Fire Dynamics, Applications and Fundamentals
This book is a part of the course by Jaipur National University, Jaipur. This book contains the course content for Fire Dynamics, Applications and Fundamentals.

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Abbreviations

BLEVE - Boiling Liquid Expanding Vapour Explosion
MW - Mega Watts
TAFF - Theoretical Adiabatic Flashing Fraction
W - Watts
Chapter I

Enclosure Fires

Aim

The aim of this chapter is to:

- introduce the enclosure fire concept
- explain the process of combustion
- describe the fire growth in an enclosure

Objectives

The objectives of this chapter are to:

- guide students through stages in fire development
- elucidate the factors influencing the fire development
- explain the fire development in terms of flow through openings

Learning outcome

At the end of this chapter, you will be able to:

- recognise other common terms describing enclosure fire stages
- identify properties of bounding surfaces
- describe fire growth in an enclosure
1.1 Introduction

Fire is a physical and chemical phenomenon which is strongly interactive by nature. The interactions between the flame, its fuel and the surroundings can be strongly non-linear and a quantitative estimation of the processes involved is often complex. The processes of interest in an enclosure fire mainly involve mass fluxes and heat fluxes to and from the fuel and the surroundings. The figure given below shows a schematic diagram of these interactions.

![Schematic diagram of heat fluxes and mass fluxes occurring in an enclosure fire](image)

**Fig. 1.1 Schematic diagram of the heat fluxes and mass fluxes occurring in an enclosure fire**

1.2 Process of Combustion

This section contains a general, qualitative description of the chemical and physical phenomena associated with fire. The discussion is divided into two parts; a general and summary discussion on the process of combustion and; a qualitative description of the development of fire in an enclosure and the consequences it has on the enclosure environment.

1.2.1 General Description of the Process of Combustion

- The study of combustion is a complex subject; it includes a number of disciplines such as fluid mechanics, heat and mass transport and chemical kinetics.
- The study of a burning candle, however, is very illustrative with regards to the natural processes. Michael Faraday, the 19th century scientist, gave lectures on “the Chemical History of a Candle” at the so called “Christmas Lectures” at the Royal Institution in London. He claimed that there was no better way by which one could introduce the study of natural philosophy than by considering the physical phenomena of a candle.
- Consider the figure given below, which shows an illustration of a burning candle and the temperature distribution through the flame. An ignition source, a match for example, heats up the wick and starts melting the solid wax.
- The wax in the wick vaporises and the gases move out by the process of diffusion, into a region where oxygen is found. The gases are oxidised in a complex series of chemical reactions, in regions where the oxygen-fuel mixture is flammable.
- The candle flame is then stable; it radiates energy to the solid wax, which melts. Since the wax vaporises and is removed from the wick, the melted wax moves up the wick, vaporises, burns and the result is a steady combustion process.
The processes occurring in the flame involves the flow of energy and the flow of mass. The flow of energy occurs by the processes of radiation, convection and conduction.

The dominant process is that of radiation; it is mainly the dirt particles produced by combustion which glow and radiate heat in all directions.

The radiation down towards the solid is the main heat transfer mode which melts the solid, but convection also plays a role. The convective heat flux is mainly upwards, transferring heat up and away from the combustion zone.

The larger and more luminous the flame, the quicker is the melting process. The radiative energy reaching the solid is however not sufficient to vaporise the wax, only to melt it. The wick is therefore introduced as a way to transport the melted wax up into the hot gases, where the combined processes of radiation, convection and conduction supply sufficient energy to vaporise the melted wax.

The burning candle also exemplifies mass transfer and phase transformation. The fuel transforms from the solid to the liquid state. The mass balance requires that the mass, which disappears from the wick by vaporisation be replaced and thus the liquid is drawn up into the wick by capillary action.

Once there, the heat transfer from the flame causes it to vaporise and the gases move away from the wick by the process of diffusion. The inner portion of the flame contains insufficient oxygen for full combustion, but some incomplete chemical reactions occur, producing soot and other products of incomplete combustion.

These products move upwards in the flame due to the convective flow and react there with oxygen. At the top of the flame nearly all the fuel has combusted to produce water and carbon dioxide, the efficiency of combustion can be seen by observing the absence of smoke emanating from the top of the candle flame.

This self sustained combustion process can most easily be changed by changing the dimensions and properties of the wick, and thereby the shape and size of the flame. A longer and thicker wick will allow more molten wax to vaporise, resulting in a larger flame and increased heat transfer to the solid. The mass and heat flow will quickly enter a balanced state, with steady burning as a result.

Other solid fuels

Without the wick the candle will not sustain a flame, as is true for many other solid fuels. Factors such as the ignition source, the type of fuel, the amount and surface area of the fuel package, determine whether the fuel can sustain a flame or not.

A pile of wooden sticks may sustain a flame while a thick log of wood may not do so. Once these factors are given, the above discussed processes of mass and energy transfer will determine whether the combustion process will decelerate, be steady or accelerate.
Also, the phase transformations of other solid fuels may be much more complicated than the melting and vaporising of the candle wax. The solid fuel may have to go through the process of decomposition before melting or vaporising and this process may require considerable energy.

- The chemical structure of the fuel may therefore determine whether the burning is sustained or not. For more complex fuels than the candle, it is difficult to predict fire growth. The difficulty is not only due to the complexity of the physical and chemical processes involved, but also due to the dependence of these processes on the geometric and other fuel factors mentioned above and the great variability in these.
- When the fuel package is burnt in an enclosure, the fire generated environment and the enclosure boundaries will interact with the fuel, as seen in fig. 1.1, making predictions of fire growth even more complex.
- It is currently beyond the state of the art of fire technology to predict the fire growth in an enclosure fire with any generality, but reasonable engineering estimates of fire growths in buildings are frequently obtained using experimental data and approximate methods.

1.2.2 General Description of Fire Growth in an Enclosure

A fire in an enclosure can develop in a multitude of different ways, mostly depending on the enclosure geometry and ventilation and the fuel type, amount and surface area. Following is a general description of various phenomena that may arise during the development of a typical fire in an enclosure.

**Ignition**

- After ignition, the fire grows and produces increasing amounts of energy, mostly due to flame spread. In the early stages the enclosure has no effect on the fire, which then is fuel-controlled. Besides releasing energy, a variety of toxic and non-toxic gases and solids are produced.
- The generation of energy and combustion products is a very complex issue as mentioned above, and the engineer must rely on measurements and approximate methods in order to estimate energy release rates and the yield of combustion products.

**Plume**

- Cold gases surround hot gases in the flame and the hotter, less dense mass will rise upwards due to the density difference, or rather, due to buoyancy. The buoyant flow including any flames is referred to as the fire plume.
- As hot gases rise, cold air will be entrained into the plume. This mixture of combustion products and air will impinge on the ceiling of the fire compartment and cause a layer of hot gases to be formed.
- Only a small portion of the mass interrupting on the ceiling originates from the fuel; the greatest portion of this mass originates from the cool air entrained laterally into the plume as it continues to move the gases towards the ceiling.
- As a result of this entrainment, the total mass flow in the plume increases and the average temperature and concentration of combustion products decreases with height.

**Ceiling jet**

- When the plume flow impinges on the ceiling, the gases spread across it as a momentum driven circular jet. The velocity and temperature of this jet is of importance since quantitative knowledge of these variables will allow estimates to be made on the response of any smoke and heat detectors and sprinkler links in the vicinity of the ceiling.
- The ceiling jet eventually reaches the walls of the enclosure and is forced to move downwards along the wall as seen in fig. 1.3.
- However, the gases in the jet are still warmer than the surrounding ambient air and the flow will turn upwards due to buoyancy. A layer of hot gases will thus be formed under the ceiling.
Gas temperatures
- Experiments have shown for a wide range of compartment fires; that it is reasonable to assume that the room becomes divided into two distinct layers; a hot upper layer consisting of a mixture of combustion products and entrained air; and a cold lower layer consisting of air.
- Further, the properties of the gases in each layer change with time but are assumed to be uniform throughout each layer. For example, it is commonly assumed when using engineering methods that the temperature is the same throughout the hot layer at any given time.

The hot layer
- The plume continues to entrain air from the lower layer and transporting it towards the ceiling. The hot upper layer therefore grows in volume and the layer interface descends towards the floor.

Heat transfer
- As the hot layer descends and increases in temperature, the heat transfer processes are enhanced. Heat is transferred by radiation and convection from the hot gas layer to the ceiling and walls which are in contact with the hot gases.
- Heat from the hot layer is also radiated towards the floor and the air in the lower layer will absorb the lower walls and some of the heat.
- Additionally, heat is transferred to the fuel bed, not only by the flame, but to an increasing extent by radiation from the hot layer and the hot enclosure boundaries. This leads to an increase in the burning rate of the fuel and the heating up of other fuel packages in the enclosure.

Vent flows
- If there is an opening to the adjacent room or out to the atmosphere, the smoke will flow out through it as soon as the hot layer reaches the top of the opening.
- Often, the increasing heat in the enclosure will cause the breakage of windows and thereby create an opening.
The fully-developed fire

- The fire may continue to grow, by the increased burning rate, by flame spread over the first ignited item or by the ignition of the secondary fuel packages. The upper layer increases in temperature and may become very hot.
- As a result of radiation from the hot layer towards other combustible material in the enclosure, a stage may arise where all the combustible material in the enclosure is ignited, with a very rapid increase in energy release rates.
- This very rapid and sudden transition from a growing fire to a fully developed fire is called flashover. At this stage, flames extend out through the opening and all the combustible material in the enclosure is involved in the fire.
- The fully-developed fire can go on for a number of hours, as long as there is sufficient fuel and oxygen available for combustion.

Oxygen starvation

- For the case where there are no openings in the enclosure or only small leakage areas, the hot layer will soon descend towards the flame region and eventually cover the flame. The air entrained into the combustion zone now contains little oxygen and the fire may die out due to oxygen starvation.
- If a window breaks at this point, or if the fire service personnel creates an opening, the hot gases will flow out through the top of the opening and cold and fresh air will flow in through its lower part.
- This may diminish the thermal load in the enclosure but the fresh air may cause an increase in the energy release rate.

Back-draft

- As a worst case, the inflowing air may mix with the unburnt products from the oxygen starved fire. Any ignition sources, such as a glowing ember, can ignite the resulting flammable mixture. This leads to an explosive or very rapid burning of gases.
- Expansion due to the heat created by combustion will force out the burning gases through the opening. This phenomenon, termed as back-draft, can be extremely hazardous and many firemen have lost their lives due to this very rapidly occurring event.
- A back-draft will usually be followed by flashover, since the thermal input will ignite all combustible fuel in the enclosure, leading to a fully developed enclosure fire.

1.3 Stages in Enclosure Fire Development

Fire development in enclosures is commonly divided into different stages. This can be done in terms of several environmental variables. However, we shall mainly discuss the stages in terms of enclosure temperatures and in terms of mass flows and pressure differences across these enclosure openings.

1.3.1 Fire Development in Terms of Enclosure Temperatures

Enclosure fires are often discussed in terms of the temperature development in the compartment and divided into different stages accordingly. Fig. 1.4 shows an idealised variation of temperature with time, along with the growth stages, for the case where there is no attempt to control the fire. Walton and Thomas lists these stages as follows:

- Ignition
- Growth
- Flashover
- Fully developed fire
- Decay
Ignition
- Ignition can be considered as a process which produces an exothermic reaction characterised by an increase in temperature greatly above the ambient. It can occur either by piloted ignition (by flaming match, spark or other pilot source) or by spontaneous ignition (through accumulation of heat in the fuel).
- The accompanying combustion process can be either flaming combustion or smouldering combustion.

Growth
- Following ignition, the fire may grow at a slow or a fast rate, depending on the type of combustion, the type of fuel, interaction with the surroundings, and access to oxygen. The fire can be described in terms of the rate of energy released and the production of combustion gases.
- A smouldering fire can produce hazardous amounts of toxic gases while the energy release rate may be relatively low.
- The growth period of such a fire may be very long and it may die out before subsequent stages are reached.
- The growth stage can also occur very rapidly, especially with flaming combustion, where the fuel is flammable enough to allow rapid flame spread over its surface, where heat flux from the first burning fuel package is sufficient to ignite adjacent fuel packages, and where sufficient oxygen and fuel are available for rapid fire growth. Fires with sufficient oxygen available for combustion are said to be fuel-controlled.

Flashover
- Flashover is the transition from the growth period to the fully-developed stage in fire development. The formal definition from the International Standards Organisation is given as ‘the rapid transition to a state of total surface involvement in a fire of combustible material within an enclosure”.
- In fire safety engineering, the word is used as the demarcation point between the two stages of a compartment fire i.e., pre-flashover and post-flashover.
- By definition, Flashover is not a precise term; several variations in definition can be found. The criteria given usually demands, the temperature in the compartment reaches from 500C to 600C. Or that the radiation to the floor of the compartment is 15 - 20 kW/m, or that flames appear from the compartment openings.
- These happenings may all be due to different mechanisms to do with the fuel properties, fuel orientation, fuel position, the compartment geometry and conditions in the upper layers. Flashover cannot be said to be a mechanism, but rather a phenomena associated with thermal instability.
**Fully-developed fire**

- At this stage the energy released in the compartment is at its greatest and is very often limited by the availability of oxygen.
- This is called ventilation-controlled burning (as opposed to fuel-controlled burning) since the oxygen needed for combustion is assumed to enter through openings.
- In ventilation-controlled fires, unburnt gases can collect at the ceiling level and as these gases leave through openings they burn, causing flames to stick out through the openings.
- The average gas temperature in the compartment during this stage is often very high, in the range of 700 C - 1200 C.

**Decay**

As the fuel is consumed by the energy released, it diminishes and thus the average gas temperature in the compartment declines. The fire may go from being ventilation-controlled to becoming fuel-controlled during this period.

**1.3.2 Fire Development in Terms of Flow Through Openings**

- A second way of dividing the enclosure fire into a number of stages is to observe the mass flows in and out through the enclosure openings while the fire progresses.
- The mass flows in turn depending on the pressure differences across the opening. The figure given below shows how the fire develops in an enclosure with a single opening in terms of the pressure profiles across the opening.
- A straight line, sloping since the weight of the column of air increases as we approach ground level, represents the pressure for the outside atmosphere.
- Assuming that the temperature of the air in the lower layer of the compartment equals the temperature outside, we have the same slope as that for the outside.
- There is a twist in the pressure line inside the compartment when we move into the upper layer the hot air is lighter than the cold air.
- The pressure of the outside atmosphere is the same for all four cases in the figure below and is denoted by the symbol $P_i$ and pressure inside the compartment is denoted $P_o$.

![Fig. 1.5 Pressure profile across the opening as the fire develops](image)

8/JNU OLE
Stage A
• In the first stage of the fire, the pressure inside is higher than the pressure outside the compartment.
• This is due to the expansion of hot gases; these have a greater volume than the cold gases.
• If the opening is not at ceiling level, cold gases will be forced out through the opening due to the hot gas expansion.
• As a result, the pressure difference across the opening is positive (with respect to the compartment) and there will be no inflow through the opening, only outflow of cold gases.

Stage B
• Stage B only lasts a few seconds and is often ignored. The smoke layer has just reached the top of the opening and the hot gases have started to flow out.
• The pressure inside even now is still higher than the pressure outside and both hot and cold gases flow out through the opening. There is no mass flow into the compartment.

Stage C
• During this stage, hot gases flow out through the top of the opening and mass balance demands that cold gases of equal mass flow in through the lower part of the opening. This stage can last for a considerable time, until the room is entirely filled with smoke or until flashover occurs.
• Stages A, B and C are associated with the growth stage mentioned above and the pre-flashover stage.

Stage D
• This stage is often termed the “well mixed” stage, where the compartment is filled with smoke which is assumed to be well mixed i.e., assumed to have some single, average temperature. This stage is associated with the fully-developed fire mentioned above.
• In many cases flashover has occurred between stages C and D.

1.3.3 Other Common Terms Describing Enclosure Fire Stages
• In fire safety engineering design, two distinctly different design situations often occur. One has to do with the pre-flashover fire, where the emphasis is on human safety. The design load in this case is characterised by an energy release rate curve, where the growth of the fire is of most importance.
• A very different design situation arises when the objective is to ensure structural stability and safety of fire fighters. Here the post-flashover fire is of greatest concern and the design load is characterised by a temperature time curve where the fully-developed fire stage is of greatest concern.
• Fire development is therefore sometimes simply divided into the pre-flashover stage and the post-flashover stage.
• After ignition and during the initial fire growth stage, the fire is said to be fuel- controlled, since, in the initial stages, there is sufficient oxygen available for combustion and the growth of the fire entirely depends on the characteristics of the fuel and its geometry.
• When the fire grows towards flashover it may become ventilation-controlled when there is not enough oxygen available to combust most of the pyrolysing fuel. The energy release rate of the fire is then determined by the amount of oxygen which enters the enclosure fuel and it is therefore termed ventilation-controlled. During the decay stage the fire will eventually return to being fuel-controlled.
• The growth stage of the fire (and the pre-flashover fire) is therefore often associated with the fuel-controlled fire. The fully-developed stage (and the post-flashover fire) is often associated with the ventilation-controlled fire.
1.4 Factors Influencing Fire Development in an Enclosure

The factors which influence the development of a fire in an enclosure can be divided into two main categories; those that have to do with the enclosure itself and those that have to do with the fuel. We can specifically mention them as follows:

- the size, and the location of the ignition source
- the type, amount, position, spacing, orientation and surface area of the fuel packages
- the geometry of the enclosure
- the size and location of the compartment openings
- the material properties of the enclosure boundaries

Ignition source

- An ignition source can consist of a spark with very low energy content, a heated surface of a large pilot flame to give couple of examples. The source of energy is chemical, electrical or mechanical.
- The greater the energy of the source, quicker is the subsequent fire growth on the fuel source. A spark or glowing cigarette may initiate smouldering combustion which may continue for a long time before flaming occurs, often producing low heat but considerable amounts of toxic gases.
- A pilot flame usually produces flaming combustion directly, resulting in flame spread and fire growth.
- The location of the ignition source is also of great importance. A pilot flame positioned at the lower end of, say, a window curtain may cause rapid upward flame spread and fire growth. The same pilot flame would cause a much slower fire growth were it placed at the top of the curtain, resulting in slow, creeping, downward flame spread.

Fuel

- The type and amount of combustible material is of course one of the main factors determining fire development in an enclosure. In building fires, the fuel usually consists of solid materials; the furniture and fittings normally seen in the enclosure interior; in some industrial applications the fuel source may also be in liquid state.
- Heavy, wood based furniture usually causes slow fire growth but can burn for a long time. Some modern interior materials include porous light-weight plastic, which causes more rapid fire growth but burns for a shorter time. A high fire load does not therefore necessarily constitute a greater hazard; rapid fire growth is more hazardous in terms of human lives.
- The position of the fuel package can have a marked effect on fire development. If the fuel package is burning away from walls, cool air is entrained into the plume from all directions. When placed close to a wall, the entrainment of cold air is limited. This not only causes higher temperatures but the flames are higher since combustion must take place over a greater distance.
- Fig. 1.6 shows temperatures measured above fires in 1.22 m high stacks of wood pallets. Curve A shows temperatures as a function of height above the pallets burning without the presence of walls. Curve B is for a similar stack near a wall and curve C is for a stack in a corner.
- The spacing and orientation of the fuel packages is also of importance. The spacing in the compartment determines to a considerable extent how quickly the fire spreads between these. Upward flame spread on a vertically oriented fuel surface will happen much more rapidly than lateral spread along a horizontally oriented fuel surface.
Fig. 1.6 The temperature in the fire plume as a function of height above a burning stack of wood pallets

- Combustible lining materials, mounted on compartment walls and/or ceiling can cause very rapid fire growth. Fig. 1.7 shows results from a small scale room test where the lining material is mounted only on the walls (with non-combustible ceiling) and when the material is mounted on both walls and ceiling.
- In both cases an initial flame was established on the lining material along one corner of the room. With material mounted on the ceiling, the flame spreads with the flow of gases (concurrent-flow flame spread), causing rapid growth.
- With a non-combustible ceiling, the flame spreads horizontally (opposed-flow flame spread) across the material, a process which is much slower and requires the lining material to be heated considerably before the flame can spread rapidly over it. As a result, the time to flashover is 4 minutes in the former case and 12 minutes in the latter.

Fig. 1.7 The energy release rate versus time

A fuel package with a large surface area will burn more rapidly than an otherwise equivalent fuel package with a small surface area. A pile of wooden sticks, for example, will burn more rapidly than a single log of wood of the same mass.
**Enclosure geometry**

- The hot smoke layer and the upper bounding surfaces of the enclosure will radiate towards the burning fuel and increase its burning rate. Other combustible items in the room will also be heated up. The temperature and thickness of the hot layer and the temperature of the upper bounding surfaces thus have considerable impact on the growth of the fire.

- A fuel package burning in a small room will cause relatively high temperatures and rapid fire growth. In a large compartment, the same burning fuel will cause lower gas temperatures, longer smoke filling time, less feedback to the fuel and slower fire growth.

- The fire plume entrains cold air as the mixture of combustion products and air moves upward towards the ceiling. The amount of cold air entrained depends on the distance between the fuel source and the hot layer interface. In an enclosure with a high ceiling, this causes relatively low gas temperatures, but due to the large amount of air entrained, the smoke filling process occurs relatively rapidly.

- The smaller the floor area, faster is the smoke filling process. With a low ceiling, heat transfer to the fuel will be greater. Additionally, the flames may reach the ceiling and spread horizontally under it. This results in considerable increase in the feedback to the fuel and to other combustibles with imminent very rapid fire growth.

- For enclosures with a high ceiling and large floor area the flames may not reach the ceiling and the feedback to the fuel is modest. Fire growth rather occurs through direct radiation from the flame to nearby objects, where the spacing of the combustibles becomes important.

- In buildings with a large floor area but a low ceiling height, the feedback from the hot layer and ceiling flames can be very intensive near the source. Further away, the hot layer has entrained cold air and has lost heat to the extensive ceiling surfaces. The heat flux to the combustible materials, in the early stage of the fire is therefore lower than the heat flux closer to the fire source.

- We can conclude that the proximity of ceilings and walls can greatly enhance fire growth. Even in large spaces, hot gases trapped under the ceiling can heat up the combustibles beneath and result in an extremely rapid fire spread over a large area. The fire which so tragically engulfed the Bradford City Football Stadium in England, 1985, is a clear reminder of this.

**Compartment openings**

- Once flaming combustion is established, the fire must have access to oxygen for continued development. In compartments of moderate volume which are closed or have very small leakage areas, the fire is soon oxygen starved and may self-extinguish or continue to burn at a very slow rate depending on the availability of oxygen.

- For compartments with ventilation openings, the size, shape and position of these become important for fire development under certain circumstances.

- During the growth phase of the fire, before it becomes ventilation-controlled, the opening may act as an exhaust for the hot gases, if its height or position is such that the hot gases are effectively removed from the enclosure. This will diminish the thermal feedback of the opening and does not have a very significant effect on fire growth during the fuel-controlled regime.

**Properties of bounding surfaces**

- The material in the bounding surfaces of the enclosure can affect the hot gas temperature considerably and thereby the heat flux of the burning fuel and other combustible objects.

- Certain bounding materials are designed to conserve energy, e.g., mineral wool will limit the amount of heat flow to the surfaces so that the hot gases will retain most of their energy.

- The material properties controlling the heat flow through construction are conductivity (k), density (p) and heat capacity (c). These are commonly collected in a property called thermal inertia and given as the product kpc.

- Insulating materials have a low thermal inertia, materials with relatively high thermal inertia, such as brick and concrete; allow more heat to be conducted into the construction, thereby lowering the hot gas temperatures.
Summary

- Fire is a physical and chemical phenomenon which is strongly interactive by nature.
- The study of combustion is a complex subject; it includes a number of disciplines such as fluid mechanics, heat and mass transport and chemical kinetics.
- A fire in an enclosure can develop in a multitude of different ways, mostly depending on the enclosure geometry and ventilation and the fuel type, amount and surface area.
- Fire development in enclosures is commonly divided into different stages namely enclosure temperatures and mass flows and pressure differences across these enclosure openings.
- Ignition can be considered as a process which produces an exothermic reaction characterised by an increase in temperature greatly above the ambient. It can occur either by piloted ignition (by flaming match, spark or other pilot source) or by spontaneous ignition (through accumulation of heat in the fuel).
- Flashover is the transition from the growth period to the fully-developed stage in fire development.
- In fully-developed fire stage the energy released in the compartment is at its greatest and is very often limited by the availability of oxygen.
- In fire safety engineering design, two distinctly different design situations often occur. One has to do with the pre-flashover fire, where the emphasis is on human safety. The design load in this case is characterised by an energy release rate curve, where the growth of the fire is of most importance.
- The factors which influence the development of a fire in an enclosure can be divided into two main categories; those that have to do with the enclosure itself and those that have to do with the fuel.

References


Recommended Reading

Self Assessment

1. Which of the following statement is true?
   a. The convective heat flux is mainly upwards, transferring heat up and away from the combustion zone.
   b. The convective heat flux is mainly downwards, transferring heat up and away from the combustion zone.
   c. The convective heat flux is mainly upwards, transferring heat downward from the ignition.
   d. The gas is mainly upwards, transferring heat up and away from the combustion zone.

2. The larger and more luminous the flame, the quicker is the ________ process.
   a. heating
   b. melting
   c. freezing
   d. evaporating

3. After__________, the fire grows and produces increasing amounts of energy, mostly due to flame spread.
   a. growth
   b. flashover
   c. decay
   d. ignition

4. In which stage, the pressure inside is higher than the pressure outside the compartment?
   a. Stage A
   b. Stage B
   c. Stage C
   d. Stage D

5. Which stage is often termed the “well mixed” stage?
   a. Stage A
   b. Stage B
   c. Stage D
   d. Stage C

6. Which of the following statement is true?
   a. Decay is the transition from the growth period to the fully-developed stage in fire development.
   b. Flashover is the transition from the growth period to the decay stage in fire development.
   c. Flashover is the transition from the growth period to the ignition stage in fire development.
   d. Flashover is the transition from the growth period to the fully-developed stage in fire development.

7. Fires with sufficient oxygen available for combustion are said to be ________
   a. gas-controlled
   b. fuel controlled
   c. ignited
   d. fume
8. The type and amount of ____________ material is of course one of the main factors determining fire development in an enclosure.
   a. polymer
   b. gas
   c. combustible
   d. wax

9. Which of the following statement is true?
   a. The smaller the floor area, slower is the smoke filling process.
   b. The larger the floor area, faster is the smoke filling process.
   c. The smaller the floor area, faster is the fuel filling process.
   d. The smaller the floor area, faster is the smoke filling process.

10. The material properties controlling the heat flow through construction are conductivity (k), ______(p) and heat capacity (c).
    a. density
    b. melting
    c. cooling
    d. quantity
Chapter II
Development and Growth of Fires in Enclosures

Aim
The aim of this chapter is to:

- analyse the factors affecting fire development
- explain different burning regimes
- discuss the fire development in compartment

Objectives
The objectives of this chapter to:

- explain fire spread concept
- determine the fire severity
- examine the concept of flashover

Learning outcome
After reading this chapter, you will be able to:

- understand the heat balance for an enclosure
- explain how to calculate heat balance
- evaluate the fire loading concept
2.1 Introduction

The growth and development of fire has been shown to be dependent to a large extent on the geometry and ventilation of the enclosure containing the Fire. Friedman reported the differences observed between Fires burning in the open and those burning in enclosures.

The following figure shows the effect of an enclosure on the burning rate of a square slab of polymethyl methacrylate that illustrates the difference between a material burning in the open and the same material burning under a hood or roof.

In the former case, except for the heat required to produce the volatiles from the fuel bed, all of the remaining heat energy is lost to the atmosphere. In the latter case however, the roof plays a significant role, the loss of heat energy is considerably reduced and an energy feedback mechanism is created which significantly increases the pyrolisation and hence the burning rate. The rapidity with which fire so tragically surrounded the Bradford City Football Stadium in 1985 clearly demonstrates the latter.

2.2 Factors Affecting Fire Development

A fire usually starts because its material is ignited by a heat source. The development of the fire within the compartment depends on many factors. They are as follows:

- The item first ignited is sufficiently flammable to allow flames to spread over its surfaces.
- The heat flux from the first fuel package is sufficient to irradiate adjacent fuel packages, which in turn will begin to burn.

- Sufficient fuel exists within the compartment; otherwise the fire may simply burn itself out.
- The fire may burn very slowly because of a restricted oxygen supply, e.g. in a well-sealed compartment the fire may eventually overpower itself.
- Provided that there is sufficient fuel and oxygen available, the fire may totally involve the compartment.

**Fig. 2.1 The effect of an enclosure on the burning rate of a square polymethyl methacrylate slab**
2.3 Flashover

- Flashover has been defined as the rapid involvement of a compartment’s combustible contents as they ignite almost simultaneously. Unfortunately, such a definition tends to regard flashover as an event.
- A better definition of flashover would be the time when flames cease to be localised and flaming can be observed throughout the compartment volume i.e., the burning activity changes from being a surface phenomenon to a volume process.
- Flashover is in fact, the transition from the growth period to the fully developed stage in fire development. It is used as the demarcation point between the two stages of a compartment fire i.e., pre-flashover and post-flashover.
- In model studies designed to study the effects of the variation of room and window geometries on flashover in residential sized rooms. Waterman chose a heat flux-time criterion to indicate flashover. A low level heat flux of 2 W/cm was used in these experiments.
- Hagglund et al. in attempting to develop a technique for predicting probable flashover, conducted several room experiments using different types of furnishings. Visual observations of flames emerging from the windows were found to correlate with an average room-gas-temperature of 600°C at the ceiling. This 600°C ‘flashover criterion’ was then applied to a further series of experiments where the size of crib fire and window opening were varied. This gave an expression for the peak burning rate required to cause flashover (Refer to the figure below).

![Fig. 2.2 Flashover, ventilation and burning rate](image)

The expression so generated was:

\[
R_{\text{peak}} = 3.0 + 0.2AH^{1/6} \text{ when } AH^{1/2} \geq 0.9
\]

\[R_{\text{peak}} = \text{‘peak burning rate’ kg min}^{-1} \text{ (i.e., minimum burning rate necessary for flashover to occur)}\]

\[A = \text{window area (m)}\]

\[H = \text{window height (m)}\]

Although this work was limited to fixed room sizes and boundary constructions, it does a useful approximation of the flashover potential of various rooms and their furnishings.

It also offers an insight into the complex phenomenon of flashover and the factors which influence its occurrence. Some of these factors are: burning rate, compartment geometry and ventilation.
2.4 Fire Development in Compartments

- The time versus temperature development of fire is shown in fig. 2.3. In the figure the curve represents the average temperature determined under test conditions.
- The period A-B is known as the growth period. It is essentially the pre-flashover period during which temperatures in the compartment remain relatively low and the chances of escape are relatively high.
- At B, the fire progresses rapidly through flashover to the fully-developed stage and it can be seen that flashover in essence is the transition from the growth period to the fully-developed period.
- During this period, all the combustibles in the compartment are burning and the temperature within the enclosure increases sharply.

![Fig. 2.3 Time/temperature fire profile](image)

- At point C the burning period ends, the temperature begins to fall and the decay period begins. During the decay period, the temperatures are such that for a period of time the direct threat to other spaces remains because of the risk of propagation by radiation or penetration of constructional components.
- In the model heat balance described above, the temperature within the compartment is assumed to be uniform and the properties of materials forming the boundary construction are assumed constant. In practice however, the temperature within the compartment during a fire will vary not only with time but also with location, and the properties of the materials forming the enclosing construction will also vary.
- Much of the interest in modelling fire development focuses on the flashover transition and full compartment involvement in the fire so that the pre-flashover situation may be overlooked. This would be a mistake. As can be seen from the above figure, the temperatures during the growth period are low and consequently can be ignored. It is the duration of the growth period however, which is very important as it determines the time available for escape and for the effective operation of the emergency services.
- During the growth period, heat from the fire causes materials in the compartment, e.g. wall lining, to evolve gases and vapours. If the rate of vapour production is sufficiently high, a vapour-air mixture will be formed within the ‘flammability limits’ which may be ignited by flames from the already burning materials. It follows that the easier a material is to ignite and the greater the rate of heat production, the faster the growth of the fire. The time required for ignition of a material and its subsequent rate of heat production is dependent not only on the nature and dimensions of the physical characteristics of the material, but also on the heat flux transferred to the material itself.
- Large areas of combustible materials, such as wall and ceiling linings, can contribute significantly to the rapid growth of a fire. Radiation from large areas of burning surfaces, the exponential rate of flame spread over vertical surfaces and relatively low ceilings interact to promote the rapid development of a fire within a compartment. Drysdale categorised the factors affecting the rate of flame spread over combustible solids (Refer to the below table).
## Table 2.1 Factors that affect the rate of flame spread on combustible solids

Along with the factors listed in the above table, other factors that affect the duration of the growth period are as follows:

- spacing of combustible fuel packages within the compartment
- mass and surface area of the combustible materials dispersed within the room
- size and location of ignition sources
- size and location of (the openings in the compartment boundaries)
- geometry of the compartment

### 2.5 Burning Regimes

Two identifiable regimes of burning are as follows.

#### 2.5.1 The Ventilation-controlled Regime

In the ventilation controlled regime, it is assumed that the rate of burning (R) i.e., the rate of mass loss is strictly controlled by the rate of ingress of air. The underlying assumption is that the rate of air supply is exactly sufficient to burn all the volatiles which are produced at the rate R. The following figure indicates the limiting ventilation rate between the ventilation and fuel-controlled regimes.

![Fig. 2.4 Limiting ventilation rates between ventilation and fuel-controlled regimes](image)
Following figure shows the relationship between temperatures attained in fires and ventilation enclosures, which have similar fire loadings.

![Diagram of Development and growth of fires in enclosures]

**Fig. 2.5 Variation in combustion gas temperature with ventilation**

- If compartment (a) represents a well-sealed compartment with no windows, the temperature profile in the compartment will be low and the fire would eventually self-extinguish due to oxygen starvation.
- With compartment (b), there is sufficient oxygen available to allow all the fuel to be consumed and the relationships between ventilation rates, fire loading, compartment geometry, and the thermal characteristics of the compartment. The boundary construction is such that the maximum fire temperatures are achieved.
- In compartment (c) there is too much ventilation and the size of the compartment reduces the effect of the boundary construction in fire development. The available excess air entrained into the fire process actually has a cooling effect and the fire burns as if it were in the open. Thus, it can be seen that more severe fires occur in the ventilation regime.

From Kawogoe’s work for a ventilation-controlled regime

\[ R = 5.5AH^{0.5} \text{ kg/min} \]

It should however be noted that, the ratio \( R/AH \) is not constant, i.e., does not equal 5.5 over a wide range of conditions. It is dependent to some extent on the geometry of the enclosure, especially the ratio of width/depth.

The relationship is also empirical, strictly speaking it applies only to wood crib fires which although are useful in exploratory experimental work to represent a standard fire may not represent a real fire in an enclosure. This is particularly so for a fire in a room containing modern furniture and materials. In an enclosure with more than one opening:

\[ A = A_1 + A_2 + A_3 \ldots \]

And \( H \) is calculated from:

\[ H = \sum A_i H_i / A \]

### 2.5.2 The Fuel-controlled Regime

Thomas has suggested a burning rate equal to the ‘charring rate’ of wood. \( R = 6 \times 10^3 A \text{ kg s}^{-1} \) (for cellulose materials), where \( A \) is the surface area of the combustible material, however, \( R/A \), is known to be function of stick size in crib fires and consequently the relationship is rather contrived. Any significant changes in the heat feedback mechanisms could influence the burning rate as expressed by the relationship above, which is empirical and does not hold for non-cellulosic Fires. The figure given below further illustrates the conditions necessary for the transition from fuel-controlled regime to ventilation-controlled regime or vice versa.
2.6 Heat Balance for an Enclosure

A heat energy balance for an enclosure will assist in developing a complete understanding of fire growth and development. This energy balance can be expressed as:

\[
\dot{Q}_T = \dot{Q}_E + \dot{Q}_B + \dot{Q}_L
\]

It means that the heat release in the enclosure should be equal to the sum of all heat losses. (See fig. 2.7)

- \(\dot{Q}_E\) = The quantity of heat released per unit time by combustion of the combustibles in the enclosure.
- \(\dot{Q}_E\) = The quantity of heat lost per unit time by radiation and convection to the boundary construction of the enclosure.
- \(\dot{Q}_B\) = The quantity of heat lost per unit time by radiation through the openings.
- \(\dot{Q}_L\) = The quantity of heat carried away per unit time by the combustion gas.

Fig. 2.6 Maximum temperatures in experimental fires correlated with ventilation

Fig. 2.7 Energy balance for an enclosure
2.6.1 Calculation of $\dot{Q}_T$

The heat release $Q_t$ is calculated by the formula:

$$\dot{Q}_T = R \times q$$

where,

$q = $ calorific value of wood (kJ/kg)

$R =$ the rate of burning (kg/min”)

It should be noted here that $Q$ in a real fire will vary with time. Kawagoe in his experimental work involving the burning of wooden cribs in enclosures within the ventilation-controlled regime found that the rate of burning was essentially independent of the amount of fuel, but increased with the size of the ventilation opening.

Correlating the rate of weight loss with the ventilation opening he obtained:

$$R = 5.5A_w \sqrt{H} \text{ kg/min}$$

Fig. 2.8 illustrates this relationship where experimental results are shown which verify the theoretical determination of $R$. The results of Kawagoe and others are summarised by Thomas who suggests the relationship for ventilation-controlled fires to be: $R/AH^{1/2} = 6 \text{ kg.min}^{-1}m^{-1/2}$.
Fig. 2.9 Burning rate and air flow factor

Where, R = burning rate
A = window area
H = window height
Thomas’s correlation is shown in fig. 2.9.
Calculation of $\dot{Q}_E$

The heat loss to the enclosure boundary is obtained from the equation:

$$\dot{Q}_E = q_R + q_c$$

$$\dot{Q}_E = A_e \frac{d\theta}{dx}$$

Where:
$q_R$ = The net heat flux radiation from the flame to the internal surfaces of the enclosure.
$q_c$ = The net heat transferred by convection from the flame to the internal surfaces of the enclosure.
$\lambda$ = The thermal conductivity of the boundary construction
$A_e$ = The total area of the enclosure surfaces exposed to the fire
$\frac{d\theta}{dx}$ = Temperature gradient in the boundary construction.

In this equation q and q are expressed as:

$q_R = A_e \varepsilon \delta (T_f^{4} - T_c^{4})$ and $q_c = h A_e (T_f - T_c)$
where,
\( E \) = emissivity of the enclosure surfaces
\( h \) = co-efficient of heat transfer by convection
\( T_g \) = temperature of the flame
\( T_c \) = temperature of the enclosure surfaces.

In the equation:

\[
\dot{Q}_E = A_E \cdot \lambda \cdot \frac{\partial \theta}{\partial x}
\]

\( A_E \cdot \lambda \cdot \frac{\partial \theta}{\partial x} \) is the term for the heat transfer by conduction through the walls and can be calculated by a graphical or numerical technique.

### 2.6.2 Calculation of \( \dot{Q}_B \)

\( \dot{Q}_B \) is the net heat lost by radiation through openings in the enclosure walls to the external environment.

\[
\dot{Q}_B = A_B \varepsilon f \delta (T_g^4 - T_o^4)
\]

Where,
\( A_B \) = area of the opening in the walls
\( \varepsilon \) = emissivity of the flame assumed to be unity.
\( \delta \) = Stephan Boltzmann constant

### 2.6.3 Calculation of \( \dot{Q}_L \)

\( \dot{Q}_L \) is the quantity of heat lost by replacing hot gases by cold air. Assuming equal inflow and outflow air and gases then:

\[
\dot{Q}_L = M_{out} \frac{C_p}{2} (T_g - T_o)
\]

where,
\( M_{out} = \frac{2}{3} CB \left( H^{2/3} \lambda \right) \left[ 2g \frac{p_o}{p_g} \right]^{1/2} \) kgs\(^{-1}\)

where,
\( C \) = discharge coefficient
\( B \) = width of the opening (m)
\( H \lambda \) = height of the opening (m)
\( p_o \) = density of external air (kg/m\(^3\))
\( p_g \) = density of Fire gases (kg m\(^{-3}\))
\( g \) = gravitational constant

### 2.7 Fire Spread

The spread of fire may be influenced by essentially three factors, which are as follows.

#### 2.7.1 Interspatial Interactions

- The determination of interspatial interactions is an integral part of design, which demands as a prerequisite, the establishment of building functional requirements related to the dedicated space. Primarily the functional requirements of different parts of a building will require the provision of separating constructional components. These components can then be utilised by increasing their fire endurance characteristics thus providing an initial barrier to fire spread.
- Buildings are designed and constructed to accommodate people and processes, among other things. Consequently the flow of people, materials and products must be incorporated in such a way as to achieve a pre-determined level of fire safety.
The minimum level of fire safety to be achieved may be prescribed by building legislation or be determined by insurance requirements or other influences.

The figure given below shows the plan of a simple factory building and fig. 2.11 shows the longitudinal elevation.

The three-storey section is devoted to administration processes and the single-storey section is concerned with production processes. Clearly, there is a general division of function although communications between both parts must obviously be provided.

Within the production-oriented section various sub-divisions are also apparent, related to the activity carried out in particular spaces, e.g. storage. For an apparently simple building such as the one illustrated, the building designer who has to satisfy the minimum legislative requirements will perhaps subconsciously carry out a notional hazard analysis.

The sequential analysis process can be outlined as follows:
- Problem definition: establish clearly the need.
- Choice of objectives: a definition of the physical needs and of the criteria within which they must be met.
- System synthesis: the creation of possible alternative systems.
- Systems analysis: analysis of alternative systems against the defined objectives.
- Systems selection: selection of the most promising alternative.
- Implementation: test the preferred solution.
- Systems engineering: monitor, modification and information feedback.

Having determined the nature and scale of the risk, the designer has several options which may be considered as follows:
- Isolation
- Containment - compartmentation
- Segregation
Isolation
If the risk is such that the threat to the building and its occupants cannot be accepted, then the risk may be removed and located at another part of the same site. This is particularly the case with industrial processes where the risk of explosion exists.

Compartmentation
• The factors which generally determine the need for compartmentation are the floor area and the cubic capacity of the spaces under consideration.
• Thus, building legislation relates these two criteria to risk and it follows that if floor areas and cubic capacities of predetermined dimensions are suitably protected by fire-resisting boundary-constructional components, the probability of fire spread beyond the compartment, of origin is diminished.
Segregation
Segregation of the risk elements of areas requires a hazard analysis study. The risks of potential threats to the building and its occupants are identified and classified. Risks of similar character and nature can then be collectively accommodated in spaces especially provided for that specific purpose.

2.7.2 Fire Loading
The term, fire load is used to describe the heat energy which could be released per square metre of floor area of a compartment or storey by the combustion of the contents of the building and any combustible parts of the superstructure itself.

\[
\text{Fire load} = \frac{M \times C}{A} \text{ KJm}^{-2}
\]

where,
- \(M\) = mass of combustible materials in the compartment or storey (kg)
- \(C\) = calorific value of the materials (kj/kg)
- \(A\) = floor area in metres (m)

![Fig. 2.12 Rates of burning of fuels in various forms](image)

- Thomas et al shows that the nature and disposition of a fuel could have a considerable effect on the rate of burning. In fig. 2.12, Curve 1 refers to materials such as books and reels of cardboard which offer a comparatively small surface area for combustion. Curve 2 represents the same type of material in a different configuration, e.g. cardboard cartons stored folded flat, and Curve 3 represents stacks of cardboard cartons.
- Thus, it can be seen that whilst the fire load is a necessary component of fire growth, it is like blood in a person’s veins, necessary for life, but not a measure of the whole person.
- The nature, disposition and height of the fuel will also contribute to fire growth and must be considered for each building, not just each building type.
- For example, two buildings may be used for storage purposes, both storing cardboard. One building uses high racks storage for cartons and the other low racks storage for folded cartons. In the latter it would be reasonable to expect a slow burning deep-seated fire which a sprinkler system may control but not extinguish, whereas in the former it would be reasonable to expect a very rapid fast growing fire with flames at ceiling level in the very early stages of development, which the sprinkler system may not be able to control.
2.7.3 Heat Transfer
Heat may be transmitted in three distinct ways in any situation or by a combination of all the three.

Conduction
- It is transfer of heat through the material from a high temperature zone to a lower temperature zone. Building regulations require hearths to be non-combustible and a minimum thickness of 150mm so as to prevent the transfer of heat by conduction (Refer to fig. 2.13 (a)).
- Heat conducted through a masonry wall can easily ignite combustibles stored against the wall at the face on the other side of the fire face (Refer to fig. 2.13(b)).

![Fig. 2.13 (a) Heat transfer by conduction](image1)

![Fig. 2.13 (b) Heat transfer by conduction](image2)


**Convection**

- It is transfer of heat through or by a fluid by the means of induced convective currents within the fluid.
- When a fire burns in a room a buoyant plume of hot smoke rises from the fuel bed, contacts the ceiling and spreads across the ceiling progressively heating up the surface and the entire volume until a point is reached when all the combustibles within the room can be easily ignited (See fig. 2.14(a)).
- In the simple design of domestic flues, etc., reliance is placed on convection to remove the smoke and toxic gases.
- Within a building a fire may develop on one floor and progress upward through the building by means of convective forces. In buildings, staircases, lift shafts and ducts provide ready-made artificial flues which will channel the fire rapidly upwards through the building until every floor above the fire floor is surrounded by fire (See fig. 2.14(b)).

**Radiation**

- It is transfer of heat through a fluid or vacuum by means of electromagnetic waves. In many fire situations, radiation may be the dominant factor controlling spread and growth.
- As the fire develops within an enclosure, all the surfaces gradually (sometimes very quickly) heat up.
  - The surfaces themselves begin to radiate heat energy (Fig. 2.15) significantly influencing:
  - the temperature rise in the enclosure
  - the burning rate of the combustibles
  - fire development and growth
Radiation is also very important when considering fire spread between buildings. Building regulations consider unprotected areas in the facades of buildings as potential radiators in a fire situation and require that buildings be sited sufficiently distant from respective site boundaries so as not to present a Fire hazard to other buildings adjoining or within the same site.

The distances quoted in building regulations are derived in relation to the amount of unprotected areas in the external walling of the building.

Unprotected areas are defined as:
- Areas of walling not having the required degree of Fire resistance
- Windows, doors or other openings
- Any part of the external wall, which has combustible material more than 1 mm thick attached or applied to its external face whether for cladding or any other purpose.

The following figure shows the elevation of a dwelling. If it is assumed that the unprotected areas act as black-body radiators at 1,000°C, it is possible to calculate the radiant intensity at various distances (m) from the burning building. Knowing the radiant intensity at various distances, buildings can be sited so as to avoid spontaneous ignition on their exposed facades.
2.8 Fire Severity

- Fire severity may be simply defined as the destructive potential of a compartment fire, i.e. the fire in a given compartment will have a potential impact upon the structural and constructional components, which form the compartment and the contents of the compartment. Inevitably, fire severity has been linked with structural performance in terms of a component's fire-resisting capabilities.

- Legislation established a direct relationship between fire-load density and fire severity. This concept has been widely utilised in building legislation to determine the fire resistance requirements of building components within buildings of various purpose groups.

- An equal-area concept (Refer to fig. 2.17) was developed on the basis of this work by calculating the area under the average temperature curve and equating it to the area under the standard temperature-time curve used in fire-resistance furnace tests.

- Fire severity is not a function of a single parameter such as the fire load density, but depends on other factors such as ventilation, burning rate, fire duration and the thermal properties of the enclosure construction. Fujita and Kawagoe recognised that the flow of air into a compartment was an important factor in the severity of fully-developed fires.

![Fig. 2.17 Equal-area concept to relate fire severity](image-url)
Butcher, using purpose-built brickwork rooms with controlled ventilation showed the effects of ventilation and fire load on fire-temperature profiles for a standard compartment (shown in the figure given above).

- Subsequent work (Heselden) was carried out using the fire load, ventilation and thermal properties of the enclosure boundary construction as variable parameters to derive expressions for the potential severity of compartment fires.

- The information has to be expressed in terms of fire-temperature histories particularly during the fully-developed period of the fire. Heselden, reporting the results of an international co-operative programme on fully-developed fires in single compartments, listed the following conclusions:

- The rate of burning and the temperature of a fire in a compartment are dependent mainly on the size and shape of the compartment and the size and shape of its ventilation opening, and also to some extent on Ore-load density.
  - Although the burning rate changes widely with scale, the burning rate per unit floor area for fires with full ventilation openings and the values of R/AH\(^{1/2}\) for openings vary only slightly with scale.
  - With large openings, temperature is independent of scale, but with \(\frac{1}{4}\) openings, temperature increases slightly with increasing scale.
  - The burning rate and temperature depend to a small extent on the thermal properties of the ceiling and wall material.
  - The intensity of radiation from the ventilation opening can be related to the rate of burning, the area of the opening and the temperature within a given compartment.
  - Intensity of radiation from the flame can be related to the rate of burning, the intensity of radiation at the ventilation opening and the dimensions of the compartment.
  - Changes in the exposure hazard caused by wind deflection of the emergent flames are likely to be more important than changes caused in the way the fire burns in the original compartment.
  - The experimental conditions used in this programme of work is shown in the figure below:
Fig. 2.19 Ratio of width/depth/height

Fig. 2.20 Ratio of ventilation opening to front wall
<table>
<thead>
<tr>
<th>Scale (compartment height)</th>
<th>1, 1 and 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ventilation opening</td>
<td>1/1 or whole of front wall (Figure 2.20)</td>
</tr>
<tr>
<td>Fire-load density</td>
<td>20, 30 and 40 kg m. The fuel</td>
</tr>
<tr>
<td>(fire load/ floor area)</td>
<td>consisted of standardised wooden cribs</td>
</tr>
<tr>
<td>Fuel thickness</td>
<td>10, 20 and 40 mm</td>
</tr>
<tr>
<td>Fuel spacing</td>
<td>1 or 1/3 stick thickness (Figure 2.21)</td>
</tr>
</tbody>
</table>

Fig. 2.21 Fuel spacing in terms of stick thickness

Winds
Wind speeds of 5 and 7 ms were used blowing perpendicularly to the plane of the ventilation opening at 60°C to this direction for tm scale Compartments having shapes 111, 211, 121 and 221.

Harmathy introduced three Fire-severity parameters. These are as follows:
- The duration of the fully-developed fire.
- The overall penetration flux, q, i.e., the heat flux incident on the interval surface of the compartment boundaries, averaged spatially over the boundary surfaces and temporarily over the period of full-fire development.
- The average temperature of the compartment gases, T averaged temporarily and spatially over the compartment volume.
Summary

- The growth and development of a fire has been shown to be dependent to a large extent on the geometry and ventilation of the enclosure containing the fire.
- Friedman reported the differences observed between fires burning in the open and those burning in enclosures.
- Flashover has been defined as the rapid involvement of a compartment’s combustible contents as they ignite almost simultaneously. Unfortunately such a definition tends to regard flashover as an event.
- In the ventilation controlled regime, it is assumed that the rate of burning (R) i.e., the rate of mass loss is strictly controlled by the rate of ingress of air. The underlying assumption is that the rate of air supply is exactly sufficient to burn all the volatiles which are produced at the rate R.
- The factors which generally determine the need for compartmentation are the floor area and the cubic capacity of the spaces under consideration.
- Segregation of the risk elements of areas requires a hazard analysis study. The risks of potential threats to the building and its occupants are identified and classified.
- The term, fire load is used to describe the heat energy which could be released per square metre of floor area of a compartment or storey by the combustion of the contents of the building and any combustible parts of the superstructure itself.
- Fire severity may be simply defined as the destructive potential of a compartment fire i.e., the potential impact that a fire in a given compartment will have upon the structural and constructional components, which form the compartment and the contents of the compartment.
- Fire severity has been linked with structural performance in terms of a component’s fire-resisting capabilities.

References


Recommended Reading

Self Assessment

1. A fire usually starts because its material is ignited by a _________ source.
   a. heat
   b. energy
   c. freezing
   d. ignition

2. ___________ has been defined as the rapid involvement of a compartment’s combustible contents as they ignite almost simultaneously.
   a. $Q_b$
   b. Flashover
   c. Fire loading
   d. Heat transfer

3. Which of the following statement is true?
   a. The Fire may burn very slowly because of a unrestricted oxygen supply, e.g. in a well-sealed compartment the fire may eventually smother itself.
   b. The Fire may burn very quickly because of a restricted oxygen supply, e.g. in a well-sealed compartment the fire may eventually smother itself.
   c. The Fire may burn very slowly because of a restricted oxygen supply, e.g. in a well-sealed compartment the fire may eventually smother itself.
   d. The Fuel may burn very slowly because of heat supply, e.g. in a well-sealed compartment the fire may eventually smother itself.

4. Which of the following statement is true?
   a. Flashover is used as the demarcation point between the two stages of a compartment fire, i.e. pre-flashover and post-flashover.
   b. Fire loading is used as the demarcation point between the two stages of a compartment fire, i.e. pre-flashover and post-flashover.
   c. Flashover is used as the demarcation point for one stage of a compartment fire, i.e. pre-flashover.
   d. Flashover is not used as the demarcation point between the two stages of a compartment fire, i.e. pre-flashover and post-flashover.

5. Which is the quantity of heat lost by replacing hot gases by cold air?
   a. $Q_B$
   b. $Q_E$
   c. $V_m$
   d. $Q_L$

6. ___________ is the net heat lost by radiation through openings in the enclosure walls to the external environment.
   a. $Q_B$
   b. $Q_E$
   c. $V_m$
   d. $Q_L$
7. It is transfer of heat through the material from a high temperature zone to a lower temperature zone
   a. Convection
   b. Radiation
   c. Conduction
   d. Heating

8. Which of the following statement is false?
   a. Fire severity has been linked with structural performance in terms of a component’s fire-resisting capabilities.
   b. The burning rate and temperature depend to a small extent on the thermal properties of the ceiling and wall material.
   c. Fire severity may be simply defined as the destructive potential of a compartment fire.
   d. The burning rate and temperature depend to a small extent on the thermal properties of the candle and flame.

9. Fujita and Kawagoe recognised that the flow of _______ into a compartment was an important factor in the severity of fully-developed fires.
   a. heat
   b. air
   c. gas
   d. flame

10. The formula to find \( Q_e \) is?
    a. \( Q_e = A_e \times \frac{d\theta}{dx} \)
    b. \( Q_e = Mout \times \frac{d\theta}{dx} \)
    c. \( Q_e = A_e \times \frac{d\theta}{dx} \)
    d. \( Q_e = A_e \times (T_g - T_o) \)
Chapter III

Energy Release Rates

Aim

The aim of the chapter is to:

- explore the factors controlling energy release rates in enclosure fires
- explain the enclosure effects
- elucidate burning rate and energy release rate

Objectives

The objectives of this chapter are to:

- explain the r-squared fire
- analyse the measurement techniques and parameters measured
- examine the design fire

Learning outcome

At the end of this chapter, you will be able to:

- understand simple and complex design fire
- describe the pool fires
- recognise energy release rates based on free burn measurements
3.1 Introduction

Energy release rate (often termed heat release rate or HRR) is measured in Watts, kilowatts or Mega Watts. The table below shows some characteristic values of energy released by various burning fuel packages and heat output from various sources.

<table>
<thead>
<tr>
<th>Source</th>
<th>Energy released</th>
</tr>
</thead>
<tbody>
<tr>
<td>A burning cigarette</td>
<td>5W</td>
</tr>
<tr>
<td>A typical light bulb</td>
<td>60W</td>
</tr>
<tr>
<td>A human being at normal exertion</td>
<td>100W</td>
</tr>
<tr>
<td>A burning wastepaper basket</td>
<td>100kW</td>
</tr>
<tr>
<td>A burning 1 m$^2$ pool of gasoline</td>
<td>2.5MW</td>
</tr>
<tr>
<td>Burning wood pallets, stacked to a height of 3 m</td>
<td>7MW</td>
</tr>
<tr>
<td>Burning polystyrene jars, in cartons, 2 m, 4.9 m high</td>
<td>30-40 MW</td>
</tr>
<tr>
<td>Output from a typical reactor at a Nuclear Power Plant</td>
<td>500-1000MW</td>
</tr>
</tbody>
</table>

Table 3.1 Rough measure of energy released from various sources

- Fire development is generally characterised in terms of energy release rate versus time. Once an engineer has arrived at such a relationship for a certain scenario, the energy release rate versus time relationship is termed as the “design fire”. Table 3.1 indicates that for many design purposes, the design fire energy output could be in the range 10 kW to 50 MW.

- There are basically two approaches available when determining the design fire for a given scenario. One is based on the knowledge of the amount and type of combustible materials in the compartment of fire origin. The other is based on the knowledge of the type of occupancy, where very little is known about the details of the fire load.

- In the first mentioned case, an object is assumed to ignite and start to burn. Then resulting energy release rate vs. time can in many cases be estimated using data from previous experiments, where energy release rate has been measured.

- However, in many design situations there is very little information available on the combustible content of the room of fire origin. In this case, knowledge of the type of occupancy, any available statistics and engineering judgment must be used to arrive at a design fire.

3.2 Factors Controlling Energy Release Rates in Enclosure Fires

The rate at which energy is released in a fire is mainly dependent on the type, quantity and orientation of fuel and on the effects that an enclosure may have on the energy release rate.

The energy release rate will vary with time. Fig. 3.1 shows a schematic graph of the energy release rate versus time measured when .2 m by 1.2 m wood pallets, stacked to different heights are burnt. Such measurements are often termed “free burn” tests, indicating that the items are burning without any effects of the enclosure in which the fire takes place.
3.2.1 Burning Rate and Energy Release Rate

- Burning rate is the mass rate of solid or liquid fuel vaporised and burned. It is expressed as mass flow per unit time, typically in kg/s or g/s and is denoted as \( m \). It can also be expressed as mass flux; burning rate per unit area, typically in kg/(m \( \times \) s). In this case it is denoted as \( m'' \).
- A general predictive formula for steady burning mass flux is given by:
  \[
  m'' = \frac{q''}{\Delta H_g} \quad (3.1)
  \]
- Where \( q'' \) is the net heat flux from the flame to the fuel and used to release the volatiles and \( H \) is called the heat of gasification.
- The net heat flux from the flame to the fuel is typically measured in kW/m. The heat of gasification is a measure of how much energy is needed to gasify some unit mass of the fuel and is typically given in kJ/kg. For liquid fuels this is the same as the heat of evaporation; the energy needed to evaporate the liquid once it has reached its boiling point.
- The heat of gasification is not a constant property for solids but is a fundamental property for liquid fuels. Because of the difficulty in quantitatively determining the net heat flux to the fuel surface, equation (3.1) is seldom used in practice and generally we need experimental results to estimate the burning rate.

3.2.2 Enclosure Effects

- When an item burns inside an enclosure, mainly two factors will influence the energy released and the burning rate. Firstly, hot gases will collect at the ceiling level and heat the ceiling and the walls. These surfaces and the hot gas layer will radiate heat towards the fuel surface, thus enhancing the burning rate.
- Secondly, the enclosure vents (doors, windows, leakage areas) may restrict the availability of oxygen needed for combustion. This causes a decrease in the amount of fuel burnt, leading to a decrease in the energy release rate and an increase in the concentration of unburnt gases.
- Fig. 3.2 shows a schematic diagram of an arbitrary item burning. One curve shows the burning rate when the object is burning in the open (free burn).
- The other curve shows the effect of burning the item in an enclosure (with an opening), where the hot surface and gases transfer heat to the fuel bed, thus increasing the burning rate (compared to the somewhat slower burning rate expected from a free burn experiment).
- If, however, the opening is relatively small, the limited availability of oxygen will cause incomplete combustion, resulting in a decrease in the energy release rate which in turn causes lower gas temperatures and less heat transfer to the fuel.
- The fuel will continue to release volatile gases at a similar or somewhat lower rate. Only a part of the gases combust, releasing energy, and the unburnt gases are collected at the ceiling level. The unburnt gases can release energy when flowing out through an opening and mix with oxygen, causing flames to appear at the opening.
- To sum up, compartment heat transfer can increase the mass loss rate of the fuel, while compartment vitiation of the available air near the floor will decrease the mass loss rate.
3.3 Energy Release Rates Based on Free Burn Measurements

The only practical way to determine the burning rate or energy release rate of an item is by direct measurement. Such measurements are termed free burn measurements, meaning that the enclosure effects are minimised; the hot gases are vented away from the fuel and there is no limitation on air supply to the fuel. Engineers can use these results as guidelines when determining the design fire for a certain scenario. In case of liquid fuels, such measurements have resulted in expressions, allowing the energy release rate to be calculated if the liquid pool diameter is known. Below, we shall briefly discuss the most common measurement techniques, methods for calculating energy release rates from pool fires and show experimentally determined energy release rate curves for various residential and industrial items.

3.3.1 Measurement Techniques and Parameters Measured

- Energy release rate: The most common method to measure energy release rate is known as oxygen consumption calorimetric.
- The basis of this method is that for most gases, liquids and solids, a more or less constant amount of energy is released per unit mass of oxygen consumed. This constant has been found to be 13100 kJ per kilogram oxygen consumed and is considered to be accurate with very few exceptions to about 5 percent for many hydrocarbon materials.
- A schematic diagram of an oxygen consumption calorimeter is shown in fig. 3.3.
- After ignition, all the combustion products are collected in a hood and removed through an exhaust duct. The flow rate and the composition of the gases are measured in the duct. This gives a measure of how much oxygen has been used for combustion. Using the above constant, the energy release rate can be computed.
3.3.2 Pool Fires

- Accidental spills of liquid fuels in industrial process and power plant systems can pose a serious fire hazard.
- Some liquids are highly volatile at ambient temperatures and can evaporate and form a flammable mixture with air leading to a possible explosion in a confined space.
- Other liquids have a high flashpoint and require localised heating to achieve ignition.
- Once ignited, however, very rapid flame spread will occur over the liquid spill surface. In a free burn condition, the burning rate will quickly reach a constant value, depending on the diameter of the spill.

Diameter dependence: Fairly extensive pool fire experiments have been carried out for a wide range of liquids. It has been found that, for diameters larger than 0.2 m, the burning rate increases with the diameter up to a certain value, which we shall call the asymptotic diameter mass loss rate, denoted \( m^* \), usually given in kg/(m s).

3.3.3 Various Products

- Most products and solid materials, however, exhibit a varying burning rate with time. Starting at ignition, the burning rate typically increases to a maximum value and then decreases until most of the combustible material is burnt.
- For a majority of the products, the burning can in most instances be divided into the stages of ignition, growth and decay.
- In this section we shall display some typical energy release rate results from free burn tests of various products and commodities.
- These can be used by the engineer as benchmarks or guidelines but cannot be used as precise estimates because there can be wide variations within a given item class. Also, the mode of ignition in each case will have some influence on the initial fire growth in time.

**Wood pallets**

A fairly common fuel source at industrial locations is a stack of wood pallets. Fig. 3.4 shows energy release rate versus time of a typical pallet stack with a height of 1.22 m, burning in the open. Each pallet is 1.22 m by 1.22 m and is 0.14 m high, so the stack in fig. 3.4 consists of roughly 9 pallets stacked on top of each other.

![Fig. 3.4 Typical energy release rate from a wood pallet stack](image)

Further experiments have shown that the peak energy release rate increases with the stack height, as can be seen in the figure given below. Fig. 3.1 also gave examples of wood pallets burning at different stack heights.
Fig. 3.5 Dependence of the pallet stack height on the peak energy release rate

Upholstered furniture and mattresses
A significant amount of data on energy release rate from upholstered furniture is available in the literature. Fig. 3.6 shows the energy release rate of a typical upholstered sofa, a two-seat sofa (loveseat) and an upholstered chair. Fig. 3.7 shows similar results for typical mattresses.
Various other items
The figure given below shows the energy release rates for trash bags of various weights. Fig. 3.9 shows the results from two experiments with television sets and fig. 3.10 shows results from three experiments with Christmas trees.

Fig. 3.8 Energy release rates for trash bags

Fig. 3.9 Energy release rates from two experiments with television sets

Fig. 3.10 Energy release rates from three experiments with Christmas trees
3.3.4 The T-squared Fire

In real fires, the initial growth period nearly always accelerates. A simple way to describe the accelerating growth is to assume that the energy release rate increases as the square of the time. By multiplying time squared by a factor \( \alpha \), various growth velocities can be simulated and the energy release rate as a function of time could be expressed as

\[
Q = \alpha t^2
\]

Where \( \alpha \) is a growth factor (often given in the units kW/s) and \( t \) is the time from established ignition, in seconds.

This relationship has been found to fit well with the growth rates exhibited by various different commodities, but only after ignition has been well established and the fire has started to grow. This starting time, denoted \( t \), both depends on the commodity in question and the manner in which it is ignited and is generally taken to be the time from ignition until flaming occurs, when significant energy begins to be released.

3.4 The Design Fire

- Building fire regulations commonly require two main objectives to be met; life safety of the occupants and; structural stability of the building. Two distinctly different design procedures are applied in each case.
- In case of structural stability, the objective is to protect property and ensure that fire fighters can gain entry to the building without the risk of a structural collapse. Here, the time-frame is relatively long (often 0.5 - 3 hours), the fire is assumed to have caused flashover and the design fire is usually given as a temperature/time curve.
- In case where the objective is to facilitate escape for the occupants, the time-frame is usually relatively short (most often less than 30 minutes) and the design fire is specified as energy release rate versus time. It is this case which we have seen and will be concentrating on in this textbook.
- When an engineer is to design a beam, the design load must be chosen. The beam cannot be designed for all possible load combinations which can occur during the building life span. Similarly, when designing for fire safety, the purpose of the design is not to simulate accurately all possible fires which could occur in the building. The engineer must first decide upon how much material can be expected to burn and how rapidly it will burn, and thus arrive at a design fire.
- The purpose of the design work is mainly to help the engineer form an opinion of the possible consequences and establish a basis for appraising the risks due to a building fire. The engineer can then compare the effectiveness of different safety measures. For example, investigate how smoke ventilation through the roof would compare with installing early warning devices with regards to allowing means of escape to the occupants.
- Exact methodology or procedure is available to the engineer to define the design fire. The engineer must use all available information on the building contents and the building type and use his engineering judgement to arrive at a design fire.
- The engineer can then perform a simple sensitivity analysis by changing the design fire to check the reliability of the design solution. An example of the simplest way to construct a design fire curve is given in fig 3.11 below.

\[
\begin{align*}
\dot{Q} &= \alpha t^2 \\
\dot{Q} &= \dot{Q} \text{ max}
\end{align*}
\]

![Fig. 3.11 A simple design fire curve](image)

The curve is divided into the growth phase, the steady phase and the decay phase. We shall, in the following, examine crude ways in which the engineer can estimate the duration and magnitude of these phases.
3.4.1 The Growth Phase

- In real fires, the initial fire development is nearly always accelerating. A suitable way to describe this mathematically is to use the $t_f$ fire described.
- The choice of the growth rate (the choice of the factor) depends on how much is known about the building contents and the building type.
- If considerable knowledge of the building contents is available, a suitable ignition scenario can be assumed and experimental data on materials can be used to determine the growth rate factor.
- In many instances, there is very scarce information available on the building contents and the engineer must make use of information on the building type. There is currently considerable ongoing activity on this. As an example, Table 3.2 gives the growth rates that have been suggested as recommendations in Swedish occupancies (not approved yet).

<table>
<thead>
<tr>
<th>Types of occupancy</th>
<th>Growth rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dwellings</td>
<td>Medium</td>
</tr>
<tr>
<td>Hotels, Nursing homes, etc.</td>
<td>Fast</td>
</tr>
<tr>
<td>Shopping centres, entertainment centres</td>
<td>Ultra fast</td>
</tr>
<tr>
<td>Schools. Offices</td>
<td>Fast</td>
</tr>
<tr>
<td>Hazardous industries</td>
<td>Not specified</td>
</tr>
</tbody>
</table>

Table 3.2 Typical growth recommended for various types of occupancies

- Note that these values are only suggested; the designer must use engineering judgment and carry out a sensitivity analysis to check the reliability of the design solution.
- It should also be noted that the initial ignition time, before the fire starts the growth phase, has not been taken into account here.
- The fire is assumed to start growing at zero time. In all instances there is a shorter or longer time to ignition, where little energy is being evolved but the smouldering fuel may produce smoke that can trigger off detection devices, even before the growth phase starts.
- This ignition phase should be taken into account for the final design solution.

3.4.2 The Steady Phase

- The growth phase of the fire can either lead to a stage where the fuel reaches a maximum burning rate (where the fire is termed fuel-bed controlled) or will lead to a stage where there is insufficient oxygen for continued combustion (where the fire is termed ventilation-controlled). In the latter case, this may lead to flashover, where excess fuel is combusted in an adjacent room or in the openings leading to the outside.
- In both cases, some assumption on the fuel must be made in order to estimate both the magnitude $Q$ and the duration $t$, of the steady phase. Where there is max considerable knowledge of the building contents, the experimental results discussed in Section 3.3 can be used directly.
- If such information is not available, some assumptions on the scenario at hand must be made to arrive at values for both. $Q$ can be assessed by considering the amount of air available for max combustion.
Any excess fuel will burn in the outside air and will not influence conditions in the fire compartment. In most cases, however, the fire compartment has openings to adjacent rooms and there may be excess fuel may be there, thus influencing the environmental conditions in the building. It is therefore essential to base the steady phase of the design fire on the amount and type of fuel, and not solely on the availability of oxygen.

3.4.3 The Decay Phase
In most practical design situations, the first 10 - 30 minutes are of interest when the objective is to ensure human safety and escape, since the fire brigade is assumed to start their rescue and fire fighting operations within that time interval.

The steady phase is therefore most often assumed to continue and no decay phase is specified.

If, however, considerable knowledge is available on the building contents, and only a limited amount of fuel can be burnt, some assumptions of the decay phase can be made. The engineer must then rely on experimental data (such as given in Section 3.3) to assess when, and how rapidly, the energy release decreases.

3.4.4 A More Complex Design Fire

- When there is exact information on the material content of the fire compartment, a more realistic design fire curve can be constructed. This requires that a number of material parameters for the fuel packages are known, that their relative positions in the compartment as well as the mode of ignition are known.
- Fig. 3.12 gives a schematic example of such a design fire where one of the fuel packages is ignited, burns and causes ignition of the other fuel package.
- The energy release rate from the first fuel package can be estimated using experimental results. Once the energy release rate from this fuel package is known, the resulting flame height can be calculated. Thus, the first fuel package is ignited at time $t_0$ and reaches steady burning at time $t_1$.
- The second fuel package ignites at time $t_2$, reaches steady burning at time $t_3$. At time $t_4$ the first fuel package reaches the decay period and at time $t_5$ only the second fuel package is burning.

It should be noted that the above procedure will only give very rough estimates and that very detailed information on the fuel packages and room geometry are required.
Summary

- Energy release rate (often termed heat release rate or HRR) is measured in Watts, kilowatts or Mega Watts.
- There are basically two approaches available when determining the design fire for a given scenario. One is based on the knowledge of the amount and type of combustible materials in the compartment of fire origin. The other is based on the knowledge of the type of occupancy, where very little is known about the details of the fire load.
- The rate at which energy is released in a fire is mainly dependent on the type, quantity and orientation of fuel and on the effects that an enclosure may have on the energy release rate.
- Burning rate is the mass rate of solid or liquid fuel vaporised and burned. It is expressed as mass flow per unit time, typically in kg/s or g/s and is denoted as m.
- Burning rate can also be expressed as mass flux; burning rate per unit area, typically in kg/(m s). In this case it is denoted as m".
- The only practical way to determine the burning rate or energy release rate of an item is by direct measurement.
- Energy release rate: The most common method to measure energy release rate is known as oxygen consumption calorimetric.
- Accidental spills of liquid fuels in industrial process and power plant systems can pose a serious fire hazard.
- A fairly common fuel source at industrial locations is a stack of wood pallets.
- Building fire regulations commonly require two main objectives to be met; life safety of the occupants and structural stability of the building.

References


Recommended Reading

Self Assessment

1. Which of the following statement is true?
   a. Fire development is generally characterised in terms of energy release rate versus time.
   b. Fire development is generally characterised in terms of gas release rate versus time.
   c. Explosion development is generally characterised in terms of energy release rate versus air.
   d. Fire development is generally characterised in terms of air release rate versus time.

2. _______ rate is the mass rate of solid or liquid fuel vaporised and burned.
   a. Flashover
   b. Melting
   c. Evaporating
   d. Burning

3. The only practical way to determine the burning rate or energy release rate of an item is by _______ measurement.
   a. indirect
   b. direct
   c. fire
   d. explosion

4. Which of the following statement is false?
   a. The rate at which energy is released in a fire is mainly dependent on the type, quantity and orientation of fuel and on the effects that an enclosure may have on the energy release rate.
   b. The energy release rate will vary with time.
   c. Accidental spills of liquid fuels in industrial process and power plant systems can pose a serious fire hazard.
   d. The energy release rate will not vary with time.

5. Which is the most common method to measure energy release rate?
   a. Direct method
   b. Indirect method
   c. Oxygen consumption calorimetric
   d. Pool fires

6. Building fire _______ commonly require two main objectives to be met; life safety of the occupants and structural stability of the building.
   a. regulations
   b. pools
   c. fumes
   d. explosion

7. In real fires, the initial fire development is nearly always _______.
   a. declining
   b. heating
   c. accelerating
   d. extinguishing
8. Which of the following statement is true?
   a. When an item burns inside an enclosure, mainly three factors will influence the energy released and the burning rate.
   b. When an item burns inside an enclosure, mainly two factors will influence the energy released and the burning rate.
   c. When an item burns inside an enclosure, mainly one factor will influence the energy released and the burning rate.
   d. When an item burns outside an enclosure, mainly two factors will influence the energy released and the burning rate.

9. The flow rate and the __________ of the gases are measured in the duct.
   a. intensity
   b. decomposition
   c. composition
   d. value

10. Which of the following is expressed as mass flow per unit time, typically in kg/s or g/s and is denoted as \( m \)?
    a. Burning time
    b. Burning rate
    c. Decomposition
    d. Flame
Chapter IV
Fire Ball, Fire Plumes and Flame Heights

Aim
The aim of the chapter is to:

• explore the flame characteristics
• elucidate fireball radius and duration
• examine the ideal plume

Objectives
The objectives of this chapter are to:

• explain intensity and fraction of energy radiated
• explain the nature of fire balls from BLEVEs
• analyse the single-step rapid BLEVE

Learning outcome
At the end of this chapter, you will be able to:

• identify the turbulent fire plume characteristics
• explain Transient Jet release
• recognise the power of fireball
4.1 Quantification of Hazards due to the Fire Ball

This helps in understanding hazards due to the flammable substances in storage tanks or process equipment. The steps involved in the calculation of the fire ball are:

- fire ball radius
- fire ball duration
- power of the fire ball
- power density
- intensity and fraction of radiations emitted
- energy received at a distance
- energy intensity received at a distance
- attenuation due to absorption in the atmosphere
- fatality caused by thermal radiations: Probit equation

4.2 Radius and Duration

It has been observed that only tonnage quantities of a spill are capable of causing fireballs. Further, whether a liquefied flammable gas spillage will cause a pool fire or a fireball, is decided by the criterion that if the TAFF (Theoretical Adiabatic Flashing Fraction) is = 0.35, a fireball will result.

The duration of the fireball has been found to be only a few seconds and during this time its size as well as height above the ground also changes. This rapidly changes the thermal radiation field with time.

The radius for the fireball is given by

\[ R = 27.5 M^{1/3} \]

And the duration

\[ t = 3.8 M^{1/3} \]

Where,

- \( M \) = mass of the hydrocarbon in the fireball, tonnes
- \( R \) = radius of the fireball, m
- \( t \) = duration, s (from ignition to ceasing of thermal radiations)

Not all the spilled liquid enters a fireball unless the TAFF is very high and any unflashed liquid hydrocarbon is evaporated fast, e.g. if it is summer time or if it is spilled on water (since the ground would soon cool down while warm water keeps replacing the cool water).

4.3 Power of the Fire Ball

We will now calculate the power or the heat intensity and damage or injury potential of a fire ball. This needs the values of heat of combustion and the adiabatic flame temperature. From tables of such values, Marshall [1] has taken representative values as 47 MJ/kg.

\[ (47 \times 10^9 J/T) \text{heat of combustion and 2300 K as the adiabatic flame temperature.} \]

The power (heat released per unit time) is given by the total heat released divided by the duration of the fire ball:

\[ P_{FB} = 47 \times 10^9 M / 3.8 \times M^{1/3} \]

\[ P_{FB} = 47 \times 10^9 M^{2/3} / 3.8 \]

Where, \( M \) = mass of hydrocarbon in fire ball, in tonnes

\( P \) = power of fireball, W/m
4.4 Power Density

Power density, power per unit volume, of the fire ball is

\[ P_{D^*} = \text{W/m}^3 \]

(This is proportional to the burn up rate per unit volume since the heat released is a linear function of the mass reacted.)

It gives the burn up rate as inversely proportional to the cube root of the mass in the fireball though the total power release increases directly to 2/3rd power of the mass.

4.5 Intensity and Fraction of Energy Radiated

The heat released in combustion is used up in two ways. They are as follows:

- Radiation
- sensible heat of combustion products and unreacted components

Radiation is the one that is of concern outside the envelope of the fire ball. The radiations are taken to emanate from the surface of the fire ball. The intensity at the surface is where

\[ I_s = \frac{P_{FB}}{4\pi R_{FB}^2} \]

Where, \( I_s \) = intensity of radiation at the surface, W/m

\( P_{FB} \) = Power of the fire ball, W

\( F_R \) = Fraction of energy radiated

\( R_{FB} \) = Radius of fire ball, m

4.6 Energy Received at a Distance

Energy received, \( E_R \) at distance \( R_c \) oriented at 90, is

\[ E_R = \frac{E_{E_T}}{1.22} \]

(E_{E_T} = Energy per tonne)

Or, distance for a particular amount of energy received is

\[ R_T = 3.35 \times 10^4 E_R^{-0.5} M^{0.5} \]

Thus, if we know the amount of energy that will cause harm to people/structures/ combustibles, we can determine the radius or the area in which such harm will occur and thus attempt to move such things away.

4.7 Energy Intensity at a Distance

Energy intensity, \( I_T \) at R

\[ I_T = \frac{E_R}{R^2} \text{W/m}^2 \]

Given \( R_{FB} = 27.5 \text{ M}^{1/3} \), substituting for M gives

\[ I_T = 1.3 \times 10^{62}, \text{ independent of } M \]

Distance for a specific intensity, \( I_T \) is

\[ R_T = 1.14 \times 10^3 R_{FB} \]

Thus, if we know the harmful potential of different energy intensities, we can determine the radius or the area in which it would occur.

4.8 Attenuation due to Absorption in the Atmosphere

Heat radiations are attenuated (reduced in intensity) as they pass through the atmosphere due to absorption by CO2, water vapour, etc. and scattering by dust particles (At the fire temperature, only the triatomic gases affect, and not diatomics O, N, etc. or monatomics Ar, Kr, etc.). The equation for energy received, \( E \), should be modified to

\[ E_{AR} = \]
Thus, more the distance the radiations have to travel, the more the attenuation. It varies with relative humidity (RH). In this equation, RH=0.2 has been assumed. Replace 1 by .96 for RH = 0.5, and by 0.92 for RH = 1.0. The various equations are summarised in Table (4.1).

4.8.1 Fatality Caused by Thermal Radiation: Probit Equation

Since intensity \( I_T \) below a certain level will not affect a person, no matter what the length of the exposure time (similar to TLV in toxicology) is, the simple formula \( L_{FB} \times D_{FB} \) will not do (\( D_{FB} \) is the duration of the fire ball). It has been proposed to take \( D_{FB} \) a measure and the Probit equation is given as:

\[
\text{Probit} = -14.9 + 2.56 \ln (D_{FB} \times 10^{-4})
\]

\( IT = J/m^2s \)

For first degree burns, the criterion is

\( D_{FB} = 5.5 \times 10^5 \)

The intensity received would reduce if attenuation is taken into account.

4.9 Effects of Thermal Radiations on the Skin

- Suitably clothed, the body can operate at extremes of temperatures like -90°C in Antarctica or +58°C in some other parts of the world. Without proper clothing, only a narrow temperature range can be tolerated.
- In fire, people may burn and die or they may die due to asphyxiation or inhalation of CO and poisonous fumes. Also, inhalation of very hot gases burns the air passages and destroys the alveoli in the lungs.
- For each death from thermal injury (at the work place or home), 20 are hospitalised for 5-6 weeks and 200 seek treatment in the casualty departments of hospitals.
- The skin can take up to 42°C. Bathing water is approximately 36°-42°C. Hot water at 70°C causes a complete loss of skin thickness in 10 seconds (the skin has cooling mechanisms too namely: blood circulation, sweating).
- The skin is made up of the epidermis, dermis and subcutaneous tissues.
- Mild radiations affect the epidermis (1 mm thick).
- Intense radiations affect the epidermis + dermis (2 mm thick).
- Most intense radiations affect the epidermis + dermis + subcutaneous tissues.
- For 3 and 2 degree burns, the following equations can be used for probable (most likely) and maximum distances:

\( 3^{rd} \) degree burns
- Probable distance = 80M\(^{0.42}\),m
- Maximum distance = 130 M\(^{0.42}\),m

\( 2^{nd} \) degree burns
- Probable distance = 120 M\(^{0.42}\),m
- Maximum distance = 130 M\(^{0.42}\),m

Where, \( M \) is the mass of the flammables in the fire ball, tonnes.

Because of the nature of the situation where experiments are difficult to conduct and the results are dependent on numerous parameters (type of flammables, amount, meteorological conditions, nearby buildings, relative humidity, dust in air, etc.), it is difficult to predict more exact values for effects.

4.10 Two-step Slow BLEVE

- In this case, there is a significant time between when the original fissure opens and when the tank fails catastrophically.
- First a small whole forms in the vapour space wall and this leads to a pressure drop which then causes a liquid boiling response that causes pressure recovery in the tank. This pressure recovery drives the crack along the length of the tank to cause a total loss of containment and BLEVE. In this case the crack velocity may be as low as 1 m/s.
4.11 Single-step Rapid BLEVE

- Let us take the example BLEVE of a 400 litre propane tank (non-ASME code) exposed to torch fire impingement from above. In this case, the tank has a 3 mm wall rather than the 6 mm needed to be an ASME code tank.
- This tank failed so rapidly that, the liquid flashing had little or no role in the tank failure. In other words, the vapour energy was sufficient to drive the failure crack the full length of the tank. In this case the crack velocity was of the order of 150 m/s.

4.12 Transient Jet Release

- If the tank has not been weakened sufficiently, then a BLEVE does not take place after thermal rupture is initiated. In this case the fissure does not run the entire tank length but is arrested in strong material.
- In this case the tank contents vent as a two-phase transient jet. If the hole is large (i.e., the hole length is of the order of the tank diameter), then the release looks very much like a BLEVE.

4.13 Fire Balls from BLEVEs

- The shapes and liftoffs of BLEVE fire balls vary significantly and depend on the detailed thermodynamic state of the liquid, and the details of tank failure. If the tank fails rapidly, then classical spherical fire balls result.
- If the failure is slow then the initial jet release sends the fire ball high into the air. If the liquid is relatively cool, then a large ground fire is possible. These differences can change the hazards to nearby objects (such as emergency responders) significantly.

4.14 Flame Characteristics

In most fire safety engineering applications, we are concerned with the so-called buoyant, turbulent diffusion flame. We shall discuss here some of the processes that characterise such flames. We will show the results from flame, height measurements and finally, give correlation equations that can be used for estimating flame heights.

**Diffusion**

- Diffusion flames refer to the case where fuel and oxygen are initially separated and mix through the process of diffusion.
- Burning and flaming occurs where the concentration of the mixture is favourable to combustion. Although the fuel and the oxidant may come together through turbulent mixing, the underlying mechanism is molecular diffusion.
- This is the process in which molecules are transported from a high to low concentration. Also opposed to this is the pre-mixed flame, as is the case with a welder’s torch, where the fuel and the oxidant are mixed before ignition.
- Flames in accidental fires are nearly always characterised as diffusion flames.

**Buoyancy**

- When a mass of hot gases is surrounded by colder gases, the hotter and less dense mass will rise upwards due to the density difference, or rather, due to buoyancy.
- The upward velocity of the flow within a flame will be dominated by the buoyancy force, if the velocity at which the fuel is injected is very low relative to the fuel source area.
- The buoyancy dominated flames are exactly opposite to the flows formed above a high-pressure gaseous fuel source (for example a ruptured pipeline under high pressure) where the flow is not buoyancy dominated, but momentum dominated; these are termed jet flames.
Turbulence

- Very small diffusion flames can be laminar, such as the flame on a candle. Larger diffusion flames are turbulent and will fluctuate with periodic oscillations with large eddies shedding at the flame edge (See fig. 4.1).
- The eddies, which are visible in all turbulent buoyant plumes, roll up along the outside of the plume and are caused due to the instability between the hot flame and the cold air.

![Fig. 4.1 Flame fluctuations due to periodic eddy shedding](image)

These random fluctuations, which are characteristic of turbulence, will give rise to periodic flame height (and shape) fluctuations. The fluctuations normally have a frequency of the order of 1-3 Hz i.e., will occur three times per second, in general this shedding depends on the fire diameter. Fig. 4.2 shows a characteristic sketch of this phenomenon where, \( L \) is the visible flame height as a function of time.

![Fig. 4.2 A characteristic sketch of flame height fluctuations](image)

In our treatment we shall only considered mean time results i.e., we shall be considering the mean flame height, denoted by \( L \), given in [m].

**Definition of the mean flame height**

In order to provide engineering equations to allow calculation of the flame height, we must first define the mean flame height. Averaging the visible flame height over time, most conveniently does this. The luminosity of the lower part of the flaming region appears fairly steady. The upper part fluctuates, or in other words, is intermittent. Fig. 4.3 is generally used to define the mean flame height.

![Fig. 4.3 Definition from mean flame height](image)
• The intermittency, denoted by I, is shown on the vertical axis, where a value of 1 indicates the appearance of a flame at all times. The horizontal axis shows the distance above the fire source, z. The height at which the intermittency is 0.5 i.e., the height at which the flame appears half the time, is defined as the mean flame height, L.

• The experimental procedures for measuring flame heights usually involve video equipment. The data achieved is fairly consistent with flame heights that are averaged by the human eye.

Flame height correlations

• Due to the turbulent nature of the flames, we cannot provide engineering equations for flame heights which are derived from the first principles. We must therefore investigate which properties influence the flame height and use experimental data to express the flame height in terms of the dominating properties.

• The non-dimensional Froude number, denoted Fr, is used in hydraulics when describing fluid flows

\[ Fr = \frac{u}{\sqrt{gD}} \]

where \( u \) is the flow velocity, \( g \) is the acceleration due to gravity and \( D \) is diameter of the flow source. The numerator is in proportion to the momentum and the denominator in proportion to the gravity or buoyancy.

• The Froude number can be expressed in terms of the energy release rate by noting that \( \dot{Q} = m\dot{H}_c \), where \( m \) is the burning rate and \( \dot{H}_c \) is the heat of combustion. Further, the burning rate can be expressed as \( m = upA \) where \( u \) is the velocity of the gas, \( p \) is the density of the gas and \( A \) is the area of the fuel source (directly related to \( D^2 \)).

• Dimensionally, the relationship between the Froude number, the energy release rate and the diameter of the source can therefore be said to be of the form

\[ Fr \propto \frac{\dot{Q}^2}{D^5} \]

The geometry of turbulent diffusion flames have been found to scale with the square root of the Froude number. Representing the flame geometry as the flame height normalised by the source diameter, \( L/D \), we can write:

\[ \sqrt{Fr} \propto \frac{L}{D} \propto \frac{\dot{Q}^2}{D^5} \times \frac{\dot{Q}}{D^{5/2}} \]

A vast number of experiments have been carried out, relating flame heights to the energy release rate and source diameter. Experimenters have found it convenient to express the data in terms of a non-dimensional energy rate, denoted \( Q^* \), and given by the expression,

\[ Q^* = \frac{\dot{Q}}{\rho_cC_pT_s\sqrt{gDD^2}} \]

where \( \rho_c, c \) and \( T_s \) refer to the properties of ambient air. This dimensionless energy release rate parameter, which can be said to represent the square root of the Froude number, has been found to be very important in controlling the geometry of fire plumes and we shall return to it in later sections. Rewriting Equation (1) as

\[ \dot{Q}^{42/5}D = \left( \frac{\dot{Q}}{\rho_cC_pT_s\sqrt{g}} \right)^{2/5} \]

we note that \( Q \) represents a dimensionless fire plume length scale.
From the above equations we see that we should be able to express flame heights as a function of the diameter and the energy release rate for a wide range of Froude numbers. Indeed, fig. 5.4 shows a representation of a great number of experimental results, where the mean flame height normalised by source diameter, \( L/D \), has been plotted against the dimensionless energy release rate \( Q^* \). Each line in the plot represents the results of separate experiments carried out by different investigators.

![Graph showing normalised flame height versus dimensionless energy release rate](image)

**Fig. 4.4 Normalised flame height versus dimensionless energy release rate**

The left side of the plot shows fires where the diameter is of the same order of magnitude as the flame height and the Froude number is low, indicating buoyancy dominated flows. The upper right hand corner represents the high Froude number, high momentum jet flame regime.

In most fire situations \( Q \) will be less than 10 and for most large fires less than 2. We are therefore mostly interested in the left hand side of fig. 4.4. Experimenters have found that the normalised mean flame height, \( L/D \), correlates well with \( Q \) over a wide range of values (roughly \( 1 < Q < 1000 \), as seen by the straight line in fig. 4.4). A great number of correlation equations for flame heights have been presented in the literature representing various regimes shown in fig. 4.4.

One of the most useful equations, presented by Heskestad, gives good results for the different regimes in fig. 4.4 except for the jet flame regime. The equation expresses the mean flame height divided by the diameter as

\[
\frac{L}{D} = 3.7 Q^{0.75} - 1.02
\]

This relationship maintains the 2/5 power of \( Q \) over the large intermediate regime while exhibiting an increasing slope at small \( Q \), as is seen in fig. 4.4. A more convenient form of Equation (2) gives the mean flame height as a function of energy release rate and diameter

\[
L = 0.235 Q^{0.25} - 1.02D
\]

Where the energy release rate is given in [kW] and the diameter given in [m], resulting in the mean flame height in [m].
4.15 Turbulent Fire Plume Characteristics

- Fire plumes can be characterised into various groups depending on the scenario under investigation.
- In this section we shall concentrate on the plume, most commonly used in fire safety engineering. The so-called buoyant axi-symmetric plume is caused by a diffusion flame formed above the burning fuel. An axis of symmetry is assumed to exist along the vertical centre line of the plume.
- Other plume categories include the various types of buoyant plumes formed when hot gases exit through an opening and entrain air as the hot gases rise.
- The axi-symmetric fire plume is conventionally divided into the three zones as shown in fig. 4.5.

Fig. 4.5 The three zones of the axi-symmetric buoyant plume

In the continuous flame zone the upward velocity is nearly zero at the base and increases with height. In the intermittent flame zone the velocity is relatively constant and in the far field zone, the velocity decreases with height. Fig. 4.6 shows some of the characteristics of a buoyant axi-symmetric plume.

Plume velocity
The highest velocity is at the centreline of the plume, as shown by the velocity profile in fig. 4.6. This centreline velocity, denoted \( u \), changes with height. The right hand side of fig. 4.6 shows that, the centreline velocity is close to zero at the fuel bed. The only mass flowing upwards at that height equals the mass loss rate of the fuel bed. The centreline velocity increases with height since more ambient air is entrained, which cools the plume and decreases the buoyancy force.
**Plume temperature**
- The highest temperature is at the plume centreline, decreasing towards the edge of the plume with a similar profile as the velocity profile.
- The centreline temperature denoted $T$, changes with height. It is roughly constant in the continuous flame region and represents mean flame temperature.
- The temperature decreases sharply above the flames as an increasing amount of ambient air is entrained into the plume. The symbol $\Delta T$ is used for the centreline plume temperature rising above the ambient temperature $T_0$. Thus, $T_0 = T_0 + \Delta T$.

**Plume mass flow rate**
- The mass flow rate in the plume, denoted by $m$, and most often given in kg/s, is the total mass flowing upwards, at a certain height, within the plume boundaries. The plume mass flow increases steadily with height since ambient air is continually entrained over the plume height.
- This mass consists of a mixture of combustion products and ambient air entrained into the plume, most of the mass stemming from the ambient air entrained and only a small portion stemming from the combustion products.
- For a burning wastebasket, with a total effect of around 100 kW, the plume mass flow rate is 2 m above and it is roughly 1 kg/s. At a height of 4 m, the plume mass flow rate is roughly 3 kg/s.
- The plume mass flow rate should not be confused with the mass burning rates released from the fuel bed. The above wastebasket would release fuel gases at roughly the rate of 0.005 kg/s. This is insignificant in relation to the mass plume rate of 1 kg/s at the height of 2 m.

**Plume radius**
- The point source plume radius, denoted $b$, spreads roughly with an angle of 15° to the vertical. This corresponds approximately to the point where the centreline temperature rise has declined to 0.5 $\Delta T$. Similar values are achieved when the plume radius is defined as the point where the centreline velocity has declined to 0.5 $u_0$.

**4.16 The Ideal Plume**
- In this section, we shall consider a very simple type of a fire plume, sometimes referred to as the ideal plume or the point-source plume. We shall set up the fundamental equations for continuity, momentum and buoyancy and thus arrive at analytical solutions for the mass flow, velocity and temperature of the gases in this simplified plume.
- The purpose is to facilitate an understanding of how plume equations are generally arrived at. Consider fig. 4.7. We assume the simple case of a point source of heat at height $z = 0$. The energy is considered to be totally transported in the plume and no radiative heat is emitted from the point source.
- The force driving the system can therefore be assumed to arise due to the density difference of the hot air above the point and the cold surrounding air. We shall further assume that the flow profile across the section of the plume, at any height, is a so called “top hat” profile.
- Therefore, the upward velocity is assumed to be constant across the width of the plume and zero outside it. The plume temperature is similarly assumed to be constant across any section of the plume. Note that in plume temperature and velocity were denoted by the symbols $T_0$ and $u_0$, the suffix “0” referring to the centreline axis. Since these properties here are assumed to be constant across the plume, we shall drop the suffix “0” in the symbols.
Here, $T$ and $P$ are the temperature and density of the surrounding ambient air, the upward velocity is denoted $u$, the temperature increase, above the ambient is denoted $T$, and the height above the point source is denoted $z$. We shall also assume that there is a relationship between the upward velocity in the plume and the horizontal entrainment velocity into the plume, $v$, such that $v = u$, which is called the entrainment coefficient.

### 4.16.1 Assumptions

To arrive at simple analytical solutions expressing the plume properties we must make many restricting assumptions. The main assumptions are:

- We assume that all the energy is injected at the point source of origin and that energy remains in the plume i.e., that there are no heat losses in the system due to radiative losses. In real fire plumes, the radiative part is typically 20% - 60% of the total energy released from many common fuel sources.

- We assume that the density variations throughout the plume height are small and only need to be considered when the difference $(p-p)$ appears directly. The ideal plume theory is therefore sometimes referred to as the weak plume theory, where, due to mixing (entrainment) of air, the plume temperature is only slightly higher than the ambient. At certain points in the derivation, we shall therefore assume $p-p$. However, when expressing the buoyancy force, which is caused by the density difference, $p-p$ assumption does not apply. This approximation is sometimes referred to as the business approximation. In practical terms this means that the equations cannot be used at heights close to the fire source but will give reasonable answers at heights further above the source.

- We assume that the velocity, temperature and force profiles are of similar form independent of the height, $z$. We further assume that these profiles are so called “top hat” profiles, so that the velocity and temperature are constant over the horizontal section at height $z$ along the radius $b$, and that $u = T = T$ outside the plume radius.

- We assume that the air entrainment at the edge of the plume is proportional to the local gas velocity in the plume, so that the entrainment velocity can be written as $v = u$, which is a constant and here taken to be $0.15$ (applies to top profile). In other words, the horizontal entrainment velocity is assumed to be 15% of the upward plume velocity. This value is difficult to measure but has been found to correspond reasonably with other experimentally measured values.
Summary

- It has been observed that only tonnage quantities of a spill are capable of causing fireballs.
- Whether a liquefied flammable gas spillage will cause a pool fire or a fireball is decided by the criterion that if the TAFF (Theoretical adiabatic Flashing Fraction) is \(= 0.35\), a fireball will result.
- The duration of the fireball has been found to be only a few seconds and during this time its size as well as height above the ground also changes. This rapidly changes the thermal radiation field with time.
- Power density, power per unit volume, of the fire ball is
  \[
  P_D = \frac{P_{FE}}{\frac{3}{2} \pi R^3} = \frac{12.368 \times 10^8 M^{2/3}}{\pi (27.5 \times M^{1/3})^3} = \frac{1.42 \times 10^8}{M^{1/3}} \text{W/m}^3
  \]
- The heat released in combustion is used up in two ways which are as radiation and sensible heat of combustion products and unreacted components.
- If the tank has not been weakened sufficiently, then a BLEVE does not take place after thermal rupture is initiated. In this case the fissure does not run the entire tank length but is arrested in strong material.
- The shapes and liftoffs of BLEVE fire balls vary significantly and depend on the detailed thermodynamic state of the liquid, and the details of tank failure. If the tank fails rapidly, then classical spherical fire balls result.
- Diffusion flames refer to the case where fuel and oxygen are initially separated and mix through the process of diffusion.
- When a mass of hot gases is surrounded by colder gases, the hotter and less dense mass will rise upwards due to the density difference, or rather, due to buoyancy.
- Fire plumes can be characterised into various groups depending on the scenario under investigation.
- The mass flow rate in the plume, denoted by \(m\), and most often given in kg/s, is the total mass flowing upwards, at a certain height, within the plume boundaries. The plume mass flow increases steadily with height since ambient air is continually entrained over the plume height.
- The point source plume radius, denoted \(b\), spreads roughly with an angle of 15° to the vertical. This corresponds approximately to the point where the centreline temperature rise has declined to 0.5 \(\Delta T_o\).

References


Recommended Reading

Self Assessment

1. The duration of the ______ has been found to be only a few seconds and during this time its size as well as height above the ground also changes.
   a. fire ball
   b. power
   c. explosion
   d. fire density

2. Which of the following statement is true?
   a. Explosion is the one that is of concern outside of the envelope of the fire ball.
   b. Radiation is the one that is of concern inside of the envelope of the fire ball.
   c. Radiation is the one that is of concern outside of the envelope of the fire flame.
   d. Radiation is the one that is of concern outside of the envelope of the fire ball.

3. Which of the following are attenuated (reduced in intensity) as they pass through the atmosphere due to absorption by CO₂, water vapour, etc. and scattering by dust particles?
   a. Flames
   b. Plumes
   c. Heat radiations
   d. Fire balls

4. __________ flames refer to the case where fuel and oxygen are initially separated and mix through the process of diffusion.
   a. Diffusion
   b. Buoyancy
   c. Turbulence
   d. Plume

5. Which of the following statement is true?
   a. Very small diffusion flames can be laminar, such as the flame on a candle.
   b. Very big diffusion flames can be laminar, such as the flame on a candle.
   c. Very small diffusion flames cannot be laminar, such as the flame on a candle.
   d. Very small diffusion flames can be laminar, such as the fireball.

6. __________ can be characterised into various groups depending on the scenario under investigation.
   a. Candle
   b. Fire plumes
   c. Fire
   d. Fire ball

7. Which of the following statement is true?
   a. The highest velocity is at the centreline of the plume.
   b. The highest velocity is at the bottom-line of the plume.
   c. The highest velocity is not at the centreline of the plume.
   d. The lowest velocity is at the centreline of the plume.
8. The centreline temperature denoted T, changes with ________.
   a. gas
   b. pressure
   c. height
   d. density

9. What is denoted as b, spreads roughly with an angle of 15° to the vertical?
   a. Point source plume radius
   b. Fire ball
   c. Fire intensity
   d. Fire explosion

10. Which of the following statement is true?
    a. The duration of the fire flame has been found to be only a few seconds during which time its size as well as height above the ground also change.
    b. The duration of the fire plume has been found to be only a few seconds during which time its size as well as height above the ground also change.
    c. The duration of the fireball has been found to be only a few seconds during which time its size as well as height above the ground also change.
    d. The duration of the fireball has been found to be only a few seconds during which time its size as well as weight above the ground also change.
Chapter V
Explosion

Aim
The aim of the chapter is to:

• explain the dense explosions
• elucidate blast damage
• examine the three basic types of energy released in an explosion

Objectives
The objectives of this chapter are to:

• determine the explosions classified based upon the density of the explosive
• discuss energy released by a chemical explosion
• analyse the inerting concept

Learning outcome
At the end of this chapter, you will be able to:

• understand the mortality index
• explain energy released by a mechanical explosion
• discuss the energy releases
5.1 Introduction

Explosion is a sudden and violent release of energy accompanied by the generation of a pressure wave and a loud noise. The rate of energy release is very large. It has the potential to cause injury to a living being, damage the plants and nearby property and cause temporary or permanent environmental degradation (Sevesco).

An injury to a living being could be fatal, leave one suffering / crippled for the rest of the life and may cause genetic alterations that may affect the future generations. As is apparent, the cost in terms of human suffering and the direct economic losses of damage to plant and structures, lost production, litigation and compensation are enormous. Hence, everything possible needs to be done to prevent an explosion.

5.2 Three Basic Types of Energy are Released in an Explosion

- Physical: High pressure vessel exploding or suffering brittle fracture. Thermal energy might create conditions for an explosion; e.g., Fire underneath an LPG container building up pressure in the container leading to an explosion; superheat in a liquid under pressure causing flashing off when the liquid is released at atmospheric pressure and the vapor cloud so formed exploding, etc.
- Chemical: Runaway chemical exothermic reactions (planned like TNT, or unplanned like in decomposition e.g. of hydrogen peroxide, lead oxide). If it occurs in a vessel, it is a uniform explosion. If in a pipe, it is a propagating explosion.
- Nuclear: Nuclear bombs, core melt down, etc.

5.3 Explosions are of Two Kinds Depending Upon the Velocity of Propagation

Deflagration
It is low burning velocity, couple of m/s (HC air mixture 1 m/s). Peak pressure is 8 bar. In a pipe, the deflagration may turn into a detonation.

Detonation
- It is a very high burning velocity, approaching the sound velocity at the temperature of the combustion products (1600 to 2000°C).
- The burning velocity is 2000 to 3000 m/s for HC air mixtures at the burning temperatures (sound velocity 330 m/s at 0°C). The flame front travels as a shock wave followed closely by a combustion wave which releases energy to sustain the shock wave.
- Experience indicates that a vapor-cloud does not undergo spontaneous detonation. Experiments to produce detonation have generally failed.
- It is likely that a deflagration may turn into a detonation; e.g. in a pipe where the expansion in volume results in the acceleration of the gas and it may reach a sonic velocity at the temperature of the reaction. The pressure increase can then be 20 to 40 times.

5.4 Explosions can be Classified Based Upon the Density of the Explosive

An explosion can be rarefied or dense. A rarefied explosive has density close to that of air. Some cases are: dust (pigment, flour, etc.), aerosol (hydrocarbon or oil droplets), and flammable vapours. A rarefied explosion may be confined or unconfined. A dense explosive, on the other hand, is quite dense and includes solid and liquid explosives. Dense explosives may be classified according to their susceptibility to shock:
- Propellants: Insensitive to shock and relatively slow burning (e.g. nitrocellulose).
- Secondary explosives: Also called high explosives (e.g. TNT which is also used as a reference substance).
- Primary explosives: Less powerful than secondary and are easily detonated by mechanical shock. Lead and mercury fulminate are examples.
Dense Explosions

- Dense explosions in air at or only near the ground level are considered. Those in water or at very high altitudes are not considered since their effects are very different.
- If a dense explosive detonates inside a casing, the casing will contain the initial pressure. This will be reflected back to the explosive and the detonation will enhance. The shock wave from the detonation will then spread throughout the mass of the explosive (or the charge). If the charge is less than critical diameter (2 to 7 mm depending on the explosive and its density), the detonation will fall away.
- Above it, a detonation velocity of 5 to 9 km/sec is produced. Initially, the gases are very highly compressed. Hence, the ideal gas law does not hold. These gases are not in chemical equilibrium either.
- Initially, the gases released will produce a fire ball. Its temperature > 2000 C, initial pressure 20 to 40 GPa or 200,000 bars. Then the products expand and cool as they move away. The initial velocity of several km/sec, is quite localised (8 m for a 100 kg high explosive). It soon decelerates to sonic velocity and a shock wave is generated which travels long distances. A crater may form on the surface of the ground.
1 tonne explosive = 60m crater volume
and D = 3

D = dia (m), V = volume of crater (m³), h = depth (m)

For 1 tonne, D = 3*7.74/h

It has been suggested that h = D/w, then for 1 tonne, D = 6.7 m (readers to check it)

5.5 Rarefied Explosions May be Confined or Unconfined

Confined: It occurs within a container / building / pipe work / vessel due to runaway reactions or air getting in. A majority of gas and vapour explosions are confined explosions.

Unconfined: It occurs in the open air though the surrounding structures may provide partial confinement. These are known as UVCE (Unconfined Vapour Cloud Explosion). In case of a multiple explosion, the first confined one may destroy the containment walls. Subsequent ones would be called unconfined explosions. This effect of UVCE depends upon:

- Quantity of material released.
- Fraction of material vaporised.
- Probability of ignition of cloud: increases with the size of the cloud.
- Distance travelled by the cloud prior to ignition: effect increases as the cloud becomes larger.
- Time delay before the ignition of the cloud.
- Probability of explosion rather than fire: In 10% of the cases either an explosion occurs, else a vapour cloud fire.
- Existence of a threshold quantity of material: A threshold quantity of 10 to 15 T minimums has been suggested. In a number of cases, no explosion occurred for less than 15 T release (table 5.1) while in some it did. Marshall states a minimum quantity of 3 T.
Table 5.1 Some data on quality released on the occurrence of fire or explosion in unconfined vapour clouds

The above table shows some data on quality released on the occurrence of fire or explosion in unconfined vapour clouds (after Marshall, 1976 a) Efficiency of an explosion: It is the ration of the energy in the last wave to that theoretically calculated by using the heat of combustion. The efficiency is taken to be 1 to 10% though sometimes greater efficiency has been calculated. Its value also depends upon whether the total vapour has been taken into account or only the one within the flammable limits, since that’s the amount which will burn / explode. While the vapour cloud above UFL may dilute and come within flammable limits and thus burn / explode, that which is below the LFL will not. The ratio of the total amount to that within the flammable limits can vary by a factor of upto 10. Further, the amount of vapour released, especially in a flashing liquid, is not exactly known because a significant part may be present as entrained droplets that may either settle out and re-evaporate slowly or may evaporate while suspended and thus add significantly to the amount of vapour. Thus, the uncertainty in the amount of vapour can be upto 100% (factor of 2). An efficiency of 3% (or yield factor, YF = 0.003) has been recommended by the Second Report of the (U.K.) Advisory Committee on Major Hazards.

Substances with yield factors of Y =.03

<table>
<thead>
<tr>
<th>Substance</th>
<th>Yield Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>3-Methyl-Butene-1</td>
</tr>
<tr>
<td>Actone</td>
<td>Methyl-Butyl-Ketone</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>Methyl Chloride</td>
</tr>
<tr>
<td>Amyl Alcohol</td>
<td>Methyl-Ethyl –ketone</td>
</tr>
<tr>
<td>Benzene</td>
<td>Methyl Formate</td>
</tr>
<tr>
<td>1,3 – Butadiene</td>
<td>Methyl Mercaptan</td>
</tr>
<tr>
<td>Butene-1</td>
<td>Methyl Fopormate</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>Methyl-Ethyl-Ketone</td>
</tr>
<tr>
<td>------------------------</td>
<td>------------------------------</td>
</tr>
<tr>
<td>Cyanogen</td>
<td>Methyl Formate</td>
</tr>
<tr>
<td>1,1 – Dichloroethane</td>
<td>Methyl-Propyl-Ketone</td>
</tr>
<tr>
<td>1,2 – Dichloroethane</td>
<td>Monochlorobenzene</td>
</tr>
<tr>
<td>Di-Methyl Ether</td>
<td>N-Amyl Acetate</td>
</tr>
<tr>
<td>Dimethyl Sulphide</td>
<td>Naphthalene</td>
</tr>
<tr>
<td>Ethane</td>
<td>N-Butane</td>
</tr>
<tr>
<td>Ethanol</td>
<td>N-Butyle Acetate</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>N-Decane</td>
</tr>
<tr>
<td>Ethalamine</td>
<td>N-Heptane</td>
</tr>
<tr>
<td>Ethyl Benzine</td>
<td>N-Hexane</td>
</tr>
<tr>
<td>Ethyl Chloride</td>
<td>N-Pentane</td>
</tr>
<tr>
<td>Ethyl Cyclohexane</td>
<td>N-Propanol</td>
</tr>
<tr>
<td>Ethyl Formate</td>
<td>N-Propyl Acetate</td>
</tr>
<tr>
<td>Ethyl Proprionate</td>
<td>O-Dichlorobenzene</td>
</tr>
<tr>
<td>Furfural Alcohol</td>
<td>P-Cymene</td>
</tr>
<tr>
<td>Hydrocyanic acid</td>
<td>Petroleum Ether</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>Phthalic Anhydride</td>
</tr>
<tr>
<td>Hydrogen Sulphide</td>
<td>Propane</td>
</tr>
<tr>
<td>Iso-Buty Alcohol</td>
<td>Propionaldehyde</td>
</tr>
<tr>
<td>Isobutylene</td>
<td>Propylene</td>
</tr>
<tr>
<td>Iso-Octane</td>
<td>Propylene Dichloride</td>
</tr>
<tr>
<td>Iso-Propl Alcohol</td>
<td>P-Xylene</td>
</tr>
<tr>
<td>Isobutylene</td>
<td>Styrene</td>
</tr>
<tr>
<td>Iso-Octane</td>
<td>Tetrafluoroethylene</td>
</tr>
<tr>
<td>Iso-Propyl Alcohol</td>
<td>Toluene</td>
</tr>
</tbody>
</table>
**Table 5.2 (a) Substances with yield factors Y = .03**

<table>
<thead>
<tr>
<th>Methalamine</th>
<th>Vinyl Acetate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>Vinyl Chloride</td>
</tr>
<tr>
<td>Methanol</td>
<td>Vinlylidene Chloride</td>
</tr>
<tr>
<td>Methyl Acetate</td>
<td>Water Gas</td>
</tr>
</tbody>
</table>

**5.6 BLEVE: (Boiling Liquid Expanding Vapour Explosion)**

- When a fire weakens a container (storage tank, reactor vessel) enough to cause rupture, the contents spill out with force and there is no opportunity for the relief valve/rupture disk to operate.

- This happens when the fire underneath a partially filled container goes out of hand. The bottom part of the container in touch with the liquid transfers the heat to the liquid which eventually boils. The latent heat of boiling takes up the heat being input. However, when the fire envelopes the top part of the container that has only vapour, heat removal is not efficient since the vapour mass and its heat capacity are much less than those of the liquid.

- The container top gets hotter and hotter; and the pressure inside keeps on increasing. The metal weakens and ruptures below its relief valve setting, sending missiles, producing shock waves and causing damage to buildings and other equipment.

- The contents are spewed out, both in liquid and vapour form. The liquid undergoes flash evaporation and entraps fine droplets.

- The vapour-mist cloud expands and moves depending upon the weather conditions. The substance, if flammable will catch fire (fire ball) and radiate heat or will explode (UVCE), if it finds an ignition source. If toxic, it will hurt the living and the flora-fauna for a significant distance depending upon its characteristics and the concentration.

![Fig. 5.1 The development of a BLEVE](image-url)
5.7 Mortality Index

Marshall has evolved a mortality index defined as fatalities per tonne of explosive (TNT equivalent) by using the data of war casualties due to shells fired during the first and second world wars, nuclear bombs dropped on Japan, chemical explosions in Flixborough, U.K. (cyclohexane), Oppau, Germany (ammonium nitrate), etc.

- Unconfined vapour cloud explosions for which the TNT equivalent could not be calculated, have also been tabulated and a mortality index calculated in case (Table 5.3). Figure 5.2 shows the fatalities for some fire balls and UVCEs for various population densities. It is quite instructive to study these figures.

- Marshall gives a correlation for the mortality index, population density and the quantity of explosive:
  \[ MI = PD \times Q^{0.33} \]

  Where,
  - \( MI \) = mortality index (number of fatalities per tonne of explosive)
  - \( PD \) = population density, thousands/sq. km
  - \( Q \) = quantity of explosive, tones

He also gives approximate relations (for a population density of 4000/sq. km)

- For radii for
  - deaths = \( 20 Q^{0.33} \) m
  - deaths + serious injuries = \( 35Q^{0.33} \) m
  - deaths + all injuries = \( 50Q^{0.33} \) m

- Basically, the injuries extend to 250% of the distance of the deaths. These equations can help in planning plant layouts, location of offices, habitation, etc.

- The above mortality index figures are for developed countries where the number of people employed to carry out a specific job is less due to a greater degree of automation and / or higher training and efficiency.

- Further, the population density in the neighborhood is low, taken as 4000 per sq. km. In contrast, the number of people employed per unit task is greater in India and other developing countries due to less automation and other social reasons.

- Further the population density is significantly higher. Hence, the mortality indeed is likely to be an order of magnitude greater than in the case of the developed countries.
Fig. 5.2 Fatalities vs. mass of spillage for fire balls and VCE’s and for various population densities

<table>
<thead>
<tr>
<th>Date</th>
<th>Location</th>
<th>Chemical</th>
<th>Liquid spilled (t)</th>
<th>Vapour involved (t)</th>
<th>Nature of incident</th>
<th>Facilities</th>
<th>Morality index (deaths/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1943 Jan. 18</td>
<td>Los Angeles, Calif</td>
<td>Butane</td>
<td>14</td>
<td></td>
<td>Fire</td>
<td>5</td>
<td>0.35</td>
</tr>
<tr>
<td>1944 Nov. 15</td>
<td>Cleveland, Ohio</td>
<td>LNG</td>
<td>180</td>
<td></td>
<td>Fire</td>
<td>213</td>
<td>1.18</td>
</tr>
<tr>
<td>1959 June 28</td>
<td>Meldrin, Ga</td>
<td>LPG</td>
<td>18</td>
<td></td>
<td>Explosion and fire</td>
<td>23</td>
<td>1.27</td>
</tr>
<tr>
<td>1962 July 26</td>
<td>New Berlin N.Y.</td>
<td>LPG</td>
<td>17</td>
<td></td>
<td>Explosion and fire</td>
<td>10</td>
<td>0.58</td>
</tr>
<tr>
<td>1967 Aug. 6</td>
<td>Lake Charles, L.A.</td>
<td>Isobutene</td>
<td>13</td>
<td></td>
<td>Explosion</td>
<td>7</td>
<td>0.53</td>
</tr>
<tr>
<td>1968 Jan 20</td>
<td>Pernis, Netherlands</td>
<td>Hydrocarbon vapour</td>
<td>50</td>
<td>2</td>
<td>Explosion</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1970 Dec. 9</td>
<td>Port Hudson, Mo.</td>
<td>Propane</td>
<td>27</td>
<td></td>
<td>Explosion</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Date</td>
<td>Location</td>
<td>Gas</td>
<td>Release</td>
<td>Type</td>
<td>Pressure</td>
<td>Fire</td>
<td>Explo</td>
</tr>
<tr>
<td>------------</td>
<td>-------------------</td>
<td>----------------</td>
<td>---------</td>
<td>----------</td>
<td>----------</td>
<td>------</td>
<td>-------</td>
</tr>
<tr>
<td>1971 July 11</td>
<td>Pensacola, Fa</td>
<td>Cyclohexane</td>
<td>30</td>
<td>No ignition</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1972 Jan.22</td>
<td>East St.Louis</td>
<td>Propylene</td>
<td>70</td>
<td>Explosion</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>1972 March 19</td>
<td>Lynchburgh, Va</td>
<td>Propane</td>
<td>9</td>
<td>Fire</td>
<td>2</td>
<td>1.33</td>
<td></td>
</tr>
<tr>
<td>1972 Sep.21</td>
<td>New Jersey</td>
<td>Propylene</td>
<td>18</td>
<td>Pressure rupture followed by fire</td>
<td>2</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>1973 Feb.23</td>
<td>Austin, Tex</td>
<td>Natural gas liquids</td>
<td>720</td>
<td>Fire</td>
<td>8</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>1974 June 1</td>
<td>Flixborough, U.K.</td>
<td>Cyclohexane</td>
<td>125</td>
<td>Explosion</td>
<td>28</td>
<td>0.70</td>
<td></td>
</tr>
<tr>
<td>1974 June 29</td>
<td>Climax, Tex.</td>
<td>Vinyl chloride</td>
<td>75</td>
<td>Explosion</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>1975 Nov.7</td>
<td>Beek, MNetherlands</td>
<td>Propylene</td>
<td>5.5</td>
<td>Explosion and fire</td>
<td>14</td>
<td>2.54</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>630</td>
<td></td>
<td>316</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td></td>
<td>39.4</td>
<td></td>
<td>19.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.2 (b) Some data on the relation between the size of flammable release and the number of fatalities

5.8 Energy Released by a Mechanical Explosion

- Energy is released when a high pressure container ruptures. The contents are suddenly released.
- Their pressure reduces to the atmospheric one and their volume expands. In case of liquids, this is rather small since liquids can't be compressed much.
- However, gases can be, and when a high pressure gas container ruptures, the gases expand isentropically releasing large amounts of energy (That's why hydrostatic testing of pressure vessels is to be preferred over pneumatic testing. In case of a failure, there is no danger of missiles flying in hydrostatic testing).
- The peak pressure is the bursting pressure measured at the vessel but it falls off fast with distance.

For an isentropic expansion of an ideal gas, the work of expansion, $W$, is given by

$$W_c =$$

where

- $P$ = Pressure
- $V$ = Volume

=$\text{Ration of heat capacities } C_p / C_v$
1.2=Initial (high pressure), and final (surroundings) conditions
Isentropic expansion of an ideal gas:
\[ P_1 = P_2 \text{ (EX-2)} \]
\[ W_e = \]

### 5.9 Energy Released by Chemical Explosions

- Chemical explosions are caused by runaway chemical reactions. These also result in a change in volume, pressure and temperature, as do the mechanical explosions.
- Further, they are based on a constant temperature expansion of gases which is not the case in chemical explosions. The situation is worse in case of liquid and solid explosions.
- The thermal heating (and associated sudden expansion) and the change in the number of moles due to the reaction are the two factors that contribute to the blast wave following a chemical explosion. However, this thermal heating which provides the maximum contribution since the change in the number of moles in gaseous explosions in air, is very small. For example, the propane combustion
\[ C_3H_8 + 5O_2 + 18.8N_2 = 3CO_2 + 4H_2O + 18.8N_2 \]
- The number of moles before and after the combustion are 24.8 and 25.8 respectively, or a change of a mere 4% while its adiabatic flame temperature is approximately 2000 K after the explosion and the mixture was at the ambient temperature before the explosion. So, the temperature rise has been about 7 folds.
- Hence, it is suggested that the release of energy due to a chemical explosion be based on the initial and final thermodynamic states.
- The maximum energy released in a reaction is the Helmholtz free energy. A Thermodynamics gives a relation
\[ dA = -SdT-PdV \]
At constant temperature, \(dT=0\)
\[ dA = -PdV \]
This is the work of expansion due to explosion.
\[ = P - R \]
Where,
\[ P=\text{product} \]
\[ R=\text{reactants} \]

It is assumed that most chemical explosions occur at ambient conditions, (doubtful). Ambient conditions are the same as the standard conditional at which thermodynamic propertries are tabulated.
\[ If = -T \]
\[ = P - R \]
\[ = S^o - Rg \ln x_i \]

Alternatively, as an approximation, one could use \( S^o \) instead of \( T \) or \( Rg \ln x_i \) instead of \( S^o \). If the change in the number of moles is not large, neglect \( T \). Then of the reaction.

Here,
\[ A = \text{Helmholtz Free Energy} \]
\[ G = \text{Gibbs Free Energy} \]
\[ H = \text{Enthalpy} \]
\[ R_g = \text{Universal Gas Constant} \]
\[ S = \text{Entropy} \]
\[ T = \text{Absolute Temperature} \]
\[ U = \text{Internal Energy} \]
\[ x_i = \text{Mole Fraction of Gaseous Components} \]
A blast can hurt both living and process equipment/structures due to the overpressure it produces. A lot of work has been done on the damage potential of TNT. Hence, a convenient way to assess the damage produced by an explosion is to first determine the amount of TNT that will release the same amount of energy, and then to determine the damage produced by that amount of TNT. The procedure has been simplified by Hopkinson’s scaling law of 1915 [2] that states “Self-similar blast (shock) waves are produced at identical scaled distances when two explosive charges of similar geometry and the same explosive but of different size are detonated in the same atmosphere”.

\[
Z = \frac{R}{M}
\]

Where,

- \( Z \) = scaled distance, ft/(lbm) , m/(kg)
- \( R \) = distance from charge, ft, m
- \( M \) = mass of explosive, lbm, kg

Effects of atmospheric pressure and temperature can be built in the above relation but are usually not necessary. Figures 5.4 (a) and (b) show peak overpressure vs. scaled distance.

Duration of the impulse also plays an important role, along with overpressure, in the resultant damage. For a 1 kilo tonne nuclear blast wave, it is 0.1 to 0.4 sec. For VCE, it will be several times. The longer the duration, the more is the damage.

Damage by chemical hazards can be predicted using Hopkinson’s scaling law if an equivalent quantity of TNT can be assigned to an explosive. The resultant damage calculations are statistical in nature because of the following reasons:

- Overpressure and impulse duration are only predicted statistically.
- Size and flight paths of missiles are also statistical
- Characteristics of the targets vary: Humans differ in age and physical conditions. Buildings and equipment differ in size, age, construction materials, design, etc.
- Angle of inclination of the target to the blast wave also influences.

It is therefore possible from the scaling law, to predict the degree of damage likely to be inflicted at any specified radius from the explosion of a given equivalent quantity of TNT or what quantity of TNT would be required for a particular damage at a particular location. One should however keep the Yield Factor in mind which is generally taken as 3%. The yield factors for several chemicals are given in Table (5.2).

Damage to human beings results from the blast waves, secondary reflections, building collapse, resultant fires, crushing, asphyxiation, secondary missiles (bricks, broken glass, etc.).

The damage to human beings and structures can also be calculated using the probit equation as discussed in the chapter on Probit Equations.

The maximum horizontal range of blast fragments can be read from Fig. 5.3 based on the equivalent mass of TNT explosive.
<table>
<thead>
<tr>
<th>Substance</th>
<th>Substances</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrolein</td>
<td>Ethylene</td>
</tr>
<tr>
<td>Carbon Disulphide</td>
<td>Ethyl Nitrie</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>Methy1 – Vinyle Ether</td>
</tr>
<tr>
<td>Di-Ethyl Ether</td>
<td>Phthalic Anhydride</td>
</tr>
<tr>
<td>Di-Vinyl Ether</td>
<td>Propane Oxide</td>
</tr>
</tbody>
</table>

**Table 5.2 (c) Substances with yield factors of \( Y = .06 \)**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Substance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylene</td>
<td>Isopropyl Nitrate</td>
</tr>
<tr>
<td>Ethylene Oxide</td>
<td>Methyl Acetylene</td>
</tr>
<tr>
<td>Ethyl Nitrate</td>
<td>Nitromethane</td>
</tr>
<tr>
<td>Hydrazine</td>
<td>Vinyl Acetylene</td>
</tr>
</tbody>
</table>

**Table 5.2 (d) Substances with yield factors of \( Y = .19 \)**

### 5.11 Inerting

- This term implies changing the environment in a system by reducing the oxygen content so as to prevent fire and explosion. Any gaseous fuel requires a minimum oxygen concentration (MOC) for a flame or explosion to propagate.
- Below the MOC, the energy released is not enough to heat the entire mixture to the ignition temperature. Thus, regardless of the fuel concentration, reducing the oxygen to below the MOC can prevent an explosion. This is used in practice in the storage of many hydrocarbons. Oxygen concentration does not need to be reduced to zero.

![Fig. 5.3 Mortality index for explosions](image-url)
Fig. 5.4 (a) Maximum horizontal range of blast fragments

Fig. 5.4 (b) Correlation between overpressure and scaled distance, English Engineering Units
Fig. 5.4 (c) Correlation between over pressure and scaled distance SI unit
Summary

- When a fire weakens a container (storage tank, reactor vessel) enough to cause rupture, the contents spill out with force and there is no opportunity for the relief valve/rupture disk to operate.
- Chemical explosions are caused by runaway chemical reactions. These also result in a change in volume, pressure and temperature, as do the mechanical explosions.
- Further, they are based on a constant temperature expansion of gases which is not the case in chemical explosions. The situation is worse in case of liquid and solid explosions.
- A blast can hurt both living and process equipment/structures due to the overpressure it produces. A lot of work has been done on the damage potential of TNT.
- Hence, a convenient way to assess the damage produced by an explosion is to first determine the amount of TNT that will release the same amount of energy, and then to determine the damage produced by that amount of TNT.
- Since the rest of the chapter deals with rarefied explosions, this is a good place to discuss the dense explosions a bit more.
- Dense explosions in air at or only near the ground level are considered. Those in water or at very high altitudes are not since their effects are very different.
- Efficiency of an explosion: It is the ration of the energy in the last wave to that theoretically calculated by using the heat of combustion. The efficiency is taken to be 1 to 10% though sometimes greater efficiency has been calculated. Its value also depends upon whether the total vapour has been taken into account or only the one within the flammable limits, since that’s the amount which will burn / explode.
- When a fire weakens a container (storage tank, reactor vessel) enough to cause rupture, the contents spill out with force and there is no opportunity for the relief valve/rupture disk to operate.
- Energy is released when a high pressure container ruptures. The contents are suddenly released. Their pressure reduces to the atmospheric one and their volume expands. In case of liquids, this is rather small since liquids can’t be compressed much.

References


Recommended Reading

1. __________ is a sudden and violent release of energy accompanied by the generation of a pressure wave and a loud noise.
   a. Explosion
   b. Plumes
   c. Fireball
   d. Flames

2. Which of the following is low burning velocity, couple of m/s (HC air mixture 1 m/s) with peak pressure 8 bar and in a pipe, the deflagration may turn into a detonation?
   a. Deflagration
   b. Detonation
   c. Dense Explosions
   d. Confined

3. __________ occurs in the open air though the surrounding structures and may provide partial confinement.
   a. Confined
   b. Plumes
   c. Unconfined
   d. Explosion

4. Which of the following statement is true?
   a. A blast can hurt both living and process equipment/structures due to the vapour it produces.
   b. An ideal plume can hurt both living and process equipment/structures due to the overpressure it produces.
   c. A blast cannot hurt both living and process equipment/structures due to the overpressure it produces.
   d. A blast can hurt both living and process equipment/structures due to the overpressure it produces.

5. Which of the following term implies changing the environment in a system by reducing the oxygen content so as to prevent fire and explosion?
   a. Blast damage
   b. Inerting
   c. Morality index
   d. BLEVE

6. __________ is released when a high pressure container ruptures.
   a. Gas
   b. Energy
   c. Pressure
   d. Vapour

7. Which of the following statement is true?
   a. Experience indicates that a gas pressure does not undergo spontaneous detonation.
   b. Experience does not indicate that a vapour-cloud does not undergo spontaneous detonation.
   c. Experience indicates that a vapour-cloud does not undergo spontaneous detonation.
   d. Experience indicates that a flame does not undergo spontaneous detonation.
8. Which of the following has the potential to cause injury to a living being, damage the plant and nearby property and cause temporary or permanent environmental degradation?
   a. Explosion
   b. Fireball
   c. Plume
   d. Candle

9. \[ _____ = PD^* Q^{0.333} \]
   a. I
   b. MI
   c. Q*
   d. Q

10. Which of the following result in a change in volume, pressure and temperature, as do the mechanical explosions?
    a. Mechanical explosions
    b. Fire ball
    c. Inertion
    d. Chemical explosions
Chapter VI
Chemical Thermodynamics

Aim
The aim of this chapter is to:

• explain the laws of thermodynamics
• analyse chemical equilibrium and its relation to free energy
• define and explain entropy

Objectives
The objectives of this chapter are to:

• explain the Joule-Thomson effect
• view the Hess’s law of constant heat summation
• comprehend the relation between molar heat capacity at constant volume and constant pressure

Learning outcome
At the end of this chapter, you will be able to:

• calculate the equilibrium constant using the Van’t Hoff isotherm
• apply the Clapeyron-Clausius equation to determine the latent heat from vapour pressure
• explain the physical significance of free energy
6.1 Introduction

Thermodynamics is the study of the effects of work, heat and energy on a system. It is only concerned with large scale observations. It is a branch of physics which deals with the energy and work of a system.

Thermodynamics literally means flow of heat. Thus, in a broad sense, it deals with the relationship of heat to all other forms of energy, light, kinetic energy, etc. The science of thermodynamics aims to determine the efficiency of these engines, i.e., the percentage of heat supplied which is converted to mechanical energy. So, for the engineer, this information is of utmost importance, because if the laws governing the transformation of heat to energy are known, more efficient engines can be designed. Although, originally the science of thermodynamics was meant to ascertain the efficiency of heat engines, now it has found wider use in diverse branches of all physical and chemical sciences.

6.2 Terminology of Thermodynamics

The basic concepts and terminology used in thermodynamics would be helpful in understanding detailed and complex topics.

- **Thermodynamic system**: The thermodynamic system is defined as any portion of matter under consideration, which is separated from the surroundings by real or imaginary boundaries. The thermodynamic system may be homogeneous or heterogeneous, but has to be macroscopic. A system is called homogeneous, if it consists of one phase. i.e., its physical and chemical properties are identical throughout the system.
- **System**: A system is called heterogeneous if it consists of parts (or phases), each of which has different physical and possibly different chemical properties.

> It is important that we define what is contained inside the system as well as what exists outside it.

**Fig. 6.1 Surroundings and system**

(Source: www.bse.ph/download/.../Module%2014%20Thermodynamics.pdf)

- **Surroundings**: The surrounding is the rest of the universe around the system. A system and its surroundings are always separated by real (fixed or movable) or imaginary boundaries, through which matter and energy may be exchanged between the two. Ordinarily, surroundings mean water or air or both. Based on the exchange of matter and energy between the system and the surroundings, a system can be classified into the following three types:
  - **Open system**: The open system is capable of exchanging both matter and energy (as heat) with the surroundings. For example, plants and living-beings are all open systems.
  - **Closed system**: The closed system is capable of exchanging only energy (as heat or work) with the surroundings. For example, a sealed flask containing gas (or matter) is a closed system.
  - **Isolated system**: The isolated system is a system, which can exchange neither matter nor energy with the surroundings. For such a system, matter and energy remain constant. There is no perfectly isolated system, but our universe can be considered as an isolated system, since by definition it does not have any surroundings.
• Extensive property: It is the property, which depends upon the amount of substance present in the system. For example, total mass, volume, energy, etc., of a system are included in extensive property, since they cannot be determined without considering the system as a whole.

• Intensive property: It is the property independent of the amount of substance present in the system. For example, viscosity, surface tension, refractive index, temperature, pressure, dielectric constant, density, specific gravity, specific heat, vapour pressure of a liquid, etc., are some of the important intensive properties.

• State of the system: It is a set of variables such as pressure, volume, temperature, composition, etc., which describe the system. Thus, when one or more variables undergo change, then the system is said to have undergone a change of state.

• The isothermal process: It is a process carried out at constant temperature. When a system undergoes an isothermal process, the system is usually kept in contact with a constant temperature bath (called a thermostat) and the system maintains its temperature constant by the exchange of heat with the thermostat.

• The adiabatic process: It is one in which no heat can leave or enter the system (i.e., thermally insulated). Thus, for carrying out the adiabatic process, the system is carefully insulated from the surroundings. It may be pointed out that in an adiabatic process; the temperature of the system may increase or decrease.

• The isobaric process: It is carried out at constant pressure. For example, a reaction taking place in an open vessel is always at atmospheric pressure and hence, such a reaction is isobaric. In the isobaric process, change in volume takes place.

• The isochoric process: It is the one in which the volume of the system is kept constant.

• The reversible process: It is one, when energy change in each step of the process can be reversed in direction by merely a small change in a variable (like temperature, pressure, etc.) acting on the system. A system that has undergone a reversible process can be restored back to its original/initial state with an infinitesimal change in the external system. To approach reversibility, two most important requirements are:
  • There must be no friction and no finite temperature differences. Reaction in the Daniels cell is an example of a reversible process.

• The irreversible process: It is the one in which the system or surroundings are not restored to their initial state at the conclusion of the reverse process. All naturally occurring processes are irreversible. They always tend to proceed in a definite direction and if left to themselves, they will never proceed in the opposite direction. For example, a clock always runs down and cannot rewind itself. Other common examples of irreversible process are:
  • flow of heat from a hotter to a colder body
  • expansion of gases from high-pressure regions to low-pressure regions through orifices
  • mixing of two gases

Irreversible processes are also called “spontaneous processes”, which means that the process takes place in one direction.

• State function: It is a thermodynamic property, which depends only on the state of the system and is independent of the path followed (or chosen) to bring about the change. For example, internal energy change ($\Delta E$), enthalpy change ($\Delta H$), free energy change ($\Delta G$), entropy change ($\Delta S$), etc.

• Internal energy: Every chemical system has some internal energy ($E$), which is a function of the temperature, the chemical nature of the substance and at times the pressure and volume of the system. The magnitude of internal energy in a given system of molecules is determined by the kinetic, rotational and vibration movement of molecules and their component atoms, as well as by the way in which the molecules are put together and the nature of individual atoms. It is impossible to determine the absolute value of the internal energy of a system. Fortunately, we are concerned only with the change in internal energy, accompanying a chemical or physical change. This change in internal energy is represented by $\Delta E$. If $E_2$ is the internal energy of the system in the final state and $E_1$ is the initial internal energy of the system (i.e., before change), then:

$$E = E_2 - E_1$$

Internal energy is a state function as it depends only on the initial and final states and not on the path followed between the states, i.e., no route is specified.
6.3 The Zeroth Law of Thermodynamics

- The zeroth law of thermodynamics begins with a simple definition of thermodynamic equilibrium. It is observed that some property of an object, like the pressure in a volume of gas, the length of a metal rod, or the electrical conductivity of a wire, can change when the object is heated or cooled.
- If two of these objects are brought into physical contact there is initially a change in the property of both objects. But, eventually, the change in property stops and the objects are said to be in thermal, or thermodynamic, equilibrium.
- Thermodynamic equilibrium leads to the large scale definition of temperature. When two objects are in thermal equilibrium they are said to have the same temperature.
- During the process of reaching thermal equilibrium, heat, which is a form of energy, is transferred between the objects. The details of the process of reaching thermal equilibrium are described in the first and second laws of thermodynamics.

6.4 The First Law of Thermodynamics

As a result of a number of experimental observations, Helmholtz, Clausius and Kelvin enunciated a generated law of nature, commonly known as the Principle of the conservation of energy or the First law of thermodynamics, which may be stated in different ways as follows:
- “Energy can neither be created nor destroyed, though it may be converted from one form to another.”
- “The total energy of an isolated system remains constant, although it may change from one form to another.”

Convention of signs regarding heat (q) and work (w)
The following sign conventions are generally accepted in thermodynamics:
Heat gained by the system is given a positive sign (+ q); while heat lost by the system is given a negative sign (- q)
The work done (w) by the system on the surroundings is given a positive sign (+w); while work done on the system a negative sign (-w). A system containing a definite mass at a definite temperature possesses definite internal energy E. Actual absorbed amount of internal energy is not known, but the change in internal energy is indicated as \( \Delta E = E_2 - E_1 \), where E_1 and E_2 are the initial and final internal energies of the system respectively. If E_2 > E_1, then the \( \Delta E \) is negative.

Mathematical formulation
Suppose heat supplied to the system is q. A part of this heat may be used up by the system itself in increasing its internal energy by \( \Delta E \) and the rest is used for performing external work, w. Then, according to the first law

\[
q = \Delta E + w \\
\text{or} \\
\Delta E = q - w \quad \text{ ... (i)}
\]

For an infinitesimally small change, the equation (i) may be written as:

\[
dE = dq - dw \quad \text{ ... (ii)}
\]

where dE is the increase in energy; dq and dw represent small quantities of heat absorbed and external work done by the system respectively.

Equation (i) and (ii) are the mathematical forms of the first law.

In a cyclic process i.e., in which the system is subjected to a series of operations such that it ultimately comes back to its initial state, so that the initial and the final states becomes identical,

\[
E_1 < E_2 \text{ or } \Delta E = 0 \]
\[
\Delta E = q - w = 0
\]
or q – w = 0
or q = w
e.i., the work done is equal to the heat absorbed in a cyclic process.

The first law of thermodynamics provides the basic principle used in heat engines, from steam turbines to nuclear reactors. It has its obvious application in transportation.

A train that runs in a steam engine operates by burning wood or coal in the engine. Heat is generated, thus increasing the temperature of the engine’s water. As the water boils, it produces steam. The expansion of this steam does work and propels the train forward. Even the jet engines of airplanes or the common automobile engines use the heat of combustion of their fuel to do work in making these vehicles move.

Limitations
This law merely states the exact equivalence of various forms of energy involved, but provides no information regarding the feasibility of the process. Moreover, this law does not say whether a gas can diffuse from low pressure to high pressure or whether water itself can flow uphill, etc.

6.5 The Joule-Thomson Effect
The Joule-Thomson effect states “when a gas under high pressure is permitted to expand to a region of low pressure, it suffers a fall in temperature.”

Suppose a volume \( V_1 \) of a gas enclosed between the piston and the porous plug at pressure \( P_1 \) is forced through the plug by moving the piston inwards and allowed to expand to a volume \( V_2 \) at a lower pressure, \( P_2 \), then,

work done by the system 1 = \( P_1 V_1 \)
and work done by the system 2 = \( P_2 V_2 \)
Net work done by the system, \( w = (P_2 V_2 - P_1 V_1) \)
But for an ideal gas, \( P_1 V_1 = P_2 V_2 \)
\( w = 0 \)

Hence, \( \Delta E = q - w = q - 0 = q \) (From the 1st law of thermodynamics)

Hence, for an ideal gas, there should be no rise or fall in temperature. However, Joule-Thomson noticed a small, but definite fall in temperature in most of the gases.

As energy of the gaseous system falls, so \( \Delta E = -ve \). Also \( q = 0 \), since the expansion is carried out adiabatically. Consequently, \( w = +ve \), i.e., while expanding by passing through a porous plug from a region of high pressure into a region of low pressure, the gas must have done some work and hence, temperature falls.

According to kinetic theory, work has to be done in order to overcome the attractive forces existing between gas molecules. This work is done at the expense of K.E. of molecules. In other words, K.E. decreases, thereby cooling results.
6.6 Enthalpy

Suppose a change of a system from state A to B is brought about at constant pressure (P), let the volume be increased from \( V_A \) to \( V_B \). Suppose heat absorbed by the system during the changes is \( q \). Therefore, by the first law of thermodynamics;

\[
q = (E_B - E_A) + \text{External work done (w)}
\]

where, \( E_B \) and \( E_A \) are the initial and final internal energies of the system. But work done (w) by the system, on the surroundings in increasing volume from \( V_A \) to \( V_B \)

\[
= P (V_B - V_A)
\]

\[
q = (E_B - E_A) + P (V_B - V_A) = (E_B + PV_B) - (E_A + PV_A) = H_B - H_A = \Delta H
\]

where, the quantity \((E+PV)\) is known as enthalpy or heat content of the system and is denoted by \( H \). Thus, enthalpy change \( \Delta H \) is equal to the heat absorbed \( (g) \).

Since \( E \) is a state (or definite) property and \( P \) and \( V \) are definite properties of a system, it follows \( H \) is also a definite property, depending upon the state of the system. Since \( H_B \) and \( H_A \) are definite properties, obviously \( \Delta H \), like \( \Delta E \), is a definite or state property, depending only on the initial and final states of the system. Thus the heat content or enthalpy change,

\[
\Delta H = (E_B + PV_B) - (E_A + PV_A) = (E_B - E_A) + P (V_B - V_A)
\]

or \( \Delta H = \Delta E + P \Delta V \)

at constant pressure, \( \Delta H > \Delta E \)

If volume is constant, i.e., \( \Delta V = 0 \), then

\( \Delta H = \Delta E \)

Thus, at constant volume, enthalpy change or heat absorbed,

\( (\Delta H) = \text{Change in internal energy (} \Delta E) \)

6.6.1 Relation between Pressure-Volume and Work

Consider a certain amount of a gas enclosed in a cylinder of cross-sectional area ‘A’ and fitted with a hypothetical, weightless and frictionless piston. Allow the gas to expand against the opposing pressure, \( P \) (see figure below). If the pressure is reduced by a very small amount \( dP \), the piston will be forced to move upward, due to the expansion of the gas by a small distance \( dl \).

The corresponding work associated with the change, \( dw \), is given by:

\[
\text{Fig. 6.3 Work in P-V form}
\]
\[ dw = \text{Force} \times \text{Distance} \]
But pressure = \( \frac{\text{Force}}{\text{Area}} \)
\[ dw = \text{Pressure} \times \text{Area} \times \text{Distance} \]
= \( P \times A \times dl \)
But the product \( A \times dl \) is the volume swept by the piston, \( dV \),
\[ dw = P \cdot dV \]
This is nothing but the work done when the volume changes by a very small amount \( dV \) against pressure \( P \).

If the volume changes from \( V_{\text{initial}} \) to \( V_{\text{final}} \), then the total work done by the gas is obtained by integration

Total work done = \( \int_{V_{\text{initial}}}^{V_{\text{final}}} dw \)
= \( \int_{V_{\text{initial}}}^{V_{\text{final}}} P \cdot dV \)

If the external pressure \( P \) is constant, then:
\[ w = P \int_{V_{\text{initial}}}^{V_{\text{final}}} dV \]
= \( P (V_{\text{final}} - V_{\text{initial}}) = P \Delta V \)

Relation between \( \Delta H \) and \( \Delta E \) in case of gaseous reaction:
Consider a reaction involving gases. Let:

\( V_{\text{initial}} = \) total volume of the gaseous reactants
\( V_{\text{final}} = \) total volume of gaseous product as
\( n_{\text{initial}} = \) number of moles of gaseous reactants
\( n_{\text{final}} = \) number of moles of gaseous products
\( T = \) constant temperature
\( P = \) constant pressure

Then, from ideal gas laws, we have:
\( PV_{\text{initial}} = n_{\text{initial}} RT \)
and \( PV_{\text{final}} = n_{\text{final}} RT \)
\( P (V_{\text{final}} - V_{\text{initial}}) = (n_{\text{final}} - n_{\text{initial}}) RT \)
or \( V = \Delta n_{g} \cdot RT \)
but \( \Delta H = \Delta E + P \Delta V \)

\[ \Delta H = \Delta E + \Delta n_{g} \cdot RT \]

...(i)

Where \( R = \) gas constant
\[ = 0.08206 \text{L} \cdot \text{atm} K^{-1} \text{mol}^{-1} = 8.343 \text{J} K^{-1} \text{mol}^{-1} \]

Equation (i) can be utilised in converting \( \Delta H \) value into \( \Delta E \) value and vice versa in reactions involving gaseous reactants and/or products.

\begin{itemize}
  \item In case of expansion, \( \Delta n_{g} \) is positive, so \( \Delta H > \Delta E \).
  \item In case of contraction, \( \Delta n_{g} \) is negative, so \( \Delta H < \Delta E \).
  \item For no change in volume, \( \Delta n_{g} = 0 \), so \( \Delta H = \Delta E \).
\end{itemize}
6.7 Thermochemical Definitions

- **Heat of reaction (ΔH):** It is the difference between the heat contents (or enthalpies) of the products and the reactants, when molar quantities of the reactants, indicated by the balanced chemical equation, react completely or mathematically, heat of reaction,

\[ \Delta H = \text{Enthalpy of product} - \text{Enthalpy of reactant} \]

**Example:** The Thermochemical equation:

\[ 2H_2 (g) + O_2 (g) \rightarrow 2H_2O (l) \]

\[ \Delta H = -285.9 \text{kJ} \]

The reaction indicates that when 2 moles of gaseous hydrogen combine with 1 mole of gaseous oxygen to produce 2 moles of liquid water, the heat content of the system decreases by 285.9 kJ or the reacting system loses 285.9 kJ. Hence, the heat of the above reaction is -285.9 kJ.

- **Enthalpy (or heat) of combustion (ΔH) of a compound or an element:** It is the change in heat content, when 1 mole of the substance is completely burnt in excess of oxygen. Since combustion reactions are always exothermic, heat of combustion is always negative.

**Example:** Heat of combustion of methane (CH\(_4\)) is -890.2 kJ mol\(^{-1}\)

\[ \text{CH}_4 (g) + 2\text{O}_2 (g) \rightarrow \text{CO}_2 (g) + 2\text{H}_2\text{O} (l) \quad \Delta H = 890.2 \text{kJ} \]

- **Enthalpy (or heat) of neutralisation of an acid (or base):** It is the change in heat content (ΔH) when one gram equivalent of the acid (or base) in dilute aqueous solution is neutralised by one gram equivalent of a dilute aqueous solution of a base (or acid).

**Example:**

\[ \text{HNO}_3 (aq) + \text{NaOH} (aq) \rightarrow \text{NaNO}_3 (aq) + \text{H}_2\text{O}; \quad \Delta H = -57 \text{kJ} \]

\[ \text{HCl} (aq) + \text{KOH} (aq) \rightarrow \text{KCl} (aq) + \text{H}_2\text{O}; \quad \Delta H = -57 \text{kJ} \]

These thermochemical equations imply that heat of neutralisation (ΔH) of a strong acid (HNO\(_3\) or HCl, etc.) by a strong base (NaOH, KOH, etc.) and vice versa is -57kJ, no matter what acid or base is employed. This is because the heat of neutralisation is in fact the heat of formation of 1 mole of water from 1 g equivalent H ions (of acid) and 1g equivalent OH ions (of base), while the other ions of the strong acid and base remain unaltered. Thus,

\[ \text{A}^- + \text{H}^+ + \text{B}^+ + \text{OH}^- \rightarrow \text{A}^- + \text{B}^+ + \text{H}_2\text{O} \quad \Delta H = -57 \text{kJ} \]

Strong acid  Strong base  Salt

or

\[ \text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} \quad \Delta H = -57 \text{kJ} \]

- **Enthalpy (or heat) of formation (ΔH) of a compound:** It is the change in heat content or enthalpy (ΔH) when one mole of the compound is formed from its elements in their commonly occurring (or standard) states.

**Example:** The equation:

\[ \text{C (graphite)} + 2\text{H}_2(g) \rightarrow \text{CH}_4(g); \quad \Delta H_f = -74.8 \text{kJ} \]

The reaction indicates that when one mole of methane gas is formed from its elements, carbon and hydrogen, 74.8 kJ of heat is given out. Thus, enthalpy (or heat) of formation of methane is -74.8kJ mol\(^{-1}\).

- **Enthalpy of formation and its stability:** The enthalpy of formation is an important property of a compound and is related to its stability. The stability of a compound is inversely proportional to its heat content (or intrinsic energy). In other words, lower the enthalpy of formation of a compound more is its stability.
A compound with enthalpy of formation \( (\Delta H) \) is positive means that the energy content of the compound is more than the energy contents of its constituent elements. Hence, such a compound is unstable. On the other hand, a compound with enthalpy of formation \( (\Delta H) \) is negative means that the energy content of the compound is less than that of its constituent elements. Consequently, such a compound is stable.

So, a compound with positive enthalpy of formation is unstable and one with negative enthalpy of formation is stable. It is quite clear that the relative stability of various compounds is inversely proportional to their enthalpies of formation.

**Example:** The enthalpies of formation \( (\Delta H) \) of HI, HBr, HCl and HF are +26.9, -36.1, -92.4 and -161.7 kJ mol\(^{-1}\) respectively. Consequently, HI is least stable, while HF is most stable. In other words, the stability of these halides is in the order: HF > HCl > HBr > HI.

- Enthalpy (or heat) of fusion of a substance: It is “the heat change in converting 1 mole of it from the solid to the liquid phase at its melting point.” Heat of fusion is always positive, because heat is needed to overcome the intermolecular forces between the constituent particles of a solid.

**Example:** Heat of fusion of water,

\[
\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l) \quad \Delta H_{\text{fusion}} = 6.0\text{kJ}
\]

- Enthalpy (or heat) of vapourisation of a liquid: It is the heat change in converting 1 mole of the substance from liquid to the gaseous state at its boiling point.

**Example:** Heat of vaporisation of water,

\[
\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(g); \quad \Delta H_{\text{vap}} = 42.00\text{kJ}
\]

- Enthalpy (or heat) of sublimation of a solid: It is the heat change in converting 1 mole of a solid directly into its vapour at a given temperature, below its melting point.

**Example:** Heat of sublimation of iodine,

\[
\text{I}_2(s) \rightarrow \text{I}_2(g); \quad \Delta H_{\text{sub}} = 62.00\text{kJ}
\]

### 6.8 Bond Energy

Bond energy can be defined as the average amount of energy required (or enthalpy change involved) during the breaking of one mole (or Avogadro’s number) of bonds of the same type, present in the molecules of a gaseous compound, into gaseous fragments, atoms, radicals, etc.

Bond energy is sometimes also called the enthalpy or heat formation of the bond. The strength of the bond joining the two atoms together depends upon the environment. For example, the energy needed to break the O–H bond in water (\(\text{H–O–H}\)) to give the H atom and OH groups is 118 kcal mol\(^{-1}\); while the energy needed to break the O–H bond in the hydroxy radical (\(\text{–O–H}\)) to give O and H atoms is 102 kcal mol\(^{-1}\). The difference in the two values can be related to the fact that OH radicals are much more reactive than oxygen atoms in combining with H atoms to form more stable molecules. These bond-breaking reactions can be written as:

\[
\text{H}_2\text{O}(g) \rightarrow \text{OH}(g) + \text{H}(g); \quad \Delta H = 118 \text{ kcal mol}^{-1}
\]

or

\[
\text{OH}(g) \rightarrow \text{O}(g) + \text{H}(g); \quad \Delta H = 102 \text{ kcal mol}^{-1}
\]

Thus, the total dissociation energy of water into 2 H and O is 220 kcal mol\(^{-1}\). Hence, the average bond energy of O–H bond in water is 110 kcal mol\(^{-1}\).

In a polyatomic molecule (i.e., containing more than one covalent bonds) such as \(\text{AB}_n\), the average bond energy is calculated by dividing the heat of formation of the compound \(\text{AB}_n\) by \(n\). For example, in case of the methane \((\text{CH}_4)\) molecule, having four C–H bonds, the mean bond energy is one-fourth of the heat of formation of methane. Thus, average bond energy of C–H bonds in methane,
Alternatively, the C–H bond energy in methane may be calculated as the average of the total dissociation energy of the C–H bonds in the series of different dissociation species. Thus, in methane,

\[
\begin{align*}
\text{CH}_4(g) &\rightarrow \text{CH}_3(g) + \text{H}(g); \quad \Delta H = 104 \text{ kcal/mol} \\
\text{CH}_3(g) &\rightarrow \text{CH}_2(g) + \text{H}(g); \quad \Delta H = 106 \text{ kcal/mol} \\
\text{CH}_2(g) &\rightarrow \text{CH}(g) + \text{H}(g); \quad \Delta H = 106 \text{ kcal/mol} \\
\text{CH}(g) &\rightarrow \text{C}(g) + \text{H}(g); \quad \Delta H = 82 \text{ kcal/mol}
\end{align*}
\]

So the bond dissociation energy value is equal to \(1/4 \times [104 + 106 + 106 + 82] = 99.5 \text{ kcal/mol}^{-1}\)

### 6.8.1 Calculation of Bond Energies

In a reaction between gaseous species, certain bonds in reactants are broken and some new bonds are formed in products. So the sum of enthalpy changes for bonds broken and bonds formed gives the enthalpy change for the reaction, i.e.,

\[
\Delta H_{\text{rxn}} = \sum \Delta H (\text{bonds broken}) + \sum \Delta H (\text{bonds formed})
\]

The enthalpy of reaction in gas phase is also given by:

\[
\Delta H_{\text{rxn}} = \sum \text{BE (reactants)} + \sum \text{BE (products)} = \text{Total energy input – Total energy released}
\]

where BE stands for average bond energy and is the summation sign.

### Variation of Bond Energy

- With the size of the atoms: Bond energy decreases with the increase in the size of atoms. For example, bond energies of H–F and H–Cl bonds are 56.5 kJ/mol and 43.1 kJ/mol respectively.
- With electronegativity bond energy increases with increase in difference in electronegativities of the atoms involved in the bond. For example, bond energy of H–Cl = 43.1 kJ/mol with electronegativity difference of 0.9 units; while bond energy of H–F = 56.5 kJ/mol with electronegativity difference of 1.9 units.

### 6.8.2 Applications of Bond Energies

#### Calculation of Heat Reaction

Suppose we want to calculate the heat of reaction:

\[
\text{C}_2\text{H}_4(g) + \text{H}_2(g) \rightarrow \text{C}_2\text{H}_6(g)
\]

Given that bond dissociation energy of C=C is 146 kcal mol\(^{-1}\); C–C is 83 kcal mol\(^{-1}\)

\[
\text{H–H} = 102 \text{ kcal/mol}^{-1} \quad \text{and} \quad \text{C–H} = 99 \text{ kcal/mol}^{-1}
\]

Now heat of reaction

\[= – \left[ \text{Bond energies of (products – reactants)} \right]\]

But in the given reaction:

\[
\begin{array}{c}
\text{H} \\
\text{C} \\
\text{H}
\end{array} + \begin{array}{c}
\text{H} \\
\text{H} \\
\text{H}
\end{array} + \begin{array}{c}
\text{H} \\
\text{H} \\
\text{H}
\end{array} \rightarrow \begin{array}{c}
\text{H} \\
\text{C} \\
\text{H}
\end{array} + \begin{array}{c}
\text{H} \\
\text{H} \\
\text{H}
\end{array}
\]

92/JNU OLE
the four C–H bonds (i.e., 2 on each carbon atom) remain unaffected;
• the double bond (C = C) in CH break up;
• the bond (H–H) in Hg breaks up;
• the product has one C–C bond plus two C–H bonds extra.

\[ \Delta H_{\text{reaction}} = - [\Delta H_{\text{C-C}} + 2\Delta H_{\text{C-H}}] - (\Delta H_{\text{C=C}} + \Delta H_{\text{H-H}}) \]
\[ = -(83+2 \times 99) + (146+102) \text{kcal} = -281+248\text{kcal} = -33\text{kcal}. \]

**Calculation of heat of formation**

Heat of formation can be calculated by taking the sum of the average bond energies involved in the molecule. For example, the heat of formation of n-pentane,

\[ 5\text{C}(g) + 12\text{H}(g) \rightarrow \text{H} \quad \text{C} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \]
\[ \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{C} \quad \text{C} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \]

Can be calculated as follows:
Since there are four C–C and twelve C–H bonds
\[ \Delta H_{f} \text{ for } \text{C}_5\text{H}_{12} = [4 \times \text{B.E for C–C} + 12 \times \text{B.E for C–H}] \]
\[ = 4 \times 79.5 + 12 \times 98.5 \text{kcal mol}^{-1} \]
\[ = 1,499.2 \text{kcal mol}^{-1} \]

**6.9 Hess’s Law of Constant Heat Summation**

According to Hess’s law “the heat change in a particular reaction is always constant and is independent of the manner in which the reaction takes place.” In other words, the overall heat change in a chemical reaction carried out either at constant pressure (or at constant volume) is the same, irrespective of the fact whether the reaction proceeds in one or several stages. This law is a direct consequence of the first law of thermodynamics, according to which heat change, \( \Delta H \) (enthalpy change) or \( \Delta E \) (internal energy change) of a reaction is state function, i.e., dependent only on the initial and final states of the system.

**Example**

Let us consider the formation of CO\(_2\). Carbon might be burned directly to CO\(_2\). On the other hand, carbon might be burned to carbon monoxide and then the latter burnt to carbon dioxide. The two procedures can be represented as follows:

**First procedure (in one-step only):**

\[ \text{C(s)} + \text{O}_2 (g) \rightarrow \text{CO}_2 (g), \quad \Delta H = -393.5 \text{ kJ} \]

**Second procedure (in two-steps):**

\[ \text{C(s)} + \frac{1}{2} \text{O}_2 (g) \rightarrow \text{O}_2 (g) \quad \Delta H = -110.5 \text{ kJ} \]
\[ \text{CO (g)} + \frac{1}{2} \text{O}_2(g) \rightarrow \text{O}_2(g) \quad \Delta H = -283.0 \text{ kJ} \]

Adding: \[ \text{C(s)} + \text{O}_2 (g) \rightarrow \text{CO}_2 (g); \quad \Delta H = -393.5 \text{ kJ} \]

**6.9.1 Applications of Hess’s Law**

Hess’s law has made it clear that thermochemical equations are simple algebraic equations, which can be added, subtracted, multiplied and divided by any number. This has led us to compute indirectly heat of formation, heat of transition, etc., which cannot be measured experimentally.

• Calculation of heat of reaction: Heat of certain reactions is extremely difficult to measure. However, Hess’s law makes it possible.
Calculation of heat of formation: The heats of formation of compounds, which either cannot be prepared directly from their elements or which synthesis reaction proceeds too slow to allow direct measurement, can be computed indirectly with the help of Hess’s law by using their heat of combustion values, which can be measured easily.

Calculation of heat of transition: The following example will illustrate the heat of transition of C (graphite) to C (diamond). Suppose heats of combustion (H) of graphite and diamond are x and y kJ mol\(^{-1}\) respectively, i.e.,

\[ \text{C (graphite)} + \text{O}_2(g) \rightarrow \text{CO}_2(g); \quad \Delta H = x \text{ kJ} \quad ...(i) \]
\[ \text{C (diamond)} + \text{O}_2(g) \rightarrow \text{CO}_2(g); \quad \Delta H = y \text{ kJ} \quad ...(ii) \]

Subtracting (ii) from (i), we get:
\[ \text{C (graphite)} \rightarrow \text{C (diamond)}; \quad \Delta H = (x-y) \text{ kJ} \]

Hence, the heat of transition (\(\Delta H\)) of graphite into diamond is \((x-y) \text{ kJmol}^{-1}\).

### 6.10 Heat Capacity

Heat capacity (C) of a substance is “the amount of heat needed to raise the temperature of 1g of it through 1°C”; whereas molar heat capacity (C) is the amount of heat required to raise the temperature of 1 mole of it through 1°C.

- Molar heat capacity is of two types:
  - Molar heat capacity at constant volume (C\(_v\)) is measured by keeping the volume constant. It is given by:
    \[
    C_v = \left(\frac{\partial E}{\partial T}\right)_v
    \]
  - Molar heat capacity at constant pressure (C\(_p\)) is measured by keeping pressure constant. It is given by:
    \[
    C_p = \left(\frac{\partial H}{\partial T}\right)_p = \frac{dq}{dT}
    \]

Relation between C\(_p\) and C\(_v\):
\[ H = E + PV \]
When the temperature is changed; then \(\Delta H = \Delta E + \Delta(PV)\)

or
\[
\frac{\Delta H}{\Delta T} = \frac{\Delta E}{\Delta T} + \frac{\Delta(PV)}{\Delta T}
\]

or
\[
C_p = C_v + \frac{\Delta(PV)}{\Delta T}
\]

For 1 mole of any ideal gas \(P_1V_2 = -RT_2\) and \(P_1V_1 = RT_1\), so that
\[
\Delta(PV) = R(T_2-T_1) = RT
\]
For 1 mole of gas
\[
C_p = C_v + R
\]
For solids and liquids, \(\Delta H = \Delta E\) and \(\Delta(PV) = 0\), so that \(C_p = C_v\)

### 6.11 Kirchoff’s Equation

The variation of heat of reaction with temperature can be derived with the help of the first law of thermodynamics. Consider a simple hypothetical reaction in which the reactant in state A at the temperature \(T_1\) yields the product in state B at the temperature \(T_2\). We may proceed from state A at \(T_1\) to B at \(T_2\) by two paths as shown in Fig. 6.4.
Let $\Delta H_1$ be the heat of reaction at temperature $T_1$ and $\Delta H$ be the heat of reaction at temperature $T_2$. Again let $C_p$ and $C'_p$ represent respectively the mean molar heat capacity of the reactants and product at constant pressure.

In the first path, the reactants are first heated from $T_1$ to $T_2$ and then allowed to react at the higher temperature, $T_2$. Therefore, the total heat change involved is given by:

$$\Delta H \text{ (path 1)} = C_p (T_2 - T_1) + \Delta H_2$$

In the second path, the reactants are allowed to react at the lower temperature, $T_1$ and then the products are heated to $T_2$. The value of total heat change ($\Delta H$) for this path is as follows:

$$\Delta H \text{ (path 2)} = \Delta H_1 + C'_p (T_2 - T_1)$$

According to the first law of thermodynamics,

$$\Delta H \text{ (path 1)} = \Delta H \text{ (path 2)}$$

or $C_p (T_2 - T_1) + H_2 = \Delta H_1 + C'_p (T_2 - T_1)$

Therefore,

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = C'_p - C_p = \Delta C_p$$  \(\text{..(iii)}\)

where $\Delta C_p$ = difference in the heat capacities of the products and the reactants at constant pressure. This equation (iii) is called Kirchoff’s equation.

The above equation may also be written as:

$$\frac{\Delta H_2 - \Delta H_1}{\Delta T} = \Delta C_p$$

[Where, $\Delta T = T_2 - T_1$]
6.12 Entropy

Entropy of a system is a measure of randomness or disorder of the system and is denoted by the symbol $S$. It is a state function (i.e., the change in entropy is independent of path). It can also be regarded as the measure of "unavailable energy".

The change in entropy of a system (or a reaction) is given by:

$$\Delta S = S_{\text{final}} - S_{\text{initial}} = S_2 - S_1$$

Entropy is expressed in Joule deg$^{-1}$ (JK$^{-1}$)

6.12.1 Physical Significance of Entropy

- Entropy has been regarded as “a measure of disorder or randomness of a system”. Thus, when a system goes from a more orderly to less orderly state, there is an increase in its randomness and hence, entropy of the system increases.

- Conversely, if the change is one in which there is an increase in orderliness, there is a decrease in entropy. For example, when a solid changes to a liquid, an increase in entropy takes place, because with the breaking of the orderly arrangement of the molecules in the crystal to the less orderly liquid state, the randomness increases. Conversely, the process of solidification brings about a more orderly state and consequently, there is a decrease in entropy.

- The process of vaporisation produces an increase in randomness in the distribution of molecules, hence an increase in entropy. This concept of entropy, as a measure of orderliness or randomness, has led to the conclusion that “all substances in their normal crystalline state at the absolute zero temperature would be in the condition of maximum orderly arrangement, because all motion has essentially ceased at OK”. In other words, entropy of a substance at OK is minimum.

- It may be added here that in any system, only a part of the total energy is made available for useful work, since some energy is always dissipated (or wasted) isothermally. This “unavailable energy” of the system is considered equal to the product of the intensity factor and a capacity factor. The intensity factor is referred to as the temperature, while the capacity factor is entropy. Thus, we can say that entropy signifies the unavailable form of energy of the system.

6.12.2 Entropy Change for an Ideal Gas

Consider the reversible expansion of an ideal gas enclosed in a container, fitted with a frictionless weightless and movable piston at constant pressure, $P$. Let the volume change from $V_1$ to $V_2$. Since the process is reversible, the pressure of the gas is approximately equal to the external pressure against which the gas is expanding at all stages. Hence, under these conditions, the work done by the gas is maximum; and is equal to $P.dV$.

We know from the first law of thermodynamics,

$$dq = dE + dw = dE + P.dV$$

$$\frac{C_v}{T} \cdot \frac{dT}{V} + \frac{RT}{V}$$

(since $C_v = \frac{dE}{dT}; P = \frac{RT}{V}$)

$$\frac{dq}{T} = C_v \cdot \frac{dT}{T} + R \frac{dV}{V}$$

$$dS = C_v \frac{dT}{T} + R \frac{dV}{V}$$

(since, $\frac{dq}{T} = dS$)

Thus, for a definite change from state 1 to 2, the total change in entropy is given by:

$$\int_{V_1}^{V_2} dS = \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{V_1}^{V_2} \frac{dV}{V}$$

$$= C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \quad \text{...(i)}$$
The corresponding expression for n moles would be:
\[ \Delta S = nC_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \]
\[ \frac{V_2}{V_1} = \frac{P_2}{P_1} \] ...(ii)

But for an ideal gas:
\[ \Delta S = nC_v \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2} \]
\[ nC_v \ln \frac{T_2}{T_1} + R \ln \frac{P_2}{P_1} \] ...(iii)

- At constant temperature, i.e., when \( T_1 = T_2 \) then for isothermal expansion of the gas, the equations (ii) and (iii) take the form:
  \[ (\Delta S)_T = nR \ln \frac{V_2}{V_1} = \frac{P_1}{P_2} = 2.303 n R \log \frac{V_2}{V_1} \] ...(iv)

- At constant pressure, i.e., when \( P_1 = P_2 \) the equation (iii):
  \[ (\Delta S)_p = nC_v \ln \frac{T_2}{T_1} = 2.303n C_p \log \frac{T_2}{T_1} \] ...(v)

In this equation \( C_v \) has been changed to \( C_p \), because the change in temperature has taken place at constant pressure.

At constant volume, i.e., for an isochoric process, \( V_1 = V_2 \), so the equation (ii) takes the form
\[ (\Delta S)_v = nC_v \ln \frac{T_2}{T_1} = 2.303n C_v \log \frac{T_2}{T_1} \]

### 6.13 Free Energy

Free energy of system, (denoted by the symbol ‘G’) is a thermodynamic state function, which is related to enthalpy and entropy as:
\[ G = H - TS \] ...(i)

Free energy change (\( \Delta G \)) of a system (or reaction) a measure of energy available for doing useful work. Thus:
[Energy available as useful work] = [Total energy available] – [Non available form of energy]

The change in free energy between two states of a system,
or \( \Delta G = G_2 - G_1 = (H_2 - T_2S_2) - (H_1 - T_1S_1) \)
\[ = (H_1H_1) - (T_2S_2 - T_1S_1) \]
\[ = \Delta H - (T_2S_2 - T_1S_1) \]
when, at constant temperature (i.e., \( T_1 = T_2 \))
\[ \Delta G = \Delta H - T \Delta S \] ...(ii)

### 6.13.1 Physical Significance of Free Energy

From the law of conservation, of energy, the total heat energy supplied to the system,
\[ q = \Delta E + W_{\text{expansion}} + W_{\text{non-expansion}} \]
\[ = \Delta E + P \Delta V + W_{\text{non-expansion}} \]
\[ = \Delta H + W_{\text{non-expansion}} \] ...(iii)
Now in a reversible change at constant temperature \( T \), we have:

\[ \Delta S + \frac{q}{T} = T \Delta S \quad \text{(iv)} \]

From (iii) and (iv), we get:

\[ T \Delta S = \Delta H + W_{\text{non-expansion}} \]

or

\[ \Delta H - T \Delta S = -W_{\text{non-expansion}} \]

\[ = (\Delta G)_{PT} \]

or

\[ - (\Delta G)_{PT} = W_{\text{non-expansion}} \quad \text{(v)} \]

i.e., \( -\Delta G \) is a measure of non-expansion or useful work obtainable in a reversible reaction at constant temperature and pressure. In other words, decrease in free energy, during a process, is equal to the “useful work” obtainable from the process.

Standard state for a substance is defined as the pure material in its most stable form (gas, liquid or solid) at the external pressure of 1 atm and at the specified temperature (most usually = 298 K). The standard state conventions are:

- For a solid: The pure substance at 1 atm external pressure.
- For a liquid: The pure substance at 1 atm external pressure.
- For a gas: An ideal gas at 1 atm partial pressure.
- For a solution: An ideal solution at 1 M concentration.

Standard free energy change (\( \Delta G^0 \)) is defined as “the free energy change for a process at 298 K in which the reactants in their standard states are converted into the products in their standard states”. Thus:

\[ \Delta G^0 = \sum G^0_{\text{products}} - \sum G^0_{\text{reactants}} \]

The value of \( \Delta G^0 \) for a reaction can be derived from the standard free energies of formation (\( \Delta G^0_f \)). The standard free energy of formation (\( \Delta G^0_f \)) of a compound is defined as “the change in free energy, when 1 mol of the compound is formed from its constituent elements in their standard states”. Thus:

\[ \Delta G^0_f = \sum G^0_{\text{products}} - \sum G^0_{\text{reactants}} \]

= [Sum of the standard free energies of formation of products] – [Sum of the standard free energies of formation of reactants]

It may be pointed here that “the standard free energy of formation of an element in its standard state is zero.”

**Relation between (\( \Delta G^0 \) and equilibrium constant \( K_{eq} \))**

The standard free energy change (\( \Delta G^0 \)) of a reaction is related to the equilibrium constant (\( K_{eq} \)) by the relation:

\[ \Delta G^0 = -2.303RT \log K_{eq} \]

where \( R \) = gas constant (= 8.314 JK\(^{-1}\)mol\(^{-1}\)), \( T \) = temperature in Kelvin.

**Relation between standard free energy changes and cell potential**

We know that decrease in free energy is equal to maximum useful work that can be obtained from a process, i.e.,

\[ -\Delta G = W_{\text{max}} \]

If the useful work involved is electrical work (e.g., in Daniel cell), then:

\[ -\Delta G = W_{\text{max}} = \text{electrical work} = nFE \]

Where \( n \) = number of electrons involved in the cell reaction; \( E \) = emf (or potential) of the cell and \( F \) = Faraday (= 96,500 C).

If reactants as well products of the cell reaction are in their standard states (i.e., 298 K and 1 atm), then:

\[ -\Delta G^0 = nFE^0 \]

Where, \( \Delta G^0 \) = standard free energy change and \( E^0 \) = standard EMF (or potential) of cell.
Feasibility of cell reaction
The cell reaction is feasible if \( \Delta G^0 \) is positive (or standard free energy change is negative). A positive value of \( \Delta G^0 \) shows that the reaction may be feasible in the reverse direction.

### 6.14 The Second Law of Thermodynamics

Statements of the second law of thermodynamics: The law can be stated in the following several ways:

- It is impossible to convert heat completely into an equivalent amount of work, without producing some other changes in some parts of the system.
- It is impossible for a self-acting machine, unaided by any external agency, to convey heat from a body at a lower temperature to a body at a higher temperature.
- Heat cannot pass by itself from a colder to a hotter body.
- Only a fraction of a given quantity of heat may be converted to work, when it is allowed to flow from a body at a higher temperature to a body at a lower temperature and that its value depends on the temperature difference and the higher temperature.
- It is impossible to convert heat from a reservoir into work by a cyclic process, without transferring it to a colder reservoir.
- All natural or spontaneous processes tend to take place in one direction and they cannot be reversed.
- The energy of the universe is constant, but the entropy approaches a maximum or the universe is approaching a condition of maximum randomness.
- All naturally occurring processes always tend to change spontaneously in a direction, which will ultimately lead to equilibrium.
- There is a general tendency in nature for energy to pass from a more to a less ordered form.

### 6.15 Gibbs – Helmholtz Equation

We know: \( G = H - TS \) and \( H = E + PV \)

\[ G = E + PV - TS \]

Upon differentiation we get:

\[ dG = dE + PdV + VdP - TdS - SdT \]

But \( dq = dE + dw = dE + PdV \) \( \text{(1st law)} \)

\[ . . . dG = dq + VdP - TdS - SdT \]

For reversible process: \( dS = dq/T \) or \( T.dS = dq \)

\[ . . . dG = VdP - SdT \]

If pressure remains constant, i.e., \( dP = 0 \) then:

\[ dG = - SdT \] \( \text{... (i)} \)

Let \( G_1 \) = initial free energy of a system at \( T \); and \( G_1 + dG_1 \) = initial free energy of the system at \( T + dT \), where \( dT \) is infinitesimally small and pressure is constant,

\[ dG_1 = -S_1dT \] \( \text{... (ii)} \)

where, \( S_1 \) is the entropy of the system in the initial state.

Now suppose that the free energy of the system in the final state is \( G_2 \) at \( T \).

Let \( G_2 + dG_2 \) be the free energy of the system at \( T + dT \) in the final state, then:

\[ dG_2 = -S_2dT \] \( \text{... (iii)} \)

where \( S_2 \) is the entropy of the system in the final state.

Subtracting (ii) from (iii), we get:

\[ dG_2 - dG_1 = -(S_2 - S_1)dT \]

or \( d(\Delta G) = -\Delta SdT \) \( \text{... (iv)} \)
At constant pressure,
\[
\left[ \frac{\partial (\Delta G)}{\partial T} \right]_p = -\Delta S \quad \text{...(v)}
\]
We know: \( \Delta G = \Delta H - T \Delta S \)
\[
-\Delta S = \frac{\Delta G - \Delta H}{T} \quad \text{...(vi)}
\]
From (v) and (vi), we get:
\[
\frac{\Delta G - \Delta H}{T} = \left[ \frac{\partial (\Delta G)}{\partial T} \right]_p
\]
or
\[
\Delta G = \Delta H + T \left[ \frac{\partial (\Delta G)}{\partial T} \right]_p
\]
This equation is called the Gibbs-Helmholtz equation in terms of free energy and enthalpy changes at constant pressure.

6.15.1 Application of the Gibbs-Helmholtz Equations

**Calculation of E.M.F. of a reversible cell**

Suppose the emf of a reversible cell, when operated at constant pressure and constant temperature, is \( E \). Let \( n \) faraday, i.e., \( nF \) coulombs of electricity is yielded by the cell, then:

Electrical work obtained = \( nFE \)

We know: Net electrical work = decrease in free energy.

Therefore, \( nF = -\Delta G \)

Substituting in the Gibbs-Helmholtz equation, we have:
\[
- nFE = \Delta H - T \left( \frac{\partial (nFE)}{\partial T} \right)_p
\]
\[
= \Delta H - nFT \left( \frac{\partial E}{\partial T} \right)_p \quad \text{(Since \( n \) and \( F \) are constant)}
\]
\[
E = \frac{-\Delta H}{nF} + T \left( \frac{\partial E}{\partial T} \right)_p
\]

Thus, by knowing \( E \) (emf. of the cell) and \( \left( \frac{\partial E}{\partial T} \right)_p \), i.e., variation of emf (with temperature at constant pressure), the value of heat of reaction (\( \Delta H \)) occurring in the cell can be calculated.

6.15.2 Significance of the Gibbs-Helmholtz Equation

The Gibbs-Helmholtz equation helps us in a better understanding of the force that causes the chemical reaction to proceed forward. We know that if \( \Delta G \) is negative, the reaction occurs spontaneously and if free energy of the reactants and the products are equal, i.e., \( \Delta G = 0 \), the reaction is in equilibrium. From the relation, \( \Delta G = \Delta H - T \Delta S \)

It is clear that \( \Delta G \) is made up of two opposing parts, viz.,

- \( \Delta H \): When the reaction is exothermic, \( \Delta H \) is negative, so \( \Delta G \) tends to be negative and consequently, the reaction tends to the spontaneous. This is supported by the fact that generally exothermic reactions at ordinary temperature and pressure are spontaneous.

- \( T \Delta S \): If \( \Delta S \) is positive, \( \Delta G \) tends to be negative. Thus, physical and chemical changes proceed spontaneously in a direction in which the entropy increases. For example, a solid substance dissolves in the solvent, because entropy (or randomness) of the system increases.
Criteria of the spontaneity of the process: For a reaction to be spontaneous, $\Delta G$ must be negative. The $\Delta G$ is negative under the following condition:

- If $\Delta H$ is negative and $\Delta S$ is positive, since both factors make $DG$ negative.
- If both $\Delta H$ and $\Delta S$ are positive and the magnitude of $T \Delta S > \Delta H$.
- If both $\Delta H$ and $\Delta S$ are negative and the magnitude of $\Delta H > T \Delta S$.

<table>
<thead>
<tr>
<th>$\Delta H$</th>
<th>$\Delta S$</th>
<th>$-T \Delta S$</th>
<th>$\Delta G$</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>-ve</td>
<td>+ve</td>
<td>-ve</td>
<td>-ve at all T</td>
<td>Spontaneous at all T</td>
</tr>
<tr>
<td>-ve</td>
<td>-ve</td>
<td>+ve</td>
<td>-ve at low T</td>
<td>Spontaneous at low T</td>
</tr>
<tr>
<td>+ve</td>
<td>-ve</td>
<td>+ve</td>
<td>+ve at high T</td>
<td>Non- spontaneous at high T</td>
</tr>
<tr>
<td>+ve</td>
<td>+ve</td>
<td>-ve</td>
<td>-ve at high T</td>
<td>Spontaneous at high T</td>
</tr>
<tr>
<td>+ve</td>
<td>-ve</td>
<td>+ve</td>
<td>+ve at all T</td>
<td>Non-spontaneous at all T</td>
</tr>
</tbody>
</table>

Table 6.1 Spontaneous and non-spontaneous reactions

6.16 Free Energy Change of an Ideal Gas in Isothermal Reversible Change

We know that,
$$G = H - TS$$
and
$$H = E + PV$$

$$G = E + PV - TS$$

Upon differentiation, we get:
$$dG = dE + P \cdot dV + V \cdot dP - T \cdot dS - S \cdot dT \quad \ldots (i)$$

From 1st law, we have
$$dq = dE + dw = dE + PdV \quad \ldots (ii)$$

$\therefore$ From (i) and (ii), we get :
$$dG = dq + V \cdot dP - T \cdot dS - S \cdot dT \quad \ldots (iii)$$

We know that for a reversible process,
$$dS = \frac{dq}{T} \quad or \quad dS = dq$$

or
$$dq - T \cdot dS = 0 \quad \ldots (iv)$$

From (iii) and (iv), we get:
$$dG = V \cdot dP S \cdot dT \quad \ldots (v)$$

If temperature is kept constant (isothermal change), i.e., $dT=0$, then the equation (r) takes the form:
$$dG = V \cdot dP \quad \ldots (vi)$$

Free energy change from state 1 to 2 at constant temperature is given by:

$$\Delta G = G_2 - G_1 = \int_{\eta_1}^{\eta_2} V \cdot dP = \int_{\eta_1}^{\eta_2} \frac{PV \cdot dP}{P} \quad \ldots (vii)$$

where $P_1$ and $P_2$ are the initial and final pressures respectively.
For n moles of an ideal gas: \( PV = nRT \)

\[ \therefore \Delta G = nRT \int_{P_1}^{P_2} \frac{dP}{P} \]

or \( \Delta G = nRT \ln \frac{P_2}{P_1} \)

\[ \therefore \Delta G = 2.303nRT \log \frac{P_2}{P_1} = 2.303nRT \frac{V_2}{V_1} \]

...(viii)

Where \( V_1 \) and \( V_2 \) are the initial and final volumes respectively.

### 6.17 The Clapeyron-Clausius Equation

Consider a system consisting of only 1 mole of a substance, which exists in two phases A and B. Let the temperature and pressure of the system be \( T \) and \( P \) respectively. Suppose the free energy/mole of the substance in two phases A and B be \( G_A \) and \( G_B \). The system being in equilibrium, so there is no free energy change i.e.,

\( G_A = G_B \)

Let the temperature of the system be raised to \( T + dT \), so that the pressure becomes \( P + dP \). Suppose the new free energies per mole of A and B phases be \( G_A + dG_A \) and \( G_B + dG_B \) respectively. As the two phases are still in equilibrium, so:

\[ G_A + dG_A = G_B + dG_B \]

We know: \( G = H - TS = E + PV - TS \) .... (iii)

\[ dG = dE + PdV + VdP - TdS - SdT \] ... (iv)

But \( dq = dE + dw = dE + PdV \) .... (v)

and \( dq/T = dS \) or \( TdS = dq \) ...(vi)

From (iv), (v) and (vi), we get: \( dG = V . dP - S . dT \) ...(vii)

As the various equilibria considered here are such in which work done is only due to volume change, so equation (vii) may be applied to phase A as well as B.

\[ dG_A = V_A dP - S_A dT \] ...(viii)

and \( dG_B = V_B dP - S_B dT \) ...(ix)

where \( V_A \) and \( V_B \) are the molar volumes of phase A and B respectively and \( S_A \) and \( S_B \) are their molar entropies.

From (vii), (viii) and (ix), we get:

\[ V_A dP - S_A dT = V_B dP - S_B dT \]

or \( \frac{dP}{dT} = \frac{S_B - S_A}{V_B - V_A} = \frac{\Delta S}{V_B - V_A} \)

...(x)

Where, \( \Delta S \) = molar entropy change and \( V_B - V_A \) is the change in volume when 1 mole of substance changes from A to B.

If molar heat of transition from phase A to B is \( q \), then

\[ \Delta S = \frac{q}{T} \] ... (xi)

From (x) and (xi), we get:

\[ \frac{dP}{dT} = \frac{q}{T(V_B - V_A)} \] ...(xii)
Applications

- Determination of latent heat from vapour pressure: If the vapour pressure at two different temperatures of the two phases in equilibrium are known, then the latent heat can be calculated by using the Clapeyron-Clausius equation.

- To study the effect of pressure on boiling point: If the boiling point of a liquid at one pressure and its latent heat of vaporisation are known, then boiling point of liquid at another pressure can be computed with the help of the integrated Clapeyron-Clausius equation (xiii).

- To study the effect of temperature on the vapour pressure of a liquid: If latent heat ($L_v$) and vapour pressure of a liquid at one temperature are known, then vapour pressure of liquid at another temperature can be calculated with the help of the Integrated Clapeyron-Clausius equation (xiii).

**6.18 The Third Law of Thermodynamics**

This law was stated by Nernst in 1906 and according to him, “at absolute zero, the entropy of a perfectly crystalline substance is taken as zero.” At absolute zero, the kinetic energy is zero and the substances (element and compounds) are in a rigid state, thereby providing them complete order. Due to total lack of disorder, the entropy of all pure elements and compounds at absolute zero is zero.

**Calculation of absolute entropy values**

Absolute value of entropy at room temperature can be measured by determining heat capacities ($C_p$) of the substance at different temperatures ($T$). Then, $C_p$ values are plotted against $T$.

The area of the curve between $T = 0$ and the required temperature gives the value of absolute entropy of a substance ($S_T$).

**6.19 Van’t Hoff Isotherm**

Consider a general reaction,

$$aA + bB \rightarrow cC + dD \quad \text{...(i)}$$

We know: $G = H - TS = E + PV - TS$

or $dG = dE + PdV + VdP - TdS - SdT$

But $d = dE + PdV$ and $dS = dq/T$

$dG = V \cdot dP - SdT$

At constant temperature, (dG) $T = V$. dP Free energy change for 1 mole of any gas at a constant temperature is given by:

$$dG = V \cdot dP = RT \cdot \frac{dP}{P} \quad \text{[:: PV = RT]}$$

Integrating:

$$\int dG = RT \int \frac{dP}{P}$$

$$G = G^0 + RT \ln P \quad \text{...(ii)}$$

Where $G^0$ integration constant and is known as standard free energy, i.e.,

$G^0 = -G$ when $P = 1$ atm

Let the energy/mole of A, B, C and D at their respective pressures $P_A$, $P_B$, $P_C$ and $P_D$ are $G_A$, $G_B$, $G_C$ and $G_D$ respectively. Then, the free energy change for the reaction (i) is given by:

$$G_{\text{products}} - G_{\text{reactants}} = \left[ cG_C + dG_D \right] - \left[ aG_A + bG_B \right] \quad \text{...(iii)}$$

Substituting the value of $G_A$, $G_B$, $G_C$ and $G_D$ in (iii) from (ii), we get:
\[ \Delta G = \left[ G^c + cRT\ln P_a + dG^a + dRT\ln P_b \right] - \left[ G^c + aRT\ln P_a + dG^a + bRT\ln P_b \right] \]

or

\[ \Delta G = \Delta G^0 + RT\ln \frac{(P_a)^d}{(P_b)^b} \]

...(iv)

Where, \( \Delta G^0 = \text{standard free energy of reaction} \)

We know that at equilibrium, \( \Delta G = 0 \)

\[ \Delta G = \Delta G^0 + RT\ln K_{eq} \]

\[ \implies \left[ \frac{(P_a)^d}{(P_b)^b} \right]_{eq} = K_{eq} \]

or

\[ \Delta G^0 = -RT\ln K_{eq} \]

...(v)

From (iv) and (v) we get:

\[ \Delta G = -RT\ln K_{eq} + RT\ln \frac{(P_a)^d}{(P_b)^b} \]

or

\[ \Delta G = -RT\ln K_{eq} - RT\ln \frac{(P_a)^d}{(P_b)^b} \]

...(vi)

This expression, called Van’t Hoff isotherm, is very important and gives a quantitative relation for free energy change accompanying a chemical reaction.

Van’t Hoff isotherm: \( \Delta G^0 = -RT\ln K_{eq} \)

or

\[ \ln K_{eq} = -\frac{\Delta G^0}{RT} = -(\Delta H^o - T\Delta S^o) = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \]

\[ \therefore \ln K_{eq} = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \text{ and } \ln K_{eq} = \Delta H^o \left[ \frac{1}{T_1} - \frac{1}{T_2} \right] \]

or

\[ \ln K_{eq} = \Delta H^o \left[ \frac{T_2 - T_1}{T_1 T_2} \right] \]

or

\[ \log K_{eq} = \frac{\Delta H^o}{2.303R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right] \]

...(vii)

This expression, called the Van’t Hoff isotherm, can be used to calculate the equilibrium constant at \( T \), if its value at \( T \) is known.
**Solved examples**

**Example 1**
Calculate the heat of formation of benzene, given the heats of combustion of benzene, carbon and hydrogen are $-780$ kcal, $-94.0$ kcal and $-68.0$ kcal, at 300 K.

**Solution**
The given data is

\[
\begin{align*}
C_6H_6(l) + 7.5O_2(g) & \rightarrow 6CO_2(g) + 3H_2O (l) & \Delta H &= -780 \text{kcal} \\
C(s) + O_2(g) & \rightarrow CO_2(g) & \Delta H &= -94.0 \text{kcal} \\
H_2(g) + 0.5 O_2(g) & \rightarrow H_2O (l) & \Delta H &= -68.0 \text{kcal}
\end{align*}
\]

Our aim is $6C(s) + 3H_2(g) \rightarrow C_6H_6(l)$; \hspace{1cm} \Delta H_f = ?

\[6 \times \text{Eq (ii)} + 3 \times \text{Eq (iii)} - \text{Eq (i)} \text{ gives:} \]

\[\Delta H = -564 \text{kcal} \]

\[6C(s) + 6O_2(g) \rightarrow 6CO_2(g); \quad \Delta H = -204 \text{kcal} \]

\[6CO_2 (g) + 3H_2O (g) \rightarrow C_6H_6(l) + 7.5O_2 (g) \quad \Delta H = +780 \text{kcal} \]

Adding: $6C(s) + 3H_2(g) \rightarrow C_6H_6(l) \quad \Delta H_f = +12 \text{kcal}$

Hence, heat of formation \( \Delta H_f \) of \( C_6H_6(l) \) is \(+12 \text{kcalmol}^{-1}\).

**Example 2**
\(\Delta G\) and \(\Delta H\) values for a reaction at 300 K are \(-16.0\) kcal and \(-10\) kcal respectively. Calculate the free energy at 330 K.

**Solution**
We know that entropy change,

\[\Delta S = \frac{\Delta H - \Delta G}{T} = \frac{-10,000 \text{cal} + 16,000 \text{cal}}{300} \]

\[= 20 \text{caldeg}^{-1}\]

\[\therefore \text{At } 330 \text{K, } \Delta G = \Delta H - T \Delta S \]

\[= -10,000 \text{cal} - 330 \times 20 \text{cal} \]

\[= -16,600 \text{cal} = -16.6 \text{kcal} \]

**Example 3**
Gibbs free energy of a reaction at 27°C and 37°C are \(-29.0\) kcal and \(-30.0\) kcal respectively. Determine its \(\Delta H\) and \(\Delta S\) in this temperature range.

**Solution**
Here \(T_1 = 300 \text{ K} ; T_2 = 310 \text{ K} ; \Delta G_{300} = -29.0 \text{ kcal} = -29,000 \text{ cal} ; \Delta G_{310} = -30.0 \text{ kcal} = -30,000 \text{ cal} .

\[\Delta G_{310} = -30.0 \text{ kcal} = -30,000 \text{ cal} .
\]

\[\therefore \Delta S = \frac{\partial \Delta G}{\partial T} = \frac{\Delta G_{310} - \Delta G_{300}}{(T_2 - T_1)} = \frac{-30,000 - 29,000}{310 - 300} = -100 \text{cal deg}^{-1}
\]

or

\[\Delta S = 100 \text{caldeg}^{-1}\]

But \(\Delta G = \Delta H - T \Delta S\)

\[\therefore \text{At } 330 \text{K (27°C)}: \]

\[-29000 \text{cal} = \Delta H - 300 \times 100 \text{cal} \]

or

\[\Delta H = -30,000 + 29, 000 \text{cal} = -1,000 \text{cal} = -1.0 \text{kcal}\]
Summary

- The thermodynamic system is defined as any portion of matter under consideration, which is separated from the surroundings by real or imaginary boundaries. The thermodynamic system may be homogeneous or heterogeneous, but has to be macroscopic. A system is called homogeneous, if it consists of one phase. i.e., its physical and chemical properties are identical throughout the system.

- The zeroth law of thermodynamics begins with a simple definition of thermodynamic equilibrium. It is observed that some property of an object, like the pressure in a volume of gas, the length of a metal rod, or the electrical conductivity of a wire, can change when the object is heated or cooled. If two of these objects are brought into physical contact there is initially a change in the property of both objects.

- The first law of thermodynamics provides the basic principle used in heat engines, from steam turbines to nuclear reactors. It has its obvious application in transportation.

- The first law merely states the exact equivalence of various forms of energy involved, but provides no information regarding the feasibility of the process. Moreover, this law does not say whether a gas can diffuse from low pressure to high pressure or whether water itself can flow uphill, etc.

- Bond energy can be defined as the average amount of energy required (or enthalpy change involved) during the breaking of one mole (or Avogadro’s number) of bonds of the same type, present in the molecules of a gaseous compound, into gaseous fragments, atoms, radicals, etc. Bond energy is sometimes also called the enthalpy or heat formation of the bond.

- The second law of thermodynamics states that it is impossible to convert heat completely into an equivalent amount of work, without producing some other changes in some parts of the system.

- The Gibbs-Helmholtz equation helps us in a better understanding of the force that causes the chemical reaction to proceed forward.

- The third law of thermodynamics states that at absolute zero, the kinetic energy is zero and the substances (element and compounds) are in a rigid state, thereby providing them complete order. Due to total lack of disorder, the entropy of all pure elements and compounds at absolute zero is zero.

References


Recommended Reading


Self Assessment

1. The __________ system is defined as any portion of matter under consideration, which is separated from the surroundings by real or imaginary boundaries.
   a. aerodynamic
   b. thermodynamic
   c. thermostatic
   d. thermocheccimal

2. A system is called homogeneous, if it consists of one phase and its physical and ______ properties are identical throughout the system.
   a. biological
   b. molecular
   c. chemical
   d. natural

3. Which law does not say whether a gas can diffuse from low pressure to high pressure or whether water itself can flow uphill?
   a. First Law of Thermodynamics
   b. First Law of faraday
   c. Second Law of Thermodynamic
   d. Third Law of Thermodynamic

4. Which of the following statement is true.
   a. The Kirchoff’s equation helps us in a better understanding of the force that causes the chemical reaction to proceed forward.
   b. The Van’t Hoff equation helps us in a better understanding of the force that causes the chemical reaction to proceed forward.
   c. The Gibbs-Helmholtz equation helps us in a better understanding of the force that causes the reaction to reverse
   d. The Gibbs-Helmholtz equation helps us in a better understanding of the force that causes the chemical reaction to proceed forward.

5. The ________ is capable of exchanging both matter and energy (as heat) with the surroundings.
   a. isolated system
   b. closed system
   c. open system
   d. remote system

6. For an isolated system, matter and ________ remain constant.
   a. state
   b. energy
   c. chemical properties
   d. physical properties
7. Helmholtz, __________ and Kelvin enunciated a generated law of nature, commonly known as the principle of the conservation of energy.
   a. Clausius
   b. Gibbs
   c. Kirchoff
   d. Van’t Hoff

8. __________ is a state function as it depends only on the initial and final states and not on the path followed between the states.
   a. External energy
   b. Static energy
   c. Internal energy
   d. Isolated energy

9. Which effect states “when a gas under high pressure is permitted to expand to a region of low pressure, it suffers a fall in temperature?”
   a. The Van’t Hoff effect
   b. The pressure – gas effect
   c. The temperature – energy effect
   d. The Joule-Thomson effect

10. The stability of a compound is __________ to its heat content.
    a. inversely proportional
    b. equal
    c. directly proportional
    d. inversely related
Chapter VII
Physicochemical Principles

**Aim**
The aim of this chapter is to:

- explore thermodynamics of combustion
- analyse rates of chemical change in combustion
- explain transport properties of gases

**Objectives**
The objectives of this chapter are to:

- explain the extent of reaction and determination of chemical equilibrium
- discuss termolecular reactions and elements of chain reaction mechanisms
- examine grouping of parameters and dimensional groups

**Learning outcome**
At the end of this chapter, you will be able to:

- understand the conduction of heat as per Fourier’s law
- state concentration dependences in global and elementary reaction rate expressions
- discuss diffusion as per Fick’s law
7.1 Introduction

From the study of chemical equilibrium involving law of mass action, we can predict how far the reaction would go, but can say nothing about how fast the equilibrium will attain. Though thermodynamics has got an enormous influence in chemical equilibrium yet has no valid application in studying the rate of reaction. The passage towards equilibrium takes some time which may be almost instantaneous or very long. The velocity of a reaction is not same even at constant temperature. Every chemical reaction has a definite velocity at a definite temperature. Modern techniques have been developed to study the reaction rate which gets completed in milliseconds or even microseconds.

This chapter discusses the principles of chemical thermodynamics and reaction kinetics. Heat and mass transport processes, some aspects of the chemistry-fluids interaction and the non-dimensionalisation of parameters as they apply to combustion processes are also introduced.

7.2 Thermodynamics of Combustion

Combustion involves the liberation of energy as the chemical reaction proceeds. The interpretation of the overall amount of energy released from and the state of equilibrium attained in the combustion process is part of the subject of thermodynamics.

7.2.1 Energy of Reaction and Overall Heat Release

The amount of energy that can be liberated from a given chemical reaction is determined from the energies of the individual reactants and products. The precise products, and hence the overall stoichiometry of the reaction, must always be established by chemical analysis. From the examples given in chapter 1 it might be presumed that the outcome can be guessed, but it is not necessarily the case.

For example, methane may react with oxygen to produce either carbon monoxide or water.

\[
\text{CH}_4 + 3/2\text{O}_2 = \text{CO} + 2\text{H}_2\text{O} \quad \ldots (7.1)
\]

Or carbon dioxide and water:

\[
\text{CH}_4 + 2\text{O}_2 = 2\text{H}_2\text{O} + \text{CO}_2 \quad \ldots (7.2)
\]

Whereas the second reaction corresponds to complete combustion, and hence to the maximum release of energy, in many circumstances the first reaction provides a better representation of what actually happens when methane is burned. Other possibilities arise from the combustion of methane at temperatures lower than those normally encountered in flames.

The energy of an individual chemical species may be given either in term of its internal energy, \( U \), or its enthalpy, \( H \), where, by definition

\[
H = U + pV \quad \ldots (7.3)
\]

The products \( pV \) relates to the mechanical work done on the system. Since neither internal energy nor enthalpy can be measured absolutely, it is necessary to choose a reference state to which all other energies may be related. This standard state is generally taken as the stable state of the pure substance at atmospheric pressure and at a specified temperature (normally 298 K). The enthalpy of each element is arbitrarily assigned the value zero in the standard state. The enthalpy change involved at some temperature, \( T \), in forming one mole of the chemical species in its standard state from its elements in their standard states is known as the standard enthalpy of formation, \( \Delta H^\theta_f \), of the compound (Table 7.1). There are extensive tabulations of these standard enthalpies.
<table>
<thead>
<tr>
<th>Species</th>
<th>Formula</th>
<th>$\Delta H^o_{f\ 298}$ (kJmol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen atom</td>
<td>H</td>
<td>217.99</td>
</tr>
<tr>
<td>Oxygen atom</td>
<td>O</td>
<td>249.19</td>
</tr>
<tr>
<td>Hydroxyl radical</td>
<td>OH</td>
<td>39.46</td>
</tr>
<tr>
<td>Hydro peroxy radical</td>
<td>HO₂</td>
<td>20.92</td>
</tr>
<tr>
<td>Water (liquid)</td>
<td>H₂O(1)</td>
<td>-285.83</td>
</tr>
<tr>
<td>Water (vapour)</td>
<td>H₂O</td>
<td>-241.81</td>
</tr>
<tr>
<td>Hydrogen peroxy (liquid)</td>
<td>H₂O₂(1)</td>
<td>-136.10</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>CO</td>
<td>-110.52</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>CO₂</td>
<td>-393.51</td>
</tr>
<tr>
<td>Methyl radical</td>
<td>CH₃</td>
<td>145.70</td>
</tr>
<tr>
<td>Methane</td>
<td>CH₄</td>
<td>-74.87</td>
</tr>
<tr>
<td>Ethyne (acetylene)</td>
<td>C₂H₂</td>
<td>226.70</td>
</tr>
<tr>
<td>Ethane</td>
<td>C₂H₆</td>
<td>52.47</td>
</tr>
<tr>
<td>Ethane</td>
<td>C₂H₆</td>
<td>-84.67</td>
</tr>
<tr>
<td>Propane</td>
<td>C₃H₈</td>
<td>-103.85</td>
</tr>
<tr>
<td>Benzene</td>
<td>C₆H₆</td>
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<td>Methanol vapour</td>
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<tr>
<td>Nitrogen atom</td>
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<td>472.7</td>
</tr>
<tr>
<td>Amine radical</td>
<td>NH₂</td>
<td>167.7</td>
</tr>
<tr>
<td>Ammonia</td>
<td>NH₃</td>
<td>-45.94</td>
</tr>
<tr>
<td>Nitric oxide</td>
<td>NO</td>
<td>90.29</td>
</tr>
<tr>
<td>Sulphur dioxide</td>
<td>SO₂</td>
<td>-296.81</td>
</tr>
</tbody>
</table>

| Species             | Formula | $\Delta H^o_{f\ 298}$ (kJmol⁻¹) |

Table 7.1 Standard enthalpies of formation
(All species are gaseous unless otherwise stated)

From Hess’s Law (which is a special case of the first law of thermodynamics), the enthalpy change in the reaction taking place under standard state conditions $\Delta H^o_\theta$ is equal to the difference between the sums of the standard enthalpies of formation of the products and the reactants. For eqn. (7.1), when the water is produced as vapour,

$$\Delta H^o_{\theta\ 298} = \Delta H^o_\theta (\text{CO}) + 2 \Delta H^o_\theta (\text{H}_2\text{O}_g) - \Delta H^o_\theta (\text{CH}_4) \quad \ldots7.4$$

$$= (-110.52) + 2(-241.81) - (-74.80)$$

$$= -519.34\text{kJmol}^{-1}$$

The negative sign indicates that energy is released, and the reaction is said to be exothermic. Although combustion processes are exothermic overall, not all of the elementary reactions involved in the overall process are necessarily exothermic. A reaction for which $\Delta H$ is positive and, therefore, energy is absorbed by the system from the surroundings, is said to be endothermic.

For the general reaction

$$\sum v_A \text{A} + \sum v_B \text{B} \ldots\ldots\ldots\ldots= \sum v_P \text{P} + \sum v_Q \text{Q} \quad \ldots\ldots\ldots\ldots\ldots(7.5)$$

$$\Delta H^o_{\theta\ 298} = \sum v_x \Delta H^o_{\theta\ 298}(X) \quad \ldots\ldots\ldots\ldots\ldots(7.6)$$
Where, the summation is performed with the stoichiometric factors, Vx, as positive for the products and negative for the reactants.

$$\Delta H$$ for a chemical reaction is quoted unambiguously only if the stoichiometric equation is also given. The units of $$\Delta H$$ are J mol\(^{-1}\), that is Joules for an extent of reaction of one mole of the reactant. The stoichiometric equation given so far imply complete conversion of the reactant when the reaction is carried out, whether or not conversion is complete or the absolute amount of energy released.

For some engineering purposes, it is preferable to use the enthalpy released per unit mass of reactants. For eqn. (7.1) this is,

$$\frac{519.27}{16 \frac{3}{2}} = 8.11 \text{ kJ g}^{-1} \text{ (of the reactant mixture)}$$

since 0.016 and 0.032 kg are the molar masses of methane and oxygen respectively. As atmospheric air is usually regarded as ‘free’, another useful quantity is the amount of energy available from unit mass of fuel. For methane burning to carbon monoxide, the energy available is,

$$\frac{5.19.27}{16} = 32.45 \text{ kJ g}^{-1}$$

These calculations relate the enthalpy changes taking place at constant pressure. The corresponding energy released when reaction takes place at constant volume is given by the internal energy change, $$\Delta U$$. For reactions involving ideal gases there is a simple relationship between $$\Delta H$$ and $$\Delta U$$, namely,

$$\Delta H = \Delta U + (\Delta v) RT \quad \ldots (7.7)$$

Where $$\Delta v$$ is the change in the number of moles of gaseous reactants to products and ideal gas behaviour is assumed. When only liquids or solids are involved, $$\Delta H \approx \Delta U$$ combustion reactions do not usually take place at room temperature, but the enthalpy change at other temperatures is easily obtained from

$$\Delta H_T = \Delta H_{298} + \int_{298}^{T} \Delta C_v dT \quad \ldots (7.8)$$

where $$\Delta C_v$$ refers to the difference between the heat capacity of the products and that of the reactants, that is

$$\Delta C_v = \sum v_x C_v(X) \quad \ldots (7.9)$$

where the summation is performed, as before, treating the stoichiometric factor v as positive for the products and negative for the reactants. $$C_v(X)$$ represents the molar heat capacity of reactant X. In practice, the enthalpy changes are not very sensitive to temperature because the heat capacities on each side of the chemical equation are approximately equal. For eqn. (7.1), $$\Delta H$$ changes from 519 kJ mol\(^{-1}\) at 298K to -503 kJ mol\(^{-1}\) at 2000 K and -542 kJ mol\(^{-1}\) at 3000K.

In real systems, the energy is released over a range of temperatures, but since both internal energy and enthalpy are state properties, this means that their values depend only on the present state of the system and not the path by which it was reached. It follows that, as long as the initial and final states of the system are fixed, the change in internal energy or enthalpy associated with the process will be independent of the route by which the change takes place. Thus, we can find the enthalpy change for a system which begins with reactants at an initial temperature $$T_0$$ and finishes with products at a final temperature $$T_f$$ by first finding the enthalpy change at $$T_0$$ and then using heat capacity data to calculate the enthalpy change involved in heating the products from $$T_0$$ to $$T_f$$.

### 7.2.2 Adiabatic Temperature Rise and Evaluation of Heat Capacities

The energy released during reaction in adiabatic conditions goes into raising the temperature of the system. For a constant volume process, such as a closed vessel explosion

$$\Delta U_T - \Delta U_{T_0} = \int_{T_0}^{T_f} C_v(products)dT \quad \ldots (7.10)$$
and similarly for a constant pressure process, typified by a premixed flame,

\[ \Delta H_{f_{\text{products}}} - \Delta H_{f_{\text{reactants}}} = \int_{T_0}^{T_f} C_p \, (\text{products}) \, dT \]

... (7.11)

under adiabatic conditions,

\[ \Delta H_{f_{\text{products}}} = \Delta U_{f_{\text{products}}} = 0 \]

... (7.12)

Heat capacities are to be found in compilations of thermodynamic data either tabulated against temperature or, more conveniently, they may be derived as polynomials in temperature of the following form

\[ C = a + bT + cT^2 + dT^3 \]

... (7.13)

or

\[ C = a + b/T + c/T^2 \]

... (7.14)

The heat capacities of some species involved in combustion are given in Table 7.2. For approximate calculations it is necessary to know only that the maximum value of \( C_p \) for gaseous molecules is given by the sum of the classical contributions to molecular energy, which on a molar basis are given by:

- Transnational motion: \( 3/2 \) \( R \)
- Rotational motion: \( 2R \) for a non-linear molecule
- \( R \) for a linear molecule
- Vibrational motion: \( R \) for each vibrational mode

<table>
<thead>
<tr>
<th>Species</th>
<th>a</th>
<th>( 10^2 ) b</th>
<th>( 10^6 ) c</th>
<th>( 10^9 ) d</th>
<th>Temperature range (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2 )</td>
<td>29.09</td>
<td>-0.1916</td>
<td>0.400</td>
<td>-0.870</td>
<td>273-1800</td>
</tr>
<tr>
<td>( \text{O}_2 )</td>
<td>25.46</td>
<td>1.519</td>
<td>-0.715</td>
<td>1.311</td>
<td>273-1800</td>
</tr>
<tr>
<td>( \text{N}_2 )</td>
<td>27.32</td>
<td>0.6226</td>
<td>-0.095</td>
<td>----</td>
<td>273-3800</td>
</tr>
<tr>
<td>( \text{CO} )</td>
<td>28.14</td>
<td>0.1674</td>
<td>0.537</td>
<td>-2.220</td>
<td>273-1800</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>22.24</td>
<td>5.977</td>
<td>-3.499</td>
<td>7.464</td>
<td>273-1800</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>32.22</td>
<td>0.1920</td>
<td>1.054</td>
<td>-3.594</td>
<td>273-1800</td>
</tr>
<tr>
<td>( \text{CH}_4 )</td>
<td>19.87</td>
<td>5.021</td>
<td>1.286</td>
<td>-11.00</td>
<td>273-1500</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_2 )</td>
<td>21.80</td>
<td>9.208</td>
<td>-6.523</td>
<td>18.20</td>
<td>273-1500</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_4 )</td>
<td>3.95</td>
<td>15.63</td>
<td>-8.339</td>
<td>17.66</td>
<td>273-1500</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_6 )</td>
<td>6.89</td>
<td>17.25</td>
<td>6.402</td>
<td>7.280</td>
<td>273-1500</td>
</tr>
<tr>
<td>( \text{C}_3\text{H}_8 )</td>
<td>-4.04</td>
<td>30.46</td>
<td>-15.71</td>
<td>31.71</td>
<td>273-1500</td>
</tr>
<tr>
<td>( \text{C}<em>6\text{H}</em>{12} )</td>
<td>-39.19</td>
<td>48.44</td>
<td>-31.55</td>
<td>77.57</td>
<td>273-1500</td>
</tr>
<tr>
<td>( \text{CH}_3\text{OH} )</td>
<td>19.04</td>
<td>9.146</td>
<td>-1.218</td>
<td>-8.033</td>
<td>273-1000</td>
</tr>
<tr>
<td>( \text{NH}_3 )</td>
<td>27.55</td>
<td>2.563</td>
<td>0.990</td>
<td>-6.686</td>
<td>273-1500</td>
</tr>
<tr>
<td>( \text{NO} )</td>
<td>27.03</td>
<td>0.9866</td>
<td>0.322</td>
<td>0.365</td>
<td>273-3800</td>
</tr>
<tr>
<td>( \text{SO}_2 )</td>
<td>25.76</td>
<td>5.791</td>
<td>-3.809</td>
<td>8.606</td>
<td>273-1800</td>
</tr>
</tbody>
</table>

Table 7.2 Molar heat capacities of some gases

\[ [C_p \,(\text{Jmol}^{-1}\text{K}^{-1}) = a + b \,(T/K0 + c \,(T/K)^2 + d \,(T/K)^3) ] \]
There are $3n-5$ vibrational modes for a linear molecule and $3n-6$ modes for a non-linear molecule comprising $n$ atoms. A mean heat capacity, suitable for approximate temperatures, is obtained by assuming that 50% of the classical vibrational modes are active, and therefore contribute to the heat capacity. The classical limits of translation and rotation contributions are established at all normal or higher temperatures. The heat capacity $C_v$, which is calculated in this way, is assumed independent of temperature. Values of $C_v$ may be then obtained from the following relationship:

$$C_p = C_v + R$$  \hspace{1cm} (7.15)

where, $R$ is the ideal gas constant.

### 7.2.3 Extent of Reaction and Determination of Chemical Equilibrium

Chemical reactions may not go to completion and so the final composition is not necessarily that shown simply by the stoichiometric equation, as in eqn. (7.1) or (7.2), for example. The second law of thermodynamics provides criteria for the position of equilibrium, and in the case of a system at constant temperature and pressure, this may be represented by a minimum in the Gibbs function (or free energy change) for the reaction, $\Delta G$, where

$$\Delta G = \Delta H - T\Delta S$$  \hspace{1cm} (7.16)

If the reactants and products behave as ideal gases (as in most combustion systems at moderate pressures), then the change in the standard Gibbs function accompanying reaction at a temperature $T$ is related to the equilibrium constant by the expression.

$$\Delta G^\circ_T = -RT\ln K^\circ$$  \hspace{1cm} (7.17)

For the generalised reaction shown in eqn (7.5):

$$K^\circ = \left(\frac{p_p / p^0}{p_r / p^0}\right)^{y_p} \left(\frac{p_r / p^0}{p_p / p^0}\right)^{y_r}$$  \hspace{1cm} (7.18)

Just as there are tabulations of standard enthalpies of formation, there are lists of standard Gibbs functions of formation for as very large number of compounds. $\Delta G^\circ_T$ for a particular reaction may be combining the tabulated $\Delta G^\circ_T$ values in a way analogous to the combination of $\Delta H_T q$ in eqn. (7.6).

$\Delta G$ must change with temperature, even if both $\Delta H$ and $\Delta S$ for the reaction are constant over a certain temperature range [eqn. (7.16)], and the equilibrium constant is a function of temperature, given by

$$\ln(K^\circ / K^\circ_T) = \frac{-\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$  \hspace{1cm} (7.19)

If the second term on the right of eqn. (7.16) could be neglected, then the condition for equilibrium would correspond to a maximum in $(\Delta H)$, the amount of heat evolved by the process. This means the reaction would always go to completion. However, the presence of the second term means that a small reduction in $(\Delta H)$ may be compensated by a corresponding change in $T\Delta S$.

The entropy, $S$, is a measure of disorder in the system, and the entropy is increased by an increase in the number of different chemical species present as a result of the chemical reaction. Since mass must be conserved, an increase in entropy is favoured when the gaseous products comprise molecular species that are 'simpler' than the reactants; that is, they contain fewer atoms. In an adiabatic methane flame, in addition to carbon dioxide and water the final products of combustion, there may be traces of residual reactants (CH$_4$ and O$_2$), other molecular products (e.g. CO and O$_2$) and free radical intermediates (e.g. H, O, OH and CH$_3$).
Table 7.3 Mole fractions of reactants and products (propane + air mixture)
(Calculated at thermodynamic equilibrium for a stoichiometric propane + air mixture)

<table>
<thead>
<tr>
<th>Species</th>
<th>Constant Pressure</th>
<th></th>
<th>Constant Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>c</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.1004</td>
<td>0.1003</td>
<td>0.1111</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.1423</td>
<td>0.1439</td>
<td>0.1481</td>
</tr>
<tr>
<td>N₂</td>
<td>0.7341</td>
<td>0.7347</td>
<td>0.7407</td>
</tr>
<tr>
<td>CO</td>
<td>0.0099</td>
<td>0.0100</td>
<td>---</td>
</tr>
<tr>
<td>H₂</td>
<td>0.0032</td>
<td>0.0033</td>
<td>---</td>
</tr>
<tr>
<td>O₂</td>
<td>0.0048</td>
<td>0.0055</td>
<td>---</td>
</tr>
<tr>
<td>CH₂O</td>
<td>&lt;10⁻⁵</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>CH₃H₄</td>
<td>&lt;10⁻⁵</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>&lt;10⁻⁵</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>&lt;10⁻⁵ CHO</td>
<td>&lt;10⁻⁵</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>CH₃</td>
<td>&lt;10⁻⁵</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>C₂H₅</td>
<td>&lt;10⁻⁵</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>i-C₃H₇</td>
<td>&lt;10⁻⁵</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>H₂</td>
<td>&lt;10⁻⁵</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>H</td>
<td>0.0035</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>O</td>
<td>0.0020</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>OH</td>
<td>0.0027</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>N</td>
<td>&lt;10</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>NO</td>
<td>0.0020</td>
<td>0.0022</td>
<td>---</td>
</tr>
<tr>
<td>NO₂</td>
<td>&lt;10⁻⁵</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Final temperature (K)</td>
<td>2219</td>
<td>2232</td>
<td>2324</td>
</tr>
</tbody>
</table>

The data in column (a) refers to calculations based on a comprehensive set of equilibria. Data in column (b) refers to calculations using a more limited set of equilibria. The data in column (c) were obtained by considering only the formation of CO₂ and H₂O.

In general, when any reaction has reached equilibrium there will be varying amounts of chemical species other than the expected final products. This is relatively unimportant in most combustion processes at low final temperatures, but the presence of the temperature multiplier in the TΔS term means that the trace materials become more important at elevated temperatures. The effect is fairly small up to about 2000K (Table 7.3) but is very remarkable at 3000 K (Table 7.4), as is appropriate to propane combustion in oxygen. A considerably lower temperature is predicted to be associated with the more complex equilibrium composition, by contrast to the final temperature (6340K) associated with the final products of combustion, CO₂ and H₂O (Table 7.4).
An alternative approach to computation, which is viable if only a few species are present, is to consider the individual chemical equilibria involved. Although a condition of equilibrium relationships are satisfied, in practice many of them will be interdependent and it is therefore necessary to consider only an appropriate subset, as discussed by Gaydon and Wolfhard. Manual calculations of the equilibrium composition of the products of combustion are possible but computer methods are usually employed.

<table>
<thead>
<tr>
<th>Species</th>
<th>Constant Pressure</th>
<th>Constant Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.1396</td>
<td>0.0896</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.3000</td>
<td>0.3182</td>
</tr>
<tr>
<td>CO</td>
<td>0.1951</td>
<td>0.2544</td>
</tr>
<tr>
<td>H₂</td>
<td>0.0697</td>
<td>0.1404</td>
</tr>
<tr>
<td>O₂</td>
<td>0.0984</td>
<td>0.1974</td>
</tr>
<tr>
<td>CH₂O</td>
<td>&lt;10⁻⁵</td>
<td>---</td>
</tr>
<tr>
<td>CH₃H₄</td>
<td>&lt;10⁻⁵</td>
<td>---</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>&lt;10⁻⁵</td>
<td>---</td>
</tr>
<tr>
<td>CHO</td>
<td>&lt;10⁻⁵</td>
<td>---</td>
</tr>
<tr>
<td>CH₃</td>
<td>&lt;10⁻⁵</td>
<td>---</td>
</tr>
<tr>
<td>C₃H₅</td>
<td>&lt;10⁻⁵</td>
<td>---</td>
</tr>
<tr>
<td>i-C₃H₇</td>
<td>&lt;10⁻⁵</td>
<td>---</td>
</tr>
<tr>
<td>H</td>
<td>0.0526</td>
<td>---</td>
</tr>
<tr>
<td>O</td>
<td>0.0441</td>
<td>---</td>
</tr>
<tr>
<td>OH</td>
<td>0.1005</td>
<td>---</td>
</tr>
<tr>
<td>HO₂</td>
<td>3x10⁻³</td>
<td>---</td>
</tr>
<tr>
<td>Final temperature (K)</td>
<td>3081</td>
<td>3420</td>
</tr>
</tbody>
</table>

Table 7.4 Mole fractions of reactants and products (propane + oxygen mixture)
(Calculated at thermodynamic equilibrium for a stoichiometric propane + oxygen mixture)
(Conditions same as table 7.3)

However, for underlying kinetic reasons, a state of chemical equilibrium may not necessarily have been established in the combustion system.

### 7.3 Rates of Chemical Change in Combustion

While all combustion processes depend on the total amount of energy released by chemical reaction, not all depend on the rate of reaction, provided that it exceeds some minimum value. Thus the overall behaviour in detonation waves, diffusion flames, burning droplets and liquid propellant rocket engines is virtually independent of chemical kinetics, whilst premixed flames, fires and internal combustion engines are sensitive to the detailed kinetics involved. The fundamentals of reaction kinetics are described in this section.
7.3.1 Reaction Rate, Kinetic Rate Laws and Order of Reaction

The quantitative behaviour of a chemical reaction is described by a rate law which specifies the rate of change of the concentration of chemical species in terms of the product of concentration terms and a rate constant (or rate coefficient) which is independent of concentration but, usually, not of temperature. For the reaction represented by the following stoichiometric equation

\[ V_A A + V_B B \ldots \ldots = v_P P + v_Q Q^+ \ldots \ldots \]

The rate law with respect to these four components takes the form

\[
\frac{-d[A]}{V_A} \frac{dt}{dt} = \frac{-d[B]}{V_B} \frac{dt}{dt} = \frac{1}{V_P} \frac{d[P]}{dt} = \frac{1}{V_Q} \frac{d[Q]}{dt} = k[A]^a[B]^b \ldots \ldots \tag{7.20}
\]

Where, \( k \) is the rate constant. The powers \( a \) and \( b \) are known as the orders of reaction with respect to the concentrations of the reaction \( A \) and \( B \), respectively, and the overall order is given by \( (a+b) \). The individual orders of reaction quantify the dependence of the species concentrations. The terms on the left-hand side of eqn. (7.20) rationalise the reaction rate in terms of changes of any of the molecular reactants or product concentrations through the respective stoichiometric coefficients representing the reactant consumption carried over to the rate expression. The square brackets signify either a molecular or a molar concentration of a species and, therefore, the reaction rate is expressed as molecules (or moles) per unit volume per unit time.

7.3.2 Concentration Dependences in Global and Elementary Reaction Rate Expressions

A distinction must be made between a rate expression which represents an overall reaction, often referred to as a global reaction, and an elementary step, as one of the components of the mechanism that makes up the overall reaction. In the latter, the chemical equation represents what is believed to happen on a molecular level.

\[ H + O_2 \rightarrow OH + O \quad \ldots \ldots \tag{7.21} \]

For example, the process is an elementary step (which is of considerable importance in combustion) in which a hydrogen atom collides with an oxygen molecule and the three atoms rearrange to give a hydroxyl radical and an oxygen atom. In this case, the rate law may be deducted directly from this concept of the molecular interaction. Doubling the concentration of oxygen molecules in the system would double the frequency of collisions of H atoms with them, and hence the rate of conversion to product species. Thus, the bimolecular interaction must have a linear dependence on \([O_2]\), i.e., be of first order with respect to it. On the basis of a similar argument with respect to the H atoms, the rate law for eqn. (7.21) is expressed as,

\[
\frac{-d[H]}{dt} = \frac{-d[O_2]}{dt} = \frac{d[OH]}{dt} = \frac{d[O]}{dt} = k[H][O_2] \ldots \ldots \tag{7.22}
\]

That is, the rate law is first order with respect to each of the reactants and second order overall. The reaction rate of an elementary reaction is never dependent on a product concentration. The forward and reverse rate constants of an elementary reaction, \( k_f \) and \( k_r \), can be related through the expression \( k_f/k_r = k_c \), where \( k_c \) is the equilibrium constant defined in terms of reactant and product concentrations.

Most combustion processes take place by a series of elementary steps, as part of a chain reaction. Thus, an overall equation which represents the stoichiometry of the reaction does not necessarily reflect the detailed events as the species react, nor does it give information about the concentration dependences in the appropriate rate law. For example, the overall stoichiometry,

\[ 2H_2 + O_2 \rightarrow 2H_2O \quad \ldots \ldots \tag{7.23} \]

may be represented by a global rate law such as,

\[
\frac{-1}{2} \frac{d[H_2]}{dt} = \frac{-d[O_2]}{dt} = \frac{1}{2} \frac{d[H_2O]}{dt} = k[H_2]^\alpha[O_2]^\beta \ldots \ldots \tag{7.24}
\]
But this cannot be regarded to represent two hydrogen molecules colliding with a single oxygen molecule to form two molecules of water. The global process is an abbreviation for a complex sequence of elementary steps, and a global rate law to represent it is an empirical representation of the dependence of the reaction rate on concentrations which applies over a very limited (specifies) range of conditions. It sometimes happens that the detailed reaction mechanism is not completely understood, or that its complexity makes it unsuitable for incorporation into a computer model, and then a global expression has to be used.

For a global reaction, the order must be established by experiment. The fractional reaction orders, as measured, should alert us to the fact that the reaction mechanism is a complex composite of elementary reactions, as would an inverse dependence on a reactant concentration or the intervention of product concentration dependence in the rate equation.

An elementary step is said to be uni-molecular if it involves only a single molecule, for example.

\[ \text{H}_2 \rightarrow 2\text{H} \quad \ldots (7.25) \]

And it might be expected to obey first order kinetics as expressed by the relationship,

\[ \frac{d[H_2]}{dt} = \frac{1}{2} \frac{d[H]}{dt} = k[H_2] \quad \ldots (7.26) \]

While uni-molecular reactions are normally first order, there are departures at low pressure, which may be important to combustion processes. In fact, the uni-molecular reaction is second order in the limit of very low pressures, and this change of overall behaviour (called the “fall-off” region) signifies that there is a more complex mechanistic substructure to the uni-molecular reaction. These types of processes are extremely well understood, and there are sophisticated theories which permit the quantitative interpretation of the behaviour.

The units of the rate constant are governed by the overall reaction order (be it a global representation or an elementary reaction), since the units on the right-hand side must equate to those on the left-hand side. Thus, a first-order rate constant has the dimensions of \([\text{time}]^{-1}\), whereas a second-order rate constant has units \([\text{concentration}]^{-1} [\text{time}]^{-1}\). In combustion reactions, the units of time are almost always seconds, whereas convenient concentration units may be \((\text{molecules}) \text{ cm}^{-3}\), \(\text{mol cm}^{-3}\), \(\text{mol dm}^{-3}\) or \(\text{mol m}^{-3}\). The concentration terms must be unified when data are being taken from different sources.

A useful parameter that gives some concepts of the timeline on which the chemistry takes place, especially with respect to first order reactions, is the half-life of the reaction. This represents the time for 50% of the reactant to be consumed, and is given by \(\ln 2/k\). For second or higher order reactions, the corresponding parameter is derived under pseudo first order conditions that is by subsuming certain (constant) reactant concentrations into the rate constant.

### 7.3.3 Temperature Dependence of the Rate Constant

The temperature dependence of a reaction is incorporated in the rate constant, and is expressed most simply in the Arrhenius form, as,

\[ k = A \exp(-E/RT) \quad \ldots (7.27) \]

The parameters \(A\) and \(E\) are independent of temperature in this well-established representation. Although they are derived experimentally, these terms have clear identities even in quite simple interpretations of reaction rate theory. Thus, \(A\) is termed the frequency factor with respect to first order reactions, since it may be identified with the rate at which chemical bonds can rearrange in a molecule and relates to a vibrational frequency (~1013 s\(^{-1}\)). In other circumstances, \(A\) is called the pre-exponential term and bears some relationship to collision frequencies between the interacting species in elementary reactions. The units of \(A\) are also the units of \(k\).

\(E\) is the activation energy barrier to reaction. It may be regarded as a measure of the energy barrier to reaction and is given as \(\text{J mol}^{-1}\) or \(\text{kJ mol}^{-1}\) in SI units. The quotient \((E/R)\) signifies a temperature coefficient, which testifies to its
experimental origin as a quantitative measure of the way in which the rate constant varies with temperature. The coefficient \( E/R \) is often quoted in rate data, rather than the activation energy.

The two-parameter representation of the temperature dependence [eqn (7.27)] is satisfactory for most reactions, especially over limited temperature ranges, and is confirmed by the linearity of the relationship in the classical Arrhenius plot \( \ln K \) versus \( 1/T \).

\[
\ln k = \ln A - \frac{E}{RT} \quad \ldots (7.28)
\]

However, in some application in combustion the rate constant has to be represented over an extremely wide temperature range (500-2500K). Where sufficient experimental measurements are available it may be found that the two-parameter representation is inadequate, which leads to a three-parameter representation of the form.

\[
k = A'T^n \exp\left(-\frac{E}{RT}\right) \quad \ldots (7.29)
\]

where ‘\( n \)’ is a number of order unity. The product \( (A'T^n) \) now has the units of the rate constant.

### 7.3.4 Termolecular Reactions and Elements of Chain Reaction Mechanisms

The termolecular reaction,

\[
H + O_2 + M \rightarrow HO_2 + M \quad \ldots (7.30)
\]

obeys third-order kinetics in certain conditions

\[
v = k [H] [O_2] [M] \quad \ldots (7.31)
\]

The symbol \( M \) is used to denote any molecule present in the system and its function is to remove some of the energy released by the formation of the new chemical bond, thereby preventing the product from immediately re-dissociating. \( M \) is termed a third body or chaperone molecule. The rate constant has dimensions of \([\text{concentration}]^2[\text{time}]^{-1}\) in this case. Third-order reactions often have rates which fall slightly with increasing temperature, which means that the measured ‘activation energy’ is slightly negative. This has no obvious physical meaning, and signifies that the mechanism of the overall process is not properly represented as a single ‘three-body interaction’. Like uni-molecular reactions, the rate constants for termolecular reaction also show pressure dependence, they become second order at a high-pressure limit.

The probability of termolecular reactions is so low that these reactions might be expected to be unimportant. However, since they provide virtually the only route for the homogeneous removal of reactive intermediates in gaseous combustion and are responsible for the liberation of considerable amounts of energy they are very important. Such reactions tend to predominate in the post-flame region, which follows the main reaction zone of a flame. Termolecular recombination reactions, such as the following reactions fall in this category.

\[
H+ OH + M \rightarrow H_2O + M; \quad \Delta H_{\phi}^{298} = -468\text{kJmol}^{-1} \quad \ldots (7.32)
\]

or

\[
CO + O + M \rightarrow CO_2 + M; \quad \Delta H_{\phi}^{298} = -532\text{kJmol}^{-1} \quad \ldots (7.33)
\]

Combustion reactions normally involve a complex mechanism, or sequence of elementary steps. The mechanisms involve chain reactions, in which an active species (usually a free radical or an atom) reacts with a stable molecule to give a product molecule and another active species which can propagate the chain. Thus, in the reaction between hydrogen and chlorine, the chain is propagated by the cycle,

\[
Cl + H_2 \rightarrow HCl + H \quad \ldots (7.34)
\]

\[
H + Cl_2 \rightarrow HCl + Cl \quad \ldots (7.35)
\]
Such reactions comprise a linear chain because each propagation step leaves the total number of active centres (H and Cl) unchanged.

Although linear-chain propagation is normal, examples are known where chain branching may also occur, that is, in which one active species produces additional species which are capable of continuing the chain.

\[ H + O_2 \rightarrow OH + O \]

In the oxidation of hydrogen, the above reaction brings about chain branching since both OH and O can react with hydrogen molecules to continue the chain. Branching chain reactions are particularly important in many combustion reactions. Typical active species involved in hydrocarbon combustion are H, O, OH, CH₃, and CHO. Reactions of such species have low energy barriers and hence their rates are rapid even though the concentrations of active species are low. With the exception of thermal ignition, in general, reactions involving only molecular reactants are too slow to sustain combustion.

The behaviour of a complex reaction mechanism is described mathematically by a set of simultaneous differential equations, equal in number to that of the chemical species involved. Analytical solution of these equations is usually impossible and therefore, uses are made of the stationary-state approximation in which the rates of change of concentrations of the active centres with respect to time are set equal to zero.

In the hydrogen + chlorine example, involving eqns. (7.34) and (7.35) amongst other reactions, one would write,

\[
\frac{d[H]}{dt} = \frac{d[C]}{dt} = 0 \quad \text{...(7.36)}
\]

This reduces a number of the differential equations to algebraic equations. It does not imply that the concentrations of radicals are invariant in time, but only that they can be related of stable specie, which have finite time derivatives. The algebraic equations can often be solved to give the stationary-state concentration of radical species. In some cases, when the rate of reaction is very high, it is not possible to use the stationary-state assumption, and then recourse must be made to numerical computation.

### 7.4 Transport Properties of Gases

The laws of conservation of energy, mass and momentum are used in the physics of combustion. Although the applications may be more complicated, the underlying principles are established in the respective transport processes in fluids, namely heat conduction, diffusion and viscosity. The transport of momentum, or viscosity, is involved only indirectly in combustion, for example when it controls the flow velocity profile in a tube. The conduction of heat is described by Fourier’s Law,

\[
\frac{q}{A} = -\lambda \frac{dT}{dx} \quad \text{...(7.37)}
\]

where \( q \) is the heat flowing in unit time through an area \( A \) and \( k \) is the thermal conductivity, which is measured in Wm⁻¹K⁻¹. The temperature gradient in the medium is \( dT/dX \) in the direction of heat flow and the negative sign indicates that the temperature gradient is in the opposite direction to the flow of heat.

Thermal diffusivity, \( \alpha \), is defined as \( k/\sigma C_p \) and thus has units of m²s⁻¹, where \( s \) is the molar density and \( C_p \) is the molar heat capacity. For a gas, simple kinetic theory can be used to show that the net heat flux through unit area is \((1/2) \sigma C_v c \lambda (dT/dx)\). In this expression \( c \) is the mean molecular velocity, and the negative sign signifies that heat flow occurs down the temperature gradient. Comparison with Fourier’s Law shows that;

\[
k = (1/2) \rho C_v c \lambda \quad \text{...(7.38)}
\]

More rigorous treatments result in a similar relationship but with a different numerical factor. Each leads to an expression close to
The mean free path ($\lambda$) is inversely proportional to the gas density and $c$ is proportional to $T^{1/2}$, so $k$ is virtually independent of pressure but increases with temperature very roughly as $T^{1/2}$. The measured value for air at room temperature is about 0.025 Wm$^{-1}$ K$^{-1}$ and hence the thermal diffusion is about $2 \times 10^5$ m$^2$ s$^{-1}$.

Diffusion is described by Fick’s Law as,

$$\frac{dn}{dx} = -D \frac{dn}{dx}$$  \hspace{1cm} \text{(7.40)}$$

where ‘n’ is the number of molecules per unit time crossing an area, A, ($dn/dx$) is the concentration gradient, and $D$ is the diffusion coefficient with the dimensions m$^2$ s$^{-1}$.

A simple kinetic theory derivation, analogous to that for thermal conductivity, yields the prediction that the self-diffusion coefficient is equal to $(1/2) c\bar{\lambda}$. The diffusion coefficient $D$ is inversely proportional to pressure and, in practice, increases with temperature according to about $T^{1.5}$. The measured value of $D$ for a gas molecule such as nitrogen diffusing in air is around $2 \times 10^{-5}$ m$^2$ s$^{-1}$.

Derivations of the equations for heat and mass fluxes pertain to the behaviour in quiescent gas or in a laminar flow (i.e., transport through a cross-section which is perpendicular to the imposed gradient as a result of molecular collisions), when there is no forced mixing induced by turbulent motion of the fluid. The expression for the diffusion coefficient comprises the product of a velocity and a scale factor. The numerical values for the thermal diffusivity and the diffusion coefficient of the same molecules are very similar and the dimensionless ratio $\alpha/D$, the Lewis number (Le), is close to unity. It represents the ratio of conductive to diffusive fluxes and theoretical solutions to many problems in combustion are obtained by setting this number equal to unity. This implies that both $\alpha$ and $D$ show the same dependence on temperature.

### 7.5 Grouping of Parameters and Dimensionless Groups

Many of the mathematical equations which represent the physics and chemistry of combustion are written in a non-dimensional form. The equation may not be so cumbersome to write when presented in this way, thereby reducing the chances of error in subsequent algebraic manipulation but that is only a peripheral advantage. The mode of application may be relatively straight forward such as in the non-dimensionalisation of a spatial co-ordinate by dividing the distance by a characteristic dimension of the system. E.g., let $r = l/r$ where $r$ is the radius of a spherical reaction vessel and $l$ is the distance from the centre to a given position along that co-ordinate.

Derivations involving this type of non-dimensionalisation become more general in application. That is, the size of the system need not be specified at the outset, but it may mean also that the equation could be applied to a different shape reactor if a characteristic dimension can be specified that replaces the radius $r$. In other circumstance, groups of parameters are collected together so that the overall phenomenology, as predicted in a mathematical equation is described by a more global ‘lumped parameter’. It may be necessary to investigate the dependence on a specific physical parameter within such a group at a later stage. Thermal diffusivity, $\alpha$, which is described in the previous section is an example of a partial non dimensionalisation. The Lewis number, which incorporates $\alpha$, is an example of a non-dimensionalised parameter, or $Le$ could be given its full identity in the form

$$Le = \frac{\alpha}{DpC_p}$$  \hspace{1cm} \text{(7.41)}$$
Summary

- Every chemical reaction has a definite velocity at a definite temperature. Modern techniques have been developed to study the reaction rate which gets completed in milliseconds or even microseconds.

- Combustion involves the liberation of energy as the chemical reaction proceeds. The interpretation of the overall amount of energy released from and the state of equilibrium attained in the combustion process is part of the subject of thermodynamics.

- The amount of energy that can be liberated from a given chemical reaction is determined from the energies of the individual reactants and products. The precise products, and hence the overall stoichiometry of the reaction, must always be established by chemical analysis.

- In general, when any reaction has reached equilibrium there will be varying amounts of chemical species other than the expected final products. This is relatively unimportant in most combustion processes at low final temperatures, but the presence of the temperature multiplier in the $T\Delta S$ term means that the trace materials become more important at elevated temperatures.

- While all combustion processes depend on the total amount of energy released by chemical reaction, not all depend on the rate of reaction, provided that it exceeds some minimum value. Thus, the overall behaviour in detonation waves, diffusion flames, burning droplets and liquid propellant rocket engines is virtually independent of chemical kinetics, whilst premixed flames, fires and internal combustion engines are sensitive to the detailed kinetics involved.

- The quantitative behaviour of a chemical reaction is described by a rate law which specifies the rate of change of the concentration of chemical species in terms of the product of concentration terms and a rate constant (or rate coefficient) which is independent of concentration but, usually, not of temperature.

- The laws of conservation of energy, mass and momentum are used in the physics of combustion. Although the applications may be more complicated, the underlying principles are established in the respective transport processes in fluids, namely heat conduction, diffusion and viscosity. The transport of momentum, or viscosity, is involved only indirectly in combustion.

References


Recommended Reading


1. Every chemical reaction has a definite ____________ at a definite temperature.
   a. reactant  
   b. product  
   c. velocity  
   d. pressure

2. __________ involves the liberation of energy as the chemical reaction proceeds.
   a. Combustion  
   b. Stoichiometry  
   c. Amalgamation  
   d. Condensation

3. What must always be established by chemical analysis?
   a. Reaction rate  
   b. Reaction kinetics  
   c. Product temperature  
   d. Stoichiometry

4. Which of the following statement is true.
   a. The positive sign indicates that energy is released, and the reaction is said to be exothermic.  
   b. The negative sign indicates that energy is released, and the reaction is said to be exothermic.  
   c. The negative sign indicates that energy is absorbed, and the reaction is said to be exothermic.  
   d. The negative sign indicates that energy is released, and the reaction is said to be endothermic.

5. A reaction for which $\Delta H$ is ________ and, therefore, energy is absorbed by the system from the surroundings, is said to be endothermic.
   a. negative  
   b. maximum  
   c. neutral  
   d. positive

6. As long as the initial and final states of the system are fixed, the change in internal energy or enthalpy associated with the process will be __________ of the route by which the change takes place.
   a. independent  
   b. regulated  
   c. dependent  
   d. determined

7. Entropy is increased by an increase in the number of different chemical __________ present as a result of the chemical reaction.
   a. reactants  
   b. gases  
   c. species  
   d. molecules
8. What is the rate constant independent of?
   a. concentration
   b. volume
   c. temperature
   d. pressure

9. In general, when any reaction has reached _____________, there will be varying amounts of chemical species other than the expected final products.
   a. end
   b. equilibrium
   c. saturation
   d. concentration

10. Many of the mathematical equations which represent the physics and chemistry of combustion are written in a ____________.
    a. dimensional form
    b. two dimensional form
    c. equation form
    d. non-dimensional form
Chapter VIII
Thermal Properties of Materials

Aim
The aim of this chapter is to:

- determine thermal properties of materials that influence their behaviour during a fire
- investigate thermal diffusivity
- introduce thermal expansion

Objectives
The objectives of this chapter are to:

- explain derivation of the heat flow equation
- examine thermal conduction due to radiation
- explain thermal inertia

Learning outcome
At the end of this chapter, you will be able to:

- recall thermal conductivity due to fluid mass transfer
- explain solution of transient heat flow equation
- discuss the variation in thermal conductivity with moisture content
8.1 Introduction

The fire hazards associated with materials, products, and assemblies used in buildings and other structures have long been a subject of concern and regulation. The hazards of flammable gases and flammable and combustible liquids are widely recognised and regulated with respect to their production, transportation, and utilisation.

This chapter considers the thermal properties of materials which influence their behaviour during a fire. These properties are: thermal conductivity, specific heat capacity, thermal diffusivity, thermal inertia, and thermal expansion.

“Thermal property” is the response of a material to the application of heat. As a solid absorbs energy in the form of heat, its temperature rises and its dimensions increase. The energy may be transported to cooler regions of the specimen if temperature gradients exist and ultimately, the specimen may melt.

8.2 Thermal Conductivity

This quantity is a measure of a material’s ability to pass heat energy through its bulk when subjected to a transient or steady state heat flux. In building materials, there are up to three distinct modes of energy transfer possible, these being:

- Thermal conduction by atomic and molecular vibration
- Thermal conduction by radiation
- Thermal conduction due to mass transfer (gaseous conduction)

8.2.1 Thermal Conduction (Molecular and Atomic Processes)

The ease with which thermal energy can be transferred down a rod or other structures depends on the type of bonding between the molecules. The materials that have a rigidly bound structure pass more energy than those with a weakly bound structure. This is due to the fact that the frequency of vibration for rigidly bound molecules is high. Thus, the rate at which energy is transferred is also high. Energy is transmitted down the rod by very-high-frequency elastic waves. These waves can be compared to sound waves, but have much higher wave frequencies. The quantum of energy associated with such a wave motion is called the phonon, which is passed from molecule to molecule in turn all the way down the length of the rod.

In an insulation-type material, the conduction process is dominated by these waves and their phonons. In comparison, the conductivity of a good thermal conductor such as a metal, is largely due to the electron drift where electrons move from regions of high temperatures to regions of lower temperature. Thus the actual thermal resistance of an insulation-type material may be considered to be due to phonon-phonon collisions or phonon-lattice framework collision processes. So if the interaction between phonons increases, as it must with an increase in temperature, this will cause the thermal resistance to increase, hence lowering the thermal conductivity.

Most masonry materials are polycrystalline, i.e., they consist of more than one crystal type, and since the phonons are scattered by crystal boundaries and by porosity, it is not surprising that such materials have lower phonon-conductivity than the single-crystal types. The situation of an amorphous type material, such as glass, is one in which the phonon-scattering process dominates, thus making the conductivity of an amorphous material independent of temperature for practical purposes.

8.2.2 Thermal Conduction due to Radiation

Surfaces having a temperature above absolute zero are capable of emitting and absorbing radiation. The rate $q$ at which this can occur is given by Stefan’s Law,

$$q = A \varepsilon \varphi \sigma (T_B^4 - T_g^4)$$

Where, $\varphi$ is the configuration factor which is dependent on the geometry and $\varepsilon$

Where,

$\varepsilon = \text{emissivity of the surface}$

$A = \text{surface area of emitter or absorber}$
\[ \sigma = \text{Steran's constant} \]
\[ T_B = \text{temperature of the body} \]
\[ T_g = \text{temperature of the surroundings} \]

Radiation passes through solids and undergoes scattering at structure imperfections, crystal boundaries and at pores. In highly porous material, this type of conductivity can be shown to be proportional to \( T^3 \) and becomes quite significant at temperatures above 500°C. However, in opaque-type-material this type of conductivity only starts to become important at 1,000°C or above.

### 8.2.3 Thermal Conductivity due to Fluid Mass Transfer

In this case a gas, such as air, which fills the pores within the material, can add to the ability of the material to pass heat energy through the material under a thermal gradient or by a buoyancy effect.

For a porous material or fibrous-type insulation, the gaseous conduction component of the thermal conductivity has been shown to have a moderate contribution to make to the overall conductivity compared to the radiant component. This contribution is shown clearly in Fig. 8.1.

![Fig. 8.1 Variation of the thermal conductivity with temperature for a medium density fibrous insulant](image)

It would now be useful to consider the variation of thermal conductivity of building materials with: temperature, density, moisture content.

**Temperature**

Experimental determination of the thermal conductivity of concrete containing crystalline and amorphous-type aggregate is shown in Fig. 8.2, which supports the theoretical predictions expressed in the previous paragraphs.

The role of radiation is quite well illustrated in the variation of medium-density fibrous insulation where it shows the thermal conductivity (\( \lambda \)) to be more or less proportional to \( T^3 \) at fire temperatures (Fig. 8.1)
Density variation (n)
This variation is quite well illustrated below, where the variation of thermal conductivity with density is shown.

Moisture content
Here, as water displaces the air in the pore spaces, the ability of the porous masonry-type material to conduct is enhanced since water is a good thermal conductor compared to stationary air. Thus as more of the air voids fill with water, the greater is the overall thermal conductivity according to the following relationship:

\[ \lambda = f[\lambda_1\%] \]

\[ \lambda_{-x} = \frac{f_x}{f_{10/0}} \left[ \lambda_{1\%} \right] \]

Where, \( f(x) \) = moisture factor which can be read from Table 8.1.

Thus moisture-laden masonry materials can have an overall thermal conductivity, which will change as they warm up and dry out.
Fig. 8.3 Variation of thermal conductivity for porous materials with density

![Graph showing variation of thermal conductivity with density]

Table 8.1 Thermal conductivity

<table>
<thead>
<tr>
<th>Water content (%)</th>
<th>1</th>
<th>2.5</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture factor</td>
<td>1.3</td>
<td>1.55</td>
<td>1.75</td>
<td>2.10</td>
<td>2.35</td>
<td>2.55</td>
<td>2.75</td>
</tr>
</tbody>
</table>

8.3 Specific Heat Capacity $C_p$

This is usually defined as the amount of thermal energy needed to “raise the temperature of 1 kg or a material by 1 degree Kelvin”. Building materials will, in general, contain water or water vapour—this is especially so during initial stages before the drying-out process has occurred under normal climatic conditions. Thus, if the temperature of such a material is raised to temperatures in excess of the ambient temperature, the remaining free water and water vapour will start to evaporate. This situation can arise during the early stages of a fire. At 100°C (boiling point), water and vapour in the pores will be removed thus making the energy needed to raise 1 kg of material by 1 kg, at this temperature, much greater than would normally be the case at temperatures greater than or less than 100°C. This type of behaviour is illustrated in Fig. 8.4, which shows how the specific heat capacity ($C_p$) for gypsum varies with temperature.
Fig. 8.4 The variation of specific heat capacity of gypsum with temperature

At much higher temperatures, chemical reactions tend to control the overall variation of Cp. This behaviour is more complex than that of the more chemically stable materials such as bricks, concrete and mineral wool (Fig. 8.5).
8.3.1 Vibrational Heat Capacity

In most solids, the principal mode of thermal energy assimilation is by the increase in vibrational energy of the atoms. Atoms in solid materials are constantly vibrating at very high frequencies and with relatively small amplitudes. Rather than being independent of one another, the vibrations of adjacent atoms are coupled by virtue of the atomic bonding. These vibrations are coordinated in such a way that travelling lattice waves are produced.
8.4 Derivation of Heat Flow Equation

Consider a slab of insulating material as shown in Fig. 8.7. Here, the heat crossing the plane AA’ may be considered to:

- heat up the slab of material between planes AA’ and plane BB’
- flow out across BB’ into the next section of the slab

Expressing this heat flow process in mathematical terms

\[
\frac{\lambda A}{dx} \frac{d\theta}{dx} = \lambda A \frac{d}{dx} \left( \theta - \delta \theta \right) + A \delta x p C_p \frac{d\theta}{dt}
\]

Rate at which energy is conducting across AA’
Rate at which energy is conducting across BB’
Rate at which slab energy is heating up
\[ \lambda A \frac{d\theta}{dx} = \lambda A \frac{d\theta}{dx} - \lambda A \frac{d}{dx} (\delta\theta) + A \delta x \rho C_p \frac{d\theta}{dt} \]

\[ \lambda A \frac{d}{dx} (\delta\theta) = A \delta x \rho C_p \frac{d\theta}{dt} \]

Using the fact that \( \delta\theta = \frac{d\theta}{dx} \cdot (\delta x) \)

Then

\[ \lambda A \frac{d^2\theta}{dx^2} \cdot \delta x = A \delta x \rho C_p \frac{d\theta}{dt} \]

\[ \frac{d^2\theta}{dx^2} = \frac{\rho C_p \frac{d\theta}{dt}}{\lambda} \]

or \( \nabla^2 \theta = \frac{1}{\alpha} \frac{d\theta}{dt} \)

where \( \alpha = \frac{\lambda}{\rho C_p} \)

and \( \nabla^2 \theta = \frac{d^2\theta}{dx^2} + \frac{d^2\theta}{dy^2} + \frac{d^2\theta}{dz^2} = \frac{1}{\alpha} \frac{d\theta}{dt} \)

for a three dimensional situation.
8.5 Thermal Diffusivity ($\alpha$)

Thermal diffusivity may be defined as:

$$\lambda = \frac{\text{thermal conductivity of the material}}{\rho C_p \text{ density of material} \times \text{specific heat of material}}$$

The thermal diffusivity is also a measure of a material’s ability to conduct heat energy in relation to its thermal storage capacity. The thermal diffusivity of a material gives an indication of the rate at which thermal energy can travel through a material, which in turn controls the rate of temperature rise within the material.

Materials having large diffusivity values respond quickly, whereas low diffusivity materials respond more slowly to a thermal heat flux. The temperature variation for steel is shown in the graph below. It is essential that this temperature variation of the diffusivity of a material is known since situations may arise where the solution of the equation which is derived in the previous paragraph is required in the fire temperature range. This may well be the case when a theoretical estimation of the fire resistance of a structure is needed.

![Graph showing variation of diffusivity of steel with temperature.](image)

Fig. 8.8 Variation of the diffusivity of steel with temperature

8.6 Solution of the Transient Heat Flow Equation

Solution of:

$$\frac{d\theta}{dt} = \frac{\alpha}{\rho C_p} \frac{d^2 \theta}{dx^2}$$

When a slab is subject to a sinusoidal temperature at the surface, i.e., $\theta = \theta \sin (2\pi/T)$ at $x = 0$ and $t = t$

A choice of solution of the form $\theta = C e^{px} \sin (2\pi fT - qx)$

Where $C$, $p$ and $q$ are constants to be determined.

Rewriting equation (1)
\[
\frac{d\theta}{dt} = 2\pi fCe^{-\alpha t} \cos(2\pi ft - qx)
\]
\[
\frac{d\theta}{dx} = -pCe^{-\alpha t} \sin(2\pi ft - qx) - aCe^{-\alpha t} \cos(2\pi ft - qx)
\]
\[
\frac{d^2\theta}{dx^2} = p^2Ce^{-\alpha t} \sin(2\pi ft - qx) + pqCe^{-\alpha t} \cos(2\pi ft - qx)
\]
\[
+ pqCe^{-\alpha t} \cos(2\pi ft - qx) - q^2Ce^{-\alpha t} \sin(2\pi ft - qx)
\]
\]
\]
\[
\text{... (2)}
\]

Substituting these expressions in equation (2)
\[
2\pi f \cos(2\pi f \ qx) - \alpha(p^2 \sin(2\pi ft \ qx) + 2pq \cos(2\pi ft \ qx) \ q^2 \sin(2\pi f \ qx))
\]
\[
2\pi f = 2pq\alpha \text{ and } \alpha(p^2 - q^2) = 0
\]

Since no sine terms on 1 hs. \((p^2 - q^2) = 0\)
\[
2\pi f = 2pq\alpha \quad \text{i.e.} \quad pq - \frac{\pi f}{\alpha}
\]
also \(p^2 = q^2 \quad \text{i.e.} \quad p = q\)
\[
\text{so } p = q \pm \sqrt{\frac{\pi f}{\alpha}}
\]
∴ Solution can be written as,
\[
\theta = C \exp \left\{ -x \sqrt{\frac{\pi f}{\alpha}} \right\} \sin \left(2\pi ft - x \sqrt{\frac{\pi f}{\alpha}}\right)
\]

Inserting boundary condition,
\[
\theta = \theta_s \sin(2\pi ft) \quad \text{at} \quad x = 0 \quad \text{and} \quad t = t
\]
∴ \(C = \theta_0\)
\[
\therefore \theta = \theta_0 \exp \left\{ -x \sqrt{\frac{\pi f}{\alpha}} \right\} \sin \left(2\pi ft - x \sqrt{\frac{\pi f}{\alpha}}\right)
\]
\[
\therefore \theta_0(x) = \theta_0 \exp \left\{ -x \sqrt{\frac{\pi f}{\alpha}} \right\}
\]
\]
\]
\]
\]
\]
\[
\text{... (3)}
\]
This means the amplitude of the heat energy wave as it moves through the material suffers damping according to eqn [3] (Fig.8.8).

Also, as this temperature wave propagates through the solid, there is a lag in time between the peaks at depth \( x \) compared to those at the surface. This phase difference can be directly found from the \( \sin(2\pi f T - x\sqrt{\pi f/\alpha}) \) term. i.e., \( x\sqrt{\pi f/\alpha} \) is \( \Phi \), the phase lag.

The time lag \( \Delta t \) between the occurrence of a peak at \( x = 0 \) compared to one at \( x = x \) can be easily shown to be

\[
\Delta t = \frac{x}{2\sqrt{\frac{1}{\pi f \alpha}}}
\]
From the above sketch, the phase lag is equal to \(2\pi f - \Delta t\) (Fig. 8.10)

\[
i.e. \quad 2\pi f/\Delta t = x\sqrt{\frac{\pi f}{\alpha}}
\]
\[
\therefore \Delta t = \frac{x}{2} \sqrt{\frac{1}{\pi f \alpha}}
\]

The period ‘t’ for such a temperature wave can now be calculated by,

\[
\tau = \frac{1}{f}
\]
\[
\therefore 2\pi \frac{1}{\tau} = \lambda \sqrt{\frac{\pi f}{\alpha}} \quad \text{i.e. when } \Delta t = \tau
\]
\[
\therefore \lambda = 2\sqrt{\frac{\pi \alpha}{f}}
\]

Using \(V = f \lambda\), the temperature wave velocity can be determined.

\[
i.e. \quad V = f \cdot 2\sqrt{\frac{\pi \alpha}{f}} = 2\sqrt{\pi f \alpha}
\]
\[
i.e. \quad V = 2\sqrt{\pi f \alpha} \quad \ldots (4)
\]

**Solved example**

Which of the following materials—A, B or C (the physical and thermal properties of which are given in the table 8.2 below) would make the most suitable insulating screen to withstand the penetration of a high temperature wave for as long as possible?

From the theory in the previous paragraph it was shown that the velocity of a temperature wave is given by eqn. (4).

\[
V = 2\sqrt{\pi f \alpha}
\]

This implies that the material possessing the smallest value of thermal diffusivity will provide the best material to insulate the effects of a high temperature wave, thus evaluating the diffusivity for each material accordingly.

\[
\alpha = \frac{\lambda}{\rho C_p}
\]

Therefore material C is the most suitable material of the three available materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>(\lambda) (Wm (^{-1})K(^{-1}))</th>
<th>(\rho) (kg/ m(^3))</th>
<th>(C_p) (kJ kg(^{-1}) K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>(6.0 \times 10^{-1})</td>
<td>11.500</td>
<td>0.84</td>
</tr>
<tr>
<td>B</td>
<td>1.0</td>
<td>1.200</td>
<td>1.60</td>
</tr>
<tr>
<td>C</td>
<td>(3.5 \times 10^{-1})</td>
<td>750</td>
<td>1.00</td>
</tr>
</tbody>
</table>

**Table 8.2 Comparison of thermal properties of material A, B and C**
8.7 Thermal Inertia

Thermal inertia may be defined as the product of \( (\rho C_p) \). It is well known that the transient response of the surface lining of a structure depends on its thermal properties, i.e., the inertia of the surface lining nearest to the heat flux input. In table 8.3, the thermal inertia of some building materials is given at ambient temperature. It is clear that inertia variation can be easily determined provided the thermal conductivity and specific heat capacity variation with temperature are known.

It has been shown that the time to flashover or for the fire growth period \( t_G \) depends on the thermal inertia \( (\rho C_p) \) of the surface covering of a compartment wall.

\[
t_G = \Phi(\lambda\rho C_p)
\]

or

\[
t_G = \text{const}(\lambda\rho C_p)^n
\]

Where \( 0 \leq n \leq 0.5 \)

Assuming a value for \( n = 0.5 \)

\[
t_G = \text{const} \sqrt[2]{\lambda \rho C_p}
\]

<table>
<thead>
<tr>
<th>Materials</th>
<th>Thermal Conductivity ( \lambda ) (W m(^{-1}) K(^{-1}))</th>
<th>Density ( \rho ) (kg m(^{-3}))</th>
<th>Specific heat capacity ( C_p ) (Jkg(^{-1})K(^{-1}))</th>
<th>Thermal inertia ( \lambda \rho C_p ) (W(^2)m(^{-1})K(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brick</td>
<td>0.80</td>
<td>2,600</td>
<td>800</td>
<td>1.66 x 10(^6)</td>
</tr>
<tr>
<td>Plasterboard</td>
<td>0.16</td>
<td>950</td>
<td>840</td>
<td>1.276 \times 1(^0)</td>
</tr>
<tr>
<td>Cellular type Insulation</td>
<td>0.03</td>
<td>20</td>
<td>1,500</td>
<td>900</td>
</tr>
<tr>
<td>Fibrous insulation</td>
<td>0.05</td>
<td>240</td>
<td>1.250</td>
<td>1.5 \times 10(^4)</td>
</tr>
</tbody>
</table>

Table 8.3 Thermal properties of typical construction material

Solved example

Compare the predicted fire growth periods for two identically constructed enclosures having the same shape and dimensions but differing internal wall linings. Enclosure A has a plaster board finish while enclosure B has a fibrous insulation lining.

Solution

Using the information provided in table 8.3,

\( (\lambda\rho C_p)_A = 130 \times 10^3 \)

\( (\lambda\rho C_p)_B = 15 \times 10^3 \)

And the fact that

\[
t_G = \text{const} \sqrt[2]{\lambda \rho C_p}
\]

then

\[
t_{GA} = \left(\frac{(\lambda\rho C_p)_A}{(\lambda\rho C_p)_B}\right)^{1/2} = \sqrt{\frac{130}{15}} \approx 3
\]

\[
\therefore t_{GB} = \frac{1}{3} t_{GA}
\]

This suggests that if a fire in enclosure A takes 20 minutes to reach flashover, then the same fire condition in enclosure B would grow to flashover in 7 or 8 minutes.
8.8 Thermal Expansion

It is well known from practical experience that metallic materials will invariably expand when heated. This fact has been shown to be the case using simple expansion experiments at school level. The tendency of a material to expand with an increase in temperature is associated with the increase in the internal kinetic energy of the atoms and molecules within the material. The co-efficient of expansion gives an indication of the expansion that is produced with the change in temperature. This expansion co-efficient may be defined as: ‘The expansion per unit length of a material when its temperature is raised by 1°C or 1K.’

In elementary physics courses, \( \alpha \) is assumed to be constant over a large temperature range especially where metals are being considered. Thus, a simple relationship can be derived relating the expansion \( \Delta f \) to the original length \( l \) and the temperature rise \( \Delta \theta \) via the co-efficient of linear expansion \( \alpha \).

\[ \Delta f = \alpha l \Delta \theta \]

Table 8.4 gives a list of the expansion co-efficients for common materials which are assumed to be independent of temperature:

<table>
<thead>
<tr>
<th>Materials</th>
<th>( \alpha/c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>-51.67 × 10</td>
</tr>
<tr>
<td>Steel</td>
<td>-51.10 × 10</td>
</tr>
<tr>
<td>Glass</td>
<td>-69.00 × 10</td>
</tr>
<tr>
<td>Aluminium</td>
<td>-52.55 × 10</td>
</tr>
</tbody>
</table>

Table 8.4 Thermal expansion co-efficient of linear thermal expansion

It must be noted that, at elevated temperatures, well in excess of 100°C, the assumption that \( \alpha \) is temperature independent is no longer valid. It has been shown for materials such as steel that the co-efficient of expansion increases quite slowly with temperature as seen in Fig. 8.11. It must be noticed that at temperatures greater than 700°C, steel starts to contract. This is of little importance since at 700°C steel has lost most of its useful strength.

![Fig. 8.11 Upper and lower limits of the co-efficient of linear expansion for steel](image-url)
For non-ferrous materials, the variation is however irregular over the lower temperature ranges. Masonry-type materials, such as cement paste, show this tendency, which is due to water removal which causes shrinkage and chemical transformations, which can cause both, expansion and shrinkage in materials (Fig. 8.12).

![Graph showing linear shrinkage of cement paste with increasing temperature](image)

**Fig. 8.12 Linear shrinkage of cement pane with increasing temperature**
(Heating rate 5°C per minute)

For composite materials such as concrete the resulting expansion, if any, depends on the type of aggregate used. Soft aggregates such as perlite have a relatively small influence on the expansion of concrete where the cement paste matrix controls the overall process. When hard aggregates such as granite are used, the influence exerted by the aggregate is much stronger and the concrete expands as shown in Fig 8.13. Table 8.5 gives a few of the coefficients of linear expansion of concrete, which use different aggregate types over a temperature range up to 100°C.
Fig. 8.13 Linear expansion with temperature of concrete made with different aggregates

<table>
<thead>
<tr>
<th>Aggregate type</th>
<th>α/c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Granite</td>
<td>9.50 × 10^{-6}</td>
</tr>
<tr>
<td>Limestone</td>
<td>6.80 × 10^{-6}</td>
</tr>
<tr>
<td>Quartz</td>
<td>1.20 × 10^{-5}</td>
</tr>
<tr>
<td>Sandstone</td>
<td>1.12 × 10^{-5}</td>
</tr>
</tbody>
</table>

Table 8.5 Co-efficient of thermal expansion materials

Thus, the knowledge of how the co-efficient of linear expansion of building materials varies with temperature to deal with issues such as fire resistance where thermal stresses induced by fire temperatures are to be evaluated.

Solved example
A zinc rod exactly 1.0 m long at 10°C is 2.33 mm short than a copper rod at the same temperature. On heating both rods to 260°C, it was found that they are now of the same length. Given that the co-efficient of linear expansion of the copper rod is 1.67 × 10^{-5}/ C, calculate the co-efficient of linear expansion for the zinc rod.

Solution
\[ l(Zn) = 1.0m \quad f(Cu) = 1.0023m \]
\[ 10°C \quad 10°C \]
\[ \Delta l(Zn) = \alpha_m \times 1.00 \times 250 \]
\[ \therefore \Delta l(Cu) = 1.67 \times 10^{-5} \times 1.0023 \times 250 \]
\[ l(Zn)_{260°C} = 1.00 + 1.00 \times \alpha_m \times 250 \]
Equating length and solving for \( \alpha_m \)
\[ \alpha_m = 2.594 \times 10^{-5} \]
Summary

- The fire hazards associated with materials, products, and assemblies used in buildings and other structures have long been a subject of concern and regulation. The hazards of flammable gases and flammable and combustible liquids are widely recognised and regulated with respect to their production, transportation, and utilisation.

- “Thermal property” is the response of a material to the application of heat. As a solid absorbs energy in the form of heat, its temperature rises and its dimensions increase. The energy may be transported to cooler regions of the specimen if temperature gradients exist, and ultimately, the specimen may melt.

- Thermal conductivity is a quantity that measures a material’s ability to pass heat energy through its bulk when subjected to a transient or steady state heat flux.

- Specific Heat Capacity ($C_p$) is usually defined as the amount of thermal energy needed to “raise the temperature of 1 kg of a material by 1 degree Kelvin”.

- The thermal diffusivity is also a measure of a material’s ability to conduct heat energy in relation to its thermal storage capacity. The thermal diffusivity of a material gives an indication of the rate at which thermal energy can travel through a material, which in turn controls the rate of temperature rise within the material.

- Thermal inertia may be defined as the product of ($\rho C_p$). It is well known that the transient response of the surface lining of a structure depends on its thermal properties, i.e., the inertia of the surface lining nearest to the heat flux input.

- The tendency of a material to expand with an increase in temperature is associated with the increase in the internal kinetic energy of the atoms and molecules within the material. The coefficient of expansion gives an indication of the expansion that is produced with the change in temperature.

References


Recommended Reading


Self Assessment

1. As a solid absorbs energy in the form of heat, its temperature rises and its _________ increase.
   a. volume
   b. mass
   c. velocity
   d. dimensions

2. What is a measure of a material’s ability to pass heat energy through its bulk when subjected to a transient or steady state heat flux known as?
   a. Thermal conductivity
   b. Thermal expansion
   c. Thermal diffusivity
   d. Thermal velocity

3. Which of the following statement is true?
   a. In building materials, there are up to five distinct modes of energy transfer possible.
   b. In building materials, there are up to three distinct modes of energy increment possible.
   c. In building materials, there are up to three distinct modes of energy transfer possible.
   d. In case of actual fire, there are up to three distinct modes of energy transfer possible.

4. The ease with which thermal energy can be transferred down a rod or other structures depends on the type of bonding between the _________.
   a. atoms
   b. molecules
   c. ions
   d. particles

5. The quantum of energy associated with a wave motion is called the ________, which is passed from molecule to molecule in turn all the way down the length of the rod.
   a. photon
   b. electron
   c. phonon
   d. ray

6. Surfaces having a temperature above __________ are capable of emitting and absorbing radiation.
   a. 10°C
   b. 20°C
   c. 0°C
   d. absolute zero

7. ___________ is usually defined as the amount of thermal energy needed to “raise the temperature of 1 kg or a material by 1 degree Kelvin.”
   a. Specific heat capacity
   b. Specific gravity
   c. Specific density
   d. Specific thermal heat
8. At much higher temperatures, _________ tend to control the overall variation of Cp.
   a. thermal energy
   b. heat
   c. chemical reactions
   d. electrons

9. The materials that have a rigidly bound structure pass ___________ than those with a weakly bound structure.
   a. less energy
   b. more heat
   c. less heat
   d. more energy

10. The thermal diffusivity is a measure of a material’s ability to conduct heat energy in relation to its ____________ capacity.
    a. thermal exchange
    b. thermal storage
    c. thermal expansion
    d. thermal condensation
Case Study I

Fire

Including the one in Phoenix, Arizona, considered one of the most progressive in North America. For its forward-thinking management and commitment to advanced fire fighting technology, the Phoenix Fire Department is often viewed as a model for city fire departments all over the continent. In 1994, its evaluation committee set several initiatives for all manufacturers that wanted to participate. At the top of the list: a breathing apparatus with an integrated, automatically activated Personal Alert Safety System (PASS). The PASS is a motion sensor that alerts other fire-fighters to an unconscious or trapped fire-fighter by both sound and light. Up until then, the only PASS devices used by fire departments in North America were standalone units that attached to a fire-fighter’s turnout gear and had to be manually activated. The problem was, up to 90% of all fire-fighters did not turn their units on. When the Phoenix FD came to Tyco Fire & Security, we were already in the process of working on this project with the fire department of New York City. The Phoenix evaluation caused us to expedite our development process. Ultimately, we were named the supplier of choice in Phoenix, which purchased more than 600 units. Shortly after, the New York Fire Department purchased more than 3,000 units. Our product, the Pak-Alert ® 1000, prompted the National Fire Protection Agency to incorporate automatic activation as a requirement in the PASS standard of 1998 for all manufacturers. More than 250,000 Pak-Alerts currently protect fire fighters worldwide. We also continue to lead the way in new products that increase the safety of fire fighters – such as SEMS, our technology that lets commanders track fire fighters inside burning buildings. It’s yet another reason fire departments know they can rely on Tyco Fire & Security when it counts.

Questions
1. What does PASS mean in the above case?
   Answer
   The PASS is a motion sensor that alerts other fire-fighters to an unconscious or trapped fire-fighter by both sound and light.

2. What were Tyco Fire & Security awarded with?
   Answer
   Tyco Fire & Security were named the supplier of choice in Phoenix, which purchased more than 600 units.

3. Which was the other product than PASS of Tyco Fire & Security?
   Answer
   The other product of Tyco Fire & Security is SEMS, technology that lets commanders track fire fighters inside burning buildings.
Case Study II

Processes influencing ozone levels in Alaskan forest fire plumes during long-range transport over the North Atlantic

A case of long-range transport of a biomass burning plume from Alaska to Europe is analyzed using a Lagrangian approach. This plume was sampled several times in the free troposphere over North America, the North Atlantic and Europe by three different aircraft during the IGAC Lagrangian 2K4 experiment which was part of the ICARTT/ITOP measurement intensive in summer 2004. Measurements in the plume showed enhanced values of CO, VOCs and NOy, mainly in form of PAN. Observed O3 levels increased by 17 ppbv over 5 days. A photochemical trajectory model, CiTTyCAT, was used to examine processes responsible for the chemical evolution of the plume. The model was initialized with upwind data and compared with downwind measurements. The influence of high aerosol loading on photolysis rates in the plume was investigated using in situ aerosol measurements in the plume and lidar retrievals of optical depth as input into a photolysis code (Fast-J), run in the model. Significant impacts on photochemistry are found with a decrease of 18% in O3 production and 24% in O3 destruction over 5 days when including aerosols. The plume is found to be chemically active with large O3 increases attributed primarily to PAN decomposition during descent of the plume toward Europe. The predicted O3 changes are very dependent on temperature changes during transport and also on water vapour levels in the lower troposphere which can lead to O3 destruction. Simulation of mixing/dilution was necessary to reproduce observed pollutant levels in the plume. Mixing was simulated using background concentrations from measurements in air masses in close proximity to the plume, and mixing timescales (averaging 6.25 days) were derived from CO changes. Observed and simulated O3/CO correlations in the plume were also compared in order to evaluate the photochemistry in the model. Observed slopes change from negative to positive over 5 days. This change, which can be attributed largely to photochemistry, is well reproduced by multiple model runs even if slope values are slightly underestimated suggesting a small underestimation in modelled photochemical O3 production. The possible impact of this biomass burning plume on O3 levels in the European boundary layer was also examined by running the model for a further 5 days and comparing with data collected at surface sites, such as Jungfraujoch, which showed small O3 increases and elevated CO levels. The model predicts significant changes in O3 over the entire 10 day period due to photochemistry but the signal is largely lost because of the effects of dilution. However, measurements in several other BB plumes over Europe show that O3 impact of Alaskan fires can be potentially significant over Europe.

Questions
1. Which approach is used to analyse the above case?
2. What was photochemical trajectory model used for?
3. Explain the impact on biomass due to burning plume on O3 level?
Case Study III

Fire Behaviour

On February 29, 2008 Firefighter Brad Holmes and Lieutenant Scott King were assigned to perform primary search of Exposure Delta at a fire in a wood frame duplex in Grove City, PA. During their search, rapidly deteriorating conditions trapped the search crew. After being rescued by the Rapid Intervention Team, both members were transported to Pittsburgh’s Mercy Hospital Burn Unit. Firefighter Brad Holmes had burns over 75% of his body, and died from his injuries on March 5, 2008. Lieutenant King suffered less serious injuries and was treated and released. A 41 year old female occupant of the dwelling also died attempting to rescue a pet.

Building Information

The fire originated in the D Side unit of a two-story, wood frame duplex at 132 Garden Avenue in Grove City, Pennsylvania. The building was originally built in the 1930s and remodelled into two separate dwelling units in the 1960s. Figure 1. Fire Unit and Exposure Bravo Floor 1

Note: This floor plan is based on data provided in NIOSH Report F2008-06 and is not drawn to scale. Windows shown as open are based on the narrative or photographic evidence. Door position is as shown based on information provided by NIOSH Investigator Steve Berardinelli (this differs from the NIOSH report which includes the fire investigators...
rough sketch showing all doors open). Windows shown as intact are not visible in the available photographs, but may be open due to fire effects or fire fighting operations (particularly those in the fire unit).

Fig. 2 Fire units and exposure bravo floor 2

Note: See the prior comments regarding windows and door position.

As illustrated in Figures 2 and 3, the floor plan of each unit was a mirror image of the other. The first floor had a living room, dining room and kitchen and a deck on Side C. The units shared a common entry on Side A. The second floors had two bedrooms and a bathroom.

The 36’ x 30’ structure was of balloon-frame construction and had a basement. Interior construction was plaster over wood lath with carpeting over hardwood floors. The unit on Side D (fire unit) had wood paneling throughout the first floor. Exterior construction was wood clapboards over wooden framing. The building was not insulated and did not contain a rated fire wall between the units. The roof covering was asphalt shingles over an undetermined type of wood sheathing.

Dispatch Information
The initial call reporting this incident was 0606 hours, but was disconnected prior to communication of the nature of the emergency. A law enforcement unit was initially dispatched to the address to investigate the interrupted call. A second call was received from an occupant of the fire unit (Side D) at 0609 reporting the fire and that his wife was trapped.

Station 95 (Chief 95, Accountability Officer (POV), Engine 95, Engine 85-2, Squad 95) and Ambulance 100 were dispatched at 0609 followed by Stations 85 (Engine 85, Engine 85-2, Squad 85) and 87 (Rescue 87) at 0611.

The law enforcement officer initially dispatched to the disconnected call arrived at 0612 and reported a working fire with entrapment. Based on this report, the Station 95 Assistant Chief (unit not specified) requested an additional engine prior to arrival. Station 77 (Engine 77, Brush 77, and Water Tender 77) was dispatched at 0614.
Weather Conditions
The temperature was 60°F (-14°C) with no wind.

Conditions on Arrival
Chief 95 arrived at 0616 and established Command. Fire was showing from the first floor unit on Side D extension and there was significant involvement of Floor 2 of the same unit. The IC did a quick 360° size-up and determined the structure was a duplex by the two separate decks at the rear of the structure. However, this information was not communicated to the responding companies. The IC spoke to law enforcement and confirmed that there was an occupant trapped, but received no information about the occupant’s last known location.

Questions
1. What stage(s) of fire and burning regime do you believe existed in the involved unit when Chief 95 arrived? (Remember that Figure 1 illustrates conditions considerably later in the incident than Chief 95’s arrival.)
2. What building factors are likely to influence fire development and extension?
3. What information should Command communicate to responding companies based on his size-up and assessment of the situation?
Bibliography

References


Recommended Reading

Self Assessment Answers

Chapter I
1. a
2. b
3. d
4. a
5. c
6. d
7. b
8. c
9. d
10. a

Chapter II
1. a
2. b
3. c
4. a
5. d
6. a
7. c
8. d
9. b
10. a

Chapter III
1. a
2. d
3. b
4. d
5. c
6. a
7. c
8. b
9. c
10. b

Chapter IV
1. a
2. d
3. c
4. a
5. a
6. b
7. a
8. c
9. a
10. c
Chapter V
1. a
2. a
3. c
4. d
5. b
6. b
7. c
8. a
9. b
10. d

Chapter VI
1. b
2. c
3. a
4. d
5. c
6. b
7. a
8. c
9. d
10. a

Chapter VII
1. c
2. a
3. d
4. b
5. d
6. a
7. c
8. a
9. b
10. d

Chapter VIII
1. d
2. a
3. c
4. b
5. c
6. d
7. a
8. c
9. d
10. b