1

ENERGY SOURCES

1.1 INTRODUCTION

One of the greatest achievements of man since the beginning of civilization has been the discovery and control of fire. Fire has also played an important role in the birth of chemistry as a science. Peking man is credited with the discovery of fire some 250,000 years ago. Empedocles (500-430 B.C.) proposed that fire was one of the four elements, viz., air, earth, water, and fire, that made up the universe. Man burned wood to heat his cave and cook his food, and later learned to make bricks and smelt metals from their ores by the use of fire. When coal, oil, and gas were discovered, they were used by him to produce mechanical and electrical power. These provided mankind with transportation and added comforts.

Wood remained the chief source of energy till the beginning of the nineteenth century. Even in the USA during the early years of the nineteenth century, more than 90% of the energy demand was met by wood. Fossil fuels were in use for purposes other than heating and cooking as far back as 5000 to 6000 B.C. During the Babylonian empire (2500-538 B.C.) crude oil and asphalt were used throughout the Middle East. The Chinese were perhaps the first to use coal around 1100 B.C. The other source of energy, apart from fuel and animal power harnessed by man, were wind power (A.D. 1300) and water mill (A.D. 1000). By A.D. 1600, more than 10,000 flour mills were in use in Great Britain alone. The use of these energy sources, viz., wood, wind power, water mills, and animal power prevailed for many centuries till the invention of the steam engine and the beginning of the industrial era of the eighteenth century. After this the use of coal started increasing at a rapid rate. Around the beginning of the twentieth century more than 85% of the energy demand was met by coal. In the first half of the twentieth century, the use of fossil fuels increased at a steady rate. The use of coal remained at an almost constant level while the use of crude and natural gas filled the gap for the ever increasing energy demand.

At present, the major share of the energy demand is met by crude oil which supplies nearly 42% of the total energy demand. Coal supplies nearly 32% and natural gas about 21% of the energy demand. Nearly 2.5% of the energy demand is met by hydraulic and nuclear sources, and the remaining by wood, wind, cow dung, etc.

At present, the USA with only 6% of the world's population is using about 33% of the energy consumed all over the world. The per capita energy consumption of the world in 1972 was equivalent to 1,984 kg of coal while for India it was only 186 kg. Fuel scarcity is felt during every major war and the price of the fuel shoots up. But during the 1973 Arab-Israel war, oil was used as a weapon by the Arab oil-exporting countries to tilt the favour of big nations towards them. This resulted in a sudden four-fold rise in the price of crude oil. The importance of fuel in human life immediately became evident as world-wide inflation started which even resulted in the fall of a few governments. The economy of many countries was shattered and they are still struggling to bring it back to shape.

India which imports about 14 million tonnes of crude had to pay more than Rs. 1000 crores instead of Rs. 240 crores it was paying for the same quantity before the war started. The import of crude in 1950 was worth about Rs. 80 crores, Rs. 108 crores in 1966, Rs. 240 crores in 1972, and it went up to Rs. 1125 crores in 1975.[1] With the price of crude increasing periodically in the international market, the import bill has risen from Rs. 1654 crores in 1978 to Rs. 3804 crores in 1979. At present, the crude oil share is more than 66% of the total raw material import bill of India. Due to the sudden rise in the price of crude oil, the consumption of crude which was increasing on an average rate of 7.5% per annum since 1960 went down in the year 1974 by 2.75% as compared to its consumption in 1973.[2]

In 1975, the total crude output by the Organization of Petroleum Exporting Countries (OPEC) was 28 million barrels per day (MBD) against the 1973 figure of 30.9 MBD, i.e., a decrease of about 9.5% in two years time. The 1973 Arab-Israel war on the other end generated a worldwide momentum to search and develop more and more sources of energy—especially the indigenous ones. Wherever possible, most of the countries are now shifting from oil to coal.

1.2 ENERGY SOURCES OF PRESENT AND FUTURE

Energy sources can be divided into two main categories:

1. Exhaustible sources, e.g., fossil fuels such as coal, crude oil, natural gas, etc.
2. Inexhaustible or continuous sources, e.g., hydraulic, wind, tidal, solar energy, etc.

Atomic or nuclear energy may be said to be an exhaustible source because the uranium and thorium deposits could be completely consumed. However, if controlled fusion reaction can be mastered, then nuclear energy can become an inexhaustible source as an unlimited supply of deuterium is always available in sea water.

It is quite difficult to predict the exact amount of reserves of any particular fuel or its future demand. Most predictions for both the reserve and expected demands have to be often revised. The ratio of a pessimistic report to an optimistic one for estimated resources is sometimes of the order of ten in a particular region. Similarly, on the consumption side, many factors such as economical, political, and scientific developments, change the predicted demand. In the draft of the fourth Five Year Plan of India, it was expected that by 1965, the coal consumption would be about 98 million tonnes per annum. Later, the estimate was revised to 90 million tonnes, but the actual consumption turned out to be only 60 million tonnes.[3] However, this does not mean that the predictions are baseless or useless. They give a fair idea of the future demand and trends.

1.3 EXHAUSTIBLE SOURCES

All fossil fuels come under the category of exhaustible sources. Table 1.1 gives the classification of fossil fuels. They are divided into three main categories, viz., solid, liquid, and gaseous fuels.[4] Table 1.1 also shows the secondary fuels, i.e., the fuels produced from primary fossil fuels. Here we shall briefly discuss the primary fuels which can be used either for producing secondary fuels or consumed directly.

Wood

As already mentioned, wood played an important role until the middle of the nineteenth century. But today the use of wood is confined to only a few rural areas in some developing countries. Its supply is very limited in the developed nations because of the increasing demand for its use in furniture and as a building material. The contribution of wood in energy supply at present is negligible and in future it is likely to go further down. Its use is limited to only cooking and space heating

Coal

Coal is one of the cheapest fuels and is available in sufficient quantities in many countries. Crude oil and natural gas are fast replacing coal because they are easy to handle and control. Coal is unsuitable for short period operations, while liquid and gaseous fuels generate power immediately. The transportation cost of coal is usually more than its production cost except near the coal mines.

The total estimated reserves of coal in the world and India are estimated to be approximately 6,641,200 and 106,260 million tonnes respectively. The

TABLE 1.1 Various Primary and Secondary Fuels

Primary fuels	*Secondary or derived fuels*		
	Solid	*Liquid*	*Gaseous*
Wood	Charcoal	Methyl alcohol	Producer gas
Peat	Peat-char	Motor spirit, oils	Producer gas
Lignite and Brown coal	Briquettes Semi-coke	Motor spirit, oils	Producer gas
Coal	Briquettes pulverised coal		
		Oil-coal mixtures	
	Semi-coke	Motor spirit, oils, tars, pitches	Town-gas, coke-oven gas, producer-gas, Water-gas
	Coke		Blast furnace gas
Petroleum	Petroleum-coke	Motor spirit, kerosene, diesel oil, fuel oils	
		Oil-Coal mixture	
Natural gas		Gasoline, synthetic fuels	Compressed butane, etc. "calor gas"
Oil shales, torbanites, boghead coals		Motor spirit, kerosene, diesel oil, fuel oils	

From G. W. Hinus, *The Elements of Fuel Technology*, 1958,

total reserve and production of coal for various countries of the world are given in Tables A.1 and A.2.

With the increase in the price of crude, the consumption of coal is expected to increase at a faster rate than it had been in the past. The demand of coal during the first half of the twentieth century remained more or less constant but is expected to increase in future. It is estimated that coal can meet its demand for another 2300 years.[5] However, if coal is used for the production of oil in future and nuclear energy and other energy sources are not developed as expected, then the above estimate may prove to be entirely wrong. The reserves of higher ranking coals, i.e., anthracite and coking bituminous coals are less as compared to the low ranking bituminous coal and lignite. On the other hand, the demand for high ranking coals is more for metallurgical use and for use as fuel. By pulverising and briquetting, low ranking coals can also be used efficiently as fuel. India has about 4000 million tonnes of coking coal and the present consumption of such coal for metallurgical use is about 17-18 million tonnes per year. It is expected that metallurgical coal will last for about 75 years while the other low ranking coals are sufficient for about 1000 years.[6] Because of the cheap price of coal so far much attention was not paid to improve the efficiency of the coal consuming equipment. It is estimated that the overall efficiency of coal consuming plants on an average is only about 18%. There is therefore, much scope to improve the efficiency of such equipment.

Crude Oil

The reserves and the present consumption of crude oil presents a most gloomy picture. The total reserves of crude petroleum for the whole world estimated in the year 1972 were 76,800 million tonnes as against an annual consumption of 2,527 million tonnes. With the steady increase in demand it can be seen easily that the total crude reserves will not be even sufficient for the next 30 years. Table A.3 gives the total reserves and production of crude oil for various countries of the world.

The picture on the Indian front is also not rosy. The total reserves at present stand at about 123 million tonnes including the offshore reserves. The present consumption is about 21 million tonnes per annum. So our total reserves of crude could be consumed in only about six years time. But at present we are producing only one-third of our demand, and the rest is met by the imports; though it is planned that by 1981 or so, India will become self-sufficient. Apart from the proven sources, geologists have expressed the view that India has 26 sedimentary basins of which only nine have been explored. Soviet geologists have even estimated that India has 1,24,000 km^2 of prospective area in West Bengal, Tamil Nadu, Kerala, Gujarat, and Maharashtra. According to them Calcutta is perched on vast fields containing oil and gas. Oil and gas fields in the Kavery basin extend to 15 km on land and 30 km inside the Bay of Bengal.[1]

For the whole world, the consumption of crude increased at an annual rate of 7.5% from 1960 to 1973. In 1974 the total consumption went down as compared to the figure of 1973, and it went down even further in 1975. It is expected that due to the increased price of crude, the consumption of crude oil will increase at an average rate of 5% from 1975 to 1985.

Natural Gas

The use of natural gas is increasing at a rapid rate. The USA has many large gas fields and is consuming a large amount of natural gas. Its share in total energy consumption is also increasing rapidly. The total world reserves of natural gas are estimated to be around 54,100 thousand million cubic metres. The Indian reserves are estimated to be about 44,000 million cubic metres against an annual production of 693 million cubic metres. Natural gas resources of the world are expected to last for about 38 years or so. Table A.4 gives the reserves and production of natural gas for various countries of the world.

Nuclear Power

It was discovered in 1939 that U^{235} could be split in a controlled manner to liberate enormous amount of energy. Now the nuclear energy from the atom has been hailed as the saviour of our civilization. It is expected and planned that by A.D. 2000 about 30% of the total world energy demand will be met by nuclear power. Actually at present atomic or nuclear power seems to be the only immediate solution of meeting the growing energy demand. The main raw material for reactors is U^{235}, though U^{233} and Pu^{239} are also fissionable but these are not available in nature. U^{233} can be produced from Th^{232} and Pu^{239} from U^{238}. U^{235} and U^{238} are available in nature in the form of uranium oxide U_3O_8 in pitch-blende. The world reserves of uranium are estimated to be about 868,880 tonnes while its annual consumption in 1972 stood at 19,185 tonnes. Table A.5 gives the reserves and production of uranium for various countries of the world.[7]

The Indian reserves are estimated to be around 76,000 tonnes, of which a large amount is of low grade. It is estimated that the Indian reserves of uranium can produce about 5 million kW of power for 20 years. Besides uranium, India also has large deposits of thorium. These reserves are estimated to be 50,000 tonnes, but it will take some time before suitable breeder reactors are commissioned for the production of power from U^{233} produced from thorium.

A much more prospective source of energy is the controlled fusion reaction. Laser induced nuclear fusion using deuterium is estimated to be sufficient to provide the total world's energy demands for 350 million years. The cost of power generated from nuclear power is already competing with the cost of thermal power generation, and it is expected that with the increase in the cost of production and transportation of fossil fuels, nuclear power will become cheaper than thermal power. However, the disposal of waste from the nuclear reactors is still a problem.

1.4 INEXHAUSTIBLE SOURCES

Hydraulic Power

Hydraulic power was used even 1,000 years ago, but its use was limited to the operation of flour mills. The potential energy of the water at the top of a hill is used for generating hydraulic power. Modern hydraulic power stations use elevation differences ranging from about 20 m to as high as 1600 m. The main disadvantage of a hydraulic power plant is its high initial cost and longer commissioning period. But these disadvantages are offset by the low cost of generation coupled with the control of floods and increased irrigation facilities. For the generation of hydraulic power, generally a dam is constructed at a suitable place to collect a large quantity of water during the rainy season. The water so collected produces a pressure head. The water is then released in a controlled manner to drive a turbine for the generation of power.

The total generation of electrical power in the world from hydraulic sources in 1971 was about 1100×10^{12} kW out of which India in the same year produced about 34×10^{12} kW. The world utilization of hydraulic power is going up at an average rate of about 4.1% while for India it is about 11.3% per annum. The total potential of the Indian production of hydraulic power is about 41×10^6 kW at 60% load factor. It can thus be seen that there is much scope for further development.

Solar Energy

All sources of energy, viz., coal, petroleum, natural gas, hydraulic power, wind power, etc. with the exception of nuclear power, derive energy from the sun. Fossil fuels are of plant origin and for the growth of plants the sun plays an important role. The wind blows because of differences in temperature and pressure in various zones caused by sunlight. Similarly, water, which provides hydraulic power, is evaporated and is carried to a higher altitude where it condenses and falls as rain or snow.

The quantity of energy received by the earth from the sun is tremendous but it is also quite diffuse. The intensity of solar energy outside the earth atmosphere is about 0.333 Kcal/m²s. Of this about 30% is lost in atmospheric layers. The total energy falling on the earth turns out to be about 708×10^{14} Kcal/s, i.e., some 30,000 times the energy consumed at present. These figures give a clear picture of how large this inexhaustible source is, but because of the low temperature at which it is available and low energy density, large size collectors are needed. Scientists all over the world are trying to tap this source of energy. The other main advantages of solar energy are that it is absolutely pollution free, inexhaustible, and specially suited to deserts and isolated places where other sources are not available. At present, most solar collectors are designed for the desalination of sea water, dehydration of food, and for space heating. With the production of suitable low cost collector materials, solar energy can play a significant role in the future.

Solar water heaters for domestic use have now become quite popular in Australia, New Zealand, Israel, and Japan. Mostly flat plate collectors are used with a top up electric heater (for cloudy days) to provide water at 60°C. Some 2.5 million solar water heaters were sold in Japan in 1973 alone. The use of small domestic water heaters and cookers has good potential for saving wood, coal, and other fossil fuels.

No full scale commercial power plants have been built so far, but the construction of a first solar power plant of 10 MW capacity is scheduled for 1980-81 in Mojave Desert at Barstow, USA. It is estimated that the total cost of the system may come out to be competitive with a fossil fuel plant.

Wind Power

Wind power was used for driving flour mills in many parts of the world. For many years wind power was harnessed for driving the ships that were sailing around the world. However, with the cheap availability of coal and electric power, and with the increasing cost of wood and steel, i.e., higher cost of the wind mill, its use has now become restricted to isolated places where electricity or other fossil fuels are not available. Because of the increasing fuel cost, interest has once again been generated for the improvement in the design of wind mills, especially for the areas where higher wind velocity is available for a considerable period of time. However, this is not expected to make any significant contribution in the near future.

Energy from Oceans

The oceans are full of energy in the form of tides, currents, and thermal gradients. Oceans energy is quite diffuse in nature and its tapping is at present uneconomical, but as in the case of solar energy, it is free from pollution and is available in abundance in coastal areas. It is estimated that the tides and tidal currents have a power of about 3×10^9 kW. The best opportunity for using energy from the oceans lies at present in utilizing the tidal energy source.

Tidal Power

The water level at the sea coast changes twice on each lunar day because of the changing position of the moon. This water can be trapped at a higher level and then regulated to convert this potential energy to some other useful form. The difference in the lengths of the lunar and the solar days gives rise to the spring (or maximum amplitude) tide and neap (or minimum amplitude) tide. When the sun and moon are nearly in line with the earth, a spring tide results, and when they are 90° out of phase with the earth, a neap tide results.

Normally, in an open sea, the difference of level of the high and low tide is only about two-thirds of a metre, but at many selective sites, it is more than two metres, e.g., at the Bay of Fundy on the east coast of Canada, the tide moves as high as 15 metres due to its deep and resonating narrow basin that resonates.

Tidal energy is only now attracting attention, although it was tapped as early as the eleventh century in Europe for small mills. The Rance river 240 MW capacity plant in France was completed in 1966 using a tide range of 11 metres. It utilizes both the upstream and downstream tide to drive a reversible axial flow Kaplan turbine producing 160 MW of power. In Kislaya Bay, Russia, a small 1,200 kW plant was installed in 1966. Russians are now thinking of installing a 6,000 kW station at Mazen Bay on the Arctic coast while in the UK a 4,000 kW project is proposed on Severn estuary. Canada is also considering installing a plant in the Bay of Fundy.

Because of the large initial investment, the power generation cost from the tidal sources is at present about 2.5 times as compared to other conventional sources. Although tidal power utilization is not going to make any significant contribution to the overall energy demand, it has potential to narrow the gap between the demand and supply of energy in the future.

Ocean Thermal Energy Conversion

A thermal gradient always exists in the oceans at a depth of about 500 to 1000 m. A temperature difference of about 15 to 20°C is available from a warm surface to cold deep water. This natural temperature difference can provide an inexhaustible source of energy especially in the tropical oceans, and can be utilized to operate a Rankine cycle working with fluids like ammonia, Freon-11, propane, etc. System studies have shown that the Ocean Thermal Energy Conversion (OTEC) power plant can operate giving a cycle efficiency of about 2.5%. At present the major difficulty posed is the very high cost of large heat exchangers which transfer heat at low temperature differences, and a suitable fluid to operate the cycle.

Geothermal Power

As we go deeper and deeper inside the earth, the temperature correspondingly becomes higher. At a depth of about five km from the surface of the earth, the temperature is around 120°C. At many places the geothermal energy manifests itself in the form of natural hot springs. Very hot springs along with steam also appear in many places. This energy can very easily be utilized to generate power. The cost of power from geothermal sources is appreciably less compared to the power from thermal and nuclear sources. The total heat reserves of the earth are more than 100 million times the total reserves of the fossil fuels on the earth. However, at present, geothermal energy can be tapped only at places where it is available at ground level.

In Larderell, Italy, a 400 MW geothermal power plant has been in operation for the past 60 years. A second commercial plant of 145 MW capacity was installed in New Zealand in 1958. Other commercial plants operating at present are the Geysers power plant of 500 MW capacity in California, a 30 MW plant in Matsukawa, Japan, and a 75 MW plant in Cerro Prieto, Mexico.

According to one geothermal study, 20,000 to 30,000 MW of power can be produced in California's Imperial valley alone. In India also there are many hot springs near Himalayas and in certain parts of Gujarat, Maharashtra, and Bihar, but it is not possible at present to use them for large scale production of power.

Energy from Waste

All human, industrial, and agricultural wastes constitute a potentially significant source of energy. Normally a large portion of such wastes is combustible organic matter, e.g., wood, paper, tar, textile, plastics, plant leaves, etc. It is estimated that in the USA, a city with a population of 1 million generates about 1600 tonnes of organic solids per day which can be utilized to generate energy in three distinct ways: (i) by burning in incinerators, (ii) by supplementary fuelling of power plants by waste material, and (iii) by conversion of the waste to synthetic fuels.

Municipal waste generally contains 50 to 60 combustible material which can give roughly half the heating value as compared to coal of the same weight. The waste is usually first shredded, then ferrous metals are separated by a magnetic separator, and other incombustibles are removed by air-classification.

One of the first plants using municipal refuse was constructed in 1954 in Berne, Switzerland using about 6800 tonnes of waste per day, which generated steam, hot water, and electricity. Due to the success of the Berne plant, almost every major town of Europe has its refuse energy plant. Recently several large incinerators have been built for the existing power plants or as boilers for steam heating systems. In Paris, several incinerators are heating space for more than 10,000 dwelling units and producing some 200 million kW hours of electricity.

Waste heat recovery has another advantage, viz. the exhaust gases are relatively free of harmful pollutants since the waste contains almost no sulphur as compared to that of coal. The main problem with waste utilization is the wide variation in its constituents especially in its water content. The incinerators, therefore, have to be provided with supplementary fossil fuels to maintain the required steam pressure. In St. Louis, Missouri, dry refuse is burnt in boilers powering the turbogenerators with a rating of 270 MW and consuming some 6800 tonnes of waste per day.

The organic waste can be converted to synthetic liquid or gaseous fuel by hydrogenation, by pyrolysis, or by bio-conversion. *Hydrogenation* is a chemical reduction process. The waste is kept in a reactor with carbon monoxide and steam at a pressure of 100 to 250 atm and a temperature of 240 to 380°C in the presence of an alkaline catalyst, such as sodium carbonate, for about an hour. About 90% of the carbon in the waste gets converted to a heavy oil similar to No. 6 fuel oil.

Pyrolysis is a destructive distillation process which is carried out in a reaction vessel in the absence of oxygen at atmospheric pressure and a temperature of about 500°C. The fuel output may be a gas or liquid, but along with it some char is also produced.

Some pilot plants are in operation using the above two methods. It is expected that the full-scale plant will be quite competitive in view of the increasing crude price. The third method, i.e., *bio-conversion* is a bacterial method of anaerobic digestion and is discussed below under the title : "bio-gas."

Bio-Gas

Bio-gas is obtained by fermentation in the sewage disposal system, or by the fermentation of cattle waste, farm waste, etc. If fermentation is carried out in the absence of air, the gas produced may have the concentration of methane as high as 75%. The remaining gas is mostly carbon-dioxide and hydrogen. A town with a population of about 35 million can produce about 1 million cubic metres of gas per day, liberating a total heat of about 5.5×10^9 kcal. This is equivalent to 200,000 tonnes of coal consumed annually. Apart from human waste, gas can also be obtained from cattle waste. It is estimated that there are about 1143 million cattle heads in the world out of which 177 millions are in India alone. Apart from fuel, the process gives good quality compost and a hygienic waste disposal system. United Nations is also taking keen interest in the development of bio-gas plants. A workshop on bio-gas was held in August 1975 under the auspices of an agency of the United Nations. This resulted in the establishment of a corporation called "Calorific Recovery Anaerobic Process Inc." to recover methane gas from cow-dung from ranches in Oklahoma, USA. The amount of gas to be produced is about 23.4 million cubic metres. This gas will be taken to neighbouring states by pipeline. The future of big bio-gas plants will depend on the success of this plant. Many developing and industrial nations are taking interest in the development of bio-gas plants with an aim to preserve their energy resources and environment. The future of bio-gas plants appears to be bright for both in India and countries abroad, especially in the tropical areas.

Synthetic Fuels: Some Alternatives to Gasoline

With the increasing gap between the demand and supply of crude oil, and with the fast depleting fossil fuel reserves, it has now become essential to find out alternatives to gasoline for automobiles, heavy vehicles, and aircrafts. Scientists are on the look out for various synthetic fuels that can replace gasoline. So far, the alternatives proposed have been quite uneconomical, and their production and studies have been only confined to pilot plants. However, with the rapidly increasing cost of crude, as evident from Fig. 1.1, coupled with the concentrated research efforts in synthetic fuels, the latter may soon compete with natural crude oil.

There are three main alternative synthetic fuels which can replace gasoline:

1. Synthetic fuels such as *ethanol* and *butanol* derived from carbohydrates.
2. Synthetic fuels such as *methanol* derived from coal.

Hydrogen from water.

The first two alternatives pose no problem regarding their use. A synthetic fuel blended with gasoline can be used directly in internal combustion engines. However, the use of a pure synthetic fuel would require little modification of the engine. Hydrogen gas can also be used as engine fuel, but further studies are needed for its handling.

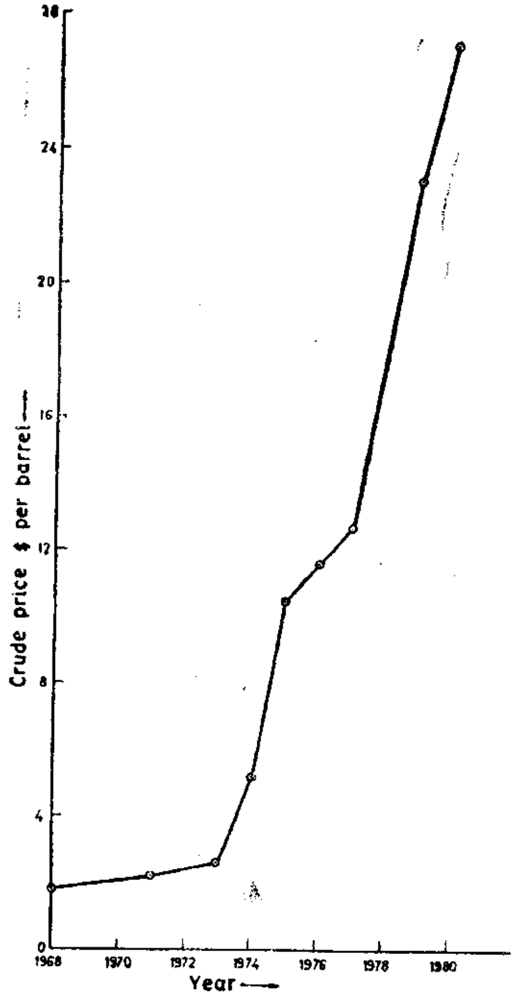

Fig. 1.1—Middle East crude oil prices.

Ethanol

Ethanol (ethyl alcohol) is produced by the yeast fermentation of a variety of carbohydrates such as saccharin (sugarcanes, sugar beets, molasses, and fruit juices), starch (cereals and potatoes), or cellulose (wood waste sulphite liquor). Fermentation yields ethanol and carbon dioxide. This process is completed in about three days. The raw material can be grown specially to produce ethanol. The concentration of alcohol is of the order of 10 to 20% which is increased by distillation. Similarly, butanol can be produced from a variety of raw materials.

Methanol

Methanol (methyl alcohol) can be produced from coal by its liquification, by pyrolysis, or by its reaction with high pressure hydrogen. This will result in liquid fuel in a similar way as described for the production of liquid fuel from municipal waste. Methanol can also be produced by the gasification of coal to give carbonmonoxide and hydrogen, which can later be converted to a liquid hydrocarbon by the catalytic process.

In South Africa, synthetic crude (syncrude) is being manufactured since 1955. The present rate of its production is about 3,660 billion barrels of gasoline and about 90 billion barrels of diesel fuel per day.

Hydrogen

Hydrogen gas is produced either by the electrolysis of water or by the thermochemical splitting of water. Electrolysis of water needs electrical energy. The common installations give about 1000 to 50,000 m^3 of gas per day. They operate usually at 60 to 70% efficiency. Some high pressure electrolyzers have achieved an efficiency up to 85%.

Hydrogen as an alternative to gasoline has the great advantage of almost eliminating the undesirable pollutants. Liquid hydrogen is used with liquid oxygen as a propellant for rockets and space vehicles. Combustion of hydrogen in internal combustion engines increases the efficiency by about 50% as compared to gasoline. The carburetion of hydrogen is also very simple, but a major drawback is in its storage and handling.

Hydrogen can be stored or transmitted in gaseous form, but being very light, it occupies a large volume. In the liquid form, at temperatures below −253°C, hydrogen would require super-insulated cryogenic containers. It can also be stored and transferred in the form of metal hydrides. Metals such as vanadium, niobium, and alloys such as the compound $LaNi_5$, when exposed to prossurized hydrogen can store more hydrogen gas than the volume of its liquid. This gas is released on heating the metal, but these metals are very expensive.

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2

SOLID FUELS

Wood, peat, coal, charcoal, coke, etc. are a few of the solid fuels. The modern trend is to go in for clean and efficient fuels with small sized furnaces where solid fuels cannot compete with liquid and gaseous fuels. But because they are cheap and easily available, solid fuels still supply approximately 33 % of the total energy requirements of the world at present. Most of the solid fuels are naturally occurring, i.e., they are of the primary type.

2.1 ORIGIN OF COAL

Coal is a firm, brittle, sedimentary, combustible rock derived from vegetable debris which has undergone a complex series of chemical and physical changes during the course of many millions of years. It consists mainly of carbon, hydrogen, and oxygen with minor proportions of nitrogen and sulphur. The inorganic materials are found as admixtures.

Coal seams occur in two main types of deposits. The first is the sequence of coal seams, each of great extent and moderate thickness. Such thicknesses seldom exceed four metres. The second type of coal field consists of more isolated deposits, less extensive than the first type, but usually of much greater thickness. These thicknesses may vary from 10 to 20 m and sometimes may be of the order of even 300 m

Two theories have been put forward as to the modes of origin of coal seams. The first, the growth-in-place or *in situ* theory says that coal seams occupy more or less the site on which the original plants grew and where their remains accumulated. According to the second, the "drift" theory, material composing the coal seams drifted there from the areas in which it grew. Some of the coal fields are the results of drift while some are resulted by *in situ* deposition.

Genesis of Coal

Geological studies have proved that coal is of plant origin. Conversion of wood to coal occurs because of the prolonged action of bacteria, fungi, temperature, and pressure. The degree of change of chemical composition of coal, within the series of fossil fuels from peat to anthracite, is known as its rank. Peat is of the lowest rank or belongs to the first stage of conversion of wood to coal, while anthracite is the most mature form of coal.

Formation of Peat from Wood

The principal chemical components of wood are: cellulose [empirical formula $n(C_6H_{10}O_5)$] 45-65%; lignin 25-35%; water and proteins in solution 10-15%; and waxes and resins 0.5-15%. Table 2.1 shows the analysis of wood.

TABLE 2.1 Analysis of Wood

Material	*Per cent*
Moisture (material as found)	30-60
Moisture (air-dried material)	10-15
Dry, ash-free material:	
Carbon	50
Hydrogen	6
Oxygen	43

When wood is subjected to bacterial processes, under nearly stagnant or slowly moving water, cellulose, lignin, and protein are partially decomposed, and their residuals combine to form products of varying composition that resemble humus, called humic acid. Humic acid occasionally occurs as a thick jelly, also called dopplerite, after its discoverer Doppler.

A typical analysis shows that peat contains humic acid (dopplerite) 70-90%, resins and waxes 5-30%. Table 2.2 shows the components of peat.

TABLE 2.2 Analysis of Peat

Material	*Per cent*
Moisture (material as found)	+90
Moisture (air-dried material)	20-25
Dr, ash-free material:	
Carbon	55-65
Hydrogen	5.5
Oxygen	32

The amount of water present in peat varies greatly and may be as high as 90%. Near the surface, peat is light in colour, but at lower depths it becomes darker and finally black.

Formation of Coal from Peat

The major ranks of coal in ascending order are:
Lignite, sub-bituminous, bituminous, semi-anthracite, and anthracite. The burial of peat under a thick layer of silt stops plant growth and eventually stops bacterial action. The gradually increasing weight of the accumulating layer of earth above the buried peat causes water to be squeezed out with the consequent consolidation of peat. The pressure increases because of the increasing thickness of deposits, and because of the movements of earth, a large lateral pressure is caused. The temperature of peat also increases with increasing depth. This high pressure of the order of a few kg/cm² to hundreds of kg/cm² and temperature (not exceeding 300°C), with changing time (from 10×10^6 years for most brown coal to 300×10^6 years for most mature anthracite) causes varying degree of metamorphosis, increasing the rank from lignite to anthracite.

With increasing rank, coal loses moisture, hydrogen, nitrogen, sulphur, and volatile matter, while carbon content and calorific value of coal increases progressively. The coking properties of coal also increase over a certain range.

Various overall reactions suggested for formation of coal from wood are:
According to Renault (1900)

$(C_6H_{10}O_5)_4 \quad C_9H_6O + 7CH_4 + 8CO_2 + 3H_2O$

Cellulose→bituminous coal + methane + carbondioxide + water

According to Parr (1910)

$(C_6H_{10}O_5)_5 \quad C_{20}H_{22}O_4 + 3CH_4 + 8H_2O + 6CO_2 + CO$

Cellulose→lignite

$(C_6H_{10}O_5)_6 = C_{22}H_{20}O_3 + 5CH_4 + 10H_2O + 8CO_2 + CO$

Cellulose→bituminous coal

The changes occurring in the series wood to anthracite, according to Mott (1942), are shown in Table 2.3.

From the reactions given in Table 2.3 it can be observed that the rate of methane evolved increases rapidly from bituminous coal to semi-anthracite, and from semi-anthracite to anthracite. This results in a fall of the hydrogen content of coal. These reactions account for large quantities of methane (fire damp) associated with coal mines containing carbonaceous coals and anthracites.

2.2 ANALYSIS OF COAL

Coal is composed of carbon, hydrogen, nitrogen, oxygen, sulphur, and inor

TABLE 2.3 Products Evolved During Formation of Anthracite from Wood

Stage	*Products evolved*	*Yield %* (*Wood= 100%*)	*Gases, m³/tonne*	
			CH_4	*CO_2*
Wood to low rank lignite	$64H_2O+8CH_4+CO_2$	73.5	38.2	4.3
Low rank lignite to low rank bituminous coal	CO_2	53.4	—	147
Low rank bituminous coal to semi-anthracite	1st stage $1.42\ H_2O+0.43\ CH_4+CO_2$	47.4	13.4	34.6
	2nd stage $3CH_4+CO_2+5H_2O$	45.1	14.4	3.0
	3rd stage $1.45\ H_2O+5.8\ CH_4+CO_2$	41.3	73.6	12.2
Semi-anthracite to anthracite	$36\ CH_4+H_2O$	37.2	145	..

With permission of IPC Business Press, from Mott R.A., *Fuel* 1942, **21**: 129. 1943, **22**: 20.

ganic impurities. The chemical constituents are determined by the proximate and ultimate analyses. Testing of coals also includes the determination of calorific value, coking, and caking properties.

Proximate Analysis

Proximate analysis is a simple test of the quality of coal. It gives in percentage the amount of moisture, volatile matter, fixed carbon, and ash content of coal.

The amount of moisture is calculated by heating 1g sample of coal to a temperature of 108–110°C, so that all the moisture is evaporated and noting the loss of weight. To find the amount of volatile matter, 1g sample of coal is heated in an air-tight crucible for seven minutes at about 950°C, the volatile matter and moisture is liberated, the loss of weight is noted and loss of weight due to moisture already found is deducted. The percentage of ash is calculated by heating 1g sample of coal in the presence of air to about 725°C so that all the fixed carbon is burned. The residue will be ash. The percentage of fixed carbon is found as 100 minus the percentage of moisture, volatile matter, and ash. The heating value of coal is often given with the proximate analysis and is found by the bomb calorimeter.

Ultimate Analysis

Ultimate analysis gives the amount of carbon, hydrogen, oxygen, nitrogen, sulphur, and ash present in a sample of coal in terms of percentage by weight. The percentage of carbon is found by burning 0.2 g sample of coal in strongly oxidizing atmosphere and weighing the amount of carbondioxide absorbed in a solution of potassium hydroxide. The weight of carbon can be computed from the weight of carbondioxide. Similarly, the water vapour emitted is absorbed in a calcium chloride tube and the amount of hydrogen found from the weight of moisture. The percentage of ash is found by burning the coal sample and weighing the residue. The percentage of nitrogen is found by the Kjeldahl method. One gram sample of coal is heated in a glass flask with boiling concentrated sulphuric acid which works as an oxidizing agent. To assist the oxidation of nitrogen, pure anhydrous potassium sulphate and selenium powder is added. The first chemical increases the boiling point, while the second works as a catalyst. The nitrogen in the coal is converted to $(NH_4)_2SO_4$. The resulting solution is diluted with water, made strongly alkaline, and boiled. $(NH_4)_2SO_4$ is decomposed, liberating ammonia, which is absorbed in a standard acid and titrated. Then the amount of nitrogen is calculated. Sulphur occurs in coal as a chemical combined with carbon of pure coal known as organic sulphur, in combination with iron as pyrites (FeS_2) known as pyritic sulphur, and as sulphates of calcium, magnesium, iron. etc. known as sulphate sulphur.

Usually the total amount of sulphur is determined, though individual forms can also be found. A simple method used for determining the total amount of sulphur is the Eschka method. In this method 1g air-dried sample is mixed with 2g of the Eschka mixture (two parts by weight of pure MgO and one part by weight of pure anhydrous Na_2CO_3) and the mixture is heated gently in a porcelain crucible until all the coal is oxidized. Sulphur is converted to sulphates and sulphites. The residue is mixed with water and little bromine—water is added to convert all sulphites into sulphates. Hydrochloric acid is added to dissolve all sulphates. The sulphate in the filtrate is precipitated as $BaSO_4$ by adding $BaCl_2$. The barium sulphate is filtered, ignited, and weighed. Then the amount of sulphur is computed. A typical analysis of various solid fuels is given in Table 2.4.

2.3 SOME OTHER TESTS

Calorific Value

The calorific value of coal is determined by using a bomb calorimeter. Approximately 1 g of coal is placed in a crucible kept inside the calorimeter. The bomb is filled with oxygen under a pressure of 25 atm for bituminous coals and 30 atm for anthracites and coke. The coal is then ignited by passing a low voltage current through the firing circuit. The rise in the

TABLE 2.4. Typical Composition of Solid Fuels

Fuel	*Proximate analysis, %*				*Ultimate analysis, %*						*Heating value, kcal/kg*	
	Moisture	*Volatile matter*	*Fixed carbon*	*Ash*	*Carbon*	H_2	O_2	N_2	S	*Ash*	*As reported*	*Dry basis*
Wood												
Oak, dry	—	—	—	—	50.2	6.0	43.3	0.1	—	0.4	—	4620
Pine, dry	—	—	—	—	52.6	7.0	40.1	—	—	0.3	—	5340
Peat	56.8	26.0	11.2	6.0	23.1	9.6	59.6	1.3	0.4	6.0	2000	4630
Lignite	34.8	28.2	30.8	6.2	42.4	6.7	43.3	0.7	0.7	6.2	4000	6110
Bituminous coal												
Low volatile	3.3	20.5	70.0	6.2	80.7	4.9	5.3	1.1	1.8	6.2	7950	8225
Medium volatile	3.1	21.8	67.9	7.2	80.1	5.0	5.2	1.5	1.0	7.2	7790	8050
High volatile	8.2	36.1	48.7	7.0	68.4	5.6	16.4	1.4	1.2	7.0	6755	7355
Sub-bituminous coal	19.6	30.5	45.9	4.0	58.8	6.0	29.6	1.3	0.3	4.0	5625	7000
Anthracite	2.3	3.1	87.7	6.9	86.7	2.2	2.9	0.8	0.5	6.9	7520	7700
Semi-Anthracite	3.0	8.4	78.9	9.7	80.2	3.6	4.7	1.1	0.7	9.7	7470	7700
Coke, by-product	0.8	1.4	87.1	10.7	85.0	0.8	1.2	1.3	1.0	10.7	7050	7100
Coke, breeze	12.0	4.2	65.8	18.0	66.8	2.5	11.2	0.9	0.6	18.0	5665	6440
Charcoal	12.0	1.9	83.1	3.0	84.6	2.3	10.7	—	—	3.0	6280	7150

With permission of Mc Graw-Hill, from M.L. Smith and K.W. Stinson, *Fuels and Combustion*, 1952, P. 13.

temperature of water is a measure of the heat released by the combustion of coal.

Swelling or Caking Test

The caking or swelling property of coal is usually measured by the crucible swelling test. In this test 1 g of air-dried coal, freshly ground to pass a 72 mesh B.S. sieve, is rapidly heated in a crucible, above a burner flame, to 820°C. After the flame from the burning volatile matter has died out or after 24 min, whichever is the greater period of time, the crucible is cooled. The coke button is removed and compared with standard numbered profiles from one to nine in half units. The result is recorded as "swelling number" or "free swelling index".

In the Roga index method, the known weight of coal and standard anthracite are mixed in a crucible and carbonized. The resulting coke is examined in a Roga drum for its resistance to abrasion.

The Gray-King assay test is also carried out to observe the coking property of coal. In this test, 20 g of the coal sample is slowly heated in a silica tube to 600°C. After cooling, the coke is compared with standard profiles numbered A to G. If the residue remained is a powder, it is classified as A. Stage B is classified as non-caking, C and D as weakly caking while E, F, and G are classified as medium caking. Strongly caking coals swell and are designated as G_1, G_2, etc. to G_{10}, the suffix indicating the number of grams of inert carbon which must be blended into a 20 g charge to give zero swelling.

The Audibert-Arnu test is only carried out for coals corresponding to type G to G_{10} of the Gray-King assay test. In this test, a pencil of compressed powdered coal topped by a steel piston is heated at a rate not exceeding 5°C/min. The percentage dilation is calculated from the observed movement of the piston. The relation between the Gray-King assay test and the Audibert-Arnu test is:

G_1 to G_4 gives a maximum dilation from 0 to 60%
G_4 to G_8 gives a maximum dilation from 60 to 130%
G_8 to G_{12} gives a maximum dilation from 130 to 400%

The Roga index correlated with the Gray-King assay approximately as Index 0-5=A-B. 5-10=B-D, 20=G, 45=G_4.

Ash Fusibility Test

In this test a moulded cone of ash is heated in a mildly reducing atmosphere. The deformation temperature is the temperature at which the tip rounds, and the hemisphere temperature is the temperature at which the specimen subsides to a hemispherical lump.

Agglutinating Index

This is determined by mixing the coal with an inert material such as graded sand and stating the proportion which fails to give a coherent mass.

Grindability Index

The grindability of coal is important in connection with pulverizing. In this test specially sized coal is submitted to a standardized grinding procedure. The index is calculated from the percentage of the sample remaining on a 74 μ sieve.

2.4 COAL PETROLOGY

Petrology is a branch of geology concerned with the study of the individual mineral components, structure, and history by visual means, i.e., by the naked eye or by an optical microscope.

Stopes and Wheeler gave the relationship between the appearance and properties of the banded components of bituminous coals. The four banded constituents were named by Stopes, viz.

Vitrain

A thin band generally 2 to 10 mm thick, brilliantly glossy and vitreous, uniform appearance.

Clarain

Bands less brilliantly glossy than vitrain but with a satin luster and a clearly striated (laminated) structure.

Durain

Hard and almost lusterless dull coal with a granular, matt surface.

Fusain

Soft charcoal like layers or pockets having a fibrous appearance.

Typical chemical composition of these banded components of medium bituminous coals are shown in Table 2.5.

Recent Petrological Terminology

These days coal components are termed as:

TABLE 2.5—Composition of Banded Constituents of Coal

	Proximate analysis, %			Ultimate analysis, ash-free-dry, %						
Constituent	*Fixed carbon*	*Moisture air-dried*	*Volatile matter*	*Ash*	*Carbon*	*Hydrogen*	*Sulphur*	*Nitrogen*	*Oxygen*	*Calorific value* kcal/kg *ash-free-dry*	*Coking power*
Vitrain	63.1	1.7	34.6	0.6	84.4	5.4	1.0	1.5	7.7	8200	Swollen coke
Clarain	57.5	1.4	37.6	3.5	82.2	5.7	2.3	1.9	7.9	8200	Swollen coke
Durain	62.0	1.2	32.2	4.6	85.8	5.3	0.9	1.4	6.6	8400	Non-swollen coke
Fusain	70.4	0.9	19.1	9.6	88.7	4.0	1.0	0.7	5.6	8250	No coke formed

After J.S.S. Brame and J.G. King, *Fuel—Solid, Liquid and Gaseous*, 1955).

Lithotype or rocktype

A macroscopic component of coal equivalent to the banded component, viz., vitrain, clarain, durain, or fusain.

Maceral

Elementary homogeneous chemical entity identified through a microscope. They include vitrinite, resinite, fusinite, etc., with their name terminating with "-inite".

Micro-lithotype

An association of macerals present in a coal band of maximum width of 50 microns. Then name termination is "-ite", e.g., vitrite, clarite, durite, fusite, etc.

2.5 CLASSIFICATION OF COAL

Coal is ordinarily classified according to rank. Most classifications are based upon some property of coal which varies with increasing maturity or rank of coal. The systems of classification fall into two categories: scientific and commercial. For scientific classification, the property used is the ultimate analysis which gives the elementary composition of coal in terms of percentages by weight of the elements present, viz., carbon, hydrogen, oxygen, nitrogen, and sulphur.

For the classification to be used and developed for commercial purposes, the property used is the proximate analysis which gives percentages of moisture content, volatile matter, ash, fixed carbon, and sulphur in coal plus calorific value in cal/g. Classification by the National Coal Board (NCB), and the Economic Commission of Europe (ECE) also includes the coking properties of coal.

Most scientific systems of classification are based on mineral matter free or moisture and ash free basis. The simplest method for determining the amount of mineral matter present is to determine the ash and sulphur contents and to make corrections for the changes taking place in these during combustion. The Parr formula for calculating mineral matter is:

$$\text{Total inorganic matter} = \text{Moisture} + 1.08\ \text{ash} + 0.55\ \text{sulphur}$$

where moisture, ash, and sulphur represent the percentages of these substances found by analysis of the coal.

Another formula for calculating the mineral matter is:

$$\text{Mineral matter} = 1.13\ \text{ash} + 0.5\ S_{pyr} + 0.8\ CO_2 + SO_{3coal} - 1.1\ SO_{3ash} + 0.5\ Cl.$$

Where

S_{pyr} = % pyritic sulphur in coal

CO_2 = % carbon dioxide, as carbonate, in coal

$SO_{3}ash$ = % sulphate in ash from coal

Cl = % chlorine in coal.

SO_{3coal} = % sulphate in coal.

Methods Based upon Ultimate Analysis

Regnault was the first to give a satisfactory classification based on ultimate analysis in 1837. In 1874, Gruner modified Regnault's classification. In 1911, Gruner's son with Bousquet modified the earlier classification, and divided coals above the rank of lignite into six classes, based upon their carbon contents. He drew up a table in which the principal features of the six classes were defined in terms of hydrogen, fixed carbon, volatile matter, calorific value, the nature of the residue obtained on carbonization, and the behaviour of the coals during combustion. In 1907 Grout plotted the ultimate analysis of a large number of coals, calculated according to the ash-free-dry basis on a tri-axial diagram and found that the humic coals lie on a narrow band, while cannel coals which are rich in hydrogen lie well above the band. In 1915 Ralston confirmed the observations made by Grout. He found that coals of equal volatile matter and equal calorific value fall on approximately straight lines, inclined at an angle to the C, H, and O axes.

Seyler's Classification

In 1900, C. A. Seyler gave a classification of coal depending upon the observation that if the elementary composition of coal, carbon, and hydrogen on the basis of dry mineral free is plotted on a chart, then there is a close relation between their composition and properties. On rectangular coordinates, representing % carbon and % hydrogen on "pure coal basis" ($C+H+O=100$), he found that all normal high rank coals are placed in a narrow band between $C=75$ and 95% and hydrogen from 3 to 5.7% within a maximum width equivalent to 0.7% hydrogen. He also found that except for anthracite, volatile matter and calorific value will also serve approximately as coordinates for the same points, provided that these alternative coordinates are set at an angle to the C—H coordinates. Any coal falling above this band are called per-hydrous and those below the band are called sub-hydrous. Seyler also devised mathematical equations to express the relationship between carbon, hydrogen, volatile matter and calorific value. He later added lines of equal caking characteristics to his chart. Seyler's chart is given in Fig. 2.1. Table 2.6 gives the important features of Seyler's classification.

Methods Based upon Proximate Analysis

The classifications based upon proximate analysis were developed for international trade. There are three major classifications, viz., the American Standards for Testing and Materials (ASTM) classification developed

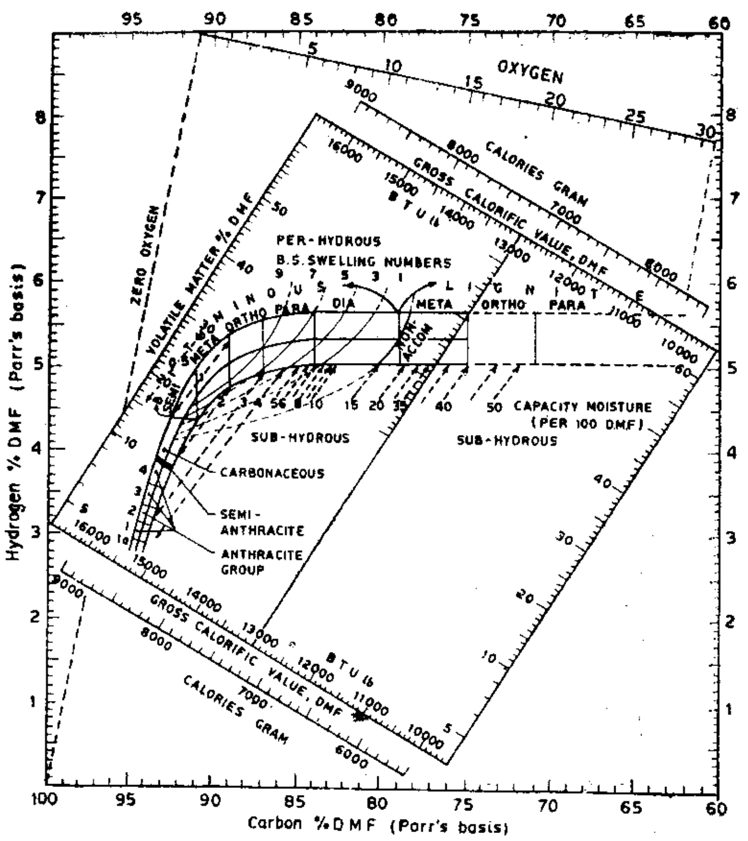


Fig. 2.1—Seylers coal classification chart (after C.A. Seyler, Proc. S. Wales Inst. Engrs., 1900)

TABLE 2.6—Seyler's Coal Classification Chart

Coal rank	*Carbon* %	*Hydrogen* %	*Volatile matter* %	*Calorific Value* Btu/lb	*Calorific Value* kcal/kg	*B.S. Swelling Index*
Anthracite	>93.3	3.0–3.9	5–10	15400	8555	1
Carbonaceous						
Semi-anthracite	93.3–91.2	3.8–4.4	10–14	17500	9722	1
Semi-bituminous		4.4–5.0	14–20	15800	8777	3.5
Bituminous						
Meta-	91.2–89.0	4.4–5.4	20–28	15700	8722	9
Ortho-	89 0–87.0	4.7–5.6	28–31	15500	8611	9
Para-	87.0–84.4	4.9–5.7	31–36	15000	8333	6
Lignitious						
Meta-	84.0–80.0	5.0–5.7	36–42	14300	7944	2
Ortho-	80.0–75.0	5.0–5.7	42–49	13300	7388	1
Lignite	<75.0	5.0–5.7	49–59	11700	6500	1

in the USA, the National Coal Board (NCB) classification developed in England and International classification or (ECE) classification developed by the Economic Commission of Europe. The international classification is based partly on the NCB system and partly upon the ASTM classification.

ASTM Classification

ASTM standards on coal and coke (ASTM 0388-38 and 389-37) give details of classification of coal and coke. Coal is classified according to rank and grade. Rank gives the maturity of coal from lignite to anthracite and grade gives the ash softening temperature, heating value, and size.

Classification according to rank is done on the basis of proximate analysis of moisture free and mineral matter free coal. Heating values are taken on moist and mineral matter free basis. Coals containing less than 31% volatile matter are divided on the basis of fixed carbon into five groups. The first

TABLE 2.7. Classification of Coals by Rank

All values reported on mineral-matter-free basis

*Fixed carbon** (*Dry basis*) %		*Volatile matter* (*Dry basis*) %	*Numerical designation* (*x–y*)
98	*m*-Anthracite	2	x=nearest whole % fixed carbon y=nearest whole Btu per lb/100
92	Anthracite	8	
86	Semi-anthracite (Non-agglomerating)	14	
78	Low-volatile bituminous	22	Btu per lb* (Moist basis)
69	Medium-volatile bituminous	31	
	High-volatile bituminous A		14,000
	High-volatile bituminous B		13,000
	High-volatile bituminous C (either agglomerating or non-weathering)		
	Sub-bituminous A (both weathering and non-agglomerating)		11,000
	Sub-bituminous B		9,500
	Sub-bituminous C		8,300
	Lignite (consolidated)		
	Brown coal (unconsolidated)		

*Samples having border line values are classed in higher bracket.

With permission of American Society for Testing and Materials from *ASTM*, D-383—38.

three groups which have a fixed carbon content greater than 86% are called anthracites while the last two containing fixed carbon between 69 and 78% are called bituminous coals. The remaining bituminous coals, sub-bituminous coals, and lignites are then classified according to their calorific value. These are divided into eight groups: three groups of bituminous coals, three groups of sub-bituminous coals, and two groups of lignites. Table 2.7 gives the details of classification according to rank.

The classification according to grade is shown in Table 2.8 giving the ash softening temperature, sulphur contents, and size of the coal.

TABLE 2.8—Classification of Coals by Grade

All values reported on as sampled basis

1. *Size designation* ($y \times x$ in.):
   y=upper limit (large size): The smallest screen which retains less than 5% of total sample
   x=lower limit (small size): The largest screen which passes less than 15% of total sample
   Large screens: Plates containing round holes of designated size, 8 in. max., 3/8 in. min.
   Small sieves . Woven-wire cloth square openings. Size of opening [(1/sieve No.)—wire dia.] in. No. 4 max., No. 200 min.
   (Surface moisture dried off coal before screen tests, if present)

2. *Ash-content designation* (value to nearest 0.1%) :

% Ash*	0	4.05	6.05	8.05	10.05	12.05	14.05	16.05	18.05	20.05
Symbol	A4	A6	A8	A10	A12	A14	A16	A^{18}	A20	A20 +

3. *Softening Temperature of Ash* (value to nearest 10°F) :

°F*	2000	2195	2395	2595	2795	
Symbol	F20 –	F20	F22	F24	F26	F28

4. *Sulphate content* (value to nearest 0.1%) :

% S*	0	0.75	1.05	1.35	1.65	2.05	3.05	5.0
Symbol	S 0.7	S 1.0	S 1.3	S 1.6	S 2.0	S 3.0	S 5.0	S 5+

5. *Calorific value** (nearest whole Btu per lb divided by 100).

*Samples having border line values are classed in a higher bracket.

With permission of American Society for Testing and Materials from *ASTM*, D-389—37.

Size grade gives the upper and lower limits of the screen size between which more than 80% of coal lies. The heating value symbol gives the heating value of coal in hundreds of Btu to the nearest hundred, e.g., symbol "132" represents heating value between 13,150 to 13,249 Btu/lb. Classification by grade may be expressed by a combination of five types of symbols, viz.

4×2 in., 132-A 8-F 24-S 1.6

The above example indicates a coal size so that 80% coal will pass between screens of 2 and 4 in. size, which have a calorific value of 13,150 to 13,249 Btu/lb., an ash content of 6.1 to 8%, an ash softening temperature of 2400 to 2590°F, and a sulphur content of 1.4 to 1.6%.

The symbols may include classification by rank, e.g., 62—146, 4×2 in., 132—A8—F24—S1.6 will also indicate a high volatile bituminous coal analyzing approximately 62% dry mineral matter free fixed carbon which had a heating value of 14,600 Btu/lb.

NCB Classification

The NCB classification is based upon volatile matter, expressed according to the dry, mineral matter free basis and the coking power of clean coal containing not greater than 10% ash. The classification by volatile matter yield is:

Anthracites	*Less than* 9.1%
Low Volatile Steam Coals	9.1-19.5%
Medium Volatile Coals	19.6-32%
High Volatile Coals	More than 32%

Each of these four main classes is sub-divided according to the caking properties of the coals assessed by the Gray-King coke type assay. Table 2.9 gives the details of NCB classification.

ECE or International Classification

According to the ECE classification, coals are first divided into nine classes. These are further divided according to coking and caking properties. The first five classes contain coals with volatile matter (dry ash free basis) upto 33%. The coals having volatile matter greater than 33% are divided into the remaining four classes according to their gross calorific value on moist ash-free basis. The classes of coals are sub-divided into groups according to their caking properties. A broad correlation exists between the crucible swelling number and the Roga index which represent the caking properties, and either may be used to determine the group number of coal. These groups are further divided into sub-groups upon their coking properties, determined by the Gray-King coke type or Audibert-Arnu dilatometer number.

A system of three digit code number is used as shown in Table 2.10. The first digit represents the class number, the second digit the group number and the third digit gives the sub-group number or we can say the second digit represents the caking index and the third digit gives the coking index. The distinction between caking and coking properties is in the rate of heating: high rate of heating gives caking properties, while slow heating gives coking properties.

Brown coal and lignites are classified as those having a calorific value on moist, ash-free basis of less than 10,260 Btu/lb (5700 kcal/kg). These are

TABLE 2.9—NCB Classification of Coals

Group	*Class*	*Sub-class*	*Volatile matter, %*	*Gray-King coke type*	*General description*
100			<9.1	A	Anthracites
	101		<6.1	A	
	102		6.1-9.0		
200			9.1-19.5	A to G_8	Low-volatile steam coals
	201		9.1-13.5	A to C	Dry steam coals
		201a	9.1-11.5	A to B	
		201b	11.6-13.5	B to C	
	202		13.6-15.0	B to G	Coking steam coals
	203		15.1-17.0	E to G_4	
	204		17.1-19.5	G_1 to G_8	
	206		9.1-19.5	A to B for V.M. 9.1-15.0 A to D for V.M. 15.1-19.5	Heat altered low-volatile steam coals
300			19.6-32.0	A to G_9	Medium volatile coals
	301		19.6-32.0	$>G_4$	Prime coking coals
		301a	19.6-27.5		
		301b	27.6-32.0		
	305		19.6-32.0	G to G_3	Mainly heat altered coals
	306		19.6-32.0	A to F	
400-900			>32.0	A to G_9	High-volatile coals
400			>32.0	G_9 or $>G_9$	Very strongly caking coals
	401		32.1-36.0		
	402		>36.0		
500			>32.0	G_5 to G_8	Strongly caking coals
	501		32.1-36.0		
	502		>36.0		
600			>32.0	G_1 to G_4	Medium caking coals
	601		32.1-36.0		
	602		>36.0		
700			>32.0	E to G	Weakly caking coals
	701		32.1-36.0		
	702		>36.0		
800			>32.0	C to	ery weakly caking coals
	801		32.1-36.0		
	802		>36.0		
900			>32.0	A to B	Non-caking coals
	901		32.1-36.0		
	902		>36.0		

TABLE 2.10—International Classification of Coals

GROUPS (determined by caking properties)			CODE NUMBERS										SUBGROUPS (determined by coking properties)		
GROUP NUMBER	ALTERNATIVE GROUP PARAMETERS: Free-swelling index (crucible-swelling number)	ALTERNATIVE GROUP PARAMETERS: Roga index	The first figure of the code number indicates the class of the coal, determined by volatile matter content up to 33%V.M. and by calorific parameter above 33 % V.M. The second figure indicates the group of coal, determined by caking properties The third figure indicates the subgroup determined by coking properties										SUB-GROUP NUMBER	ALTERNATIVE SUBGROUP PARAMETERS: Dilatometer	ALTERNATIVE SUBGROUP PARAMETERS: Gray–King
3	>4	>45					435	535	635				5	>140	$>G_8$
						334 VA	434 VB	534 VC	634				4	>50–140	G_5–G_8
						333	433	533	633	733 VD			3	>0–50	G_1–G_4
						332 a, 332 b	432	532	632	732	832		2	≤0	E - G
2	$2\frac{1}{2}$–4	>20-45				323	423	523	623	723 VIA	823		3	>0-50	G_1–G_4
						322 IV	422	522	622	722	822		2	≤0	E–G
						321	421	521	621	721 VIB	821		1	Contraction only	B–D
1	1–2	>5–20			212	312	412	512	612	712	812		2	≤0	E–G
					211	311 III	411	511	611	711 VII	811		1	Contraction only	B–D
0	0–$\frac{1}{2}$	>0–5		100 I: A, B	200 II	300	400	500	600	700	800	900	0	Nonsoftening	A
CLASS NUMBER →			0	1	2	3	4	5	6	7	8	9	As an indication, the following classes have an approximate volatile-matter content of:		
CLASS PARAMETERS	volatile matter (dry, ash-free) →		0-3	>3–10 >3–6.5, >6.5–10	>10–14	>14–20	>20–28	>28–33	>33	>33	>33	>33	Class 6: volatile matter 33–41 % Class 7: 33–44 % Class 8: 35–50 % Class 9: 42–50 %		
	Calorific parameter a/ →			—	—	—	—	—	>13,950	>12,960–13,950	>10,980–12,960	>10,260–10,980			
			CLASSES (Detemined by volatile matter up to 33% V.M. and by calorific parameter above 33 % V M)												

From Bureau of Mines, *Rept. Invest.* 5435 classified by a code number which is a combination of the class number and group number. The class number represents the total moisture of the coal as mined and the group number represents the percentage tar yield from the dry, ash free coal.

2.6 OTHER SOLID FUELS

Wood

Wood is still extensively used as a fuel for cooking and house heating in tropical and developing countries. Wood is used in its natural state or as waste in the form of wood shavings, saw dust, scraps, etc. Wood charcoal is also used for heating.

Wood is classified as hard and soft wood. Hard wood refers to a botanical group of trees which have broad leaves. Soft wood or conifers refers to trees which have needle or scale-like leaves and remain evergreen for most part of the year. The presence of considerable quantities of resins and oils, e.g., in long leaf pine and eucalyptus tend to raise the heating value of wood. Generally, soft wood burns faster than hard wood.

Freshly cut wood contains approximately 25-50 moisture. In air-dried fully seasoned wood it reduces to 15—20%. The composition of wood gives approximately 15—20% moisture, 40—50% cellulose, 0.4—2% resins and waxes, 2—4% soluble water, and approximately 30% lignin. A typical proximate analysis of dry wood is as follows: Volatile matter, 81.5%, Fixed carbon, 17.5, and Ash 1%. The ultimate analysis and calorific values of typical wood are given in Table 2.4. The calorific value of pure cellulose is 4150 kcal/kg. The measurement of molecular weight of cellulose indicates values of 16,000 to 2,000,000, the lower values, suggesting some degradation in the process of preparation. The basic configuration of cellulose is shown in Fig. 2.2.

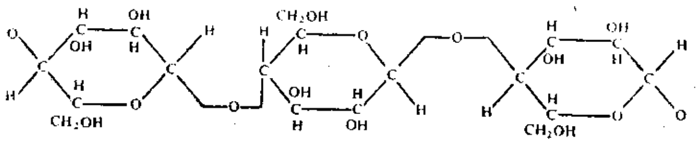


Fig. 2.2.

Within the cells of wood and at their surface are compounds like tannins, starches, resins, oils, dyes, alkaloids , and sugars.

Wood Charcoal

When wood is burned in a closed retort with insufficient air, the volatile matter is driven off leaving behind charcoal as residue. The charcoal intended for use as a fuel in the blast furnace is made from cardwood by low temperature distillation in by-product retorts, in brick kilns, and formerly in heaps covered with earth called "meilers". The yield of charcoal in meilers is less than 20% while in metal retorts is about 35%. Typical proximate and ultimate analysis of charcoal is given in Table 2.4. The charcoal has an average heating value of about 6,000 kcal/kg. It ignites and burns easily without smoke. Charcoal is also used for both absorption and adsorption. It is porous in nature with a large surface area.

Coke

Coke is a fused cellular porous structure that remains after the free moisture and the major portion of the volatile matter have been distilled from coal. It is produced by heating coal in absence of air so that coal decomposes thermally. The process is known as carbonization and is similar to pyrolysis.

Coal is carbonized in coke ovens in horizontal or inclined retorts and in intermittent or continuous vertical retorts. The process of carbonization can be observed in a laboratory by heating the coal in the absence of air and raising the temperature at a slow controlled rate. Various characteristics, decomposition temperature, and physical changes can be observed. The decomposition temperature depends upon the rank and coking properties of coal.

When raw coal known as "green" coal is heated, free moisture is driven off first, followed by carbondioxide, carbonmonoxide, and combined moisture around 300°C. At the critical softening or fusion temperature of around 350 to 400°C, the outer layer of coal melts and creates a fusion zone. Simultaneously, saturated paraffin hydrocarbons (methane, etc.), some unsaturated hydrocarbons, and hydrogen are also liberated. The plastic layer formed due to fusion is impervious to gases. Thus a gas pressure is created inside the lump of coal which makes it swell. This plastic layer moves towards the centre with continued heating. On further heating to about 500°C, the plastic layer begins to resolidify to form a soft, dull black char known as semi-coke. At about 550°C, this semi-coke decomposes, shrinks, and becomes much harder. This residue is known as coke. The formation of coke continues upto 1,000°C. During this heating, the coke is further devolatilized and its colour changes from black to silvery gray. Shrinking and hardening continues, and the formation of graphite lattice commences. On the basis of carbonization temperature, coke is divided into three broad classes.

Coke carbonized from 900°C to 1200°C is called *high temperature coke.* The volatile product gets decomposed yielding a relatively large quantity of gas having low heating value, a minimum of tar, and coke containing graphite form of carbon. Coke carbonized at a temperature below 750°C, generally between 500 to 600°C is known as *low temperature coke.* Low temperature carbonization yields a relatively small quantity of gas which has high calorific value, maximum of tar, and the coke consists of active carbon. Coke carbonized at a temperature between 750 to 900°C, generally around 850°C, is known as *medium temperature coke.*

Yield of coke from coal varies from 60 to 80%. Low temperature coke is used as a fuel while high temperature coke is used for metallurgical purposes. The typical proximate and ultimate analysis of coke is given in Table 2.4.

Fuel Briquettes

Fuel briquetting is the term applied to the process of agglutinating fine sizes of coal, lignite, or other fuels. The purpose of briquetting is to form a composite large size of briquette which is easy to burn in a conventional equipment.

Heat, pressure, and a binder, or a combination of these are mediums used for briquetting. Brown coals and some bituminous coals can be briquetted without a binder by applying heat and pressure. Anthracite, some low volatile bituminous coals, and lignite are difficult to briquette without a binder because of its non-coking characteristics and neither do these become plastic when heated. The binder used is generally coal tar or petroleum asphalt. Sometimes two binders are used. A main or primary binder is added to the dried and preheated coal such as asphalt coal tar or pitch. A secondary binder such as flour or starch is either used as a paste or used dry, and heated with coal in a preheater to reduce the quantity of the bituminous binder. Such briquettes are stronger, cleaner, and produce less smoke.

3

LIQUID FUELS

Liquid fuels are derived from two main sources: from crude oil, i.e., from naturally occurring petroleum, and from coal. The liquid fuel obtained from coal is negligible as compared to the fuel obtained from petroleum. Based on their use, liquid fuels can be divided into two classes, viz.

1. Light oils or spirits, suitable for IC engines
2. Heavy oils, suitable mainly for burning in furnaces.

3.1 ORIGIN OF PETROLEUM

Many theories have been advanced for the origin of petroleum but none has been proved or agreed upon universally. The theory of vegetable origin is most widely accepted today. It holds that petroleum was formed from enormous quantities of animal and vegetable debris accumulated in sea basins and estuaries, and buried there by sand and silt. This debris, when subjected to anaerobic bacterial action under reducing condition, gets decomposed. The partially decomposed debris, when subjected to high pressure and temperature due to the depth and movement of earth, distills as a black viscous product known as crude oil. The approximate composition of petroleum is: carbon 80–89%, hydrogen 12–14%, nitrogen 0.3–1.0%, sulphur 0.3–3.0% and oxygen 2–3%.

3.2 CHEMISTRY OF PETROLEUM

The main components of petroleum are hydrocarbons, i.e., they contain only carbon and hydrogen. Carbon combines with hydrogen in various amounts to form a variety of compounds. Many types of hydrocarbons are found in petroleum, but most of them fall into five main classes: normal paraffins, iso-paraffins, olefins, naphthenes, and aromatics.

Normal Paraffins

Normal paraffins are given the suffix "ane", e.g., methane, ethane, propane, etc. The first letter indicates the number of carbon atoms present in a molecule. Their general formula is C_nH_{2n+2}. The term "normal" derives from the non-branched nature of the carbon chain of molecule. Figure 3.1 shows the structure of *n*-butane and *n*-octane.

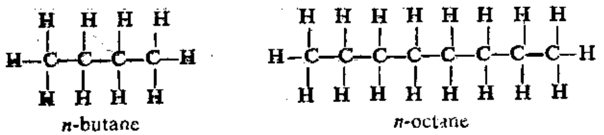


Fig. 3.1

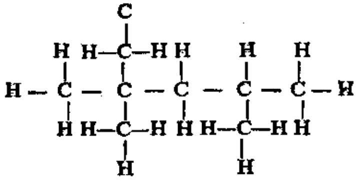
These compounds are usually quite stable and have a lower specific gravity. The compounds which have a lower molecular weight (methane, ethane, propane, and butane) are gases at room temperature and pressure. The medium molecular weight species are liquids (five to sixteen carbon atoms) while the heavier ones are solids. The properties of various hydrocarbons are given in Appendix Table A.6. These hydrocarbons are clean in burning, and are thus desirable in illuminating oils such as kerosene. The spontaneous ignition point of paraffinic hydrocarbons is fairly low.

Iso-paraffins

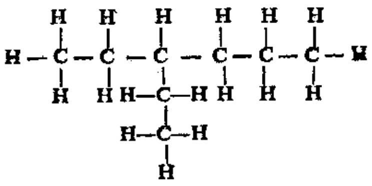
Iso-paraffins are isomers of normal paraffins. Their chemical formula remains the same as that of normal paraffins but the arrangement of atoms is modified. The isomers can have various arrangements. To specify any particular isomer a more precise nomenclature is required. The system of nomenclature can be explained by means of specific examples: 2,2,4-trimethylpentane and 3-ethylhexane. Their structures are shown in Fig. 3.2. To understand the nomenclature, we start from the end: pentane indicates five carbon atoms of a paraffin molecule, trimethyl indicates that there are three methyl groups attached to the main carbon chain, 2,2,4 gives the number of carbon atoms in the main chain to which the methyl group is attached. Similarly, 3-ethylhexane will have a structure as shown in Fig. 3.2. The physical properties of iso-paraffins resemble those of normal paraffins.

Olefins

Olefins are generally named with the suffix "ene", e.g., pentene, octene, etc. They have a straight carbon chain but with one or more carbon atoms doubly bonded together. Olefins are thus unsaturated hydrocarbons. The molecular structure of a monolefin and diolefin is shown in Fig. 3.3. The chemical formula for monolefin is C_nH_{2n} while for diolefin is C_nH_{2n-2}. The monolefin has one double bond while diolefin has two. The olefins are



2,2,4-trimethyl-pentane (iso-octane)



3-ethylhexane (iso-octane)

Fig. 3.2

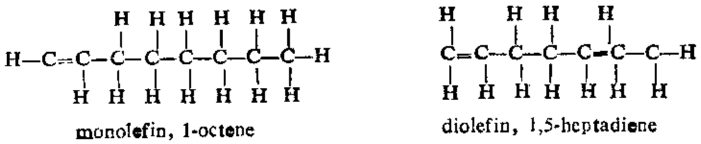
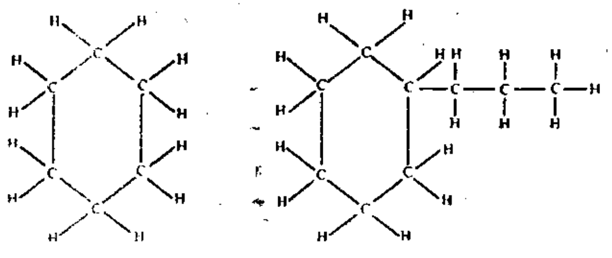


Fig. 3.3

usually distinguished by their characteristic odour. They are chemically active as compared to other hydrocarbons and have good burning characteristics because they get oxidized and polymerized easily. The thermodynamic properties of olefins are similar to normal paraffins. Their vapour pressure is slightly higher, while the specific heat and enthalpy are slightly lower. But their burning characteristics are quite different. The olefins are present in large quantities in cracked oils.

Naphthenes

Naphthenes are designated by the term "cyclo" in their name because of the carbon ring in the molecule. In the naphthene carbon ring, only a single carbon-carbon bond appears. They have the same general formula, C_nH_{2n} as for monolefins but they are saturated. The simplest naphthene is cyclopropane, C_3H_6. The molecular structure of cyclo-hexane and n-propylcyclo-hexane is shown in Fig. 3.4.



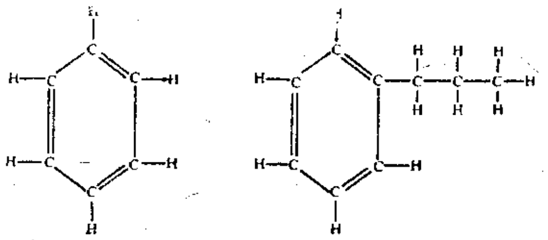
Cyclo-hexane *n*-propyl-cyclohexane

Fig. 3.4

These hydrocarbons are not found in large volumes in light oils, but are usually found in heavy oils. They have good burning characteristics.

Aromatics

Aromatics are those hydrocarbons which have a benzene ring in their molecular structure. The benzene ring consists of six carbon atoms in a ring, with alternate carbon atoms double bonded. This leaves each carbon atom with a single valence. An aromatic which has a single hydrogen atom in the benzene ring replaced by a normal alkyl (methyl, ethyl, etc.) group is called an alkylbenzene compound, e.g., *n*-propyl-benzene. The structure of benzene and *n*-propyl-benzene is shown in Fig. 3.5.



Benzene *n*-propyl-benzene

Fig. 3.5

The thermodynamic properties of aromatics are similar to those of naphthenes. Their burning characteristics in gasoline engines are excellent. But because aromatic compounds contain a higher proportion of carbon, they have a tendency to smoke. They are undesirable in kerosene and should be in a limited quantity in diesel oil. Aromatics have a higher specific gravity, are very stable under heat, and are chemically active to a moderate degree.

3.3 REFINING OF PETROLEUM

Crude oil contains a variety of hydrocarbons ranging from the simplest hydrocarbon methane gas to the most complex hydrocarbons such as paraffin wax and bitumen. It contains gases dissolved under pressure, solids as suspended particles and also in a dissolved state.

Crude oils are of three main classes named according to the type of hydrocarbon which predominates the oil: if the aliphatic groups are greater than 75%, the crude oil is called paraffinic; if the naphthenic rings are greater than 70%, the crude oil is called naphthenic, and if the aromatic rings are greater than 60%, the crude oil is called asphaltic. But most crude oils are of a mixed type.

The crude oil which comes from wells contains impurities of water, inorganic solids like sand, and gases such as methane, ethane, etc. These gases are partially removed in storage tanks. The crude oil is first passed through a centrifugal separator which removes most of the water, solid impurities, and wet gases. The crude oil is then sent for distillation. The modern refining processes include distillation, cracking, polymerization, etc. The main aim is to economically obtain the maximum quantity of gasoline along with the desired properties of various products.

Fractional Distillation

Distillation is a process of separation on a molecular basis or, we can say, on the basis of the boiling point of various fractions. The crude oil is first heated to a temperature of about 300 to 350°C in a tube heater which evaporates most of the crude oil. These vapours are then condensed in a tall cylindrical tower, approximately 1.5 to 2 m in diameter and 25 to 30 m high. This tower is known as the fractionating column. The oil pressure in the heater is kept around 3 kg/cm^2. This pressure reduces undue volatilization. The hot crude oil enters the fractionating column as a mist or spray at its lower end. The column is kept at nearly atmospheric pressure. Most of the crude oil, therefore, gets vapourized and rises up. During its ascent it cools down. A number of bubble caps are fitted inside the column. The heavier fractions which have the highest boiling points get liquefied first, while the remaining fractions rise and condense in order of their boiling points. Various fractions are taken out at an approximate temperature difference of 50°C. The uncondensed gases leave the tower from the top, and are sent for absorption. The various fractions taken out are shown in Fig. 3.6. Table 3.1 gives the yield and boiling range of a typical crude oil in primary or straight run distillation.

Sometimes, these primary fractions can be used as they are but they usually have to be treated further for improvement in desired properties and for increased production of gasoline. The other important refining methods are as follows.

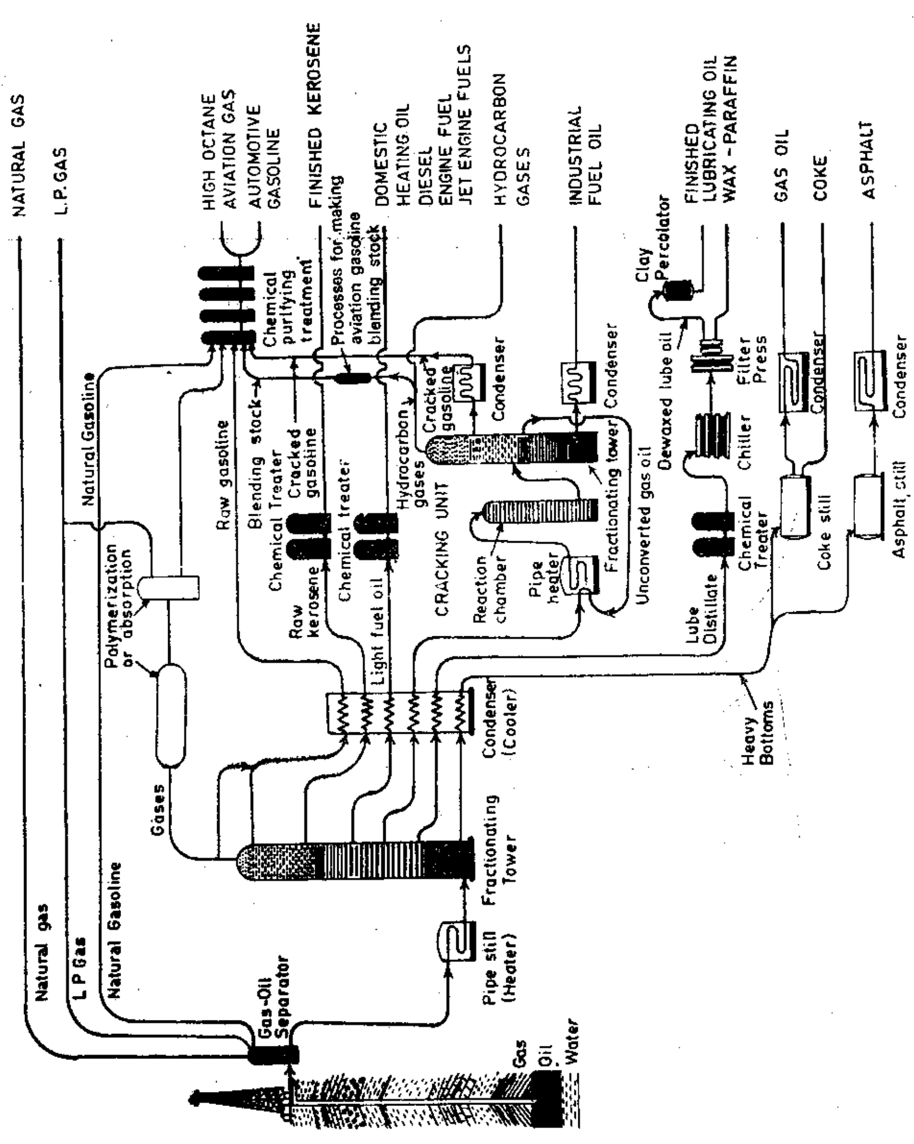


Fig. 3.6—Schematic diagram of petroleum refinery (After *American Petroleum Institute*).

TABLE 3.1—Yield and Boiling Range of Petroleum Fractions

Distillate	*Boiling range,* °C	*Yield,* %
Light Gasoline including gases	—	8
Heavy Gasoline	30 -65	12
Naphtha	65–250	5
Kerosene	150–250	15
Gas oil (Diesel oil, Fuel oil, No. 2 Fuel oil)	150–400	5
Residue (Nos.5 and 6 Fuel oil)	320–540	55

Cracking

Cracking means the breaking of heavy molecules into lighter hydrocarbons. In this process, a straight run residue is heated to a temperature of about 500°C. At this elevated temperature, heavy oils decompose to give lower hydrocarbons which have a low boiling range and a heavy residue of coke. The cracking process is of two types: thermal and catalytic. In thermal cracking, the residue of straight run distillation is first heated and compressed to a pressure of about 70 kg/cm^2 and is then sent to a reaction chamber where its temperature is increased to about 540°C. The cracked products are sent to a fractionating column similar to the primary column. The catalytic cracking process can be carried out at a lower temperature and pressure in the presence of a catalyst, thus giving an extra yield of gasoline. The catalysts used are aluminium silicate, sulphuric acid, hydrofluoric acid, anhydrous aluminium chloride, etc. Solid catalyst may be mixed with liquid crude, or kept in a reaction chamber in the form of pellets or balls. Catalytic cracking may be done in series of thermal cracking using the residue oil of thermally cracked oil. The products obtained by thermal cracking are gasoline, No. 2 oil, and Nos. 5 and 6 fuel oils, while catalytic cracking gives gasoline, No. 2 oil, and slurry oil. This slurry oil is generally blended into No. 6 fuel oil.

Vacuum Distillation Process

The residue of straight run processes can be refined to yield more gasoline by vacuum distillation. The difference is that the reaction occurs in vacuum instead of at high pressure. Due to the high temperature and low pressure, heavy distillates are squeezed out of the residue. The remaining residue is called vacuum bottoms. The distillate is usually subjected to the catalytic cracking process. These vacuum bottoms can be used as charge for the visbreaking process or to make asphalt or blended to make No. 6 oil.

Visbreaking

This process is similar to thermal cracking except that the pressure and temperature used are lower. The purpose of this process is to obtain large volumes of distillate for catalytic cracking from vacuum bottoms. The products are gasoline and heavy oil, while the residue is mixed with vacuum bottoms to give No. 6 fuel oil.

Reforming Process

The purpose of the reforming process is to change the chemical nature of various hydrocarbons to give the desired physical properties. These include thermal and catalytic reforming. The main difference between the refining and reforming processes is that the former is carried out on crude, residue, or heavy oils, while the latter is done on gasoline.

Thermal Reforming

Thermal reforming is similar to thermal cracking. The straight run gasoline is subjected to a temperature of 500-600°C and a pressure of around 80 kg/cm². The purpose is to produce *n*-paraffins of lower molecular weight, and the synthesis of desired iso-paraffins and aromatic species. As the components of straight run gasoline are already of a lower molecular weight they require a higher temperature and longer time for reforming. The extent of reforming is controlled by quenching the hot vapours with cold oil called *quenching oil*. These quenched vapours are then passed in to a fractionating column to remove residual gases from the reformed gasoline.

Catalytic Reforming

The present requirement of gasoline is an octane number around 100. The most attractive method of achieving this objective is catalytic reforming. There are many versions of this process, but the dominant reaction is the dehydrogenation of naphthenes with the production of aromatic hydrocarbons. Thus benzene is produced from cyclohexane and toluene from methyl-cyclohexane. These reactions provide an excess of hydrogen. Other reactions include the hydrogenation (saturation) of olefins, the isomerization of paraffins, and desulphurization. The hydrogen produced in the dehydrogenation of naphthene, combines with sulphur to give hydrogen sulphide which can be later removed from the system. Benzene, toluene, and xylenes are sometimes separated for use as high grade aviation gasoline. Usually the feed is naphthas of boiling range 90 to 200°C mixed with cracked gasoline or naphtha. The temperature is kept around 480 to 540°C and pressure varies from 14 to 21 kg/cm². The catalyst used often contains 0.75% by weight of platinum. It contains 8 to 10% of molybdena on an alumina support. Small amounts of chlorine and fluorine compounds may also be added.

Plat-forming

This is a typical fixed bed reforming process with platinum as a catalyst. The catalyst used is not regenerated but it gets poisoned. Several reactors are used in series operating at temperatures varying from 455°C initially to 527°C finally and pressures of 35 to 50 kg/cm². The main reactions are aromatization hydrocracking. Aromatization is endothermic and takes place in the first reactor. Hydrogen is supplied to the first reactor. Hydrocracking is exothermic and takes place in the latter reactors. Water and oxygen are removed in the preheater in the beginning. The excess hydrogen and hydrogen sulphide are removed by scrubbing with mono- and diethanolamines.

3.4 OTHER CONVERSION PROCESSES

Some other conversion processes are employed in crude oil refining for converting lighter gases to gasoline. These include polymerization, alkylation, and isomerization.

Polymerization

Light gases resulting from fractional distillation and cracking can be polymerized to give heavier hydrocarbons, thus increasing the yield of gasoline from the escaping gases. Polymerization is the reverse of cracking. Ethylene, propylene, butylene, etc. are quite reactive and can easily be polymerized in the presence of a catalyst at higher temperatures and pressures to give liquid hydrocarbons, e.g., C_6H_{12}, C_8H_{14}, C_7H_{14}, etc. The catalysts used commonly are phosphoric acid and sulphuric acid. The temperature varies between 190 to 230°C and pressure is of the order of 85 kg/cm².

Alkylation

This is a process for combining two molecules, one of iso-paraffin with that of an olefin to produce a branch chained iso-paraffin. The catalyst generally used is either 98% sulphuric acid or hydrofluoric acid. With sulphuric acid the temperature is kept at 5-7°C while with hydrofluoric acid the reaction temperature is kept at 25-45°C. The reaction time is 20 to 30 min. Hydrofluoric acid is preferred as chilling is costlier than heating in a refinery. The process is used for increasing the yield of gasoline by using light gases to form heavier liquid paraffins.

Isomerization

In gasoline, certain types of hydrocarbons are preferred, e.g., aromatic(ring) or iso-paraffin (branch chained) are preferred to long chained *n*-paraffins. The process of changing one type of molecule to another type with the same molecular weight is known as isomerization. It is usually carried out in the presence of a catalyst: Aluminium chloride ($AlCl_3$) activated by anhydrous hydrochloric acid. The temperature and pressure suitable for such reactions are 110°C and 21 kg/cm² for butane isomerization. For isomerization of heavier paraffins, higher pressures and temperatures are required.

Absorption Process

Gases leaving the oil well and fractionating columns invariably contain heavier hydrocarbons in the vapour state. These can be recovered either by chilling the gases, which is costly, or by absorption in either kerosene or light oil. Kerosene and light oil absorb only the heavier vapours, while the lighter hydrocarbon gases are not absorbed. These heavier vapours can be recovered by heating the absorber in a steam stripper.

3.5 PROPERTIES AND TESTS FOR PETROLEUM PRODUCTS

Various tests are carried out to determine the properties of any petroleum fraction. This helps in choosing a particular fraction for specific use and also or blending the various fractions to obtain a mixture of desired properties.

Gravity

In general, the specific gravity of any substance is defined as the ratio of density of that substance to that of water at the same temperature. The temperature usually specified is 15°C. However, the term gravity, as used in the oil industry, does not mean the specific gravity. The oil industry employs the API gravity scale, devised by the American Petroleum Institute and the National Bureau of Standards. It is expressed in degrees API.

$$\text{Deg. API gravity} = \frac{141.5}{\text{Specific gravity at } 15.5^\circ\text{C } (60^\circ\text{F})} - 131.5$$

The gravity of an oil is found by using a standard hydrometer, taking care that either the test is carried out at 15.5°C or the necessary correction is made to convert the gravity to that at standard temperature. To determine the specific gravity the most accurate method is to weigh a known volume in a specific gravity bottle at 15.5°C. The specific gravity or gravity of any oil can give the indication of its viscosity, carbon residue, heat of combustion, grade of oil, and the percentage of carbon and hydrogen present in the oil.

Viscosity

The viscosity of an oil is the measure of its resistance to flow. The standard measuring instruments are: the Redwood viscometer, and the Saybolt viscosimeter, of both the universal and Furol types. The principle of all these instruments is the same. A certain quantity of oil is allowed to flow through a standardized orifice tube placed at the bottom of a cup and the time required is noted down in seconds. During the test the temperature is kept constant

at 25°C, 38°C, or 99°C. The viscosity is expressed as viscosity in SSF, SSU, or Redwood viscosity at, say, 38°C.

Nowadays, the kinematic viscosity of oil is specified. The U-tube kinematic viscosimeter allows an accurately reproducible volume of liquid to pass through a capillary at a constant temperature by the application of an accurately reproducible force. The time taken for a liquid to flow is proportional to the ratio of the dynamic viscosity to the density of the fluid, i.e., to its kinematic viscosity. It is expressed in units, centistokes. The kinematic viscosity of a fluid of viscosity greater than 10 centistokes is given by the expression:

$$\nu = Ct$$

where ν is the kinematic viscosity

C is the viscosimeter constant

t is the time of flow in seconds.

For fluids which have a viscosity less than 10 centistokes, the expression is:

$$\nu = Ct - \frac{B}{t}$$

where B is the coefficient of kinetic energy, which may be determined experimentally, or eliminated by choosing long flow times. The viscosity of one scale can be converted to another by using conversion tables.

Flash Point and Fire Point

As fuel oils are heated, vapours are produced which at a certain temperature "flash" when ignited by an external flame. This temperature is called the flash point of the oil. If heating is continued, sufficient vapours are finally driven off to produce continuous burning and not just a single flash. This temperature is called the fire point.

Two different types of instruments are used to test flash and fire points: the Pensky-Martens or closed cup flash tester and the Cleveland or open cup tester. The Abel close cup test is also used. The flash points of kerosene and fuel oils are determined by a closed cup type of apparatus containing still air above the oil (a condition similar to the one, in the storage tank).

To determine the flash or fire point, the oil is placed in the cup. The temperature of oil is raised at a standard slow rate of about 5 to 6°C/min. The Pilot flame is dipped for two seconds at regular intervals of temperature.

Calorific Value

The bomb calorimeter is used for determining the calorific value of oil. The apparatus and procedure is the same as the one used for the determination of the calorific value of coal.

Reid Vapour Pressure

This is a measure of the vapour pressure of an oil at 38°C expressed in kg cm^2 or in millimeters of mercury. The vapour pressure is a measure of the tendency of gasoline to "vapour lock" or generate vapour bubbles in the oil line.

In this test a sample of oil at 38°C is permitted to vapourize into a chamber of air saturated with water vapour. The volume of the chamber is four times the volume of the bomb containing the oil. The pressure in the air chamber, corrected for initial chamber air temperature, gives the Reid vapour pressure.

Cloud and Pour Points

The temperature at which an oil will just flow under standardized conditions is known as the pour point. The oil will not flow satisfactorily at temperatures below its pour point.

To conduct the test, a sample of the oil is placed in a small bottle or a jar fitted with a thermometer at the top. The sample is first heated and then cooled in a standard manner. Finally, it is kept in a refrigerator or in a cooling medium and the temperature and fluidity of the sample is observed at temperature intervals of 3°C. So long as the oil is fluid it returns to the cooling bath until it becomes solid. The pour point is set at 3°C above the temperature at which the oil becomes solid.

The cloud point is the temperature at which haze or a cloud first appears in a sample of oil, when cooled in a prescribed manner. The oil sample is first dehydrated and filtered at a temperature greater than 25°C above the anticipated cloud point. It is then placed in a test tube and cooled progressively. The sample is inspected for cloudiness at temperature intervals of 1°C. The cloud point indicates the temperature at which wax or the other compounds begin to solidify, which can result in a blocked filter or iol line.

Aniline Point and Diesel Index

This is an approximate measure of the aromatic content of a mixture of hydrocarbons. It is defined as the lowest temperature at which an oil is completely miscible with an equal volume of aniline. Since aromatics dissolve aniline more readily than paraffins or iso-paraffins, the lower the aniline point, the higher the proporton of aromatics in the oil. The cetane number of any oil is dependent on the aromatic content of the oil. The aniline point therefore, can be used to indicate the probable behaviour of an oil in a diesel engine.

The diesel index is an expression developed to correlate the aniline point and API gravity with the cetane number:

$$\text{Diesel index} = \frac{GA}{100}$$

where, G is the API gravity of an oil
A is the aniline point of the oil.

Gum in Motor Fuel and Oxygen Stability

Usually the unsaturated hydrocarbons containing more than one double-bond are chemically unstable. They react either with air or with each other to form a rubber like substance called gum. This gum can precipitate in the fuel feed system and in engines to cause difficulties.

Two classifications of gum are recognized: preformed or existent gum, and potential gum or gum stability. The former represents the gum content at the time of the test and the latter is an approximate measure of the tendency to form gum during storage.

For existent gum, 50 ml of sample is evaporated in a glass dish of specified size on a steam bath for one hour, or until the evaporation is complete, while heated air from a small jet impinges on the surface. The dish is transferred to a drying oven for one hour, and weighed after cooling. The weight in mg/100ml is reported as existent gum.

To measure the oxygen stability, 50 ml of the gasoline is placed in a glass dish inside a steel bomb, filled with oxygen at 7 kg/cm^2. The bomb assembly is placed in a boiling water bath and connected to a sensitive pressure/time recorder. The time interval, between placing the bomb in the water bath and recording a drop of 0.14 kg/cm^2 (2 lb/in.^{2}) from the maximum pressure, is recorded in minutes as the induction period, i.e., the oxygen stability is recorded in minutes. The oxygen stability is sometimes also expressed as the gum formed during some fixed time, say 16 hours, in mg/100 ml under standard test conditions.

Sulphur

Sulphur, in one form or another, is always present in crude oil and its products, though it is one of the most undesirable of the elements. The most important trouble due to sulphur is the corrosion by its combustion products. It is also harmful in glass and ceramic industries, as it causes discoloration and pitting of the products.

Sulphur is determined by various methods, viz., the oxygen bomb method, lamp method, iodate titration method, and the sodium peroxide fusion bomb method. The copper strip method is also used.

The apparatus for the oxygen bomb method is the same as the one used for the determination of calorific value. The contents of the bomb after ignition are washed with distilled water into a beaker. Hydrochloric acid is added to the boiling solution to precipitate the sulphuric acid as barium sulphate. After cooling and allowing it to stand for 24 hrs, the precipitate is filtered off, washed, dried, and weighed. The weight of sulphur can be calculated from the weight of barium sulphate.

The iodate titration method is quite rapid and takes only about 5 to 10 minutes for completion. The sample is burned with excess oxygen and the gaseous products are passed through hydrochloric acid solution, where sulphurdioxide is absorbed. The solution is then titrated using potassium iodate as the indicator.

The copper strip test, generally used for light distillates, detects the presence of corrosive chemical compounds, but does not indicate the amount. In this method, a piece of mechanically cleaned pure standard size strip of copper is completely immersed in 40 ml of the sample. The sample is then heated in a boiling water bath for three hours. The copper strip is then compared visually with standard reference strips, rated from Nos. 1 to 4, with their colours ranging from light orange to jet black.

Water and Sediments

Water and sediments are usually present in heavier oils and can cause a number of difficulties. The water and sediments are referred as bottom sediment and water, and abbreviated as BSW. There are three different methods for testing BSW. The first is the test by centrifuge. This test is conducted by mixing the oil with benzol in a glass tube which is then whirled in a centrifuge. The water and sediments settle at the bottom. The tube is usually calibrated to give a direct reading.

The volume of water is best determined by the distillation test. 100 ml of oil is placed in a flask with 25 ml of dry toluene. The flask is heated gently until 25 ml of toluene has distilled into a graduated tube. The water distilled with the toluene separates to the bottom of the tube. Its volume is recorded in ml, or the weight in mg or percent.

The sediments are measured by the solvent extraction method. The test is conducted by placing 10 g of oil sample into a porous fused alumina crucible of known weight. The crucible is suspended inside a flask containing 100 ml of benzene at the bottom. The top of the flask is covered by a small, coiled, water cooled condenser. The flask is heated until the condensed benzene vapour, dripping from the condenser to the crucible, dissolves all the oil. The crucible is then dried, reweighed, and the increase in weight recorded in percent or in mg sediment/100 ml oil.

Carbon Residue

When a sample of oil is burned in the absence of air, the oil may leave some carbonaceous residue. This is known as "carbon residue" or carbon content of an oil. It should not be confused with the fixed carbon of the chemical compounds and the free carbon which may be present in oil, the carbon formed on burner tips, walls of furnaces, or the combustion chamber due to incomplete combustion. The carbon residue is usually tested by either the Conradson carbon test or the Ramsbottom carbon test.

In the Conradson test, a known weight of oil, say 10 g, is placed inside a porcelain crucible which is again placed inside two iron crucibles, and heated by the Maker gas burner. In the absence of air, the heating expels all the volatile material, leaving behind only the carbon residue. After cooling, the porcelain crucible is reweighed and the result recorded as per cent weight "Conradson carbon".

In the Ramsbottom test, a known weight of oil is heated in a hemispherical glass bulb of standard dimensions by a bath of molten solder at 550°C for 20 minutes. The residue carbon is weighed and recorded as percent weight "Ramsbottom coke".

Ash Content

Ash is the percentage by weight of an inorganic residue obtained by combustion of an oil in the presence of air. Mostly, it consists of inorganic impurities and salts present in the oil.

To determine the ash content, 20 g of oil is placed in a clean, dry, weighed silica dish. This is placed inside a cold electric muffle furnace. The temperature is raised slowly until the oil burns. A flame is then applied to the surface. When the combustion is complete, the temperature is raised to 800°C and kept for one hour. The crucible and ash are then cooled, reweighed, and the weight of ash obtained by the difference.

Colour

Colour and colour changes of an oil are important for the control of quality of refinery products. Colour itself is of no importance but a change indicates some deviation from the regular process. The Saybolt Chromometer or the ASTM Union Colorimeter is used to determine the colour of petroleum products. The procedure is to match the sample with standard colour discs.

Distillation

The distillation of oil is carried out in a standard distillation flask of 250 ml capacity attached to a water cooled condenser. A thermometer is fixep at the top and 100 ml of oil is poured in the flask and heated by a small gas flame. The initial boiling point (ibp), the end point (ep), and as many intermediate temperatures as desired may be recorded. However, the 10, 50, and 90 per cent point are of greatest significance. Ten per cent point means the temperature at which 10% of the oil by volume will evaporate. A boiling point curve can also be obtained indicating the percent of oil evaporated at a particular temperature.

Knock Characteristics of Motor Fuels

In spark ignition engines, spontaneous ignition before the spark passes generates ultra high velocity pressure waves giving rise to "knock". The phenomenon is apparent as a sharp metallic hammering from the engine cylinder. The Co-operative Fuel Research (CFR) engine is used to determine the octane number. Pure normal heptane is arbitrarily assigned an octane number of zero, and pure 2,2,4-trimethyl-pentane (iso-octane) is assigned an octane number of 100. The percentage of standard iso-octane by volume with *n*-heptane in the matching blend is designated as the octane number. Fuels with a higher octane rating are preferred. If the octane number of a fuel is greater than 100, it is referred to as the "performance number". To test the fuel, various blends of *n*-heptane and iso-octane are used in a CFR engine and their knock characteristic is matched with that of the fuel under test.

In compression ignition engines, when fuels with long delay times or high spontaneous ignition temperatures are injected, a violent combustion with sudden increase in pressure results causing what is called the "diesel knock". This characteristic is measured in terms of the "cetane number" of the fuel. The cetane number of a diesel oil is the percentage by volume of cetane in a cetane, α-methyl naphthalene mixture that has the same performance in a standard compression ignition engine as that of the fuel under test. Pure cetane is assigned a cetane number of 100 and α-methyl naphthalene is given a rating of zero.

3.6 VARIOUS PETROLEUM PRODUCTS

Motor Gasoline

Motor gasoline is an ideal fuel for spark ignition engines. The main advantage of a gasoline engine is its light weight per B.H.P. developed. This makes it most suitable for automotive vehicles.

The desired properties of fuel for otto-cycle engines are low boiling point and high octane rating. The temperature at which the first 10% of gasoline evaporates is a measure of the ease of starting. The normal boiling range of motor gasoline is 30°C to 300°C. At 70°C, a minimum of 10% gasoline by volume should evaporate. It is necessary to have a low boiling point of gasoline because the vapour burns easily and more efficiently than liquid droplets. But on the other hand, for low boiling point fuel, storage, transportation, and supply are difficult. If the vapour pressure of the fuel is high, there will be a tendency for the fuel line to get vapour-locked. The loss of fuel is more due to the breathing of the storage tank which increases the danger of fire.

The second most important desirable property is high octane rating. With a higher compression ratio the efficiency of the otto-cycle increases, but the higher compression ratio results in knocking. Octane rating can be increased by increasing the concentration of highly branched iso-paraffin, olefin, and aromatic hydrocarbons. It can also be increased by adding certain compounds such as tetra ethyl lead (TEL).

The other desirable property is the low freezing point, although this is not specified. Benzene in petrol freezes at 5.5°C and *m*-xylene at −25°C. Remaining components freeze at temperatures below −25°C. The gasoline should not contain a large amount of impurities such as gum, carbon, sulphur, water, sediment, etc. The presence of gum causes valve sticking and heavy intake manifold deposits. Sulphur forms acidic compounds in the engine and exhaust. Sulphur also inhibits the action of tetra ethyl lead. Table A.7 gives the requirements of 83 and 93 octane rating gasolines. As the gasoline engines are spark ignition engines, they demand some very exacting specifications.

Aviation Gasoline

The desired properties of aviation gasoline are slightly different than for motor gasoline. Various grades of aviation gasolines are available. Table A.8 gives the requirements for various grades of aviation gasolines. The grade number indicates its octane number or performance number. The aviation gasoline requires a lower boiling range, of the order of 30°C to 150°C, or sometimes as low as 30 to 75°C. The freezing point of aviation gasoline should be less than −60°C, as aeroplanes operate at high altitudes where temperatures are fairly low. Crystal formation at low pressures may cause trouble in the feed line and filters. Similarly, the limits for sulphur, gum formation, etc., for aviation gasoline are also lower as compared to motor gasoline.

Aviation Turbine Fuels

The requirements of jet fuels are less exacting than those for gasolines. Kerosene, gasoline, and the lighter gas oils have all been used as fuel for jet engines and gas turbines.

In gas turbines or jet engines, the fuel is injected into the hot compressed air where it is ignited and burned. Cold secondary air is admitted to keep the turbine blade temperature below 910°C. For the aviation turbine, a high heating value fuel with less weight is required. Its octane rating or volatility need not be high, it is essential that it has a low freezing point. It should leave less deposit, and should be safe and clean in storage and burning. Although high volatile fuels are better for easy starting, they can create a vapour-lock in the fuel supply line. The breathing loss is also high. On these counts, kerosene or a near related fuel is found to be most suitable. Table A.9 gives the requirements for aviation turbine fuels of the kerosene type. Three grades of fuel oil requirements are given for different types of combustion chambers. In jet fuel, paraffins and naphthenes are preferred as compared to olefins and aromatics. Olefins are unsuitable because of their high chemical activity and gum forming tendencies. Aromatics are good solvents for plastics and cause smoke and carbon deposit. Aromatics are restricted to a maximum of 25% in aviation turbine fuels. Table A.10 gives the requirements for aviation turbine fuels of the high flash point type.

Kerosene

Kerosene oil is extensively used for lighting and heating. Its boiling range is 150 to 300°C. It mainly consists of paraffins. Its viscosity should be less than 2.5 centistokes for easy flow of fuel through capillaries or the wick. Another important desirable property is the smoke point. The smoke point is the height to which the flame may be raised before the smoke starts, when kerosene is burned in a standard lamp under controlled conditions. Similarly, its char value should be less than 30 mg per kg of kerosene. The char is the deposit on the upper edge of the wick. The flash point, sulphur content, etc. are a few of the other properties to be controlled. Table A.11 gives the requirements for kerosene.

Diesel Fuels

Diesel fuels are used in compression ignition engines. The normal boiling range for the diesel fuel is 200 to 370°C. High speed diesel may use oils with initial boiling point as low as 140°C. The 50% distillation point should not exceed 300°C. The chief requirements for diesel fuels are high cetane number, freedom from impurities, and a fairly high flash point. With good diesel fuel, the delay time is short.

The spontaneous ignition temperature of *n*-paraffins is much lower than that of aromatics or olefins. Therefore, straight chain hydrocarbons are preferred to branched chain hydrocarbons or aromatics. All types of light fuel oils with low octane numbers can be satisfactorily used as high speed diesel fuels whereas high octane fuel oils are unsatisfactory. A good motor gasoline will make a poor diesel engine fuel and vice versa. Requirements for high speed diesel oil are more exacting than that for light diesel oil. Table A.12 gives the requirements for high speed diesel and light diesel oil fuels. Slow speed diesel engines can use a wide variety of oils while high speed engines require limited variation in properties.

Fuel Oils

There are many types of oils produced by the refining of petroleum. We can use a different oil for a different furnace. Normally, in any combustion furnace or burner only one type of fuel can burn efficiently. If we change the fuel, either the combustion will become difficult or it will produce less heat. The ASTM has standardized five grades of fuel oil for easy selection of fuel. These are designated as Nos. 1, 2, 4, 5 and 6 oils.

Nos. 1 and 2 oils are distillate oils with a boiling range of 150 to 350°C at atmospheric pressure. No. 1 oil is slightly heavier than kerosene and is used for domestic heating. But these days both No. 1 oil and kerosene are put in the same class. The No.2 oil distillate follows No. 1 in straight run refining. This is usually called gas oil. There is no such thing as a No. 3 oil. No. 4 oil is a variable and complex oil. Nos. 5 and 6 oils are heavy black residuals

obtained from various refining processes. The requirements of various grades of fuel oils are given in Table 3.2. The Indian Standards Institution has classified the oils as low viscosity, medium viscosity, and high viscosity oils. Their specifications are given in Table A.13. An analysis of various fuel oils of the same grade shows wide variation. This is due to the difference of source and the type of oil. Nevertheless, their properties lie within a certain range. Sometimes the properties of some samples do not meet all the requirements of the given grade.

TABLE 3.2 Detailed Requirements for Fuel Oils

	Grades of Fuel Oil					
Properties	*No.1*	*No.2*	*No. 4*	*No. 5 light*	*No. 5 heavy*	*No.6*
Flash point, °C, min	38 or legal	38 or legal	55 or legal	55 or legal	55 or legal	65
Pour point, °C,max	−17.8	−7^{c}	−7	—	—	—
Water and sediment, % by volume, Max	max trace	0.10	0.50	1.00	1.00	2.00^{g}
Carbon residue on 10% Bottoms % max	0.15	0.35	—	—	—	—
Ash % by weight, max	—	—	0.1	0.10	0.10	—
Distillation temperature, °C, 10% max	215	d	—	—	—	—
90 % point, min	—	282	—	—	—	—
max	288	338	—	—	—	—
Kinematic viscosity, C.S. At 38° C, min	1.4	2.0^{e}	(5.8)	(32)	(75)	—
max	2.2	3.6	(26.4)	(65)	(162)	—
At 50°C, min	—	—	—	—	(42)	(92)
max	—	—	—	—	(81)	(638)
Gravity, deg. API, min	35	30	—	—	—	—
Copper strip corrosion, max	No.3	—	—	—	—	—
Sulphur, % max^{a}	0.5	0.7	no limit	no limit	no limit	no limit

With permission of American Society for Testing and Materials, from *ASTM* D 396-67.

(a) **Recognizing the necessity for low sulphur fuel oils used in connection with heat** treatment, non-ferrous metal, glass, ceramic furnace, and other special uses, a sulphur requirement may be specified as given. Other sulphur limits may be specified only by mutual agreement between the purchaser and the seller.

(b) It is the intent of these classifications that failure to meet any requirement of a given grade does not automatically place an oil in the next lower grade unless in fact it meets all requirements of the lower grade.

(c) The lower or higher pour points may be specified whenever required by the condition of storage or use.

(d) The 10% distillation temperature point may be specified at 226°C max for use in other than atomizing burners

(Contd.)

(e) When a pour point less than −17.8°C (0°F) is specified, the minimum viscosity shall be 1.8 C.S. and the minimum 90% Point shall be waived.

(f) Viscosity values in parentheses are for information only and not necessarily limiting.

(g) The amount of water by distillation plus the sediment by extraction shall not exceed 2.00%. The amount of sediment by extraction shall not exceed 0.5%. A deduction in quantity shall be made for all water and sediment in excess of 1%.

Oil Shales

Oil shales are similar to sedimentary rocks containing crude oil known as kerogen. Large deposits of oil shales are found around the world. It contains oils from 30 to 725 litres per tonne. The total reserves in the USA alone can yield 48 $\times 10^{12}$ litres of oil. The production of oil from shale consists of mining and recovery of oil from shale. The shales are crushed, and its subsequent destructive distillation in retorts yields gas, crude shale oil, and ammonia. The residue in the retort is not a fuel and is used for the manufacture of bricks. In Sweden, oil is recovered from Shale *in situ* by heating the mines electrically and distilling the oil. Once the crude oil is produced, its refining and reforming processes are similar to those applied to crude petroleum. Because of the limited resources of petroleum, the future of the recovery of oil from shale is bright.

4

GASEOUS FUELS

Gaseous fuels have a number of advantages over solid or liquid fuels. They burn without any smoke and ash, their combustion is complete with a small percentage of excess air, and the control of gas flames is relatively easy. The disadvantage is the difficulty in storing large quantities of gaseous fuels as compared to liquid and solid fuels.

The gaseous fuels may be classified as: natural and manufactured gases. The natural gases are generally associated with petroleum and coal deposits. Sometimes, natural gas is found in abundance in gas wells. The manufactured gases are produced from wood, peat, coal, petroleum, oil, shale, etc. or they are produced as by-products. The combustible components of these gases are mostly methane, carbonmonoxide, and hydrogen in varying proportions. The characteristics of a particular type of gas will depend upon the percentage of the components present in the gas.

4.1 NATURAL GASES

Natural Gas from Petroleum Deposits

Most of the natural gas is found in oil wells and gas fields. It consists mainly of methane with small percentages of ethane, propane, butane, carbondioxide, nitrogen, and hydrogen sulphide. Natural gas is nearly odourless and colourless. If it contains a large percentage of sulphur, the sulphur is removed before using the gas; otherwise it is supplied after separating the oil from the gas containing C_3 and C_4 hydrocarbons, or it may be used in the natural state. The usual range of composition of the natural gas after removing water and oil is:

Methane	68–96%
Ethane	3–30%

The gross calorific value of the gas is 9000 to 11,000 kcal/m^3. The value is usually taken at 15°C and 76 cm Hg. The gas containing hydrocarbon vapours other than methane and ethane is named "wet gas". The wet gas is 'unstable'. Therefore, it is "rectified" or "stabilized", i.e., the wet components of the gas are removed by fractional distillation.

Natural Gas from Coal Mines

Methane is associated with many coal seams and is known as "fire damp". This gas is released slowly during coal mining. The quantity of gas may be as high as 85 m³/tonne for some high ranking coals. Usually this gas is expelled with the help of ventilators to avoid explosion during mining. But if the gas yield is sufficient, it can be recovered by drainage through a series of bore holes sited some 45 metres behind the coal face. The gas consists of mainly: 93 to 99% methane, upto 3% ethane, up to 4% carbondioxide, and nitrogen and inerts less than 6%.

4.2 MANUFACTURED GASES

The gases are mostly manufactured by the carbonization of solid fuels. Sometimes these gases are treated to increase their calorific value. Manufactured gases are usually used near the place of their manufacture while the natural gases may be supplied through pipelines to various consuming centres. Gaseous fuels are usually produced either by carbonization or by the gasification of coal.

Liquefied Petroleum Gas

During the refining of petroleum, large quantities of butane and propane are liberated from the top of the fractionating column and from other refining processes. These gases can be compressed and liquefied at atmospheric temperature. Butane and propane are also present in natural gas and can be separated and removed. Butane liquefies at 21.1°C (70°F) under a pressure of 2.1 kg/cm² (30 psi) while propane liquefies at 8.8 kg/cm² (125 psi). These liquefied fractions can be stored under pressure in steel cylinders. Thus large volumes of the gas can be stored in liquid form in small cylinders. It is an ideal fuel for domestic and mobile use. Propane is usually sold for industrial use because of its high liquefacation pressure. Liquefied petroleum gas or L.P. gas contains some fractions of methane and unsaturated hydrocarbons. The calorific value of LP gas is very high. It is 22,700 kcal/m³ for propane and 28,500 kcal/m³ for butane. Commercial liquid butane contains about 80% saturated and unsaturated C_4 hydrocarbons, less than 20% of C_3 and less than 2% of C_5 hydrocarbons. Commercial liquid propane contains less than 5% of C_2 and less than 10% of C_4 hydrocarbons, with the remaining saturated and unsaturated C_3 hydrocarbons. The total sulphur should be less than 0.02% and the gas should be free from H_2S and water vapour. Table A.14 gives the requirements for liquefied petroleum gas.

As the specific gravity of butane and propane are more than that of air, in case of leakage they have a tendency to settle down and form an explosive mixture with air. Therefore, these gases are mixed with any odouring agent so that the leakage may be immediately detected.

Refinery Oil Gas

During the refining of petroleum, various gases are evolved which cannot be converted to liquid gasoline. Such gases contain many light hydrocarbons with small percentages of hydrogen and carbonmonoxide. These gases are generally utilized in the refinery itself, as it is not economical to transport them.

Wood Gas

This is a by-product obtained from the carbonization of wood to form charcoal. It is usually not collected and is of little commercial interest. The typical yield composition and properties of wood gas are given in Table 4.1. The wood is either carbonized at a low temperature around 350°C or at a high temperature in the range of 1000 to 1200°C.

TABLE 4.1 Typical Yield and Composition of Wood Gas

	Low temperature carbonization	*High temperature carbonization*
Yield (m³/t), dry wood	125	550
Calorific value of gas (kcal/m³), gross	3125	3075
Composition, % by volume		
CO_2	30	20
C_nH_m	4	2
CO	25	25
CH_4	14	12
H_2	20	35
N_2	7	6

Peat Gas

Peat gas is similar in composition to low temperature carbonized wood gas. It is manufactured by the carbonization of air dried peat, and used for heating ovens.

Coal Gas (Town Gas)

High temperature carbonization of coal is one of the oldest methods used for the manufacture of gas for town supply. For this reason coal gas is also known as town gas. Carbonization of coal is usually done at a temperature between 950 to 1,350°C. The main product of high temperature carbonization is gas while coke is a secondary by-product. Coke produced by high temperature carbonization is unfit for metallurgical use. Coal gas is produced in horizontal, inclined, or vertical retorts which are continuously or intermittently fired. Usually, high volatile bituminous coal is used for the production of gas. The composition of the gas is controlled by the temperature and duration of coking. The coal gas calorific value should be approximately 4450 kcal/m³ and the maximum sulphur permitted is 0.46 gm/m³. If the coal gas produced has a calorific value higher than the one prescribed, it is reduced by passing steam which reduces the calorific value; but the amount of gas produced per ton of coal is increased. The typical analysis and properties of coal gas are given in Table 4.2.

Coke Oven Gas

The difference between coke oven gas and coal gas is that in coke oven gas, the carbonization temperature is lower and more closely controlled. The temperature is kept between 600 to 1000°C. In the case of coke oven practice, the primary aim is to get good quality coke; the gas is a by-product. The composition of coke oven gas is usually similar to coal gas, but steaming is never practiced in the coke oven process because of the danger to refractory walls and to maintain the quality of coke. The typical composition and properties of coke oven gas are given in Table 4.2.

Producer Gas

Coal gas, coke oven gas, peat gas, and wood gas are produced by carbonization, i.e., by the decomposition of solid fuel in the absence of air. Producer gas, water gas, and blast furnace gas are produced by the gasification of coal. Gasification refers to the process of partial combustion of the entire solid fuel in the presence of a limited amount of air or oxygen. This partial combustion of carbon yields carbonmonoxide which is a combustible gas.

The process of gasification can be best understood from Fig. 4.1 for the production of producer gas. In the gas producer, a mixture of air and steam is supplied from the bottom of a nearly 2 m thick coal bed. From the top, coal is supplied and gas is removed. In the first 15—20 cm height, oxidation of coal takes place at a temperature around 1200°C. The resultant carbondioxide reduces the middle layer of the coal when the temperature reduces to about 800°C because the reaction is endothermic. On the top 50 cm, steam reacts with carbonmonoxide and carbon to give carbondioxide and hydrogen. The temperature in this zone reduces further and the distillation of fresh coal takes place at about 400°C. As air contains large quantities of nitrogen, it appears in the producer gas, and consequently the calorific value of producer gas is low, being about 1150 to 1350 kcal/m³. The producer gas may be produced from coal or coke. The addition of steam increases the calorific value of the gas. Producer gas can be used either in hot or cold condition. If used in the hot condition, it gives sensible heat while in the cold

TABLE 4.2—Typical Analysis of Fuel Gases

S.No.	Name	Components, % by volume										Sp. gravity	kcal/m³ at 15.5°C and atm. 1 pressure	
		CO_2	O_2	N_2	CO	H_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}	Others		Gross	Net
1.	Natural gas	0.8	—	8.4	—	—	84.1	6.7	—	—	—	0.63	8650	7800
2.	Propane	—	—	—	—	—	—	2.2	97.3	0.5	—	1.55	22700	21000
3.	Butane	—	—	—	—	—	—	—	6.0	94.0	—	2.04	28500	26300
4.	Coal gas	1.7	0.8	8.1	7.3	49.5	29.2	—	—	—	3.4	0.42	4620	4150
5.	Coke oven gas	2.2	0.8	8.1	6.3	46.5	32.1	—	—	—	4.0	0.44	5050	4520
6.	Producer gas	4.5	0.6	50.9	27.0	14.0	3.0	—	—	—	—	0.86	1450	1360
7.	Blast furnace gas	11.5	—	60.0	27.5	1.0	—	—	—	—	—	1.02	820	820
8.	Blue water gas	5.5	0.9	27.6	28.2	32.5	4.6	—	—	—	0.7	0.7	2300	2125
9.	Carburetted water gas	6.0	0.9	12.4	26.8	32.2	13.5	—	—	—	8.2	0.66	4700	4000
10.	Bio-gas(sewage)	22.0	—	6.0	—	2.0	68.0	—	—	—	—	0.79	6150	5520

(After "Gaseous Fuels, *American Gas Association*, 1948.

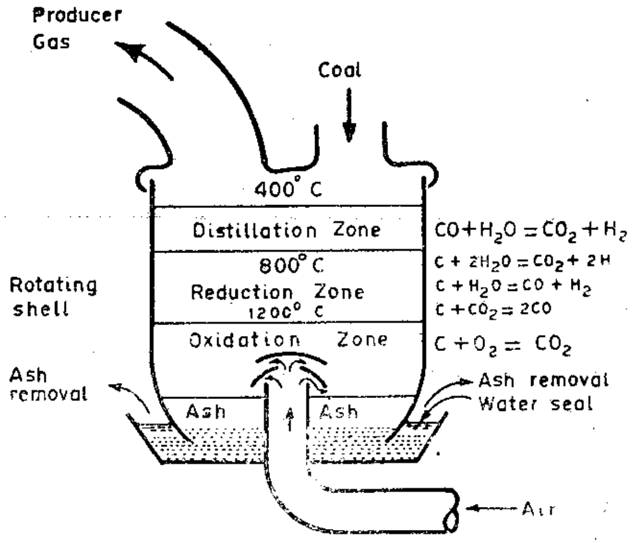


Fig. 4.1 Gas producer.

condition it can be used after cleaning. The yield of a typical producer gas plant using bituminous coal is 3450 m³/tonne of dry coal with gross calorific value at S.T.P. 1600 kcal/m³. Because of the low cost, producer gas is used in large scale for industrial furnaces. A typical composition of producer is shown in Table 4.2.

Blast Furnace Gas

Blast furnace gas is a low grade producer gas. It is produced in the blast furnace for the smelting of iron ore with coke as a by-product. In the blast furnace, coke reacts with air and ore to give carbondioxide which rises upwards and reacts with coke to give carbonmonoxide. The blast furance gas has a low calorific value in the range of 800 to 900 kcal/m³. It contains large quantities of dust. This dust is removed by dust catchers or cyclones. It can be further cleaned by water washing, bag filtering, or by electrical precipitation. The blast furnace produces about 4000 m³ of gas per tonne of coke produced. Because of its low calorific value, it cannot produce high temperature. It is used for operating gas engines, to heat by-product coke ovens, and in various other heating processes. Ninety per cent of its sensible heat can be used in the regenerative heat exchanger. Sometimes, it is enriched by coke oven gas or by creosote vapours to increase its calorific value to about 2250 kcal/m³.

Blue Water Gas (BWG)

Blue water gas or water gas is produced by passing steam on red hot coke. The resulting gas contains large quantities of carbonmonoxide and hydrogen. The reaction is highly endothermic. Therefore, to heat the coke, air is blasted. The purpose of passing air and steam at different intervals is to ensure that the large quantity of nitrogen does not reach the gas. The cycle of operation consists of the blow, purge, and make periods. In the blow period, air is blown for about one minute with the stack valve open. The rate of air blown is approximately 60 m³ per min per m² cross-section of the generator. The temperature attained is about 1450°C. During the purge period of approximately 10 to 20 s, steam is passed with the stack valve open which pushes the remaining nitrogen from the generator. During the make period of 2 to 3 min. steam is passed with the stack valve closed. During the first minute, steam is blown upwards, and then the direction of steam is reversed for the next minute to equalize the temperature. The temperature of coke during the endothermic reaction falls to about 1000°C, then for 10 to 20 s, the direction of steam is changed to remove the combustible gases in the ash pit. The gross calorific value of water gas produced is about 2250 to 2650 kcal/m³. The gas is called blue water gas because the combustion of carbonmonoxide gives a blue flame. About 45% of carbon in the fuel is used during the blow period.

This process gives an intermittent supply of gas. To produce water gas continuously with less wastage of heat, one method is to supply oxygen and steam together. Four types of continuous processes have been developed, viz., non-slagging generators operating at nearly atmospheric pressure, slagging generators operating at nearly atmospheric pressure, pressure gasification (Lurgi process), and gasification of fluidized coal.

Carburetted Water Gas (CWG)

Water gas has a low calorific value. In order to increase the calorific value, it is enriched by hydrocarbon gases. The resultant gas is known as carburetted water gas. Enrichment is usually done in a carburettor which is a heated fire brick chequer-work sprayed with suitable fuel oil. The fuel oil used is generally of a boiling range of 200 to 300°C which cracks at a temperature between 730 and 760°C. About a litre of fuel oil is consumed for the enrichment of 3m³ of water gas for raising its calorific value from 2550 to 4450 kcal/m³. Heating of chequer-work is achieved by blowing stack gases of blow period with some added air to complete the combustion of carbonmonoxide. The temperature of the carburettor is kept around 1000°C. Oil is sprayed during the make period which vapourizes the oil and the cracking is completed in the superheater maintained at a temperature between 650 to 750°C. About 75% of the oil is cracked. The carbon deposited during cracking is burned during the blow period. The gas is cleaned before use by passing through a washer, similar to the water seal, by which water vapour, tar, dust, and some sulphur compounds are removed.

Bio-Gas

This is a gas produced by the fermentation of animal or human waste. The fermentation takes place in an air free closed space. The gas produced consists of mostly methane, carbondioxide, and hydrogen. The typical composition of a bio-gas is:

$$60\%\ CH_4,\ 30\%\ CO_2 \text{ and } 10\%\ H_2.$$

The calorific value of the gas can be increased by absorbing carbondioxide. The fermentation of cow-dung takes place in about seven days but a continuous yield of gas can be obtained by adding fresh slurry of water and cattle waste daily in the plant. The most suitable temperature for fermentation is about 37°C. The fermentation can be catalyzed by adding certain type of bacteria. The gas obtained is odourless and gives a clean, blue, smokeless flame. Small domestic gas plants for a farmer with two or three cattle are becoming popular in India. Big sewage disposal plants are also working in some cities.

4.3 PROPERTIES AND TESTING OF FUEL GASES

The properties of fuel gases which are generally specified are their calorific value, specific gravity, and composition. Apart from these, sometimes their odour, inflammability limits, ignition temperature, maximum flame temperature, etc., are also reported. Here, however, we shall discuss only the three main propeties.

Specific Gravity or Density

The gas gravity or gas density is the density compared to that of dry air at the same temperature and pressure. To obtain its approximate value, the Schilling effusion apparatus is used. This apparatus is based upon the relationship between the molecular weight and rate of effusion or escape of the gas through a very small hole. The time required for a measured volume of air and the sample gas is measured. Then the gas gravity is calculated as:

$$\text{Gas gravity} = \frac{M_g}{M_a} = \left(\frac{t_g}{t_a}\right)^2$$

where M is the average molecular weight and t is the time of effusion. Subscript "a" stands for air and "g" for gas.

The pressure balance or gas balance is another technique for the accurate measurement of gas density. The apparatus consists of a beam balance with a sealed bulb and a counter weight on the beam. The bulb and beam are placed in a gas-tight casing fitted with a manometer. The casing is filled with

a gas under pressure. With a change in the gas pressure, the buoyancy force on the bulb changes. By adjusting the gas pressure in the casing, balance is obtained. The above procedure is repeated with air. The gas gravity is calculated using Boyle's and Charles' laws:

$$\text{Gas gravity} = \frac{\text{density of gas}}{\text{density of air}} = \left(\frac{P_g}{P_a}\right)\left(\frac{T_a}{T_g}\right)$$

where P_g and P_a are the pressures of the gas and air respectively expressed usually in the height of the mercury column (by adding manometer readings to the barometric reading). T_a and T_g are the temperatures expressed in deg. Kelvin.

The density of gas can also be measured by the direct weighing of two similar glass flasks, one filled with air and the other with gas at the same temperature and pressure on an accurate analytical balance.

Calorific Value

The heating value, also called the calorific value or the heat of combustion of a fuel gas, is generally determined at constant pressure by the Boys or Junkers gas calorimeter. Both calorimeters are similar in principle and working. In the apparatus, gas enters the pressure regulator, flows through a wet gas meter, and then into the burner. This burner is mounted in a water jacket. The gas is metered, burned and the heat absorbed by the water passing through the jacket. The water rate is experimentally determined and the air rate is estimated. The flue gases first rise up, then go downwards, and again upwards through the heat exchanger. The gross or higher heating value is measured because the flue gases generally leave at a temperature quite near the atmospheric temperature. The calorific value can be calculated by measuring the gas flow rate, water flow rate, rise in temperature of water air humidity, gas pressure, etc. The calorific value is generally expressed as gross or total in kcal per cubic metre of the gas, measured at 15.5°C and 76 cm of Hg.

Analysis of Fuel Gas

The analysis of a fuel gas is carried out to measure the percentage of various components present in the gas. The determination of carbondioxide, oxygen, and carbonmonoxide is relatively quite simple. But the determination of various hydrocarbons and other components needs expensive and sophisticated instruments.

To determine the percentage of carbondioxide, oxygen, and carbonmonoxide, the Orsat apparatus is used. A measured quantity, usually 100 ml of gas sample, is collected in a burette. The gas is then passed to three pipettes, containing respectively, solutions of caustic potash, alkaline pyrogallic acid, and ammoniacal cuprous chloride. The first pipette absorbs CO_2.

After its absorption, the volume of the remaining gas is measured. Next, oxygen is absorbed and the remaining volume of the sample is noted. Lastly, CO is absorbed and the reduction in volume is noted. Care is taken to read the volume of gas in the burette always at atmospheric pressure with the help of a levelling bottle.

Spectrometry

The mass spectrometer is a very useful and accurate instrument. It operates on the principle that ions of different masses, when accelerated through a circular path, separate into individual ion beams of different radii depending upon the mass and velocity of each ion. A spectrum of ion beam intensity versus ion mass is obtained and compared with standards from pure substances.

The infrared spectrometer is widely used for gas analysis. The principle of operation is that each gas or vapour absorbs infrared radiation at a particular wavelength.

Gas Chromatography

Gas chromatography is also quite an accurate tool for gas analysis. Basically the apparatus consists of a long column packed with either an adsorbent or an inert solid coated with a high boiling organic liquid. A small amount of gas is injected at one end of the column and an inert carrier gas is passed through the column. Solid adsorbent materials are usually charcoal, alumina, silica gel, etc., while the carrier gas may be nitrogen, argon, etc. The solid adsorbent provides varying affinities for each component, and therefore, they flow through the column at different speeds. They come out at the other end of the column at different intervals. A detector element is placed at the outlet which gives different peaks on a chromatograph. Various detectors can be used which compare some property of the carrier gas and the individual components of the sample as they pass through. Differences in density, surface potential, dielectric constant, heat of adsorption, and thermal conductivity are among the properties that may be used. Normally, thermal conductivity is used for hydrocarbons. The relative area covered under the peak gives the total amount of a particular component, and the time interval at which the particular component comes out of the column is an indication of the component.

5

INTRODUCTION TO THE COMBUSTION OF FUELS

5.1 GENERAL CONSIDERATION

All conventional fossil fuels, whether solid, liquid, or gaseous, contain basically carbon and/or hydrogen which invariably react with the oxygen in the air, forming carbon dioxide, carbon monoxide or water vapour. The heat energy released as a result of combustion can be utilized for heating purposes, or for generation of high pressure steam in a boiler, or as power from an engine or a gas turbine, etc.

The solid fuels are burned in beds in chunk or pellet form or in pulverized form suspended in the air stream. The liquid fuels are burned either by vapourizing and mixing with the air before ignition when they behave like gaseous fuels, or in the form of fine droplets which get evaporated while mixing with the air stream and during burning. The gaseous fuels are either burned in burners where the fuel and air are premixed, or the fuel and air flow separately into a burner or a furnace and simultaneously mix together as combustion proceeds. The first type of burning gives a premixed flame whereas the second type is called burning with a diffusion flame.

All solid fuels contain basic elements such as carbon, hydrogen, and sulphur or its compounds. The combustion reactions can, therefore, be dealt with the help of a few simple reaction equations which will cover the combustion of other types of fuels as well. The proportions of various elements or compounds obey the law of combining weights: "Different elements combine in fixed and definite proportions by weight."

As the weights of reactants involved are not simple integers, the numerical ratios of atoms or molecules are used in combustion calculations. The kilogram-mole or gram-mole is widely used in combustion calculations as a unit of weight. The molecular weight of any substance in kg represents one kilogram-mole or 1 kmol. 1 kmol of hydrogen has a mass of 2.016 kg and 1 kmol of carbon has a mass of 12 kg. Thus 1 kmol of methane (CH_4) has a mass of 16.032 kg. Consider a reaction:

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2H_2O \tag{5.1}$$

Here we can say that 16.032 kg of methane reacts with 64 kg of oxygen to form 44 kg of carbon dioxide and 36.032 kg of water. We can also simply state that 1 kmol of methane reacts with 2 kmols of oxygen to form 1 kmol of carbon dioxide and 2 kmols of water. This has the advantage of permitting easy conversion between the mass and volumetric quantities for the gaseous fuels and the products of combustion. If the gases are considered ideal, then according to Avogadro's hypothesis: "All gases contain the same number of molecules per unit volume." This simply implies that 1 kmol of any gaseous substance occupies the same volume (22.4 m^3 at NTP, i.e., 101.3 or 16.032 kN/m^2 and 273K). For example, 44 kg of carbon dioxide or 32 kg of oxygen kg of methane will occupy a volume of 22.4 m^3 at NTP.

The reaction Eq. (5.1) may also be written as: 1 volume of methane reacts with 2 volumes of oxygen to form 1 volume of carbon dioxide and 2 volumes of water vapour. However, it should be clearly understood that in any reaction, the mass is conserved but the number of moles or volumes may or may not be conserved. In Eq. (5.1) the moles are also conserved although this is not a general rule. Now, consider the reaction:

$$2\,CO + O_2 \rightarrow 2CO_2 \tag{5.2}$$

This shows that 2 moles of carbon monoxide react with 1 mole of oxygen to form 2 moles of carbon dioxide. The reaction Eq. (5.2) indicates that 3 moles of the reactants produce 2 moles of the products. Considering the mass balance, we can say that 88 kg of the reactants produce 88 kg of the products.

5.2 COMBUSTION STOICHIOMETRY

A balanced chemical equation for complete combustion of the reactants with no excess air in the products is known as a stoichiometric equation. A stoichiometric mixture of the reactants is one in which the molal proportions of the reactants are exactly as given by the stoichiometric coefficients so that no excess of any constituent is present. In general, a chemical reaction may be written as:

$$aA + bB \rightarrow cC + dD \tag{5.3}$$

where the reactants A and B react to form the products C and D. The small letters *a*, *b*, *c*, and *d* are known as the stoichiometric coefficients. The principal reactions for the combustion of any fuel are summarized below:

$$\begin{aligned}
&C + O_2 \rightarrow CO_2\\
&C + \tfrac{1}{2}O_2 \rightarrow CO\\
&CO + \tfrac{1}{2}O_2 \rightarrow CO_2\\
&H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O\\
&S + O_2 \rightarrow SO_2\\
&C_m\,H_n + \left(m + \frac{n}{4}\right)O_2 \rightarrow m\,CO_2 + \frac{n}{2}H_2O
\end{aligned} \tag{5.4}$$

where C_mH_n represents any hydrocarbon fuel.

For the combustion of any fuel, the most common oxidizer is air which, for general purposes, may be considered as a mixture of 21% oxygen and 79% nitrogen (on volume basis), i.e. one mole of oxygen is accompanied by 79/21 (=3.76) mole of nitrogen. The chemical equation for the stoichiometric combustion of carbon with air is written as:

$$C + O_2 + 3.76\,N_2 \rightarrow CO_2 + 3.76\,N_2 \tag{5.5}$$

The minimum amount of air required for the complete combustion of a fuel is known as "theoretical air". However, in practice it is difficult to achieve the complete combustion with theoretical air. Therefore, the coal fired boilers are supplied with 10 to 20% excess air; pulverized fuel fired boilers need about 20% excess air and natural gas fired boilers require only about 5% excess air. Internal combustion engines are also supplied with some excess air and gas turbines run on very lean mixtures up to about 400% of the theoretical quantity. The fuel rich mixtures, or mixtures with stoichiometric or less than stoichiometric air give incomplete combustion that result in some quantity of undesirable carbon monoxide in the exhaust gases and also some loss of heat energy.

Theoretical Air Required for Complete Combustion

If the fuel composition is known, the requirement of oxygen or air can be calculated either by mass balance or by the mole method according to Eq. (5.4).

On Mass Basis

12 kg of carbon requires 32 kg of oxygen to form 44 kg of carbon dioxide or 1 kg C + $\frac{3}{8}$ kg O_2 → $\frac{11}{3}$ kg CO_2.

Similarly,

$$1 \text{ kg C} + \tfrac{4}{3} \text{ kg } O_2 \rightarrow \tfrac{7}{3} \text{ kg CO}$$
$$1 \text{ kg C} + \tfrac{8}{7} \text{ kg } O_2 \rightarrow \tfrac{11}{7} \text{ kg } CO_2$$
$$1 \text{ kg } H_2 + 8 \text{ kg } O_2 \rightarrow 9 \text{ kg } H_2O$$
$$1 \text{ kg S} + 1 \text{ kg } O_2 \rightarrow 2 \text{ kg } SO_2$$

$$\text{and } 1 \text{ kg } C_mH_n + \left(\frac{(m+n/4)32}{12m+n}\right) \text{kg } O_2 \rightarrow \frac{44m}{12m+n} \text{kg } CO_2 + \frac{9n}{12m+n} \text{kg } H_2O$$

On Molal Basis

$$1 \text{ kmol C} + 1 \text{ kmol } O_2 \rightarrow 1 \text{ kmol } CO_2$$
$$1 \text{ kmol C} + \tfrac{1}{2} \text{ kmol } O_2 \rightarrow 1 \text{ kmol CO}$$
$$1 \text{ kmol CO} + \tfrac{1}{2} \text{ kmol } O_2 \rightarrow 1 \text{ kmol } CO_2$$
$$1 \text{ kmol } H_2 + \tfrac{1}{2} \text{ kmol } O_2 \rightarrow 1 \text{ kmol } H_2O$$
$$1 \text{ kmol S} + 1 \text{ kmol } O_2 \rightarrow 1 \text{ kmol } SO_2$$
$$1 \text{ kmol } C_mH_n + \left(m + \frac{n}{4}\right) \text{kmol } O_2 \rightarrow m \text{ kmol } CO_2 + \frac{n}{2} \text{kmol } H_2O.$$

Conversion of Gravimetric Analysis to Volumetric Basis and Vice Versa

If the composition of a fuel is given on gravimetric (or weight) basis, it can be converted to volumetric (or mole) basis as follows: Divide the weight of each constituent of the fuel by its molecular weight. This will give the relative volume (or moles) of each constituent. Add all the relative volumes of the constituents. Then

$$\frac{\text{Individual (relative) volume of the constituent}}{\text{Total (relative) volume of all the constituents}} \times 100$$

will give the percentage by volume of each constituent in the fuel.

Similarly, if the volumetric composition of a fuel is given, it can be converted to gravimetric (or weight) basis as follows: Multiply the individual volume of each constituent by its molecular weight. This will give the relative weight of each constituent. Add all the relative weights of the constituents. Then

$$\frac{\text{Individual (relative) weight of the constituent}}{\text{total (relative) weights of all the constituents}} \times 100$$

will give the percentge by weight of each constituent in the fuel.

Calculation of the Minimum Amount of Air for a Fuel of Known Composition

Calculate the minimum volume of air required to burn 1 kg of coal having the following composition by weight:

C 72.4%, H_2 5.3%, N_2 1.8%, O_2 8.5%, moisture 7.2%, S 0.9%, and ash 3.9%.

On Weight Basis

Taking 1 kg coal as the basis, the weight of oxgyen required to burn carbon in 1 kg coal is

$$0.724 \times \frac{32}{12} = 1.92 \text{ kg}$$

Similarly, for combustion of hydrogen in fuel, the oxygen required is

$$0.053 \times \frac{16}{2} = 0.424 \text{ kg}$$

and for the combustion of sulphur in fuel, the oxygen required is

$$0.009 \times \frac{32}{32} = 0.009 \text{ kg}$$

i.e., the total oxygen required is 2.363 kg per kg coal. But 0.085 kg oxygen is available in the coal. Therefore, the oxygen needed is (2.363 — 0.085) =2 278 kg per kg coal. Air contains 23% of oxygen by weight. Therefore, the weight of air to be supplied is $2.278 \times \frac{100}{23} = 9.90$ kg per kg coal. Taking the mean molecular weight of air as 29, the density of air at NTP is $\frac{29}{22.4} = 1.29$ kg/m^3 (22.4 m^3 is the gas molecular volume).

Therefore, the volume of air required for combustion

$$\frac{9.90}{1.29} = 7.67 \text{ m}^3 \text{ per kg coal.}$$

On Mole Basis

Consider 100 kg coal which has

$$C = \frac{72.4}{12} = 6.03 \text{ kmol} \qquad O_2 = \frac{8.5}{32} = 0.265 \text{ kmol}$$

$$H_2 = \frac{5.3}{2} = 2.65 \text{ kmol} \qquad H_2O = \frac{7.2}{18} = 0.4 \text{ kmol}$$

$$N_2 = \frac{1.8}{28} = 0.064 \text{ kmol} \qquad S = \frac{0.9}{32} = 0.028 \text{ kmol}$$

We know that 1 kmol carbon requires 1 kmol oxygen. Therefore, the oxygen required for combustion of 6.03 kmol of carbon is (6.03 × 1) = 6.03 kmol. Similarly, for hydrogen, the oxygen required is (2.65 × ½) = 1.325 kmol and for sulphur, the oxygen required is (0.028 × 1) = 0.028 kmol. The total oxygen required is (6.03 + 1.325 + 0.028) = 7.383 kmol. The oxygen present in 100 kg coal is 0.265 kmol. Therefore, the net oxygen required is (7.383 − 0.256) = 7.118 kmol, and the air required is

$$7.118 \times \frac{100}{21} = 33.89 \text{ kmol/100 kg coal}$$
$$= 0.3389 \text{ kmol/kg coal.}$$

Therefore, the volume of air to be supplied is

$$0.3389 \times 22.4 = 7.59 \text{ m}^3\text{/kg coal.}$$

Calculation of the Composition of Dry Flue Gases if Fuel Composition is Known

Calculate the volumetric analysis of the flue gases when the coal of analysis as given in the previous section is burned with 20% excess air.

From the previous section, we know that the theoretical air required is 33.89 kmol/100 kg coal. Therefore, the actual air is

$$\left(33.89 \times \frac{120}{100}\right) = 40.67 \text{ kmol/100 kg coal}$$

The amount of N associated with this air is

$$\frac{79}{100} \times 40.67 = 32.13 \text{ kmol}$$

The amount of O_2 associated with this air is

$$\frac{21}{100} \times 40.67 = 8.54 \text{ kmol}$$

The amount of oxygen required for combustion is 7.118 kmol. Therefore, the excess oxygen which will appear in exhaust gases will be (8.54 − 7.118) = 1.422 kmol. Thus by combustion of 100 kg of coal the dry flue gases will contain:

CO_2 = 6.03 kmol from combustion of 6.03 kmol of C
SO_2 = 0.028 kmol from combustion of 0.028 kmol of S
N_2 = 32.13 kmol of N_2 from air + 0.064 kmol of N_2 from fuel
= 32.194 kmol
O_2 = 1.422 kmol as excess oxygen.

Total volume = (6.03 + 0.028 + 32.194 + 1.422) = 39.674 kmol. Therefore, the volumetric composition of the dry flue gases is

$$CO_2 = \frac{6.03}{39.674} \times 100 = 15.120\%$$

$$SO_2 = \frac{0.028}{39.674} \times 100 = 0.07\%$$

$$N_2 = \frac{32.13}{39.674} \times 100 = 81.15\%$$

$$O_2 = \frac{1.422}{39.674} \times 100 = 3.58\%$$

Calculation of the Composition of Fuel and Excess Air Supplied from the Exhaust Gas Analysis

Sometimes, the composition of the fuel is unknown and it becomes necessary to judge whether the amount of air supplied is sufficient, insufficient, or in excess. This can be obtained by analyzing the sample of exhaust gases and then carrying out the nitrogen, oxygen, and carbon balances, provided the fuel does not contain nitrogen. The following example will illustrate the calculation procedure:

The composition of dry flue gases obtained by burning a liquid fuel containing only hydrogen and carbon is

CO_2 10.7%, O_2 5.1%, N_2 84.2%.

Calculate the composition of the fuel by weight and the excess air used.

Fuel Composition

Consider 100 kmol of dry flue gases. They will contain 10.7 kmol of O_2 (from CO_2) + 5.1 kmol of O_2 (as free oxygen) = 15.8 kmol.

Using the nitrogen balance, the actual air used is $84.2 \times \frac{100}{79}$ = 106.58 kmol/100 kmol of flue gases and the oxygen in the air supplied is $\frac{21}{100} \times 106.58 = 22.38$ kmol.

Therefore, the amount of oxygen present in the water produced by the combustion of hydrogen is

$$(22.38 - 15.8) = 6.58 \text{ kmol } O_2.$$

We know that 1 kmol H_2 combines with 1/2 kmol O_2 to produce water. Therefore, the amount of hydrogen present is 6.58 × 2 = 13.16 kmol/kmol of fuel.

The hydrogen present (by weight) is 13.16 × 2 = 26.32 kg/100 kmol of dry flue gases and the carbon present is 12 × 10.7 = 128.4 kg/100 kmol of dry flue gases. Therefore, the composition of fuel (by weight) is 128.4 kg C and 26.32 kg H_2 and on percentage basis

$$C = \frac{128.4}{128.4 + 26.32} \times 100\% = 82.99\%$$

$$H = \frac{26.32}{128.4 + 26.32} \times 100\% = 17.01\%$$

Excess Air Supplied

Let us first calculate the minimum weight of air required. In 100 kmol flue gases, CO_2 present is 10.7 kmol, i.e., carbon is 10.7 kmol, and hydrogen is 13.16 kmol. The amount of O_2 required to burn 10.7 kmol C and 13.16 kmol H_2 is

$$\left(10.7 + \frac{13.16}{2}\right) = 17.28 \text{ kmol/100 kmol dry flue gases}$$

Actual oxygen supplied is 22.38 kmol/100 kmol dry flue gases.

$$\text{Therefore, \% excess air} = \frac{22.38 - 17.28}{17.28} \times 100\% = 29.5\%$$

5.3 DEWPOINT OF PRODUCTS

The products of combustion containing water vapour are termed as "wet" products, although the water vapour present is in the form of superheated steam. According to Dalton's law of partial pressures, the partial pressures of the individual gases present in the mixture are proportional to their molal percentages. If the water vapour present in the wet products of combustion is cooled down to the point of condensation, the vapour would turn into a liquid and its volume would be reduced. Now all the space of the products would be occupied by carbon dioxide, carbon monoxide, oxygen, and nitrogen, called the "dry" products of combustion (if all the water vapour is condensed). Knowing the partial pressure exerted by the water vapour before condensing, it is possible to determine the dewpoint of the products, i.e., the saturation temperature corresponding to the partial pressure by means of the steam tables. This temperature is useful in avoiding the corrosion of metals. Water in the liquid form not only rusts metals, but also reacts with SO_2 (from sulphur in fuels) forming H_2SO_3 and attacks the metals violently.

5.4 FLUE GAS ANALYSIS

A flue gas usually contains carbon dioxide, carbon monoxide, nitrogen, water vapour, and often oxygen. The presence of sulphur dioxide is normally ignored. It is possible to judge the completeness of combustion from the presence or absence of carbon monoxide in the products, or in the case of coal, it serves to give an estimate of the carbon and hydrogen content of the fuel. It is, therefore, desirable to know the flue gas analysis.

The analysis of a flue gas is determined by using an Orsat apparatus. It consists of three absorption pipettes and a measuring burette, all housed in a wooden frame. The flue gas sample is forced from the measuring burette in to the absorption pipettes containing chemical reagents by means of a levelling bottle by creating a hydrostatic head. Carbon monoxide, oxygen, and carbon dioxide are absorbed in the absorption pipettes containing acid solution of cuprous chloride for absorbing carbon monoxide, pyrogallic acid for oxygen, and potassium hydroxide for carbon dioxide. The decrease in volume of carbon monoxide, oxygen, and carbon dioxide after each absorption gives the measure of the different gases. Nitrogen is determined by the difference in the total volume of the gases taken initially and the total volume of the gases absorbed in the pipettes. The Orsat apparatus gives the flue gas analysis on a dry basis.

Example 5.1

A fuel gas has the following percentage volumetric analysis:

H_2 : 48, CH_4 : 26, CO_2 : 11, CO : 5, N_2 : 10

The percentage volumetric analysis of the dry exhaust gases is

CO_2 : 8.8, O_2 : 5.5, N_2 : 85.7

Determine the air/fuel ratio by volume if air contains 21% O_2 by volume.

Solution

The chemical equation for the reaction of 100 mols of fuel gas with air may be written as

$$48\,H_2 + 26\,CH_4 + 11\,CO_2 + 5\,CO + 10\,N_2 + x\,[O_2 + 3.76\,N_2] \rightarrow aCO_2 + bH_2O + cO_2 + dN_2$$

A balance of each element enables us to evaluate each of the unknown coefficients

C balance: $26 + 11 + 5 = a$

$a = 42 \quad (1)$

H_2 balance: $48 + 52 = b$

$b = 100 \quad (2)$

O_2 balance: $11 + 2.5 + x = \frac{b}{2} + \text{—} + c \quad (3)$

$$N_2 \text{ balance:} \quad 10 + 3.76\,x = d \qquad (4)$$

From Eqs. (3) and (4), we have

$$a + c + d = 23.5 - 50 + 4.76\,x$$
$$= 4.76\,x - 36.5$$

Now % CO_2 by volume in dry gas may be written as

$$\frac{a}{a + c + d} \times 100 = 8.8$$

or $$\frac{42}{4.76x - 26.5} = .088$$

or $$4.76x = 497.4$$

The air-fuel ratio by volume is

$$AF = \frac{\text{Total mols of air}}{\text{mols of fuel gas}} = \frac{497.4}{100}$$
$$AF = 4.974. : 1$$

Example 5.2

Find the dew point temperature of the high temperature products of combustion of C_8H_{16} with 20 per cent deficiency of air if the total pressure is 1 atm.

Solution

With deficiency of air we assume here that all the hydrogen in the fuel is converted to water vapour and the carbon is converted to both CO and CO_2. The reaction equation for combustion of C_8H_{16} with 20 per cent deficiency of air may be written as:

$$C_8H_{16} + 0.8 \times 12\,(O_2 + 3.76\,N_2) \rightarrow a\,CO + b\,CO_2 + 8H_2O + 36.1\,N_2$$

In this case the carbon balance and oxygen balance lead to the following equations:

$$\text{C balance} : 8 = a + b$$

$$O_2 \text{ balance} : 9.6 = \frac{a}{2} + b + 4$$

Solving these equations, we get

$$a = 4.8$$
$$b = 3.2$$

Hence the reaction equation is

$$C_8H_{16} + 9.6\,(O_2 + 3.76\,N_2) \rightarrow 4.8\,CO + 3.2\,CO_2 + 8H_2O + 36.1\,N_2$$

The total mols of the products are 52.1. The partial pressure of the water vapour in the products is $\frac{8}{52.1} \times 1 \text{ atm} = 0.153$ atm.

From steam tables the saturation temperature corresponding to this pressure is nearly 54.7°C. When the products of combustion are cooled to 54.7°C at constant pressure, the dew point temperature of the products is reached. For temperatures lower than this value, water will condense out of the products.

Example 5.3

A fuel has the following per cent analysis by weight:

C : 82, H_2 : 10, S : 3, O_2 : 2.5, Ash : 2.5

For an air/fuel ratio of 12:1, calculate

(a) the mixture strength as a percentage rich or lean, and
(b) the volumetric analysis of the dry products of combustion.

Air contains 23 per cent O_2 by weight.

Solution

Consider 100 kg of fuel. The basic chemical equations involved are

$$C + O_2 \rightarrow CO_2$$
$$2H_2 + O_2 \rightarrow 2H_2O$$
$$S + O_2 \rightarrow SO_2$$
$$2C + O_2 \rightarrow 2CO$$

The fuel is made up of

82 kg C
10 kg H_2
3 kg S
2.5 kg O_2
2.5 kg ash

Of these only the first three require oxygen for combustion. Thus

82 kg C require $\frac{82}{12} \times 32 = 218.6$ kg oxygen for combustion

10 kg H_2 require $\frac{10}{4} \times 32 = 80$ kg oxygen for combustion

3 kg S require $\frac{3}{32} \times 32 = 3$ kg oxygen for combustion

Thus the stoichiometric requirement of oxygen for the fuel is

$$218.6 + 80 + 3 - 2.5 = 299.1 \text{ kg } O_2 \text{ per 100 kg fuel.}$$

Therefore, air required for complete combustion is

$$\frac{299.1}{0.23} = 1300 \text{ kg air per 100 kg fuel.}$$

Stoichiometric fuel-air ratio $= \frac{100}{1300} = \frac{1}{13}$

Actual fuel-air ratio $= \frac{1}{12}$

Therefore equivalence ratio $\phi = (F/A)_{actual}\ (F/A)_{stoic} = \frac{13}{12} = 1.803$

i.e. the mixture is 8.3 per cent rich.
Thus deficiency of air $= 13 - 12 = 1$ kg per kg of fuel
The weight of air saved by burning 1 kg C to CO instead of

$$CO_2 \rightarrow \frac{16}{12} \times \frac{1}{0.23}\,\text{kg}$$

Therefore 1 kg of air will be saved when $\frac{1 \times 0.23 \times 12}{16} = 0.1725$ kg C burns to CO

$$CO \text{ formed} = 0.1725 \times \frac{18}{12} = 0.403 \text{ kg per kg of fuel}$$

$$CO_2 \text{ formed} = (0.82 - 0.1725) \times \frac{44}{12} = 2.38 \text{ kg per kg of fuel}$$

N_2 supplied $= 12 \times 0.77 = 9.25$ kg per kg of fuel

SO_2 formed $= 0.06$ kg per kg of fuel

Dry analysis in tabular form

Product	m	M	$\frac{m}{M}$	% vol $= \frac{m/M}{\Sigma m/M} \times 100$
CO	0.304	28	0.0144	3.6
CO_2	2.38	44	0.0541	13.5
N_2	9.25	28	0.3310	82.67
SO_2	0.06	64	0.00094	0.23
			0.40044	100.00

6

FUNDAMENTALS OF CHEMICAL KINETICS

A majority of propulsive devices, e.g., steam engines and steam turbines, gasoline and diesel engines, electricity-driven and jet-propelled vehicles, ramjet and rocket engines, are dependent on the occurrence of chemical reactions involving one or more substances. The reactions involved are usually the combustion or oxidation processes. The combustible substance is called the "fuel", and the air or oxygen is the "oxidizer". The process can be divided into two parts: how fast does the reaction occur, and what are the chemical changes that take place during the reaction. The former question is concerned with the subject of chemical kinetics which is the most important chemical aspect of flames. The latter question is complex and difficult to answer, and is concerned with the mechanism of the reaction. However, the determination of the final changes on the completion of the reaction is generally much easier and involves the application of chemical thermodynamics.

This chapter deals with chemical kinetics, defined as that branch of physical chemistry concerned with the speed or velocity of a reaction in chemical processes. It seeks to define the rate of chemical reactions in terms of several variables such as pressure, temperature, composition, presence or absence of catalysts and external energy sources, etc. The speed or velocity of a chemical reaction determines its usefulness as a source of propulsion energy. For example, the slow burning of gasoline in a spirit lamp can be contrasted with the same chemical reactions occurring in a gasoline engine or jet engine.

Further, the subject of chemical kinetics seeks a more precise definition of the mechanism or path of a chemical reaction about which much cannot be said in a definite way at present.

6.1 RATE OF REACTION

According to the law of mass action, the rates of direct and reverse reactions are at every moment proportional to the active concentration of the reactants present in the mixture. Also, according to the kinetic theory the number of molecular collisions are proportional to the concentration of any species present in the mixture. If the appearance and disappearance of any species is only due to the reaction and there is no diffusion, supply, or removal of the reacting substance, then the reaction rate will change according to change in the concentration of the reactants.

The reaction rate may be calculated as the change per unit time in the concentration of any reactant and can be expressed as dC/dt. If the concentration C is reducing with time, as is the case with the reactants, it should be written as $(-dC/dt)$. Consider the reaction:

$$aA + bB + \dots = lL + mM + \dots \tag{6.1}$$

The rate of reaction will be

$$\frac{d[A]}{dt} = -\frac{a}{b}\frac{d[B]}{dt} = \frac{a}{l}\frac{d[L]}{dt} = \frac{a}{m}\frac{d[M]}{dt} \tag{6.2}$$

where [A], [B], ..., [L], [M] denote the concentrations of the substances A, B, L, M, etc.

A reaction is called unilateral if it proceeds in only one direction and there is no reverse reaction. Although at high temperatures, the reverse reaction always occurs but many reactions can be considered as unilateral under given conditions. A reaction is called homogeneous if it takes place uniformly throughout the bulk of a single physical phase. If the reaction takes place at the interface between two different phases, the reaction is said to be heterogeneous.

6.2 REACTION ORDER AND MOLECULARITY

These two terms are sometimes not clearly distinguished. The term "molecularity" is used for the elementary reaction, i.e., for one step reaction only. It gives the number of molecules or particles taking part in the reaction in a single step to give the products. It is a whole number. An elementary reaction may be unimolecular, bimolecular, or trimolecular. The "reaction order" is defined for an overall reaction. The order of a reaction is indicated by the number of reacting species whose concentrations determine the rate of the process. A first order reaction is one in which the rate of the reaction is proportional to the instantaneous concentration of a single species. A reaction will be termed of order n if the rate of reaction involving a single reactant is written

$$-\frac{dC}{dt} = kC^n \tag{6.3}$$

where K is called the specific reaction rate, specific rate constant, or velocity constant. Sometimes, for an elementary reaction, the molecularity and order of reaction are the same. The reaction may be of zero order or may have a fractional value. For rate calculations, the reactions are classified according to their order.

Half-Life

It is convenient to express the time interval required to reduce the concentration of a species to half its initial value, because this time is independent of the change in concentration. It relates to the rate constant and is designated as the half-life of a species or half-life of a reaction. It is represented by the symbol $t_{1/2}$.

Zero Order Reactions

For a zero order reaction, the rate of reaction will be independent of the concentration of its reactants.
Considering the general reaction

$$aA + bB \rightarrow \text{products} \tag{6.4}$$

to be a zero order reaction, the rate equation will be

$$-\frac{dc}{dt} = k^{\circ}C = k \tag{6.5}$$

Where C represents the concentration of reactants. The integration of Eq. (6.5) gives

$$C = -kt + \text{const.} \tag{6.6}$$

The constant of integration can be determined from the condition of the reaction. If the initial concentration of C be C_0 at $t = 0$, then

$$C - C_0 = -kt \tag{6.7}$$

gives the concentration of reactants at any time t. The half-life of the reaction will be given by Eq. (6.7) when $t = t_{1/2}$ and $C = C_0/2$

$$\therefore t_{1/2} = \frac{C_0}{2k} \tag{6.8}$$

There are very few cases of zero order reactions. The decomposition of nitrous oxide gas on hot platinum wire is given by the reaction

$$2N_2O \rightarrow 2N_2 + O_2$$

The decomposition of ammonia gas on hot platinum wire is written as

$$2NH_3 \rightarrow N_2 + 3H_2$$

These are examples of zero order hetrogeneous reactions. The reaction rates of the above reactions are found to be independent of the concentration of nitrous oxide or ammonia. This phenomenon can be explained if we assume that the platinum surface becomes saturated with very small concentrations of the reactants and the reaction goes on at a steady rate as the surface remains saturated most of the time.

First Order Reactions

For a first order reaction, the rate of reaction is proportional to the concentration of only one of the reacting species. Consider a general reaction

$$aA + bB \rightarrow lL + mM \tag{6.9}$$

to be of first order. Let the reaction rate be independent of the concentration of B and is dependent on the concentration of species A only. If the concentration of A is represented by [A]

Then $$-\frac{d[A]}{dt} = k_A \; [A] \tag{6.10}$$

The integration of Eq. (6.10) gives

$$\ln [A] = -k_A t + \text{const} \tag{6.11}$$

If the initial concentration of A is $[A_0]$ at time $t = 0$

Then $$\ln \frac{[A]}{[A_0]} = -k_A t \tag{6.12}$$

or $$2.303 \log_{10} \frac{[A]}{[A_0]} = -k_A t$$

or $$[A] = [A_0] \, e^{-k_A t} \tag{6.13}$$

For a first order reaction, its half-life will be given by Eq. (6.13) when $t = t_{1/2}$ and $[A] = \frac{[A_0]}{2}$

Therefore,

$$t_{1/2} = \frac{\ln 2}{k_A} = \frac{0.693}{k_A} \tag{6.14}$$

From Eq. (6.13), it is clear that a graph between $\log_e [A]$ against time t will be a straight line and minus the slope of this line is equal to the specific rate constant. Figure 6.1 shows such a graphical representation for a first order reaction.

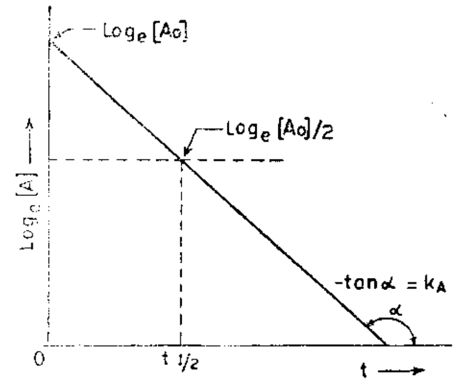


Fig. 6.1 Representation of first order reactions.

There are many first order reactions. The dissociation of the oxygen molecule

$$O_2 \rightarrow 2O$$

representing the decay of the unstable element or decomposition of N_2O_5 as

$$N_2O_5 \rightarrow 2NO_2 + \tfrac{1}{2} O_2$$

are examples of first order reactions..

Unimolecular Reactions

Before considering a second order reaction, it would be better to understand the mechanism of unimolecular reactions. For a unimolecular reaction, concept that collision of two molecules is necessary for any reaction to take place, fails because by definition, a unimolecular reaction will become bimolecular if collision is responsible for the reaction. The unimolecular reaction is the disintegration of a stable molecule. Some examples have been given in the preceding section. But normally a stable molecule should not decompose. Lindemann[1] proposed the following mechanism to explain a unimolecular reaction

$$A \rightarrow \text{products} \tag{6.15}$$

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A^* + B \tag{6.16}$$

i.e., when a molecule of A collides with one of B the result may be an activated molecule of A represented by A*. Molecule B may either be a molecule of A or any other molecule which remains unaffected by the collision. This means, by collision molecule A acquires some energy and this activated molecule is capable of disintegrating according to the equation

$$A^* \xrightarrow{k_3} P \text{ (products)} \tag{6.17}$$

During the course of collision, an activated molecule may loose its energy to return to its original condition by the reverse reaction (6.16) or may follow the path of reaction (6.17).

Assuming k_1 as the rate constant for the forward reaction, k_2 the rate constant for the reverse reaction and k_3 for the reaction (6.17), the rate equation for concentration of A* may be written as

$$\frac{d[A^*]}{dt} = k_1 [A] [B] - k_2 [A^*] [B] - k_3 [A^*] \tag{6.18}$$

and for the formation of the product

$$\frac{d[P]}{dt} = k_3 [A^*] \tag{6.19}$$

In the steady state condition, the concentration of the activated molecule of A will not change much with time. Therefore, we may write

$$\frac{d[A^*]}{dt} = 0$$

From Eq. (6.18)

$$[A^*] = \frac{k_1 [A] [B]}{k_2 [B] + k_3} \tag{6.20}$$

Substituting this value in Eq. 6.19

$$\frac{d[P]}{dt} = k_3 \frac{k_1 [A] [B]}{k_2 [B] + k_3}$$

or
$$\frac{d[P]}{dt} = \frac{k_1 [A] [B]}{1 + \frac{k_2}{k_3} [B]} \tag{6.21}$$

If the concentration of B, i.e., the total number of moles per unit volume, is large (say, the pressure is high) or if

the ratio $\frac{k_2}{k_3}$ [B] is large, i.e. $\frac{k_2}{k_3} [B] \gg 1$,

then
$$\frac{d [P]}{dt} = \frac{k_1 [A] [B]}{\frac{k_2}{k_3} [B]} = \frac{k_1 k_3}{k_2} [A] \tag{6.22}$$

the expression shows the reaction to be of the first order.

If $\frac{k_2}{k_3} [B] \ll 1$

Equation (6.21) may be written as

$$\frac{d [P]}{dt} = k_1 [A] [B] \tag{6.23}$$

This expression appears to be of the bimolecular type. There are many reactions which behave like first order reactions at high pressures and second order reactions at low pressures. Such a behaviour supports the Lindemann mechanism.

Second Order Reaction

For a second order reaction, the rate of reaction is proportional to the first power of the product of the concentrations of two species, or is proportional to the square of the concentration of a single reacting species. A general second order reaction can be written as

$$aA + bB \rightarrow \text{products} \tag{6.24}$$

The second order rate equation can be of two types:

Type I
$$-\frac{d[A]}{dt} = k_A [A]^2 \tag{6.25}$$

Type II
$$-\frac{d[A]}{dt} = k_A [A] [B] \tag{6.26}$$

Let us first consider the Type I rate equation.
The integration of Eq. (6.25) gives

$$\frac{1}{[A]} = k_A t + \text{const.} \tag{6.27}$$

The integration of the above equation between limits $[A] = [A_0]$ at $t = 0$ and [A] at time t gives

$$\frac{1}{[A]} - \frac{1}{[A_0]} = k_A t \tag{6.28}$$

o
$$K_A = \frac{1}{t} \left\{ \frac{[A_0] - [A]}{[A_0] [A]} \right\} \tag{6.29}$$

and
$$t_{1/2} = \frac{1}{k_A [A_0]} \tag{6.30}$$

i.e., for a second order reaction, the half-life varies inversely as the initial concentration. The gas-phase thermal decomposition of hydrogen iodide or of NO_2 are typical examples of the second order reaction of type I as represented by Eq. (6.25). The reactions are as follows

$2HI \rightarrow H_2 + I_2$ and

$2NO_2 \rightarrow 2NO + O_2$

For second order reaction of type II

$$-\frac{d [A]}{dt} = k_A [A] [B] \tag{6.26}$$

or
$$-\frac{d [B]}{dt} = k_B [A] [B] \tag{6.31}$$

where $-\frac{k_A}{a} = \frac{k_B}{b}$

If $[A_0]$ and $[B_0]$ are the concentrations at $t = 0$ and x represents the concentration of A which has reacted, then the remaining concentration of A is

$$[A] = [A_0] - x \tag{6.32}$$

and for B,

$$[B] = [B_0] - \frac{b}{a} x \tag{6.33}$$

From Eqs. (6.32) and (6.33)

$$d [A] = - d x = \frac{a}{b} d [B] \tag{6.34}$$

Substituting this in Eq. (6.26)

$$\frac{d [A]}{dt} = - \frac{dx}{dt} = - k_A \left([A_0] - x \right) \left([B_0] - \frac{b}{a} x \right)$$

or
$$\frac{dx}{\left([A_0]-x\right)\left([B_0]-\frac{b}{a}x\right)}=k_A\,dt \tag{6.35}$$

The integration of Eq. (6.35) gives

$$\ln\frac{1-x/[A_0]}{1-b\,x/a\,[B_0]}=\left(\frac{b}{a}[A_0]-[B_0]\right)k_A\,t \tag{6.36}$$

From Eqs. (6.32) and (6.33)

$$\ln\frac{[A]/[A_0]}{[B]/[B_0]}=\frac{b[A_0]-a\,[B_0]}{a}\,k_A\,t$$

or
$$\ln\frac{[A]}{[B]}=\frac{b[A_0]-a[B_0]}{a}k_A\,t+\ln\frac{[A_0]}{[B_0]} \tag{6.37}$$

Equations (6.29) and (6.37) can be plotted to give concentration time relationships as shown in Fig. 6.2.

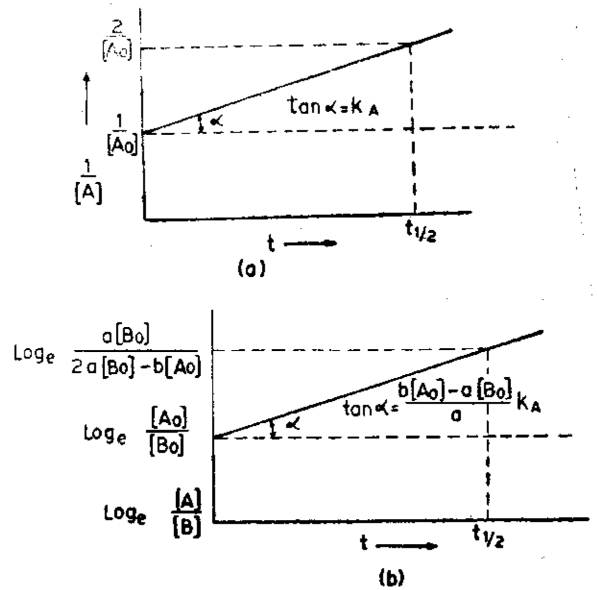


Fig. 6.2 Representation of second order reactions.

The slope of the line in Fig. 6.2(a) gives the value of the specific rate constant for the second order reaction of Type I. For the second order reaction of Type II, the specific rate constant can be calculated if the initial concentrations and slope of the line in Fig. 6.2(b) is given by the relations

$$\tan\alpha=\frac{(b[A_0]-a[B_0])}{a}k_A$$

are known.

From Eq. (6.37), the half-life of species A can be obtained.

$$t_{1/2}=\frac{a}{k_A b[A_0]-a\,[B_0]}\ln\frac{a[B_0]}{2\,a\,[B_0]-b[A_0]} \tag{6.38}$$

Such type of second order reactions are quite common, e.g., gas-phase formation of hydrogen iodide

$$H_2+I_2\rightarrow 2HI$$

and reactions of free radicals with molecules such as

$$H+Br_2=HBr+Br$$

If species A and B are present in stoichiometric or nearly stoichiometric concentrations, i.e., ($a[A_0]\approx b[B_0]$) then Eq. (6.37) becomes less useful as $\ln\frac{[A]\,[B_0]}{[B]\,[A_0]}$ will change little with time. Under these conditions a modified solution can be obtained as follows.

The rate equation is

$$\frac{d[A]}{dt}=k_A\,[A]\,[B]$$

where the instantaneous concentration of B can be written as

$$[B]=[B_0]-\frac{b}{a}([A_0]-[A])$$
$$=\frac{b}{a}\left([A]+\frac{a}{b}[B_0]-[A_0]\right)$$

or
$$[B]=\frac{b}{a}([A]+\Delta) \tag{6.39}$$

where $\Delta=\frac{a}{b}[B_0]-[A_0]$

The rate equation can be written as

$$-\frac{d[A]}{dt}=\frac{b}{a}\,k_A\,[A]\,([A]+\Delta) \tag{6.40}$$

If $[A']=([A']+\Delta/2)$, the rate equation becomes

$$-\frac{d[A']}{dt}=\frac{b}{a}k_A\left([A']+\frac{\Delta}{2}\right)([A']-\Delta/2)$$

$$\text{or} \qquad -\frac{d[A']}{dt} = \frac{b}{a} k_A \left([A']^2 - \Delta^2/4\right)$$

$$\text{or} \qquad -\frac{d[A']}{dt} = \frac{b}{a} k_A [A']^2 \left\{1 - \left(\frac{\Delta}{2}[A]\right)^2\right\} \qquad (6.41)$$

The terms in brackets in Eq. (6.41) do not change significantly even though [A] changes as the reaction proceeds. Under these conditions this term can be assumed to be constant and replaced by its average value over the course of the reaction. Therefore,

$$-\frac{d[A]}{dt} = \frac{b}{a} k_A [A']^2 \left\{1 - \frac{\Delta^2}{4[A'_0][A'_f]}\right\} \qquad (6.42)$$

where $[A'_0]$ and $[A_f]$ are the initial and final values of $[A']$. The integration of this gives

$$\frac{1}{[A']} - \frac{1}{[A'_0]} = \frac{b k_A t}{a} \left\{1 - \frac{\Delta^2}{4[A'_0][A'_f]}\right\} \qquad (6.43)$$

This result resembles Eq. (6.28)

Third Order Reactions

The third order reactions can be classified into three types. The reaction is

$$aA + bB + cC \rightarrow \text{products} \qquad (6.44)$$

The rate equations are written as

$$\text{Type I} \qquad -\frac{d[A]}{dt} = k_A [A]^3 \qquad (6.45)$$

$$\text{Type II} \qquad -\frac{d[A]}{dt} = k_A [A]^2 [B] \qquad (6.46)$$

$$\text{Type III} \qquad -\frac{d[A]}{dt} = k_A [A][B][C] \qquad (6.47)$$

Type I

Equation (6.45) can be integrated directly. If $[A] = [A_0]$ at $t = 0$ then

$$\frac{1}{[A]^2} - \frac{1}{[A_0]^2} = 2 k_A t \qquad (6.48)$$

and half-life may be written as

$$t_{1/2} = \frac{3}{2k_A [A_0]^2} \qquad (6.49)$$

Type II

Assuming initial concentrations as $[A_0]$ and $[B_0]$, then at time t

$$[B] = [B_0] + \frac{b}{a}([A_0] - [A])$$

$$\text{or} \qquad [B] = \frac{b}{a}\left([A] + \frac{a}{b}[B_0] - [A_0]\right)$$

$$\text{or} \qquad [B] = \frac{b}{a}([A] + \Delta) \qquad (6.50)$$

$$\text{where} \qquad \Delta = \frac{a}{b}[B_0] - [A_0]$$

Eq. (6.46) becomes

$$\frac{d[A]}{dt} = -k_A \frac{b}{a} [A]^2 ([A] + \Delta) \qquad (6.51)$$

which on rearranging the terms becomes

$$d[A]\left(\frac{\Delta^2}{[A]^2} + \frac{1}{[A] + \Delta} - \frac{1}{[A]}\right) = -\Delta^2 \frac{b}{a} k_A \, dt \qquad (6.52)$$

The integration of Eq. (6.52) between the limits $[A] = [A_0]$ at $t = 0$ and $[A] = [A]$ at time t gives

$$\Delta\left(\frac{1}{[A]} - \frac{1}{[A_0]}\right) + \ln\left(\frac{[A]}{[A_0]} \frac{[A_0]+\Delta}{[A]+\Delta}\right) = \Delta^2 \frac{b}{a} k_A t \qquad (6.53)$$

Replacing $([A] + \Delta)$ by $\frac{a}{b}[B]$, Eq. (6.53) becomes

$$\Delta\left(\frac{1}{[A]} - \frac{1}{[A_0]}\right) + \ln\left(\frac{[A]}{[A_0]} \frac{[B_0]}{[B]}\right) = \frac{\Delta^2 b}{a} k_A t \qquad (6.54)$$

Replacing Δ as $\Delta = \frac{a}{b}[B_0] - [A_0] = \frac{a[B_0] - b[A_0]}{b}$

Eq. (6.54) becomes

$$\left(\frac{a[B_0] - b[A_0]}{b}\right)\left(\frac{1}{[A]} - \frac{1}{[A_0]}\right) + \ln\left(\frac{[A]}{[A_0]} \frac{[B_0]}{[B]}\right)$$

$$= \frac{(a[B_0] - b[A_0])}{ab} k_A t$$

or
$$\left(\frac{a}{a[B_0]-b[A_0]}\right)\left(\frac{1}{[A]}-\frac{1}{[A_0]}\right)+\frac{ab}{(a[B_0]-b[A_0])^2}\ln\left(\frac{[A]}{[B]}\frac{[B_0]}{[A_0]}\right) = k_A\,t \tag{6.55}$$

and the half-life may be written as

$$t_{1/2} = \frac{a}{[A_0]\,k_A\,(a[B_0]-b[A_0])} - \frac{ab\ln(2-b\,[A_0]/a\,[B_0])}{k_A\,(a[B_0]-b\,[A_0])} \tag{6.56}$$

If $(a/b)\,[B_0]-[A_0] < 0.3\ [A_0]$, Eqs. (6.55) and (6.56) fail to give satisfactory values. Therefore, Eq. (6.51) may be written as

$$\frac{d\,[A']}{dt} = -k_A\frac{b}{a}[A']^3\left\{1-\frac{\Delta^2[A]^2-2\,\Delta/9)}{3[A']^3}\right\} \tag{6.57}$$

where, $[A'] = ([A]+\Delta/3)$

We can assume an average value for $[A']$ between $[A_0]$ and the final value of $[A]$, and assume the terms in the bracket to be constant. Equation (6.57) can be integrated directly to give

$$\frac{1}{[A']^2}-\frac{1}{[A']^2} = \frac{2b}{a}k_A\,t\left\{1-\frac{\Delta^2\left([A_0']+[A']-\frac{4\Delta}{9}\right)}{6\,([A'_0]\,[A'_t])^{3/2}}\right\} \tag{6.58}$$

Type III

$$\frac{d[A]}{dt} = -k_A\,[A]\,[B]\,[C] \tag{6.47}$$

Assuming the initial concentrations to be $[A_0]$, $[B_0]$ and $[C_0]$,

$$[B] = [B_0]-\frac{b}{a}([A_0]-[A]) = \frac{b}{a}([A]+\Delta_b) \tag{6.59}$$

and
$$[C] = [C_0]-\frac{c}{a}([A_0]-[A]) = \frac{c}{a}([A]+\Delta_c) \tag{6.60}$$

where,
$$\Delta_b = \frac{a}{b}[B_0]-[A_0]$$

and
$$\Delta_c = \frac{a}{c}[C_0]-[A_0]$$

are the differences in the initial stoichiometric concentrations. On substituting values of $[A]$, $[B]$ and $[C]$ in Eq. (6.47), we get

$$-\frac{d[A]}{dt} = \frac{bc}{a^2}k_A\,[A]\,([A]+\Delta_b)\,([A]+\Delta_c) \tag{6.61}$$

On rearranging the terms and integrating, we get

$$(\Delta_c-\Delta_b)\ln\frac{[A_0]}{[A]}-\Delta_c\ln\left(\frac{[A_0]+\Delta_b}{[A]+\Delta_b}\right)+\Delta_b\ln\left(\frac{[A_0]+\Delta_c}{[A]+\Delta_c}\right) = \frac{bc}{a^2}k_A\Delta_b\,\Delta_c\,(\Delta_c-\Delta_b)t \tag{6.62}$$

There are very few examples of third order reactions. Equation (6.62) is quite complex and is only of academic interest.

Fractional-Order and Higher-Order Reactions

In general, for a fractional or higher order reaction, we may write the rate equation as

$$-\frac{d[A]}{dt} = k_A\,[A]^n \tag{6.63}$$

where n represents the order of the reaction.
The integration of this equation between the limits gives

$$\frac{1}{[A]^{n-1}}-\frac{1}{[A_0]^{n-1}} = (n-1)\,k_A\,t \tag{6.64}$$

and the half life is given by

$$t_{1/2} = \frac{2^{n-1}-1}{k_A\,[A_0]^{n-1}\,(n-1)} \tag{6.65}$$

The solution is valid for all values of n except for the case when n is unity. In practice, it is difficult to have a reaction order higher than three, but reaction orders up to five have been reported in literature. A summary of the important equations for different order reactions is given in Table 6.1

To determine the order of a reaction, the concentration of reactants at various time intervals is measured and a graph is plotted between time t and functions such as $\log C$, $1/C$, $1/C^2, \ldots,\ 1/C^n$, etc. A function giving a straight line will give the order of the reaction. The reaction order can also be calculated by half-life values at different concentrations. If the half-life is calculated with different equations, an equation which gives a constant value of half life will indicate the correct reaction order.

6.3 COMPLEX REACTIONS

Occasionally, the order of a reaction calculated indicates whether its value is fractional, or of an order higher than three. Reactions of fifth and higher orders are also reported in literature, but on molecular considerations alone, it is obvious that a reaction with a molecularity higher than three is quite difficult because the chances of a simultaneous collision of four different particles are quite unlikely. This is because the reaction given by the stoichiometric equation does not proceed in a single step but may be a combination of many first and/or second order steps. These steps may occur simultaneously. Such reactions which consist of more than one steps are called complex reactions. In the reaction

$$KClO_3+6FeSO_4+3H_2SO_4 \rightarrow KCl+3Fe_2\ (SO_4)_3+3H_2O$$

Obviously the possibility of the simultaneous collision of ten molecules is negligible. Therefore, it must be taking place in several elementary steps.

Example 6.1

A first order reaction is 30 per cent complete at the end of 140 s. What is the value of the reaction rate constant in s^{-1}? In how many seconds will the reaction be 60 per cent complete?

Solution

For a first order reaction:

$$\log_e \frac{[A]}{[A_0]} = -kt$$

where $[A_0]$ is the initial concentration of the reactants at time $t = 0$ and $[A]$ is the concentration at time t.

Let x represent the concentration of A which has reacted. Then at time t the remaining concentration of A is

$$[A] = [A_0] - x$$

Substituting in the above equation, we have

$$k = \frac{1}{t} \log_e \frac{[A_0]}{[A_0]-x}$$

Considering $[A_0] = 100$ per cent

$$k = \frac{1}{140} \log_e \frac{100}{100-30}$$
$$= 0.00256\ s^{-1}$$

The time when the reaction is 60 per cent complete may be calculated from the equation

$$t = \frac{1}{k} \log_e \frac{100}{100-60}$$
$$= \frac{1}{0.00256} \log_e \frac{100}{40}$$
$$= 358\ s.$$

Example 6.2

A second order reaction involving reactants with initial concentration of 0.05 mol/1 is found to be 25 per cent complete in 150 s. Calculate:

(a) The reaction rate constant
(b) The half life of the reaction
(c) The time it would take for the reaction to be 25 per cent complete if the initial concentrations were 0.005 mol/1.

Solution

Consider the second order reaction of Type I

$$-\frac{d[A]}{dt} = k\ [A]^2$$

The above rate equation can be converted to

$$\frac{1}{[A]} - \frac{1}{[A_0]} = kt$$

where $[A_0]$ is the initial concentration of A at time $t = 0$.
Let x represent the concentration of A which has reacted.
Then at time t, the remaining concentration of A is

$$[A] = [A_0] - x$$

Substituting in the above equation we have

$$\frac{1}{([A_0] - x)} - \frac{1}{[A_0]} = kt$$

(a) When $x = 25$ per cent, $t = 150$ s and $[A_0] = 0.05$ mol/1
The above equation may be written as

$$k = \frac{x}{t\ [A_0]\ ([A_0] - x)}$$

Substituting the values we have

$$k = \frac{25}{150 \times 0.05 \times (100-25)} = 0.0445\ 1/\text{mols}$$

(b) The half-life of a second order reaction of Type I is given by

$$t_{1/2} = 1/k\ [A_0]$$
$$= 1/(0.0445)\ (0.05)$$
$$= 222.5\ s$$

(c) If $[A_0] = 0.005$ mol/l, then the time for the reaction to be 25 per cent complete is given by

$$t = \frac{x}{k\ [A_0]\ ([A_0] - x)} = \frac{25}{0.0445 \times 0.005 \times (100-25)}$$
$$= 1500\ s$$

TABLE 6.1 Summary of Important Equations for Different Order Reactions
(With permission of McGraw-Hill from S.W. Benson: *Foundations of Chemical Kinetics*, 1960, p. 24)

Reaction order	*Differential equation*	*Rate constant K_A from integrated equation*	*Half-life $t_{1/2}$*
0	$-\frac{d[A]}{dt} = k_A$	$\frac{[A_0]-[A]}{t}$	$\frac{[A_0]}{2k_A}$
1	$-\frac{d[A]}{dt} = k_A[A]$	$\frac{1}{t}\ln\frac{[A_0]}{[A]}$	$\frac{1}{k_A}\ln 2$
2 Type I	$-\frac{d[A]}{dt} = k_A[A]^2$	$\frac{1}{t}\left(\frac{1}{[A]}-\frac{1}{[A_0]}\right)$	$\frac{1}{k_A[A_0]}$
Type II	$-\frac{d[A]}{dt} = k_A[AB]$	$\frac{a\ln([A]/[A_0])([B_0]/[B])}{t(b[A_0]-a[B_0])}$	$\frac{a}{k_A(a[B_0]-b[A_0])}\ln\left(2-\frac{b[A_0]}{a[B_0]}\right)$
3 Type I	$-\frac{d[A]}{dt} = k_A[A]^3$	$\frac{1}{2t}\left(\frac{1}{[A]^2}-\frac{1}{[A_0]^2}\right)$	$\frac{3}{2k_A[A_0]^2}$
Type II	$-\frac{d[A]}{dt} = k_A[A]^2[B]$	$\frac{-a}{t(b[A_0]-a[B_0])}\left(\frac{1}{[A]}-\frac{1}{[A_0]}\right) + \frac{ab}{t(b[A_0]-a[B_0])^2}\ln\frac{[A]}{[A_0]}\frac{[B_0]}{[B]}$	$\frac{-a}{k_A[A_0](b[A_0])-a[B_0])} - \frac{ab\ln(2-b[A_0]/a[B_0])}{k_A(b[A_0]-a[B_0])^2}$
Type III	$-\frac{d[A]}{dt} = k_A[A][B][C]$	See text	
n	$-\frac{d[A]}{dt} = k_A A^n$	$\frac{1}{(n-1)t}\left(\frac{1}{[A]^{n-1}}-\frac{1}{[A_0]^{n-1}}\right)$	$\frac{(2^{n-1}-1)}{k_A[A_0]^{n-1}(n-1)}$

Similarly, the reaction: $2NO + 2H_2 \rightarrow N_2 + 2H_2O$ is kinetically of third order, which it can well be, because the reaction takes place in the following two steps:

(i) $2NO + H_2 \rightarrow N_2 + H_2O_2$
(ii) $N_2O_2 + H_2 \rightarrow 2H_2O$.

The first reaction is trimolecular and is a slow reaction. The chances of the simultaneous collision of two NO molecules with one hydrogen molecule are less. Once H_2O_2 is formed, it reacts rapidly with hydrogen to give H_2O. The second step takes place rapidly. Therefore, the net rate of the reaction is governed by the first step only. The complex reaction can be categorized as: (i) opposing or reversible reactions, (ii) concurrent or parallel reactions, and (iii) consecutive reactions.

Reversible Reactions

Reversible reactions are those reactions in which the products may react themselves to form the original reactants with measurable rates. The mixture initially consists of only the reactants, but as the reaction proceeds in the forward direction, the products appear which start reacting to give the reactants. As the rate of reaction is proportional to the concentration of reactants, the rate of the forward reaction goes on reducing with the consumption of reactants while the rate of the reverse reaction increases. Ultimately, an equilibrium state is reached when the rates of the forward and reverse reactions are the same. This final equilibrium state can also be computed with thermodynamic considerations. Reversible reactions are the simplest form of simultaneous reactions.

A first order reversible reaction can be written as

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} L \tag{6.66}$$

We can write the rate expression as

$$\frac{d[A]}{dt} = -k_1[A] + k_2[L] \tag{6.67}$$

If the initial concentrations are $[A_0]$ and $[L_0]$ at $t = 0$, then at any instant

$$[A] + [L] = [A_0] + [L_0]$$

or $$[L] = [A_0] + [L_0] - [A] \tag{6.68}$$

On substituting the values in Eq. (6.67)

$$\frac{d[A]}{dt} = -k_1[A] + k_2([A_0] + [L_0] - [A])$$

or $$\frac{d[A]}{dt} = k_2([A_0] + [L_0]) - (k_1 + k_2)[A] \tag{6.69}$$

The integration of the above equation gives

$$\ln\left(\frac{k_1[A]-k_2[L]}{k_1[A_0]-k_2[L_0]}\right)=-(k_1+k_2)t \qquad (6.70)$$

At equilibrium, the rates of the forward and reverse reactions are the same. Therefore,

$$k_1[A_e]=k_2[L_e]$$

or

$$\frac{k_1}{k_2}=\frac{[L_e]}{[A_e]}=K \qquad (6.71)$$

where K is called the equilibrium constant and $[A_e]$ and $[L_e]$ represent the equilibrium concentration of the reactants and products respectively. Equations (6.70) and (6.71) yield

$$\ln\left(\frac{K[A]-[L]}{K[A_e]-[L_e]}\right)=(k_1+k_2)t \qquad (6.72)$$

The value of K can be calculated from thermodynamic considerations and Eq. (6.72) can thus give the value of k_1+k_2. Equation (6.71) gives the value of k_1/k_2. Thus k_1 and k_2 can be calculated. If the value of K is very large or very small, it means that either the forward or reverse reaction is very slow. As the value of K depends only upon the temperature, so also does the rate of the forward and reverse reactions.

For a second order reversible reaction given by

$$A+B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} L+M \qquad (6.73)$$

the rate equation may be written as

$$\frac{d[A]}{dt}=-k_1[A][B]+k_2[L][M] \qquad (6.74)$$

If the initial concentrations are $[A_0]$, $[B_0]$, $[L_0]$, and $[M_0]$ and after time t, x moles of the products are formed, then

$$\frac{dx}{dt}=k_1([A_0]-x)([B_0]-x)-k_2([L_0]+x)([M_0]+x) \qquad (6.75)$$

Equation (6.75) can be expressed in the following standard form

$$\frac{dx}{\alpha+\beta x+\gamma x^2}=dt \qquad (6.76)$$

This equation can be integrated directly. The particular form of the integral will depend on the relation of the coefficients α, β, and γ,

$$q=\beta^2-4\alpha\gamma$$

the integration of Eq. (6.76) leads to an expression which can be written in the following form.

$$\ln\frac{x+(\beta-q^{1/2})/2\gamma}{x+(\beta+q^{1/2})/2\gamma}=t\,q^{1/2}+\theta \qquad (6.77)$$

where θ is an integration constant determined by the initial condition $x=0$ at $t=0$ which gives

$$\theta=\ln\frac{\beta-q^{1/2}}{\beta+q^{1/2}} \qquad (6.78)$$

To use Eq. (6.77) experimentally, the value of k_1 and k_2 must be known, or at least their ratio should be known. Once the value of K is known, the data can be plotted and individual specific rate constants can be determined.

If initially at $t=0$, $[L]=[M]=0$ then Eq. (6.74) can be written as:

$$-\frac{d[A]}{dt}=-k_1[A]([B_0]-[A_0]+A)+k_2([A_0]-[A])^2 \qquad (6.79)$$

which on integration gives

$$\ln\left\{\frac{([A_0]-[A_e])([A]-[A_e]+Q)}{([A]-[A_e])([A_0]+[A_e]+Q)}\right\}=(k_1-k_2)Qt \qquad (6.80)$$

where $Q=\{1/(K-1)\}\sqrt{k^2([B_e]-[A_e])^2+4[A_e][B_e]K}$ (6.81)

and $K=\dfrac{k_1}{k_2}$

The equilibrium concentration of A is written as:

$$[A_e]=\frac{-\{K([B_0]-[A_0])+2[A_0]\}+Q(K-1)}{2(K-1)} \qquad (6.82)$$

If $[A]=[B]$ then Eq. (6.82) reduces to

$$\ln\frac{(K-\sqrt{K})\{[A](K-1)+A_0(\sqrt{K}+1)\}}{(K+\sqrt{K})\{[A](K-1)-A_0(\sqrt{K}-1)\}}=(k_1-k_2)\left(\frac{2[A_0]\sqrt{K}}{K-1}\right)t \qquad (6.83)$$

The homogeneous gas-phase decomposition of hydrogen iodide is represented by Eq. (6.83).

The mathematical analysis of the third and higher order reversible reactions is quite difficult. The analysis of the mixed first-second order reaction is given in standard text-books on kinetics.

Figure 6.3 gives the result of Bodenstein's[2] experiment on the dissociation and formation of hydrogen iodide. Initially the reactant is pure hydrogen-iodide. The upper curve represents the dissociation of hydrogen iodide and the lower curve represents its formation. Both the curves approach a limiting concentration of hydrogen iodide corresponding to the equilibrium concentration for the given temperature. The rate of reaction for the dissociation of hydrogen iodide also goes on decreasing from its initial maximum value, because the concentration of hydrogen iodide is decreasing with increasing time. The curves correspond to the isothermal reaction. For the changing temperature, the reaction rate will vary.

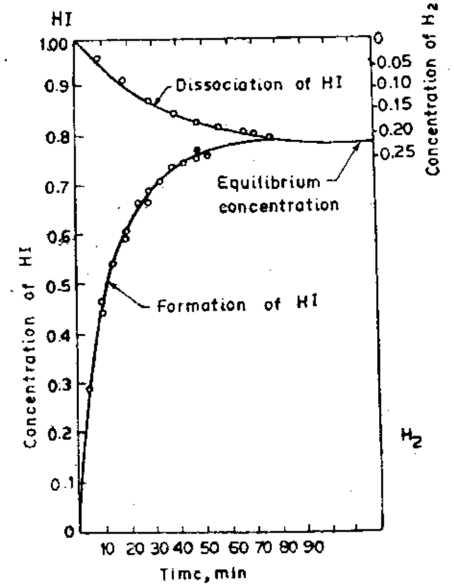


Fig. 6.3 **Formation and dissociation of hydrogen iodide (from L.N. Khitrin, *The Physics of Combustion and Explosion*, Israel Program for Scientific Translations, 1962).**

Parallel Reactions

Parallel reactions are called concurrent or collateral reactions. They consist of several simultaneously proceeding reactions involving a given substance. Thus the reactants can react in more than one independent way to give either the same or different products. The reactants A and B can react as

$$A + B \rightarrow C + D$$
$$A + B \rightarrow L + M$$
or
$$A + B \rightarrow P + Q \tag{6.84}$$

A parallel reaction is called a conjugate reaction if the second reaction takes place only in conjunction with the first.

The simplest first order parallel reaction can be represented as

$$A \xrightarrow{k_1} L$$
$$A \xrightarrow{k_2} M$$
$$A \xrightarrow{k_3} N, \text{ etc.}$$

The rate equation for the consumption of A will be

$$-\frac{d[A]}{dt} = k_1[A] + k_2[A] + k_3[A]$$

or

$$-\frac{d[A]}{dt} = (k_1 + k_2 + k_3)[A]$$

or

$$-\frac{d[A]}{dt} = k[A] \tag{6.85}$$

where $k = k_1 + k_2 + k_3$

If the initial concentration of A is $[A_0]$, then the integration of Eq. (6.85) will give

$$[A] = [A_0]\,e^{-kt} \tag{6.86}$$

If the initial concentrations of L, M, and N are $[L_0]$, $[M_0]$, and $[N_0]$ respectively, then the concentrations of the products will be given by

$$[L] = [L_0] + \frac{k_1[A_0]}{k}(1-e^{-kt}) \tag{6.87}$$

$$[M] = [M_0] + \frac{k_2[A_0]}{k}(1-e^{-kt}) \tag{6.88}$$

and

$$[N] = [N_0] + \frac{k_3[A_0]}{k}(1-e^{-kt}) \tag{6.89}$$

If $[L_0] = [M_0] = [N_0] = 0$,

The above equations simplify to

$[L] : [M] : [N] = k_1 : k_2 : k_3$

In such a case, the ratio of the concentrations of products is independent of time, but is only dependent on the ratio of the corresponding specific rate constants. The overall rate coefficient k can be determined by Eq. (6.86). Then the two known individual rate constants can give the value of the third by using the expression: $k = k_1 + k_2 + k_3$.

Normally, any reaction scheme consists of the first, second, and mixed order reactions. For such cases, each individual reaction can be treated independently if we consider the scheme

$$A \xrightarrow{k_1} L$$
$$A + B \xrightarrow{k_2} M + N$$
$$A + C \xrightarrow{k_3} P$$

The three parallel reactions are consuming species A to give different products. Therefore, the first reaction appears to be of the first order, the second of the second order, and the third of the second order mixed. We can write the rate equation for the consumption of A as

$$-\frac{d[A]}{dt} = k_1 [A] + k_2 [A][B] + k_3 [A][C] \tag{6.90}$$

The solutions for such mixed order schemes are not direct. If we at least know the ratio of the specific rate constants, then there exists a possibility of calculating the rate constants by numerical integration.

Consecutive Reactions

Consecutive or successive reactions are a set of reactions where the products of the first reaction become reactants for the second, and the products of the second react to give new products. Such reactions are given by the following schemes

$$\text{(i)}\quad A \xrightarrow{k_1} B \xrightarrow{k_2} C \tag{6.91}$$

$$\text{(ii)}\quad A + B \xrightarrow{k_1} L + M \xrightarrow{k_2} N + P \tag{6.92}$$

As in the case of parallel reactions, only the first order reactions given by Eq. (6.91) can be treated exactly. For higher order and mixed order consecutive reactions, the solution becomes quite complicated. Let us consider the example of reaction Eq. (6.91) in which there are two consecutive first order reactions. We can write

$$\frac{d[A]}{dt} = -k_1 [A] \tag{6.93}$$

$$\frac{d[B]}{dt} = k_1 [A] - k_2 [B] \tag{6.94}$$

$$\frac{d[C]}{dt} = k_2 [B] \tag{6.95}$$

Such a scheme indicates that B is **an intermediate unstable molecule and the** overall reaction is A → C.

The integration of Eq. (6.93) gives

$$[A] = [A_0]\, e^{-k_1 t} \tag{6.96}$$

where $[A_0]$ is the initial concentration of A.

Substituting the value of A in Eq. (6.94) we get

$$\frac{d[B]}{dt} = k_1 [A_0]\, e^{-k_1 t} - k_2 [B]$$

or

$$\frac{d[B]}{dt} + k_2 [B] = k_1 [A_0]\, e^{-k_1 t} \tag{6.97}$$

Equation (6.97) is a first order linear differential equation. The general solution of this equation may be written as the sum of the complementary function and the particular integral

$$[B] = [B_0]\, e^{-k_2 t} + \frac{k_1 [A]_0}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t}) \tag{6.98}$$

Remembering that

$$[A_0] + [B_0] + [C_0] = [A] + [B] + [C] = \text{const.}$$

The solution of Eq. (6.95) for [C] may be now easily written as

$$[C] = [A_0] - [A] + [B_0] - [B_0] + [C_0] \tag{6.99}$$

On rearranging the terms and by substituting the value of [A] and [B] from Eqs. (6.96) and (6.98) we get

$$[C] = [A_0]\, 1 - ek^{1-t} + \frac{k_1}{k_2 - k_1}(e^{-k_1 t} - e^{-k t})$$

$$+ [B_0]\,(1 - e^{-k_2 t}) + [C_0] \tag{6.100}$$

The concentration of A for such consecutive reactions will decrease exponentially. The concentrations of B and C will depend on the relative values of k_1 and k_2. The concentration of B will increase, attain a maximum value and will start decreasing unless $k_1 [A_0] \ll k_2 [B_0]$, while the concentration of C will increase with time.

An actual combustion process consists of many first, second, or mixed first-second order reactions. The reaction scheme also has all types of parallel consecutive, and reversible reactions. Almost every reaction has a unique scheme and that too varies with the change of different parameters, e.g., initial concentration, pressure, temperature, etc. The kinetics of simple hydrogen-oxygen reaction dealt with in the next chapter will give an idea of how complicated the mathematics of kinetics is and how to use the available experimental and theoretical data.

6.4 CHAIN REACTIONS

Bodenstein is credited with the discovery of chain reactions in 1913.[3] He found that the quantum yields of some photochemical reactions were very high. According to the Stark Einstein photochemical law, not more than one or two molecules would react per every quantum absorbed.[4,5] However, Bodenstein's conclusion was that the primary photochemical step was followed by a long chain of chemical conversions involving many molecules of primary compounds. In 1918, Nernst studied the reaction between chlorine and hydrogen and proposed the mechanism that the active centres in this reaction are free chlorine and hydrogen atoms.[6] These active centres of valence unsaturated free chlorine and hydrogen atoms are formed in the course of the reaction. Later, Bodenstein studied in detail the reaction of hydrogen with chlorine and bromine. A further development of the chain theory was the discovery of branched chain reactions by Semenoy and Hinshelwood[7]. The theory implies that, on an average, one step of a branched chain reaction involves the formation of more than one new active centre per every disappearing centre. Thus the rate of the generation of active centres will exceed the rate of their consumption in the course of a branched reaction.

The mechanism of a chain reaction can be understood by the scheme given in Fig. 6.4. According to this scheme an active centre (A) is first formed by the reaction path (0) which represents the thermal or external generation of chain carriers. These chain carriers may be free atoms, radicals, or molecules. The active centres so formed can take one of the two paths: by path (2) by which the active centre is deactivated, and by path (1) by which it yields a reaction product C and a certain number ϵ of active centres A. These active centres will again follow one of the two routes, i.e., path (2) for deactivation and path (1) to give products and (ϵA) active centres.

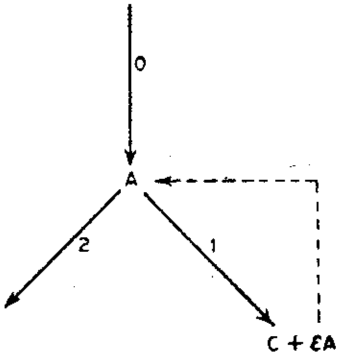


Fig. 6.4 Schematic representation of a chain reaction.

Let us assume ν_1 as the frequency or specific rate of reaction (1) and ν_2 that of reaction (2). Then the ratio of the regeneration of the active centres to that of their consumption may be written as

$$\frac{\epsilon \nu_1}{\nu_1 + \nu_2} = \epsilon w_1 \tag{6.101}$$

where, $w_1 = \frac{\nu_1}{\nu_1 + \nu_2}$ is called the probability for reaction (1). The

probability of reaction (2) will be

$$w_2 = \nu_2/(\nu_1 + \nu_2), \text{ and } w_1 + w_2 = 1.$$

For an unbranched chain reaction,

$$\epsilon \nu_1 \leqslant (\nu_1 + \nu_2), \text{ i.e., } \epsilon w_1 \leqslant 1$$

and for a branched chain reaction $\epsilon\nu_1 > (\nu_1 + \nu_2)$, i.e., $\epsilon w_1 > 1$.

An unbranched chain reaction may be represented by a zig-zag line as shown in Fig. 6.5(a), each straight horizontal line representing one chain cycle and a number of such cycles representing a chain length. Figures 6.5(b) and 6.5(c) represent branched chain reactions. Figure 6.5(c) represents branching in each step while Fig. 6.5(b) shows where the chances of branching in each step is less than one. For Fig. 6.5(b), $2 > \epsilon > 1$ or $1 > \delta > o$, and for Fig. 6.5(c), $\epsilon \geqslant 2$ or $\delta \geqslant 1$, where δ is defined as the probability of branching per chain step, $\delta = \epsilon - 1$. The reaction of hydrogen with halogens is a typical unbranched chain reaction, while the reaction of hydrogen and oxygen is an example of a branched chain reaction.

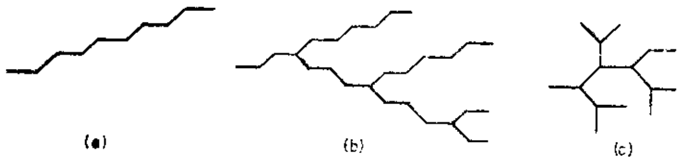


Fig. 6.5 Schematic representation of (a) an unbranched, (b) a branched, and (c) a continuously branched chain reaction.

Kinetics of Chain Reactions

The mechanism of a chain reaction may be divided into three steps.

1. *Initiation.* Formation of active centre or chain carrier by path (0)
2. *Propagation.* Formation of products and more chain carriers by path (1)
3. *Termination.* Deactivation of chain carriers by path (2).

If (A) is the concentration of active centres and [C] that of the reaction products: w_0 the rate of primary generation of active centres by path (0) and W the rate of the reaction, we may write the following equations:

$$\frac{d[A]}{dt} = w_0 + \nu_1 \epsilon [A] - \nu_1 [A] - \nu_2 [A]$$

or
$$\frac{d[A]}{dt} = w_0 - [A]\{\nu_1 (1-\epsilon) + \nu_2\} \tag{6.102}$$

and
$$w_1 = \frac{d[C]}{dt} = \nu_1 [A] \tag{6.103}$$

Assuming that the temperature is constant (i.e., the reaction is isothermal) and that w_0, ν_1 and ν_2 also remain constant, we obtain by integrating Eq. (6.102)

$$[A] = [A_o]\, e^{(-t/\tau)} + W_0\, \{1 - e^{(-t/\tau)}\} \tag{6.104}$$

where τ is the "life time" of the chain carrier, i.e., the average time before a chain carrier is destroyed by either path (1) or path (2) of the reaction scheme given in Fig. (6.4). It is given by

$$\tau = \frac{1}{\nu_1 (1 - \epsilon) + \nu_2} \tag{6.105}$$

and $[A_o]$=initial concentration of the active centres. If at $t = 0$, $[A_0] = 0$. Then Eq. (6.104) reduces to

$$[A] = W_0\, \tau\, \{1 - e^{-t/\tau}\} \tag{6.106}$$

Eqs. (6.103) and (6.106) give

$$W = \frac{d[C]}{dt} = \nu_1 W_0 \tau \{1 - e^{-t/\tau}\} \tag{6.107}$$

Equations (6.106) and (6.107) show that if t approaches zero, the concentration of the chain carriers will increase following the law of proportionality, i.e.,

$$W = \nu_1 W_0\, t \tag{6.108}$$

and

$$[A] = W_0\, t \tag{6.109}$$

Any further variations in W and [A] will depend on the type of the reaction, i.e., whether the reaction is unbranched or branched.

Unbranched Chain Reactions

For the unbranched chain reaction, $\delta = \epsilon - 1 = 0$ or $\epsilon = 1$.
Therefore, from Eq. (6.105)

$$\tau = 1/\nu_2 \tag{6.110}$$

It is obvious that for the unbranched chain reaction, the concentration of active centres will initially increase according to the law given by Eqs. (6.108) and (6.109), and after a sufficiently long period of $(t \gg \tau)$, the concentration [A] will assume a steady state maximum value.

At such a time, $\frac{d[A]}{dt} = 0$

Therefore, from Eq. (6.102)

$$W_0 - [A]\,[\nu_1 (1 - \epsilon) + \nu_2] = 0$$

Therefore $\qquad W_0 - [A_{max}]\, \nu_2 = 0 \qquad$ since $\epsilon = 1$

or

$$[A_{max}] = \frac{W_0}{\nu_2} \tag{6.111}$$

Therefore, from Eq. (6.103)

$$W_{max} = W_0 \frac{\nu_1}{\nu_2} \tag{6.112}$$

The chain length ν is defined as the ratio $W : W_0$, thus we have for an unbranched chain reaction from Eq. (6.112)

$$\nu = \frac{\nu_1}{\nu_2} \tag{6.113}$$

In actual practice W does not remain constant after attaining the maximum value, but will start decreasing. This is because the concentration of the reactants and correspondingly that of the chain carriers gradually starts decreasing. Therefore, the reaction rate also starts decreasing. However, if the products are continuously replaced by the reactants, the process will assume a steady rate. Figure 6.6 gives an idea of the steady state unbranched chain reaction rate and of the actual unbranched chain reaction rate.

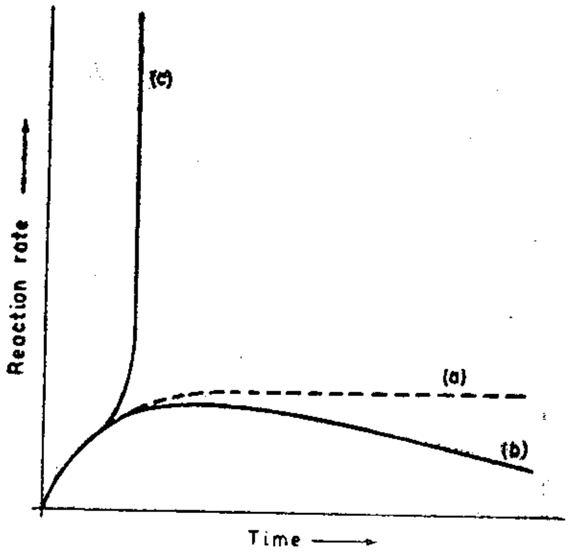


Fig. 6.6 Time dependence of reaction rate for (a) a steady state unbranched, (b) an actual unbranched, and (c) a branched chain reaction.

Branched Chain Reactions

For branched chain reaction $\epsilon w_1 > 1$. Therefore, Eq. (6.102) can be rewritten in the form

$$\frac{d[A]}{dt} = W_0 + (\epsilon w_1 - 1)(\nu_1 + \nu_2)[A]$$

or

$$\frac{d[A]}{dt} = W_0 + \phi[A] \tag{6.114}$$

where,

$$\phi = (\epsilon W_1 - 1)(\nu_1 + \nu_2) \tag{6.115}$$

Assuming that at $t=0$, $[A_0]=0$, and that the reaction proceeds under isothermal conditions so that ν_1, ν_2, and W_0 are constants, we may integrate and write Eq. (6.114) as

$$[A] = \frac{W_0}{\phi}[e\phi^t - 1] \tag{6.116}$$

Therefore, from Eq. (6.103)

$$W = \frac{W_0\,\nu_1}{\phi}[e\,\phi^t - 1] \tag{6.117}$$

From Eq. (6.117), it follows that the rate of a branched chain near $t=0$ is given by

$$W = W_0\,\nu_1\,t \tag{6.118}$$

and when t assumes a high value, Eq. (6.117) can be written as

$$W = \frac{W_0\,\nu_1}{\phi}\,e\phi^t \tag{6.119}$$

i.e., the reaction will obey the exponential law, theoretically derived by Semenov. The exponential auto-catalytic acceleration of the reaction is a characteristic feature of branched chain reactions. Figure 6.6(c) shows the reaction rate with increasing time. It is seen that for a branched chain reaction, the reaction rate increases so rapidly that after some time an explosion takes place. This explosion is not a thermal explosion because it has been assumed that the reaction takes place isothermally.

Degenerate Branching

The change of sign in the value of ϕ can be accounted for by a change in the ratio of branching to termination rates. The value of ϕ is given by the expression:

$$\phi = (\nu_1 + \nu_2)(\epsilon W_1 - 1)$$

where,

$$\epsilon = \delta + 1 \text{ and } W_1 = \nu_1/(\nu_1 + \nu_2)$$

Therefore, we may write

$$\phi = (\nu_1 + \nu_2)\{(\delta + 1)(\nu_1/(\nu_1 + \nu_2) - 1\}$$

$$= (\nu_1 + \nu_2)\left(\frac{\nu_1\delta + \nu_1 - \nu_1 - \nu_2}{(\nu_1 + \nu_2)}\right)$$

or

$$\phi = \nu_1\,\delta - \nu_2 \tag{6.120}$$

This means that the value of ϕ depends upon the relative magnitudes of $\delta\nu_1$ and ν_2. If $\delta\nu_1 > \nu_2$, ϕ is +ve which results in an explosion with accumulation of some chain carriers in the course of the reaction. When $\delta\nu_1 < \nu_2$, ϕ is −ve and Eq. (6.119) becomes the same as that for a linear chain reaction. The rate of linear chain reaction assumes its steady state maximum value for $\phi=0$.

Sometimes, it is found that the value of ϕ is initially positive but decreases to zero, and finally assumes an increasingly negative value as the reaction proceeds.

When there is an accumulation of reaction products, they enter into side reactions with the chain carriers in the system. The system initially appears to exhibit an increase in the reaction rate, then it becomes almost constant for a short period and finally decreases. An explosion does not occur under such a condition and this phenomenon is generally referred to as "degenerate explosion". Figure 6.7 shows a rate curve which is exhibited in reactions leading to degenerate explosion.

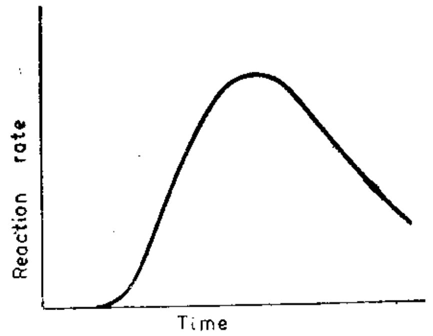


Fig. 6.7 Reaction rate for a degenerate branching reaction.

This phenomenon of degenerate branching can be explained for a case where the reactants form an unstable intermediate compound with a fairly long half life. This intermediate compound then can decompose to either give unreactive stable molecules or produce a carrier. Initially when the concentration of the intermediate compound increases, there appears to be no reaction but with further increase in its concentration, the decomposition also starts resulting in an increase in the concentration of chain carriers. After some time, as the concentration of the intermediate compound starts falling, the reaction rate also reduces. The coal flames appearing during the oxidation of hydrocarbons are a typical example of degenerate branching.

6.5 THEORIES OF REACTION KINETICS

The basic theories of reaction kinetics are based on the assumption that molecular collisions are in one way or another responsible for the occurrence of the reaction. Since we observe reactions which take place with half lives which range from milliseconds to days, it is at once obvious that all molecular collisions cannot lead to a reaction. For example, in nitrogen at 1 atm pressure and 25°C temperature, a single atom undergoes 6.5×10^9 collisions per second with its neighbours. Therefore, for even the most rapid observable reactions, only an extremely small fraction of the collisions is effective in causing a reaction.

Another experimentally observed fact is that an increase of temperature almost invariably increases the rate of a chemical reaction to a marked extent. For homogeneous processes, the specific rate may be doubled or trebled for each 10°C rise of temperature. This marked influence of temperature cannot be attributed to an increase in the frequency of collisions because the latter will increase only by about 2% for a rise of 10°C at ordinary temperature. An acceptable theory of reaction rates must provide a satisfactory explanation of this increase in the reaction rate with temperature.

The Arrhenius Equation

In 1889 Arrhenius[8] suggested an experimental formulation of the effect of temperature on rates in the following form:

$$k = A\ e^{-E/RT} \tag{6.121}$$

where k is the reaction rate constant at some temperature, T is the absolute temperature, R is the universal gas constant, and A and E are the empirical constants.

Arrhenius derived the relation by the the consideration of an equilibrium process

$$\mathrm{A} + \mathrm{B} \underset{\overleftarrow{k}}{\overset{\overrightarrow{k}}{\rightleftharpoons}} \mathrm{C} + \mathrm{D} \tag{6.122}$$

The equilibrium is established by equating the rates of two opposing reactions

$$\overrightarrow{k}\,[\mathrm{A}]\,[\mathrm{B}] = \overleftarrow{k}\,[\mathrm{C}]\,[\mathrm{D}] \tag{6.123}$$

The equilibrium constant K is given by

$$K = \frac{[\mathrm{C}]\,[\mathrm{D}]}{[\mathrm{A}]\,[\mathrm{B}]} = \frac{\overrightarrow{k}}{\overleftarrow{k}} \tag{6.124}$$

The law for the variation of equilibrium constant is

$$\frac{d\,(\ln K)}{dT} = \frac{\Delta H}{RT^2} \tag{6.125}$$

where H is the heat of the reaction.

Equation (6.125) may be written as

$$\frac{d\,(\ln \overrightarrow{k})}{dT} - \frac{d\,(\ln \overleftarrow{k})}{dT} = \frac{\Delta H}{RT^2} \tag{6.126}$$

Arrhenius suggested that ΔH could be split into two parts $\overrightarrow{E}$ and $\overleftarrow{E}$ such that

$$\Delta H = \overrightarrow{E} - \overleftarrow{E}$$

Equation (6.126) may be written as

$$\frac{d\,(\ln \overrightarrow{k})}{dT} - \frac{d\,(\ln \overleftarrow{k})}{dT} = \frac{\overrightarrow{E}}{RT^2} - \frac{\overleftarrow{E}}{RT^2} \tag{6.127}$$

He further suggested that Eq. (6.127) could be separated into two equations

$$\frac{d\,(\ln \overrightarrow{k})}{dT} = \frac{\overrightarrow{E}}{RT^2}$$

and

$$\frac{d\,(\ln \overleftarrow{k})}{dT} = \frac{\overleftarrow{E}}{RT^2}$$

or, in general,

$$\frac{d\,(\ln k)}{dT} = \frac{E}{RT^2} \tag{6.128}$$

The integration of Eq. (6.128) gives

$$\ln k = -\frac{E}{RT} + A$$

or

$$k = A\ e^{-E/RT} \tag{6.121}$$

This is called the Arrhenius equation.

According to Eq. (6.121), a plot of $\ln k$ versus $1/T$ should give a straight line with a slope of $-E/R$ or $-E/2.303\ R = E/4.57$, if common logarithms are used, and an intercept of $\ln A$ (Fig. 6.8). The Arrhenius equation is widely applicable, not only to homogeneous gas reactions, but also to reactions in solution and to heterogeneous processes. It, however, frequently fails for chain reactions. The energy E, called the "energy of activation", is of great theoretical importance. It is determined from the measurements of specific rates at two or more temperatures.

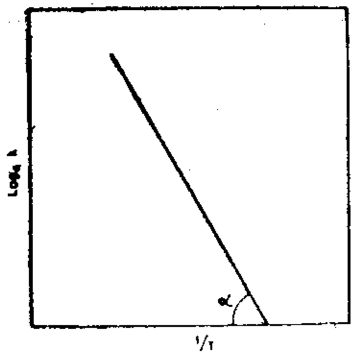


Fig. 6.8 Effect of temperature on reaction rate constant.

On an experimental basis, it has been found that both E and A are not totally independent of temperature. For a wide range of temperatures, it is found that the plot of $\log_e k$ vs $1/T$, instead of being a straight line, assumes a shape such that we can divide the plot in more than one segment of straight lines with different slopes. At high temperatures, the slope increases, indicating that the value of E changes with temperature. The value of A is given by the intercept of the straight line on the y-axis.

Activation Energy

To explain Eq. (6.121), Arrhenius postulated that in every system an equilibrium exists between the normal and "active" species, and that only the latter could take part in a chemical reaction. According to him, the heat of formation of such active molecules is equal to or greater than E of Eq. (6.121). This minimum energy which a molecule must possess to be active is called the activation energy.

The marked influence of temperature on the reaction rate is thus explained, because a rise of temperature will favour the formation of active molecules. Though the number of collisions between molecules is only slightly affected, the concentration of active molecules can be doubled by a 10°C rise of temperature so that the rate of reaction is greatly increased.

It follows that the overall reaction can be looked upon as taking place by the following two step process:

$$\text{Reactants} \rightarrow \text{Activated Reactants} \rightleftharpoons \text{Products}$$

The energy change for the formation of activated reactants is $\overrightarrow{E}$ and for the second part of the process $\overleftarrow{E}$. These energy changes are illustrated for both exothermic and endothermic reactions in Fig. (6.9). It may be noted that the Arrhenius theory gives no information regarding the numerical values of activation energies, although it is clear from Fig. (6.9) that $\overleftarrow{E}$ must be greater than ΔH for an endothermic reaction and $\overleftarrow{E}$ greater than the absolute value of ΔH for an exothermic reaction, where ΔH is the

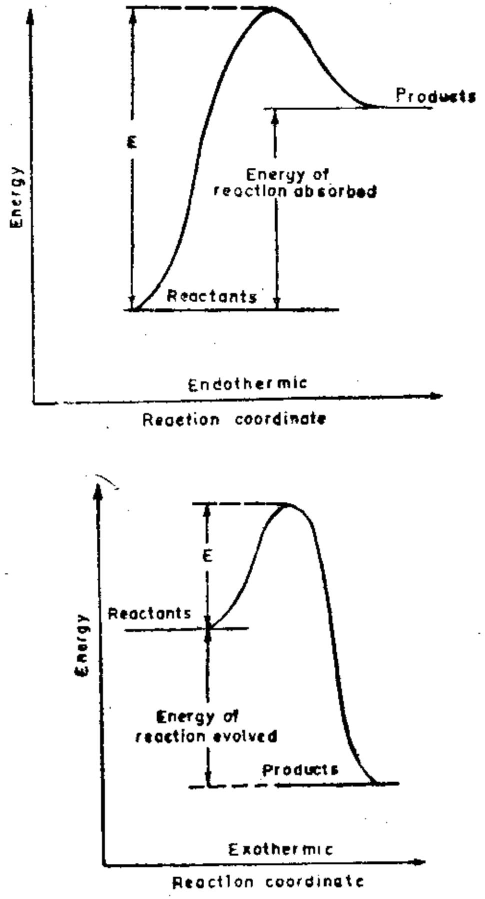


Fig. 6.9 Reaction paths exothermic and endothermic reaction showing activation energy.

enthalpy change of reaction (and is taken to be negative for an exothermic reaction). It is apparent that $\Delta H = \vec{E} - \overleftarrow{E}$.

Thus the activation energy of a chemical reaction may be looked upon as the energy of the highest point of the reaction path over a potential surface connecting reactants and products.

If we assume that the curve gives the path of the reaction, the reactant will have to rise to an energy level given by peak of the path, and then only it can go to the product side. If H_{react} is the average energy of the reactant molecules, only those molecules of the reactant will result in products which have an energy equal to or greater than $H_{react} + E$. So for any exothermic reaction, $E \geqslant 0$ and for an endothermic reaction, $E \geqslant \Delta H$. For a reversible reaction as suggested by Arrhenius

$$\Delta H = \vec{E} - \overleftarrow{E}$$

In a physical sense we can say that only those collisions will result in reaction products which have a kinetic energy greater than the value of E.

Example 6.3

For a second order reaction the values of the rate constant k at the given temperatures are as follows:

Temperature T, °C	$k \times 10^2$ l/mol-s
330	78
355	180
380	410
385	475

Calculate the activation energy of reaction E and compare the result with the value determined graphically.

Solution

The Arrhenius equation is written as

$$k = A\, e^{-E/RT}$$

This equation is applicable to experimental data for reactions of all orders. The activation energy of reaction E can be calculated directly from the values of the reaction rate constants at two different temperatures.

From the above equation we can write

$$\text{At temperature } T_1\text{: } \log_e k_1 = \log_e A - \frac{E}{RT_1}$$

$$\text{At temperature } T_2\text{: } \log_e k_2 = \log_e A - \frac{E}{RT_2}$$

Subtracting the two equations we write

$$\log_e \frac{k_1}{k_2} = \frac{E}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

After rearrangement and conversion to logarithms to the base 10 gives

$$E = \frac{2.3\, R T_1 T_2}{(T_1 - T_2)} \log_{10} \frac{k_1}{k_2}$$

Converting the temperatures °C in the given table to K we write:

T (K)	$k \times 10^2$ (l/mol-s)
603	78
628	180
653	410
658	457

Selecting the values of k at temperatures of 628 K and 653 K and substituting the values in the above equation for E

$$E = \frac{2.3 \times 1.987 \times 628 \times 653}{653 - 628} \log_{10} \frac{410 \times 10^{-2}}{180 \times 10^{-2}}$$
$$= 26{,}800 \text{ cal/mol}$$

Compare the answer with the value of E determined graphically as follows. The values of $\log_{10} k$ versus $1/T$ are plotted on a graph paper. This plot gives a straight line with a slope of

$$-E/2.3\,R = -5.75 \times 10^3.$$

The value of E is therefore, equal to

$$E = 2.3 \times 1.987 \times 5.75 \times 10^3$$
$$= 26{,}200 \text{ cal/mol.}$$

Collision Theory

The collision theory is the earlier theory of reaction rates, originally advanced by Lewis in 1918[9]. According to this theory, two species A and B can react with each other only if they collide. A collision means that the centres of the reactant molecules must come close enough to have a distance equal to the sum of their gas-kinetic radii. The rate of reaction will, therefore, be related to the number of collisions between the two species A and B. From the kinetic theory of gases, the number of collisions, Z_{AB} is given by:

$$Z_{AB} = n_A\, n_B \left(\frac{\sigma_A + \sigma_B}{2}\right)\left(\frac{8\pi kT}{\mu}\right)^{\frac{1}{2}} \qquad (6.129)$$

where Z_{AB} is the number of collision per cm^3 per s

n_A, n_B are the number of A and B molecules per cm^3

σ_A, σ_B are the molecular diameters of A and B.

$\mu = \frac{m_A\ m_B}{m_A + m_B}$ is the "reduced mass" of A and B.

$\mathbf{k}$ = Boltzmann constant.

According to this expression, the relation between the reaction rate and the concentration of reactants is the same as that given by the law of mass action. But the rate of reaction given by this expression is much higher than observed practically for many reactions. The effect of temperature on the reaction rate by this expression turns out to be proportional to $\sqrt{T}$ which is not the observed effect for any reaction as given by the Arrhenius equation. The expression can be modified by assuming that only those collisions are effective which possess a kinetic energy greater than a critical value.

Now, according to the Maxwell-Boltzmann theory, in any system which has a large number of molecules N_0, the number of molecules N which has a kinetic energy greater than E ($E = \frac{1}{2} mV^2$, where m is the molecular weight and V the moleucular velocity) is given by

$$\frac{N}{N_0} = D\, e^{-E/RT} \tag{6.130}$$

where D is a constant.

Now if we make the assumption that only those molecules take part in a reaction which have a kinetic energy greater than E, we can write the reaction rate for the reaction between molecules A and B as

$$-\frac{d[A]}{dt} = k\,[A]\,[B]$$

or

$$-\frac{d\,[A]}{dt} = n_A\, n_B \left(\frac{\sigma_A + \sigma_B}{2}\right)\left(\frac{8\pi \mathbf{k} T}{\mu}\right)^{\frac{1}{2}} e^{-E/RT} \tag{6.131}$$

or we may write the rate constant k as

$$k = Z\, e^{-E/RT} \tag{6.132}$$

where, $Z = \left(\frac{\sigma_A + \sigma_B}{2}\right)^2 \left(\frac{8\pi \mathbf{k} T}{\mu}\right)^{\frac{1}{2}}$ is called the collision number.

Equation (6.132) can be written as

$$k = Z'\, T^{1/2}\, e^{-E/RT} \tag{6.133}$$

where Z is a temperature independent term. Now Eq. (6.132) correctly predicts the effect of temperature on the reaction rate.
It is found that the reaction rate calculated from Eq. (6.132) turns out to be generally quite high. Therefore, the expression is modified to:

$$k = PZ\, e^{-E/RT} \tag{6.134}$$

where P is called the "steric factor" or probability factor, which has a value less than unity.

The explanation for multiplying with such a factor is that all collisions with sufficient energy are not capable of reaction, unless the collisions between the molecules takes place along a particular axis. Thus this factor takes into account the orientation of a molecule before collision. The factor P may have a value as low as 10^{-8} for a complex molecule while for a simple molecule it may have a value of about 0.1

Before proceeding further it is well to mention that the fraction of collisions having an energy greater than E given by the expression $e^{-E/RT}$, is true for collisions involving only two degrees of freedom. For complex molecules having n degrees of freedom for the activation energy E, the fraction is given as:

$$\frac{e^{-E/RT}\,(E/RT)^{n/2-1}}{\left(\frac{n}{2} - 1\right)} \tag{6.135}$$

Potential Energy Surface

Arrhenius pointed out that for any reaction to occur, a potential barrier has to be overcome. Unless some critical amount of energy is available a reaction will not take place, even if the collision of two molecules occurs with proper orientation.

Marcelin[10] suggested that the activation energy can be treated conveniently in terms of the concept of potential energy surface, which results when the potential energy is plotted against suitable bond distances and angles. For a reaction between two atoms, their nuclii distances versus potential energy will give a curve on the x-y plot. But if three atoms are involved, say in a reaction of the type

$$\text{A+B—C} \rightarrow \text{A—B+C} \tag{6.136}$$

The system will require three distances A-B, B-C, and A-C to be represented with the potential energy co-ordinate, and will need a four dimensional co-ordinate system. If we fix a suitable angle, say A-B-C=180° and represent distances A-B and B-C in a three dimensional co-ordinate system, a suitable model as given in Fig. 6.10 can be constructed. On face 1276, the curve shows the potential energy curve for molecule A-B. Point R corresponds to the dissociation of molecule and point Q to the classical ground state. It is assumed that the distance B-C is large enough not to disturb A-B potential curve. Similarly, on face 2347, the potential energy curve for B-C is shown. A section through the minimum path is shown in Fig. 6.11. This section is known as the potential energy profile.

The reaction path is represented on the potential energy surface from P to Q. The system will travel along a path where the energy is not too high. Calculations show that on this surface there are two valleys which

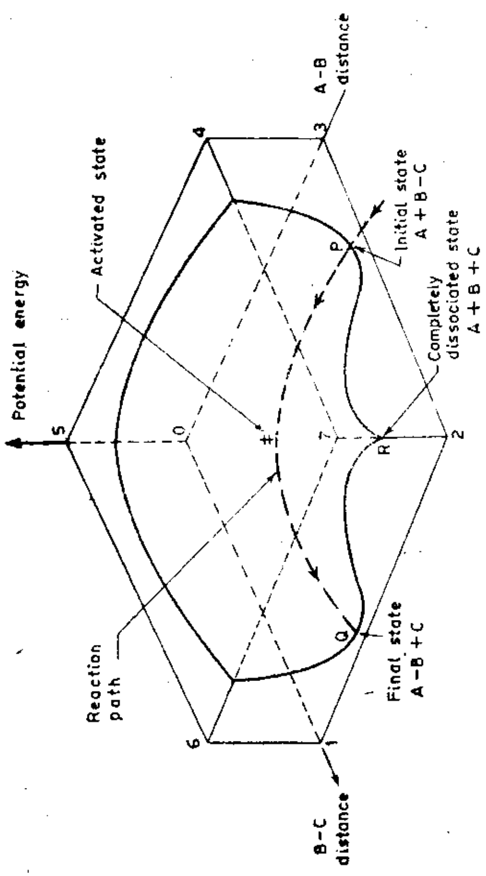


Fig. 6.10 Variation of potential energy for a triatomic molecule as a function of the inter-nuclear distance (from K.J. Laidler, *Theories of Chemical Reaction Rates*, McGraw-Hill, 1969).

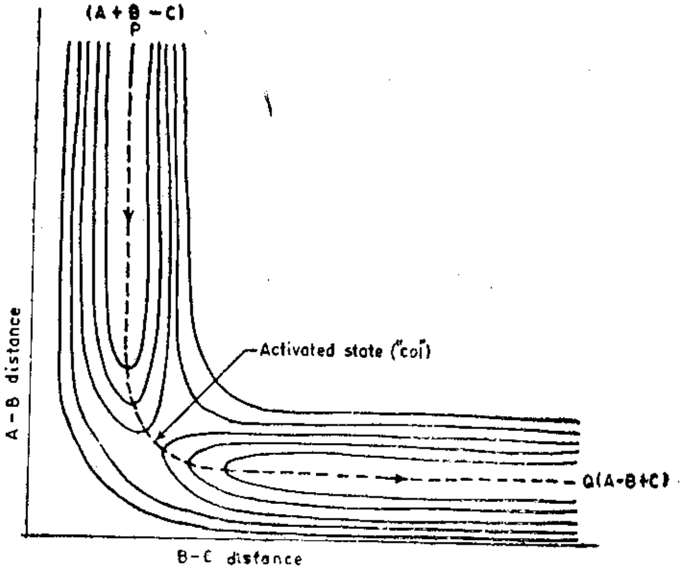


Fig. 6.11 A contour diagram indicating minimum energy path for a reaction A + B — C → A — B + C (from K.J. Laidler, *Theories of Chemical Reaction Rates*, McGraw-Hill, 1969).

meet in the interior at "Col" or "Saddle point". This is shown in Figs. (6.10) and (6.11).

A section through the minimum path is shown in Fig. 6.12 as potential energy profile. The system corresponding to the small area around the saddle point is known as the "activated complex" and is denoted by symbol [‡]. The potential energy surface for a reaction involving more than three atoms is a hyper surface in multidimensional space.

Activated Complex Theory

In the molecular collision theory, molecules were assumed to be hard spheres. This resulted in considerable error in the results obtained. It was found that a satisfactory theory could be formulated by considering an activated complex which is a molecular system whose configuration corresponds to the saddle point region on the potential energy surface. In this theory, the activated complex is regarded as being in equilibrium with the reactants. The activated complex theory is also named as the absolute rate theory, theory of absolute reaction rates, or the transition state theory.

The Equilibrium Hypothesis

The activated complex theory involves the hypothesis that even when the reactants and products are not in equilibrium, then the activated

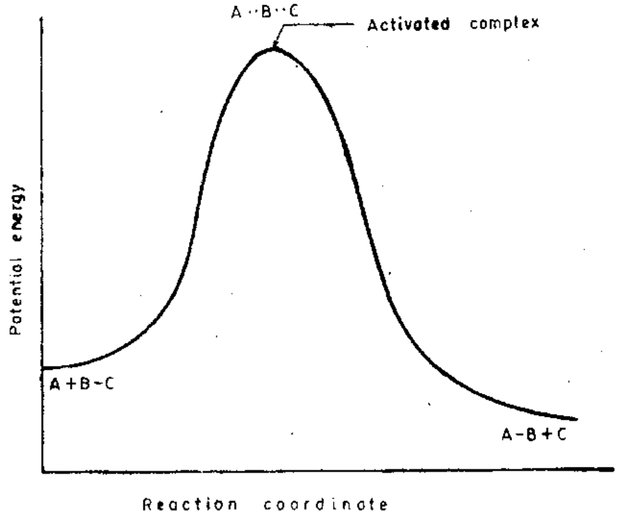


Fig. 6.12 Potential energy profile for a reaction A + B — C → A — B + C (from K.J. Laidler, *Theories of Chemical Reaction Rates*, McGraw-Hill, 1969).

complex is in equilibrium with the reactants. However, for simplicity we consider a reaction

$$A + B \rightleftharpoons C + D \tag{6.137}$$

After it has attained equilibrium with the activated complex X, it is in equilibrium with the concentrations of A and B.

The Rate Equation

The rate equation can be derived by different considerations but the results obtained are the same. We take the derivation with the assumption that the motion of the activated complex over the saddle point is a very loose vibration. For equilibrium between the reactants and activated complexes, we may write

$$K^{\ddagger} = \frac{[X^{\ddagger}]}{[A]\,[B]} \tag{6.138}$$

where $K^{\ddagger}$ is the equilibrium constant which we may write in terms of the appropriate partition functions

$$\frac{[X^{\ddagger}]}{[A]\,[B]} = \frac{Q}{Q_A\,Q_B} e^{-E_0/RT} \tag{6.139}$$

The partition function must be evaluated with respect to the zero point levels of the respective molecules. E_0 the difference between the zero point energy per mole of the activated complexes and that of the reactants.

Partition functions can be factorized into its components of translational, rotational, vibrational, and electronic energy as shown in Table 6.2 with their values. For a molecule of N atoms, there will be $3N_A$ partition functions, of which three are for translational motion, three for rotational motion (or two for a linear molecule) and therefore, $3N_A$—6 for vibrational motion ($3N_A$—5 for a linear molecule).

TABLE 6.2 Partition Functions

(from K.J. Laidler, *Chemical Kinetics*, McGraw-Hill, 1965)

Motion	*Degrees of freedom*	*Partition function*	*Order of magnitude*
Translational	3	$\frac{(2\pi m\mathbf{k}T)^{3/2}}{\mathbf{h}^3}$ (per unit volume)	10^{24}-10^{25}
Rotational (linear molecule)	2	$\frac{8\pi^2 I\mathbf{k}T}{\mathbf{h}^2}$	10-10^2
Rotational (non-linear molecule)	3	$\frac{8\pi^2 (8\pi^3 ABC)^{1/2} (\mathbf{k}T)^{3/2}}{\mathbf{h}^3}$	10^2-10^3
Vibrational (per normal mode)	1	$\frac{1}{1-e^{-h\nu/kT}}$	1-10
Restricted rotation	1	$\frac{(8\pi^3 I'\,\mathbf{k}T)^{1/2}}{\mathbf{h}}$	1-10

where m = Mass of the molecule
I = Moment of inertia of a linear molecule
A, B, C = Moment of inertia of nonlinear molecules about the three axes at right angle to one another
I' = Moment of inertia for restricted rotation
ν = Normal mode vibrational energy
$\mathbf{k}$ = Boltzmann constant
T = Temperature, K
$\mathbf{h}$ = Planck's constant

The same is true for the activated complex which consists of $N_A + N_B$ atoms. This gives $3(N_A + N_B)$ —6 vibrational terms if the molecule is nonlinear. One of these vibrational factors is of a different character from the rest, since it corresponds to a very loose vibration and thus allows the complex to dissociate into products C and D. for this one degree of freedom, one may, therefore, employ, in place of the ordinary factor $(1-e^{-h\nu/kT})^{-1}$ the value of this function calculated in the limit at which ν tends to zero. This is evaluated by expanding the exponential and taking only the first term.

$$\lim_{\nu \to 0} \frac{1}{1-e^{-h\nu/kT}} = \frac{1}{1-(1-h\nu/kT)} = \frac{kT}{h\nu} \tag{6.140}$$

The equilibrium constant may, therefore, be expressed by including the term $\frac{kT}{h\nu}$ and replacing $Q'^{\ddagger}$ as $Q^{\ddagger}$ which now refers only to $3(N_A + N_B) - 7$ degrees of vibrational freedom, [$3(N_A + N_B) - 6$ for a linear complex] where N_A and N_B are the numbers of atoms in the activated complex. The resulting expression is

$$\frac{[X^{\ddagger}]}{[A]\,[B]} = \frac{(Q_{\ddagger}\, kT/h\nu)}{Q_A\, Q_B}\, e^{-E_0/RT} \tag{6.141}$$

or

$$\nu[X^{\ddagger}] = [A]\,[B]\, \frac{kT}{h} \frac{Q_{\ddagger}}{Q_A Q_B}\, e^{-E_0/RT} \tag{6.142}$$

Here ν is the frequency of vibration of the activated complexes and is, therefore, the frequency of decomposition. The left hand side of the equation therefore, represents the rate of decomposition, i.e., the rate of reaction or

$$v = [A]\,[B]\, \frac{kT}{h} \frac{Q_{\ddagger}}{Q_A Q_B}\, e^{-E_0/RT} \tag{6.143}$$

If the activated complex is made of a molecules of A and b molecules of B, then the rate of reaction will be given by

$$v = [A]^a\,[B]^b\, \frac{kT}{h}\, \frac{Q_{\ddagger}}{Q_A\, Q_B}\, e^{-E_0/RT} \tag{6.144}$$

Therefore, the reaction rate constant

$$k = \frac{kT}{h}\, \frac{Q_{\ddagger}}{Q_A\, Q_B} e^{-E_0/RT} \tag{6.145}$$

$\frac{kT}{h}$ has the dimensions of frequency and its value is about 6×10^{12} s^{-1} at 300 K.

Thermodynamical Formulation of Reaction Rates

If we wish to express Eq. (6.145) in terms of a thermodynamic function instead of a partition function, let us consider the reaction

$$A + B \rightleftharpoons X^{\ddagger}$$

Therefore,

$$K^{\ddagger} = \frac{[X^{\ddagger}]}{[A]\,[B]} = \frac{Q_{\ddagger}}{Q_A\, Q_B}\, e^{-E_0/RT}$$

Now if we assume $Q^{\ddagger}$ as $Q_{\ddagger}$ and $K^{\ddagger}$ to be a special type of equilibrium constant then

$$K^{\ddagger} = \frac{[X^{\ddagger}]}{[A]\,[B]} = \frac{Q_{\ddagger}}{Q_A\, Q_B}\, e^{-E_0/RT} \tag{6.146}$$

By comparing Eqs. (6.145) and (6.146), we obtain

$$k = \frac{kT}{h} K^{\ddagger} \tag{6.147}$$

If we express $K^{\ddagger}$ in terms of the Gibbs free energy, then

$$k = \frac{kT}{h}\, e^{-\Delta G^{\ddagger}/RT} \tag{6.148}$$

as $\Delta G = \Delta H - T\,\Delta S$

Therefore,

$$k = \frac{kT}{h}\, e^{\Delta S_{\ddagger}/R}\, e^{-\Delta H_{\ddagger}/RT} \tag{6.149}$$

If k is expressed in litres mole^{-1} s^{-1}, the standard state for free energy and entropy of activation is 1 mole/litres.

If we want to express Eq. (6.149) in terms of the experimental value of activation energy instead of $\Delta H^{\ddagger}$, then differentiating the logarithmic form of Eq. (6.147) we get

$$\frac{d \ln K^{\ddagger}}{dT} = \frac{1}{T} + \frac{d \ln K^{\ddagger}}{dT} \tag{6.150}$$

Also, the variation of $K^{\ddagger}$ with temperature may be expressed as

$$\frac{d \ln K^{\ddagger}}{dT} = \frac{\Delta E^{\ddagger}}{RT^2} \tag{6.151}$$

Equations (6.150) and (6.151) give

$$\frac{d \ln k}{dT} = \frac{1}{T} = \frac{\Delta E^{\ddagger}}{RT^2} = \frac{RT + \Delta E^{\ddagger}}{RT^2}$$

Now the experimental activation energy may be defined as

$$\frac{d \ln k}{dT} = \frac{E_{exp}}{RT^2}$$

Therefore, $E_{exp} = RT + \Delta E^{\ddagger}$

Now as

$$\Delta H^{\ddagger} = \Delta E^{\ddagger} + P\Delta V^{\ddagger}$$

Therefore, $E_{exp} = \Delta H^{\ddagger} - P\,\Delta V^{\ddagger} + RT$

For a unimolecular reaction and the reactions in solution $\Delta V^{\ddagger} = 0$.

Therefore, $E_{exp} = \Delta^{\ddagger} + RT$

or $$k = \frac{\mathbf{k}T}{\mathbf{h}} e^{\Delta S^{\ddagger}/R} e^{-E_{exp} - RT/RT}$$

or $$k = e \frac{\mathbf{k}T}{\mathbf{h}} e^{\Delta S^{\ddagger}/R} e^{-E_{exp}/RT} \tag{6.152}$$

For other gas reactions

$$P\,\Delta V^{\ddagger} = \Delta n^{\ddagger} RT$$

where $\Delta n^{\ddagger}$ is the increase in the number of molecules when activated complex is formed from the reactants. For a bimolecular reaction $\Delta n^{\ddagger} = -1$ as two reactant molecules from one activated complex molecule, we have

$$E_{exp} = \Delta H^{\ddagger} + 2RT$$

or for a bimolecular reaction

$$k = e^{2} \frac{\mathbf{k}T}{\mathbf{h}} e^{\Delta S^{\ddagger}/R} e^{-E_{exp}/RT} \tag{6.153}$$

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7

KINETICS OF CHEMICAL CHAIN REACTIONS

Of the hundreds of chemical reactions observed experimentally only a few reactions, if any, can be described in terms of a single chemical change. A majority of the reactions follow a more or less complex mechanism or path of reaction involving the formation and destruction of chain carriers (atoms and radicals). Usually, the concentration of these chain carriers in a reaction is extremely low. As a result of this, it is difficult to establish the mechanism of a reaction from the measurements of the reaction rate constant, activation energy, and the order of a chemical reaction.

Combustion leads to high temperatures and reaction rates of chemical reactions. But the studies of physico-chemical parameters are carried out at relatively low temperatures where the reaction rates are observed to be low. The advantage of this is that the reaction is spread over a period of time while the disadvantage is that the elementary reactions may differ in importance from those governing high temperature processes. However, it is a fact that the mechanism of even the simplest reactions is not fully understood as yet.

In this chapter we shall consider the details of some of the better understood chemical reactions, including some of the methods used for the study of their mechanisms.

7.1 REACTION OF BROMINE WITH HYDROGEN

The reaction of bromine with hydrogen is one of the simple and well understood unbranched chain reactions. The mechanism of reaction for other halogens, e.g. chlorine, iodine, and fluorine is essentially similar but the reaction rate for different reactions varies to a large extent because of the different values of activation energy and heat of reaction, etc. Let us consider the reaction.

$$H_2 + Br_2 \rightleftharpoons 2HBr \tag{7.1}$$

If this reaction is considered to be of the second order, the measured reaction rate is found to be much higher than the calculated value, assuming the reaction to be a simple one step bimolecular reaction. The reaction rate of the hydrogen bromine reaction in the temperature range of 200 to 300°C was measured by Bodenstein and Lind[1] in 1906 and they proposed the following empirical equation.

$$\frac{d[HBr]}{dt} = \frac{k[H_2]\,[Br_2]}{1+k'\,[HBr]\,/\,[Br_2]} \tag{7.2}$$

where $k'=1/10$ is called the inhibition constant and is independent of temperature, k is proportional to $e^{-40{,}200/RT}$ which indicates that the activation energy for the reaction is 4.2 kcal/g-mol.

The mechanism of hydrogen-bromine reaction involves the following simple reactions

$$\left.\begin{array}{l}
\text{(i)}\ Br_2+M \xrightarrow{k_1} 2Br+M-46.1\ \text{kcal}\\
\text{(ii)}\ Br+H_2 \xrightarrow{k_2} HBr+H-16.6\ \text{kcal}\\
\text{(iii)}\ H+Br_2 \xrightarrow{k_3} HBr+Br+41.4\ \text{kcal}\\
\text{(iv)}\ H+HBr \xrightarrow{k_4} H_2+Br+16.6\ \text{kcal}\\
\text{(v)}\ 2\ Br \xrightarrow{k_5} Br_2+46.1\ \text{kcal}\\
\text{(vi)}\ Br+HBr \xrightarrow{k_6} H+Br_2-41.4\ \text{kcal}\\
\text{(vii)}\ H_2+Br_2 \xrightarrow{k_7} 2\ HBr+24.7\ \text{kcal}\\
\text{(viii)}\ H_2+M \xrightarrow{k_8} 2H+M-104.2\ \text{kcal}\\
\text{(ix)}\ 2H+M \xrightarrow{k_9} H_2+M+104.2\ \text{kcal}\\
\text{(x)}\ H+Br+M \xrightarrow{k_{10}} HBr+M+87.5\ \text{kcal}\\
\text{(xi)}\ HBr+M \xrightarrow{k_{11}} H+Br+M-87.5\ \text{kcal}
\end{array}\right. \tag{7.3}$$

On examining the reactions we find that reactions (i) and (v), (ii) and (iv), (viii) and (ix), and (x) and (xi) are reversible. In 1919, Christiansen[2], Herzfeld[3], and Polanyl[4] proposed the mechanism of H_2-Br_2 reaction in terms of the first five reactions.

Reaction (i) is a chain initiation reaction, reactions (ii), (iii), (iv) are chain propagation reactions, and reaction (v) is a chain ending reaction. Therefore, the mechanism is fully described by the first five reactions as the frequency of reactions (vi) to (xi) is quite low.

HBr is formed in reactions (ii) and (iii) and is consumed in reaction (iv). Therefore,

$$\frac{d[HBr]}{dt} = k_2[Br]\,[H_2]+k_3\,[H]\,[Br_2]-k_4\,[H]\,[HBr] \tag{7.4}$$

where the terms in brackets indicate the concentration of species. As it is difficult to measure the concentration of free H and Br atoms, we shall have to remove the terms containing concentration of H and Br in order to solve Eq. (7.4.)

Writing the rate of formation of Br and H

$$\frac{d[Br]}{dt} = 2k_1\,[Br_2]-k_2\,[Br][H_2]+k_3\,[H]\,[Br_2]+k_4\,[H]\,[HBr] -2[k_5]\,[Br]^2 \tag{7.5}$$

$$\frac{d[H]}{dt} = k_2\,[Br]\,[H_2]-k_3\,[H]\,[Br_2]-k_4[H]\,[HBr] \tag{7.6}$$

The complete solution of these equations is quite difficult. For simplicity, we may safely assume that the steady state occurs after a certain time, i.e., the concentrations of H and Br remain essentially constant.

It therefore, follows that

$$\frac{d[Br]}{dt} = \frac{d[H]}{dt} = 0$$

We may rewrite Eqs. (7.5) and (7.6) as

$$2k_1[Br_2]-k_2[Br][H_2]+k_3[H]\,[Br_2]+k_4[H]\,[HBr]-2k_5[Br]^2=0 \tag{7.7}$$

and

$$k_2[Br]\,[H_2]-k_3\,[H]\,[Br_2]-k_4\,[H][HBr]=0 \tag{7.8}$$

Equations (7.5), (7.6), (7.7), etc. can be solved simultaneously. For convenience we may replace the kinetic terms with Roman numerals. Thus Eqs. (7.7) and (7.8) may be written as

$$2I-II+III+IV-2V=0 \tag{7.7a}$$

$$II-III-IV=0 \tag{7.8a}$$

By adding Eq. (7.7a) and Eq. (7.8a)

$$2I-2V=0$$

or

$$2k_1(Br_2)-2\,k_5\,[Br]^2=0$$

or

$$[Br]=\{(k_1/k_5)\,[Br_2]\}^{\frac{1}{2}} \tag{7.9}$$

Rewriting Eq. (7.8),

$$[H]=\frac{k_2\,[H_2]}{k_3\,[Br_2]+k_4\,[HBr]}[Br]$$

Substituting the value of [Br] from Eq. (7.9)

$$[H]=\frac{k_2\,(k_1/k_5)^{\frac{1}{2}}\,[H_2]\,[Br_2]^{\frac{1}{2}}}{k_3\,[Br_2]+k_4\,[HBr]} \tag{7.10}$$

By subtracting Eq. (7.8) from Eq. (7.4) we have

$$\frac{d[HBr]}{dt} = 2k_3[H]\,[Br_2] \tag{7.11}$$

Substituting the value of [H] from Eq. (7.10) in the above equation

$$\frac{d\,[\mathrm{HBr}]}{dt}=\frac{2k_3\;k_2(k_1/k_5)^{1/2}[\mathrm{H_2}]\,[\mathrm{Br_2}]^{3/2}}{k_3[\mathrm{Br_2}]+k_4]\mathrm{HBr}]}$$

$$=\frac{2k_2(k_1/k_5)^{1/2}[\mathrm{H_2}]\,[\mathrm{Br_2}]^{3/2}}{1+k_4\{[\mathrm{HBr}]/k_3\,([\mathrm{Br_2}])\}} \tag{7.12}$$

If we compare the experimental Eq. (7.2) and the theoretical result derived in Eq. (7.12), we find that the equations are similar and give

$$k=2k_2\,(k_1//k_5)^{1/2} \tag{7.13}$$

and

$$k'=k_4/k_3 \tag{7.14}$$

If we consider Eq. (7.13), reactions (i) and (v) are reversible reactions. Therefore, $k_1/k_5=\mathrm{K}$ for reaction (i). Thus the equilibrium constant can be determined. It is found to be $e^{-45,200/RT}$

Therefore $\quad k=2k_2\;(B.\,e^{-45,200/RT})^{1/2}$ (7.15)

where B is a proportionality constant. The value of k can be measured experimentally. The value of k_2 can thus be calculated. Jost[5] gave the value of k_2 as

$$k_2=10^{12\cdot3}T^{1/2}\;e^{-17,600/RT}\text{ litres mole}^{-1}\text{ s}^{-1} \tag{7.16}$$

This can be compared with the collision theory which gives

$$k_2=PZT^{1/2}\;e^{-E/RT} \tag{7.17}$$

where $Z=(N/1000)\,\sigma^2{}_{12}\left\{8\pi R\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\right\}^{1/2}$

By comparing Eqs. (7.16) and (7.17),

$$PZ=10^{12\cdot3}$$

The activation energy is thus 17.6 kcal and since the reaction is endothermic to the extent of 16.4 kcal, therefore the activation energy for the reverse reaction (iv) is 1.2 kcal.

The value of k', i.e., k_4/k_3 is found to be independent of temperature indicating that the activation energy of reaction (iiii) is the same as that of reaction (iv). Therefore, the activation energy of reaction (iii) is also approximately 1.2 kcal. As the value of k' is about 1/10, the reaction rate for (iii) is ten times that for (iv). This difference should be accounted for in terms of the frequency factor, that for (iv) being one-tenth of (iii).

7.2 REACTION OF HYDROGEN WITH OXYGEN

Explosion Limits

The hydrogen-oxygen reaction is a typical example of a branched chain reaction. Because of its simplicity, this reaction has been studied by many

workers and its mechanism is well undrstood. The reaction rate of the reaction of hydrogen with oxygen is dependent to a large extent on the pressure and temperature. To understand the mechanism fully, we shall first discuss the effect of pressure on the reaction rate. Normally, because of the measurable rates, this reaction has been studied between 450° and 600°C. Figure 7.1 illustrates the effect of total pressure on the reaction rate at a constant temperature, say 550°C. At very low pressures, the rate of the reaction increases as expected in a normal unbranched chain reaction but as the pressure is increased by a few mm of Hg, the mixture suddenly explodes. This pressure is known as the first explosion limit, and is indicated by point B in Fig. 7.1. Between pressures B and D, the reaction is explosive but at E it again becomes slow and increases in the normal way up to pressure F. Pressure E is known as the second explosion limit and pressure F, the third explosion limit. It is difficult to reproduce the first explosion limit because it varies according to the experimental conditions and size of the vessel etc. but the second and third explosion limits are well defined at 550°C. The second explosion limit is around 100 mm of Hg. The position of the explosion limits changes if the temperature is changed. The first and second explosion limits are not a thermal explosion but because of the branched chain reactions the rate of reaction becomes very high. Between the limits, i.e., in the range of AB and EF, the chain terminating reactions are as fast as the chain initiation and propagation reactions. Therefore, the rate of the reaction is reduced.

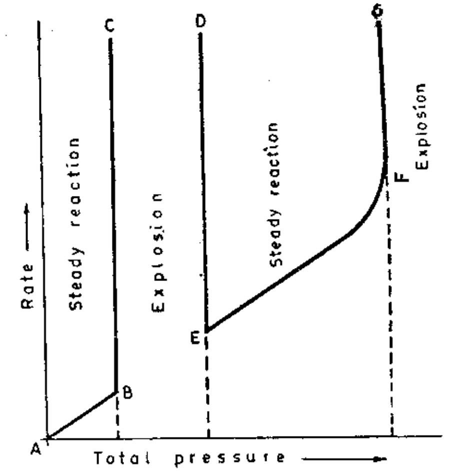


Fig. 7.1 Variation in the rate of H_2/O_2 reaction with total pressure.

If we observe the effect of temperature on the explosion limits, we get a reaction peninsula. Figure 7.2 gives the plot between temperature and pressure for hydrogen-oxygen reaction. Points B, E and F of Fig. 7.1

can be obtained from Figure 7.2 by taking pressures at isotherm of 550°C. In Fig. 7.2 the shaded portion indicates that the reaction rate is explosive. This means that below 460°C the hydrogen-oxygen reaction remains steady up to very high pressures. At about 460°C the first and second explosion limits are almost the same. But at about 600°C, we get three distinct explosion limits. Therefore, various explosions can be explained well if we study the general rate equation for the branched chain reaction rate as given by Hinshelwood. The reaction rate v is written as

$$v = \frac{F}{f_s+f_g+A(1-\alpha)} \tag{7.18}$$

where F is the rate of the chain initiation, f_s and f_g are the rates of destruction of the radicals at the surface and in the gas phase respectively, and A is a function related to the chain branching process. If α is greater than unity as in a branched chain reaction, the term $A\,(1-\alpha)$ becomes negative. If it is sufficiently negative so that it equals the term f_s+f_g, the denominator approaches zero or the reaction rate becomes infinite. The magnitudes of f_s+f_g and α depend upon the concentration of various species. If we consider the hydrogen-oxygen reaction, then at extremely low pressures, the wall termination of the radicals beomes predominant and the rate is measurable. As the pressure increases, f_s reduces and at pressure B the mixture becomes explosive. If we increase the pressure, between pressure E and F, the gas phase destruction of radicals becomes predominant and between these pressures the reaction is controlled. Thermal explosion takes place at the higher pressure. This also explains the effect of the diameter of the combustion vessel on the first explosion limit and its independence on the second limit.

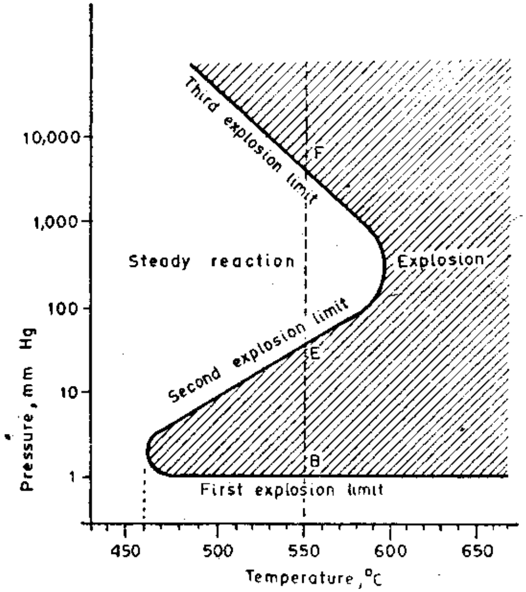


Fig. 7.2 Explosion limits for hydrogen-oxygen reaction

Hydrogen-Oxygen Reaction Mechanism

The hydrogen-oxygen reaction is a branched chain reaction. Because of its simplicity the mechanism of this reaction has been studied by many scientists. The reaction rate can be controlled between 450 and 600°C, but above 600°C the mixture becomes explosive. The reaction is explosive and is given as

$$2H_2+O_2 \longrightarrow 2H_2O \tag{7.19}$$

It appears to be of third order but consists of many elementary steps. The mechanism of reaction can be divided into three parts: (i) mechanism below the first explosion limit, (ii) between the second and third limits and (iii) near the third limit. First we shall study the reaction between the second and third limits. Hinshelwood[6] proposed the following mechanism:

$$\left.\begin{array}{ll}
\text{(i)} & H_2+O_2 \xrightarrow{k_1} 2\,OH-18.6 \text{ kcal/g-mol (initiation)} \\
\text{(ii)} & OH+H_2 \xrightarrow{k_2} H_2O+H+14.7 \text{ kcal/g-mol (propagation)} \\
\text{(iii)} & H+O_2 \xrightarrow{k_3} OH+O-16.7 \text{ kcal/g-mol (branching)} \\
\text{(iv)} & O+H_2 \xrightarrow{k_4} OH+H-1.9 \text{ kcal/g-mol (branching)} \\
\text{(v)} & H+O_2+M \xrightarrow{k_5} HO_2+M+47.0 \text{ kcal/g-mol (termination in gas phase)} \\
\text{(vi)} & HO_2 \rightarrow \text{Destruction by wall (termination at wall)}
\end{array}\right\} \tag{7.20}$$

In this simple mechanism, Hinshelwood proposed that the initiation of the chain carrier is by the gas phase reaction of hydrogen and oxygen molecules. The initiation reaction may be written as

$$H_2+O_2 \rightarrow HO_2+H-56.3 \text{ kcal/g-mol}$$

but on energy consideration, reaction (i) appears to be preferable. The initiation of the chain carrier can also be due to the heterogeneous reaction on the surface. Patrick and Robb have given a few convincing arguments for the heterogeneous generation of carriers. Branching [steps (iii) and (iv)] and propagation [step (ii)] are well established. Chain termination occurs because of step (iv). The HO_2 radical is quite inactive and it diffuses to the wall where it is absorbed and destroyed by the reaction with another HO_2 radical or any free atom. For the rate of reaction we may write the rate of change of concentration of chain carriers. The equations may be written as

$$\frac{d[OH]}{dt} = I+III+IV-II \tag{7.21}$$

$$\frac{d[H]}{dt} = II-III+IV-V \tag{7.22}$$

$$\frac{d[O]}{dt} = III-IV \tag{7.23}$$

$$\frac{d[H_2O]}{dt} = II \tag{7.24}$$

where I indicates the rate of initiation of chain carriers OH.

$II=k_2\,[OH]\,[H_2]$,

$III=k_3\,[H]\,[O_2]$, etc.

Equation (7.24) gives the rate of formation of water or it may be referred to as the overall rate of the reaction.

To solve these equations without the knowledge of the reaction rate constants is quite difficult. Blackmore[7] used the calculated and known values of the rate constants and solved these equations on an analog computer. He found that the concentrations of the chain carriers, H, OH, and O assume steady state values in a very short time, i.e., in about 4×10^{-3} s. Therefore, we may safely assume that the left hand sides of Eqs. (7.21) and (7.23) become zero instantaneously. Therefore, these equations may be written as

$$I+III+IV-II=0 \tag{7.21a}$$

$$II-III+IV-V=0 \tag{7.22a}$$

$$III-IV=0 \tag{7.23a}$$

Adding Eqs. (7.21a) and (7.22a) we get

$$I+2\,IV-V=0 \tag{7.25}$$

From Eqs. (7.23a) and (7.25) we may write

$$I+2\,III-V=0 \tag{7.26}$$

or $\quad I+2k_3[H]\,[O_2]-k_5\,[H]\,[O_2]\,[M]=O$

or
$$[H]=\frac{I}{[O_2]\,(k_5\,[M]-2k_3)} \tag{7.27}$$

Adding Eqs. (7.22a) and (7.23a) we get

$II=V$

i.e.,
$$k_2\,[OH]\,[H_2]=k_5\,[H]\,[O_2]\,[M] \tag{7.28}$$

Substituting the value of (H) from Eq. (7.27)

$$k_2\,[OH]\,[H_2]=\frac{k_5\,I\,[O_2]\,[M]}{[O_2]\,(k_5\,[M]-2k_3)}$$

or
$$k_2\,[OH]\,[H_2]=\frac{k_5\,I\,M}{(k_5\,M-2k_3)} \tag{7.29}$$

The left hand side of this equation gives the overall rate of the reaction. From Eq. (7.25,) therefore, we may write

$$\frac{d\,[H_2O]}{dt}=\frac{k_5\,I\,[M]}{k_5\,[M]-2k_3} \tag{7.30}$$

Reaction (v) is a chain termination reaction. The higher the pressure the higher will be value of [M] which controls the reaction rate. If $k_5\,[M]=2k_3$, the denominator of Eq. (7.30) becomes zero indicating an infinite rate of reaction which explains the pressure of second explosion limits.

If $k_5\,[M]>>2k_3$, then Eq. (7.30) can be written as

$$\frac{d\,[H_2O]}{dt}=\frac{k_5\,I\,[M]}{k_5\,[M]}\approx I \tag{7.31}$$

The value of I equals $2\,k_1\,[O_2]\,[H]$ which indicates that the rate of reaction increases with increasing pressure. This is because at higher pressures the concentration of oxygen and hydrogen increases. The pressure of the second explosion limit can be calculated from the condition $k_5\,[M]=2\,k_3$.

or
$$[M]=\frac{2\,k_3}{k_5} \tag{7.32}$$

where [M] can be regarded as the total pressure. According to the above mechanism, the rate of reaction and the value of the second explosion limit appear to be independent of the nature and shape of the reaction vessel. Baldwin and co-workers[8] have proved experimentally that the reaction in this range is independent of the size of the vessel. But if the vessel is coated with boric acid, boric oxide (B_2O_3) or is made of pyrex, the rate of the reaction is quite slow and it increases as the vessel surface ages. Similarly, if the vessel wall is coated with potassium chloride (KCl) or calcium chloride (CaCl) or is made of porcelain, then the rate reaches its maximum value immediately. This dependence of the reaction rate on the nature of the surface is explained by the following mechanism.

$$\begin{aligned}
&\text{(i)} && H_2+O_2\xrightarrow{k_1}2\,OH\\
&\text{(ii)} && OH+H_2\xrightarrow{k_2}H_2O+H\\
&\text{(iii)} && H+O_2\xrightarrow{k_3}OH+O\\
&\text{(iv)} && O+H_2\xrightarrow{k_4}OH+H\\
&\text{(v)} && O_2+H+M\xrightarrow{k_5}HO_2+M\\
&\text{(vii)} && HO_2+HO_2\xrightarrow{k_7}H_2O_2+O_2\\
&\text{(viii)} && H+HO_2\xrightarrow{k_8}2\,OH\\
&\text{(ix)} && HO_2+H_2\xrightarrow{k_9}H_2O_2+H\\
&\text{(x)} && H_2O_2+M\xrightarrow{k_{10}}2\,OH+M\\
&\text{(xi)} && H+H_2O_2\xrightarrow{k_{11}}H_2O+OH\\
&\text{(xii)} && OH+H_2O_2\xrightarrow{k_{12}}H_2O+HO_2
\end{aligned} \tag{7.33}$$

According to this mechanism, the HO_2 radical is not destroyed on the wall but will react homogeneously with another HO_2 radical, or with the

H atom or with the H_2 molecule to produce chain carriers OH, H, and hydrogen peroxide. The hydrogen peroxide then reacts accor ing to reactions (x), (xi) and (xii). This scheme contains two additional branching steps (viii) and (x) and a few additional propagation steps. According to this reaction scheme, the rate of reaction increases with increased pressure because step (x) contains concentration of M which increases as the pressure increases. This step also explains the reason for the third explosion limit. At higher pressures due to the increased rate of step (x), the production of the chain carrier increases rapidly to produce the explosion. Therefore, it may be said that if the surface of the vessel is such that it easily destroys the radical HO_2, the simple mechanism proposed by Hinshelwood[6] will prevail. However, if because of the higher pressure or because of the nature of the surface, the HO_2 radicals prefer a homogeneous gas reaction, the above mentioned extended mechanism will prevail.

The rate equation for this mechanism can be written as

$$\frac{d[OH]}{dt} = 2\,I + III + IV - II + 2\,X + 2\,VIII + XI - XII \tag{7.34}$$

$$\frac{d[O]}{dt} = III - IV \tag{7.35}$$

$$\frac{d[H]}{dt} = II - III - IV - V - VIII + IX - XI \tag{7.36}$$

$$\frac{d[HO_2]}{dt} = V - VIII - 2\,VII - IX + XII \tag{7.37}$$

$$\frac{d[H_2O_2]}{dt} = VII + IX - X - XI - XII \tag{7.38}$$

It is again quite difficult to find the solutions for these equations. Blackmore[7] has shown that by solving these equations on an analog computer, the concentrations of OH, H, and O reach their steady state concentration values in a very short time, while the concentrations of HO_2 and H_2O_2 increase slowly. Even after 40 s, the concentrations of HO_2 and H_2O_2 assume about half of their final steady state values. The proposed mechanism is further supported by the experimental observation that the addition of H_2O_2 to the system increases the reaction rate and the value of the second explosion limit.

The reaction mechanism operating below the first explosion limit, i.e., at low pressures was proposed by Baldwin[9] as

(i) $OH + H_2 \xrightarrow{k_1} H_2O + H$

(ii) $H + O_2 \xrightarrow{k_2} OH + O$

(iii) $O + H_2 \xrightarrow{k_3} OH + H$

(iv) $H + O_2 + M \xrightarrow{k_4} HO_2 + M$

(contd.)

(v) $HO_2 \xrightarrow{k_5}$ destruction (7.39)

(vi) $H \xrightarrow{k_6}$ destruction

(vii) $OH \xrightarrow{k_7}$ destruction

The first five steps are the same as in the simple mechanism suggested by Hinshelwood, but Baldwin omitted the initiation reaction. Later, Clark, Simmons, and Balckmore,[10] by numerical analysis, have shown that the omission of the initiation reaction below the first limit does not affect the condition of the reaction. By omitting this reaction, calculations are simplified but the result itself is not affected.

The rate equations for the change of concentrations of chain carriers with respect to time may be written as

$$\frac{d[OH]}{dt} = -I + II + III - VII \tag{7.40}$$

$$\frac{d[H]}{dt} = I - II + III - IV - VI \tag{7.41}$$

$$\frac{d[O]}{dt} = II - III \tag{7.42}$$

As it has been found that the concentrations of H, OH, and O assume steady state values in a very short time, we may write

$$\frac{d[OH]}{dt} = \frac{d[H]}{dt} = \frac{d[O]}{dt} = 0$$

Therefore, Eqs. (7.40 to 7.42) may be written as

$$II + III - I - VII = 0 \tag{7.40a}$$

$$I - II + III - IV - VI = 0 \tag{7.41a}$$

and $$II - III = 0 \tag{7.42a}$$

Adding Eqs. (7.40a) and (7.42a)

$$2\,II - I - VII = 0$$

or $$I = 2\,II - VII \tag{7.43}$$

Adding Eqs. (7.41a) and (7.42a) we get

$$I - IV - VI = 0$$

or $$I = IV + VI \tag{7.44}$$

Equating Eqs. (7.43) and (7.44)

$$2\,II - VII = IV + VI$$

or $$2\,II - IV = VI + VII$$

Writing the above in full form gives

$$2k_2[H][O_2] - k_4[H][O_2][M] = k_6[H] + k_7[OH]$$

or $$2k_2 [H] [O_2] \left(1 - \frac{k_4 [M]}{2k_2}\right) = k_6 [H] + k_7 [OH]$$

or $$\left(1 - \frac{k_4 [M]}{2k_2}\right) = \frac{k_6 [H]}{2k_2 [H] [O_2]} + \frac{k_7 [OH]}{2k_2 [H] [O_2]} \tag{7.45}$$

Substituting the value of $2k_2$ [H] [O_2] in the second term on the right hand side of Eq. (7.43) we get

$$\left(1 - \frac{k_4 [M]}{2k_2}\right) = \frac{k_6}{2k_2 [O]_2} + \frac{k_7}{k_1 [H_2] + k_7} \tag{7.46}$$

From the reaction between the second and third limits, the condition for the second limit can be written as

$$[M] = \frac{2k_3}{k_5}$$

Comparing the mechanism of Hinshelwood for the reaction between the second and third limits with the mechanism of Baldwin for the reaction below the first limit, we find that the reactions (iii) and (v) of Hinshelwood are the same as reactions (ii) and (i) of Baldwin. Therefore, the second limit pressure P_2 is given by the expression

$$P_2 = \frac{2k_2}{k_4} \tag{7.47}$$

Near the first limit [M] for Eq. (7.46) will represent the **first limit pressure P_1.**

Therefore, we may write Eq. (7.46) at the first limit as

$$\left(1 - \frac{P_1}{P_2}\right) = \frac{k_6}{2k_2 [O_2]} + \frac{k_7}{k_1 [H_2] + k_7} \tag{7.48}$$

The numerator of the terms on the right hand side of the above equation is the rate constant for the wall destruction of carriers H and OH. It is obvious that below the first limit these carriers will easily diffuse to the wall of the vessel and the hetrogenous chain termination will become predominant.

The values of k_6 and k_7 are related to the diffusion coefficient D, thermal velocity v, and chain breaking efficiency σ for H and OH. If σ_H is smaller than 10^{-2}–10^{-3}, then $k_6 = a \frac{\sigma_H v_H}{d}$ s^{-1} where a is a numerical factor dependent on the geometry of the reaction vessel and d is the diameter of the vessel. If σ_H is relatively large ($5 \times 10^{-2} < \sigma_H < 1$), then

$$k_6 = b \frac{D}{d^2} \ s^{-1} \tag{7.49}$$

where b is also a coefficient dependent on the geometry of the reaction vessel. The value of σ_H is governed by the nature of the surface of the reaction vessel.

THE CARBON MONOXIDE-OXYGEN REACTIONS

The study of the oxidation of carbon monoxide is quite important for combustion processes because carbon monoxide generally constitutes a part of the fuel or appears as an intermediate product during the combustion of inorganic or organic fuels. The mechanism of this reaction is not so well understood. Though the reaction is similar to the hydrogen-oxygen reaction in many respects, a generalizaton of the two processes cannot be made. The combustion of carbon monoxide has been studied by many workers and many experimental results have been well established, but quite a few questions still remain to be answered.

The carbon monoxide oxidation exhibits a reaction peninsula similar in shape to the hydrogen-oxygen peninsula. The explosion region is confined between the two limits. The first limit was observed by Sagulin[11] and the second by Koop, Kowalsly, Sagulin, and Semenov[12]. Figure 7.3 shows the variation of the explosion limit with temperature. The effect was first studied by Semenov et al. Though the shape of the peninsula is the same as that of the hydrogen-oxygen explosion limit, it lies in the region of higher temperature and pressure. The shaded portion of the diagram indicates the explosion zone. The slow reaction zone can be divided into different parts.

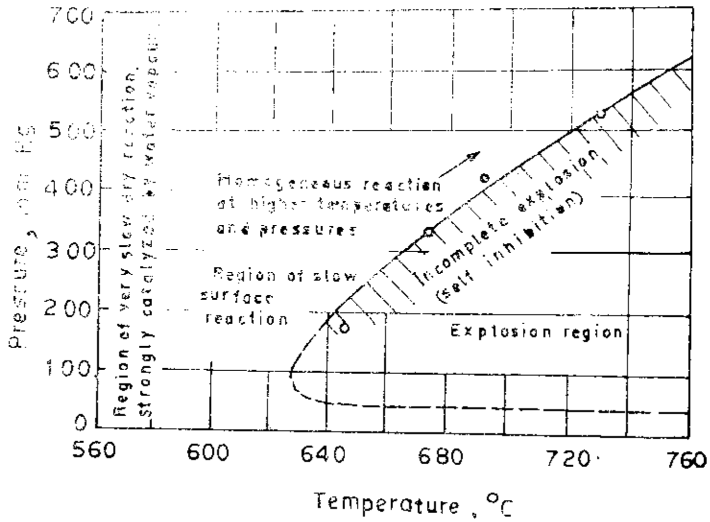


Fig. 7.3 Explosion limits of carbon monoxide and oxygen reaction [from G. Hadman, H.W. Thompson, and C.N. Hinshelwood, *Proc. Roy. Soc. (London)*, A 138, 297, 1932].

At low temperatures and high pressures the reaction is observed to be quite slow but the addition of a little amount of water vapour speeds up the reaction. Figure 7.3 also shows the zone of slow surface reaction, and zone of gas phase homogeneous reaction at higher temperatures and pressures. Few other experimental observations reported by Lewis, Von Elbe, and Roth[13] are the effects of vessel size, CO-O_2 ratio and the effect of nitrogen on the second explosion limit. It has been reported that a decrease in the diameter reduces the second limit pressure. The second limit pressure is also found to decrease if the percentage of carbon monoxide is increased in the mixture. However, it remains unaffected if some of the mixture of carbon monoxide and oxygen is replaced by the same amount of nitrogen or oxygen. Dixon and Bone[14,15] observed that the ignition of the mixture, if very dry, is quite difficult even with a strong spark. In general, the reaction is found to be strongly catalyzed by water vapour or hydrogen, but the second limit pressure is found to remain the same even by increasing their concentration.

Topley's[16] work shows that the dry mixture sometimes explodes after a few minutes. The carbon monoxide flame is one of the most luminous. It was reported by Kondratiev[17] that at 100 torr pressure and 1000 K, one quantum of radiation is emitted for every 125 molecules of CO_2 formed which is too large. From all these experimental results it may be concluded that the carbon monoxide-oxygen reaction mechanism is of the branched chain type, where wall termination of carriers and third body molecules M play an important role. Chain carrier initiation is quite difficult in dry mixtures. The carrier concentration which can be derived from carbon monoxide and oxygen builds up slowly. An excited molecule is formed during the reaction which emits radiation. Lewis and Von Elbe[18] initially proposed that O, O_3, and CO play the role of chain carriers but as the presence of CO_3 radical has not been proved, it is generally omitted in the reaction scheme. First the excited CO_2 molecule was supposed to emit light but Hornbeck[19] has shown that the light emitted is by the exited oxygen molecules. Based on these facts Griffing and Laidler proposed the following scheme:

$$\begin{array}{rl}
\text{(i)} & CO+O_2 \longrightarrow CO+O \\
\text{(ii)} & O+CO+M \longrightarrow CO_2^*+M \\
\text{iii)} & O+O_2+M \longrightarrow O_3+M \\
\text{(iv)} & O_3+CO \longrightarrow CO_2+2\,O \\
\text{(v)} & O_3+CO+M \longrightarrow CO_2+O_2+M \\
\text{(vi)} & CO_2^*+M \longrightarrow O+CO+M \\
\text{(vii)} & CO_2^*+O_2 \longrightarrow CO_2+2\,O \\
\text{(viii)} & CO_2^* \longrightarrow CO_2+h\nu \\
\text{(ix)} & CO_2^*+O_2 \longrightarrow CO_2+O^*_2 \\
\text{(x)} & O_2^* \longrightarrow O_2+h\nu
\end{array} \qquad (7.50)$$

In the above scheme CO_2^* and O_2^* indicate the electronically excited state and, $h\nu$ indicates the release of radiation.

The initiation of the O atom is as given by reaction (i) as this initiation step is exothermic whereas the other possible steps are endothermic. Theoretically it can be shown that the reaction of the O atom and the CO molecule will always result in an electronically exited CO_2 molecule. The likelihood of the reaction of O_2 with O is quite high because of the very low, almost nil, activation energy of the reaction. The possibility of the branching reaction is explained by reaction (iv) while reaction (v) gives the chain termination step. The other reactions after reaction (v) are the possible reactions of

CO_2^*. It is found that the possibility of reaction (viii) is quite low. Most of the CO_2^* molecules are supposed to take step (ix) and the O_2^* produced reacts according to step (x).

This mechanism does not include the effect of wall termination. For the reaction near the first limit, such reactions assume a major role, so the wall termination of O, O_3, CO_2^*, and O_2^* can be included in the scheme to explain the effect of surface on the reaction mechanism. The upper limit can be computed by writing the steady state equations for the concentrations of O, O_3, and CO_2^*, solving for [O], and equating to zero the denominator of the factor multiplying [O] in the final expression, i.e., giving a condition for [O] to be infinite. The simple expression obtained with the valid assumption of $k_3\,[O] \gg k_2\,[CO]$ is $k_5\,[M]=k_4$ where [M] is any molecule of carbon monoxide, oxygen, or any other constituent of the mixture. This expression confirms the experimental fact that by replacing some of the mixture by nitrogen, the second limit pressure remains unaffected. Also, the activation energy of reaction (iv) corresponds to the value of 35 kcal which can be obtained by variation of the upper limit with the second limit pressure. The value of the light yield obtained with the above scheme is also consistent with the experimental value. But the above scheme cannot correctly predict the behaviour of the second limit with a change in the concentration of carbon monoxide and the size of vessel.

7.4 WATER CATALYZED CARBON MONOXIDE-OXYGEN REACTION

The presence of water has a marked affect on the reaction rate of the oxidation of carbon monoxide outside the explosion region. As hydrogen and water are invariably present in a fuel, the study of carbon monoxide oxidation in the presence of water is quite useful.

It has been found that in the presence of water the initiation of reaction is quite easy in comparison to the dry $CO\text{-}O_2$ mixture. In the region of slow surface reaction (Fig. 7.3) it has been found that an increase in the surface to volume ratio increases the reaction rate. While at higher pressures and temperatures in the homogeneous reaction zone, the rate of reaction decreases by increasing the surface to volume ratio. The presence of water also catalyzes the reaction. Also, the reaction is strongly catalyzed in the presence of water, at low temperature and higher pressure. In the slow surface reaction region, the initiation of reaction is surfacee catalyzed which results in an increased rate with a large surface to volume ratio. At other regions, the wall termination of chain carriers are responsible for the decreasing rate with increasing surface to volume ratio.

It has been found that the second limit remains unaffected by increasing the concentrations of water or hydrogen, while the lower limit temperature and pressure reduce by increasing the concentration of H_2 or H_2O and approach the value of the $H_2\text{-}O_2$ peninsula. Keeping in view the above experimental observations, Lewis and Von Elbe[20] proposed the following mechanism:

$$
\begin{array}{rll}
\text{(i)} & H_2O+CO \longrightarrow CO_2+H_2 & \text{(Surface)} \\
\text{(ii)} & H_2+O_2 \longrightarrow H_2O_2 & \text{(Surface)} \\
\text{(iii)} & H_2O_2+M \longrightarrow 2\,OH+M & \\
\text{(iv)} & H_2O_2+CO \longrightarrow CO_2+H_2O & \\
\text{(v)} & OH+CO \longrightarrow CO_2+H & \\
\text{(vi)} & H+O_2 \longrightarrow OH+O & \\
\text{(vii)} & H+O_2+M \longrightarrow HO_2+M & \\
\text{(viii)} & O+H_2 \longrightarrow OH+H & \\
\text{(ix)} & O+O_2+M \longrightarrow O_3+M & \\
\text{(x)} & HO_2+CO \longrightarrow CO_2+OH & \\
\text{(xi)} & HO_2 \xrightarrow{\text{Surface}} \text{Destruction} &
\end{array}
\qquad (7.51)
$$

According to this scheme, the inotiation reaction is a surface reaction. First, a hydrogen molecule is produced at the surface of the reaction vessel which reacts with a oxygen molecule to produce H_2O_2 which can disintegrate to produce two chain carriers or can react with CO molecule to give H_2O and CO_2. Reactions (iii), (vi) and (viii) are branching reactions. In the above scheme, reactions (vi), (vii), (viii) and (x) are the same as proposed in the H_2-O_2 reaction mechanism. Reactions (i) and (iii) correspond to the initiation reaction in H_2—O_2 reaction. Thus almost all the reactions of the H_2—O_2 reaction scheme are incorporated except the reaction $H_2+OH \rightarrow H_2O+H$. This reaction is omitted because the concentration of hydrogen molecule is very low in wet $CO+O_2$ mixture. Therefore, the chances of a chain carrier colliding with hydrogen molecule are quite low. The probability of the occurrence of reaction (ix) is also quite low. However, the O_3 produced is consumed by the following mechanism.

$$O_3+CO+M \longrightarrow CO_2+O_2+M$$

$$O_3 \xrightarrow{\text{wall}} \text{Destruction}$$

or it can react with a CO molecule to give two carriers as

$$O_3+CO \longrightarrow CO_2+2O$$

Near the explosion peninsula, this branching reaction becomes important with the increased concentration of O atoms. The O_3 concentration also increases and this branching reaction leads to explosion. This also explains why the presence of H_2 or H_2O does not affect the second limit pressure. Although the initiation is by hydrogen molecule for explosion, the branching reaction with O_3 molecule is responsible for the higher reaction rate.

7.5 HYDROCARBON OXIDATION

Most liquid and many gaseous fuels consist of a mixture of various hydrocarbons. The physical and chemical nature of the various constituents in a fuel vary widely. As such the study of the kinetics of a fuel is quite difficult. Normally, for kinetic considerations a single constituent of fuel, i.e., a pure hydrocarbon is studied separately. These studies reveal that though the physical and chemical properties vary with the structure of a hydrocarbon, the oxidation process of hydrocarbon fuels has many common features. Therefore, the result obtained by studying the behaviour of one hydrocarbon, can predict the behaviour of a set of hydrocarbons. For example, the phenomenon of cool flames is observed in parafins above ethane and is common with various olefins, naphthenes, alcohols, aldehydes, and ethers. It is also observed that a few intermediate compounds are always found during the oxidation of hydrocarbons.

The mechanism of degenerate branch explosion is common to many hydrocarbons. The reaction mechanism for such explosions was explained by Semenov[21]. During a reaction, an intermediate unstable compound with appreciable half life is produced which disintegrates to give products. It is observed that in the oxidation process of many hydrocarbons, a hydroperoxide is formed which disintegrates either to give a ketone molecule and water or an oxygen heterocyclin compound and a chain carrier. Before taking up the chemical steps which are involved in the oxidation of a hydrocarbon, we shall discuss a few well established physical observations and laboratory results.

Prettre[22] first studied the oxidation of many hydrocarbons systematically. He passed the mixture of various hydrocarbon vapours and air through a pyrex glass or quartz reaction vessel. The reaction vessel was of 10 cm in length and 5.4 cm in diameter and kept in an electric furnace whose temperature was raised slowly. The mixture flow was slow with a known rate of 0.3 to 6 litres/hr.

The physical observations for the rich pentane—air mixture with increasing temperature were as given in Table 7.1.

It was found that the effect of fuel/air ratio on these temperatures was not much for the rich mixtures. The luminous wave observed at 260 C is called the cool flame. The term cool flame is used because the flame which is visible is unable to char an ordinary paper because of its low temperature. Normally, in a cool flame light is emitted by electronically excited formaldehyde.

The phenomenon observed for a lean mixture of pentane with air is given in Table 7.2.

It was also found that for higher hydrocarbons, the phenomenon observed was similar, but occurred at slightly low temperatures. It was also observed that the temperature at which luminescence appears increases from paraffin to the corresponding olefin or naphthene and from unsaturated cyclic compound to the corresponding saturated cyclic compound. It was observed that

TABLE 7.1

Temp. °C	*Phenomenon observed*
220	Bluish luminosity develops.
240	Luminosity increases strongly and uniformly.
260	A bright luminous wave is formed which starts at the exit of the tube and travels sowly against the stream at a speed of the order of 10 cm/s. A succession of such waves forms at the exit and disappears at the entrance.
260-290	Wave becomes more diffuse and travels more slowly.
290	Discrete waves appear leaving a luminous column in the tube, with zone of greater brightness which moves slowly against the stream.
350	Luminosity becomes uniform again.
670	Ignition occurs with comparative brilliance at the tube entrance, with the flame intermittently becoming extinct and reigniting.

TABLE 7.2

Temp. °C	*Phenomenon observed*
240	Light blue luminiscence becomes visible.
300-330	Luminiscence increases.
330-525	Luminiscence constant.
525-550	Luminiscence cannot be distinguished owing to glow of the walls.
660-670	Ignition.

aromatic compounds are much more resistant to oxidation than paraffins or naphthenes. This order of reactivity is parallel to the knocking tendency of fuels established in engine tests. Other notable observations are that the cool flame always appears at the exit point and that a definite induction period is necessary for its appearance.

In hydrocarbon oxidation, where a cool flame phenomenon is observed, acetaldehyde always appears as a major product between 200 and 300°C. Acetaldehyde in small concentrations catalyzes the oxidation in the range of luminiscence. Similarly, the addition of peroxides has an accelerating effect on the oxidation process, while lead tetraethyl represses the luminiscence and the cool flames in paraffins.

Neumann and Aivazov[23] conducted more accurate experiments on pentane-oxygen mixtures. They also recorded the pressure measurements. A typical pressure variation with the appearence of cool flame is shown in Fig. 7.4. AB represents the period where the mixture is warmed. BC represents the delay period τ during which the mixture prepares itself for the reaction and CD represents the cool flame zone. The cool flame phenomenon appears at C and ends at D. After D the pressure first drops along DE and then rises slowly and steadily. The accurate measurement of pressure during the CD zone gives the shape of the curve as shown in Fig. 7.5. Each cool flame which appears in the reaction vessel gives a sharp pressure pulse. After the passage of cool flame the pressure is increased slightly because of increase in the number of moles. The sudden rise and fall of pressure during a pulse indicates an increase and then a fall in temperature because of heat transfer. Raising the pressure or over-heating the mixture increases the pressure rise in the cool flame and accelerates the reaction after it.

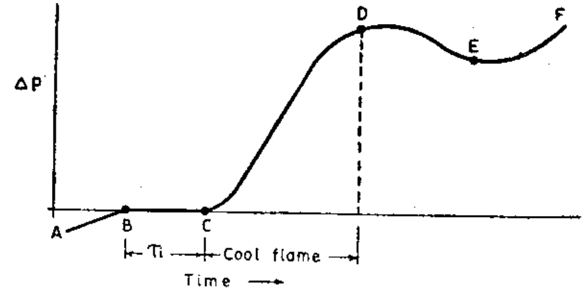


Fig. 7.4 Variation of pressure with appearance of cool flames.

The oxidation process of hydrocarbon can be divided in three parts: (i) slow oxidation usually in the temperature range of 20 to 500°C, (ii) cool

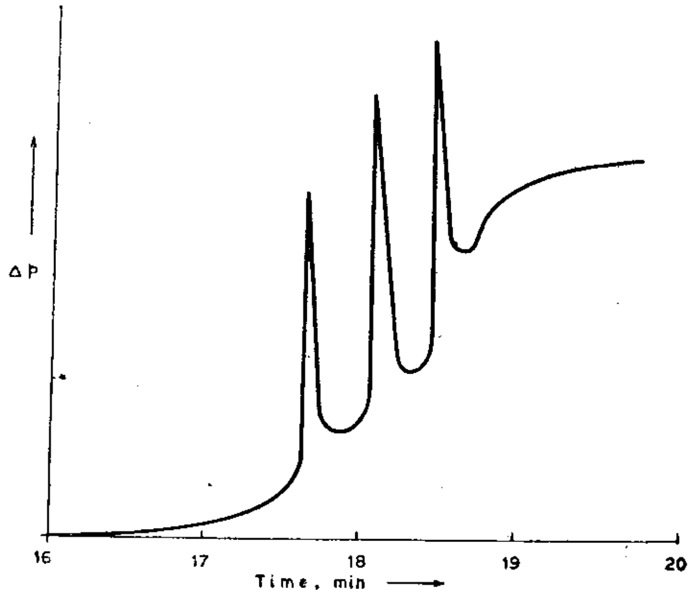


Fig. 7.5 Variation of reaction rate with time during the cool-flame oxidation.

flame zone normally between 250 and 350°C and (iii) hot flames, i.e., combustion at high temperatures. The pressure-temperature diagram of the oxidation of propane with oxygen given by Newitt and Thornes[24] is shown in Fig. 7.6. The diagram indicates the zone of slow oxidation to the left of curve ABC and the right hand side of curve JAL indicates the explosion zone. The pressure-temperature diagram for the other hydrocarbons gives a similar shape but the values of temperature and pressure may differ. The well defined explosion peninsula which points towards the low pressure side is bounded by a cool flame zone. The vertical line at a particular pressure indicates the explosion limit where it cuts the curve. In the diagram at 450 mm of Hg, we can get three explosion limits. However, it may be noted that these three limits correspond to three different temperatures at a given pressure while the explosion limits of hydrogen-oxygen or carbon monoxide-oxygen mixture correspond to different pressures at a particular temperature. Curve ABC gives the zone of cool flames.

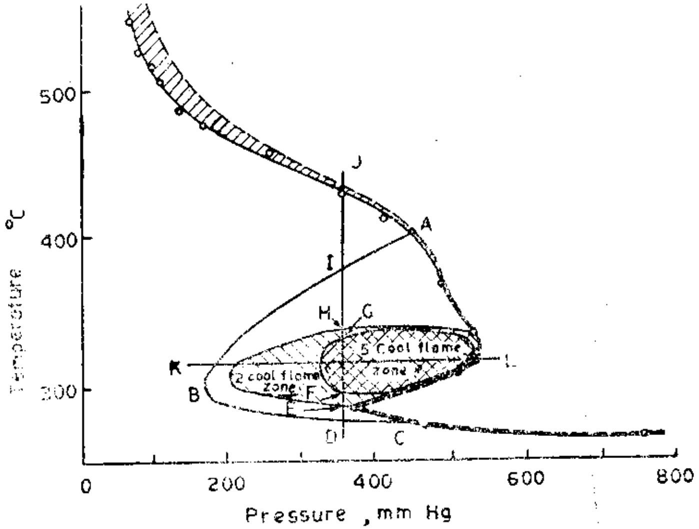


Fig. 7.6 Cool flame and second-stage ignition of $C_3H_8+O_2$ mixture (With permission of the Chemical Society, from the *Journal of Society*, p. 1656, 1937).

As we move in the positive *x*-axis direction along the line K-L, we pass from a zone of slow reaction to one cool flame zone, then to the two cool-flame zone, 4-5 cool fiame zone and utlimately the explosion zone. If a cool flame is followed by the hot one, the ignition is called a two-stage ignition process. Figure 7.7 shows the reaction rate in terms of pressure rise for 35% $C_5H_{12}+65\%$ O_2 mixture at 260°C and various initial pressures. Curve (1) is for the slow reaction zone, curve (2) for the cool flame zone and curves (3) and (4) for pressures in the two-stage ignition zone. In this zone a cool flame appears, after the delay period τ_1. The ordinary hot flame appears after the lapse of another delay period τ_2. For a mixture of C_5H_{12} and $4O_2$ at 340 mm Hg and 318°C, τ_1 was found to be about 8.2 s, while the explosion took place after 9.1 sec indicating τ_2 as 1.01 s. The delay period τ_1 for the cool flames decreases with increasing temperature. The relationship between τ_1, temperature and pressure was given by Neiman[25] and others as:

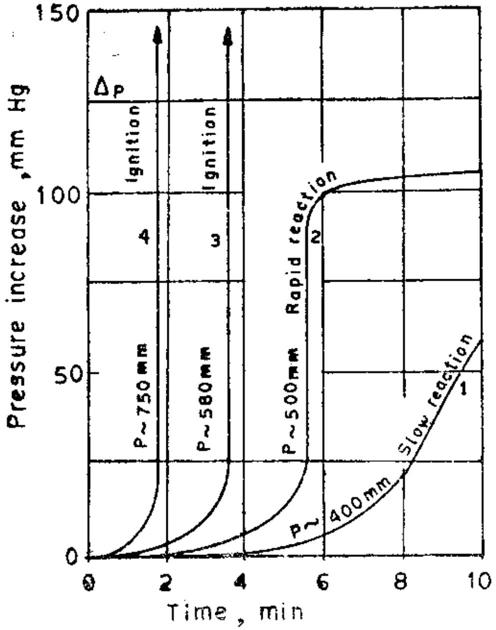


Fig. 7.7 Pressure rise versus time for 35% C_5H_{12} +65% O_2 at 260°C and various initial pressures [With permission of the Combustion Institute, from *Third Symposium (International) on Combustion*, p. 398, 1949].

$$\tau_1 = Ap^{-n} \exp(B/T) \tag{7.52}$$

where *A*, *B*, and *n* are constant. The above expression is similar to the expression of the reaction rate for the branched chain reaction. The constant *B* can be treated as E/R.

However, the dependence of τ_2 on temperature and pressure is of a complicated nature. According to Aivazov et al.[26], the value of τ_2 for the mixture of C_4H_{10} and O_2 increases with temperature, reaches a maximum value of 320°C, and starts decreasing. However, at a higher temperature, we may get an equation for τ_2 similar to the Eq. (7.52) for τ_1. The first stage ignition is because of the chain branching. However, before the reaction rate assumes an infinite value, the reaction rate is arrested because of the consumption of intermediate compounds. The second stage ignition is because

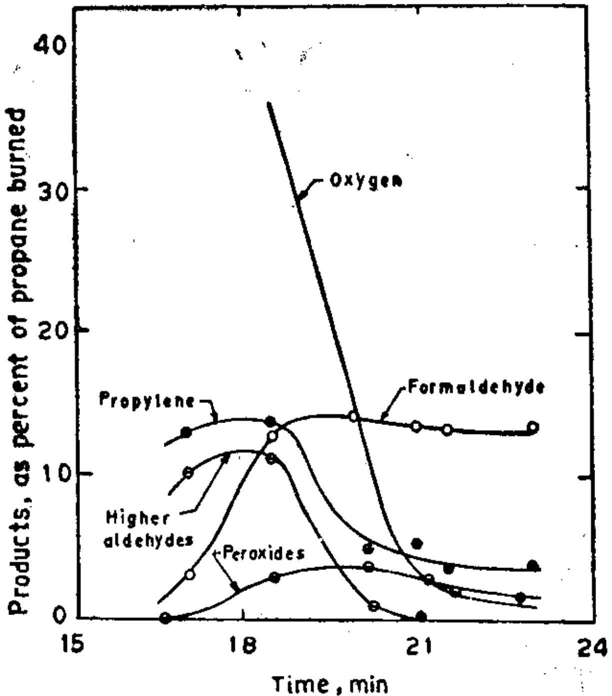


Fig. 7.8 Products from the reaction of a $C_3H_8+O_2$ mixture at 460 mm Hg and 274°C (below the cool flame zone) [With permission of the Chemical Society, from the *Journal of Chemical Society*, p. 1659, 1937].

of the heat liberated due to the exothermic reaction which leads to the increased rate of reaction.

The products of reaction for the propane-oxygen mixture in the various zones are shown in Figs. 7.8, 7.9 and 7.10 as reported by Newitt and Thornes[24]. Figure 7.8 corresponds to reactions below the cool flame zone, Fig. 7.9 above the cool flame zone, and Fig. 7.10 in the cool flame zone. Above the cool flame zone, formaldehyde is present in large proportion, the other major products being propylene and peroxides. Few workers have reported the presence of methyl alcohol which is also not reported by Newitt and Thornes.

Figure 7.8 shows that as the concentration of formaldehyde increases, that of the higher aldehydes decreases. This is because formaldehyde is produced by the oxidative degradation of acetaldehyde. Figure 7.10 shows that the final products contain propylene and higher aldehydes in larger proportions and appear earlier than formaldehyde. The shaded portion indicates the passage of cool flames. This figure also indicates that the cool flame results in the decrease in the concentrations of propylene and the higher aldehydes. The conentration drops sharply after some interval and rises again. Figure

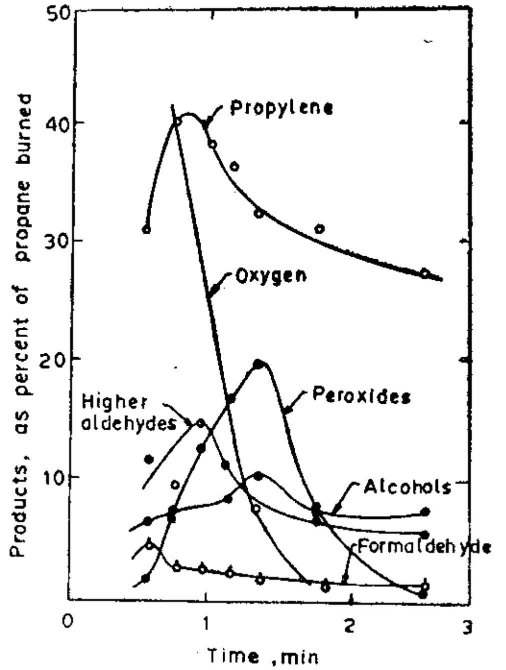


Fig. 7.9 Products from the reaction of a $C_3H_8+O_2$ mixture at 360 mm Hg and 400°C (above the cool flame zone) [With permission of the Chemical Society, from the *Journal of Chemical Society*, p. 1659, 1937].

7.9 which gives the zone of slow reaction above the cool flame zone, indicates that the reaction rate is much faster than in the first two zones and the oxygen concentration falls rapidly. The final products mainly contain propylene, alcohols, and higher aldehydes. Peroxides are produced in good quantity during the course of reaction but are ultimately consumed.

7.6 MECHANISM OF HYDROCARBON COMBUSTION

The study of the mechanism of hydrocarbon combustion can be divided into two main parts, viz., the low temperature oxidation process and the high temperature oxidation process. In high temperature oxidation, if a sufficient quantity of air or oxygen is present the end-products will always be water vapour and carbon dioxide irrespective of the structure of hydrocarbon, while in the slow oxidation process, various intermediate compounds are produced with an appreciable half-life. The chemical structure of these compounds depends upon the temperature, pressure, initial structure of fuel and time elapsed after the reaction started.

First let us consider the process of low temperature oxidation. The low temperature oxidation means the slow oxidation process, i.e., to the left of the explosion line given in Fig. 7.6. The cool flame zone is also included. It is clear from Figs. 7.8, 7.9, and 7.10 that the major products of combustion in all the three cases, i.e., below the cool flame zone, in the cool flame zone,

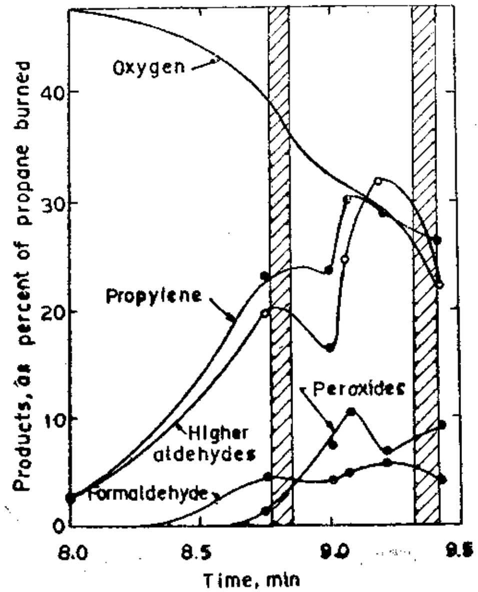


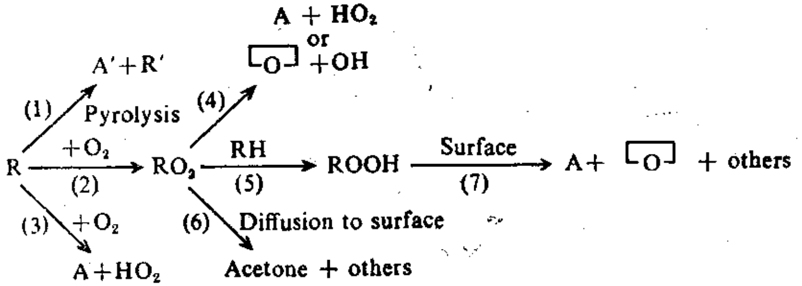
Fig. 7.10 Products from the reaction of a $C_3H_8+O_2$ mixture at 400 mm Hg and 294°C (in the cool flame zone) [With permission of the Chemical Society, from the *Journal of Chemical Society*, p. 1660, 1937].

and above the cool flame zone are the same but their proportions vary in the end state. The major products are olefins, peroxides, aldehydes, ketones and alcohols. Based on the various experimental facts, the mechanism of slow oxidation proposed recently by Knox and Kinnear[27], and for the oxidation of pentane in particular, can be taken as a general case which explains in a simple manner the various possible reactions.

As the oxidation of a hydrocarbon involves many intermediate products and various cracked products of a heavier molecule at high temperatures, it is quite difficult to give the reaction mechanism of various hydrocarbons. We shall first take a general hydrocarbon (say, a paraffin) represented by RH, where $R=C_nH_{2n+1}$, and then explain the various important reactions of one of the simplest paraffin molecules, C_3H_8 which exhibits the cool flames and other phenomena common to the heavier hydrocarbon molecules. Due to complexity, the mechanism of hydrocarbon oxidation cannot be completely described by a single set of reactions. After the production of radical R which may be the result of any one of the following reactions,

$$RH+O_2 \longrightarrow R+HO_2$$
$$RH+OH \longrightarrow R+H_2O$$
$$RH+O \longrightarrow R+OH$$

Knox and Kinnear[27] proposed the following **sets of reactions** (Fig. 7.11):



where *RH* is any n-paraffin, *R* is the alkane radical, *A* is the olefin of the hydrocarbon, *A′* is a lower olefin, *R′* is a lower alkane radical and $\boxed{O}$ is the oxygen hetrocyclic compound.

Fig. 7.11 Mechanism of oxidation pentane (With permission of the Combustion Institute from *Thirteenth Symposium (International) on Combustion*, p. 222, 1971).

In the above mechanism at low temperatures, i.e., below the cool flame zone, reactions 2, 5, and 7 appear to dominate reactions 1, 3, 4, and 6. In the cool flame region, reactions (4), (5), and (6) proceed with equal importance. As the temperature is increased, the pyrolysis reaction (4) dominates reactions (5) and (6). At still higher temperatures, i.e., above the cool flames, the pyrolysis of the alkane radical R increases, i.e., reaction (1) proceeds at a rapid rate. Although at various temperatures all the reactions given above and many other reactions will be occuring simultaneously, this simple scheme covers all the major products at various temperature ranges of the slow oxidation process. How important one reaction is as compared to another can be known once we know the various rate constants and concentrations of the reactants at different times. Plenty of work is still going on in this field and a large amount of literature is available.

If we consider the oxidation of propane based on the above mechanism and a few other possible reactions, the following reactions will occur.

$$C_3H_8+O_2 \rightarrow C_3H_7+HO_2$$
$$C_3H_7 \xrightarrow{(1)} C_2H_4+CH_2 \xrightarrow{+C_3H_8} CH_4+C_3H_7$$
$$C_3H_7+O_2 \xrightarrow{(3)} C_3H_6+HO_2$$
$$C_3H_7O_2 \xrightarrow{(2)} C_3H_7O_2$$
$$C_3H_7+O_2 \xrightarrow{(4)} C_3H_6+HO_2$$
$$C_3H_7O_2 \xrightarrow{(4)} OH+C_2H_5CHO$$
$$C_3H_7O_2+RH \xrightarrow{(5)} C_3H_7O_2H+C_3H_7$$
$$C_3H_7O_2H \xrightarrow{(7)} C_3H_7O+OH$$
$$C_3H_7O \rightarrow CH_3CHO+CH_3$$
$$C_3H_7O \rightarrow C_2H_5+HCHO$$

Apart from these reactions, the methyl radical and methane produced will repeat a similar set of reactions. As propane can be attacked by the H-abstracting radicals at either the primary or secondary position, the initial C_3H_7 radicals will consist of both primary and secondary isomers. But because the attack on the primary hydrogen atom is higher, ultimately the secondary isomers will become abundant. CH_4 and CO are also formed by the radical sensitized decomposition of CH_3CHO while the decomposition of HCHO produces small amounts of H_2 and CO.

Blue cool flames are produced by the electronically excited HCHO molecules. The possible reactions for the formation of HCHO* are:

H-abstraction from CH_3O as

$$CH_3O+\left\{\begin{matrix}CH_3\\OH\\C_3H_7\end{matrix}\right\}\rightarrow HCHO^*+\left\{\begin{matrix}CH_4\\HOH\\C_3H_8\end{matrix}\right\}$$

where CH_3O is formed as

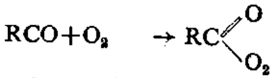
$$2CH_3O_2\ (RO_2)\rightarrow 2CH_3O+O_2$$

or from CH_3OOH molecule.

The formaldehyde and acetaldehyde formed are quite active and the reactions proceed as

$$\begin{aligned}
&R+CH_2O &&\rightarrow CHO+RH\\
&R+CH_3CHO &&\rightarrow CH_3CO+RH\\
&M+CH_3CO &&\rightarrow CO+CH_3+M\\
&M+CHO &&\rightarrow CO+H+M
\end{aligned}$$

or



$$RCO+O_2 \rightarrow RC\genfrac{}{}{0pt}{}{\diagup O}{\diagdown O_2}$$

$$\begin{aligned}
&RCO_3+R'H &&\rightarrow RCO_3H+R'\\
&RCO_3H &&\rightarrow RCO_2+OH\\
&RCO_2+R'H &&\rightarrow RCO_2H+R'\\
&RCO_2 &&\rightarrow R+CO_2
\end{aligned}$$

In general, it is found that the rate of oxidation decreases with an increase in the surface to volume ratio. Also the coated surface of potassium chloride inhibits the oxidation process. The cool flame region generally coincides with the formation of higher concentrations of peroxides and aldehydes.

For hot flame oxidation, it can be said that the reaction mechanism is quite similar to the reaction mechanism of H_2-O_2 mixture as:

$$\begin{aligned}
&OH+H_2 \rightarrow H_2O+H &\qquad& OH+RH \rightarrow H_2O+R\\
&O+H_2 \rightarrow OH+H && O+RH \rightarrow OH+R\\
&H+O_2 \rightarrow OH+O && R+O_2 \rightarrow RO+O\\
&H+O_2 \rightarrow HO_2 && R+O_2 \rightarrow RO_2\\
&HO_2+H_2 \rightarrow H_2O_2+H && RO_2+RH \rightarrow ROOH+R
\end{aligned}$$

but because of the thermal cracking of a hydrocarbon molecule the reaction mechanism of hydrocarbon oxidation is quite complicated as compared to that of the H_2-O_2 mixture. As in almost all reactions, the methyl radical and formaldehyde are produced, the mechanism of methane oxidation as proposed by Lewis and Von Elbe may be written as

$$\begin{aligned}
&OH+CH_4 &&\rightarrow H_2O+CH_3\\
&CH_3+O_2 &&\rightarrow HCHO+OH\\
&OH+HCHO &&\rightarrow H_2O+CHO\\
&CHO+O_2 &&\rightarrow CO+HO_2\\
&CHO+O_2+M &&\rightarrow CHO_3+M\\
&CHO_3+HCHO &&\rightarrow 2CO+H_2O+OH
\end{aligned}$$

The formation of CO_2 is either from CO or from the reaction given in the slow oxidation process of propane.

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8

THERMODYNAMICS OF COMBUSTION

Thermodynamics generally considers the inter-relationships between the properties of a system and the effect of energy transfers on them as the system undergoes a process involving a state change. For many purposes, it is sufficient to consider only processes during which the system experiences no chemical reaction. However, when we are analysing a combustion process, we are dealing with a system which is experiencing a state change involving a chemical reaction, and therefore, we must include the effects of this reaction in our analysis. When we do this, we are dealing with the thermodynamics of chemically reactive systems.

The object of this chapter is to develop the means of determining: (i) the amount of energy released in a combustion process, and (ii) the state of the projects of combustion (flame temperature, equilibrium composition, and other properties).

Both these objectives involve the application of the principle of conservation of chemical elements and the laws of thermodynamics (conservation of energy and maximization of entropy).

A combustion process usually means an exothermic oxidation process. The oxygen in the air reacts with the carbon and hydrogen of a fuel to form carbon monoxide, carbon dioxide, and water vapour. Thus the combustion of methane with stoichiometric air may be written as

$$CH_4+2O_2+2(3.76)\ N_2 \rightarrow CO_2+2H_2O+7.52\ N_2 \tag{8.1}$$

For stoichiometric combustion of pure hydrocarbon C_mH_n, the equation may be written as:

$$C_mH_n+\left(m+\frac{n}{4}\right)O_2+3.76\left(m+\frac{n}{4}\right)N_2 \rightarrow$$
$$mCO_2+\frac{n}{2}\ H_2O+3.76\left(m+\frac{n}{4}\right)N_2 \tag{8.2}$$

The relationship between fuel and air is usually given in terms of the air-fuel ratio (AF) or the fuel-air (FA). The air-fuel ratio refers to the mass of air supplied per unit mass of fuel, while the fuel-air ratio refers to the mass of fuel supplied per unit mass of air.

$$AF=\frac{\text{mass of air}}{\text{mass of fuel}}$$

and

$$FA=\frac{\text{mass of fuel}}{\text{mass of air}}$$

In actual combustion processes, we may have e moles excess oxygen or $-e$ moles deficiency per mole of C_mH_n. In this case, using Eq. (8.2) we have

$$C_mH_n+\left(m+\frac{n}{4}+e\right)(O_2+3.76\ N_2) \rightarrow mx\ CO+m\ (1-x)\ CO_2$$
$$+\frac{n}{2}\ H_2O+\left(\frac{mx}{2}+e\right)O_2+3.76\left(m+\frac{n}{4}+e\right)N_2 \tag{8.3}$$

Equation (8.) may be written in the general from as:

$$\sum_R n_iC_i \rightarrow \sum_P n_jC_j \tag{8.4}$$

where n_i and n_j are the number of moles of the reactant (R) and product (P) of the chemical species C_i and C_j respectively (per mole of fuel).

8.1 COMBUSTION PROCESS AND THE FIRST LAW

In a combustion process, we are interested in the conversion of chemical energy into thermal energy. The conversion of one form of energy to another is governed by the first law of thermodynamics. All matters contain energy in the form of molecular motion. The amount of energy varies upon the structure, nature, and state of matter. Recalling the first law of thermodynamics for a process in a closed system, the general mathematical expression is

$$\Delta U=Q-W \tag{8.5}$$

where ΔU represents the change of internal energy of the system, Q is the thermal energy or heat transfer to or from the system and W is the work done on or by the system. We will adopt the standard sign convention, i.e., the heat flowing into the system from the surroundings is taken as positive and the heat going out is taken as negative. Similarly, the work done by the system is considered positive and the work done on the system negative.

The internal energy U is a function of state and is independent of path. In combustion calculations, the change in enthalpy is more useful than the change in internal energy. Enthalpy is defined mathematically as

$$H=U+PV \tag{8.6}$$

where H=total enthalpy of the system

U=total internal energy of the system

PV=pressure volume product or potential external work function of the system (or flow work)

Enthalpy is also sometimes referred to as the total heat content of the system. As U, P, and V are functions of the state, H too is a function of state, i.e., it is a property of the system. But as in the case of internal energy, it is difficult to give any absolute value to the enthalpy of a system. Only the change of enthalpy can be measured experimentally. If we consider a change in enthalpy from state 1 to state 2,

$$H_2-H_1=U_2-U_1+P_2V_2-P_1V_1$$

or

$$\Delta H=\Delta U+(P_2V_2-P_1V_1) \tag{8.7}$$

If the process is carried out at constant pressure, then

$$\Delta H=\Delta U+P\cdot\Delta V \tag{8.8}$$

For energy transfer in the form of heat, the change of enthalpy is equal to the heat added in the case of ideal gases under constant pressure, i.e.,

$$Q=-\Delta H \tag{8.9}$$

where Q=heat added by surroundings

ΔH=enthalpy given up by the system (in heat units)

8.2 ENERGY BALANCE OF CHEMICAL REACTIONS

Internal Energy and Enthalpy of Combustion

Energy is associated with any molecule in the form of forces which bind different atoms together into a single particle. This means that the reactants and products of any reaction have a definite amount of energy associated with them. The energy released in any chemical reaction will, therefore, depend upon the chemical nature of the reactants and products. The state is usually defined by the temperature and pressure.

Internal Energy of Reaction

If a chemical reaction takes place at constant volume (as in the bomb calorimeter) and the products are brought back to the initial temperature of the reactants, the energy liberated or absorbed is known as the "internal energy of reaction" or the "heat of reaction of constant volume" and is symbolized as ΔU_R.

In the case of reactions occurring at constant volume, the relationship between the internal energy of the reactants (per mole of the fuel), U_R and that of the products, U_P is

$$Q=U_P-U_R \tag{8.10}$$

where Q is the amount of heat added to the system during the process (per mole of fuel).

Equation (8.10) applied to this process gives

$$Q=\sum_P n_ju_j-\sum_R n_iu_i \tag{8.11}$$

Here $\quad Q=n_f\cdot\Delta U_R$ (by definition of ΔU_R) $\qquad$ (8.12)

where n_f is the number of moles of fuel in the reactants.

Assuming complete combustion, i.e., $x=1$ and $e=0$ in Eq. (8.3)

$$\sum_P n_ju_j=n_f\,(m\cdot u_{CO_2}+Nu_{H_2O}+U) \tag{8.13}$$

where n_fU = internal energy of excess O_2+inerts

$$\sum_R n_i\,u_i=n_f\left[u_f+\left(m+\frac{n}{4}\right)u_{O_2}+U\right] \tag{8.14}$$

Substituting Eqs. (8.12), (8.13) and (8.14) into Eq. (8.11) we get

$$\Delta U_R=m\ u_{CO_2}+\frac{n}{2}u_{H_2O}-u_f-\left(m+\frac{n}{4}\right)u_{O_2} \tag{8.15}$$

Equation (8.15) shows that the internal energy of the fuel (u_f) includes the internal energy of the reaction (ΔU_R). Values of u may be obtained recalling that

$$u=h-pv=h-R_0\,T=h-1.987\ T \tag{8.16}$$

Making this substitution, Eq. (8.17) becomes (for a constant volume process)

$$Q=\left[\sum_P n_j\,h_j-n_P\,(1.987)\ T_P\right]-\left[\sum_R n_i\,h_i-n_R\,(1.987)\ T_R\right] \tag{8.17}$$

where $n_P=\Sigma n_j$=moles of products per mole of fuel

$n_R=\Sigma n_i$=moles of reactants per mole of fuel

T_P=temperature of products

T_R=temperature of reactants

Enthalpy of Combustion

The upper enthalpy of combustion of a fuel is defined as the heat which is rejected when 1 mole of the fuel is combined with sufficient oxygen (or air) to completely burn the fuel (to CO_2 and H_2O in the case of hydrocarbons), provided that the products are returned to the temperature of the reactants and the process takes place at constant pressure. The heat of vaporization of the water formed is deducted from this gross enthalpy of combustion to yield the lower enthalpy of combustion. The value of the enthalpy of combustion, ΔH_R is a function of the temperature chosen and is usually designated at 25°C and expressed in kilocalories per kg-mole (or calories per g-mole). Values of enthalpy of combustion for various hydrocarbons are given in Table A.16.

The lower enthalpies of combustion for hydrogen, carbon monoxide, and carbon may be ascertained by the following relationship (Fig. 8.1).

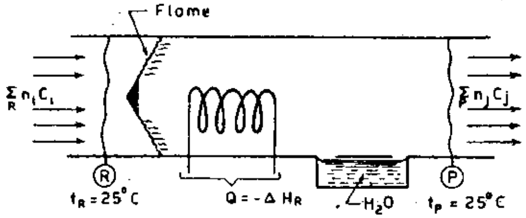

Fig. 8.1 Diagrammatic representation of the process used to determine the enthalpy of combustion.

For the constant pressure process under consideration, the steady flow energy equation becomes:

$$\sum_R n_i h_i + \Delta H_R = \sum_P n_j h_j + n_{H_2O} h_{fg,\ H_2O} \tag{8.18}$$

where n_i and n_j = as previously defined

h_i and h_j = molal enthalpies of reactants and products

$h_{fg,\ H_2O}$ = heat of vaporization of H_2O

n_{H_2O} = number of g moles of H_2O per mole fuel.

The heat of reaction at constant volume (ΔU_R) and the heat of reaction at constant pressure (ΔH_R) are related as follows:

$$\Delta H_R = (H_P - H_R)_P \tag{8.19}$$

For a constant volume process

$$\Delta U_R = (U_P - U_R)_V \tag{8.20}$$

Now subtracting Eq. (8.20) from Eq. (8.19), we have

$$\Delta H_R - \Delta U_R = (H_P - H_R) - (U_P - U_R) \tag{8.21}$$

From the definition of the enthalpy of a perfect gas

$$H = U + PV = U + nR_0T$$

Therefore, Eq. (8.21) can be written as

$$\Delta H_R - \Delta U_R = (H_P - H_R) - (H_P - n_P R_0 T - H_R + n_R R_0 T)$$

$$= (n_P - n_R) R_0 T$$

or

$$\Delta H_R - \Delta U_R = \Delta n\, R_0 T \tag{8.22}$$

where Δn represents the difference in the number of moles of gases of the products and reactants.

The enthalpy of a reaction also varies if the reaction occurs at different pressure or temperature. Therefore, to compare the values of the enthalpy of reaction for different reactions, it becomes essential to specify the state at which the reaction takes place.

Since most gases behave as an ideal gas at 1 atm and usually the reaction takes place at atmospheric temperature, the values of ΔU_R or ΔH_R, usually tabulated at 1 atm and 25°C, are called the standard internal energy of reaction and the standard enthalpy of reaction respectively.

This state of 1 atm and 25°C is called the standard condition. The standard values are generally represented by the superscript°, i.e. by ΔU_R° and H_R° or sometimes as $\Delta U_{R,\ 298}^\circ$ and $\Delta H_{R,\ 298}^\circ$ on molal basis. $\Delta H_{R,T}$ indicates the heat of reaction at temperature T.

Any exothermic reaction indicates the heat released from the system to the surroundings. By our sign convention, the heat flowing out of the system will be negative. For example, in the case of the reaction of propane with oxygen:

$$C_3H_8(g) + 5\,O_2(g) \rightarrow 3CO_2(g) + 4H_2O\ (l) \tag{8.23}$$

$$\Delta H_R^\circ = -2221493 \text{ kJ/kg-mol } (-530600 \text{ kcal/kg-mol})$$

This reaction indicates that the reaction is exothermic. To understand the significance of the negative sign it is easier to reason that the total internal energy or enthalpy of the products after combustion will be less than that of the reactants, i.e., because of the exothermic reaction, reactants have lost the energy. Hence a negative sign indicates that the reaction has released energy. While writing the equations, the terms (g) and (l) indicate the phase of the reactants or the products, because the change of enthalpy or internal energy of any reaction will depend upon the phase of the reactants and products. The term (g) indicates the gaseous state, (l) the liquid state, (s) the solid state (sometimes (c) is also used to indicate the solid state, i.e., crystals), and (ag) the hypothetical ideal solution.

The enthalpy of reaction is dependent upon the temperature at which the reaction takes place as is the enthalpy of different constituents. See Fig. 8.2 in which point 'a' represents the enthalpy of the reactants. Therefore, 'ab' will represent standard enthalpy of reaction $\Delta H_{R,\ 298}^\circ$ If we consider the reaction at any other temperature, say T, then $\Delta H_{R,T}$. is not equal to $\Delta H_{R,\ 298}^\circ$ Usually for an exothermic reaction, ΔH_R. increases with increase in temperature. The problem of heat of reaction at temperatures other than at 298 K becomes more important if the reaction occurs only at a higher temperature. To establish a relation between the change in the heat of reaction and the temperature, the following analysis gives useful results.

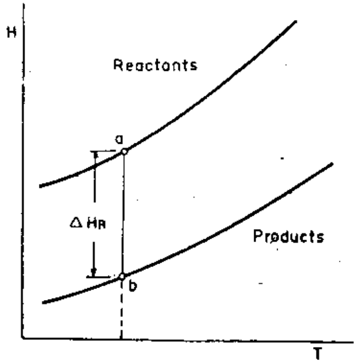

Fig. 8.2 Enthalpy of a reaction as a function of temperature.

Change of reaction enthalpy ΔH_R with temperature

$$\frac{d}{dT}(\Delta H_R) = \frac{d\,(H_P - H_R)}{dT}$$

$$= \left(\frac{dH}{dT}\right)_P - \left(\frac{dH}{dT}\right)_R$$

$$= (C_P)_P - (C_P)_R$$

This can be written as:

$$\frac{d\,(\Delta H_R)}{dT} = \Delta C_P \qquad (8.24)$$

Similarly, we can write

$$\frac{d\,(\Delta U_R)}{dT} = \Delta C_V \qquad (8.25)$$

These equations are often known as Kirchhoff's equations, which can be integrated.

Integrating Eq. (8.24) we get

$$\int_{T_1}^{T_2} d\,(\Delta H_R) = \int_{T_2}^{T_2} \Delta C_P \cdot dT$$

or $$\Delta H_{R,\,T_2} - \Delta H_{R,\,T_1} = \int_{T_2}^{T_1} \Delta C_P \cdot dT$$

Taking the mean value of C_P for a small temperature range, we get,

$$\Delta H_{R,\,T_2} = \Delta H_{R,\,T_1} + \Delta C_P\,(T_2 - T_1) \qquad (8.26)$$

By an analysis analogous to that used in developing Eq. (8.18) from Eq. (8.11), we conclude that the relationship between ΔH_R (experimentally determined in a constant pressure calorimeter) and h_f (molal enthalpy of fuel) is:

$$\Delta H_R = \left[m \cdot h_{CO_2} + \frac{n}{2}\,h_{H_2O} \right] - \left[h_f + \left(m + \frac{n}{4}\right) h_{O_2} \right. \qquad (8.27)$$

The enthalpy values for those compounds which have zero values of ΔH_R are seen to have zero values of enthalpy at 0 K. For these substances, the values of h are approximately the same as those calculated using values of a, b, c, and d in C_P equations. Note that

$$h = \int_0^T C_P\,dT = aT + b\,\frac{T^2}{2} + c\,\frac{T^3}{3} + d\,\frac{T^4}{4} \qquad (8.28)$$

For compounds having non-zero values of ΔH_R (H_2 OH, CO, NO, C, CH_4, etc.) the value of h is found by Eq. (8.27) at 298 K:

$$h_{298} = (-\Delta H_R)_{298} - \left[\left(m + \frac{n}{4}\right) h_{O_2} \right]_{298} + \left[m \cdot h_{CO_2} + \frac{n}{2}\,h_{H_2O} \right]_{298} \qquad (8.29)$$

Thus, if ΔH_R values at 298 K (25°C), are known, h_f at 298 K can also be determined by Eq. (8.29). At other temperatures, h_f may be obtained by:

$$h = h_{298} + \int_{298}^{T} C_P\,dT \qquad (8.30)$$

In Eq. (8.30), $C_P = a + bT + cT^2 + dT^3$. Values of a, b, c and d from Table A.18 are used to evaluate h for fuels in Eq. (8.30).

Enthalpy of Formation

There are numerous hydrocarbons and other fuels which can react in a number of ways. It is often difficult to find the enthalpy of reaction for each one of them. This problem can be simplified by introducing the concept of enthalpy of formation, sometimes called the standard enthalpy, change of formation, or standard heat of formation. This is defined as the energy released or absorbed when a chemical compound is formed from its elements, the products and the elements being at their standard state. The standard state referred to is the one at 1 atm pressure and 25°C temperature.

The reacting elements are defined as stable elements in their standard state at given initial pressure and temperature. For example, the stable form of hydrogen is H_2 gaseous molecule, standard state of carbon is solid carbon atom C, and sulphur exists in the rhombic crystalline form. Similarly, the products should be in their standard state e.g., the standard state of H_2O vapour can be calculated at 1 atm and 25°C taking into account the latent heat of vaporization. The standard enthalpy of formation is represented by the symbol $\Delta H_{f,\,298}^{\circ}$.

It is obvious from the definition of the enthalpy of formation that the enthalpy of elements in their standard state and at standard condition of 1 atm and 25° is taken to be zero. Thus

$$\text{for } H_2\,(g){:}\quad \Delta H_{f,298}^{\circ} = 0$$

Table A.15 shows the selected values of $\Delta H_{f,298}^{\circ}$ for various compounds.

From the definition of ΔH_f° on molal basis:

$$\Delta H_f^{\circ} = h^{\circ}_{\text{comp}} - \Sigma n_i\,h_i \qquad (8.31)$$

Here h_i is the molal enthalpy of the ith elemental substance involved in the formation reaction and n_i is the number of moles of the ith elemental substance involved in forming a single mole of the compound. For example, the enthalpy of formation of CO_2 will be the amount of heat released by the combustion of solid carbon with gaseous oxygen to give gaseous carbon dioxide at standard conditions.

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

$$\Delta H^\circ_{f,\,CO_2} = \overset{\circ}{h}_{CO_2} - (\overset{\circ}{h}_C + \overset{\circ}{h}_{O_2}) \qquad (8.32)$$

$$\therefore \quad \overset{\circ}{h}_{CO_2} = \Delta H^\circ_{f,\,CO_2} = -393.769 \text{ kJ/mole}$$

If we know the enthalpies of formation for different elements and compounds, it is quite easy to calculate the enthalpy of reaction for any particular reaction either with the help of a single reaction equation or with the help of a set of selected chemical equations.

$$\Delta H_R = H_P - H_R = \Sigma(n_j\, h_j)_P - \Sigma(n_i\, h_i)_R$$

$$= \sum_P n_j \;\Delta H^\circ_f - \sum_R n_i \;\Delta H^\circ_f \qquad (8.33)$$

The principle of constant heat summation, i.e., Hess's law is quite useful for using a set of chemical reactions because enthalpy is a function of state only. Hess's law says that if the simple reaction equations are added or subtracted to give an overall reaction scheme, then the corresponding ΔH_R values can also be added or subtracted to give an overall value of enthalpy change.

Example 8.1

Determine the enthalpy of formation (ΔH°_f) of propane using the table of values of enthalpy of combustion (ΔH°_R) of C_3H_8 (g), enthalpy of formation (ΔH°_f) of CO_2 (g) and enthalpy of formation (ΔH°_f) of H_2O (1).

Solution

The relevant chemical equation is

$$C_3H_8\,(g) + 5\,O_2\,(g) \rightarrow 3\,CO_2\,(g) + 4\,H_2O\,(1)$$

The enthalpy of combustion for any reaction is related to the enthalpy of formation data for the reactants and products. For the above reaction we write:

$$\Delta H^\circ_R = 3(\Delta H^\circ_f)_{CO_2} + 4(\Delta H^\circ_f)_{H_2O} - 1\,(\Delta H^\circ_f)_{C_3H_8} - 5(\Delta H^\circ_f)_{O_2}$$

The enthalpy of formation data for CO_2 (g) and H_2O (1) and the enthalpy of combustion for C_3H_8 (g) are found in Tables A.15 and A.16 respectively.

Therefore, $(\Delta H^\circ_f)_{C_3H_8} = 3\,(-393769) + 4\,(-286028)$

$$-5\,(0.0) - 1\,(-2221493) = -103926 \text{ kJ/kmol}$$

Compare this answer with the value of ΔH°_f for C_3H_8 (g) in Table A.15.

Example 8.2

Determine the internal energy of reaction, ΔU_R for methane at 300°C.

Solution

The combustion of methane with stoichiometric amount of oxygen is given by the chemical equation

$$CH_4\,(g) + 2\,O_2\,(g) \rightarrow CO_2\,(g) + 2\,H_2O\,(g)$$

The symbol (g) in the above equation indicates the gas phase.

The enthalpy of combustion for the reaction is written as

$$\Delta H_R = \sum_P n_j\, h_j - \sum_R n_i\, h_i$$

We know $\Delta H_R - \Delta U_R = (\sum_P n_j - \sum_R n_i) R_0 T$

Therefore, $(\Delta U_R)_{573K} = [\sum_P (h_j - R_0 T) - \sum_R (h_i - R_0 T)]_{573K}$.

The absolute enthalpy of a substance at any temperature T is given by the equation

$$h_T = \Delta H^\circ_f + (h_T - h_{298})$$

Applying this equation to the problem we have

$$(\Delta U_R)_{573} = 1(\Delta H^\circ_f)_{CO_2} + (h_{573} - h_{298})_{CO_2} - 1.987 \times 573 + 2(\Delta H^\circ_f)_{H_2O}$$
$$+2(h_{573} - h_{298})_{H_2O} - 2 \times 1.987 \times 573 - 1(\Delta H^\circ_f)_{CH_4}$$
$$-1 \int_{298}^{573} (C_p)_{CH_4}\, dT - 1 \times 1.987 \times 573 - 2(\Delta H^\circ_f)_{O_2}$$
$$-2\,(h_{573} - h_{298})_{O_2} - 2 \times 1.987 \times 573 \text{ kcal/kmol } CH_4$$

where $\int_{298}^{573} (C_p)_{CH_4}\, dT = (h_{573} - h_{298})_{CH_4}$

$$= \int_{298}^{573} (a + bT + cT^2 + dT^3)_{CH_4}\, dT$$

Substituting the data for C_p of methane from Table A.18 and integrating

$$(\Delta h)_{CH_4} = \int_{298}^{578} (19.87 + 5.021 \times 10^{-2} T + 1.268 \times 10^{-5}\, T^2 - 11 \times 10^{-9}\, T^3)\, dT$$
$$= 11883.55 \text{ kJ/kmol } CH_4 = 2838 \text{ kcal/kmol } CH_4$$

Hence substituting the values of ΔH°_f from Table A.15 and $(h_{573} - h_{298})$ from Tables A.20, A.21 and A.23 after interpolation for the specific components we get:

$$(\Delta U_{R,CH_4})573 = [(-94154) + 2790 - 1138.55] + 2[(-57798) + 2278.15$$
$$-1138.55] - [(-17825) + 2838 - 1138.55] - 2[(0.0) + 2006.2 - 1138.55]$$
$$= (-92502.55) + (-113316.8) - (-7150) - (1735.3)$$
$$= -191359 \text{ kJ/kmol}$$

Example 8.3

Methane gas at 400 K is supplied along with 120 per cent stoichiometric air (preheated to 500 K) to a furnace. Combustion which occurs at 1 atm pressure, goes to completion and the temperature of the products of combustion is 2000 K. Determine the heat transfer to or from the furnace in kJ/kmol of fuel.

Solution

The chemical equation for complete combustion of methane with 120 per cent theoretical air is

$$CH_4+1.2\times 2(O_2+3.76\ N_2)\rightarrow CO_2+2\ H_2O+9.024\ N_2+0.4\ O_2$$

The energy balance for the combustion process is written as

$$Q=\sum_P n_i\,(\Delta H_f^\circ+h_T-h_{298})_i-\sum_R n_i\,(\Delta H_f^\circ+h_T-h_{298})_i$$

The enthalpy of formation data are given in Table A.15 and the values of enthalpy (h_T-h_{298}) for the gases are available in Tables A.19, A.20, A.21 and A.23. The enthalpy change for methane from 298 to 400 K is calculated as follows:

$$(C_p)_{CH_4}=(a+bT+cT^2+dT^3)$$

where the coefficients *a*, *b*, *c* and *d* for methane are listed in Table A.18.

$$(C_p)_{CH_4}=19.87+5.021\times 10^{-2}T+1.268\times 10^{-5}\ T^2-11\times 10^{-9}T^3$$

Therefore, the enthalpy change is given by:

$$(h_{400}-h_{298})_{CH_4}=\int_{298}^{400}(C_p)_{CH_4}\,dT$$

$$=19.87\ (400-298)+\frac{5.021\times 10^{-2}}{2}\left[(400)^2-(298)^2\right]$$

$$+\frac{1.268\times 10^{-5}}{3}\left[(400)^3-(298)^3\right]$$

$$-\frac{11\times 10^{-9}}{4}\left[(400)^4-(298)^4\right]$$

$$=2026.74+1787.3+158.6-48.6$$

$$=3924\ \text{kJ/kmol}\ CH_4$$

Substituting the data from the Appendix tables stated above and the enthalpy change for methane, we get

$$Q=1(-393769+91512)+2(-241997+72736)+9.024\ (0.0+56178)$$
$$+0.4\ (0.0+58239)\ -1\ (-74920+3924)-2.4\ (0.0+6092)$$
$$-9.024\ (0.0+5915)$$
$$=-302257-338552+506950.27+23295.6+70995.96-14620.8$$
$$-53376.96$$
$$=-107565\ \text{kJ/kmol}\ CH_4$$

Bond Energies

All chemical reactions are nothing but the rearrangement of the molecules of different elements in the form of various compounds. The atoms of one element are joined with the atoms of other elements with the help of a force called the bond energy. If we want to break any molecule into its atoms, a definite amount of energy is needed. This energy will be equal to the change in enthalpy. Consider an equation:

$$AB(g)\ \rightarrow\ A(g)+B(g) \qquad (8.34)$$
$$\text{Enthalpy change}=\Delta H^\circ_{298}$$

If the molecule and its atoms are at their standard state and at standard condition of 1 atm and 25°C, the enthalpy change equals the standard bond dissociation energy DH° for the bond A-B

$$DH^\circ\ (\text{A-B})=\Delta H^\circ_{298}$$

For example, two O-H bonds of water can be broken in succession:

$$\text{HO-H(g)}\ \rightarrow\ \text{HO(g)+H(g)},\ \Delta H^\circ=+494\ \text{kJ/mole}$$
$$\text{O-H(g)}\ \rightarrow\ \text{O(g)+H(g)},\ \Delta H^\circ=+431\ \text{kJ/mole}$$
$$\therefore\quad DH^\circ\ (\text{HO-H})=494\ \text{kJ/mole}$$
$$DH^\circ\ (\text{O-H})=431\ \text{kJ/mole}$$

Similarly, if we remove hydrogen atoms from methane one by one, the standard bond dissociation energies will be as follows:

$$DH^\circ\ (CH_3\text{-H})=435\ \text{kJ/mole}$$
$$DH^\circ\ (CH_2\text{-H})=444\ \text{kJ/mole}$$
$$DH^\circ\ (\text{CH-H})=444\ \text{kJ/mole}$$
$$DH^\circ\ (\text{C-H})=339\ \text{kJ/mole}$$

Average Bond Dissociation Energies

An approximate average bond energy can be calculated by assuming the molecule to break into its atoms in the gas phase. Consider the example of methane gas which would give

$$CH_4(g)\ \rightarrow\ C(g)+4H(g) \qquad (8.35)$$

four atoms of hydrogen gas and one atom of carbon in gaseous form. This reaction involves the breaking of four C–H bonds.

$$\Delta H^\circ=\Delta H_f^\circ\ [C(g)]+4\Delta H_f^\circ\ [H(g)]-\Delta H_f^\circ\ [CH_4(g)]$$
$$=715.0+4\ (217.9)-(-74.85)$$
$$=1661\ \text{kJ/mole}$$

It is to be noted that ΔH_f° (C) and ΔH_f° (H) are not zero because they are not taken at their standard state, i.e., solid for carbon and H_2 molecule for hydrogen. Therefore, the average bond dissociation energy for the C–H bond works out to be:

$$DH_{av}\ (\text{C–H})=\frac{\Delta H^\circ}{4}=\frac{1661}{4}=415.25\ \text{kJ/mole}$$

Similarly, if we consider ethane, it will involve the breaking of six C–H bonds and one C–C bond.

The calculation of average bond energies for various molecules indicates that there is very little variation of bond energy for similar bonds. The concept of bond energy can, therefore, be well utilized to calculate an approximate enthalpy of formation of any new molecule of known structure. Table 8.1 shows the average bond energies for a few single and multiple bonds in kJ/mole.

TABLE 8.1 Average Bond Dissociation Energies for a Selection of Single and Multiple Bonds (kJ/mole)

	I	Br	Cl	F	O	C	H
H	297	368	431	569	460	414	435
C	226	289	343	444	339	343	—
O	—	—	205	184	146	—	—
F	243	251	255	159	—	—	—
Cl	209	218	243	—	kJ/mole	—	—
Br	180	192	—	—	—	—	—
I	151	—	—	—	—	—	—

C=C : 611 kJ/mole
C≡C : 833 kJ/mole
C=C : 741 kJ/mole
C≡N : 879 kJ/mole

8.3 ADIABATIC FLAME TEMPERATURE

The adiabatic flame temperature, adiabatic combustion temperature, or the theoretical reaction temperature is the maximum possible temperature attained by the products of reaction when the reaction goes to completion and all the heat released is used to heat up the products. To attain maximum temperature, the fuel must be mixed with a stoichiometric amount of oxygen and the reaction should be complete. If the combustion of fuel takes place with air instead of oxygen, the temperature attained will be lower because some of the heat will be used to raise the temperature of the nitrogen in the air.

The calculation of the adiabatic flame temperature is useful for the consideration of metallurgical limitations of the materials used in combustion chambers and gives an idea of the possible maximum temperature that can be attained for any fuel. In practice, it is difficult to obtain theoretical temperatures because of incomplete combustion, excess air usually supplied, heat losses due to radiation, conduction and convection, dissociation of products, etc.

In any reacting mixture, the sum of the enthalpies of the reactants equals the standard enthalpy of the reaction and the total enthalpy of the products. The temperature of the products which will correspond to this total enthalpy can be calculated. For such calculations, one should know the heat capacities and latent heat for each of the products of the reaction. The heat capacity usually varies with temperature, especially if the temperature range is large. It cannot be taken as a constant. The variation of C_p with temperature is usually given in a tabular form or as a chart. The value of C_p is usually known as a power series. The number of terms commonly used to describe C_p varies from two to four. The general expression is:

$$C_p=a+bT+cT^2+dT^3 \tag{8.36}$$

the values of a, b, c, and d are given for various reactants and products. Thus C_p can be calculated for any particular temperature or the heat required to heat up the products can be calculated as:

$$\begin{aligned} q &= n\int_{T_2}^{T_1} C_p \cdot dT \\ &= n\int_{T_1}^{T_2} (a+bT+cT^2+dT^3)\, dT \\ &= n\left[aT+b\frac{T^2}{2}+c\frac{T^3}{3}+d\frac{T^4}{4} \right]_{T_1}^{T_2} \end{aligned} \tag{8.37}$$

But usually, the value of T_2 is unknown.

The enthalpy of each of the products of reaction can be expressed by an equation similar to Eq. (8.28) and all these can be added together to represent H_p for the products. The equation can be solved by the trial and error or the graphical method. If some of the products change their phase during heating, the equation may be written as:

$$q=n\left[aT+\tfrac{1}{2}\,bT^2+\tfrac{1}{3}\,cT^3+\tfrac{1}{4}\,dT^4\right]_{T_1}^{T_2}+n\lambda \tag{8.38}$$

where λ is the latent enthalpy change for the product.

The procedure of calculation can be simplified if we know $h-h^\circ_{298}$ and ΔH°_f for all the reactants and the products. Joint Army Navy Air Force (JANAF) tables[1] give comprehensive values of $h-h^\circ_{298}$ up to a temperature 5000 K. The procedure can be better understood with the help of Fig. 8.3. Let us assume that the initial reactant temperature is T_i (and not 298 K), and the products will be at some final temperature T_f where the sum of the enthalpies of the products of combustion equals that of the reactants. To calculate this temperature, we proceed by the indirect path 1–2–3–4. The energy available by cooling the reactants from state (1) to state (2) plus the additional energy released by combustion at 298 K from state (2) to state (3) must equal the change in enthalpy of the products of combustion from state (3) to state (4).

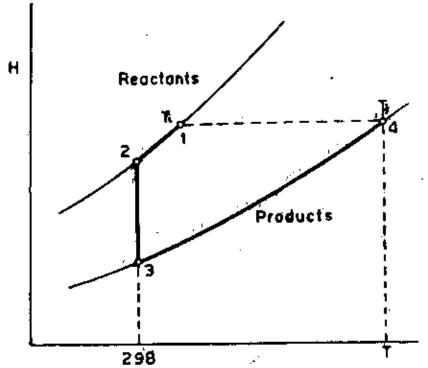

Fig. 8.3 Process diagram for calculation of the adiabatic frame temperature.

We know that the absolute enthalpy of a substance at any temperature T with respect to know data at 25°C is given by

$$h_T = \Delta H^\circ_{f,\,298} + (h_T - h_{298}) \tag{8.39}$$

In most combustion processes, there is no shaft work and the change in potential energy is negligible. Whether the kinetic energy term is important or not depends upon the particular application. Hence the energy balance for the combustion process reduces to:

$$Q = \Delta H + \Delta KE$$
$$= \sum_P n_j(H_j + KE_j) - \sum_R n_i\,(H_i + KE_i) \tag{8.40}$$

where the value of n_i comes directly from the balanced chemical equation and Q is the heat transfer for n_i moles of fuel. In most cases the value of n_i for the fuel itself will be unity. The values of H_i and H_j must be, of course, the absolute enthalpy values for the various substances involved as found from Eq. (8.39). If Eq. (8.39) is substituted into Eq. (8.40) then

$$Q = \sum_P n_j\,[\Delta H^\circ_f + (h_T - h_{298})] - \sum_R n_i\,[\Delta H^\circ_f + (h_T - h_{298})] \tag{8.41}$$

where the kinetic energy terms have been neglected.

Or
$$Q = \sum_P n_j\,\Delta H^\circ_f - \sum_R n_i \Delta H^\circ_f + \sum_P n_j\,(h_T - h_{298}) - \sum_R n_i\,(h_T - h_{298}) \tag{8.42}$$

However, according to Eq. (8.33)

$$\Delta H^\circ_R = \sum_P n_j\,\Delta H^\circ_f - \sum_R n_i\,\Delta H^\circ_f \tag{8.43}$$

Hence
$$Q = \Delta H^\circ_{R,\,298} + \sum_P n_j\,(h_T - h_{298}) - \sum_R n_i\,(h_T - h_{298}) \tag{8.44}$$

The above equation is only useful if the enthalpy of reaction for the desired reaction is available from a table. Otherwise, since data on enthalpy of formation are available, Eq. (8.42) should be used.

When the correct final flame temperature is tried, the heat transfer term Q in Eq. (8.44) will vanish ($Q=0$ for adiabatic combustion; $H_P = H_R$). Thus the procedure is to guess the final flame temperature T_f, and then compute the enthalpy of the products of combustion corresponding to this guessed temperature. The value of H_P obtained is then compared with H_R, and iteration carried out with T_s until $H_P = H_R$ as required for an adiabatic constant pressure flame, i.e., the summation of the enthalpies of the products equals that of the unburned gas mixture.

Example 8.4

Methane and 200 per cent theoretical air at 1 atm and 25°C react at constant pressure in a steady flow process. Determine the adiabatic flame temperature in K.

Solution

The stoichiometric equation for the reaction is

$$CH_4 + 2(O_2 + 3.76\ N_2) \rightarrow CO_2 + 2H_2O + 7.52\ N_2$$

For 200 per cent theoretical air (or 100 per cent excess air) the equation becomes

$$CH_4 + 4O_2 + 15.04\ N_2 \rightarrow CO_2 + 2H_2O + 2O_2 + 15.04\ N_2$$

The absolute enthalpy of a substance at any temperature T is given by the equation

$$h_T = \Delta H^\circ_f + (h_T - h_{298})$$

Applying this equation to this problem we have

$$\sum_R n_i(\Delta H^\circ_f + h_T - h_{298})_i = \sum_P n_j(\Delta H^\circ_f + h_T - h_{298})_j$$

As the final temperature of the combustion products is unknown, all the values of the terms in this equation are known except the $(h_T - h_{298})$ values for the products. From the tables in the Appendix, substituting the known values of the terms in the equation gives

$$1\,(-17895) = 1(-94154 + h_T - h_{298})_{CO_2} + 2(-57798 + h_T - h_{298})_{H_2O(g)}$$
$$+ 2(h_T - h_{298})_{O_2} + 15.04(h_T - h_{298})_{N_2}$$

or
$$191855 = 1(h_T - h_{298})_{CO_2} + 2(h_T - h_{298})_{H_2O} + 2(h_T - h_{298})_{O_2}$$
$$+ 15.04(h_T - h_{298})_{N_2}$$

The final value of the adiabatic flame temperature is obtained by trial-and-error method of solution. We guess a value of the temperature T for which $(h_T - h_{298})$ value of each of the products is known. This would enable us to evaluate the right hand side of the above equation. The following Table shows the summary of the iteration process at temperatures close to the final value.

$n_j(h_T - h_{298})_j$	1400 K	1500 K	1480 K
$1\ (h_T - h_{298})_{CO_2}$	13362	14750	14472
$2\ (h_T - h_{298})_{H_2O}$	20768	22986	2(11271)
$2\ (h_T - h_{298})_{O_2}$	17670	19412	2(9532)
$15.04\ (h_T - h_{298})_{N_2}$	125584	138052	15.04(9013)
$\sum_P n_j(h_T - h_{298})_j$	177384	195200	191634

The value of $\sum_P n_j(h_T - h_{298})_j$ should be 191855. The data in the above Table shows that the adiabatic flame temperature is close to 1480 K.

8.4 EQUILIBRIUM COMPOSITION OF GASEOUS MIXTURES

Definition

A system is said to be in equilibrium when there is no tendency for spontaneous change in its state with respect to time. Further, the equilibrium is stable if a small disturbance brings about not more than a correspondingly small change in state. For example, a system comprising a mixture of equal volumes of hydrogen and oxygen at room temperature and pressure is not in a state of stable equilibrium, since a very small spark could bring about a great change of state (through combustion). In this chapter when the term equilibrium is used, it is understood to mean stable equilibrium.

By equilibrium composition we mean that chemical composition (proportions of each chemical compound) in which the system is in a stable equilibrium state. In any molecular collision, there is a possibility of a chemical reaction, i.e., at least one of the molecules involved may lose its chemical identity. Whether or not such a reaction will occur in a given collision depends on the species of molecules involved, their relative velocity of approach at a given distance apart, their spins and vibrational modes, their respective orientations, and various other factors.

A system comprising many thousands of molecules and/or atoms is in a state of chemical equilibrium when there is no tendency for the concentration of any chemical species to change with time. This does not mean that new species are not being created and old ones continuously destroyed (from the molecular viewpoint). A system is in chemical equilibrium if the rate of formation and the rate of destruction of each species present are equal.

The Equilibrium Composition of a Single Chemical Species

With the possible exception of monoatomic gases (argon, krypton, xenon, etc.) it is theoretically impossible to have a single species gaseous system. To clarify this statement, let us take oxygen gas as an example. Consider a system comprising nothing but oxygen, i.e. no atoms other than those of oxygen are present within the system. At room temperature and pressure (in the absence of strong electrical or magnetic fields) nearly all of the oxygen at a given instant exists in the molecular form with two atoms whose nuclei are held close together by a chemical bond. These nuclei rotate around a central axis and vibrate very rapidly. All the while, each such molecule is experiencing millions of collisions per second with the neighbouring molecules. Occasionally one or more of these collisions will impart so much energy (in the form of rotation and vibration) to the diatomic molecule that the two atoms will separate completely. Each one then may wander about until it happens to be "captured" by another free oxygen atoms to form a new O_2 molecule, or perhaps by an oxygen molecule to form an O_3 molecule. Therefore, it can be seen why at any instant in a system comprising millions of molecules, there are also present oxygen atoms (called dissociation products from the process: $O_2 \rightarrow 2O$) as well as O_3 molecules. The same applies to any other gas such as hydrogen, carbon monoxide, carbon dioxide, etc.

Further, since the mean translational kinetic energy, as well as the rotational and vibrational energy (according to the principles of equipartition of energy) vary directly with the temperature, it can be seen that the population of dissociated species increases with temperature. But how does this precisely happen? To answer this question, we must start from fundamental thermodynamic considerations. We shall see that the equilibrium composition at a given temperature can be best specified by the use of the "equilibrium constant".

The Equilibrium Composition of a Mixture of Reacting Species

Consider the case of a system comprising a mixture of reacting species, such as hydrogen and oxygen. Here we shall see that we have not only molecular hydrogen, oxygen, and water present, but also such species as OH, O, H, HO_2, H_2, O_2, and others. Due to either the relative weakness of the chemical bonds joining the atoms or the great affinity between the two atoms which frequently meet, many of the species are very unstable (short lived). The exact equilibrium composition (% of each component) depends only on the temperature, pressure, and on the relative numbers of different types of atoms present. For the case cited above comprising only hydrogen and oxygen

$$\text{Composition} = f(T, p, [O], [H])$$

where [O] and [H] represent the concentration of oxygen and hydrogen atoms present in the mixture.

The Law of Mass Action

The law of mass action states that "the rate at which a chemical reaction proceeds is proportional to the concentrations of the active species present".

Consider a general reaction

$$A + B \rightarrow C \tag{8.45}$$

The rate at which this occurs (the time rate of formation of C from A and B) at a given temperature may be assumed to be proportional to the number of A–B collisions per unit time. This collision rate is, in turn, proportional to the mole fractions of both A and B. Thus

$$\overrightarrow{\text{rate}} = \vec{k}\,(x_A)\,(x_B) \tag{8.46}$$

where x_A and x_B are the mole fractions of the species A and B and k is the proportionality or rate constant. The reverse of the step represented by Eq. (8.45) can also take place

$$A+B \leftarrow C \tag{8.47}$$

then the rate of such a reaction is given as

$$\overleftarrow{\text{rate}} = \overleftarrow{k}\,(x_C) \tag{8.48}$$

Consider the reaction

$$O+O \rightleftharpoons O_2 \tag{8.49}$$

$$\overrightarrow{\text{rate}} = \overrightarrow{k}\,[x_O]\,[x_O] = \overrightarrow{k}\,[x_O]^2 \tag{8.50}$$

and $$\overleftarrow{\text{rate}} = \overleftarrow{k}\,[x_{O_2}] \tag{8.51}$$

In general, for a reaction

$$aA+bB+cC\ldots \rightleftharpoons lL+mM+nN$$

$$\overrightarrow{\text{rate}} = \overrightarrow{k}\,[x_A]^a\,[x_B]^b\,[x_C]^c \tag{8.52}$$

$$\overleftarrow{\text{rate}} = \overleftarrow{k}\,[x_L]^l\,]x_M]^m\,[x_N]^n \tag{8.53}$$

In the equilibrium state, the rate of reaction in the forward direction is the same as the rate of reaction in the reverse direction, i.e., the state of equilibrium Eqs. (8.52) and (8.53) are the same. Therefore,

$$\frac{(x_L)^l\,(x_M)^m\,(x_N)^n}{(x_A)^a\,(x_B)^b\,(x_C)^c} = \frac{\overrightarrow{k}}{\overleftarrow{k}} = K_x \tag{8.54}$$

where K_x is defined as the equilibrium constant. The subscript x shows that the equilibrium constant is expressed in terms of mole fractions. In Eq. 8.54 x_A, x_B, x_L, etc., represent the actual mole fractions present in the equilibrium state while suffixes l, m, a, b, etc. represent the numbers which appear in the stoichiometric chemical equation.

For the reaction $2O \rightleftharpoons O_2$,

$$K = \frac{(x_{O_2})}{(x_O)^2} \tag{8.55}$$

The equilibrium constant is a function of temperature only.

The units of K will be

$$(\text{Units of concentration})^{l+m-\ldots-a-b\ldots}$$

where the concentration may be expressed in g-mol/g-mol of mixture or in molecules/cm^3 of mixture.

In the case of ideal gases, the equilibrium constant can be defined conveniently in terms of partial pressures, as for the ideal gas mixture, the partial pressures of the components are proportional to the mole fractions, i.e.,

$$p_i = x_i\,p_{\text{total}} \tag{8.56}$$

Thus,

$$K_p = \frac{(p_L)^l\,(p_M)^m\ldots}{(p_A)^a\,(p_B)^b\ldots}$$

or $$K_p = \frac{(x_L)^l\,(x_M)^m\ldots}{(x_A)^a\,(x)_B^b\ldots}\,(p_{\text{total}})^{l+m+\ldots-a-b\ldots} \tag{8.57}$$

where x_L = mole fraction of $L = \dfrac{n_L}{\Sigma n_j}$

K_p = equilibrium constant expressed in terms of partial pressures.

p_L = partial pressure of component L in atmospheres,

p_{total} = total pressure of mixture in atmospheres.

Example 8.5

Carbon monoxide and 200 per cent theoretical oxygen react to give products at high temperature and 1 atm pressure. The relative concentrations of CO and CO$_2$ in the products are determined to be 2 : 3. Find K_p for the reaction.

Solution

The chemical equation for the reaction is

$$CO+O_2 \rightarrow aCO+bCO_2+dO_2$$

A balance of each element enables us to evaluate each of the unknown coefficients

C balance: $1 = a+b$ (1)

O$_2$ balance: $\dfrac{3}{2} = \dfrac{a}{2}+b+d$ (2)

Further $\dfrac{a}{b} = \dfrac{2}{3}$ (3)

From Eqs. (1) and (3) we have

$$1 = a+\frac{3}{2}\,a$$

$$a = \frac{2}{5} = 0.4$$

and $b = 0.6$

From Eq. (2), $d = 0.7$

Thus $CO+O_2 \rightarrow 0.4\,CO+0.6\,CO_2+0.7\,O_2$

The expression for K_p for the reaction $CO_2 \rightleftharpoons CO+\frac{1}{2}\,O_2$ may be written as

$$K_p = \frac{(p_{CO})\,(p_{O_2})^{1/2}}{p_{CO_2}} = \frac{(x_{CO})\,(x_{O_2})^{1/2}}{(x_{CO_2})}\,(p_T)^{1/2}$$

where $x_{CO}=\frac{n_{CO}}{\Sigma n_j}=\frac{0.4}{1.7}=0.236$

$$x_{CO_2}=\frac{n_{CO_2}}{\Sigma n_j}=\frac{0.6}{1.7}=0.353$$

$$x_{O_2}=\frac{n_{O_2}}{\Sigma n_j}=\frac{0.7}{1.7}=0.412$$

Substituting these values into the equation for K_p we have

$$K_p=\frac{(0.236)\,(0.412)^{1/2}}{(0.353)}\,(1)^{1/2}=0.429$$

Equilibrium Criteria

Firstly, we shall assume that at the equilibrium state, the reaction is stopped, and all the gases in the mixture are ideal gases. For any system at pressure, P and temperature T, we have from the First Law of Thermodynamics:

$$dQ=dU+dW \tag{8.58}$$

and from the Second Law,

$$dS\geqslant\frac{dQ}{T}$$

or
$$dS-\frac{dQ}{T}\geqslant 0 \tag{8.59}$$

we know at constant pressure

$$dW=P\,dV \tag{8.60}$$

From Eqs. (8.58), (8.59), and (8.60)

$$TdS-dU-PdV\geqslant 0 \tag{8.61}$$

This is the general equation for any reacting mixture at temperature T and pressure P. It shows that any reaction that takes place will increase the entropy.

For a particular case, i.e., when the reaction is taking place in an isolated closed chamber where $dU=0$, $dV=0$, Eq. (8.61) will yield:

$$dS\geqslant 0 \tag{8.62}$$

This equation can be expressed as:

$(dS)_{U,V,N}>0$, spontaneous process

$(dS)_{U,V,N}=0$, reversible process

$(dS)_{U,V,N}<0$, unnatural process

where subscripts U, V, N indicate constant energy, volume apn mass. Figure 8.4 shows the change in composition of the mixture with entropy. It is obvious that the reaction cannot proceed from B to C because it will mean a decrease in entropy. Therefore for the equilibrium at constant volume and energy, the composition will correspond to point B, i.e., where the entropy is maximum.

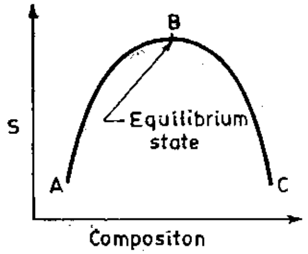

Fig. 8.4 Equilibrium at constant volume and energy.

If the reaction takes place at constant volume and temperature, we will observe its effect on the Helmholtz function. The Helmholtz function is given by

$$A=U-TS \tag{8.63}$$

Differentiating,

$$dA=dU-TdS-S\,dT \tag{8.64}$$

At constant temperature,

$$dA=dU-TdS \tag{8.65}$$

From Eqs. (8.60), (8.61) and (8.65)

$$-dA+p\,dV=TdS-dU+ndv\geqslant 0$$

or
$$-dA-dW=Tds-dQ\geqslant 0 \tag{8.66}$$

Equation (8.66) states that for a closed reacting system at constant temperature and volume,

$$dA\leqslant -dW \tag{8.67}$$

But at constant volume, $dW=0$. Therefore

$$dA\leqslant 0$$

or $(dA)_{T,V,N}<0$, spontaneous process

$(dA)_{T,V,N}=0$, reversible process

$(dA)_{T,V,N}>0$, unnatural process

i.e., for any process at constant temperature and volume, the Helmholtz function must decrease. If it is zero, it means an equilibrium is reached. Figure 8.5 indicates point B, which gives a minimum value of the Helmholtz function. This point will correspond to the equilibrium composition.

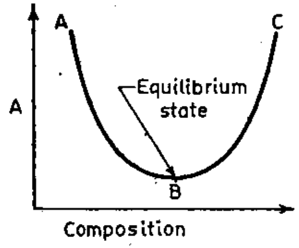

Fig. 8.5 Equilibrium at constant volume and temperature.

Now if we consider that the reaction is taking place at constant temperature and pressure, we can study the effect of Gibbs function. The Gibbs function is defined as

$$G=U+pV-Ts \tag{8.68}$$

Differentiating,

$$dG=dU+pdV+Vdp-Tds-S\,dT \tag{8.69}$$

At constant temperature and pressure, it reduces to

$$dG = dU + pdV - Tds$$

or $$-dG = TdS - dU - pdV \geqslant 0$$

or $$dG \leqslant 0 \tag{8.70}$$

i.e., for any reaction at constant temperature and pressure, Gibbs function will decrease, or

$(dG)_{T,\,P,\,N} <$ spontaneous reaction
$(dG)_{T,\,P,\,N} =$ reversible reaction
$(dG)_{T,\,P,\,N} >$ unnatural reaction

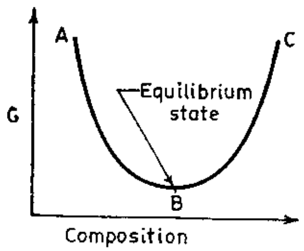

Fig. 8.6 Equilibrium at constant pressure and temperature.

Figure 8.6 shows that for a reactive mixture, point B will give minimum value of the Gibbs function and this point will correspond to the equilibrium composition. Thus, we know what the general conditions for any reactive mixture to be in equilibrium are and these conditions can be expressed in simple thermodynamic terms for the particular cases.

Relationship Between Gibbs Function and Equilibrium Constant

We have seen that for any reactive mixture of ideal gases, $(dG)_{T,P} = 0$. The Gibbs function for a mixture of ideal gases can be found easily by the application of Gibbs-Dalton law, which states that the properties of an ideal gas in a mixture are assumed to be the same as those for the pure when maintained at the volume and temperature of the mixture, or in other words, a gas is maintained at the partial pressure of the gas in the mixture.

To find the value of the Gibbs function at a pressure other than at 1 atm at the same temperature, we can use the relation

$$dg = vdp - s\,dT \tag{8.71}$$

If the temperature remains same, the relation reduces to

$$dg = vdp \tag{8.72}$$

Let g be the value of the Gibbs function at temperature T and pressure p, and g_0 be the value of the Gibbs function at temperature T and pressure $p = 1$ atm

$$g - g_0 = \int_{p_0}^{p} vdp$$

or $$g - g_0 = \int_{p}^{p} RT\,\frac{dp}{p}$$

or $$g - g_0 = RT\log\frac{p}{p_0} \tag{8.73}$$

If the pressure is expressed in atmosphere and $p = 1$

Then, $$g - g_0 = RT\log p. \tag{8.74}$$

Now let us consider a reaction

$$aA + bB = lL + mM$$

Assuming all components are ideal gases, so that at equilibrium at temperature T and pressure p, the partial pressures of the components are p_A, p_B, p_L, and p_M, then we can write the value of the Gibbs function at temperature T and at partial pressure equivalent to the partial pressure of each component as

$$\begin{aligned} g_A - g_A^\circ &= RT\log p_A \\ g_B - g_B^\circ &= RT\log p_B \\ g_L - g_L^\circ &= RT\log p_L \\ g_M - g_M^\circ &= RT\log p_M \end{aligned} \tag{8.75}$$

Now if we consider the change in Gibbs function from the initial components of A and B to the final products L and M, then

$$\Delta G = G_{\text{products}} - G_{\text{reactants}}$$

or $$\Delta G = l\,g_L + m\,g_M - a\,g_A - b\,g_B \tag{8.76}$$

Substituting the values of g_L, g_M, g_A and g_B from Eq. (8.75)

$$\Delta G = l\,(g_L^\circ + RT\log p_L) + m\,(g_M^\circ + RT\log p_M) - a\,(g_A^\circ + RT\log p_A)$$
$$- b\,(g_B^\circ + RT\log p_B) \tag{8.77}$$

Similar to Eq. (8.76) we can write

$$\Delta G^\circ = l\,g_L^\circ + m\,g_M^\circ - a\,g_A^\circ - b\,g_B^\circ \tag{8.78}$$

i.e., when each constituent is at a pressure of 1 atm and at a temperature T, by Eqs. (8.77) and (8.78) we can write

$$\Delta G = \Delta G^\circ + RT\log p_L^l + \log p_M^m - \log p_A^a - \log p_B^b$$

or $$\Delta G = \Delta G^\circ + RT\log\frac{p_L^l\;p_M^m}{p_A^a\;p_B^b} \tag{8.79}$$

We have already seen that for any reacting mixture $(\Delta G)_{T,\,P} = 0$

$$\Delta G^\circ = -RT \log \frac{p_L^l \; p_M^m}{p_A^a \; p_B^b} \tag{8.80}$$

The equilibrium constant is defined as

$$K_p = \frac{p_L^l \; p_M^m}{p_A^a \; p_B^b}$$

$$\therefore \quad \Delta G^\circ = -RT \log K_p$$

$$\text{or} \quad K_p = e^{-\Delta G^\circ/RT} \tag{8.81}$$

For equilibrium constant the following points should be noted:

1. During the actual reaction, K_p is independent of pressure because ΔG° is defined at a standard pressure of 1 atm.
2. For the given reaction, K_p is defined with the products in the numerator and the reactants in the denominator. Some authors give a reverse definition. Therefore, before using any tabulated value, the definition given for K_p should be observed.
3. If the reaction is written in the reverse direction, the value of K_p will change, e.g.,
   If we write
   $$H_2 + \tfrac{1}{2} O_2 \rightarrow H_2O \tag{8.82}$$
   $$\text{or} \quad H_2O \rightarrow H_2 + \tfrac{1}{2} O_2 \tag{8.83}$$
   The value of K_p for Eq. (8.83) will be the reciprocal of the value of K_p for Eq. (8.82).
4. The stoichiometric equation must also be well defined for a given value of K_p. If we consider the following two reaction equations
   $$H_2 + \tfrac{1}{2} O_2 \rightarrow H_2O \tag{8.82}$$
   $$2\,H_2 + O_2 \rightarrow 2\,H_2O \tag{8.84}$$
   Although the equations are the same, the K_p value of Eq. (8.84) will be square of the K_p value of Eq. (8.82).
5. It should be noted that ΔG° is not equal to zero for a reaction except at a particular temperature, while ΔG will always be zero for a reaction at equilibrium.

8.5 CALCULATION OF EQUILIBRIUM COMPOSITION AND TEMPERATURE

The object is to outline a procedure which may be used for computing the equilibrium composition and final state of the products after constant pressure or constant volume combustion at prescribed initial conditions.

Constant Pressure Combustion

The equilibrium composition and temperature of the products resulting from a combustion process at constant pressure can be determined by applying the laws of conservation of mass and energy, laws of chemical equilibrium and the concentration condition (combination of Avogadro's and Dalton's laws and the equation of state for the gas phase). Suppose one has a carbon–hydrogen–oxygen–nitrogen reaction system and the initial state of the reactants is specified by temperature T_i, pressure P_i, and the number of moles n_i of each component. Assume that the equilibrium products of combustion consist of the following ten chemical species:

$$CO_2,\ CO,\ O_2,\ H_2O,\ H_2,\ OH,\ H,\ O,\ N_2,\ NO$$

In order to fix the state of the equilibrium products, one must know the final equilibrium temperature T_e, pressure p_e and the number of moles n_j of each of ten chemical species above. Thus, there are 12 unknown quantities and, therefore, 12 equations are required to solve for the unknowns. These equations are obtained as given below.

Mass Conservation (Four Equations)

The conservation of the total number of atoms from reactants to products may be expressed by

$$\Sigma\, n_i C_i = \Sigma\, n_j C_j$$

or

$$w + x + y + z = [\Sigma n_j]\,[3X_{CO_2} + 2X_{CO} + 3X_{H_2O} + 2X_{H_2} + X_H + 2X_{O_2} + X_O + 2X_{OH} + 2X_{N_2} + 2X_{NO}] \tag{8.85}$$

where w, x, y, z = number of atoms of carbon, hydrogen, oxygen, and nitrogen respectively

C = collective number of atoms

n_i = number of moles of i^{th} reactant

n_j = number of moles of j^{th} combustion product

X = mole fraction

The conservation of the number of atoms of each element from reactants to products may be expressed by the conservation of the atomic ratios α, β and γ.

$$\alpha\,[2X_{CO_2} + X_{CO} + X_{H_2O} + 2X_{O_2} + X_O + X_{OH} + X_{NO}] = X_{CO_2} + X_{CO} \tag{8.86}$$

$$\beta\,[2X_{H_2O} + 2X_{H_2} + X_H + X_{OH}] = X_{CO_2} + X_{CO} \tag{8.87}$$

$$\gamma\,[2X_{CO_2} + X_{CO} + X_{H_2O} + 2X_{O_2} + X_O + X_{OH} + X_{NO}] = 2X_{N_2} + X_{NO} \tag{8.88}$$

where α = atomic ratio of carbon to oxygen

β = atomic ratio of carbon to hydrogen

γ = atomic ratio of nitrogen to oxygen

Chemical Equilibrium (Six Equations)

The number of these equations is equal to the number of chemical species in the equilibrium products minus the number of elements. Let us consider the following dissociation reactions:

$$CO_2 \rightleftharpoons CO + \tfrac{1}{2} O_2;\ K_1 = (X_{CO}\ X_{O_2}^{1/2}/X_{CO_2})\ \ P_e^{1/2} \tag{8.89}$$

$$H_2O \rightleftharpoons H_2 + \tfrac{1}{2} O_2;\ K_2 = (X_{H_2}\ X_{O_2}^{1/2}/X_{H_2O})\ \ P_e^{1/2} \tag{8.90}$$

$$H_2O \rightleftharpoons OH + \tfrac{1}{2} H_2;\ K_3 = (X_{OH}\ X_{H_2}^{1/2}/X_{H_2O})\ \ P_e^{1/2} \tag{8.91}$$

$$\tfrac{1}{2} O_2 \rightleftharpoons O;\ K_4 = (X_O/X_{O_2}^{1/2})\ \ \ P_e^{1/2} \tag{8.92}$$

$$\tfrac{1}{2} H_2 \rightleftharpoons H;\ K_5 = (X_H/X_{H_2}^{1/2})\ \ \ P_e^{1/2} \tag{8.93}$$

$$\tfrac{1}{2} N_2 + \tfrac{1}{2} O_2 \rightleftharpoons NO;\ K_6 = X_{NO}/(\ X_{N_2}^{1/2}\ \ X_{O_2}^{1/2}) \tag{8.94}$$

Concentration Condition (One Equation)

Since the summation of mole fractions equals unity, we can write:

$$X_{CO_2} + X_{CO} + X_{H_2O} + X_{H_2} + X_{OH} + X_H + X_{O_2} + X_O + X_{N_2} + X_{NO} - 1 = 0 \tag{8.95}$$

Energy Conservation (One Equation)

For adiabatic constant pressure combustion, the total enthalpy of the products is equal to the total enthalpy of the reactants. Thus

$$H_j = H_i \tag{8.96}$$

where $H_i = n_f(h_{T_i}^{0})_f + n_{O_2}(h_{T_i}^{0})_{O_2} + n_{N_2}(h_{T_i}^{0})_{N_2}$

$H_j = (\Sigma n_j)\{\Sigma X_j (h_T^{0})_j\}$

n_f = number of moles of fuel

Equation (8.96) assumes that there is no heat transfer, i.e., the combustion process is adiabatic.

The given twelve Eqs. (8.85) to (8.96) can be solved simultaneously to determine the equilibrium temperature and composition of the products.

Constant Volume Combustion

For constant volume combustion calculations, it is more convenient to express the various equations in terms of mole numbers rather than mole fractions. In Eqs. (8.86) to (8.88) this is easily done by simply replacing X by n (this amounts to multiplying both sides of the equations by Σn_j).

Equation (8.85) is rewritten by multiplying out the right hand side. Equation (8.89) is expressed as

$$K_1 = \frac{p_{CO}\ p_{O_2}^{1/2}}{p_{CO_2}} = \frac{n_{CO}\ n_{O_2}^{1/2}}{n_{CO_2}}\left(\frac{p_e}{\Sigma n_j}\right)^{1/2} \tag{8.97}$$

where $$\frac{p_e}{\Sigma n_j} = \frac{T_e}{T_i} = \frac{p_i}{\Sigma n_i} \tag{8.98}$$

since $\Sigma n_i = \dfrac{p_i V}{R_0 T_i};\ \Sigma n_j = \dfrac{p_e V}{R_0 T_e};\ p_j = \dfrac{n_j}{\Sigma n_j} p_e$

Equations (8.90) to (8.94) can also be transformed in the same manner and written as:

$$K_2 = \frac{p_{H_2}\ p_{O_2}^{1/2}}{p_{H_2O}} = \frac{n_{H_2}\ (n_{O_2})^{1/2}}{n_{H_2O}}\left(\frac{p_e}{\Sigma n_j}\right)^{1/2} \tag{8.99}$$

$$K_3 = \frac{p_{OH}\ p_{H_2}^{1/2}}{p_{H_2O}} = \frac{n_{OH}\ (n_{H_2})^{1/2}}{n_{H_2O}}\left(\frac{p_e}{\Sigma n_j}\right)^{1/2} \tag{8.100}$$

$$K_4 = \frac{p_O}{p_{O_2}^{1/2}} = \frac{n_O}{(n_{O_2})^{1/2}}\left(\frac{p_e}{\Sigma n_j}\right)^{1/2} \tag{8.101}$$

$$K_5 = \frac{p_H}{p_{H_2}^{1/2}} = \frac{n_H}{(n_{H_2})^{1/2}}\left(\frac{p_e}{\Sigma n_j}\right)^{1/2} \tag{8.102}$$

$$K_6 = \frac{p_{NO}}{p_{N_2}^{1/2}\ p_{O_2}^{1/2}} = \frac{n_{NO}}{(n_{N_2}\ n_{O_2})^{1/2}} \tag{8.103}$$

The energy conservation for this case is expressed by

$E_j = E_i$

where $E_i = n_f\,(h_{T_i}^{0})_f + n_{O_2}\ (h_{T_i}^{0})_{O_2} + n_{N_2}(h_{T_i}^{0})_{N_2} - R_0\ T_i\ \Sigma n_i$

$E_j = \Sigma n_j\ [(h_T^{0})_j - R_0 T]$

Method of Solution

The method of solving the Eqs. (8.85) to (8.96) is briefly outlined here and is essentially similar to that given by Kopa, et al.[2] with minor modifications:

Step 1. A trial value of equilibrium temperature T_e is assumed and the equilibrium constants K_1 to K_6 computed at this temperature.

Step 2. Experience shows that the mole numbers of the compounds H_2, H_2O, CO_2 and N_2 display the best behaviour. For this reason, the mole fractions of all other species are expressed in terms of X_{H_2} (=A), X_{H_2O}

(=B), X_{CO_2} (=C), and $X_{N_2}^{1/2}$ (=D) by using Eqs. (8.89) to (8.94) and the known values of K_1 to K_6 and $P_e = P_i$.

Step 3. Equations (8.86) to (8.88) and (8.95) are rewritten in the form:

$$F\,(A, B, C, D) = 0$$
$$G\,(A, B, C, D) = 0$$
$$H\,(A, B, C, D) = 0$$
$$J\,(A, B, C, D) = 0$$

Step 4. The four equations in step 3 above with four unknowns are linearized by using the Taylor series expansion and neglecting the higher powers of small terms.

$$F = F_0 + F_A\,\delta A + F_B\,\delta B + F_C\,\delta C + F_D\,\delta D$$
$$G = G_0 + G_A\,\delta A + G_B\,\delta B + G_C\,\delta C + G_D\,\delta D$$
$$H = H_0 + H_A\,\delta A + H_B\,\delta B + H_C\,\delta C + H_D\,\delta D$$
$$J = J_0 + J_A\,\delta A + J_B\,\delta B + J_C\,\delta C + J_D\,\delta D$$

where $F_A = \dfrac{\partial F}{\partial A}$ etc., and $F_0 = F\,(A_0, B_0, C_0, D_0)$ etc.

Step 5. Starting from assumed initial values A_0, B_0, C_0, and D_0 of A, B, C, and D, the set of equations obtained in Step 4 is solved (by the Gauss-Jordan elimination method) for δA, δB, δC, and δD, which are then applied as corrections to A_0, B_0, C_0, and D_0 to yield new values of A, B, etc. This process is repeated until the absolute values of the ratios δA/A, δB/B, δC/C and δD/D are each below an assigned minimum (of the order of 10^{-7}). Once A, B, C, and D are computed, the composition of the equilibrium products is readily obtained.

Step 6. Once the equilibrium composition of the products is known, the total number of moles of the products, Σn_j, is calculated from Eq. (8.85) and the enthalpy of the products calculated and compared with that of the reactants. If the two corresponding energies do not tally, the assumed value of T_e is either increased (if $H_i > H_j$) or decreased (if $H_i < H_j$) and the steps outlined are repeated until two successive test temperatures bracket the desired value. Further adjustments are then made by interpolation. As the temperature and the energy have no linear relation, exact equivalence $H_i = H_j$ is difficult to achieve. In order to save time say, while using a computer for solving such problems, a maximum difference of the order of 100 kcal between H_i and H_j (per kmol fuel) is considered acceptable. This difference has negligible effect on T_e.

The method of solution for the constant volume case is entirely analogous to the above.

As an illustration of the above procedure, a computer flow chart[3] is given in Appendix B. This can be used for computing the equilibrium composition and final state of the products after constant volume combustion in any C—H—O—N system, provided that the products of combustion are assumed to consist of the ten chemical species viz. CO_2, CO, H_2O, H_2, OH, H, O_2, O, N_2 and NO.

Example 8.6

Determine the equilibrium composition for the constant pressure combustion of $CO + \frac{1}{2}\,O_2$ at 3000 K and 10 atm pressure.

Solution

We consider the following dissociation reaction

$$CO_2 \rightleftharpoons CO + (\tfrac{1}{2})O_2$$

Dissociation of O_2 around 300 K is not considered appreciable. We shall, therefore, assume that the equilibrium mixture contains only CO, CO_2 and O_2. The value of equilibrium constant K_p at 3000 K for dissociation of CO_2 is 0.327 from Table A.17.

$$\text{Therefore,}\quad K_p = \frac{(n_{CO})\,(n_{O_2})^{1/2}}{(n_{CO_2})}\left(\frac{P_T}{\Sigma\, n_j}\right)^{1/2} \tag{1}$$

The overall reaction may be written as

$$CO + (1/2)O_2 \rightarrow aCO + bCO_2 + dO_2 \tag{2}$$

where a, b and d represent the number of moles of CO, CO_2 and O_2 present in the equilibrium mixture. Here $\Sigma\, n_j = a + b + d$. Substitution of the values in Eq. (1) yields

$$K_p = \frac{a\,(d)^{1/2}}{b}\left(\frac{10}{a+b+d}\right)^{1/2} \tag{3}$$

Equation (3) has three unknowns. Two mass balance equations may be written as

$$\text{C balance: } 1 = a + b \tag{4}$$

$$O_2\ \text{balance: } 1 = \frac{a}{2} + b + d \tag{5}$$

From Eq. (4) $\quad b = 1 - a$

From Eq. (5) $\quad d = 1 - \dfrac{a}{2} - 1 + a = \dfrac{a}{2}$

Also $\quad \Sigma\, n_j = a + b + d = a + (1-a) + \dfrac{a}{2} = 1 + \dfrac{a}{2}$

Substituting the values in Eq. (3) we have

$$K_p = \frac{a\left(\dfrac{a}{2}\right)^{1/2}}{(1-a)}\left(\frac{10}{1+\dfrac{a}{2}}\right)^{1/2}$$

or

$$K_p^2 = a \cdot \frac{a^2}{2} \cdot \frac{10}{1+\dfrac{a}{2}} \cdot \frac{1}{1-a^2}$$

$$(0.327)^2 = \frac{a^3}{2} \cdot \frac{10}{\left(1+\dfrac{a}{2}\right)} \cdot \frac{1}{(1+a^2-2a)}$$

$$0.11 = \frac{10\,a^3}{a^3-3a+2}$$

or $$9.89\,a^3+0.33\,a-0.22=0$$

This equation may be solved by a suitable technique. The equation is satisfied within accuracy for the value of $a=0.245$. The chemical equation for the reaction may be written as

$$CO+(1/2)O_2 \rightarrow 0.245\,CO+0.755\,CO_2+0.123\,O_2$$

The results are shown below in a tabular form.

Species	*Initial moles*	*Final moles*
CO	1	0.245
O_2	0.5	0.123
CO_2	—	0.755

Example 8.7

One mole of CO_2 is mixed with one mole of H_2. Determine the equilibrium composition for the reaction $CO_2+H_2 \rightleftharpoons CO+H_2O$, if the temperature and pressure are 2500 K and 1 atm. Assume that only CO, CO_2, H_2, H_2O and O_2 are present in the products.

Solution

We shall consider the following reactions

$$CO_2 \rightleftharpoons CO+(1/2)\,O_2 \tag{I}$$

and $$CO_2+H_2 \rightleftharpoons CO+H_2O \tag{II}$$

From Table A.17 we find the values of K_p for these reactions at 2500 K as

$$\log_{10} K_{p_I} = -1.440$$

Therefore, $K_{p_I}=10^{-1.440}=.0312$ and $\log_{10} K_{p_{II}}=+0.784$

Therefore, $K_{p_{II}}=10^{+0.784}=6.1$

Thus $$K_{p_I}=\frac{(p_{CO})\,(p_{O_2})^{1/2}}{(p_{CO_2})}=\frac{(n_{CO})\,(n_{O_2})^{1/2}}{(n_{CO_2})}\left(\frac{P_T}{\Sigma\,n_j}\right)^{1/2} \tag{1}$$

and $$K_{p_{II}}=\frac{(p_{CO})\,(p_{H_2O})}{(p_{CO_2})\,(p_{H_2})}=\frac{(n_{CO})\,(n_{H_2O})}{(n_{CO_2})\,(n_{H_2})}\left(\frac{P_T}{\Sigma\,n_j}\right)^{0} \tag{2}$$

where $P_T=1$ atm and $\Sigma\,n_j=n_{CO}+n_{CO_2}+n_{H_2}+n_{H_2O}+n_{O_2}$

The overall reaction may be written as

$$CO_2+H_2 \rightarrow n_{CO}+n_{CO_2}+n_{H_2}+n_{H_2O}+n_{O_2}$$

We may write the mass balance equations in terms of the atomic species present as follows:

$$\text{C balance: } 1=n_{CO}+n_{CO_2} \tag{3}$$

$$\text{O}_2 \text{ balance: } 1=(1/2)\,n_{CO}+n_{CO_2}+(1/2)\,n_{H_2O}+n_{O_2} \tag{4}$$

$$\text{H}_2 \text{ balance: } 1=n_{H_2}+n_{H_2O} \tag{5}$$

Thus we have five equations with five unknowns. Let us arbitrarily consider n_{CO_2} and n_{H_2O} as independent variables.

Then
$$n_{CO}=1-n_{CO_2}$$
$$n_{O_2}=1-(1/2)\,n_{CO}-n_{CO_2}-(1/2)\,n_{H_2O}$$
$$=(1/2)\,(1-n_{CO_2}-n_{H_2O})$$
$$n_{H_2}=1-n_{H_2O}$$
$$\Sigma\,n_j=n_{CO}+n_{CO_2}+n_{H_2}+n_{H_2O}+n_{O_2}$$
$$=(1-n_{CO_2})+n_{CO_2}+(1-n_{H_2O})+n_{H_2O}+(1/2)\,(1-n_{CO_2}-n_{H_2O})$$
$$=(1/2)\,(5-n_{CO_2}-n_{H_2O})$$

Substituting these values into the equations for K_{p_I} and $K_{p_{II}}$, we have

$$0.0312=\frac{(1-n_{CO_2})\,(1-n_{CO_2}-n_{H_2O})^{1/2}}{n_{CO_2}}\;\frac{1}{(5-n_{CO_2}-n_{H_2O})^{1/2}} \tag{6}$$

and $$6.1=\frac{(1-n_{CO_2})\,(n_{H_2O})}{(n_{CO_2})\,(1-n_{H_2O})} \tag{7}$$

Equations (6) and (7) may be solved simultaneously by applying suitable numerical methods. The results are given below in a tabular form.

Species	*Initial moles*	*Final moles*
CO_2	1	0.29
H_2	1	0.29
CO	—	0.71
H_2O	—	0.71
O_2	—	0.005

Compare the answer if we consider the situation where the reacting species include CO, CO_2, H_2 and H_2O. In this case we should write

$$CO_2+H_2 \rightleftharpoons CO+H_2O$$

In view of the expected equilibrium reaction among the constituents, the overall reaction would be written as

$$CO_2+H_2 \rightarrow n_{CO}+n_{CO_2}+n_{H_2}+n_{H_2O}$$

Writing the mass balance relationships for C, O_2 and H_2, and K_p for the water-gas reaction, the four equations may be solved simultaneously.

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9

LAMINAR FLAME PROPAGATION

Laminar flame propagation is one of the most interesting and important problems in combustion research. The study of a laminar flame is an ancient combustion problem and requires the simultaneous consideration of transport phenomena and chemical kinetics for its solution. The ultimate objective of combustion research is the acquisition of a complete understanding of the mechanism of ignition, structure, and mode of propagation of flames.

Although a lot of work has been done in the past several decades, the science of combustion is not yet fully developed. For any combustible mixture the thermodynamic properties, both of the unburned gas and of the equilibrium products, are generally known to an adequate degree of precision. What is lacking is a detailed knowledge of the kinetics of combustion reactions and the actual mechanism of flame propagation.

An attempt has been made to summarize the available information on laminar flame propagation. The structure of laminar flames and a brief survey of the theories of flame propagation are presented in this chapter. The methods of measuring burning velocity along with the effects of physical and chemical variables are discussed in the next chapter.

9.1 PREMIXED FLAMES

Before proceeding further, let us consider the definitions of a few terms pertaining to premixed flames. A combustible mixture is one which is capable of propagating a flame indefinitely away from the ignition source. In a premixed flame the gaseous mixture is prepared prior to combustion within certain limits of the fuel/air ratio known as the lean and rich limits

of inflammability. A flame is a thermal wave in which rapid exothermic chemical reactions occur and which travel with subsonic velocities. Subsonic flame propagation is also termed as a deflagration wave. Luminosity in a flame is not essential but is almost always present. In a premixed flame, the reactants may be introduced into the reaction zone or the reaction zone may move into the reactants. The flame velocity or burning velocity, S_u, of a combustible mixture is the velocity at which the unburned gas moves through the combustion wave in a direction normal to the wave surface.

Burning velocity is considered a fundamental constant and is a useful combustion parameter characterizing the overall reaction rate in a premixed flame. It depends on the initial temperature, pressure, and composition of the gaseous combustible mixture. As the kinetics of the combustion reactions for hydrocarbon mixtures are not yet known in great detail for determining S_u from first principles, the experimental techniques are commonly employed.

9.2 THE STRUCTURE OF A LAMINAR FLAME

The combustion process in a flame is a combination of chemical reaction, heat transfer by conduction, convection and radiation, mass transfer by diffusion, and the flow pattern. The shape and size of a flame is governed by all these factors. A mathematical equation can be written separately for each variable. But because of many simultaneously occurring phenomena, a mathematical model even for a simplest flame will be quite complicated. Therefore, to determine the temperature and concentration gradients across a flame front and to study the factors governing the shape and size of a flame, experimental approach is preferred by most of the workers. Such studies give an insight into the structure of a flame and help in understanding the important properties of a combustion wave, e.g., burning velocity, quenching distance, flame stability, etc.

The study of the temperature and concentration gradients across the combustion wave is often referred to as the structure of the reaction zone or the microscopic structure of a flame. The study of the shape of a flame is referred to as its macroscopic structure. We shall first consider the microscopic structure of an assumed simple one dimensional flame front which gives the variation of temperature and concentration in and near the flame front. This discussion will be applicable to all shapes and sizes of flames. The microscopic structure of a burner flame which is widely used in practice and the combustion wave in tubes will also be considered. The flame front geometry in a flat flame burner and a spherical combustion bomb is quite simple and as such needs no explanation.

Temperature Profile

We shall consider a one dimensional flame front so that the flame propagation and diffusion of mass is normal to the wave surface and parallel to each other. Let us consider a stream tube of unburned gas following in the positive x-direction. The flame is a steady, stationary combustion wave as shown in Fig. 9.1. A mass element, shown hatched in the figure is moving from the unburned side to the burned side. T_u is supposed to be the boundary before which there is no chemical reaction and no heat and mass transfer due to diffusion. As soon as this mass element crosses the T_u boundary, it receives heat due to conduction from the hotter elements ahead of it, i.e., from the downstream elements. The nature of the temperature profile during this movement up to boundary 'I' is found to be convex towards the x-axis $\left(\frac{\partial^2 T}{\partial x^2} > 0\right)$ which means that a mass element in this region gains heat by conduction from the hotter elements downstream faster than it loses heat to the cooler elements upstream. As there is little chemical reaction in this region, little heat is evolved.

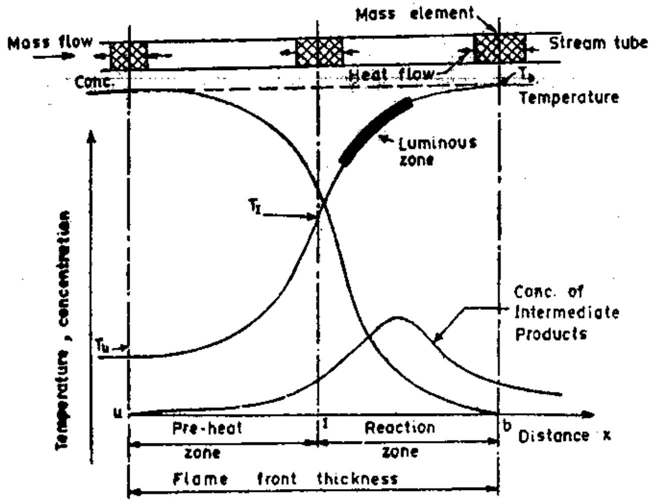

Fig. 9.1 **Structure of a combustion wave (With permission of Academic Press, from B. Lewis and G. Von Elbe, *Combustion, Flames and Explosions of Gases*, 1951, p. 269).**

Because of the increasing temperature, the chemical reaction rate also increases as the element moves from left to right. At temperature T_I, this mass element, due to increased chemical reaction in itself starts acting as a source of heat giving more energy to the upstream elements. But the temperature still continues to rise because of the evolution of heat due to the chemical reaction. The temperature profile, however, after boundary "I" changes its nature and becomes concave towards the x-axis $\left(\frac{\partial^2 T}{\partial x^3} < 0\right)$.

The luminous zone shown by the shaded rectangle on the temperature profile was first considered to give the reaction zone thickness. But the reaction also takes place before and after the luminous zone. The reaction may be said to be taking place between the initial temperature T_u and the final temperature T_b. In Fig. 9.1, T_u represents the boundary where the temperature of the mixture starts rising and T_b represents the boundary where the final temperature T_b is attained. The inflexion point T_I may be called the ignition temperature. The zone between the T_u and T_I boundaries is referred to as the "preheat zone" and between the T_I and T_b boundaries as the "reaction zone".

In the perheat zone we may say that the rise in temperature is due to conduction alone or the heat received by this zone is more than that received by other zones. Assuming there is no heat release due to reaction in the preheat zone and that the thermal conductivity and specific heat remain constant, the preheat zone thickness can be calculated theoretically. As the density and conductivity of gaseous fuels with air and oxygen do not vary much, it may be said, therefore, that the preheat zone thickness depends mainly on the burning velocity and pressure. Theoretically the temperature in the preheat zone rises exponentially. Therefore, in order to define the thickness of the preheat zone, it is important to define the location of the T_u boundary. If T_u is the initial mixture temperature the preheat zone thickness will become infinite. Generally, T_u is taken to be a point where the temperature rise is 1% of the rise in preheat zone temperature. However, if the temperature rise is say 10% of the rise in the preheat zone temperature, the thickness will reduce to half, and if the temperature rise is taken as 0.1%, the preheat zone thickness will be doubled.

The preheat zone thickness is roughly given by the distance between the inner edge of the luminous zone and the schlieren edge of the flame. The ignition point T_I does not have any relation with the ignition or the spontaneous ignition temperature. Dixon-Lewis and Wilson[1] found that for the methane-air mixture most of the reaction takes place between temperatures of 1450 and 2100 K. They suggested that the ignition point should be about 1100 to 1300 K for the methane-air mixture. However, for acetylene, ethylene, and propane-air mixtures, experiments have shown the ignition point to be below 800°C and as low as 400°C.

Figure 9.2 shows the temperature profile of the propane-air flame along with the theoretical curve for the preheat zone. Figure 9.3 shows the heat release rate. Both these curves were obtained by Friedman and Burke[2] on a flat burner for low pressure propane-air mixture. The dotted curve in Fig. 9.3 represents the percentage of the heat released. It is observed that only about 60% of the heat is released up to the end of the luminous zone and the rest of the heat is released in the after burning region where CO is converted to CO_2.

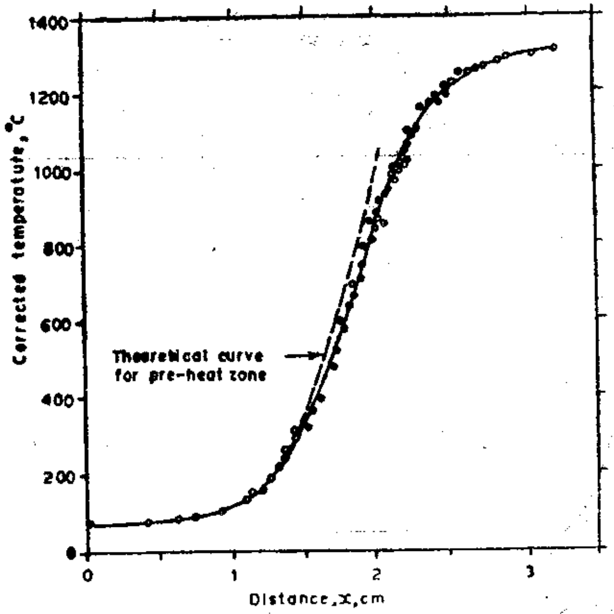

Fig. 9.2 Temperature profile in a flat flame for a propane-air mixture (From R. Friedman and E. Burke, *J. Chem. Phys.*, 22: 824, 1954).

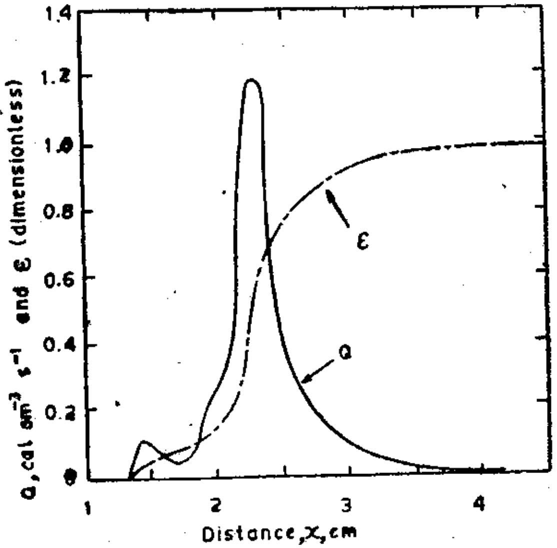

Fig. 9.3 Heat release rate in a low pressure flat flame (From R. Friedman and E. Burke, *J. Chem. Phys.*, 22: 824, 1954).

Concentration Profile

Analogous considerations apply for the variation in molecular concentrations. As a result of the chemical reaction, concentration gradients are produced which give rise to the diffusion of the reactants diffusing from the boundary u to b and the products diffusing from the boundary b to u. The intermediate products which originate in the reaction zone diffuse in both the directions. The concentration profile is symmetrically opposite to the temperature profile showing that the loss of reactants from a mass element results in the gain of temperature by the element.

The concentration profile of various components for the methane-oxygen flame is shown in Fig. 9.4. The data were obtained by Fristrom, Grunfelder, and Favin[3] on a flat flame burner at low pressures. Figure 9.5 gives the concentration of unstable intermediate species. These data were obtained by Westenberg and Fristrom[4] using Electron Spin Resonance (ESR) spectrometry. Most of the studies were carried out at low pressure because at lower pressures the reaction zone thickness is increased and the measurement of the various variables becomes comparatively easy. These figures

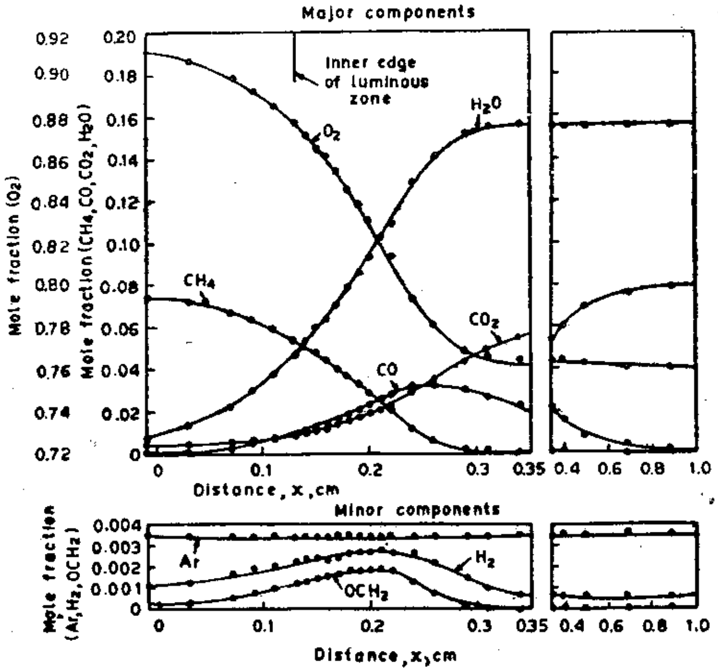

Fig. 9.4 Concentration profile in 0.1 atm CH_4-O_2 flat flame (With permission of the American Chemical Society, from the *Journal of Physical Chemistry*, 1960, LXIV: 1391).

give an idea of the microstructure of different flames. Basically the microstructure of most of the flames gives similar profiles except for the very

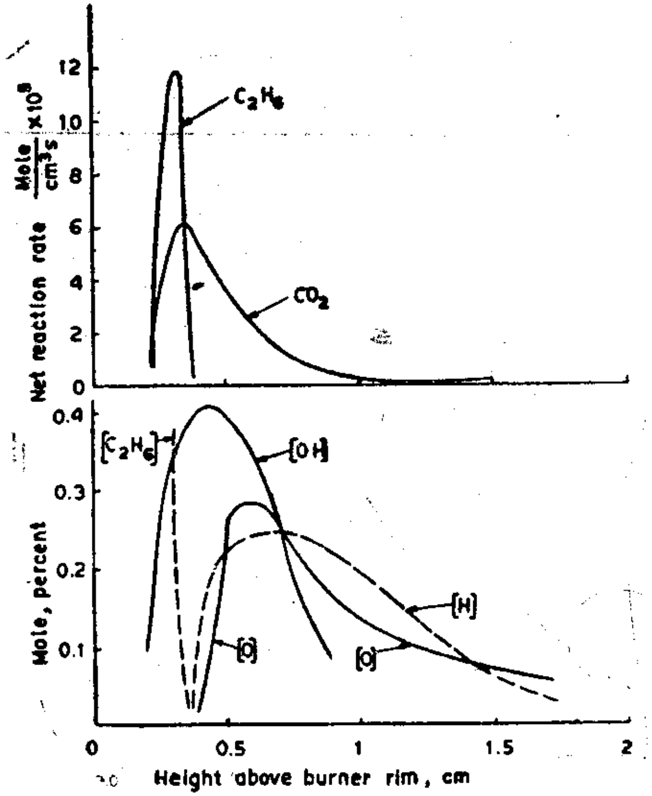

Fig. 9.5 **Concentration profiles of unstable species in 0.1 atm C_2H_6-O_2 flame [With permission of the Combustion Institute, from *Tenth Symposium (International) on Combustion*, 1965, p. 475].**

fast burning mixtures, say the hydrogen-oxygen mixture, where the diffusion of hydrogen also plays an important role.

The Bunsen Flame

The shape of a flame is mainly governed by two factors: the flow pattern of the mixture or products and the quenching effect of solid surfaces. In the case of a burner flame both factors are important. Michelson[6] first calculated the theoretical shape of the bunsen burner flame assuming the velocity profile in the burner tube to be parabolic, the flame to be of zero thickness, burning velocity to be constant over the entire flame surface, and flow lines to remain parallel to the tube axis up to the flame surface. However, the actual visible flame differed from Michelson's model in the following respects. The tip of an actual bunsen flame is rounded instead of pointed one as given theoretically. The base of the theoretical flame is equal to the inner diameter of the tube while the actual flame overlaps the burner base. The schlieren image of the bunsen cone resembles in a better way with the theoretical shape of Michelson's model. The deviations at the base and tip are explained as follows:

The burning velocity across the burner does not remain constant because of the quenching effect of the burner rim. It reduces to zero at the burner surface and increases with distance from the tube. At the tip of the flame, i.e., near the axis of the burner tube, the unburned gas receives an increasing amount of heat and active centres due to the excessive curvature of flame, thereby rapidly increasing the burning velocity.

Figure 9.6(c) shows the variation of the burning velocity across the burner tube. It is clear that there is a steep gradient near the burner rim and axis. In the middle portion the burning velocity remains almost constant. Therefore, the base and tip effects are quite important for a small diameter burner and their influence reduces on increasing the diameter of the burner. Figure 9.6(a) and (b) show the theoretical and experimental shapes of the flame front and flow pattern. In the theoretical model, the stream lines remain parallel to one another and there is no expansion. In practice, the flow lines expand as soon as they come out of the burner tube. The divergence of the flow lines is marked just before the flame front. As a result of the pressure field established by the flame the flow lines not only diverge but at the axis the flow velocity is reduced. Because of the reduced flow velocity and increased burning velocity at the tip a rounded tip is formed.

On reducing the tube diameter or the pressure, the flame shape deforms by an increasing amount so that a sort of hemispherical flame shape is produced. Further reduction results in a nearly flat flame having the shape of a water meniscus or sometimes a button shaped flame. The shape of a simple burner flame becomes complex because of the tip and base effects. The shape can be improved a bit by using a constant velocity nozzle or orifice so that instead of a parabolic flow pattern a constant velocity profile is obtained except near the rim. This results in almost a straight sided cone except near the base and tip where the burning velocity is changed. The structure of a burner flame is best understood from a schlieren photograph using particle tracks which gives the exact magnitude and pattern of flow velocity. The schlieren image of a flame is also supposed to give a true flame profile.

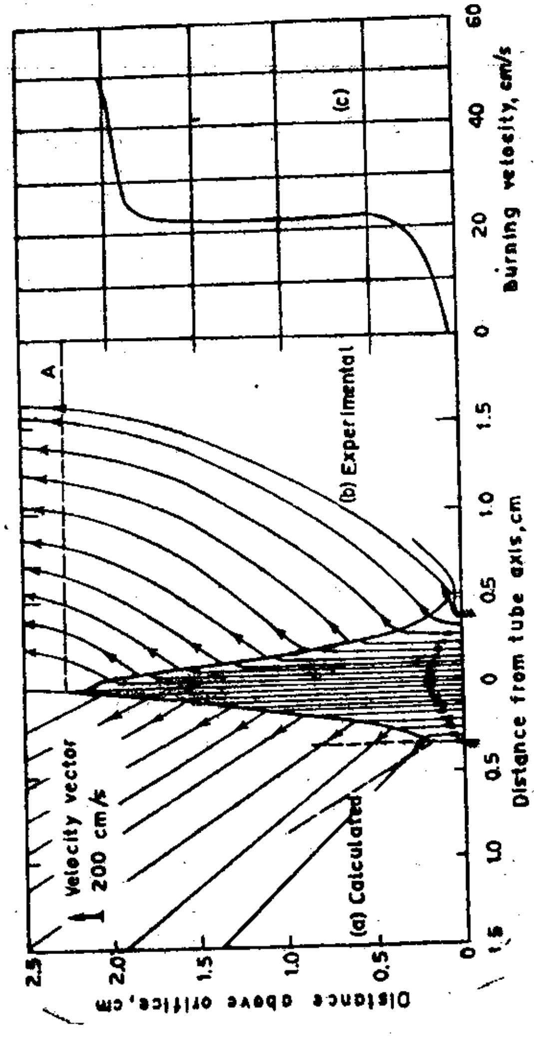

Fig. 9.6 **Burning velocity and flow pattern across a burner tube: (a) calculated and (b) and (c) experimental for a natural gas-air flame (With permission of Academic Press, from B. Lewis and G. Von Elbe,** ***Combustion, Flames and Explosions of Gases*****, 1951, p. 269).**

Flames in Tubes

The flame propagation rate was first measured by the time taken by a flame propagating between two fixed points in a tube. Gouy's[6] definition of burning velocity brought the concept of flame shape and size. Coward and Hartwell[7] studied the shape of a flame in a tube and suggested that if each element of a flame consumes some amount of the combustible mixture, an initial curve shaped flame will ultimately assume a flat shape. So they suggested that the convection currents cause a small movement of gases ahead of the flame which resists the tendency of the flame to assume a flat shape.

If, in a tube with one end closed and filled with a combustible mixture, the mixture is ignited at the open end, a flame will travel towards the closed end. As a result of combustion, the burned gases expand and move towards the open end as there is no other opening. The burned gases flowing in a tube have a Poiseuille-type flow with maximum velocity at the centre and low velocity near the walls on account of frictional drag. The accelerated flow near the axis of tube results in a central thrust towards the closed end. This pushes the unburned gases from the central portion towards the walls. This results in the flow pattern shown in Fig. 9.7.

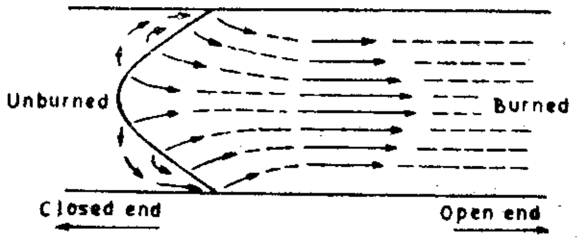

Fig. 9.7 **Flow pattern and particle velocity for a laminar combustion wave moving from open to closed end. Observer is stationary with respect to tube (With permission of Academic Press, from B. Lewis and G. Von Elbe:** ***Combustion, Flames and Explosions of Gases*****, 1951, p. 292).**

This gives the direction of the gas flow of the combustion wave and the magnitude and direction of the burned gases flowing towards the open end.

If a stationary flame is maintained in a tube by flowing a mixture with constant velocity, the flow pattern as shown in Fig. 9.8 will be obtained. Similar results of the gas flow pattern in a tube are obtained by the use of the particle track method. However, the flame shape is slightly different because the wall quenching effect reduces the burning velocity near the walls of the tube.

Frank Kamenetsky[8] discussed the flame shape in a tube and suggested that if the walls of the tube are hot and the heat is flowing from outside to inside, the curvature of flame will be towards the burned side. But if the heat is flowing out from the combustion wave to the walls of tube, the curvature of flame will be towards the unburned gas.

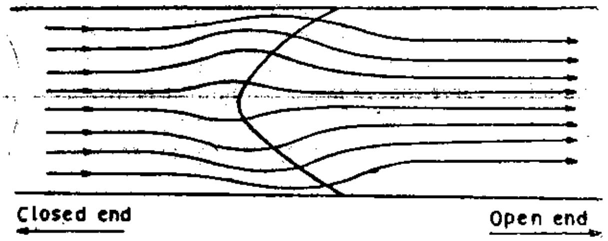

Fig. 9.8 **Flow lines in a laminar combustion wave moving from open to closed end of a tube. Observer is moving with the combustion wave (With permission of Academic Press, from B. Lewis and G. Von Elbe, *Combustion, Flames and Explosions of Gases*, 1951, p. 294).**

Ball[9] calculated the shape of the flame on hydrodynamic considerations alone and gave the shape of flame and gas flow pattern as shown in Fig. 9.9. In the calculation he assumed the flame to be of zero thickness, constant burning velocity across the entire cross section, gases as ideal gases, and flow to be incompressible. As the solution was not exact his calculation did not give a precise description of the flame shape at the tip and near the wall. The first order analytical solution indicated the flame to be perpendicular to the axis at the tip and tangent to the walls. However, because of the quenching effect of the wall, Ball's assumption of

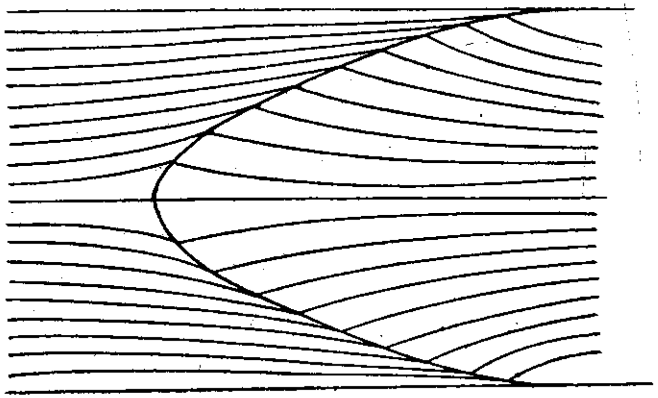

Fig. 9.9 **Calculated shape of the flame and flow lines in a tube (With permission of the Combustion Institute, from *Fourth Symposium (International) on Combustion*, 1953, p. 41.)**

constant burning velocity near the wall is not valid. The shape of flame and flow pattern obtained by him resemble the one obtained experimentally as shown in Fig. 9.8. The actual flame, in a horizontal tube with one end closed and where the mixture ignited by a spark at the open end, is hook-shaped as shown in the Fig. 9.10.

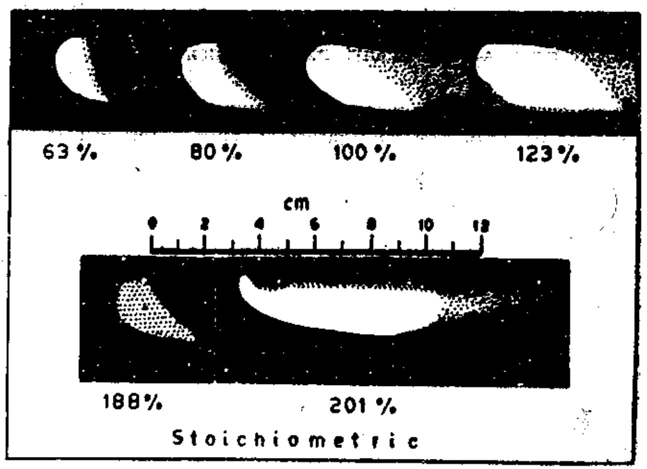

Fig. 9.10 **Actual flame shapes in a horizontal tube open at the ignition end for propaneair mixtures (With permission of the Combustion Institute, from *Fourth Symposium (International) on Combustion*, 1953, p. 41).**

It is observed that the shape of the flame is independent of the mode of ignition. If the spark is located at the bottom of the tube, an inverted hook shape is developed, but within a few centimeters of flame travel the shape changes to the normal hook shape. If the mixture is ignited by a pilot flame, hot body, or spark located at any other portion, the shape of flame is same after it has propagated a distance of a few centimeters. The flame is hook shaped and unsymmetrical because of the convection current of hot gases. It is also observed that for most of the hydrocarbon-air mixture, near the maximum burning velocity, the flame shape is constant in a 2.54 cm diameter tube. It is further reported that by placing an orifice at the open end of the tube the fluctuations in the flame shape are reduced as it absorbs the pressure disturbance. By placing a second orifice at the close end thus permitting a flow of compressed unburned gas to the atmosphere also stabilizes the flame shape. If the tube is very long or the diameter large, then after some travel the flame becomes turbulent. The turbulence can be avoided by using a tube of small diameter or a tube of short length thus reducing Reynold's flow number.

The flame shape is observed to change near the lean and rich side of the mixture. If the mixture is quite rich the flame assumes an elongated shape which does not touch the bottom of the tube. Several other flame shapes are also obtained, the explanation of which is difficult. It is further observed that the oscillation of the gas column as a whole can produce oscillation in the flame travel which do not change the shape of the flame.

9.3 THEORIES OF LAMINAR FLAME PROPAGATION

The mechanism of flame propagation in combustible mixtures has received a great deal of theoretical consideration and considerable research work is in progress to establish specifically the factors which control the rate of flame propagation. The various factors which have been thought of as being the most important in controlling the rate of flame propagation are:

1. Rate of heat transfer from the reaction zone to the adjacent heating zone
2. Diffusion of active radicals or chain carriers from the reaction zone into the unburned gas
3. Mechanism of the reaction
4. Chemical kinetics of individual reactions in the mechanism.

Some attempts have also been made at forming general theories which would include all possible factors, but due to mathematical difficulties and insufficiency of data, it is extremely difficult to get complete solutions without making drastic approximations. The problem is exceedingly complex because, not only the rate of the combustion process but also many physical variables such as temperature, pressure, air/fuel ratio, vessel size, and humidity affect the mechanism markedly.

As stated earlier, a flame (or a deflagration wave) travels with subsonic velocities. A detonation, as distinguished from a flame, travels with supersonic velocities. The velocity of a detonation wave is determined by the equations of conservation of mass, momentum and energy, whereas the velocity of flame propagation depends upon the detailed chemical kinetics and the coefficients of diffusion and thermal conductivity.

An incomplete knowledge of chemical kinetics, precise values of the various parameters at high temperature and complicated mathematical equations are the major hurdles in the determination of an accurate theoretical value of velocity of flame propagation.

The current theories of laminar flame propagation may be broadly divided into:

1. Thermal theories
2. Diffusion theories
3. Comprehensive theories

These theories are briefly discussed here.

Thermal Theories

The first attempt to determine the velocity of laminar flame propagation was made by Mallard and Le Chatelier[10]. They equated the sensible heat gain in the preheat zone to the heat conducted from the reaction zone at the T_I boundary (Fig. 9.1). Assuming that there is no reaction before T_I, the temperature gradient is expressed as:

$$-\left(\frac{dT}{dx}\right)_I \approx \frac{T_b-T_I}{x_b-x_I} \tag{9.1}$$

The quantity of heat necessary to heat S_u cm³ of fresh gas (that passes through the burning surface per cm² per sec) to the ignition temperature is:

$$\bar{C}_p\,(\rho_u S_u)\,(T_I-T_u)$$

The heat transfer by conduction from the reaction zone is

$$-k\left(\frac{dT}{dx}\right)$$

hence
$$\bar{C}_p\,(\rho_u S_u)(T_I-T_u)=k\,\frac{T_b-T_I}{x_b-x_I} \tag{9.2}$$

or
$$S_u=\frac{k}{\bar{C}_p\,\rho_u\,(x_b-x_I)}\cdot\frac{T_b-T_I}{T_I-T_u} \tag{9.3}$$

where $\bar{C}_p$ is the mean specific heat from T_u to T_I.

According to Fig. 9.1, the T-x curve is linear in the reaction zone and the slope is equal to that at x_I as determined by approaching x_I through the preheat zone. The chemical reaction rate is involved indirectly through the reaction zone thickness (x_b-x_I). All authors since Mallard and Le Chatelier have given some consideration to include the reaction rate in their equation for the velocity of laminar flame propagation. It may be noted that it is not easy to determine the ignition temperature for use in such equations.

After a considerable period, Jouguet and Nusselt[11] independently computed the velocity of laminar flame propagation considering the reaction rate and thermal conduction. Jouguet assumed the relation between temperature and reaction rate to be linear, viz. $\mathbf{k}=k_0T$ where $\mathbf{k}$ is the reaction rate constant which differs greatly from the law of Arrhenius. This simplified the mathematics but the result could not give the correct relation between the temperature and reaction rate.

Assuming a steady state, one dimensional, adiabatic flow with a flat stationary flame conducting heat in the x direction only and having a fixed ignition point, Jouguet wrote the continuity, momentum and energy equations for the two zones, namely the preheat zone before temperature T_I and the reaction zone from T_I and T_b. The boundary conditions are:

At $x=-\infty$, $T=T_u$, $\frac{dT}{dx}=0$ and chemical variable $\alpha=0$

at $x=+\infty,\ T=T_b,\ \frac{dT}{dx}=0$ and $\alpha=1$

By solving the two sets of equations and equating the values of T for the two zones for the point $x=0$ where $T=T_I$, he obtained the following expression for the velocity of flame propagation.

$$S_u=\frac{T_0}{\sqrt{P_0}}\sqrt{\frac{nRkk_0}{C_p}\left(\frac{T_b-T_I}{T_I-T_u}\right)} \tag{9.4}$$

where k is the thermal conductivity of the gas mixture. This relationship is correct for a unimolecular reaction when the reaction rate constant **k** is proportional to the temperature.

After the publication of Jouguet's work many equations for the velocity of flame propagation based on the thermal mechanism were given by Daniell, Damköhler Bechert, Bartholome and Emmons, Harr and Strong etc.[11] Other workers who have presented thermal theories of flame propagation are Zeldovich and Frank-Kamenetsky[12], Semenov[13], and Boys and Corner[14]. A particularly convenient approximate theory has been presented by Vonkarman and Penner[15]. Zeldovich and Frank-Kamenetsky have derived an equation for flame velocity which includes diffusion of molecules but not free radicals and atoms. Therefore, it emphasizes thermal mechanism. Semenov derived an equation which has been widely used in literature for predicting the flame velocities of hydrocarbons and comparing with the experimental values. It merits some discussion here. He assumed the ignition temperature near the flame temperature where most of the reaction takes place and by approximation eliminated it from the final expression.

Semenov Equation

In the derivation of the Semenov equation, an ignition temperature is used as a mathematical device for computation. Semenov assumed that this ignition temperature is near the flame temperature where most of the reaction takes place. The chemical reaction rate is an exponential function of the temperature viz.

$$\omega\propto\exp\left(-\frac{E_{act}}{RT}\right) \tag{9.5}$$

where ω is the reaction rate and E_{act} is the activation energy.

Using approxiamation, Semenov eliminated the ignition temperature from the final equation. This resulted in a form of equation more useful than the previous equations. Semenov used the following assumptions in the derivation of his equation:

1. The flame is one dimensional.
2. The flame is steady with respect to time.

3. Velocity gradients may be neglected, hence, viscosity terms in the momentum and energy equations may be ignored.
4. Pressure is essentially constant across the flame front, hence the equation for conservation of momentum can be ignored.
5. The effect of gravity is negligible.
6. The loss of energy by radiation is negligible.
7. Diffusion is important in as far as it affects the energy balance.
8. Flame velocity may be described in terms of an overall chemical reaction; equations are set up in terms of zero order, first order (monomolecular) or second order (bimolecular) reactions.
9. Specific heat C_p and thermal conductivity k are constant.
10. Thermal diffusivity $k/C_p\,\rho$ is equal to molecular diffusivity D.
11. The total number of molecules is constant.

The physical model of such one dimensional adiabatic flame is shown in Fig. 9.11.

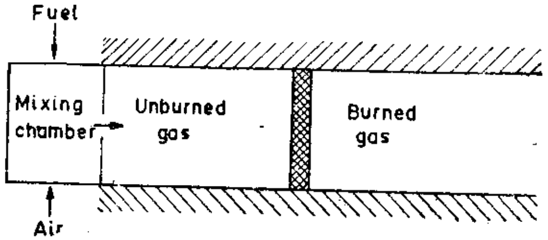

Fig. 9.11 Physical model of one-dimensional adiabatic flame.

The basic equations are as follows:

Continuity equation:

$$D\rho\frac{d^2C'}{dx^2}-G\frac{dC'}{dx}+\omega=0 \tag{9.6}$$

where $C'=C_{rt,\,0}\,\rho_0-\frac{C_{rt}}{\rho}$

and $C_{rt,\,0}$ is the concentration of reactant molecules at initial conditions, molecules/cm^3

The energy equation is given as:

$$\frac{k}{C_p}\frac{d^2T}{dx^2}-G\frac{dT}{dx}+\omega\frac{Q_{r0}}{C_p} \tag{9.7}$$

where $G=\rho U=\rho_0\,S_u$

Equation of state:

$$\frac{\rho}{\rho_0}=\frac{T_0}{T} \tag{9.8}$$

where G=mass flow rate

ω=reaction rate

x=distance

U=velocity, cm/s

Q_{rc}=heat of reaction cal/molecule of reactant.

It is assumed that there is no chemical reaction in the preheat zone x_u to x_i and in the reaction zone the energy loss due to mass transfer may be neglected in comparison with the chemical reaction and heat conduction terms. The energy equation is solved for S_u by integrating over the preheat zone (x_u to x_i) and the reaction zone (x_i to x_b) separately and establishing the condition of continuity by equating dT/dx at $x=x_i$ for the two zones. The resulting equation is:

$$S_u=\sqrt{\frac{2\kappa}{C_{ri,0}\,\rho_u\,\bar{C}_p\,(T_b-T_u)}\int_0^{T_b}\omega dT} \tag{9.9}$$

It is assumed that the overall reaction is second-order (bimolecular) with respect to fuel and oxygen, and the reaction rate follows an Arrhenius type temperature relation. The reaction rate integral is evaluated as follows:

$$\int_0^{T_b}\omega dT=\int_0^{T_b} C_f\, C_{O_2}\, PZ \exp\left(-\frac{E_{act}}{RT}\right) \tag{9.10a}$$

$$\approx C_{f\,eff}\, C_{O_2,eff}\, PZ\,\frac{RT_b^2}{E_{act}}\,\exp\left(-\frac{E_{act}}{RT_b}\right) \tag{9.10b}$$

where, $C_{f,\,eff}$ and $C_{O_2,eff}$ are the effective mean concentrations of fuel and oxygen in the reaction zone (molecules/cm^3); P is the steric factor; E_{act} is the activation energy (cal/mole); Z is the collision number.

Semenov states that the approximation for the exponential term obtained from Eqs. (9.10a) and (9.10b) is satisfactory for

$$\frac{RT_b}{E_{act}}\leqslant 0.1$$

Approximate solutions must be obtained for the effective concentration terms. The relation between concentration and temperature is first established for a zero-order reaction as follows: A new variable $\theta=C_p(T-T_u)\,Q_{re}$ is introduced into the energy equation to give :

$$\frac{k}{C_p}\,\frac{d^2\theta}{dx^2}-G\frac{d\theta}{dx}+\omega=0 \tag{9.11}$$

which is formally identical with the continuity Eq. (9.6) because by assumption (10), $k/C_p=D\rho$. It can be shown that the boundary conditions

of these equations coincide at x_u and x_b. If $C'=\theta$ for the entire interval, a relation between concentration and temperature is obtained

$$C_p\, T+C_{rt}\, Q_{re}=C_p\, T_u+C_{ri,\,0}\, Q_{re}=C_p\, T_b \tag{9.12}$$

Equation (9.12) implies that the sum of chemical and thermal energies is constant throughout the flame (a condition that holds only where assumption (10) is valid). Following the approximation technique used by Semenov this relation is modified for $C_{f,eff}$ and $C_{O_2,\,eff}$ for bimolecular reaction as follows:

$$\left.\begin{aligned} C_{f,\,eff}&=C_{f,\,0}\,\frac{T_u}{T_b}\left(1-\frac{1-\beta}{\phi}\right)\\ C_{O_2,\,eff}&=C_{O_2,\,0}\,\frac{T_u}{T_b}\cdot\beta\end{aligned}\right\} \tag{9.13}$$

For lean mixtures $\phi<1$

$$\left.\begin{aligned} C_{f,\,eff}&=C_{f,\,0}\,\frac{T_u}{T_b}\,\beta\\ C_{O_2,\,eff}&=C_{O_2,\,0}\,\frac{T_u}{T_b}[1-\phi\,(1-\beta)]\end{aligned}\right\} \tag{9.14}$$

where

$$\beta=\frac{RT_b^2}{E_{act}\,(T_b-T_u)} \tag{9.15}$$

and

$$C_{O_2,\,0}=\frac{C_{f,\,0}}{\phi}\left(\frac{C_{f,\,0}}{C_{O_2,\,0}}\right)_{st} \tag{9.16}$$

where $\left(\frac{C_{f,\,0}}{C_{O_2,\,0}}\right)_{st}$ is the stoichiometric fuel oxygen ratio. Correction may now be applied to some of the assumptions as follows: Assumption (9) is corrected by the use of a mean value of k/C_p for the preheat zone, and it is assumed that the physical properties in the reaction zone may be represented by their values at T_b. For the bimolecular reaction, assumptions (10) and (11) are corrected by inserting the factors $(k/Cp\rho D)_b^2$ and m^2 respectively under the square root sign in Eq. (9.9) (m is the ratio of moles of reactants to moles of products in the stoichiometric reaction). These correction factors and Eqs. (9.8), (9.10b), (9.13), (9.14), and (9.15) are substituted into the flame velocity Eq. (9.9). After collecting the terms, the resulting equation for the rich mixture can be written as

$$S_u=\frac{K\beta}{C_{p,\,b}\,D_b}\sqrt{\frac{2k_b^3\,PZ\,C_{f,\,0}\left(1-\dfrac{1-\beta}{\phi}\right)}{\rho_u^3\,C_p\,\phi\left(\dfrac{C_{f,\,0}}{C_{O_2,\,0}}\right)_{st}}\exp\left(-\frac{E_{act}}{RT_b}\right)} \tag{9.17}$$

For lean mixtures, the term $[1(1-\beta/\phi)]$ is replaced by $[1-\phi\,(1-\beta)]$ and for stoichiometric mixtures it becomes simply β.

The Semenov equation can also be written in the following form:

$$S_u=\left[\frac{2k_b\, Ka_0\, C_{p,b}^2}{\rho_u\, C_p^3}\left(\frac{T_u}{T_b}\right)^2\left(\frac{k}{\bar{C}_p\,\rho\, D}\right)_b^2\left(\frac{n_1}{n_2}\right)^2\left(\frac{RT_b}{E_{act}}\right)\frac{\exp\left(-\frac{E_{act}}{RT_b}\right)}{(T_b-T_u)^3}\right]^{\frac{1}{2}} \tag{9.18}$$

where K=constant

C_p=mean constant pressure specific heat of mixture, T_u to T_b (cal/g K)

a_0=number of molecules of combustible per unit volume of initial mixture,

$\frac{n_1}{n_2}$=moles of reactants per mole of products from stoichiometric equation

R=gas constant (cal/mole K).

Thus, the Semenov equation though based primarily on a thermal mechanism gives satisfactory relative predictions for flame velocities as either the initial temperature or the equivalence ratio is varied. This equation is more comprehensive than other thermal theory equations.

Diffusion Theories

Several approximate equations for burning velocity have been proposed by numerous investigators which take into account the effect of diffusion of active centres (free atoms and radicals) into the unburned gas.

Because of the steep concentration gradient in the reaction zone and the high diffusivity coefficients of hydrogen atoms, hydroxyl radicals, and other chain carriers, the effect of diffusion has been considered of major importance.

Because of the low activation energies of chemical reactions involving atoms and free radicals, even the small percentage of these active particles in the preheat zone, results in appreciable reactions i.e., the reaction rate is not very dependent on the temperature. In some cases the diffusion effect can even dominate the thermal effect for transfer of energy and initiating the reaction in the preheat zone thickness. By spectroscopical examination it has been found that the relative concentration of hydroxyl radicals remains high in the unburned gas ahead of the visible flame zone. Gaydon and Wolfhard[16] have shown that the width of the reaction zone for several hydrocarbon-air and ogygen flames is roughly equal to the diffusion limit of hydrogen atoms from the flame front into the unburned gas. The diffusion model of flame propagation qualitatively follows the known features of the structure of the flame and the oxidation reaction.

Tanford-Pease Equation

Tanford and Pease[17] have derived an approximate equation for flame velocity based on the diffusion model. In addition to the first six assumptions listed in the thermal theories, the following simplifications and assumptions were made:

1. Chain branching does not occur.
2. The rate controlling step (or steps) in the chemical chain reaction is the reaction of an active particle, such as the hydrogen atom, with a fuel molecule, for example,

$$H+CH_4 \rightarrow \text{products} \tag{9.19}$$

3. The number of active particles is calculated from the linear continuity equation

$$D_i\left(\frac{d^2C_i}{dx^2}\right)+S_u\left(\frac{dC_i}{dx}\right)+I_i=0 \tag{9.20}$$

where I_i is the rate of production of the active species regardless of the reaction order of process (molecules/cm³ sec).

4. The rate of formation of combustion products per unit area of flame surface can be written as the integral of a sum of number of terms, one for each active particle:

$$\frac{d\,(\text{product})}{dt}=\int_{x_u}^{x_\infty}\left(\sum_i k_i\,\frac{dC_i}{dx}\right)C_f\,dx \tag{9.21}$$

where k_i is the specific rate constant for reaction between the i^{th} active species.

5. Through each unit area of the flame surface, the unburned gas is converted at the flame velocity to products of complete combustion, so that another expression for product formation is

$$\frac{d\,(\text{product})}{dt}=C_{t,0}\,X_p\,S_u \tag{9.22}$$

where $C_{t,0}$ is the total number of molecules per cubic centimetre at initial conditions and X_p is the mole fraction of potential combustion product in the unburned gas.

6. The fuel concentration, combustion zone temperature, and the diffusion coefficient are expressed as constant mean values, $C_{f,m}$, T_m and D_m respectively. The ratio T_m/T_u is called θ_m and T_m is arbitrarily assigned the value 0.7 T_b.

The continuity Eq. (9.20) is solved for C_i which is then differentiated to give $\partial C_i/\partial x$. By equating the two simplified expressions for product formation by Eqs. (9.21) and (9.22), substituting for $\partial C_i/\partial x$, and making the indicated integration, there is obtained the square root law for flame velocity.