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# INTERNAL COMBUSTION ENGINE FUNDAMENTALS

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# CHAPTER

# 1

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## ENGINE TYPES AND THEIR OPERATION

### 1.1 INTRODUCTION AND HISTORICAL PERSPECTIVE

The purpose of internal combustion engines is the production of mechanical power from the chemical energy contained in the fuel. In *internal* combustion engines, as distinct from *external* combustion engines, this energy is released by burning or oxidizing the fuel *inside* the engine. The fuel-air mixture before combustion and the burned products after combustion are the actual working fluids. The work transfers which provide the desired power output occur directly between these working fluids and the mechanical components of the engine. The internal combustion engines which are the subject of this book are spark-ignition engines (sometimes called Otto engines, or gasoline or petrol engines, though other fuels can be used) and compression-ignition or diesel engines.† Because of their simplicity, ruggedness and high power/weight ratio, these two types of engine have found wide application in transportation (land, sea, and air) and power generation. It is the fact that combustion takes place inside the work-

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† The gas turbine is also, by this definition, an "internal combustion engine." Conventionally, however, the term is used for spark-ignition and compression-ignition engines. The operating principles of gas turbines are fundamentally different, and they are not discussed as separate engines in this book.

producing part of these engines that makes their design and operating characteristics fundamentally different from those of other types of engine.

Practical heat engines have served mankind for over two and a half centuries. For the first 150 years, water, raised to steam, was interposed between the combustion gases produced by burning the fuel and the work-producing piston-in-cylinder expander. It was not until the 1860s that the internal combustion engine became a practical reality.<sup>1, 2</sup> The early engines developed for commercial use burned coal-gas air mixtures at atmospheric pressure—there was no compression before combustion. J. J. E. Lenoir (1822–1900) developed the first marketable engine of this type. Gas and air were drawn into the cylinder during the first half of the piston stroke. The charge was then ignited with a spark, the pressure increased, and the burned gases then delivered power to the piston for the second half of the stroke. The cycle was completed with an exhaust stroke. Some 5000 of these engines were built between 1860 and 1865 in sizes up to six horsepower. Efficiency was at best about 5 percent.

A more successful development—an atmospheric engine introduced in 1867 by Nicolaus A. Otto (1832–1891) and Eugen Langen (1833–1895)—used the pressure rise resulting from combustion of the fuel-air charge early in the outward stroke to accelerate a free piston and rack assembly so its momentum would generate a vacuum in the cylinder. Atmospheric pressure then pushed the piston inward, with the rack engaged through a roller clutch to the output shaft. Production engines, of which about 5000 were built, obtained thermal efficiencies of up to 11 percent. A slide valve controlled intake, ignition by a gas flame, and exhaust.

To overcome this engine's shortcomings of low thermal efficiency and excessive weight, Otto proposed an engine cycle with four piston strokes: an intake stroke, then a compression stroke before ignition, an expansion or power stroke where work was delivered to the crankshaft, and finally an exhaust stroke. He also proposed incorporating a stratified-charge induction system, though this was not achieved in practice. His prototype four-stroke engine first ran in 1876. A comparison between the Otto engine and its atmospheric-type predecessor indicates the reason for its success (see Table 1.1): the enormous reduction in engine weight and volume. This was the breakthrough that effectively founded the internal combustion engine industry. By 1890, almost 50,000 of these engines had been sold in Europe and the United States.

In 1884, an unpublished French patent issued in 1862 to Alphonse Beau de Rochas (1815–1893) was found which described the principles of the four-stroke cycle. This chance discovery cast doubt on the validity of Otto's own patent for this concept, and in Germany it was declared invalid. Beau de Rochas also outlined the conditions under which maximum efficiency in an internal combustion engine could be achieved. These were:

1. The largest possible cylinder volume with the minimum boundary surface
2. The greatest possible working speed

**TABLE 1.1**  
**Comparison of Otto four-stroke cycle and Otto-Langen engines<sup>2</sup>**

	Otto and Langen	Otto four-stroke
Brake horsepower	2	2
Weight, lb, approx.	4000	1250
Piston displacement, in <sup>3</sup>	4900	310
Power strokes per min	28	80
Shaft speed, rev/min	90	160
Mechanical efficiency, %	68	84
Overall efficiency, %	11	14
Expansion ratio	10	2.5

3. The greatest possible expansion ratio
4. The greatest possible pressure at the beginning of expansion

The first two conditions hold heat losses from the charge to a minimum. The third condition recognizes that the greater the expansion of the postcombustion gases, the greater the work extracted. The fourth condition recognizes that higher initial pressures make greater expansion possible, and give higher pressures throughout the process, both resulting in greater work transfer. Although Beau de Rochas' unpublished writings predate Otto's developments, he never reduced these ideas to practice. Thus Otto, in the broader sense, was the inventor of the modern internal combustion engine as we know it today.

Further developments followed fast once the full impact of what Otto had achieved became apparent. By the 1880s several engineers (e.g., Dugald Clerk, 1854–1913, and James Robson, 1833–1913, in England and Karl Benz, 1844–1929, in Germany) had successfully developed two-stroke internal combustion engines where the exhaust and intake processes occur during the end of the power stroke and the beginning of the compression stroke. James Atkinson (1846–1914) in England made an engine with a longer expansion than compression stroke, which had a high efficiency for the times but mechanical weaknesses. It was recognized that efficiency was a direct function of expansion ratio, yet compression ratios were limited to less than four if serious knock problems were to be avoided with the available fuels. Substantial carburetor and ignition system developments were required, and occurred, before high-speed gasoline engines suitable for automobiles became available in the late 1880s. Stationary engine progress also continued. By the late 1890s, large single-cylinder engines of 1.3-m bore fueled by low-energy blast furnace gas produced 600 bhp at 90 rev/min. In Britain, legal restrictions on volatile fuels turned their engine builders toward kerosene. Low compression ratio "oil" engines with heated external fuel vaporizers and electric ignition were developed with efficiencies comparable to those of gas engines (14 to 18 percent). The Hornsby-Ackroyd engine became the most

popular oil engine in Britain, and was also built in large numbers in the United States.<sup>2</sup>

In 1892, the German engineer Rudolf Diesel (1858–1913) outlined in his patent a new form of internal combustion engine. His concept of initiating combustion by injecting a liquid fuel into air heated solely by compression permitted a doubling of efficiency over other internal combustion engines. Much greater expansion ratios, without detonation or knock, were now possible. However, even with the efforts of Diesel and the resources of M.A.N. in Ausburg combined, it took five years to develop a practical engine.

Engine developments, perhaps less fundamental but nonetheless important to the steadily widening internal combustion engine markets, have continued ever since.<sup>2–4</sup> One more recent major development has been the rotary internal combustion engine. Although a wide variety of experimental rotary engines have been proposed over the years,<sup>5</sup> the first practical rotary internal combustion engine, the Wankel, was not successfully tested until 1957. That engine, which evolved through many years of research and development, was based on the designs of the German inventor Felix Wankel.<sup>6, 7</sup>

Fuels have also had a major impact on engine development. The earliest engines used for generating mechanical power burned gas. Gasoline, and lighter fractions of crude oil, became available in the late 1800s and various types of carburetors were developed to vaporize the fuel and mix it with air. Before 1905 there were few problems with gasoline; though compression ratios were low (4 or less) to avoid knock, the highly volatile fuel made starting easy and gave good cold weather performance. However, a serious crude oil shortage developed, and to meet the fivefold increase in gasoline demand between 1907 and 1915, the yield from crude had to be raised. Through the work of William Burton (1865–1954) and his associates of Standard Oil of Indiana, a thermal cracking process was developed whereby heavier oils were heated under pressure and decomposed into less complex more volatile compounds. These thermally cracked gasolines satisfied demand, but their higher boiling point range created cold weather starting problems. Fortunately, electrically driven starters, introduced in 1912, came along just in time.

On the farm, kerosene was the logical fuel for internal combustion engines since it was used for heat and light. Many early farm engines had heated carburetors or vaporizers to enable them to operate with such a fuel.

The period following World War I saw a tremendous advance in our understanding of how fuels affect combustion, and especially the problem of knock. The antiknock effect of tetraethyl lead was discovered at General Motors,<sup>4</sup> and it became commercially available as a gasoline additive in the United States in 1923. In the late 1930s, Eugene Houdry found that vaporized oils passed over an activated catalyst at 450 to 480°C were converted to high-quality gasoline in much higher yields than was possible with thermal cracking. These advances, and others, permitted fuels with better and better antiknock properties to be produced in large quantities; thus engine compression ratios steadily increased, improving power and efficiency.

During the past three decades, new factors for change have become important and now significantly affect engine design and operation. These factors are, first, the need to control the automotive contribution to urban air pollution and, second, the need to achieve significant improvements in automotive fuel consumption.

The automotive air-pollution problem became apparent in the 1940s in the Los Angeles basin. In 1952, it was demonstrated by Prof. A. J. Haagen-Smit that the smog problem there resulted from reactions between oxides of nitrogen and hydrocarbon compounds in the presence of sunlight.<sup>8</sup> In due course it became clear that the automobile was a major contributor to hydrocarbon and oxides of nitrogen emissions, as well as the prime cause of high carbon monoxide levels in urban areas. Diesel engines are a significant source of small soot or smoke particles, as well as hydrocarbons and oxides of nitrogen. Table 1.2 outlines the dimensions of the problem. As a result of these developments, emission standards for automobiles were introduced first in California, then nationwide in the United States, starting in the early 1960s. Emission standards in Japan and Europe, and for other engine applications, have followed. Substantial reductions in emissions from spark-ignition and diesel engines have been achieved. Both the use of catalysts in spark-ignition engine exhaust systems for emissions control and concern over the toxicity of lead antiknock additives have resulted in the reappearance of unleaded gasoline as a major part of the automotive fuels market. Also, the maximum lead content in leaded gasoline has been substantially reduced. The emission-control requirements and these fuel developments have produced significant changes in the way internal combustion engines are designed and operated.

Internal combustion engines are also an important source of noise. There are several sources of engine noise: the exhaust system, the intake system, the fan used for cooling, and the engine block surface. The noise may be generated by aerodynamic effects, may be due to forces that result from the combustion process, or may result from mechanical excitation by rotating or reciprocating engine components. Vehicle noise legislation to reduce emissions to the environment was first introduced in the early 1970s.

During the 1970s the price of crude petroleum rose rapidly to several times its cost (in real terms) in 1970, and concern built up regarding the longer-term availability of petroleum. Pressures for substantial improvements in internal combustion engine efficiency (in all its many applications) have become very substantial indeed. Yet emission-control requirements have made improving engine fuel consumption more difficult, and the removal and reduction of lead in gasoline has forced spark-ignition engine compression ratios to be reduced. Much work is being done on the use of alternative fuels to gasoline and diesel. Of the non-petroleum-based fuels, natural gas, and methanol and ethanol (methyl and ethyl alcohols) are receiving the greatest attention, while synthetic gasoline and diesel made from shale oil or coal, and hydrogen could be longer-term possibilities.

It might be thought that after over a century of development, the internal

TABLE 1.2  
The automotive urban air-pollution problem

Pollutant	Impact	Mobile source emissions as % of total†	Automobile emissions		Truck emissions††	
			Uncontrolled vehicles, g/km‡	Reduction in new vehicles, % ¶	SI engines, g/km	Diesel, g/km
Oxides of nitrogen (NO and NO <sub>2</sub> )	Reactant in photochemical smog; NO <sub>2</sub> is toxic	40-60	2.5	75	7	12
Carbon monoxide (CO)	Toxic	90	65	95	150	17
Unburned hydrocarbons (HC, many hydrocarbon compounds)	Reactant in photochemical smog	30-50	10	90	17‡‡	3
Particulates (soot and absorbed hydrocarbon compounds)	Reduces visibility; some of HC compounds mutagenic	50	0.5§	40§	n	0.5

† Depends on type of urban area and source mix.

‡ Average values for pre-1968 automobiles which had no emission controls, determined by U.S. test procedure which simulates typical urban and highway driving. Exhaust emissions, except for HC where 55 percent are exhaust emissions, 20 percent are evaporative emissions from fuel tank and carburetor, and 25 percent are crankcase blowby gases.

§ Diesel engine automobiles only. Particulate emissions from spark-ignition engines are negligible.

¶ Compares emissions from new spark-ignition engine automobiles with uncontrolled automobile levels in previous column. Varies from country to country. The United States, Canada, Western Europe, and Japan have standards with different degrees of severity. The United States, Europe, and Japan have different test procedures. Standards are strictest in the United States and Japan.

†† Representative average emission levels for trucks.

‡‡ With 95 percent exhaust emissions and 5 percent evaporative emissions.

n = negligible.

combustion engine has reached its peak and little potential for further improvement remains. Such is not the case. Conventional spark-ignition and diesel engines continue to show substantial improvements in efficiency, power, and degree of emission control. New materials now becoming available offer the possibilities of reduced engine weight, cost, and heat losses, and of different and more efficient internal combustion engine systems. Alternative types of internal combustion engines, such as the stratified-charge (which combines characteristics normally associated with either the spark-ignition or diesel) with its wider fuel tolerance, may become sufficiently attractive to reach large-scale production. The engine development opportunities of the future are substantial. While they



present a formidable challenge to automotive engineers, they will be made possible in large part by the enormous expansion of our knowledge of engine processes which the last twenty years has witnessed.

## 1.2 ENGINE CLASSIFICATIONS

There are many different types of internal combustion engines. They can be classified by:

1. *Application.* Automobile, truck, locomotive, light aircraft, marine, portable power system, power generation
2. *Basic engine design.* Reciprocating engines (in turn subdivided by arrangement of cylinders: e.g., in-line, V, radial, opposed), rotary engines (Wankel and other geometries)
3. *Working cycle.* Four-stroke cycle: naturally aspirated (admitting atmospheric air), supercharged (admitting precompressed fresh mixture), and turbocharged (admitting fresh mixture compressed in a compressor driven by an exhaust turbine), two-stroke cycle: crankcase scavenged, supercharged, and turbocharged
4. *Valve or port design and location.* Overhead (or I-head) valves, underhead (or L-head) valves, rotary valves, cross-scavenged porting (inlet and exhaust ports on opposite sides of cylinder at one end), loop-scavenged porting (inlet and exhaust ports on same side of cylinder at one end), through- or uniflow-scavenged (inlet and exhaust ports or valves at different ends of cylinder)
5. *Fuel.* Gasoline (or petrol), fuel oil (or diesel fuel), natural gas, liquid petroleum gas, alcohols (methanol, ethanol), hydrogen, dual fuel
6. *Method of mixture preparation.* Carburetion, fuel injection into the intake ports or intake manifold, fuel injection into the engine cylinder
7. *Method of ignition.* Spark ignition (in conventional engines where the mixture is uniform and in stratified-charge engines where the mixture is non-uniform), compression ignition (in conventional diesels, as well as ignition in gas engines by pilot injection of fuel oil)
8. *Combustion chamber design.* Open chamber (many designs: e.g., disc, wedge, hemisphere, bowl-in-piston), divided chamber (small and large auxiliary chambers; many designs: e.g., swirl chambers, prechambers)
9. *Method of load control.* Throttling of fuel and air flow together so mixture composition is essentially unchanged, control of fuel flow alone, a combination of these
10. *Method of cooling.* Water cooled, air cooled, uncooled (other than by natural convection and radiation)

All these distinctions are important and they illustrate the breadth of engine designs available. Because this book approaches the operating and emissions

**TABLE 1.3**  
**Classification of reciprocating engines by application**

Class	Service	Approximate engine power range, kW	Predominant type		
			D or SI	Cycle	Cooling
Road vehicles	Motorcycles, scooters	0.75-70	SI	2, 4	A
	Small passenger cars	15-75	SI	4	A, W
	Large passenger cars	75-200	SI	4	W
	Light commercial	35-150	SI, D	4	W
	Heavy (long-distance) commercial	120-400	D	4	W
Off-road vehicles	Light vehicles (factory, airport, etc.)	1.5-15	SI	2, 4	A, W
	Agricultural	3-150	SI, D	2, 4	A, W
	Earth moving	40-750	D	2, 4	W
	Military	40-2000	D	2, 4	A, W
Railroad	Rail cars	150-400	D	2, 4	W
	Locomotives	400-3000	D	2, 4	W
Marine	Outboard	0.4-75	SI	2	W
	Inboard motorcrafts	4-750	SI, D	4	W
	Light naval craft	30-2200	D	2, 4	W
	Ships	3500-22,000	D	2, 4	W
Airborne vehicles	Ships' auxiliaries	75-750	D	4	W
	Airplanes	45-2700	SI	4	A
Home use	Helicopters	45-1500	SI	4	A
	Lawn mowers	0.7-3	SI	2, 4	A
	Snow blowers	2-5	SI	2, 4	A
Stationary	Light tractors	2-8	SI	4	A
	Building service	7-400	D	2, 4	W
	Electric power	35-22,000	D	2, 4	W
	Gas pipeline	750-5000	SI	2, 4	W

SI = spark-ignition; D = diesel; A = air cooled; W = water cooled.

Source: Adapted from Taylor.<sup>9</sup>

characteristics of internal combustion engines from a fundamental point of view, the method of ignition has been selected as the primary classifying feature. From the method of ignition—spark-ignition or compression-ignition†—follow the important characteristics of the fuel used, method of mixture preparation, combustion chamber design, method of load control, details of the combustion process, engine emissions, and operating characteristics. Some of the other classifications are used as subcategories within this basic classification. The engine operating cycle—four-stroke or two-stroke—is next in importance; the principles of these two cycles are described in the following section.

Table 1.3 shows the most common applications of internal combustion

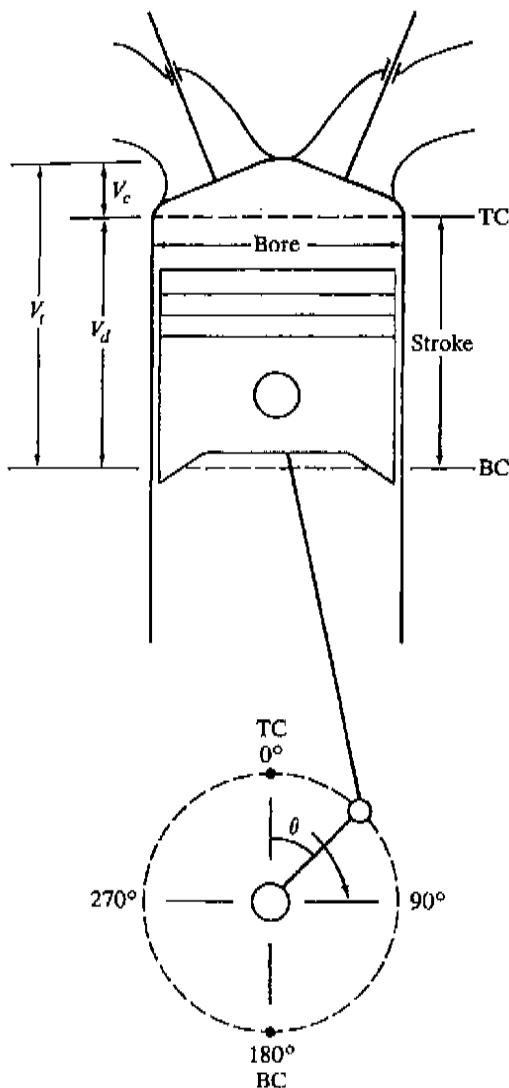
† In the remainder of the book, these terms will often be abbreviated by SI and CI, respectively.

engines, the predominant type of engine used in each classification listed, and the approximate engine power range in each type of service.

### 1.3 ENGINE OPERATING CYCLES

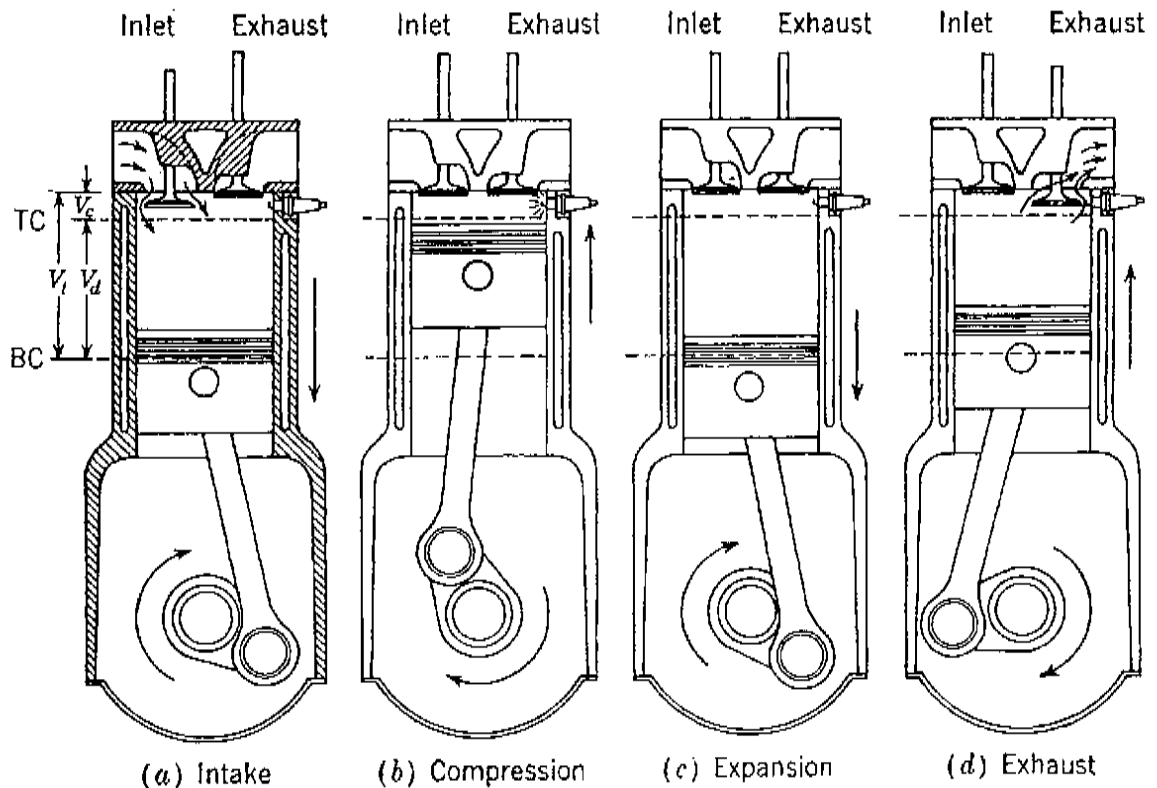
Most of this book is about reciprocating engines, where the piston moves back and forth in a cylinder and transmits power through a connecting rod and crank mechanism to the drive shaft as shown in Fig. 1-1. The steady rotation of the crank produces a cyclical piston motion. The piston comes to rest at the top-center (TC) crank position and bottom-center (BC) crank position when the cylinder volume is a minimum or maximum, respectively.† The minimum cylinder volume is called the clearance volume  $V_c$ . The volume swept out by the

† These crank positions are also referred to as top-dead-center (TDC) and bottom-dead-center (BDC).



**FIGURE 1-1**

Basic geometry of the reciprocating internal combustion engine.  $V_c$ ,  $V_d$  and  $V_t$  indicate clearance, displaced, and total cylinder volumes.



**FIGURE 1-2**  
The four-stroke operating cycle.<sup>10</sup>

piston, the difference between the maximum or total volume  $V_t$  and the clearance volume, is called the displaced or swept volume  $V_d$ . The ratio of maximum volume to minimum volume is the compression ratio  $r_c$ . Typical values of  $r_c$  are 8 to 12 for SI engines and 12 to 24 for CI engines.

The majority of reciprocating engines operate on what is known as the *four-stroke cycle*. Each cylinder requires four strokes of its piston—two revolutions of the crankshaft—to complete the sequence of events which produces one power stroke. Both SI and CI engines use this cycle which comprises (see Fig. 1-2):

1. *An intake stroke*, which starts with the piston at TC and ends with the piston at BC, which draws fresh mixture into the cylinder. To increase the mass inducted, the inlet valve opens shortly before the stroke starts and closes after it ends.
2. *A compression stroke*, when both valves are closed and the mixture inside the cylinder is compressed to a small fraction of its initial volume. Toward the end of the compression stroke, combustion is initiated and the cylinder pressure rises more rapidly.
3. *A power stroke*, or expansion stroke, which starts with the piston at TC and ends at BC as the high-temperature, high-pressure, gases push the piston down and force the crank to rotate. About five times as much work is done on the piston during the power stroke as the piston had to do during compression.

- As the piston approaches BC the exhaust valve opens to initiate the exhaust process and drop the cylinder pressure to close to the exhaust pressure.
4. *An exhaust stroke*, where the remaining burned gases exit the cylinder: first, because the cylinder pressure may be substantially higher than the exhaust pressure; then as they are swept out by the piston as it moves toward TC. As the piston approaches TC the inlet valve opens. Just after TC the exhaust valve closes and the cycle starts again.

Though often called the Otto cycle after its inventor, Nicolaus Otto, who built the first engine operating on these principles in 1876, the more descriptive four-stroke nomenclature is preferred.

The four-stroke cycle requires, for each engine cylinder, two crankshaft revolutions for each power stroke. To obtain a higher power output from a given engine size, and a simpler valve design, the *two-stroke* cycle was developed. The two-stroke cycle is applicable to both SI and CI engines.

Figure 1-3 shows one of the simplest types of two-stroke engine designs. Ports in the cylinder liner, opened and closed by the piston motion, control the exhaust and inlet flows while the piston is close to BC. The two strokes are:

1. *A compression stroke*, which starts by closing the inlet and exhaust ports, and then compresses the cylinder contents and draws fresh charge into the crankcase. As the piston approaches TC, combustion is initiated.

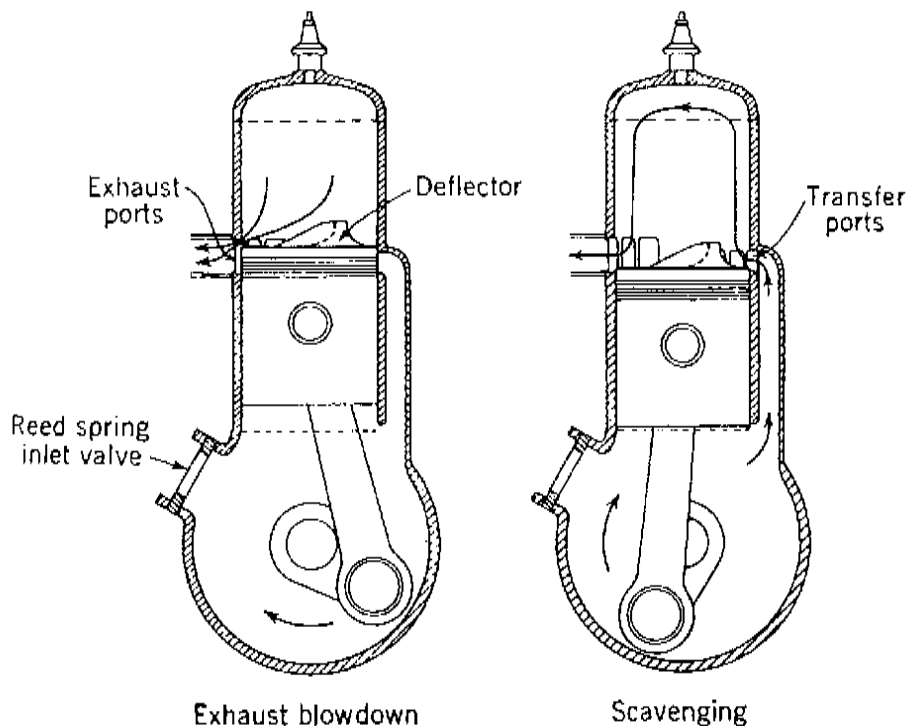


FIGURE 1-3 The two-stroke operating cycle. A crankcase-scavenged engine is shown.<sup>10</sup>

2. *A power or expansion stroke*, similar to that in the four-stroke cycle until the piston approaches BC, when first the exhaust ports and then the intake ports are uncovered (Fig. 1-3). Most of the burnt gases exit the cylinder in an exhaust blowdown process. When the inlet ports are uncovered, the fresh charge which has been compressed in the crankcase flows into the cylinder. The piston and the ports are generally shaped to deflect the incoming charge from flowing directly into the exhaust ports and to achieve effective scavenging of the residual gases.

Each engine cycle with one power stroke is completed in one crankshaft revolution. However, it is difficult to fill completely the displaced volume with fresh charge, and some of the fresh mixture flows directly out of the cylinder during the scavenging process.† The example shown is a *cross-scavenged* design; other approaches use *loop-scavenging* or *uniflow* systems (see Sec. 6.6).

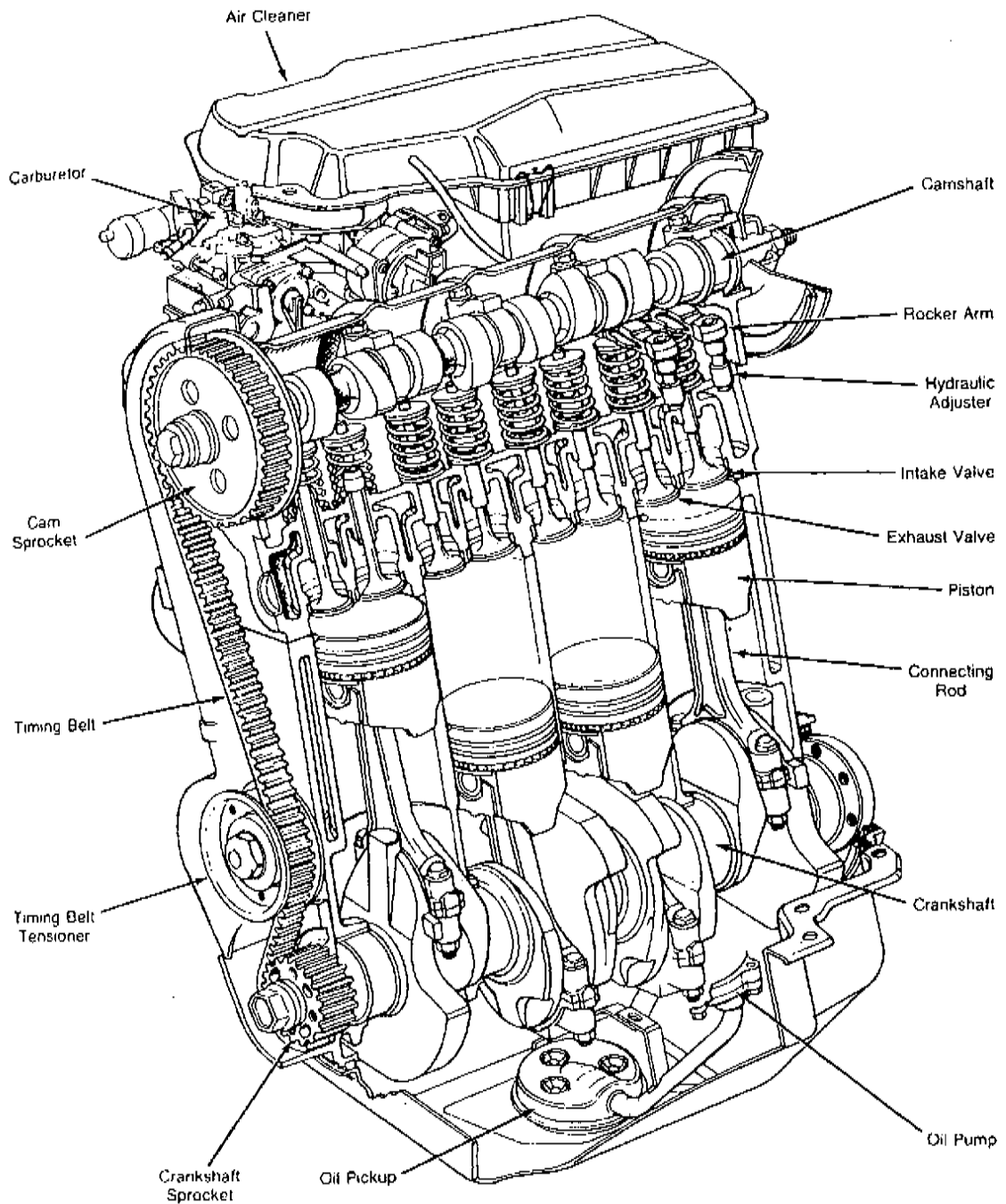
#### 1.4 ENGINE COMPONENTS

Labeled cutaway drawings of a four-stroke SI engine and a two-stroke CI engine are shown in Figs. 1-4 and 1-5, respectively. The spark-ignition engine is a four-cylinder in-line automobile engine. The diesel is a large V eight-cylinder design with a uniflow scavenging process. The function of the major components of these engines and their construction materials will now be reviewed.

The engine cylinders are contained in the engine block. The block has traditionally been made of gray cast iron because of its good wear resistance and low cost. Passages for the cooling water are cast into the block. Heavy-duty and truck engines often use removable cylinder sleeves pressed into the block that can be replaced when worn. These are called *wet liners* or *dry liners* depending on whether the sleeve is in direct contact with the cooling water. Aluminum is being used increasingly in smaller SI engine blocks to reduce engine weight. Iron cylinder liners may be inserted at the casting stage, or later on in the machining and assembly process. The crankcase is often integral with the cylinder block.

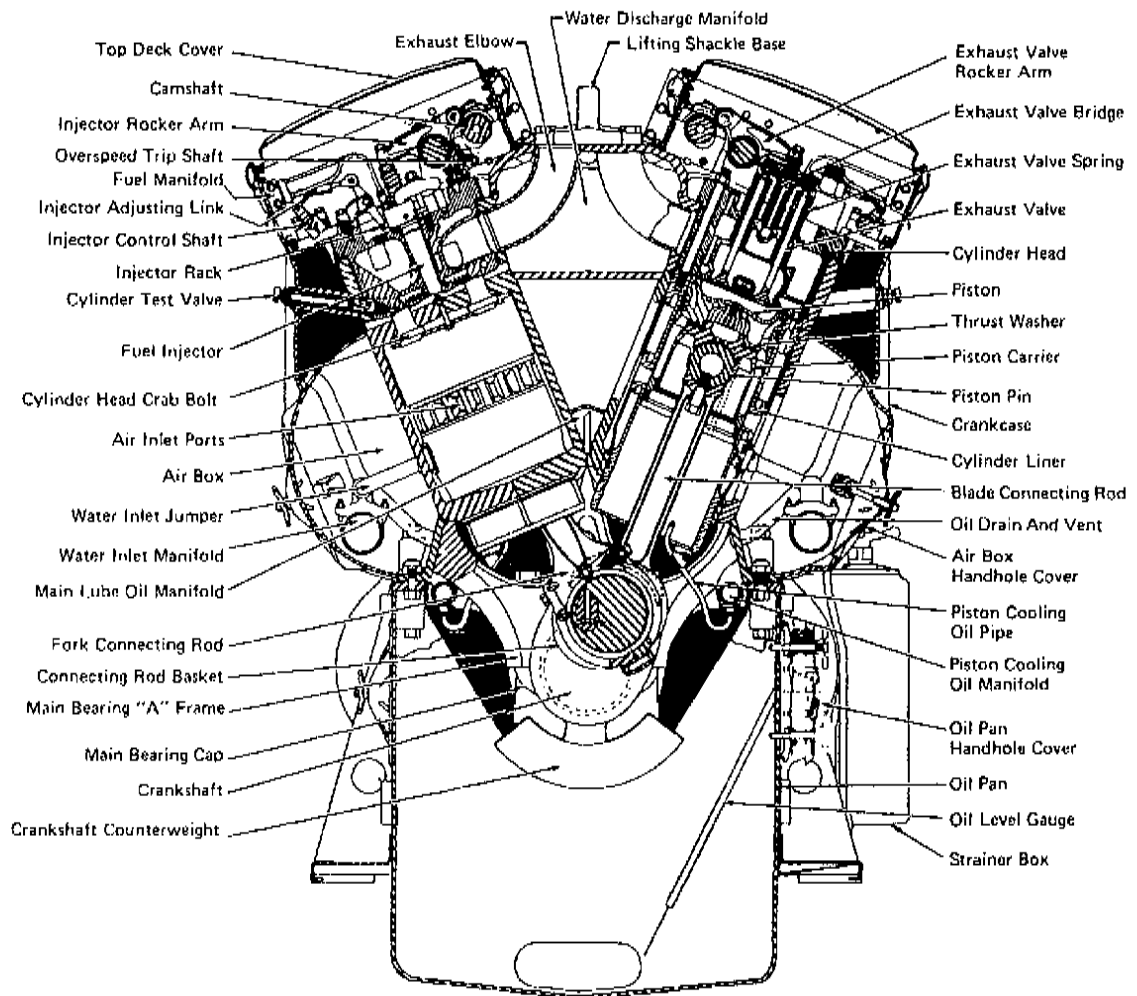
The crankshaft has traditionally been a steel forging; nodular cast iron crankshafts are also accepted normal practice in automotive engines. The crankshaft is supported in main bearings. The maximum number of main bearings is one more than the number of cylinders; there may be less. The crank has eccentric portions (crank throws); the connecting rod big-end bearings attach to the crank pin on each throw. Both main and connecting rod bearings use steel-backed precision inserts with bronze, babbitt, or aluminum as the bearing materials. The crankcase is sealed at the bottom with a pressed-steel or cast aluminum oil pan which acts as an oil reservoir for the lubricating system.

† It is primarily for this reason that two-stroke SI engines are at a disadvantage because the lost fresh charge contains fuel and air.



**FIGURE 1-4**  
 Cutaway drawing of Chrysler 2.2-liter displacement four-cylinder spark-ignition engine.<sup>11</sup> Bore 87.5 mm, stroke 92 mm, compression ratio 8.9, maximum power 65 kW at 5000 rev/min.

Pistons are made of aluminum in small engines or cast iron in larger slower-speed engines. The piston both seals the cylinder and transmits the combustion-generated gas pressure to the crank pin via the connecting rod. The connecting rod, usually a steel or alloy forging (though sometimes aluminum in small engines), is fastened to the piston by means of a steel piston pin through the rod upper end. The piston pin is usually hollow to reduce its weight.



**FIGURE 1-5**

Cross-section drawing of an Electro-Motive two-stroke cycle diesel engine. This engine uses a uniflow scavenging process with inlet ports in the cylinder liner and four exhaust valves in the cylinder head. Bore 230.2 mm, stroke 254 mm, displaced volume per cylinder 10.57 liters, rated speed 750-900 rev/min. (Courtesy Electro-Motive Division, General Motors Corporation.)

The oscillating motion of the connecting rod exerts an oscillating force on the cylinder walls via the piston skirt (the region below the piston rings). The piston skirt is usually shaped to provide appropriate thrust surfaces. The piston is fitted with rings which ride in grooves cut in the piston head to seal against gas leakage and control oil flow. The upper rings are compression rings which are forced outward against the cylinder wall and downward onto the groove face. The lower rings scrape the surplus oil from the cylinder wall and return it to the crankcase. The crankcase must be ventilated to remove gases which blow by the piston rings, to prevent pressure buildup.

The cylinder head (or heads in V engines) seals off the cylinders and is made of cast iron or aluminum. It must be strong and rigid to distribute the gas forces acting on the head as uniformly as possible through the engine block. The cylinder head contains the spark plug (for an SI engine) or fuel injector (for a CI engine), and, in overhead valve engines, parts of the valve mechanism. **FORD 1109**



The valves shown in Fig. 1-4 are poppet valves, the valve type normally used in four-stroke engines. Valves are made from forged alloy steel; the cooling of the exhaust valve which operates at about 700°C may be enhanced by using a hollow stem partially filled with sodium which through evaporation and condensation carries heat from the hot valve head to the cooler stem. Most modern spark-ignition engines have overhead valve locations (sometimes called valve-in-head or I-head configurations) as shown in Fig. 1-4. This geometry leads to a compact combustion chamber with minimum heat losses and flame travel time, and improves the breathing capacity. Previous geometries such as the L head where valves are to one side of the cylinder are now only used in small engines.

The valve stem moves in a valve guide, which can be an integral part of the cylinder head (or engine block for L-head engines), or may be a separate unit pressed into the head (or block). The valve seats may be cut in the head or block metal (if cast iron) or hard steel inserts may be pressed into the head or block. A valve spring, attached to the valve stem with a spring washer and split keeper, holds the valve closed. A valve rotator turns the valves a few degrees on opening to wipe the valve seat, avoid local hot spots, and prevent deposits building up in the valve guide.

A camshaft made of cast iron or forged steel with one cam per valve is used to open and close the valves. The cam surfaces are hardened to obtain adequate life. In four-stroke cycle engines, camshafts turn at one-half the crankshaft speed. Mechanical or hydraulic lifters or tappets slide in the block and ride on the cam. Depending on valve and camshaft location, additional members are required to transmit the tappet motion to the valve stem; e.g., in in-head valve engines with the camshaft at the side, a push rod and rocker arm are used. A recent trend in automotive engines is to mount the camshaft over the head with the cams acting either directly or through a pivoted follower on the valve. Camshafts are gear, belt, or chain driven from the crankshaft.

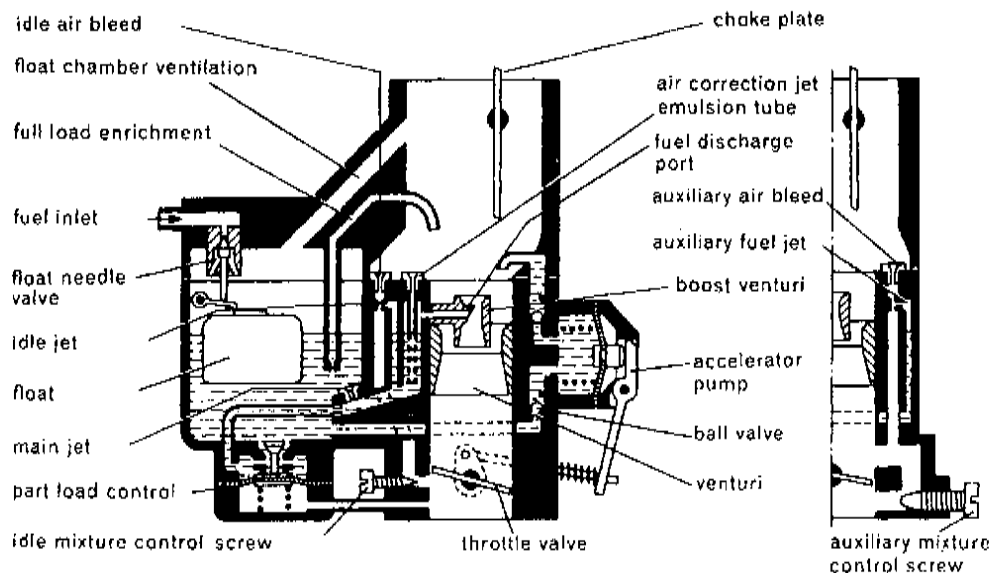
An intake manifold (aluminum or cast iron) and an exhaust manifold (generally of cast iron) complete the SI engine assembly. Other engine components specific to spark-ignition engines—carburetor, fuel injectors, ignition systems—are described more fully in the remaining sections in this chapter.

The two-stroke cycle CI engine shown in Fig. 1-5 is of the uniflow scavenged design. The burned gases exhaust through four valves in the cylinder head. These valves are controlled through cam-driven rocker arms. Fresh air is compressed and fed to the air box by a Roots blower. The air inlet ports at the bottom of each cylinder liner are uncovered by the descending piston, and the scavenging air flows upward along the cylinder axis. The fuel injectors are mounted in the cylinder head and are driven by the camshaft through rocker arms. Diesel fuel-injection systems are discussed in more detail in Sec. 1.7.

## 1.5 SPARK-IGNITION ENGINE OPERATION

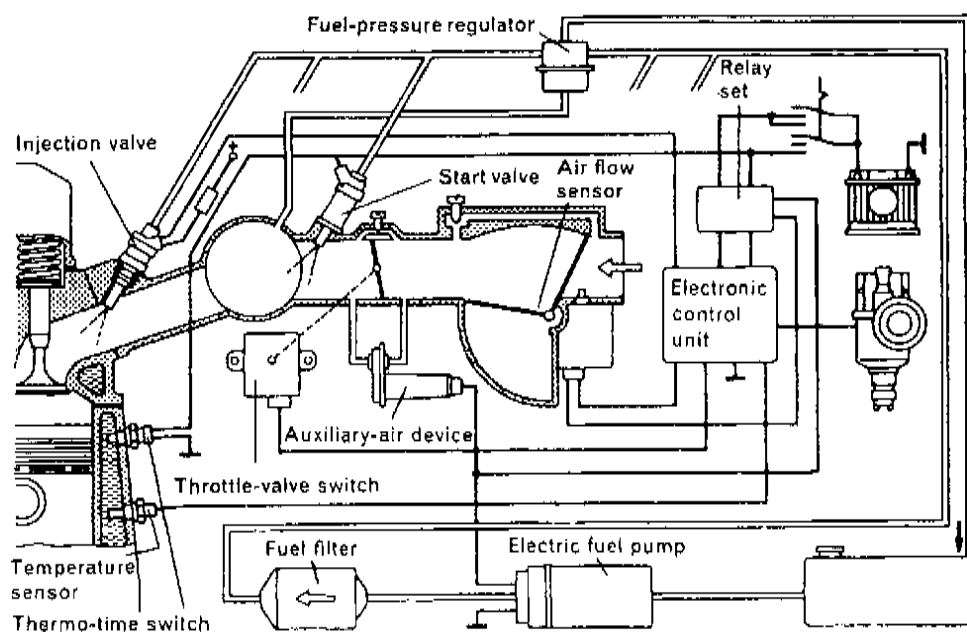
In SI engines the air and fuel are usually mixed together in the intake system prior to entry to the engine cylinder, using a carburetor (Fig. 1-6) or fuel-injection system (Fig. 1-7). In automobile applications, the temperature of the air entering

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**FIGURE 1-6**  
Cross section of single-barrel downdraft carburetor.<sup>12</sup> (Courtesy Robert Bosch GmbH and SAE.)

the intake system is controlled by mixing ambient air with air heated by contact with the exhaust manifold. The ratio of mass flow of air to mass flow of fuel must be held approximately constant at about 15 to ensure reliable combustion. The



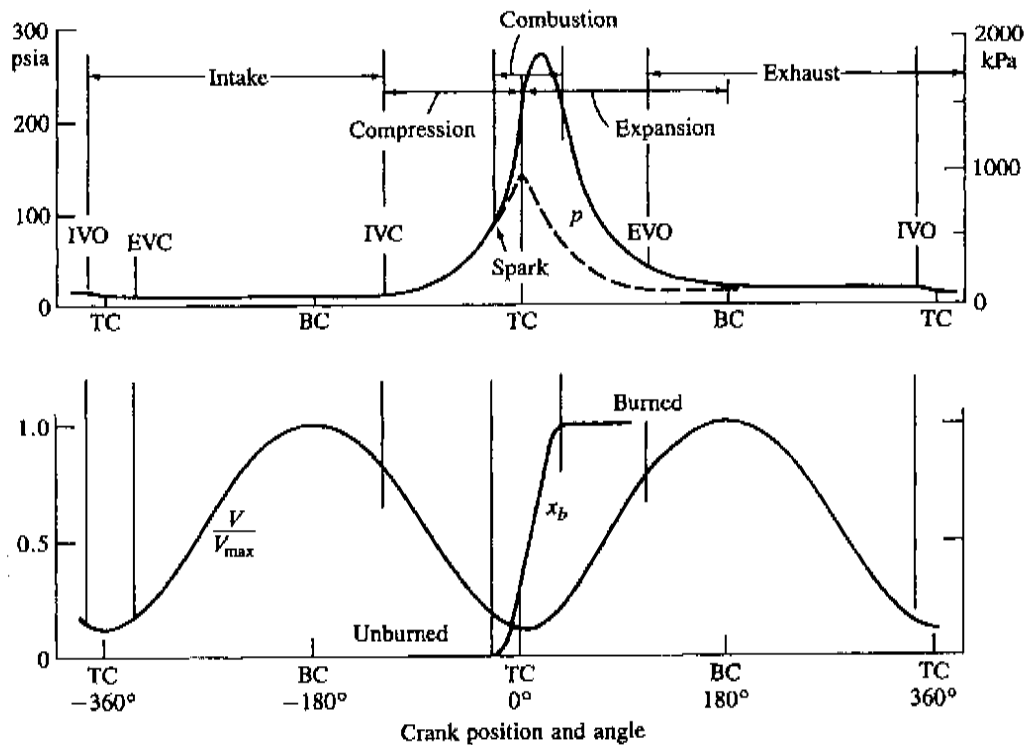
**FIGURE 1-7**  
Schematic drawing of L-Jetronic port electronic fuel-injection system.<sup>12</sup> (Courtesy Robert Bosch GmbH and SAE.)

carburetor meters an appropriate fuel flow for the engine air flow in the following manner. The air flow through the venturi (a converging-diverging nozzle) sets up a pressure difference between the venturi inlet and throat which is used to meter an appropriate amount of fuel from the float chamber, through a series of orifices, into the air flow at the venturi throat. Just downstream of the venturi is a throttle valve or plate which controls the combined air and fuel flow, and thus the engine output. The intake flow is throttled to below atmospheric pressure by reducing the flow area when the power required (at any engine speed) is below the maximum which is obtained when the throttle is wide open. The intake manifold is usually heated to promote faster evaporation of the liquid fuel and obtain more uniform fuel distribution between cylinders.

Fuel injection into the intake manifold or inlet port is an increasingly common alternative to a carburetor. With port injection, fuel is injected through individual injectors from a low-pressure fuel supply system into each intake port. There are several different types of systems: mechanical injection using an injection pump driven by the engine; mechanical, driveless, continuous injection; electronically controlled, driveless, injection. Figure 1-7 shows an example of an electronically controlled system. In this system, the air flow rate is measured directly; the injection valves are actuated twice per cam shaft revolution by injection pulses whose duration is determined by the electronic control unit to provide the desired amount of fuel per cylinder per cycle.<sup>12</sup> An alternative approach is to use a single fuel injector located above the throttle plate in the position normally occupied by the carburetor. This approach permits electronic control of the fuel flow at reduced cost.

The sequence of events which take place inside the engine cylinder is illustrated in Fig. 1-8. Several variables are plotted against crank angle through the entire four-stroke cycle. Crank angle is a useful independent variable because engine processes occupy almost constant crank angle intervals over a wide range of engine speeds. The figure shows the valve timing and volume relationship for a typical automotive spark-ignition engine. To maintain high mixture flows at high engine speeds (and hence high power outputs) the inlet valve, which opens before TC, closes substantially after BC. During intake, the inducted fuel and air mix in the cylinder with the *residual* burned gases remaining from the previous cycle. After the intake valve closes, the cylinder contents are compressed to above atmospheric pressure and temperature as the cylinder volume is reduced. Some heat transfer to the piston, cylinder head, and cylinder walls occurs but the effect on unburned gas properties is modest.

Between 10 and 40 crank angle degrees before TC an electrical discharge across the spark plug starts the combustion process. A distributor, a rotating switch driven off the camshaft, interrupts the current from the battery through the primary circuit of the ignition coil. The secondary winding of the ignition coil, connected to the spark plug, produces a high voltage across the plug electrodes as the magnetic field collapses. Traditionally, cam-operated breaker points have been used; in most automotive engines, the switching is now done electronically. A turbulent flame develops from the spark discharge, propagates



**FIGURE 1-8**

Sequence of events in four-stroke spark-ignition engine operating cycle. Cylinder pressure  $p$  (solid line, firing cycle; dashed line, motored cycle), cylinder volume  $V/V_{max}$ , and mass fraction burned  $x_b$ , are plotted against crank angle.

across the mixture of air, fuel, and residual gas in the cylinder, and extinguishes at the combustion chamber wall. The duration of this burning process varies with engine design and operation, but is typically 40 to 60 crank angle degrees, as shown in Fig. 1-8. As fuel-air mixture burns in the flame, the cylinder pressure in Fig. 1-8 (solid line) rises above the level due to compression alone (dashed line). This latter curve—called the motored cylinder pressure—is the pressure trace obtained from a motored or nonfiring engine.† Note that due to differences in the flow pattern and mixture composition between cylinders, and within each cylinder cycle-by-cycle, the development of each combustion process differs somewhat. As a result, the shape of the pressure versus crank angle curve in each cylinder, and cycle-by-cycle, is not exactly the same.

There is an optimum spark timing which, for a given mass of fuel and air inside the cylinder, gives maximum torque. More advanced (earlier) timing or retarded (later) timing than this optimum gives lower output. Called *maximum*

† In practice, the intake and compression processes of a firing engine and a motored engine are not exactly the same due to the presence of burned gases from the previous cycle under firing conditions.

*brake-torque* (MBT) timing,† this optimum timing is an empirical compromise between starting combustion too early in the compression stroke (when the work transfer is to the cylinder gases) and completing combustion too late in the expansion stroke (and so lowering peak expansion stroke pressures).

About two-thirds of the way through the expansion stroke, the exhaust valve starts to open. The cylinder pressure is greater than the exhaust manifold pressure and a *blowdown* process occurs. The burned gases flow through the valve into the exhaust port and manifold until the cylinder pressure and exhaust pressure equilibrate. The duration of this process depends on the pressure level in the cylinder. The piston then *displaces* the burned gases from the cylinder into the manifold during the exhaust stroke. The exhaust valve opens before the end of the expansion stroke to ensure that the blowdown process does not last too far into the exhaust stroke. The actual timing is a compromise which balances reduced work transfer to the piston before BC against reduced work transfer to the cylinder contents after BC.

The exhaust valve remains open until just after TC; the intake opens just before TC. The valves are opened and closed slowly to avoid noise and excessive cam wear. To ensure the valves are fully open when piston velocities are at their highest, the valve open periods often overlap. If the intake flow is throttled to below exhaust manifold pressure, then backflow of burned gases into the intake manifold occurs when the intake valve is first opened.

## 1.6 EXAMPLES OF SPARK-IGNITION ENGINES

This section presents examples of production spark-ignition engines to illustrate the different types of engines in common use.

Small SI engines are used in many applications: in the home (e.g., lawn mowers, chain saws), in portable power generation, as outboard motorboat engines, and in motorcycles. These are often single-cylinder engines. In the above applications, light weight, small bulk, and low cost in relation to the power generated are the most important characteristics; fuel consumption, engine vibration, and engine durability are less important. A single-cylinder engine gives only one power stroke per revolution (two-stroke cycle) or two revolutions (four-stroke cycle). Hence, the torque pulses are widely spaced, and engine vibration and smoothness are significant problems.

Multicylinder engines are invariably used in automotive practice. As rated power increases, the advantages of smaller cylinders in regard to size, weight, and improved engine balance and smoothness point toward increasing the number of

† MBT timing has traditionally been defined as the minimum spark advance for best torque. Since the torque first increases and then decreases as spark timing is advanced, the definition used here is more precise.

cylinders per engine. An upper limit on cylinder size is dictated by dynamic considerations: the inertial forces that are created by accelerating and decelerating the reciprocating masses of the piston and connecting rod would quickly limit the maximum speed of the engine. Thus, the displaced volume is spread out amongst several smaller cylinders. The increased frequency of power strokes with a multi-cylinder engine produces much smoother torque characteristics. Multicylinder engines can also achieve a much better state of balance than single-cylinder engines. A force must be applied to the piston to accelerate it during the first half of its travel from bottom-center or top-center. The piston then exerts a force as it decelerates during the second part of the stroke. It is desirable to cancel these inertia forces through the choice of number and arrangement of cylinders to achieve a *primary balance*. Note, however, that the motion of the piston is more rapid during the upper half of its stroke than during the lower half (a consequence of the connecting rod and crank mechanism evident from Fig. 1-1; see also Sec. 2.2). The resulting inequality in piston acceleration and deceleration produces corresponding differences in inertia forces generated. Certain combinations of cylinder number and arrangement will balance out these secondary inertia force effects.

Four-cylinder in-line engines are the most common arrangements for automobile engines up to about 2.5-liter displacement. An example of this in-line arrangement was shown in Fig. 1-4. It is compact—an important consideration for small passenger cars. It provides two torque pulses per revolution of the crankshaft and primary inertia forces (though not secondary forces) are balanced. V engines and opposed-piston engines are occasionally used with this number of cylinders.

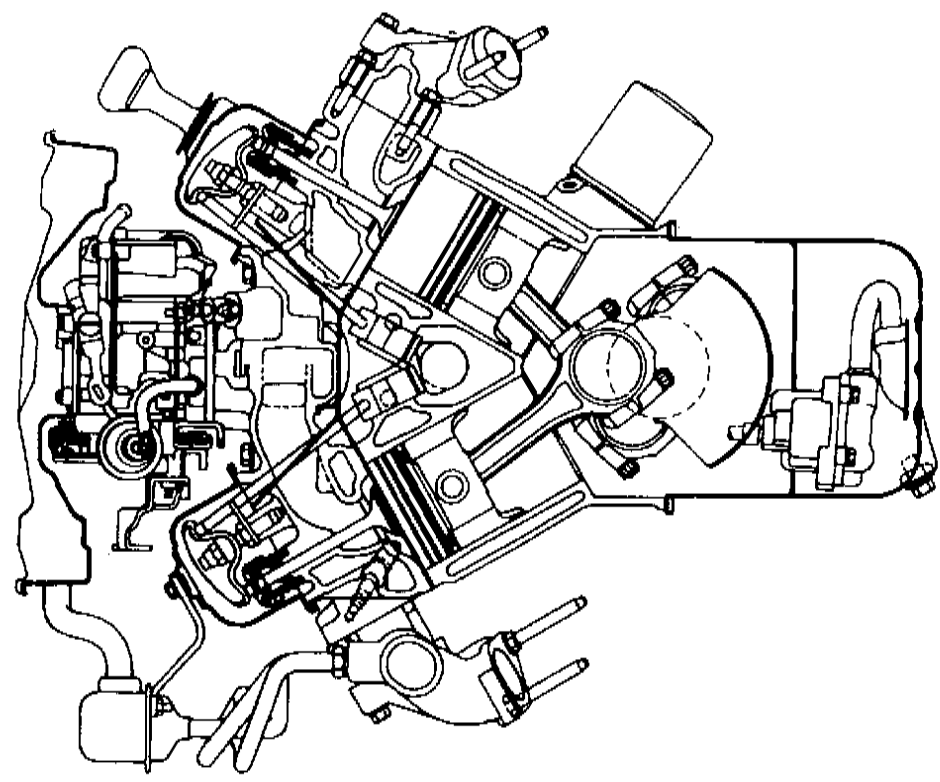
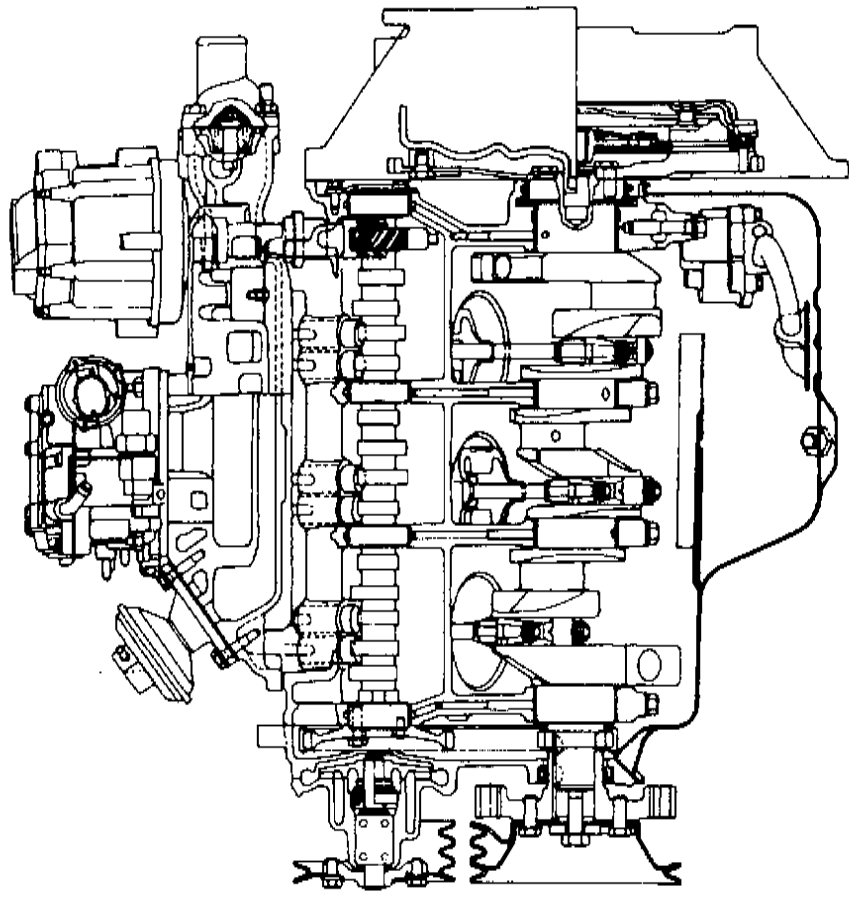
The V arrangement, with two banks of cylinders set at  $90^\circ$  or a more acute angle to each other, provides a compact block and is used extensively for larger displacement engines. Figure 1-9 shows a V-6 engine, the six cylinders being arranged in two banks of three with a  $60^\circ$  angle between their axis. Six cylinders are usually used in the 2.5- to 4.5-liter displacement range. Six-cylinder engines provide smoother operation with three torque pulses per revolution. The in-line arrangement results in a long engine, however, giving rise to crankshaft torsional vibration and making even distribution of air and fuel to each cylinder more difficult. The V-6 arrangement is much more compact, and the example shown provides primary balance of the reciprocating components. With the V engine, however, a rocking moment is imposed on the crankshaft due to the secondary inertia forces, which results in the engine being less well balanced than the in-line version. The V-8 and V-12 arrangements are also commonly used to provide compact, smooth, low-vibration, larger-displacement, spark-ignition engines.

Turbochargers are used to increase the maximum power that can be obtained from a given displacement engine. The work transfer to the piston per cycle, in each cylinder, which controls the power the engine can deliver, depends on the amount of fuel burned per cylinder per cycle. This depends on the amount of fresh air that is inducted each cycle. Increasing the air density prior to entry into the engine thus increases the maximum power that an engine of given dis-

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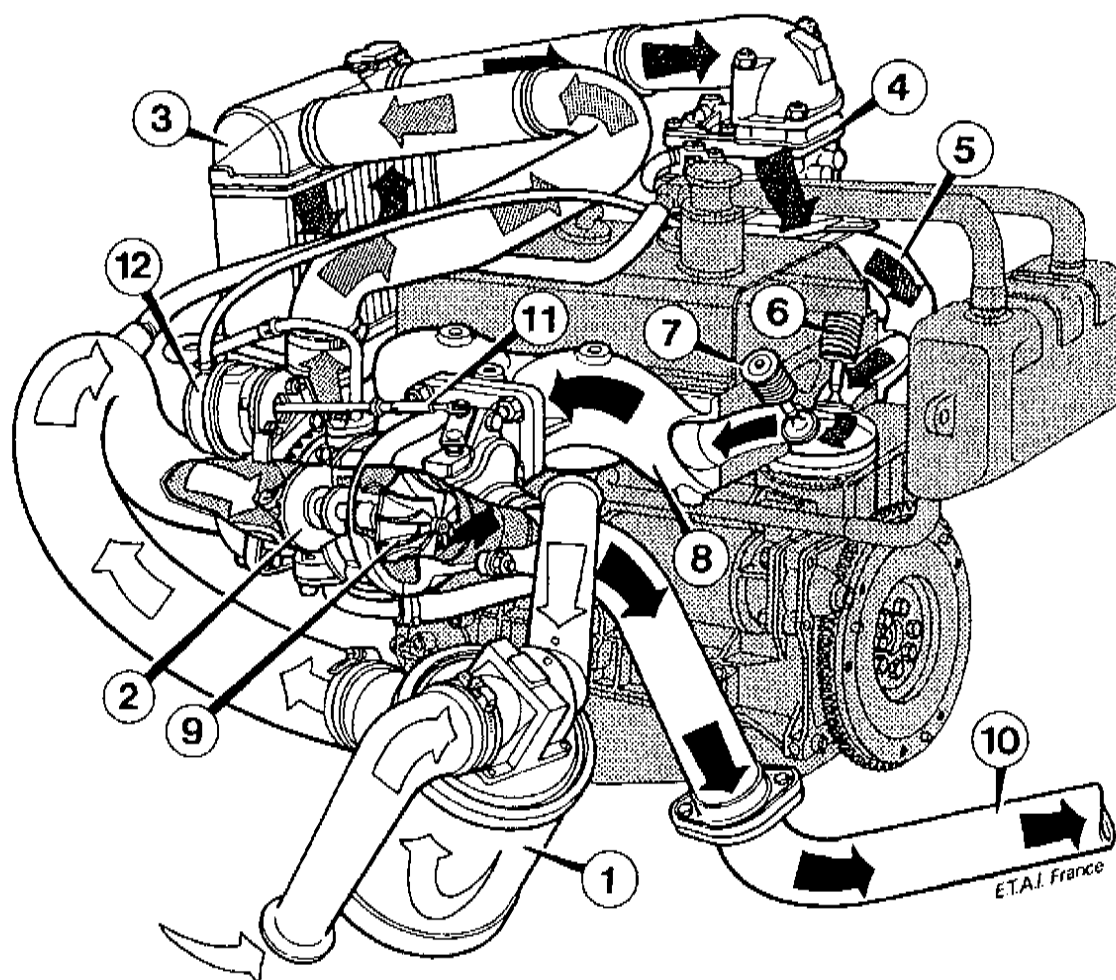
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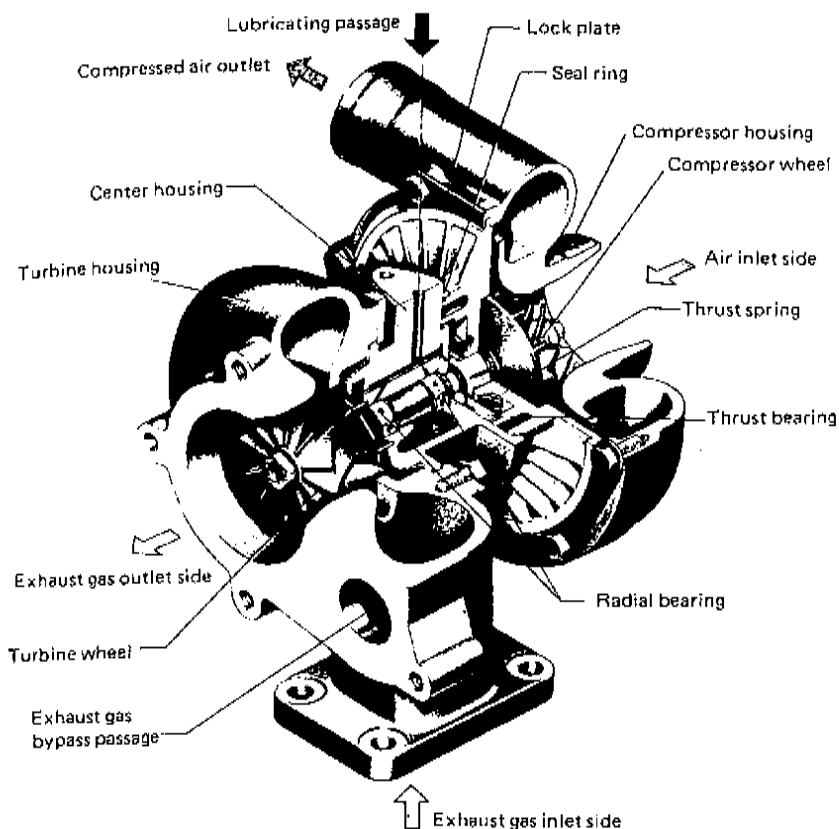
**FIGURE 1-9**  
 Cross-section drawings of General Motors 60 degree V-6 spark-ignition engine.<sup>13</sup> Displacement 2.8 liter, bore 89 mm, stroke 76 mm, compression ratio 8.5, maximum power 86 kW at 4800 rev/min.

placement can deliver. Figure 1-10 shows an example of a turbocharged four-cylinder spark-ignition engine. The turbocharger, a compressor-turbine combination, uses the energy available in the engine exhaust stream to achieve compression of the intake flow. The air flow passes through the compressor (2), intercooler (3), carburetor (4), manifold (5), and inlet valve (6) as shown. Engine inlet pressures (or boost) of up to about 100 kPa above atmospheric pressure are typical. The exhaust flow through the valve (7) and manifold (8) drives the turbine (9) which powers the compressor. A wastegate (valve) just upstream of the turbine bypasses some of the exhaust gas flow when necessary to prevent the boost pressure becoming too high. The wastegate linkage (11) is controlled by a boost pressure regulator. While this turbocharged engine configuration has the carburetor downstream of the compressor, some turbocharged spark-ignition engines have the carburetor upstream of the compressor so that it operates at or below atmospheric pressure. Figure 1-11 shows a cutaway drawing of a small automotive turbocharger. The arrangements of the compressor and turbine



**FIGURE 1-10**  
Turbocharged four-cylinder automotive spark-ignition engine. (Courtesy Regie Nationale des Usines.)



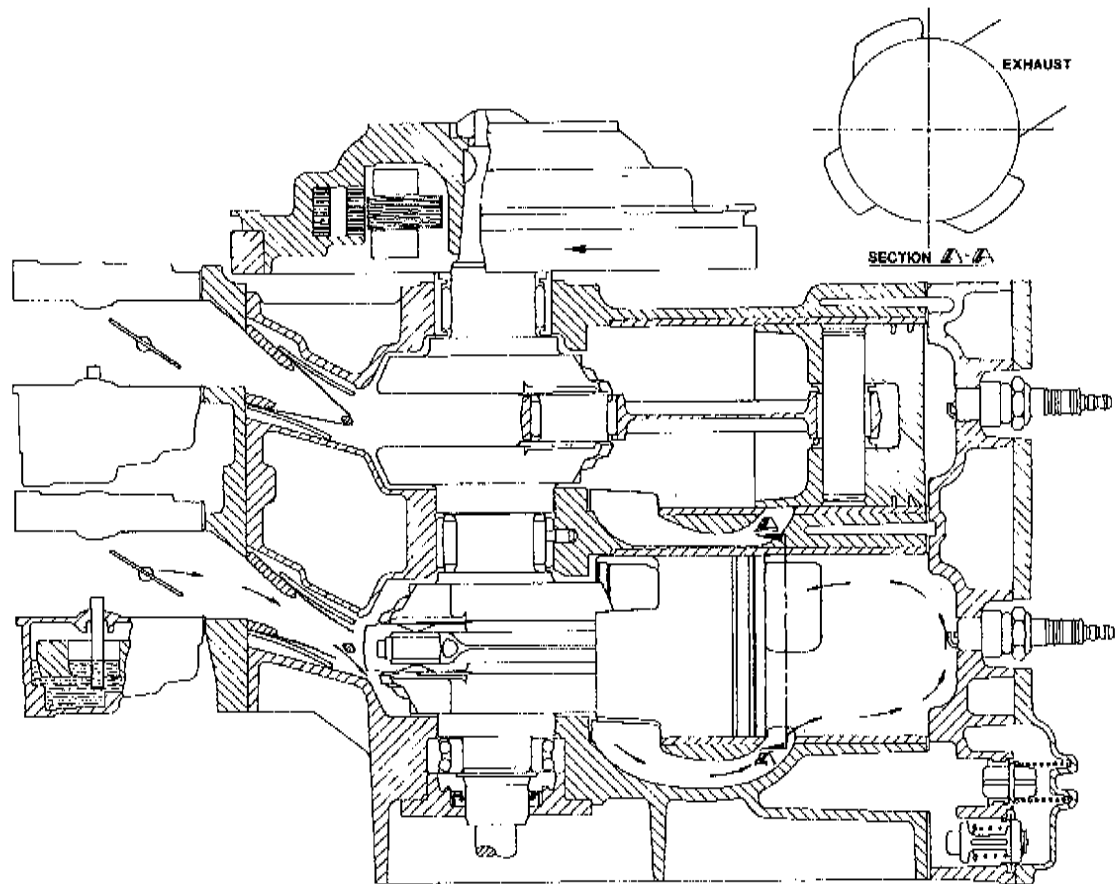


**FIGURE 1-11**  
Cutaway view of small automotive engine turbocharger. (Courtesy Nissan Motor Co., Ltd.)

rotors connected via the central shaft and of the turbine and compressor flow passages are evident.

Figure 1-12 shows a two-stroke cycle spark-ignition engine. The two-stroke cycle spark-ignition engine is used for small-engine applications where low cost and weight/power ratio are important and when the use factor is low. Examples of such applications are outboard motorboat engines, motorcycles, and chain saws. All such engines are of the carburetor crankcase-compression type which is one of the simplest prime movers available. It has three moving parts per cylinder: the piston, connecting rod, and the crank. The prime advantage of the two-stroke cycle spark-ignition engine relative to the four-stroke cycle engine is its higher power per unit displaced volume due to twice the number of power strokes per crank revolution. This is offset by the lower fresh charge density achieved by the two-stroke cycle gas-exchange process and the loss of fresh mixture which goes straight through the engine during scavenging. Also, oil consumption is higher in two-stroke cycle engines due to the need to add oil to the fuel to lubricate the piston ring and piston surfaces.

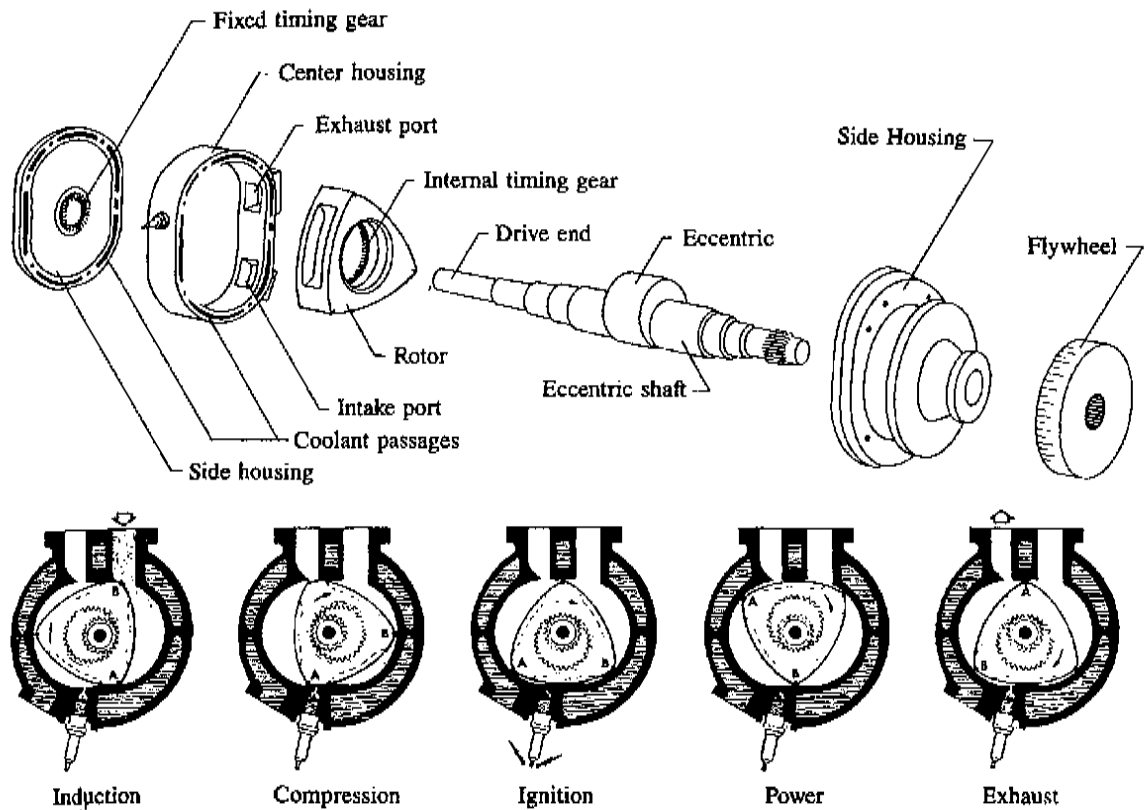
The Wankel rotary engine is an alternative to the reciprocating engine geometry of the engines illustrated above. It is used when its compactness and higher engine speed (which result in high power/weight and power/volume ratios), and inherent balance and smoothness, offset its higher heat transfer, and



**FIGURE 1-12**

Cutaway drawing of two-cylinder two-stroke cycle loop-scavenged marine spark-ignition engine. Displaced volume 737 cm<sup>3</sup>, maximum power 41 kW at 5500 rev/min. (Courtesy Outboard Marine Corporation.)

its sealing and leakage problems. Figure 1-13 shows the major mechanical parts of a simple single-rotor Wankel engine and illustrates its geometry. There are two rotating parts: the triangular-shaped rotor and the output shaft with its integral eccentric. The rotor revolves directly on the eccentric. The rotor has an internal timing gear which meshes with the fixed timing gear on one side housing to maintain the correct phase relationship between the rotor and eccentric shaft rotations. Thus the rotor rotates and orbits around the shaft axis. Breathing is through ports in the center housing (and sometimes the side housings). The combustion chamber lies between the center housing and rotor surface and is sealed by seals at the apex of the rotor and around the perimeters of the rotor sides. Figure 1-13 also shows how the Wankel rotary geometry operates with the four-stroke cycle. The figure shows the induction, compression, power, and exhaust processes of the four-stroke cycle for the chamber defined by rotor surface AB. The remaining two chambers defined by the other rotor surfaces undergo exactly the same sequence. As the rotor makes one complete rotation, during which the eccentric shaft rotates through three revolutions, each chamber produces one power "stroke." Three power pulses occur, therefore, for each rotor revolution;

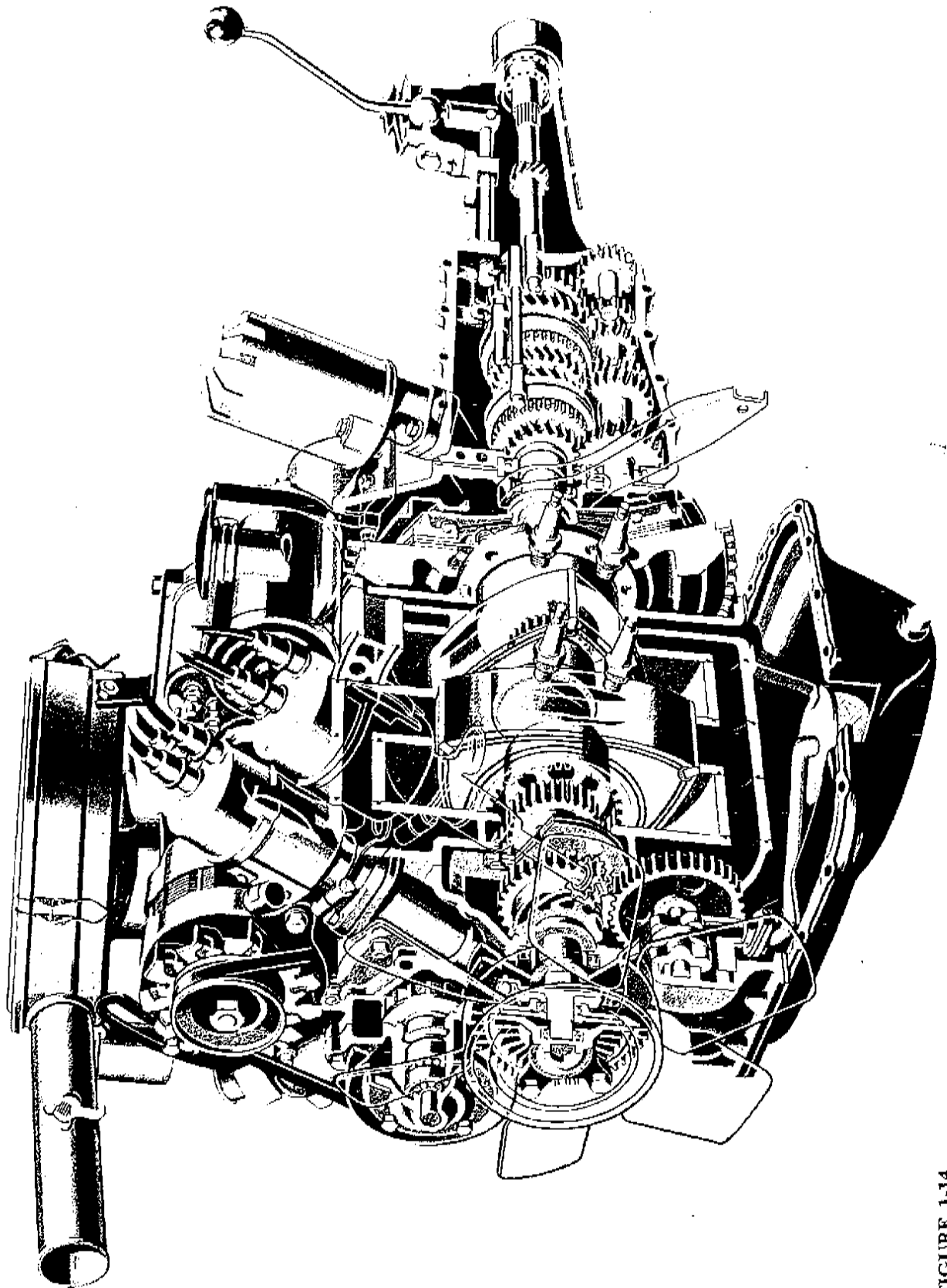


**FIGURE 1-13**  
 (a) Major components of the Wankel rotary engine; (b) induction, compression, power, and exhaust processes of the four-stroke cycle for the chamber defined by rotor surface AB. (From *Mobil Technical Bulletin, Rotary Engines*, © Mobil Oil Corporation, 1971.)

thus for each eccentric (output) shaft revolution there is one power pulse. Figure 1-14 shows a cutaway drawing of a two-rotor automobile Wankel engine. The two rotors are out of phase to provide a greater number of torque pulses per shaft revolution. Note the combustion chamber cut out in each rotor face, the rotor apex, and side seals. Two spark plugs per firing chamber are often used to obtain a faster combustion process.

### 1.7 COMPRESSION-IGNITION ENGINE OPERATION

In compression-ignition engines, air alone is inducted into the cylinder. The fuel (in most applications a light fuel oil, though heated residual fuel is used in marine and power-generation applications) is injected directly into the engine cylinder just before the combustion process is required to start. Load control is achieved by varying the amount of fuel injected each cycle; the air flow at a given engine speed is essentially unchanged. There are a great variety of CI engine designs in use in a wide range of applications—automobile, truck, locomotive, marine, power generation. Naturally aspirated engines where atmospheric air is inducted, turbocharged engines where the inlet air is compressed by an exhaust-driven



**FIGURE 1-14**  
Cutaway drawing of two-rotor Wankel spark-ignition engine. Displacement of each working chamber 573 cm<sup>3</sup>, compression ratio 9.4, maximum

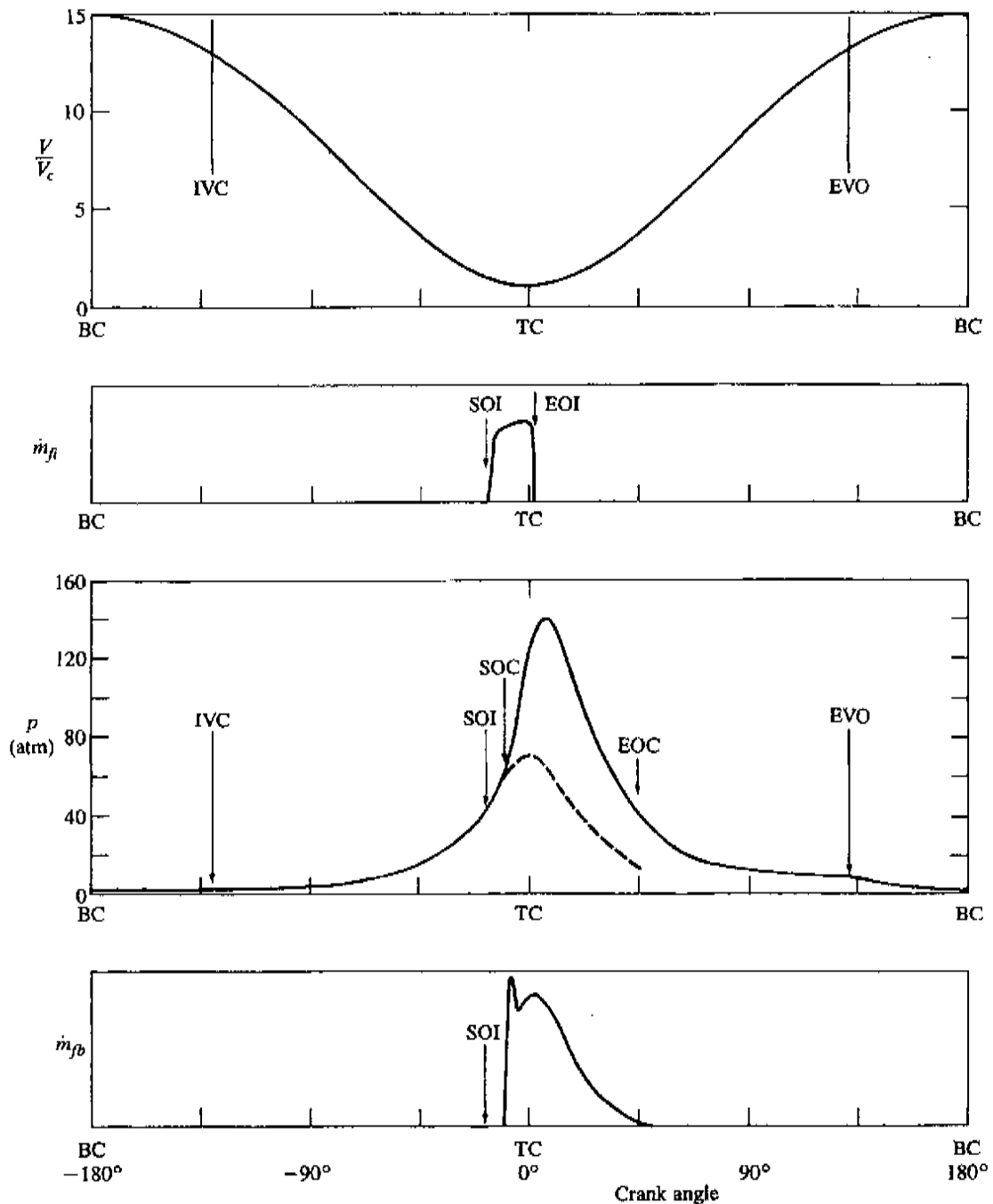
turbine-compressor combination, and supercharged engines where the air is compressed by a mechanically driven pump or blower are common. Turbocharging and supercharging increase engine output by increasing the air mass flow per unit displaced volume, thereby allowing an increase in fuel flow. These methods are used, usually in larger engines, to reduce engine size and weight for a given power output. Except in smaller engine sizes, the two-stroke cycle is competitive with the four-stroke cycle, in large part because, with the diesel cycle, only air is lost in the cylinder scavenging process.

The operation of a typical four-stroke naturally aspirated CI engine is illustrated in Fig. 1-15. The compression ratio of diesels is much higher than typical SI engine values, and is in the range 12 to 24, depending on the type of diesel engine and whether the engine is naturally aspirated or turbocharged. The valve timings used are similar to those of SI engines. Air at close-to-atmospheric pressure is inducted during the intake stroke and then compressed to a pressure of about 4 MPa (600 lb/in<sup>2</sup>) and temperature of about 800 K (1000°F) during the compression stroke. At about 20° before TC, fuel injection into the engine cylinder commences; a typical rate of injection profile is shown in Fig. 1-15b. The liquid fuel jet atomizes into drops and entrains air. The liquid fuel evaporates; fuel vapor then mixes with air to within combustible proportions. The air temperature and pressure are above the fuel's ignition point. Therefore after a short *delay period*, spontaneous ignition (autoignition) of parts of the nonuniform fuel-air mixture initiates the combustion process, and the cylinder pressure (solid line in Fig. 1-15c) rises above the nonfiring engine level. The flame spreads rapidly through that portion of the injected fuel which has already mixed with sufficient air to burn. As the expansion process proceeds, mixing between fuel, air, and burning gases continues, accompanied by further combustion (see Fig. 1-15d). At full load, the mass of fuel injected is about 5 percent of the mass of air in the cylinder. Increasing levels of black smoke in the exhaust limit the amount of fuel that can be burned efficiently. The exhaust process is similar to that of the four-stroke SI engine. At the end of the exhaust stroke, the cycle starts again.

In the two-stroke CI engine cycle, compression, fuel injection, combustion, and expansion processes are similar to the equivalent four-stroke cycle processes; it is the intake and exhaust pressure which are different. The sequence of events in a loop-scavenged two-stroke engine is illustrated in Fig. 1-16. In loop-scavenged engines both exhaust and inlet ports are at the same end of the cylinder and are uncovered as the piston approaches BC (see Fig. 1-16a). After the exhaust ports open, the cylinder pressure falls rapidly in a blowdown process (Fig. 1-16b). The inlet ports then open, and once the cylinder pressure  $p$  falls below the inlet pressure  $p_i$ , air flows into the cylinder. The burned gases, displaced by this fresh air, continue to flow out of the exhaust port (along with some of the fresh air). Once the ports close as the piston starts the compression stroke, compression, fuel-injection, fuel-air mixing, combustion and expansion processes proceed as in the four-stroke CI engine cycle.

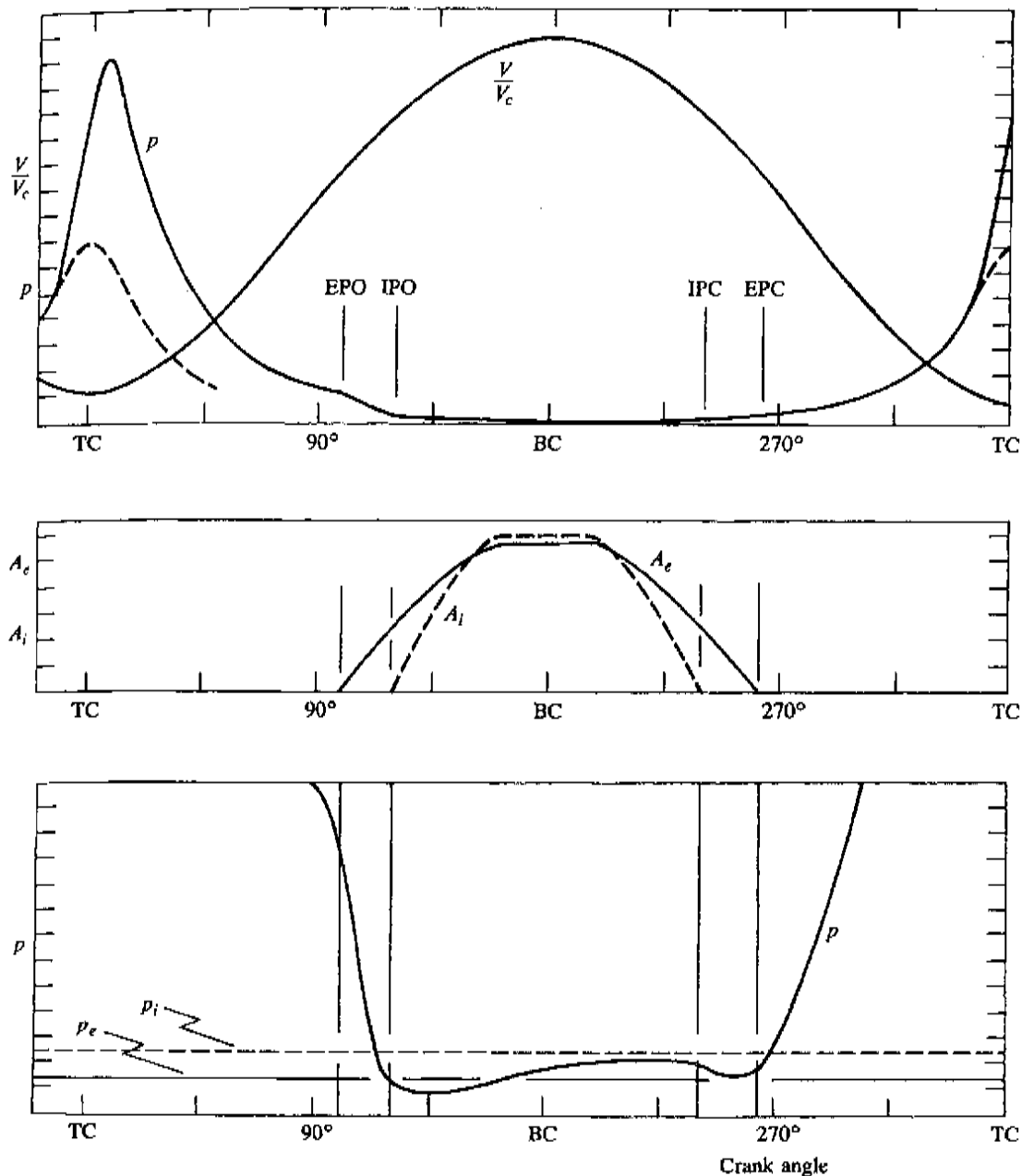
The diesel fuel-injection system consists of an injection pump, delivery pipes, and fuel injector nozzles. Several different types of injection pumps and

FIGURE 1-14  
Cutaway drawing of two-rotor Wankel spark-ignition engine. Displacement of each working chamber 573 cm<sup>3</sup> compression ratio 9.4 maximum

**FIGURE 1-15**

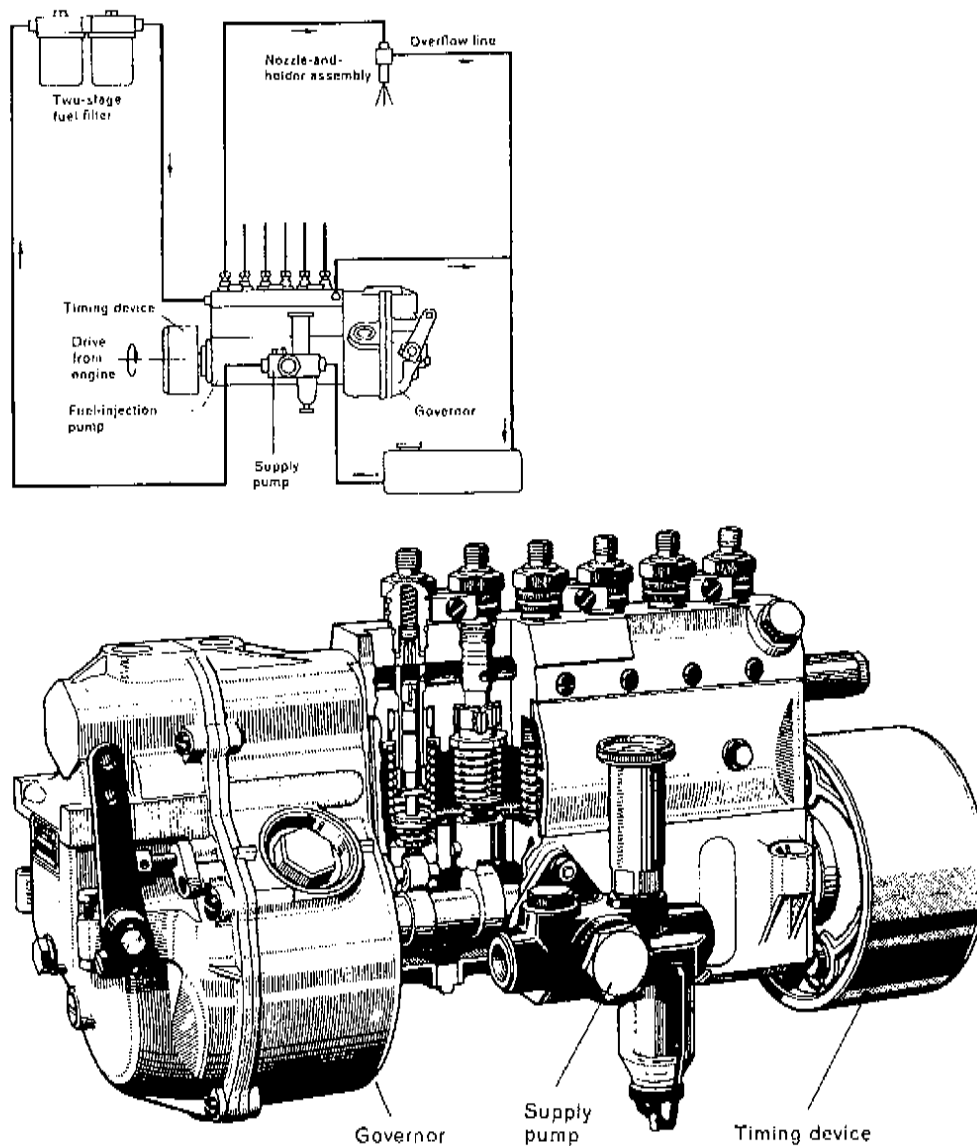
Sequence of events during compression, combustion, and expansion processes of a naturally aspirated compression-ignition engine operating cycle. Cylinder volume/clearance volume  $V/V_c$ , rate of fuel injection  $\dot{m}_{fi}$ , cylinder pressure  $p$  (solid line, firing cycle; dashed line, motored cycle), and rate of fuel burning (or fuel chemical energy release rate)  $\dot{m}_{fb}$  are plotted against crank angle.

nozzles are used. In one common fuel pump (an in-line pump design shown in Fig. 1-17) a set of cam-driven plungers (one for each cylinder) operate in closely fitting barrels. Early in the stroke of the plunger, the inlet port is closed and the fuel trapped above the plunger is forced through a check valve into the injection



**FIGURE 1-16** Sequence of events during expansion, gas exchange, and compression processes in a loop-scavenged two-stroke cycle compression-ignition engine. Cylinder volume/clearance volume  $V/V_c$ , cylinder pressure  $p$ , exhaust port open area  $A_e$ , and intake port open area  $A_i$  are plotted against crank angle.

line. The injection nozzle (Fig. 1-18) has one or more holes through which the fuel sprays into the cylinder. A spring-loaded valve closes these holes until the pressure in the injection line, acting on part of the valve surface, overcomes the spring force and opens the valve. Injection starts shortly after the line pressure begins to rise. Thus, the phase of the pump camshaft relative to the engine crankshaft controls the start of injection. Injection is stopped when the inlet port of the pump is uncovered by a helical groove in the pump plunger, because the high

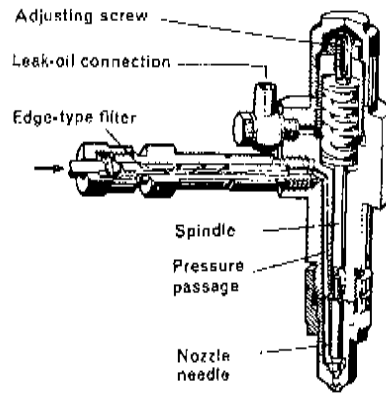
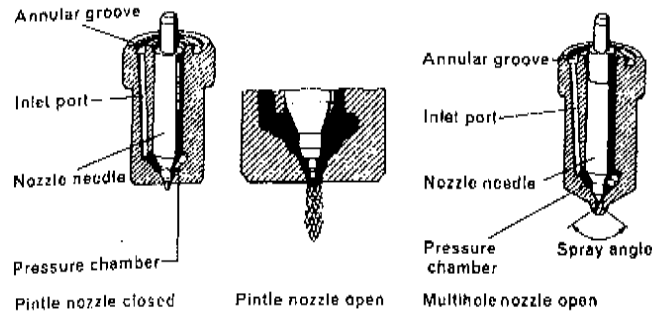


**FIGURE 1-17**  
Diesel fuel system with in-line fuel-injection pump (type PI).<sup>1,2</sup> (Courtesy Robert Bosch GmbH.)

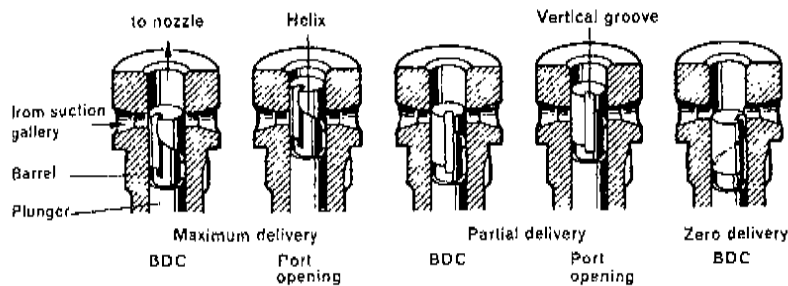
pressure above the plunger is then released (Fig. 1-18). The amount of fuel injected (which controls the load) is determined by the injection pump cam design and the position of the helical groove. Thus for a given cam design, rotating the plunger and its helical groove varies the load.

Distributor-type pumps have only one pump plunger and barrel, which meters and distributes the fuel to all the injection nozzles. A schematic of a distributor-type pump is shown in Fig. 1-19. The unit contains a low-pressure fuel pump (on left), a high-pressure injection pump (on right), an overspeed governor, and an injection timer. High pressure is generated by the plunger which is made to describe a combined rotary and stroke movement by the rotating eccentric disc or cam plate; the rotary motion distributes the fuel to the individual injection nozzles.





Nozzle-holder assembly with nozzle



Fuel delivery control (lower helix)

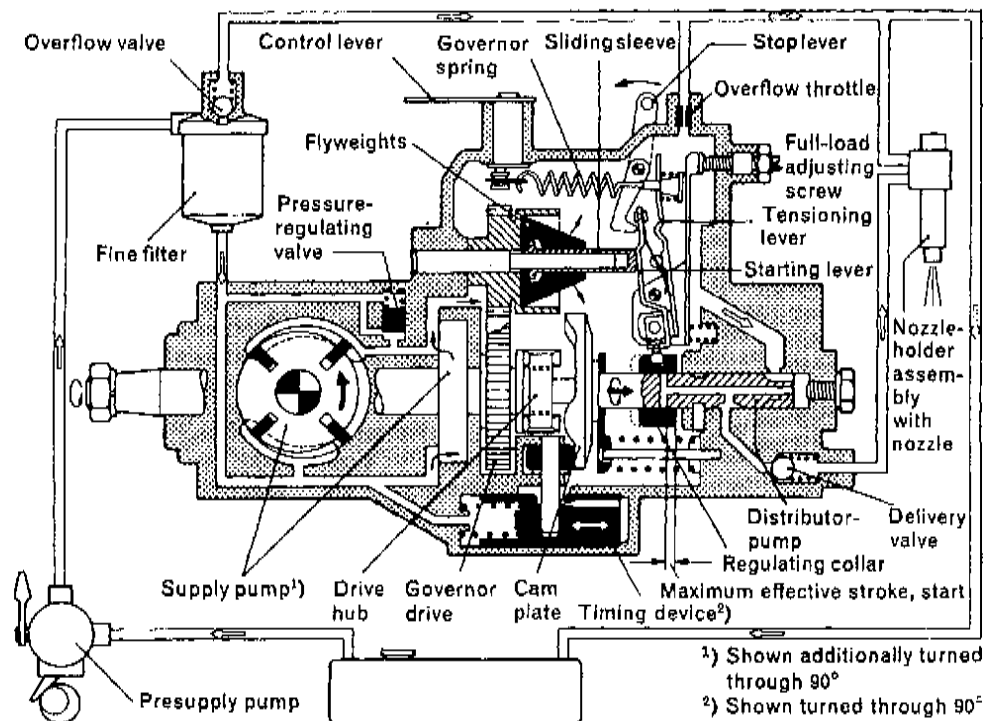
FIGURE 1-18

Details of fuel-injection nozzles, nozzle holder assembly and fuel-delivery control.<sup>1,2</sup> (Courtesy Robert Bosch GmbH.)

Distributor pumps can operate at higher speed and take up less space than in-line pumps. They are normally used on smaller diesel engines. In-line pumps are used in the mid-engine-size range. In the larger diesels, individual single-barrel injection pumps, close mounted to each cylinder with an external drive as shown in Fig. 1-5, are normally used.

## 1.8 EXAMPLES OF DIESEL ENGINES

A large number of diesel engine configurations and designs are in common use. The very large marine and stationary power-generating diesels are two-stroke



**FIGURE 1-19**

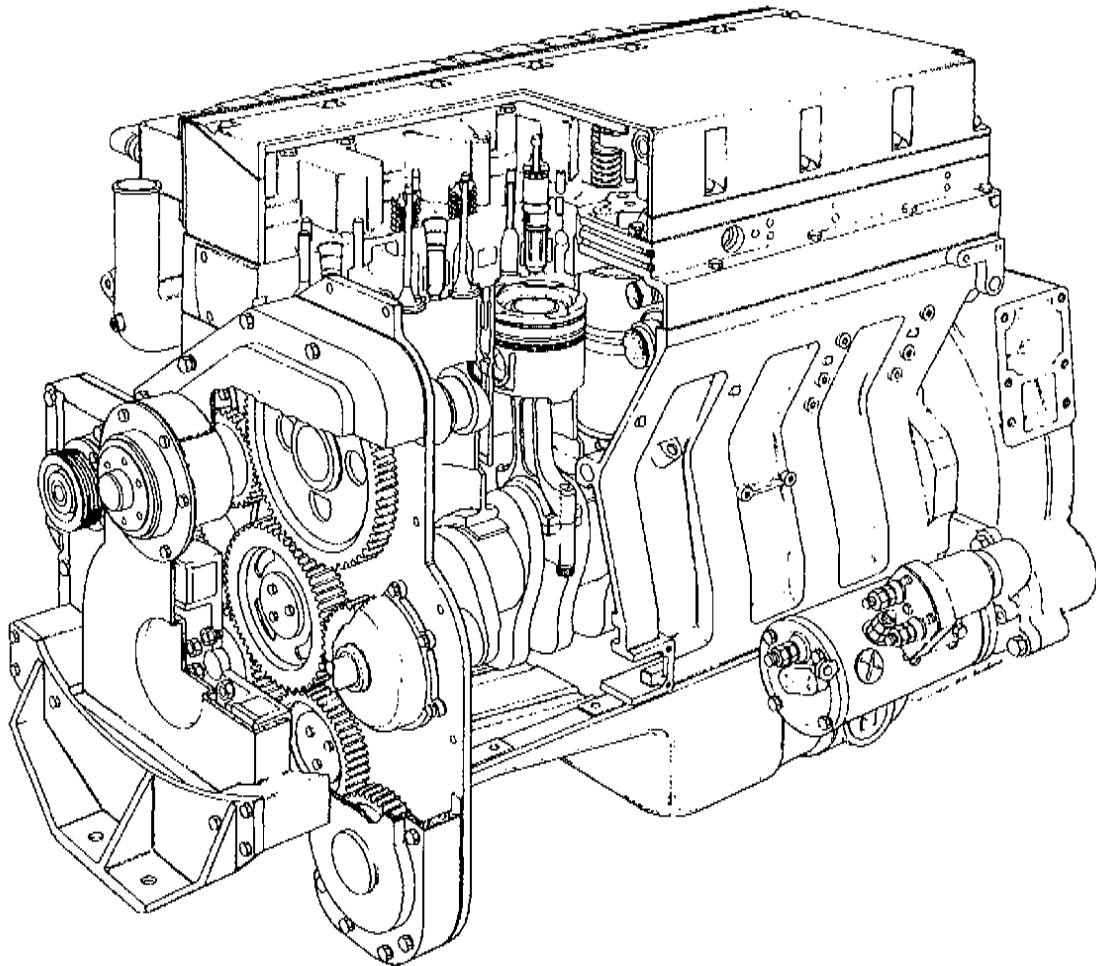
Diesel fuel system with distributor-type fuel-injection pump with mechanical governor.<sup>12</sup> (Courtesy Robert Bosch GmbH.)

cycle engines. Small- and medium-size engines use the four-stroke cycle. Because air capacity is an important constraint on the amount of fuel that can be burned in the diesel engine, and therefore on the engine's power, turbocharging is used extensively. All large engines are turbocharged. The majority of smaller diesels are not turbocharged, though they can be turbocharged and many are. The details of the engine design also vary significantly over the diesel size range. In particular, different combustion chamber geometries and fuel-injection characteristics are required to deal effectively with a major diesel engine design problem—achieving sufficiently rapid fuel-air mixing rates to complete the fuel-burning process in the time available. A wide variety of inlet port geometries, cylinder head and piston shapes, and fuel-injection patterns are used to accomplish this over the diesel size range.

Figure 1-20 shows a diesel engine typical of the medium-duty truck application. The design shown is a six-cylinder in-line engine. The drawing indicates that diesel engines are generally substantially heavier than spark-ignition engines because stress levels are higher due to the significantly higher pressure levels of the diesel cycle. The engine shown has a displacement of 10 liters, a compression ratio of 16.3, and is usually turbocharged. The engine has pressed-in cylinder liners to achieve better cylinder wear characteristics. This type of diesel is called a *direct-injection* diesel. The fuel is injected into a combustion chamber directly above the piston crown. The combustion chamber shown is a “bowl-in-piston” design, which puts most of the clearance volume into a compact shape. With this

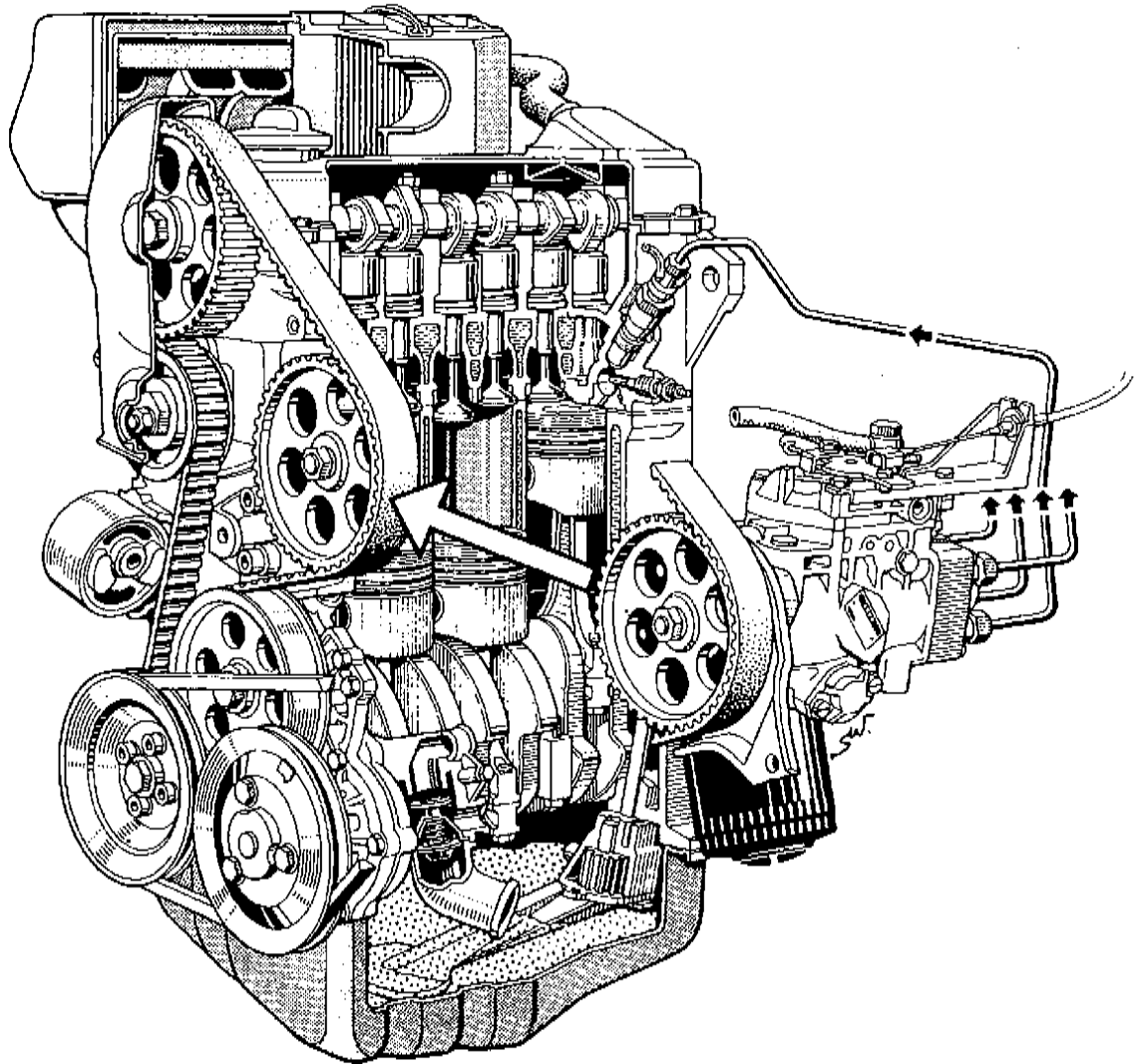
size of diesel engine, it is often necessary to use a swirling air flow rotating about the cylinder axis, which is created by suitable design of the inlet port and valve, to achieve adequate fuel-air mixing and fuel burning rates. The fuel injector, shown left-of-center in the drawing, has a multihole nozzle, typically with three to five holes. The fuel jets move out radially from the center of the piston bowl into the (swirling) air flow. The in-line fuel-injection pump is normally used with this type of diesel engine.

Figure 1-21 shows a four-cylinder in-line overhead-valve-cam design automobile diesel engine. The smallest diesels such as this operate at higher engine speed than larger engines; hence the time available for burning the fuel is less and the fuel-injection and combustion system must achieve faster fuel-air mixing rates. This is accomplished by using an *indirect-injection* type of diesel. Fuel is injected into an auxiliary combustion chamber which is separated from the main combustion chamber above the piston by a flow restriction or nozzle. During the latter stages of the compression process, air is forced through this nozzle from the



**FIGURE 1-20**

Direct-injection four-stroke cycle six-cylinder turbocharged Cummins diesel engine. Displaced volume 10 liters, bore 125 mm, stroke 136 mm, compression ratio 16.3, maximum power 168 to 246 kW at rated speed of 2100 rev/min. (Courtesy Cummins Engine Company, Inc.)



**FIGURE 1-21**

Four-cylinder naturally aspirated indirect-injection automobile Volkswagen diesel engine.<sup>14</sup> Displaced volume 1.47 liters, bore 76.5 mm, stroke 80 mm, maximum power 37 kW at 5000 rev/min.

cylinder into the prechamber at high velocity. Fuel is injected into this highly turbulent and often rapidly swirling flow in this auxiliary or prechamber, and very high mixing rates are achieved. Combustion starts in the prechamber, and the resulting pressure rise in the prechamber forces burning gases, fuel, and air into the main chamber. Since this outflow is also extremely vigorous, rapid mixing then occurs in the main chamber as the burning jet mixes with the remaining air and combustion is completed. A distributor-type fuel pump, which is normally used in this engine size range, driven off the camshaft at half the crankshaft speed by a toothed belt, is shown on the right of the figure. It supplies high-pressure fuel pulses to the pintle-type injector nozzles in turn. A glow plug is also shown in the auxiliary chamber; this plug is electrically heated prior to and during cold engine start-up to raise the temperature of the air charge and the fuel sufficiently to achieve autoignition. The compression ratio of this engine is 23. Indirect-injection diesel engines require higher compression ratios than direct-injection engines to start adequately when cold.

Diesel engines are turbocharged to achieve higher power/weight ratios. By increasing the density of the inlet air, a given displaced volume can induct more air. Hence more fuel can be injected and burned, and more power delivered, while avoiding excessive black smoke in the exhaust. All the larger diesels are turbocharged; smaller diesels can be and often are. Figure 1-22 shows how a turbocharger connects to a direct-injection diesel.

All the above diesels are water cooled; some production diesels are air cooled. Figure 1-23 shows a V-8 air-cooled direct-injection naturally aspirated

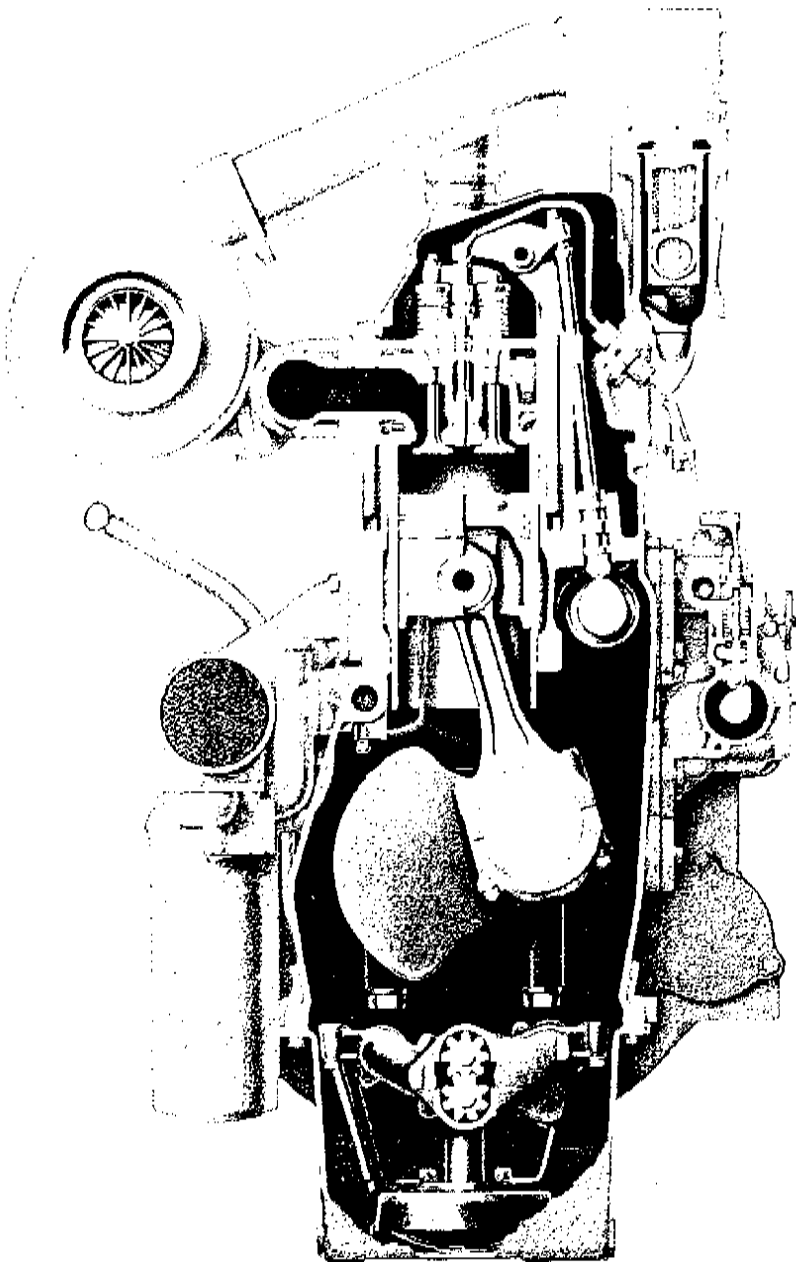
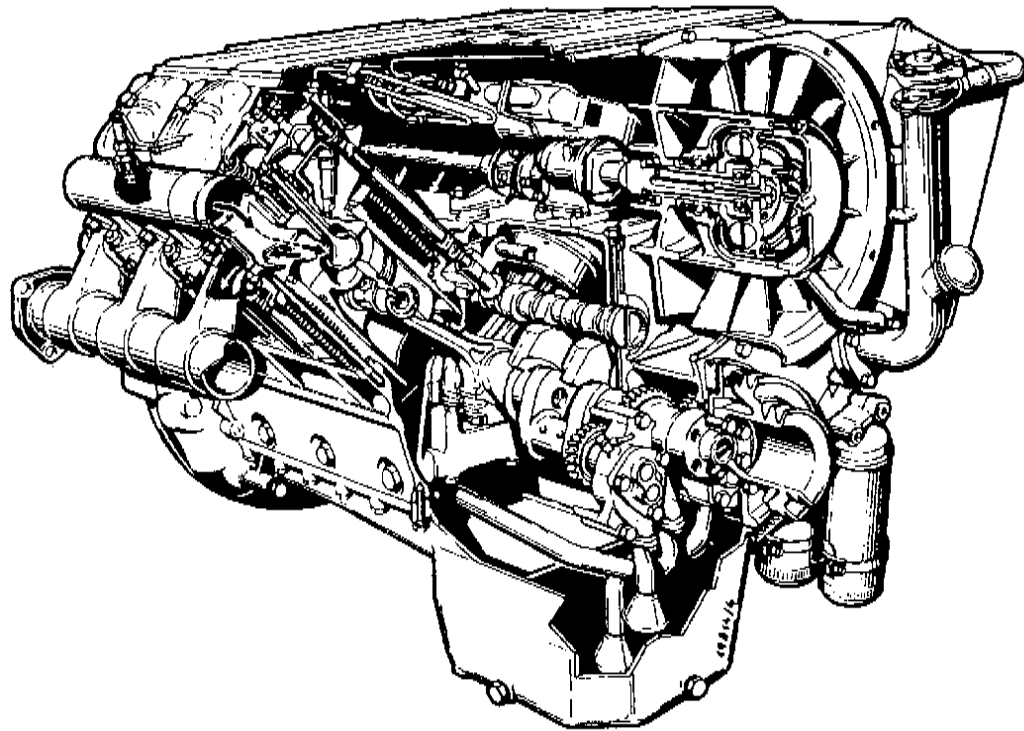


FIGURE 1-22

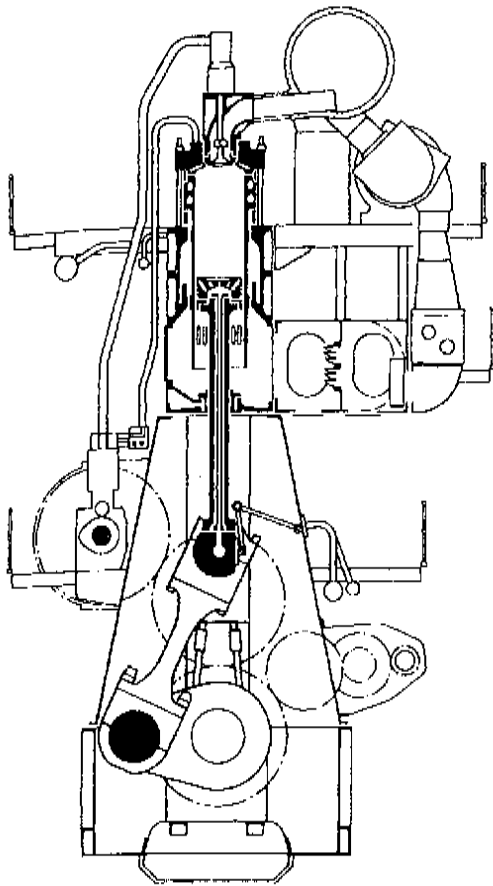
Turbocharged aftercooled direct-injection four-stroke cycle Caterpillar six-cylinder in-line heavy-duty truck diesel engine. Bore 137.2 mm, stroke 165.1 mm, rated power 200–300 kW and rated speed of 1600–2100 rev/min depending on application. (Courtesy Caterpillar Tractor Company.)

**FIGURE 1-23**

V-8 air-cooled direct-injection naturally aspirated diesel engine. Displacement 13.4 liter, bore 128 mm, stroke 130 mm, compression ratio 17, maximum rated power 188 kW at rated speed of 2300 rev/min. (Courtesy Klöcker-Humboldt-Deutz AG.<sup>15</sup>)

diesel. The primary advantage compared to the water-cooled engines is lower engine weight. The fins on the cylinder block and head are necessary to increase the external heat-transfer surface area to achieve the required heat rejection. An air blower, shown on the right of the cutaway drawing, provides forced air convection over the block. The blower is driven off the injection pump shaft, which in turn is driven off the camshaft. The in-line injection pump is placed between the two banks of cylinders. The injection nozzles are located at an angle to the cylinder axis. The combustion chamber and fuel-injection characteristics are similar to those of the engine in Fig. 1-22. The nozzle shown injects four fuel sprays into a reentrant bowl-in-piston combustion chamber.

Diesels are also made in very large engine sizes. These large engines are used for marine propulsion and electrical power generation and operate on the two-stroke cycle in contrast to the small- and medium-size diesels illustrated above. Figure 1-24 shows such a two-stroke cycle marine engine, available with from 4 to 12 cylinders, with a maximum bore of 0.6–0.9 m and stroke of 2–3 m, which operates at speeds of about 100 rev/min. These engines are normally of the crosshead type to reduce side forces on the cylinder. The gas exchange between cycles is controlled by first opening the exhaust valves, and then the piston uncovering inlet ports in the cylinder liner. Expanding exhaust gases leave the cylinder via the exhaust valves and manifold and pass through the turbocharger

**FIGURE 1-24**

Large Sulzer two-stroke turbocharged marine diesel engine. Bore 840 mm, stroke 2900 mm, rated power 1.9 MW per cylinder at 78 rev/min, 4 to 12 cylinders. (Courtesy Sulzer Brothers Ltd.)

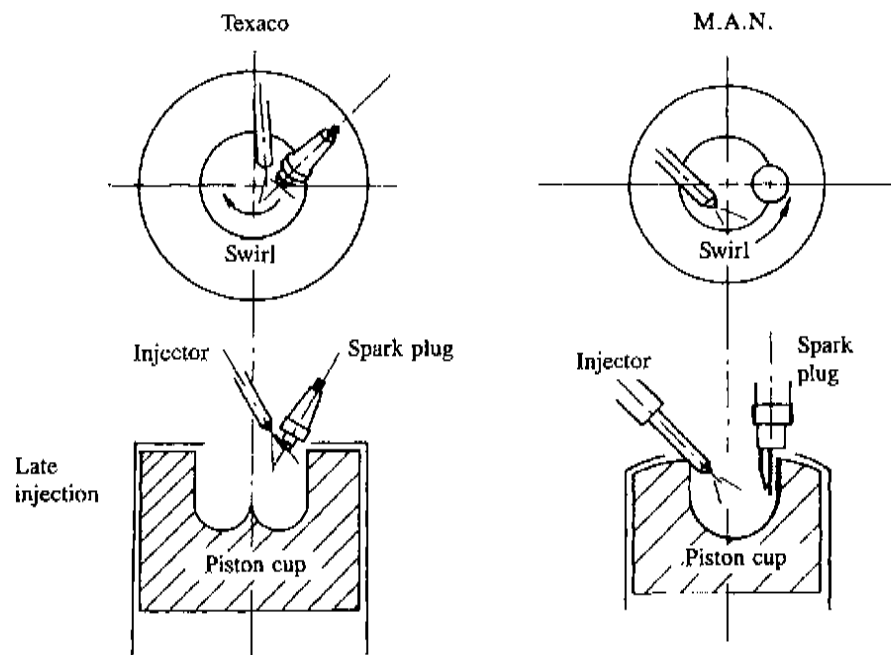
turbine. Compressed air enters via the inlet ports and induces forced scavenging; air is supplied from the turbocharger and cooler. At part load electrically driven blowers cut in to compress the scavenge air. Because these large engines operate at low speed, the motion induced by the centrally injected fuel jets is sufficient to mix the fuel with air and burn it in the time available. A simple open combustion chamber shape can be used, therefore, which achieves efficient combustion even with the low-quality heavy fuels used with these types of engines. The pistons are water cooled in these very large engines. The splash oil piston cooling used in medium- and small-size diesels is not adequate.

## 1.9 STRATIFIED-CHARGE ENGINES

Since the 1920s, attempts have been made to develop a hybrid internal combustion engine that combines the best features of the spark-ignition engine and the diesel. The goals have been to operate such an engine at close to the optimum compression ratio for efficiency (in the 12 to 15 range) by: (1) injecting the fuel directly into the combustion chamber during the compression process (and thereby avoid the knock or spontaneous ignition problem that limits conventional spark-ignition engines with their premixed charge); (2) igniting the fuel as it mixes with air with a spark plug to provide direct control of the ignition process

(and thereby avoid the fuel ignition-quality requirement of the diesel); (3) controlling the engine power level by varying the amount of fuel injected per cycle (with the air flow unthrottled to minimize work done pumping the fresh charge into the cylinder). Such engines are often called *stratified-charge engines* from the need to produce in the mixing process between the fuel jet and the air in the cylinder a "stratified" fuel-air mixture, with an easily ignitable composition at the spark plug at the time of ignition. Because such engines avoid the spark-ignition engine requirement for fuels with a high antiknock quality and the diesel requirement for fuels with high ignition quality, they are usually fuel-tolerant and will operate with a wide range of liquid fuels.

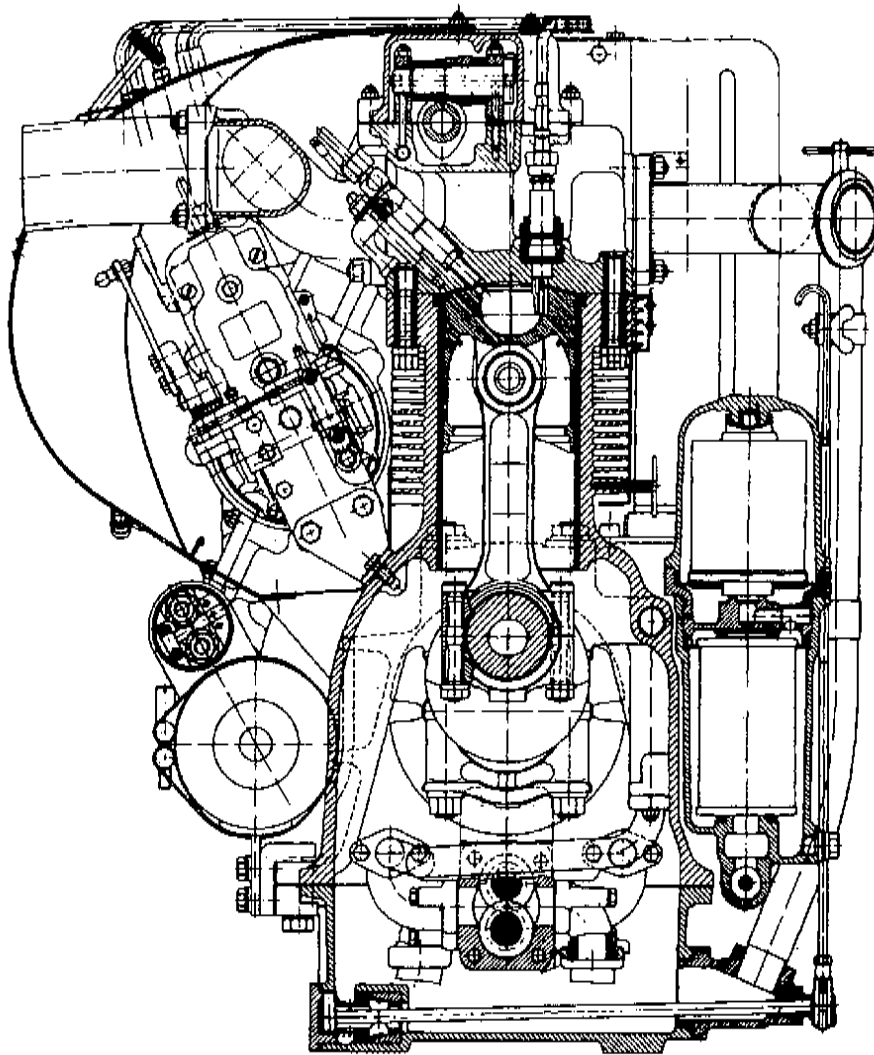
Many different types of stratified-charge engine have been proposed, and some have been partially or fully developed. A few have even been used in practice in automotive applications. The operating principles of those that are truly fuel-tolerant or multifuel engines are illustrated in Fig. 1-25. The combustion chamber is usually a bowl-in-piston design, and a high degree of air swirl is created during intake and enhanced in the piston bowl during compression to achieve rapid fuel-air mixing. Fuel is injected into the cylinder, tangentially into the bowl, during the latter stages of compression. A long-duration spark discharge ignites the developing fuel-air jet as it passes the spark plug. The flame spreads downstream, and envelopes and consumes the fuel-air mixture. Mixing continues, and the final stages of combustion are completed during expansion. Most successful designs of this type of engine have used the four-stroke cycle. This concept is usually called a *direct-injection stratified-charge engine*. The engine can be turbocharged to increase its power density.



**FIGURE 1-25**

Two multifuel stratified-charge engines which have been used in commercial practice: the Texaco Controlled Combustion System (TCCS)<sup>16</sup> and the M.A.N.-FM System.<sup>17</sup>

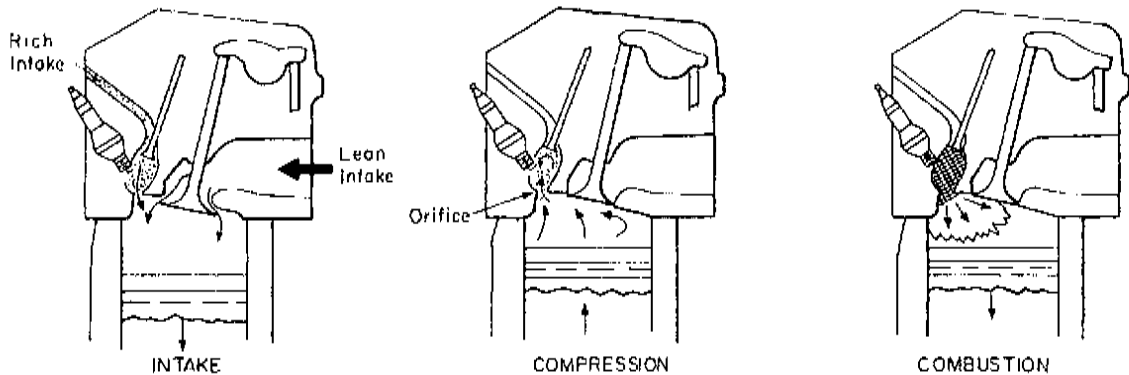




**FIGURE 1-26**  
Sectional drawing of M.A.N. high-speed multifuel four-cylinder direct-injection stratified-charge engine. Bore 94.5 mm, stroke 100 mm, displacement 2.65 liters, compression ratio 16.5, rated power 52 kW at 3800 rev/min.<sup>17</sup>

A commercial multifuel engine is shown in Fig. 1-26. In this particular design, the fuel injector comes diagonally through the cylinder head from the upper left and injects the fuel onto the hot wall of the deep spherical piston bowl. The fuel is carried around the wall of the bowl by the swirling flow, evaporated off the wall, mixed with air, and then ignited by the discharge at the spark plug which enters the chamber vertically on the right. This particular engine is air cooled, so the cylinder block and head are finned to increase surface area.

An alternative stratified-charge engine concept, which has also been mass produced, uses a small *prechamber* fed during intake with an auxiliary fuel system to obtain an easily ignitable mixture around the spark plug. This concept, first proposed by Ricardo in the 1920s and extensively developed in the Soviet Union and Japan, is often called a *jet-ignition* or *torch-ignition* stratified-charge engine. Its operating principles are illustrated in Fig. 1-27 which shows a three-valve



**FIGURE 1-27**

Schematic of three-valve torch-ignition stratified-charge spark-ignition engine.

carbureted version of the concept.<sup>18</sup> A separate carburetor and intake manifold feeds a fuel-rich mixture (which contains fuel beyond the amount that can be burned with the available air) through a separate small intake valve into the prechamber which contains the spark plug. At the same time, a very lean mixture (which contains excess air beyond that required to burn the fuel completely) is fed to the main combustion chamber through the main carburetor and intake manifold. During intake the rich prechamber flow fully purges the prechamber volume. After intake valve closing, lean mixture from the main chamber is compressed into the prechamber bringing the mixture at the spark plug to an easily ignitable, slightly rich, composition. After combustion starts in the prechamber, rich burning mixture issues as a jet through the orifice into the main chamber, entraining and igniting the lean main chamber charge. Though called a stratified-charge engine, this engine is really a jet-ignition concept whose primary function is to extend the operating limit of conventionally ignited spark-ignition engines to mixtures leaner than could normally be burned.

## PROBLEMS

- 1.1. Describe the major functions of the following reciprocating engine components: piston, connecting rod, crankshaft, cams and camshaft, valves, intake and exhaust manifolds.
- 1.2. Indicate on an appropriate sketch the different forces that act on the piston, and the direction of these forces, during the engine's expansion stroke with the piston, connecting rod, and crank in the positions shown in Fig. 1-1.
- 1.3. List five important differences between the design and operating characteristics of spark-ignition and compression-ignition (diesel) engines.
- 1.4. Indicate the approximate crank angle at which the following events in the four-stroke and two-stroke internal combustion engine cycles occur on a line representing the full cycle ( $720^\circ$  for the four-stroke cycle;  $360^\circ$  for the two-stroke cycle): bottom- and top-center crank positions, inlet and exhaust valve or port opening and closing, start of combustion process, end of combustion process, maximum cylinder pressure.

- 1.5. The two-stroke cycle has twice as many power strokes per crank revolution as the four-stroke cycle. However, two-stroke cycle engine power outputs per unit displaced volume are less than twice the power output of an equivalent four-stroke cycle engine at the same engine speed. Suggest reasons why this potential advantage of the two-stroke cycle is offset in practice.
- 1.6. Suggest reasons why multicylinder engines prove more attractive than single-cylinder engines once the total engine displaced volume exceeds a few hundred cubic centimeters.
- 1.7. The Wankel rotary spark-ignition engine, while lighter and more compact than a reciprocating spark-ignition engine of equal maximum power, typically has worse efficiency due to significantly higher gas leakage from the combustion chamber and higher total heat loss from the hot combustion gases to the chamber walls. Based on the design details in Figs. 1-4, 1-13, and 1-14 suggest reasons for these higher losses.

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# CHAPTER 3

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## THERMOCHEMISTRY OF FUEL-AIR MIXTURES

### 3.1 CHARACTERIZATION OF FLAMES

Combustion of the fuel-air mixture inside the engine cylinder is one of the processes that controls engine power, efficiency, and emissions. Some background in relevant combustion phenomena is therefore a necessary preliminary to understanding engine operation. These combustion phenomena are different for the two main types of engines—spark-ignition and diesel—which are the subject of this book. In spark-ignition engines, the fuel is normally mixed with air in the engine intake system. Following the compression of this fuel-air mixture, an electrical discharge initiates the combustion process; a flame develops from the “kernel” created by the spark discharge and propagates across the cylinder to the combustion chamber walls. At the walls, the flame is “quenched” or extinguished as heat transfer and destruction of active species at the wall become the dominant processes. An undesirable combustion phenomenon—the “spontaneous” ignition of a substantial mass of fuel-air mixture ahead of the flame, before the flame can propagate through this mixture (which is called the end-gas)—can also occur. This autoignition or self-explosion combustion phenomenon is the cause of spark-ignition engine knock which, due to the high pressures generated, can lead to engine damage.

In the diesel engine, the fuel is injected into the cylinder into air already at high pressure and temperature, near the end of the compression stroke. The autoignition, or self-ignition, of portions of the developing mixture of already

injected and vaporized fuel with this hot air starts the combustion process, which spreads rapidly. Burning then proceeds as fuel and air mix to the appropriate composition for combustion to take place. Thus, fuel-air mixing plays a controlling role in the diesel combustion process.

Chapters 3 and 4 focus on the thermochemistry of combustion: i.e., the composition and thermodynamic properties of the pre- and postcombustion working fluids in engines and the energy changes associated with the combustion processes that take place inside the engine cylinder. Later chapters (9 and 10) deal with the phenomenological aspects of engine combustion: i.e., the details of the physical and chemical processes by which the fuel-air mixture is converted to burned products. At this point it is useful to review briefly the key combustion phenomena which occur in engines to provide an appropriate background for the material which follows. More detailed information on these combustion phenomena can be found in texts on combustion such as those of Fristrom and Westenberg<sup>1</sup> and Glassman.<sup>2</sup>

The combustion process is a fast exothermic gas-phase reaction (where oxygen is usually one of the reactants). A flame is a combustion reaction which can propagate subsonically through space; motion of the flame relative to the unburned gas is the important feature. Flame structure does not depend on whether the flame moves relative to the observer or remains stationary as the gas moves through it. The existence of flame motion implies that the reaction is confined to a zone which is small in thickness compared to the dimensions of the apparatus—in our case the engine combustion chamber. The reaction zone is usually called the flame front. This flame characteristic of spatial propagation is the result of the strong coupling between chemical reaction, the transport processes of mass diffusion and heat conduction, and fluid flow. The generation of heat and active species accelerate the chemical reaction; the supply of fresh reactants, governed by the convection velocity, limits the reaction. When these processes are in balance, a steady-state flame results.<sup>1</sup>

Flames are usually classified according to the following overall characteristics. The first of these has to do with the composition of the reactants as they enter the reaction zone. If the fuel and oxidizer are essentially uniformly mixed together, the flame is designated as *premixed*. If the reactants are not premixed and must mix together in the same region where reaction takes place, the flame is called a *diffusion* flame because the mixing must be accomplished by a diffusion process. The second means of classification relates to the basic character of the gas flow through the reaction zone: whether it is *laminar* or *turbulent*. In laminar (or streamlined) flow, mixing and transport are done by molecular processes. Laminar flows only occur at low Reynolds number. The Reynolds number (density  $\times$  velocity  $\times$  lengthscale/viscosity) is the ratio of inertial to viscous forces. In turbulent flows, mixing and transport are enhanced (usually by a substantial factor) by the macroscopic relative motion of eddies or lumps of fluid which are the characteristic feature of a turbulent (high Reynolds number) flow. A third area of classification is whether the flame is *steady* or *unsteady*. The distinguishing feature here is whether the flame structure and motion change with

time. The final characterizing feature is the *initial phase* of the reactants—gas, liquid, or solid.

Flames in engines are unsteady, an obvious consequence of the internal combustion engine's operating cycle. Engine flames are turbulent. Only with substantial augmentation of laminar transport processes by the turbulent convection processes can mixing and burning rates and flame-propagation rates be made fast enough to complete the engine combustion process within the time available.

The conventional spark-ignition flame is thus a premixed unsteady turbulent flame, and the fuel-air mixture through which the flame propagates is in the gaseous state. The diesel engine combustion process is predominantly an unsteady turbulent diffusion flame, and the fuel is initially in the liquid phase. Both these flames are extremely complicated because they involve the coupling of the complex chemical mechanism, by which fuel and oxidizer react to form products, with the turbulent convective transport process. The diesel combustion process is even more complicated than the spark-ignition combustion process, because vaporization of liquid fuel and fuel-air mixing processes are involved too. Chapters 9 and 10 contain a more detailed discussion of the spark-ignition engine and diesel combustion processes, respectively. This chapter reviews the basic thermodynamic and chemical composition aspects of engine combustion.

### 3.2 IDEAL GAS MODEL

The gas species that make up the working fluids in internal combustion engines (e.g., oxygen, nitrogen, fuel vapor, carbon dioxide, water vapor, etc.) can usually be treated as ideal gases. The relationships between the thermodynamic properties of an ideal gas and of ideal gas mixtures are reviewed in App. B. There can be found the various forms of the ideal gas law:

$$pV = mRT = m \frac{\tilde{R}}{M} T = n\tilde{R}T \quad (3.1)$$

where  $p$  is the pressure,  $V$  the volume,  $m$  the mass of gas,  $R$  the gas constant for the gas,  $T$  the temperature,  $\tilde{R}$  the universal gas constant,  $M$  the molecular weight, and  $n$  the number of moles. Relations for evaluating the specific internal energy  $u$ , enthalpy  $h$ , and entropy  $s$ , specific heats at constant volume  $c_v$  and constant pressure  $c_p$ , on a per unit mass basis and on a per mole basis (where the notation  $\tilde{u}$ ,  $\tilde{h}$ ,  $\tilde{s}$ ,  $\tilde{c}_v$ , and  $\tilde{c}_p$  is used) of an ideal gas, are developed. Also given are equations for calculating the thermodynamic properties of mixtures of ideal gases.

### 3.3 COMPOSITION OF AIR AND FUELS

Normally in engines, fuels are burned with air. Dry air is a mixture of gases that has a representative composition by volume of 20.95 percent oxygen, 78.09 percent nitrogen, 0.93 percent argon, and trace amounts of carbon dioxide, neon, helium, methane, and other gases. Table 3.1 shows the relative proportions of the major constituents of dry air.<sup>3</sup>

TABLE 3.1  
Principle constituents of dry air

Gas	ppm by volume	Molecular weight	Mole fraction	Molar ratio
O <sub>2</sub>	209,500	31.998	0.2095	1
N <sub>2</sub>	780,900	28.012	0.7905	3.773
Ar	9,300	39.948		
CO <sub>2</sub>	300	44.009		
Air	1,000,000	28.962	1.0000	4.773

In combustion, oxygen is the reactive component of air. It is usually sufficiently accurate to regard air as consisting of 21 percent oxygen and 79 percent inert gases taken as nitrogen (often called atmospheric or apparent nitrogen). For each mole of oxygen in air there are

$$\frac{1 - 0.2095}{0.2095} = 3.773$$

moles of atmospheric nitrogen. The molecular weight of air is obtained from Table 3.1 with Eq. (B.17) as 28.962, usually approximated by 29. Because atmospheric nitrogen contains traces of other species, its molecular weight is slightly different from that of pure molecular nitrogen, i.e.,

$$M_{aN_2} = \frac{28.962 - 0.2095 \times 31.998}{1 - 0.2095} = 28.16$$

In the following sections, *nitrogen* will refer to atmospheric nitrogen and a molecular weight of 28.16 will be used. An air composition of 3.773 moles of nitrogen per mole of oxygen will be assumed.

The density of dry air can be obtained from Eq. (3.1) with  $R = 8314.3 \text{ J/kmol} \cdot \text{K}$  and  $M = 28.962$ :

$$\rho(\text{kg/m}^3) = \frac{3.483 \times 10^{-3} p(\text{Pa})}{T(\text{K})} \tag{3.2a}$$

or

$$\rho(\text{lbm/ft}^3) = \frac{2.699 p(\text{lb/in}^2)}{T(^{\circ}\text{R})} \tag{3.2b}$$

Thus, the value for the density of dry air at 1 atmosphere ( $1.0133 \times 10^5 \text{ Pa}$ ,  $14.696 \text{ lb/in}^2$ ) and  $25^{\circ}\text{C}$  ( $77^{\circ}\text{F}$ ) is  $1.184 \text{ kg/m}^3$  ( $0.0739 \text{ lbm/ft}^3$ ).

Actual air normally contains water vapor, the amount depending on temperature and degree of saturation. Typically the proportion by mass is about 1 percent, though it can rise to about 4 percent under extreme conditions. The *relative humidity* compares the water vapor content of air with that required to saturate. It is defined as:

The ratio of the partial pressure of water vapor actually present to the saturation pressure at the same temperature.

Water vapor content is measured with a wet- and dry-bulb psychrometer. This consists of two thermometers exposed to a stream of moist air. The dry-bulb temperature is the temperature of the air. The bulb of the other thermometer is wetted by a wick in contact with a water reservoir. The wet-bulb temperature is lower than the dry-bulb temperature due to evaporation of water from the wick. It is a good approximation to assume that the wet-bulb temperature is the adiabatic saturation temperature. Water vapor pressure can be obtained from observed wet- and dry-bulb temperatures and a psychrometric chart such as Fig. 3-1.<sup>4</sup> The effect of humidity on the properties of air is given in Fig. 3-2.<sup>5</sup>

The fuels most commonly used in internal combustion engines (gasoline or petrol, and diesel fuels) are blends of many different hydrocarbon compounds obtained by refining petroleum or crude oil. These fuels are predominantly carbon and hydrogen (typically about 86 percent carbon and 14 percent hydrogen by weight) though diesel fuels can contain up to about 1 percent sulfur. Other fuels of interest are alcohols (which contain oxygen), gaseous fuels (natural gas and liquid petroleum gas), and single hydrocarbon compounds (e.g., methane, propane, isooctane) which are often used in engine research. Properties of the more common internal combustion engine fuels are summarized in App. D.

Some knowledge of the different classes of organic compounds and their

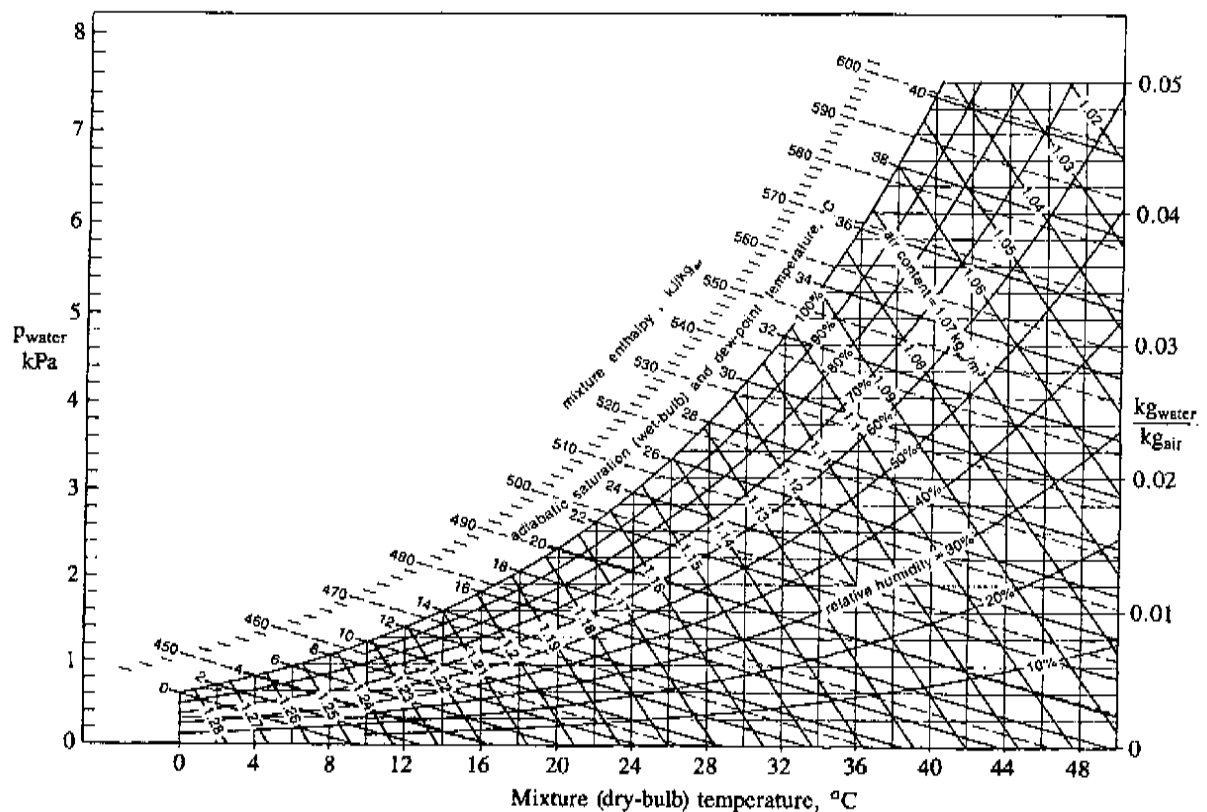
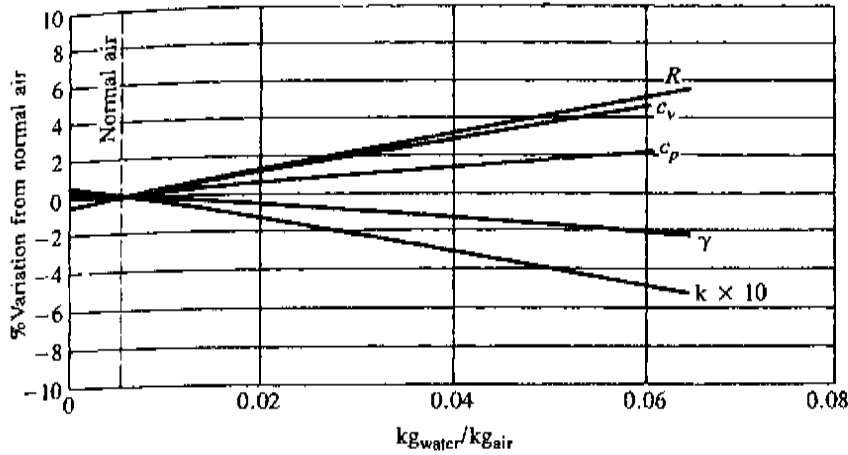


FIGURE 3-1  
Psychrometric chart for air-water mixtures at 1 atmosphere. (From Reynolds.<sup>4</sup>)



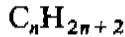
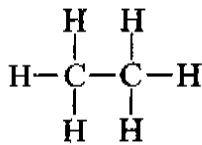


**FIGURE 3-2**  
Effect of humidity on properties of air:  $R$  is the gas constant;  $c_v$  and  $c_p$  are specific heats at constant volume and pressure, respectively;  $\gamma = c_p/c_v$ ;  $k$  is the thermal conductivity. (From Taylor.<sup>5</sup>)

molecular structure is necessary in order to understand combustion mechanisms.<sup>6</sup> The different classes are as follows:

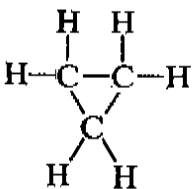
### Alkyl Compounds

#### Paraffins (alkanes)



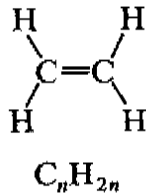
Single-bonded open-chain saturated hydrocarbon molecules: i.e., no more hydrogen can be added. For the larger molecules straight-chain and branched-chain configurations exist. These are called normal ( $n$ -) and iso compounds, respectively. Examples:  $CH_4$ , methane;  $C_2H_6$ , ethane;  $C_3H_8$ , propane;  $C_8H_{18}$ ,  $n$ -octane and isooctane. There are several "isooctanes," depending on the relative position of the branches. By isooctane is usually meant 2,2,4-trimethylpentane, indicating five carbon atoms in the straight chain (pentane) with three methyl ( $CH_3$ ) branches located respectively at C-atoms 2, 2, and 4. Radicals deficient in one hydrogen take the name methyl, ethyl, propyl, etc.

#### Cycloparaffins or naphenes (cyclanes)

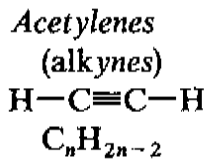


Single bond (no double bond) ring hydrocarbons. Unsaturated, since ring can be broken and additional hydrogen added. Examples:  $C_3H_6$ , cyclopropane (three C-atom ring);  $C_4H_8$ , cyclobutane (four C-atom ring);  $C_5H_{10}$ , cyclopentane (five C-atom ring).

*Olefins*  
(alkenes)

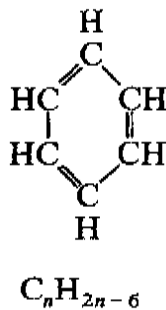


Open-chain hydrocarbons containing a double bond; hence they are unsaturated. Examples are:  $\text{C}_2\text{H}_4$ , ethene (or ethylene);  $\text{C}_3\text{H}_6$ , propene (or propylene);  $\text{C}_4\text{H}_8$ , butene (or butylene); . . . . From butene upwards several structural isomers are possible depending on the location of the double bond in the basic carbon chain. Straight- and branched-chain structures exist. Diolefins contain two double bonds.



Open-chain unsaturated hydrocarbons containing one carbon-carbon triple bond. First member is acetylene,  $\text{H}-\text{C}\equiv\text{C}-\text{H}$ . Additional members of the alkyne series comprise open-chain molecules, similar to higher alkenes but with each double bond replaced by a triple bond.

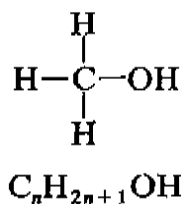
**Aromatics**



Building block for aromatic hydrocarbons is the benzene ( $\text{C}_6\text{H}_6$ ) ring structure shown. This ring structure is very stable and accommodates additional  $-\text{CH}_2$  groups in side chains and not by ring expansion. Examples:  $\text{C}_7\text{H}_8$ , toluene;  $\text{C}_8\text{H}_{10}$ , xylene (several structural arrangements); . . . . More complex aromatic hydrocarbons incorporate ethyl, propyl, and heavier alkyl side chains in a variety of structural arrangements.

**Alcohols**

*Monohydric*  
*alcohols*

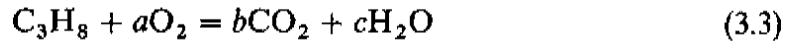


In these organic compounds, one hydroxyl ( $-\text{OH}$ ) group is substituted for one hydrogen atom. Thus methane becomes methyl alcohol,  $\text{CH}_3\text{OH}$  (also called methanol); ethane becomes ethyl alcohol,  $\text{C}_2\text{H}_5\text{OH}$  (ethanol); etc.

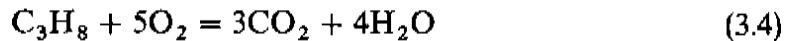
### 3.4 COMBUSTION STOICHIOMETRY

This section develops relations between the composition of the reactants (fuel and air) of a combustible mixture and the composition of the products. Since these relations depend only on the conservation of mass of each chemical element in the reactants, only the relative elemental composition of the fuel and the relative proportions of fuel and air are needed.

If sufficient oxygen is available, a hydrocarbon fuel can be completely oxidized. The carbon in the fuel is then converted to carbon dioxide  $\text{CO}_2$  and the hydrogen to water  $\text{H}_2\text{O}$ . For example, consider the overall chemical equation for the complete combustion of one mole of propane  $\text{C}_3\text{H}_8$ :

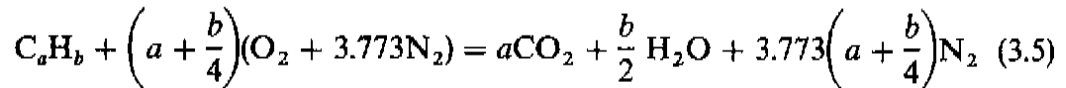


A carbon balance between the reactants and products gives  $b = 3$ . A hydrogen balance gives  $2c = 8$ , or  $c = 4$ . An oxygen balance gives  $2b + c = 10 = 2a$ , or  $a = 5$ . Thus Eq. (3.3) becomes



Note that Eq. (3.4) only relates the elemental composition of the reactant and product species; it does not indicate the process by which combustion proceeds, which is much more complex.

Air contains nitrogen, but when the products are at low temperatures the nitrogen is not significantly affected by the reaction. Consider the complete combustion of a general hydrocarbon fuel of average molecular composition  $\text{C}_a\text{H}_b$  with air. The overall complete combustion equation is



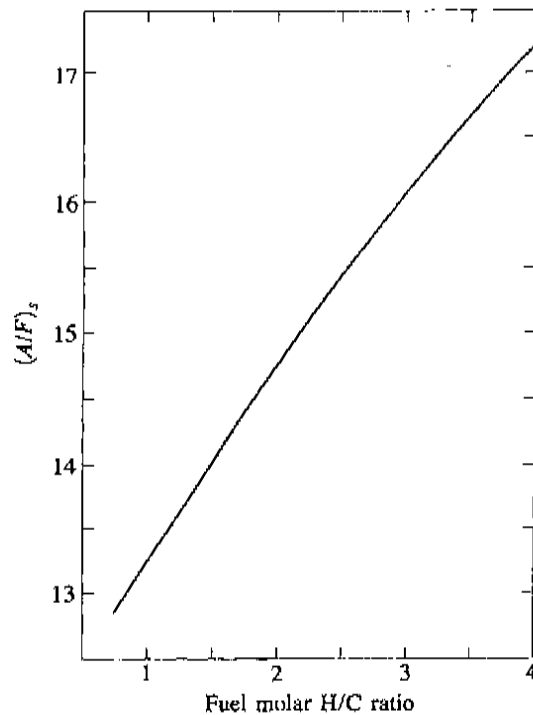
Note that only the *ratios* of the numbers in front of the symbol for each chemical species are defined by Eq. (3.5); i.e., only the relative proportions on a molar basis are obtained. Thus the fuel composition could have been written  $\text{CH}_y$ , where  $y = b/a$ .

Equation (3.5) defines the *stoichiometric* (or chemically correct or theoretical) proportions of fuel and air; i.e., there is just enough oxygen for conversion of all the fuel into completely oxidized products. The stoichiometric air/fuel or fuel/air ratios (see Sec. 2.9) depend on fuel composition. From Eq. (3.5):

$$\begin{aligned} \left(\frac{A}{F}\right)_s &= \left(\frac{F}{A}\right)_s^{-1} = \frac{(1 + y/4)(32 + 3.773 \times 28.16)}{12.011 + 1.008y} \\ &= \frac{34.56(4 + y)}{12.011 + 1.008y} \end{aligned} \quad (3.6)$$

The molecular weights of oxygen, atmospheric nitrogen, atomic carbon, and atomic hydrogen are, respectively, 32, 28.16, 12.011, and 1.008.  $(A/F)_s$  depends only on  $y$ ; Fig. 3-3 shows the variation in  $(A/F)_s$  as  $y$  varies from 1 (e.g., benzene) to 4 (methane).

**Example 3.1.** A hydrocarbon fuel of composition 84.1 percent by mass C and 15.9 percent by mass H has a molecular weight of 114.15. Determine the number of moles of air required for stoichiometric combustion and the number of moles of products produced per mole of fuel. Calculate  $(A/F)_s$ ,  $(F/A)_s$ , and the molecular weights of the reactants and the products.



**FIGURE 3-3**  
Stoichiometric air/fuel ratio for air-hydrocarbon fuel mixtures as a function of fuel molar H/C ratio.

Assume a fuel composition  $C_a H_b$ . The molecular weight relation gives

$$114.15 = 12.011a + 1.008b$$

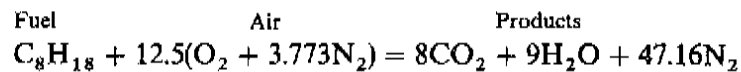
The gravimetric analysis of the fuel gives

$$\frac{b}{a} = \frac{15.9/1.008}{84.1/12.011} = 2.25$$

Thus

$$a = 8 \quad b = 18^\dagger$$

The fuel is octane  $C_8H_{18}$ . Equation (3.5) then becomes



In moles:

$$\begin{array}{rcl} 1 & + 12.5(1 + 3.773) & = 8 + 9 + 47.16 \\ 1 & + 59.66 & = 64.16 \end{array}$$

Relative mass:

$$\begin{array}{rcl} 114.15 + 59.66 \times 28.96 & = & 8 \times 44.01 + 9 \times 18.02 + 47.16 \times 28.16 \\ 114.5 + 1727.8 & = & 1842.3 \end{array}$$

$^\dagger$  Note that for fuels which are mixtures of hydrocarbons,  $a$  and  $b$  need not be integers.

Per unit mass fuel:

$$1 + 15.14 = 16.14$$

Thus for stoichiometric combustion, 1 mole of fuel requires 59.66 moles of air and produces 64.16 moles of products. The stoichiometric  $(A/F)_s$  is 15.14 and  $(F/A)_s$  is 0.0661.

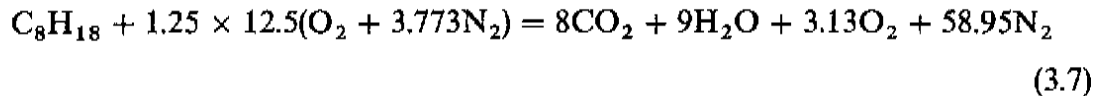
The molecular weights of the reactants  $M_R$  and products  $M_P$  are

$$M_R = \frac{1}{n} \sum n_i M_i = \frac{1}{60.66} (1 \times 114.15 + 59.66 \times 28.96)$$

$$M_P = \frac{1}{n} \sum n_i M_i = \frac{1}{64.16} (8 \times 44.01 + 9 \times 18.02 + 47.16 \times 28.16)$$

or  $M_R = 30.36 \quad M_P = 28.71$

Fuel-air mixtures with more than or less than the stoichiometric air requirement can be burned. With excess air or fuel-lean combustion, the extra air appears in the products in unchanged form. For example, the combustion of isooctane with 25 percent excess air, or 1.25 times the stoichiometric air requirement, gives



With less than the stoichiometric air requirement, i.e., with fuel-rich combustion, there is insufficient oxygen to oxidize fully the fuel C and H to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The products are a mixture of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  with carbon monoxide CO and hydrogen  $\text{H}_2$  (as well as  $\text{N}_2$ ). The product composition cannot be determined from an element balance alone and an additional assumption about the chemical composition of the product species must be made (see Secs. 4.2 and 4.9.2).

Because the composition of the combustion products is significantly different for fuel-lean and fuel-rich mixtures, and because the stoichiometric fuel/air ratio depends on fuel composition, the ratio of the actual fuel/air ratio to the stoichiometric ratio (or its inverse) is a more informative parameter for defining mixture composition. The *fuel/air equivalence ratio*  $\phi$ ,

$$\phi = \frac{(F/A)_{\text{actual}}}{(F/A)_s} \quad (3.8)$$

will be used throughout this text for this purpose. The inverse of  $\phi$ , the *relative air/fuel ratio*  $\lambda$ ,

$$\lambda = \phi^{-1} = \frac{(A/F)_{\text{actual}}}{(A/F)_s} \quad (3.9)$$

is also sometimes used.

For fuel-lean mixtures:  $\phi < 1, \lambda > 1$

For stoichiometric mixtures:  $\phi = \lambda = 1$

For fuel-rich mixtures:  $\phi > 1, \lambda < 1$

When the fuel contains oxygen (e.g., with alcohols), the procedure for determining the overall combustion equation is the same except that fuel oxygen is included in the oxygen balance between reactants and products. For methyl alcohol (methanol),  $\text{CH}_3\text{OH}$ , the stoichiometric combustion equation is



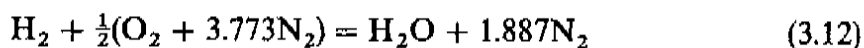
and  $(A/F)_s = 6.47$ . For ethyl alcohol (ethanol),  $\text{C}_2\text{H}_5\text{OH}$ , the stoichiometric combustion equation is



and  $(A/F)_s = 9.00$ .

If there are significant amounts of sulfur in the fuel, the appropriate oxidation product for determining the stoichiometric air and fuel proportions is sulfur dioxide,  $\text{SO}_2$ .

For hydrogen fuel, the stoichiometric equation is



and the stoichiometric  $(A/F)$  ratio is 34.3.

Note that the composition of the products of combustion in Eqs. (3.7) and (3.10) to (3.12) may not occur in practice. At normal combustion temperatures significant dissociation of  $\text{CO}_2$  and of  $\text{H}_2\text{O}$  occurs (see Sec. 3.7.1). Whether, at low temperatures, recombination brings the product composition to that indicated by these overall chemical equations depends on the rate of cooling of the product gases. More general relationships for the composition of unburned and burned gas mixtures are developed in Chap. 4.

The stoichiometric  $(A/F)$  and  $(F/A)$  ratios of common fuels and representative single hydrocarbon and other compounds are given in App. D along with other fuel data.

### 3.5 THE FIRST LAW OF THERMODYNAMICS AND COMBUSTION†

#### 3.5.1 Energy and Enthalpy Balances

In a combustion process, fuel and oxidizer react to produce products of different composition. The actual path by which this transformation takes place is understood only for simple fuels such as hydrogen and methane. For fuels with more complicated structure, the details are not well defined. Nonetheless, the first law

† The approach used here follows that developed by Spalding and Cole.<sup>7</sup>

of thermodynamics can be used to relate the end states of mixtures undergoing a combustion process; its application does not require that the details of the process be known.

The first law of thermodynamics relates changes in internal energy (or enthalpy) to heat and work transfer interactions. In applying the first law to a system whose chemical composition changes, care must be exercised in relating the reference states at which zero internal energy or enthalpy for each species or groups of species are assigned. We are not free, when chemical reactions occur, to choose independently the zero internal energy or enthalpy reference states of chemical substances transformed into each other by reaction.

Consider a system of mass  $m$  which changes its composition from reactants to products by chemical reaction as indicated in Fig. 3-4. Applying the first law to the system between its initial and final states gives

$$Q_{R-P} - W_{R-P} = U_P - U_R \tag{3.13}$$

Heat transfer  $Q_{R-P}$  and work transfer  $W_{R-P}$  due to normal force displacements may occur across the system boundary. The standard thermodynamic sign convention for each energy transfer interaction—positive for heat transfer *to* the system and positive for work transfer *from* the system—is used.

We will consider a series of special processes: first, a *constant volume* process where the initial and final temperatures are the same,  $T'$ . Then Eq. (3.13) becomes

$$Q_{R-P} = U'_P - U'_R = (\Delta U)_{V, T'} \tag{3.14}$$

The internal energy of the system has changed by an amount  $(\Delta U)_{V, T'}$ , which can be measured or calculated. Combustion processes are exothermic [i.e.,  $Q_{R-P}$  and  $(\Delta U)_{V, T'}$  are negative]; therefore the system's internal energy decreases. If Eq. (3.14) is expressed per mole of fuel, then  $(\Delta U)_{V, T'}$  is known as the increase in

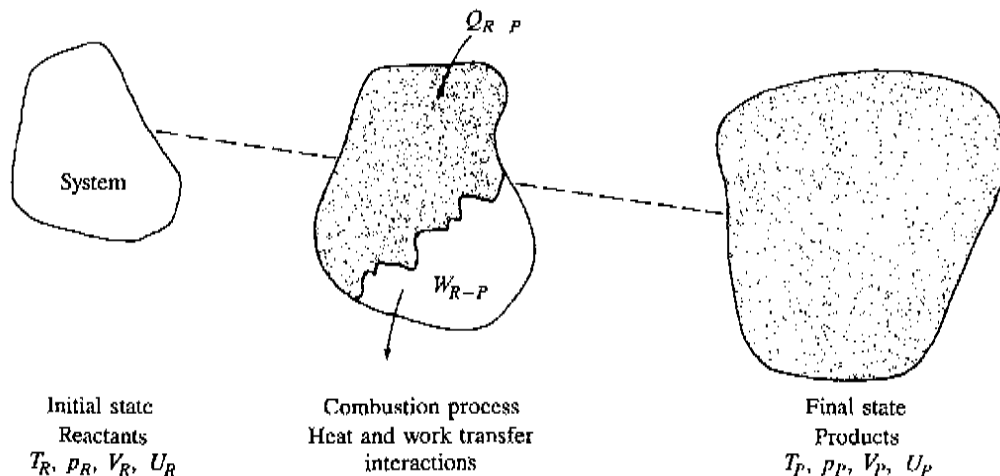


FIGURE 3-4 System changing from reactants to products for first law analysis.

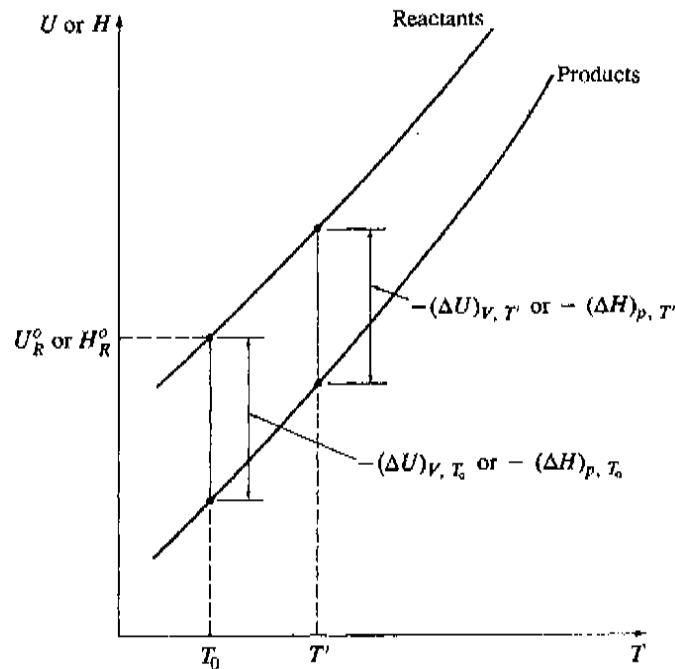


FIGURE 3-5

Schematic plot of internal energy ( $U$ ) or enthalpy ( $H$ ) of reactants and products as a function of temperature.

internal energy at constant volume, and  $-(\Delta U)_{V, T'}$  is known as the *heat of reaction at constant volume* at temperature  $T'$ .

Next, consider a *constant pressure* process where the initial and final temperatures are the same,  $T'$ . For a constant pressure process

$$W_{R-P} = \int_R^P p \, dV = p(V_P - V_R) \quad (3.15)$$

so Eq. (3.13) becomes

$$Q_{R-P} - p(V'_P - V'_R) = U'_P - U'_R$$

or

$$\begin{aligned} Q_{R-P} &= (U'_P + pV'_P) - (U'_R + pV'_R) \\ &= H'_P - H'_R = (\Delta H)_{p, T'} \end{aligned} \quad (3.16)$$

The enthalpy of the system has changed by an amount  $(\Delta H)_{p, T'}$ , which can be measured or calculated. Again for combustion reactions,  $(\Delta H)_{p, T'}$  is a negative quantity. If Eq. (3.16) is written per mole of fuel,  $(\Delta H)_{p, T'}$  is called the increase in enthalpy at constant pressure and  $-(\Delta H)_{p, T'}$  is called the *heat of reaction at constant pressure* at  $T'$ .

These processes can be displayed, respectively, on the internal energy or enthalpy versus temperature plot shown schematically in Fig. 3-5. If  $U$  (or  $H$ ) for the reactants is arbitrarily assigned a value  $U_R^0$  (or  $H_R^0$ ) at some reference temperature  $T_0$ , then the value of  $(\Delta U)_{V, T_0}$  [or  $(\Delta H)_{p, T_0}$ ] fixes the relationship between  $U(T)$  or  $H(T)$ , respectively, for the products and the reactants. Note that the slope of these lines (the specific heat at constant volume or pressure if the diagram is expressed per unit mass or per mole) increases with increasing tem-



perature; also, the magnitude of  $(\Delta U)_{V, T'}$  [or  $(\Delta H)_{p, T'}$ ] decreases with increasing temperature because  $c_v$  (or  $c_p$ ) for the products is greater than for the reactants.

The difference between  $(\Delta H)_{p, T'}$  and  $(\Delta U)_{V, T'}$  is

$$(\Delta H)_{p, T'} - (\Delta U)_{V, T'} = p(V_P - V_R) \tag{3.17}$$

Only if the volumes of the products and reactants in the constant pressure process are the same are  $(\Delta H)_{p, T'}$  and  $(\Delta U)_{V, T'}$  equal. If all the reactant and product species are ideal gases, then the ideal gas law Eq. (3.1) gives

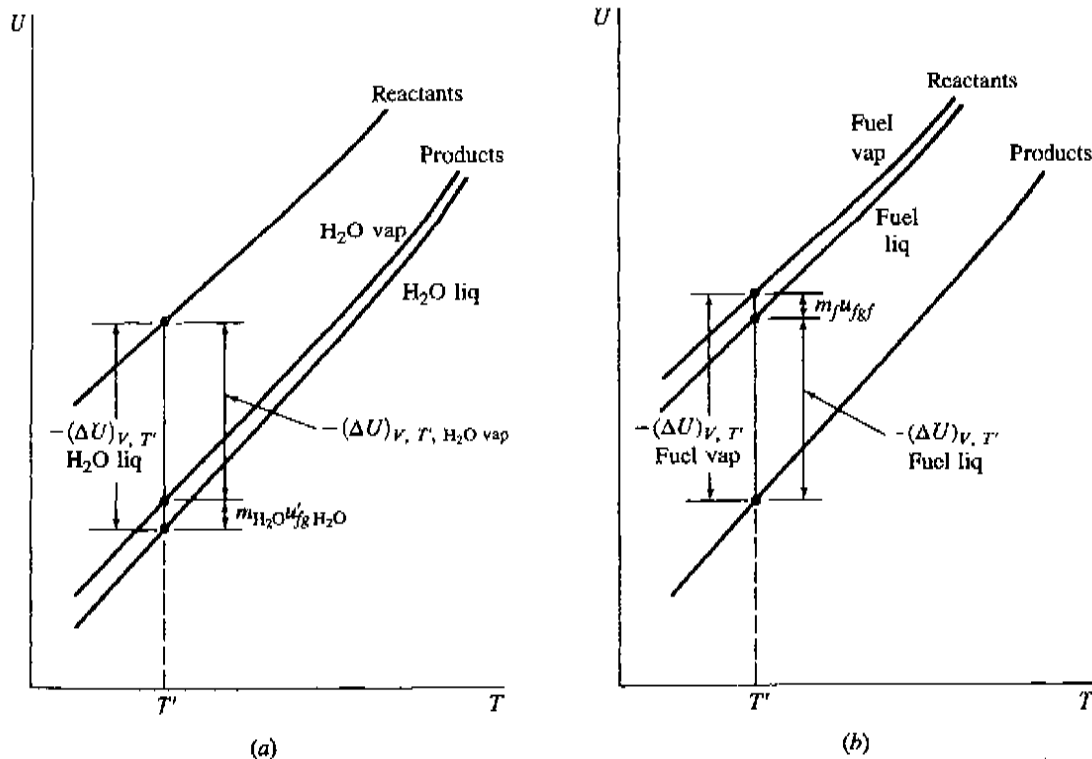
$$(\Delta H)_{p, T'} - (\Delta U)_{V, T'} = \tilde{R}(n'_P - n'_R)T' \tag{3.18}$$

Note that any inert gases do not contribute to  $(n'_P - n'_R)$ .

With a hydrocarbon fuel, one of the products,  $H_2O$ , can be in the gaseous or liquid phase. The internal energy (or enthalpy) of the products in the constant volume (or constant pressure) processes described above in Fig. 3-5 will depend on the relative proportions of the water in the gaseous and liquid phases. The limiting cases of all vapor and all liquid are shown in Fig. 3-6a for a  $U-T$  plot. The internal energy differences between the curves is

$$|(\Delta U)_{V, T', H_2O \text{ liq}}| - |(\Delta U)_{V, T', H_2O \text{ vap}}| = m_{H_2O} u'_{fg, H_2O} \tag{3.19}$$

where  $m_{H_2O}$  is the mass of water in the products and  $u'_{fg, H_2O}$  is the internal energy of vaporization of water at the temperature and pressure of the products. Similar



**FIGURE 3-6**  
Schematic plots of internal energy of reactants and products as a function of temperature. (a) Effect of water in products as either vapor or liquid. (b) Effect of fuel in reactants as either vapor or liquid.

curves and relationships apply for enthalpy:

$$|(\Delta H)_{p, T, \text{H}_2\text{O liq}}| - |(\Delta H)_{p, T, \text{H}_2\text{O vap}}| = m_{\text{H}_2\text{O}} h'_{f\theta \text{H}_2\text{O}} \quad (3.20)$$

For some fuels, the reactants may contain the fuel as either liquid or vapor. The  $U$ - $T$  (or  $H$ - $T$ ) line for the reactants with the fuel as liquid or as vapor will be different, as indicated in Fig. 3-6b. The vertical distance between the two reactant curves is  $m_f u_{f\theta f}$  (or  $m_f h_{f\theta f}$ ) where the subscript  $f$  denotes fuel.

### 3.5.2 Enthalpies of Formation

For fuels which are single hydrocarbon compounds, or where the precise fuel composition is known, the internal energies or enthalpies of the reactants and the products can be related through the enthalpies of formation of the reactants and products.

The *enthalpy of formation*  $\Delta \bar{h}_f^\circ$  of a chemical compound is the enthalpy increase associated with the reaction of forming one mole of the given compound from its elements, with each substance in its thermodynamic standard state at the given temperature.

The *standard state* is the state at one atmosphere pressure and the temperature under consideration. We will denote the standard state by the superscript  $^\circ$ .

Since thermodynamic calculations are made as a difference between an initial and a final state, it is necessary to select a *datum state* to which all other thermodynamic states can be referred. While a number of datum states have been used in the literature, the most common datum is 298.15 K (25°C) and 1 atmosphere. We will use this datum throughout this text. Elements at their *reference state* are arbitrarily assigned zero enthalpy at the datum temperature. The reference state of each element is its stable standard state; e.g., for oxygen at 298.15 K, the reference state is  $\text{O}_2$  gas.

Enthalpies of formation are tabulated as a function of temperature for all commonly occurring species. For inorganic compounds, the *JANAF Thermochemical Tables* are the primary reference source.<sup>8</sup> These tables include values of the molar specific heat at constant pressure, standard entropy, standard Gibbs free energy (called free energy in the tables), standard enthalpy, enthalpy of formation and Gibbs free energy of formation, and  $\log_{10}$  equilibrium constant for the formation of each species from its elements. Some primary references for thermodynamic data on fuel compounds are Maxwell,<sup>9</sup> Rossini *et al.*,<sup>10</sup> and Stull *et al.*<sup>11</sup> Enthalpies of formation of species relevant to hydrocarbon fuel combustion are tabulated in Table 3.2. Selected values of thermodynamic properties of relevant species are tabulated in App. D.

For a given combustion reaction, the enthalpy of the products at the standard state relative to the enthalpy datum is then given by

$$H_p^\circ = \sum_{\text{products}} n_i \Delta \bar{h}_{f,i}^\circ \quad (3.21a)$$

TABLE 3.2  
Standard enthalpies of formation

Species	State†	$\Delta \bar{h}_f^\circ$ , MJ/kmol
O <sub>2</sub>	Gas	0
N <sub>2</sub>	Gas	0
H <sub>2</sub>	Gas	0
C	Gas	0
CO <sub>2</sub>	Gas	-393.52
H <sub>2</sub> O	Gas	-241.83
H <sub>2</sub> O	Liquid	-285.84
CO	Gas	-110.54
CH <sub>4</sub>	Gas	-74.87
C <sub>3</sub> H <sub>8</sub>	Gas	-103.85
CH <sub>3</sub> OH	Gas	-201.17
CH <sub>3</sub> OH	Liquid	-238.58
C <sub>8</sub> H <sub>18</sub>	Gas	-208.45
C <sub>8</sub> H <sub>18</sub>	Liquid	-249.35

† At 298.15 K (25°C) and 1 atm.

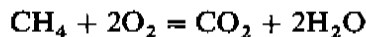
and the enthalpy of the reactants is given by

$$H_R^\circ = \sum_{\text{reactants}} n_i \Delta \bar{h}_{f,i}^\circ \quad (3.21b)$$

The enthalpy increase,  $(\Delta H)_{p, T_0}$ , is then obtained from the difference  $(H_P^\circ - H_R^\circ)$ . The internal energy increase can be obtained with Eq. (3.17).

**Example 3.2.** Calculate the enthalpy of the products and reactants, and the enthalpy increase and internal energy increase of the reaction, of a stoichiometric mixture of methane and oxygen at 298.15 K.

The stoichiometric reaction is



Thus, for H<sub>2</sub>O gas, from Table 3.2 and Eq. (3.21a, b):

$$H_P^\circ = -393.52 + 2(-241.83) = -877.18 \text{ MJ/kmol CH}_4$$

For H<sub>2</sub>O liquid:

$$H_P^\circ = -393.52 + 2(-285.84) = -965.20 \text{ MJ/kmol CH}_4$$

$$H_R^\circ = -74.87 \text{ MJ/kmol CH}_4$$

Hence for H<sub>2</sub>O gas:

$$(\Delta H)_P^\circ = -877.18 + 74.87 = -802.31 \text{ MJ/kmol CH}_4$$

and for H<sub>2</sub>O liquid:

$$(\Delta H)_P^\circ = -965.20 + 74.87 = -890.33 \text{ MJ/kmol CH}_4$$

Use Eq. (3.18) to find  $(\Delta U)_V^\circ$ . With  $H_2O$  gas, the number of moles of reactants and products are equal, so

$$(\Delta U)_V^\circ = (\Delta H)_p^\circ = -802.3 \text{ MJ/kmol } CH_4$$

For  $H_2O$  liquid:

$$(\Delta U)_V^\circ = -890.33 - 8.3143 \times 10^{-3}(1 - 3)298.15 \text{ MJ/kmol } CH_4$$

$$(\Delta U)_V^\circ = -885.4 \text{ MJ/kmol } CH_4$$

Note that the presence of nitrogen in the mixture or oxygen in excess of the stoichiometric amount would not change any of these calculations.

### 3.5.3 Heating Values

For fuels where the precise fuel composition is not known, the enthalpy of the reactants cannot be determined from the enthalpies of formation of the reactant species. The *heating value* of the fuel is then measured directly.

The heating value  $Q_{HV}$  or calorific value of a fuel is the magnitude of the heat of reaction at constant pressure or at constant volume at a standard temperature [usually  $25^\circ C$  ( $77^\circ F$ )] for the complete combustion of unit mass of fuel. Thus

$$Q_{HV,p} = -(\Delta H)_{p, T_0} \quad (3.22a)$$

and

$$Q_{HV,v} = -(\Delta U)_{v, T_0} \quad (3.22b)$$

Complete combustion means that all carbon is converted to  $CO_2$ , all hydrogen is converted to  $H_2O$ , and any sulfur present is converted to  $SO_2$ . The heating value is usually expressed in joules per kilogram or joules per kilomole of fuel (British thermal units per pound-mass or British thermal units per pound-mole). It is therefore unnecessary to specify how much oxidant was mixed with the fuel, though this must exceed the stoichiometric requirement. It is immaterial whether the oxidant is air or oxygen.

For fuels containing hydrogen, we have shown that whether the  $H_2O$  in the products is in the liquid or gaseous phase affects the value of the heat of reaction. The term *higher heating value*  $Q_{HHV}$  (or gross heating value) is used when the  $H_2O$  formed is all condensed to the liquid phase; the term *lower heating value*  $Q_{LHV}$  (or net heating value) is used when the  $H_2O$  formed is all in the vapor phase. The two heating values at constant pressure are related by

$$Q_{HHV,p} = Q_{LHV,p} + \left( \frac{m_{H_2O}}{m_f} \right) h_{f_g, H_2O} \quad (3.23)$$

where  $(m_{H_2O}/m_f)$  is the ratio of mass of  $H_2O$  produced to mass of fuel burned. A similar expression with  $u_{f_g, H_2O}$  replacing  $h_{f_g, H_2O}$  applies for the higher and lower heating value at constant volume.

The heating value at constant pressure is the more commonly used; often the qualification "at constant pressure" is omitted. The difference between the heating values at constant pressure and constant volume is small.

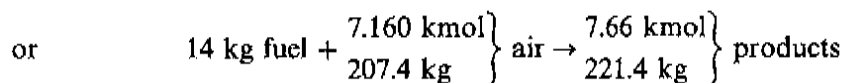
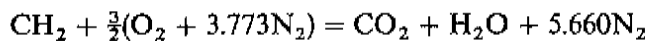
Heating values† of fuels are measured in calorimeters. For gaseous fuels, it is most convenient and accurate to use a continuous-flow atmosphere pressure calorimeter. The entering fuel is saturated with water vapor and mixed with sufficient saturated air for complete combustion at the reference temperature. The mixture is burned in a burner and the combustion products cooled with water-cooled metal tube coils to close to the inlet temperature. The heat transferred to the cooling water is calculated from the measured water flow rate and water temperature rise. The heating value determined by this process is the higher heating value at constant pressure.

For liquid and solid fuels, it is more satisfactory to burn the fuel with oxygen under pressure at constant volume in a bomb calorimeter. A sample of the fuel is placed in the bomb calorimeter, which is a stainless-steel container immersed in cooling water at the standard temperature. Sufficient water is placed in the bomb to ensure that the water produced in the combustion process will condense. Oxygen at 30 atmospheres is admitted to the bomb. A length of firing cotton is suspended into the sample from an electrically heated wire filament to act as a source of ignition. When combustion is complete the temperature rise of the bomb and cooling water is measured. The heating value determined by this process is the higher heating value at constant volume.

The heating values of common fuels are tabulated with other fuel data in App. D. The following example illustrates how the enthalpy of a reactant mixture relative to the enthalpy datum we have defined can be determined from the measured heating value of the fuel.

**Example 3.3.** Liquid kerosene fuel of the lower heating value (determined in a bomb calorimeter) of 43.2 MJ/kg and average molar H/C ratio of 2 is mixed with the stoichiometric air requirement at 298.15 K. Calculate the enthalpy of the reactant mixture relative to the datum of zero enthalpy for C, O<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub> at 298.15 K.

The combustion equation per mole of C can be written



where  $M = 28.962$  for atmospheric air.

The heating value given is at constant volume,  $-(\Delta U)_V^\circ$ .  $(\Delta H)_p^\circ$  is obtained from Eq. (3.18), noting that the fuel is in the liquid phase:

$$\begin{aligned} (\Delta H)_p^\circ &= -43.2 + 8.3143 \times 10^{-3} (7.66 - 7.160) \times \frac{298.15}{14} \\ &= -43.2 + 0.09 = -43.1 \text{ MJ/kg fuel} \end{aligned}$$

† Standard methods for measuring heating values are defined by the American Society for Testing Materials.

The enthalpy of the products per kilogram of mixture is found from the enthalpies of formation (with H<sub>2</sub>O vapor):

$$h_p = \frac{1(-393.52) + 1(-241.83)}{221.4} \\ = 2.87 \text{ MJ/kg}$$

The enthalpy of the reactants per kilogram of mixture is then

$$h_R = h_p - (\Delta h)_p^\circ = 2.87 + \frac{43.1 \times 14}{221.4} = 5.59 \text{ MJ/kg}$$

### 3.5.4 Adiabatic Combustion Processes

We now use the relationships developed above to examine two other special processes important in engine analysis: constant-volume and constant-pressure adiabatic combustion. For an adiabatic constant-volume process, Eq. (3.13) becomes

$$U_P - U_R = 0 \quad (3.24)$$

when  $U_P$  and  $U_R$  are evaluated relative to the same datum (e.g., the enthalpies of C, O<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub> are zero at 298.15 K, the datum used throughout this text).

Frequently, however, the tables or graphs of internal energy or enthalpy for species and reactant or product mixtures which are available give internal energies or enthalpies relative to the species or mixture value at some reference temperature  $T_0$ , i.e.,  $U(T) - U(T_0)$  or  $H(T) - H(T_0)$  are tabulated. Since

$$U_P(T_0) - U_R(T_0) = (\Delta U)_{V, T_0}$$

it follows from Eq. (3.24) that

$$[U_P(T) - U_P(T_0)] - [U_R(T) - U_R(T_0)] = -(\Delta U)_{V, T_0} \quad (3.25)$$

relates the product and reactant states. Figure 3-7 illustrates the adiabatic constant-volume combustion process on a  $U$ - $T$  diagram. Given the initial state of the reactants ( $T_R, V$ ) we can determine the final state of the products ( $T_P, V$ ).

For an adiabatic constant-pressure combustion process, Eq. (3.13) gives

$$H_P - H_R = 0$$

which combines with Eq. (3.16) to give

$$[H_P(T) - H_P(T_0)] - [H_R(T) - H_R(T_0)] = -(\Delta H)_{P, T_0} \quad (3.26)$$

Figure 3-7 illustrates this process also. Given the initial reactant state ( $T_R, p$ ) we can determine the final product state ( $T_P, p$ ).

Note that while in Figs. 3-5, 3-6, and 3-7 we have shown  $U$  and  $H$  for the reactants and products to be functions of  $T$  only, in practice for the products at high temperature  $U$  and  $H$  will be functions of  $p$  and  $T$ . The analysis presented here is general; however, to determine the final state of the products in an adia-

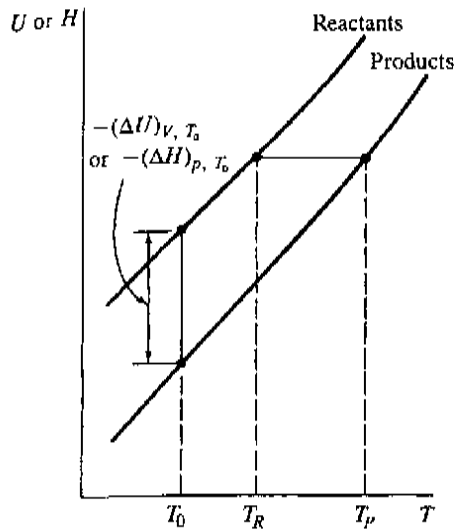


FIGURE 3-7  
Adiabatic constant-volume combustion process on  $U-T$  diagram or adiabatic constant-pressure combustion process on  $H-T$  diagram.

batic combustion process, the constant-volume or constant-pressure constraint must also be used explicitly.

The final temperature of the products in an adiabatic combustion process is called the *adiabatic flame temperature*. Examples of typical adiabatic flame temperatures are shown later in Fig. 3-11.

### 3.5.5 Combustion Efficiency of an Internal Combustion Engine

In practice, the exhaust gas of an internal combustion engine contains incomplete combustion products (e.g., CO, H<sub>2</sub>, unburned hydrocarbons, soot) as well as complete combustion products (CO<sub>2</sub> and H<sub>2</sub>O) (see Sec. 4.9). Under lean operating conditions the amounts of incomplete combustion products are small. Under fuel-rich operating conditions these amounts become more substantial since there is insufficient oxygen to complete combustion. Because a fraction of the fuel's chemical energy is not fully released inside the engine during the combustion process, it is useful to define a *combustion efficiency*. The engine can be analyzed as an open system which exchanges heat and work with its surrounding environment (the atmosphere). Reactants (fuel and air) flow into the system; products (exhaust gases) flow out. Consider a mass  $m$  which passes through the control volume surrounding the engine shown in Fig. 3-8; the *net chemical energy release* due to combustion within the engine is given by

$$[H_R(T_A) - H_P(T_A)] = m \left( \sum_{i, \text{ reactants}} n_i \Delta \tilde{h}_{f,i}^\circ - \sum_{i, \text{ products}} n_i \Delta \tilde{h}_{f,i}^\circ \right)$$

Enthalpy is the appropriate property since  $p_R = p_P = p_{atm}$ .  $n_i$  is the number of moles of species  $i$  in the reactants or products per unit mass of working fluid and  $\Delta \tilde{h}_{f,i}^\circ$  is the standard enthalpy of formation of species  $i$  at ambient temperature  $T_A$ .

The amount of fuel energy *supplied* to the control volume around the engine which can be released by combustion is  $m_f Q_{HV}$ . Hence, the *combustion*

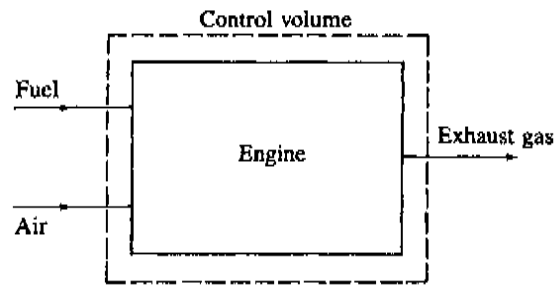


FIGURE 3-8  
Control volume surrounding engine.

*efficiency*—the fraction of the fuel energy supplied which is released in the combustion process—is given by<sup>12</sup>

$$\eta_c = \frac{H_R(T_A) - H_P(T_A)}{m_f Q_{HV}} \quad (3.27)$$

Note that  $m$  and  $m_f$  could be replaced by the average mass flow rates  $\dot{m}$  and  $\dot{m}_f$ .

Figure 3-9 shows how combustion efficiency varies with the fuel/air equivalence ratio for internal combustion engines. For spark-ignition engines, for lean equivalence ratios, the combustion efficiency is usually in the range 95 to 98 percent. For mixtures richer than stoichiometric, lack of oxygen prevents complete combustion of the fuel carbon and hydrogen, and the combustion efficiency steadily decreases as the mixture becomes richer. Combustion efficiency is little affected by other engine operating and design variables, provided the engine com-

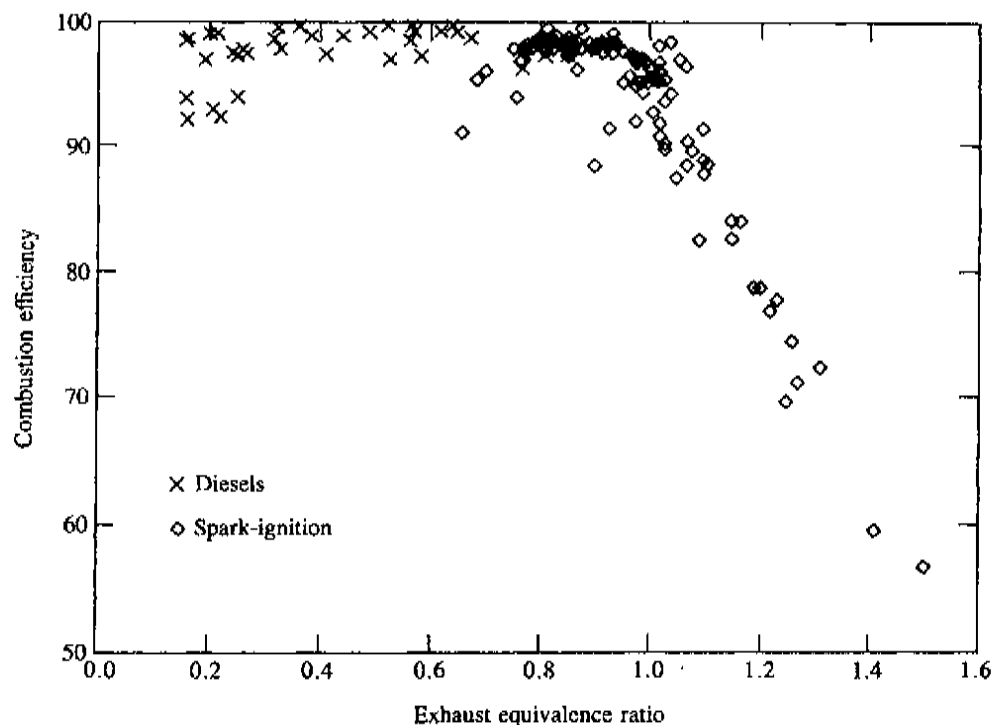


FIGURE 3-9  
Variation of engine combustion efficiency with fuel/air equivalence ratio.



combustion process remains stable. For diesel engines, which always operate lean, the combustion efficiency is normally higher—about 98 percent. Details of exhaust gas composition, on which these combustion efficiencies are based, can be found in Sec. 4.9.

## 3.6 THE SECOND LAW OF THERMODYNAMICS APPLIED TO COMBUSTION

### 3.6.1 Entropy

In App. B, it is shown how the entropy of a mixture of ideal gases of known composition can be calculated. The discussion earlier relating enthalpies (or internal energies) of reactant and product mixtures applies to entropy also. The standard state entropies of chemical species are tabulated in the JANAF tables relative to zero entropy at 0 K. If the entropies of the elements at a datum temperature are arbitrarily set equal to zero, then the values of the entropy of a reactant mixture of given composition and of the resulting product mixture of given composition are both determined.

### 3.6.2 Maximum Work from an Internal Combustion Engine and Efficiency

An internal combustion engine can be analyzed as an open system which exchanges heat and work with its surrounding environment (the atmosphere). Reactants (fuel and air) flow into the system; products (exhaust gases) flow out. By applying the second law of thermodynamics to a control volume surrounding the engine, as illustrated in Fig. 3-8, we can derive an expression for the maximum useful work that the engine can deliver.

Consider a mass  $m$  of fluid as it passes through the control volume surrounding the engine. The first law gives

$$\Delta Q - \Delta W_U = \Delta H$$

where  $\Delta W_U$  is the useful work transfer (i.e., non- $p dV$  work) to the environment and  $\Delta H = H_P - H_R$ . Since the heat transfer  $\Delta Q$  occurs only with the atmosphere at temperature  $T_A$ , from the second law

$$\frac{\Delta Q}{T_A} \leq \Delta S$$

These equations combine to give

$$\Delta W_U \leq -(\Delta H - T_A \Delta S) = -\Delta B$$

where  $B$  is the steady-flow availability function,  $H - T_A S$ .<sup>13</sup> Usually  $p_R = p_A$  and  $T_R = T_A$ . The maximum work will be obtained when  $p_P = p_A$  and  $T_P = T_A$ .

TABLE 3.3  
Enthalpies and free energies of combustion reactions

Reaction†	$\Delta\bar{h}_{298}^{\circ}$ , MJ/kmol	$\Delta\bar{g}_{298}^{\circ}$ , MJ/kmol
$C + O_2 \rightarrow CO_2$	-393.52	-394.40
$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	-240.91	-232.78
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	-802.30	-800.76
$CH_4O(l) + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O$	-638.59	-685.35
$C_3H_8(g) + 5O_2 \rightarrow 3CO_2 + 4H_2O$	-2044.0	-2074.1
$C_6H_6(l) + \frac{15}{2}O_2 \rightarrow 6CO_2 + 3H_2O$	-3135.2	-3175.1
$C_8H_{18}(l) + \frac{25}{2}O_2 \rightarrow 8CO_2 + 9H_2O$	-5074.6	-5219.9

† H<sub>2</sub>O (gas) in products.

Under these conditions,

$$\Delta W_U \leq -[(H - TS)_{P_{T_A, P_A}} - (H - TS)_{R_{T_A, P_A}}] = -(\Delta G)_{T_A, P_A}$$

or 
$$\Delta W_{U \max} = -(\Delta G)_{T_A, P_A} \quad (3.28)$$

$G$  is the Gibbs free energy,  $H - TS$ , and  $(\Delta G)_{T_A, P_A}$  is the Gibbs free energy increase in the reaction of the fuel-air mixture to products at atmospheric temperature and pressure.  $-(\Delta G)_{T_A, P_A}$  will be a maximum when combustion is complete.

A fundamental measure of the effectiveness of any practical internal combustion engine is the ratio of the actual work delivered compared with this maximum work. This ratio will be called the *availability conversion efficiency*  $\eta_a$ :

$$\eta_a = \frac{\Delta W}{\Delta W_{U \max}} = \frac{\Delta W}{(\Delta G)_{T_A, P_A}} \quad (3.29)$$

The property *availability* is the maximum useful work transfer that can be obtained from a system atmosphere (or control-volume atmosphere) combination at a given state. This efficiency therefore defines the fraction of the availability of the unburned fuel and air which, passing through the engine and interacting only with the atmosphere, is actually converted to useful work. Availability analysis of engine operation is proving valuable in identifying where the significant irreversibilities or losses in availability occur. This topic is discussed more fully in Sec. 5.7.

$(\Delta G)_{T_A, P_A}$ , or  $(\Delta g)_{T_A, P_A}$ , is not an easy quantity to evaluate for practical fuels; it is the heating value,  $-(\Delta h)_{T_A}$ , which is usually measured. Values of  $(\Delta g)_{298}^{\circ}$  and  $(\Delta h)_{298}^{\circ}$  for selected fuel combustion reactions are given in Table 3.3. For the pure hydrocarbons they are closely comparable because at 298 K,  $\Delta\bar{s}^{\circ} \ll \Delta\bar{h}^{\circ}/T$ . For hydrogen and methanol the differences are larger, however. Because for practical fuels  $-(\Delta h)_{298}^{\circ}$  is measured directly as the heating value of the fuel, it is standard practice to use the following definition of efficiency:

$$\eta_f = \frac{W_c}{m_f Q_{HV}} \quad (3.30)$$

which was defined as the *fuel conversion efficiency* in Sec. 2.8. Note that sometimes the higher heating value is used in Eq. (3.30) and sometimes the lower heating value. Whichever value is used should be explicitly stated. The normal practice in internal combustion engine analysis is to use the lower heating value at constant pressure, since the engine overall is a steady flow device and the water in the exhaust is always in vapor form. We will use  $Q_{LHV}$  in Eq. (3.30) throughout this text. The fuel conversion efficiency is the most commonly used definition of engine efficiency because it uses an easily measured quantity, the heating value, to define the usable fuel energy supplied to the engine. For hydrocarbon fuels, since  $\Delta\tilde{h}^\circ \approx \Delta\tilde{g}^\circ$ , the fuel conversion efficiency and the availability conversion efficiency are closely comparable in value.

In practice, not all the fuel energy supplied to the engine is released by the combustion process since combustion is incomplete: the combustion efficiency [Eq. (3.27)] is less than unity. It is sometimes useful to separate out the effects of incomplete combustion by defining an efficiency which relates the actual work per cycle to the amount of fuel chemical energy released in the combustion process. We will call this the *thermal conversion efficiency*  $\eta_t$ :

$$\eta_t = \frac{W_c}{H_R(T_A) - H_P(T_A)} = \frac{W_c}{(\Delta H)_{T_A}} = \frac{W_c}{\eta_c m_f Q_{HV}} \quad (3.31)$$

Obviously the fuel conversion, thermal conversion, and combustion efficiencies are related by

$$\eta_f = \eta_c \eta_t \quad (3.32)$$

It is important to understand that there is a fundamental difference between availability conversion efficiency as defined by Eq. (3.29) [and the fuel conversion efficiency for internal combustion engines, Eq. (3.30), which closely approximates it] and the efficiency of a thermodynamic heat engine. The second law limit to the availability conversion efficiency is unity. For a thermodynamic heat engine (which experiences heat-transfer interactions with at least two heat reservoirs) the efficiency is limited to a value substantially less than unity by the temperatures of the heat reservoirs available.<sup>13</sup>

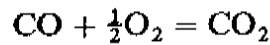
### 3.7 CHEMICALLY REACTING GAS MIXTURES

The working fluids in engines are mixtures of gases. Depending on the problem under consideration and the portion of the engine cycle in which it occurs chemical reactions may: (1) be so slow that they have a negligible effect on mixture composition (the mixture composition is essentially "frozen"); (2) be so rapid that the mixture state changes and the composition remains in chemical equilibrium; (3) be one of the rate-controlling processes that determine how the composition of the mixture changes with time.

### 3.7.1 Chemical Equilibrium

It is a good approximation for performance estimates in engines to regard the burned gases produced by the combustion of fuel and air as in chemical equilibrium.† By this we mean that the chemical reactions, by which individual species in the burned gases react together, produce and remove each species at equal rates. No net change in species composition results.

For example, if the temperature of a mass of carbon dioxide gas in a vessel is increased sufficiently, some of the  $\text{CO}_2$  molecules *dissociate* into  $\text{CO}$  and  $\text{O}_2$  molecules. If the mixture of  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{O}_2$  is in equilibrium, then  $\text{CO}_2$  molecules are dissociating into  $\text{CO}$  and  $\text{O}_2$  at the same rate as  $\text{CO}$  and  $\text{O}_2$  molecules are *recombining* in the proportions required to satisfy the equation



In combustion products of hydrocarbon fuels, the major species present at low temperatures are  $\text{N}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{O}_2$  or  $\text{CO}$  and  $\text{H}_2$ . At higher temperatures (greater than about 2200 K), these major species dissociate and react to form additional species in significant amounts. For example, the adiabatic combustion of a stoichiometric mixture of a typical hydrocarbon fuel with air produces products with species mole fractions of:  $\text{N}_2 \sim 0.7$ ;  $\text{H}_2\text{O}$ ,  $\text{CO}_2 \sim 0.1$ ;  $\text{CO}$ ,  $\text{OH}$ ,  $\text{O}_2$ ,  $\text{NO}$ ,  $\text{H}_2 \sim 0.01$ ;  $\text{H}$ ,  $\text{O} \sim 0.001$ ; and other species in lesser amounts.

The second law of thermodynamics defines the criterion for chemical equilibrium as follows. Consider a system of chemically reacting substances undergoing a constant-pressure, constant-temperature process. In the absence of shear work (and electrical work, gravity, motion, capillarity), the first law gives

$$\delta Q = dH$$

The second law gives

$$\delta Q \leq T dS$$

Combining these gives

$$dH - T dS \leq 0$$

Since we are considering constant-temperature processes, this equation holds for finite changes:

$$\Delta H - T \Delta S = \Delta G \leq 0$$

Thus, reactions can only occur (at constant pressure and temperature) if  $G$  ( $= H - TS$ ) for the products is less than  $G$  for the reactants. Hence at equilibrium

$$(\Delta G)_{p, T} = 0 \quad (3.33)$$

† This assumption is not valid late in the expansion stroke and during the exhaust process (see Sec. 4.9). Nor does it take account of pollutant formation processes (see Chap. 11).

Consider a reactive mixture of ideal gases. The reactant species  $M_a, M_b,$  etc., and product species  $M_l, M_m,$  etc., are related by the general reaction whose stoichiometry is given by

$$\nu_a M_a + \nu_b M_b + \dots = \nu_l M_l + \nu_m M_m + \dots \tag{3.34a}$$

This can be written as

$$\sum_i \nu_i M_i = 0 \tag{3.34b}$$

where the  $\nu_i$  are the stoichiometric coefficients and by convention are positive for the product species and negative for the reactant species.

Let an amount  $\delta n_a$  of  $M_a$  react with  $\delta n_b$  of  $M_b,$  etc., and produce  $\delta n_l$  of  $M_l,$   $\delta n_m$  of  $M_m,$  etc. These amounts are in proportion:

$$\delta n_i = \nu_i \delta n \tag{3.35}$$

The change in Gibbs free energy of a mixture of ideal gases, at constant pressure and temperature, as the composition changes is given by

$$(\Delta G)_{p, T} = \sum_i \tilde{\mu}_i \delta n_i \tag{3.36}$$

where  $\delta n_i$  is the change in number of moles of species  $i$  and  $\tilde{\mu}$  is the *chemical potential*. The chemical potential, an intensive property, is defined as

$$\tilde{\mu}_i = \left( \frac{\partial G}{\partial n_i} \right)_{p, T, n_j(j \neq i)} \tag{3.37}$$

It is equal in magnitude to the specific Gibbs free energy at a given temperature and pressure. For an ideal gas, it follows from Eqs. (B.13), (B.15) and (3.37) that

$$\tilde{\mu}_i = \tilde{\mu}_i^\circ(T) + \tilde{R}T \ln \frac{p_i}{p_0} \tag{3.38}$$

where  $\tilde{\mu}_i^\circ$  equals  $\tilde{g}_i^\circ,$  the standard specific Gibbs free energy of formation. The standard state pressure  $p_0$  is usually one atmosphere.

Substitution in Eq. (3.36) gives, at equilibrium,

$$\sum \left( \tilde{\mu}_i^\circ + \tilde{R}T \ln \frac{p_i}{p_0} \right) \delta n_i = 0$$

or

$$\sum \left( \tilde{\mu}_i^\circ + \tilde{R}T \ln \frac{p_i}{p_0} \right) \nu_i \delta n = 0$$

We can divide by  $\delta n$  and rearrange, to obtain

$$\sum \ln \left( \frac{p_i}{p_0} \right)^{\nu_i} = - \frac{(\sum \tilde{\mu}_i^\circ \nu_i)}{\tilde{R}T} = - \frac{\Delta G^\circ}{\tilde{R}T} = \ln K_p \tag{3.39}$$

$K_p$  is the equilibrium constant at constant pressure:

$$K_p = \prod_i \left( \frac{p_i}{p_0} \right)^{\nu_i} \tag{3.40}$$

It is obtained from the Gibbs free energy of the reaction which can be calculated from the Gibbs free energy of formation of each species in the reaction, as indicated in Eq. (3.39) above. It is a function of temperature only.

In the JANAF tables,<sup>8</sup> to simplify the calculation of equilibrium constants, values of  $\log_{10} (K_p)_i$ , the equilibrium constants of formation of one mole of each species from their elements in their standard states, are tabulated against temperature. The equilibrium constant for a specific reaction is then obtained via the relation

$$\log_{10} (K_p)_{\text{reaction}} = \sum_i \nu_i \log_{10} (K_p)_i \quad (3.41)$$

With the JANAF table values of  $(K_p)_i$ , the pressures in Eqs. (3.40) and (3.41) must be in atmospheres.

The effect of pressure on the equilibrium composition can be deduced from Eq. (3.40). Substitution of the mole fractions  $\tilde{x}_i$  and mixture pressure  $p$  gives

$$\prod_i \left( \frac{p_i}{p_0} \right)^{\nu_i} = \prod_i \left( \tilde{x}_i \frac{p}{p_0} \right)^{\nu_i} = \left( \frac{p}{p_0} \right)^{\sum_i \nu_i} \prod_i \tilde{x}_i^{\nu_i} = K_p$$

If  $\sum_i \nu_i = 0$ , changes in pressure have no effect on the composition. If  $\sum_i \nu_i > 0$  (dissociation reactions), then the mole fractions of the dissociation products decrease as pressure increases. If  $\sum_i \nu_i < 0$  (recombination reactions), the converse is true.

An equilibrium constant,  $K_c$ , based on concentrations (usually expressed in gram moles per cubic centimeter) is also used:

$$K_c = \prod_i [M_i]^{\nu_i} \quad (3.42)$$

Equation (3.40) can be used to relate  $K_p$  and  $K_c$ :

$$K_p = K_c (\bar{R}T)^{\sum_i \nu_i} \quad (3.43)$$

for  $p_0 = 1$  atmosphere. For  $\sum_i \nu_i = 0$ ,  $K_p$  and  $K_c$  are equal.

**Example 3.4.** A stoichiometric mixture of CO and O<sub>2</sub> in a closed vessel, initially at 1 atm and 300 K, is exploded. Calculate the composition of the products of combustion at 2500 K and the gas pressure.

The combustion equation is



The JANAF tables give  $\log_{10} K_p$  (equilibrium constants of formation from the elements in their standard state) at 2500 K of CO<sub>2</sub>, CO, and O<sub>2</sub> as 8.280, 6.840, and 0, respectively. Thus, the equilibrium constant for the CO combustion reaction above is, from Eq. (3.41),

$$\log_{10} K_p = 8.280 - 6.840 = 1.440$$

which gives  $K_p = 27.5$ .

If the degree of dissociation in the products is  $\alpha$  (i.e., a fraction  $\alpha$  of the  $\text{CO}_2$  formed by complete combustion is dissociated), the product composition is

$$\text{CO}_2, (1 - \alpha); \quad \text{CO}, \alpha; \quad \text{O}_2, \frac{\alpha}{2}$$

For this mixture, the number of moles of reactants  $n_R$  is  $\frac{3}{2}$ ; the number of moles of products  $n_P$  is  $(1 + \alpha/2)$ .

The ideal gas law gives

$$p_R V = n_R \bar{R} T_R \quad p_P V = n_P \bar{R} T_P$$

Thus

$$\frac{p_P}{n_P} = \frac{1}{1.5} \times \frac{2500}{300} = 5.555 \text{ atm/mol}$$

The equilibrium relation [Eq. (3.40)] gives

$$\frac{1 - \alpha}{\alpha(\alpha/2)^{1/2}} \left(\frac{n_P}{p_P}\right)^{1/2} = 27.5$$

which can be solved to give  $\alpha = 0.074$ .

The composition of the products in mole fractions is, therefore,

$$x_{\text{CO}_2} = \frac{1 - \alpha}{n_P} = 0.893$$

$$x_{\text{CO}} = \frac{\alpha}{n_P} = 0.071$$

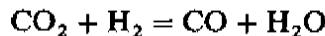
$$x_{\text{O}_2} = \frac{\alpha/2}{n_P} = 0.037$$

The pressure of the product mixture is

$$p = 5.555 n_P = 5.76 \text{ atm}$$

**Example 3.5.** In fuel-rich combustion product mixtures, equilibrium between the species  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ , and  $\text{H}_2$  is often assumed to determine the burned gas composition. For  $\phi = 1.2$ , for  $\text{C}_8\text{H}_{18}$ -air combustion products, determine the mole fractions of the product species at 1700 K.

The reaction relating these species (often called the water gas reaction) is

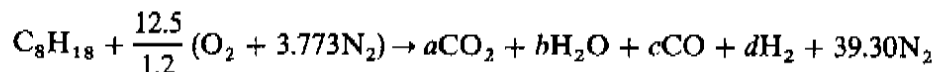


From the JANAF tables,  $\log_{10} K_p$  of formation for these species at 1700 K are:  $\text{CO}_2$ , 12.180;  $\text{H}_2$ , 0;  $\text{CO}$ , 8.011;  $\text{H}_2\text{O}(g)$ , 4.699. The equilibrium constant for the above reaction is, from Eq. (3.41),

$$\log_{10} K_p = 8.011 + 4.699 - 12.180 = 0.530$$

from which  $K_p = 3.388$ .

The combustion reaction for  $\text{C}_8\text{H}_{18}$ -air with  $\phi = 1.2$  can be written



A carbon balance gives:  $a + c = 8$

A hydrogen balance gives:  $2b + 2d = 18$

An oxygen balance gives:  $2a + b + c = 20.83$

The equilibrium relation gives  $(bc)/(ad) = 3.388$  (since the equilibrated reaction has the same number of moles as there are reactants or products, the moles of each species can be substituted for the partial pressures).

These four equations can be solved to obtain

$$c^2 - 19.3c + 47.3 = 0$$

which gives  $c = 2.89$ ,  $a = 5.12$ ,  $b = 7.72$ , and  $d = 1.29$ . The total number of moles of products is

$$a + b + c + d + 39.3 = 56.3$$

and the mole fractions of the species in the burned gas mixture are

$$\text{CO}_2, 0.0908; \quad \text{H}_2\text{O}, 0.137; \quad \text{CO}, 0.051; \quad \text{H}_2, 0.023; \quad \text{N}_2, 0.698$$

Our development of the equilibrium relationship for one reaction has placed no restrictions on the occurrence of simultaneous equilibria. Consider a mixture of  $N$  reacting gases in equilibrium. If there are  $C$  chemical elements, conservation of elements will provide  $C$  equations which relate the concentrations of these  $N$  species. Any set of  $(N - C)$  chemical reactions, each in equilibrium, which includes each species at least once will then provide the additional equations required to determine the concentration of each species in the mixture. Unfortunately, this complete set of equations is a coupled set of  $C$  linear and  $(N - C)$  nonlinear equations which is difficult to solve for cases where  $(N - C) > 2$ . For complex systems such as this, the following approach to equilibrium composition calculations is now more widely used.

Standardized computer methods for the calculation of complex chemical equilibrium compositions have been developed. A generally available and well-documented example is the NASA program of this type.<sup>14</sup> The approach taken is to minimize explicitly the Gibbs free energy of the reacting mixture (at constant temperature and pressure) subject to the constraints of element mass conservation. The basic equations for the NASA program are the following.

If the stoichiometric coefficients  $a_{ij}$  are the number of kilomoles of element  $i$  per kilomole of species  $j$ ,  $b_i^*$  is the number of kilomoles of element  $i$  per kilogram of mixture, and  $n_j$  is the number of kilomoles of species  $j$  per kilogram of mixture, element mass balance constraints are

$$\sum_{j=1}^n a_{ij} n_j - b_i^* = 0 \quad \text{for } i = 1, 2, \dots, l \quad (3.44)$$

The Gibbs free energy per kilogram of mixture is

$$g = \sum_{j=1}^n \bar{\mu}_j n_j \quad (3.45)$$



For gases, the chemical potential  $\tilde{\mu}_j$  is

$$\tilde{\mu}_j = \tilde{\mu}_j^\circ + \tilde{R}T \ln \left( \frac{n_j}{n} \right) + \tilde{R}T \ln p \quad (3.46)$$

where  $\tilde{\mu}_j^\circ$  is the chemical potential in the standard state and  $p$  is the mixture pressure in atmospheres. Using the method of lagrangian multipliers, the term

$$G = g + \sum_{i=1}^l \lambda_i \sum_{j=1}^n (a_{ij} n_j - b_i^*)$$

is defined. The condition for equilibrium then becomes

$$\delta G = \sum_{j=1}^n \left( \mu_j + \sum_{i=1}^l \lambda_i a_{ij} \right) \delta n_j + \sum_{i=1}^l \sum_{j=1}^n (a_{ij} n_j - b_i^*) \delta \lambda_i = 0 \quad (3.47)$$

Treating the variations  $\delta n_j$  and  $\delta \lambda_i$  as independent gives

$$\tilde{\mu}_j + \sum_{i=1}^l \lambda_i a_{ij} = 0 \quad \text{for } j = 1, \dots, n \quad (3.48)$$

and the original mass balance equation (3.44). Equations (3.44) and (3.48) permit the determination of equilibrium compositions for thermodynamic states specified by a temperature  $T$  and pressure  $p$ .

In the NASA program, the thermodynamic state may be specified by other pairs of state variables: enthalpy and pressure (useful for constant-pressure combustion processes); temperature and volume; internal energy and volume (useful for constant-volume combustion processes); entropy and pressure, and entropy and volume (useful for isentropic compressions and expansions). The equations required to obtain mixture composition are not all linear in the composition variables and an iteration procedure is generally required to obtain their solution. Once the composition is determined, additional relations, such as those in App. B which define the thermodynamic properties of gas mixtures, must then be used.

For each species, standard state enthalpies  $\tilde{h}^\circ$  are obtained by combining standard enthalpies of formation at the datum temperature (298.15 K)  $\Delta \tilde{h}_{f298}^\circ$  with sensible enthalpies ( $\tilde{h}^\circ - \tilde{h}_{298}^\circ$ ), i.e.,

$$\tilde{h}^\circ = \Delta \tilde{h}_{f298}^\circ + (\tilde{h}^\circ - \tilde{h}_{298}^\circ) \quad (3.49)$$

For the elements in their reference state,  $\Delta \tilde{h}_{f298}^\circ$  is zero [the elements important in combustion are C (solid, graphite),  $\text{H}_2(g)$ ,  $\text{O}_2(g)$ ,  $\text{N}_2(g)$ ].

For each species, the thermodynamic quantities specific heat, enthalpy, and entropy as functions of temperature are given in the form:

$$\frac{\tilde{c}_p^\circ}{\tilde{R}} = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4 \quad (3.50a)$$

$$\frac{\tilde{h}^\circ}{\tilde{R}T} = a_1 + \frac{a_2}{2} T + \frac{a_3}{3} T^2 + \frac{a_4}{4} T^3 + \frac{a_5}{5} T^4 + \frac{a_6}{T} \quad (3.50b)$$

$$\frac{\tilde{s}^{\circ}}{\bar{R}} = a_1 \ln T + a_2 T + \frac{a_3}{2} T^2 + \frac{a_4}{3} T^3 + \frac{a_5}{4} T^4 + a_7 \quad (3.50c)$$

The coefficients are obtained by least-squares matching with thermodynamic property data from the JANAF tables. Usually two sets of coefficients are included for two adjacent temperature intervals (in the NASA program these are 300 to 1000 K and 1000 to 5000 K) (see Sec. 4.7).

In some equilibrium programs, the species to be included in the mixture must be specified as an input to the calculation. In the NASA program, all allowable species are included in the calculation, though species may be specifically omitted from consideration.

For each reactant composition and pair of thermodynamic state variables, the program calculates and prints out the following:

1. *Thermodynamic mixture properties* (obtained from the equilibrium composition and the appropriate gas mixture rule; see App. B).  $p$ ,  $T$ ,  $\rho$ ,  $h$ ,  $s$ ,  $M$ ,  $(\partial \ln V / \partial \ln p)_T$ ,  $(\partial \ln V / \partial \ln T)_p$ ,  $c_p$ ,  $\gamma_s$ , and  $a$  (sound speed)
2. *Equilibrium composition*. Mole fractions of each species (which are present in significant amounts),  $\tilde{x}_i$

Figure 3-10 shows how the equilibrium composition of the products of combustion of isooctane-air mixtures at selected temperatures and 30 atm pressure varies with the equivalence ratio. At low temperatures, the products are  $N_2$ ,  $CO_2$ ,  $H_2O$ , and  $O_2$  for lean mixtures and  $N_2$ ,  $CO_2$ ,  $H_2O$ ,  $CO$ , and  $H_2$  for rich mixtures. As temperature increases, the burned-gas mixture composition becomes much more complex with dissociation products such as  $OH$ ,  $O$ , and  $H$  becoming significant.

Figure 3-11 shows adiabatic flame temperatures for typical engine conditions as a function of the equivalence ratio, obtained with the NASA program using the methodology of Sec. 3.5.4. The isooctane-air unburned mixture state was 700 K and 10 atm. Flame temperatures for adiabatic combustion at constant pressure (where  $p_R$  and  $H_R$  are specified) and at constant volume (where  $V_R$  and  $U_R$  are specified) are shown. Flame temperatures at constant volume are higher, because the final pressure is higher and dissociation is less. Maximum flame temperatures occur slightly rich of stoichiometric.

### 3.7.2 Chemical Reaction Rates

Whether a system is in chemical equilibrium depends on whether the time constants of the controlling chemical reactions are short compared with time scales over which the system conditions (temperature and pressure) change. Chemical processes in engines are often not in equilibrium. Important examples of nonequilibrium phenomena are the flame reaction zone where the fuel is oxidized, and the air-pollutant formation mechanisms. Such nonequilibrium processes are controlled by the rates at which the actual chemical reactions which convert

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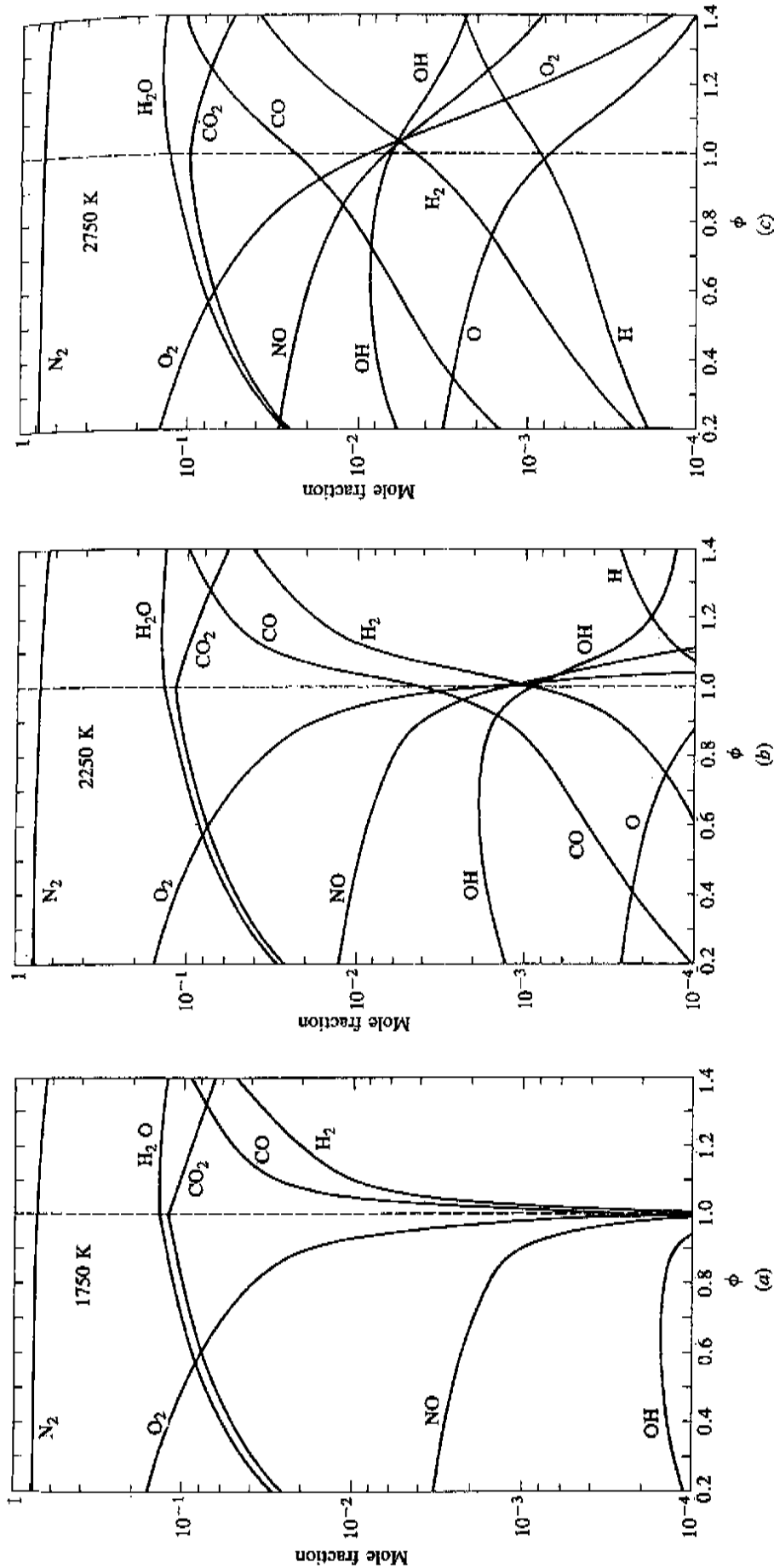
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**FIGURE 3-10** Mole fractions of equilibrium combustion products of isoctane-air mixtures as a function of fuel/air equivalence ratio at 30 atmospheres and (a) 1750 K; (b) 2250 K; and (c) 2750 K.

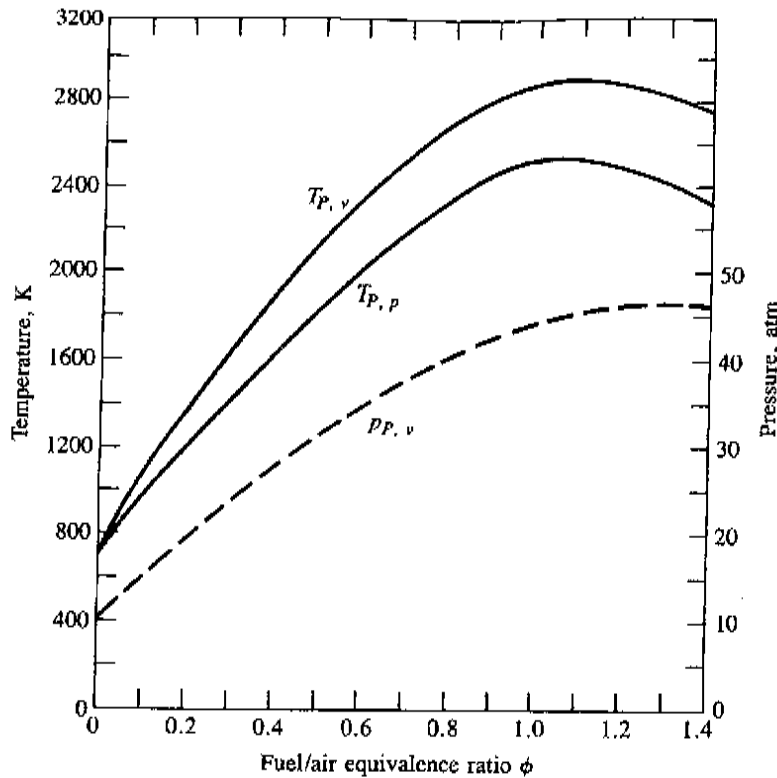


FIGURE 3-11

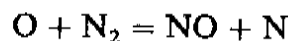
Equilibrium product temperatures for constant-volume ( $T_{P,v}$ ) and constant-pressure ( $T_{P,p}$ ) adiabatic combustion of isooctane-air mixture initially at 700 K and 10 atm, as a function of fuel/air equivalence ratio. Pressure ( $p_{P,v}$ ) is equilibrium pressure for adiabatic constant-volume combustion.

reactants to products occur. The rates at which chemical reactions proceed depend on the concentration of the reactants, temperature, and whether any catalyst is present. This field is called chemical kinetics and some of its basic relations will now be reviewed.<sup>2</sup>

Most of the chemical reactions of interest in combustion are binary reactions, where two reactant molecules,  $M_a$  and  $M_b$ , with the capability of reacting together collide and form two product molecules,  $M_c$  and  $M_d$ ; i.e.,



An important example of such a reaction is the rate-controlling step in the process by which the pollutant nitric oxide, NO, forms:



This is a second-order reaction since the stoichiometric coefficients of the reactants  $\nu_a$  and  $\nu_b$  are each unity and sum to 2. (The only first-order reactions are decomposition processes.) Third-order reactions are important in combustion, also. Examples are the recombination reactions by which radical species such as H, O, and OH combine during the final stage of the fuel oxidation process: e.g.,



M is any molecule (such as N<sub>2</sub>) which takes part in the collision and carries away the excess energy.

The law of mass action states that the rate at which product species are produced and the rate at which reactant species are removed is proportional to the product of the concentrations of reactant species, with the concentration of each species raised to the power of its stoichiometric coefficient  $v_i$ . Thus, for reaction (3.51) above, the reaction rate  $R^+$  in the forward (+) direction, reactants to products, is given by

$$R^+ = -\frac{d[M_a]^+}{dt} = \frac{d[M_c]^+}{dt} = k^+[M_a][M_b] \quad (3.53)$$

If the reaction can also proceed in the reverse (-) direction, then the backward rate  $R^-$  is given by

$$R^- = -\frac{d[M_c]^-}{dt} = \frac{d[M_a]^-}{dt} = k^-[M_c][M_d] \quad (3.54)$$

$k^+$  and  $k^-$  are the rate constants in the forward and reverse directions for this reaction. The net rate of production of products or removal of reactants is, therefore,

$$\begin{aligned} R^+ - R^- &= \frac{d[M_c]^+}{dt} + \frac{d[M_c]^-}{dt} = -\frac{d[M_a]^+}{dt} - \frac{d[M_a]^-}{dt} \\ &= k^+[M_a][M_b] - k^-[M_c][M_d] \end{aligned} \quad (3.55)$$

These results can be stated more generally as follows. Any reaction can be written as

$$\sum_{i=1}^n v_{R_i} M_{R_i} = \sum_{i=1}^m v_{P_i} M_{P_i} \quad (3.56)$$

where  $v_i$  is the stoichiometric coefficient of species  $M_i$ , subscripts  $R$  and  $P$  denote reactants and products, respectively, and there are  $n$  reactant species and  $m$  product species. The forward reaction rate  $R^+$  and the reverse reaction rate  $R^-$  are given by

$$\begin{aligned} R^+ &= k^+ \prod_{i=1}^n [M_{R_i}]^{v_{R_i}} \\ R^- &= k^- \prod_{i=1}^m [M_{P_i}]^{v_{P_i}} \end{aligned} \quad (3.57)$$

The net rate of removal of reactant species  $M_{R_i}$  is

$$-\frac{d[M_{R_i}]}{dt} = v_{R_i}(R^+ - R^-) \quad (3.58a)$$

and the net rate of production of product species  $M_{P_i}$  is

$$\frac{d[M_{P_i}]}{dt} = \nu_{P_i}(R^+ - R^-) \quad (3.58b)$$

The rate constants,  $k$ , usually follow the Arrhenius form:

$$k = A \exp\left(-\frac{E_A}{RT}\right) \quad (3.59)$$

where  $A$  is called the frequency or preexponential factor and may be a (moderate) function of temperature;  $E_A$  is the activation energy. The Boltzmann factor  $\exp(-E_A/RT)$  defines the fraction of all collisions that have an energy greater than  $E_A$ —i.e., sufficient energy to make the reaction take place. The functional dependence of  $k$  on  $T$  and the constants in the Arrhenius form, Eq. (3.59), if that is appropriate, are determined experimentally.

At equilibrium, the forward and reverse reaction rates are equal. Then, from Eq. (3.55), with  $R^+ - R^- = 0$ :

$$\frac{k^+}{k^-} = \frac{[M_c][M_d]}{[M_a][M_b]} = K_c$$

where  $K_c$  is the equilibrium constant based on concentrations defined by Eq. (3.42). It can be related to  $K_p$ , the equilibrium constant based on partial pressures, by Eq. (3.43).

The chemical reaction mechanisms of importance in combustion are much more complex than the above illustrations of rate-controlled processes. Such mechanisms usually involve both parallel and sequential interdependent reactions. The methodology reviewed above still holds; however, one must sum algebraically the forward and reverse rates of all the reactions which produce (or remove) a species of interest. In such complex mechanisms it is often useful to assume that (some of) the reactive intermediate species or radicals are in *steady state*. That is, these radicals react so quickly once they are formed that their concentrations do not rise but are maintained in steady state with the species with which they react. The net rate at which their concentration changes with time is set equal to zero.

## PROBLEMS

- 3.1. Isooctane is supplied to a four-cylinder spark-ignition engine at 2 g/s. Calculate the air flow rate for stoichiometric combustion. If the engine is operating at 1500 rev/min, estimate the mass of fuel and air entering each cylinder per cycle. The engine displaced volume is 2.4 liters. What is the volumetric efficiency?
- 3.2. Calculate the exhaust gas composition of a butane-fueled spark-ignition engine operating with equivalence ratio of 0.9. Assume the fuel is fully burned within the cylinder. Butane is  $C_4H_{10}$ .

- 3.3. The molar composition of dry exhaust gas of a propane-fueled SI engine is given below (water was removed before the measurement). Calculate the equivalence ratio.

(3.58b)

$$\text{CO}_2 = 10.8\%, \quad \text{O}_2 = 4.5\%, \quad \text{CO} = 0\%, \quad \text{H}_2 = 0\%$$

- 3.4. Evaluate and compare the lower heating values per unit mass of stoichiometric mixture and per unit volume of stoichiometric mixture (at standard atmospheric conditions) for methane, isooctane, methyl alcohol, and hydrogen. Assume the fuel is fully vaporized.

(3.59)

- 3.5. The measured engine fuel flow rate is 0.4 g/s, air flow rate is 5.6 g/s, and exhaust gas composition (measured dry) is  $\text{CO}_2 = 13.0\%$ ,  $\text{CO} = 2.8\%$  with  $\text{O}_2$  essentially zero. Unburned hydrocarbon emissions can be neglected. Compare the equivalence ratio calculated from the fuel and air flow with the equivalence ratio calculated from exhaust gas composition. The fuel is gasoline with a H/C ratio of 1.87. Assume a  $\text{H}_2$  concentration equal to one-third the CO concentration.

- 3.6. The brake fuel conversion efficiency of an engine is 0.3. The mechanical efficiency is 0.8. The combustion efficiency is 0.94. The heat losses to the coolant and oil are 60 kW. The fuel chemical energy entering the engine per unit time,  $\dot{m}_f Q_{HV}$ , is 190 kW. What percentage of this energy becomes (a) brake work; (b) friction work; (c) heat losses; (d) exhaust chemical energy; (e) exhaust sensible energy.

- 3.7. An upper estimate can be made of the amount of NO formed in an engine from considering the equilibrium of the reaction  $\text{N}_2 + \text{O}_2 = 2\text{NO}$ . Calculate the NO concentration at equilibrium at 2500 K and 30 atm.  $\log_{10} K_p = -1.2$  for this reaction at 2500 K. Assume N/O ratio in the combustion products is 15.  $\text{N}_2$ ,  $\text{O}_2$ , and NO are the only species present.

- 3.8. Carbon monoxide reacts with air at 1 atm and 1000 K in an exhaust gas reactor. The mole fractions of the exhaust gas-air mixture flowing into the reactor are  $\text{CO}$ , 3%;  $\text{O}_2$ , 7%;  $\text{N}_2$ , 74%;  $\text{CO}_2$ , 6%;  $\text{H}_2\text{O}$ , 10%.

(a) Calculate the concentration of CO and  $\text{O}_2$  in gram moles per  $\text{cm}^3$  in the entering mixture.

(b) The rate of reaction is given by

$$d[\text{CO}]/dt = -4.3 \times 10^{11} \times [\text{CO}][\text{O}_2]^{0.25} \exp[-E/(RT)]$$

[ ] denotes concentration in gram moles per  $\text{cm}^3$ ,  $E/R = 20,000$  K. Calculate the initial reaction rate of CO,  $d[\text{CO}]/dt$ : time is in seconds.

(c) The equilibrium constant  $K_p$  for the reaction  $\text{CO} + \frac{1}{2}\text{O}_2 = \text{CO}_2$  at 1000 K is  $10^{10}$ . Find the equilibrium CO concentration.

(d) Determine the time to reach this equilibrium concentration of CO using the initial reaction rate. (The actual time will be longer but this calculation indicates approximately the time required.)

- 3.9. The exhaust gases of a hydrogen-fueled engine contain 22.3 percent  $\text{H}_2\text{O}$ , 7.44 percent  $\text{O}_2$ , and 70.2 percent  $\text{N}_2$ . At what equivalence ratio is it operating?

- 3.10. Gas is sampled at 1 atmosphere pressure from the exhaust manifold of an internal combustion engine and analyzed. The mole fractions of species in the exhaust are:

$$\text{H}_2\text{O}, 0.0468; \quad \text{CO}_2, 0.0585; \quad \text{O}_2, 0.123; \quad \text{N}_2, 0.772$$

Other species such as CO and unburned hydrocarbons can be neglected.

(a) The fuel is a synthetic fuel derived from coal containing only carbon and hydrogen. What is the ratio of hydrogen atoms to carbon atoms in the fuel?

- (b) Calculate the fuel/air equivalence ratio at which this engine is operating.
- (c) Is the internal combustion engine a conventional spark-ignition or a diesel engine? Explain.
- (d) The engine has a displaced volume of 2 liters. Estimate approximately the percentage by which the fuel flow rate would be increased if this engine were operated at its maximum load at this same speed (2000 rev/min). Explain briefly what limits the equivalence ratio at maximum load.
- 3.11. The following are approximate values of the relative molecular mass (molecular weights): oxygen  $O_2$ , 32; nitrogen  $N_2$ , 28; hydrogen  $H_2$ , 2; carbon C, 12. Determine the stoichiometric fuel/air and air/fuel ratios on a mass basis, and the lower heating value per unit mass of stoichiometric mixture for the following fuels:
- Methane ( $CH_4$ ), isooctane ( $C_8H_{18}$ ), benzene ( $C_6H_6$ ), hydrogen ( $H_2$ ), methyl alcohol ( $CH_3OH$ )
- Heating values for these fuels are given in App. D.
- 3.12. Liquid petroleum gas (LPG) is used to fuel spark-ignition engines. A typical sample of the fuel consists of
- 70 percent by volume propane  $C_3H_8$   
5 percent by volume butane  $C_4H_{10}$   
25 percent by volume propene  $C_3H_6$
- The higher heating values of the fuels are: propane, 50.38 MJ/kg; butane, 49.56 MJ/kg; propylene (propene), 48.95 MJ/kg.
- (a) Work out the overall combustion reaction for stoichiometric combustion of 1 mole of LPG with air, and the stoichiometric  $F/A$  and  $A/F$ .
- (b) What are the higher and lower heating values for combustion of this fuel with excess air, per unit mass of LPG?
- 3.13. A spark-ignition engine is operated on isooctane fuel ( $C_8H_{18}$ ). The exhaust gases are cooled, dried to remove water, and then analyzed for  $CO_2$ ,  $CO$ ,  $H_2$ ,  $O_2$ . Using the overall combustion reaction for a range of equivalence ratios from 0.5 to 1.5, calculate the mole fractions of  $CO_2$ ,  $CO$ ,  $H_2$ , and  $O_2$  in the dry exhaust gas, and plot the results as a function of equivalence ratio. Assume:
- (a) that all the fuel is burnt inside the engine (almost true) and that the ratio of moles  $CO$  to moles  $H_2$  in the exhaust is 3 : 1, and
- (b) that there is no hydrogen in the exhaust for lean mixtures.
- For high-power engine operation the air/fuel ratio is 14 : 1. What is the exhaust gas composition, in mole fractions, before the water is removed?

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# CHAPTER

# 7

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## SI ENGINE FUEL METERING AND MANIFOLD PHENOMENA

### 7.1 SPARK-IGNITION ENGINE MIXTURE REQUIREMENTS

The task of the engine induction and fuel systems is to prepare from ambient air and fuel in the tank an air-fuel mixture that satisfies the requirements of the engine over its entire operating regime. In principle, the optimum air/fuel ratio for a spark-ignition engine is that which gives the required power output with the lowest fuel consumption, consistent with smooth and reliable operation. In practice, the constraints of emissions control may dictate a different air/fuel ratio, and may also require the recycling of a fraction of the exhaust gases (EGR) into the intake system. The relative proportions of fuel and air that provide the lowest fuel consumption, smooth reliable operation, and satisfy the emissions requirements, at the required power level, depend on engine speed and load. Mixture requirements and preparation are usually discussed in terms of the air/fuel ratio or fuel/air ratio (see Sec. 2.9) and percent EGR [see Eq. (4.2)]. While the fuel metering system is designed to provide the appropriate fuel flow for the *actual* air flow at each speed and load, the relative proportions of fuel and air can be stated more generally in terms of the fuel/air equivalence ratio  $\phi$ , which is the actual fuel/air ratio normalized by dividing by the stoichiometric fuel/air ratio [Eq.

(3.8)]. The combustion characteristics of fuel-air mixtures and the properties of combustion products, which govern engine performance, efficiency, and emissions, correlate best for a wide range of fuels relative to the stoichiometric mixture proportions. Where appropriate, therefore, the equivalence ratio will be used as the defining parameter. A typical value for the stoichiometric air/fuel ratio of gasoline is 14.6.† Thus, for gasoline,

$$\phi \approx \frac{14.6}{A/F} \quad (7.1)$$

The effects of equivalence ratio variations on engine combustion, emissions, and performance are discussed more fully in Chaps. 9, 11, and 15. A brief summary is sufficient here. Mixture requirements are different for full-load (wide-open throttle) and for part-load operation. At the former operating condition, complete utilization of the *inducted air* to obtain maximum power for a given displaced volume is the critical issue. Where less than the maximum power at a given speed is required, efficient utilization of the *fuel* is the critical issue. At wide-open throttle, maximum power for a given volumetric efficiency is obtained with rich-of-stoichiometric mixtures,  $\phi \approx 1.1$  (see the discussion of the fuel-air cycle results in Sec. 5.5.3). Mixtures that are richer still are sometimes used to increase volumetric efficiency by increasing the amount of charge cooling that accompanies fuel vaporization [see Eq. (6.5)], thereby increasing the inducted air density.

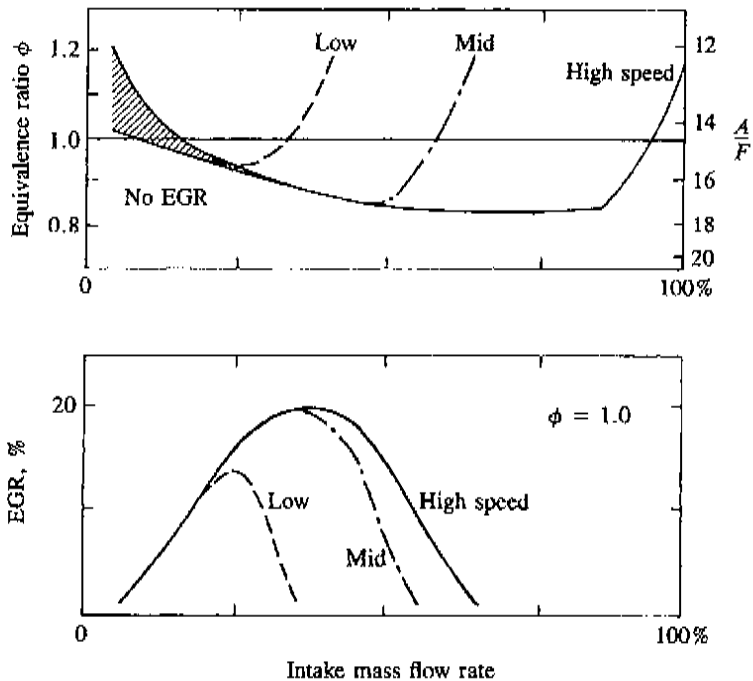
At part-load (or part-throttle) operating conditions, it is advantageous to dilute the fuel-air mixture, either with excess air or with recycled exhaust gas. This dilution improves the fuel conversion efficiency for three reasons:<sup>1</sup> (1) the expansion stroke work for a given expansion ratio is increased as a result of the change in thermodynamic properties of the burned gases—see Secs. 5.5.3 and 5.7.4; (2) for a given mean effective pressure, the intake pressure increases with increasing dilution, so pumping work decreases—see Fig. 5-10; (3) the heat losses to the walls are reduced because the burned gas temperatures are lower. In the absence of strict engine  $\text{NO}_x$  emission requirements, excess air is the obvious diluent, and at part throttle engines have traditionally operated lean. When tight control of  $\text{NO}_x$ , HC, and CO emissions is required, operation of the engine with a stoichiometric mixture is advantageous so that a three-way catalyst‡ can be used to clean up the exhaust. The appropriate diluent is then recycled exhaust gases which significantly reduces  $\text{NO}_x$  emissions from the engine itself. The amount of diluent that the engine will tolerate at any given speed and load depends on the details of the engine's combustion process. Increasing excess air

† Typical value only. Most gasolines have  $(A/F)_s$  in the range 14.4 to 14.7.  $(A/F)_s$  could lie between 14.1 and 15.2.

‡ A three-way catalyst system, when operated with a close-to-stoichiometric mixture, achieves substantial reductions in  $\text{NO}_x$ , CO, and HC emissions simultaneously; see Sec. 11.6.2.

or the amount of recycled exhaust slows down the combustion process and increases its variability from cycle to cycle. A certain minimum combustion repeatability or stability level is required to maintain smooth engine operation. Deterioration in combustion stability therefore limits the amount of dilution an engine can tolerate. As load decreases, less dilution of the *fresh* mixture can be tolerated because the internal dilution of the mixture with residual gas increases (see Sec. 6.4). At idle conditions, the fresh mixture will not usually tolerate any EGR and may need to be stoichiometric or fuel-rich to obtain adequate combustion stability.

Mixture composition requirements over the engine load and speed range are illustrated schematically for the two approaches outlined above in Fig. 7-1. If stoichiometric operation and EGR are not required for emissions control, as load increases the mixture is leaned out from a fuel-rich or close-to-stoichiometric composition at very light load. As wide-open throttle operation is approached at each engine speed, the mixture is steadily enriched to rich-of-stoichiometric at the maximum bmep point. With the stoichiometric operating conditions required for three-way-catalyst-equipped engines, when EGR is used, the percentage of recycled exhaust increases from zero at light load to a maximum at mid-load, and then decreases to zero as wide-open throttle conditions are approached so maximum bmep can be obtained. Combinations of these strategies are possible. For example, lean operation at light load can be used for best efficiency, and



**FIGURE 7-1**  
 Typical mixture requirements for two common operating strategies. Top diagram shows equivalence ratio variation with intake mass flow rate (percent of maximum flow at rated speed) at constant low, mid, and high engine speeds. Bottom diagram shows recycled exhaust (EGR) schedule as a function of intake flow rate, for low, mid, and high speeds for stoichiometric operation.

stoichiometric mixtures (with a three-way catalyst) and/or EGR can be used at mid loads to control  $\text{NO}_x$  emissions.

In practical spark-ignition engine induction systems, the fuel and air distribution between engine cylinders is not uniform (and also varies in each individual cylinder on a cycle-by-cycle basis). A spread of one or more air/fuel ratios between the leanest and richest cylinders over the engine's load and speed range is not uncommon in engines with conventional carburetors. The average mixture composition must be chosen to avoid excessive combustion variability in the leanest operating cylinder. Thus, as the spread in mixture nonuniformity increases, the mean equivalence ratio must be moved toward stoichiometric and away from the equivalence ratio which gives minimum fuel consumption.

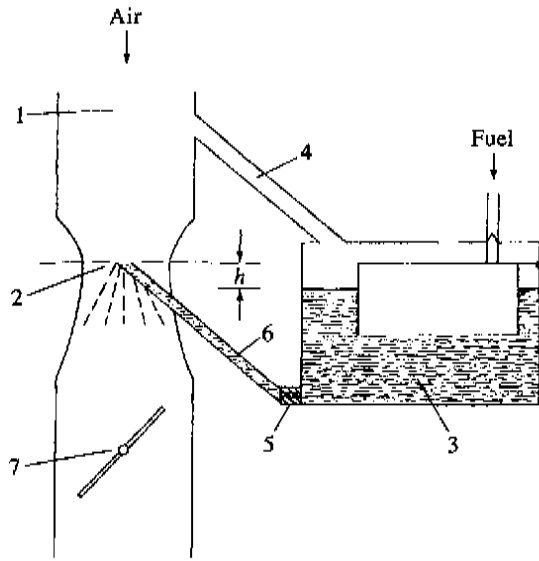
## 7.2 CARBURETORS

### 7.2.1 Carburetor Fundamentals

A carburetor has been the most common device used to control the fuel flow into the intake manifold and distribute the fuel across the air stream. In a carburetor, the air flows through a converging-diverging nozzle called a venturi. The pressure difference set up between the carburetor inlet and the throat of the nozzle (which depends on the air flow rate) is used to meter the appropriate fuel flow for that air flow. The fuel enters the air stream through the fuel discharge tube or ports in the carburetor body and is atomized and convected by the air stream past the throttle plate and into the intake manifold. Fuel evaporation starts within the carburetor and continues in the manifold as fuel droplets move with the air flow and as liquid fuel flows over the throttle and along the manifold walls. A modern carburetor which meters the appropriate fuel flow into the air stream over the complete engine operating range is a highly developed and complex device. There are many types of carburetors; they share the same basic concepts which we will now examine.

Figure 7-2 shows the essential components of an elementary carburetor. The air enters the intake section of the carburetor (1) from the air cleaner which removes suspended dust particles. The air then flows into the carburetor venturi (a converging-diverging nozzle) (2) where the air velocity increases and the pressure decreases. The fuel level is maintained at a constant height in the float chamber (3) which is connected via an air duct (4) to the carburetor intake section (1). The fuel flows through the main jet (a calibrated orifice) (5) as a result of the pressure difference between the float chamber and the venturi throat and through the fuel discharge nozzle (6) into the venturi throat where the air stream atomizes the liquid fuel. The fuel-air mixture flows through the diverging section of the venturi where the flow decelerates and some pressure recovery occurs. The flow then passes the throttle valve (7) and enters the intake manifold.

Note that the flow may be unsteady even when engine load and speed are constant, due to the periodic filling of each of the engine cylinders which draws air through the carburetor venturi. The induction time,  $1/(2N)$  (20 ms at 1500



**FIGURE 7-2**  
Schematic of elementary carburetor.

- 1 Inlet section
- 2 Venturi throat
- 3 Float chamber
- 4 Pressure equalizing passage
- 5 Calibrated orifice
- 6 Fuel discharge tube
- 7 Throttle plate

rev/min), is the characteristic time of this periodic cylinder filling process. Generally, the characteristic times of changes in throttle setting are longer; it takes several engine operating cycles to reestablish steady-state engine operation after a sudden change in throttle position.<sup>2</sup> It is usually assumed that the flow processes in the carburetor can be modeled as quasi steady.

**FLOW THROUGH THE VENTURI.** Equation (C.8) in App. C relates the mass flow rate of a gas through a flow restriction to the upstream stagnation pressure and temperature, and the pressure at the throat. For the carburetor venturi:

$$\dot{m}_a = \frac{C_{D_T} A_T p_0}{\sqrt{RT_0}} \left( \frac{p_T}{p_0} \right)^{1/\gamma} \left\{ \frac{2\gamma}{\gamma - 1} \left[ 1 - \left( \frac{p_T}{p_0} \right)^{(\gamma-1)/\gamma} \right] \right\}^{1/2} \quad (7.2)$$

where  $C_{D_T}$  and  $A_T$  are the discharge coefficient and area of the venturi throat, respectively. If we assume the velocity at the carburetor inlet can be neglected, Eq. (7.2) can be rearranged in terms of the pressure drop from upstream conditions to the venturi throat for the air stream,  $\Delta p_a = p_0 - p_T$ , as

$$\dot{m}_a = C_{D_T} A_T (2\rho_{a0} \Delta p_a)^{1/2} \Phi \quad (7.3)$$

where

$$\Phi = \left[ \left( \frac{\gamma}{\gamma - 1} \right) \frac{(p_T/p_0)^{2/\gamma} - (p_T/p_0)^{(\gamma+1)/\gamma}}{1 - (p_T/p_0)} \right]^{1/2} \quad (7.4)$$

and accounts for the effects of compressibility. Figure C-3 shows the value of  $\Phi$  as a function of pressure drop. For the normal carburetor operating range, where  $\Delta p_a/p_0 \leq 0.1$ , the effects of compressibility which reduce  $\Phi$  below 1.0 are small.

**FLOW THROUGH THE FUEL ORIFICE.** Since the fuel is a liquid and therefore essentially incompressible, the fuel flow rate through the main fuel jet is given by

Eq. (C.2) in App. C as

$$\dot{m}_f = C_{D_o} A_o (2\rho_f \Delta p_f)^{1/2} \quad (7.5)$$

where  $C_{D_o}$  and  $A_o$  are the discharge coefficient and area of the orifice, respectively,  $\Delta p_f$  is the pressure difference across the orifice, and the orifice area is assumed much less than the passage area. Usually, the fuel level in the float chamber is held below the fuel discharge nozzle, as shown in Fig. 7-2, to prevent fuel spillage when the engine is inclined to the horizontal (e.g., in a vehicle on a slope). Thus,

$$\Delta p_f = \Delta p_a - \rho_f gh$$

where  $h$  is typically of order 10 mm.

The discharge coefficient  $C_{D_o}$  in Eq. (7.5) represents the effect of all deviations from the ideal one-dimensional isentropic flow. It is influenced by many factors of which the most important are the following: (1) fluid mass flow rate; (2) orifice length/diameter ratio; (3) orifice/approach-area ratio; (4) orifice surface area; (5) orifice surface roughness; (6) orifice inlet and exit chamfers; (7) fluid specific gravity; (8) fluid viscosity; and (9) fluid surface tension. The use of the orifice Reynolds number,  $Re_o = \rho VD_o/\mu$ , as a correlating parameter for the discharge coefficient accounts for effects of mass flow rate, fluid density and viscosity, and length scale to a good first approximation. The discharge coefficient of a typical carburetor main fuel-metering system orifice increases smoothly with increasing  $Re_o$ .<sup>3</sup>

**CARBURETOR PERFORMANCE.** The air/fuel ratio delivered by this carburetor is given by

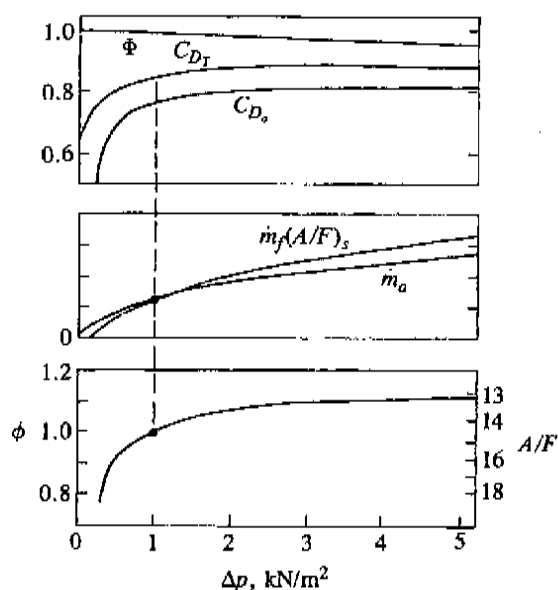
$$\left(\frac{A}{F}\right) = \frac{\dot{m}_a}{\dot{m}_f} = \left(\frac{C_{D_T}}{C_{D_o}}\right) \left(\frac{A_T}{A_o}\right) \left(\frac{\rho_{a0}}{\rho_f}\right)^{1/2} \left(\frac{\Delta p_a}{\Delta p_a - \rho_f gh}\right)^{1/2} \Phi \quad (7.6)$$

and the equivalence ratio  $\phi [= (A/F)_s / (A/F)]$  by

$$\phi = \frac{(A/F)_s}{\Phi} \left(\frac{C_{D_o}}{C_{D_T}}\right) \left(\frac{A_o}{A_T}\right) \left(\frac{\rho_f}{\rho_{a0}}\right)^{1/2} \left(1 - \frac{\rho_f gh}{\Delta p_a}\right)^{1/2} \quad (7.7)$$

where  $(A/F)_s$  is the stoichiometric air/fuel ratio. The terms  $A_o$ ,  $A_T$ ,  $\rho_f$ , and  $\rho_{a0}$  are all constant for a given carburetor, fuel, and ambient conditions. Also, except for very low flows,  $\rho_f gh \ll \Delta p_a$ . The discharge coefficients,  $C_{D_o}$  and  $C_{D_T}$ , and  $\Phi$  vary with flow rates, however. Hence, the equivalence ratio of the mixture delivered by an elementary carburetor is not constant.

Figure 7-3 illustrates the performance of the elementary carburetor. The top set of curves shows how  $\Phi$ ,  $C_{D_T}$ , and  $C_{D_o}$  typically vary with the venturi pressure drop.<sup>4</sup> Note that for  $\Delta p_a \leq \rho_f gh$  there is no fuel flow. Once fuel starts to flow, as a consequence of these variations the fuel flow rate increases more rapidly than the air flow rate. The carburetor delivers a mixture of increasing fuel/air equivalence ratio as the flow rate increases. Suppose the venturi and orifice are sized to



**FIGURE 7-3**  
Performance of elementary carburetor: variation of  $C_{D_T}$ ,  $C_{D_o}$ ,  $\Phi$ ,  $\dot{m}_f(A/F)_s$ ,  $\dot{m}_a$ , and equivalence ratio  $\phi$  with venturi pressure drop.

give a stoichiometric mixture at an air flow rate corresponding to  $1 \text{ kN/m}^2$  venturi pressure drop (middle graph in Fig. 7-3). At higher air flow rates, the carburetor will deliver a fuel-rich mixture; at very high flow rates it will eventually deliver an essentially constant equivalence ratio. At lower air flow rates, the mixture delivered leans out rapidly. Thus, the elementary carburetor cannot provide the variation in mixture ratio which the engine requires over the complete load range at any given speed (see Fig. 7-1).

The deficiencies of the elementary carburetor can be summarized as follows:

1. At low loads the mixture becomes leaner; the engine requires the mixture to be enriched at low loads.
2. At intermediate loads, the mixture equivalence ratio increases slightly as the air flow increases. The engine requires an almost constant equivalence ratio.
3. As the air flow approaches the maximum wide-open throttle value, the equivalence ratio remains essentially constant. However, the mixture equivalence ratio should increase to 1.1 or greater to provide maximum engine power.
4. The elementary carburetor cannot compensate for transient phenomena in the intake manifold. Nor can it enrich the mixture during engine starting and warm-up.
5. The elementary carburetor cannot adjust to changes in ambient air density (due primarily to changes in altitude).

### 7.2.2 Modern Carburetor Design

The changes required in the elementary carburetor so that it provides the equivalence ratio versus air flow distribution shown in Fig. 7-1 are:



1. The *main metering system* must be compensated to provide essentially constant lean or stoichiometric mixtures over the 20 to 80 percent air flow range.
2. An *idle system* must be added to meter the fuel flow at idle and light loads.
3. An *enrichment system* must be added so the engine can provide its maximum power as wide-open throttle is approached.
4. An *accelerator pump* which injects additional fuel when the throttle is opened rapidly is required to maintain constant the equivalence ratio delivered to the engine cylinder.
5. A *choke* must be added to enrich the mixture during engine starting and warm-up to ensure a combustible mixture within each cylinder at the time of ignition.
6. *Altitude compensation* is required to adjust the fuel flow to changes in air density.

In addition, it is necessary to increase the magnitude of the pressure drop available for controlling the fuel flow. Two common methods used to achieve this are the following.

**BOOST VENTURIS.** The carburetor venturi should give as large a vacuum at the throat as possible at maximum air flow, within the constraints of a low pressure loss across the complete venturi and diffuser. In a single venturi, as the diameter of the throat is decreased at a given air flow to increase the flow velocity and hence the metering signal at the throat, the pressure loss increases. A higher vacuum signal at the venturi throat and higher velocities for improved atomization can be obtained without increasing the overall pressure loss through the use of multiple venturis. Figure 7-4 shows the geometry and the pressure distribution in a typical double-venturi system. A boost venturi is positioned upstream of the throat of the larger main venturi, with its discharge at the location of maximum velocity in the main venturi. Only a fraction of the air flows through the boost venturi. Since the pressure at the boost venturi *exit* equals the pressure

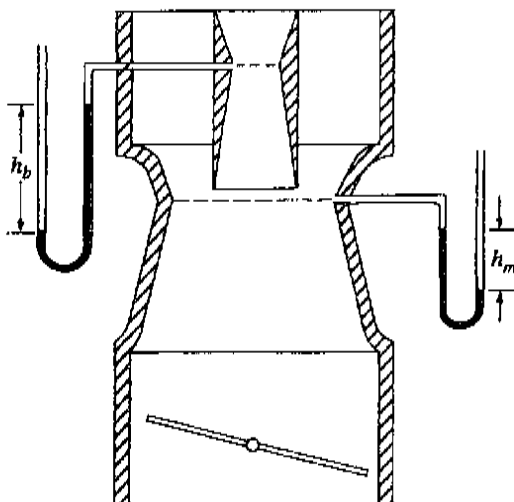


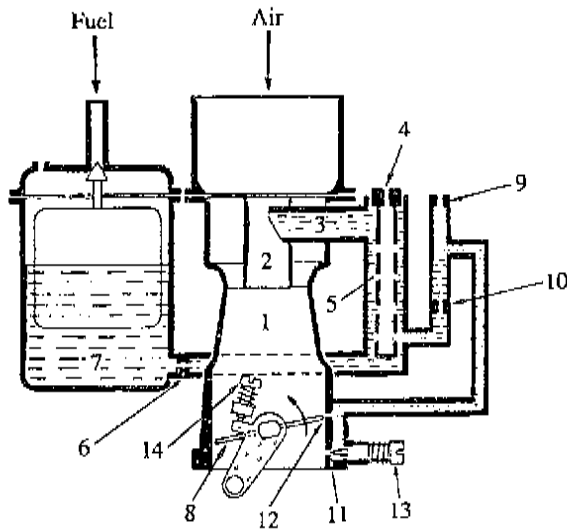
FIGURE 7-4  
Schematic of carburetor double-venturi system.

at the main venturi *throat*, a higher vacuum  $\Delta p_b = \rho_m g h_b$  is obtained at the boost venturi throat which can be used to obtain more precise metering of the fuel ( $\rho_m$  is the manometer fluid density). Best results are obtained with the boost venturi exit slightly upstream ( $\approx 5$  mm) of the main venturi throat. Because only a fraction of the total air flow goes through the boost venturi, the use of multiple venturis makes it possible to obtain a high velocity air stream (up to 200 m/s) where the fuel is introduced at the boost venturi throat, and adequate vacuum, and to reduce the pressure loss across the total venturi system, without increasing the height of the carburetor. The fuel is better atomized in the smaller boost venturi with its higher air velocity, and since this air and fuel mixture is discharged centrally into the surrounding venturi, a more homogeneous mixture results. The vacuum developed at the venturi throat of a typical double-venturi system is about twice the theoretical vacuum of a single venturi of the same flow area.<sup>5</sup> A triple-venturi system can be used to give further increases in metering signal. The overall discharge coefficient of a multiple-venturi carburetor is lower than a single-venturi carburetor of equal cross-sectional area. The throat area of the main venturi in a multiple-venturi system is usually increased, therefore, above the single-venturi size to compensate for this. Some decrease in air stream velocity is tolerated to maintain a high discharge coefficient (and hence a high volumetric efficiency).<sup>6</sup>

**MULTIPLE-BARREL CARBURETORS.** Use of carburetors with venturi systems in parallel is a common way of maintaining an adequate part-load metering signal, high volumetric efficiency at wide-open throttle, and minimum carburetor height as engine size and maximum air flow increases. As venturi size in a single-barrel carburetor is increased to provide a higher engine air flow at maximum power, the venturi length increases and the metering signal generated at low flows decreases. Maximum wide-open throttle air flow is some 30 to 70 times the idle air flow (the value depending on engine displacement). Two-barrel carburetors usually consist of two single-barrel carburetors mounted in parallel. Four-barrel carburetors consist of a pair of two-barrel carburetors in parallel, with throttle plates compounded on two shafts. Air flows through the primary barrel(s) at low and intermediate engine loads. At higher loads, the throttle plate(s) on the secondary barrel(s) (usually of larger cross-sectional area) start to open when the air flow exceeds about 50 percent of the maximum engine air flow.

There are many different designs of complete carburetors. The operating principles of the methods most commonly used to achieve the above listed modifications will now be reviewed. Figure 7-5 shows a schematic of a conventional modern carburetor and the names of the various components and fuel passages.

**COMPENSATION OF MAIN METERING SYSTEM.** Figure 7-6 shows a main fuel-metering system with air-bleed compensation. As the pressure at the venturi throat decreases, air is bled through an orifice (or series of orifices) into the main fuel well. This flow reduces the pressure difference across the main fuel-metering orifice which no longer experiences the full venturi vacuum. The mixing of bleed

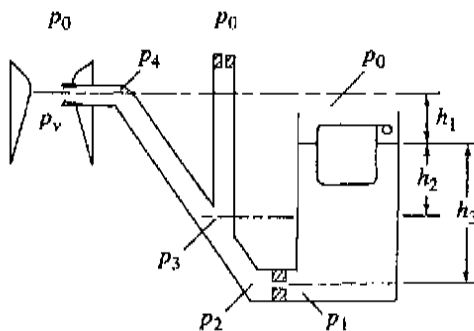


**FIGURE 7-5**  
Schematic of modern carburetor.

- |                                      |  |
|--------------------------------------|--|
| 1 Main venturi                       | 8 Throttle plate                         |
| 2 Boost venturi                      | 9 Idle air-bleed orifice                 |
| 3 Main metering spray tube or nozzle | 10 Idle fuel orifice                     |
| 4 Air-bleed orifice                  | 11 Idle mixture orifice                  |
| 5 Emulsion tube or well              | 12 Transition orifice                    |
| 6 Main fuel-metering orifice         | 13 Idle mixture adjusting screw          |
| 7 Float chamber                      | 14 Idle throttle setting adjusting screw |

Fuel enters the air stream from the main metering system through (3). At idle, fuel enters air at (11). During transition, fuel enters at (11), (12), and (3). (Courtesy S.p.A.E. Weber.)

air with the fuel forms an emulsion which atomizes more uniformly to smaller drop sizes on injection at the venturi throat. The schematic in Fig. 7-6 illustrates the operating principle. When the engine is not running, the fuel is at the same level in the float bowl and in the main well. With the engine running, as the throttle plate is opened, the air flow and the vacuum in the venturi throat increase. For  $\Delta p_v (= p_0 - p_v) < \rho_f g h_1$ , there is no fuel flow from the main metering system. For  $\rho_f g h_1 < \Delta p_v < \rho_f g h_2$ , only fuel flows through the main well and nozzle, and the system operates just like an elementary carburetor. For  $\Delta p_v > \rho_f g h_2$ , air enters the main well together with fuel. The amount of air entering the well is controlled by the size of the main air-bleed orifice. The amount of air is



**FIGURE 7-6**  
Schematic of main metering system with air-bleed compensation.

small and does not significantly affect the composition of the mixture. The air-bleed mass flow rate is given by

$$\dot{m}_{ab} = C_{D_b} A_b [2(p_0 - p_3)\rho_a]^{1/2} \quad (7.8)$$

where  $C_{D_b}$  and  $A_b$  are the discharge coefficient and the area of the air-bleed orifice. The fuel mass flow rate through the fuel orifice is given by

$$\dot{m}_f = C_{D_o} A_o [2(p_1 - p_2)\rho_f]^{1/2} \quad (7.9)$$

where

$$p_1 = p_0 + \rho_f g h_3 \quad \text{and} \quad p_2 = p_3 + \rho_f g (h_3 - h_2)$$

The density of the emulsion  $\rho_{em}$  in the main well and nozzle is usually approximated by

$$\rho_{em} = \frac{\dot{m}_{ab} + \dot{m}_f}{\dot{m}_{ab}/\rho_a + \dot{m}_f/\rho_f} \quad (7.10)$$

Since typical values are  $\rho_f = 730 \text{ kg/m}^3$  and  $\rho_a = 1.14 \text{ kg/m}^3$ , usually  $\rho_f \gg \rho_{em} \gg \rho_a$ . Thus, as the air-bleed flow rate increases, the height of the column of emulsion becomes less significant. However, the decrease in emulsion density due to increasing air bleed increases the flow velocity, which results in a significant pressure drop across the main nozzle. This pressure drop depends on nozzle length and diameter, fuel flow rate, bleed air flow rate, relative velocity between fuel and bleed air, and fuel properties. It is determined empirically, and has been found to correlate with  $\rho_{em}$  [as defined by Eq. (7.10)].<sup>2, 6</sup> The pressure loss at the main discharge nozzle with two-phase flow can be several times the pressure loss with single-phase flow.

Figure 7-7 illustrates the behavior of the system shown in Fig. 7-6:  $\dot{m}_a$ ,  $\dot{m}_f$ , and the fuel/air equivalence ratio  $\phi$  are plotted against  $\Delta p_v$ . Once the bleed system is operating ( $\Delta p_v > \rho_f g h_2$ ) the fuel flow rate is reduced below its equivalent elementary carburetor value (the  $A_b = 0$  line). As the bleed orifice area is increased, in the limit of large  $A_b$  and neglecting the pressure losses in the main nozzle, the fuel flow rate remains constant ( $A_b \rightarrow \infty$ ). An appropriate choice of bleed orifice area  $A_b$  will provide the desired equivalence ratio versus pressure drop or air flow characteristic.

Additional control flexibility is obtained in practice through use of a second orifice, or of a series of holes in the main well or emulsion tube as shown in Fig. 7-5. Main metering systems with controlled air bleed provide reliable and stable control of mixture composition at part throttle engine operation. They are simple, have considerable design flexibility, and atomize the fuel effectively. In some carburetor designs, an additional compensation system consisting of a tapered rod or needle in the main metering orifice is used. The effective open area of the main metering orifice, and hence the fuel flow rate, can thus be directly related to throttle position (and manifold vacuum).

A wide range of two-phase flow patterns can be generated by bleeding an air flow into a liquid flow. Fundamental studies of the generation and flow of

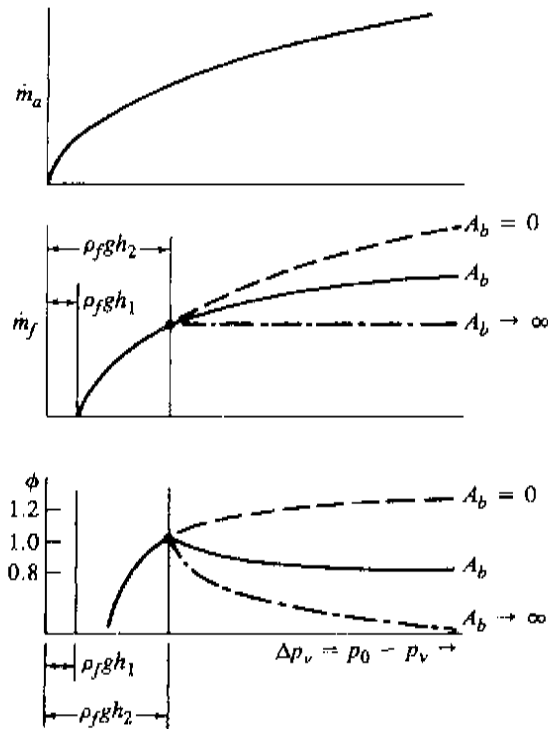


FIGURE 7-7

Metering characteristics of system with air-bleed compensation: mass flow rate of air  $\dot{m}_a$ , mass flow rate of fuel  $\dot{m}_f$ , and equivalence ratio  $\phi$  as functions of venturi pressure drop for different air-bleed orifice areas  $A_b$ .

two-phase mixtures in small diameter tubes with bleed holes similar to those used in carburetors have been carried out.<sup>7</sup> For a given pipe and bleed hole size, the type of flow pattern set up depends on the flow rates of the two phases.

**IDLE SYSTEM.** The idle system is required because at low air flows through the carburetor insufficient vacuum is created at the venturi throat to draw fuel into the air stream. However, at idle and light loads, the manifold vacuum is high, with the pressure drop occurring across the almost-closed throttle plate. This low manifold pressure at idle is exploited for the idle fuel system by connecting the main fuel well to an orifice in the throttle body downstream of the throttle plate. Figure 7-5 shows the essential features of an idle system. The main well (5) is connected through one or more orifices (10), past one or more idle air-bleed orifices (or holes) (9), past an idle mixture adjusting screw (13), to the idle discharge port (11) in the throttle body. Emulsifying air is admitted into the idle system [at (9) and (12)] to reduce the pressure drop across the idle port and permit larger-sized ports (which are easier to manufacture) to be used. Satisfactory engine operation at idle is obtained empirically by means of the idle throttle position stop adjustment (14) and the idle mixture adjustment (13). As the throttle is opened from its idle position, the idle metering system performs a transitional function. One or more holes (12) located above the idle discharge port (11) assist as air bleeds when the throttle is at or near its idle position. As the throttle plate opens and the air flow increases, these additional discharge holes are exposed to the manifold vacuum. Additional fuel is forced out of these holes into the air stream to provide the appropriate mixture ratio. As the throttle plate is opened further, the main fuel metering system starts to supply fuel also. Because the two

systems are coupled, they interact and the main system behavior in this *transition region* is modified by the fuel flow through the idle system. The total combined fuel flow provides a rich (or close-to-stoichiometric) mixture at idle, a progressive leaning of the mixture as air flow increases, and eventually (as the main system takes over full control of the fuel flow rate) an approximately constant mixture composition.

**POWER ENRICHMENT SYSTEM.** This system delivers additional fuel to enrich the mixture as wide-open throttle is approached so the engine can deliver its maximum power. The additional fuel is normally introduced via a submerged valve which communicates directly with the main discharge nozzle, bypassing the metering orifice. The valve, which is spring loaded, is operated either mechanically through a linkage with the throttle plate (opening as the throttle approaches its wide-open position) or pneumatically (using manifold vacuum).

**ACCELERATOR PUMP.** When the throttle plate is opened rapidly, the fuel-air mixture flowing into the engine cylinder leans out temporarily. The primary reason for this is the time lag between fuel flow into the air stream at the carburetor and the fuel flow past the inlet valve (see Sec. 7.6.3). While much of the fuel flow into the cylinder is fuel vapor or small fuel droplets carried by the air stream, a fraction of the fuel flows onto the manifold and port walls and forms a liquid film. The fuel which impacts on the walls evaporates more slowly than fuel carried by the air stream and introduces a lag between the air/fuel ratio produced at the carburetor and the air/fuel ratio delivered to the cylinder. An accelerator pump is used as the throttle plate is opened rapidly to supply additional fuel into the air stream at the carburetor to compensate for this leaning effect. Typically, fuel is supplied to the accelerator pump chamber from the float chamber via a small hole in the bottom of the fuel bowl, past a check valve. A pump diaphragm and stem is actuated by a rod attached to the throttle plate lever. When the throttle is opened to increase air flow, the rod-driven diaphragm will increase the fuel pressure which shuts the valve and discharges fuel past a discharge check valve or weight in the discharge passage, through the accelerator pump discharge nozzle(s), and into the air stream. A calibrated orifice controls the fuel flow. A spring connects the rod and diaphragm to extend the fuel discharge over the appropriate time period and to reduce the mechanical strain on the linkage.

**CHOKE.** When a cold engine is started, especially at low ambient temperatures, the following factors introduce additional special requirements for the complete carburetor:

1. Because the starter-cranked engine turns slowly (70 to 150 rev/min) the intake manifold vacuum developed during engine start-up is low.
2. This low manifold vacuum draws a lower-than-normal fuel flow from the carburetor idle system.

3. Because of the low manifold temperature and vacuum, fuel evaporation in the carburetor, manifold, and inlet port is much reduced.

Thus, during cranking, the mixture which reaches the engine cylinder would be too lean to ignite. Until normal manifold conditions are established, fuel distribution is also impaired. To overcome these deficiencies and ensure prompt starts and smooth operation during engine warm-up, the carburetor must supply a fuel-rich mixture. This is obtained with a choke. Once normal manifold conditions are established, the choke must be excluded. The primary element of a typical choke system is a plate, upstream of the carburetor, which can close off the intake system. At engine start-up, the choke plate is closed to restrict the air flow into the carburetor barrel. This causes almost full manifold vacuum within the venturi which draws a large fuel flow through the main orifice. When the engine starts, the choke is partly opened to admit the necessary air flow and reduce the vacuum in the venturi to avoid flooding the intake with fuel. As the engine warms up, the choke is opened either manually or automatically with a thermostatic control. For normal engine operation the choke plate is fully open and does not influence carburetor performance. A manifold vacuum control is often used to close the choke plate partially if the engine is accelerated during warm-up. During engine warm-up the idle speed is increased to prevent engine stalling. A fast idle cam is rotated into position by the automatic choke lever.

**ALTITUDE COMPENSATION.** An inherent characteristic of the conventional float type carburetor is that it meters fuel flow in proportion to the air *volume* flow rate. Air density changes with ambient pressure and temperature, with changes due to changes in pressure with altitude being most significant. For example, at 1500 m above sea level, mean atmospheric pressure is 634 mmHg or 83.4 percent of the mean sea-level value. While ambient temperature variations, winter to summer, can produce changes of comparable magnitude, the temperature of the air entering the carburetor for warmed-up engine operation is controlled to within much closer tolerances by drawing an appropriate fraction of the air from around the exhaust manifold.

Equation (7.6) shows how the air/fuel ratio delivered by the main metering system will vary with inlet air conditions. The primary dependence is through the  $\sqrt{\rho_{a0}}$  term; depending on what is held constant (e.g., throttle setting or air mass flow rate) there may be an additional, much smaller dependence through  $\Phi$  and  $\Delta p_a$  (see Ref. 5). To a good approximation, the enrichment  $E$  with increasing altitude  $z$  is given by

$$1 + E = \frac{(F/A)_z}{(F/A)_0} = \left( \frac{\rho_{a0}}{\rho_{az}} \right)^{1/2} \quad (7.11)$$

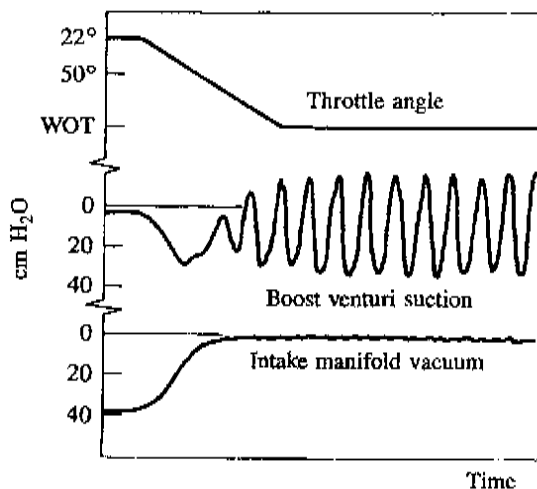
For  $z = 1500$  m,  $E = 9.5$  percent; thus, a cruise equivalence ratio of 0.9 or  $(A/F) = 16.2$  would be enriched to close to stoichiometric.

The effects of increase in altitude on the carburetor flow curve shown in Fig. 7-1 are: (1) to enrich the entire part-throttle portion of the curve and (2) to

bring in the power-enrichment system at a lower air flow rate due to decreased manifold vacuum. To reduce the impact to changes in altitude on engine emissions of CO and HC, modern carburetors are altitude compensated. A number of methods can be used to compensate for changes in ambient pressure with altitude:

1. *Venturi bypass method.* To keep the air volume flow rate through the venturi equal to what it was at sea-level atmospheric pressure (calibration condition), a bypass circuit around the venturi for the additional volume flow is provided.
2. *Auxiliary jet method.* An auxiliary fuel metering orifice with a pressure-controlled tapered metering rod connects the fuel bowl to the main well in parallel with the main metering orifice.
3. *Fuel bowl back-suction method.* As altitude increases, an aneroid bellows moves a tapered rod from an orifice near the venturi throat, admitting to the bowl an increasing amount of the vacuum signal developed at the throat.
4. *Compensated air-bleed method.* The orifices in the bleed circuits to each carburetor system are fitted with tapered metering pins actuated by a single aneroid bellows.<sup>8</sup>

**TRANSIENT EFFECTS.** The pulsating and transient nature of the flow through a carburetor during actual engine operation is illustrated by the data shown in Fig. 7-8.<sup>2</sup> The changes in pressure with time in the intake manifold and at the boost venturi throat of a standard two-barrel carburetor installed on a production V-8 engine are shown as the throttle is opened from light load (22°) to wide-open throttle at 1000 rev/min. Note the rapid increase in boost venturi suction as the throttle is suddenly opened. This results from the sudden large increase in the air flow rate and corresponding increase in air velocity within the boost venturi. Note also that the pressure fluctuations decay rapidly, and within a few engine revolutions have stabilized at the periodic values associated with the new throttle angle. At wide-open throttle, the pulsating nature of the flow as each



**FIGURE 7-8**

Throttle angle, boost venturi suction, and intake manifold vacuum variation with time as throttle is opened from light load (22°) to wide-open throttle at 1000 rev/min. Standard two-barrel carburetor and production V-8 engine.<sup>2</sup>



cylinder draws in its charge is evident. The pressure drop across the main metering jet also fluctuates. The pulsations in the venturi air flow (and hence fuel flow) due to the filling of each cylinder in turn are negligibly small at small throttle angles and increase to a maximum at wide-open throttle. At small throttle openings, the choked flow at the throttle plate prevents the manifold pressure fluctuations from propagating upstream into the venturi. The effective time-averaged boost venturi suction is greater for the pulsating flow case than for the steady flow case. If the ratio of the effective metering signal for a pulse cycle to that for steady air flow at the same average mass flow is denoted as  $1 + \Omega$ , where  $\Omega$  is the pulsation factor, then  $\Omega$  is related to the amplitude and frequency of pressure waves within the intake manifold as well as the damping effect of the throttle plate. An empirical equation for  $\Omega$  is

$$\Omega = \frac{\text{constant} \times (1 - M)p_m n_R}{N n_{c/b}} \quad (7.12)$$

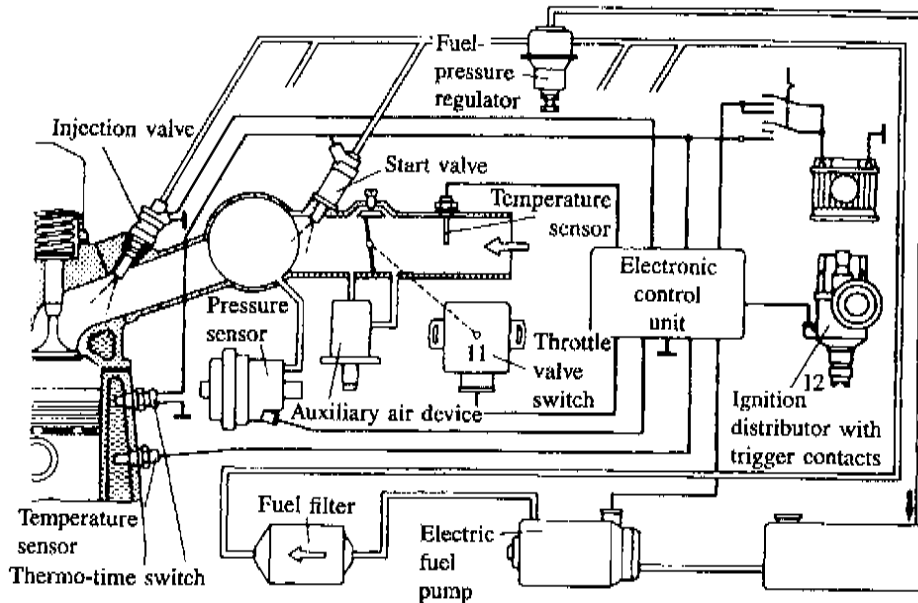
where  $M$  is the throttle plate Mach number,  $p_m$  the manifold pressure,  $n_R$  the number of revolutions per power stroke,  $N$  the crank speed, and  $n_{c/b}$  the number of cylinders per barrel. The value of the constant depends on carburetor and engine geometry. For  $p_m$  in kilonewtons per square meter and  $N$  in revolutions per minute a typical value for the constant is 7.3.<sup>2</sup> Thus, at wide-open throttle at 1500 rev/min,  $\Omega$  has a value of about 0.2. The transient behavior of the air and fuel flows in the manifold are discussed more fully in Sec. 7.6.

## 7.3 FUEL-INJECTION SYSTEMS

### 7.3.1 Multipoint Port Injection

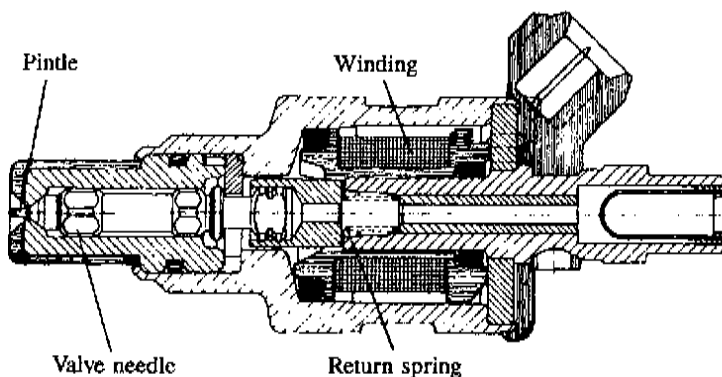
The fuel-injection systems for conventional spark-ignition engines inject the fuel into the engine intake system. This section reviews systems where the fuel is injected into the intake port of each engine cylinder. Thus these systems require one injector per cylinder (plus, in some systems, one or more injectors to supplement the fuel flow during starting and warm-up). There are both mechanical injection systems and electronically controlled injection systems. The advantages of port fuel injection are increased power and torque through improved volumetric efficiency and more uniform fuel distribution, more rapid engine response to changes in throttle position, and more precise control of the equivalence ratio during cold-start and engine warm-up. Fuel injection allows the amount of fuel injected per cycle, for each cylinder, to be varied in response to inputs derived from sensors which define actual engine operating conditions. Two basic approaches have been developed; the major difference between the two is the method used to determine the air flow rate.

Figure 7-9 shows a schematic of a *speed-density* system, where engine speed and manifold pressure and air temperature are used to calculate the engine air flow. The electrically driven fuel pump delivers the fuel through a filter to the fuel line. A pressure regulator maintains the pressure in the line at a fixed value (e.g.,



**FIGURE 7-9**  
 Speed-density electronic multipoint port fuel-injection system: Bosch D-Jetronic System.<sup>9</sup> (Courtesy Robert Bosch GmbH and SAE.)

270 kN/m<sup>2</sup>, 39 lb/in<sup>2</sup>, usually relative to manifold pressure to maintain a constant fuel pressure drop across the injectors). Branch lines lead to each injector; the excess fuel returns to the tank via a second line. The inducted air flows through the air filter, past the throttle plate to the intake manifold. Separate runners and branches lead to each inlet port and engine cylinder. An electromagnetically actuated fuel-injection valve (see Fig. 7-10) is located either in the intake manifold tube or the intake port of each cylinder. The major components of the injector are the valve housing, the injector spindle, the magnetic plunger to which the spindle is connected, the helical spring, and the solenoid coil. When the solenoid is not excited, the solenoid plunger of the magnetic circuit is forced, with its seal, against the valve seat by the helical spring and closes the fuel passage. When the solenoid coil is excited, the plunger is attracted and lifts the spindle about



**FIGURE 7-10**  
 Cross section of fuel injector.<sup>10</sup>

0.15 mm so that fuel can flow through the calibrated annular passage around the valve stem. The front end of the injector spindle is shaped as an atomizing pintle with a ground top to atomize the injected fuel. The relatively narrow spray cone of the injector, shown in the photo in Fig. 7-11, minimizes the intake manifold wall wetting with liquid fuel. The mass of fuel injected per injection is controlled by varying the duration of the current pulse that excites the solenoid coil. Typical injection times for automobile applications range from about 1.5 to 10 ms.<sup>11</sup>

The appropriate coil excitation pulse duration or width is set by the electronic control unit (ECU). In the speed-density system, the primary inputs to the ECU are the outputs from the manifold pressure sensor, the engine speed sensor (usually integral with the distributor), and the temperature sensors installed in the intake manifold to monitor air temperature and engine block to monitor the water-jacket temperature—the latter being used to indicate fuel-enrichment requirements during cold-start and warm-up. For warm-engine operation, the mass of air per cylinder per cycle  $m_a$  is given by

$$m_a = \eta_v(N)\rho_a(T_i, p_i)V_d = \frac{\eta_v V_d p_i}{R_a T_i} \quad (7.13)$$

where  $\eta_v$  is the volumetric efficiency,  $N$  is engine speed,  $\rho_a$  is the inlet air density, and  $V_d$  is the displaced volume per cylinder. The electronic control unit forms the pulse which excites the injector solenoids. The pulse width depends primarily on the manifold pressure; it also depends on the variation in volumetric efficiency  $\eta_v$  with speed  $N$  and variations in air density due to variations in air temperature. The control unit also initiates mixture enrichment during cold-engine operation and during accelerations that are detected by the throttle sensor.

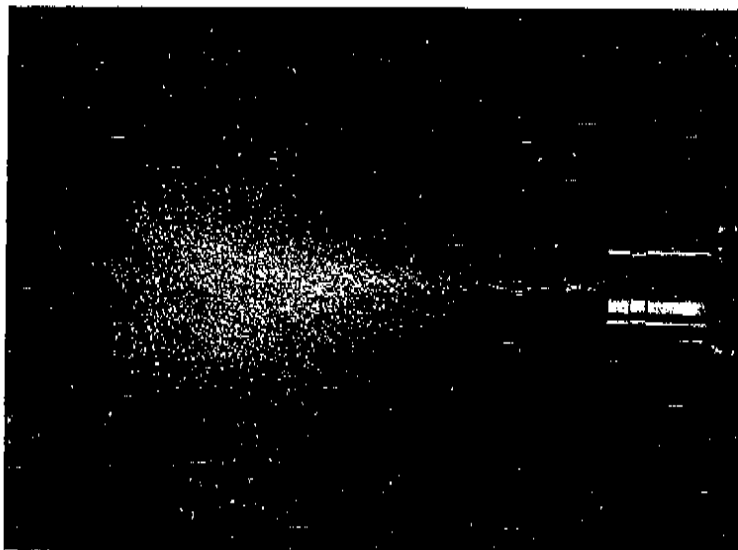
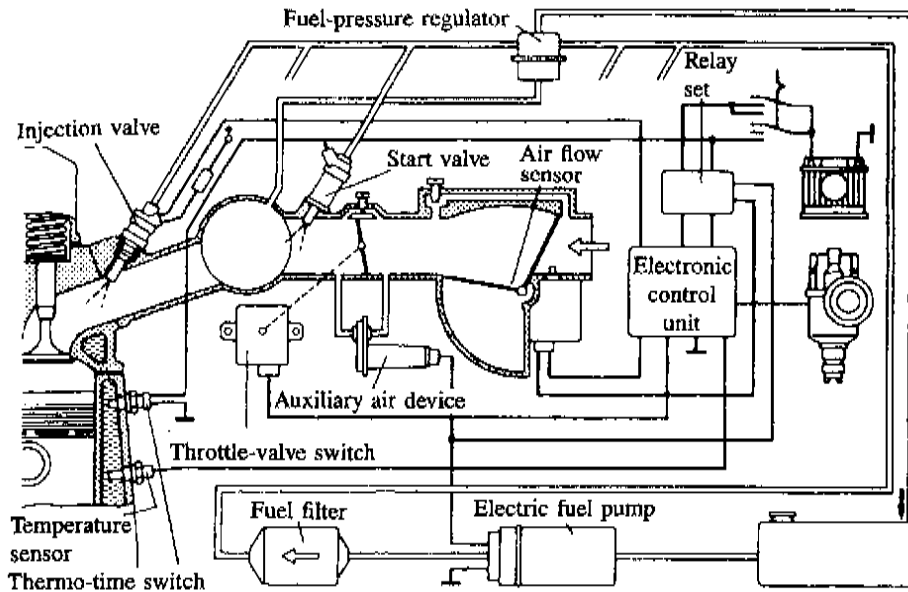


FIGURE 7-11

Short time-exposure photograph of liquid fuel spray from Bosch-type injector. (Courtesy Robert Bosch GmbH.)



**FIGURE 7-12**

Electronic multipoint port fuel-injection system with air-flow meter: Bosch L-Jetronic system.<sup>9</sup> (Courtesy Robert Bosch GmbH and SAE.)

Figure 7-12 shows an alternative EFI system (the Bosch L-Jetronic) which uses an air-flow meter to measure air flow directly. The air-flow meter is placed upstream of the throttle. The meter shown measures the force exerted on a plate as it is displaced by the flowing air stream; it provides a voltage proportional to the air flow rate. An alternative air-flow measuring approach is to use a hot-wire air mass flow meter.<sup>10</sup> The advantages of direct air-flow measurement are:<sup>12</sup> (1) automatic compensation for tolerances, combustion chamber deposit buildup, wear and changes in valve adjustments; (2) the dependence of volumetric efficiency on speed and exhaust backpressure is automatically accounted for; (3) less acceleration enrichment is required because the air-flow signal precedes the filling of the cylinders; (4) improved idling stability; and (5) lack of sensitivity of the system to EGR since only the fresh air flow is measured.

The mass of air inducted per cycle to each cylinder,  $m_a$ , varies as

$$m_a \propto \frac{\dot{m}_a}{N} \quad (7.14)$$

Thus the primary signals for the electronic control unit are air flow and engine speed. The pulse width is inversely proportional to speed and directly proportional to air flow. The engine block temperature sensor, starter switch, and throttle valve switch provide input signals for the necessary adjustments for cold-start, warm-up, idling, and wide-open throttle enrichment.

For cold-start enrichment, one (or more) cold-start injector valve is used to inject additional fuel into the intake manifold (see Figs. 7-9 and 7-12). Since short opening and closing times are not important, this valve can be designed to

provide extremely fine atomization of the fuel to minimize the enrichment required.

Mechanical, air-flow-based metering, continuous injection systems are also used. Figure 7-13 shows a schematic of the Bosch K-Jetronic system.<sup>9, 10</sup> Air is drawn through the air filter, flows past the air-flow sensor, past the throttle valve, into the intake manifold, and into the individual cylinders. The fuel is sucked out of the tank by a roller-cell pump and fed through the fuel accumulator and filter to the fuel distributor. A primary pressure regulator in the fuel distributor maintains the fuel pressure constant. Excess fuel not required by the engine flows back to the tank. The mixture-control unit consists of the air-flow sensor and fuel distributor. It is the most important part of the system, and provides the desired metering of fuel to the individual cylinders by controlling the cross section of the metering slits in the fuel distributor. Downstream of each of these metering slits is a differential pressure valve which for different flow rates maintains the pressure drop at the slits constant.

Fuel-injection systems offer several options regarding the timing and location of each injection relative to the intake event.<sup>10</sup> The K-Jetronic mechanical injection system injects fuel continuously in front of the intake valves with the spray directed toward the valves. Thus about three-quarters of the fuel required for any engine cycle is stored temporarily in front of the intake valve, and one-quarter enters the cylinder directly during the intake process.

With electronically controlled injection systems, the fuel is injected intermittently toward the intake valves. The fuel-injection pulse width to provide the appropriate mass of fuel for each cylinder air charge varies from about 1.5 to 10 ms over the engine load and speed range. In crank angle degrees this varies

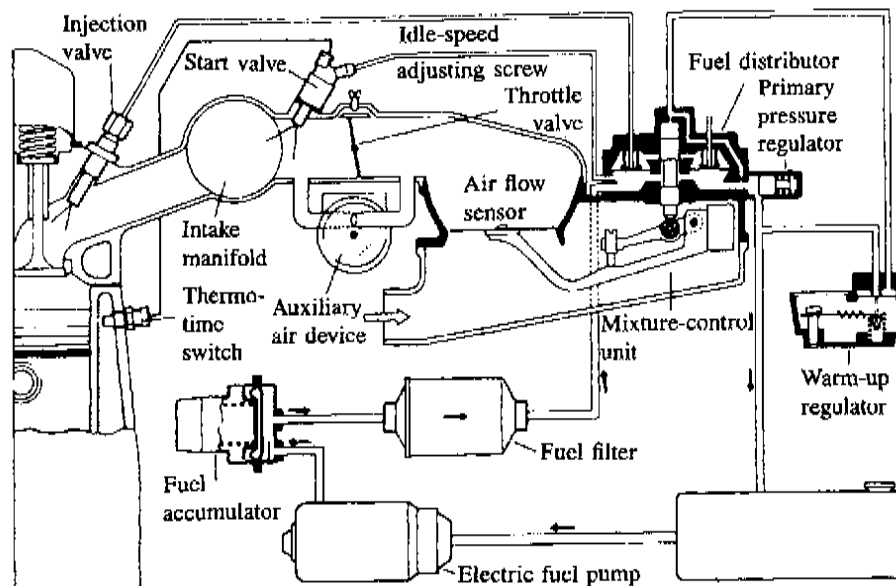
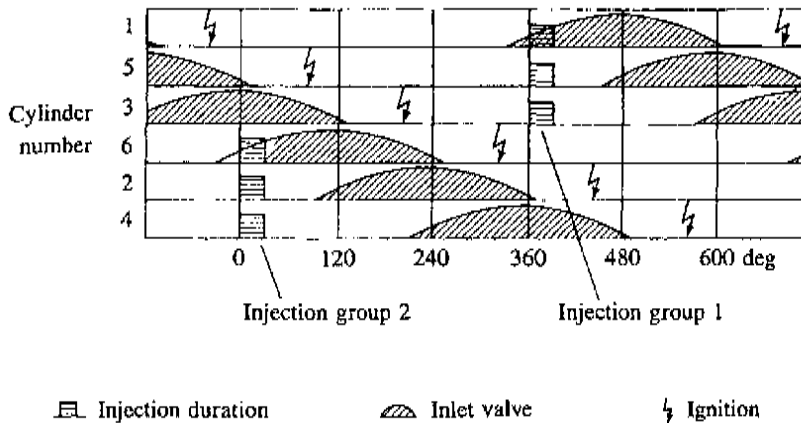


FIGURE 7-13

Mechanical multipoint port fuel-injection system: Bosch K-Jetronic system.<sup>9</sup> (Courtesy Robert Bosch GmbH and SAE.)

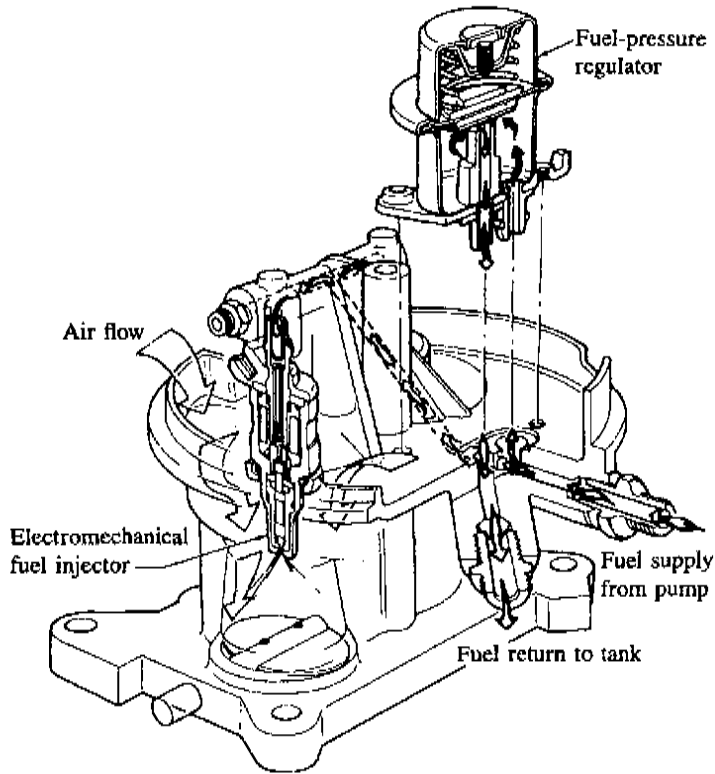


**FIGURE 7-14**  
Injection pulse diagram for D-Jetronic system in six-cylinder engine.<sup>10</sup>

from about  $10^\circ$  at light load and low speed to about  $300^\circ$  at maximum speed and load. Thus the pulse width varies from being much less than to greater than the duration of the intake stroke. To reduce the complexity of the electronic control unit, groups of injectors are often operated simultaneously. In the Bosch L-Jetronic system, all injectors are operated simultaneously. To achieve adequate mixture uniformity, given the short pulse width relative to the intake process over much of the engine load-speed range, fuel is injected twice per cycle; each injection contributes half the fuel quantity required by each cylinder per cycle. (This approach is called simultaneous double-firing.) In the speed-density system, the injectors are usually divided into groups, each group being pulsed simultaneously. For example, for a six-cylinder engine, two groups of three injectors may be used. Injection for each group is timed to occur while the inlet valves are closed or just starting to open, as shown in Fig. 7-14. The other group of injectors inject one crank revolution later. Sequential injection timing, where the phasing of *each* injection pulse relative to its intake valve lift profile is the same, is another option. Engine performance and emissions do change as the timing of the start of injection relative to inlet valve opening is varied. Injection with valve lift at its maximum, or decreasing, is least desirable.<sup>10</sup>

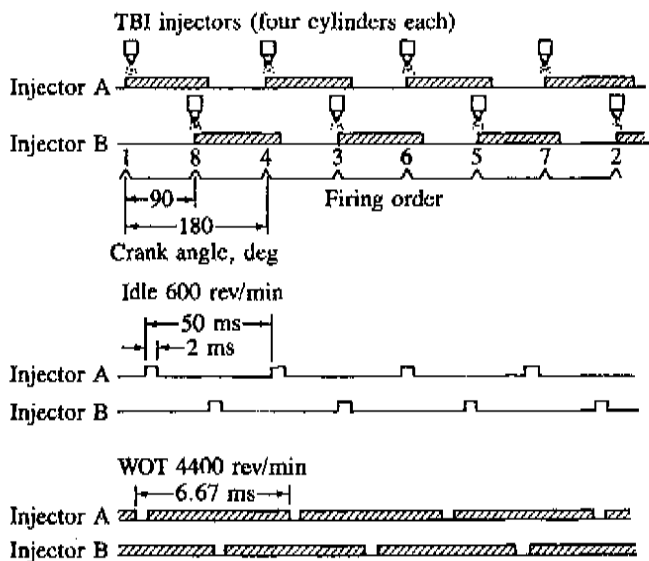
### 7.3.2 Single-Point Throttle-Body Injection

Single-point fuel-injection systems, where one or two electronically controlled injectors meter the fuel into the air flow directly above the throttle body, are also used. They provide straightforward electronic control of fuel metering at lower cost than multipoint port injection systems. However, as with carburetor systems, the problems associated with slower transport of fuel than the air from upstream of the throttle plate to the cylinder must now be overcome (see Sec. 7.6). Figure 7-15 shows a cutaway of one such system.<sup>13</sup> Two injectors, each in a separate air-flow passage with its own throttle plate, meter the fuel in response to calibrations of air flow based on intake manifold pressure, air temperature, and



**FIGURE 7-15**  
Cutaway drawing of a two-injector throttle-body electronic fuel-injection system.<sup>13</sup>

engine speed using the speed-density EFI logic described in the previous section. Injectors are fired alternatively or simultaneously, depending on load and speed and control logic used. Under alternative firing, each injection pulse corresponds to one cylinder filling. Smoothing of the fuel-injection pulses over time is achieved by proper placement of the fuel injector assembly above the throttle bore and plate. The walls and plate accumulate liquid fuel which flows in a sheet toward the annular throttle opening (see Sec. 7.6.3). The high air velocity created



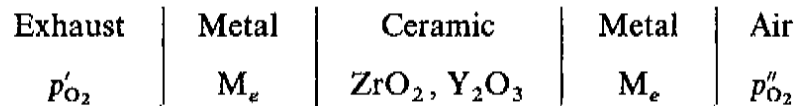
**FIGURE 7-16**  
Injector fuel delivery schedule for two-injector throttle-body injection system for eight-cylinder engine with dual plane intake manifold. Each injection nozzle feeds one plane of the manifold and its four cylinders.<sup>14</sup>

by the pressure drop across the throttle shears and atomizes the liquid sheet. Vigorous mixing of fuel and air then occurs, especially at part throttle, and provides good mixture uniformity and distribution between cylinders. Injector fuel delivery scheduling is illustrated in Fig. 7-16 for an eight-cylinder engine for a throttle-body fuel-injection system.<sup>14</sup>

### 7.4 FEEDBACK SYSTEMS

It is possible to reduce engine emissions of the three pollutants—unburned hydrocarbons, carbon monoxide, and oxides of nitrogen—with a single catalyst in the exhaust system if the engine is operated very close to the stoichiometric air/fuel ratio. Such systems (called three-way catalyst systems) are described in more detail in Sec. 11.6.2. The engine operating air/fuel ratio is maintained close to stoichiometric through the use of a sensor in the exhaust system, which provides a voltage signal dependent on the oxygen concentration in the exhaust gas stream. This signal is the input to a feedback system which controls the fuel feed to the intake.

The sensor [called an oxygen sensor or lambda sensor— $\lambda$  being the symbol used for the relative air/fuel ratio, Eq. (3.9)] is an oxygen concentration cell with a solid electrolyte through which the current is carried by oxygen ions. The electrolyte is yttria ( $Y_2O_3$ )-stabilized zirconia ( $ZrO_2$ ) ceramic which separates two gas chambers (the exhaust manifold and the atmosphere) which have different oxygen partial pressures. The cell can be represented as a series of interfaces as follows:



$p''_{O_2}$  is the oxygen partial pressure of the air ( $\approx 20 \text{ kN/m}^2$ ) and  $p'_{O_2}$  is the equilibrium oxygen partial pressure in the exhaust gases. An electrochemical reaction takes place at the metal electrodes:

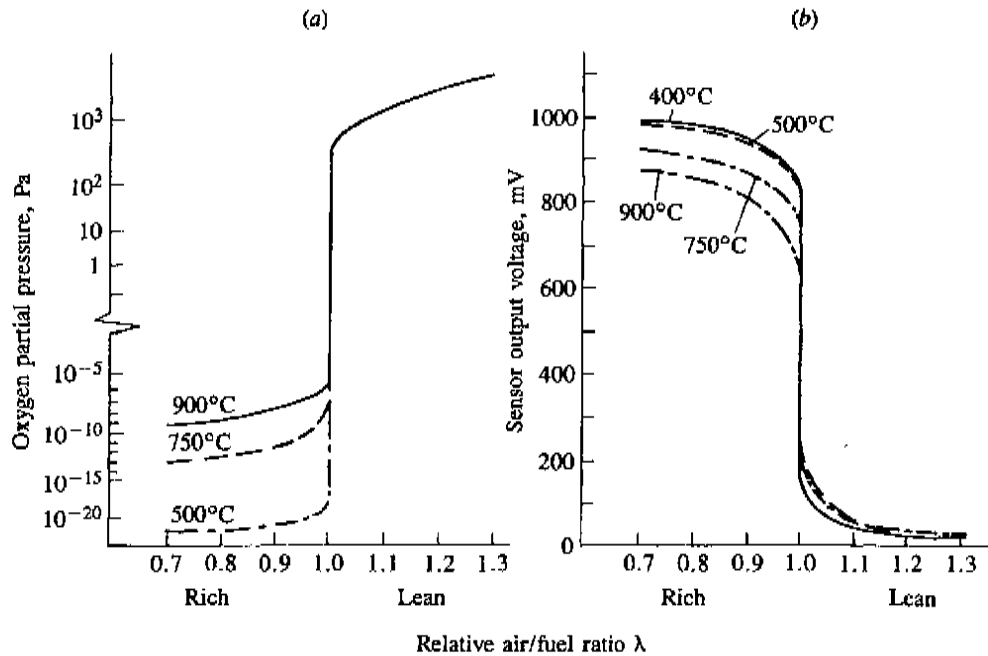


and the oxygen ions transport the current across the cell. The open-circuit output voltage of the cell  $V_o$  can be related to the oxygen partial pressures  $p'_{O_2}$  and  $p''_{O_2}$  through the Nernst equation:

$$V_o = \frac{RT}{4F} \ln \left( \frac{p''_{O_2}}{p'_{O_2}} \right) \tag{7.15}$$

where  $F$  is the Faraday constant. Equilibrium is established in the exhaust gases by the catalytic activity of the platinum metal electrodes. The oxygen partial pressure in equilibrated exhaust gases decreases by many orders of magnitude as the equivalence ratio changes from 0.99 to 1.01, as shown in Fig. 7-17a. Thus the sensor output voltage increases rapidly in this transition from a lean to a rich





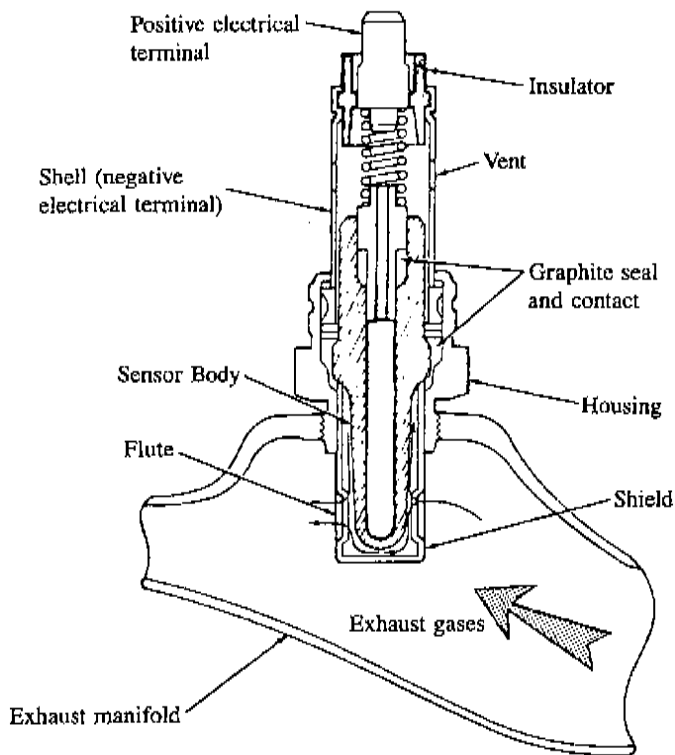
**FIGURE 7-17**

Oxygen-sensor characteristics. Variation as a function of relative air/fuel ratio and temperature of: (a) oxygen partial pressure in equilibrated combustion products; (b) sensor output voltage.<sup>15</sup>

mixture at the stoichiometric point, as shown in Fig. 7-17b. Since this transition is not temperature dependent, it is well suited as a sensor signal for a feedback system.<sup>15</sup>

Figure 7-18 shows a cross-section drawing of a lambda sensor, screwed into the wall of the exhaust manifold. This location provides rapid warm-up of the sensor following engine start-up. It also gives the shortest flow time from the fuel injector or carburetor location to the sensor—a delay time which is important in the operation of the feedback system. The sensor body is made of  $ZrO_2$  ceramic stabilized with  $Y_2O_3$  to give adequate low-temperature electrical conductivity. The inner and outer electrodes are 10- $\mu m$  thick porous platinum layers to provide the required catalytic equilibration. The outer electrode which is exposed to the exhaust gases is protected against corrosion and erosion by a 100- $\mu m$  spinal coat and a slotted shield. Air passes to the inner electrode through holes in the protective sleeve. The shield, protective sleeve, and housing are made from heat- and corrosion-resistant steel alloys. Such sensors were first developed for air/fuel ratio control at close to the stoichiometric value. Use of a similar sensor to control air/fuel ratios at lean-of-stoichiometric values during part-throttle engine operation is also feasible.

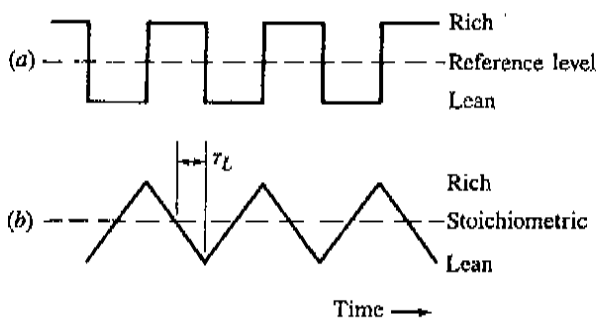
For closed-loop feedback control at close-to-stoichiometric, use is made of the sensor's low-voltage output for lean mixtures and a high-voltage output for rich mixtures. A control voltage reference level is chosen at about the mid-point of the steep transition in Fig. 7-17b. In the electronic control unit the sensor signal is compared to the reference voltage in the comparator as shown in Fig. 7-19a. The comparator output is then integrated in the integral controller whose



**FIGURE 7-18**  
Cross-section drawing of exhaust oxygen sensor.<sup>16</sup>

output varies the fuel quantity linearly in the opposite direction to the sign of the comparator signal. There is a time lag  $\tau_L$  in the loop composed of the transport time of fuel-air mixture from the point of fuel admission in the intake system to the sensor location in the exhaust, and the sensor and control system time delay. Because of this time lag, the controller continues to influence the fuel flow rate in the same direction, although the reference point  $\phi = 1.0$  has been passed, as shown in Fig. 7-19b. Thus, oscillations in the equivalence ratio delivered to the engine exist even under steady-state conditions of closed-loop control. This behavior of the control system is called the *limit cycle*. The frequency  $f$  of this limit cycle is given by

$$f_{LC} = \frac{1}{4\tau_L} \tag{7.16}$$



**FIGURE 7-19**  
Operation of electronic control unit for closed-loop feedback: (a) sensor signal compared with reference level; (b) controller output voltage—the integrated comparator output.<sup>12</sup>

and the change in equivalence ratio peak-to-peak is

$$\Delta\phi = 2K\tau_L \quad (7.17)$$

where  $K$  is the integrator gain (in equivalence ratio units per unit time).

Depending on the details of the three-way catalyst used for cleanup of all three pollutants (CO, HC, and  $\text{NO}_x$ ) in the exhaust, the optimum average equivalence ratio may not be precisely the stoichiometric value. Furthermore, the reference voltage for maximum sensor durability may not correspond exactly to the stoichiometric point or the desired catalyst mean operating point. While a small shift ( $\sim \pm 1$  percent) in operating point from the stoichiometric can be obtained by varying the reference voltage level, larger shifts are obtained by modifying the control loop to provide a steady-state bias. One method of providing a bias—*asymmetrical gain rate biasing*<sup>17</sup>—uses two separate integrator circuits with different gain rates  $K^+$  and  $K^-$  to integrate the comparator output, depending on whether the comparator output is positive (rich) or negative (lean). An alternative biasing technique incorporates an additional delay time  $\tau_D$  so that the controller output continues decreasing (or increasing) even though the sensor signal has switched from the high to the low level (or vice versa). By introducing this additional delay only on the negative slope of the sensor signal, a net lean bias is produced. Introducing the additional delay on the positive slope of the sensor signal produces a net rich bias.<sup>12</sup>

Note that the sensor only operates at elevated temperatures. During engine start-up and warm-up, the feedback system does not operate and conventional controls are required to obtain the appropriate fuel-air mixture for satisfactory engine operation.

## 7.5 FLOW PAST THROTTLE PLATE

Except at or close to wide-open throttle, the throttle provides the minimum flow area in the entire intake system. Under typical road-load conditions, more than 90 percent of the total pressure loss occurs across the throttle plate. The minimum-to-maximum flow area ratio is large—typically of order 100. Throttle

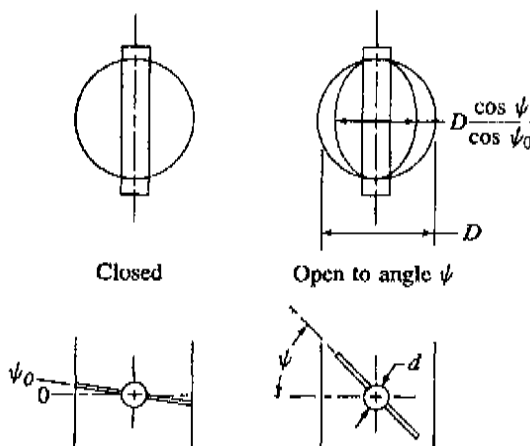
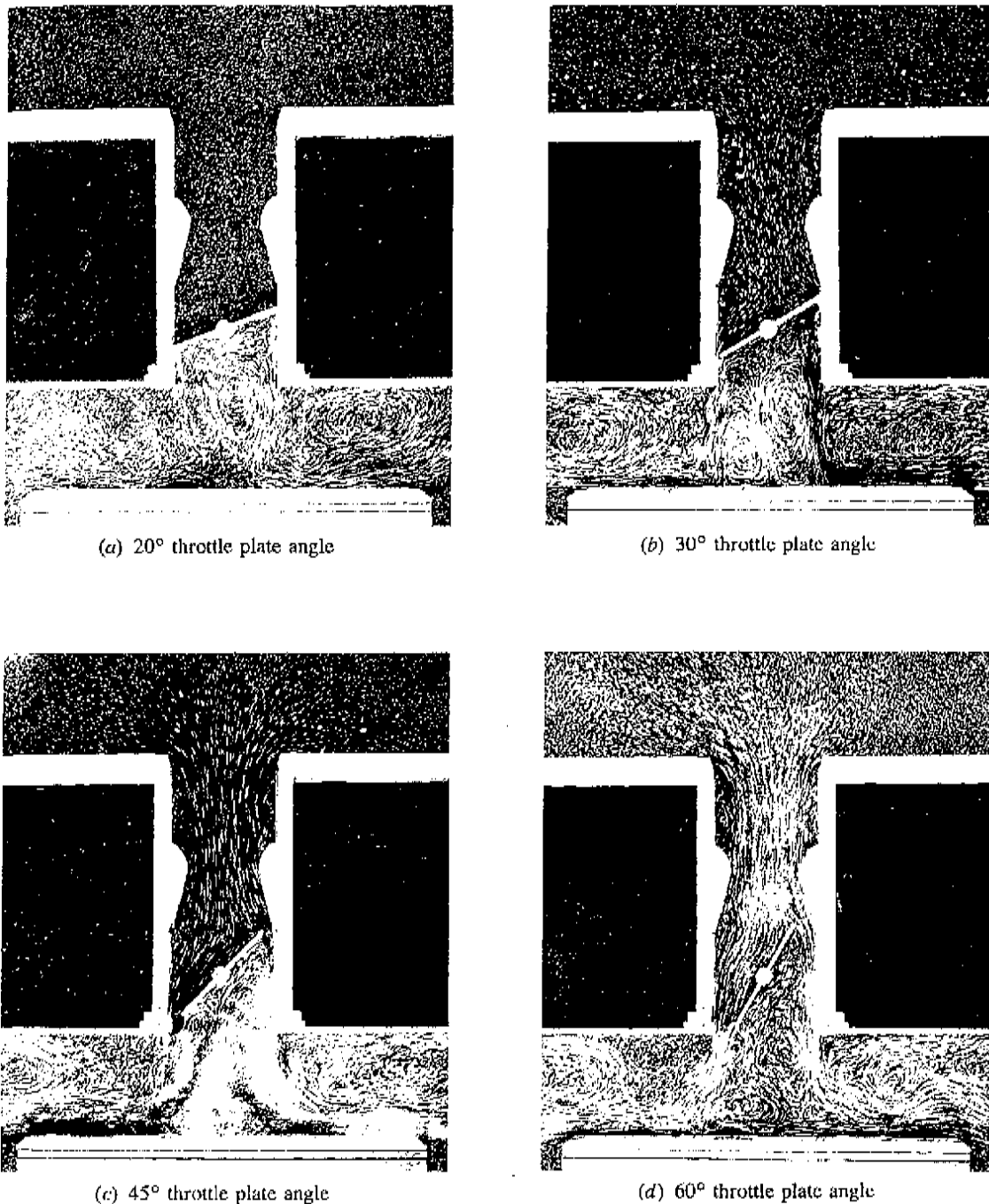


FIGURE 7-20  
Throttle plate geometry.<sup>2</sup>

**FIGURE 7-21**

Photographs of flow in two-dimensional hydraulic analog of carburetor venturi, throttle plate, and manifold plenum floor at different throttle plate angles.<sup>18</sup>

plate geometry and parameters are illustrated in Fig. 7-20. A throttle plate of conventional design such as Fig. 7-20 creates a three-dimensional flow field. At part-throttle operating conditions the throttle plate angle is in the 20 to 45° range and jets issue from the “crescent moon”-shaped open areas on either side of the throttle plate. The jets are primarily two dimensional. Figure 7-21 shows photographs taken of a two-dimensional hydraulic analog of a typical carburetor

venturi and throttle plate in steady flow at different throttle angles. The path lines traced by the particles in the flow indicate the relative magnitude of the flow velocity.<sup>18</sup> The flow accelerates through the carburetor venturi (separation occurs at the corners of the entrance section); it then divides on either side of the throttle plate. There is a stagnation point on the upstream side of the throttle plate. The wake of the throttle plate contains two vortices which rotate in opposite directions. The jets on either side of the wake (at part throttle) are at or near sonic velocity. There is little or no mixing between the two jets. Thus, if maldistribution of the fuel-air mixture occurs above the throttle plate, it is not corrected immediately below the throttle plate.

In analyzing the flow through the throttle plate, the following factors should be considered:<sup>2, 19, 20</sup>

1. The throttle plate shaft is usually of sufficient size to affect the throttle open area.
2. To prevent binding in the throttle bore, the throttle plate is usually completely closed at some nonzero angle (5, 10, or 15°).
3. The discharge coefficient of the throttle plate is less than that of a smooth converging-diverging nozzle, and varies with throttle angle, pressure ratio, and throttle plate Reynolds number.
4. Due to the manufacturing tolerances involved, there is usually some minimum leakage area even when the throttle plate is closed against the throttle bore. This leakage area can be significant at small throttle openings.
5. The measured pressure drop across the throttle depends ( $\pm 10$  percent) on the circumferential location of the downstream pressure tap.
6. The pressure loss across the throttle plate under the actual flow conditions (which are unsteady even when the engine speed and load are constant, see Fig. 7-8) may be less than under steady flow conditions.

The throttle plate open area  $A_{th}$ , as a function of angle  $\psi$  for the geometry in Fig. 7-20, is given by<sup>2</sup>

$$\frac{4A_{th}}{\pi D^2} = \left(1 - \frac{\cos \psi}{\cos \psi_0}\right) + \frac{2}{\pi} \left[ \frac{a}{\cos \psi} (\cos^2 \psi - a^2 \cos^2 \psi_0)^{1/2} - \frac{\cos \psi}{\cos \psi_0} \sin^{-1} \left( \frac{a \cos \psi_0}{\cos \psi} \right) - a(1 - a^2)^{1/2} + \sin^{-1} a \right] \quad (7.18)$$

where  $a = d/D$ ,  $d$  is the throttle shaft diameter,  $D$  is the throttle bore diameter, and  $\psi_0$  is the throttle plate angle when tightly closed against the throttle bore. When  $\psi = \cos^{-1}(a \cos \psi_0)$ , the throttle open area reaches its maximum value ( $\approx \pi D^2/4 - dD$ ). The throttle plate discharge coefficient (which varies with  $A_{th}$ ), and minimum leakage area, must be determined experimentally.

The mass flow rate through the throttle valve can be calculated from standard orifice equations for compressible fluid flow [see App. C, Eqs. (C-8) and

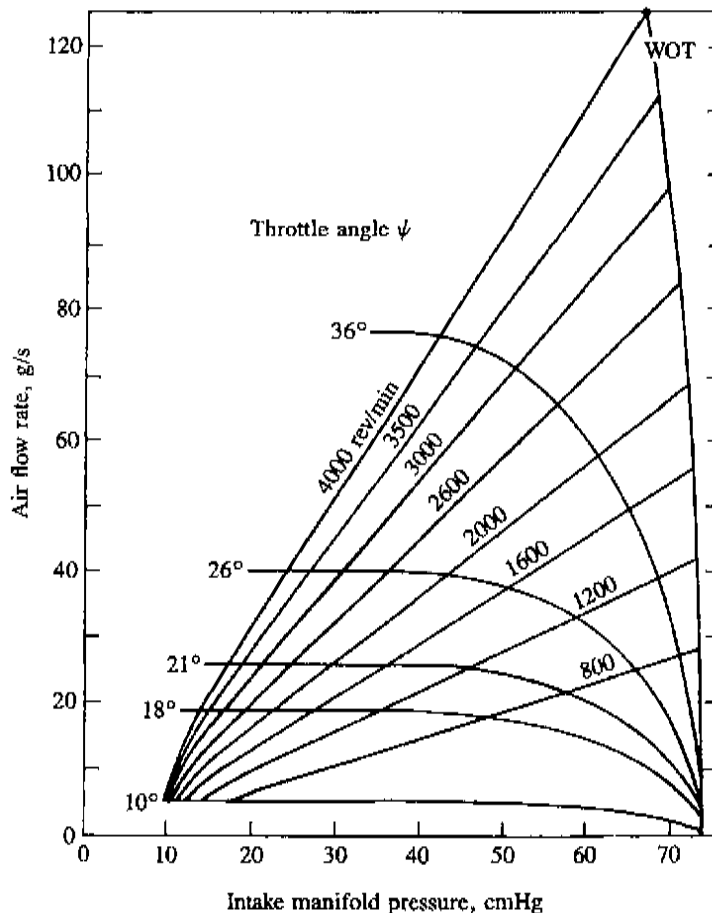
(C-9)]. For pressure ratios across the throttle less than the critical value ( $p_T/p_0 = 0.528$ ), the mass flow rate is given by

$$\dot{m}_{th} = \frac{C_D A_{th} p_0}{\sqrt{RT_0}} \left(\frac{p_T}{p_0}\right)^{1/\gamma} \left\{ \frac{2\gamma}{\gamma-1} \left[ 1 - \left(\frac{p_T}{p_0}\right)^{(\gamma-1)/\gamma} \right] \right\}^{1/2} \quad (7.19)$$

where  $A_{th}$  is the throttle plate open area [Eq. (7.18)],  $p_0$  and  $T_0$  are the upstream pressure and temperature,  $p_T$  is the pressure downstream of the throttle plate (assumed equal to the pressure at the minimum area: i.e., no pressure recovery occurs), and  $C_D$  is the discharge coefficient (determined experimentally). For pressure ratios greater than the critical ratio, when the flow at the throttle plate is choked,

$$\dot{m}_{th} = \frac{C_D A_{th} p_0}{\sqrt{RT_0}} \gamma^{1/2} \left(\frac{2}{\gamma+1}\right)^{(\gamma+1)/2(\gamma-1)} \quad (7.20)$$

The relation between air flow rate, throttle angle, intake manifold pressure, and engine speed for a two-barrel carburetor and a 4.7-dm<sup>3</sup> (288-in<sup>3</sup>) displacement eight-cylinder production engine is shown in Fig. 7-22. While the lines are predictions from a quasi-steady computer simulation, the agreement with data is excellent. The figure shows that for an intake manifold pressure below the critical



**FIGURE 7-22**  
Variation in air flow rate past a throttle, with inlet manifold pressure, throttle angle, and engine speed. 4.7-dm<sup>3</sup> displacement eight-cylinder engine.<sup>2</sup>

value ( $0.528 \times p_{\text{atm}} = 53.5 \text{ kN/m}^2 = 40.1 \text{ cmHg}$ ) the air flow rate at a given throttle position is independent of manifold pressure and engine speed because the flow at the throttle plate is choked.<sup>2</sup>

## 7.6 FLOW IN INTAKE MANIFOLDS

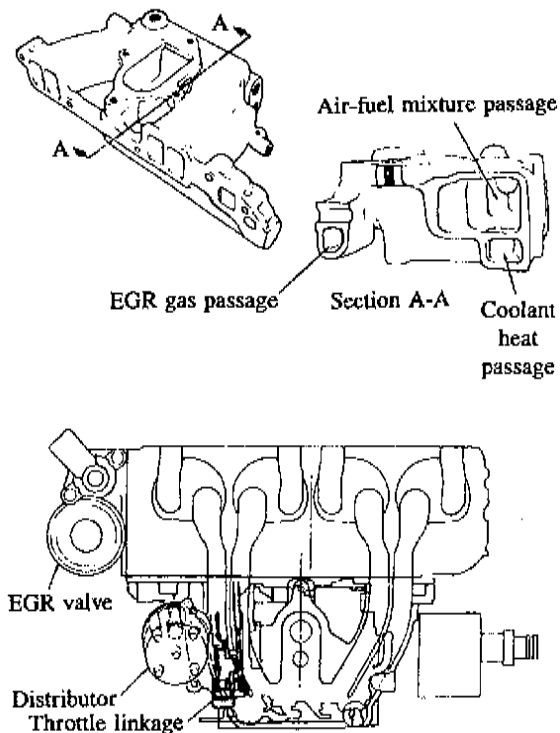
### 7.6.1 Design Requirements

The details of the air and fuel flow in intake manifolds are extremely complex. The combination of pulsating flow into each cylinder, different geometry flow paths from the plenum beneath the throttle through each runner and branch of the manifold to each inlet port, liquid fuel atomization, vaporization and transport phenomena, and the mixing of EGR with the fresh mixture under steady-state engine operating conditions are difficult enough areas to untangle. During engine transients, when the throttle position is changed, the fact that the processes which govern the air and the fuel flow to the cylinder are substantially different introduces additional problems. This section reviews our current understanding of these phenomena.

Intake manifolds consist typically of a plenum, to the inlet of which bolts the throttle body, with individual runners feeding branches which lead to each cylinder (or the plenum can feed the branches directly). Important design criteria are: low air flow resistance; good distribution of air and fuel between cylinders; runner and branch lengths that take advantage of ram and tuning effects; sufficient (but not excessive) heating to ensure adequate fuel vaporization with carbureted or throttle-body injected engines. Some compromises are necessary; e.g., runner and branch sizes must be large enough to permit adequate flow without allowing the air velocity to become too low to transport the fuel droplets. Some of these design choices are illustrated in Fig. 7-23 which shows an inlet manifold and carburetor arrangement for a modern four-cylinder  $1.8\text{-dm}^3$  engine. In this design the four branches that link the plenum beneath the carburetor and throttle with the inlet ports are similar in length and geometry, to provide closely comparable flow paths. This manifold is heated by engine coolant as shown and uses an electrically heated grid beneath the carburetor to promote rapid fuel evaporation.<sup>21</sup> Exhaust gas heated stoves at the floor of the plenum are also used in some intake manifolds to achieve adequate fuel vaporization and distribution. Note that with EGR, the intake manifold may contain passages to bring the exhaust gas to the plenum or throttle body.

With port fuel-injection systems, the task of the inlet manifold is to control the air (and EGR) flow. Fuel does not have to be transported from the throttle body through the entire manifold. Larger and longer runners and branches, with larger angle bends, can be used to provide equal runner lengths and take greater advantage of ram and tuning effects. With port fuel injection it is not normally necessary to heat the manifold.

A large number of different manifold arrangements are used in practice. Different cylinder arrangements (e.g., four, V-six, in-line-six, etc.) provide quite different air and fuel distribution problems. Air-flow phenomena in manifolds can



**FIGURE 7-23**  
Inlet manifold for four-cylinder 1.8-dm<sup>3</sup> displacement spark-ignition engine.<sup>21</sup>

be considered as unaffected by the fuel flow. The reverse is definitely not the case: the fuel flow—liquid and vapor—depends strongly on the air flow. These two topics will therefore be reviewed in sequence.

### 7.6.2 Air-Flow Phenomena

The air flow out of the manifold occurs in a series of pulses, one going to each cylinder. Each pulse is approximately sinusoidal in shape. For four- and eight-cylinder engines, these flow pulses sequence such that the outflow is essentially zero between pulses. For six-cylinder arrangements the pulses will overlap. When the engine is throttled, backflow from the cylinder into the intake manifold occurs during the early part of the intake process until the cylinder pressure falls below the manifold pressure. Backflow can also occur early in the compression stroke before the inlet valve closes, due to rising cylinder pressure. The flow at the throttle will fluctuate as a consequence of the pulsed flow out of the manifold into the cylinders. At high intake vacuum, the flow will be continuously inward at the throttle and flow pulsations will be small. When the outflow to the cylinder which is undergoing its intake stroke is greater than the flow through the throttle, the cylinder will draw mixture from the rest of the intake manifold. During the portion of the intake stroke when the flow into the cylinder is lower than the flow through the throttle, mixture will flow back into the rest of the manifold. At wide-open throttle when the flow restriction at the throttle is a minimum, flow pulsations at the throttle location will be much more pronounced.<sup>19</sup>

The air flows to each cylinder of a multicylinder engine, even under steady operating conditions, are not identical. This is due to differences in runner and



branch length and other geometric details of the flow path to each cylinder. Also, as each cylinder's intake flow commences, air is drawn from the branch and runner leading to the cylinder, the plenum, and the other runners and branches feeding the plenum, as well as past the throttle. This "drawing down" of other parts of the intake manifold depends on the arrangement of the plenum, runners, and branches, and the firing order of the cylinders. Thus the air flow to each individual cylinder is affected by the details of its own branch, how that branch connects to the rest of the intake manifold, and the cylinder firing order.<sup>22</sup> The differences between the air flows to individual cylinders have been measured. Variations in the average air mass flow rate to each individual cylinder of up to about 5 percent above and below the average are quite common. Larger peak-to-peak variations ( $\pm 15$  percent) have been measured. The extent of each cylinder's difference from the average flow varied significantly as engine speed and load were varied.<sup>23, 24</sup>

Typical quantities that characterize manifold air flow are given in Table 7.1 for a four- and an eight-cylinder spark-ignition engine. The volume of mixture pulled into each cylinder per cycle is about the same as the volume of one direct flow path between the throttle plate and inlet valve. Thus, one stroke loads the manifold, the next one pulls the charge into the cylinder.

An additional phenomenon becomes important when engine load is changed by opening or closing the throttle: the mass of air in the induction system volume takes a finite time to adjust to the new engine operating conditions. For example, as the throttle is opened the air flow into the manifold increases as the throttle open area increases. However, due to the finite volume of

**TABLE 7.1**  
**Parameters that characterize manifold air flow**

Engine geometry	I-4†	V-8‡
Typical flow-path distance between throttle bore and intake valve, cm	33	30
Average intake-passage flow area, cm <sup>2</sup>	9.4	16
Volume of one direct flow path from throttle bore to intake valve, cm <sup>3</sup>	300	500
<b>Range of speeds, etc.</b>	<b>Maximum</b>	<b>Minimum</b>
Crankshaft, rev/min	5000	650
Peak air velocity in manifold branch, m/s	130†, 100‡	15
Peak Reynolds number in manifold branch	$4 \times 10^5$	$5 \times 10^4$
Duration of individual cylinder intake process, ms	6	46

† 1.8-dm<sup>3</sup> four-cylinder in-line SI engine.<sup>21</sup>

‡ 5.6-dm<sup>3</sup> V eight-cylinder SI engine.<sup>25</sup>

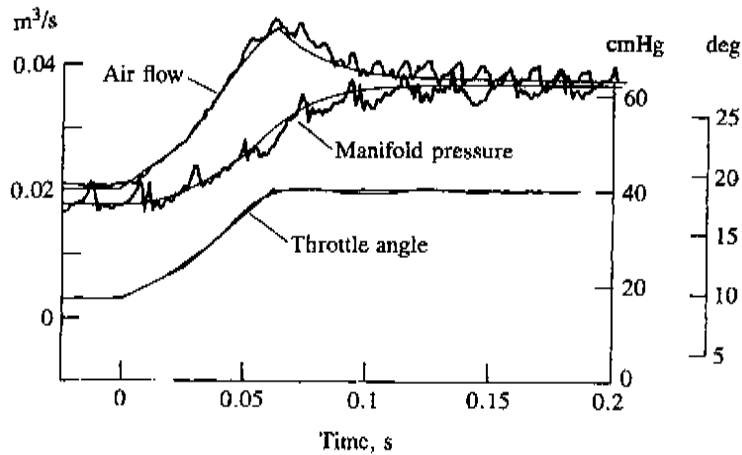


FIGURE 7-24

Throttle angle, intake manifold pressure, and air flow rate past the throttle versus time for 10° part-load throttle opening. 5-dm<sup>3</sup> V-8 engine.<sup>25</sup>

the manifold, the pressure level in the manifold increases more slowly than would be the case if steady-state conditions prevailed at each throttle position. Thus, the pressure difference across the throttle is larger than it would be under steady flow conditions and the throttle air flow overshoots its steady-state value. The air flow into each cylinder depends on the pressure in the manifold, so this lags the throttle air flow. This transient air-flow phenomenon affects fuel metering. For throttle-body injection or a carburetor, fuel flow should be related to throttle air flow. For port fuel injection, fuel flow should be related to cylinder air flow. Actual results for the air flow rate and manifold pressure in response to an opening of the throttle (increase in throttle angle) are shown in Fig. 7-24. The overshoot in throttle air flow and lag in manifold pressure as the throttle angle is increased are evident. Opposite effects will occur for a decrease in throttle angle.

**AIR-FLOW MODELS.** Several models of the flow in an intake manifold have been proposed.<sup>26, 27</sup> One simple manifold model that describes many of the above phenomena is the *plenum* or *filling and emptying* model. It is based on the assumption that at any given time the manifold pressure is uniform. The continuity equation for air flow into and out of the intake manifold is

$$\frac{dm_{a,m}}{dt} = \dot{m}_{a,th} - \sum \dot{m}_{a,cyl} \quad (7.21)$$

where  $m_{a,m}$  is the mass of air in the manifold, and  $\dot{m}_{a,th}$  and  $\dot{m}_{a,cyl}$  are the air mass flow rates past the throttle and into each cylinder, respectively. The flow rate past the throttle is given by Eq. (7.19) or (7.20). For manifold pressures sufficiently low to choke the flow past the throttle plate, the flow rate is independent of manifold pressure. The mass flow rate to the engine cylinders can be modeled at several levels of accuracy. The air flow through the valve to each cylinder can be computed from the valve area, discharge coefficient, and pressure

difference across the valve; or a sine wave function can be assumed. In the general case, Eq. (7.21) must be combined with the first law for an open system (see Sec. 14.2.2). For calculating the manifold response to a change in load or throttle setting, simplifying assumptions can be made. A quasi-steady approximation for the cylinder air flow:

$$\sum \dot{m}_{a, \text{cyl}} = \frac{\eta_v \rho_{a, m} V_d N}{2}$$

is usually adequate, and the air temperature can be assumed constant.<sup>25</sup> Then, using the ideal gas law for the manifold,  $p_m V_m = m_{a, m} R_a T_m$ , Eq. (7.21) can be written as

$$\frac{dp_m}{dt} + \frac{\eta_v V_d N}{2V_m} p_m = \dot{m}_{a, \text{th}} \frac{RT_m}{V_m} \quad (7.22)$$

Both  $\eta_v$  and  $\dot{m}_{a, \text{th}}$  have some dependence on  $p_m$  [e.g., see Eq. (6.2)]. In the absence of this weak dependence, Eq. (7.22) would be a first-order equation for  $p_m$  with a time constant  $\tau = 2V_m/(\eta_v V_d N) \approx V_m/\dot{V}_{\text{cyl}}$ , which is 2 to 4 times the intake stroke duration. The smooth curves in Fig. 7-24 are predictions made with Eq. (7.22) and show good agreement with the data. The plenum model is useful for investigating manifold pressure variations that result from load changes. It provides no information concerning pressure variations associated with momentum effects.

*Helmholtz resonator models* for the intake system have been proposed. This type of model can predict the resonant frequencies of the combined intake and engine cylinder system, and hence the engine speeds at which increases in air flow due to intake tuning occur. It does not predict the magnitude of the increase in volumetric efficiency. The Helmholtz resonator theory analyzes what happens during one inlet stroke, as the air in the manifold pipe is acted on by a forcing function produced by the piston motion. As the piston moves downward during the intake stroke, a reduced pressure occurs at the inlet valve relative to the pressure at the open end of the inlet pipe. A rarefaction wave travels down the intake pipe to the open end and is reflected as a compression wave. A positive tuning effect occurs when the compression wave arrives at the inlet valve as the valve is closing.<sup>27</sup> A single-cylinder engine modeled as a Helmholtz resonator is shown in Fig. 7-25a. The effective resonator volume  $V_{\text{eff}}$  is chosen to be one-half of the displaced volume plus the clearance volume; the piston velocity is then close to its maximum and the pressure in the inlet system close to its minimum. The tuning peak occurs when the natural frequency of the cylinder volume coupled to the pipe is about twice the piston frequency. For a single-cylinder, fed by a single pipe open to the atmosphere, the resonant tuning speed  $N_r$  is given by

$$N_r(\text{rev/min}) = \frac{955}{K} a \left( \frac{A}{lV_{\text{eff}}} \right)^{1/2} \quad (7.23)$$

where  $a$  is the sound speed (m/s),  $A$  the effective cross-sectional area of the inlet system ( $\text{cm}^2$ ),  $l$  the effective length of the inlet system (cm),  $K$  a constant equal to about 2 for most engines, and  $V_{\text{eff}} = V_d(r_c + 1)/[2(r_c - 1)]$  ( $\text{cm}^3$ ).<sup>28</sup>

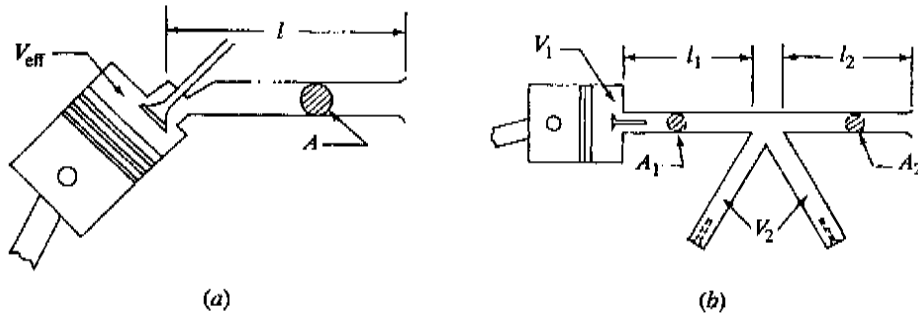


FIGURE 7-25 Helmholtz resonator models for (a) single-cylinder engine and (b) multicylinder engine.<sup>27</sup>

The Helmholtz theory for multicylinder engines treats the pipes of cylinders not undergoing induction as an additional volume. The two pipes,  $(l_1, A_1)$  and  $(l_2, A_2)$ , and two volumes,  $V_1$  and  $V_2$ , in Fig. 7-25b form a vibrating system with two degrees of freedom and two resonant frequencies. The following equation, based on an electrical analog (in which capacitors represent volumes and inductors pipes), gives the two frequencies at which the manifold shown in Fig. 7-25b would be tuned:<sup>28</sup>

$$f_{\mp} = \frac{1}{2\pi} \left\{ \frac{(\alpha\beta + \alpha + 1) \mp [(\alpha\beta + \alpha + 1)^2 - 4\alpha\beta]^{1/2}}{2\alpha\beta L_1 C_1} \right\}^{1/2} \quad (7.24)$$

where  $\alpha = L_2/L_1$ ,  $\beta = C_2/C_1$ ,  $C_1 = V_1$ ,  $C_2 = V_2$ ,  $L_1 = (l/A)_1$ ,  $L_2 = (l/A)_2$ , and  $V_{\text{eff}} = V_1$ . The Helmholtz theory predicts the engine speeds at which positive tuning resonances occur with reasonable accuracy.<sup>27</sup>

The dynamics of the flow in multicylinder intake (and exhaust) systems can be modeled most completely using one-dimensional unsteady compressible flow equations. The standard method of solution of the governing equations has been the method of characteristics (see Benson<sup>29</sup>). Recently, finite difference techniques which are more efficient have been used.<sup>30</sup> The assumptions usually made in this type of analysis are:

1. The intake (or exhaust) system can be modeled as a combination of pipes, junctions, and plenums.
2. Flow in the pipes is one dimensional and no axial heat conduction occurs.
3. States in the engine cylinders and plenums are uniform in space.
4. Boundary conditions are considered quasi steady.
5. Coefficients of discharge, heat transfer, pipe friction, and bend losses for steady flow are valid for unsteady flow.
6. The gases can be modeled as ideal gases.

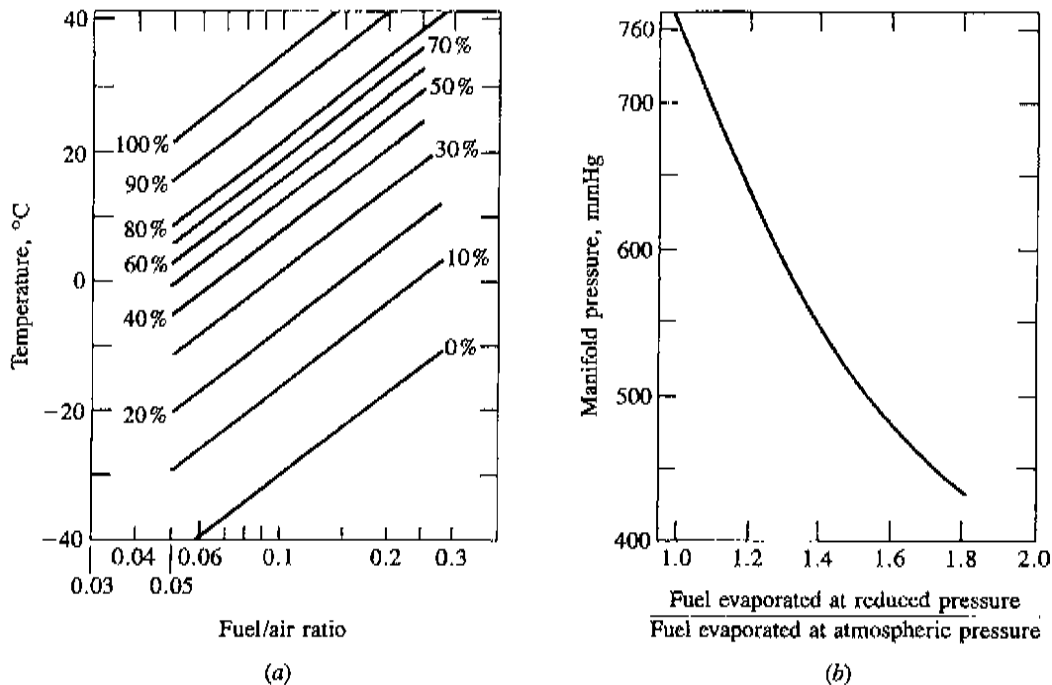
This approach to intake and exhaust flow analysis is discussed more fully in Sec. 14.3.4.

### 7.6.3 Fuel-Flow Phenomena

**TRANSPORT PROCESSES.** With conventional spark-ignition engine liquid-fuel metering systems, the fuel enters the air stream as a liquid jet. The liquid jet atomizes into droplets. These mix with the air and also deposit on the walls of the intake system components. The droplets vaporize; vaporization of the liquid fuel on the walls occurs. The flow of liquid fuel along the walls can be significant. The transport of fuel as vapor, droplets, and liquid streams or films can all be important. The fuel transport processes in the intake system are obviously extremely complex.

The details of the fuel transport process are different for multipoint fuel-injection systems than for carburetor and throttle-body injection systems. For the latter systems, fuel must be transported past the throttle plate and through the complete intake manifold. For the former systems, the liquid fuel is injected in the inlet port, toward the back of the intake valve. For all these practical fuel metering systems, the quality of the mixture entering the engine is imperfect. The fuel, air, recycled exhaust, mixture is not homogeneous; the fuel may not be fully vaporized as it enters the engine. The charge going to each cylinder is not usually uniform in fuel/air ratio throughout its volume, and the distribution of fuel between the different engine cylinders is not exactly equal. During engine transients, when engine fuel and air requirements and manifold conditions change, it is obvious that the above fuel transport processes will not all vary with time in the same way. Thus, in addition to the transient non-quasi-steady air-flow phenomena described above, there are transient fuel-flow phenomena. These have to be compensated for in the fuel metering strategy.

Since gasoline, the standard spark-ignition engine fuel, is a mixture of a large number of individual hydrocarbons it has a boiling temperature range rather than a single boiling point. Typically, this range is 30 to 200°C. Individual hydrocarbons have the saturation pressure-temperature relationships of a pure substance. The lower the molecular weight, the higher will be the saturated vapor pressure at a given temperature. The boiling point of hydrocarbons depends primarily on their molecular weight: the vapor pressure also depends on molecular structure. The equilibrium state of a hydrocarbon-air mixture depends therefore on the vapor pressure of the hydrocarbon at the given temperature, the relative amounts of the hydrocarbon and air, and the total pressure of the mixture. The equilibrium fraction of fuel evaporated at a given temperature and pressure can be calculated from Bridgeman charts<sup>31</sup> and the distillation characteristics of the fuel (defined by the ASTM distillation curve<sup>32</sup>). Figure 7-26a shows the effect of mixture temperature on percent of indolene fuel (a specific gasoline) evaporated at equilibrium at atmospheric pressure. Figure 7-26b shows the effect of reduced manifold pressure on the amount evaporated.<sup>18</sup> While insufficient time is usually available in the manifold to establish equilibrium, the trends shown are indicative of what happens in practice: lower pressures increase the relative amount of fuel vaporized and charge heating is usually required to vaporize a substantial fraction of the fuel.



**FIGURE 7-26**

(a) Percentage of indolene fuel evaporated at equilibrium at 1 atmosphere pressure. (b) Effect of pressure on amount of indolene fuel evaporated.<sup>18</sup>

For carbureted and throttle-body injection systems, the fuel path is the following. Until the throttle plate is close to fully opened, most of the fuel metered into the air stream impacts on the throttle plate and throttle-body walls. Only a modest fraction of the fuel vaporizes upstream of the throttle. The liquid is re-entrained as the air flows at high velocity past the throttle plate. The fuel does not usually divide equally on either side of the throttle plate axis. The air undergoes a 90° bend in the plenum beneath the throttle; much of the fuel which has not evaporated is impacted on the manifold floor. Observations of fuel behavior in intake manifolds with viewing ports or transparent sections show that there is substantial liquid fuel on the walls with carburetor fuel metering systems. Figure 7-27 shows the engine conditions under which liquid fuel was observed on the floor of the manifold plenum beneath the throttle plate and in the manifold runners, in a standard four-cylinder production engine.<sup>23</sup> This manifold was heated by engine coolant at 90°C. The greatest amount of liquid was present at high engine loads and low speeds. Heating the manifold to a higher temperature with steam at 115°C resulted in a substantial reduction in the amount of liquid: there was no extensive puddling on the plenum floor, liquid films or rivulets were observed in a zone bounded by 120 mmHg vacuum and 2500 rev/min, and there were no films or rivulets in the manifold runner. Depending on engine operating conditions, transport of fuel as a liquid film or rivulet in the manifold and vaporization from these liquid fuel films and rivulets and subsequent transport as vapor may occur.

Vaporized fuel and liquid droplets which remain suspended in the air

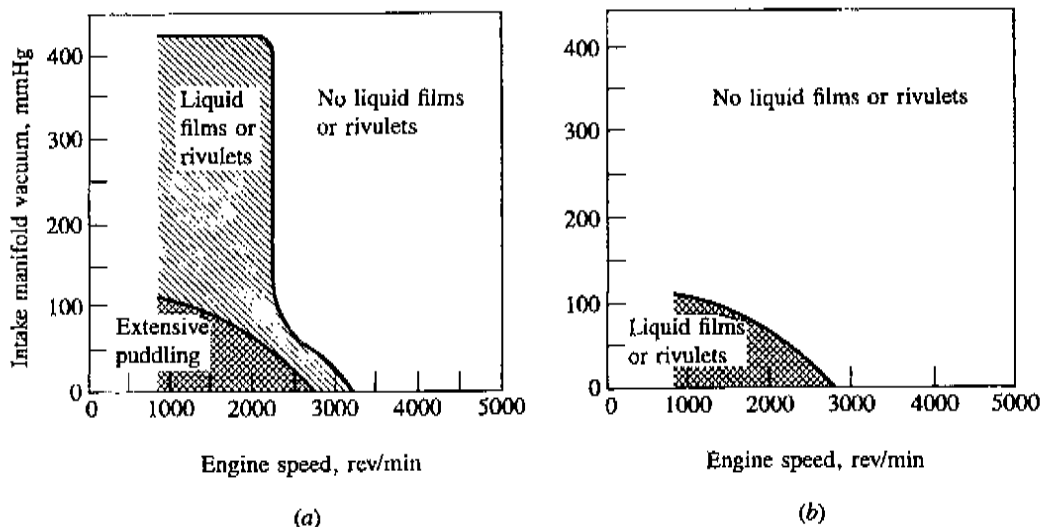


FIGURE 7-27

Regions of engine load and speed range where extensive pools or puddles, liquid films, or rivulets were observed: (a) on manifold plenum floor and (b) in manifold runner. Four-cylinder automobile engine. Manifold heated by coolant at 90°C.<sup>23</sup>

stream will be transported with the air stream. However, droplet deposition on the manifold walls may occur due to gravitational settling and to inertial effects as the flow goes round bends in the manifold.

The fuel transport processes for port fuel-injection systems are different and will depend significantly on the timing and duration of the injection pulse. Fuel is injected onto the back of the inlet valve (and surrounding port wall), usually while the valve is closed or only partly open. Vaporization of liquid fuel off the valve and walls occurs, enhanced by the backflow of hot residual gases from the cylinder (especially at part load). There is evidence that, even under fully warmed-up engine conditions, some fuel is carried as liquid drops into the cylinder.<sup>33</sup>

**FUEL DROPLET BEHAVIOR.** With carburetor and throttle-body injection systems, the liquid fuel atomizes as it enters the air stream. In the carburetor venturi this occurs as the fuel-air emulsion from the fuel jet(s) enters the high-velocity ( $> 100$  m/s) air stream. With an injector, the velocity of the liquid jet as it exits the nozzle is high enough to shatter the flowing liquid, and its interaction with the coaxial air flow further atomizes the fuel. Typical droplet-size distributions are not well defined; size would vary over the load and speed range. Droplet diameters in the 25 to 100  $\mu\text{m}$  range are usually assumed to be representative; larger drops are also produced. The liquid fuel drops are accelerated by the surrounding air stream and start to vaporize. Vaporization rates have been calculated using established formulas for heat and mass transfer between a droplet and a surrounding flowing gas stream (see Ref. 34 for a review of methods of calculating droplet vaporization rates). Calculations of fuel vaporization in a carburetor venturi and upstream of the throttle plate show that the temperature

of the liquid fuel droplets decreases rapidly (by up to about  $30^\circ\text{C}^{35}$ ), and the fraction of the fuel vaporized is small (in the 2 to 15 percent range<sup>35, 36</sup>).

Liquid fuel drops, due to their density being many times that of the air, will not exactly follow the air flow. Droplet impaction on the walls may occur as the flow changes direction, and the greater inertia of the droplets causes them to move across the streamlines to the outer wall. Deposition on the manifold floor due to gravity may also occur. The equation of motion for an individual droplet in a flowing gas stream is

$$\left(\frac{1}{6}\pi D_d^3 \rho_f\right)\mathbf{a} = m_d \mathbf{g} - \frac{1}{2}(\mathbf{v}_d - \mathbf{v}_g) |\mathbf{v}_d - \mathbf{v}_g| \rho_g C_D \frac{\pi D_d^2}{4} \quad (7.25)$$

where  $D_d$  is the droplet diameter,  $\rho_f$  and  $\rho_g$  are liquid and gas densities,  $\mathbf{v}_d$  and  $\mathbf{v}_g$  are the droplet and gas velocities,  $\mathbf{a}$  is the droplet acceleration,  $\mathbf{g}$  acceleration due to gravity, and  $C_D$  is the drag coefficient. For  $6 < \text{Re} < 500$  the drag coefficient of an evaporating droplet is a strong function of the Reynolds number,  $\text{Re}$ : e.g.,

$$C_D = 27 \text{Re}^{-0.84} \quad (7.26)$$

where  $\text{Re} = (\rho_g D_d |\mathbf{v}_d - \mathbf{v}_g| / \mu_g)$ .

Studies of droplet impaction and evaporation using the above equations and typical manifold conditions and geometries indicate the following.<sup>26, 35, 37</sup> For  $90^\circ$  bends, drops of less than  $10 \mu\text{m}$  diameter are essentially carried by the gas stream (<10 percent impaction); almost all droplets larger than  $25 \mu\text{m}$  impact on the walls. Droplet sizes produced first in the carburetor venturi or fuel injector spray and then by secondary atomization as liquid fuel is entrained from the throttle plate and throttle-body walls depend on the local gas velocity: higher local relative velocities between the gas and liquid produce smaller drop sizes. Approximate estimates which combine the two phenomena outlined above show that at low engine air flow rates, almost all of the fuel will impact first on the throttle plate and then on the manifold floor as the flow turns  $90^\circ$  into the manifold runners. At high air flows, because the drops are smaller, a substantial fraction of the drops may stay entrained in the air flow. Secondary atomization at the throttle at part-load operating conditions is important to the fuel transport process: the very high air velocities at the edge of the throttle plate produce droplets of order or less than  $10 \mu\text{m}$  diameter. However, coalescence and deposition on the walls and subsequent reentrainment probably increase the mean droplet size. In the manifold, gravitational settling of large ( $>100 \mu\text{m}$ ) droplets would occur at low air flow rates,<sup>38</sup> but these drops are also likely to impact the walls due to their inertia as the flow is turned.

Estimates of droplet evaporation rates in the manifold indicate the following. With a representative residence time in the manifold of about one crank revolution (10 ms at 6000 rev/min, 100 ms at 600 rev/min), only drops of size less than about  $10 \mu\text{m}$  will evaporate at the maximum speed;  $100 \mu\text{m}$  droplets will not vaporize fully at any speed. Most of these large droplets impact on the walls, anyway. Drops small enough to be carried by the air stream are likely to vaporize in the manifold.<sup>26</sup>

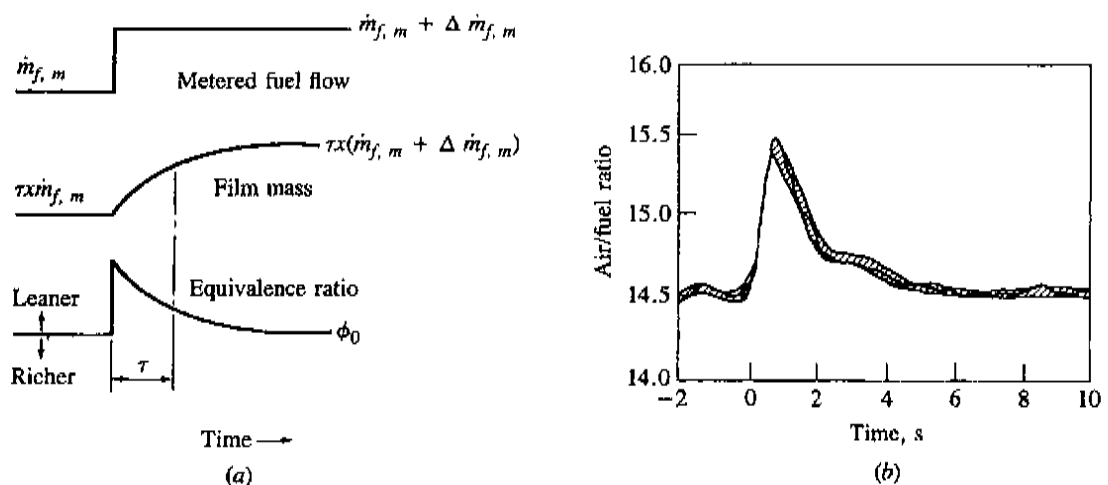


**FUEL-FILM BEHAVIOR.** The fuel which impacts on the wall will also vaporize and, depending on where in the manifold deposition occurs and the local manifold geometry, may be transported along the manifold as a liquid film or rivulet. If the vaporization rate off the wall is sufficiently high, then a liquid film will not build up. Any liquid film or pool on the manifold floor or walls is important because it introduces additional fuel transport processes—deposition, liquid transport, and evaporation—which together have a much longer time constant than the air transport process. Thus changes in the air and the fuel flow into each engine cylinder, during a change in engine load, will not occur in phase with each other unless compensation is made for the slower fuel transport.

Several models of the behavior of liquid-fuel wall-films have been developed. One approach analyzes a liquid puddle on the floor of the manifold plenum.<sup>38</sup> Metered fuel enters the puddle; fuel leaves primarily through vaporization. The equation for rate of change of mass of fuel in the puddle is

$$\dot{m}_{f,p} = \dot{m}_{f,in} - \dot{m}_{f,out} = x\dot{m}_{f,m} - \frac{m_{f,p}}{\tau} \quad (7.27)$$

where  $m_{f,p}$  is the mass of fuel in the puddle,  $\dot{m}_{f,m}$  is the metered fuel flow rate, and  $x$  is the fraction of the metered flow that enters the puddle. It is assumed that the reentrainment/evaporation rate is proportional to the mass of fuel in the puddle divided by the characteristic time  $\tau$  of the reentrainment/evaporation process. The puddle behavior predicted by this model in response to a step increase in engine load is shown in Fig. 7-28a. Because only part  $(1 - x)$  of the fuel flows directly with the air, as the throttle is opened rapidly a lean air/fuel ratio excursion is predicted. Figure 7-28b shows that this behavior (without any metering compensation) is observed in practice. Estimates of the volume of fuel in the puddle (for a 5-liter V-8 engine) are of order  $1000 \text{ mm}^3$ , and increase with



**FIGURE 7-28**

(a) Predicted behavior of the fuel film for an uncompensated step change in engine operating conditions. (b) Observed variation in air/fuel ratio for uncompensated throttle opening at 1600 rev/min which increased manifold pressure from 48 to 61 cmHg.<sup>38</sup>

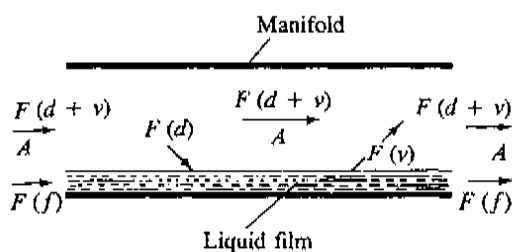


FIGURE 7-29

Schematic of fuel flow paths in the manifold when liquid film flows along the manifold runner floor.

- A Air
- F Fuel
- f Liquid fuel film
- d Liquid fuel droplets
- v Fuel vapor

increasing load and speed. The time constant is of order 2 seconds for a fully warmed-up engine; it varies with engine operating conditions and is especially sensitive to intake manifold temperature. Such models have been used primarily to develop fuel metering strategies which compensate for the fuel transport lag.<sup>36</sup>

An alternative model, for liquid film flow in the manifold runner and branch, has been developed.<sup>37</sup> Fuel is deposited on the manifold walls and forms a film which flows toward the cylinder due to the shear force at the gas/liquid interface as shown in Fig. 7-29. Vaporization from the film also occurs. An analysis of the dynamics of the fuel film leads to expressions for steady-state film velocity and thickness. As air and metered fuel flows change due to a throttle position change, the characteristic time for reestablishing steady state is  $l/(2u_f)$ , where  $l$  is the manifold length and  $u_f$  the average film velocity. This characteristic response time is of order 1 second for typical manifold conditions, in approximate agreement with values obtained from transient engine experiments.

A more extensive analysis of both fuel droplet and film evaporation in a complete carburetor, throttle, manifold system,<sup>35</sup> with a multicomponent model for gasoline based on its distillation curve, indicates the following phenomena are important. Secondary atomization of the liquid fuel at the throttle, which produces the smallest droplet sizes when the throttle open angle is small, significantly increases the fraction of fuel evaporation in the manifold. Increasing inlet air temperature increases the fraction of fuel vaporized; this effect is larger at lower loads since secondary atomization under these conditions increases the liquid fuel surface area significantly. Heating the wall, which heats the liquid film on the wall directly, provides a greater increase in fraction evaporated than does equivalent heating of the air flow upstream of the carburetor. Due to the multicomponent nature of the fuel, the residual liquid fuel composition changes significantly as fuel is transported from the carburetor to the manifold exit. Of the full boiling range liquid composition at entry, all the light ends, most of the mid-range components, but only a modest amount of the high boiling point fraction have evaporated at the manifold exit. The predicted fuel fraction evaporated ranged from 40 to 60 percent for the conditions examined. One set of measurements of the fraction of fuel vaporized in the manifold of a warmed-up four-cylinder engine showed that 70 to 80 percent of the fuel had vaporized, confirming that under these operating conditions "most" but not necessarily "all" the fuel enters the cylinder in vapor form.<sup>39</sup>

The engine operating range where fuel puddling, fuel films, and rivulets are observed (see Fig. 7-27) can now be explained. At light load, secondary atom-

ization at the throttle and the lower manifold pressure would reduce the amount of liquid fuel impinging on the manifold plenum floor. Also, typical manifold heating at light load substantially exceeds the heat required to vaporize the fuel completely,<sup>40</sup> and manifold floor temperatures are of order 15°C higher than at full load. All the above is consistent with less liquid on the floor and none in the runners at light load, compared to what occurs at full load. At high speed, drop sizes produced in the carburetor are much smaller, so impingement on the walls is much reduced.

The fuel flow to each cylinder per cycle is not exactly the same. There is a *geometric variation* where fuel is not divided equally among individual cylinders. There is also a *time variation* under steady-state engine conditions where the air/fuel ratio in a given cylinder varies cycle-by-cycle.<sup>41</sup> Data on time-averaged air/fuel ratios in each cylinder of multicylinder engines show that the extent of the maldistribution varies from engine to engine, and for a particular engine varies over the load and speed range. Spreads in the equivalence ratio (maximum to minimum) of about 5 percent of the mean value are typical at light load for carbureted engines. Largest variations between cylinders usually occur at wide-open throttle. WOT spreads in the equivalence ratio of about 15 percent of the mean appear to be typical, again for carbureted engines, while spreads as high as 20 to 30 percent are not uncommon at particular speeds for some engines.<sup>23, 40</sup> Time variations are less well defined; the limited data available suggest they could be of comparable magnitude.<sup>41</sup>

With multipoint port fuel-injection systems, the fuel transport processes are substantially different and are not well understood. Air-flow phenomena are comparable to those with carbureted or throttle-body injection systems. However, manifold design can be optimized for air flow alone since fuel transport from the throttle through the manifold is no longer a design constraint. Because the manufacture and operation of individual fuel injectors are not identical, there is still some variation in fuel mass injected cylinder-to-cylinder and cycle-to-cycle. Since individual cylinder air flows depend on the design of the manifold, whereas the amount of fuel injected does not, uniform air distribution is especially important with port injection systems. The fuel vaporization and transport processes will depend on the duration of injection and the timing of injection pulse(s) relative to the intake valve-lift profile. Some of the injected fuel will impinge on the port walls, valve stem, and backside of the valve, especially when injection toward a closed valve occurs. Backflow of hot residual gases at part-load operation will have a substantial effect on fuel vaporization. Compensation for fuel lag during transient engine operation is still required; sudden throttle openings are accompanied by a "lean spike" in the mixture delivered to the engine, comparable to though smaller than that shown in Fig. 7-28 for a throttle-body fuel-injection system. Thus wall wetting, evaporation off the wall, and liquid flow along the wall are all likely to be important with port fuel-injection systems also.

With port fuel-injection systems, liquid fuel enters the cylinder and droplets are present during intake and compression. Limited measurements have been made of the distribution, size, and number density of these fuel droplets. During

intake, the droplet number density in the clearance volume increased to a maximum at the end of injection (the injection lasted from 45 to 153° ATC) and then decreased due to evaporation during compression to a very small value at the time of ignition. Average droplet size during intake was 10 to 20  $\mu\text{m}$  in diameter; it increased during compression as the smaller drops in the distribution evaporated. At the conditions tested, some 10 to 20 percent of the fuel was in droplet form at the end of injection. At ignition, the surviving droplets contained a negligible fraction of the fuel. During injection, the distribution of droplets across the clearance volume was nonuniform. It became much more uniform with time, after injection ended.<sup>33</sup>

## PROBLEMS

- 7.1. The equivalence ratio in a conventional spark-ignition engine varies from no load (idle) to full load, at a fixed engine speed, as shown at the top of Fig. P7-1. (By load is meant the percentage of the maximum brake torque at that speed.) Also shown is the variation in total friction (pumping plus mechanical rubbing plus accessory friction). Using formats similar to those shown, draw *carefully proportioned qualitative* graphs of the following parameters versus load (0 to 100 percent):

- Combustion efficiency,  $\eta_c$
- Gross indicated fuel conversion efficiency,  $\eta_{f,ig}$
- Gross indicated mean effective pressure,  $\text{imep}_g$
- Brake mean effective pressure,  $\text{bmep}$
- Mechanical efficiency,  $\eta_m$

Indicate clearly where the maximum occurs if there is one, and where the value is zero or unity or some other obvious value, if appropriate. Provide a *brief justification* for the shape of the curves you draw.

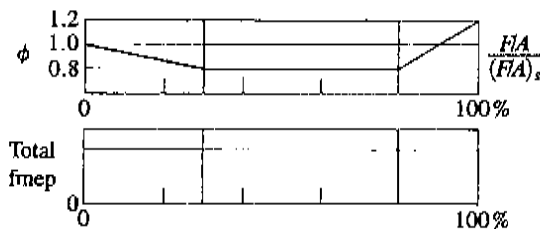


FIGURE P7-1

- 7.2. The four-cylinder spark-ignition engine shown in the figure uses an oxygen sensor in the exhaust system to determine whether the exhaust gas composition is lean or rich of the stoichiometric point, and a throttle-body injection system with feedback to maintain engine operation close to stoichiometric. However, since there is a time delay between a change in the fuel/air ratio at the injector location and the detection of that change by the sensor (corresponding to the flow time between the injector and the sensor), the control system shown results in oscillations in fuel/air ratio about the stoichiometric point.

- (a) Estimate the average flow time between the injector and the sensor at an engine speed of 2000 rev/min.

- (b) The sensor and control unit provide a voltage  $V$  of  $+V_s$  volts when the fuel/air equivalence ratio  $\phi$  is less than one and a voltage of  $-V_s$  volts when  $\phi$  is greater than one. The feedback injection system provides a fuel/air ratio ( $F/A$ ) given by

$$\left(\frac{F}{A}\right) = \left(\frac{F}{A}\right)_{t=0} (1 + CVt)$$

where  $t$  is the time (in seconds) after the voltage signal last changed sign,  $(F/A)_{t=0}$  is the fuel/air ratio at the injector at  $t = 0$ , and  $C$  is a constant. Develop carefully proportioned quantitative sketches of the variation in the fuel/air ratio at the injector and at the exhaust sensor, with time, showing the phase relation between the two curves. Explain briefly how you developed these graphs.

- (c) Find the value of the constant  $C$ , in volts<sup>-1</sup>-seconds<sup>-1</sup> (the feedback system gain), such that  $(F/A)$  variations about the stoichiometric value do not exceed  $\pm 10$  percent for  $V_s = 1$  V.

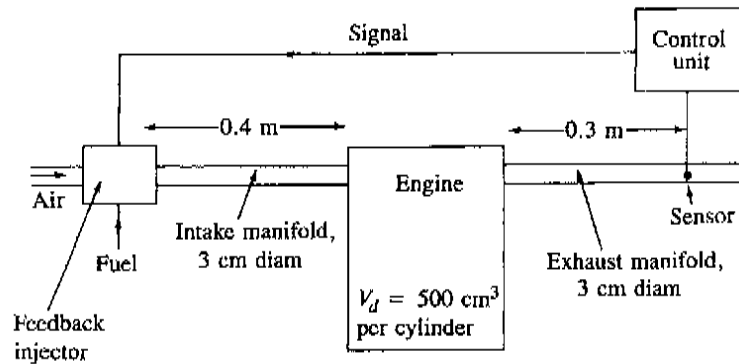


FIGURE P7-2

- 7.3. In many spark-ignition engines, liquid fuel is added to the inlet air upstream of the inlet manifold above the throttle. The inlet manifold is heated to ensure that under steady-state conditions the fuel is vaporized before the mixture enters the cylinder.
- (a) At normal wide-open throttle operating conditions, in a four-stroke cycle 1.6-dm<sup>3</sup> displacement four-cylinder engine, at 2500 rev/min, the temperature of the air entering the carburetor is 40°C. The heat of vaporization of the fuel is 350 kJ/kg and the rate of heat transfer to the intake mixture is 1.4 kW. Estimate the temperature of the inlet mixture as it passes through the inlet valve, assuming that the fuel is fully vaporized. The volumetric efficiency is 0.85. The air density is 1.06 kg/m<sup>3</sup> and  $c_p$  for air is 1 kJ/kg · K. You may neglect the effects of the heat capacity of the liquid and vapor fuel.
- (b) With port electronic fuel-injection systems, the fuel is injected directly into the intake port. The intake manifold is no longer heated. However, the fuel is only partly vaporized prior to entering the cylinder. Estimate the mixture temperature as it passes through the inlet valve with the EFI system, assuming that the air temperature entering the intake manifold is still 40°C and 50 percent of the fuel is vaporized.
- (c) Estimate the ratio of the maximum indicated power obtained at these conditions with this engine with a carburetor, to the maximum power obtained with port fuel injection. Assume that the inlet valve is the dominant restriction in the flow into the engine and that the pressure ratio across the inlet valve is the same for both carbureted and port-injection fueled engines. The intake mixture pressure and equivalence ratio remain the same in both these cases.

- 7.4. Port fuel-injection systems are replacing carburetors in automobile spark-ignition engines. List the major advantages and any disadvantages of fuel metering with port fuel injection relative to carburetion.
- 7.5. With multipoint port fuel injection and single-point injection systems, the fuel flow rate is controlled by the injection pulse duration. If each injector operates continuously at the maximum rated power point (wide-open throttle,  $A/F = 12$ , 5500 rev/min) of an automobile spark-ignition engine, estimate approximately the injection pulse duration (in crank angle degrees) for the same engine at idle. Idle conditions are: 700 rev/min, 0.3 atm inlet manifold pressure, stoichiometric mixture.
- 7.6. The fuel-air cycle results indicate that the maximum imep is obtained with gasoline-air mixtures at equivalence ratios of about 1.0. In practice, the maximum wide-open throttle power of a spark-ignition engine at a given speed is obtained with an air/fuel ratio of about 12. The vaporization of the additional gasoline lowers the temperature of the inlet air and the richer mixture has a lower ratio of specific heats  $\gamma_u$  during compression. Estimate approximately the change in mixture temperature due to vaporization of the additional fuel used to decrease  $A/F$  from 14.6 (an equivalence ratio of 1.0) to 12.2 in the intake system, and the combined effect of vaporization and lower  $\gamma_u$  on the unburned mixture temperature at WOT when the cylinder pressure is at its peak of 40 atm. (The principal effect of the richer mixture is its impact on knock.)
- 7.7. (a) Plot dimensionless throttle plate open area  $4A_{th}/(\pi D^2)$  as a function of throttle plate angle  $\psi$ . Assume  $\psi_0 = 10^\circ$ ,  $D$  (throttle bore diameter) = 57 mm,  $d$  (throttle shaft diameter) = 10.4 mm. What is the throttle plate area?
- (b) Estimate the average velocity of the air flowing through the throttle plate open area for  $\psi = 26^\circ$  at 3000 rev/min and  $\psi = 36^\circ$  at 2000 rev/min. Use the relationship between  $\psi$ , engine speed, and inlet manifold pressure given in Fig. 7-22. Assume a discharge coefficient  $C_D = 0.8$ .
- (c) For the throttle of part (a), estimate and plot the total force on the throttle plate and shaft, and the force parallel and perpendicular to the throttle bore axis (i.e., in the mean flow direction and normal to that direction) as a function of throttle angle at 2000 rev/min. Again use Fig. 7-22 for the relationship between  $\psi$  and inlet manifold pressure.
- 7.8. For the engine and intake manifold shown in Fig. 7-23, estimate the ratio of the intake manifold runner cross-sectional area to  $(\pi B^2/4)$ , the ratio of the length of the flow path from the intake manifold entrance to the inlet valve seat to the bore, the ratio of the volume of each inlet port to each cylinder's displaced volume, and the ratio of the volume of each intake manifold runner to each cylinder's displaced volume. The cylinder bore is 89 mm.

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## CHAPTER

# 11

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## POLLUTANT FORMATION AND CONTROL

### 11.1 NATURE AND EXTENT OF PROBLEM

Spark-ignition and diesel engines are a major source of urban air pollution. The spark-ignition engine exhaust gases contain oxides of nitrogen (nitric oxide,  $\text{NO}$ , and small amounts of nitrogen dioxide,  $\text{NO}_2$ —collectively known as  $\text{NO}_x$ ), carbon monoxide ( $\text{CO}$ ), and organic compounds which are unburned or partially burned hydrocarbons ( $\text{HC}$ ). The relative amounts depend on engine design and operating conditions but are of order:  $\text{NO}_x$ , 500 to 1000 ppm or 20 g/kg fuel;  $\text{CO}$ , 1 to 2 percent or 200 g/kg fuel; and  $\text{HC}$ , 3000 ppm (as  $\text{C}_1$ ) or 25 g/kg fuel. Piston blowby gases, and fuel evaporation and release to the atmosphere through vents in the fuel tank and carburetor after engine shut-down, are also sources of unburned hydrocarbons. However, in most modern engines these nonexhaust sources are effectively controlled by returning the blowby gases from the crankcase to the engine intake system and by venting the fuel tank and carburetor float bowl through a vapor-absorbing carbon cannister which is purged by some of the engine intake air during normal engine operation. In diesel engine exhaust, concentrations of  $\text{NO}_x$  are comparable to those from SI engines. Diesel hydrocarbon emissions are significant though exhaust concentrations are lower by about a factor of 5 than typical SI engine levels. The hydrocarbons in the exhaust may also condense to form white smoke during engine starting and warm-up.

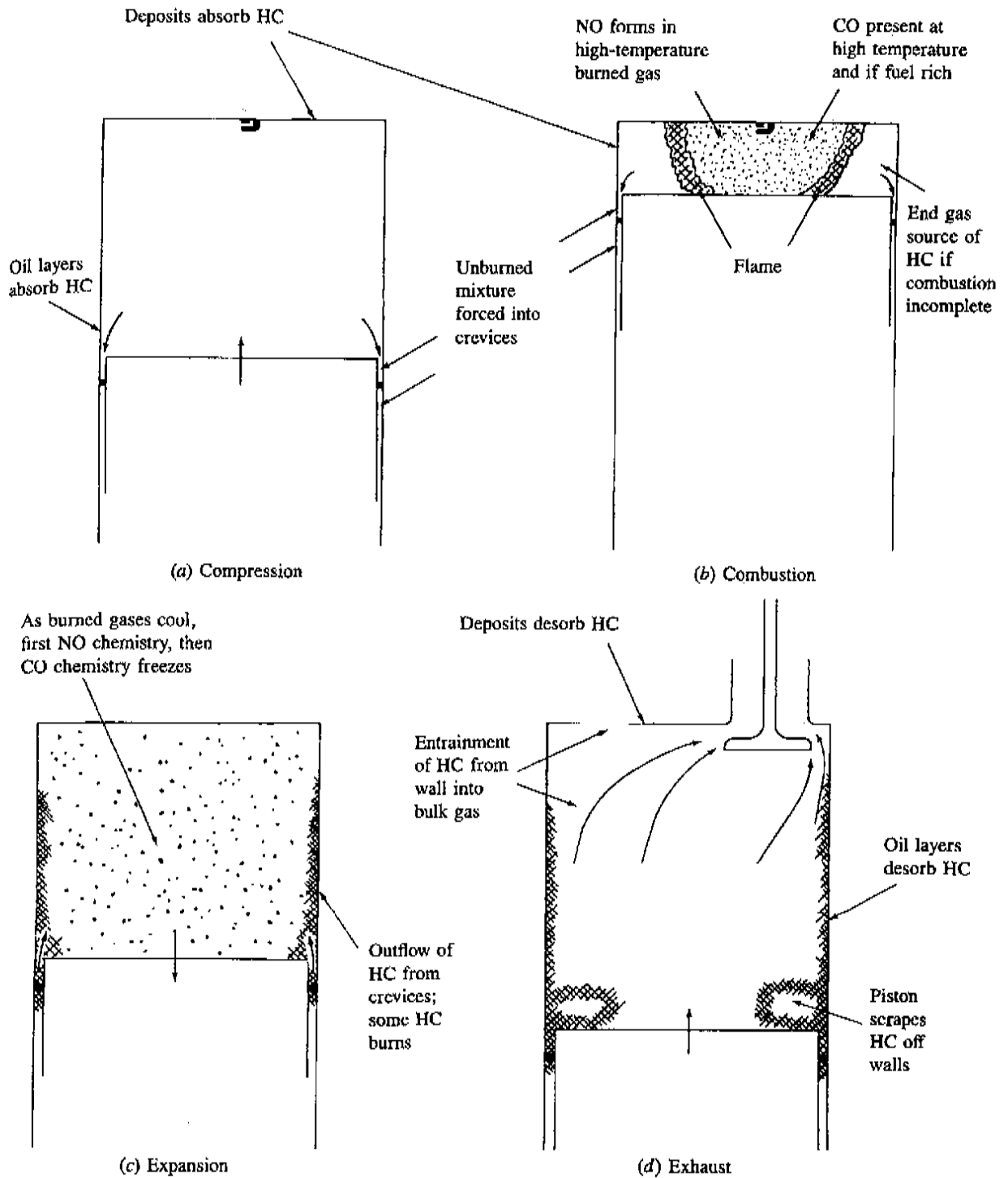
Specific hydrocarbon compounds in the exhaust gases are the source of diesel odor. Diesel engines are an important source of particulate emissions; between about 0.2 and 0.5 percent of the fuel mass is emitted as small ( $\sim 0.1 \mu\text{m}$  diameter) particles which consist primarily of soot with some additional absorbed hydrocarbon material. Diesel engines are not a significant source of carbon monoxide.

Use of alcohol fuels in either of these engines substantially increases aldehyde emissions. While these are not yet subject to regulation, aldehydes would be a significant pollutant if these fuels were to be used in quantities comparable to gasoline and diesel. Currently used fuels, gasoline and diesel, contain sulfur: gasoline in small amounts ( $\leq 600$  ppm by weight S), diesel fuel in larger amounts ( $\leq 0.5$  percent). The sulphur is oxidized (or burned) to produce sulfur dioxide,  $\text{SO}_2$ , of which a fraction can be oxidized to sulfur trioxide,  $\text{SO}_3$ , which combines with water to form a sulfuric acid aerosol.

In general, the concentrations of these pollutants in internal combustion engine exhaust differ from values calculated assuming chemical equilibrium. Thus the detailed chemical mechanisms by which these pollutants form and the kinetics of these processes are important in determining emission levels. For some pollutant species, e.g., carbon monoxide, organic compounds, and particulates, the formation and destruction reactions are intimately coupled with the primary fuel combustion process. Thus an understanding of the formation of these species requires knowledge of the combustion chemistry. For nitrogen oxides and sulfur oxides, the formation and destruction processes are not part of the fuel combustion process. However, the reactions which produce these species take place in an environment created by the combustion reactions, so the two processes are still intimately linked. A summary of the mechanisms by which these pollutants form in internal combustion engines provides an introduction to this chapter. In subsequent sections, the details of the basic formation mechanisms of each pollutant and the application of these mechanisms to the combustion process in both spark-ignition and compression-ignition engines will be developed.

The processes by which pollutants form within the cylinder of a conventional spark-ignition engine are illustrated qualitatively in Fig. 11-1. The schematic shows the combustion chamber during four different phases of the engine operating cycle: compression, combustion, expansion, and exhaust. Nitric oxide (NO) forms throughout the high-temperature burned gases behind the flame through chemical reactions involving nitrogen and oxygen atoms and molecules, which do not attain chemical equilibrium. The higher the burned gas temperature, the higher the rate of formation of NO. As the burned gases cool during the expansion stroke the reactions involving NO freeze, and leave NO concentrations far in excess of levels corresponding to equilibrium at exhaust conditions. Carbon monoxide also forms during the combustion process. With rich fuel-air mixtures, there is insufficient oxygen to burn fully all the carbon in the fuel to  $\text{CO}_2$ ; also, in the high-temperature products, even with lean mixtures, dissociation ensures there are significant CO levels. Later, in the expansion stroke, the CO oxidation process also freezes as the burned gas temperature falls.

The unburned hydrocarbon emissions have several different sources.



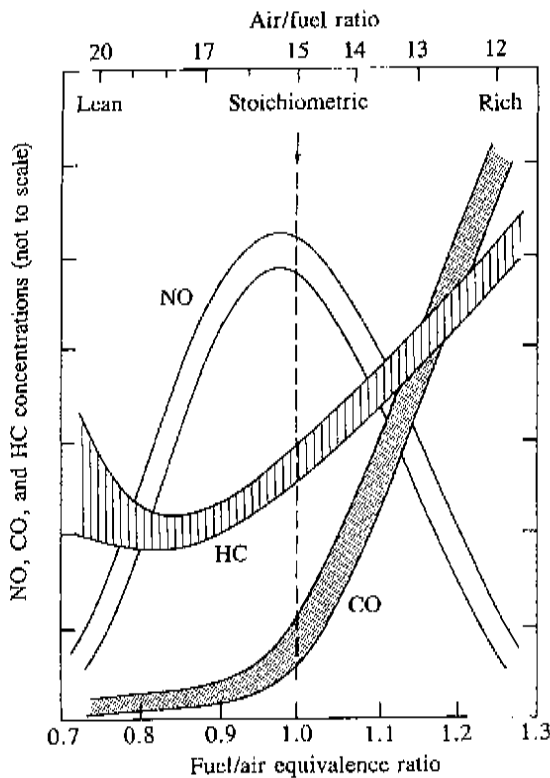
**FIGURE 11-1**  
 Summary of HC, CO, and NO pollutant formation mechanisms in a spark-ignition engine.

During compression and combustion, the increasing cylinder pressure forces some of the gas in the cylinder into crevices, or narrow volumes, connected to the combustion chamber: the volumes between the piston, rings, and cylinder wall are the largest of these. Most of this gas is unburned fuel-air mixture; much of it

escapes the primary combustion process because the entrance to these crevices is too narrow for the flame to enter. This gas, which leaves these crevices later in the expansion and exhaust processes, is one source of unburned hydrocarbon emissions. Another possible source is the combustion chamber walls. A quench layer containing unburned and partially burned fuel-air mixture is left at the wall when the flame is extinguished as it approaches the wall. While it has been shown that the unburned HC in these thin ( $\leq 0.1$  mm) layers burn up rapidly when the combustion chamber walls are clean, it has also been shown that the porous deposits on the walls of engines in actual operation do increase engine HC emissions. A third source of unburned hydrocarbons is believed to be any engine oil left in a thin film on the cylinder wall, piston and perhaps on the cylinder head. These oil layers can absorb and desorb fuel hydrocarbon components, before and after combustion, respectively, thus permitting a fraction of the fuel to escape the primary combustion process unburned. A final source of HC in engines is incomplete combustion due to bulk quenching of the flame in that fraction of the engine cycles where combustion is especially slow (see Sec. 9.4.3). Such conditions are most likely to occur during transient engine operation when the air/fuel ratio, spark timing, and the fraction of the exhaust recycled for emission control may not be properly matched.

The unburned hydrocarbons exit the cylinder by being entrained in the bulk-gas flow during blowdown and at the end of the exhaust stroke as the piston pushes gas scraped off the wall out of the exhaust valve. Substantial oxidation of the hydrocarbons which escape the primary combustion process by any of the above processes can occur during expansion and exhaust. The amount of oxidation depends on the temperature and oxygen concentration time histories of these HC as they mix with the bulk gases.

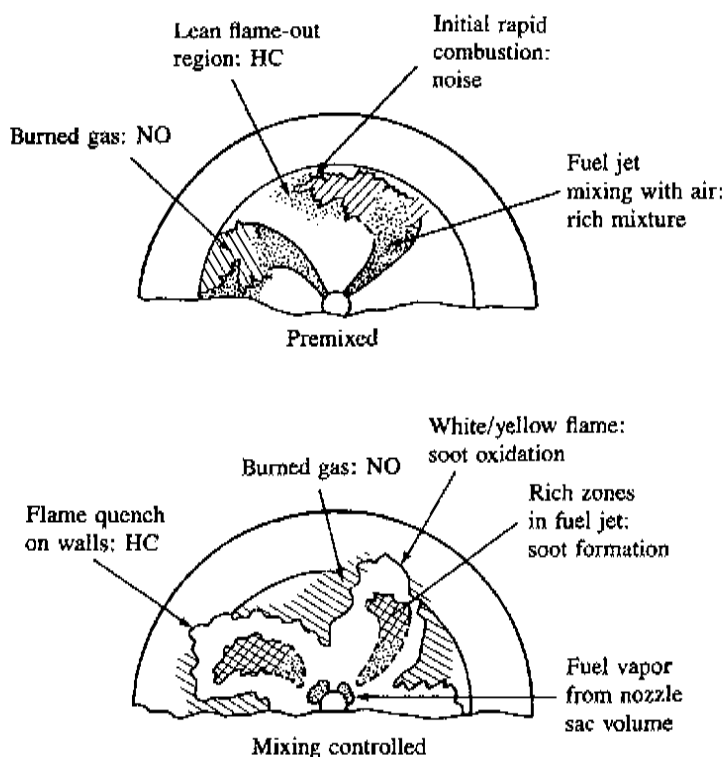
One of the most important variables in determining spark-ignition engine emissions is the fuel/air equivalence ratio,  $\phi$ . Figure 11-2 shows qualitatively how NO, CO, and HC exhaust emissions vary with this parameter. The spark-ignition engine has normally been operated close to stoichiometric, or slightly fuel-rich, to ensure smooth and reliable operation. Figure 11-2 shows that leaner mixtures give lower emissions until the combustion quality becomes poor (and eventually misfire occurs), when HC emissions rise sharply and engine operation becomes erratic. The shapes of these curves indicate the complexities of emission control. In a cold engine, when fuel vaporization is slow, the fuel flow is increased to provide an easily combustible fuel-rich mixture in the cylinder. Thus, until the engine warms up and this enrichment is removed, CO and HC emissions are high. At part-load conditions, lean mixtures could be used which would produce lower HC and CO emissions (at least until the combustion quality deteriorates) and moderate NO emissions. Use of recycled exhaust to dilute the engine intake mixture lowers the NO levels, but also deteriorates combustion quality. Exhaust gas recirculation (EGR) is used with stoichiometric mixtures in many engine control systems. Note that the highest power levels are obtained from the engine with slightly rich-of-stoichiometric mixtures and no recycled exhaust to dilute the incoming charge. As we will see, several emission control techniques are required



**FIGURE 11-2**  
Variation of HC, CO, and NO concentration in the exhaust of a conventional spark-ignition engine with fuel/air equivalence ratio.

to reduce emissions of all three pollutants, over all engine operating modes, and achieve acceptable average levels.

In the diesel engine, the fuel is injected into the cylinder just before combustion starts, so throughout most of the critical parts of the cycle the fuel distribution is nonuniform. The pollutant formation processes are strongly dependent on the fuel distribution and how that distribution changes with time due to mixing. Figure 11-3 illustrates how various parts of the fuel jet and the flame affect the formation of NO, unburned HC, and soot (or particulates) during the "premixed" and "mixing-controlled" phases of diesel combustion in a direct-injection engine with swirl. Nitric oxide forms in the high-temperature burned gas regions as before, but temperature and fuel/air ratio distributions within the burned gases are now nonuniform and formation rates are highest in the close-to-stoichiometric regions. Soot forms in the rich unburned-fuel-containing core of the fuel sprays, within the flame region, where the fuel vapor is heated by mixing with hot burned gases. Soot then oxidizes in the flame zone when it contacts unburned oxygen, giving rise to the yellow luminous character of the flame. Hydrocarbons and aldehydes originate in regions where the flame quenches both on the walls and where excessive dilution with air prevents the combustion process from either starting or going to completion. Fuel that vaporizes from the nozzle sac volume during the later stages of combustion is also a source of HC. Combustion generated noise is controlled by the early part of the combustion process, the initial rapid heat release immediately following the ignition-delay period.



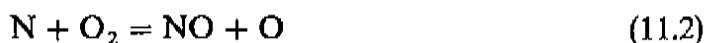
**FIGURE 11-3**  
Summary of pollutant formation mechanisms in a direct-injection compression-ignition engine during "premixed" and "mixing-controlled" combustion phases.

## 11.2 NITROGEN OXIDES

### 11.2.1 Kinetics of NO Formation

While nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>) are usually grouped together as NO<sub>x</sub> emissions, nitric oxide is the predominant oxide of nitrogen produced inside the engine cylinder. The principal source of NO is the oxidation of atmospheric (molecular) nitrogen. However, if the fuel contains significant nitrogen, the oxidation of the fuel nitrogen-containing compounds is an additional source of NO. Gasolines contain negligible amounts of nitrogen; although diesel fuels contain more nitrogen, current levels are not significant.

The mechanism of NO formation from atmospheric nitrogen has been studied extensively.<sup>1</sup> It is generally accepted that in combustion of near-stoichiometric fuel-air mixtures the principal reactions governing the formation of NO from molecular nitrogen (and its destruction) are†



† This is often called the extended Zeldovich mechanism. Zeldovich<sup>1</sup> was the first to suggest the importance of reactions (11.1) and (11.2). Lavoie *et al.*<sup>2</sup> added reaction (11.3) to the mechanism; it does contribute significantly.

**TABLE 11.1**  
**Rate constants for NO formation mechanism<sup>1</sup>**

Reaction	Rate constant, cm <sup>3</sup> /mol·s	Temperature range, K	Uncertainty, factor of or %
(1) O + N <sub>2</sub> → NO + N	7.6 × 10 <sup>13</sup> exp [-38,000/T]	2000-5000	2
(-1) N + NO → N <sub>2</sub> + O	1.6 × 10 <sup>13</sup>	300-5000	±20% at 300 K 2 at 2000-5000 K
(2) N + O <sub>2</sub> → NO + O	6.4 × 10 <sup>9</sup> T exp [-3150/T]	300-3000	±30% 300-1500 K 2 at 3000 K
(-2) O + NO → O <sub>2</sub> + N	1.5 × 10 <sup>9</sup> T exp [-19,500/T]	1000-3000	±30% at 1000 K 2 at 3000 K
(3) N + OH → NO + H	4.1 × 10 <sup>13</sup>	300-2500	±80%
(-3) H + NO → OH + N	2.0 × 10 <sup>14</sup> exp [-23,650/T]	2200-4500	2

The forward and reverse rate constants ( $k_i^+$  and  $k_i^-$ , respectively) for these reactions have been measured in numerous experimental studies. Recommended values for these rate constants taken from a critical review of this published data are given in Table 11.1. Note that the equilibrium constant for each reaction,  $K_{c,i}$  (see Sec. 3.7.2), is related to the forward and reverse rate constants by  $K_{c,i} = k_i^+/k_i^-$ . The rate of formation of NO via reactions (11.1) to (11.3) is given by [see Eqs. (3.55) and (3.58)]

$$\frac{d[\text{NO}]}{dt} = k_1^+ [\text{O}][\text{N}_2] + k_2^+ [\text{N}][\text{O}_2] + k_3^+ [\text{N}][\text{OH}] - k_1^- [\text{NO}][\text{N}] - k_2^- [\text{NO}][\text{O}] - k_3^- [\text{NO}][\text{H}] \quad (11.4)$$

where [ ] denote species concentrations in moles per cubic centimeter when  $k_i$  have the values given in Table 11.1. The forward rate constant for reaction (11.1) and the reverse rate constants for reactions (11.2) and (11.3) have large activation energies which results in a strong temperature dependence of NO formation rates.

A similar relation to (11.4) can be written for  $d[\text{N}]/dt$ :

$$\frac{d[\text{N}]}{dt} = k_1^+ [\text{O}][\text{N}_2] - k_2^+ [\text{N}][\text{O}_2] - k_3^+ [\text{N}][\text{OH}] - k_1^- [\text{NO}][\text{N}] + k_2^- [\text{NO}][\text{O}] + k_3^- [\text{NO}][\text{H}] \quad (11.5)$$

Since [N] is much less than the concentrations of other species of interest ( $\sim 10^{-8}$  mole fraction), the steady-state approximation is appropriate:  $d[\text{N}]/dt$  is set equal to zero and Eq. (11.5) used to eliminate [N]. The NO formation rate then becomes

$$\frac{d[\text{NO}]}{dt} = 2k_1^+ [\text{O}][\text{N}_2] \frac{1 - [\text{NO}]^2/(K[\text{O}_2][\text{N}_2])}{1 + k_1^- [\text{NO}]/(k_2^+ [\text{O}_2] + k_3^+ [\text{OH}])} \quad (11.6)$$

where  $K = (k_1^+/k_1^-)(k_2^-/k_2^+)$ .

TABLE 11.2  
 Typical values of  $R_1$ ,  $R_1/R_2$ , and  $R_1/(R_2 + R_3)$ †

Equivalence ratio	$R_1$ ‡	$R_1/R_2$	$R_1/(R_2 + R_3)$
0.8	$5.8 \times 10^{-5}$	1.2	0.33
1.0	$2.8 \times 10^{-5}$	2.5	0.26
1.2	$7.6 \times 10^{-6}$	9.1	0.14

† At 10 atm pressure and 2600 K.

‡ Units  $\text{gmol}/\text{cm}^3 \cdot \text{s}$ .

NO forms in both the flame front and the postflame gases. In engines, however, combustion occurs at high pressure so the flame reaction zone is extremely thin ( $\sim 0.1$  mm) and residence time within this zone is short. Also, the cylinder pressure rises during most of the combustion process, so burned gases produced early in the combustion process are compressed to a higher temperature than they reached immediately after combustion. Thus, NO formation in the postflame gases almost always dominates any flame-front-produced NO. It is, therefore, appropriate to assume that the combustion and NO formation processes are decoupled and to approximate the concentrations of O,  $\text{O}_2$ , OH, H, and  $\text{N}_2$  by their equilibrium values at the local pressure and equilibrium temperature.

To introduce this equilibrium assumption it is convenient to use the notation  $R_1 = k_1^+ [\text{O}]_e [\text{N}_2]_e = k_1^- [\text{NO}]_e [\text{N}]_e$ , where  $[\ ]_e$  denotes equilibrium concentration, for the one-way equilibrium rate for reaction (11.1), with similar definitions for  $R_2 = k_2^+ [\text{N}]_e [\text{O}_2]_e = k_2^- [\text{NO}]_e [\text{O}]_e$  and  $R_3 = k_3^+ [\text{N}]_e [\text{OH}]_e = k_3^- [\text{NO}]_e [\text{H}]_e$ . Substituting  $[\text{O}]_e$ ,  $[\text{O}_2]_e$ ,  $[\text{OH}]_e$ ,  $[\text{H}]_e$ , and  $[\text{N}_2]_e$  for  $[\text{O}]$ ,  $[\text{O}_2]$ ,  $[\text{OH}]$ ,  $[\text{H}]$ , and  $[\text{N}_2]$  in Eq. (11.6) yields

$$\frac{d[\text{NO}]}{dt} = \frac{2R_1 \{1 - ([\text{NO}]/[\text{NO}]_e)^2\}}{1 + ([\text{NO}]/[\text{NO}]_e)R_1/(R_2 + R_3)} \quad (11.7)$$

Typical values of  $R_1$ ,  $R_1/R_2$  and  $R_1/(R_2 + R_3)$  are given in Table 11.2. The difference between  $R_1/R_2$  and  $R_1/(R_2 + R_3)$  indicates the relative importance of adding reaction (11.3) to the mechanism.

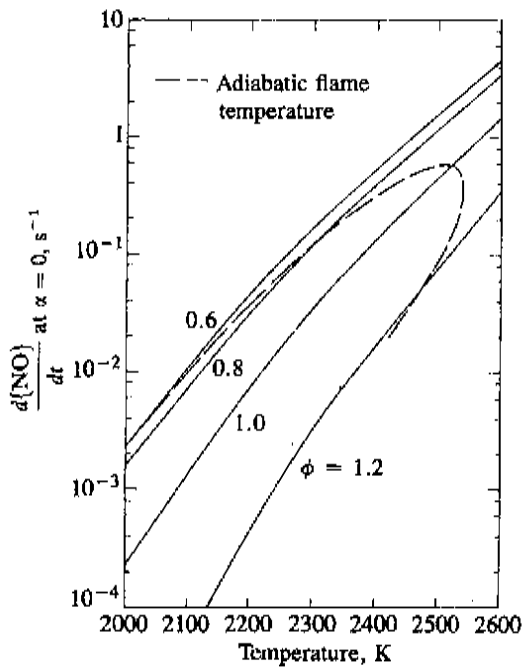
The strong temperature dependence of the NO formation rate can be demonstrated by considering the initial value of  $d[\text{NO}]/dt$  when  $[\text{NO}]/[\text{NO}]_e \ll 1$ . Then, from Eq. (11.7),

$$\frac{d[\text{NO}]}{dt} = 2R_1 = 2k_1^+ [\text{O}]_e [\text{N}_2]_e \quad (11.8)$$

The equilibrium oxygen atom concentration is given by

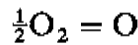
$$[\text{O}]_e = \frac{K_{p(\text{O})} [\text{O}_2]_e^{1/2}}{(\bar{R}T)^{1/2}} \quad (11.9)$$





**FIGURE 11-4**  
Initial NO formation rate, mass fraction per second (for  $[NO]/[NO]_e \ll 1$ ), as a function of temperature for different equivalence ratios ( $\phi$ ) and 15 atm pressure. Dashed line shows adiabatic flame temperature for kerosene combustion with 700 K, 15 atm air.<sup>3</sup>

where  $K_{p(O)}$  is the equilibrium constant for the reaction



and is given by

$$K_{p(O)} = 3.6 \times 10^3 \exp\left(\frac{-31,090}{T}\right) \text{ atm}^{1/2} \quad (11.10)$$

The initial NO formation rate may then be written [combining Eqs. (11.8), (11.9), and (11.10) with  $k_1^+$  from Table 11.1] as

$$\frac{d[NO]}{dt} = \frac{6 \times 10^{16}}{T^{1/2}} \exp\left(\frac{-69,090}{T}\right) [O_2]_e^{1/2} [N_2]_e \text{ mol/cm}^3 \cdot \text{s} \quad (11.11)$$

The strong dependence of  $d[NO]/dt$  on temperature in the exponential term is evident. High temperatures and high oxygen concentrations result in high NO formation rates. Figure 11-4 shows the NO formation rate as a function of gas temperature and fuel/air equivalence ratio in postflame gases. Also shown is the adiabatic flame temperature attained by a fuel-air mixture initially at 700 K at a constant pressure of 15 atm. For adiabatic constant-pressure combustion (an appropriate model for each element of fuel that burns in an engine), this initial NO formation rate peaks at the stoichiometric composition, and decreases rapidly as the mixture becomes leaner or richer.

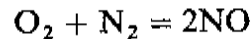
A characteristic time for the NO formation process,  $\tau_{NO}$ , can be defined by

$$\tau_{NO}^{-1} = \frac{1}{[NO]_e} \frac{d[NO]}{dt} \quad (11.12)$$

$[\text{NO}]_e$  can be obtained from the equilibrium constant

$$K_{\text{NO}} = 20.3 \times \exp(-21,650/T)$$

for the reaction



as  $[\text{NO}]_e = (K_{\text{NO}}[\text{O}_2]_e[\text{N}_2]_e)^{1/2}$ . Equations (11.11) and (11.12) can be combined to give

$$\tau_{\text{NO}} = \frac{8 \times 10^{-16} T \exp(58,300/T)}{p^{1/2}} \quad (11.13)$$

where  $\tau_{\text{NO}}$  is in seconds,  $T$  in kelvins, and  $p$  in atmospheres. Use has been made of the fact that  $\bar{x}_{\text{N}_2} \approx 0.71$ . For engine combustion conditions,  $\tau_{\text{NO}}$  is usually comparable to or longer than the times characteristic of changes in engine conditions so the formation process is kinetically controlled. However, for close-to-stoichiometric conditions at the maximum pressures and burned gas temperatures,  $\tau_{\text{NO}}$  is of the same order as typical combustion times (1 ms) and equilibrium NO concentrations may be attained.

Evidence that this formation model is valid under conditions typical of those found in engines is provided by high-pressure combustion bomb studies. Newhall and Shahed<sup>4</sup> have measured the NO production, using the  $q$ -band absorption technique, behind hydrogen-air and propane-air planar flames propagating axially in a cylindrical bomb. Some results are compared with predictions made with this kinetic scheme (coupled with an "unmixed" combustion calculation to determine local pressure and temperature; see Sec. 9.2.1) in Fig. 11-5. The agreement is excellent. Note that the NO concentration rises smoothly from

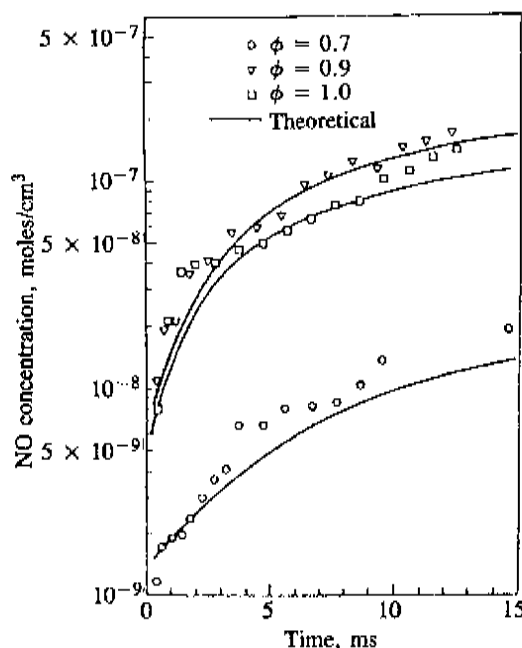


FIGURE 11-5

Measured and calculated rate-limited NO concentrations behind flame in high-pressure cylindrical bomb experiments with  $\text{H}_2$ -air mixture.  $\phi$  = equivalence ratio.<sup>4</sup>

TABLE 11.3  
Typical nitrogen content of distillate fuels<sup>1</sup>

Fraction	Average nitrogen, wt %	Range, wt %
Crude	0.65	—
Heavy distillates	1.40	0.60–2.15
Light distillates	0.07	0–0.60

close to zero, indicating that at these high pressures there is negligible NO production within the flame front itself.

Fuel nitrogen is also a source of NO via a different and yet to be fully explained mechanism. Table 11.3 shows the typical nitrogen content of petroleum-derived fuels. During distillation, the fuel nitrogen is concentrated in the higher boiling fractions. In distillate fuels, the nitrogen can exist as amines and ring compounds (e.g., pyridine, quinoline, and carbazoles). During combustion these compounds are likely to undergo some thermal decomposition prior to entering the combustion zone. The precursors to NO formation will therefore be low molecular weight nitrogen-containing compounds such as NH<sub>3</sub>, HCN, and CN. The detailed information on the kinetics of NO formation from these compounds is limited. Oxidation to NO is usually rapid, occurring on a time scale comparable to that of the combustion reactions. The NO yield (amount of fuel nitrogen converted to NO) is sensitive to the fuel/air equivalence ratio. Relatively high NO yields (approaching 100 percent) are obtained for lean and stoichiometric mixtures; relatively low yields are found for rich mixtures. NO yields are only weakly dependent on temperature, in contrast to the strong temperature dependence of NO formed from atmospheric nitrogen.<sup>1</sup>

### 11.2.2 Formation of NO<sub>2</sub>

Chemical equilibrium considerations indicate that for burned gases at typical flame temperatures, NO<sub>2</sub>/NO ratios should be negligibly small. While experimental data show this is true for spark-ignition engines, in diesels NO<sub>2</sub> can be 10 to 30 percent of the total exhaust oxides of nitrogen emissions.<sup>5</sup> A plausible mechanism for the persistence of NO<sub>2</sub> is the following.<sup>6</sup> NO formed in the flame zone can be rapidly converted to NO<sub>2</sub> via reactions such as



Subsequently, conversion of this NO<sub>2</sub> to NO occurs via



unless the NO<sub>2</sub> formed in the flame is quenched by mixing with cooler fluid. This explanation is consistent with the highest NO<sub>2</sub>/NO ratio occurring at light load in diesels, when cooler regions which could quench the conversion back to NO are widespread.<sup>5</sup>

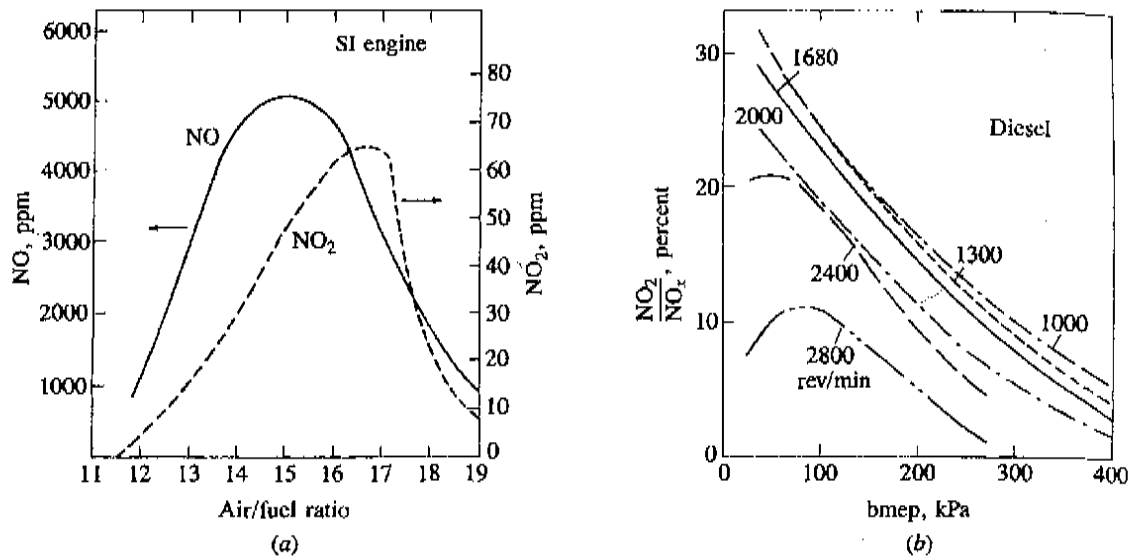


FIGURE 11-6

(a) NO and NO<sub>2</sub> concentrations in SI engine exhaust as function of air/fuel ratio, 1500 rev/min, wide-open throttle; (b) NO<sub>2</sub> as percent of total NO<sub>x</sub> in diesel exhaust as function of load and speed.<sup>5</sup>

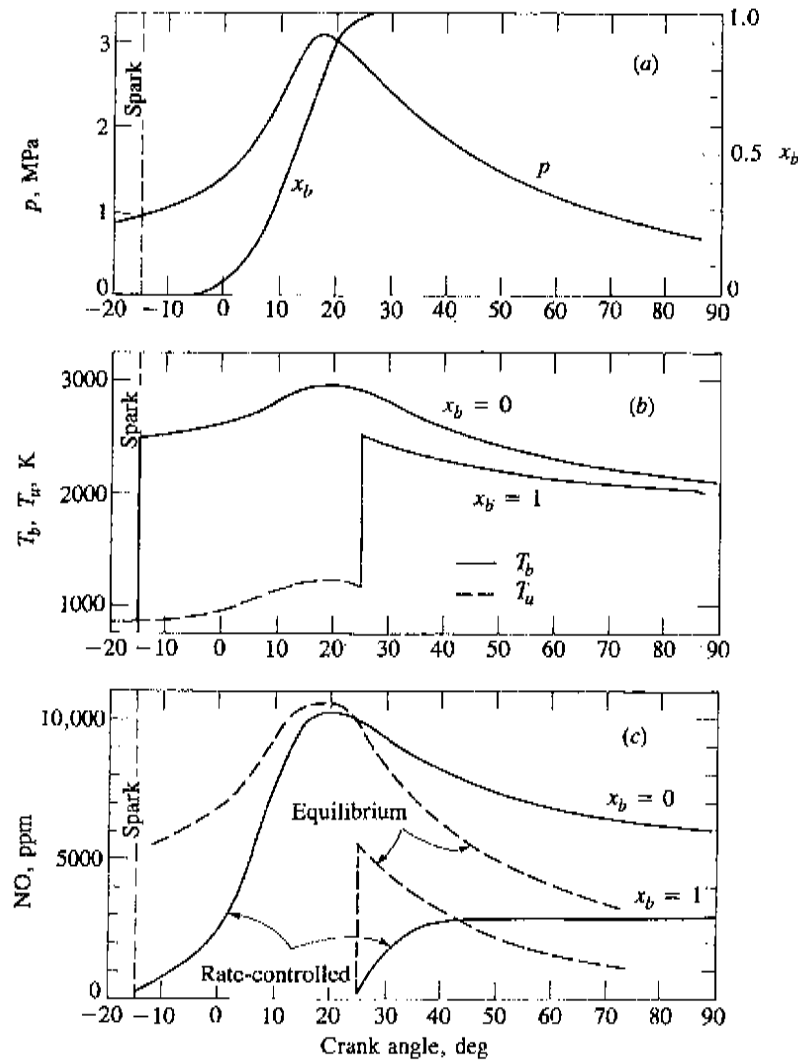
Figure 11-6 shows examples of NO and NO<sub>2</sub> emissions data from a spark-ignition and a diesel engine. The maximum value for the ratio (NO<sub>2</sub>/NO) for the SI engine is 2 percent, at an equivalence ratio of about 0.85. For the diesel this ratio is higher, and is highest at light load and depends on engine speed.

It is customary to measure total oxides of nitrogen emissions, NO plus NO<sub>2</sub>, with a chemiluminescence analyzer and call the combination NO<sub>x</sub>. It is always important to check carefully whether specific emissions data for NO<sub>x</sub> are given in terms of mass of NO or mass of NO<sub>2</sub>, which have molecular weights of 30 and 46, respectively.

### 11.2.3 NO Formation in Spark-Ignition Engines

In conventional spark-ignition engines the fuel and air (and any recycled exhaust) are mixed together in the engine intake system, and vigorous mixing with the residual gas within the cylinder occurs during the intake process. Thus the fuel/air ratio and the amount of diluent (residual gas plus any recycled exhaust) is approximately uniform throughout the charge within the cylinder during combustion.† Since the composition is essentially uniform, the nature of the NO formation process within the cylinder can be understood by coupling the kinetic mechanism developed in Sec. 11.2.1 with the burned gas temperature distribution and pressure in the cylinder during the combustion and expansion processes. The

† It is well known that the mixture composition within the cylinder is not completely uniform and varies from one cycle to the next. Both these factors contribute to cycle-by-cycle combustion variations. For the present discussion, the assumption of mixture uniformity is adequate.



**FIGURE 11-7** Illustration of SI engine NO formation model: (a) measured cylinder pressure  $p$  and calculated mass fraction burned  $x_b$ ; (b) calculated temperature of unburned gas  $T_u$  and burned gas  $T_b$  in early- and late-burning elements; (c) calculated NO concentrations in early- and late-burning elements for rate-controlled model and at equilibrium.<sup>7</sup>

temperature distribution which develops in the burned gases due to the passage of the flame across the combustion chamber has been discussed in Sec. 9.2.1. Mixture which burns early is compressed to higher temperatures after combustion, as the cylinder pressure continues to rise; mixture which burns later is compressed primarily as unburned mixture and ends up after combustion at a lower burned gas temperature. Figure 11-7a and b shows measured cylinder pressure data from an operating engine, with estimates of the mass fraction burned ( $x_b$ ) and the temperatures of a gas element which burned just after spark discharge and a gas element which burned at the end of the burning process. The model used to estimate these temperatures assumed no mixing between mixture elements which burn at different times. This assumption is more realistic than the

alternative idealization that the burned gases mix rapidly and are thus uniform (see Sec. 9.2.1). If the NO formation kinetic model [Eq. (11.7)] is used to calculate NO concentrations in these burned gas elements, using the equilibrium concentrations of the species O, O<sub>2</sub>, N<sub>2</sub>, OH, and H corresponding to the average fuel/air equivalence ratio and burned gas fraction of the mixture and these pressure and temperature profiles, the rate-limited concentration profiles in Fig. 11-7c are obtained. Also shown are the NO concentrations that would correspond to chemical equilibrium at these conditions. The rate-controlled concentrations rise from the residual gas NO concentration, lagging the equilibrium levels, then cross the equilibrium levels and "freeze" well above the equilibrium values corresponding to exhaust conditions. Depending on details of engine operating conditions, the rate-limited concentrations may or may not come close to equilibrium levels at peak cylinder pressure and gas temperature. Also, the amount of decomposition from peak NO levels which occurs during expansion depends on engine conditions as well as whether the mixture element burned early or late.<sup>7</sup>

Once the NO chemistry has frozen during the early part of the expansion stroke, integration over all elements will give the final average NO concentration in the cylinder which equals the exhaust concentration. Thus, if {NO} is the local mass fraction of NO, then the average exhaust NO mass fraction is given by

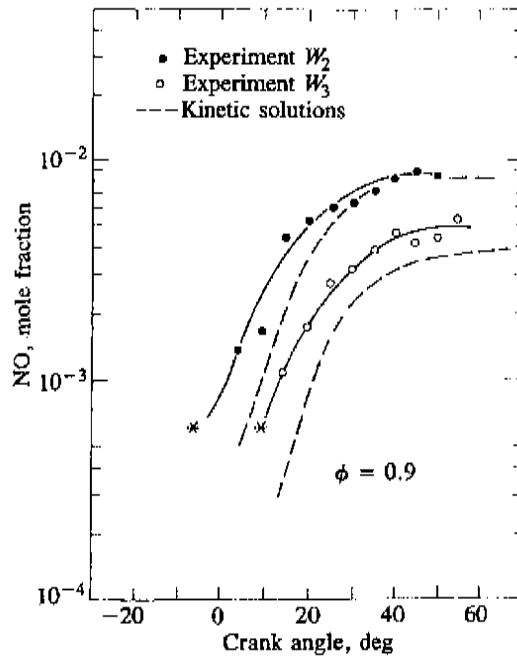
$$\{\overline{\text{NO}}\} = \int_0^1 \{\text{NO}\}_f dx_b \quad (11.16)$$

where {NO}<sub>f</sub> is the final frozen NO mass fraction in the element of charge which burned when the mass fraction burned was x<sub>b</sub>. Note that {NO} = [NO]M<sub>NO</sub>/ρ, where M<sub>NO</sub> = 30, the molecular weight of NO. The average exhaust concentration of NO as a mole fraction is given by

$$\tilde{x}_{\text{NOav}} = \{\overline{\text{NO}}\} \frac{M_{\text{exh}}}{M_{\text{NO}}} \quad (11.17)$$

and the exhaust concentration in ppm is  $\tilde{x}_{\text{NOav}} \times 10^6$ . The earlier burning fractions of the charge contribute much more to the exhausted NO than do later burning fractions of the charge: frozen NO concentrations in these early-burning elements can be an order of magnitude higher than concentrations in late-burning elements. In the absence of vigorous bulk gas motion, the highest NO concentrations occur nearest the spark plug.

Substantial experimental evidence supports this description of NO formation in spark-ignition engines. The NO concentration gradient across the burned gas in the engine cylinder, due to the temperature gradient, has been demonstrated using gas sampling techniques<sup>8,9</sup> and using measurements of the chemiluminescent radiation from the reaction  $\text{NO} + \text{O} \rightarrow \text{NO}_2 + h\nu$  to determine the local NO concentration. Figure 11-8 shows NO concentration data as a function of crank angle, taken by Lavoie<sup>10</sup> through two different windows in the cylinder head of a specially constructed L-head engine where each window was a different distance from the spark plug. The stars indicate the estimated initial NO concentration that results from mixing of the residual gas with the fresh charge, at the



**FIGURE 11-8** Spectroscopically measured NO concentrations through two windows  $W_3$  and  $W_2$  in special L-head SI engine ( $W_2$  is closer to spark than  $W_3$ ). The asterisks mark estimated initial conditions and flame arrival times. The dashed lines are calculated rate-limited concentrations for parts of charge burning at these flame arrival times with zero initial NO concentration.<sup>10</sup>

time of arrival of the flame at each window. The observed NO mole fractions rise smoothly from these initial values and then freeze about one-third of the way through the expansion process. NO levels observed at window  $W_2$ , closest to the spark plug, were substantially higher than those observed at window  $W_3$ . The dashed lines show calculated NO concentrations obtained using the NO formation kinetic model with an "unmixed" thermodynamic analysis for elements that burned at the time of flame arrival at each window. Since the calculated values started from zero NO concentration at the flame front (and not the diluted residual gas NO level indicated by the star), the calculations initially fall below the data. However, the difference between the two measurement locations and the frozen levels are predicted with reasonable accuracy. Thus, the rate-limited formation process, freezing of NO chemistry during expansion, and the existence of NO concentration gradients across the combustion chamber have all been observed.

The most important engine variables that affect NO emissions are the fuel/air equivalence ratio, the burned gas fraction of the *in-cylinder* unburned mixture, and spark timing. The burned gas fraction depends on the amount of diluent such as recycled exhaust gas (EGR) used for NO<sub>x</sub> emissions control, as well as the residual gas fraction. Fuel properties will affect burned gas conditions; the effect of normal variations in gasoline properties is modest, however. The effect of variations in these parameters can be explained with the NO formation mechanism described above: changes in the time history of temperature and oxygen concentration in the burned gases during the combustion process and early part of the expansion stroke are the important factors.<sup>11</sup>

**EQUIVALENCE RATIO.** Figure 11-9 shows the effect of variations in the fuel/air equivalence ratio on NO emissions. Maximum burned gas temperatures occur at

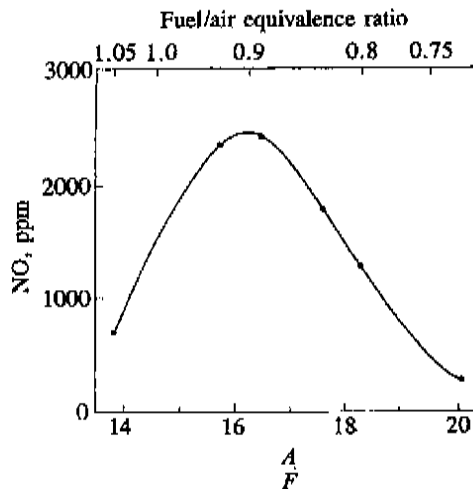


FIGURE 11-9

Variation of exhaust NO concentration with  $A/F$  and fuel/air equivalence ratio. Spark-ignition engine, 1600 rev/min,  $\eta_b = 50$  percent, MBT timing.<sup>12</sup>

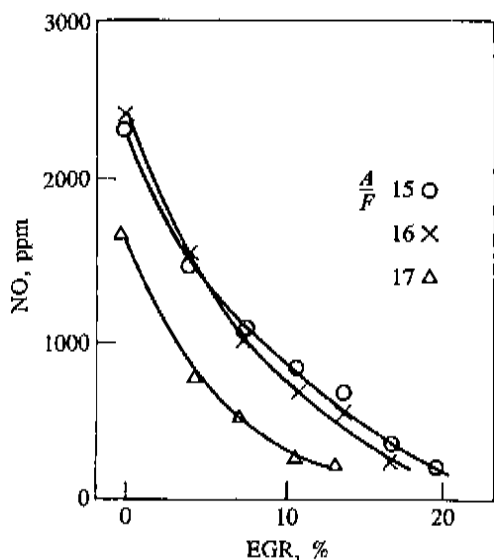
$\phi \approx 1.1$ ; however, at this equivalence ratio oxygen concentrations are low. As the mixture is enriched, burned gas temperatures fall. As the mixture is leaned out, increasing oxygen concentration initially offsets the falling gas temperatures and NO emissions peak at  $\phi \approx 0.9$ . Detailed predictions of NO concentrations in the burned gases suggest that the concentration versus time histories under fuel-lean conditions are different in character from those for fuel-rich conditions. In lean mixtures NO concentrations freeze early in the expansion process and little NO decomposition occurs. In rich mixtures, substantial NO decomposition occurs from the peak concentrations present when the cylinder pressure is a maximum. Thus in lean mixtures, gas conditions at the time of peak pressure are especially significant.<sup>7</sup>

**BURNED GAS FRACTION.** The unburned mixture in the cylinder contains fuel vapor, air, and burned gases. The burned gases are residual gas from the previous cycle and any exhaust gas recycled to the intake for  $\text{NO}_x$  emissions control. The residual gas fraction is influenced by load, valve timing (especially the extent of valve overlap), and, to a lesser degree, by speed, air/fuel ratio, and compression ratio as described in Sec. 6.4. The burned gases act as a diluent in the unburned mixture; the absolute temperature reached after combustion varies inversely with the burned gas mass fraction. Hence increasing the burned gas fraction reduces NO emissions levels. However, it also reduces the combustion rate and, therefore, makes stable combustion more difficult to achieve (see Secs. 9.3 and 9.4).

Figure 11-10 shows the effect of increasing the burned gas fraction by recycling exhaust gases to the intake system just below the throttle plate. Substantial reductions in NO concentrations are achieved with 15 to 25 percent EGR, which is about the maximum amount of EGR the engine will tolerate under normal part-throttle conditions. Of course, increasing the EGR at fixed engine load and speed increases the inlet manifold pressure, while fuel flow and air flow remain approximately constant.

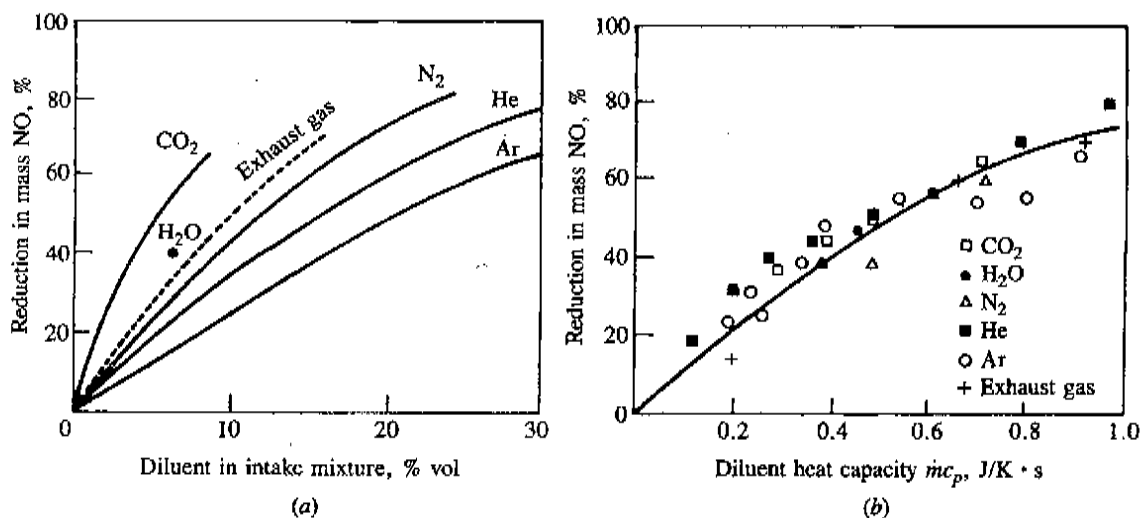
The primary effect of the burned gas diluent in the unburned mixture on the NO formation process is that it reduces flame temperatures by increasing the





**FIGURE 11-10**  
Variation of exhaust NO concentration with per cent recycled exhaust gas (EGR). Spark-ignition engine, 1600 rev/min,  $\eta_v = 50$  percent, MBT timing.<sup>12</sup>

heat capacity of the cylinder charge, per unit mass of fuel. Figure 11-11 shows the effect of different diluent gases added to the engine intake flow, in a single-cylinder engine operated at constant speed, fuel flow, and air flow.<sup>13</sup> The data in Fig. 11-11a show that equal volume percentages of the different diluents produce different reductions in NO emissions. The same data when plotted against diluent heat capacity (diluent mass flow rate  $\times$  specific heat,  $c_p$ ) collapse to a single



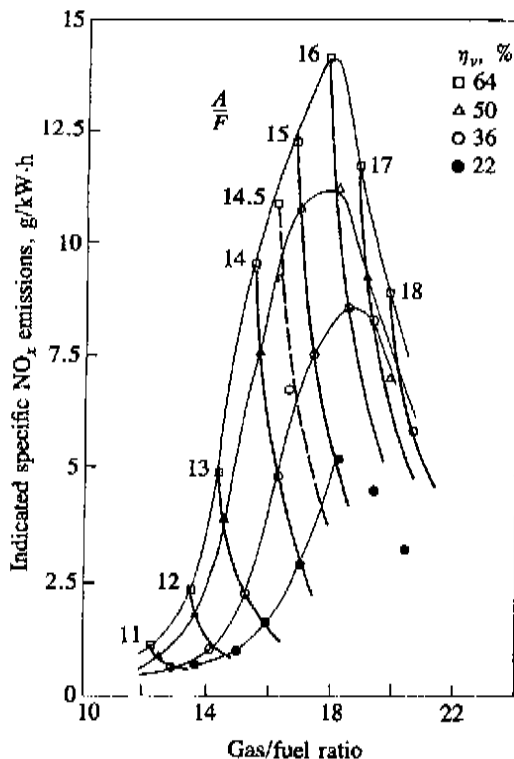
**FIGURE 11-11**  
(a) Percentage reduction in mass NO emissions with various diluents. (b) Correlation of NO reduction with diluent heat capacity. Spark-ignition engine operated at 1600 rev/min, constant brake load (intake pressure  $\sim 0.5$  atm), with MBT spark timing.<sup>13</sup>

curve.† A similar study where the burned gas fraction in the unburned charge was varied by changing the valve overlap, compression ratio, and EGR, separately, showed that, under more realistic engine operating conditions, it is the heat capacity of the total diluent mass in the in-cylinder mixture that is important. Whether the diluent mass is changed by varying the valve overlap, EGR, or even the compression ratio is not important.<sup>14</sup>

**EXCESS AIR AND EGR.** Because of the above, it is possible to correlate the influence of engine operating variables (such as air/fuel ratio, engine speed, and load) and design variables (such as valve timing and compression ratio) on NO emissions with two parameters which define the in-cylinder mixture composition: the fuel/air equivalence ratio (often the air/fuel ratio is used instead) and the gas/fuel ratio. The gas/fuel ratio ( $G/F$ ) is given by

$$\frac{G}{F} = \frac{\text{total mass in cylinder}}{\text{fuel mass in cylinder}} = \frac{A}{F} \left( 1 + \frac{x_b}{1 - x_b} \right) \quad (11.18)$$

where  $x_b$  is the burned gas fraction [Eq. (4.3)]. These together define the relative proportions of fuel, air, and burned gases in the in-cylinder mixture, and hence



**FIGURE 11-12**

Correlation between gas/fuel ratio ( $G/F$ ) and indicated specific NO<sub>x</sub> emissions at various air/fuel ratios ( $A/F$ ) and volumetric efficiencies ( $\eta_v$ ). Spark-ignition engine operated at 1400 rev/min with spark timing retarded to give 0.95 of maximum brake torque.<sup>15</sup>

† Some of the scatter in Fig. 11-11 is due to the fact that the residual gas fraction is slightly different for each diluent.

will correlate NO emissions.† Figure 11-12 shows the correlation of specific NO emissions, from a four-cylinder engine, over a wide range of engine operating conditions with the air/fuel ratio and gas/fuel ratio. Lines of constant air/fuel ratio and volumetric efficiency are shown; the direction of increasing dilution with residual gas and EGR at constant air/fuel ratio is to the right. Excessive dilution results in poor combustion quality, partial burning, and, eventually, misfire (see Sec. 9.4.3). Lowest NO emissions consistent with good fuel consumption (avoiding the use of rich mixtures) are obtained with a stoichiometric mixture, with as much dilution as the engine will tolerate without excessive deterioration in combustion quality.<sup>15</sup>

Comparisons between predictions made with the NO formation model (described at the beginning of this section) and experimental data show good agreement with normal amounts of dilution.<sup>16</sup> With extreme dilution, at NO levels of about 100 ppm or less, the NO formed within the flame reaction zone cannot, apparently, be neglected. Within the flame, the concentrations of radicals such as O, OH, and H can be substantially in excess of equilibrium levels, resulting in much higher formation rates within the flame than in the postflame gases. It is believed that the mechanism [reactions (11.1) to (11.3)] and the formation rate equation (11.6) are valid. However, neglecting flame-front-formed NO is no longer an appropriate assumption.<sup>17</sup>

**SPARK TIMING.** Spark timing significantly affects NO emission levels. Advancing the timing so that combustion occurs earlier in the cycle increases the peak cylinder pressure (because more fuel is burned before TC and the peak pressure moves closer to TC where the cylinder volume is smaller); retarding the timing decreases the peak cylinder pressure (because more of the fuel burns after TC). Higher peak cylinder pressures result in higher peak burned gas temperatures, and hence higher NO formation rates. For lower peak cylinder pressures, lower NO formation rates result. Figure 11-13 shows typical NO emission data for a spark-ignition engine as a function of spark timing. NO emission levels steadily decrease as spark timing is retarded from MBT timing and moved closer to TC. Since exact determination of MBT timing is difficult (and not critical for fuel consumption and power where the variation with timing around MBT is modest), there is always considerable uncertainty in NO emissions at MBT timing. Often, therefore, an alternative reference timing is used, where spark is retarded from MBT timing to the point where torque is decreased by 1 or 2 percent from the maximum value. Great care with spark timing is necessary to obtain accurate NO emissions measurements under MBT-timing operating conditions.

† Spark timing also affects NO emissions, as discussed next. The above discussion relates to engines run with timing at MBT or with torque at a fixed percentage of (and close to) the maximum.

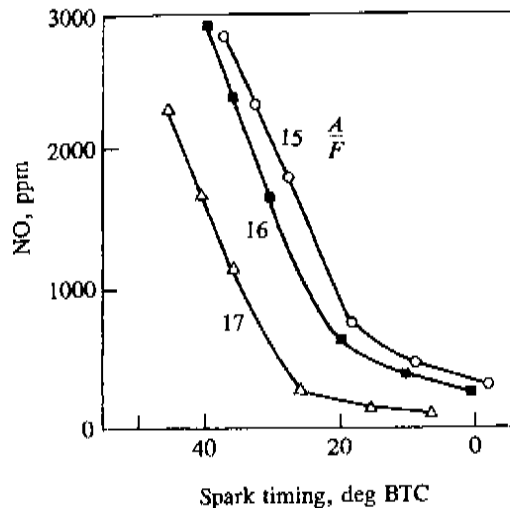


FIGURE 11-13

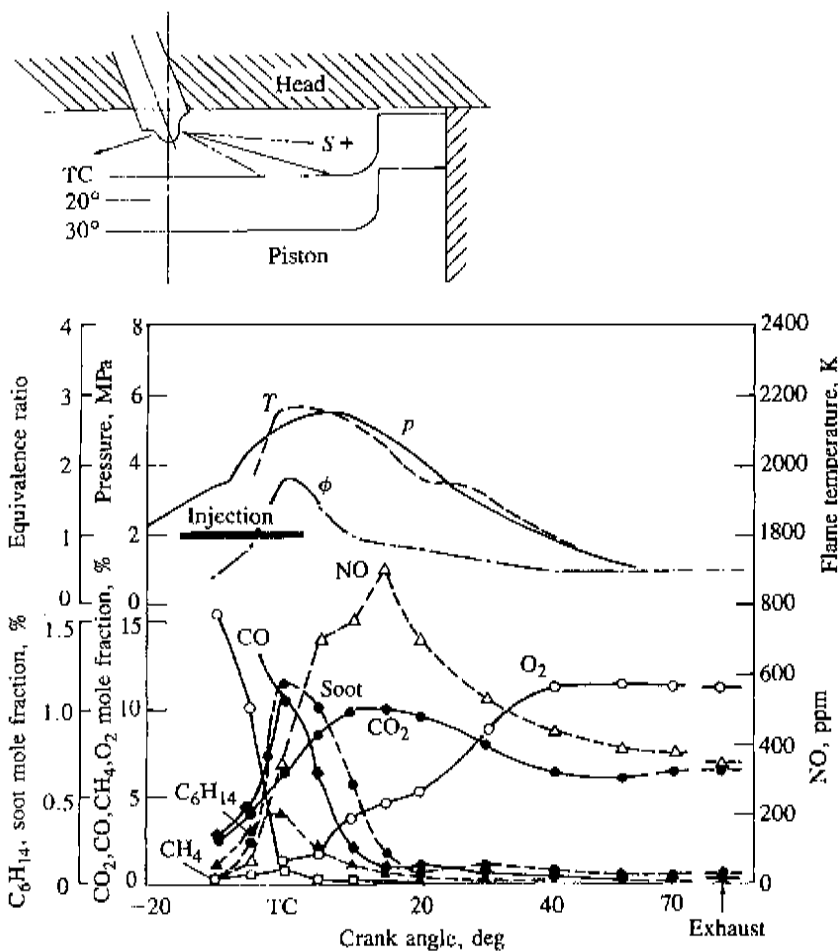
Variation of exhaust NO concentration with spark retard. 1600 rev/min,  $\eta_v = 50$  percent; left-hand end of curve corresponds to MBT timing for each  $A/F$ .<sup>12</sup>

#### 11.2.4 NO<sub>x</sub> Formation in Compression-Ignition Engines

The kinetic mechanisms for NO and NO<sub>2</sub> formation described in Secs. 11.2.1 and 11.2.2 and the assumptions made regarding equilibration of species in the C—O—H system apply to diesels as well as to spark-ignition engines. The critical difference, of course, is that injection of fuel into the cylinder occurs just before combustion starts, and that nonuniform burned gas temperature and composition result from this nonuniform fuel distribution during combustion. The fuel-air mixing and combustion processes are extremely complex. During the "premixed" or uncontrolled diesel combustion phase immediately following the ignition delay, fuel-air mixture with a spread in composition about stoichiometric burns due to spontaneous ignition and flame propagation. During the mixing controlled combustion phase, the burning mixture is likely to be closer to stoichiometric (the flame structure is that of a turbulent, though unsteady, diffusion flame). However, throughout the combustion process mixing between already burned gases, air, and lean and rich unburned fuel vapor-air mixture occurs, changing the composition of any gas elements that burned at a particular equivalence ratio. In addition to these composition (and hence temperature) changes due to mixing, temperature changes due to compression and expansion occur as the cylinder pressure rises and falls.

The discussion in Sec. 11.2.1 showed that the critical equivalence ratio for NO formation in high-temperature high-pressure burned gases typical of engines is close to stoichiometric. Figure 11-4 is relevant here: it shows the initial NO formation rate in combustion products formed by burning a mixture of a typical hydrocarbon fuel with air (initially at 700 K, at a constant pressure of 15 atm). NO formation rates are within a factor of 2 of the maximum value for  $0.85 \lesssim \phi \lesssim 1.1$ .

The critical time period is when burned gas temperatures are at a maximum: i.e., between the start of combustion and shortly after the occurrence of peak cylinder pressure. Mixture which burns early in the combustion process



**FIGURE 11-14** Concentrations of soot, NO, and other combustion product species measured at outer edge of bowl-in-piston combustion chamber (location *S*) of quiescent DI diesel with rapid sampling valve. Cylinder gas pressure *p*, mean temperature *T*, and local equivalence ratio  $\phi$  shown. Bore = 95 mm, stroke = 110 mm,  $r_c = 14.6$ . Four-hole nozzle with hole diameter = 0.2 mm.<sup>18</sup>

is especially important since it is compressed to a higher temperature, increasing the NO formation rate, as combustion proceeds and cylinder pressure increases. After the time of peak pressure, burned gas temperatures decrease as the cylinder gases expand. The decreasing temperature due to expansion *and* due to mixing of high-temperature gas with air or cooler burned gas freezes the NO chemistry. This second effect (which occurs only in the diesel) means that freezing occurs more rapidly in the diesel than in the spark-ignition engine, and much less decomposition of the NO occurs.

The above description is supported by the NO concentration data obtained from experiments where gas was sampled from within the cylinder of normally operating diesel engines with special gas-sampling valves and analyzed. Figure 11-14 shows time histories of major species concentrations, through the combustion process, determined with a rapid-acting sampling valve (1 ms open time) in a quiescent *direct-injection diesel* engine. Concentrations at different positions in the combustion chamber were obtained; the sample valve location for the Fig.

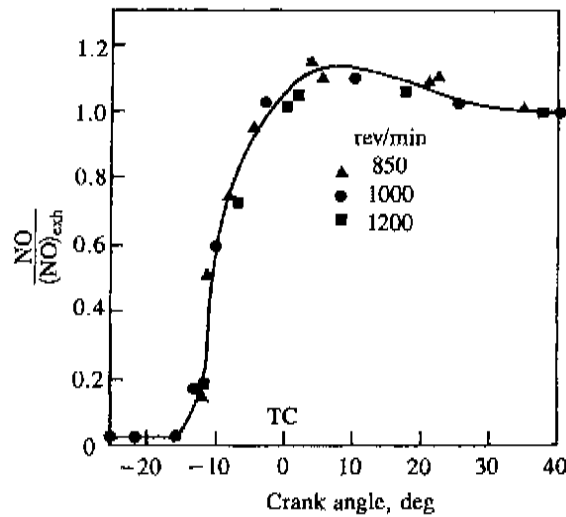
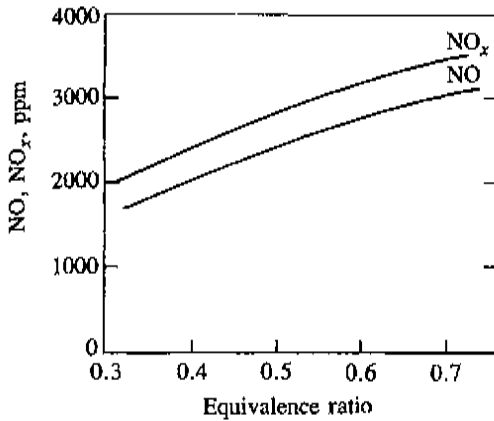


FIGURE 11-15

Ratio of cylinder-average NO concentration at given crank angle (determined from cylinder-dumping experiments) to exhaust NO concentration. DI diesel, equivalence ratio = 0.6, injection timing at 27° BTC.<sup>19</sup>

11-14 data is shown. Local NO concentrations rise from the residual gas value following the start of combustion, to a peak at the point where the local burned gas equivalence ratio changes from rich to lean (where the CO<sub>2</sub> concentration has its maximum value). As the local burned gas equivalence ratio becomes leaner due to mixing with excess air, NO concentrations decrease since formation becomes much slower as dilution occurs. At the time of peak NO concentrations within the bowl (15° ATC), most of the bowl region was filled with flame. The total amount of NO within the cylinder of this type of direct-injection diesel during the NO formation process has also been measured.<sup>19</sup> At a predetermined time in one cycle, once steady-state warmed-up engine operation had been achieved, the contents of the cylinder were dumped into an evacuated tank by rapidly cutting open a diaphragm which had previously sealed off the tank system. Figure 11-15 shows how the ratio of the average cylinder NO concentration divided by the exhaust concentration varies during the combustion process. NO concentrations reach a maximum shortly after the time of peak pressure. There is a modest amount of NO decomposition. Variations in engine speed have little effect on the shape of this curve. The 20 crank angle degrees after the start of combustion is the critical time period.

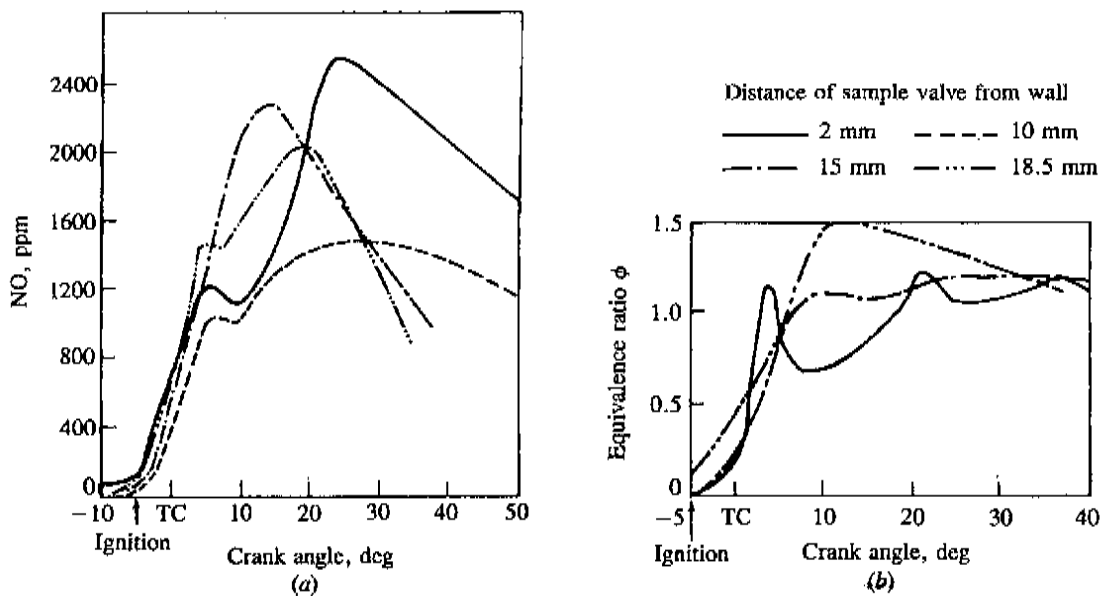
Results from similar cylinder-dumping experiments where injection timing and load (defined by the overall equivalence ratio) were varied also showed that almost all of the NO forms within the 20° following the start of combustion. As injection timing is retarded, so the combustion process is retarded; NO formation occurs later, and concentrations are lower since peak temperatures are lower. The effect of the overall equivalence ratio on NO<sub>x</sub> concentrations is shown in Fig. 11-16. At high load, with higher peak pressures, and hence temperatures, and larger regions of close-to-stoichiometric burned gas, NO levels increase. Both NO and NO<sub>x</sub> concentrations were measured; NO<sub>2</sub> is 10 to 20 percent of total NO<sub>x</sub>. Though NO levels decrease with a decreasing overall equivalence ratio, they do so much less rapidly than do spark-ignition engine NO emissions (see Fig. 11-9) due to the nonuniform fuel distribution in the diesel. Though the



**FIGURE 11-16**  
Exhaust NO<sub>x</sub> and NO concentrations as a function of overall equivalence ratio or engine load. DI diesel, 1000 rev/min, injection timing at 27° BTC.<sup>19</sup>

amount of fuel injected decreases proportionally as the overall equivalence ratio is decreased, much of the fuel still burns close to stoichiometric. Thus NO emissions should be roughly proportional to the mass of fuel injected (provided burned gas pressures and temperatures do not change greatly).

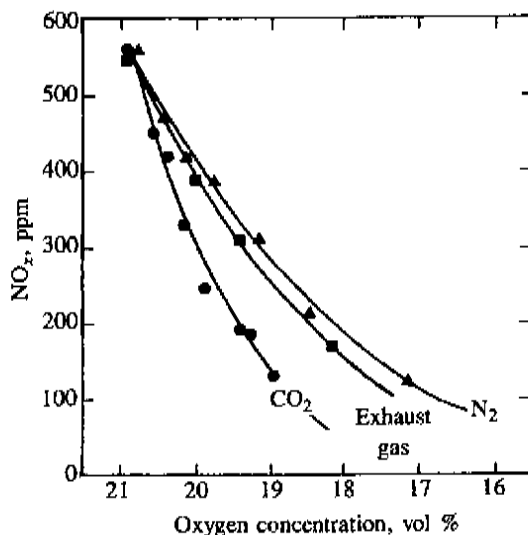
Similar gas-sampling studies have been done with *indirect-injection* diesel engines. Modeling studies suggest that most of the NO forms within the pre-chamber and is then transported into the main chamber where the reactions freeze as rapid mixing with air occurs. However, the prechamber, except at light load, operates rich overall so some additional NO can form as the rich combustion products are diluted through the stoichiometric composition.<sup>20</sup> Figure 11-17 shows local NO concentrations and equivalence ratios as a function of crank angle determined with a rapid-acting sampling valve at different locations



**FIGURE 11-17**  
(a) NO concentrations measured with rapid sampling valve and (b) calculated equivalence ratios at different distances from the wall in swirl chamber of IDI diesel engine, as function of crank angle. Engine speed = 1000 rev/min, injection at 13° BTC, ignition at 5° BTC.<sup>21</sup>

within the prechamber of a Comet swirl chamber IDI engine.<sup>21</sup> The gas mixture rapidly becomes stoichiometric or fuel-rich. Composition nonuniformities across the prechamber are substantial. Peak NO concentrations, as expected, correspond approximately to locally stoichiometric regions. Because the mixture remains fuel-rich in the prechamber as the burned gases expand (after the time of peak pressure which occurs between 6 and 10° ATC), substantial NO decomposition within the prechamber can occur. However, by this time much of the gas (and NO) in the prechamber has been transferred to the main chamber where freezing of the NO chemistry will occur. Cylinder-gas dumping experiments, where both main chamber and prechamber gases were dumped and quenched, confirm this description. Cylinder average NO concentrations, determined by rapidly opening a diaphragm which separated the engine cylinder from an evacuated tank at predetermined points in the cycle of an otherwise normally operated IDI engine, rise rapidly once combustion starts, until the NO chemistry is effectively frozen at about 15° ATC. Little net NO decomposition occurs.<sup>22</sup> Heat-release-rate diagrams obtained from pressure data analysis for the same IDI engine indicate that combustion is only about one-half complete at the time the NO formation process ceases.

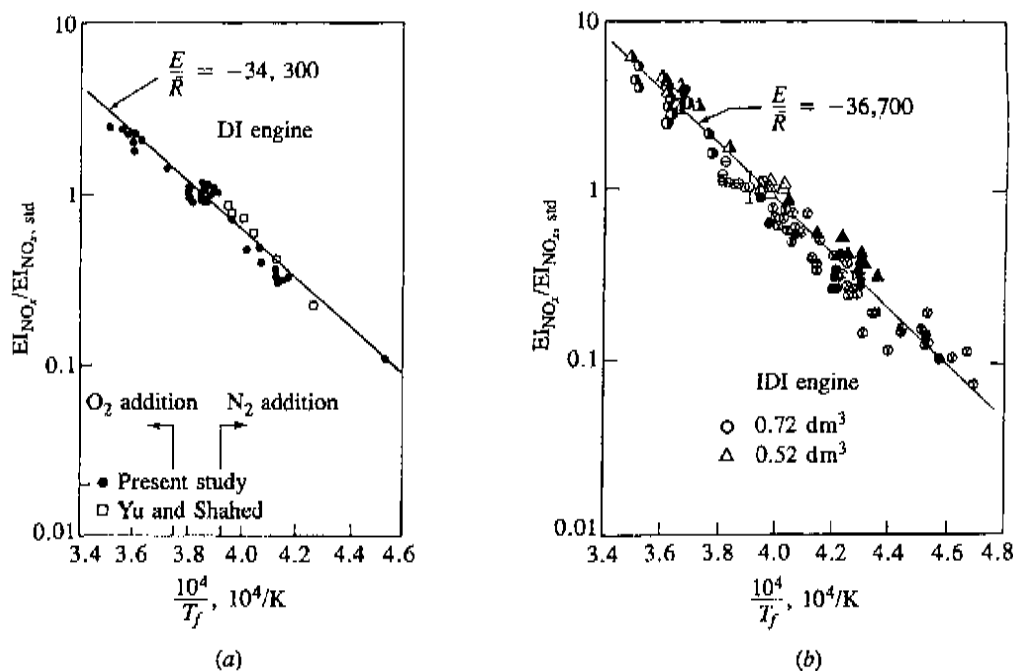
Diluents added to the intake air (such as recycled exhaust) are effective at reducing the NO formation rate, and therefore NO<sub>x</sub> exhaust emissions. As with spark-ignition engines, the effect is primarily one of reducing the burned gas temperature for a given mass of fuel and oxygen burned. Figure 11-18 shows the effect of dilution of the intake air with N<sub>2</sub>, CO<sub>2</sub>, and exhaust gas on NO<sub>x</sub> exhaust levels.<sup>23</sup> The heat capacity of CO<sub>2</sub> (per mole) at the temperatures relevant to diesel combustion is about twice that of N<sub>2</sub>. That of exhaust gas is slightly higher than that of N<sub>2</sub>. Therefore these data show that the effect is primarily one of reduced burned gas temperatures. Note that the composition of the exhaust gas of a diesel varies with load. At idle, there is little CO<sub>2</sub> and H<sub>2</sub>O, and the composition does not differ much from that of air. At high load the heat



**FIGURE 11-18**

Effect of reduction in oxygen concentration by different diluents (exhaust gas, CO<sub>2</sub>, N<sub>2</sub>) on NO<sub>x</sub> emissions in DI diesel. Bore = 140 mm, stroke = 152 mm,  $r_c = 14.3$ . Speed = 1300 rev/min, fuel rate = 142 mm<sup>3</sup>/stroke, injection timing at 4° BTC.<sup>23</sup>





**FIGURE 11-19** Correlation of NO<sub>x</sub> emissions index EI<sub>NO<sub>x</sub></sub> for a wide range of operating conditions with reciprocal of stoichiometric mixture flame temperature for: (a) DI engines; (b) IDI engines. Flame temperatures varied by addition of different diluents and oxygen.<sup>25,26</sup> Values of EI<sub>NO<sub>x</sub></sub> normalized with value at standard conditions.

capacity increases as the concentrations of CO<sub>2</sub> and H<sub>2</sub>O are substantially higher. Similar studies in an *indirect-injection* engine show comparable trends. Addition of diluents [exhaust gas (EGR) and nitrogen] reduce peak flame temperatures and NO<sub>x</sub> emissions; also, addition of oxygen (which corresponds to a *reduction* in diluent fraction) increases flame temperatures and therefore increases NO<sub>x</sub> emissions.<sup>24</sup>

Confirmation that NO forms in the close-to-stoichiometric burned gas regions and the magnitude of the stoichiometric burned gas temperature controls NO<sub>x</sub> emissions is given by the following. Plee *et al.*<sup>25,26</sup> have shown that the effects of changes in intake gas composition (with EGR, nitrogen, argon, and oxygen addition) and temperature on NO<sub>x</sub> emissions can be correlated by

$$EI_{NO_x} = \text{constant} \times \exp\left(\frac{E}{\bar{R}T_f}\right) \quad (11.19)$$

T<sub>f</sub>(kelvin) is the stoichiometric adiabatic flame temperature (evaluated at a suitable reference point: fuel-air mixture at top-center pressure and air temperature) and E is an overall activation energy. Figure 11-19 shows EI<sub>NO<sub>x</sub></sub> for a range of intake air compositions and temperatures, and two DI and two IDI engines for several loads and speeds, normalized by the engine NO<sub>x</sub> level obtained for standard air, plotted on a log scale against the reciprocal of the stoichiometric adiabatic flame at TC conditions. A single value of E/ $\bar{R}$  correlates the data over two

orders of magnitude. There is, of course, some scatter since the model used is overly simple, and load, speed, and other engine design and operating parameters affect the process. The overriding importance of the burned gas temperature of close-to-stoichiometric mixture is clear, however.

### 11.3 CARBON MONOXIDE

Carbon monoxide (CO) emissions from internal combustion engines are controlled primarily by the fuel/air equivalence ratio. Figure 11-20 shows CO levels in the exhaust of a conventional spark-ignition engine for several different fuel compositions.<sup>27</sup> When the data are plotted against the relative air/fuel ratio or the equivalence ratio, they are correlated by a single curve. For fuel-rich mixtures CO concentrations in the exhaust increase steadily with increasing equivalence ratio, as the amount of excess fuel increases. For fuel-lean mixtures, CO concentrations in the exhaust vary little with equivalence ratio and are of order  $10^{-3}$  mole fraction.

Since spark-ignition engines often operate close to stoichiometric at part load and fuel rich at full load (see Sec. 7.1), CO emissions are significant and must be controlled. Diesels, however, always operate well on the lean side of stoichiometric; CO emissions from diesels are low enough to be unimportant, therefore, and will not be discussed further.

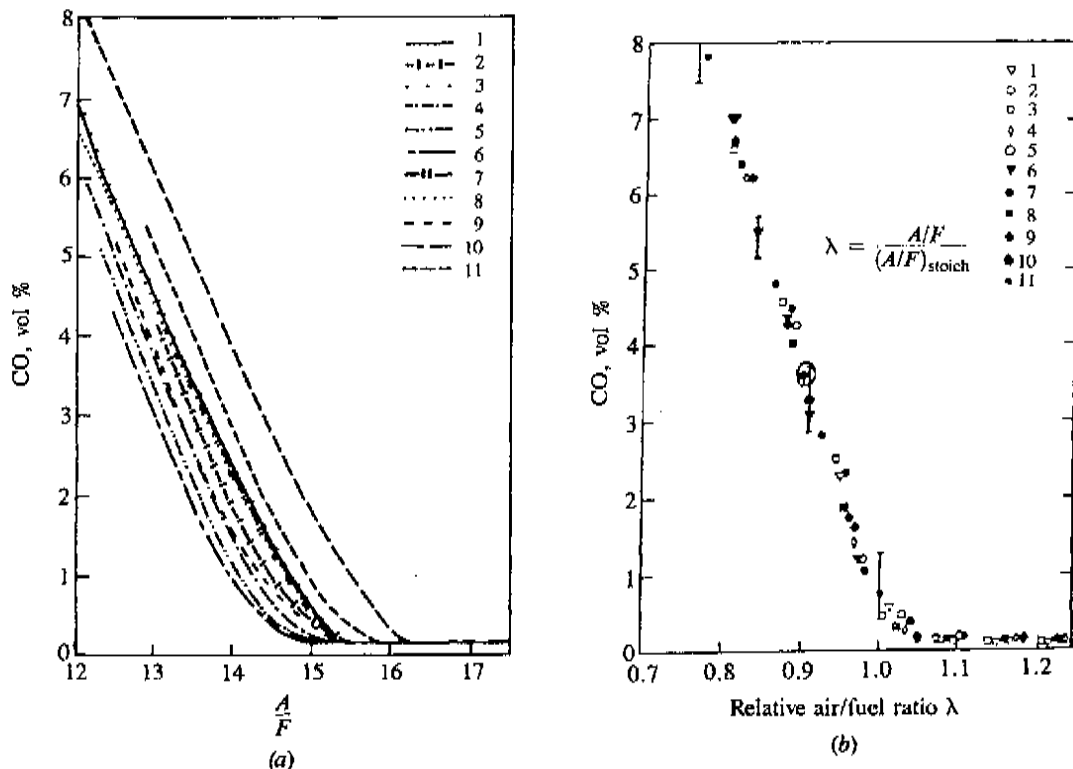
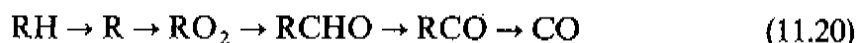


FIGURE 11-20

Variation of SI engine CO emissions with eleven fuels of different H/C ratio: (a) with air/fuel ratio; (b) with relative air/fuel ratio  $\lambda$ .<sup>27</sup>

The levels of CO observed in spark-ignition engine exhaust gases are lower than the maximum values measured within the combustion chamber, but are significantly higher than equilibrium values for the exhaust conditions. Thus the processes which govern CO exhaust levels are kinetically controlled. In premixed hydrocarbon-air flames, the CO concentration increases rapidly in the flame zone to a maximum value, which is larger than the equilibrium value for adiabatic combustion of the fuel-air mixture. CO formation is one of the principal reaction steps in the hydrocarbon combustion mechanism, which may be summarized by<sup>1</sup>



where R stands for the hydrocarbon radical. The CO formed in the combustion process via this path is then oxidized to CO<sub>2</sub> at a slower rate. The principal CO oxidation reaction in hydrocarbon-air flames is



The rate constant for this reaction is<sup>1</sup>

$$k_{CO}^+ = 6.76 \times 10^{10} \exp\left(\frac{T}{1102}\right) \text{ cm}^3/\text{gmol} \quad (11.22)$$

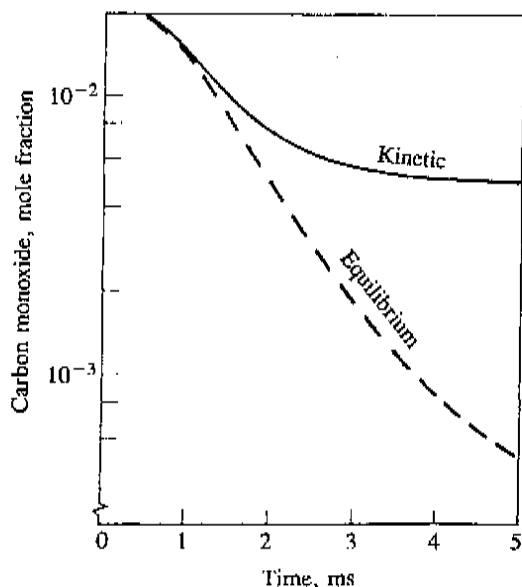
It is generally assumed that in the postflame combustion products in a spark-ignition engine, at conditions close to peak cycle temperatures (2800 K) and pressures (15 to 40 atm), the carbon-oxygen-hydrogen system is equilibrated. Thus CO concentrations in the immediate postflame burned gases are close to equilibrium. However, as the burned gases cool during the expansion and exhaust strokes, depending on the temperature and cooling rate, the CO oxidation process [reaction (11.21)] may not remain locally equilibrated.

Newhall carried out a series of kinetic calculations for an engine expansion stroke assuming the burned gas at the time of peak cylinder pressure was uniform and in equilibrium.<sup>28</sup> Of the reactions important to CO chemistry, only three-body radical-recombination reactions such as



were found to be rate controlling. The bimolecular exchange reactions and the CO oxidation reaction (11.21) were sufficiently fast to be continuously equilibrated. Only during the later stages of the expansion stroke was the CO concentration predicted to depart from equilibrium, as shown in Fig. 11-21. Using this technique to predict average CO levels at the end of expansion over a range of equivalence ratios (rich to lean), Newhall obtained a good match to experimental data (see Fig. 11-22). The kinetically controlled aspects of the CO emissions mechanism have thus been confirmed.

These calculations showed that a partial equilibrium amongst the bimolecular exchange reactions occurred *a posteriori*. Analyses based explicitly on this partial equilibrium assumption (which are considerably simpler) have been

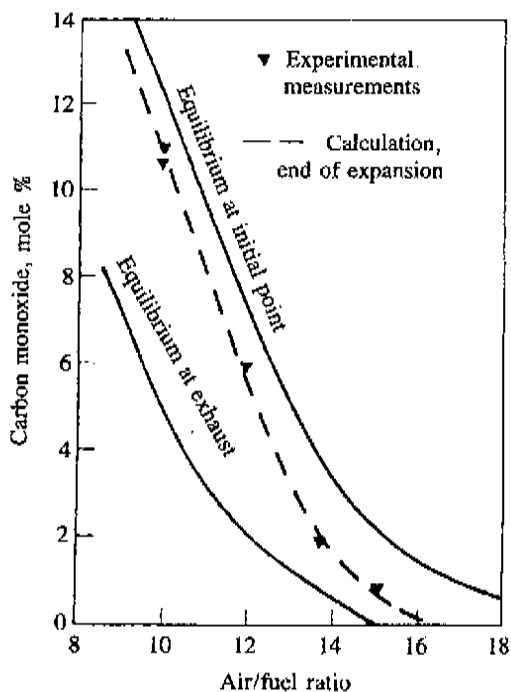


**FIGURE 11-21**  
Results of kinetic calculations of CO concentrations during expansion stroke following TC combustion in SI engine; stoichiometric mixture.<sup>28</sup>

carried out.<sup>29, 30</sup> The appropriate three-body atom and radical recombination reactions [e.g., (11.23) to (11.25)] were treated as the rate-limiting constraint on the total number of particles or moles per unit volume of burnt gases, i.e.,

$$\left(\frac{1}{V}\right) \frac{dn}{dt} = \sum_{i=1}^k (R_i^- - R_i^+) \quad (11.26)$$

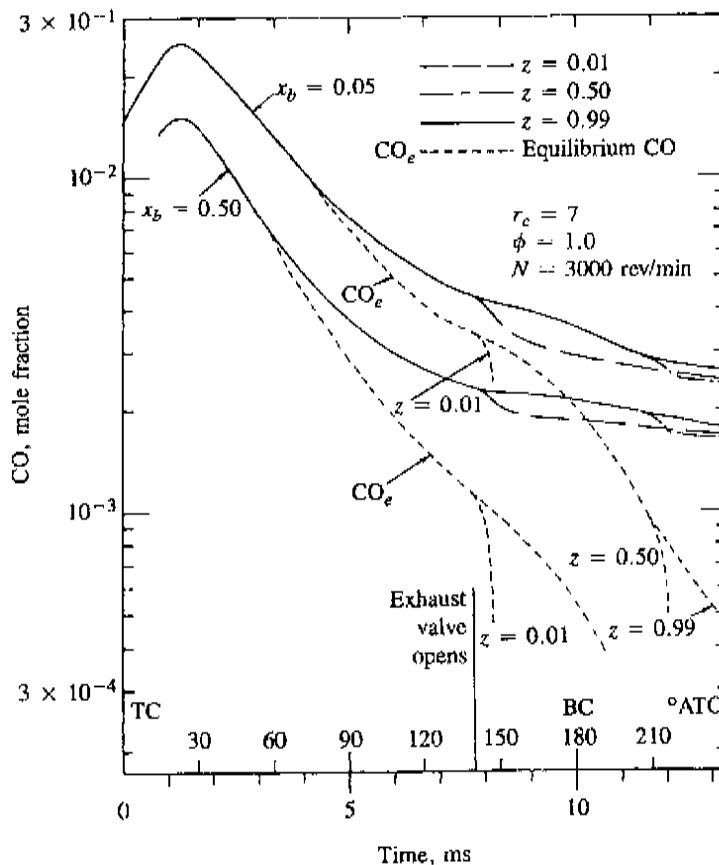
$V$  is the volume of the elemental system considered,  $n$  is the total number of moles,  $R_i^+$  and  $R_i^-$  are the forward and backward rates for reaction  $i$ , and  $k$  represents the number of three-body recombination reactions included. All other



**FIGURE 11-22**  
Predicted CO concentration at end of expansion stroke, compared with measured exhaust concentrations, as function of air/fuel ratio. Equilibrium levels at TC combustion and exhaust conditions also shown.<sup>28</sup>

reactions were assumed to be equilibrated. The studies using this simplified kinetic model have confirmed that at peak cylinder pressures and temperatures, equilibration times for CO are faster than times characteristic of changes in burnt gas conditions due to compression or expansion. Thus the CO concentration rapidly equilibrates in the burnt gases just downstream of the reaction zone following combustion of the hydrocarbon fuel. However, it has already been pointed out in Sec. 9.2.1 that the burnt gases are not uniform in temperature. Also, the blowdown of cylinder pressure to the exhaust manifold level during the exhaust process and the decrease in gas temperature that accompanies it occupies a substantial portion of the cycle—about 60 crank angle degrees. Thus, the temperature- and pressure-time profiles of parts of the charge at different locations throughout the cylinder differ, depending on when these parts of the charge burn and when they exit the cylinder through the exhaust valve and enter the exhaust manifold.

The results of an idealized calculation which illustrate these effects are shown in Fig. 11-23. The CO mole fractions in different elements or parts of the burnt gas mixture are plotted versus crank angle;  $x_b$  is the fraction of the total charge which had burned when each element shown burned;  $z$  is the mass fraction which had left the cylinder at the time each element left the cylinder. The partial equilibrium calculations show the burned gases are close to equilibrium until about 60 crank angle degrees after top-center. During the exhaust blowdown process after the exhaust valve opens, gas which leaves the cylinder early



**FIGURE 11-23**  
CO concentrations in selected elements of SI engine cylinder charge, which burn at different times and which exit the cylinder at different times.  $x_b$  is mass fraction burned when element burned.  $z$  is fraction of gas which has already left cylinder during exhaust process prior to element leaving cylinder. Speed = 3000 rev/min,  $r_c = 7$ , equivalence ratio = 1.0.<sup>30</sup>

( $z \ll 1$ ) cools more rapidly than gas which leaves late ( $z \approx 1$ ). In these calculations, mixing between gas elements which burn at different times was neglected. It can be seen that a CO gradient exists across the burned gases and that the CO concentration in the exhaust gases is unlikely to be uniform. Experiments with single-cylinder engines support these conclusions that CO is in equilibrium during the combustion process but deviates from equilibrium late in the expansion stroke (e.g., see Refs. 10 and 31).

Conclusions from these detailed studies are as follows. The measured average exhaust CO concentrations for fuel-rich mixtures are close to equilibrium concentrations in the burned gases during the expansion process. For close-to-stoichiometric mixtures, the partial equilibrium CO predictions are in agreement with measurements and are orders of magnitude above CO equilibrium concentrations corresponding to exhaust conditions. For fuel-lean mixtures, measured CO emissions are substantially higher than predictions from any of the models based on kinetically controlled bulk gas phenomena. One possible explanation of this lean-mixture discrepancy is that only partial oxidation to CO may occur of some of the unburned hydrocarbons emerging during expansion and exhaust from crevices in the combustion chamber and from any oil layers or deposits on the chamber walls.

While many questions about details of the CO oxidation mechanisms remain, as a practical matter exhaust emissions are determined by the fuel/air equivalence ratio. The degree of control achieved within the engine to date has come from improving mixture uniformity and leaning-out the intake mixture. In multicylinder engines, because CO increases rapidly as the inlet mixture becomes richer than stoichiometric, cylinder-to-cylinder variations in equivalence ratio about the mean value are important; nonuniform distribution can significantly increase average emissions. Thus improved cylinder-to-cylinder fuel/air ratio distribution has become essential. Also, because it is necessary to enrich the fuel-air mixture when the engine is cold, CO emissions during engine warm-up are much higher than emissions in the fully warmed-up state. Further, in transient engine operation during acceleration and deceleration, control of fuel metering has had to be improved. Additional reductions in CO beyond what can be achieved in the engine are possible with exhaust treatment devices, which are reviewed in Sec. 11.6. Oxidation of CO in the exhaust system without use of special exhaust treatment devices does not occur to any significant degree because the exhaust gas temperature is too low (Fig. 11-23 shows that the CO oxidation reactions effectively freeze as the gas passes through the exhaust valve).

## 11.4 UNBURNED HYDROCARBON EMISSIONS

### 11.4.1 Background

Hydrocarbons, or more appropriately organic emissions, are the consequence of incomplete combustion of the hydrocarbon fuel. The level of unburned hydrocarbons (HC) in the exhaust gases is generally specified in terms of the total hydro-

**TABLE 11.4**  
**Hydrocarbon composition of spark-ignition engine exhaust**  
**(by class)<sup>33</sup>**

	Carbon, percent of total HC			
	Paraffins	Olefins	Acetylene	Aromatics
Without catalyst	33	27	8	32
With catalyst	57	15	2	26

carbon concentration expressed in parts per million carbon atoms ( $C_1$ ).<sup>†</sup> While total hydrocarbon emission is a useful measure of combustion inefficiency, it is not necessarily a significant index of pollutant emissions. Engine exhaust gases contain a wide variety of hydrocarbon compounds. Table 11.4 shows the average breakdown by class of the hydrocarbons in spark-ignition engine exhaust gases, both with and without a catalytic converter, with gasoline fuel. Some of these hydrocarbons are nearly inert physiologically and are virtually unreactive from the standpoint of photochemical smog. Others are highly reactive in the smog-producing chemistry. (Some hydrocarbons are known carcinogens; see Sec. 11.5.2). Based on their potential for oxidant formation in the photochemical smog chemistry, hydrocarbon compounds are divided into nonreactive and reactive categories. Table 11.5 shows one reactivity scale which has been used to estimate the overall reactivity of exhaust gas hydrocarbon mixtures. Other scales are used for the same purpose.<sup>34</sup> Scales that assign high values for reactivity to the olefins (like Table 11.5), which react most rapidly in the photochemical smog reaction, probably best approximate smog-formation potential near the sources of hydrocarbon pollution. The simplest scale, which divides the HC into two classes—methane and nonmethane hydrocarbons—probably best approximates the end result for all HC emissions. All hydrocarbons except methane react, given enough time. More detailed breakdowns of the composition of spark-ignition and diesel engine exhaust HC are available in the literature.<sup>33, 35</sup>

Fuel composition can significantly influence the composition and magnitude of the organic emissions. Fuels containing high proportions of aromatics and olefins produce relatively higher concentrations of reactive hydrocarbons. However, many of the organic compounds found in the exhaust are not present

<sup>†</sup> This is because the standard detection instrument, a flame ionization detector (FID), is effectively a carbon atom counter: e.g., one propane molecule generates three times the response generated by one methane molecule. Some data in the literature are presented as ppm propane ( $C_3$ ), or ppm hexane ( $C_6$ ); to convert to ppm  $C_1$  multiply by 3 or by 6, respectively. Older measurements of hydrocarbon emissions were made with nondispersive infrared (NDIR) detectors which had different sensitivities for the different hydrocarbon compounds. For gasoline-fueled engines, HC emissions determined by FID analyzers are about twice the levels determined by NDIR analyzers,<sup>32</sup> though this scaling is not exact.

**TABLE 11.5**  
**Reactivity of classes of hydrocarbons**

Hydrocarbons	Relative reactivity†
C <sub>1</sub> -C <sub>4</sub> paraffins	0
Acetylene	
Benzene	
C <sub>4</sub> and higher molecular weight paraffins	2
Monoalkyl benzenes	
<i>Ortho</i> - and <i>para</i> -dialkyl benzenes	
Cyclic paraffins	
Ethylene	5
<i>Meta</i> -dialkyl benzenes	
Aldehydes	
1-Olefins (except ethylene)	10
Diolefins	
Tri- and tetraalkyl benzenes	
Internally bonded olefins	30
Internally bonded olefins with substitution at the double bond	100
Cycloolefins	

† General Motors Reactivity Scale (0-100). Based on the NO<sub>2</sub> formation rate for the hydrocarbon relative to the NO<sub>2</sub> formation rate for 2,3-dimethyl-2-benzene.<sup>3,4</sup>

in the fuel, indicating that significant pyrolysis and synthesis occur during the combustion process.

Oxygenates are present in engine exhaust, and are known to participate in the formation of photochemical smog. Some oxygenates are also irritants and odorants. The oxygenates are generally categorized as carbonyls, phenols, and other noncarbonyls. The carbonyls of interest are low molecular weight aldehydes and aliphatic ketones. The volatile aldehydes are eye and respiratory tract irritants. Formaldehyde is a major component ( $\lesssim 20$  percent of total carbonyls). Carbonyls account for about 10 percent of the HC emissions from diesel passenger car engines, but only a few percent of spark-ignition engine HC emissions. Phenols are odorants and irritants: levels are much lower than aldehyde levels. Other noncarbonyls include methanol, ethanol, nitromethane, methyl formate. Whether these are significant with conventional hydrocarbon fuels is unclear.<sup>3,5</sup> Use of alcohol fuels increases oxygenate emissions. Both methanol and aldehyde emissions increase substantially above gasoline-fueled levels with methanol-fueled spark-ignition engines.



### 11.4.2 Flame Quenching and Oxidation Fundamentals

Flame quenching or extinction occurs at the walls of engine combustion chambers. The cool walls of the chamber act as a sink for heat and the active radical species generated within the flame. Quenching of the flame occurs under several different geometrical configurations: the flame may be propagating normal to, parallel to, or at an angle to the wall; the flame may quench at the entrance to a crevice—a thin volume with a narrow entrance to the combustion chamber such as the region between the piston crown and the cylinder wall. When the flame quenches, it leaves a layer or volume of unburned mixture ahead of the flame. (Whether this results in unburned hydrocarbon emissions depends on the extent to which these quench region hydrocarbons can subsequently be oxidized.)

Flame-quenching processes are analyzed by relating the heat release within the flame to the heat loss to the walls under conditions where quenching just occurs. This ratio, a Peclet number (Pe), is approximately constant for any given geometrical configuration. The simplest configuration for study is the two-plate quench process, where the minimum spacing between two parallel plates through which a flame will propagate is determined. The Peclet number for this two-plate configuration is given by:

$$Pe_2 = \frac{\rho_u S_L c_{p,f} (T_f - T_u)}{k_f (T_f - T_u) / d_{q2}} = \frac{\rho_u S_L c_{p,f} d_{q2}}{k_f} \tag{11.27}$$

which is approximately constant over a wide range of conditions.  $\rho$ ,  $S_L$ ,  $c_p$ ,  $T$ , and  $k$  are the density, laminar flame speed, specific heat at constant pressure, gas temperature, and thermal conductivity, respectively, with the subscripts  $u$  and  $f$  referring to unburned and flame conditions.  $d_{q2}$  is the two-plate quench distance. The wall temperature and unburned gas temperature are assumed to be equal; this assumption is also appropriate in the engine context since there is ample time during the compression stroke for a thermal boundary layer to build up to a thickness of at least the quench distance.

Lavoic<sup>36</sup> has developed empirical correlations for two-plate quench-distance data for propane-air mixtures; only limited data for liquid hydrocarbon fuels such as isooctane are available. The data in the pressure range 3 to 40 atm are well fitted by

$$Pe_2 = \frac{9.5}{\phi} \left( \frac{p}{3} \right)^{0.26 \min(1, 1/\phi^2)} \tag{11.28}$$

where  $p$  is the pressure in atmospheres and  $\phi$  is the fuel/air equivalence ratio. The two-plate quench distance  $d_{q2}$  is then obtained from Eq. (11.27) and Prandtl number and viscosity relations for the flame conditions (see Sec. 4.8 or Ref. 36). Thus the minimum size crevice region into which a flame will propagate can be determined.

For the process of a flame front quenching on a single wall, there are many possible geometries. The simplest is where the flame front is parallel to the wall

and approaches it head on. The one-wall quench distance  $d_{q1}$ , defined as the position of closest approach of the reaction zone to the wall, scales with flame properties in a similar way to the two-plate quench distance. Thus, a one-wall Peclet number relation can be formed:

$$Pe_1 = \frac{\rho_u S_L c_{p,u} d_{q1}}{k_u} \approx 8 \quad (11.29)$$

where the subscript  $u$  denotes properties evaluated at unburned gas conditions.

Using the wall temperature as representative of the unburned gas temperature (because the thermal boundary-layer thickness is greater than typical quench distances), Lavoie showed that

$$\frac{d_{q1}}{d_{q2}} = \frac{Pe_1}{Pe_2} = 0.2 \quad (11.30)$$

is a reasonable fit to the single-wall quench data. Typical two-wall quench distances for spark-ignition engine conditions are 0.2 to 1 mm; these distances represent the minimum crevice size the flame will enter. Single-wall quench distances are, therefore, in the range 0.04 to 0.2 mm.

While a fraction of the fuel hydrocarbons can escape the primary combustion process unburned or only partially reacted, oxidation of some of these hydrocarbons can occur during the expansion and exhaust processes. Hydrocarbon oxidation rates have been determined in a number of different studies and several different empirical correlations of the data in the form of overall reaction rate equations have been proposed. A reasonable fit to the experimental data on unburned HC burnup is the rate expression:<sup>36</sup>

$$\frac{d[\text{HC}]}{dt} = -6.7 \times 10^{15} \exp\left(\frac{-18,735}{T}\right) \tilde{x}_{\text{HC}} \tilde{x}_{\text{O}_2} \left(\frac{p}{RT}\right)^2 \quad (11.31)$$

where  $[ ]$  denotes concentration in moles per cubic centimeter,  $\tilde{x}_{\text{HC}}$  and  $\tilde{x}_{\text{O}_2}$  are the mole fractions of HC and  $\text{O}_2$ , respectively,  $t$  is in seconds,  $T$  in kelvins, and the density term  $(p/RT)$  has units of moles per cubic centimeter. The spread in the data about this equation is substantial, however.

Studies of combustion of premixed fuel-air mixtures at high pressure in closed vessels or bombs have been useful in identifying the mechanisms by which hydrocarbons escape complete combustion. The residual unburned hydrocarbons left in the bomb following a combustion experiment have been shown to come primarily from crevices in the bomb walls. Unburned HC levels were proportional to total crevice volume, and decreased to very low values ( $\sim 10$  ppm C) as all the crevices were filled with solid material. Thus wall quench hydrocarbons apparently diffuse into the burned gases and oxidize following the quenching event.<sup>37</sup> Analytical studies of the flame quenching process, and postquench diffusion and oxidation with kinetic models of the hydrocarbon oxidation process, are in agreement with these bomb data.<sup>38</sup> Flame quenching can be thought of as a two-stage process. The first step is the extinction of the flame at a short distance from the cold wall, determined by a balance between thermal conduction of heat

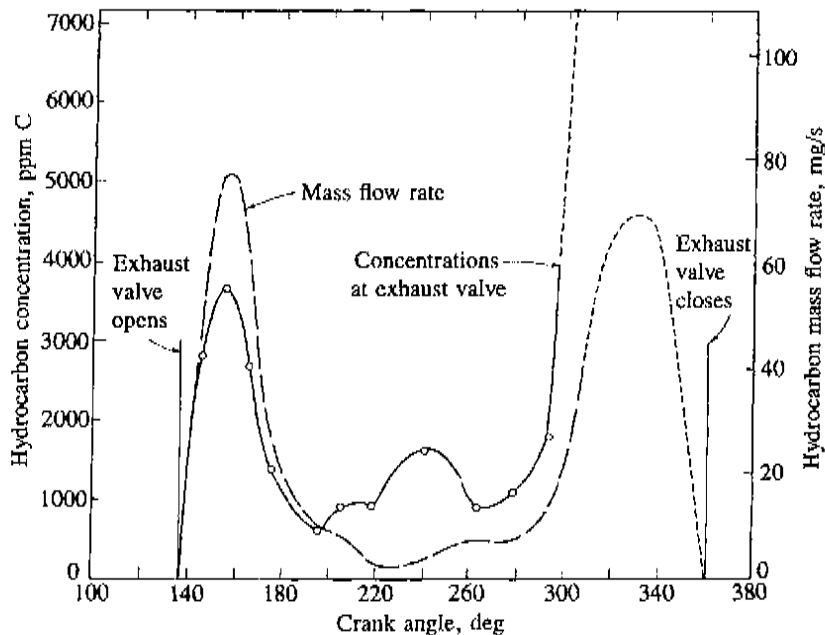
from the hot reaction zone to the wall and heat released in the reaction zone by the flame reactions. The second step is the postquench diffusion and oxidation occurring on a time scale of one or a few milliseconds after quenching. The diffusion and oxidation process ultimately reduces the mass of wall quench hydrocarbons to several orders of magnitude below its value at the time of quenching.

Closed-vessel combustion experiments have also been used to show that oil layers on the walls of the bomb cause an increase in residual unburned HC levels after combustion is complete. The additional HC that result in experiments with oil films present are primarily (>95 percent) fuel molecules, and are directly proportional to the amount of oil placed on the walls of the reactor and the solubility of the specific fuel in the oil. These results show that absorption of fuel in the oil occurs prior to ignition. This dissolved fuel is then desorbed into the burned gases well after combustion is complete. Thus fuel absorption into and desorption from any oil layers is a potentially important engine HC mechanism.<sup>39</sup>

### 11.4.3 HC Emissions from Spark-Ignition Engines

Unburned hydrocarbon levels in the exhaust of a spark-ignition engine under normal operating conditions are typically in the range 1000 to 3000 ppm C<sub>1</sub>. This corresponds to between about 1 and 2½ percent of the fuel flow into the engine; the engine combustion efficiency is high. As indicated in Fig. 11-2, HC emissions rise rapidly as the mixture becomes substantially richer than stoichiometric. When combustion quality deteriorates, e.g., with very lean mixtures, HC emissions can rise rapidly due to incomplete combustion or misfire in a fraction of the engine's operating cycles. As outlined in Sec. 11.1, there are several mechanisms that contribute to total HC emissions. Also, any HC escaping the primary combustion process may oxidize in the expansion and exhaust processes. While a complete description of the HC emissions process cannot yet be given, there are sufficient fundamental data available to indicate which mechanisms are likely to be most important, and thus how major engine variables influence HC emission levels.

Four possible HC emissions formation mechanisms for spark-ignition engines (where the fuel-air mixture is essentially premixed) have been proposed: (1) flame quenching at the combustion chamber walls, leaving a layer of unburned fuel-air mixture adjacent to the wall; (2) the filling of crevice volumes with unburned mixture which, since the flame quenches at the crevice entrance, escapes the primary combustion process; (3) absorption of fuel vapor into oil layers on the cylinder wall during intake and compression, followed by desorption of fuel vapor into the cylinder during expansion and exhaust; (4) incomplete combustion in a fraction of the engine's operating cycles (either partial burning or complete misfire), occurring when combustion quality is poor (e.g., during engine transients when A/F, EGR, and spark timing may not be adequately controlled). In addition, as deposits build up on the combustion chamber walls,



**FIGURE 11-24**

Variation in HC concentration and HC mass flow rate at the exhaust valve during the exhaust process. SI engine operating at 1200 rev/min and  $\phi = 1.2$ , unthrottled.<sup>40</sup>

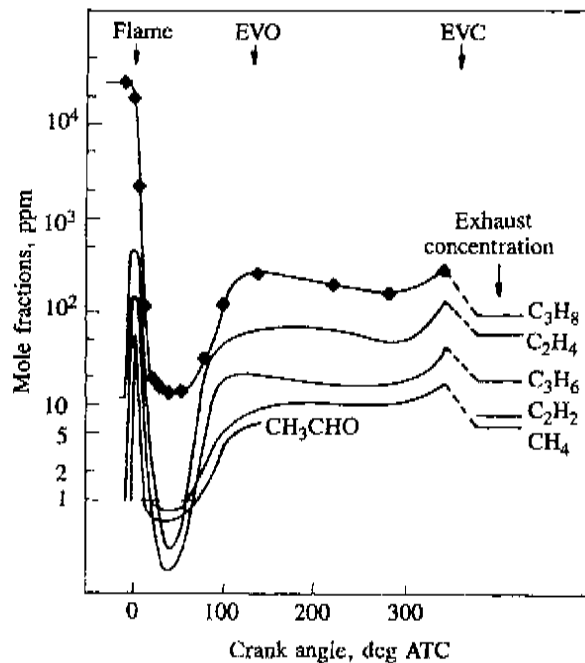
HC emissions increase. Whether the deposits constitute an additional mechanism or merely modify one of the above mechanisms is unclear.

All these processes (except misfire) result in unburned hydrocarbons close to the combustion chamber walls, and not in the bulk of the cylinder gases. Thus, the distribution of HC in the exhaust gases would not be expected to be uniform. Experiments have been done to determine the unburned HC concentration distribution in the exhaust port during the exhaust process to provide insight into the details of the formation mechanisms. Gas concentrations were measured with a rapid-acting sampling valve placed at the exhaust port exit. Figure 11-24 shows results from these time-resolved HC concentration measurements. HC concentrations vary significantly during the exhaust process. Gas which remains in the exhaust port between exhaust pulses has a high HC concentration, so purging techniques where air or nitrogen was bled into the exhaust port were used to displace this high HC gas while the exhaust valve was closed. The high HC concentration in the blowdown exhaust gases is clearly discernible, as is the rapid rise in HC concentration toward the end of the exhaust stroke. The cylinder-exit HC concentrations were then multiplied by the instantaneous exhaust gas mass flow rate to obtain the instantaneous HC mass emission rate from the cylinder throughout the exhaust process, also shown in Fig. 11-24. The unburned HC are exhausted in two peaks of approximately equal mass: the first of these coincides with the exhaust blowdown mass flow pulse (which removes the majority of the mass from the cylinder); the second occurs toward the end of the exhaust stroke where HC concentrations are very high and the mass flow rate is relatively low.<sup>40</sup> Other experiments have confirmed these observations.<sup>41</sup> Clearly, mixing of

unburned HC with the bulk cylinder gases occurs during expansion and/or the exhaust blowdown process. Then, the final stages of piston motion during the exhaust stroke push most of the remaining fraction of the cylinder mass with its high HC concentration into the exhaust. This would be expected to leave a high concentration of HC in the residual gas in the cylinder. Experiments conducted in which the valve mechanism of a single-cylinder engine was arranged to disengage during operation and trap residual gases in the cylinder confirm this. For one set of typical engine operating conditions, approximately one-third of the hydrocarbons left unburned in an engine combustion event was retained in the cylinder and recycled.<sup>42</sup>

**FLAME QUENCHING AT THE WALLS.** The existence of quench layers on the cold combustion chamber walls of a spark-ignition engine was shown photographically by Daniel.<sup>43</sup> Photographs of the flame region immediately after flame arrival at the wall through a window in the cylinder head showed a thin non-radiating layer adjacent to the wall. The quench layer thicknesses measured were in the range 0.05 to 0.4 mm (thinnest at high load), in rough agreement with predictions based on experiments in combustion bombs. However, more recent work in bombs and engines indicates that diffusion of hydrocarbons from the quench layer into the burned gases and its subsequent oxidation occur on a time scale of a few milliseconds, at least with smooth clean combustion chamber walls. The constant-volume combustion bomb data which suggested this conclusion and the kinetic calculations which support this explanation of why quench layers are not significant with smooth clean walls have already been described in Sec. 11.4.2. The following evidence shows these conclusions are also valid in an engine.

A special rapid-acting poppet valve was used in a single-cylinder engine to sample the gases from a torus-shaped region, of height of order 0.25 mm and diameter about 6 mm, adjacent to the wall over a 1-ms period. Sampling was repeated every cycle to provide a steady stream of sampled gases for analysis. Figure 11-25 shows the variation in concentrations of HC species through the combustion, expansion, and exhaust processes. The fuel was propane ( $C_3H_8$ ). The fuel concentration drops rapidly to a low value when the flame arrives at the valve; at the same time, intermediate hydrocarbon product concentrations rise and then fall sharply to values below 1 ppm. Beginning at 60° ATC, all HC concentrations rise and vary somewhat during the remainder of the cycle in a way that depends strongly on engine operating conditions. The observed rapid rise in partial oxidation products immediately after flame arrival is consistent with the flame quenching short of the wall. The presence of  $CH_2O$  and  $CH_3CHO$  in significant quantities indicates that low-temperature oxidation processes are occurring. However, since all HC product concentrations fall rapidly within 2 ms of flame arrival to very low values, the unburned HC in the quench layer diffuse into the bulk burned gases and oxidize. The increase in HC concentrations later in the cycle results from the sampling of hydrocarbons from sources other than quench layers.<sup>44</sup>



**FIGURE 11-25**

Concentrations (mole fractions) of selected hydrocarbons adjacent to combustion chamber wall, as a function of crank angle during combustion, expansion, and exhaust processes. Mass sampled with rapid-acting valve held constant at  $7.6 \times 10^{-6}$  g per pulse. Total exhaust HC = 400 ppm C. Engine speed = 1250 rev/min, imep = 380 kPa, equivalence ratio = 0.9, MBT spark timing, no EGR.<sup>44</sup>

Though quench layers on clean smooth combustion chamber walls are not a significant source of unburned hydrocarbons, it has been shown that wall surface finish does affect exhaust HC levels. Comparisons have been made between the standard "rough" as-cast cylinder head surfaces and the same cylinder heads when smoothed. The average exhaust HC concentration decreased by 103 ppm C, or 14 percent; the smoothed surface area was 32 percent of the total combustion chamber surface area.<sup>45</sup> Buildup of deposits on the combustion chamber surfaces also affect HC emission levels, as will be discussed later.

**CREVICE HC MECHANISM.** The crevices in the combustion chamber walls—small volumes with narrow entrances—into which the flame is unable to penetrate have been shown to be a major source of unburned HC. The largest of these crevice regions is the volumes between the piston, piston rings, and cylinder wall. Other crevice volumes in production engines are the threads around the spark plug, the space around the plug center electrode, crevices around the intake and exhaust valve heads, and the head gasket crevice. Table 8.1 shows the size and relative importance of these crevice regions in one cylinder of a production V-6 engine determined from measurements of cold-engine components. Total crevice volume is a few percent of the clearance volume and the piston and ring pack crevices are the dominant contributor.

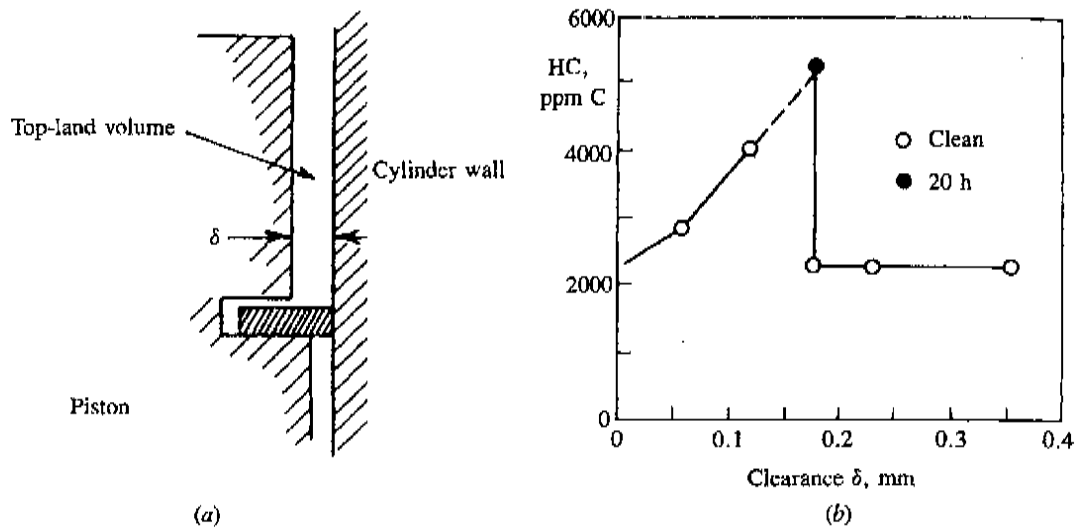
The important crevice processes occurring during the engine cycle are the following. As the cylinder pressure rises during compression, unburned mixture is forced into the crevice regions. Since these volumes are thin they have a large surface/volume ratio; the gas flowing into each crevice cools by heat transfer to close to the wall temperature. During combustion, while the pressure continues to rise, unburned mixture continues to flow into the crevice volumes. When the

flame arrives at each crevice, it can either propagate into the crevice and fully or partially burn the fuel and air within the crevice or it can quench at the crevice entrance. Whether the flame quenches depends on crevice entrance geometry, the composition of the unburned mixture, and its thermodynamic state as described in Sec. 11.4.2. After flame arrival and quenching, burned gases will flow into each crevice until the cylinder pressure starts to decrease. Once the crevice gas pressure is higher than the cylinder pressure, gas flows back from each crevice into the cylinder.

The most important of these crevices, the volumes between the piston, piston rings, and cylinder wall, is shown schematically in Fig. 8-27. This crevice consists of a series of volumes, connected by flow restrictions such as the ring side clearance and ring gap whose geometry changes as the ring moves up and down in the ring groove sealing either at the top or bottom ring surface. The gas flow, pressure distribution, and ring motion are therefore coupled, and their behavior during the compression and expansion strokes has already been discussed in Sec. 8.6. During compression and combustion, mass flows *into* the volumes in this total crevice region. Once the cylinder pressure starts to decrease (after about 15° ATC) gas flows out of the top of these crevice regions in Fig. 8-27 into the cylinder at low velocity adjacent to the cylinder wall. The important result is that the fraction of the total cylinder charge (5 to 10 percent) trapped in these regions at the time of peak cylinder pressure escapes the primary combustion process. Most of this gas flows back into the cylinder during the expansion process. Depending on spark plug location in relation to the position of the top ring gap, well above 50 percent of this gas can be unburned fuel-air mixture. Its potential contribution to unburned HC emissions is obvious.

There is substantial evidence to support the above description of crevice HC phenomena and the piston ring crevice region in particular. Visualization studies in a special engine have identified the spark plug crevice outflow, low-velocity gas expansion out of the volume above the first ring after the time of peak pressure, and the jet-like flows through the top ring gap later in the expansion process when the pressure difference across the ring changes sign.<sup>46</sup> Gas sampling from the volume above the top ring, using a rapid-acting sample valve mounted in the piston crown, has shown that the gas composition in this region corresponds to unburned fuel-air mixture until flame arrival at the crevice entrance closest to the sampling valve location. Next, product gases enter the crevice as the cylinder pressure continues to rise. Then, during expansion as gas flows out of this region, the composition of the gas sampled reverts back toward that of the unburned mixture which enters the crevice region earlier.<sup>47</sup>

Direct evidence that the piston and ring crevice regions are a major contributor to exhaust HC emissions comes from experiments where the volume of this crevice region was substantially changed. Wentworth<sup>48</sup> almost completely eliminated this crevice by moving the top piston ring as close to the crown of the piston as possible, and sealing this ring at top and bottom in its groove with O rings. Tests of this sealed ring-orifice design in a production engine showed reductions of between 47 and 74 percent from baseline HC levels over a range of



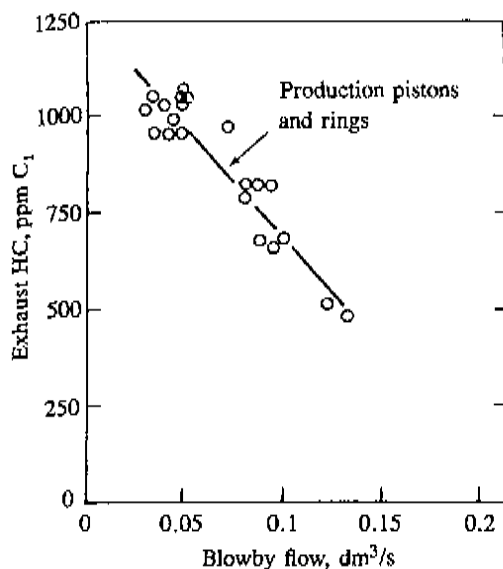
**FIGURE 11-26** (a) Piston top-land crevice volume. (b) Effect of increasing top-land clearance on exhaust hydrocarbon emissions. Unthrottled spark-ignition engine,  $r_c = 6,885$  rev/min,  $A/F = 13$ , MBT timing.<sup>49</sup>

speeds and loads. Haskell and Legate,<sup>49</sup> in experiments in a single-cylinder CFR engine, steadily increased the piston top-land clearance (see Fig. 11-26a) and measured the effect on exhaust HC emissions. Figure 11-26b shows the results: HC emissions increase as the top-land clearance increases until the clearance equals about 0.18 mm, when emissions drop to the zero clearance level. This clearance (0.18 mm) is close to the two-plate quench distance estimated from Eq. (11.27). For piston top-land clearances above this value, the flame can enter the crevice and burn up much of the crevice HC.

The relative importance of the different crevices in the combustion chamber walls has been examined by using the cylinder head and piston of a four-cylinder production engine to form two constant-volume reactors or combustion bombs.<sup>50</sup> The cylinder head was sealed with a steel plate across the head gasket plane to make one reactor; the piston and ring pack and cylinder wall, again sealed with a plate at the head gasket plane, formed the second reactor. Each reactor was filled with a propane-air mixture and combustion initiated with a spark discharge across a spark plug; following combustion the burned gases were exhausted, sampled, and analyzed. The crevices were sequentially filled with epoxy or viton rubber, and after filling each crevice, the exhaust HC emission level determined. It was found that the ring pack crevices produced approximately 80 percent of the total scaled HC emissions, the head gasket crevice about 13 percent, and the spark plug threads 5 percent. All other HC sources in these reactors produced less than 2 percent of the total HC. While these numbers cannot be applied directly to an operating engine (the crevice filling and emptying rates in the bomb experiments are substantially different from these rates in an engine), they do underline the importance of the ring pack crevice region.

Blowby is the gas that flows from the combustion chamber, past the piston and into the crankcase. It is forced through any leakage paths afforded by the





**FIGURE 11-27**

Effect of increasing crankcase blowby on exhaust hydrocarbon emissions. Production pistons and rings. SI engine at 1200 rev/min, intake manifold pressure 0.6 atm,  $A/F = 14.2$ .<sup>51</sup>

piston-bore-ring assembly in response to combustion chamber pressure. Blowby of gases from the cylinder to the crankcase removes gas from this crevice region and thereby prevents some of the crevice gases from returning to the cylinder. Crankcase blowby gases used to be vented directly to the atmosphere and constituted a significant source of HC emissions. The crankcase is now vented to the engine intake system, the blowby gases are recycled, and this source of HC emissions is now fully controlled. Blowby at a given speed and load is controlled primarily by the greatest flow resistance in the flow path between the cylinder and the crankcase. This is the smallest of the compression ring ring-gap areas. Figure 8-30 shows how blowby increases linearly with the smallest gap area. Figure 11-27 shows how exhaust HC levels decrease as blowby increases and more crevice HC flows to the crankcase. Crankcase blowby gases represent a direct performance loss. They are a smaller efficiency loss because crankcase gases are now recycled to the engine intake system.

The location of the ring gap in relation to the spark plug also affects HC emission levels. Experiments have shown that HC emissions are highest when the top ring gap is farthest from the spark plug; the gas flowing into the crevice directly above the gap is then unburned mixture for the longest possible time. With the top ring gap closest to the spark plug, HC exhaust levels are lowest because burned gas reaches the gap location at the earliest time in the combustion process. The difference, highest to lowest, was between 9 and 42 percent of the average level for any set of operating conditions, and in most cases was above 20 percent.<sup>51</sup>

The fate of these crevice HC when they flow back into the cylinder during expansion and exhaust is not well understood. Both jet-like flows (e.g., that from the ring gap) and low-velocity creeping flows (e.g., that from the piston top-land crevice) have been observed (see Fig. 8-29). While the former could mix rapidly with the high-temperature bulk burned gases, the latter will enter the cool gases

**TABLE 11.6**  
**Amount of gas flowing into and out of crevice regions†**

	% mass	ppm C
Total gas in all crevice regions	8.2	
Total gas back to combustion chamber	7.0	
Unburned back to combustion chamber	3.7–7.0‡	5000–9400
Unburned to blowby	0.5–1.2‡	
Total unburned escaping primary combustion	4.2–8.2‡	

† For V-6 engine operating at 2000 rev/min and wide-open throttle.

‡ Depends on spark plug and ring gap location.

in the cylinder wall boundary layer and mix and (probably) burn much more slowly. Hydrocarbon transport and oxidation processes are discussed more fully below.

Table 11.6 presents a summary of estimates of the total mass of gas and mass of unburned mixture in the piston, ring, and cylinder wall crevice region for a typical spark-ignition engine.<sup>46</sup> When compared to exhaust HC levels, it is clear that these crevices are a major source of unburned hydrocarbons.

**ABSORPTION AND DESORPTION IN ENGINE OIL.** The presence of lubricating oil in the fuel or on the walls of the combustion chamber is known to result in an increase in exhaust hydrocarbon levels. In experiments where exhaust HC concentrations rose irregularly with time, with engine operating conditions nominally constant, it was shown that oil was present on the piston top during these high emission periods. When engine oil was added to the fuel, HC emissions increased, the amount of additional HC in the exhaust increasing with the increasing amount of oil added. The increase in exhaust HC was primarily unreacted fuel (isooctane) and not oil or oil-derived compounds.<sup>51</sup> The increase in HC can be substantial: exhaust HC levels from a clean engine can double or triple when operated on a fuel containing 5 percent lubricating oil over a period of order 10 minutes. (With deposits from leaded-fuel operation present on the combustion chamber walls, however, a much smaller increase in exhaust HC was observed.) It has been proposed that fuel vapor absorption into and desorption from oil layers on the walls of the combustion chamber could explain these phenomena.<sup>49</sup>

The absorption and desorption mechanism would work as follows. The fuel vapor concentration within the cylinder is close to the inlet manifold concentration during intake and compression. Thus, for about one crankshaft revolution, any oil film on the walls will absorb fuel vapor. During the latter part of compression, the fuel vapor pressure is increasing so, by Henry's law, absorption will continue even if the oil was saturated during intake. During combustion the fuel vapor concentration in the bulk gases goes essentially to zero so the absorbed fuel vapor will desorb from the liquid oil film into the gaseous combustion products. Desorption could continue throughout the expansion and exhaust strokes.

Some of the desorbed fuel vapor will mix with the high-temperature combustion products and oxidize. However, desorbed vapor that remains in the cool boundary layer or mixes with the cooler bulk gases late in the cycle may escape full oxidation and contribute to unburned HC emissions.

Experiments, where measured amounts of oil were placed on the piston crown, confirm that oil layers on the combustion chamber surface increase exhaust HC emissions. The exhaust HC levels increased in proportion to the amount of oil added when the engine was fueled with isooctane. Addition of 0.6 cm<sup>3</sup> of oil produced an increase of 1000 ppm C in exhaust HC concentration. Fuel and fuel oxidation species, not oil oxidation products, were responsible for most of this increase. Similar experiments performed with propane fuel showed no increase in exhaust HC emissions when oil was added to the cylinder. The increase in exhaust HC is proportional to the solubility of the fuel in the oil. The exhaust HC levels decreased steadily back to the normal engine HC level before oil addition, over a period of several minutes. At higher coolant temperatures, the increase in HC on oil addition is less, and HC concentrations decreased back to the normal level more quickly. Increasing oil temperature would decrease viscosity, increasing the rate of drainage into the sump. It also changes the solubility and diffusion rate of the fuel in the oil.<sup>52</sup>

At the outer surface of the oil layer, the concentration of fuel vapor dissolved in the oil is given by Henry's law for dilute solutions in equilibrium:

$$\bar{x}_f = \frac{p_f}{H} \tag{11.32}$$

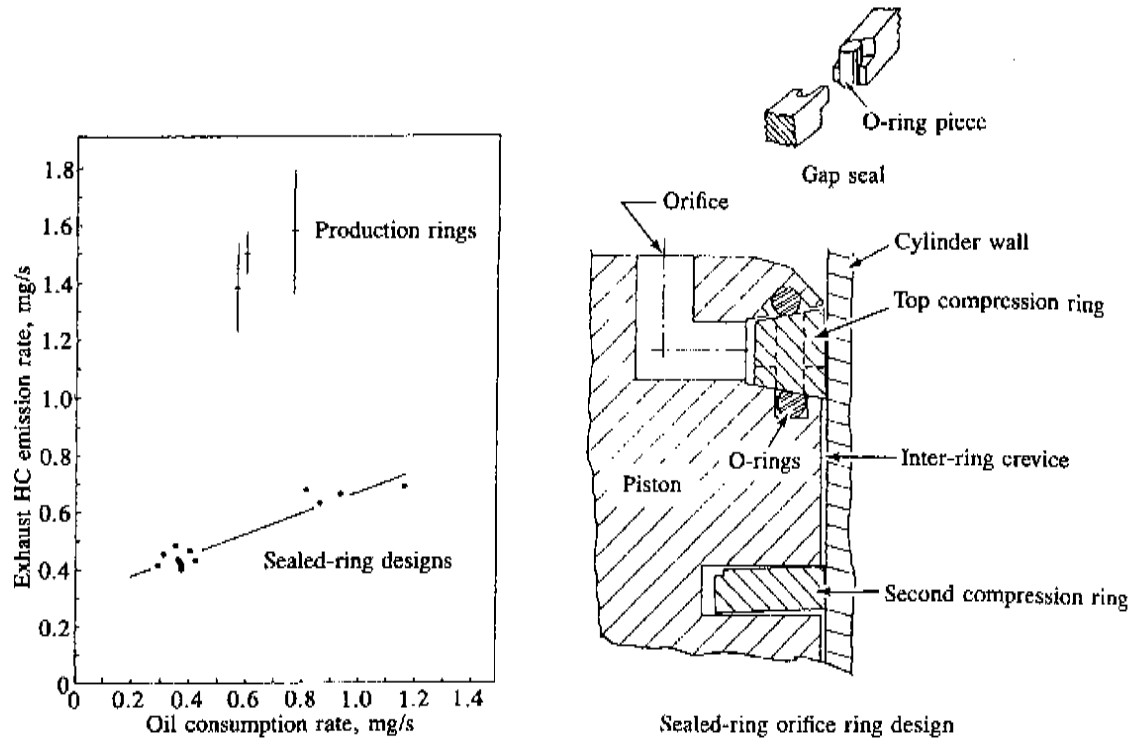
where  $\bar{x}_f$  is the mole fraction of fuel vapor in the oil,  $p_f$  is the partial pressure of fuel vapor in the gas, and  $H$  is Henry's constant. If the oil layer is sufficiently thin, and hence diffusion sufficiently rapid, Eq. (11.32) can be used to estimate the mole fraction of the fuel dissolved in the oil. Since  $p_f = n_{f,c} \tilde{R}T/V$  (where  $n_{f,c}$  is the number of moles of fuel in the cylinder,  $T$  is the temperature, and  $V$  the cylinder volume) and  $x_f = n_{f,o}/(n_{f,o} + n_o) = n_{f,o}/n_o$  for  $n_o \gg n_{f,o}$  (where  $n_{f,o}$  is the number of moles of fuel dissolved in the oil and  $n_o$  is the number of moles of oil),<sup>53</sup> then

$$\frac{n_{f,o}}{n_{f,c}} = \frac{n_o \tilde{R}T}{HV} \tag{11.33}$$

Diffusion is sufficiently rapid for Eq. (11.33) to be valid if the diffusion time constant  $\tau_d$  is much less than characteristic engine times: i.e.,

$$\tau_d \approx \frac{\delta^2}{D} \ll N^{-1}$$

where  $\delta$  is the oil layer thickness,  $D$  is the diffusion coefficient for fuel vapor in the oil, and  $N$  is engine speed.  $D$  for a hydrocarbon through a motor oil is of order 10<sup>-6</sup> cm<sup>2</sup>/s at 300 K and of order 10<sup>-5</sup> cm<sup>2</sup>/s at 400 K. Oil film thicknesses on the cylinder wall vary during the operating cycle between about 1 and 10  $\mu$ m.<sup>54, 55</sup> Thus diffusion times for engine conditions are 10<sup>-1</sup> to 10<sup>-3</sup> s; for the thinnest oil layers approximate equilibration would be achieved. A theoretical



**FIGURE 11-28**

Correlation between exhaust hydrocarbon emissions and oil consumption rate. Production piston rings and sealed ring-orifice ring designs. SI engine at 1600 rev/min, imep = 422 kPa, equivalence ratio = 0.9,  $r_c = 8.0$ , intake pressure = 54 kPa, MBT spark timing.<sup>57</sup>

study of this problem—the one-dimensional cyclic absorption and desorption of a dilute amount of gas in a thin (constant thickness) isothermal liquid layer where diffusion effects are important—has been carried out. It suggests that oil layers on the cylinder wall could be a significant contributor to HC emission levels.<sup>56</sup>

Correlations between engine oil consumption and exhaust HC emissions provide a perspective on the relative importance of oil absorption/desorption and crevice mechanisms. Wentworth measured oil consumption and HC emissions in a spark-ignition engine for a range of piston ring designs.<sup>57</sup> Some of these designs were of the sealed ring-orifice type which effectively eliminates all the crevices between the piston, piston rings, and cylinder, and prevents any significant gas flow into or out of the ring region. HC emissions increase with increasing oil consumption for both production ring designs and the sealed ring-orifice designs, as shown in Fig. 11-28. Extrapolation to zero oil consumption from normal consumption levels shows a reduction in exhaust HC levels, but this decrease is significantly less than the difference in emission levels between the production and the sealed ring-orifice designs which effectively remove the major crevice region. The production piston used had a chamfered top land. The HC emissions for a normal piston top-land design would probably be higher.

**POOR COMBUSTION QUALITY.** Flame extinction in the bulk gas, before all of the flame front reaches the wall, is a source of HC emissions under certain engine

operating conditions. As the cylinder pressure falls during the expansion stroke, the temperature of the unburned mixture ahead of the flame decreases. This slows the burning rate [the laminar flame speed decreases so the burning rate in Eq. (9.52) decreases]. If the pressure and temperature fall too rapidly, the flame can be extinguished. This type of bulk quench has been observed in spark-ignition engines; it results in very high HC concentrations for that particular cycle. Engine conditions where bulk quenching is most likely to occur are at idle and light load where engine speed is low and the residual gas fraction is high, with high dilution with excessive EGR or overly lean mixtures, and with substantially retarded combustion. Even if steady-state engine calibrations of  $A/F$ , EGR, and spark-timing are such that bulk quenching does not occur, under transient engine operation these variables may not be appropriately set to avoid bulk quenching in some engine cycles due to the different dynamic characteristics of the engine subsystems which control these variables.

The existence of zones of stable and unstable engine operation with lean or dilute mixtures has already been discussed (see Sec. 9.4.3). Detailed engine combustion studies have shown that, as mixture composition becomes more dilute (e.g., by increasing EGR) and unburned gas temperature and pressure during combustion become lower, combustion quality (or variability) and engine stability deteriorate. The standard deviation in a parameter such as indicated mean effective pressure (which depends for its magnitude on the proper timing of the start of combustion and on the duration of the combustion process) increases due first to an increase in the number of slower burning cycles, then as conditions worsen to the occurrence of partial burning cycles, and finally to some misfiring cycles. Figure 9-36 showed how unburned hydrocarbon emissions from a spark-ignition engine rise as the EGR rate is increased at constant load and speed, and combustion quality (defined by the ratio of standard deviation in imep to the average imep) deteriorates. Initially the increase in HC is modest and is caused by changes in the other HC emission mechanisms described above. However, when partial burning cycles are detected, HC emissions rise more rapidly due to incomplete combustion of the fuel in the cylinder in these cycles. When misfiring cycles—no combustion—occur the rise in HC becomes more rapid still.

The relative importance of bulk gas quenching in a fraction of the engine's operating cycles due to inadequate combustion quality as a source of HC, compared with the other sources described in this section, has yet to be established. However, one obvious technique for reducing its importance, burning the mixture faster so that combustion is completed before conditions conducive to slow and partial burning exist in the cylinder, does reduce engine exhaust HC emissions. Figure 11-29 shows a comparison of HC emissions from a moderate burn rate engine with HC emissions with a faster burn rate [i.e., with improved combustion quality—lower coefficient of variation in imep,  $COV_{imep}$ , Eq. (9.50)], achieved by the use of two spark plugs instead of one.<sup>58</sup> The exhaust measurements show lower HC emissions when significant amounts of EGR are used for  $NO_x$  control for the faster, and hence less variable, combustion process. Such evidence suggests that occasional partial burning cycles may occur, even under

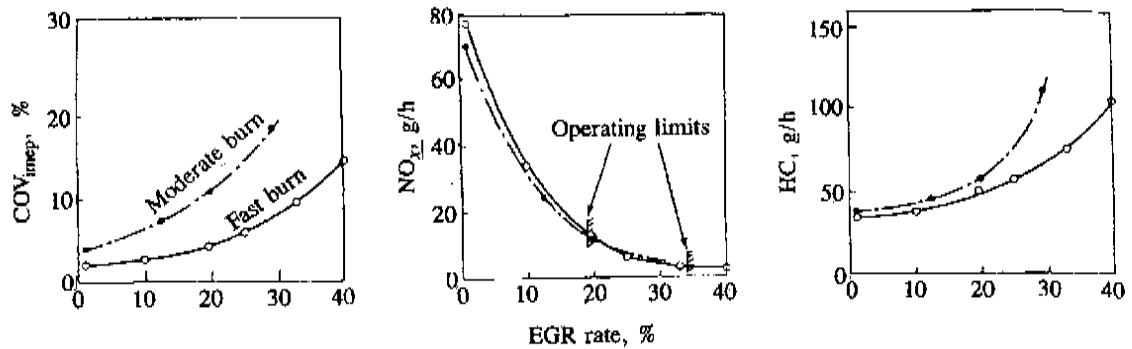


FIGURE 11-29

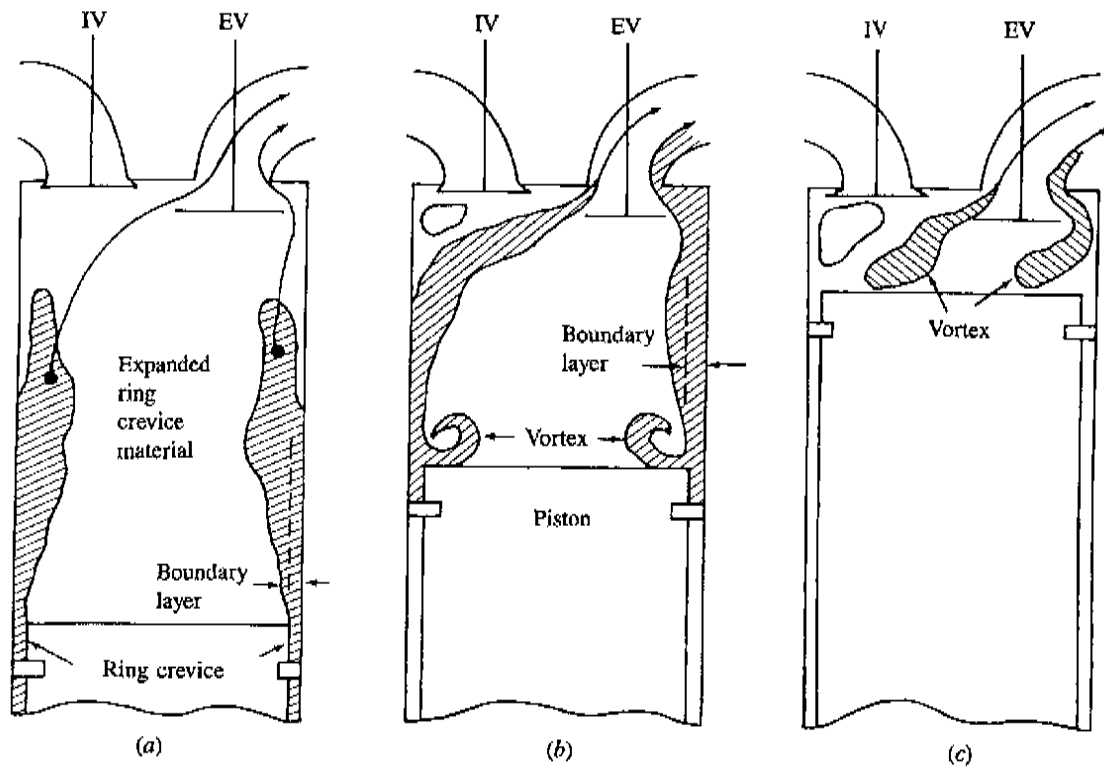
Effect of increasing burn rate on tolerance to recycled exhaust gas (EGR) and HC and NO<sub>x</sub> emissions levels. COV<sub>imep</sub> defined by Eq. (9.50). SI engine at 1400 rev/min, 324 kPa imep, equivalence ratio = 1.0, MBT timing.<sup>58</sup>

conditions where combustion appears to be “normal,” and that this mechanism is important in practice.

**EFFECT OF DEPOSITS.** Deposit buildup on the combustion chamber walls (which occurs in vehicles over several thousands of miles) is known to increase unburned HC emissions. With leaded gasoline operation, the increase in HC emissions varies between about 7 and 20 percent. The removal of the deposits results typically in a reduction in HC emissions to close to clean engine levels. With unleaded gasoline, while the deposit composition is completely different (carbonaceous rather than lead oxide), the increase in HC emissions with accumulated mileage is comparable. Soft sooty deposits, such as those which accumulate after running the engine on a rich mixture, also cause an increase in HC emissions. Again, when the deposits were removed the emission rate fell about 25 percent to the original level.<sup>59</sup> Studies with simulated deposits (pieces of metal-foam sheet 0.6 mm thick) attached to the cylinder head and piston also showed increases in HC emissions. The increase varied between about 10 and 100 ppm C/cm<sup>2</sup> of simulated deposit area. The effect for a given area of deposit varied with deposit location. Locations close to the exhaust valve, where the flow direction during the exhaust process would be expected to be directly into the exhaust port, showed the highest increase in emissions.<sup>45</sup>

It is believed that absorption and desorption of hydrocarbons by these surface deposits is the mechanism that leads to an increase in emissions. Deposits can also build up in the piston ring crevice regions. A reduction in volume of these crevice regions would decrease HC emissions (and such a decrease has been observed). However, changes in piston-cylinder wall clearance due to deposits can affect the flame-quenching process and could increase emissions.<sup>49</sup>

**HYDROCARBON TRANSPORT MECHANISMS.** All of the above mechanisms (except misfire) result in high hydrocarbon concentrations adjacent to the combustion chamber walls. While any jet-type flows out of crevices during the expansion



**FIGURE 11-30** Schematic of flow processes by which ring crevice HC and HC desorbed from cylinder wall oil film exit the cylinder: (a) exhaust blowdown process; (b) during exhaust stroke; (c) end of exhaust stroke.<sup>60</sup>

sion and exhaust strokes can transport unburned HC into the bulk gases, most of the HC will remain near the wall. Two mechanisms by which gas near the cylinder wall exits the cylinder have been demonstrated. One is entrainment in the vigorous gas flow out of the cylinder which occurs during the exhaust blowdown process. The other is the vortex generated in the piston crown-cylinder wall corner during the exhaust stroke.

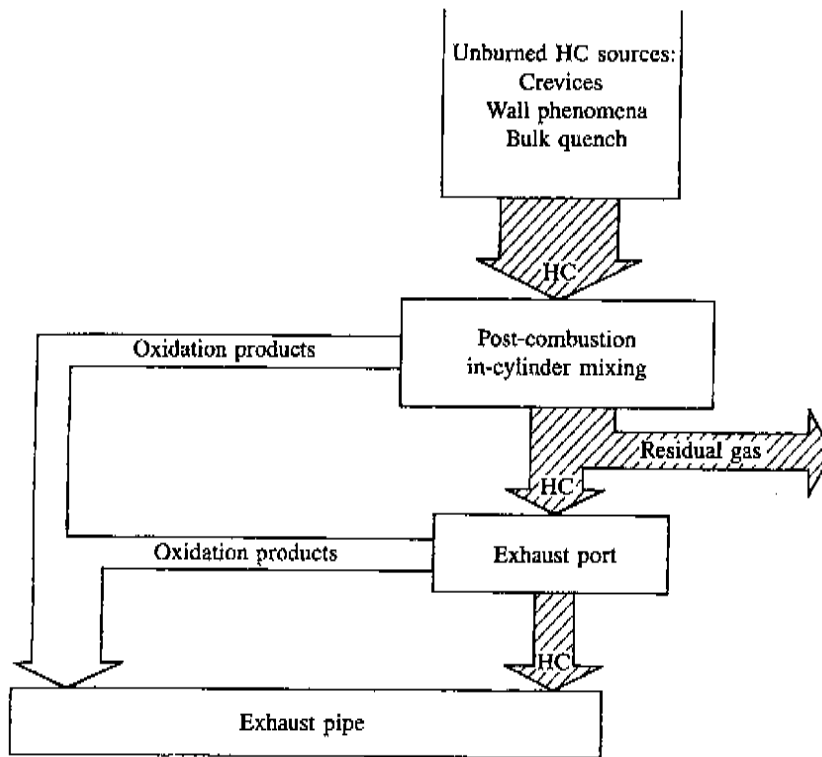
Figure 11-30 illustrates these flow processes. In Fig. 11-30a the engine cylinder is shown as the exhaust valve opens during the blowdown process. At this time the unburned HC from the ring crevice regions, laid along the wall during expansion (and possibly HC from the oil film on the cylinder wall), is expanding into the cylinder as the cylinder pressure falls. Some of this material will be entrained by the bulk gases in the rapid motion which occurs during exhaust blowdown (see Sec. 6.5). The rapid thinning of the thermal boundary-layer regions on the combustion chamber walls during blowdown, which would result from entrainment of the denser hydrocarbon-containing gas adjacent to the wall, has been observed in schlieren movies taken in a transparent engine.<sup>46</sup> This process, plus entrainment of any HC from the spark plug and head gasket crevices, would contribute to unburned HC in the blowdown gases which contain about half the total HC emissions (see Fig. 11-24). During the exhaust stroke this bulk gas entrainment process will continue, exhausting additional unburned HC, as shown in Fig. 11-30b.

The second mechanism starts at the beginning of the exhaust stroke in the piston crown-cylinder wall corner. The piston motion during the exhaust stroke scrapes the boundary-layer gases off the cylinder wall (which contain the remainder of the piston and ring crevice hydrocarbons), rolls them up into a vortex, and pushes them toward the top of the cylinder. This piston crown-cylinder wall corner flow is discussed in Sec. 8.7, and has been observed in transparent engines as well as in water-flow engine analog studies. At the end of the exhaust stroke, the height of this vortex is comparable to the engine clearance height. As shown in Fig. 11-30c, a recirculation flow is likely to build up in the upper corner of the cylinder away from the exhaust valve, causing the vortex to detach from the wall and partly sweep out of the cylinder. In the corner nearest the valve, the flow is deflected around the valve, also tending to pull part of the vortex out of the chamber. In this way it is possible for a large part of the vortex, which now contains a substantial fraction of the unburned HC originally located adjacent to the cylinder wall, to leave the cylinder at the end of the exhaust stroke. This vortex flow is thought to be the mechanism that leads to the high HC concentrations measured at the end of the exhaust process, which contributes the other half of the exhausted HC mass (see Fig. 11-24), and to be responsible for the HC concentrations measured in the residual gases being much higher than average exhaust HC levels.<sup>42</sup> This study showed that at close to wide-open-throttle conditions, only about two-thirds of the HC which fail to oxidize inside the cylinder were exhausted, though 95 percent of the gas within the cylinder flows out through the exhaust valve. The residual gas HC concentration was about 11 times the average exhaust level. At part-throttle conditions, where the residual gas fraction is higher, it has been estimated that only about half of the unreacted HC in the cylinder will enter the exhaust.<sup>61</sup>

**HYDROCARBON OXIDATION.** Unburned hydrocarbons which escape the primary engine combustion process by the mechanisms described above must then survive the expansion and exhaust process without oxidizing if they are to appear in the exhaust. Since the formation mechanisms produce unburned HC at temperatures close to the wall temperature, mixing with bulk burned gas must take place first to raise the HC temperature to the point where reaction can occur. The sequence of processes which links the source mechanisms to hydrocarbons at the exhaust exit is illustrated in Fig. 11-31; it involves mixing and oxidation in both the cylinder and the exhaust system.

There is considerable evidence that substantial oxidation does occur. The oxidation of unburned HC in the quench layers formed on the combustion chamber walls on a time scale of order 1 ms after the flame is extinguished has already been discussed. Because the quench layers are thin, diffusion of HC into the bulk burned gas is rapid. Because the burned gases are still at a high temperature, oxidation then occurs quickly. Measurements of in-cylinder HC concentrations by gas sampling prior to exhaust valve opening show levels about 1.5 to 2 times the average exhaust level.<sup>44, 63</sup> The exhaust unburned HC are a mixture of fuel hydrocarbon compounds and pyrolysis and partial oxidation pro-





**FIGURE 11-31**  
Schematic of complete SI engine HC formation and oxidation mechanism within the cylinder and exhaust system.<sup>62</sup>

ducts. While the relative proportion of fuel compared to reaction product hydrocarbon compounds varies substantially with engine operating conditions, an average value for passenger car vehicle exhausts is that fuel compounds comprise 40 percent of the total HC. Though partially reacted HC are produced in the flame-quenching process, these are closest to the high-temperature burned gases and are likely to mix and burn rapidly. That such a large fraction of the exhaust HC are reaction products indicates that substantial postformation HC reactions are occurring. There is direct evidence that HC oxidation in the exhaust system occurs.<sup>64</sup> Since in-cylinder gas temperatures are higher, it is likely that mixing of unburned HC with the bulk cylinder gases limits the amount of oxidation rather than the reaction kinetics directly.

Overall empirically based expressions for the rate of oxidation of hydrocarbons of the form of Eq. (11.31) have been developed and used to examine in-cylinder and exhaust burnup. A characteristic time  $\tau_{HC}$  for this burnup process can be defined:

$$\frac{1}{\tau_{HC}} = \frac{1}{[HC]} \frac{d[HC]}{dt} \quad (11.34)$$

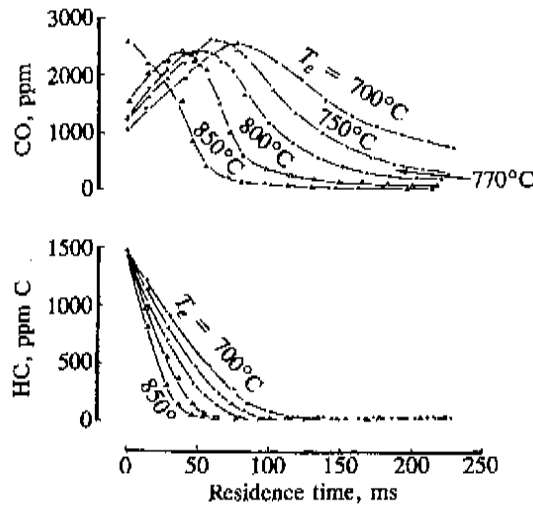
Using an expression similar to Eq. (11.31) for  $d[HC]/dt$ , Weiss and Keck<sup>63</sup> have shown that any HC mixing with the burned gases in the cylinder prior to exhaust

blowdown will oxidize. The in-cylinder gas temperature prior to blowdown generally exceeds 1250 K; the characteristic reaction time  $\tau_{\text{HC}}$  is then less than 1 ms. During blowdown the temperature falls rapidly to values typically less than 1000 K;  $\tau_{\text{HC}}$  is then greater than about 50 ms. An experimental study of HC exiting from a simulated crevice volume has shown that complete HC oxidation only occurs when the cylinder gas temperature is above 1400 K.<sup>65</sup> Thus a large fraction of the HC leaving crevice regions or oil layers during the exhaust process can be expected to survive with little further oxidation. Gas-sampling data show little decrease in in-cylinder HC concentrations during the exhaust stroke, thus supporting this conclusion.<sup>44, 63</sup> Overall, probably about half of the unburned HC formed by the source mechanisms described above will oxidize within the engine cylinder (the exact amount cannot yet be predicted with any accuracy; it is likely to depend on engine design and operating conditions<sup>61</sup>).

As shown schematically in Fig. 11-31, oxidation of HC in the exhaust system can occur. Often this is enhanced by air addition into the port region to ensure that adequate oxygen for burnup is available. However, since the gas temperature steadily decreases as the exhaust gases flow through the exhaust port and manifold, the potential for HC burnup rapidly diminishes. To oxidize the hydrocarbons in the gas phase, a residence time of order 50 ms or longer at temperatures in excess of 600°C are required. To oxidize carbon monoxide temperatures in excess of 700°C are required. Average exhaust gas temperatures at the cylinder exit (at the exhaust valve plane) are about 800°C; average gas temperatures at the exhaust port exit are about 600°C.† Figure 6-21 shows an example of the measured cylinder pressure, measured gas temperature at the exhaust port exit, and estimated mass flow rate into the port and gas temperature in the cylinder, during the exhaust process at a part-throttle operating condition. Port residence time and gas temperatures vary significantly through the process. Precise values of these variables obviously depend on engine operating conditions. It is apparent that only in the exhaust port and upstream end of the manifold can any significant gas-phase HC oxidation occur.

The importance of exhaust gas temperature to exhaust system emissions burnup is illustrated by the results shown in Fig. 11-32.<sup>66</sup> The exhaust system of a four-cylinder engine was modified by installing a section of heated and insulated pipe to maintain the exhaust gas temperature constant in the absence of any HC or CO burnup. The exhaust temperature entering this test section was varied by adjusting the engine operating conditions. The figure shows CO and HC concentrations as functions of residence time in the exhaust test section (or effectively as a function of distance from the engine).  $T_e$  is the entering gas temperature. The exhaust composition was fuel lean with 3 percent O<sub>2</sub> in the burned

† Note that there is a significant variation in the temperature of the exhaust gases throughout the exhaust process. The gas exhausted first is about 100 K hotter than the gas exhausted at the end of the process (see Sec. 6.5).



**FIGURE 11-32**

Effect of exhaust gas temperature on HC and CO burnup in the exhaust. SI engine at 1600 rev/min, engine air flow =  $7.7 \text{ dm}^3/\text{s}$ , lean mixture with 3%  $\text{O}_2$  and 13% ( $\text{CO} + \text{CO}_2$ ) in exhaust.<sup>66</sup>

gas stream. HC oxidation starts immediately (for  $T \gtrsim 600^\circ\text{C}$ ), the rate of oxidation increasing rapidly with increasing temperature. Under fuel-lean conditions, incomplete HC oxidation can result in an increase in CO levels. CO oxidation commences later, when the gas temperature rises above the entering value due to heat released by the already occurring HC oxidation. The further heat released by CO oxidation accelerates the CO burnup process. These data underline the importance of the exhaust port heat-transfer and mixing processes. Both mixing between the hotter blowdown gases (with their lower HC concentration) and the cooler end-of-exhaust gases (with their higher HC concentration) and mixing between burned exhaust gas and secondary air are important.

Engine experiments where the exhaust gas reactions were quenched by timed injection of cold carbon dioxide at selected locations within the exhaust port have shown that significant reductions in HC concentration in the port can occur. Parallel modeling studies of the HC burnup process (based on instantaneous mass flow rate, estimated exhaust gas temperature, and an overall hydrocarbon reaction-rate expression), which predicted closely comparable magnitudes and trends, indicated that gas temperature and port residence time are the critical variables. The percent of unburned HC exiting the cylinder which reacted in the exhaust system (with most of the reaction occurring in the port) varied between a few and 40 percent. Engine operating conditions that gave highest exhaust temperatures (stoichiometric operation, higher speeds, retarded spark timing, lower compression ratio) and longest residence times (lighter load) gave relatively higher percent reductions. Air injection at the exhaust valve-stem base, phased to coincide with the exhaust process, showed that for stoichiometric and slightly rich conditions secondary air flow rates up to 30 percent of the exhaust flow substantially increased the degree of burnup. The timing of the secondary air flow relative to the exhaust flow and the location of the air injection point in the port are known to be critical.<sup>64</sup>

Reductions in exhaust port heat losses through the use of larger port cross-sectional areas (to reduce flow velocity and surface area per unit volume), inser-

tion of port liners to provide higher port wall temperatures, and attention to port design details to minimize hot exhaust gas impingement on the walls are known to increase the degree of reaction occurring in the port.

**SUMMARY.** It will be apparent from the above that the HC emissions formation process in spark-ignition engines is extremely complex and that there are several paths by which a small but important amount of the fuel escapes combustion. It is appropriate here to summarize the overall structure of the spark-ignition engine hydrocarbon emission problem and identify the key factors and engine variables that influence the different parts of that problem. Table 11.7 provides such a summary. The total process is divided into four sequential steps: (1) the formation of unburned hydrocarbon emissions; (2) the oxidation of a fraction of these HC emissions within the cylinder, following mixing with the bulk gases; (3) the flow of a fraction of the unoxidized HC from the cylinder into the exhaust; (4) the oxidation in the exhaust system of a fraction of the HC that exit the cylinder. The detailed processes and the design and operating variables that influence each of these steps in a significant way are listed.

The four separate formation mechanisms identified in step 1 have substantial, though as yet incomplete, evidence behind them. They are listed in the most likely order of importance. Each has been extensively described in this section. It is through each of these mechanisms that fuel or fuel-air mixture escapes the primary combustion process. That fuel must then survive the expansion and exhaust processes and pass through the exhaust system without oxidation if it is to end up in the atmosphere as HC emissions. The rate of mixing of these unburned HC with the hot bulk cylinder gases, the temperature and composition of the gases with which these HC mix, and the subsequent temperature-time and composition-time histories of the mixture will govern the amount of in-cylinder oxidation that occurs. The distribution of these HC around the combustion chamber is nonuniform (and changes with time); they are concentrated close to the walls of the chamber. The fraction of these HC that will exit the chamber during the exhaust process will depend on the details of the in-cylinder flow patterns that take them through the exhaust valve. Overall, the magnitude of the residual fraction will be one major factor; the residual gas is known to be much richer in HC than the average exhaust. In particular, the flow patterns in the cylinder toward the end of the exhaust stroke as the gas scraped off the cylinder wall by the piston moves toward the exhaust valve will be important. Finally, a fraction of the unburned HC which leave the cylinder through the exhaust valve will burn up within the exhaust system. Gas-phase oxidation in the exhaust ports and hotter parts of the exhaust manifold is significant. The amount depends on the gas temperature, composition, and residence time. If catalysts or a thermal reactor are included in the exhaust system, very substantial additional reduction in HC emission levels can occur. These devices and their operating characteristics are described in Sec. 11.6.

**TABLE 11.7**  
**Critical factors and engine variables in HC emissions mechanisms**

<p>1. <i>Formation of HC</i></p> <p>(a) <i>Crevice</i></p> <ol style="list-style-type: none"> <li>(1) Crevice volume</li> <li>(2) Crevice location (relative to spark plug)</li> <li>(3) Load</li> <li>(4) Crevice wall temperature</li> <li>(5) Mixture composition†</li> </ol> <p>(b) <i>Oil layers</i></p> <ol style="list-style-type: none"> <li>(1) Oil consumption</li> <li>(2) Wall temperature</li> <li>(3) Speed</li> </ol> <p>(c) <i>Incomplete combustion</i></p> <ol style="list-style-type: none"> <li>(1) Burn rate and variability</li> <li>(2) Mixture composition†</li> <li>(3) Load</li> <li>(4) Spark timing‡</li> </ol> <p>(d) <i>Combustion chamber walls</i></p> <ol style="list-style-type: none"> <li>(1) Deposits</li> <li>(2) Wall roughness</li> </ol>	<p>2. <i>In-cylinder mixing and oxidation</i></p> <p>(a) <i>Mixing rate with bulk gas</i></p> <ol style="list-style-type: none"> <li>(1) Speed</li> <li>(2) Swirl ratio</li> <li>(3) Combustion chamber shape</li> </ol> <p>(b) <i>Bulk gas temperature during expansion and exhaust</i></p> <ol style="list-style-type: none"> <li>(1) Speed</li> <li>(2) Spark timing‡</li> <li>(3) Mixture composition†</li> <li>(4) Compression ratio</li> <li>(5) Heat losses to walls</li> </ol> <p>(c) <i>Bulk gas oxygen concentration</i></p> <ol style="list-style-type: none"> <li>(1) Equivalence ratio</li> </ol> <p>(d) <i>Wall temperature</i></p> <ol style="list-style-type: none"> <li>(1) Important if HC source near wall</li> <li>(2) For crevices: importance depends on geometry</li> </ol>
<p>3. <i>Fraction HC flowing out of cylinder</i></p> <p>(a) <i>Residual fraction</i></p> <ol style="list-style-type: none"> <li>(1) Load</li> <li>(2) Exhaust pressure</li> <li>(3) Valve overlap</li> <li>(4) Compression ratio</li> <li>(5) Speed</li> </ol> <p>(b) <i>In-cylinder flow during exhaust stroke</i></p> <ol style="list-style-type: none"> <li>(1) Valve overlap</li> <li>(2) Exhaust valve size and location</li> <li>(3) Combustion chamber shape</li> <li>(4) Compression ratio</li> <li>(5) Speed</li> </ol>	<p>4. <i>Oxidation in exhaust system</i></p> <p>(a) <i>Exhaust gas temperature</i></p> <ol style="list-style-type: none"> <li>(1) Speed</li> <li>(2) Spark timing‡</li> <li>(3) Mixture composition†</li> <li>(4) Compression ratio</li> <li>(5) Secondary air flow</li> <li>(6) Heat losses in cylinder and exhaust</li> </ol> <p>(b) <i>Oxygen concentration</i></p> <ol style="list-style-type: none"> <li>(1) Equivalence ratio</li> <li>(2) Secondary air flow and addition point</li> </ol> <p>(c) <i>Residence time</i></p> <ol style="list-style-type: none"> <li>(1) Speed</li> <li>(2) Load</li> <li>(3) Volume of critical exhaust system component</li> </ol> <p>(d) <i>Exhaust reactor§</i></p> <ol style="list-style-type: none"> <li>(1) Oxidation catalyst</li> <li>(2) Three-way catalyst</li> <li>(3) Thermal reactor</li> </ol>

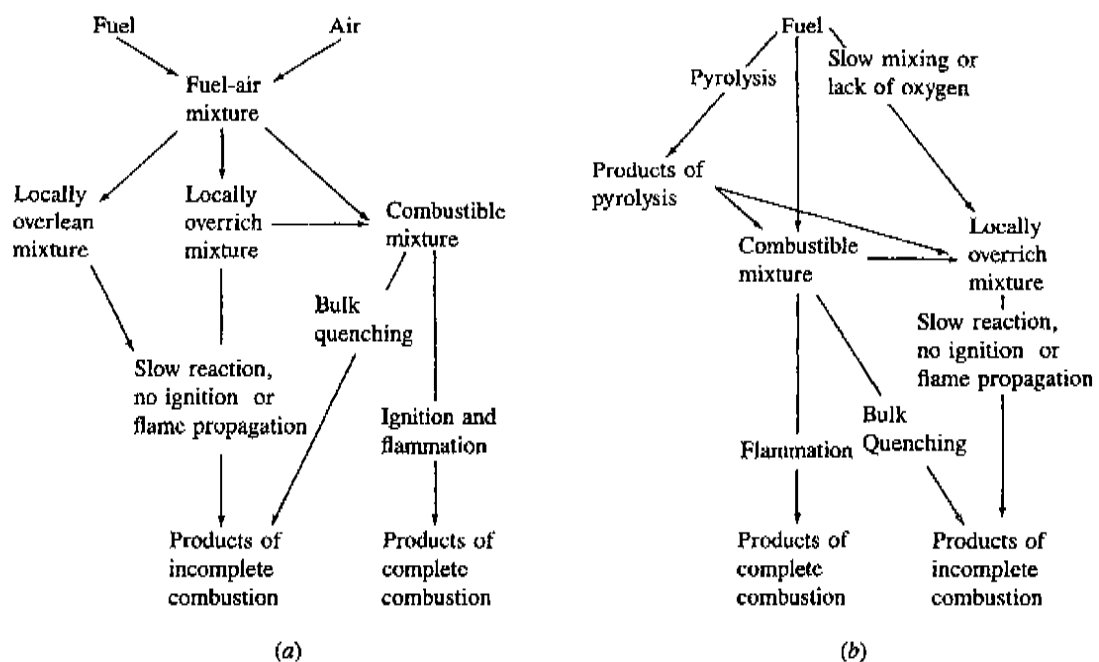
† Fuel/air equivalence ratio and burned gas fraction (residual plus recycled exhaust gas).

‡ Relative to MBT timing.

§ Of at least as great an importance as engine details if present in total emission control system. See Sec. 11.6.

### 11.4.4 Hydrocarbon Emission Mechanisms in Diesel Engines

**BACKGROUND.** Diesel fuel contains hydrocarbon compounds with higher boiling points, and hence higher molecular weights, than gasoline. Also, substantial pyrolysis of fuel compounds occurs within the fuel sprays during the diesel combustion process. Thus, the composition of the unburned and partially oxidized hydrocarbons in the diesel exhaust is much more complex than in the spark-ignition engine and extends over a larger molecular size range. Gaseous hydrocarbon emissions from diesels are measured using a hot particulate filter (at 190°C) and a heated flame ionization detector. Thus the HC constituents vary from methane to the heaviest hydrocarbons which remain in the vapor phase in the heated sampling line (which is also maintained at about 190°C). Any hydrocarbons heavier than this are therefore condensed and, with the solid-phase soot, are filtered from the exhaust gas stream upstream of the detector. The particulate emission measurement procedure measures a portion of total engine hydrocarbon emissions also. Particulates are collected by filtering from a diluted exhaust gas stream at a temperature of 52°C or less. Those hydrocarbons that condense at or below this temperature are absorbed onto the soot. They are the extractable fraction of the particulate: i.e., that fraction which can be removed by a powerful solvent, typically between about 15 and 45 percent of the total particulate mass. This section discusses gaseous hydrocarbon emissions; particulate emissions—soot and extractable material—are discussed in Sec. 11.5.



**FIGURE 11-33**

Schematic representation of diesel hydrocarbon formation mechanisms: (a) for fuel injected during delay period; (b) for fuel injected while combustion is occurring.<sup>23</sup>

The complex heterogeneous nature of diesel combustion, where fuel evaporation, fuel-air and burned-unburned gas mixing, and combustion can occur simultaneously, has been discussed extensively in Chap. 10. As a result of this complexity, there are many processes that could contribute to diesel engine hydrocarbon emissions. In Chap. 10 the diesel's compression-ignition combustion process was divided into four stages: (1) the ignition delay which is the time between the start of injection and ignition; (2) the premixed or rapid combustion phase, during which the fuel that has mixed to within combustible limits during the delay period burns; (3) the mixing controlled combustion phase, during which the rate of burning depends on the rate of fuel-air mixing to within the combustible limits; (4) the late combustion phase where heat release continues at a low rate governed by the mixing of residual combustibles with excess oxygen and the kinetics of the oxidation process. There are two primary paths by which fuel can escape this normal combustion process unburned: the fuel-air mixture can become too lean to autoignite or to support a propagating flame at the conditions prevailing inside the combustion chamber, or, during the primary combustion process, the fuel-air mixture may be too rich to ignite or support a flame. This fuel can then be consumed only by slower thermal oxidation reactions later in the expansion process after mixing with additional air. Thus, hydrocarbons remain unconsumed due to incomplete mixing or to quenching of the oxidation process.†

Figure 11-33 shows schematically how these processes can produce incomplete combustion products. Fuel injected during the ignition delay (Fig. 11-33a) will mix with air to produce a wide range of equivalence ratios. Some of this fuel will have mixed rapidly to equivalence ratios lower than the lean limit of combustion (locally overlean mixture), some will be within the combustible range, and some will have mixed more slowly and be too rich to burn (locally overrich mixture). The overlean mixture will not autoignite or support a propagating flame at conditions prevailing inside the combustion chamber (though some of this mixture may burn later if it mixes with high-temperature burned products early in the expansion stroke). In the "premixed" combustible mixture, ignition occurs where the local conditions are most favorable for autoignition. Unless quenched by thermal boundary layers or rapid mixing with air, subsequent autoignition or flame fronts propagating from the ignition sites consume the combustible mixture. Complete combustion of overrich mixture depends on further mixing with air or lean already-burned gases within the time available before rapid expansion and cooling occurs. Of all these possible mechanisms, the overlean mixture path is believed to be the most important.<sup>23</sup>

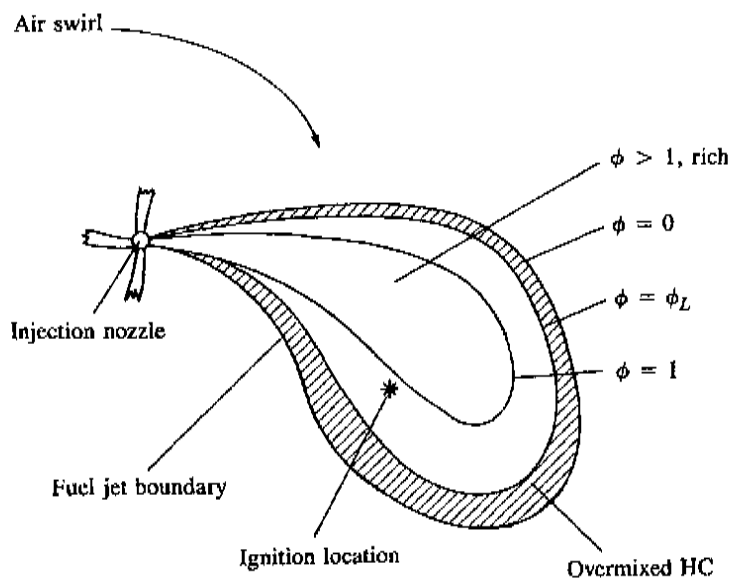
For the fuel injected after the ignition delay period is over (Fig. 11-33b), rapid oxidation of fuel or the products of fuel pyrolysis, as these mix with air,

† Note that under normal engine operating conditions, the combustion inefficiency is less than 2 percent; see Sec. 4.9.4 and Fig. 3-9.

results in complete combustion. Slow mixing of fuel and pyrolysis products with air, resulting in overrich mixture or quenching of the combustion reactions, can result in incomplete combustion products, pyrolysis products, and unburned fuel being present in the exhaust.<sup>23</sup>

Hydrocarbon emission levels from diesels vary widely with operating conditions, and different HC formation mechanisms are likely to be most important at different operating modes. Engine idling and light-load operation produce significantly higher hydrocarbon emissions than full-load operation. However, when the engine is overfueled, HC emissions increase very substantially. As will be explained more fully below, overmixing (overleaning) is an important source of HC, especially under light-load operation. Undermixing, resulting in overrich mixture during the combustion period, is the mechanism by which some of the fuel remaining in the injector nozzle sac volume escapes combustion, and is also the cause of very high HC emissions during overfueling. Wall temperatures affect HC emissions, suggesting that wall quenching is important, and under especially adverse conditions very high cyclic variability in the combustion process can cause an increase in HC due to partial burning and misfiring cycles.

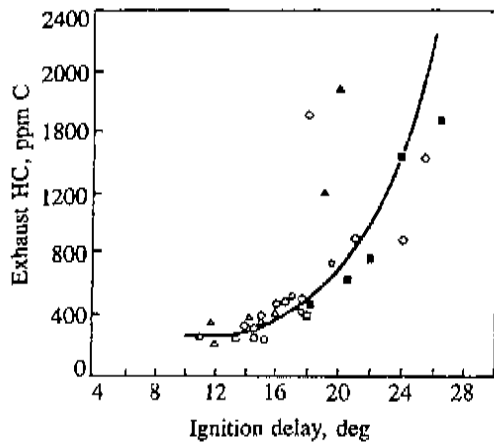
**OVERLEANING.** As soon as fuel injection into the cylinder commences, a distribution in the fuel/air equivalence ratio across the fuel sprays develops. The amount of fuel that is mixed leaner than the lean combustion limit ( $\phi_L \sim 0.3$ ) increases rapidly with time.<sup>23</sup> Figure 11-34 illustrates this equivalence ratio distribution in the fuel spray at the time of ignition. In a swirling flow, ignition occurs in the slightly lean-of-stoichiometric region downstream of the spray core



**FIGURE 11-34**

Schematic of diesel engine fuel spray showing equivalence ratio ( $\phi$ ) contours at time of ignition.  $\phi_L$  = equivalence ratio at lean combustion limit ( $\approx 0.3$ ). Shaded region contains fuel mixed leaner than  $\phi_L$ .<sup>67</sup>





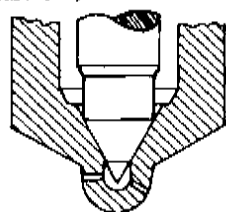
**FIGURE 11-35**  
Correlation of exhaust HC concentration with duration of ignition delay for DI diesel engine. Various fuels, engine loads, injection timings, boost pressures, at 2800 rev/min.<sup>67</sup>

where the fuel which has spent most time within the combustible limits is located. However, the fuel close to the spray boundary has already mixed beyond the lean limit of combustion and will not autoignite or sustain a fast reaction front. This mixture can only oxidize by relatively slow thermal-oxidation reactions which will be incomplete. Within this region, unburned fuel, fuel decomposition products, and partial oxidation products (aldehydes and other oxygenates) will exist; some of these will escape the cylinder without being burned. The magnitude of the unburned HC from these overlean regions will depend on the amount of fuel injected during the ignition delay, the mixing rate with air during this period, and the extent to which prevailing cylinder conditions are conducive to autoignition. A correlation of unburned HC emissions with the length of the ignition delay would be expected. The data in Fig. 11-35 from a direct-injection naturally aspirated engine show that a good correlation between these variables exists. As the delay period increases beyond its minimum value (due to changes in engine operating conditions), HC emissions increase at an increasing rate.<sup>67</sup> Thus, overleaning of fuel injected during the ignition delay period is a significant source of hydrocarbon emissions, especially under conditions where the ignition delay is long.

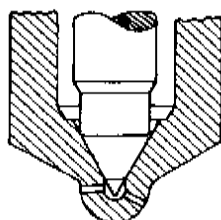
**UNDERMIXING.** Two sources of fuel which enter the cylinder during combustion and which result in HC emissions due to slow or under mixing with air have been identified. One is fuel that leaves the injector nozzle at low velocity, often late in the combustion process. The most important source here is the nozzle sac volume, though secondary injections can increase HC emissions if the problem is severe. The second source is the excess fuel that enters the cylinder under overfueling conditions.

At the end of the fuel-injection process, the injector sac volume (the small volume left in the tip of the injector after the needle seats) is left filled with fuel. As the combustion and expansion processes proceed, this fuel is heated and vaporizes, and enters the cylinder at low velocity through the nozzle holes. This fuel vapor (and perhaps large drops of fuel also) will mix relatively slowly with air

Standard sac, volume =  $1.35 \text{ mm}^3$



Reduced sac, volume =  $0.6 \text{ mm}^3$



Valve covers orifice

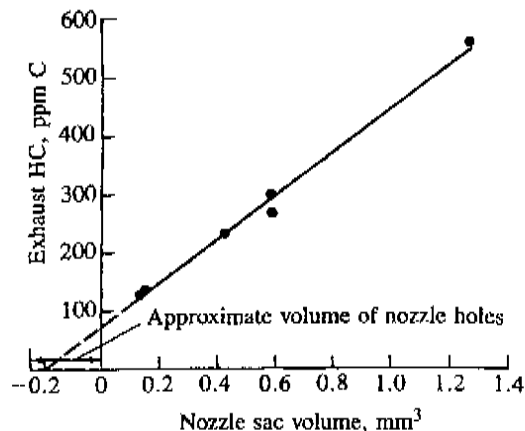
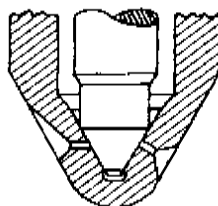
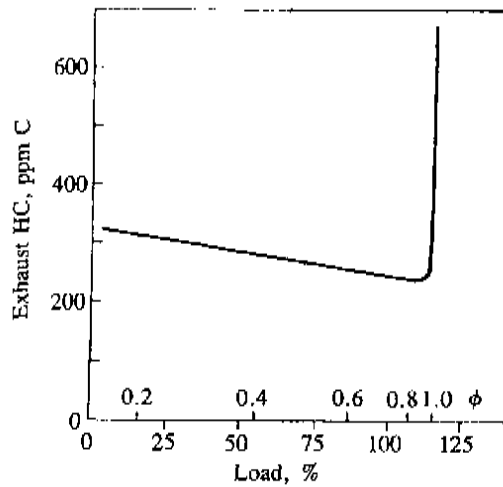


FIGURE 11-36

Effect of nozzle sac volume on exhaust HC concentration, DI diesel engine, at minimum ignition delay.  $V_d = 1 \text{ dm}^3/\text{cylinder}$ , 1700–2800 rev/min.<sup>67</sup>

and may escape the primary combustion process. Figure 11-36 shows HC emissions at the minimum ignition delay for a direct-injection diesel engine as a function of sac volume, along with drawings of some of the injector nozzles used. The correlation between HC emissions (under conditions when the overleaning mechanism is least significant) and sac volume is striking. The extrapolation to zero HC emissions suggests that the fuel in the nozzle holes also contributes. Not all the fuel in the sac volume is exhausted as unburned hydrocarbons. For example, in Fig. 11-36 a volume of  $1 \text{ mm}^3$  gives 350 ppm  $C_1$  while  $1 \text{ mm}^3$  of fuel would give 1660 ppm  $C_1$ . The sac volume may not be fully filled with fuel. Also, the higher-boiling-point fractions of the fuel may remain in the nozzle. Significant oxidation may also occur. In indirect-injection engines, similar trends have been observed, but the HC emission levels at short ignition delay conditions are substantially lower. The sac volume in current production nozzles helps to equalize the fuel pressures immediately upstream of the nozzle orifices. A small sac volume makes this equalization less complete and exhaust smoke deteriorates. The contribution of sac and hole volumes to exhaust HC can be reduced to below  $0.75 \text{ g/kW} \cdot \text{h}$  for a  $1 \text{ dm}^3$  per cylinder displacement DI engine.<sup>67</sup>

In DI engines, exhaust smoke limits the full-load equivalence ratio to about 0.7. Under transient conditions as the engine goes through an acceleration process, overfueling can occur. Even though the overall equivalence ratio may remain lean, locally overrich conditions may exist through the expansion stroke and into the exhaust process. Figure 11-37 shows the effect of increasing the amount of fuel injected at constant speed, with the injection timing adjusted to keep the ignition delay at its minimum value (when HC emissions from overleaning are lowest). HC emissions are unaffected by an increasing equivalence ratio until a critical value of about 0.9 is reached when levels increase dramatically. A



**FIGURE 11-37**  
Effect of overfueling on exhaust HC concentration. DI diesel engine, speed = 1700 rev/min, injection timing at full-load 15° BTC.<sup>67</sup>

similar trend exists for IDI engines.<sup>67</sup> This mechanism is not significant under normal operating conditions, but can contribute HC emissions under acceleration conditions if overfueling occurs. However, it produces less HC than does overleaning at light load and idle.<sup>23</sup>

**QUENCHING AND MISFIRE.** Hydrocarbon emissions have been shown to be sensitive to oil and coolant temperature: when these temperatures were increased from 40 to 90°C in a DI diesel, HC emissions decreased by 30 percent. Since ignition delay was maintained constant, overmixing phenomena should remain approximately constant. Thus, wall quenching of the flame may also be a significant source of HC, depending on the degree of spray impingement on the combustion chamber walls.

While cycle-by-cycle variation in the combustion process in diesel engines is generally much less than in spark-ignition engines, it can become significant under adverse conditions such as low compression temperatures and pressures and retarded injection timings. Substantial variations, cycle-by-cycle, in HC emissions are thought to result. In the limit, if misfire (no combustion) occurs in a fraction of the operating cycles, then engine HC emissions rise as the percentage of misfires increases. However, complete misfires in a well-designed and adequately controlled engine are unlikely to occur over the normal operating range.<sup>23</sup>

**SUMMARY.** There are two major causes of HC emissions in diesel engines under normal operating conditions: (1) fuel mixed to leaner than the lean combustion limit during the delay period; (2) undermixing of fuel which leaves the fuel injector nozzle at low velocity, late in the combustion process. At light load and idle, overmixing is especially important, particularly in engines of relatively small cylinder size at high speed. In IDI engines, the contribution from fuel in the nozzle sac volume is less important than with DI engines. However, other sources of low velocity and late fuel injection such as secondary injection can be significant.

## 11.5 PARTICULATE EMISSIONS

### 11.5.1 Spark-Ignition Engine Particulates

There are three classes of spark-ignition engine particulate emissions: lead, organic particulates (including soot), and sulfates.

Significant sulfate emissions can occur with oxidation-catalyst equipped engines. Unleaded gasoline contains 150 to 600 ppm by weight sulfur, which is oxidized within the engine cylinder to sulfur dioxide,  $\text{SO}_2$ . This  $\text{SO}_2$  can be oxidized by the exhaust catalyst to  $\text{SO}_3$  which combines with water at ambient temperatures to form a sulfuric acid aerosol. Levels of sulfate emissions depend on the fuel sulfur content, the operating conditions of the engine, and the details of the catalyst system used. Typical average automobile sulfate emission rates are 20 mg/km or less.<sup>68</sup>

For automobile engines operated with regular and premium leaded gasolines (which contain about 0.15 g Pb/liter or  $\text{dm}^3$ ) the particulate emission rates are typically 100 to 150 mg/km. This particulate is dominated by lead compounds: 25 to 60 percent of the emitted mass is lead.<sup>69</sup> The particulate emission rates are considerably higher when the engine is cold, following start-up. The exhaust temperature has a significant effect on emission levels. The particle size distribution with leaded fuel is about 80 percent by mass below 2  $\mu\text{m}$  diameter and about 40 percent below 0.2  $\mu\text{m}$  diameter. Most of these particles are presumed to form and grow in the exhaust system due to vapor phase condensation enhanced by coagulation. Some of the particles are emitted directly, without settling. Some of the particles either form or are deposited on the walls where agglomeration may occur. Many of these are removed when the exhaust flow rate is suddenly increased, and these particles together with rust and scale account for the increase in mass and size of particles emitted during acceleration. Only a fraction (between 10 and 50 percent) of the lead consumed in the fuel is exhausted, the remainder being deposited within the engine and exhaust system.

Use of unleaded gasoline reduces particulate emissions to about 20 mg/km in automobiles without catalysts. This particulate is primarily soluble (condensed) organic material. Soot emissions (black smoke) can result from combustion of overly rich mixtures. In properly adjusted spark-ignition engines, soot in the exhaust is not a significant problem.

### 11.5.2 Characteristics of Diesel Particulates

**MEASUREMENT TECHNIQUES.** Diesel particulates consist principally of combustion generated carbonaceous material (soot) on which some organic compounds have become absorbed. Most particulate material results from incomplete combustion of fuel hydrocarbons; some is contributed by the lubricating oil. The emission rates are typically 0.2 to 0.6 g/km for light-duty diesels in an automobile. In larger direct-injection engines, particulate emission rates are 0.5 to 1.5 g/brake kW · h. The composition of the particulate material depends on the conditions in the engine exhaust and particulate collection system. At tem-

temperatures above 500°C, the individual particles are principally clusters of many small spheres or spherules of carbon (with a small amount of hydrogen) with individual spherule diameters of about 15 to 30 nm. As temperatures decrease below 500°C, the particles become coated with adsorbed and condensed high molecular weight organic compounds which include: unburned hydrocarbons, oxygenated hydrocarbons (ketones, esters, ethers, organic acids), and polynuclear aromatic hydrocarbons. The condensed material also includes inorganic species such as sulfur dioxide, nitrogen dioxide, and sulfuric acid (sulfates).

The objective of most particulate measurement techniques is to determine the amount of particulate being emitted to the atmosphere. Techniques for particulate measurement and characterization range from simple smoke meter opacity readings to analyses using dilution tunnels. Most techniques require lengthy sample-collection periods because the emission rate of individual species is usually low. The physical conditions under which particulate measurements are made are critical because the emitted species are unstable and may be altered through loss to surfaces, change in size distribution (through collisions), and chemical interactions among other species in the exhaust at any time during the measurement process (including sampling, storage, or examination). The most basic information is normally obtained on a mass basis: for example, grams per kilometer for a vehicle, grams per kilowatt-hour for an engine, grams per kilogram of fuel or milligrams per cubic meter of exhaust (at standard conditions). Smoke meters measure the relative quantity of light that passes through the exhaust or the relative reflectance of particulate collected on filter paper. They do not measure mass directly. They are used to determine visible smoke emissions and provide an approximate indication of mass emission levels. Visible smoke from heavy-duty diesels at high load is regulated. In the standard mass emission measurement procedure, dilution tunnels are used to simulate the physical and chemical processes the particulate emissions undergo in the atmosphere. In the dilution tunnel, the raw exhaust gases are diluted with ambient air to a temperature of 52°C or less, and a sample stream from the diluted exhaust is filtered to remove the particulate material.

**PARTICULATE COMPOSITION AND STRUCTURE.** The structure of diesel particulate material is apparent from the photomicrographs shown in Fig. 11-38 of particulates collected from the exhaust of an IDI diesel engine. The samples are seen to consist of collections of primary particles (spherules) agglomerated into aggregates (hereafter called particles). Individual particles range in appearance from clusters of spherules to chains of spherules. Clusters may contain as many as 4000 spherules. Occasional liquid hydrocarbon and sulfate droplets have been identified. The spherules are combustion generated soot particles which vary in diameter between 10 and 80 nm, although most are in the 15 to 30 nm range. Figure 11-39 shows a typical distribution of spherule size (solid line) determined by sizing and counting images in the photomicrographs. The number-mean diameter ( $= \sum N_i d_i / N$ ) is 28 nm. The volume contribution of these

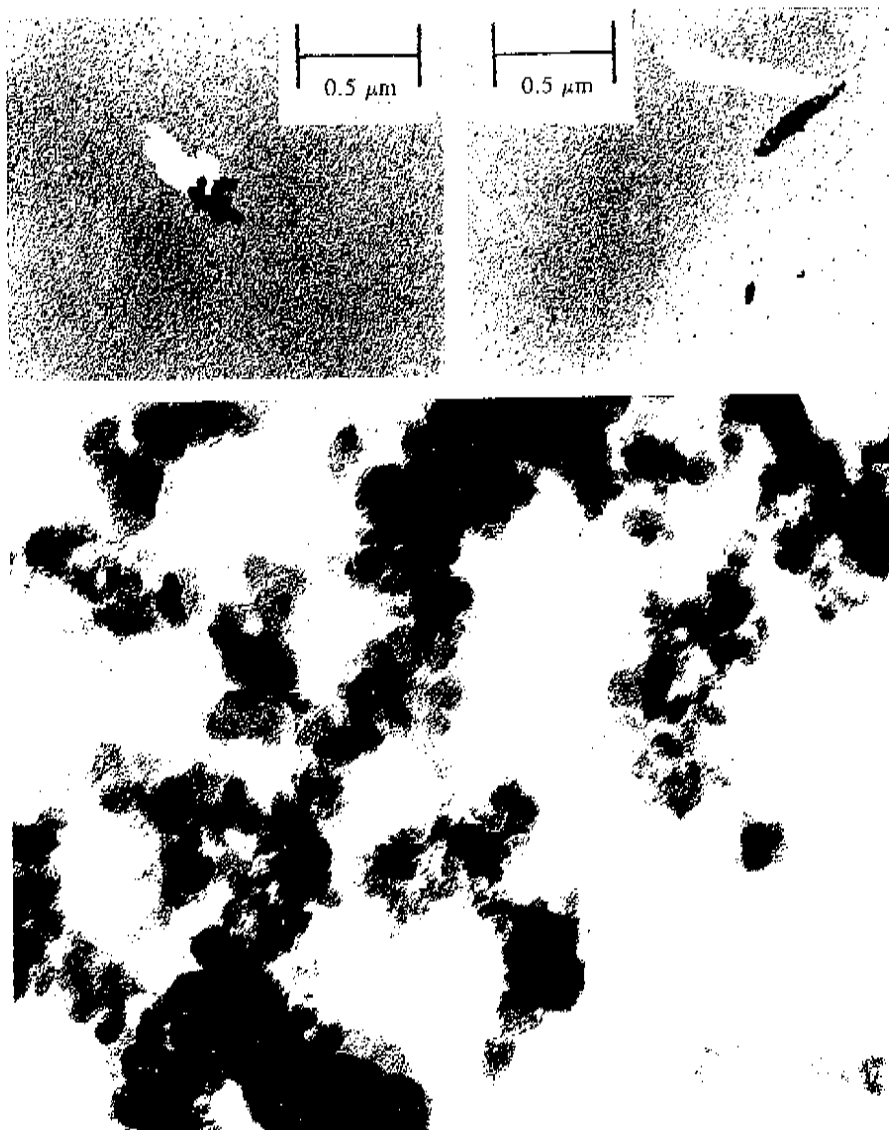


FIGURE 11-38 Photomicrographs of diesel particulates: cluster (upper left), chain (upper right), and collection from filter (bottom).<sup>70</sup>

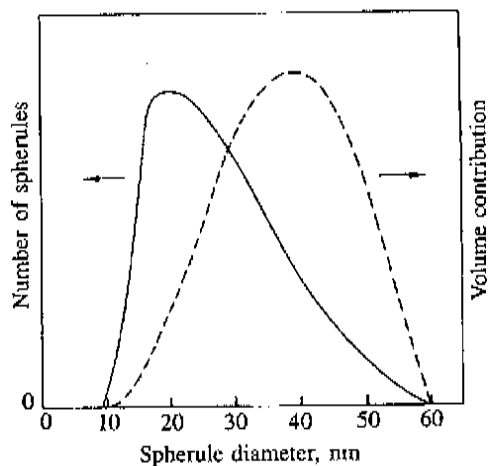


FIGURE 11-39 Typical distributions of spherule diameter and volume.<sup>70</sup>

TABLE 11.8  
Chemical composition of particular matter<sup>70</sup>

	Idle	48 km/h
Extractable		
composition	$C_{23}H_{29}O_{4.7}N_{0.21}$	$C_{24}H_{30}O_{2.6}N_{0.18}$
H/C	1.26	1.63
Dry soot		
composition	$CH_{0.27}O_{0.22}N_{0.01}$	$CH_{0.21}O_{0.15}N_{0.01}$
H/C	0.27	0.21

spherules is shown as the dashed curve in Fig. 11-39. The volume-mean diameter,  $(\sum N_i d_i^3 / N)^{1/3}$ , is 31 nm.

Determination of the *particle* size distribution with a similar technique involves assigning a single dimension to a complex and irregular aggregate, and introduces uncertainties arising from only having two-dimensional images of particles available. Other approaches based on inertial impactors and electrical aerosol analysers have been used. Some of the data suggest that the particle size distribution is bimodal. The smaller-size range is thought to be liquid hydrocarbon drops and/or individual spherules characterized by number-mean diameters of 10 to 20 nm; the larger-size range is thought to be the particles of agglomerated spherules characterized by number-mean diameters of 100 to 150 nm. However, other particulate samples have not shown a bimodal distribution: volume-mean diameters ranged from 50 to 220 nm with no notable trend with either speed or load.<sup>70</sup>

The exhaust particulate is usually partitioned with an extraction solvent into a soluble fraction and a dry-soot fraction. Two commonly used solvents are dichloromethane and a benzene-ethanol mixture. Typically 15 to 30 mass percent is extractable, though the range of observations is much larger (~10 to 90 percent). Thermogravimetric analysis (weighing the sample as it is heated) produces comparable results. Typical average chemical compositions of the two particulate fractions are given in Table 11.8. Dry soot has a much lower H/C ratio than the extractable material. Although most of the particulate emissions are formed through incomplete combustion of fuel hydrocarbons, engine oil may also contribute significantly. The number-average molecular weight of the extractable material shown in Table 11.8 ranged from about 360 to 400 for a variety of engine conditions. This fell between the average molecular weight of the fuel (199) and that of the lubricating oil (443 when fresh and 489 when aged).<sup>70</sup> Radioactive tracer studies in a light-duty IDI diesel have shown that the oil was the origin of between 2 to 25 percent by mass of the total particulate and 16 to 80 percent of the extractable organic portion, the greatest percentages being measured at the highest engine speed studied (3000 rev/min). All of the oil contribution appeared in the extractable material. The contributions from the different individual compounds in the fuel have also been studied. All the compounds tested—paraffins,

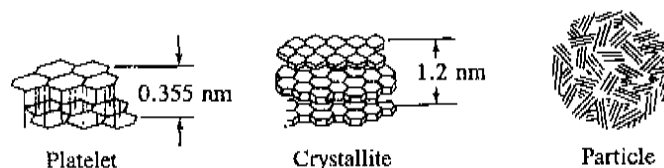


**FIGURE 11-40**  
Lattice-imaging micrograph of a diesel particulate.<sup>72</sup>

olefins, and aromatics—contributed to the particulate emissions; as a group, aromatics were the greatest contributors. Eighty percent of the carbon-14 used to tag individual fuel compounds was found in the *insoluble* fraction and 20 percent in the *soluble* particulate fraction.<sup>71</sup>

In addition to the elements listed in Table 11.8, trace amounts of sulfur, zinc, phosphorus, calcium, iron, silicon, and chromium have been found in particulates. Sulfur and traces of calcium, iron, silicon, and chromium are found in diesel fuel; zinc, phosphorus, and calcium compounds are frequently used in lubricating oil additives.<sup>70</sup>

A lattice image of a diesel particle is shown in Fig. 11-40; it suggests a concentric lamellate structure arranged around the center of each spherule. This arrangement of concentric lamellas is similar to the structure of carbon black. This is not surprising; the environment in which diesel soot is produced is similar to that in which oil furnace blacks are made. The carbon atoms are bonded together in hexagonal face-centered arrays in planes, commonly referred to as platelets. As illustrated in Fig. 11-41, the mean layer spacing is 0.355 nm (only slightly larger than graphite). Platelets are arranged in layers to form crystallites. Typically, there are 2 to 5 platelets per crystallite, and on the order of  $10^3$  crys-



**FIGURE 11-41**  
Substructure of carbon particle.<sup>73</sup>



tallites per spherule. The crystallites are arranged with their planes more or less parallel to the particle surface. This structure of unordered layers is called turbo-static. The spherules, 10 to 50 nm in diameter, are fused together to form particles as shown in Fig. 11-40. A single spherule contains  $10^5$  to  $10^6$  carbon atoms.<sup>70, 73</sup>

A surface area of about  $200 \text{ m}^2/\text{g}$  has been measured for diesel soot. A smooth-surfaced 30-nm diameter sphere with a density of  $2 \text{ g/cm}^3$  would have a surface/mass ratio of  $100 \text{ m}^2/\text{g}$ , so the measured value is about twice the superficial area. Approximating a particle of agglomerated spherules by a single sphere of 200 nm diameter gives a surface/mass ratio of  $15 \text{ m}^2/\text{g}$ .<sup>70</sup> These data and estimates of superficial area per unit mass indicate that diesel soot has low porosity.

**SOLUBLE FRACTION COMPONENTS.** The extractable organic fraction of diesel particulate emissions includes compounds that may cause health and environmental hazards. Thus chemical and biological characterization of the soluble organic fraction are important. Both soxhlet and sonification methods are used to extract the organic fraction from particulate samples. Because the particulates are mixtures of polar and nonpolar components, full extraction requires different solvents; any one solvent is a compromise. Methylene chloride is the most commonly used extractant, however. Since a complex mixture of organic compounds is associated with diesel particulates, a preliminary fractionation scheme is used to group similar types of compounds before final separation and identification. The scheme most frequently used results in seven fractions generally labeled as: basics, acidics, paraffins, aromatics, transitionals, oxygenates, and ether insolubles. Table 11.9 indicates the types of components in each fraction and the approximate proportions. The biological activity of the soluble organic fraction and its subfractions is most commonly assessed with the Ames *Salmonella*/microsomal test. With this test, a quantitative dose-response curve showing the mutagenicity of a sample compound is obtained. The Ames test uses a mutant strain of *Salmonella typhimurium* that is incapable of producing histidine. Mutagenicity is defined as the ability of a tested compound to revert—back-mutate—this bacterium to its wild state, where it regains its ability to produce histidine.<sup>35</sup>

### 11.5.3 Particulate Distribution within the Cylinder

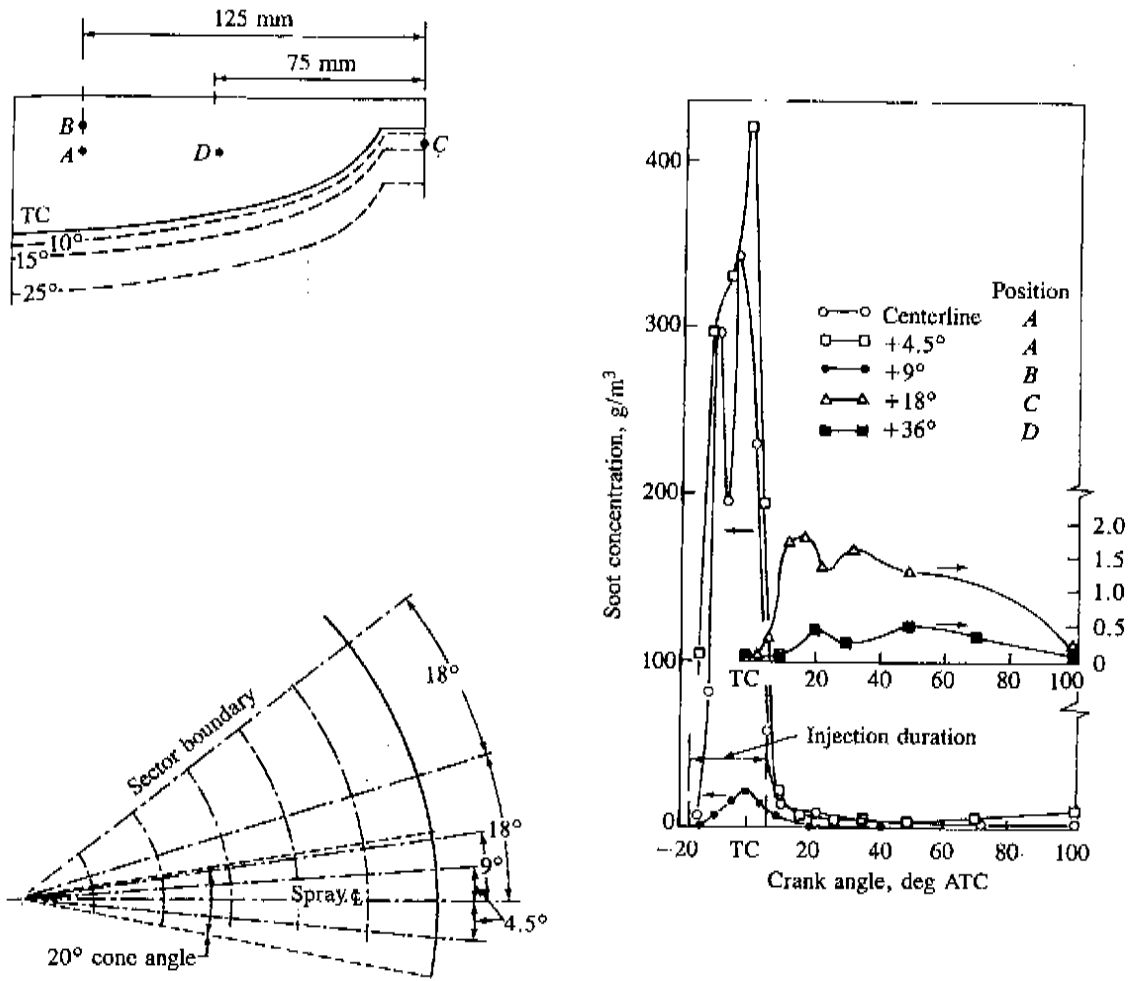
Measurements have been made of the particulate distribution within the combustion chamber of operating diesel engines. The results provide valuable information on the particulate formation and oxidation processes and how these relate to the fuel distribution and heat-release development within the combustion chamber. Techniques used to obtain particulate concentration data include: use of rapid-acting poppet or needle valves which draw a small gas sample from the cylinder at a specific location and time for analysis (e.g., Refs. 21

TABLE 11-9  
 Components of the soluble organic fraction<sup>35</sup>

Fraction	Components of fraction	Percent of total
Acidic	Aromatic or aliphatic Acidic functional groups Phenolic and carboxylic acids	3-15
Basic	Aromatic or aliphatic Basic functional groups Amines	<1-2
Paraffin	Aliphatics, normal and branched Numerous isomers From unburned fuel and/or lubricant	34-65
Aromatic	From unburned fuel, partial combustion, and recombination of combustion products; from lubricants Single ring compounds Polynuclear aromatics	3-14
Oxygenated	Polar functional groups but not acidic or basic Aldehydes, ketones, or alcohols Aromatic phenols and quinones	7-15
Transitional	Aliphatic and aromatic Carbonyl functional groups Ketones, aldehydes, esters, ethers	1-6
Insoluble	Aliphatic and aromatic Hydroxyl and carbonyl groups High molecular weight organic species Inorganic compounds Glass fibers from filters	6-25

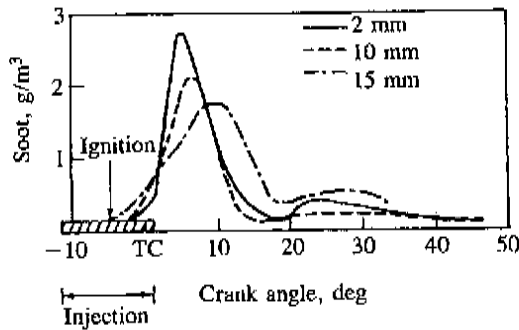
and 74), optical absorption techniques (e.g., Refs. 75 and 76), and cylinder dumping where the cylinder contents are rapidly emptied into an evacuated tank at a preset time in the cycle (e.g., Ref. 77). Both DI and IDI engines have been studied. Of course, concentration data taken at specific locations in the cylinder during the engine cycle are not necessarily representative of the cylinder contents in general; nor do they represent the time history of a given mass of gas. The fuel distribution, mixing, and heat-release patterns in the cylinder are highly nonuniform during the soot-formation process, and the details of gas motion in the vicinity of the sampling location as the piston changes position are usually unknown.

In direct-injection diesel engines, the highest particulate concentrations are found in the core region of each fuel spray where local average equivalence ratios are very rich (see Secs. 10.5.6 and 10.7.2). Soot concentrations rise rapidly soon after combustion starts. Figure 11-42 shows a set of sample-valve soot-concentration data from a large (30.5-cm bore, 38.1-cm stroke), quiescent, direct-



**FIGURE 11-42** Particulate concentrations, in  $\text{g}/\text{m}^3$  at standard temperature and pressure, in various regions of the fuel spray as a function of crank angle in quiescent DI diesel engine, measured with rapid sampling valve. Different sample valve locations in combustion chamber and spray indicated on left. Cylinder bore = 30.5 cm, stroke = 38.1 cm,  $r_c = 12.9$ , engine speed = 500 rev/min, bmp = 827 kPa.<sup>74</sup>

injection diesel engine which illustrates these points.<sup>74</sup> The particulate concentrations on the fuel spray axis close to the injector orifice are remarkably high ( $\sim 200$  to  $400 \text{ g}/\text{m}^3$  at standard temperature and pressure). This corresponds to a large fraction of the fuel carbon in the extremely rich fuel vapor core being sampled as particulate (as soot and condensed HC species). Such high particulate fractions of the local fuel carbon ( $\sim 50$  percent) have also been found in the very fuel rich cores of high-pressure liquid-fueled turbulent diffusion flames. Pyrolysis of the fuel is therefore an important source of soot. These very high local soot concentrations decrease rapidly once fuel injection ceases and the rich core mixes to leaner equivalence ratios. Soot concentrations in the spray close to the piston bowl outer radius and at the cylinder wall rise later, are an order of magnitude less, and decay more slowly. Away from the fuel spray core, soot concentrations



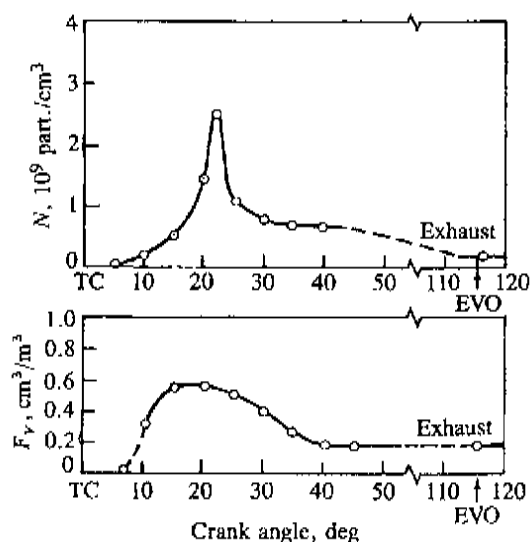
**FIGURE 11-43**

Particulate concentrations at various distances from wall of prechamber in swirl-chamber IDI diesel engine, measured with rapid sampling valve. Engine speed = 1000 rev/min, injection at 12° BTC, ignition at 5° BTC.<sup>21</sup>

decrease rapidly with increasing distance from the centerline. A useful comparison with these soot concentrations is the fuel concentration in a *stoichiometric* mixture, about 75 g fuel/m<sup>3</sup>. Approximate estimates of the mean soot concentration inside the cylinder through the combustion process suggests that almost all (over 90 percent) of the soot formed is oxidized prior to exhaust. Similar results have been obtained in a small direct-injection engine with swirl.<sup>78, 79</sup> Peak soot concentrations in the outer regions of the fuel spray were comparable (~10 g/m<sup>3</sup>). Measurements were not made in the spray core near the injector orifice; however, based on the equivalence ratio results in Fig. 10-46, soot concentrations would be expected to be lower due to the more rapid mixing with air that occurs with swirl.

Similar data are available from sampling in the prechamber of an IDI swirl chamber engine.<sup>21</sup> Figure 11-43 shows soot concentrations 2, 10, and 15 mm from the wall of the prechamber. Equivalence ratio distributions from this study have already been shown in Fig. 11-17. Concentrations peak 5 to 10° ATC at levels ~2 g/m<sup>3</sup>; these are substantially lower than DI engine peak soot concentrations (presumably due to the more rapid mixing of fuel and air in the IDI engine). Concentrations in the prechamber at these locations then decrease substantially.

A better indication of average concentrations within the cylinder is given by total cylinder sampling experiments. Measurements of the total number of soot particles and soot volume fraction through the combustion process have been made in an IDI passenger car diesel. The contents of the engine cylinder, at a preselected point in the cycle, were rapidly expelled through a blowdown port, diluted, and collected in a sample bag. Figure 11-44 shows one set of results. Particles first appear shortly after the start of combustion (4 to 5° ATC). The number density rises to a maximum at 20° ATC and then falls rapidly as a result of particle coagulation and, possibly, oxidation. The exhaust particulate number density is less than one-tenth of the peak value. The volume fraction soot data (soot mass concentration is proportional to volume fraction) show a much flatter maximum earlier in the combustion process and a decrease (due to oxidation) from 20 to 40° ATC to about one-third of the peak value. Oxidation apparently ceases at about 40° ATC at these conditions.



**FIGURE 11-44** Cylinder-average particle-number density  $N$  and particle-volume fraction  $F_v$ , as a function of crank angle in IDI diesel engine determined from cylinder-dumping experiments. 1000 rev/min,  $\phi = 0.32$ , injection starts at  $3.5^\circ$  BTC. Gas volumes at standard temperature and pressure.<sup>77</sup>

### 11.5.4 Soot Formation Fundamentals

The soot particles, whose characteristics have been described in the above two sections, form primarily from the carbon in the diesel fuel. Thus, the formation process starts with a fuel molecule containing 12 to 22 carbon atoms and an H/C ratio of about 2, and ends up with particles typically a few hundred nanometers in diameter, composed of spherules 20 to 30 nm in diameter each containing some  $10^5$  carbon atoms and having an H/C ratio of about 0.1. Most of the information available on the fundamentals of soot formation in combustion comes from studies in simple premixed and diffusion flames, stirred reactors, shock tubes, and constant-volume combustion bombs. A recent review<sup>80</sup> summarizes the extensive literature available from such studies. Also, the production of carbon black requires a high yield of soot from pyrolysis of a hydrocarbon feedstock, and the literature from that field has much to contribute (see Ref. 81). However, the characteristics of diesel combustion which make it unsuitable for more fundamental studies—the high gas temperatures and pressures, complex fuel composition, dominance of turbulent mixing, the unsteady nature of the process, and the three-dimensional geometry—also make it difficult to interpret fundamental ideas regarding soot formation in the diesel context. There is much about the soot formation process in diesel engines, therefore, that is poorly and incompletely understood.

Soot formation takes place in the diesel combustion environment at temperatures between about 1000 and 2800 K, at pressures of 50 to 100 atm, and with sufficient air *overall* to burn fully all the fuel. The time available for the formation of solid soot particles from a fraction of the fuel is in the order of milliseconds. The resulting aerosol—dispersed solid-phase particles in a gas—can be characterized by the total amount of condensed phase (often expressed as the soot volume fraction,  $F_v$ , the volume of soot/total volume), the number of soot particles per unit volume ( $N$ ), and the size of the particles (e.g., average diameter  $d$ ).  $F_v$ ,  $N$ , and  $d$  are mutually dependent [e.g., for spherical particles  $F_v =$

$(\pi/6)Nd^3]$ , and any two of these variables characterize the system. It is most convenient to consider  $N$  and  $F_V$  as the independent variables since they each relate to the "almost-separate" stages of soot particle generation (the source of  $N$ ) and soot particle growth (the source of  $F_V$ ).

These stages can be summarized as follows:<sup>80</sup>

1. Particle formation, where the first condensed phase material arises from the fuel molecules via their oxidation and/or pyrolysis products. These products typically include various unsaturated hydrocarbons, particularly acetylene and its higher analogues ( $C_{2n}H_2$ ), and polycyclic aromatic hydrocarbons (PAH). These two types of molecules are considered the most likely precursors of soot in flames. The condensation reactions of gas-phase species such as these lead to the appearance of the first recognizable soot particles (often called nuclei). These first particles are very small ( $d < 2$  nm) and the formation of large numbers of them involve negligible soot loading in the region of their formation.
2. Particle growth, which includes both surface growth, coagulation, and aggregation. Surface growth, by which the bulk of the solid-phase material is generated, involves the attachment of gas-phase species to the surface of particles and their incorporation into the particulate phase. Figure 11-45, where the log of the molecular weight of a species is plotted against its hydrogen mole fraction  $\tilde{x}_H$ , illustrates some important points about this process. Starting with a fuel molecule of  $\tilde{x}_H \approx 0.5$  it is apparent that neither purely polyacetylene chain

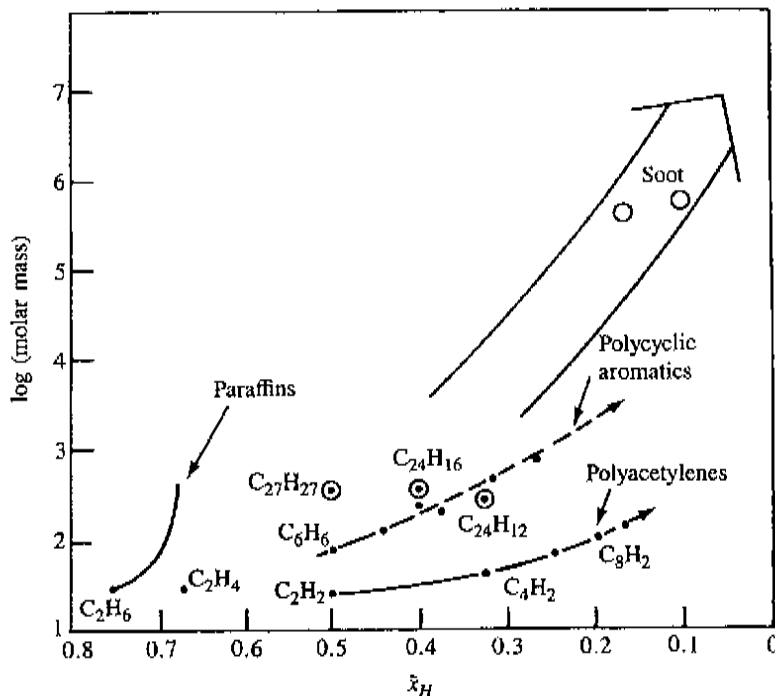


FIGURE 11-45

Paths to soot formation on plot of species molecular weight  $M$  versus hydrogen mole fraction  $\tilde{x}_H$ .<sup>80</sup>

growth nor purely PAH growth would lead to soot particles which have  $\bar{x}_H$  in the range 0.1 to 0.2. What is required is condensation of species with the right hydrogen content, or condensation of species with higher hydrogen content followed by dehydrogenation, or a combination of both these processes. Obviously some polyacetylenes and some PAH can satisfy these requirements, as can saturated platelets (e.g.,  $C_{27}H_{27}$ ; see Sec. 11.5.2). Surface growth reactions lead to an increase in the amount of soot ( $F_V$ ) but the number of particles ( $N$ ) remains unchanged. The opposite is true for growth by coagulation, where the particles collide and coalesce, which decreases  $N$  with  $F_V$  constant. Once surface growth stops, continued aggregation of particles into chains and clusters can occur.

These stages of particle generation and growth constitute the soot formation process. At each stage in the process oxidation can occur where soot or soot precursors are burned in the presence of oxidizing species to form gaseous products such as CO and  $CO_2$ . The eventual emission of soot from the engine will depend on the balance between these processes of formation and burnout. The emitted soot is then subject to a further mass addition process as the exhaust gases cool and are diluted with air. Adsorption into the soot particle surface and condensation to form new particles of hydrocarbon species in the exhaust gases occurs in the exhaust system and in the dilution tunnel which simulates what happens in the atmosphere. Figure 11-46 illustrates the relationship between these processes.<sup>70</sup> Although they are illustrated as discrete processes, there is some overlap, and they may occur concurrently in a given elemental mixture region within the diesel combustion chamber. Of course, due also to the non-homogeneous nature of the mixture and the duration of fuel injection and its overlap with combustion, at any given time different processes are in progress in different regions or packets of fluid. The fundamentals of each of these processes will now be reviewed.

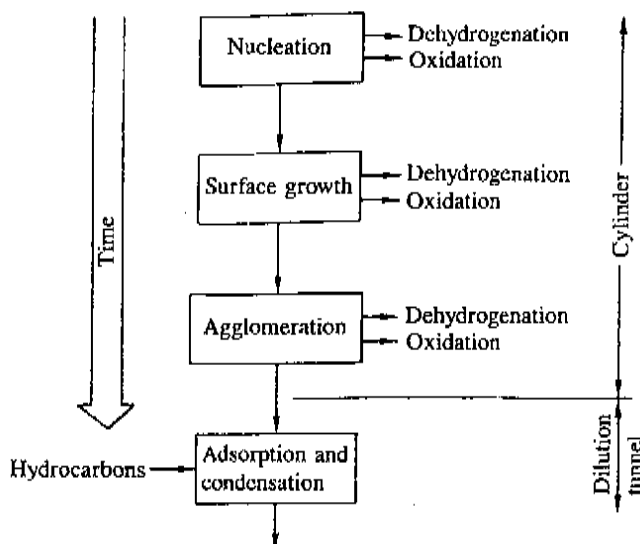
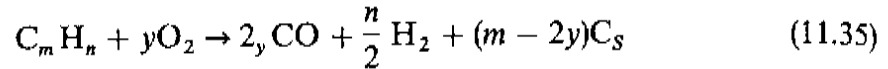


FIGURE 11-46 Processes leading to net production of diesel particulates.<sup>70</sup>

**SOOT PARTICLE FORMATION.** Empirically, it has been found useful to define the composition of the fuel-oxidizer mixture at the onset of soot formation in flames by the carbon/oxygen ratio. Equilibrium considerations indicate that soot formation should occur when, in



$m$  becomes larger than  $2y$ : i.e., the C/O ratio exceeds unity. The corresponding fuel/air equivalence ratio is given by

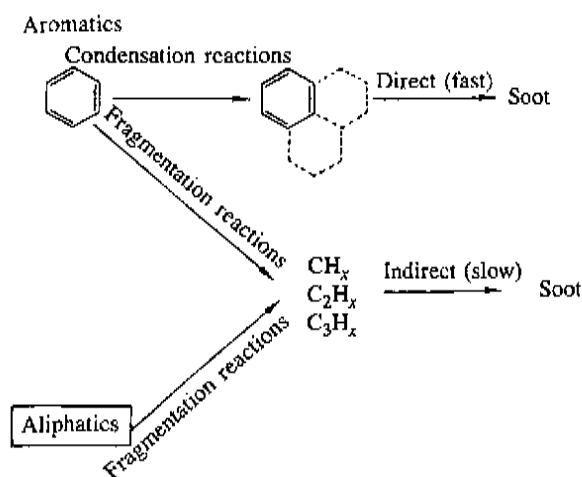
$$\phi = 2 \left( \frac{C}{O} \right) (1 + \delta) \quad (11.36)$$

where  $\delta = n/(4m)$ ;  $\phi$  is 3 for  $(C/O) = 1$ , with  $n/m = 2$ . The experimentally observed critical C/O ratios are less than unity, however, varying with fuel composition and details of the experimental setup from about 0.5 to 0.8. The critical C/O ratio for soot formation increases with increasing temperature but is only weakly dependent on pressure. Beyond the carbon formation limit, the yield of soot increases rapidly with increasing C/O ratio and is strongly enhanced by increasing pressure.<sup>80</sup>

It is obvious that soot formation is a nonequilibrium process. Yet despite decades of study, the precise details of the chemistry leading to the establishment of soot nuclei still elude investigators. Several different theories have been advanced to explain the pyrolysis process—the extensive decomposition and atomic rearrangement of the fuel molecules—that culminates in nucleation. Reviews of these theories can be found in Refs. 73, 80, and 81. Often-cited mechanisms are thermal cracking that results in fragmentation of fuel molecules into smaller ones, condensation reactions and polymerization that result in larger molecules, and dehydrogenation that lowers the H/C ratio of the hydrocarbons destined to become soot. Three different paths to the production of soot appear to exist, depending on the formation temperature. At the lowest temperatures ( $\lesssim 1700$  K) only aromatics or highly unsaturated aliphatic compounds of high molecular weight are very effective in forming solid carbon through pyrolysis. At intermediate temperatures typical of diffusion flames ( $\gtrsim 1800$  K), all normally used hydrocarbon fuels produce soot if burned at sufficiently rich stoichiometry, but appear to do so by following a different path. At very high temperatures, above the range of interest for diesel combustion, a third nucleation process seems likely that involves carbon vapor.<sup>70</sup>

A simple mechanistic model for nucleation in the low and intermediate temperature ranges which has considerable experimental support for its basic features has been advanced by Graham et al.<sup>82</sup> It is illustrated in Fig. 11-47. At low temperatures, an aromatic hydrocarbon can produce soot via a relatively fast direct route that involves condensation of the aromatic rings into a graphitelike structure. Above about 1800 K, however, a slower, less-direct route is favored that entails ring breakup into smaller hydrocarbon fragments. These fragments then polymerize to form larger unsaturated molecules that ultimately produce





**FIGURE 11-47**  
Mechanistic model for formation of soot from aromatic and aliphatic hydrocarbon compounds.<sup>70</sup>

soot nuclei. Aliphatic molecules can only follow this latter less-direct route. Experimental measurements in flames suggest that polyunsaturated hydrocarbon compounds are involved in nucleation, and acetylenes and polyacetylenes have been detected that decrease in concentration as the mass of carbon formed increases. Such observations fit the indirect path in Fig. 11-47. Results of studies of pyrolysis of benzene between 1300 and 1700 K support a physical condensation mechanism for the low-temperature path. This mechanism begins with the transformation of the initial hydrocarbon into macromolecules by a gas-phase reaction. The partial pressure of these macromolecules grows until supersaturation becomes sufficient to force their condensation into liquid microdroplets. These become nuclei, and subsequently formed gaseous macromolecules then contribute to nuclei growth.<sup>70</sup>

**SOOT PARTICLE GROWTH.** Nucleation produces a large number of very small particles with an insignificant soot loading. The bulk of the solid-phase material is generated by surface growth, which involves the gas-phase deposition of hydrocarbon intermediates on the surfaces of the spherules that develop from the nuclei. A qualitative description of the changes that occur as a function of time in a premixed flame during nucleation and surface growth is shown in Fig. 11-48. The soot fraction  $F_v$ , in units of soot volume per unit volume of gas, is related to the number density  $N$  and the volume-mean diameter of the soot particles by

$$F_v = \frac{\pi}{6} N d^3 \tag{11.37}$$

$d$  is the actual diameter of the spherules, or the diameter of a sphere of equivalent volume to an agglomerated particle. The rate of change of particle number density with time  $t$  can be written

$$\frac{dN}{dt} = \dot{N}_n - \dot{N}_a \tag{11.38}$$

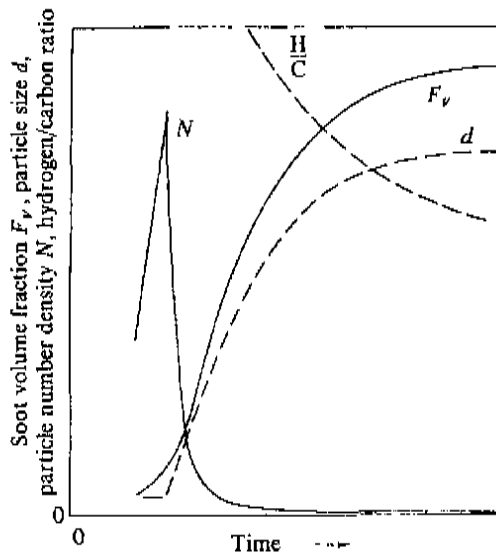


FIGURE 11-48

Variation in soot volume fraction  $F_v$ , particle number density  $N$ , particle size  $d$ , and soot hydrogen/carbon ratio with time in a flame.<sup>70</sup>

where  $\dot{N}_n$  is the rate at which fresh nuclei appear and  $\dot{N}_a$  is the rate of agglomeration of spherules or particles that collide and stick. At the peak of the  $N$  curve,  $\dot{N}_n = \dot{N}_a$ . To the left of the peak,  $\dot{N}_n > \dot{N}_a$ , the particle diameter remains essentially constant at the minimum detectable diameter and the (small) rise in soot volume is dominated by nucleation. To the right of the peak in the  $N$  curve,  $\dot{N}_a > \dot{N}_n$ . The number of agglomerating collisions is high because of the high number density; at the same time nucleation ends because there is enough dispersed surface area for gaseous deposition of hydrocarbon intermediates so the probability of generating new nuclei falls to zero. With nucleation halted slightly to the right of the  $N$  curve peak, all the subsequent increase in soot volume fraction (the majority) stems from surface growth. To the right of the  $N$  curve peak, the number density falls in the case illustrated by three orders of magnitude. This is the result of agglomeration, which is responsible for a portion of the increase in particle diameter. Agglomeration does not contribute to the rise in soot volume fraction,  $F_v$ . Surface growth that takes place on nuclei and on spherules is responsible for forming the concentric shells (somewhat distorted and warped) that constitute the outer portions of spherules and which are distinct from the less-organized spherule center (see Figs. 11-40 and 11-41). Surface growth on agglomerated particles may partly fill in the crevices at the junctures of adjoining spherules to provide the nodular structure evident in Fig. 11-40.<sup>70</sup>

Once particles have formed, interparticle collisions can lead to agglomeration, thereby decreasing the number of particles and increasing their size. Three types of agglomeration have been identified in soot formation. During the early stages of particle growth, collision of two spherical particles may result in their *coagulation* into a single spheroid. This is easy to visualize in hydrocarbon pyrolysis where the beginnings of a soot particle may have the viscosity of a tarry liquid.<sup>70</sup> Also, when the individual particles are small, rapid surface growth will quickly restore the original spherical shape.<sup>73</sup> This process occurs up to diameters of about 10 nm. On the other hand, if spherules have solidified before colli-

sion and surface growth rates have diminished, the resulting particles resemble a cluster in which the original spherules retain much of their individual identity. After surface growth essentially ceases, continued coalescence of the soot particles results in the formation of chainlike structures of discrete spherules. This suggests electrostatic forces are significant. Positive charge measured on these particle chains is claimed to be the cause of their chainlike structure.<sup>70, 73</sup> This latter coalescence once surface growth ceases is termed *aggregation*.

It has been shown experimentally that during coagulation the rate of decrease of particle number density was proportional to the product of a coagulation coefficient and the square of the number density:

$$-\frac{dN}{dt} = KN^2 \quad (11.39)$$

This is the Smoluchowski equation for coagulation of a liquid colloid. Based on brownian motion, this equation is applicable when the Knudsen number (ratio of mean free path to particle diameter) exceeds 10.  $K$  depends on such factors as particle size and shape, size distribution, and the temperature, pressure, and density of the gas. Equation (11.39) has been used to predict coagulation rates in low-pressure sooting flames.<sup>73, 80</sup> It has also been modified so that it applies where the particle size and mean free path are comparable by using a more complex expression for  $K$  (see Ref. 83). These studies show that under conditions approximating those in engine flames, the fraction of the initial number density  $N_0$  remaining at time  $t$  is given approximately by

$$\frac{N}{N_0} \approx (KN_0 t)^{-1} \quad (11.40)$$

Thus as  $t$  increases,  $N/N_0$  decreases rapidly. Although these coagulation calculations are simplistic (in that many of the assumptions made are not strictly valid since soot particles are not initially distributed homogeneously in the combustion space, they are not monodisperse, and surface growth and oxidation may be taking place during agglomeration), an overall conclusion is that the rate of coagulation of spherules and particles to larger particles is very sensitive to number density. Thus the number of particles decreases rapidly with advancing crank angle in the diesel engine during the early part of the expansion process (see Fig. 11-44) and agglomeration is essentially complete well before the exhaust valve opens.

Throughout the soot formation process in a flame, the H/C ratio of the hydrocarbons formed in the pyrolysis and nucleation process and of the soot particles continually decreases. The H/C ratio decreases from a value of about 2, typical of common fuels, to of order 1 in the youngest soot particles that can be sampled, and then to 0.2 to 0.3 once surface growth has ceased in the fully agglomerated soot.<sup>80</sup> The latter stages of this process are indicated in Fig. 11-48. The addition of mass to the soot particles occurs by reaction with gas-phase molecules. The reacting gas-phase hydrocarbons appear to be principally acetylenes, with larger polymers adding faster than the smaller. Small polyacetylenes

undergo further polymerization in the gas phase, presumably by the same mechanism leading to nucleation. As a result of preferential addition of the larger polymers, the H/C ratio of the particles decreases toward its steady-state value. Thus most of the polyacetylenes added must be of very high molecular weight or dehydrogenation must also take place.<sup>73, 80</sup>

### 11.5.5 Soot Oxidation

In the overall soot formation process, shown schematically in Fig. 11-46, oxidation of soot at the precursor, nuclei, and particle stages can occur. The engine cylinder soot-concentration data reviewed in Sec. 11.5.3 indicate that a large fraction of the soot formed is oxidized within the cylinder before the exhaust process commences. In the discussion of diesel combustion movies in Sec. 10.3.1, dark brown regions were observed in the color photographs (see color plate, Fig. 10-4); these were interpreted as soot particle clouds, and were seen to be surrounded by a diffusion flame which appeared white from the luminosity of the high-temperature soot particles consumed in this flame. As air mixed with this soot-rich region, the white flame eradicated the dark soot clouds as the particles were burned up.

In general, the rate of heterogeneous reactions such as the oxidation of soot depends on the diffusion of reactants to and products from the surface as well as the kinetics of the reaction. For particles less than about 1  $\mu\text{m}$  diameter, diffusional resistance is minimal. The soot oxidation process in the diesel cylinder is kinetically controlled, therefore, since particle sizes are smaller than this limit. There are many species in or near the flame that could oxidize soot: examples are  $\text{O}_2$ ,  $\text{O}$ ,  $\text{OH}$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ . Recent reviews of soot formation<sup>70, 73, 80</sup> have concluded that at high oxygen partial pressures, soot oxidation can be correlated with a semiempirical formula based on pyrographite oxidation studies. For fuel-rich and close-to-stoichiometric combustion products, however, oxidation by  $\text{OH}$  has been shown to be more important than  $\text{O}_2$  attack, at least at atmospheric pressure.

It is argued on the basis of structural similarities that the rates of oxidation of soot and of pyrographites should be the same. This is a significant simplification. It has proved difficult to follow the oxidation of soot aerosols in flames, and if care is taken to avoid diffusional resistance, studies of bulk samples of pyrographite can then be used as a basis for understanding soot oxidation. The semiempirical formula of Nagle and Strickland-Constable has been shown<sup>84</sup> to correlate pyrographite oxidation for oxygen partial pressures  $p_{\text{O}_2} < 1$  atm and temperatures between 1100 and 2500 K. This formula is based on the concept that there are two types of sites on the carbon surface available for  $\text{O}_2$  attack. For the more reactive type *A* sites, the oxidation rate is controlled by the fraction of sites not covered by surface oxides (and therefore is of mixed order, between 0 and 1 in  $p_{\text{O}_2}$ ). Type *B* sites are less reactive, and react at a rate which is first order in  $p_{\text{O}_2}$ . A thermal rearrangement of *A* sites into *B* sites is also allowed (with rate constant  $k_T$ ). A steady-state analysis of this mechanism gives a surface mass oxi-

**TABLE 11.10**  
**Rate constants for Nagle and Strickland-Constable soot oxidation mechanism<sup>84</sup>**

Rate constant	Units
$k_A = 20 \exp(-15,100/T)$	$\text{g/cm}^2 \cdot \text{s} \cdot \text{atm}$
$k_B = 4.46 \times 10^{-3} \exp(-7640/T)$	$\text{g/cm}^2 \cdot \text{s} \cdot \text{atm}$
$k_T = 1.51 \times 10^5 \exp(-48,800/T)$	$\text{g/cm}^2 \cdot \text{s}$
$k_Z = 21.3 \exp(2060/T)$	$\text{atm}^{-1}$

oxidation rate  $w$  ( $\text{g C/cm}^2 \cdot \text{s}$ ):

$$\frac{w}{12} = \left( \frac{k_A p_{\text{O}_2}}{1 + k_Z p_{\text{O}_2}} \right) x + k_B p_{\text{O}_2} (1 - x) \quad (11.41)$$

where  $x$  is the fraction of the surface occupied by type  $A$  sites and is given by

$$x = \left( 1 + \frac{k_T}{p_{\text{O}_2} k_B} \right)^{-1} \quad (11.42)$$

The empirical rate constants determined by Nagle and Strickland-Constable for this model are listed in Table 11.10. According to this mechanism, the reaction is first order at low oxygen partial pressures, but approaches zero order at higher pressures. At a given oxygen pressure, the rate initially increases exponentially with temperature (equivalent activation energy is  $k_A/k_Z$  or 34,100 cal/mol). Beyond a certain temperature the rate decreases as the thermal rearrangement favors formation of less reactive  $B$  sites. When, at sufficiently high temperature, the surface is completely covered with  $B$  sites, the rate is first order in oxygen partial pressure and increases again with temperature.<sup>80</sup>

Park and Appleton<sup>84</sup> have compared this formula with oxidation rate data obtained from pyrographite samples, carbon black particles, and with the available flame soot oxidation data. Figure 11-49 shows both the soot oxidation rate predicted by Eqs. (11.41) and (11.42) as a function of temperature and oxygen partial pressure, and the above-mentioned data. The formula correlates the data shown to within a factor of 2. Under diesel engine conditions, the  $\text{O}_2$  partial pressure can be high ( $\sim$ several atmospheres), as can the temperatures of close-to-stoichiometric mixtures ( $\lesssim 2800$  K).

Equations (11.41) and (11.42) have been used to estimate the amount of soot that can be oxidized in a typical IDI diesel engine. It was assumed that soot was present in stoichiometric combustion products at selected times in the cycle and that mixing with air leaned out the burned gas mixture at different rates until the overall fuel/air equivalence ratio was reached. The surface recession rate during this process was computed. Figure 11-50 shows sample results at an engine speed of 1600 rev/min and an overall cylinder equivalence ratio of 0.58. Fast, intermediate, and slow mixing occurred in 30, 70, and 140°, respectively. The surface recession rate rises to a maximum as  $p_{\text{O}_2}$  increases and then decreases as the

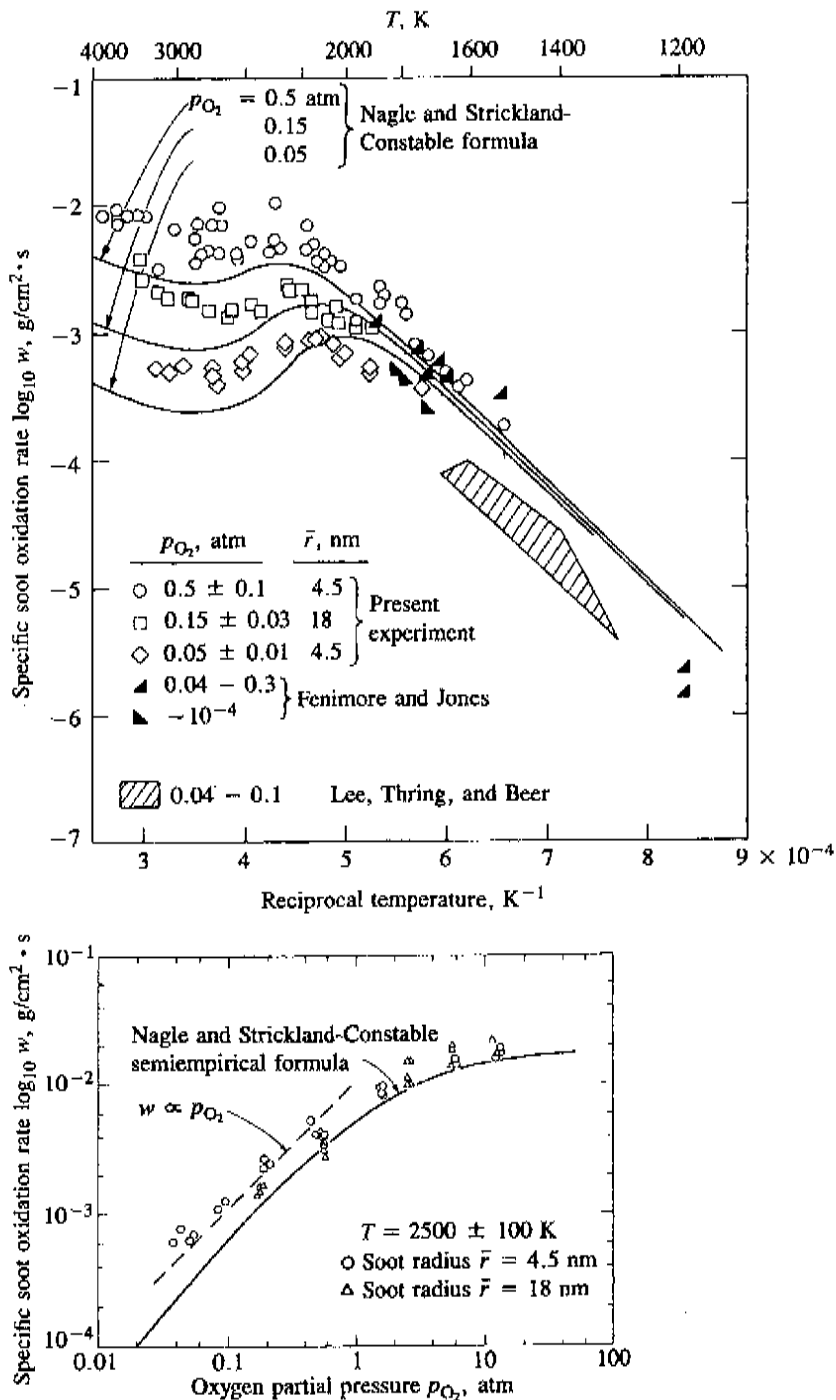
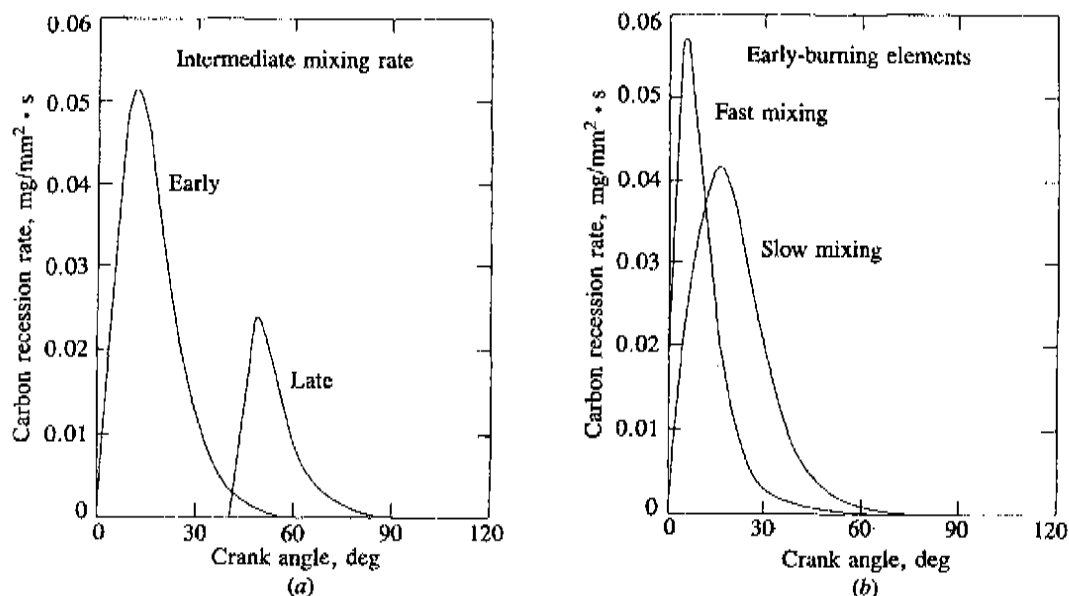


FIGURE 11-49

Specific soot oxidation rate measurements and predictions as a function of temperature and oxygen partial pressure.<sup>84</sup>

falling gas temperature more than offsets the increasing oxygen concentration. While the shape of the recession rate versus time curves depends on the mixing rate, the total amount of carbon burned (the area under each curve in Fig. 11-50b) is about the same ( $0.1 \mu\text{g}/\text{mm}^2$ ). However, the point in the cycle at which the soot-containing burned gas mixture passes through stoichiometric is much


**FIGURE 11-50**

Soot particle burnup rate in diesel combustion environment: (a) in early- and late-burned fuel-air elements with intermediate mixing rate; (b) for fast and slow mixing for early-burning elements.<sup>83</sup>

more important. For the late mixing element shown (mixing lean of stoichiometric at 40° ATC), the total carbon mass oxidized is only 40 percent of that for the early mixing calculation. This is due primarily to the decreasing gas temperatures as the expansion stroke proceeds, and not the longer time available for burnup.<sup>83</sup>

For a spherical particle, the mass burning rate  $w$  (g/cm<sup>2</sup> · s) can be converted to a surface recession rate using

$$\frac{dr}{dt} = \frac{-w}{\rho}$$

where  $\rho$  is the density ( $\approx 2$  g/cm<sup>3</sup>). The integrated values of  $w(t)$  when divided by  $\rho$  then give the maximum radius of a soot particle that can be burned up. Integrated values of 0.1  $\mu\text{g}/\text{mm}^2$  (estimated for TC start of burnup) correspond to a radius of about 50 nm or diameter of 100 nm. Individual spherule diameters are about 30 nm, so soot which mixes with air early in the expansion stroke is likely to be fully burned. Thus the soot present in the exhaust would be expected to come from regions which mix with air too late for the oxidation rate to be sufficient for particle burnup.

Agglomeration will have an indirect influence on the amount of soot oxidized through its effect on surface area. In the limiting case of a spherical cluster,  $n$  monodisperse spherules ( $10 \lesssim n \lesssim 100$ ) can be imagined as compacted into a single solid sphere of equal volume. Alternatively, the same  $n$  spherules can be imagined compacted into a cylinder of diameter equal to that of the original spherules. Since oxidative attack is essentially an exterior surface phenomenon, the surface/volume ratio is the appropriate measure of the effect of particle shape on soot mass burnup rate. It can be shown that the surface/volume ratios for the

single sphere, cylinder, and individual spherule are in the ratio  $n^{-1/3}$ ,  $\frac{2}{3}$ , and 1, respectively. Thus agglomeration will decrease the relative oxidation rate. In the limit spherical clusters are less desirable than a chain; the larger the cluster the bigger the relative reduction in surface area. However, the densely packed spherule limit does not appear to be approached in practice. A specific surface area, of about  $200 \text{ m}^2/\text{g}$  for diesel soot, has been measured.<sup>85</sup> A smooth-surfaced 30-nm diameter spherule with a  $2\text{-g}/\text{cm}^3$  density has a surface/mass ratio of  $100 \text{ m}^2/\text{g}$ ; the measured value is about twice this value, indicating low porosity and an agglomerate structure which is loosely rather than densely packed.<sup>83</sup>

Equation (11.41) shows a maximum recession rate in combustion products corresponding to a fuel/air equivalence ratio of about 0.9. Recent evidence shows that in an atmospheric pressure environment with rich and close-to-stoichiometric combustion products where  $\text{O}_2$  mole fractions are low, oxidation by OH radical attack is much more significant than oxidation by O or  $\text{O}_2$ . The OH radical may be important in oxidizing soot in the flame zone under close-to-stoichiometric conditions.

### 11.5.6 Adsorption and Condensation

The final process in the particulate formation sequence illustrated in Fig. 11-46 is adsorption and condensation of hydrocarbons. This occurs primarily after the cylinder gases have been exhausted from the engine, as these exhaust gases are diluted with air. In the standard particulate mass emission measurement process this occurs in a dilution tunnel which simulates approximately the actual atmospheric dilution process. A diluted exhaust gas sample is filtered to remove the particulate. After equilibrating the collection filter at controlled conditions to remove water vapor, the particulate mass is obtained by weighing. In the prescribed EPA procedure, the filter temperature must not exceed  $52^\circ\text{C}$ . For a given exhaust gas temperature, the filter (and sample) temperature depends on the dilution ratio, as shown in Fig. 11-51.

The effect of the dilution ratio (and the dependent sample temperature) on collected particulate mass is shown in Fig. 11-52 for a standard dilution tunnel,

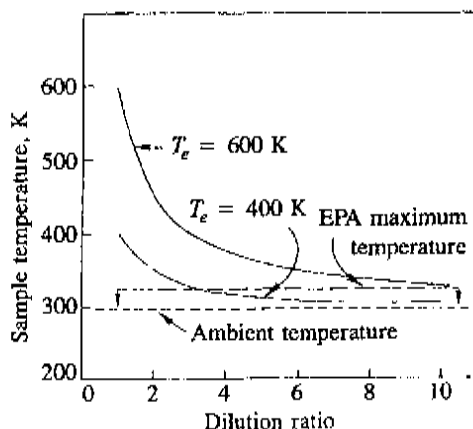
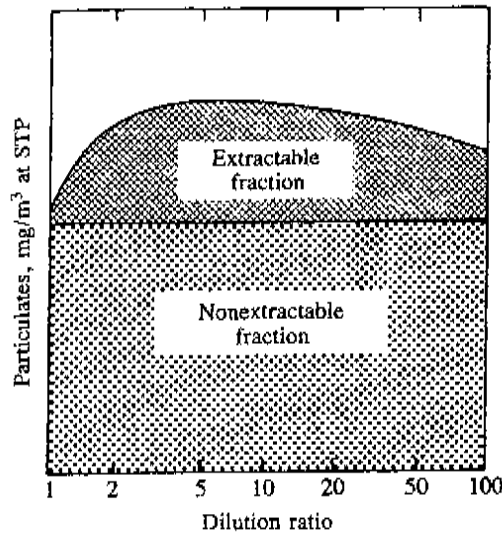


FIGURE 11-51

Effect of exhaust gas dilution ratio on the temperature of the collected particulate sample as a function of engine exhaust temperature  $T_e$ .<sup>70</sup>





**FIGURE 11-52**  
 Typical effect of dilution ratio on particulate mass emission and its partitioning between extractable and nonextractable fractions.<sup>70</sup>

where the total sample is partitioned into extractable and nonextractable fractions. The nonextractable fraction is the carbonaceous soot generated during combustion and is not affected by the dilution process. With no dilution (dilution ratio of unity) the difference between the total and nonextractable mass is small; the bulk of the extractable fraction is acquired after the exhaust gas is mixed with dilution air. Extensive studies of this dilution process have shown that both adsorption and condensation occur. Adsorption involves the adherence of molecules of unburned hydrocarbons to the surfaces of the soot particles by chemical or physical (van der Waals) forces. This depends on the fraction of the available particle surface area occupied by hydrocarbons and on the partial pressure of the gaseous hydrocarbons that drives the adsorption process. As the dilution ratio increases from unity, the effect of decreasing temperature on the number of active sites dominates and, as shown in Fig. 11-52, the extractable fraction increases. At high dilution ratios, the sample temperature becomes insensitive to the dilution ratio (see Fig. 11-51) but the decreasing hydrocarbon partial pressure causes the extractable mass to fall again. Condensation will occur whenever the vapor pressure of the gaseous hydrocarbon exceeds its saturated vapor pressure. Increasing dilution decreases hydrocarbon concentrations and hence vapor pressure. However, the associated reduction in temperature does reduce the saturation pressure. High exhaust concentrations of hydrocarbons are the conditions where condensation is likely to be most significant, and the hydrocarbons most likely to condense are those of low volatility. Sources of low-volatility hydrocarbons are the high-boiling-point end of the fuel, unburned hydrocarbons that have been pyrolyzed but not consumed in the combustion process, and the lubricating oil.<sup>70</sup>

Experiments with a passenger car IDI diesel, where the oil was tagged with a radioactive tracer, have shown that the oil can contribute from 2 to 25 percent of the total particulate mass, with the greatest contribution occurring at high speed. On average, over half of the extractable mass was traceable to the oil. All the material traceable to the oil was found in the extractable fraction, indicating that the oil did not participate in the combustion process. However, the oil is not

always a significant contributor; in another engine, fuel was the dominant source of extractable material.<sup>70, 71</sup>

## 11.6 EXHAUST GAS TREATMENT

### 11.6.1 Available Options

Our discussion so far has focused on *engine* emissions. Further reductions in emissions can be obtained by removing pollutants from the exhaust gases in the engine exhaust system. Devices developed to achieve this result include catalytic converters (oxidizing catalysts for HC and CO, reducing catalysts for NO<sub>x</sub>, and three-way catalysts for all three pollutants), thermal reactors (for HC and CO), and traps or filters for particulates.

The temperature of exhaust gas in a spark-ignition engine can vary from 300 to 400°C during idle to about 900°C at high-power operation. The most common range is 400 to 600°C. Spark-ignition engines usually operate at fuel/air equivalence ratios between about 0.9 and 1.2 (see Sec. 7.1). The exhaust gas may therefore contain modest amounts of oxygen (when lean) or more substantial amounts of CO (when rich). In contrast, diesel engines, where load is controlled by the amount of fuel injected, always operate lean. The exhaust gas therefore contains substantial oxygen and is at a lower temperature (200 to 500°C). Removal of gaseous pollutants from the exhaust gases after they leave the engine cylinder can be either thermal or catalytic. In order to oxidize the hydrocarbons in the gas phase without a catalyst, a residence time of order or greater than 50 ms and temperatures in excess of 600°C are required. To oxidize CO, temperatures in excess of 700°C are required. Temperatures high enough for some homogeneous thermal oxidation can be obtained by spark retard (with some loss in efficiency) and insulation of the exhaust ports and manifold. The residence time can be increased by increasing the exhaust manifold volume to form a *thermal reactor* (see Sec. 11.6.3). However, this approach has limited application.

Catalytic oxidation of CO and hydrocarbons in the exhaust can be achieved at temperatures as low as 250°C. Thus effective removal of these pollutants occurs over a much wider range of exhaust temperatures than can be achieved with thermal oxidation. The only satisfactory method known for the removal of NO from exhaust gas involves catalytic processes. Removal of NO by catalytic oxidation to NO<sub>2</sub> requires temperatures < 400°C (from equilibrium considerations) and subsequent removal of the NO<sub>2</sub> produced. Catalytic reaction of NO with added ammonia NH<sub>3</sub> is not practical because of the transient variations in NO produced in the engine. Reduction of NO by CO, hydrocarbons, or H<sub>2</sub> in the exhaust to produce N<sub>2</sub> is the preferred catalytic process. It is only feasible in spark-ignition engine exhausts. Use of catalysts in spark-ignition engines for CO, HC, and NO removal has become widespread. Catalysts are discussed in Sec. 11.6.2.

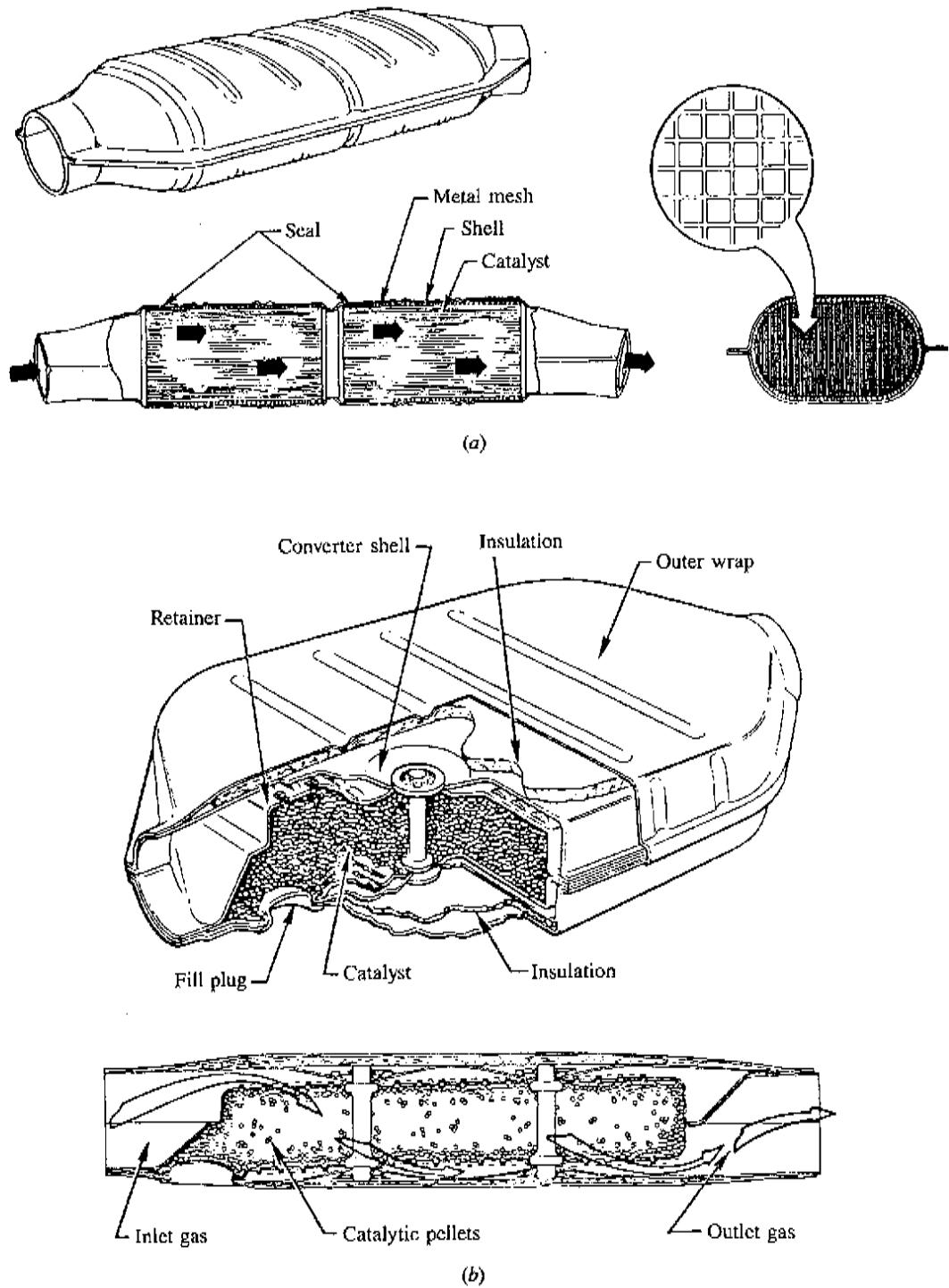
Particulates in the exhaust gas stream can be removed by a trap. Due to the small particle size involved, some type of filter is the most effective trapping

method. The accumulation of mass within the trap and the increase in exhaust manifold pressure during trap operation are major development problems. Diesel particulates, once trapped, can be burned up either by initiating oxidation within the trap with an external heat source or by using a trap which contains catalytically active material. The operation of particulate traps is reviewed briefly in Sec. 11.6.4.

### 11.6.2 Catalytic Converters

The catalytic converters used in spark-ignition engines consist of an active catalytic material in a specially designed metal casing which directs the exhaust gas flow through the catalyst bed. The active material employed for CO and HC oxidation or NO reduction (normally noble metals, though base metals oxides can be used) must be distributed over a large surface area so that the mass-transfer characteristics between the gas phase and the active catalyst surface are sufficient to allow close to 100 percent conversion with high catalytic activity. The two configurations commonly used are shown in Fig. 11-53. One system employs a ceramic honeycomb structure or monolith held in a metal can in the exhaust stream. The active (noble metal) catalyst material is impregnated into a highly porous alumina washcoat about 20  $\mu\text{m}$  thick that is applied to the passageway walls. The typical monolith has square-cross-section passageways with inside dimensions of  $\sim 1$  mm separated by thin (0.15 to 0.3 mm) porous walls. The number of passageways per square centimeter varies between about 30 and 60. The washcoat, 5 to 15 percent of the weight of the monolith, has a surface area of 100 to 200  $\text{m}^2/\text{g}$ . The other converter design uses a bed of spherical ceramic pellets to provide a large surface area in contact with the flow. With pellet catalysts, the noble metal catalyst is impregnated into the highly porous surface of the spherical alumina pellets (typically 3 mm diameter) to a depth of about 250  $\mu\text{m}$ . The pellet material is chosen to have good crush and abrasion resistance after exposure to temperatures of order 1000°C. The gas flow is directed down through the bed as shown to provide a large flow area and low pressure drop. The gas flow is turbulent which results in high mass-transfer rates; in the monolith catalyst passageways, it is laminar.

**OXIDATION CATALYSTS.** The function of an oxidation catalyst is to oxidize CO and hydrocarbons to  $\text{CO}_2$  and water in an exhaust gas stream which typically contains  $\sim 12$  percent  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , 100 to 2000 ppm NO,  $\sim 20$  ppm  $\text{SO}_2$ , 1 to 5 percent  $\text{O}_2$ , 0.2 to 5 percent CO, and 1000 to 6000 ppm  $\text{C}_1$  HC, often with small amounts of lead and phosphorus. About half the hydrocarbons emitted by the SI engine are unburned fuel compounds. The saturated hydrocarbons (which comprise some 20 to 30 percent) are the most difficult to oxidize. The ease of oxidation increases with increasing molecular weight. Sufficient oxygen must be present to oxidize the CO and HC. This may be supplied by the engine itself



**FIGURE 11-53** Catalytic converters for spark-ignition engine emission control: (a) monolith design; (b) pelletized design.<sup>62</sup>

running lean of stoichiometric or with a pump that introduces air into the exhaust ports just downstream of the valve. Venturi air addition into the exhaust port using the pressure pulsations generated by the exhaust process can also be used to add the required air.

Because of their high intrinsic activity, noble metals are most suitable as the catalytic material. They show higher specific activity for HC oxidation, are more thermally resistant to loss of low-temperature activity, and are much less deactivated by the sulfur in the fuel than base metal oxides. A mixture of platinum (Pt) and palladium (Pd) is most commonly used. For the oxidation of CO, olefins, and methane, the specific activity of Pd is higher than that of Pt. For the oxidation of aromatic compounds, Pt and Pd have similar activity. For oxidation of paraffin hydrocarbons (with molecular size greater than  $C_3$ ), Pt is more active than Pd. Pure noble metals sinter rapidly in the 500 to 900°C temperature range experienced by exhaust catalysts. Since catalytic behavior is manifested exclusively by surface atoms, the noble metals are dispersed as finely as possible on an inert support such as  $\gamma\text{-Al}_2\text{O}_3$  which prevents particle-to-particle metal contact and suppresses sintering. The particle size of the noble metal particles in a fresh catalyst is less than 50 nm. This can increase to  $\sim 100$  nm when the catalyst is exposed to the high temperatures of the exhaust in vehicle operation. Typical noble metal concentrations in a commercial honeycomb catalyst are between 1 and 2 g/dm<sup>3</sup> of honeycomb volume, with Pt/Pd = 2 on a weight basis. As a rough rule of thumb, the ceramic honeycomb volume required is about half the engine displaced volume. This gives a space velocity through the converter (volume flow rate of exhaust divided by converter volume) over the normal engine operating range of 5 to 30 per second.<sup>68</sup>

The *conversion efficiency* of a catalyst is the ratio of the rate of mass removal in the catalyst of the particular constituent of interest to the mass flow rate of that constituent into the catalyst: e.g., for HC,

$$\eta_{\text{cat}} = \frac{\dot{m}_{\text{HC, in}} - \dot{m}_{\text{HC, out}}}{\dot{m}_{\text{HC, in}}} = 1 - \frac{\dot{m}_{\text{HC, out}}}{\dot{m}_{\text{HC, in}}} \quad (11.43)$$

The variation of conversion efficiency of a typical oxidizing catalytic converter with temperature is shown in Fig. 11-54. At high enough temperatures, the steady-state conversion efficiencies of a new oxidation catalyst are typically 98 to 99 percent for CO and 95 percent or above for HC. However, the catalyst is ineffective until its temperature has risen above 250 to 300°C. The term *light-off temperature* is often used to describe the temperature at which the catalyst becomes more than 50 percent effective.

The above numbers apply to fresh noble metal oxidation catalysts; as catalysts spend time in service their effectiveness deteriorates. Catalysis involves the adsorption of the reactants onto surface sites of high activity, followed by chemical reaction, then desorption of the products. Catalyst degradation involves both the deactivation of these sites by catalyst poisons and a reduction in the effective area of these sites through sintering. Poisoning affects both the warm-up and

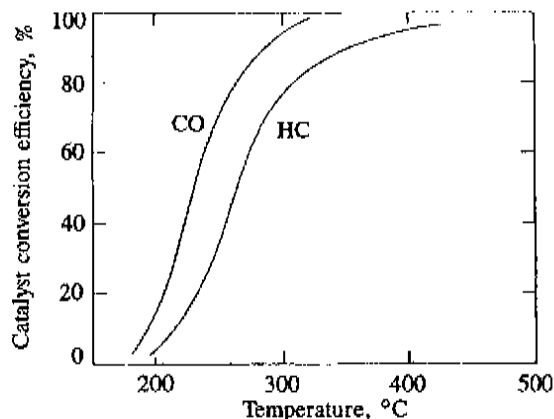


FIGURE 11-54

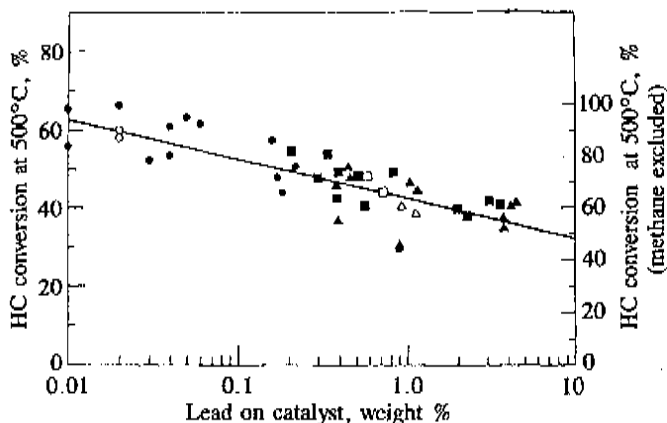
Conversion efficiency for CO and HC as a function of temperature for typical oxidizing catalytic converter.<sup>62</sup>

steady-state performance of the catalyst. When poisoning occurs, catalytic activity is impeded through prolonged contact with interfering elements that either physically block the active sites or interact chemically with the active material. The lead in fuel antiknock agents and the phosphorus in oil additives are the most important poisons. Though lead antiknock agents are not added to the gasoline used with catalyst-equipped vehicles, this "unleaded" fuel can be contaminated with small amounts ( $\sim 10 \text{ mg Pb/dm}^3$ ) from the fuel distribution system. Between 10 and 30 percent of the lead in the fuel ends up on the catalyst. Its effect on catalyst conversion efficiency depends on the amount of lead on the catalyst, as shown in Fig. 11-55. Lead depresses the catalytic oxidation of HC to a greater extent than oxidation of CO. The oxidation activity of saturated hydrocarbons is particularly depressed. The extent of the poisoning that results from traces of critical elements in the fuel and oil depends on which elements are present and the amounts absorbed, as well as the composition of the catalyst and its operating conditions (especially its temperature).<sup>68</sup> Sintering is promoted by exposure of the catalyst to high operating temperatures. It involves the migration and agglomeration of sites, thus decreasing their active surface area. Sintering slows warm-up but has minimal effect on the steady-state conversion efficiency.

The oxidation kinetics of CO over Pt and Pd noble metal catalysts can be described by

$$\frac{d[\text{CO}]}{dt} = \frac{K_1 p_{\text{CO}} p_{\text{O}_2}}{(1 + K_2 p_{\text{CO}} + K_3 p_{\text{HC}})^2 (1 + K_4 p_{\text{NO}}^n)} \quad (11.44)$$

where  $K_1$  to  $K_4$  and  $n$  are constants at any given temperature, and  $p_{\text{CO}}$ ,  $p_{\text{O}_2}$ ,  $p_{\text{HC}}$ , and  $p_{\text{NO}}$  are the partial pressures of carbon monoxide, oxygen, hydrocarbons, and nitric oxide, respectively. A similar relationship can be written for the olefinic and aromatic HC oxidation rate (these being the most reactive hydrocarbons). These relationships incorporate the fact that the rates of CO and HC oxidation are inhibited by high CO and reactive HC concentrations, and that NO concentrations in the range 0 to 1000 ppm strongly inhibit oxidation also. The oxidation rate of paraffin hydrocarbons varies with the first power of the HC partial pres-



**FIGURE 11-55**  
 HC conversion efficiency as a function of lead concentration on catalyst. Total HC conversion on left; non-methane HC conversion on right. 0.001–0.013 g Pb/dm<sup>3</sup> in fuel.<sup>68</sup>

sure, is inhibited by CO, olefins, and NO, and increases as the O<sub>2</sub> partial pressure is decreased to near-stoichiometric values.<sup>68</sup>

It will be apparent from the above that two extremely important considerations for successful use of catalysts for automotive applications are the test procedure that is used to measure emissions and the methods used to determine if the catalyst has the required durability. The U.S. Federal Test Procedure requires that the vehicle under test be at a temperature of 16 to 30°C for 12 hours prior to the test and that emissions are measured from the time the ignition key is turned on until the test has ended. In spark-ignition engines the mixture fed into the engine during start-up is enriched substantially (carburetors have a choke to accomplish this; additional fuel is injected with port or manifold fuel injection). The rationale is that if sufficient fuel is added to the inlet air, enough will evaporate to start the engine. However, until the rest of the fuel is consumed, the engine then runs rich and emits high concentrations of CO and HC. The catalyst is cold at this time, and until it warms up, these emissions will pass through without reaction. It is important that the catalyst be brought to its light-off temperature as quickly as possible (preferably in less than 60 s) and that mixture enrichment during start-up be held to a minimum. Thus catalysts should have low thermal inertia for rapid warm-up and low light-off temperatures for CO and HC, so they become effective quickly. The closer they are placed to the engine the faster they will reach light-off. However, they will then experience higher temperatures when fully warmed up and so be more susceptible to thermal degradation. While it is not too difficult to prepare catalysts that are highly effective when fresh, it is much more difficult to maintain effectiveness over extended mileage (50,000 miles) in which the catalyst is exposed to high temperatures and catalyst poisons. These can degrade both cold-start and warmed-up performance. Also, catalyst durability is affected by engine durability. Any engine malfunction that will expose the catalyst to excessive amounts of unburned fuel (such as ignition failure, misfire with too lean a mixture, or excessively rich operation) will severely overheat the catalyst.

Oxidation-catalyst-equipped vehicles may emit sulfuric acid aerosol. Unleaded gasoline contains 150 to 600 ppm by weight of S, which leaves the

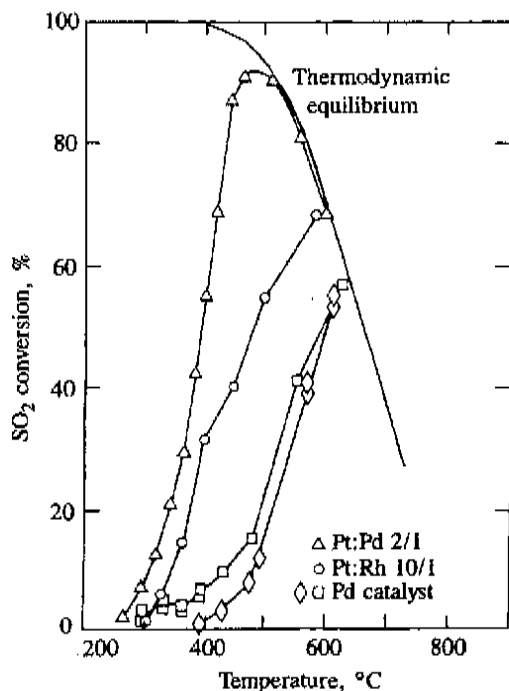


FIGURE 11-56

SO<sub>2</sub> conversion to SO<sub>3</sub> as a function of temperature with 5% O<sub>2</sub> concentration and no reducing gases present. Space velocity (volume flow per unit volume)  $\sim 10 \text{ s}^{-1}$ . Results for Pt-Pd, Pt-Rh, and Pd catalysts.<sup>68</sup>

combustion chamber as SO<sub>2</sub>. This SO<sub>2</sub> can be oxidized by the catalyst to SO<sub>3</sub> which combines with water at ambient conditions to form an H<sub>2</sub>SO<sub>4</sub> aerosol. The SO<sub>3</sub> can be chemisorbed on the alumina catalyst surface; when large pellet beds are used, considerable storage of SO<sub>3</sub> at temperatures  $< 500^\circ\text{C}$  can occur. At higher catalyst temperatures, this stored SO<sub>3</sub> is emitted as an SO<sub>3</sub>-SO<sub>2</sub> mixture. SO<sub>3</sub> production can be controlled by lowering or raising the catalyst temperature. Figure 11-56 shows that at low temperatures SO<sub>3</sub> production is kinetically limited; at high temperatures SO<sub>3</sub> production is thermodynamically limited. Palladium and rhodium produce less SO<sub>3</sub> than Pt and have comparable HC and CO catalytic activity. By decreasing oxygen concentrations leaving the catalyst to  $\sim 1$  percent, SO<sub>3</sub> production can be substantially reduced.<sup>68</sup>

**NO CATALYSIS.** NO is removed by reduction using the CO, hydrocarbons, and H<sub>2</sub> in the exhaust. The reactions are shown in Table 11.11. No catalyst is available for the decomposition of NO to O<sub>2</sub> and N<sub>2</sub> (thermodynamically favored at exhaust temperatures) which is sufficiently active for use in engine exhausts. NO reduction can be carried out under rich conditions where there is an excess of reducing species over oxidizing species. The catalyst used under these conditions is referred to as an *NO reduction catalyst*. Such a system requires a follow-up oxidation catalyst, together with addition of air from an air pump before the oxidation catalyst, to remove the remaining CO and hydrocarbons. Such a two-bed system can remove all three pollutants (NO, CO, and HC) from the exhaust. However, the rich operation necessary for NO reduction results in a fuel consumption penalty and constrains the performance of the NO catalyst since a fraction of the NO removed is converted to ammonia NH<sub>3</sub> rather than N<sub>2</sub>. NH<sub>3</sub>



**TABLE 11.11**  
**Possible NO reactions under**  
**reducing conditions<sup>68</sup>**

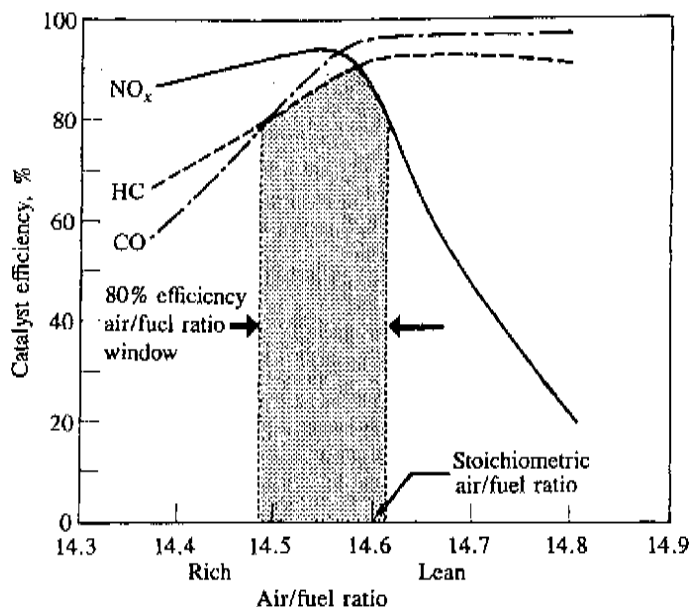
- 
1.  $\text{NO} + \text{CO} \rightarrow \frac{1}{2}\text{N}_2 + \text{CO}_2$
  2.  $2\text{NO} + 5\text{CO} + 3\text{H}_2\text{O} \rightarrow 2\text{NH}_3 + 5\text{CO}_2$
  3.  $2\text{NO} + \text{CO} \rightarrow \text{N}_2\text{O} + \text{CO}_2$
  4.  $\text{NO} + \text{H}_2 \rightarrow \frac{1}{2}\text{N}_2 + \text{H}_2\text{O}$
  5.  $2\text{NO} + 5\text{H}_2 \rightarrow 2\text{NH}_3 + 2\text{H}_2\text{O}$
  6.  $2\text{NO} + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$
- 

Reactions 3 and 6 occur at 200°C, which is below that usually found in auto exhausts.

formation under rich operation in the first bed must be small in this two-bed system because the second (oxidation) catalyst readily oxidizes  $\text{NH}_3$  back to NO. Reduction of NO by CO or  $\text{H}_2$  can be accomplished by base metal catalysts (e.g., CuO, NiO) in the temperature range 350 to 600°C. However, these catalyst materials are deactivated by sulfur and have shown limited thermal stability when used in vehicle exhausts. Alumina-supported noble metal catalysts reduce NO with CO- $\text{H}_2$  mixtures. Their NO-reduction activity is in the order  $\text{Ru} > \text{Rh} > \text{Pd} > \text{Pt}$ . Ruthenium (Ru) and rhodium (Rh) produce considerably less  $\text{NH}_3$  than Pd or Pt under slightly rich conditions. While these properties make ruthenium a desirable NO catalyst, it forms volatile oxides under oxidizing conditions which results in loss of ruthenium from the alumina support.<sup>68</sup>

**THREE-WAY CATALYSTS.** If an engine is operated at all times with an air/fuel ratio at or close to stoichiometric, then both NO reduction and CO and HC oxidation can be done in a single catalyst bed. The catalyst effectively brings the exhaust gas composition to a near-equilibrium state at these exhaust conditions; i.e., a composition of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{N}_2$ . Enough reducing gases will be present to reduce NO and enough  $\text{O}_2$  to oxidize the CO and hydrocarbons. Such a catalyst is called a *three-way catalyst* since it removes all three pollutants simultaneously. Figure 11-57 shows the conversion efficiency for NO, CO, and HC as a function of the air/fuel ratio. There is a narrow range of air/fuel ratios near stoichiometric in which high conversion efficiencies for all three pollutants are achieved. The width of this window is narrow, about 0.1 air/fuel ratios ( $7 \times 10^{-3}$  in equivalence ratio units) for catalyst with high mileage use, and depends on catalyst formulation and engine operating conditions.

This window is sufficiently narrow to be beyond the control capabilities of an ordinary carburetor, though it can sometimes be achieved with sophisticated carburetors and fuel-injection systems. Thus closed-loop control of equivalence ratio has been introduced. An oxygen sensor in the exhaust is used to indicate whether the engine is operating on the rich or lean side of stoichiometric, and provide a signal for adjusting the fuel system to achieve the desired air-fuel mixture (see Sec. 7.4). Holding the equivalence ratio precisely on the chosen near-

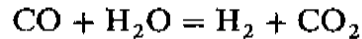


**FIGURE 11-57**  
Conversion efficiency for NO, CO, and HC for a three-way catalyst as a function of exhaust gas air/fuel ratio.<sup>68</sup>

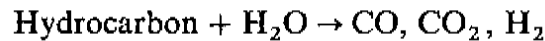
stoichiometric value is not a practical expectation of such a feedback system, and the equivalence ratio oscillates around the set point in an approximately periodic manner as the fuel flow is varied. Experimental data show that there is a considerable widening of the air/fuel ratio window where all three pollutants are effectively removed, with cyclic variation of the fuel flow. The maximum conversion in the middle of the window is reduced, however, from its value when there are no fluctuations. The effect of fluctuations depends on the frequency; frequencies of about 0.5 to 1 hertz are most effective and the usable window (at lower conversion efficiencies) can be broadened to about 1 air/fuel ratio. Some of the benefits of fluctuations in equivalence or air/fuel ratios are available even without any deliberate attempt to produce such variations with closed-loop feedback. Open-loop systems exhibit variations in the air/fuel ratio during normal vehicle operation.

Because of these cyclic variations in exhaust gas composition about a set point close to stoichiometric, it is desirable that the catalyst be able to reduce NO when a slight excess of oxygen is present (on the lean side) and remove CO and HC when there is a slight deficiency of oxygen (on the rich side). Rhodium is the principal ingredient used in commercial catalysts to remove NO. It is very active for NO reduction, is much less inhibited by CO and sulfur compounds, and produces less NH<sub>3</sub> than Pt. To remove NO under slightly lean-of-stoichiometric conditions, the catalyst must react the CO, H<sub>2</sub>, or HC with NO rather than with O<sub>2</sub>, as the exhaust gas passes through the catalyst bed. Rhodium shows some NO reduction activity slightly lean of stoichiometric. On the rich side, the three-way catalyst window is determined by hydrocarbon and CO removal. Platinum is most commonly used for HC and CO oxidation; it has good activity under stoichiometric and slightly lean conditions. When sufficient rhodium is present, the participation of Pt in NO removal is minimal. In the rich

regime, the three-way catalyst consumes all the oxygen that is present in the exhaust, and as a consequence removes an equivalent amount of CO, H<sub>2</sub>, and hydrocarbons; it is thought that the H<sub>2</sub> is removed first. In addition, the water-gas shift reaction



and the steam-reforming reaction

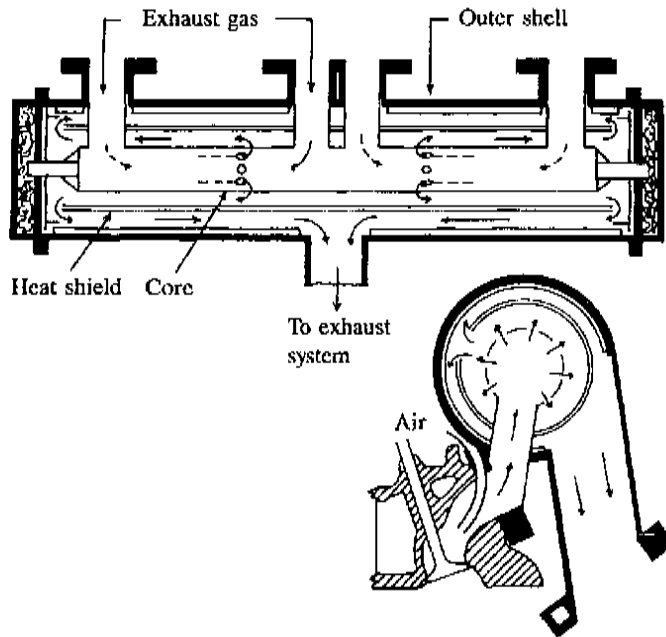


can consume CO and HC. The exhaust contains an H<sub>2</sub>/CO ratio of about  $\frac{1}{3}$  (see Sec. 4.9.1), where the equilibrium ratio at 500°C is about 4. Considerable CO removal can be expected if the water-gas shift equilibrium is approached. Platinum is active in promoting this equilibrium. For large molecular weight paraffin hydrocarbons, and for olefins and aromatic hydrocarbons, the equilibrium for the steam-reforming reactions lies to the right. This reaction can therefore lead to considerable hydrocarbon removal. Rhodium is particularly active in the steam-reforming reaction; platinum is also active.<sup>68</sup>

The conversions of NO, CO, and hydrocarbons in a three-way catalyst operated with cyclical variations in equivalence ratio are larger than estimates based on summation of steady-state values during the cycle. At least part of the improved performance is thought to be due to the ability of the catalyst to undergo reduction-oxidation reactions. Such a catalyst component is usually referred to as an oxygen-storage component. In its oxidized state it can provide oxygen for CO and hydrocarbon oxidation in a rich exhaust gas environment, and in the process be reduced. When the exhaust cycles to lean conditions, this reduced component can react with O<sub>2</sub> or NO (which removes NO directly or indirectly by reducing the O<sub>2</sub> concentration). The oxidized component can then oxidize CO and HC in the next rich cycle, etc. Components such as ReO<sub>2</sub> or CeO<sub>2</sub> which exhibit this "redox" behavior can be included in three-way catalyst formulations. Commercial three-way catalysts contain platinum and rhodium (the ratio Pt/Rh varying substantially in the range 2 to 17) with some A<sub>2</sub>O<sub>3</sub>, NiO, and CeO<sub>2</sub>. Alumina is the preferred support material.<sup>68</sup>

### 11.6.3 Thermal Reactors

In Secs. 11.3 and 11.4.2 it was explained that oxidation of CO and HC occurred during the expansion and exhaust processes in the cylinder of a conventional spark-ignition engine and, under certain circumstances, in the exhaust system. Oxidation after passage through the exhaust port can be enhanced with a *thermal reactor*—an enlarged exhaust manifold that bolts directly onto the cylinder head. Its function is to promote rapid mixing of the hot exhaust gases with any secondary air injected into the exhaust port (required with fuel-rich engine operation to produce a net oxidizing atmosphere), to remove nonuniformities in temperature and composition in the exhaust gases, and to retain the gases at a high enough



**FIGURE 11-58**  
Schematic of exhaust thermal reactor  
for HC and CO oxidation.

temperature for sufficient time to oxidize much of the HC and CO which exits the cylinder. An example of a thermal reactor design is shown in Fig. 11-58.

The temperature levels typically required for bulk gas oxidation of HC and CO in a reactor are about 600 and 700°C, respectively. Note that they are considerably higher than those required for equivalent conversion in a catalytic converter and that higher temperatures are required for CO oxidation than for HC oxidation. The exhaust gas temperature in the manifold of a conventional engine is not sufficient to achieve any substantial reduction in engine exhaust port emissions. To achieve greater reductions, the reactor must be designed to reduce heat losses and increase residence time. In addition, to achieve rapid warm-up after engine start, a low thermal inertia reactor is desirable. Typically, a thin steel liner acts as the core of the reactor inside a cast-iron outer casing; with suitably arranged flow paths, this construction holds heat losses to a minimum by thermally isolating the core.

The effectiveness of the reactor depends on its operating temperature, the availability of excess oxygen mixed throughout the reacting gases, and the reactor volume. The operating temperature depends on the reactor inlet gas temperature, heat losses, and the amount of HC, CO, and H<sub>2</sub> burned up in the reactor. This latter factor is important: 1.5 percent CO removal results in a 220 K temperature rise. As a consequence, reactors with fuel-rich cylinder exhaust gas and secondary air give greater fractional reductions in HC and CO emissions than reactors with fuel-lean cylinder exhaust (which do not require any secondary air). As has already been explained, a higher core gas temperature is required to burn up the same fraction of CO which enters the reactor as of HC which enters. For lean engine exhaust gas, where the reactor core gas temperatures are a hundred degrees K lower than under fuel-rich operation, substan-

tial reductions in CO emissions are difficult to achieve. For very lean operation, HC burnup becomes marginal.

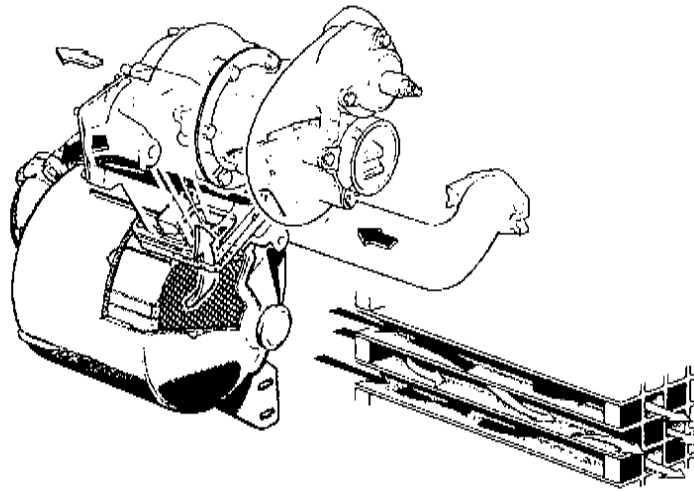
A practical limitation to reactor effectiveness with fuel-rich engine operation is mixing of secondary air and engine exhaust gases in the exhaust port and the reactor core. The secondary air flow with a conventional air pump is effectively shut off by the exhaust blowdown process, and virtually no oxidation occurs in the exhaust port because the air and exhaust gases are segregated. Mixing in the reactor itself is promoted by suitably arranging the reactor inlet and exit ports and by using baffles. In systems with conventional secondary air pumps, maximum reductions in CO and HC occur with 10 to 20 percent excess air in the mixture. However, even with very high reactor core gas temperatures, 100 percent HC and CO oxidation is not achieved due to incomplete mixing. Improved control of secondary air flow has been shown to increase significantly CO emissions burnup.

#### 11.6.4 Particulate Traps

An exhaust treatment technology that substantially reduces diesel engine particulate emissions is the trap oxidizer. A temperature-tolerant filter or trap removes the particulate material from the exhaust gas; the filter is then "cleaned off" by oxidizing the accumulated particulates. This technology is difficult to implement because: (1) the filter, even when clean, increases the pressure in the exhaust system; (2) this pressure increase steadily rises as the filter collects particulate matter; (3) under normal diesel engine operating conditions the collected particulate matter will not ignite and oxidize; (4) once ignition of the particulate occurs, the burnup process must be carefully controlled to prevent excessively high temperatures and trap damage or destruction. Trap oxidizers have been put into production for light-duty automobile diesel engines. Their use with heavy-duty diesel engines poses more difficult problems due to higher particulate loading and lower exhaust temperatures.

Types of particulate filters include: ceramic monoliths, alumina-coated wire mesh, ceramic foam, ceramic fiber mat, woven silica-fiber rope wound on a porous tube. Each of these has different inherent pressure loss and filtering efficiency. Regeneration of the trap by burning up the filtered particulate material can be accomplished by raising its temperature to the ignition point while providing oxygen-containing exhaust gas to support combustion and carry away the heat released. Diesel particulate matter ignites at about 500 to 600°C. This is above the normal temperature of diesel exhaust so either the exhaust gas flowing through the trap during regeneration must be heated (positive regeneration) or ignition must be made to occur at a lower temperature with catalytic materials on the trap or added to the fuel (catalytic regeneration). Catalytic coatings on the trap reduce the ignition temperature by up to 200°C.

Figure 11-59 shows a ceramic-coated trap oxidizer mounted on the exhaust system of a turbocharged IDI diesel engine. The trap is a ceramic honeycomb with half the cells closed at the inlet end and the other half of the cells closed at



**FIGURE 11-59**  
Catalytic ceramic-monolith particulate trap oxidizer mounted on exhaust of turbocharged automobile diesel engine.<sup>86</sup>

the exit end. Thus the particulate laden exhaust is forced to flow through the porous ceramic cell walls. The outside of the honeycomb is insulated and the trap is mounted close to the engine to maintain as high a trap temperature as possible. The pressure drop across the unloaded trap increases from 0.02 atm at 1000 rev/min to 0.15 atm at the maximum engine speed of 4500 rev/min. As the trap loads up, the pressure drop increases, requiring more fuel to be injected to compensate for the loss in power. This leads to higher exhaust temperature which eventually results in catalytic ignition of the particulate. The particulate oxidation rate depends on the trap temperature. With suitable trap location and design, the regeneration process is largely self-regulating. The particulate emissions from the engine are reduced by 70 percent or more.<sup>86</sup>

## PROBLEMS

- 11.1. Figure 11-2 shows concentrations of NO, CO, and HC in a spark-ignition engine exhaust as a function of fuel/air equivalence ratio. Assume the concentration scale is parts per million. Explain the trends shown as the mixture is first made richer and then leaner than stoichiometric.
- 11.2. Figure 11-2 is for a spark-ignition engine. Construct a similar qualitative graph of NO, CO, and HC concentrations versus equivalence ratio for a direct-injection four-stroke cycle diesel engine.
- 11.3. A spark-ignition engine driving a car uses, on average, 120 grams of gasoline per mile traveled. The average emissions from the engine (upstream of the catalyst) are 1.5, 2, and 20 grams per mile of NO<sub>x</sub> (as NO<sub>2</sub>), HC, and CO, respectively. The engine operates with a stoichiometric gasoline-air mixture. Find the average concentrations in parts per million of NO<sub>x</sub>, HC (as ppm C<sub>1</sub>), and CO in the engine exhaust.
- 11.4. Calculate the average combustion inefficiency corresponding to the spark-ignition engine emissions levels given in Prob. 11.3. Include any hydrogen you estimate would be present in the exhaust stream.

- 11.5. A three-way catalytic converter is used with the spark-ignition engine in Prob. 11.3. For 10 percent of the driving time, the catalyst is cold and ineffective, and does not reduce the engine's emissions. For 90 percent of the time, the catalyst is hot and has conversion efficiencies as given in Fig. 11-57. Estimate the average *vehicle* emissions of  $\text{NO}_x$ , HC, and CO in grams per mile.
- 11.6. Figure 15-11 shows the variation in NO and HC emissions as concentrations (ppm) in the exhaust of a spark-ignition engine as a function of speed and load. Convert these data to graphs of indicated specific NO and HC emissions ( $\text{g/kW}\cdot\text{h}$ ) versus speed and imep. Assume  $\eta_p$  (based on atmospheric air density) = imep (kPa)  $\times 10^{-3}$ .
- 11.7. Use the data in Fig. 11-44 to estimate:
- The exhaust particulate emissions as a fraction of the maximum particulate loading during the cycle.
  - The maximum measured soot loading and the exhaust soot loading as fractions of the fuel carbon.
  - The equivalent sphere size of each soot particle at the number density peak ( $22^\circ$  ATC) and in the exhaust.
- Assume a particulate density of  $2 \text{ g/cm}^3$ . Note that the gas volumes in Fig. 11-44 are determined at standard temperature and pressure.
- 11.8. Explain the following emissions trends. Highest marks will be given for succinct summaries of the *important* technical issues.
- Nitric oxide (NO) emissions from diesels and spark-ignition engines as the equivalence ratio is varied show significantly different behavior (see Figs. 11-9 and 11-16). Redraw these graphs on the same plot and explain the different trends for these two types of engines as  $\phi$  decreases on the lean side of stoichiometric.
  - Recirculation of a fraction of the exhaust gases to the intake is used to control engine nitric oxide emissions at part load. Exhaust gas recycle is usually more effective with spark-ignition engines than with diesels, as shown in Fig. P11-8. Explain why these trends are different.

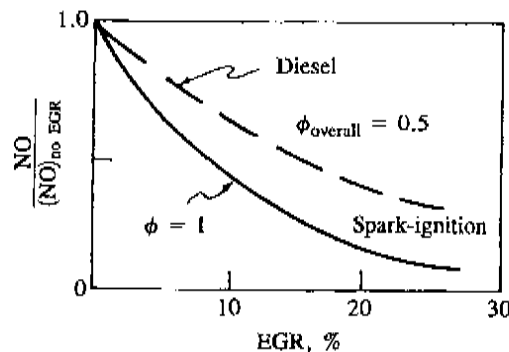


FIGURE P11-8

- Brake specific particulate emissions from diesels are a major problem. Particulate emissions from conventional spark-ignition engines are negligible. Briefly explain why the particulate emission levels from these two types of engines are so different in magnitude.

(d) Diesels have low carbon monoxide (CO) emissions. Spark-ignition engine CO emissions when *averaged* over a typical urban automobile trip (cold engine start, warm-up, cruise, idle, acceleration, etc.) are substantial and require a catalyst for effective control. Explain this difference in average CO emissions (upstream of any catalyst) from these two types of engines.

11.9. The following questions refer to an engine with these geometric and operating characteristics (see Fig. 11-26a):  $\phi = 1.0$ ; compression ratio = 8 : 1; bore = 100 mm; stroke = 100 mm; piston diameter above top ring = 99.4 mm; distance from piston crown top to top ring = 9.52 mm; volumetric efficiency = 0.8; temperature in cylinder at the start of compression = 333 K; pressure in cylinder at start of compression = 1 atm; mixture temperature before entering cylinder = 30°C; brake specific fuel consumption = 300 g/kW · h.

A substantial fraction of spark-ignition engine hydrocarbon emissions comes from the crevice between the piston crown and cylinder wall. Gas is forced into this crevice as the cylinder pressure increases and flows out of this crevice as the cylinder pressure decreases. The gas in the crevice can be assumed to be at the wall temperature, 400 K. The gas pushed into the crevice ahead of the flame is unburned mixture; the gas pushed in behind the flame is burned mixture. About two-thirds of the crevice gas is unburned. The maximum cylinder pressure is 3 MPa.

- Calculate the mass fraction of the cylinder gas which is in the crevice between the piston and cylinder wall and above the first piston ring, at the time of peak pressure.
- Assuming that half of the unburned fuel in this region is oxidized within the cylinder and a further one-third is oxidized in the exhaust port, calculate the engine HC emissions from this source in parts per million (ppm  $C_1$ ) by volume.
- Calculate the ratio of brake specific hydrocarbon emissions to brake specific fuel consumption.
- Calculate the brake specific hydrocarbon emissions in grams of HC per kilowatt-hour.

11.10. Nitric oxide, NO, forms via reactions (11.1) to (11.3). Reaction (11.1) is “slow” and reactions (11.2) and (11.3) are “fast,” so the initial rate of formation of NO is given by Eq. (11.8):

$$\frac{d[\text{NO}]}{dt} = 2k_1^+ [\text{N}_2]_e [\text{O}]_e$$

where [ ] denote concentrations in gram-moles per cubic centimeter,  $k_1^+$  is the rate constant for reaction (11.1), and the factor of 2 enters because the N atom formed in (11.1) immediately reacts via (11.2) or (11.3) to give an additional NO molecule:

$$k_1^+ = 7.6 \times 10^{13} \exp\left(\frac{-38,000}{T}\right) \quad \text{cm}^3/\text{gmol} \cdot \text{s}$$

where  $T$  is in kelvin.

Using the equilibrium composition data provided for mole fraction atomic oxygen (O), molecular nitrogen ( $\text{N}_2$ ), and nitric oxide (NO):

- Plot the formation rate of NO as a function of the equivalence ratio at 3000 K and 5.5 MPa, and as a function of temperature for a stoichiometric mixture at 5.5 MPa.



- (b) Estimate approximately the time taken to reach equilibrium NO levels at  $\phi = 1$ , 2750 K and 3000 K, 5.5 MPa.
- (c) If the stoichiometric mixture inducted into the engine reaches 3000 K and 5.5 MPa after combustion, in the absence of any exhaust gas recirculation, calculate the percentage of the exhaust that must be recycled to the intake (at the initial intake temperature) to reduce the NO formation rate by a factor of 4 (assume the final pressure 5.5 MPa stays the same; of course, the final temperature decreases as the exhaust gas is recycled).

$p = 5.5 \text{ MPa}$				$\phi = 1.0, p = 5.5 \text{ MPa}$			
		Mole fraction				Mole fraction	
$\phi$	$T(\text{K})$	O	$\text{N}_2$	$T(\text{K})$	O	$\text{N}_2$	NO
0.9	3000	$2.1 \times 10^{-3}$	0.73	2500	$6 \times 10^{-5}$	0.73	—
1.0	3000	$1.5 \times 10^{-3}$	0.73	2750	$5 \times 10^{-4}$	0.73	$4 \times 10^{-3}$
1.1	3000	$1 \times 10^{-3}$	0.73	3000	$1.5 \times 10^{-3}$	0.73	$8 \times 10^{-3}$

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