CHAPTER 3

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 "kernal" 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[1] and Glassman.[2]

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.[1]

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 × velocity × 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:

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

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.[3]

TABLE 3.1
Principle constituents of dry air

Gas	ppm by volume	Molecular weight	Mole fraction	Molar ratio
O_2	209,500	31.998	0.2095	1
N_2	780,900	28.012	0.7905	3.773
Ar	9,300	39.948		
CO_2	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 $R = 8314.3$ J/kmol·K and $M = 28.962$:

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

or

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

Thus, the value for the density of dry air at 1 atmosphere (1.0133×10^5 Pa, 14.696 lbf/in^2) and 25°C (77°F) is 1.184 kg/m^3 (0.0739 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.[4] The effect of humidity on the properties of air is given in Fig. 3-2.[5]

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
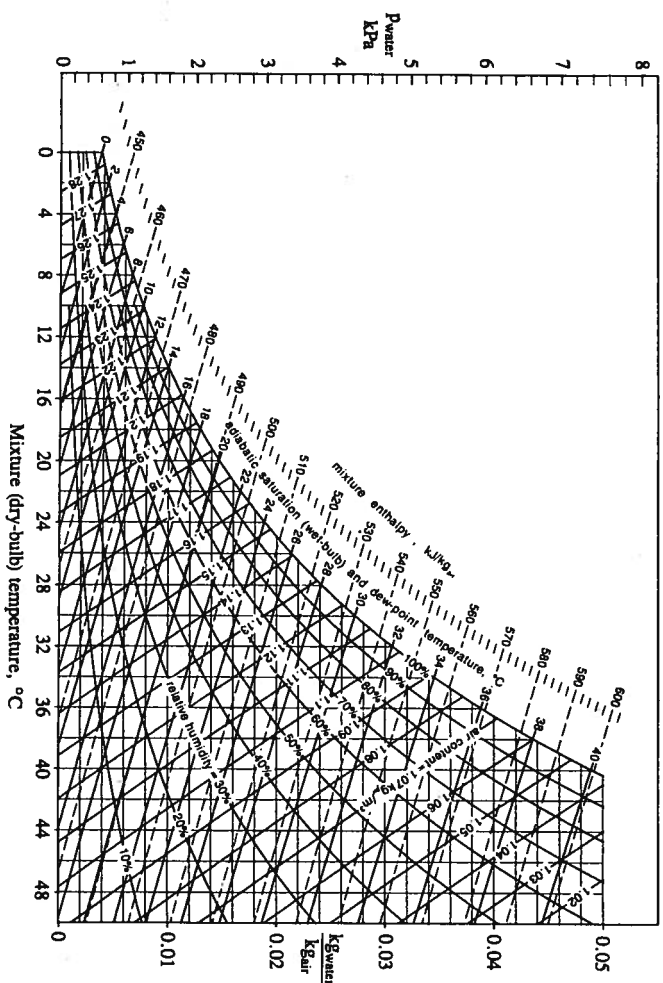
FIGURE 3-1
Psychrometric chart for air-water mixtures at 1 atmosphere. (From Reynolds.[4])
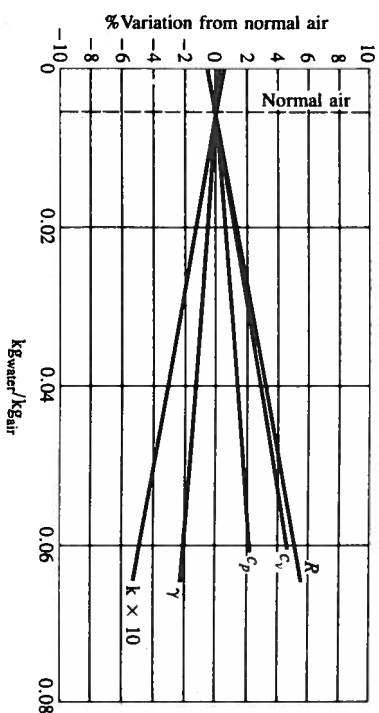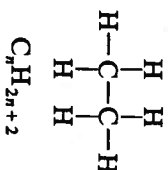
FIGURE 3-2
Effect of humidity on properties of air: R is the gas constant; c_v and c_p are specific heats at constant volume and pressure, respectively; $\gamma = c_p/c_v$; k is the thermal conductivity. (From Taylor.[5])

molecular structure is necessary in order to understand combustion mechanisms.[6] The different classes are as follows:

Alkyl Compounds

Paraffins (alkanes)

C_nH_{2n+2}

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 napthenes (cyclanes)

C_nH_{2n}

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).
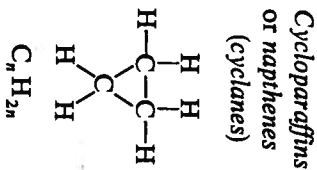
Olefins (alkenes)
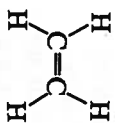
Open-chain hydrocarbons containing a double bond; hence they are unsaturated. Examples are: C_2H_4, ethene (or ethylene); C_3H_6, propene (or propylene); C_4H_8, butene (or butylene); .... From butene upwards several structural isomers are possible depending on the location of the double bond in the basic carbon chain. Straight- and branched-chain structures exist. Diolefins contain two double bonds.

C_nH_{2n}

Acetylenes (alkynes)

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

C_nH_{2n-2}
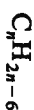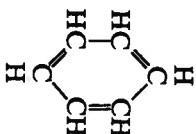
Aromatics

Building block for aromatic hydrocarbons is the benzene (C_6H_6) ring structure shown. This ring structure is very stable and accommodates additional $-CH_2$ groups in side chains and not by ring expansion. Examples: C_7H_8, toluene; C_8H_{10}, xylene (several structural arrangements); .... More complex aromatic hydrocarbons incorporate ethyl, propyl, and heavier alkyl side chains in a variety of structural arrangements.

C_nH_{2n-6}

Alcohols

Monohydric alcohols
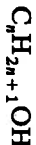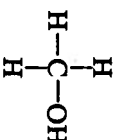
In these organic compounds, one hydroxyl (—OH) group is substituted for one hydrogen atom. Thus methane becomes methyl alcohol, CH_3OH (also called methanol); ethane becomes ethyl alcohol, C_2H_5OH (ethanol); etc.

$C_nH_{2n+1}OH$

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 air 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 CO_2 and the hydrogen to water H_2O. For example, consider the overall chemical equation for the complete combustion of one mole of propane C_3H_8:

$$C_3H_8 + aO_2 = bCO_2 + cH_2O \tag{3.3}$$
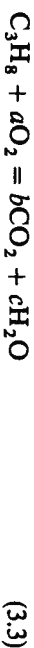
A carbon balance between the reactants and products gives $b = 3$. A hydrogen balance gives $2c = 8$, or $c = 4$. An oxygen balance gives $2b + c = 10 = 2a$, or $a = 5$. Thus Eq. (3.3) becomes

$$C_3H_8 + 5O_2 = 3CO_2 + 4H_2O \tag{3.4}$$
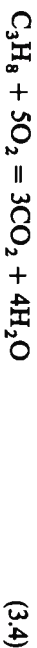
Note that Eq. (3.4) only relates the elemental composition of the reactant and product species; it does not indicate the process by which combustion proceeds, which is much more complex.

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 C_aH_b with air. The overall complete combustion equation is

$$C_aH_b + \left(a + \frac{b}{4}\right)(O_2 + 3.773N_2) = aCO_2 + \frac{b}{2}H_2O + 3.773\left(a + \frac{b}{4}\right)N_2 \tag{3.5}$$

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 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):

$$\left(\frac{A}{F}\right)_s = \left(\frac{F}{A}\right)_s^{-1} = \frac{(1 + y/4)(32 + 3.773 \times 28.16)}{12.011 + 1.008y}$$

$$= \frac{34.56(4 + y)}{12.011 + 1.008y} \tag{3.6}$$

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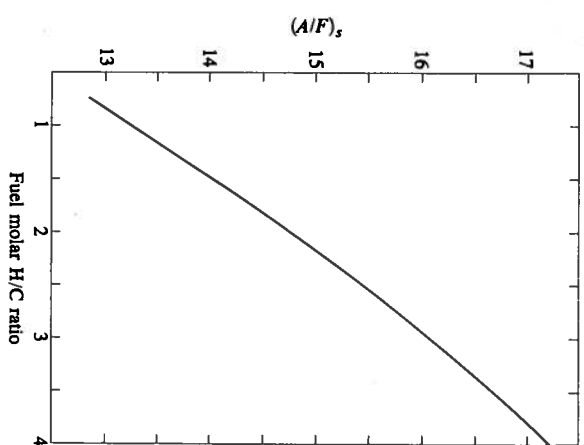
FIGURE 3-3
Stoichiometric air/fuel ratio for air–hydrocarbon fuel mixtures as a function of fuel molar H/C ratio.

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

$$a = 8 \qquad b = 18\dagger$$

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

$$\underset{\text{Fuel}}{C_8H_{18}} + \underset{\text{Air}}{12.5(O_2 + 3.773N_2)} = \underset{\text{Products}}{8CO_2 + 9H_2O + 47.16N_2}$$

In moles:

$$1 \;+\; 12.5(1 + 3.773) \;=\; 8 + 9 + 47.16$$
$$1 \;+\; 59.66 \;=\; 64.16$$

Relative mass:

$$114.15 + 59.66 \times 28.96 \;=\; 8 \times 44.01 + 9 \times 18.02 + 47.16 \times 28.16$$
$$114.5 + 1727.8 \;=\; 1842.3$$

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† 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

$$M_R = 30.36 \qquad M_P = 28.71$$

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

$$C_8H_{18} + 1.25 \times 12.5(O_2 + 3.773N_2) = 8CO_2 + 9H_2O + 3.13O_2 + 58.95N_2 \qquad (3.7)$$
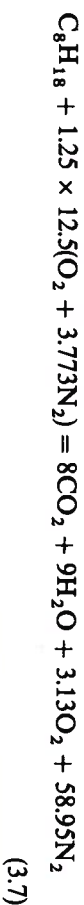
With less than the stoichiometric air requirement, i.e., with fuel-rich combustion, there is insufficient oxygen to oxidize fully the fuel C and H to CO_2 and H_2O. The products are a mixture of CO_2 and H_2O with carbon monoxide CO and hydrogen H_2 (as well as N_2). The product composition cannot be 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* φ,

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

will be used throughout this text for this purpose. The inverse of φ, the *relative air/fuel ratio* λ,

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

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), CH_3OH, the stoichiometric combustion equation is

$$CH_3OH + 1.5(O_2 + 3.773N_2) = CO_2 + 2H_2O + 5.66N_2 \qquad (3.10)$$

and $(A/F)_s = 6.47$. For ethyl alcohol (ethanol), C_2H_5OH, the stoichiometric combustion equation is

$$C_2H_5OH + 3(O_2 + 3.773N_2) = 2CO_2 + 3H_2O + 11.32N_2 \qquad (3.11)$$

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, SO_2.

For hydrogen fuel, the stoichiometric equation is

$$H_2 + \tfrac{1}{2}(O_2 + 3.773N_2) = H_2O + 1.887N_2 \qquad (3.12)$$

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 CO_2 and of H_2O 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

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† The approach used here follows that developed by Spalding and Cole.[7]

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 temperatures gives

$$Q_{R-P} - W_{R-P} = U_P - U_R \qquad (3.13)$$

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

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

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

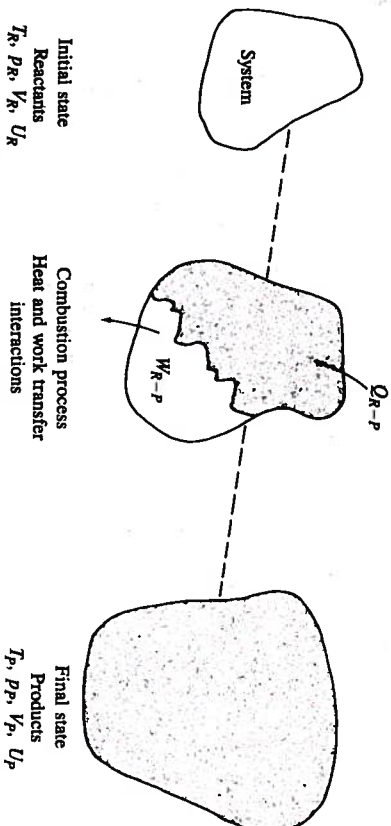

Initial state
Reactants
T_R, p_R, V_R, U_R

Combustion process
Heat and work transfer interactions

Final state
Products
T_P, p_P, V_P, U_P

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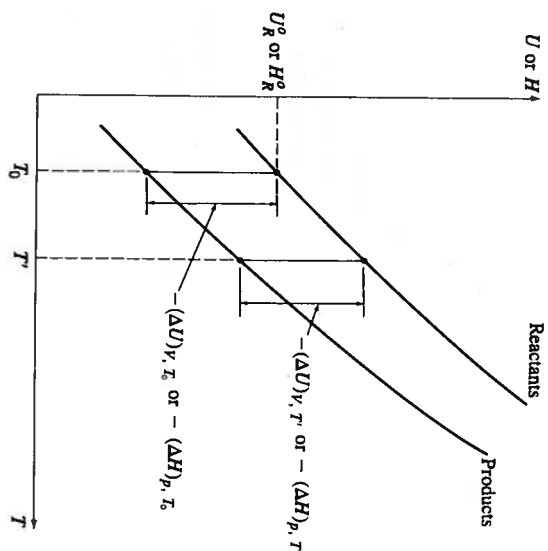System changing from reactants to products for first law analysis.

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

$$Q_{R-P} = (U_P' + pV_P') - (U_R' + pV_R')$$
$$= H_P' - H_R' = (\Delta H)_{p,T'} \quad (3.16)$$

$-(\Delta H)_{p,T'}$ is called the *heat of reaction at constant pressure at T'*.

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° (or H_R°) 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-

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perature; also, the magnitude of $(\Delta U)_{V,T}$ [or $(\Delta H)_{p,T}$] decreases with increasing temperature because c_p (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

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

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

$$(\Delta H)_{p,T'} - (\Delta U)_{V,T'} = \tilde{R}(n_P' - n_R')T' \quad (3.18)$$

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

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

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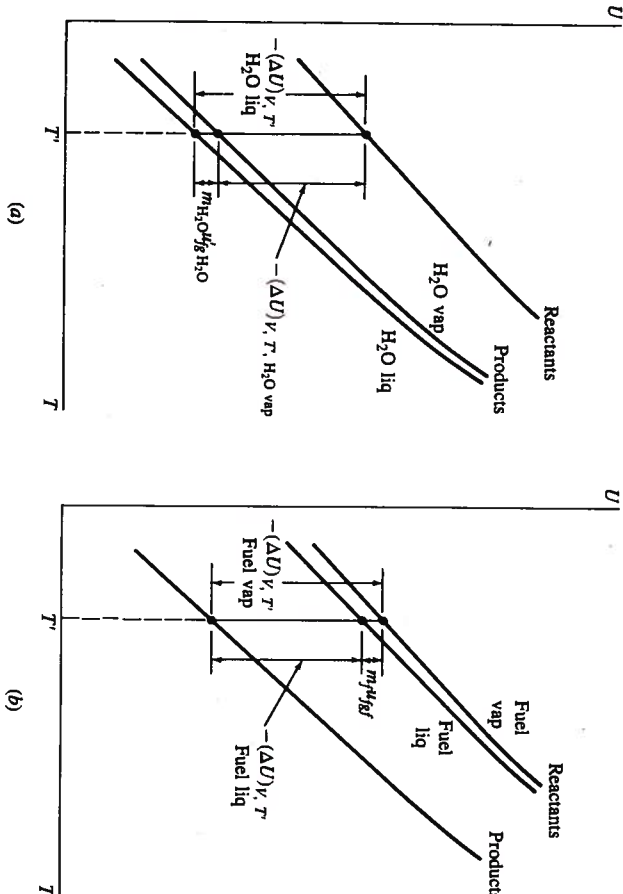
FIGURE 3-6
Schematic plots of internal energy of reactants and products as a function of temperature. (a) Effect of water in products as either vapor or liquid. (b) Effect of fuel in reactants as either vapor or liquid.

curves and relationships apply for enthalpy:

$$|(\Delta H)_{p,T,\,H_2O\,liq}| - |(\Delta H)_{p,T,\,H_2O\,vap}| = m_{H_2O}\,h_{fg\,H_2O} \qquad (3.20)$$

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 $m_f u_{fg\,f}$ (or $m_f h_{fg\,f}$) 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 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 °.

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 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.[8] 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,[9] Rossini et al,[10] and Stull et al.[11] 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

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

TABLE 3.2
Standard enthalpies of formation

Species	State†	$\Delta \bar{h}_f^\circ$, MJ/kmol
O$_2$	Gas	0
N$_2$	Gas	0
H$_2$	Gas	0
C	Gas	0
CO$_2$	Gas	−393.52
H$_2$O	Gas	−241.83
H$_2$O	Liquid	−285.84
CO	Gas	−110.54
CH$_4$	Gas	−74.87
C$_3$H$_8$	Gas	−103.85
CH$_3$OH	Gas	−201.17
CH$_3$OH	Liquid	−238.58
C$_8$H$_{18}$	Gas	−208.45
C$_8$H$_{18}$	Liquid	−249.35

† At 298.15 K (25°C) and 1 atm.

and the enthalpy of the reactants is given by

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

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

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

Thus, for H$_2$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$_2$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$_2$O gas:

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

and for H$_2$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

For H_2O liquid:

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

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

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

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°C (77°F)] for the complete combustion of unit mass of fuel. Thus

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

and

$$Q_{HV_V} = -(\Delta U)_{V, T_0} \qquad (3.22b)$$

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 and constant volume are related by

$$Q_{HHV_p} = Q_{LHV_p} + \left(\frac{m_{H_2O}}{m_f}\right) h_{fg\,H_2O} \qquad (3.23)$$

where (m_{H_2O}/m_f) is the ratio of mass of H_2O produced to mass of fuel burned. A similar expression with $u_{fg\,H_2O}$ replacing $h_{fg\,H_2O}$ 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.
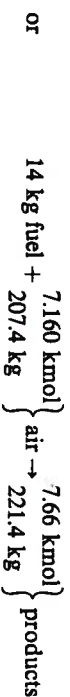
Heating values† of fuels are measured in calorimeters. For gaseous fuels, it is most convenient and accurate to use a continuous-flow atmospheric pressure calorimeter. The entering fuel is saturated with water vapor and mixed with sufficient saturated air for complete combustion at the reference temperature. 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_2, N_2, and H_2 at 298.15 K.

The combustion equation per mole of C can be written

$$CH_2 + \tfrac{3}{2}(O_2 + 3.773N_2) = CO_2 + H_2O + 5.660N_2$$

or

$$14 \text{ kg fuel} + \left.\begin{array}{c} 7.160 \text{ kmol} \\ 207.4 \text{ kg} \end{array}\right\} \text{air} \rightarrow \left.\begin{array}{c} 7.66 \text{ kmol} \\ 221.4 \text{ kg} \end{array}\right\} \text{products}$$

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:

$$(\Delta H)_p^\circ = -43.2 + 8.3143 \times 10^{-3}(7.66 - 7.160) \times \frac{298.15}{14}$$

$$= -43.2 + 0.09 = -43.1 \text{ MJ/kg fuel}$$

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† 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_2O 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

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

when U_P and U_R are evaluated relative to the same datum (e.g., the enthalpies of C, O_2, N_2, and H_2 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

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

it follows from Eq. (3.24) that

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

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

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

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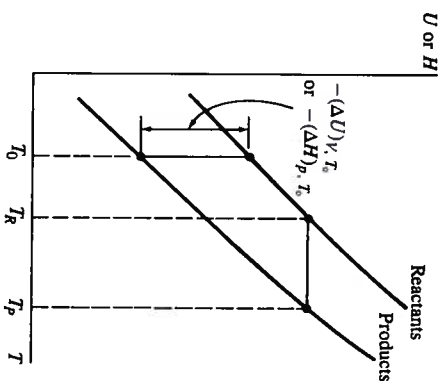
FIGURE 3-7
Adiabatic constant-volume combustion process on U-T diagram or adiabatic constant-pressure combustion process on H-T diagram.

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_2, unburned hydrocarbons, soot) as well as complete combustion products (CO_2 and H_2O) (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

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

Enthalpy is the appropriate property since $p_R = p_P = p_{\text{atm}}$. n_i is the number of moles of species i in the reactants or products per unit mass of working fluid and $\Delta\bar{f}_{f,i}^\circ$ 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*
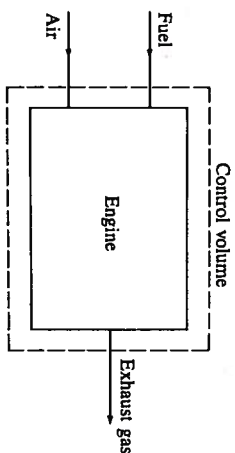
FIGURE 3-8
Control volume surrounding engine.

efficiency—the fraction of the fuel energy supplied which is released in the combustion process—is given by[12]

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

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-
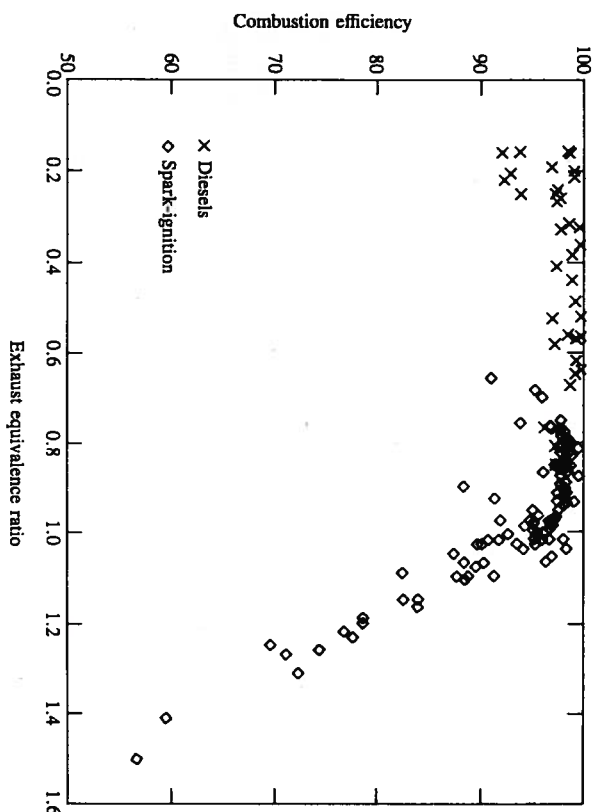

FIGURE 3-9
Variation of engine combustion efficiency with fuel/air equivalence ratio.

bustion 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 ΔW_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 ΔQ 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, $H - T_A S$.[13] 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†	$\Delta\bar{h}°_{298}$, MJ/kmol	$\Delta\bar{g}°_{298}$, MJ/kmol
$C + O_2 \to CO_2$	−393.52	−394.40
$H_2 + \frac{1}{2}O_2 \to H_2O$	−240.91	−232.78
$CH_4 + 2O_2 \to CO_2 + 2H_2O$	−802.30	−800.76
$CH_4O(l) + \frac{3}{2}O_2 \to CO_2 + 2H_2O$	−638.59	−685.35
$C_3H_8(g) + 5O_2 \to 3CO_2 + 4H_2O$	−2044.0	−2074.1
$C_6H_6(l) + \frac{15}{2}O_2 \to 6CO_2 + 3H_2O$	−3135.2	−3175.1
$C_8H_{18}(l) + \frac{25}{2}O_2 \to 8CO_2 + 9H_2O$	−5074.6	−5219.9

† H_2O (gas) in products.

Under these conditions,

$$\Delta W_U \le -[(H - TS)_{P_{T_A,P_A}} - (H - TS)_{R_{T_A}}] = -(\Delta G)_{T_A,P_A} \quad (3.28)$$

or

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

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* η_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 $(\Delta g)_{298}$ and $(\Delta h)_{298}$ for selected fuel combustion reactions are given in Table 3.3. For the pure hydrocarbons they are closely comparable because at 298 K, $\Delta\bar{s}° \le \Delta\bar{h}°/T$. For hydrogen and methanol the differences are larger, however. Because for practical fuels $-(\Delta h)_{298}$ 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 $\Delta\bar{h}° \approx \Delta\bar{g}°$, 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* η_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.[13]

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 CO_2 molecules *dissociate* into CO and O_2 molecules. If the mixture of CO_2, CO, and O_2 is in equilibrium, then CO_2 molecules are dissociating into CO and O_2 at the same rate as CO and O_2 molecules are *recombining* in the proportions required to satisfy the equation

$$CO + \tfrac{1}{2}O_2 = CO_2$$

In combustion products of hydrocarbon fuels, the major species present at low temperatures are N_2, H_2O, CO_2, and O_2 or CO and 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: $N_2 \sim 0.7$; H_2O, $CO_2 \sim 0.1$; CO, OH, O_2, NO, $H_2 \sim 0.01$; H, O ~ 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

The second law gives

Combining these gives

$$\delta Q = dH$$

$$\delta Q \leq T \, dS$$

$$dH - T \, dS \leq 0$$

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

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

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† 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

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

This can be written as

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

where the ν_i are the stoichiometric coefficients and by convention are positive for the product species and negative for the reactant species.

Let an amount δn_a of M_a react with δn_b of M_b, etc., and produce δn_l of M_l, δn_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 δn_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

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

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,

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

or

$$\sum_i \left(\tilde{\mu}_i^{\circ} + \tilde{R}T \ln \frac{p_i}{p_0} \right)_{\nu_i} \delta n = 0 \tag{3.39}$$

We can divide by δn and rearrange, to obtain

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

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,[8] 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

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

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:

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

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

$$K_p = K_c(\tilde{R}T)^{\sum_i \nu_i} \qquad (3.43)$$

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_2 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

$$CO + \tfrac{1}{2}O_2 = CO_2$$

The JANAF tables give $\log_{10} K_p$ (equilibrium constants of formation from the elements in their standard state) at 2500 K of CO_2, CO, and O_2 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 α (i.e., a fraction α of the CO_2 formed by complete combustion is dissociated), the product composition is

$$CO_2, (1-\alpha); \quad CO, \alpha; \quad O_2, \frac{\alpha}{2}$$
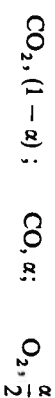
For this mixture, the number of moles of reactants n_R is $\frac{3}{2}$; the number of moles of products n_P is $(1 + \alpha/2)$.
The ideal gas law gives

$$p_R V = n_R \tilde{R} T_R \qquad p_P V = n_P \tilde{R} T_P \qquad \frac{p_P}{n_P} = \frac{\tilde{R} T_P}{V}$$

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,

$$x_{CO_2} = \frac{1-\alpha}{n_P} = 0.893$$

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

$$x_{O_2} = \frac{\alpha/2}{n_P} = 0.037$$

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 CO_2, H_2O, CO, and H_2 is often assumed to determine the burned gas composition. For $\phi = 1.2$, for C_8H_{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
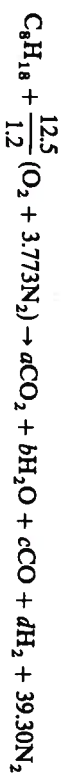
$$CO_2 + H_2 = CO + H_2O$$

From the JANAF tables, $\log_{10} K_p$ of formation for these species at 1700 K are: CO_2, 12.180; H_2, 0; CO, 8.011; $H_2O(g)$, 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 C_8H_{18}-air with $\phi = 1.2$ can be written

$$C_8H_{18} + \frac{12.5}{1.2}(O_2 + 3.773 N_2) \to a CO_2 + b H_2O + c CO + d H_2 + 39.30 N_2$$

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

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

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

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

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

CO_2, 0.0908; H_2O, 0.137; CO, 0.051; H_2, 0.023; 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.[14] 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, the element mass balance constraints are

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

The Gibbs free energy per kilogram of mixture is

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

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 δn_j and $\delta \lambda_i$ as independent gives

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

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) $\Delta \tilde{h}_{f,298}^\circ$ with sensible enthalpies $(\tilde{h}^\circ - \tilde{h}_{298}^\circ)$, i.e.,

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

For the elements in their reference state, $\Delta \tilde{h}_{f,298}^\circ$ is zero [the elements important in combustion are C (solid, graphite), $H_2(g)$, $O_2(g)$, $N_2(g)$].

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

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

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

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

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, ρ, h, s, M, $(\partial \ln V/\partial \ln p)_T$, $(\partial \ln V/\partial \ln T)_p$, c_p, γ_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
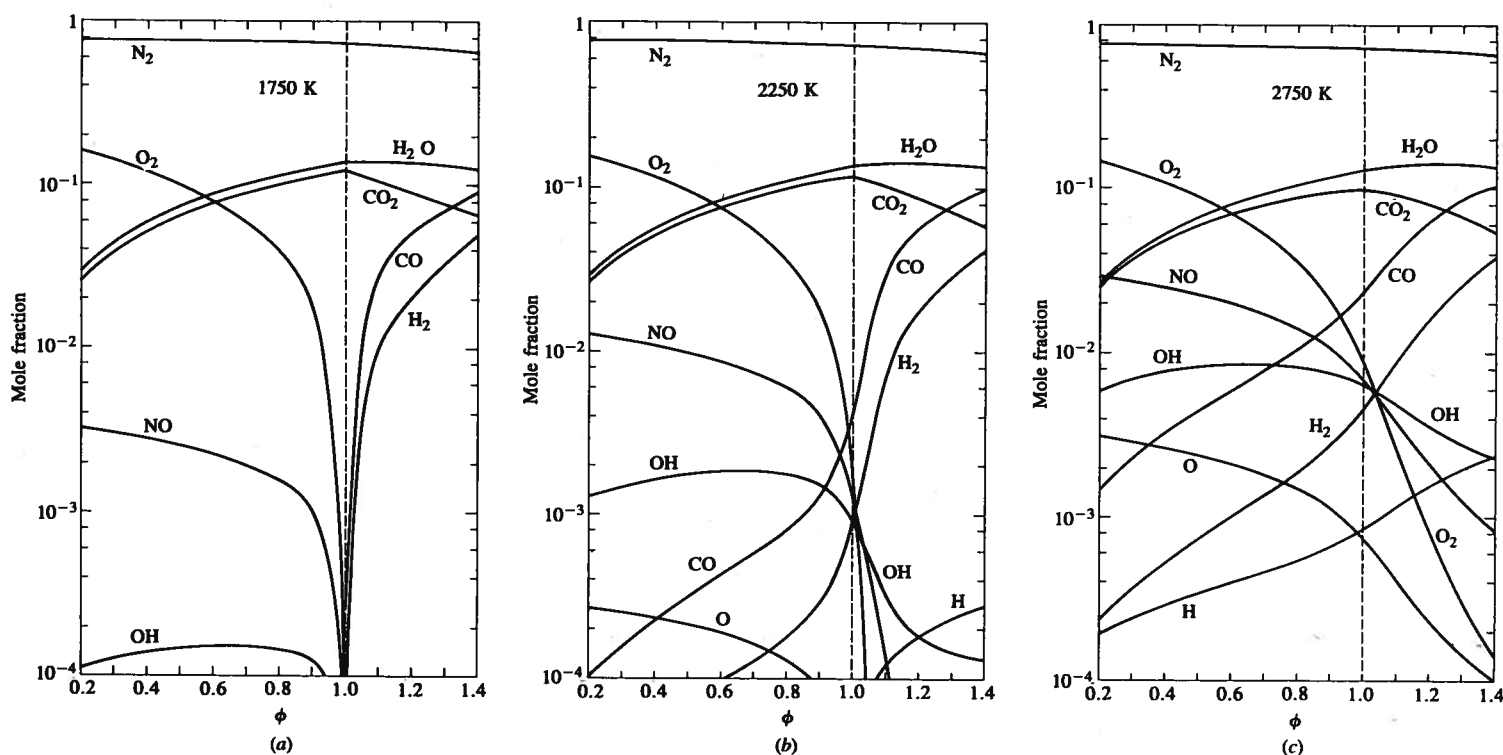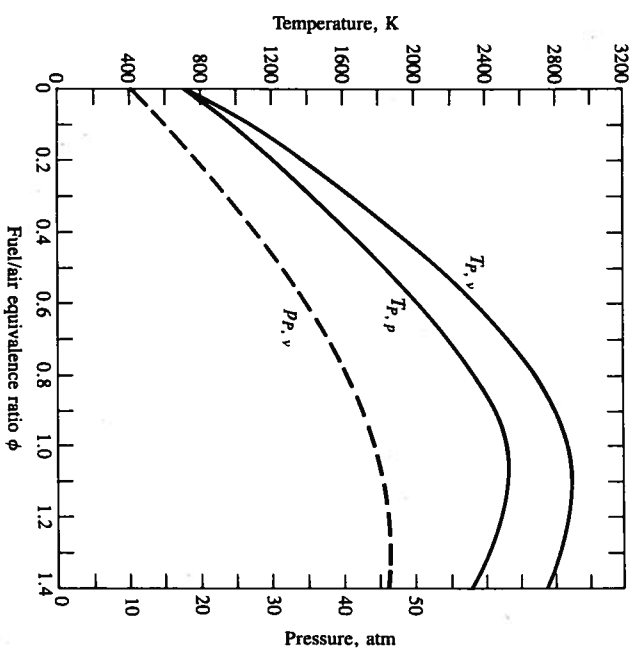

FIGURE 3-10
Mole fractions of equilibrium combustion products of isooctane-air mixtures as a function of fuel/air equivalence ratio at 30 atmospheres and (a) 1750 K; (b) 2250 K; and (c) 2750 K.

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.[2]

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.,

$$M_a + M_b = M_c + M_d \qquad (3.51)$$

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

$$O + N_2 = NO + N$$

This is a second-order reaction since the stoichiometric coefficients of the reactants ν_a and ν_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.,

$$H + H + M = H_2 + M^* \qquad (3.52)$$

M is any molecule (such as N_2) which takes part in the collision and carries away the excess energy.

The law of mass action states that 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 ν_i. Thus, for reaction (3.51) above, the reaction rate R^+ in the forward (+) direction, reactants to products, is given by

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

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

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

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,

$$R^+ - R^- = -\frac{d[M_c]^+}{dt} + \frac{d[M_c]^-}{dt} = -\frac{d[M_a]^+}{dt} - \frac{d[M_a]^-}{dt}$$
$$= k^+[M_a][M_b] - k^-[M_c][M_d] \qquad (3.55)$$

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

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

where ν_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

$$R^+ = k^+ \prod_{i=1}^{n} [M_{R_i}]^{\nu_{R_i}}$$

$$R^- = k^- \prod_{i=1}^{m} [M_{P_i}]^{\nu_{P_i}} \qquad (3.57)$$

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

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

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

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

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

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

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.

$$CO_2 = 10.8\%, \quad O_2 = 4.5\%, \quad CO = 0\%, \quad H_2 = 0\%$$

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.

3.5 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 $CO_2 = 13.0\%$, $CO = 2.8\%$ with 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 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 $N_2 + O_2 = 2NO$. 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. N_2, 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 CO, 3%; O_2, 7%; N_2, 74%; CO_2, 6%; H_2O, 10%.
(a) Calculate the concentration of CO and O_2 in gram moles per cm³ in the entering mixture.
(b) The rate of reaction is given by

$$d[CO]/dt = -4.3 \times 10^{11} \times [CO][O_2]^{0.25} \exp[-E/(RT)]$$

[ ] denotes concentration in gram moles per cm³, $E/R = 20{,}000$ K. Calculate the initial reaction rate of CO, $d[CO]/dt$ time is in seconds.
(c) The equilibrium constant K_p for the reaction $CO + \frac{1}{2}O_2 = CO_2$ 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 H_2O, 7.44 percent O_2, and 70.2 percent 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:

$$H_2O, \ 0.0048; \quad CO_2, \ 0.0585; \quad O_2, \ 0.123; \quad N_2, \ 0.772$$

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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