FUNDAMENTALS OF THERMODYNAMICS

SEVENTH EDITION

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Many thermodynamic problems involve chemical reactions. Among the most familiar of these is the combustion of hydrocarbon fuels, for this process is utilized in most of our power-generating devices. However, we can all think of a host of other processes involving chemical reactions, including those that occur in the human body.

This chapter considers a first- and second-law analysis of systems undergoing a chemical reaction. In many respects, this chapter is simply an extension of our previous consideration of the first and second laws. However, a number of new terms are introduced, and it will also be necessary to introduce the third law of thermodynamics.

In this chapter the combustion process is considered in detail. There are two reasons for this emphasis. First, the combustion process is important in many problems and devices with which the engineer is concerned. Second, the combustion process provides an excellent means of teaching the basic principles of the thermodynamics of chemical reactions. The student should keep both of these objectives in mind as the study of this chapter progresses.

Chemical equilibrium will be considered in Chapter 16; therefore, the subject of dissociation will be deferred until then.

15.1 FUELS

A thermodynamics textbook is not the place for a detailed treatment of fuels. However, some knowledge of them is a prerequisite to a consideration of combustion, and this section is therefore devoted to a brief discussion of some of the hydrocarbon fuels. Most fuels fall into one of three categories—coal, liquid hydrocarbons, or gaseous hydrocarbons.

Coal consists of the remains of vegetation deposits of past geologic ages after subject to biochemical actions, high pressure, temperature, and submersion. The characteristics of coal vary considerably with location, and even within a given mine there is some variation in composition.

A sample of coal is analyzed on one of two bases. The proximate analysis specifies, on a mass basis, the relative amounts of moisture, volatile matter, fixed carbon, and ash; the ultimate analysis specifies, on a mass basis, the relative amounts of carbon, sulfur, hydrogen, nitrogen, oxygen, and ash. The ultimate analysis may be given on an “as-received” basis or on a dry basis. In the latter case, the ultimate analysis does not include the moisture as determined by the proximate analysis.

A number of other properties of coal are important in evaluating a coal for a given use. Some of these are the fusibility of the ash, the grindability or ease of pulverization, the weathering characteristics, and size.

Most liquid and gaseous hydrocarbon fuels are a mixture of many different hydrocarbons. For example, gasoline consists primarily of a mixture of about 40 hydrocarbons, with many others present in very small quantities. In discussing hydrocarbon fuels, therefore,
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### Table 15.1

Characteristics of Some of the Hydrocarbon Families

<table>
<thead>
<tr>
<th>Family</th>
<th>Formula</th>
<th>Structure</th>
<th>Saturated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffin</td>
<td>(C_nH_{2n+2})</td>
<td>Chain</td>
<td>Yes</td>
</tr>
<tr>
<td>Olefin</td>
<td>(C_nH_{2n})</td>
<td>Chain</td>
<td>No</td>
</tr>
<tr>
<td>Diolefin</td>
<td>(C_nH_{2n-2})</td>
<td>Chain</td>
<td>No</td>
</tr>
<tr>
<td>Naphthene</td>
<td>(C_nH_{2n})</td>
<td>Ring</td>
<td>Yes</td>
</tr>
<tr>
<td>Aromatic</td>
<td>(C_nH_{2n})</td>
<td>Ring</td>
<td>No</td>
</tr>
<tr>
<td>Benzene</td>
<td>(C_nH_{2n-6})</td>
<td>Ring</td>
<td>No</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>(C_nH_{2n-12})</td>
<td>Ring</td>
<td>No</td>
</tr>
</tbody>
</table>

A brief consideration should be given to the most important families of hydrocarbons, which are summarized in Table 15.1.

Three concepts should be defined. The first pertains to the structure of the molecule. The important types are the ring and chain structures; the difference between the two is illustrated in Fig. 15.1. The same figure illustrates the definition of saturated and unsaturated hydrocarbons. An unsaturated hydrocarbon has two or more adjacent carbon atoms joined by a double or triple bond, whereas in a saturated hydrocarbon all the carbon atoms are joined by a single bond. The third term to be defined is an isomer. Two hydrocarbons with the same number of carbon and hydrogen atoms and different structures are called isomers. Thus, there are several different octanes \((C_8H_{18})\), each having 8 carbon atoms and 18 hydrogen atoms, but each with a different structure.

The various hydrocarbon families are identified by a common suffix. The compounds comprising the paraffin family all end in -ane (e.g., propane and octane). Similarly, the compounds comprising the olefin family end in -ylene or -ene (e.g., propene and octene), and the diolefin family ends in -diene (e.g., butadiene). The napthenic family has the same chemical formula as the olefin family but has a ring rather than a chain structure. The hydrocarbons in the napthenic family are named by adding the prefix cyclo- (as cyclopentane).

The aromatic family includes the benzene series \((C_6H_{12})\) and the naphthalene series \((C_{10}H_{12})\). The benzene series has a ring structure and is unsaturated.

Most liquid hydrocarbon fuels are mixtures of hydrocarbons that are derived from crude oil through distillation and cracking processes. The separation of air into its two major components, nitrogen and oxygen, using a distillation column was discussed briefly in Section 1.5. In a similar but much more complicated manner, a fractional distillation column is used to separate petroleum into its various constituents. This process is shown schematically in Fig. 15.2. Liquid crude oil is gasified and enters near the bottom of the distillation column. The heavier fractions have higher boiling points and condense out at
FUELS

Fractions decreasing in density and boiling point

Crude oil

Fractions increasing in density and boiling point

Distillation column

170°C

C_{14} to C_{32} diesel oil

20°C

C_{5} to C_{6} gases

270°C

C_{50} to C_{70} fuel oil

600°C

120°C

C_{10} to C_{14} kerosene (paraffin oil)

70°C

C_{5} to C_{8} gasoline

170°C

C_{30} to C_{35} lubricating oil

Fractions decreasing in density and boiling point

Fractions increasing in density and boiling point

Lubricating oils, waxes, polishes

Diesel fuels

Jet fuel, paraffin for lighting and heating

Chemicals

Gasoline for vehicles

Asphalt for roads and roofing

Fuel for ships, factories, and central heating

Liquefied petroleum gas

C_{5} to C_{9} naphtha

FIGURE 15.2
Petroleum distillation column.

a) Schematic diagram.

b) Photo of a distillation column in a refinery.
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the higher temperatures in the lower part of the column, while the lighter fractions condense out at the lower temperatures in the upper portion of the column. Some of the common fuels produced in this manner are gasoline, kerosene, jet engine fuel, diesel fuel, and fuel oil.

Alcohols, presently seeing increased usage as fuel in internal combustion engines, are a family of hydrocarbons in which one of the hydrogen atoms is replaced by an OH radical. Thus, methyl alcohol, or methanol, is CH₃OH, and ethanol is C₂H₅OH. Ethanol is one of the class of biofuels, produced from crops or waste matter by chemical conversion processes. There is extensive research and development in the area of biofuels at the present time, as well as in the development of processes for producing gaseous and liquid hydrocarbon fuels from coal, oil shale, and tar sands deposits. Several alternative techniques have been demonstrated to be feasible, and these resources promise to provide an increasing proportion of our fuel supplies in future years.

It should also be noted here in our discussion of fuels that there is currently a great deal of development effort to use hydrogen as a fuel for transportation usage, especially in connection with fuel cells. Liquid hydrogen has been used successfully for many years as a rocket fuel but is not suitable for vehicular use, especially because of the energy cost to produce it (at about 20 K), as well as serious transfer and storage problems. Instead, hydrogen would need to be stored as a very high-pressure gas or in a metal hydride system. There remain many problems in using hydrogen as a fuel. It must be produced either from water or a hydrocarbon, both of which require a large energy expenditure. Hydrogen gas in air has a very broad flammability range—almost any percentage of hydrogen, small or large, is flammable. It also has a very low ignition energy; the slightest spark will ignite a mixture of hydrogen in air. Finally, hydrogen burns with a colorless flame, which can be dangerous. The incentive to use hydrogen as a fuel is that its only product of combustion or reaction is water, but it is still necessary to include the production, transfer, and storage in the overall consideration.

For the combustion of liquid fuels, it is convenient to express the composition in terms of a single hydrocarbon, even though it is a mixture of many hydrocarbons. Thus, gasoline

<table>
<thead>
<tr>
<th>Table 15.2</th>
<th>Volumetric Analyses of Some Typical Gaseous Fuels</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Constituent</strong></td>
<td><strong>Various Natural Gases</strong></td>
</tr>
<tr>
<td></td>
<td><strong>A</strong></td>
</tr>
<tr>
<td>Methane</td>
<td>93.9</td>
</tr>
<tr>
<td>Ethane</td>
<td>3.6</td>
</tr>
<tr>
<td>Propane</td>
<td>1.2</td>
</tr>
<tr>
<td>Butanes plusa</td>
<td>1.3</td>
</tr>
<tr>
<td>Ethene</td>
<td>6.1</td>
</tr>
<tr>
<td>Benzene</td>
<td>2.8</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>14.0</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>7.5</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.6</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>27.0</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>4.5</td>
</tr>
</tbody>
</table>

*This includes butane and all heavier hydrocarbons*
THE COMBUSTION PROCESS

is usually considered to be octane, \( C_8H_{18} \), and diesel fuel is considered to be dodecane, \( C_{12}H_{26} \). The composition of a hydrocarbon fuel may also be given in terms of percentage of carbon and hydrogen.

The two primary sources of gaseous hydrocarbon fuels are natural gas wells and certain chemical manufacturing processes. Table 15.2 gives the composition of a number of gaseous fuels. The major constituent of natural gas is methane, which distinguishes it from manufactured gas.

15.2 THE COMBUSTION PROCESS

The combustion process consists of the oxidation of constituents in the fuel that are capable of being oxidized and can therefore be represented by a chemical equation. During a combustion process, the mass of each element remains the same. Thus, writing chemical equations and solving problems concerning quantities of the various constituents basically involve the conservation of mass of each element. This chapter presents a brief review of this subject, particularly as it applies to the combustion process.

Consider first the reaction of carbon with oxygen.

\[
\text{Reactants} \quad \text{Products} \quad \text{C} + \text{O}_2 \rightarrow \text{CO}_2
\]

This equation states that 1 kmol of carbon reacts with 1 kmol of oxygen to form 1 kmol of carbon dioxide. This also means that 12 kg of carbon react with 32 kg of oxygen to form 44 kg of carbon dioxide. All the initial substances that undergo the combustion process are called the reactants, and the substances that result from the combustion process are called the products.

When a hydrocarbon fuel is burned, both the carbon and the hydrogen are oxidized. Consider the combustion of methane as an example.

\[
\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad (15.1)
\]

Here the products of combustion include both carbon dioxide and water. The water may be in the vapor, liquid, or solid phase, depending on the temperature and pressure of the products of combustion.

In the combustion process, many intermediate products are formed during the chemical reaction. In this book we are concerned with the initial and final products and not with the intermediate products, but this aspect is very important in a detailed consideration of combustion.

In most combustion processes, the oxygen is supplied as air rather than as pure oxygen. The composition of air on a molal basis is approximately 21% oxygen, 78% nitrogen, and 1% argon. We assume that the nitrogen and the argon do not undergo chemical reaction (except for dissociation, which will be considered in Chapter 16). They do leave at the same temperature as the other products, however, and therefore undergo a change of state if the products are at a temperature other than the original air temperature. At the high temperatures achieved in internal-combustion engines, there is actually some reaction between the nitrogen and oxygen, and this gives rise to the air pollution problem associated with the oxides of nitrogen in the engine exhaust.

In combustion calculations concerning air, the argon is usually neglected, and the air is considered to be composed of 21% oxygen and 79% nitrogen by volume. When
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this assumption is made, the nitrogen is sometimes referred to as atmospheric nitrogen. A
molecular weight of 28.16 (which takes the argon into account) compared to 28.013 for pure nitrogen. This
distinction will not be made in this text, and we will consider the 79% nitrogen to be pure nitrogen.

The assumption that air is 21.0% oxygen and 79.0% nitrogen by volume leads to the conclusion
that for each mole of oxygen, 79.0/21.0 = 3.76 moles of nitrogen are involved. Therefore, when the oxygen for the
combustion of methane is supplied as air, the reaction can be written

\[
\text{CH}_4 + 2\text{O}_2 + 2(3.76)\text{N}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 7.52\text{N}_2
\]  

(15.2)

The minimum amount of air that supplies sufficient oxygen for the complete combustion of
all the carbon, hydrogen, and any other elements in the fuel that may oxidize is called the theoretical air. When
complete combustion is achieved with theoretical air, the products contain no oxygen. A general combustion reaction
with a hydrocarbon fuel and air is thus written

\[
\text{C}_x\text{H}_y + v_2\text{O}_2 + 3.76\text{N}_2 \rightarrow v_2\text{O}_2 + v_2\text{H}_2\text{O} + v_2\text{N}_2
\]  

(15.3)

with the coefficients to the substances called stoichiometric coefficients. The balance of
atoms yields the theoretical amount of air as

\[
\begin{align*}
\text{C:} & \quad v_2\text{CO}_2 = x \\
\text{H:} & \quad 2v_2\text{H}_2\text{O} = y \\
\text{N}_2: & \quad v_2\text{N}_2 = 3.76 \times v_2\text{O}_2
\end{align*}
\]

and the total number of moles of air for 1 mole of fuel becomes

\[
n_{\text{air}} = v_2\text{O}_2 \times 4.76 = 4.76(x + y/4)
\]

This amount of air is equal to 100% theoretical air. In practice, complete combustion is not likely to
be achieved unless the amount of air supplied is somewhat greater than the theoretical amount. Two important
parameters often used to express the ratio of fuel and air are the air–fuel ratio (designated AF) and its reciprocal, the fuel–air ratio (designated FA). These ratios are usually expressed on a mass basis, but a mole basis is used at times.

\[
AF_{\text{mass}} = \frac{m_{\text{air}}}{m_{\text{fuel}}}
\]  

(15.4)

\[
AF_{\text{mole}} = \frac{n_{\text{air}}}{n_{\text{fuel}}}
\]  

(15.5)

They are related through the molecular masses as

\[
AF_{\text{mass}} = \frac{m_{\text{air}}}{m_{\text{fuel}}} = \frac{n_{\text{air}}M_{\text{air}}}{n_{\text{fuel}}M_{\text{fuel}}} = AF_{\text{mole}} \frac{M_{\text{air}}}{M_{\text{fuel}}}
\]

and a subscript \(s\) is used to indicate the ratio for 100% theoretical air, also called a stoichiometric mixture. In an actual combustion process, an amount of air is expressed as a fraction of the theoretical amount, called percent theoretical air. A similar ratio named the equivalence ratio equals the actual fuel–air ratio divided by the theoretical fuel–air ratio as

\[
\Phi = \frac{FA}{FA_s} = \frac{AF}{AF_s}
\]  

(15.6)
the reciprocal of percent theoretical air. Since the percent theoretical air and the equivalence ratio are both ratios of the stoichiometric air–fuel ratio and the actual air–fuel ratio, the molecular masses cancel out and they are the same whether a mass basis or a mole basis is used.

Thus, 150% theoretical air means that the air actually supplied is 1.5 times the theoretical air and the equivalence ratio is $2/3$. The complete combustion of methane with 150% theoretical air is written

$$\text{CH}_4 + 1.5 \times (2\text{O}_2 + 3.76\text{N}_2) \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + \text{O}_2 + 11.28\text{N}_2 \quad (15.7)$$

having balanced all the stoichiometric coefficients from conservation of all the atoms.

The amount of air actually supplied may also be expressed in terms of percent excess air. The excess air is the amount of air supplied over and above the theoretical air. Thus, 150% theoretical air is equivalent to 50% excess air. The terms theoretical air, excess air, and equivalence ratio are all in current use and give an equivalent information about the reactant mixture of fuel and air.

When the amount of air supplied is less than the theoretical air required, the combustion is incomplete. If there is only a slight deficiency of air, the usual result is that some of the carbon unites with the oxygen to form carbon monoxide (CO) instead of carbon dioxide (CO$_2$). If the air supplied is considerably less than the theoretical air, there may also be some hydrocarbons in the products of combustion.

Even when some excess air is supplied, small amounts of carbon monoxide may be present, the exact amount depending on a number of factors including the mixing and turbulence during combustion. Thus, the combustion of methane with 110% theoretical air might be as follows:

$$\text{CH}_4 + 2(1.1)\text{O}_2 + 2(1.1)3.76\text{N}_2 \rightarrow$$

$$+ 0.95 \text{CO}_2 + 0.05 \text{CO} + 2\text{H}_2\text{O} + 0.225\text{O}_2 + 8.27\text{N}_2 \quad (15.8)$$

The material covered so far in this section is illustrated by the following examples.

**EXAMPLE 15.1** Calculate the theoretical air–fuel ratio for the combustion of octane, \( \text{C}_8\text{H}_{18} \).

**Solution**

The combustion equation is

$$\text{C}_8\text{H}_{18} + 12.5\text{O}_2 + 12.5(3.76)\text{N}_2 \rightarrow 8\text{CO}_2 + 9\text{H}_2\text{O} + 47.0\text{N}_2$$

The air–fuel ratio on a mole basis is

$$\text{AF} = \frac{12.5 + 47.0}{1} = 59.5 \text{kmol air/kmol fuel}$$

The theoretical air–fuel ratio on a mass basis is found by introducing the molecular mass of the air and fuel.

$$\text{AF} = \frac{59.5(28.97)}{114.2} = 15.0 \text{kg air/kg fuel}$$
EXAMPLE 15.2
Determine the molar analysis of the products of combustion when octane, \( \text{C}_8\text{H}_{18} \), is burned with 200% theoretical air, and determine the dew point of the products if the pressure is 0.1 MPa.

**Solution**

The equation for the combustion of octane with 200% theoretical air is

\[
\text{C}_8\text{H}_{18} + 12.5(2) \text{ O}_2 + 12.5(2)(3.76) \text{ N}_2 \rightarrow 8 \text{ CO}_2 + 9 \text{ H}_2\text{O} + 12.5 \text{ O}_2 + 94.0 \text{ N}_2
\]

Total kmols of product = 8 + 9 + 12.5 + 94.0 = 123.5

Molar analysis of products:

- \( \text{CO}_2 \): \( \frac{8}{123.5} = 6.47\% \)
- \( \text{H}_2\text{O} \): \( \frac{9}{123.5} = 7.29\% \)
- \( \text{O}_2 \): \( \frac{12.5}{123.5} = 10.12\% \)
- \( \text{N}_2 \): \( \frac{94}{123.5} = 76.12\% \)

100.00%

The partial pressure of the water is 100(0.0729) = 7.29 kPa, so the saturation temperature corresponding to this pressure is 39.7 \( ^\circ \text{C} \), which is also the dew-point temperature.

The water condensed from the products of combustion usually contains some dissolved gases and therefore may be quite corrosive. For this reason, the products of combustion are often kept above the dew point until discharged to the atmosphere.

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EXAMPLE 15.2E
Determine the molar analysis of the products of combustion when octane, \( \text{C}_8\text{H}_{18} \), is burned with 200% theoretical air, and determine the dew point of the products if the pressure is 14.7 lbf/in.\(^2\).

**Solution**

The equation for the combustion of octane with 200% theoretical air is

\[
\text{C}_8\text{H}_{18} + 12.5(2) \text{ O}_2 + 12.5(2)(3.76) \text{ N}_2 \rightarrow 8 \text{ CO}_2 + 9 \text{ H}_2\text{O} + 12.5 \text{ O}_2 + 94.0 \text{ N}_2
\]

Total moles of product = 8 + 9 + 12.5 + 94.0 = 123.5

Molar analysis of products:

- \( \text{CO}_2 \): \( \frac{8}{123.5} = 6.47\% \)
- \( \text{H}_2\text{O} \): \( \frac{9}{123.5} = 7.29\% \)
- \( \text{O}_2 \): \( \frac{12.5}{123.5} = 10.12\% \)
- \( \text{N}_2 \): \( \frac{94}{123.5} = 76.12\% \)

100.00%

The partial pressure of the \( \text{H}_2\text{O} \) is 14.7(0.0729) = 1.072 lbf/in.\(^2\).

The saturation temperature corresponding to this pressure is 104 \( ^\circ \text{F} \), which is also the dew-point temperature.
The water condensed from the products of combustion usually contains some dissolved gases and therefore may be quite corrosive. For this reason, the products of combustion are often kept above the dew point until discharged to the atmosphere.

**EXAMPLE 15.3** Producer gas from bituminous coal (see Table 15.2) is burned with 20% excess air. Calculate the air–fuel ratio on a volumetric basis and on a mass basis.

**Solution**

To calculate the theoretical air requirement, let us write the combustion equation for the combustible substances in 1 kmol of fuel.

\[
\begin{align*}
0.14H_2 + 0.070O_2 & \rightarrow 0.14H_2O \\
0.27CO + 0.135O_2 & \rightarrow 0.27CO_2 \\
0.03CH_4 + 0.06O_2 & \rightarrow 0.03CO_2 + 0.06H_2O \\
& 0.265 = \text{kmol oxygen required/kmol fuel} \\
& -0.006 = \text{oxygen in fuel/kmol fuel} \\
& -0.259 = \text{kmol oxygen required from air/kmol fuel}
\end{align*}
\]

Therefore, the complete combustion equation for 1 kmol of fuel is

\[
\begin{align*}
\text{fuel} & \rightarrow 0.20H_2O + 0.345CO_2 + 1.482N_2 \\
+0.259 & = \text{kmol air/kmol fuel} \\
\text{air} & = 0.259 \times 1.233 \times 1.200 = 1.48
\end{align*}
\]

If the air and fuel are at the same pressure and temperature, this also represents the ratio of the volume of air to the volume of fuel.

For 20% excess air, \( \frac{\text{kmol air}}{\text{kmol fuel}} = 1.48 \times 1.200 = 1.48 \)

The air–fuel ratio on a mass basis is

\[
AF = \frac{0.14(2) + 0.27(28) + 0.03(16) + 0.006(12) + 0.509(28) + 0.045(44)}{24.74} = 1.73 \text{ kg air/kg fuel}
\]

An analysis of the products of combustion affords a very simple method for calculating the actual amount of air supplied in a combustion process. There are various experimental methods by which such an analysis can be made. Some yield results on a “dry” basis, that
is, the fractional analysis of all the components, except for water vapor. Other experimental
procedures give results that include the water vapor. In this presentation we are not concerned
with the experimental devices and procedures, but rather with the use of such information
in a thermodynamic analysis of the chemical reaction. The following examples illustrate
how an analysis of the products can be used to determine the chemical reaction and the
composition of the fuel.

The basic principle in using the analysis of the products of combustion to obtain the
actual fuel–air ratio is conservation of the mass of each element. Thus, in changing from
reactants to products, we can make a carbon balance, hydrogen balance, oxygen balance, and
nitrogen balance (plus any other elements that may be involved). Furthermore, we recognize
that there is a definite ratio between the amounts of some of these elements. Thus, the ratio
between the nitrogen and oxygen supplied in the air is fixed, as well as the ratio between
carbon and hydrogen if the composition of a hydrocarbon fuel is known.

**EXAMPLE 15.4**

Methane (CH₄) is burned with atmospheric air. The analysis of the products on a dry basis
is as follows:

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>10.00%</td>
</tr>
<tr>
<td>O₂</td>
<td>2.37</td>
</tr>
<tr>
<td>CO</td>
<td>0.53</td>
</tr>
<tr>
<td>N₂</td>
<td>87.10</td>
</tr>
<tr>
<td></td>
<td>100.00%</td>
</tr>
</tbody>
</table>

Calculate the air–fuel ratio and the percent theoretical air and determine the com-
bustion equation.

**Solution**

The solution consists of writing the combustion equation for 100 kmol of dry products,
introducing letter coefficients for the unknown quantities, and then solving for them.

From the analysis of the products, the following equation can be written, keeping in
mind that this analysis is on a dry basis.

\[ a \text{CH}_4 + b \text{O}_2 + c \text{N}_2 \rightarrow 10.0 \text{CO}_2 + 0.53 \text{CO} + 2.37 \text{O}_2 + d \text{H}_2\text{O} + 87.1 \text{N}_2 \]

A balance for each of the elements will enable us to solve for all the unknown
coefficients:

**Nitrogen balance:**

\[ \frac{c}{b} = \frac{87.1}{3.76} = 23.16 \]

Since all the nitrogen comes from the air

**Carbon balance:**

\[ a = 10.00 + 0.53 = 10.53 \]

**Hydrogen balance:**

\[ d = 2a = 21.06 \]

**Oxygen balance:** All the unknown coefficients have been solved for, and therefore
the oxygen balance provides a check on the accuracy. Thus, b can also be determined by
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an oxygen balance

\[ \frac{b}{2} = 10.00 + \frac{0.53}{2} + 2.37 + \frac{21.06}{2} = 23.16 \]

Substituting these values for \( a, b, c, \) and \( d, \) we have

\[ 10.53 \text{CH}_4 + 23.16 \text{O}_2 + 87.1 \text{N}_2 \rightarrow 10.00 \text{CO}_2 + 0.53 \text{CO} + 2.37 \text{O}_2 + 21.06 \text{H}_2\text{O} + 87.1 \text{N}_2 \]

Dividing through by 10.53 yields the combustion equation per kmol of fuel.

\[ \text{CH}_4 + 2.2 \text{O}_2 + 8.27 \text{N}_2 \rightarrow 0.95 \text{CO}_2 + 0.05 \text{CO} + 2 \text{H}_2\text{O} + 0.225 \text{O}_2 + 8.27 \text{N}_2 \]

The air-fuel ratio on a mole basis is

\[ \frac{2.2 + 8.27}{10.47} = 10.47 \text{ kmol air/kmol fuel} \]

The air-fuel ratio on a mass basis is found by introducing the molecular masses.

\[ AF = \frac{10.47 \times 28.97}{16.0} = 18.97 \text{ kg air/kg fuel} \]

The theoretical air-fuel ratio is found by writing the combustion equation for theoretical air.

\[ \text{CH}_4 + 2\text{O}_2 + 2(3.76)\text{N}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} + 7.52 \text{N}_2 \]

\[ \frac{\text{AF}_\text{theo}}{10.0} = \frac{2(3.76)28.97}{18.0} = 17.23 \text{ kg air/kg fuel} \]

The percent theoretical air is \( \frac{18.97}{17.23} = 110\% \)

EXAMPLE 15.5  Coal from Jenkin, Kentucky, has the following ultimate analysis on a dry basis, percent by mass:

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent by Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur</td>
<td>0.6</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>5.7</td>
</tr>
<tr>
<td>Carbon</td>
<td>79.2</td>
</tr>
<tr>
<td>Oxygen</td>
<td>10.0</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.5</td>
</tr>
<tr>
<td>Ash</td>
<td>3.0</td>
</tr>
</tbody>
</table>

This coal is to be burned with 30% excess air. Calculate the air-fuel ratio on a mass basis.

Solution

One approach to this problem is to write the combustion equation for each of the combustible elements per 100 kg of fuel. The molal composition per 100 kg of fuel is
found first.

\[
\begin{align*}
\text{kmol} \ S/100 \text{kg fuel} &= 0.6 \frac{32}{32} = 0.02 \\
\text{kmol} \ H_2/100 \text{kg fuel} &= 5.7 \frac{2}{2} = 2.85 \\
\text{kmol} \ C/100 \text{kg fuel} &= 79.2 \frac{12}{12} = 6.60 \\
\text{kmol} \ O_2/100 \text{kg fuel} &= 10 \frac{32}{32} = 0.31 \\
\text{kmol} \ N_2/100 \text{kg fuel} &= 1.5 \frac{28}{28} = 0.05
\end{align*}
\]

The combustion equations for the combustible elements are now written, which enables us to find the theoretical oxygen required.

\[
\begin{align*}
0.025 S + 0.02 O_2 &\rightarrow 0.02 SO_2 \\
2.85 H_2 + 1.42 O_2 &\rightarrow 2.85 H_2O \\
6.60 C + 6.60 O_2 &\rightarrow 6.60 CO_2
\end{align*}
\]

\[
8.04 \text{kmol} \ O_2 \text{required/100 kg fuel}
\]

\[
8.04 \times 0.02 = 0.16 \text{kmol} \ O_2 \text{in fuel/100 kg fuel}
\]

\[
7.73 \text{kmol} \ O_2 \text{from air/100 kg fuel}
\]

\[
AF_{theo} = \frac{7.73 + 7.73(3.76)28.97}{100} = 10.63 \text{ kg air/kg fuel}
\]

For 30% excess air the air-fuel ratio is

\[
AF = 1.3 \times 10.63 = 13.82 \text{ kg air/kg fuel}
\]

In-Text Concept Questions

a. How many kmoles of air are needed to burn 1 kmol of carbon?

b. If I burn 1 kmol of hydrogen (H\(_2\)) with 6 kmol of air, what is the air-fuel ratio on a mole basis and what is the percent theoretical air?

c. For the 110% theoretical air in Eq. 15.8, what is the equivalence ratio? Is that mixture rich or lean?

d. In most cases, combustion products are exhausted above the dew point. Why?

15.3 ENTHALPY OF FORMATION

In the first 14 chapters of this book, the problems always concerned a fixed chemical composition and never a change of composition through a chemical reaction. Therefore, in dealing with a thermodynamic property, we used tables of thermodynamic properties for the given substance, and in each of these tables the thermodynamic properties were given...
relative to some arbitrary base. In the steam tables, for example, the internal energy of saturated liquid at 0.01 °C is assumed to be zero. This procedure is quite adequate when there is no change in composition because we are concerned with the changes in the properties of a given substance. The properties at the condition of the reference state cancel out in the calculation. When dealing with reference states in Section 14.10, we noted that for a given substance (perhaps a component of a mixture), we are free to choose a reference state condition—for example, a hypothetical ideal gas—as long as we then carry out a consistent calculation from that state and condition to the real desired state. We also noted that we are free to choose a reference state value, as long as there is no subsequent inconsistency in the calculation of the change in a property because of a chemical reaction with a resulting change in the amount of a given substance. Now that we are to include the possibility of a chemical reaction, it will become necessary to choose these reference state values on a common and consistent basis. We will use as our reference state a temperature of 25 °C, a pressure of 0.1 MPa, and a hypothetical ideal-gas condition for those substances that are gases.

Consider the simple steady-state combustion process shown in Fig. 15.3. This idealized reaction involves the combustion of solid carbon with gaseous (ideal-gas) oxygen, each of which enters the control volume at the reference state, 25 °C and 0.1 MPa. The carbon dioxide (ideal gas) formed by the reaction leaves the chamber at the reference state, 25 °C and 0.1 MPa. If the heat transfer could be accurately measured, it would be found to be −393 522 kJ/kmol of carbon dioxide formed. The chemical reaction can be written

\[
\text{C} + \text{O}_2 \rightarrow \text{CO}_2
\]

Applying the first law to this process, we have

\[
Q_{cv} + H_R = H_P
\]

(15.10)

where the subscripts \(R\) and \(P\) refer to the reactants and products, respectively. We will find it convenient to also write the first law for such a process in the form

\[
Q_{cv} + \sum_R n_R h_R = \sum_P n_P h_P
\]

(15.11)

where the summations refer, respectively, to all the reactants or all the products.

Thus, a measurement of the heat transfer would give us the difference between the enthalpy of the products and the reactants, where each is in the reference state condition. Suppose, however, that we assign the value of zero to the enthalpy of all the elements at the reference state. In this case, the enthalpy of the reactants is zero, and

\[
Q_{cv} = H_P = -393 522 \text{ kJ/kmol}
\]

FIGURE 15.3
Example of the combustion process.

1 kmol O\(_2\)
25 °C, 0.1 MPa

1 kmol CO\(_2\)
25 °C, 0.1 MPa

1 kmol C
25 °C, 0.1 MPa
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The enthalpy of (hypothetical) ideal-gas carbon dioxide at 25°C, 0.1 MPa pressure (with reference to this arbitrary base in which the enthalpy of the elements is chosen to be zero), is called the enthalpy of formation. We designate this with the symbol $h_f$. Thus, for carbon dioxide

$$h_f^0 = -393,522 \text{ kJ/kmol}$$

The enthalpy of carbon dioxide in any other state, relative to this base in which the enthalpy of the elements is zero, would be found by adding the change of enthalpy between ideal gas at 25°C, 0.1 MPa, and the given state to the enthalpy of formation. That is, the enthalpy at any temperature and pressure, $h_T$, $P$, is

$$h_T, P = (h_f^0)_{298,0.1 \text{ MPa}} + (\Delta h)_{298,0.1 \text{ MPa} \rightarrow T, P}$$

(15.12)

where the term $(\Delta h)_{298,0.1 \text{ MPa} \rightarrow T, P}$ represents the difference in enthalpy between any given state and the enthalpy of ideal gas at 298.15 K, 0.1 MPa. For convenience we usually drop the subscripts in the examples that follow.

The procedure that we have demonstrated for carbon dioxide can be applied to any compound. Table A.10 gives values of the enthalpy of formation for a number of substances in the units kJ/kmol (or Btu/lbmol in Table F.11).

Three further observations should be made in regard to enthalpy of formation.

1. We have demonstrated the concept of enthalpy of formation in terms of the measurement of the heat transfer in an idealized chemical reaction in which a compound is formed from the elements. Actually, the enthalpy of formation is usually found by the application of statistical thermodynamics, using observed spectroscopic data.

2. The justification of this procedure of arbitrarily assigning the value of zero to the enthalpy of the elements at 25°C, 0.1 MPa, rests on the fact that in the absence of nuclear reactions the mass of each element is conserved in a chemical reaction. No conflicts or ambiguities arise with this choice of reference state, and it proves to be very convenient in studying chemical reactions from a thermodynamic point of view.

3. In certain cases, an element or compound can exist in more than one state at 25°C, 0.1 MPa. Carbon, for example, can be in the form of graphite or diamond. It is essential that the state to which a given value is related be clearly identified. Thus, in Table A.10, the enthalpy of formation of graphite is given the value of zero, and the enthalpy of each substance that contains carbon is given relative to this base. Another example is that oxygen may exist in the monatomic or diatomic form and also as ozone, O$_3$. The value chosen as zero is for the form that is chemically stable at the reference state, which in the case of oxygen is the diatomic form. Then each of the other forms must have an enthalpy of formation consistent with the chemical reaction and heat transfer for the reaction that produces that form of oxygen.

It will be noted from Table A.10 that two values are given for the enthalpy of formation for water; one is for liquid water and the other for gaseous (hypothetical ideal-gas) water, both at the reference state of 25°C, 0.1 MPa. It is convenient to use the hypothetical ideal-gas reference in connection with the ideal-gas table property changes given.
in Table A.9 and to use the real liquid reference in connection with real water property changes as given in the steam tables, Table B.1. The real-liquid reference state properties are obtained from those at the hypothetical ideal-gas reference by following the procedure of calculation described in Section 14.10. The same procedure can be followed for other substances that have a saturation pressure less than 0.1 MPa at the reference temperature of 25°C.

Frequently, students are bothered by the minus sign when the enthalpy of formation is negative. For example, the enthalpy of formation of carbon dioxide is negative. This is quite evident because the heat transfer is negative during the steady-flow chemical reaction, and the enthalpy of the carbon dioxide must be less than the sum of enthalpy of the carbon and oxygen initially, both of which are assigned the value of zero. This is analogous to the situation we would have in the steam tables if we let the enthalpy of saturated vapor be zero at 0.1 MPa pressure. In this case the enthalpy of the liquid would be negative, and we would simply use the negative value for the enthalpy of the liquid when solving problems.

**15.4 FIRST-LAW ANALYSIS OF REACTING SYSTEMS**

The significance of the enthalpy of formation is that it is most convenient in performing a first-law analysis of a reacting system, for the enthalpies of different substances can be added or subtracted, since they are all given relative to the same base.

In such problems, we will write the first law for a steady-state, steady-flow process in the form

\[ Q_{c.v.} + H_R = W_{c.v.} + H_P \]

or

\[ Q_{c.v.} + \sum n_i h_i = W_{c.v.} + \sum p_i e_i \]

where \( R \) and \( P \) refer to the reactants and products, respectively. In each problem it is necessary to choose one parameter as the basis of the solution. Usually this is taken as 1 kmol of fuel.

**EXAMPLE 15.6** Consider the following reaction, which occurs in a steady-state, steady-flow process.

\[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O(l)} \]

The reactants and products are each at a total pressure of 0.1 MPa and 25°C. Determine the heat transfer per kilomole of fuel entering the combustion chamber.

Control volume: Combustion chamber.

Inlet state: P and T known; state fixed.

Exit state: P and T known; state fixed.

Process: Steady state.

Model: Three gases ideal gases; real liquid water.
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Analysis

First law:

\[ Q_{c.v.} + \sum n_i \delta h_i = \sum n_i R_{eq} \]

Solution

Using values from Table A.10, we have

\[ \sum n_i \delta h_i = (\delta h^0_{CH4}) = -74 873 \text{ kJ} \]

\[ \sum n_i R_{eq} = (\delta h^0_{CO2}) + 2(\delta h^0_{H2O(l)}) \]

\[ = -393 522 + 2(-285 830) = -965 182 \text{ kJ} \]

\[ Q_{c.v.} = -965 182 - (-74 873) = -890 309 \text{ kJ} \]

In most instances, however, the substances that comprise the reactants and products in a chemical reaction are not at a temperature of 25°C and a pressure of 0.1 MPa (the state at which the enthalpy of formation is given). Therefore, the change of enthalpy between 25°C and 0.1 MPa and the given state must be known. For a solid or liquid, this change of enthalpy can usually be found from a table of thermodynamic properties or from specific heat data. For gases, the change of enthalpy can usually be found by one of the following procedures.

1. Assume ideal-gas behavior between 25°C, 0.1 MPa, and the given state. In this case, the enthalpy is a function of the temperature only and can be found by an equation of \( C_p^{0} \) or from tabulated values of enthalpy as a function of temperature (which assumes ideal-gas behavior). Table A.6 gives an equation for \( C_p^{0} \) for a number of substances and Table A.9 gives values of \( \delta h^0 \) (that is, the \( \Delta h \) of Eq. 15.12) in kJ/kmol. \( (C_{p}^{0}\text{ref}) \) refers to 25°C or 298.15 K. For simplicity this is designated \( \Delta h^0 \). The superscript 0 is used to designate that this is the enthalpy at 0.1 MPa pressure, based on ideal-gas behavior, that is, the standard-state enthalpy.

2. If a table of thermodynamic properties is available, \( \Delta h \) can be found directly from these tables if a real-substance behavior reference state is being used, such as that described above for liquid water. If a hypothetical ideal-gas reference state is being used, then it is necessary to account for the real-substance correction to properties at that state to gain entry to the tables.

3. If the deviation from ideal-gas behavior is significant but no tables of thermodynamic properties are available, the value of \( \Delta h \) can be found from the generalized tables or charts and the values for \( C_p^{0} \) or \( \Delta h \) at 0.1 MPa pressure as indicated above.

Thus, in general, for applying the first law to a steady-state process involving a chemical reaction and negligible changes in kinetic and potential energy, we can write

\[ Q_{c.v.} + \sum n_i (\delta h_i + \Delta h_i) = W_{c.v.} + \sum n_i (R_{eq} + \Delta h_{eq}) \]  (15.13)
EXAMPLE 15.7 Calculate the enthalpy of water (on a kmole basis) at 3.5 MPa, 300 °C, relative to the 25 °C and 0.1 MPa base, using the following procedures.

1. Assume the steam to be an ideal gas with the value of \( C_p^0 \) given in Table A.6.
2. Assume the steam to be an ideal gas with the value for \( \Delta \bar{H} \) as given in Table A.9.
3. The steam tables.
4. The specific heat behavior given in 2 above and the generalized charts.

Solution

For each of these procedures, we can write

\[
\bar{h}_{T, P} = (\bar{h}^0_f + \Delta \bar{H})
\]

The only difference is in the procedure by which we calculate \( \Delta \bar{H} \). From Table A.10 we note that

\[
(\bar{h}^0_f)_{H_2O(g)} = -241 826 \text{ kJ/kmol}
\]

1. Using the specific heat equation for \( H_2O(g) \) from Table A.6,

\[
C_p = 1.79 + 0.107\theta + 0.586\theta^2 - 0.20\theta^3, \theta = T/1000
\]

The specific heat at the average temperature

\[
T_{avg} = \frac{298.15 + 573.15}{2} = 435.65 \text{ K}
\]

is

\[
C_{p\theta} = 1.79 + 0.107(0.43565) + 0.586(0.43565)^2 - 0.2(0.43565)^3
\]

\[
= 1.9313 \text{ kJ/kg K}
\]

Therefore,

\[
\Delta \bar{H} = M C_{p\theta} \Delta T\]

\[
= 18.015 \times 1.9313(573.15 - 298.15) = 9568 \text{ kJ/kmol}
\]

\[
\bar{h}_{T, P} = -241 826 + 9568 = -232 258 \text{ kJ/kmol}
\]

2. Using Table A.9 for \( H_2O(g) \),

\[
\Delta \bar{H} = 9539 \text{ kJ/kmol}
\]

\[
\bar{h}_{T, P} = -241 826 + 9539 = -232 287 \text{ kJ/kmol}
\]

3. Using the steam tables, either the liquid reference or the gaseous reference state may be used.
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For the liquid,
\[ \Delta h = 18.015(2977.5 - 104.9) = 51.750 \text{ kJ/kmol} \]
\[ P_{T_P} = -285.830 + 51.750 = -234.080 \text{ kJ/kmol} \]

For the gas,
\[ \Delta h = 18.015(2977.5 - 2547.2) = 7752 \text{ kJ/kmol} \]
\[ P_{T_P} = -241.826 + 7752 = -234.074 \text{ kJ/kmol} \]

The very small difference results from using the enthalpy of saturated vapor at 25°C (which is almost but not exactly an ideal gas) in calculating the \( \Delta h \).

4. When using the generalized charts, we use the notation introduced in Chapter 14.
\[ P_{T_P} = P_0 - (P_2 - P_1) + (P_2^* - P_1^*) + (P_1^* - P_1) \]

where the subscript 2 refers to the state at 3.5 MPa, 300 °C, and state 1 refers to the state at 0.1 MPa, 25°C.

From part 2,
\[ P_2 - P_1 = 9539 \text{ kJ/kmol} \]
\[ P_1^* = P_2 = 0 \text{ (ideal-gas reference)} \]
\[ P_{T_P} = \frac{3.5}{273.09} = 0.158, \quad T_2 = \frac{573.2}{647.3} = 0.886 \]

From the generalized enthalpy chart, Fig. D.2,
\[ \frac{P_{T_P}}{P_{T_0}} = 0.21, \quad \frac{P_2 - P_1}{P_{T_P}} = 0.21 \times 8.3145 \times 647.3 = 1130 \text{ kJ/kmol} \]
\[ P_{T_P} = -241.826 - 1130 + 9539 = -233.417 \text{ kJ/kmol} \]

Note that if the software is used including the acentric factor correction (value from Table D.4), as discussed in Section 14.7, the enthalpy correction is found to be 0.298 instead of 0.21 and the enthalpy is then \(-233.996 \text{ kJ/kmol}\), which is considerably closer to the values found for the steam tables in procedure 3 above, the most accurate value.

The approach that is used in a given problem will depend on the data available for the given substance.

EXAMPLE 15.8

A small gas turbine uses \( C_8H_{18}(l) \) for fuel and 400% theoretical air. The air and fuel enter at 25°C, and the products of combustion leave at 900 K. The output of the engine and the fuel consumption are measured, and it is found that the specific fuel consumption is
0.25 kg/s of fuel per megawatt output. Determine the heat transfer from the engine per kilomole of fuel. Assume complete combustion.

Control volume: Gas-turbine engine.
Inlet states: T known for fuel and air.
Exit state: T known for combustion products.
Process: Steady state.
Model: All gases ideal gases, Table A.9; liquid octane, Table A.10.

Analysis

The combustion equation is

\[ C_{8}H_{18}(l) + \frac{4}{12.5}O_{2} + \frac{4}{12.5}(3.76)N_{2} \rightarrow 8CO_{2} + 9H_{2}O + 37.5O_{2} + 188N_{2} \]

First law:

\[ Q_{c.v.} + \sum n_{i}(\Delta h_{f})_{i} = W_{c.v.} + \sum P_{ne}(\Delta h_{e})_{e} \]

Solution

Since the air is composed of elements and enters at 25°C, the enthalpy of the reactants is equal to that of the fuel.

\[ \sum n_{i}(\Delta h_{f})_{i} = (\Delta h_{f})_{C_{8}H_{18}(l)} = -250\,105\,kJ/kmol\,fuel \]

Considering the products, we have

\[ \sum n_{e}(\Delta h_{e})_{e} = n_{CO_{2}}(\Delta h_{e})_{CO_{2}} + n_{H_{2}O}(\Delta h_{e})_{H_{2}O} + n_{O_{2}}(\Delta h_{e})_{O_{2}} + n_{N_{2}}(\Delta h_{e})_{N_{2}} \]

\[ = 8(-393.522 + 28.030) + 9(-241.826 + 21.937) + 37.5(19.241) + 188(18.225) \]

\[ = -755\,476\,kJ/kmol\,fuel \]

\[ W_{c.v.} = \frac{1000\,kJ/s}{\frac{25\,kg/s}{kmol}} = 456\,920\,kJ/kmol\,fuel \]

Therefore, from the first law,

\[ Q_{c.v.} = -755\,476 + 456\,920 - (-250\,105) \]

\[ = -48\,451\,kJ/kmol\,fuel \]
of fuel per horsepower-hour. Determine the heat transfer from the engine per pound mole of fuel. Assume complete combustion.

Control volume: Gas-turbine engine.
Inlet states: T known for fuel and air.
Exit state: T known for combustion products.
Process: Steady state.
Model: All gases ideal gases, Table F.6; liquid octane, Table F.11.

Analysis

The combustion equation is

\[
C_8H_{18}^{(l)} + 4(12.5)O_2 + 4(12.5)(3.76)N_2 \rightarrow 8CO_2 + 9H_2O + 37.5O_2 + 188.0N_2
\]

First law:

\[
Q_{c,v} + \sum_{i} R n_i (h^0_f + \Delta h) = W_{c,v} + \sum_{e} P n_e (h^0_f + \Delta h)
\]

Solution

Since the air is composed of elements and enters at 77 F, the enthalpy of the reactants is equal to that of the fuel.

\[
\sum_{i} n_i (h^0_f + \Delta h) = (h^0_f)_{C_8H_{18}^{(l)}} = -107526 \text{ Btu/lb mol}
\]

Considering the products

\[
\sum_{e} n_e (h^0_f + \Delta h) = n_{CO_2}(h^0_f + \Delta h)_{CO_2} + n_{H_2O}(h^0_f + \Delta h)_{H_2O} + n_{O_2}(\Delta h)_{O_2} + n_{N_2}(\Delta h)_{N_2}
\]

\[
= 8(-169184 + 11391) + 9(-103966 + 8867) + 37.5(7784) + 188(7374)
\]

\[
= -439803 \text{ Btu/lb mol fuel}
\]

\[
W_{c,v} = 2544 \times 114.23 = 290601 \text{ Btu/lb mol fuel}
\]

Therefore, from the first law,

\[
Q_{c,v} = -439803 + 290601 - (-107526)
\]

\[
= -41876 \text{ Btu/lb mol fuel}
\]

EXAMPLE 15.9 A mixture of 1 kmol of gaseous ethene and 3 kmol of oxygen at 25°C reacts in a constant-volume bomb. Heat is transferred until the products are cooled to 600 K. Determine the amount of heat transfer from the system.

Control mass: Constant-volume bomb.
Initial state: T known.
Final state:  T known.
Process:  Constant volume.

Analysis
The chemical reaction is
\[ C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O(g) \]
First law:
\[ Q + U_R = U_F \]
\[ Q + \sum n_i (\Delta h^f_i + \Delta h - RT) = \sum P_n (\Delta h^f_i + \Delta h - RT) \]

Solution
Using values from Tables A.9 and A.10, gives
\[ \sum n_i (\Delta h^f_i + \Delta h - RT) = (\Delta h^f_i - RT)_{C_2H_4} - n_0 (\Delta h^f_i - RT)_{O_2} = (\Delta h^f_i)_{C_2H_4} - 4RT \]
\[ = 52467 - 4 \times 70945 \times 298.2 = 42550 \text{kJ} \]
\[ \sum P_n (\Delta h^f_i + \Delta h - RT) = 2(\Delta h^f_i)_{CO_2} + 2(\Delta h^f_i)_{H_2O(l)} - 4RT \]
\[ = 2(-393522 + 12906) + 2(-241826 + 10499) \]
\[ = -21243841 \text{kJ} \]
Therefore,
\[ Q = -1243841 - 42550 = -1286391 \text{kJ} \]

For a real-gas mixture, a pseudocritical method such as Kay’s rule, Eq. 14.83, could be used to evaluate the nonideal-gas contribution to enthalpy at the temperature and pressure of the mixture and this value added to the ideal-gas mixture enthalpy at that temperature, as in the procedure developed in Section 14.10.

15.5 ENTHALPY AND INTERNAL ENERGY OF COMBUSTION; HEAT OF REACTION
The enthalpy of combustion, \( h_{RP} \), is defined as the difference between the enthalpy of the products and the enthalpy of the reactants when complete combustion occurs at a given temperature and pressure. That is,
\[ h_{RP} = H_P - H_R \]
\[ h_{RP} = \sum e_x (\Delta h^f_x + \Delta h) - \sum n_i (\Delta h^f_i + \Delta h_i) \] (15.14)
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The usual parameter for expressing the enthalpy of combustion is a unit mass of fuel, such as a kilogram \( h_{RP} \) or a kilomole \( \overline{h}_{RP} \) of fuel. As the enthalpy of formation is fixed, we can separate the terms as

\[
H = H^0 + \Delta H
\]

where

\[
H_k^0 = \sum n_i \overline{H}_i^0; \quad \Delta H_k = \sum n_i \Delta \overline{H}_i
\]

and

\[
H_p^0 = \sum n_i \overline{H}_i^0; \quad \Delta H_p = \sum n_i \Delta \overline{H}_i
\]

Now the difference in enthalpies is written

\[
H_P - H_k = H_P^0 - H_k^0 + \Delta H_P - \Delta H_k
\]

explicitly showing the reference enthalpy of combustion, \( h_{RP}^0 \), and the two departure terms \( \Delta H_P \) and \( \Delta H_k \). The latter two terms for the products and reactants are nonzero if they exist at a state other than the reference state.

The tabulated values of the enthalpy of combustion of fuels are usually given for a temperature of 25 °C and a pressure of 0.1 MPa. The enthalpy of combustion for a number of hydrocarbon fuels at this temperature and pressure, which we designate \( h_{RP}^0 \), is given in Table 15.3.

The internal energy of combustion is defined in a similar manner.

\[
u_{RP} = U_P - U_R = \sum n_i (\overline{H}_i^0 + \Delta \overline{H} - P \overline{V})_i - \sum n_i (\overline{H}_i^0 + \Delta \overline{H} - P \overline{V})_i
\]  

(15.16)

When all the gaseous constituents can be considered as ideal gases, and the volume of the liquid and solid constituents is negligible compared to the value of the gaseous constituents, this relation for \( \overline{u}_{RP} \) reduces to

\[
\pi_{RP} = \pi_{RP}^0 - \overline{p}(n_{gaseous \ products} - n_{gaseous \ reactants})
\]  

(15.17)

Frequently the term heating value or heat of reaction is used. This represents the heat transferred from the chamber during combustion or reaction at constant temperature. In the case of a constant pressure or steady-flow process, we conclude from the first law of thermodynamics that it is equal to the negative of the enthalpy of combustion. For this reason, this heat transfer is sometimes designated the constant-pressure heating value for combustion processes.

In the case of a constant-volume process, the heat transfer is equal to the negative of the internal energy of combustion. This is sometimes designated the constant-volume heating value in the case of combustion.

When the term heating value is used, the terms higher and lower heating value are used. The higher heating value is the heat transfer with liquid water in the products, and the lower heating value is the heat transfer with vapor water in the products.
### Table 15.3

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Formula</th>
<th>Liq. HC</th>
<th>Gas HC</th>
<th>Liq. HC</th>
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CHAPTER FIFTEEN
CHEMICAL REACTIONS

EXAMPLE 15.10
Calculate the enthalpy of combustion of propane at 25°C on both a kilomole and kilogram basis under the following conditions:

1. Liquid propane with liquid water in the products.
2. Liquid propane with gaseous water in the products.
3. Gaseous propane with liquid water in the products.
4. Gaseous propane with gaseous water in the products.

This example is designed to show how the enthalpy of combustion can be determined from enthalpies of formation. The enthalpy of evaporation of propane is 370 kJ/kg.

Analysis and Solution
The basic combustion equation is

\[ \text{C}_3\text{H}_8 + 5 \text{O}_2 \rightarrow 3 \text{CO}_2 + 4 \text{H}_2\text{O} \]

From Table A.10 \( (h_f)_\text{C}_3\text{H}_8(\text{g}) = -103\,900 \) kJ/kmol. Therefore,

\[ (h_f)_\text{C}_3\text{H}_8(\text{l}) = -103\,900 - 44\,097(370) = -120\,216 \text{ kJ/kmol} \]

1. Liquid propane–liquid water:

\[ (h_f)_\text{RP} = 3(h_f)_\text{CO}_2 + 4(h_f)_\text{H}_2\text{O}(\text{l}) - (h_f)_\text{C}_3\text{H}_8(\text{l}) \]

\[ = 3(-393\,522) + 4(-285\,830) - (-120\,216) \]

\[ = -2\,203\,670 \text{ kJ/kmol} \]

The higher heating value of liquid propane is 49 973 kJ/kg.

2. Liquid propane–gaseous water:

\[ (h_f)_\text{RP} = 3(h_f)_\text{CO}_2 + 4(h_f)_\text{H}_2\text{O}(\text{g}) - (h_f)_\text{C}_3\text{H}_8(\text{l}) \]

\[ = 3(-393\,522) + 4(-241\,826) - (-120\,216) \]

\[ = -2\,027\,654 \text{ kJ/kmol} \]

The lower heating value of liquid propane is 45 982 kJ/kg.

3. Gaseous propane–liquid water:

\[ (h_f)_\text{RP} = 3(h_f)_\text{CO}_2 + 4(h_f)_\text{H}_2\text{O}(\text{l}) - (h_f)_\text{C}_3\text{H}_8(\text{g}) \]

\[ = 3(-393\,522) + 4(-285\,830) - (-103\,900) \]

\[ = -2\,219\,986 \text{ kJ/kmol} \]

The higher heating value of gaseous propane is 50 343 kJ/kg.
4. Gaseous propane–gaseous water:

$$h_{RP} = 3(h_{f}^{0})_{CO_{2}} + 4(h_{f}^{0})_{H_{2}O(g)} - (h_{f}^{0})_{C_{3}H_{8}(g)}$$

$$= 3(-393.522) + 4(-241.826) - (-103.900)$$

$$= -2,043,970 \text{ kJ/kmol}$$

$$= -46,352 \text{ kJ/kg}$$

The lower heating value of gaseous propane is 46,352 kJ/kg.

Each of the four values calculated in this example corresponds to the appropriate value given in Table 15.3.

EXAMPLE 15.11

Calculate the enthalpy of combustion of gaseous propane at 500 K. (At this temperature all the water formed during combustion will be vapor.) This example will demonstrate how the enthalpy of combustion of propane varies with temperature. The average constant-pressure specific heat of propane between 25°C and 500 K is 2.1 kJ/kg K.

Analysis

The combustion equation is

$$C_{8}H_{18}(g) + 5O_{2} \rightarrow 3CO_{2} + 4H_{2}O(g)$$

The enthalpy of combustion is, from Eq. 15.13,

$$h_{R} = \sum_{i} n_{i}(h_{T}^{0} + \Delta h_{i})$$

Solution

$$h_{R} = \sum_{i} n_{i}(h_{T}^{0} + \Delta h_{i})$$

$$= -103,900 + 2.1 \times 44.097(500 - 298.2) + 5(6086)$$

$$= -54,783 \text{ kJ/kmol}$$

$$h_{R} = n_{CO_{2}}(h_{T}^{0} + \Delta h_{CO_{2}}) + n_{H_{2}O}(h_{T}^{0} + \Delta h_{H_{2}O})$$

$$= 3(-393.522 + 8305) + 4(-241.826 + 6922)$$

$$= -2,695,267 \text{ kJ/kmol}$$

$$h_{R} = -2,040,484$$

$$= -46,273 \text{ kJ/kg}$$

This compares with a value of -46,352 at 25°C.
CHAPTER FIFTEEN
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This problem could also have been solved using the given value of the enthalpy of combustion at 25°C by noting that

$$
\Pi_{\text{f,comb}} = (\Delta H_p)_{500} - (\Delta H_s)_{500} \\
= n_{\text{CO}_2}(\Delta h)_{\text{CO}_2} + n_{\text{H}_2\text{O}}(\Delta h)_{\text{H}_2\text{O}} \\
- [\Delta H_f^{\text{avg}}(\Delta T)_{\text{C}_3\text{H}_8}] - n_{\text{O}_2}(\Delta h)_{\text{O}_2} \\
= n_{\text{CO}_2}(\Delta h)_{\text{CO}_2} + n_{\text{H}_2\text{O}}(\Delta h)_{\text{H}_2\text{O}} \\
- [\Delta H_f^{\text{avg}}(\Delta T)_{\text{C}_3\text{H}_8}] - n_{\text{O}_2}(\Delta h)_{\text{O}_2} \\
= -46,352 \times 44.097 + 3(6305) + 4(6922) \\
- 2.1 \times 44.097(500 - 298.2) - 5(6086) \\
= -2,040,499 \text{kJ/mol} \\
= -2,040,499/44.097 = -46,273 \text{kJ/kg}
$$

15.6 ADIABATIC FLAME TEMPERATURE

Consider a given combustion process that takes place adiabatically and with no work or changes in kinetic or potential energy involved. For such a process the temperature of the products is referred to as the adiabatic flame temperature. With the assumptions of no work and no changes in kinetic or potential energy, this is the maximum temperature that can be achieved for the given reactants because any heat transfer from the reacting substances and any incomplete combustion would tend to lower the temperature of the products.

For a given fuel and given pressure and temperature of the reactants, the maximum adiabatic flame temperature that can be achieved is with a stoichiometric mixture. The adiabatic flame temperature can be controlled by the amount of excess air that is used. This is important, for example, in gas turbines, where the maximum permissible temperature is determined by metallurgical considerations in the turbine and close control of the temperature of the products is essential.

Example 15.12 shows how the adiabatic flame temperature may be found. The dissociation that takes place in the combustion products, which has a significant effect on the adiabatic flame temperature, will be considered in the next chapter.

EXAMPLE 15.12
Liquid octane at 25°C is burned with 400% theoretical air at 25°C in a steady-state process. Determine the adiabatic flame temperature.

Control volume: Combustion chamber.
Inlet states: T known for fuel and air.
Process: Steady state.
Model: Gases ideal gases, Table A.9: liquid octane, Table A.10.
ADIABATIC FLAME TEMPERATURE

Analysis

The reaction is
\[ C_8H_{18} + 4(12.5)O_2 + 4(12.5)(3.76)N_2 \rightarrow 8CO_2 + 9H_2O(g) + 37.5 O_2 + 188.0 N_2 \]

First law: Since the process is adiabatic,
\[ H_f = H_p \]
\[ \sum n_i (\bar{H}_f + \Delta \bar{H}_i) = \sum n_e (\bar{H}_f + \Delta \bar{H}_e) \]
where \( \Delta \bar{H}_e \) refers to each constituent in the products at the adiabatic flame temperature.

Solution

From Tables A.9 and A.10,
\[ H_f = \sum n_i (\bar{H}_f + \Delta \bar{H}_i) = (\bar{H}_f)_C = -250,105 \text{ kJ/kg fuel} \]
\[ H_p = \sum n_e (\bar{H}_f + \Delta \bar{H}_e) = 8(-393,522 + 28,030) + 9(-241,826 + 21,892) + 37.5(19,249) + 188(18,222) = -755,769 \text{ kJ/kg fuel} \]

By trial-and-error solution, a temperature of the products is found that satisfies this equation. Assume that
\[ T_F = 900 \text{ K} \]
\[ H_p = \sum n_e (\bar{H}_f + \Delta \bar{H}_e) = 8(-393,522 + 28,030) + 9(-241,826 + 21,892) + 37.5(19,249) + 188(18,222) = -755,769 \text{ kJ/kg fuel} \]

Assume that
\[ T_F = 1000 \text{ K} \]
\[ H_p = \sum n_e (\bar{H}_f + \Delta \bar{H}_e) = 8(-393,522 + 33,400) + 9(-241,826 + 25,956) + 37.5(22,710) + 188(21,461) = 62,487 \text{ kJ/kg fuel} \]

Since \( H_p = H_f = -250,105 \text{ kJ/kg fuel} \), we find by linear interpolation that the adiabatic flame temperature is 961.8 K. Because the ideal-gas enthalpy is not really a linear function of temperature, the true answer will be slightly different from this value.
In-Text Concept Questions

e. How is a fuel enthalpy of combustion connected to its enthalpy of formation?
f. What are the higher and lower heating values HHV, LHV of n-butane?
g. What is the value of $h_{fg}$ for n-octane?
h. What happens to the adiabatic flame temperature when I burn rich and when I burn lean?

15.7 THE THIRD LAW OF THERMODYNAMICS AND ABSOLUTE ENTROPY

As we consider a second-law analysis of chemical reactions, we face the same problem we had with the first law: What base should be used for the entropy of the various substances? This problem leads directly to a consideration of the third law of thermodynamics.

The third law of thermodynamics was formulated during the early twentieth century. The initial work was done primarily by W. H. Nernst (1864–1941) and Max Planck (1858–1947). The third law deals with the entropy of substances at absolute zero temperature and in essence states that the entropy of a perfect crystal is zero at absolute zero. From a statistical point of view, this means that the crystal structure has the maximum degree of order. Furthermore, because the temperature is absolute zero, the thermal energy is minimum. It also follows that a substance that does not have a perfect crystalline structure at absolute zero, but instead has a degree of randomness, such as a solid solution or a glassy solid, has a finite value of entropy at absolute zero. The experimental evidence on which the third law rests is primarily data on chemical reactions at low temperatures and measurements of heat capacity at temperatures approaching absolute zero. In contrast to the first and second laws, which lead, respectively, to the properties of internal energy and entropy, the third law deals only with the question of entropy at absolute zero. However, the implications of the third law are quite profound, particularly in respect to chemical equilibrium.

The relevance of the third law is that it provides an absolute base from which to measure the entropy of each substance. The entropy relative to this base is termed the absolute entropy. The increase in entropy between absolute zero and any given state can be found either from calorimetric data or by procedures based on statistical thermodynamics. The calorimetric method gives precise measurements of specific-heat data over the temperature range, as well as of the energy associated with phase transformations. These measurements are in agreement with the calculations based on statistical thermodynamics and observed molecular data.

Table A.10 gives the absolute entropy at 25°C and 0.1 MPa pressure for a number of substances. Table A.9 gives the absolute entropy for a number of gases at 0.1 MPa pressure and various temperatures. For gases the numbers in all these tables are the hypothetical ideal-gas values. The pressure $P^0$ of 0.1 MPa is termed the standard-state pressure, and the absolute entropy as given in these tables is designated $s^0$. The temperature is designated in kelvins with a subscript such as $s^0_{298}$.

If the value of the absolute entropy is known at the standard-state pressure of 0.1 MPa and a given temperature, it is a straightforward procedure to calculate the entropy change from this state (whether hypothetical ideal gas or real substance) to another desired state.
following the procedure described in Section 14.10. If the substance is listed in Table A.9, then
\[ s_{T,P} = s_{0}^{T} - R \ln \frac{P}{P_{0}} + (s_{T,P} - s_{0}^{T}) \] (15.18)
In this expression, the first term on the right side is the value from Table A.9, the second is the ideal-gas term to account for a change in pressure from \( P_{0} \) to \( P \), and the third is the term that corrects for real-substance behavior, as given in the generalized entropy chart in Appendix A. If the real-substance behavior is to be evaluated from an equation of state or thermodynamic table of properties, the term for the change in pressure should be made to a low pressure \( P^* \), at which ideal-gas behavior is a reasonable assumption, but it is also listed in the tables. Then
\[ s_{T,P} = s_{0}^{T} - R \ln \frac{P^*}{P_{0}} + (s_{T,P} - s_{0}^{T}) \] (15.19)
If the substance is not one of those listed in Table A.9, and the absolute entropy is known only at one temperature \( T_{0} \), as given in Table A.10, for example, then it will be necessary to calculate from
\[ s_{T} = s_{0}^{T} + \int_{T_{0}}^{T} \frac{s_{mix}}{T} dT \] (15.20)
and then proceed with the calculation of Eq. 15.17 or 15.19.

If Eq. 15.18 is being used to calculate the absolute entropy of a substance in a region in which the ideal-gas model is a valid representation of the behavior of that substance, then the last term on the right side of Eq. 15.18 simply drops out of the calculation.

For calculation of the absolute entropy of a mixture of ideal gases at \( T, P \), the mixture entropy is given in terms of the component partial entropies as
\[ s_{mix} = \sum y_{i} s_{i}^* \] (15.21)
where
\[ s_{i}^* = s_{0}^{T_{i}} - R \ln \frac{P_{i}}{P_{0}} - R \ln \frac{y_{i}P}{P_{0}} \] (15.22)
For a real-gas mixture, a correction can be added to the ideal-gas entropy calculated from Eqs. 15.21 and 15.22 by using a pseudocritical method such as was discussed in Section 14.10. The corrected expression is
\[ s_{mix} = s_{mix}^{*} + (s - s_{0}^{T}) \] (15.23)
in which the second term on the right side is the correction term from the generalized entropy chart.

15.8 SECOND-LAW ANALYSIS OF REACTING SYSTEMS

The concepts of reversible work, irreversibility, and availability (exergy) were introduced in Chapter 10. These concepts included both the first and second laws of thermodynamics. We will now develop this matter further, and we will be particularly concerned with determining the maximum work (availability) that can be done through a combustion process and with examining the irreversibilities associated with such processes.
CHAPTER FIFTEEN

CHEMICAL REACTIONS

The reversible work for a steady-state process in which there is no heat transfer with reservoirs other than the surroundings, and also in the absence of changes in kinetic and potential energy, is, from Eq. 10.14 on a total mass basis,

\[ W_{\text{rev}} = \sum m_i (h_i - T_0 s_i) - \sum m_e (h_e - T_0 s_e) \]

Applying this equation to a steady-state process that involves a chemical reaction, and introducing the symbols from this chapter, we have

\[ W_{\text{rev}} = \sum R n_i (h_0 f_i + \Delta_h - T_0 s_i) - \sum P n_e (h_0 f_e + \Delta_h - T_0 s_e) \]  \tag{15.24}

Similarly, the irreversibility for such a process can be written as

\[ I = W_{\text{rev}} - W = \sum R n_i T_0 s_i - \sum P n_e T_0 s_e - Q_{\text{c.v.}} \]  \tag{15.25}

The availability, \( \psi \), for a steady-flow process, in the absence of kinetic and potential energy changes, is given by Eq. 10.22 as

\[ \psi = (h - T_0 s) - (h_0 - T_0 s_0) \]

We further note that if a steady-state chemical reaction takes place in such a manner that both the reactants and products are in temperature equilibrium with the surroundings, the Gibbs function \( g = h - T s \), defined in Eq. 14.14, becomes a significant variable. For such a process, in the absence of changes in kinetic and potential energy, the reversible work is given by the relation

\[ W_{\text{rev}} = \sum R n_i g_i - \sum P n_e g_e = -\Delta G \]  \tag{15.26}

in which

\[ \Delta G = \Delta H - T \Delta S \]  \tag{15.27}

We should keep in mind that Eq. 15.26 is a special case and that the reversible work is given by Eq. 15.24 if the reactants and products are not in temperature equilibrium with the surroundings.

Let us now consider the maximum work that can be done during a chemical reaction. For example, consider 1 kmol of hydrocarbon fuel and the necessary air for complete combustion, each at 0.1 MPa pressure and 25°C, the pressure and temperature of the surroundings. What is the maximum work that can be done as this fuel reacts with the air? From the considerations covered in Chapter 10, we conclude that the maximum work would be done if this chemical reaction took place reversibly and the products were finally in pressure and temperature equilibrium with the surroundings. We conclude that this reversible work could be calculated from the relation in Eq. 15.26,

\[ W_{\text{rev}} = \sum R n_i g_i - \sum P n_e g_e = -\Delta G \]

However, since the final state is in equilibrium with the surroundings, we could consider this amount of work to be the availability of the fuel and air.
EXAMPLE 15.13  Ethene (g) at 25°C and 0.1 MPa pressure is burned with 400% theoretical air at 25°C and 0.1 MPa pressure. Assume that this reaction takes place reversibly at 25°C and that the products leave at 25°C and 0.1 MPa pressure. To simplify this problem further, assume that the oxygen and nitrogen are separated before the reaction takes place (each at 0.1 MPa, 25°C), that the constituents in the products are separated, and that each is at 25°C and 0.1 MPa. Thus, the reaction takes place as shown in Fig. 15.4. This is not a realistic situation, since the oxygen and nitrogen in the air entering are in fact mixed, as would also be the products of combustion exiting the chamber. This is a commonly used model, however, for the purposes of establishing a standard for comparison with other chemical reactions. For the same reason, we also assume that all the water formed is a gas (a hypothetical state at the given T and P).

Determine the reversible work for this process (that is, the work that would be done if this chemical reaction took place reversibly and isothermally).

Control volume: Combustion chamber.
Inlet states: P, T known for each gas.
Exit states: P, T known for each gas.
Model: All ideal gases, Tables A.9 and A.10.
Sketch: Figure 15.4.

Analysis

The equation for this chemical reaction is

\[ \text{C}_2\text{H}_4(g) + 3(4)\text{O}_2 + 3(4)(3.76)\text{N}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O}(g) + 9\text{O}_2 + 45.1\text{N}_2 \]

The reversible work for this process is equal to the decrease in Gibbs function during this reaction, Eq. 15.26. Since each component is at the standard-state pressure P°, we write Eqs. 15.26 and 15.27 as

\[ W^\text{rev} = -\Delta G^0 \quad \Delta G^0 = \Delta H^0 - T\Delta S^0 \]

We also note that the 45.1 N₂ cancels out of both sides in these expressions, as does 9 of the 12 O₂.

\[ \begin{align*}
\text{C}_2\text{H}_4 & \quad \text{O}_2 & \quad \text{N}_2 \\
\text{CO}_2 & \quad \text{H}_2\text{O} & \quad \text{O}_2 \\
\text{Each at} & \quad T = 25^\circ C & \quad P = 0.1 \text{MPa} \\
\end{align*} \]

\[ \begin{align*}
\text{C}_2\text{H}_4 & \quad \text{O}_2 & \quad \text{N}_2 \\
\text{CO}_2 & \quad \text{H}_2\text{O} & \quad \text{O}_2 \\
\text{Each at} & \quad T = 25^\circ C & \quad P = 0.1 \text{MPa} \\
\end{align*} \]
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Solution

Using values from Tables A.8 and A.9 at 25 °C,

\[ \Delta H^0 = 2n_f^0(CO_2) + 2n_f^0(H_2O) - n_f^0(C_2H_4) - 3n_f^0(O_2) \]

\[ = 2(-393.522) + 2(-241.826) - (+52.467) - 3(0) \]

\[ = -1323.163 \text{ kJ/kmol fuel} \]

\[ \Delta S^0 = 2s_f^0(CO_2) + 2s_f^0(H_2O) - s_f^0(C_2H_4) - 3s_f^0(O_2) \]

\[ = 2(213.795) + 2(188.843) - (219.330) - 3(205.148) \]

\[ = -29.516 \text{ kJ/kmol fuel} \]

\[ \Delta G^0 = -1323.163 - 298.15(-29.516) \]

\[ = -1314.363 \text{ kJ/kmol C}_2\text{H}_4 \]

\[ W^{rev} = -\Delta G^0 = 1314.363 \text{ kJ/kmol C}_2\text{H}_4 \]

\[ = \frac{1314.363}{28.054} = 46.851 \text{ kJ/kg} \]

Therefore, we might say that when 1 kg of ethene is at 25 °C and the standard-state

Thus, it would seem logical to rate the efficiency of a device designed to do work by
utilizing a combustion process, such as an internal-combustion engine or a steam power
plant, as the ratio of the actual work to the reversible work or, in Example 15.13, the decrease
in Gibbs function for the chemical reaction, instead of comparing the actual work to the
heating value, as is commonly done. This is, in fact, the basic principle of the second-law
efficiency, which was introduced in connection with availability analysis in Chapter 10. As
noted from Example 15.13, the difference between the decrease in Gibbs function and the
heating value is small, which is typical for hydrocarbon fuels. The difference in the two types
of efficiencies will, therefore, not usually be large. We must always be careful, however,
when discussing efficiencies, to note the definition of the efficiency under consideration.

It is of particular interest to study the irreversibility that takes place during a com-
bustion process. The following examples illustrate this matter. We consider the same hy-
drocarbon fuel that was used in Example 15.13, ethene gas at 25 °C and 100 kPa. We
determined its availability and found it to be 46.851 kJ/kg. Now let us burn this fuel
with 400% theoretical air in a steady-state adiabatic process. In this case, the fuel and air
each enter the combustion chamber at 25 °C and the products exit at the adiabatic flame
temperature, but for the purpose of illustrating the calculation procedure, let each of the
three pressures be 200 kPa in this case. The result, then, is not exactly comparable to
Example 15.13, but the difference is fairly minor. Since the process is adiabatic, the ir-
reversibility for the process can be calculated directly from the increase in entropy using
Eq. 15.25.
EXAMPLE 15.14

Ethene gas at 25°C and 200 kPa enters a steady-state adiabatic combustion chamber along with 400% theoretical air at 25°C, 200 kPa, as shown in Fig. 15.5. The product gas mixture exits at the adiabatic flame temperature and 200 kPa. Calculate the irreversibility per kmol of ethene for this process.

Control volume: Combustion chamber
Inlet states: P, T known for each component gas stream
Exit state: P, T known
Model: All ideal gases, Tables A.9 and A.10
Sketch: Fig. 15.5

**FIGURE 15.5** Sketch for Example 15.14.

Analysis

The combustion equation is

\[
\text{C}_2\text{H}_4(g) + 12 \text{O}_2 + 12(3.76) \text{N}_2 \rightarrow 2 \text{CO}_2 + 2 \text{H}_2\text{O}(g) + 9 \text{O}_2 + 45.1 \text{N}_2
\]

The adiabatic flame temperature is determined first.

First law:

\[
H_f = H_i = \sum n_i (h_i^0) = \sum n_i (h_i^0 + \Delta h_i^0)
\]

Solution

\[
52 467 = 2(-393 522 + \Delta h_{\text{CO}_2}) + 2[-241 826 + \Delta h_{\text{H}_2\text{O}}(g)] + 9 \Delta h_{\text{O}_2} + 45.1 \Delta h_{\text{N}_2}
\]

By a trial-and-error solution we find the adiabatic flame temperature to be 1016 K. We now proceed to find the change in entropy during this adiabatic combustion process.

\[
S_f = S_{\text{C}_2\text{H}_4} + S_{\text{air}}
\]

From Eq. 15.17,

\[
S_{\text{C}_2\text{H}_4} = 1 \left( 219 330 - 8 3145 \log \frac{200}{100} \right) = 213 567 \text{kJ/K}
\]
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From Eqs. 15.21 and 15.22,

\[ S_{\text{air}} = 12 \left( 205.147 - 8.3145 \ln \frac{0.21 \times 200}{100} \right) 
+ 45.1 \left( 191.610 - 8.3145 \ln \frac{0.79 \times 200}{100} \right) \]

\[ = 12(212.360) + 45.1(187.807) = 11 018.416 \text{ kJ/k} \]

\[ S_{\text{SR}} = 213.567 + 11 018.416 = 11 231.983 \text{ kJ/k} \]

For a multicomponent product gas mixture, it is convenient to set up a table, as follows:

<table>
<thead>
<tr>
<th>Comp</th>
<th>( n_i )</th>
<th>( y_i )</th>
<th>( R \ln \frac{P_i}{P_0} )</th>
<th>( S_i )</th>
<th>( S_{\text{P}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO2</td>
<td>2</td>
<td>0.0344</td>
<td>-22.254</td>
<td>270.194</td>
<td>292.448</td>
</tr>
<tr>
<td>H2O</td>
<td>2</td>
<td>0.0344</td>
<td>-22.254</td>
<td>233.355</td>
<td>255.609</td>
</tr>
<tr>
<td>O2</td>
<td>9</td>
<td>0.1549</td>
<td>-9.743</td>
<td>244.135</td>
<td>253.878</td>
</tr>
<tr>
<td>N2</td>
<td>45.1</td>
<td>0.7763</td>
<td>+3.658</td>
<td>228.691</td>
<td>228.033</td>
</tr>
</tbody>
</table>

Then, with values from this table for \( n_i \) and \( S_{i} \) for each component \( i \),

\[ S_{\text{P}} = \sum n_i S_i = 13 530.004 \text{ kJ/K} \]

Since this is an adiabatic process, the irreversibility is, from Eq. 15.25,

\[ I = T_0(S_{\text{P}} - S_{\text{R}}) = 298.15(13 530.004 - 11 231.983) = 685.155 \text{ kJ/kmol C}_2\text{H}_4 
= \frac{685.155}{28.034} = 24.423 \text{ kJ/kg} \]

From the result of Example 15.14, we find that the irreversibility of that combustion process was 50% of the availability of the same fuel, as found at standard-state conditions in Example 15.13. We conclude that a typical combustion process is highly irreversible.

15.9 FUEL CELLS

The previous examples raise the question of the possibility of a reversible chemical reaction. Some reactions can be made to approach reversibility by having them take place in an electrolytic cell, as described in Chapter 1. When a potential exactly equal to the electromotive force of the cell is applied, no reaction takes place. When the applied potential is increased slightly, the reaction proceeds in one direction, and if the applied potential is decreased slightly, the reaction proceeds in the opposite direction. The work done is the electrical energy supplied or delivered.
Consider a reversible reaction occurring at constant temperature equal to that of its environment. The work output of the fuel cell is

\[ W = -\left( \sum n_e \nu_e - \sum n_i \nu_i \right) = -\Delta G \]

where \( \Delta G \) is the change in Gibbs function for the overall chemical reaction. We also realize that the work is given in terms of the charged electrons flowing through an electrical potential \( \nu \) as

\[ W = \eta n_e \nu \]

in which \( n_e \) is the number of kilomoles of electrons flowing through the external circuit and

\[ \nu = 6.022 \times 10^{23} \text{electrons/kmol} \times 1.602 \times 10^{-20} \text{kJ/electron} \]

\[ = 96485 \text{kJ/kmol} \]

Thus, for a given reaction, the maximum (reversible reaction) electrical potential \( \nu^0 \) of a fuel cell at a given temperature is

\[ \nu^0 = -\frac{\Delta G}{96485n_e} \quad (15.28) \]

**EXAMPLE 15.15** Calculate the reversible electromotive force (EMF) at 25°C for the hydrogen-oxygen fuel cell described in Section 1.2.

**Solution**

The anode side reaction was stated to be

\[ 2H_2 \rightarrow 4H^+ + 4e^- \]

and the cathode side reaction is

\[ 4H^+ + 4e^- + O_2 \rightarrow 2H_2O \]

Therefore, the overall reaction is, in kilomoles,

\[ 2H_2 + O_2 \rightarrow 2H_2O \]

for which 4 kmol of electrons flow through the external circuit. Let us assume that each component is at its standard-state pressure of 0.1 MPa and that the water formed is liquid. Then

\[ \Delta H^0 = 2h_{f,H_2O(l)}^0 - 2h_{f,H_2}^0 - h_{f,O_2}^0 = 2(-285.830) - 2(0) - 1(0) = -571.660 \text{kJ} \]

\[ \Delta S^0 = 2s_{f,H_2O(l)}^0 - 2s_{f,H_2}^0 - s_{f,O_2}^0 = 2(69.950) - 2(130.678) - 1(205.148) = -326.604 \text{kJ/K} \]

\[ \Delta G^0 = -571.660 - 298.15(0) - 326.604 \approx -874.283 \text{kJ} \]

Therefore, from Eq. 15.28,

\[ \nu^0 = \frac{-874.283}{96485 \times 4} = 1.229 \text{V} \]
In Example 15.15, we found the shift in the Gibbs function and the reversible EMF at 25°C. In practice, however, many fuel cells operate at an elevated temperature where the water leaves as a gas and not as a liquid; thus, it carries away more energy. The computations can be done for a range of temperatures, leading to lower EMF as the temperature increases.

This behavior is shown in Fig. 15.6.

A variety of fuel cells are being investigated for use in stationary as well as mobile power plants. The low-temperature fuel cells use hydrogen as the fuel, whereas the higher-temperature cells can use methane and carbon monoxide that are then internally reformed into hydrogen and carbon dioxide. The most important fuel cells are listed in Table 15.4 with their main characteristics.

The low-temperature fuel cells are very sensitive to being poisoned by carbon monoxide gas so they require an external reformer and purifier to deliver hydrogen gas. The higher-temperature fuel cells can reform natural gas, mainly methane, but also ethane and propane, as shown in Table 15.2, into hydrogen gas and carbon monoxide inside the cell. The latest research is being done with gasified coal as a fuel and operating the cell at higher pressures like 15 atm. As the fuel cell has exhaust gas with a small amount of fuel in it, additional combustion can occur and then combine the fuel cell with a gas turbine or steam power plant to utilize the exhaust gas energy. These combined-cycle power plants strive to have an efficiency of up to 60%.

TABLE 15.4

<table>
<thead>
<tr>
<th>Fuel Cell Types</th>
<th>PEC</th>
<th>PRC</th>
<th>MCC</th>
<th>SOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>80°C</td>
<td>200°C</td>
<td>650°C</td>
<td>900°C</td>
</tr>
<tr>
<td>Fuel</td>
<td>Hydrogen, H₂</td>
<td>Hydrogen, H₂</td>
<td>CO₂, hydrogen</td>
<td>Natural gas</td>
</tr>
<tr>
<td>Charge, nₑ</td>
<td>2e⁻ per H₂</td>
<td>2e⁻ per H₂</td>
<td>2e⁻ per H₂</td>
<td>2e⁻ per CH₄</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Pt</td>
<td>Pt</td>
<td>Ni</td>
<td>ZrO₂</td>
</tr>
<tr>
<td>Poison</td>
<td>CO</td>
<td>CO</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
A model can be developed for the various processes that occur in a fuel cell to predict the performance. From the thermodynamic analysis, we found the theoretical voltage created by the process as the EMF from the Gibbs function. At both electrodes, there are activation losses that lower the voltage and a leak current $i_{\text{leak}}$ that does not go through the cell. The electrolyte or membrane of the cell has an ohmic resistance, $\text{ASR}_{\text{ohmic}}$, to the ion transfer and thus also produces a loss. Finally, at high currents, there is a significant cell concentration loss that depletes one electrode for reactants and at the other electrode generates a high concentration of products, both of which increase the loss of voltage across the electrodes.

The output voltage, $V$, generated by a fuel cell becomes

$$V = \text{EMF} - b \ln \left( \frac{i + i_{\text{leak}}}{i_0} \right) - i \text{ASR}_{\text{ohmic}} - c \ln \frac{i_L}{i_L - (i + i_{\text{leak}})}$$

where $i$ is current density [amp/cm²], $\text{ASR}_{\text{ohmic}}$ is the resistance [ohm cm²] and $b$ and $c$ are cell constants [volts], the current densities $i_0$ is a reference, and $i_L$ is the limit.

Two examples of this equation are shown in Fig. 15.7, where for the PEC (Polymer Electrolyte Cell) cell activation losses are high due to the low temperature and ohmic losses tend to be low. Just the opposite is the case for the high-temperature SOC (Solid Oxide Cell) cell. As the current density increases toward the limit, the voltage drops sharply in both cases, and if the power per unit area ($Vi$) were shown, it would have a maximum in the middle range of current density.

This result resembles that of a heat engine with heat exchangers of a given size. As the power output is increased, the higher heat transfer requires a larger temperature difference, (recall Eqs. 7.14–7.16), which in turn lowers the temperature difference across the heat engine and causes it to operate with lower efficiency.

**In-Text Concept Questions**

i. Is the irreversibility in a combustion process significant? Explain your answer.

j. If the air–fuel ratio is larger than stoichiometric, is it more or less reversible?

k. What makes the fuel cell attractive from a power-generating point of view?
process using gasoline or diesel oil as the fuel. On a larger scale, newer power plants use natural gas (methane) in gas turbines, and older plants use oil or coal as the primary fuel in the boiler-steam generator. Jet engines and rockets use combustion to generate high-speed flows for the motion of the airplane or rocket.

Most of the heat engines described in Chapter 7, and with simple models as cycles in Chapters 11 and 12, have the high-temperature heat transfer generated from a combustion process. It is thus not a heat transfer but an energy conversion process changing from the reactants to the much higher-temperature products of combustion. For the Rankine and Stirling cycles the combustion is external to the cycle, whereas in the internal combustion engines, as in the gasoline and diesel engines, combustion takes place in the working substance of the cycle.

In external combustion the products deliver energy to the cycle by heat transfer, which cools the products, so it is never a constant temperature source of energy. The combustion takes place in a steady flow arrangement with careful monitoring of the air-fuel mixture, including safety and pollution control aspects. In internal combustion the Brayton cycle, as the model of a gas turbine, is a steady flow arrangement, and the gasoline/diesel engines are piston/cylinder engines with intermittent combustion. The latter process is somewhat difficult to control, as it involves a transient process.

A number of different parameters can be defined for evaluating the performance of an actual combustion process, depending on the nature of the process and the system considered. In the combustion chamber of a gas turbine, for example, the objective is to raise the temperature of the products to a given temperature (usually the maximum temperature the metals in the turbine can withstand). If we had a combustion process that achieved complete combustion and that was adiabatic, the temperature of the products would be the adiabatic flame temperature. Let us designate the fuel-air ratio needed to reach a given temperature under these conditions as the ideal fuel-air ratio. In the actual combustion chamber, the combustion will be incomplete to some extent, and there will be some heat transfer to the surroundings. Therefore, more fuel will be required to reach the given temperature, and this we designate as the actual fuel-air ratio. The combustion efficiency, $\eta_{\text{comb}}$, is defined here as

$$\eta_{\text{comb}} = \frac{F_{\text{ideal}}}{F_{\text{actual}}}$$ (15.30)

On the other hand, in the furnace of a steam generator (boiler), the purpose is to transfer the maximum possible amount of heat to the steam (water). In practice, the efficiency of a steam generator is defined as the ratio of the heat transferred to the steam to the higher heating value of the fuel. For a coal this is the heating value as measured in a bomb calorimeter, which is the constant-volume heating value, and it corresponds to the internal energy of combustion. We observe a minor inconsistency, since the boiler involves a flow process, and the change in enthalpy is the significant factor. In most cases, however, the error thus introduced is less than the experimental error involved in measuring the heating value, and the efficiency of a steam generator is defined by the relation

$$\eta_{\text{steam generator}} = \frac{\text{heat transferred to steam} \text{ kg fuel}}{\text{higher heating value of the fuel}}$$ (15.31)

Often the combustion of a fuel uses atmospheric air as the oxidizer, in which case the reactants also hold some water vapor. Assuming we know the humidity ratio for the moist air, $\omega$, we would like to know the composition of air per mole of oxygen as

$$1 \text{ O}_2 + 3.76 \text{ N}_2 + x \text{ H}_2\text{O}$$
Since the humidity ratio is, \( \omega = \frac{m_w}{m_a} \), the number of moles of water is
\[
n_w = \frac{n_v}{M_v} = \frac{\omega m_a}{M_v}
\]
and the number of moles of dry air per mole of oxygen is \((1 + 3.76)/1\), so we get
\[
x = \frac{n_v}{n_{\text{oxygen}}} = \frac{\omega}{4.76} \frac{M_a}{M_v} = 7.655\omega
\]
This amount of water is found in the products together with the water produced by the oxidation of the hydrogen in the fuel.

In an internal-combustion engine the purpose is to do work. The logical way to evaluate the performance of an internal-combustion engine would be to compare the actual work done to the maximum work that would be done by a reversible change of state from the reactants to the products. This, as we noted previously, is called the second-law efficiency.

In practice, however, the efficiency of an internal-combustion engine is defined as the ratio of the actual work to the negative of the enthalpy of combustion of the fuel (that is, the constant-pressure heating value). This ratio is usually called the thermal efficiency, \( \eta_{th} \):
\[
\eta_{th} = \frac{w}{-h_{RP}} = \frac{w}{\text{heating value}}
\]
When Eq. 15.33 is applied, the same scaling for the work and heating value must be used. So, if the heating value is per kg (kmol) fuel, then the work is per kg (kmol) fuel. For the work and heat transfer in the cycle analysis, we used the specific values as per kg of working substance, where for constant pressure combustion we have \( h_P = h_R + q_H \). Since the heating value is per kg fuel and \( q_H \) is per kg mixture, we have
\[
m_{tot} = m_{fuel} + m_{air} = m_{fuel}(1 + AF_{mass})
\]
and thus
\[
q_H = \frac{HV}{AF_{mass} + 1}
\]
where a scaling of the \( HV \) and \( AF \) on a mass basis must be used.

The overall efficiency of a gas turbine or steam power plant is defined in the same way. It should be pointed out that in an internal-combustion engine or fuel-burning steam power plant, the fact that the combustion is itself irreversible is a significant factor in the relatively low thermal efficiency of these devices.

One other factor should be pointed out regarding efficiency. We have noted that the enthalpy of combustion of a hydrocarbon fuel varies considerably with the phase of the water in the products, which leads to the concept of higher and lower heating values. Therefore, when we consider the thermal efficiency of an engine, the heating value used to determine this efficiency must be borne in mind. Two engines made by different manufacturers may have identical performance, but if one manufacturer bases his or her efficiency on the higher heating value and the other on the lower heating value, the latter will be able to claim a higher thermal efficiency. This claim is not significant, of course, as the performance is the same; this would be revealed by consideration of how the efficiency was defined.

The whole matter of the efficiencies of devices that undergo combustion processes is treated in detail in textbooks dealing with particular applications; our discussion is intended only as an introduction to the subject. Two examples are given, however, to illustrate these remarks.
EXAMPLE 15.16  The combustion chamber of a gas turbine uses a liquid hydrocarbon fuel that has an approximate composition of C₈H₁₈. During testing, the following data are obtained:

\[
\begin{align*}
T_{\text{air}} &= 400 \text{ K} \\
V_{\text{air}} &= 100 \text{ m/s} \\
T_{\text{fuel}} &= 50 \degree \text{C} \\
V_{\text{products}} &= 150 \text{ m/s} \\
T_{\text{products}} &= 1100 \text{ K} \\
FA_{\text{actual}} &= 0.0211 \text{ kg fuel/kg air}
\end{align*}
\]

Calculate the combustion efficiency for this process.

**Control volume:** Combustion chamber.

**Inlet states:** T known for air and fuel.

**Exit state:** T known.

**Model:** Air and products—ideal gas, Table A.9. Fuel—Table A.10.

**Analysis**

For the ideal chemical reaction the heat transfer is zero. Therefore, writing the first law for a control volume that includes the combustion chamber, we have

\[
H_k + KE_a = H_f + KE_p
\]

\[
H_k + KE_a = \sum_n \left( \frac{\dot{m}_n}{M_n} \left( c_{p,n} \Delta T + \frac{1}{2} \dot{V}_n \right) \right)
\]

\[
= c_{p,\text{air}}(50 - 25) + n_{O_2} \left( \Delta T + \frac{1}{2} \dot{V}_{O_2} \right)_{O_2} + 3.76n_{O_2} \left( \Delta T + \frac{1}{2} \dot{V}_{O_2} \right)_{N_2}
\]

\[
H_f + KE_p = \sum_n \left( \frac{\dot{m}_n}{M_n} \left( c_{p,n} \Delta T + \frac{1}{2} \dot{V}_n \right) \right)
\]

\[
= 8 \left( \frac{c_{p,\text{CO}_2} \dot{V}_{\text{CO}_2}}{M_{\text{CO}_2}} \right) + 9 \left( \frac{c_{p,\text{H}_2} \dot{V}_{\text{H}_2}}{M_{\text{H}_2}} \right)_{H_2O} + (n_{O_2} - 12.5) \left( \frac{c_{p,\text{CO}_2} \dot{V}_{\text{CO}_2}}{M_{\text{CO}_2}} \right)_{O_2} + 3.76n_{O_2} \left( \frac{c_{p,\text{N}_2} \dot{V}_{\text{N}_2}}{M_{\text{N}_2}} \right)_{N_2}
\]
Solution

\[
H_R + KE_R = -250105 + 2.23 \times 11423(50 - 25)
\]
+ \(n_{O_2} \left[ 3034 + 32 \times (100)^2 \right] \)
+ \(3.76n_{O_2} \left[ 2971 + 28.02 \times (100)^2 \right] \)
+ \(2 \times 1000 \)

\[
= -243737 + 14892n_{O_2}
\]

\[
H_P + KE_P = 8 \left[ -393522 + 38891 + \frac{44.01 \times (150)^2}{2 \times 1000} \right]
\]
+ \(9 \left[ -241826 + 30147 + \frac{18.02 \times (150)^2}{2 \times 1000} \right] \)
+ \(3.7n_{O_2} \left[ 24758 + \frac{28.02 \times (150)^2}{2 \times 1000} \right] \)

\[
= -5068599 + 120853n_{O_2}
\]

Therefore,

\[-243737 + 14892n_{O_2} = -5068599 + 120853n_{O_2} \]

\[
f_{a,\text{ideal}} = \frac{11423}{216.72 \times 28.97} = 0.0182 \text{ kg fuel/kg air}
\]

\[
\eta_{\text{comb}} = \frac{0.0182}{0.0211} \times 100 = 86.2 \text{ percent}
\]

**EXAMPLE 15.17** In a certain steam power plant, 325,000 kg of water per hour enters the boiler at a pressure of 10 MPa and a temperature of 200°C. Steam leaves the boiler at 8 MPa, 500°C. The power output of the turbine is 81,000 kW. Coal is used at the rate of 26,700 kg/h and has a higher heating value of 33,250 kJ/kg. Determine the efficiency of the steam generator and the overall thermal efficiency of the plant.

In power plants, the efficiency of the boiler and the overall efficiency of the plant are based on the higher heating value of the fuel.
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Solution

The efficiency of the boiler is defined by Eq. 15.31 as
\[ \eta_{\text{steam generator}} = \frac{\text{heat transferred to H}_2\text{O}}{\text{kg fuel}} \text{ higher heating value} \]

Therefore,
\[ \eta_{\text{steam generator}} = \frac{325 \text{,}000(339.8 - 85.6)}{26 \text{,}700 \times 33 \text{,}250} \times 100 = 93.1\% \]

The thermal efficiency is defined by Eq. 15.33,
\[ \eta_{\text{th}} = \frac{\text{w}}{\text{heating value}} = \frac{81 \text{,}000 \times 3600}{26 \text{,}700 \times 33 \text{,}250} \times 100 = 32.8\% \]

SUMMARY

A n introduction to combustion of hydrocarbon fuels and chemical reactions in general is given. A simple oxidation of a hydrocarbon fuel with pure oxygen or air burns the hydrogen to water and the carbon to carbon dioxide. We apply the continuity equation for each kind of atom to balance the stoichiometric coefficients of the species in the reactants and the products. The reactant mixture composition is described by the air–fuel ratio on a mass or mole basis or by the percent theoretical air or equivalence ratio according to the practice of the particular area of use. The products of a given fuel for a stoichiometric mixture and complete combustion are unique, whereas actual combustion can lead to incomplete combustion and more complex products described by measurements on a dry or wet basis. As water is part of the products, they have a dew point, so it is possible to see water condensing out from the products as they are cooled.

Due to the chemical changes from the reactants to the products, we need to measure energy from an absolute reference. Chemically pure substances (not compounds like carbon monoxide) in their ground state (graphite for carbon, not diamond form) are assigned a value of 0 for the formation enthalpy at the reference temperature and pressure (25°C, 100 kPa). Stable compounds have a negative formation enthalpy and unstable compounds have a positive formation enthalpy. The shift in the enthalpy from the reactants to the products is the enthalpy of combustion, which is also the negative of the heating value HV . When a combustion process takes place without any heat transfer, the resulting product temperature is the adiabatic flame temperature. The enthalpy of combustion, the heating value (lower or higher), and the adiabatic flame temperature depend on the mixture (fuel and air–fuel ratio), and the reactants supply temperature. When a single unique number for these properties is used, it is understood to be for a stoichiometric mixture at the reference conditions.

Similarly to enthalpy, an absolute value of entropy is needed for the application of the second law. The absolute entropy is zero for a perfect crystal at 0 K, which is the third law of thermodynamics. The combustion process is an irreversible process; thus, a loss of availability (exergy) is associated with it. This irreversibility is increased by mixtures different from stoichiometric mixture and by dilution of the oxygen (i.e., nitrogen in air), which lowers the adiabatic flame temperature. From the concept of flow exergy we apply the second law to find the reversible work given by the change in Gibbs function. A process that has less irreversibility than combustion at high temperature is the chemical conversion in a fuel cell, where we approach a chemical equilibrium process (covered in
detail in the following chapter). Here the energy release is directly converted into electrical power output, a system under intense study and development for future energy conversion systems.

You should have learned a number of skills and acquired abilities from studying this chapter that will allow you to:

- Write the combustion equation for the stoichiometric reaction of any fuel.
- Balance the stoichiometric coefficients for a reaction with a set of products measured on a dry basis.
- Handle the combustion of fuel mixtures as well as moist air oxidizers.
- Apply the energy equation with absolute values of enthalpy or internal energy.
- Deal with condensation of water in low-temperature products of combustion.
- Calculate the adiabatic flame temperature for a given set of reactants.
- Know the difference between enthalpy of formation and enthalpy of combustion.
- Know the definition of the higher and lower heating values.
- Apply the second law to a combustion problem and find irreversibilities.
- Calculate the change in Gibbs function and the reversible work.
- Know how a fuel cell operates and how to find its electrical potential.
- Know some basic definition of combustion efficiencies.

### KEY CONCEPTS AND FORMULAS

<table>
<thead>
<tr>
<th>Reaction</th>
<th>fuel + oxidizer → products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrocarbon + Air → Carbon dioxide + Water + Nitrogen</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Stoichiometric ratio</th>
<th>No excess fuel, no excess oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stoichiometric coefficients</td>
<td>Factors to balance atoms between reactants and products</td>
</tr>
<tr>
<td>Stoichiometric reaction</td>
<td>$C_xH_y + O_{2/3} \rightarrow CO_2 + H_2O + N_2$</td>
</tr>
</tbody>
</table>

| Air-fuel ratio | $AF_{max} = \frac{m_{air}}{m_{fuel}} = \frac{AF}{AF_{s}}$ |

| Equivalence ratio | $\Phi = \frac{AF}{AF_{s}} = \frac{AF}{AF_{s}}$ |

<table>
<thead>
<tr>
<th>Enthalpy of formation</th>
<th>$H_F^i$, zero for chemically pure substance, ground state</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enthalpy of combustion</td>
<td>$H_V = H_F - H_R$</td>
</tr>
<tr>
<td>Heating value $H_V$</td>
<td>$H_V = -\eta_F$</td>
</tr>
</tbody>
</table>

| Inflow energy of combustion | $U_F = U_F - U_R = H_F - H_R$ if ideal gases |
| A diabatic flame temperature | $H = H_k$ if flow; $U = U_k$ if constant volume |

| Reversible work | $W_{rev} = G_k - G_p = -\Delta G = -\Delta H - T \Delta S$ |

This requires that any $Q$ is transferred at the local $T$.

<table>
<thead>
<tr>
<th>Gibbs function</th>
<th>$G = H - TS$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irreversibility</td>
<td>$\eta = \frac{W_{rev} - W}{T_S\Delta S/m} = \frac{T_S\Delta S}{T_S\Delta S}$ for 1 kmol fuel</td>
</tr>
</tbody>
</table>
CHAPTER FIFTEEN  CHEMICAL REACTIONS

CONCEPT-STUDY GUIDE PROBLEMS

15.1 Is mass conserved in combustion? Is the number of moles constant?
15.2 Does all combustion take place with air?
15.3 Why would I sometimes need an air–fuel ratio on a mole basis? on a mass basis?
15.4 Why is there no significant difference between the number of moles of reactants and the number of products in combustion of hydrocarbon fuels with air?
15.5 Why are products measured on a dry basis?
15.6 What is the dew point of hydrogen burned with stoichiometric pure oxygen? With air?
15.7 How does the dew point change as equivalence ratio goes from 0.9 to 1 to 1.1?
15.8 Why does combustion contribute to global warming?
15.9 What is the enthalpy of formation for oxygen as O2? If O? For carbon dioxide?
15.10 If the nitrogen content of air can be lowered, will the adiabatic flame temperature increase or decrease?
15.11 Does the enthalpy of combustion depend on the air–fuel ratio?
15.12 Why do some fuels not have entries for liquid fuel in Table 15.2?
15.13 Is a heating value a fixed number for a fuel?
15.14 Is an adiabatic flame temperature a fixed number for a fuel?
15.15 Does it make a difference for the enthalpy of combustion whether I burn with pure oxygen or air? What about the adiabatic flame temperature?
15.16 A welder uses a bottle with acetylene and a bottle with oxygen. Why should he use the oxygen bottle instead of air?
15.17 Some gas welding is done using bottles of fuel, oxygen, and argon. Why do you think argon is used?
15.18 Is combustion a reversible process?

HOMEWORK PROBLEMS

Fuels and the Combustion Process

15.19 In a picnic grill, gaseous propane is fed to a burner together with stoichiometric air. Find the air–fuel ratio on a mass basis and the total reactant mass for 1 kg of propane burned.
15.20 Calculate the theoretical air–fuel ratio on a mass and mole basis for the combustion of ethanol, C2H5OH.
15.21 A certain fuel oil has the composition C10H22. If this fuel is burned with 150% theoretical air, what is the composition of the products of combustion?
15.22 Methane is burned with 200% theoretical air. Find the composition and the dew point of the products.
15.23 Natural gas B from Table 15.2 is burned with 20% excess air. Determine the composition of the products.
15.24 For complete stoichiometric combustion of gasoline, C8H18, determine the fuel molecular weight, the combustion products, and the mass of carbon dioxide produced per kilogram of fuel burned.
15.25 A Pennsylvania coal contains 74.2% C, 5.1% H, 6.7% O (dry basis, mass percent) plus ash and small percentages of N and S. This coal is fed into a gasifier along with oxygen and steam, as shown in Fig. P15.25. The exiting product gas composition is measured on a mole basis to: 39.9% CO, 30.8% H2, 11.4% CO2, 16.4% H2O plus small percentages of CH4, N2, and H2S. How many kilograms of coal are required to produce 100 kmol of product gas? How much oxygen and steam are required?

15.26 Liquid propane is burned with dry air. A volumetric analysis of the products of combustion yields the following volume percent composition on a dry basis: 8.6% CO2, 0.6% CO, 7.2% O2, and 83.6% N2. Determine the percent of theoretical air used in this combustion process.
15.27 In a combustion process with decane, C₁₀H₂₂, and air, the dry product mole fractions are 83.61% N₂, 4.91% O₂, 10.56% CO₂, and 0.92% CO. Find the equivalence ratio and the percent theoretical air of the reactants.

15.28 A sample of pine bark has the following ultimate analysis on a dry basis, percent by mass: 5.6% H, 53.4% C, 0.1% S, 0.1% N, 37.9% O, and 2.9% ash. This bark will be used as a fuel by burning it with 100% theoretical air in a furnace. Determine the air–fuel ratio on a mass basis.

15.29 Methanol, CH₃OH, is burned with 200% theoretical air in an engine, and the products are brought to 100 kPa, 30°C. How much water is condensed per kilogram of fuel?

15.30 The coal gasifier in an integrated gasification combined cycle (IGCC) power plant produces a gas mixture with the following volumetric percent composition:

<table>
<thead>
<tr>
<th>Product</th>
<th>% vol.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>0.3</td>
</tr>
<tr>
<td>H₂</td>
<td>29.6</td>
</tr>
<tr>
<td>CO</td>
<td>41.0</td>
</tr>
<tr>
<td>CO₂</td>
<td>10.0</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.8</td>
</tr>
<tr>
<td>H₂S</td>
<td>17.0</td>
</tr>
<tr>
<td>NH₃</td>
<td>1.1</td>
</tr>
<tr>
<td>N₂</td>
<td>0.2</td>
</tr>
</tbody>
</table>

This gas is cooled to 40°C, 3 MPa, and the H₂S and NH₃ are removed in water scrubbers. Assuming that the resulting mixture, which is sent to the combustors, is saturated with water, determine the mixture composition and the theoretical air–fuel ratio in the combustors.

15.31 Butane is burned with dry air at 40°C, 100 kPa, with AF = 26 on a mass basis. For complete combustion, find the equivalence ratio, the percentage of theoretical air, and the dew point of the products. How much water (kg/kg fuel) is condensed out, if any, when the products are cooled down to ambient temperature, 40°C?

15.32 The output gas mixture of a certain air-blown coal gasifier has the composition of producer gas as listed in Table 15.2. Consider the combustion of this gas with 120% theoretical air at 100 kPa pressure. Determine the dew point of the products and find how many kilograms of water will be condensed per kilogram of fuel if the products are cooled to 10°C below the dew-point temperature.

15.33 The hot exhaust gas from an internal-combustion engine is analyzed and found to have the following percent composition on a volumetric basis at the engine exhaust manifold: 10% CO₂, 2% CO, 13% H₂O, 3% O₂, and 72% N₂. This gas is fed to an exhaust gas reactor and mixed with a certain amount of air to eliminate the CO₂ as shown in Fig. P15.33. It has been determined that a mole fraction of 10% O₂ in the mixture at state 3 will ensure that no CO remains. What must be the ratio of flows entering the reactor?

![FIGURE P15.33](image)

15.34 Hydrogen is burned with stoichiometric air in a steady-flow process where the reactants are supplied at 100 kPa, 298 K. The products are cooled to 800 K in a heat exchanger. Find the heat transfer per kmol hydrogen.

15.35 Butane gas and 200% theoretical air, both at 25°C, enter a steady-flow combustor. The products of combustion exit at 1000 K. Calculate the heat transfer from the combuster per kilomol of butane burned.

15.36 One alternative to using petroleum or natural gas as fuels is ethanol (C₂H₅OH), which is commonly produced from grain by fermentation. Consider a combustion process in which liquid ethanol is burned with 120% theoretical air in a steady-flow process. The reactants enter the combustion chamber at 25°C, and the products exit at 60°C, 100 kPa. Calculate the heat transfer per kilomole of ethanol.

15.37 Do the previous problem with the ethanol fuel delivered as a vapor.

15.38 Liquid methanol is burned with stoichiometric air, both supplied at P₀, T₀ in a constant-pressure process, and the products exit a heat exchanger at 900 K. Find the heat transfer per kilomol fuel.

15.39 Another alternative fuel to be seriously considered is hydrogen. It can be produced from water by various techniques that are under extensive study. Its biggest problems at the present time are cost,
CHAPTER FIFTEEN
CHEMICAL REACTIONS

storage, and safety. Repeat Problem 15.36 using hydrogen gas as the fuel instead of ethanol.

15.40 The combustion of heptane, \( \text{C}_7\text{H}_{16} \), takes place in a steady-flow burner where fuel and air are added as gases at \( P_0, T_0 \). The mixture has 125% theoretical air, and the products pass through a heat exchanger, where they are cooled to 600 K. Find the heat transfer from the heat exchanger per kmol of heptane burned.

15.41 In a new high-efficiency furnace, natural gas, assumed to be 90% methane and 10% ethane (by volume) and 110% theoretical air each enter at \( 25 ^\circ \text{C}, 100 \text{kPa} \), and the products (assumed to be 100% gaseous) exit the furnace at \( 40 ^\circ \text{C}, 100 \text{kPa} \). What is the heat transfer for this process? Compare this to the performance of an older furnace where the products exit at \( 250 ^\circ \text{C}, 100 \text{kPa} \).

15.42 Repeat the previous problem but take into account the actual phase behavior of the products exiting the furnace.

15.43 Pentene, \( \text{C}_5\text{H}_{10} \), is burned with pure \( \text{O}_2 \) in a steady-flow process. The products at one point are brought to 700 K and used in a heat exchanger, where they are cooled to \( 25 ^\circ \text{C} \). Find the specific heat transfer in the heat exchanger.

15.44 A rigid container has a 1:1 mole ratio of propane and butane gas together with a stoichiometric ratio of air at \( P_0, T_0 \). The charge burns, and there is heat transfer to a final temperature of 1000 K. Find the final pressure and the heat transfer per kmol of fuel mixture.

15.45 A rigid vessel initially contains 2 kmol of \( \text{C} \) and 2 kmol of \( \text{O}_2 \) at 25 C, 200 kPa. Combustion occurs, and the resulting products consist of 1 kmol of \( \text{CO}_2 \), 1 kmol of \( \text{CO} \), and excess \( \text{O}_2 \) at a temperature of 1000 K. Determine the final pressure in the vessel and the heat transfer per kmol of fuel mixture.

15.46 A closed, insulated container is charged with a stoichiometric ratio of \( \text{O}_2 \) and \( \text{H}_2 \) at 25 C and 150 kPa. After combustion, liquid water at 25 C is sprayed in such that the final temperature is 1200 K. What is the final pressure?

15.47 In a gas turbine, natural gas (methane) and stoichiometric air flow into the combustion chamber at 1000 kPa, 500 K. Secondary air (see Fig. P15.84), also at 1000 kPa, 500 K, is added right after the combustion to result in a product mixture temperature of 1500 K. Find the air-fuel ratio mass basis for the primary reactant flow and the ratio of the secondary air to the primary air (mass flow rates ratio).

15.48 Methane, \( \text{CH}_4 \), is burned in a steady-flow adiabatic process with two different oxidizers: Case A: Pure \( \text{O}_2 \), and case B: A mixture of \( \text{O}_2 + \alpha \text{Ar} \). The reactants are supplied at \( T_0, P_0 \) and the products for both cases should be at 1800 K. Find the required equivalence ratio in case A and the amount of argon, \( \alpha \), for a stoichiometric ratio in case B.

15.49 Gaseous propane mixes with air, both supplied at 500 K, 0.1 MPa. The mixture goes into a combustion chamber, and products of combustion exit at 1300 K, 0.1 MPa. The products analyzed on a dry basis are 11.42% \( \text{CO}_2 \), 0.79% \( \text{CO} \), 2.68% \( \text{O}_2 \), and 85.11% \( \text{N}_2 \) on a volume basis. Find the equivalence ratio and the heat transfer per kmol of fuel.

15.50 Find the enthalpy of combustion and the heating value for pure carbon.

15.51 Phenol has an entry in Table 15.3, but it does not have a corresponding value of the enthalpy of formation in Table A.10. Can you calculate it?

15.52 Some type of wood can be characterized as \( \text{C}_1\text{H}_{1.5}\text{O}_{0.7} \) with a lower heating value of 19 500 kJ/kg. Find its formation enthalpy.

15.53 Do Problem 15.36 using Table 15.3 instead of Table A.10 for the solution.

15.54 Liquid pentane is burned with dry air, and the products are measured on a dry basis as 10.1% \( \text{CO}_2 \), 0.2% \( \text{CO} \), 5.9% \( \text{O}_2 \), and remainder \( \text{N}_2 \). Find the enthalpy of formation for the fuel and the actual equivalence ratio.

15.55 Agriculturally derived butanol, \( \text{C}_4\text{H}_{10}\text{O} \), with a molecular mass of 74.12, also called biobutanol, has a lower heating value LHV = 33 075 kJ/kg for liquid fuel. Find its formation enthalpy.

15.56 Do Problem 15.38 using Table 15.3 instead of Table A.10 for the solution.

15.57 Wet biomass waste from a food-processing plant is fed to a catalytic reactor, where in a steady-flow process it is converted into a low-energy fuel gas suitable for firing the processing plant boilers. The fuel gas has a composition of 50% \( \text{CH}_4 \), 45% \( \text{CO}_2 \),...
and 5% H₂ on a volumetric basis. Determine the lower heating value of this fuel gas mixture per unit volume.

15.58 Determine the lower heating value of the gas generated from coal, as described in Problem 15.30. Do not include the components removed by the water scrubbers.

15.59 In a picnic grill, gaseous propane and stoichiometric air are mixed and fed to a burner, both at $P_0$, $T_0$. After combustion, the products cool down and exit at 500 K. How much heat transfer was given out for 1 kg propane?

15.60 Do Problem 15.40 using Table 15.3 instead of Table A.10 for the solution.

15.61 Propylbenzene, $C_9H_{12}$, is listed in Table 15.3 but not in Table A.9. No molecular mass is listed in the book. Find the molecular mass, the enthalpy of formation for the liquid fuel, and the enthalpy of evaporation.

15.62 Consider natural gas A in Table 15.2. Calculate the enthalpy of combustion at 25°C, assuming that the products include vapor water. Repeat the answer for liquid water in the products.

15.63 Redo the previous problem for natural gas D in Table 15.3.

15.64 Gaseous propane and stoichiometric air are mixed and fed to a burner, both at $P_0$, $T_0$. After combustion, the products eventually cool down to $T_0$. How much heat was transferred for 1 kg propane?

15.65 Blast furnace gas in a steel mill is available at 250°C to be burned for the generation of steam. The composition of this gas is as follows on a volumetric basis:

<table>
<thead>
<tr>
<th>Component</th>
<th>CH₄</th>
<th>H₂</th>
<th>CO</th>
<th>CO₂</th>
<th>N₂</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percent by volume</td>
<td>0.1</td>
<td>2.4</td>
<td>23.3</td>
<td>14.4</td>
<td>56.4</td>
<td>3.4</td>
</tr>
</tbody>
</table>

Find the lower heating value (kJ/m³) of this gas at 250°C and ambient pressure.

15.66 A burner receives a mixture of two fuels with mass fraction 40% n-butane and 60% methanol, both vapor. The fuel is burned with stoichiometric air. Find the product composition and the lower heating value of this fuel mixture (kJ/kg fuel mix).

15.67 In an experiment, a 1:1 mole ratio propane and butane is burned in a steady-flow with stoichiometric air. Both fuels and air are supplied as gases at 298 K and 100 kPa. The products are cooled to 1000 K as they give heat to some application. Find the lower heating value (per kg fuel mixture) and the total heat transfer for 1 kmol of fuel mixture used.

15.68 Liquid nitrromethane is added to the air in a carburetor to make a stoichiometric mixture where both fuel and air are added at 298 K, 100 kPa. After combustion, a constant-pressure heat exchanger brings the products to 600 K before being exhausted. A 4.4% the nitrogen in the fuel becomes N₂ gas. Find the total heat transfer per kmol fuel in the whole process.

15.69 Natural gas, we assume methane, is burned with 200% theoretical air, shown in Fig. P15.69, and the reactants are supplied as gases at the reference temperature and pressure. The products are flowing through a heat exchanger, where they give off energy to some water flowing in at 20°C, 500 kPa, and out at 700°C, 500 kPa. The products exit at 400 K to the chimney. How much energy per kmole fuel can the products deliver, and how many kilograms of water per kilogram of fuel can they heat?

![FIGURE P15.69](image-url)

15.70 An isobaric combustion process receives gaseous benzene, C₆H₆, and air in a stoichiometric ratio at $P_0$, $T_0$. To limit the product temperature to 2000 K, liquid water is sprayed in after the combustion. Find the number of kmol of liquid water added per kmol of fuel and the dew point of the combined products.

15.71 Gasoline, $C_7H_{17}$, is burned in a steady-state burner with stoichiometric air at $P_0$, $T_0$, shown in Fig. P15.71. The gasoline is flowing as a liquid at $T_0$ to a carburetor, where it is mixed with...
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CHEMICAL REACTIONS

Air to produce a fuel air–gas mixture at $T_0$. The carburetor takes some heat transfer from the hot products to do the heating. After the combustion, the products go through a heat exchanger, which they leave at 600 K. The gasoline consumption is 10 kg/h. How much power is given out in the heat exchanger, and how much power does the carburetor need?

15.71 Adiabatic Flame Temperature

In a rocket, hydrogen is burned with air, both reactants supplied as gases at $P_0$, $T_0$. The combustion is adiabatic, and the mixture is stoichiometric (100% theoretical air). Find the products’ dew point and the adiabatic flame temperature ($\sim 2500$ K).

15.72 In a rocket, hydrogen is burned with air, both reactants supplied as gases at $P_0$, $T_0$. The combustion is adiabatic, and the mixture is stoichiometric (100% theoretical air). Find the products’ dew point and the adiabatic flame temperature ($\sim 2500$ K).

15.73 Hydrogen gas is burned with pure $O_2$ in a steady-flow burner, shown in Fig. P15.73, where both reactants are supplied in a stoichiometric ratio at the reference pressure and temperature. What is the adiabatic flame temperature?

15.74 Some type of wood can be characterized as $C_{12}H_{16}$ with a lower heating value of 19 500 kJ/kg. Find its adiabatic flame temperature when burned with stoichiometric air at 100 kPa, 298 K.

15.75 Carbon is burned with air in a furnace with 150% theoretical air, and both reactants are supplied at the reference pressure and temperature. What is the adiabatic flame temperature?

15.76 Hydrogen gas is burned with 200% theoretical air in a steady-flow burner where both reactants are supplied at the reference pressure and temperature. What is the adiabatic flame temperature?

15.77 What is the adiabatic flame temperature before the secondary air is added in Problem 15.47?

15.78 Butane gas at 25°C is mixed with 150% theoretical air at 600 K and is burned in an adiabatic steady-flow combustor. What is the temperature of the products exiting the combustor?

15.79 A gas turbine burns methane with 200% theoretical air. The air and fuel come in through two separate compressors bringing them from 100 kPa, 298 K, to 1400 kPa, and after mixing they enter the combustion chamber at 600 K. Find the adiabatic flame temperature using constant specific heat for the $\Delta H_f$ terms.

15.80 Extend the solution to the previous problem by using Table A.9 for the $\Delta H_f$ terms.

15.81 A stoichiometric mixture of benzene, $C_6H_6$, and air is mixed from the reactants flowing at 25°C, 100 kPa. Find the adiabatic flame temperature. What is the error if constant-specific heat at $T_0$ for the products from Table A.5 is used?

15.82 A gas turbine burns natural gas (assume methane) where the air is supplied to the combustor at 1000 kPa, 500 K, and the fuel is at 298 K, 1000 kPa. What is the equivalence ratio and the percent theoretical air if the adiabatic flame temperature should be limited to 1800 K?

15.83 A cetylene gas at 25°C, 100 kPa, is fed to the head of a cutting torch. Calculate the adiabatic flame temperature if the acetylene is burned with a. 100% theoretical air at 25°C. b. 100% theoretical oxygen at 25°C.

15.84 Liquid $n$-butane at $T_{ad}$, is sprayed into a gas turbine, as in Fig. P15.84, with primary air flowing at 1.0 MPa, 400 K, in a stoichiometric ratio. After complete combustion, the products are at the
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adiabatic flame temperature, which is too high, so secondary air at 1.0 MPa, 400 K, is added, with the resulting mixture being at 1400 K. Show that \( T_{ad} > 1400 \) K and find the ratio of secondary to primary airflow.

15.85 Ethene, \( \text{C}_2\text{H}_4 \), burns with 150% theoretical air in a steady-flow, constant-pressure process with reactants entering at \( P_0, T_0 \). Find the adiabatic flame temperature.

15.86 Natural gas, we assume methane, is burned with 200% theoretical air, and the reactants are supplied as gases at the reference temperature and pressure. The products are flowing through a heat exchanger and then out the exhaust, as in Fig. P15.86. What is the adiabatic flame temperature right after combustion before the heat exchanger?

15.87 Solid carbon is burned with stoichiometric air in a steady-flow process. The reactants at \( T_0, P_0 \) are heated in a preheater to \( T_2 = 500 \) K, as shown in Fig. P15.87, with the energy given by the product gases before flowing to a second heat exchanger, which they leave at \( T_4 \). Find the temperature of the products \( T_4 \) and the heat transfer per kmol of fuel (4 to 5) in the second heat exchanger.

15.88 Liquid butane at 25 °C is mixed with 150% theoretical air at 600 K and is burned in a steady-flow burner. Use the enthalpy of combustion from Table 15.3 to find the adiabatic flame temperature out of the burner.

15.89 Gaseous ethanol, \( \text{C}_2\text{H}_5\text{OH} \), is burned with pure oxygen in a constant-volume combustion bomb. The reactants are charged in a stoichiometric ratio at the reference condition. Assume no heat transfer and find the final temperature (>5000 K).

15.90 The enthalpy of formation of magnesium oxide, \( \text{MgO}(s) \), is \( -601827 \text{ kJ/kmol} \) at 25 °C. The melting point of magnesium oxide is approximately 3000 K, and the increase in enthalpy between 298 and 3000 K is \( 128449 \text{ kJ/kmol} \). The enthalpy of sublimation at 3000 K is estimated at 418 000 kJ/kmol, and the specific heat of magnesium oxide vapor above 3000 K is estimated at 37.24 kJ/kmol K.

a. Determine the enthalpy of combustion per kilogram of magnesium.
b. Estimate the adiabatic flame temperature when magnesium is burned with theoretical oxygen.

15.91 Consider the combustion of hydrogen with pure \( \text{O}_2 \) in a stoichiometric ratio under steady-flow adiabatic conditions. The reactants enter separately at 298 K, 100 kPa, and the product(s) exit at a pressure of 100 kPa. What is the exit temperature, and what is the irreversibility?

15.92 Consider the combustion of methanol, \( \text{CH}_3\text{OH} \), with 25% excess air. The combustion products are passed through a heat exchanger and exit at 200 kPa, 400 K. Calculate the absolute entropy of the products exiting the heat exchanger assuming all the water is vapor.

15.93 Two kilomoles of ammonia are burned in a steady-flow process with \( x \) kmol of oxygen. The products, consisting of \( \text{H}_2\text{O}, \text{N}_2 \), and the excess \( \text{O}_2 \), exit at 200 °C, 7 M Pa. Calculate \( x \) if half the \( \text{H}_2\text{O} \) in the products is condensed.

15.94 Propene, \( \text{C}_3\text{H}_6 \), is burned with air in a steady-flow burner with reactants at \( P_0, T_0 \). The mixture is
lean, so the adiabatic flame temperature is 1800 K. Find the entropy generation per kmol fuel, neglecting all the partial-pressure corrections.

15.95 A flow of hydrogen gas is mixed with a flow of oxygen in a stoichiometric ratio, both at 298 K and 50 kPa. The mixture burns without any heat transfer in complete combustion. Find the adiabatic flame temperature and the amount of entropy generated per kmol hydrogen in the process.

15.96 Calculate the irreversibility for the process described in Problem 15.45.

15.97 Consider the combustion of methanol, CH₃OH, with 25% excess air. The combustion products are passed through a heat exchanger and exit at 200 kPa, 40°C. Calculate the absolute entropy of the products exiting the heat exchanger per kilomole of methanol burned, using proper amounts of liquid and vapor water.

15.98 Graphite, C, at P₀, T₀ is burned with air coming in at P₀, 500 K, in a ratio so that the products exit at P₀, 1200 K. Find the equivalence ratio, the percent theoretical air, and the total irreversibility.

15.99 A new inventor claims to have built a device that will take 0.001 kg/s of water from the faucet at 10°C, 100 kPa, and produce separate streams of hydrogen and oxygen gas, each at 400 K, 175 kPa. It is stated that this device operates in a 25°C room on 10-kW electrical power input. How do you evaluate this claim?

15.100 Hydrogen peroxide, H₂O₂, enters a gas generator at 25°C, 500 kPa, at the rate of 0.1 kg/s and is decomposed to steam and oxygen exiting at 800 K, 500 kPa. The resulting mixture is expanded through a turbine to atmospheric pressure, 100 kPa, as shown in Fig. P15.100. Determine the power output of the turbine and the heat transfer rate in the gas generator. The enthalpy of formation of liquid H₂O₂ is −187 583 kJ/kmol.

15.101 Methane is burned with air, both of which are supplied at the reference conditions. There is enough excess air to give a flame temperature of 1800 K. What are the percent theoretical air and the irreversibility in the process?

15.102 Pentane gas at 25°C, 150 kPa, enters an insulated steady-flow combustion chamber. Sufficient excess air to hold the combustion products temperature to 1800 K enters separately at 500 K, 150 kPa. Calculate the percent theoretical air required and the irreversibility of the process per kmol of pentane burned.

15.103 A closed, rigid container is charged with propane, C₃H₈, and 150% theoretical air at 100 kPa, 298 K. The mixture is ignited and burns with complete combustion. Heat is transferred to a reservoir at 500 K so the final temperature of the products is 700 K. Find the final pressure, the heat transfer per kmol fuel, and the total entropy generated per kmol fuel in the process.

Problems Involving Generalized Charts or Real Mixtures

15.104 A gas mixture of 50% ethane and 50% propane by volume enters a combustion chamber at 350 K, 10 MPa. Determine the enthalpy per kmole of this mixture relative to the thermochemical base of enthalpy using Kay’s rule.

15.105 Liquid butane at 25°C is mixed with 150% theoretical air at 100 kPa, 298 K. The mixture is ignited and burns in an adiabatic steady-state combustor. Use the generalized charts for the liquid fuel and find the properties of liquid oxygen.

15.106 Repeat Problem 15.135, but assume that saturated-liquid oxygen at 90 K is used instead of 25°C oxygen gas in the combustion process. Use the generalized charts to determine the properties of liquid oxygen.

15.107 A mixture of 80% ethane and 20% methane on a mole basis is throttled from 10 MPa, 65°C, to 100 kPa and is fed to a combustion chamber, where it undergoes complete combustion with air, which enters at 100 kPa, 600 K. The amount of air is such that the products of combustion exit at 100 kPa, 1200 K. Assume that the combustion
Liquid hexane enters a combustion chamber at 15.109

For a PEC fuel cell operating at 350 K, the

15.112

15.111

Assume that the basic hydrogen–oxygen fuel cell

operates at 600 K instead of 298 K, as in Example

15.15. For a SOC fuel cell operating at 900 K can be described by

EMF = 1.26 V and the constants in Eq. 15.29

as : b = 0.12, C = 0.14, A, 4.5 = 0.04Ω cm2 ,

li = 0.01, l1, = 2, l2 = 0.13 all A/cm2 . Find

the voltage and the power density for the current
density i = 0.25, 0.75 and 1.0 A/cm2 .

15.115

Redo the previous problem, but assume that the

fuel cell operates at 1200 K instead of at room
temperature.

15.116

A SOC fuel cell at 900 K can be described by

EMF = 1.26 V and the constants in Eq. 15.29

as : b = 0.12, C = 0.14, A, 4.5 = 0.04Ω cm2 ,

li = 0.01, l1, = 2, l2 = 0.13 all A/cm2 . Find

the voltage and the power density for the current
density i = 0.25, 0.75 and 1.0 A/cm2 .

15.117

A assume the SOC fuel cell in the previous prob-

lem. How large an area does the fuel cell have to
deliver 1 kW with a current density of 1 A/cm2 ?

15.118

A PEC fuel cell operating at 25°C generates

1.0 V that also account for losses. For a total power

of 1 kW, what is the hydrogen mass flow rate?

15.119

A basic hydrogen-oxygen fuel cell operates at 600

K, instead of 25 K, as in Example 15.15. For a

total power of 5 kW, find the hydrogen mass flow

rate and the exergy in the exhaust flow.

Combustion Applications and Efficiency

15.120

For the combustion of methane, 150% theoretical

air is used at 25°C, 100 kPa, and relative humidity

of 70%. Find the composition and dew point of

the products.

15.121

Pentane is burned with 120% theoretical air in a

constant-pressure process at 100 kPa. The prod-

ucts are cooled to ambient temperature, 20°C.

How much mass of water is condensed per kilo-

gram of fuel? Repeat the answer, assuming that the

air used in the combustion has a relative humidity

of 90%.

15.122

A gas turbine burns methane with 150% theoreti-

cal air. A assume the air is 25°C, 100 kPa, and has a

relative humidity of 80%. How large a fraction of

the product mixture water comes from the moist

inlet air?

15.123

In an engine, a mixture of liquid octane and

ethanol, mole ratio 9:1, and stoichiometric air are

taken in at T0, P0. In the engine, the enthalpy of

combustion is used so that 30% goes out as work,

30% goes out as heat loss, and the rest goes out.
CHAPTER FIFTEEN

CHEMICAL REACTIONS

15.124 The gas turbine cycle in Problem 12.21 has \( q_H = 960 \text{ kJ/kg} \) air added by combustion. Assume the fuel is methane gas and \( q_H \) is from the heating value at \( T_0 \). Find the air–fuel ratio on a mass basis.

15.125 A gas turbine burns methane with 200% theoretical air. The air and fuel come in through two separate compressors bringing them from 100 kPa, 298 K, to 1400 kPa and enter a mixing chamber and a combustion chamber. What are the specific compressor work and \( q_H \) to be used in Brayton cycle calculation? Use constant specific heat to solve the problem.

15.126 Find the equivalent heat transfer \( q_H \) to be used in a cycle calculation for constant-pressure combustion when the fuel is (a) methane and (b) gaseous octane. In both cases, use water vapor in the products and a stoichiometric mixture.

15.127 Consider the steady-state combustion of propane at 25°C with air at 400 K. The products exit the combustion chamber at 1200 K. Asume that the combustion efficiency is 90% and that 95% of the carbon in the propane burns to form CO\(_2\); the remaining 5% forms CO. Determine the ideal fuel–air ratio and the heat transfer from the combustion chamber.

15.128 A gasoline engine is converted to run on propane as shown in Fig. P15.128. Assume the propane enters the engine at 25°C, at the rate of 40 kg/h. Only 90% theoretical air enters at 25°C, so 90% of the C burns to form CO\(_2\) and 10% of the C burns to form CO. The combustion products, also including H\(_2\)O, H\(_2\), and N\(_2\), exit the exhaust pipe at 1000 K. Heat loss from the engine (primarily to the cooling water) is 120 kW. What is the power output of the engine? What is the thermal efficiency?

15.129 A small air-cooled gasoline engine is tested, and the output is found to be 1.0 kW. The temperature of the products is measured as 600 K. The products (complete combustion) flow out of the exhaust valve at 1100 K. Assume that the heat loss carried away by the cooling water, at 100°C, is equal to the work output. Find the efficiency of the engine expressed as (work/lower heating value) and the second-law efficiency.

Review Problems

15.130 A gasoline engine uses liquid octane and air, both supplied at \( P_0, T_0 \), in a stoichiometric ratio. The products (complete combustion) flow out of the exhaust valve at 1100 K. Assume that the heat loss carried away by the cooling water, at 100°C, is equal to the work output. Find the efficiency of the engine expressed as (work/lower heating value) and the second-law efficiency.

15.131 Repeat Problem 15.25 for a certain Utah coal that contains, according to the coal analysis, 68.2% C, 4.8% H, and 15.7% O on a mass basis. The exiting product gas contains 30.9% CO, 26.7% H\(_2\), 15.9% CO\(_2\), and 25.7% H\(_2\)O on a mole basis.

15.132 Many coals from the western United States have a high moisture content. Consider the following sample of Wyoming coal, for which the ultimate analysis on an as-received basis is, by mass:

<table>
<thead>
<tr>
<th>Component</th>
<th>Moisture</th>
<th>H</th>
<th>C</th>
<th>S</th>
<th>N</th>
<th>O</th>
<th>Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>% mass</td>
<td>28.9</td>
<td>3.5</td>
<td>48.6</td>
<td>0.5</td>
<td>0.7</td>
<td>12.0</td>
<td>5.8</td>
</tr>
</tbody>
</table>

This coal is burned in the steam generator of a large power plant with 150% theoretical air. Determine the air–fuel ratio on a mass basis.

15.133 A fuel, C\(_x\)\(_H_\)\(_y\), is burned with dry air, and the product composition is measured on a dry mole basis to be 9.6% CO\(_2\), 7.3% O\(_2\), and 83.1% N\(_2\). Find the fuel composition \( x/y \) and the percent theoretical air used.

15.134 In an engine, liquid octane and ethanol, mole ratio 9:1, and stoichiometric air are taken in at 298 K, 100 kPa. After complete combustion, the products run out of the exhaust system, where they are cooled to 10°C. Find the dew point of the products.
HOMEWORK PROBLEMS

15.135 In a test of rocket propellant performance, liquid hydrazine (N₂H₄) at 100 kPa, 25°C, and O₂ gas at 100 kPa, 25°C, are fed to a combustion chamber in the ratio of 0.5 kg O₂/kg N₂H₄. Determine the temperature of the products exiting the chamber. Assume that only H₂O, H₂, and N₂ are present. The enthalpy of formation of liquid hydrazine is +50 417 kJ/kmol.

15.136 Find the lower heating value for the fuel blend in Problem 15.134 with scaling as in Table 15.3.

15.137 E85 is a liquid mixture of 85% ethanol and 15% gasoline (assume octane) by mass. Find the lower heating value for this blend.

15.138 Determine the higher heating value of the sample Wyoming coal as specified in Problem 15.132.

15.139 Ethene, C₂H₄, and propane, C₃H₈, in a 1:1 mole ratio as gases are burned with 120% theoretical air in a gas turbine. Fuel is added at 25°C, 1 MPa, and the air comes from the atmosphere, at 25°C, 100 kPa, through a compressor to 1 MPa and is mixed with the fuel. The turbine work is such that the exit temperature is 800 K with an exit pressure of 100 kPa. Find the mixture temperature before combustion and the work, assuming an adiabatic turbine.

15.140 A study is to be made using liquid ammonia as the fuel in a gas-turbine engine. Consider the compression and combustion processes of this engine.
   a. Air enters the compressor at 100 kPa, 25°C, and is compressed to 1600 kPa, where the isentropic compressor efficiency is 87%. Determine the exit temperature and the work input per kilomole.
   b. Two kilomoles of liquid ammonia at 25°C, 100 kPa, through a compressor to 1 MPa and is mixed with the fuel. The turbine work is such that the exit temperature is 800 K with an exit pressure of 100 kPa. Find the mixture temperature before combustion and the work, assuming an adiabatic turbine.
   c. Assuming complete combustion while the piston is at top dead center (at minimum volume) in an adiabatic process. Determine the temperature and pressure after combustion and the increase in entropy during the combustion process.
   d. What is the irreversibility for this process?

15.141 Liquid acetylene, C₂H₂, is stored in a high-pressure storage tank at ambient temperature,
CHAPTER FIFTEEN  CHEMICAL REACTIONS

25°C. The liquid is fed to an insulated combustor/steam boiler at a steady rate of 1 kg/s, along with 140% theoretical oxygen, O₂, which enters at 500 K, as shown in Fig. P15.148. The combustion products exit the unit at 500 kPa, 350 K. Liquid water enters the boiler at 10°C, at the rate of 15 kg/s, and superheated steam exits at 200 kPa.

a. Calculate the absolute entropy, per kmol, of liquid acetylene at the storage tank state.

b. Determine the phase(s) of the combustion products exiting the combustor boiler unit and the amount of each if more than one.

c. Determine the temperature of the steam at the boiler exit.

FIGURE P15.148

ENGLISH UNIT PROBLEMS

15.149E The output gas mixture of a certain air-blown coal gasifier has the composition of producer gas as listed in Table 15.2. Consider the combustion of this gas with 120% theoretical air at 15.7 lbf/in.² pressure. Find the dew point of the products and the mass of water condensed per pound-mass of fuel if the products are cooled 20°F below the dew-point temperature.

Energy and Enthalpy of Formation

15.150E What is the enthalpy of formation for oxygen as O₂? If O? For carbon dioxide?

15.151E One alternative to using petroleum or natural gas as fuels is ethanol (C₂H₅OH), which is commonly produced from grain by fermentation. Consider a combustion process in which liquid ethanol is burned with 120% theoretical air in a steady-flow process. The reactants enter the combustion chamber at 77°F, and the products exit at 140°F. 15.7 lbf/in.². Calculate the heat transfer per pound mole of ethanol, using the enthalpy of formation of ethanol gas plus the generalized tables or charts.

15.152E Liquid methanol is burned with stoichiometric air, both supplied at P₀, T₀ in a constant pressure, process, and the product exits a heat exchanger at 1600 R. Find the heat transfer per lbmol fuel.

In a new high-efficiency furnace, natural gas, assumed to be 90% methane and 10% ethane (by volume) and 110% theoretical air, each enter at 77°F, 15.7 lbf/in.², and the products (assumed to be 100% gaseous) exit the furnace at 100°F. 15.7 lbf/in.². What is the heat transfer for this process? Compare this to an older furnace where the products exit at 450°F, 15.7 lbf/in.².

15.154E Repeat the previous problem, but take into account the actual phase behavior of the products exiting the furnace.

15.155E Pentene, C₅H₁₀, is burned with pure O₂ in a steady-state process. The products at one point are brought to 1300 R, and used in a heat exchanger, where they are cooled to 77°F. Find the specific heat transfer in the heat exchanger.

15.156E A rigid vessel initially contains 2 lbm of carbon and 2 lbm of oxygen at 77°F and 20 lbf/in.². Combustion occurs, and the resulting products consist of 1 lbm of CO₂, 1 lbm of CO, and excess O₂ at a temperature of 1800 R. Determine the final pressure in the vessel and the heat transfer from the vessel during the process.

A closed, insulated container is charged with a stoichiometric ratio of oxygen and hydrogen at 77°F and 20 lbf/in.². After combustion, liquid water at 77°F is sprayed in such a way that the final temperature is 2100 R. What is the final pressure?

15.158E Methane, CH₄, is burned in a steady-state process with two different oxidizers: case A—pure oxygen, O₂, and case B—a mixture of O₂ + xAr. The reactants are supplied at T₀, P₀, and
the products are at 3200 R in both cases. Find the required equivalence ratio in case A and the amount of argon, \( x \), for a stoichiometric ratio in case B.

### Enthalpy of Combustion and Heating Value

15.159E What is the higher heating value, HHV, of \( n \)-butane?

15.160E Find the enthalpy of combustion and the heating value for pure carbon.

15.161E Blast furnace gas in a steel mill is available at 500 F to be burned for the generation of steam. The composition of this gas is as follows on a volumetric basis:

<table>
<thead>
<tr>
<th>Component</th>
<th>CH(_4)</th>
<th>H(_2)</th>
<th>CO</th>
<th>CO(_2)</th>
<th>N(_2)</th>
<th>H(_2)O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percent by volume</td>
<td>0.1</td>
<td>2.4</td>
<td>23.3</td>
<td>14.4</td>
<td>56.4</td>
<td>3.4</td>
</tr>
</tbody>
</table>

Find the lower heating value (Btu/ft\(^3\)) of this gas at 500 F and \( P_0 \).

15.162E A burner receives a mixture of two fuels with mass fraction 40% \( n \)-butane and 60% methanol, both vapor. The fuel is burned with stoichiometric air. Find the product composition and the lower heating value of this fuel mixture (Btu/lbm fuel mix).

### Adiabatic Flame Temperature

15.163E Hydrogen gas is burned with pure oxygen in a steady-flow burner where both reactants are supplied in a stoichiometric ratio at the reference pressure and temperature. What is the adiabatic flame temperature?

15.164E Some type of wood can be characterized as \( C_1H_1.5O_0.7\) with a lower heating value of 8380 Btu/lbm. Find its adiabatic flame temperature when burned with stoichiometric air at 1 atm., 77 F.

15.165E Carbon is burned with air in a furnace with 150% theoretical air, and both reactants are supplied at the reference pressure and temperature. What is the adiabatic flame temperature?

15.166E Butane gas at 77 F is mixed with 150% theoretical air at 1000 R and is burned in an adiabatic steady-state combustor. What is the temperature of the products exiting the combustor?

15.167E A acetylene gas at 77 F, 15.7 lbf/in.\(^2\), is fed to the head of a cutting torch. Calculate the adiabatic flame temperature if the acetylene is burned with 100% theoretical air at 77 F. Repeat the answer for 100% theoretical oxygen at 77 F.

15.168E Liquid \( n \)-butane at \( T_0 \), is sprayed into a gas turbine with primary air flowing at 150 lbf/in.\(^2\), 700 R in a stoichiometric ratio. After complete combustion, the products are at the adiabatic flame temperature, which is too high. Therefore, secondary air at 150 lbf/in.\(^2\), 700 R, is added (see Fig. P15.84), with the resulting mixture being at 2500 R. Show that \( T_{ad} \geq 2500 \text{ R} \) and find the ratio of secondary to primary airflow.

### Second Law for the Combustion Process

15.170E Solid carbon is burned with stoichiometric air in a steady-state, constant-pressure process, with reactants entering at \( P_0, T_0 \). Find the adiabatic flame temperature.
15.174E Hydrogen peroxide, $\text{H}_2\text{O}_2$, enters a gas generator at 77 °F, 75 lbf/in.², at the rate of 0.2 lbm/s and is decomposed to steam and oxygen exiting at 1500 R, 75 lbf/in.². The resulting mixture is expanded through a turbine to atmospheric pressure, 14.7 lbf/in.², as shown in Fig. P15.100. Determine the power output of the turbine and the heat-transfer rate in the gas generator. The enthalpy of formation of liquid $\text{H}_2\text{O}_2$ is $-80541 \text{ Btu/lb mol}$.

15.175E Methane is burned with air, both of which are supplied at the reference conditions. There is enough excess air to give a flame temperature of 3200 R. What are the percent theoretical air and the irreversibility in the process?

15.176E In Example 15.16, a basic hydrogen–oxygen fuel cell reaction was analyzed at 25 °C, 100 kPa. Repeat this calculation, assuming that the fuel cell operates on air at 77 °F, 14.7 lbf/in.², instead of on pure oxygen at this state.

15.177E Pentane is burned with 120% theoretical air in a constant-pressure process at 14.7 lbf/in.². The products are cooled to ambient temperature, 70 °F. How much mass of water is condensed per pound-mass of fuel? Repeat the problem, assuming that the air used in the combustion has a relative humidity of 90%.

15.178E A small air-cooled gasoline engine is tested, and the output is found to be 2.0 hp. The temperature of the products is measured and found to be 730 °F. The products are analyzed on a dry volumetric basis, with the following result: 11.4% CO₂, 2.9% CO, 1.6% O₂, and 84.1% N₂. The fuel may be considered to be liquid octane. The fuel and air enter the engine at 77 °F, and the flow rate of fuel to the engine is 1.8 lbm/h. Determine the rate of heat transfer from the engine and its thermal efficiency.

15.180E In a test of rocket propellant performance, liquid hydrazine ($\text{N}_2\text{H}_4$) at 14.7 lbf/in.², 77 °F, and oxygen gas at 14.7 lbf/in.², 77 °F, are fed to a combustion chamber. The heat transfer from the chamber to the surroundings is estimated to be 45 Btu/lbm. Determine the temperature of the products exiting the chamber. Assume that only $\text{H}_2\text{O}$, $\text{H}_2$, and $\text{N}_2$ are present. The enthalpy of formation of liquid hydrazine is $+21647 \text{ Btu/lb mole}$.

15.181E In Problem 15.180E, assume that saturated liquid oxygen at 170 R is used in the combustion process. Use the generalized charts to determine the properties of liquid oxygen.

15.182E Ethene, C₂H₄, and propane, C₃H₈, in a 1:1 mole ratio as gases are burned with 120% theoretical air in a gas turbine. Fuel is added at 77 °F, 150 lbf/in.², and the air comes from the atmosphere, 77 °F, 15 lbf/in.², through a compressor to 150 lbf/in.² and mixed with the fuel. The turbine work is such that the exit temperature is 1500 R with an exit pressure of 14.7 lbf/in.². Find the mixture temperature before combustion and also the work, assuming an adiabatic turbine.
combustion with 200–300% theoretical air and exhaust to the atmosphere.

15.185 A car that runs on natural gas has it stored in a heavy tank with a maximum pressure of 3600 psi (25 MPa). Size the tank for a range of 300 miles (500 km), assuming a car engine that has a 30% efficiency requiring about 25 hp (20 kW) to drive the car at 55 mi/h (90 km/h).

15.186 The Cheng cycle, shown in Fig. P13.178, is powered by the combustion of natural gas (essentially methane) being burned with 250–300% theoretical air. In the case with a single water-condensing heat exchanger, where $T_6 = 40^\circ C$ and $\Phi_1 = 100\%$, is any makeup water needed at state 8 or is there a surplus? Does the humidity in the compressed atmospheric air at state 1 make any difference? Study the problem over a range of air-fuel ratios.

15.187 The cogenerating power plant shown in Problem 11.73 burns 170 kg/s air with natural gas, CH$_4$. The setup is shown in Fig. P15.187 where a fraction of the air flow out of the compressor with pressure ratio $\frac{15.8}{1}$ is used to preheat the feed-water in the steam cycle. The fuel flow rate is 3.2 kg/s. Analyze the system, determining the total heat transfer to the steam cycle from the turbine exhaust gases, the heat transfer in the preheater, and the gas turbine inlet temperature.

15.188 Consider the combustor in the Cheng cycle (see Problems 13.178 and 15.144). A atmospheric air is compressed to 1.25 MPa, state 1. It is burned with natural gas, CH$_4$, with the products leaving at state 2. The fuel should add a total of about 15 MW to the cycle, with an air flow of 12 kg/s. For a compressor with an intercooler, estimate the temperatures $T_3$, $T_7$, and the fuel flow rate.

15.189 Study the coal gasification process that will produce methane, CH$_4$, or methanol, CH$_3$OH. What is involved in such a process? Compare the heating values of the gas products with those of the original coal. Discuss the merits of this conversion.

15.190 Ethanol, C$_2$H$_5$OH, can be produced from corn or biomass. Investigate the process and the chemical reactions that occur. For different raw materials, estimate the amount of ethanol that can be obtained per mass of the raw material.

15.191 A diesel engine is used as a stationary power plant in remote locations such as a ship, oil drilling rig, or farm. Assume diesel fuel is used with 300% theoretical air in a 1000-hp diesel engine. Estimate the amount of fuel used, the efficiency, and the potential use of the exhaust gases for heating rooms or water. Investigate if other fuels can be used.

15.192 When a power plant burns coal or some blends of oil, the combustion process can generate pollutants as SO$_x$ and NO$_x$. Investigate the use of scrubbers to remove these products. Explain the processes that take place and the effect on the power plant operation (energy, exhaust pressures, etc.).
Introduction to Phase and Chemical Equilibrium

Up to this point, we have assumed that we are dealing either with systems that are in equilibrium or with those in which the deviation from equilibrium is infinitesimal, as in a quasi-equilibrium or reversible process. For irreversible processes, we made no attempt to describe the state of the system during the process but dealt only with the initial and final states of the system, in the case of a control mass, or the inlet and exit states as well in the case of a control volume. For any case, we either considered the system to be in equilibrium throughout or at least made the assumption of local equilibrium.

In this chapter we examine the criteria for equilibrium and from them derive certain relations that will enable us, under certain conditions, to determine the properties of a system when it is in equilibrium. The specific case we will consider is that involving chemical equilibrium in a single phase (homogeneous equilibrium) as well as certain related topics.

16.1 REQUIREMENTS FOR EQUILIBRIUM

As a general requirement for equilibrium, we postulate that a system is in equilibrium when there is no possibility that it can do any work when it is isolated from its surroundings. In applying this criterion, it is helpful to divide the system into two or more subsystems and consider the possibility of doing work by any conceivable interaction between these two subsystems. For example, in Fig. 16.1 a system has been divided into two systems and an engine, of any conceivable variety, placed between these subsystems. A system may be so defined as to include the immediate surroundings. In this case, we can let the immediate surroundings be a subsystem and thus consider the general case of the equilibrium between a system and its surroundings.

The first requirement for equilibrium is that the two subsystems have the same temperature; otherwise, we could operate a heat engine between the two systems and do work. Thus, we conclude that one requirement for equilibrium is that a system must be at a uniform temperature to be in equilibrium. It is also evident that there must be no unbalanced mechanical forces between the two systems, or else one could operate a turbine or piston engine between the two systems and do work.

We would like to establish general criteria for equilibrium that would apply to all simple compressible substances, including those that undergo chemical reactions. We will find that the Gibbs function is a particularly significant property in defining the criteria for equilibrium.

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Let us first consider a qualitative example to illustrate this point. Consider a natural gas well that is 1 km deep, and let us assume that the temperature of the gas is constant throughout the gas well. Suppose we have analyzed the composition of the gas at the top of the well, and we would like to know the composition of the gas at the bottom of the well. Furthermore, let us assume that equilibrium conditions prevail in the well. If this is true, we would expect that an engine such as that shown in Fig. 16.2 (which operates on the basis of the pressure and composition change with elevation and does not involve combustion) would not be capable of doing any work.

If we consider a steady-state process for a control volume around this engine, the reversible work for the change of state from $i$ to $e$ is given by Eq. 10.14 on a total mass basis:

$$\dot{W}_{\text{rev}} = \dot{m}_i \left( h_i + \frac{V_i^2}{2} + gZ_i - T_0 s_i \right) - \dot{m}_e \left( h_e + \frac{V_e^2}{2} + gZ_e - T_0 s_e \right)$$

Furthermore, since $T_i = T_e = T_0 = \text{constant}$, this reduces to the form of the Gibbs function $g = h - Ts$, Eq. 14.14, and the reversible work is

$$\dot{W}_{\text{rev}} = \dot{m}_i \left( g_i + V_i^2 + gZ_i \right) - \dot{m}_e \left( g_e + V_e^2 + gZ_e \right)$$

However,

$$\dot{W}_{\text{rev}} = 0, \quad \dot{m}_i = \dot{m}_e \quad \text{and} \quad \frac{V_i^2}{2} = \frac{V_e^2}{2}$$

Then we can write

$$g_i + gZ_i = g_e + gZ_e$$
CHAPTER SIXTEEN
INTRODUCTION TO PHASE AND CHEMICAL EQUILIBRIUM

Equilibrium point

\[ T = \text{constant} \]
\[ P = \text{constant} \]

and the requirement for equilibrium in the well between two levels that are a distance \( dZ \) apart would be

\[ dg_T + gdZ_T = 0 \]

In contrast to a deep gas well, most of the systems that we consider are of such size that \( \Delta Z \) is negligibly small, and therefore we consider the pressure to be uniform throughout.

This leads to the general statement of equilibrium that applies to simple compressible substances that may undergo a change in chemical composition, namely, that at equilibrium

\[ dG_T = 0 \quad (16.1) \]

In the case of a chemical reaction, it is helpful to think of the equilibrium state as the state in which the Gibbs function is a minimum. For example, consider a control mass consisting initially of \( n_A \) moles of substance \( A \) and \( n_B \) moles of substance \( B \), which react in accordance with the relation

\[ v_A A + v_B B \leftrightarrow v_C C + v_D D \]

Let the reaction take place at constant pressure and temperature. If we plot \( G \) for this control mass as a function of \( n_A \), the number of moles of \( A \) present, we would have a curve as shown in Fig. 16.3. At the minimum point on the curve, \( dG_T = 0 \), and this will be the equilibrium composition for this system at the given temperature and pressure. The subject of chemical equilibrium will be developed further in Section 16.4.

16.2 EQUILIBRIUM BETWEEN TWO PHASES OF A PURE SUBSTANCE

As another example of this requirement for equilibrium, let us consider the equilibrium between two phases of a pure substance. Consider a control mass consisting of two phases of a pure substance at equilibrium. We know that under these conditions the two phases are at the same pressure and temperature. Consider the change of state associated with a transfer of \( dn \) moles from phase 1 to phase 2 while the temperature and pressure remain constant. That is,

\[ dn^1 = -dn^2 \]
The Gibbs function of this control mass is given by

\[ G = f(T, P, n^1, n^2) \]

where \( n^1 \) and \( n^2 \) designate the number of moles in each phase. Therefore,

\[ dG = \left( \frac{\partial G}{\partial T} \right)_{P, n^1, n^2} dT + \left( \frac{\partial G}{\partial P} \right)_{T, n^1, n^2} dP + \left( \frac{\partial G}{\partial n^1} \right)_{T, P, n^2} dn^1 + \left( \frac{\partial G}{\partial n^2} \right)_{T, P, n^1} dn^2 \]

By definition,

\[ \left( \frac{\partial G}{\partial n^1} \right)_{T, P, n^2} = g_1 \quad \left( \frac{\partial G}{\partial n^2} \right)_{T, P, n^1} = g_2 \]

Therefore, at constant temperature and pressure,

\[ dG = g_1 dn^1 + g_2 dn^2 = dn^1(g_1 - g_2) \]

Now at equilibrium (Eq. 16.1)

\[ dG_{T, P} = 0 \]

Therefore, at equilibrium, we have

\[ g_1 = g_2 \] (16.2)

That is, under equilibrium conditions, the Gibbs function of each phase of a pure substance is equal. Let us check this by determining the Gibbs function of saturated liquid (water) and saturated vapor (steam) at 300 kPa. From the steam tables:

For the liquid:

\[ g_f = h_f - T s_f = 561.47 - 406.7 \times 1.6718 = -118.4 \text{ kJ/kg} \]

For the vapor:

\[ g_g = h_g - T s_g = 2725.3 - 406.7 \times 6.9919 = -118.4 \text{ kJ/kg} \]

Equation 16.2 can also be derived by applying the relation

\[ T ds = dh - v dP \]

to the change of phase that takes place at constant pressure and temperature. For this process this relation can be integrated as follows:

\[ \int_{s_1}^{s_2} T ds = \int_{h_1}^{h_2} dh \]

\[ T (s_2 - s_1) = (h_2 - h_1) \]

\[ h_1 - T s_1 = h_2 - T s_2 \]

\[ \Delta g = \Delta h - s \Delta T \]
Consider a control mass that consists of a saturated liquid and a saturated vapor in equilibrium, and let this system undergo a change of pressure $dP$. The corresponding change in temperature, as determined from the vapor-pressure curve, is $dT$. Both phases will undergo the change in Gibbs function, $dg$, but since the phases always have the same value of the Gibbs function when they are in equilibrium, it follows that

$$dg_f = dg_g$$

But, from Eq. 14.15,

$$dg = v dP - s dT$$

it follows that

$$dg_f = v_f dP - s_f dT$$
$$dg_g = v_g dP - s_g dT$$

Since

$$dg_f = dg_g$$

it follows that

$$v_f dP - s_f dT = v_g dP - s_g dT$$

$$dP \left( \frac{v_g - v_f}{s_g - s_f} \right) = dT$$

$$\frac{dP}{dT} = \frac{s_{fg}}{v_{fg}} = \frac{h_{fg}}{Tv_{fg}}$$

(16.3)

In summary, when different phases of a pure substance are in equilibrium, each phase has the same value of the Gibbs function per unit mass. This fact is relevant to different solid phases of a pure substance and is important in metallurgical applications of thermodynamics. Example 16.1 illustrates this principle.

**EXAMPLE 16.1** What pressure is required to make diamonds from graphite at a temperature of 25°C? The following data are given for a temperature of 25°C and a pressure of 0.1 MPa.

<table>
<thead>
<tr>
<th>Graphite</th>
<th>Diamond</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g$</td>
<td>2867.8 kJ/mol</td>
</tr>
<tr>
<td>$v$</td>
<td>0.004 444 m³/kg</td>
</tr>
<tr>
<td>$\beta_T$</td>
<td>0.004 284 m³/kg</td>
</tr>
<tr>
<td>$h_T$</td>
<td>$0.304 \times 10^{-4}$ MPa</td>
</tr>
<tr>
<td>$r_T$</td>
<td>$0.016 \times 10^{-4}$ MPa</td>
</tr>
</tbody>
</table>

**Analysis and Solution**

The basic principle in the solution is that graphite and diamond can exist in equilibrium when they have the same value of the Gibbs function. At 0.1 MPa pressure the Gibbs function of the diamond is greater than that of the graphite. However, the rate of increase in Gibbs function with pressure is greater for the graphite than for the diamond, therefore, at some pressure they can exist in equilibrium. Our problem is to find this pressure.
We have already considered the relation
\[ dg = v \, dP - s \, dT \]
Since we are considering a process that takes place at constant temperature, this reduces to
\[ dg_T = v \, dP \]  \hspace{1cm} (a)
Now at any pressure \( P \) and the given temperature, the specific volume can be found from the following relation, which utilizes isothermal compressibility factor.
\[ v = v^0 + \int_{P=0}^{P} \left( \frac{\partial v}{\partial P} \right)_T \, dP = v^0 + \int_{P=0}^{P} \left( \frac{\partial v}{\partial P} \right)_T \, dP \]
\[ = v^0 - \int_{P=0}^{P} \beta_T \, dP \]  \hspace{1cm} (b)
The superscript \(^0\) will be used in this example to indicate the properties at a pressure of 0.1 MPa and a temperature of 25 \(^\circ\)C.
The specific volume changes only slightly with pressure, so that \( v \approx v^0 \). Also, we assume that \( \beta_T \) is constant and that we are considering a very high pressure. With these assumptions, this equation can be integrated to give
\[ v = v^0 - v^0 \beta_T \, P \]
We can now substitute this into Eq. (a) to give the relation
\[ dg_T = v^0 \left[ (1 - \beta_T \, P) \right] \, dP \]
If we assume that \( P^0 \ll P \), this reduces to
\[ g - g^0 = v^0 \left( P - \beta_T \, P^{1/2} \right) ] \]  \hspace{1cm} (e)
For the graphite, \( g^0 = 0 \) and we can write
\[ g_0 = v^0 \left[ P - \beta_T \, P^{1/2} \right] ] \]
For the diamond, \( g^0 \) has a definite value and we have
\[ g_0 = g^0 + v^0 \left[ P - \beta_T \, P^{1/2} \right] ] \]
But at equilibrium the Gibbs function of the graphite and diamond are equal:
\[ g_0 = g_0 \]
Therefore,
\[
\begin{align*}
  v_0^G \left[ P - \left( \beta T \right) G \right] &= g_0^G + v_0^D \left[ P - \left( \beta T \right) D \right] \\
  (v_0^G - v_0^D)P &= \left[ v_0^G \left( \beta T \right) G - v_0^D \left( \beta T \right) D \right] P^2/2 = g_0^D (0.000 444 - 0.000 284)P \\
  (0.000 444 \times 0.304 \times 10^{-4} - 0.000 284 \times 0.016 \times 10^{-6})P^2/2 &= 2867.8 \times 17.011 \times 10^6
\end{align*}
\]
Solving this for \( P \) we find
\[ P = 1493 \text{ MPa} \]
That is, at 1493 MPa, 25\( ^\circ \text{C} \), graphite and diamond can exist in equilibrium, and the possibility exists for conversion from graphite to diamonds.

16.3 METASTABLE EQUILIBRIUM

Although the limited scope of this book precludes an extensive treatment of metastable equilibrium, a brief introduction to the subject is presented in this section. Let us first consider an example of metastable equilibrium.

Consider a slightly superheated vapor, such as steam, expanding in a convergent-divergent nozzle, as shown in Fig. 16.4. A surprising the process is reversible and adiabatic, the
steam will follow path 1-a on the T-s diagram, and at point a we would expect condensation to occur. However, if point a is reached in the divergent section of the nozzle, it is observed that no condensation occurs until point b is reached, and at this point the condensation occurs very abruptly in what is referred to as a condensation shock. Between points a and b the steam exists as a vapor, but the temperature is below the saturation temperature for the given pressure. This is known as a metastable state. The possibility of a metastable state exists with any phase transformation. The dotted lines on the equilibrium diagram shown in Fig. 16.5 represent possible metastable states for solid-liquid-vapor equilibrium.

The nature of a metastable state is often pictured schematically by the kind of diagram shown in Fig. 16.6. The ball is in a stable position (the “metastable state”) for small displacements, but with a large displacement it moves to a new equilibrium position. The steam expanding in the nozzle is in a metastable state between a and b. This means that droplets smaller than a certain critical size will reevaporate, and only when droplets larger than this critical size have formed (this corresponds to moving the ball out of the depression) will the new equilibrium state appear.

16.4 CHEMICAL EQUILIBRIUM

We now turn our attention to chemical equilibrium and consider first a chemical reaction involving only one phase. This is referred to as a homogeneous chemical reaction; it may be helpful to visualize this as a gaseous phase, but the basic considerations apply to any phase.

Consider a vessel, Fig. 16.7, that contains four compounds, A, B, C, and D, which are in chemical equilibrium at a given pressure and temperature. For example, these might consist of CO₂, H₂, CO, and H₂O in equilibrium. Let the number of moles of each component be designated n₁, n₂, n₃, and n₄. Furthermore, let the chemical reaction that takes place
CHAPTER SIXTEEN  INTRODUCTION TO PHASE AND CHEMICAL EQUILIBRIUM

between these four constituents be

\[ v_A A + v_B B \rightleftharpoons v_C C + v_D D \]  \hspace{1cm} (16.4)

where the \( v \)'s are the stoichiometric coefficients. It should be emphasized that there is a very definite relation between the \( v \)'s (the stoichiometric coefficients), whereas the \( n \)'s (the number of moles present) for any constituent can be varied simply by varying the amount of that component in the reaction vessel.

Let us now consider how the requirement for equilibrium, namely, that \( \Delta G, T = 0 \) at equilibrium, applies to a homogeneous chemical reaction. Let us assume that the four components are in chemical equilibrium and then assume that from this equilibrium state, while the temperature and pressure remain constant, the reaction proceeds an infinitesimal amount toward the right as Eq. 16.4 is written. This results in a decrease in the moles of \( A \) and \( B \) and an increase in the moles of \( C \) and \( D \). Let us designate the degree of reaction by \( \epsilon \) and define the degree of reaction by the relations

\[
\begin{align*}
\Delta n_A &= -v_A \, d\epsilon \\
\Delta n_B &= -v_B \, d\epsilon \\
\Delta n_C &= +v_C \, d\epsilon \\
\Delta n_D &= +v_D \, d\epsilon 
\end{align*}
\hspace{1cm} (16.5)
\]

That is, the change in the number of moles of any component during a chemical reaction is given by the product of the stoichiometric coefficients (the \( v \)'s) and the degree of reaction.

Let us evaluate the change in the Gibbs function associated with this chemical reaction that proceeds to the right in the amount \( d\epsilon \). In doing so we use, as would be expected, the Gibbs function of each component in the mixture—the partial molal Gibbs function (or its equivalent, the chemical potential):

\[
d\Delta G, T = \left( v_C \, \Delta G_C + v_D \, \Delta G_D - v_A \, \Delta G_A - v_B \, \Delta G_B \right) \, d\epsilon
\hspace{1cm} (16.6)
\]

We now need to develop expressions for the partial molal Gibbs functions in terms of properties that we are able to calculate. From the definition of the Gibbs function, Eq. 14.14,

\[ G = H - T S \]

For a mixture of two components \( A \) and \( B \), we differentiate this equation with respect to \( n_A \) at constant \( T \), \( P \), and \( n_B \), which results in

\[
\left( \frac{d\Delta G}{d n_A} \right)_{T,P,n_B} = \left( \frac{dH}{dn_A} \right)_{T,P,n_B} - T \left( \frac{dS}{dn_A} \right)_{T,P,n_B}
\]

All three of these quantities satisfy the definition of partial molal properties according to Eq. 14.65, such that

\[ \Delta G = \Delta H - T \Delta S \]

For an ideal-gas mixture, enthalpy is not a function of pressure, and

\[ \Delta H = \Delta H^0 = \Delta H^0_{T,P} \]

(16.8)
Entropy is, however, a function of pressure, so that the partial entropy of \( A \) can be expressed by Eq. 15.22 in terms of the standard-state value,

\[
\bar{s}_A = s^{\text{ref},A}_{\text{STP}} = s^{0}_A P_0 = s^0_A - R \ln \left( \frac{y_A P}{P_0} \right)
\]  

(16.9)

Now, substituting Eqs. 16.8 and 16.9 into Eq. 16.7,

\[
\begin{align*}
G_A &= h^0_A - T s^0_A + R T \ln \left( \frac{y_A P}{P_0} \right)
\end{align*}
\]

(16.10)

Equation 16.10 is an expression for the partial Gibbs function of a component in a mixture in terms of a specific reference value, the pure-substance standard-state Gibbs function at the same temperature, and a function of the temperature, pressure, and composition of the mixture. This expression can be applied to each of the components in Eq. 16.6, resulting in

\[
dG_{TP} = \left[ v_C \left( g^0_C + R T \ln \left( \frac{y_C P}{P_0} \right) \right) \right] + \left[ v_D \left( g^0_D + R T \ln \left( \frac{y_D P}{P_0} \right) \right) \right] - \left[ v_A \left( g^0_A + R T \ln \left( \frac{y_A P}{P_0} \right) \right) \right] - \left[ v_B \left( g^0_B + R T \ln \left( \frac{y_B P}{P_0} \right) \right) \right]
\]

(16.11)

Let us define \( \Delta G^0 \) as follows:

\[
\Delta G^0 = v_C g^0_C + v_D g^0_D - v_A g^0_A - v_B g^0_B
\]  

(16.12)

That is, \( \Delta G^0 \) is the change in the Gibbs function that would occur if the chemical reaction given by Eq. 16.4 (which involves the stoichiometric amounts of each component) proceeded completely from left to right, with the reactants \( A \) and \( B \) initially separated and at temperature \( T \) and the standard-state pressure and the products \( C \) and \( D \) finally separated and at temperature \( T \) and the standard-state pressure. Note also that \( \Delta G^0 \) for a given reaction is a function of only the temperature. This will be most important to bear in mind as we proceed with our developments of homogeneous chemical equilibrium. Let us now digress from our development to consider an example involving the calculation of \( \Delta G^0 \).

**EXAMPLE 16.2** Determine the value of \( \Delta G^0 \) for the reaction \( 2H_2O \rightleftharpoons 2H_2 + O_2 \) at 25°C and at 2000 K, with the water in the gaseous phase.

**Solution** At any given temperature, the standard-state Gibbs function change of Eq. 16.12 can be calculated from the relation

\[
\Delta G^0 = \Delta H^0 - T \Delta S^0
\]
At 25°C,
\[ \Delta H^0 = 2\Delta h_f^0(H_2) + \Delta h_f^0(O_2) - 2\Delta h_f^0(H_2O) \]
\[ = 2(0) + 1(0) - 2(-241.826) = 483.652 \text{ kJ} \]
\[ \Delta S^0 = 2\Delta s_f^0(H_2) + 2\Delta s_f^0(O_2) - 2\Delta s_f^0(H_2O) \]
\[ = 2(130.678) + 1(205.148) - 2(188.834) = 88.836 \text{ kJ/K} \]
Therefore, at 25°C,
\[ \Delta G^0 = 483.652 - 298.15(88.836) = 457.166 \text{ kJ} \]

At 2000 K,
\[ \Delta H^0 = 2(\Delta h_{2000}^0 - \Delta h_{298}^0)_{H_2} + (\Delta h_{2000}^0 - \Delta h_{298}^0)_{O_2} - 2(\Delta h_f^0 + \Delta h_{2000}^0 - \Delta h_{298}^0)_{H_2O} \]
\[ = 2(52.942) + (59.176) - 2(-241.826 + 72.788) = 503.136 \text{ kJ} \]
\[ \Delta S^0 = 2(\Delta s_{2000}^0)_{H_2} + (\Delta s_{2000}^0)_{O_2} - 2(\Delta s_f^0)_{H_2O} \]
\[ = 2(188.419) + (268.748) - 2(264.769) = 116.048 \text{ kJ/K} \]
Therefore,
\[ \Delta G^0 = 503.136 - 2000 \times 116.048 = 271.040 \text{ kJ} \]

Returning now to our development, substituting Eq. 16.12 into Eq. 16.11 and rearranging, we can write
\[ dG_T, P = \left\{ \Delta G^0 + R \ln \left[ \frac{y_v A^v}{y_v B^v} \frac{y_v C^v}{y_v D^v} \left( \frac{P}{P_0} \right)^{v_A-v_B-v_C+v_D} \right] \right\} d\varepsilon \] (16.13)
At equilibrium, \( dG_T, P = 0 \). Therefore, since \( d\varepsilon \) is arbitrary,
\[ \ln \left[ \frac{y_v A^v}{y_v B^v} \frac{y_v C^v}{y_v D^v} \left( \frac{P}{P_0} \right)^{v_A-v_B-v_C+v_D} \right] = -\frac{\Delta G^0}{RT} \] (16.14)
For convenience, we define the equilibrium constant \( K \) as
\[ \ln K = -\frac{\Delta G^0}{RT} \] (16.15)
which we note must be a function of temperature only for a given reaction, since \( \Delta G^0 \) is given by Eq. 16.12 in terms of the properties of the pure substances at a given temperature and the standard-state pressure.
Combining Eqs. 16.14 and 16.15, we have
\[ K = \frac{y_v A^v}{y_v B^v} \frac{y_v C^v}{y_v D^v} \left( \frac{P}{P_0} \right)^{v_A-v_B-v_C+v_D} \] (16.16)


which is the chemical equilibrium equation corresponding to the reaction equation, Eq. 16.4.

From the equilibrium constant definition in Eqs. 16.15 and 16.16 we can draw a few conclusions. If the shift in the Gibbs function is large and positive, \( \ln K \) is large and negative, leading to a very small value of \( K \). At a given \( P \) in Eq. 16.16 this leads to relatively small values of the RHS (component C and D) concentrations relative to the LHS component concentrations; the reaction is shifted to the left. The opposite is the case of a shift in the Gibbs function that is large and negative, giving a large value of \( K \) and the reaction is shifted to the right, as shown in Fig. 16.8. If the shift in Gibbs function is zero, then \( K \) is zero, and \( K \) is exactly equal to 1. The reaction is in the middle, with all concentrations of the same order of magnitude, unless the stoichiometric coefficients are extreme.

The other trends we can see are the influences of the temperature and pressure. For a higher temperature but the same shift in the Gibbs function, the absolute value of \( \ln K \) is smaller, which means \( K \) is closer to 1 and the reaction is more centered. For low temperatures, the reaction is shifted toward the side with the smallest Gibbs function \( \Delta G^0 \).

The pressure has an influence only if the power in Eq. 16.16 is different from zero. That is so when the number of moles on the RHS (\( v_\text{C} + v_\text{D} \)) is different from the number of moles on the LHS (\( v_\text{A} + v_\text{B} \)). Assuming we have more moles on the RHS, then, we see that the power is positive. So, if the pressure is larger than the reference pressure, the whole pressure factor is larger than 1, which reduces the RHS concentrations as \( K \) is fixed for a given temperature. You can argue all the other combinations, and the result is that a higher pressure pushes the reaction toward the side with fewer moles, and a lower pressure pushes the reaction toward the side with more moles. The reaction tries to counteract the externally imposed pressure variation.

**EXAMPLE 16.3**

Determine the equilibrium constant \( K \), expressed as \( \ln K \), for the reaction \( 2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_2 + \text{O}_2 \) at 25°C and at 2000 K.

**Solution**

We have already found, in Example 16.2, \( \Delta G^0 \) for this reaction at these two temperatures. Therefore, at 25°C,

\[
(\ln K)_{298} = \frac{\Delta G^0}{RT} = -\frac{457.166}{8.3145 \times 298.15} = -184.42
\]

At 2000 K, we have

\[
(\ln K)_{2000} = \frac{\Delta G^0}{RT} = -\frac{271.040}{8.3145 \times 2000} = -16.299
\]
Table A.11 gives the values of the equilibrium constant for a number of reactions. Note again that for each reaction the value of the equilibrium constant is determined from the properties of each of the pure constituents at the standard-state pressure and is a function of temperature only.

For other reaction equations, the chemical equilibrium constant can be calculated as in Example 16.3. Sometimes you can write a reaction scheme as a linear combination of the elementary reactions that are already tabulated, as for example in Table A.11. Assume we can write a reaction III as a linear combination of reaction I and reaction II, which means

\[
\begin{align*}
\text{LHS}_{\text{III}} &= a \text{LHS}_{\text{I}} + b \text{LHS}_{\text{II}} \\
\text{RHS}_{\text{III}} &= a \text{RHS}_{\text{I}} + b \text{RHS}_{\text{II}}
\end{align*}
\]  

(16.17)

From the definition of the shift in the Gibbs function, Eq. 16.12, it follows that

\[
\Delta G^0_{\text{III}} = G^0_{\text{RHS}_{\text{III}}} - G^0_{\text{LHS}_{\text{III}}} = a \Delta G^0_{\text{I}} + b \Delta G^0_{\text{II}}
\]

Then from the definition of the equilibrium constant in Eq. 16.15 we get

\[
\ln K_{\text{III}} = -\frac{\Delta G^0_{\text{III}}}{RT} = -a \frac{\Delta G^0_{\text{I}}}{RT} - b \frac{\Delta G^0_{\text{II}}}{RT} = a \ln K_{\text{I}} + b \ln K_{\text{II}}
\]

or

\[
K_{\text{III}} = K_{\text{I}}^a K_{\text{II}}^b
\]  

(16.18)

**EXAMPLE 16.4** Show that the equilibrium constant for the reaction called the water-gas reaction

\[
\text{III: } \text{H}_2 + \text{CO}_2 \rightleftharpoons \text{H}_2\text{O} + \text{CO}
\]

can be calculated from values listed in Table A.11.

**Solution**

Using the reaction equations from Table A.11,

\[
\begin{align*}
\text{I: } &2\text{CO}_2 \rightleftharpoons 2\text{CO} + \text{O}_2 \\
\text{II: } &2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_2 + \text{O}_2
\end{align*}
\]

It is seen that

\[
\text{III } = \frac{1}{2} \text{I } - \frac{1}{2} \text{II}
\]

so that

\[
K_{\text{III}} = \left( \frac{K_{\text{I}}}{K_{\text{II}}} \right)^{\frac{1}{2}}
\]

where \( K_{\text{III}} \) is calculated from the Table A.11 values

\[
\ln K_{\text{III}} = \frac{1}{2}(\ln K_{\text{I}} - \ln K_{\text{II}})
\]

We now consider a number of examples that illustrate the procedure for determining the equilibrium composition for a homogeneous reaction and the influence of certain variables on the equilibrium composition.
EXAMPLE 16.5  One kilomole of carbon at 25 °C and 0.1 MPa pressure reacts with 1 kmol of oxygen at 25 °C and 0.1 MPa pressure to form an equilibrium mixture of CO₂, CO, and O₂ at 3000 K, 0.1 MPa pressure, in a steady-state process. Determine the equilibrium composition and the heat transfer for this process.

**Control volume:** Combustion chamber.
**Inlet states:** P, T known for carbon and for oxygen.
**Exit state:** P, T known.
**Process:** Steady-state.
**Sketch:** Figure 16.9.
**Model:** Table A.10 for carbon; ideal gases, Tables A.9 and A.10.

**Analysis and Solution**
It is convenient to view the overall process as though it occurs in two separate steps, a combustion process followed by a heating and dissociation of the combustion product carbon dioxide, as indicated in Fig. 16.9. This two-step process is represented as

**Combustion:**
\[ C + O_2 \rightarrow CO_2 \]

**Dissociation reaction:**
\[ 2CO_2 \rightleftharpoons 2CO + O_2 \]

That is, the energy released by the combustion of C and O₂ heats the CO₂ formed to high temperature, which causes dissociation of part of the CO₂ to CO and O₂. Thus, the overall reaction can be written

\[ C + O_2 \rightarrow aCO_2 + bCO + dO_2 \]

where the unknown coefficients a, b, and d must be found by solution of the equilibrium equation associated with the dissociation reaction. Once this is accomplished, we can write the first law for a control volume around the combustion chamber to calculate the heat transfer.

From the combustion equation we find that the initial composition for the dissociation reaction is 1 kmol CO₂. Therefore, letting \( z \) be the number of kilomoles of CO₂,
dissociated, we find

\[
2\text{CO}_2 \rightleftharpoons 2\text{CO} + \text{O}_2
\]

Initial:
\[
\begin{array}{lll}
1 & 0 & 0
\end{array}
\]

Change:
\[
-2z & +2z & +z
\]

At equilibrium:
\[
\begin{array}{ll}
(1 - 2z) & z
\end{array}
\]

Therefore, the overall reaction is

\[
\text{C} + \text{O}_2 \rightarrow (1 - 2z)\text{CO}_2 + 2z\text{CO} + z\text{O}_2
\]

and the total number of kilomoles at equilibrium is

\[
n = (1 - 2z) + 2z + z = 1 + z
\]

The equilibrium mole fractions are

\[
\begin{align*}
y_{\text{CO}_2} &= \frac{1 - 2z}{1 + z} \\
y_{\text{CO}} &= \frac{2z}{1 + z} \\
y_{\text{O}_2} &= \frac{z}{1 + z}
\end{align*}
\]

From Table A.11 we find that the value of the equilibrium constant at 3000 K for the dissociation reaction considered here is

\[
\ln K = -2.217
\]

\[
K = 0.1089
\]

Substituting these quantities along with \(P = 0.1 \text{ MPa}\) into Eq. 16.16, we have the equilibrium equation,

\[
K = 0.1089 = \frac{y_{\text{CO}_2} y_{\text{O}_2}}{y_{\text{CO}} y_{\text{O}_2}} \frac{P}{P_0} \left( \frac{2z}{1 - 2z} \right)^{2 - 1 - 2} \left( \frac{Z}{1 + z} \right)^{2 - 1 - 2} (1)
\]

or, in more convenient form,

\[
\frac{K}{P/P_0} = \frac{0.1089}{z} = \left( \frac{2z}{1 - 2z} \right) \left( \frac{Z}{1 + z} \right)
\]

To obtain the physically meaningful root of this mathematical relation, we note that the number of moles of each component must be greater than zero. Thus, the root of interest to us must lie in the range

\[
0 \leq z \leq 0.5
\]

Solving the equilibrium equation by trial and error, we find

\[
z = 0.2189
\]

Therefore, the overall process is

\[
\text{C} + \text{O}_2 \rightarrow 0.5622 \text{CO}_2 + 0.4378 \text{CO} + 0.2189 \text{O}_2
\]
where the equilibrium mole fractions are

\[ y_{CO_2} = \frac{0.5622}{1.2189} = 0.4612 \]

\[ y_{CO} = \frac{0.4378}{1.2189} = 0.3592 \]

\[ y_{O_2} = \frac{0.2189}{1.2189} = 0.1796 \]

The heat transfer from the combustion chamber to the surroundings can be calculated using the enthalpies of formation and Table A.9. For this process

\[ H_R = (h_{f}^{0} + h_{f}^{0} + h_{f}^{0} - h_{f}^{0} - h_{f}^{0})_{CO_2} + \]

\[ (h_{f}^{0} + h_{f}^{0} + h_{f}^{0} - h_{f}^{0} - h_{f}^{0})_{CO} + \]

\[ (h_{f}^{0} + h_{f}^{0} + h_{f}^{0} - h_{f}^{0} - h_{f}^{0})_{O_2} = 0 \]

\[ 0.5622(-393.522 + 152.853) + 0.4378(-110.527 + 93.504) + 0.2189(98.013) = -121.302 \text{ kJ} \]

Substituting into the first law gives

\[ Q_{c.v.} = H_P - H_R = -121.302 \text{ kJ/kmol C burned} \]

**EXAMPLE 16.6** One kilomole of carbon at 25°C reacts with 2 kmol of oxygen at 25°C to form an equilibrium mixture of CO₂, CO, and O₂ at 3000 K, 0.1 MPa pressure. Determine the equilibrium composition.

Control volume: Combustion chamber.

Inlet states: T known for carbon and for oxygen.

Exit state: P, T known.

Process: Steady state.

Model: Ideal-gas mixture at equilibrium.
Analysis and Solution

The overall process can be imagined to occur in two steps, as in the previous example. The combustion process is

\[ C + 2O_2 \rightarrow CO_2 + O_2 \]

and the subsequent dissociation reaction is

\[ 2CO_2 \rightleftharpoons 2CO + O_2 \]

Initial: 1 0 1

Change: \(-2z\) \(+2z\) \(+z\)

At equilibrium: \((1 - 2z)\) \(2z\) \((1 + z)\)

We find that in this case the overall process is

\[ C + 2O_2 \rightarrow (1 - 2z)CO_2 + 2zCO + (1 + z)O_2 \]

and the total number of kilomoles at equilibrium is

\[ n = (1 - 2z) + 2z + (1 + z) = 2 + z \]

The mole fractions are

\[ y_{CO_2} = \frac{1 - 2z}{2 + z} \quad y_{CO} = \frac{2z}{2 + z} \quad y_{O_2} = \frac{1 + z}{2 + z} \]

The equilibrium constant for the reaction \(2CO_2 \rightleftharpoons 2CO + O_2\) at 3000 K was found in Example 16.5 to be 0.1089. Therefore, with these expressions, quantities, and \(P = 0.1 \text{ MPa}\) substituted, the equilibrium equation is

\[ K = \frac{0.1089}{y_{CO_2}^2 y_{O_2}} = \frac{y_{CO}^2 y_{O_2}}{y_{CO_2}^2} = \frac{(2z)^2 (1 + z)^2}{(1 - 2z)^2 (2 + z)} \]

or

\[ \frac{K P}{P^2} = \frac{0.1089}{1} = \frac{(2z)^2 (1 + z)^2}{(1 - 2z)^2 (2 + z)} \]

We note that in order for the number of kilomoles of each component to be greater than zero,

\[ 0 \leq z \leq 0.5 \]

Solving the equilibrium equation for \(z\), we find

\[ z = 0.1553 \]

so that the overall process is

\[ C + 2O_2 \rightarrow 0.6894 \text{ CO}_2 + 0.3106 \text{ CO} + 1.1553 \text{ O}_2 \]

When we compare this result with that of Example 16.5, we notice that there is more CO₂ and less CO. The presence of additional O₂ shifts the dissociation reaction more to the left side.
The mole fractions of the components in the equilibrium mixture are

\[ y_{CO_2} = \frac{0.6894}{2.1553} = 0.320 \]
\[ y_{CO} = \frac{0.3106}{2.1553} = 0.144 \]
\[ y_{O_2} = \frac{1.1553}{2.1553} = 0.536 \]

The heat transferred from the chamber in this process could be found by the same procedure followed in Example 16.5, considering the overall process.

In-Text Concept Questions

a. For a mixture of O$_2$ and O the pressure is increased at constant T; what happens to the composition?

b. For a mixture of O$_2$ and O the temperature is increased at constant P; what happens to the composition?

c. For a mixture of O$_2$ and O I add some argon, keeping constant T, P; what happens to the moles of O?

16.5 SIMULTANEOUS REACTIONS

In developing the equilibrium equation and equilibrium constant expressions of Section 16.4, it was assumed that there was only a single chemical reaction equation relating the substances present in the system. To demonstrate the more general situation in which there is more than one chemical reaction, we will now analyze a case involving two simultaneous reactions by a procedure analogous to that followed in Section 16.4. These results are then readily extended to systems involving several simultaneous reactions.

Consider a mixture of substances A, B, C, D, L, M, and N as indicated in Fig. 16.10. These substances are assumed to exist at a condition of chemical equilibrium at temperature T and pressure P, and are related by the two independent reactions

\[ \begin{align*}
(A) & \quad v_{A1}A + v_{B}B \rightleftharpoons v_{C}C + v_{D}D \\
(B) & \quad v_{A2}A + v_{L}L \rightleftharpoons v_{M}M + v_{N}N
\end{align*} \tag{16.19} \tag{16.20} \]

We have considered the situation where one of the components (substance A) is involved in each of the reactions in order to demonstrate the effect of this condition on the resulting equations. As in the previous section, the changes in amounts of the components are related by the various stoichiometric coefficients (which are not the same as the number of moles of each substance present in the vessel). We also realize that the coefficients $v_{A1}$ and $v_{A2}$ are not necessarily the same. That is, substance A does not in general take part in each of the reactions to the same extent.

Development of the requirement for equilibrium is completely analogous to that of Section 16.4. We consider that each reaction proceeds an infinitesimal amount toward the right side. This results in a decrease in the number of moles of A, B, and L, and an increase
in the moles of \( C, D, M, \) and \( N \). Letting the degrees of reaction be \( \epsilon_1 \) and \( \epsilon_2 \) for reactions 1 and 2, respectively, the changes in the number of moles are, for infinitesimal shifts from the equilibrium composition,

\[
\begin{align*}
\Delta n_A &= -v_A \Delta \epsilon_1 - v_A \Delta \epsilon_2 \\
\Delta n_B &= -v_B \Delta \epsilon_2 \\
\Delta n_C &= +v_C \Delta \epsilon_1 \\
\Delta n_D &= +v_D \Delta \epsilon_1 \\
\Delta n_M &= +v_M \Delta \epsilon_2 \\
\Delta n_N &= +v_N \Delta \epsilon_2
\end{align*}
\]

(16.21)

The change in Gibbs function for the mixture in the vessel at constant temperature and pressure is

\[
dG_T, P = G_A \Delta n_A + G_B \Delta n_B + G_C \Delta n_C + G_D \Delta n_D + G_M \Delta n_M + G_N \Delta n_N
\]

Substituting the expressions of Eq. 16.21 and collecting terms,

\[
dG_T, P = \left( v_C G_C + v_D G_D - v_A g_0 A \right) \Delta \epsilon_1 + \left( v_M G_M + v_N G_N - v_A g_0 A \right) \Delta \epsilon_2
\]

(16.22)

It is convenient to again express each of the partial molal Gibbs functions in terms of

\[
\Delta G_0 = g_0^i + RT \ln \left( \frac{y_i P}{y_0^i P_0} \right)
\]

Equation 16.22 written in this form becomes

\[
dG_T, P = \left( \Delta G_0^1 + RT \ln \left( \frac{y_C^{\epsilon_1} y_D^{\epsilon_1}}{y_A^{\epsilon_1} y_B^{\epsilon_1}} \right) \right) \Delta \epsilon_1 + \left( \Delta G_0^2 + RT \ln \left( \frac{y_M^{\epsilon_2} y_N^{\epsilon_2}}{y_A^{\epsilon_2} y_L^{\epsilon_2}} \right) \right) \Delta \epsilon_2
\]

(16.23)

In this equation the standard-state change in Gibbs function for each reaction is defined as

\[
\Delta G_0^1 = v_C g_C^0 + v_D g_D^0 - v_A g_A^0 - v_B g_B^0
\]

(16.24)

\[
\Delta G_0^2 = v_M g_M^0 + v_N g_N^0 - v_A g_A^0 - v_L g_L^0
\]

(16.25)

Equation 16.23 expresses the change in Gibbs function of the system at constant \( T, P \), for infinitesimal degrees of reaction of both reactions 1 and 2, Eqs. 16.19 and 16.20. The requirement for equilibrium is that \( dG_T, P = 0 \). Therefore, since reactions 1 and 2 are independent, \( d\epsilon_1 \) and \( d\epsilon_2 \) can be independently varied. It follows that at equilibrium each of the bracketed terms of Eq. 16.23 must be zero. Defining equilibrium constants for the two reactions by

\[
\ln K_1 = -\frac{\Delta G_0^1}{RT}
\]

(16.26)
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and

\[ \ln K_2 = -\frac{\Delta G^0_2}{RT} \]  

we find that, at equilibrium

\[ K_1 = \frac{y^A_y^C}{y^B_y^D} \left( \frac{P}{P_0} \right)^{2v_A - v_C - v_D} \]  

and

\[ K_2 = \frac{y^M_y^N}{y^L_y^A} \left( \frac{P}{P_0} \right)^{2v_M - v_A - v_L} \]  

These expressions for the equilibrium composition of the mixture must be solved simultaneously. The following example demonstrates and clarifies this procedure.

EXAMPLE 16.7

One kilomole of water vapor is heated to 3000 K, 0.1 MPa pressure. Determine the equilibrium composition, assuming that H₂O, H₂,O₂, and OH are present.

Control volume: Heat exchanger.

Exit state: P, T known.

Model: Ideal-gas mixture at equilibrium.

Analysis and Solution

There are two independent reactions relating the four components of the mixture at equilibrium. These can be written as

(1): \( 2 \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{O}_2 \)

(2): \( 2 \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + 2 \text{OH} \)

Let \( 2a \) be the number of kilomoles of water dissociating according to reaction 1 during the heating, and let \( 2b \) be the number of kilomoles of water dissociating according to reaction 2. Since the initial composition is 1 kmol water, the changes according to the two reactions are

(1): \( 2 \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{O}_2 \)

Change: \(-2a + 2a + a\)

(2): \( 2 \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + 2 \text{OH} \)

Change: \(-2b + b + 2b\)

Therefore, the number of kilomoles of each component at equilibrium is its initial number plus the change, so that at equilibrium

\[ n_{\text{H}_2\text{O}} = 1 - 2a - 2b \]

\[ n_{\text{H}_2} = 2a + b \]

\[ n_{\text{O}_2} = a \]

\[ n_{\text{OH}} = 2b \]

\[ n = 1 + a + b \]
The overall chemical reaction that occurs during the heating process can be written:

\[
H_2O \rightarrow (1 - 2a - 2b)H_2O + (2a + b)H_2 + aO_2 + 2bOH
\]

The RHS of this expression is the equilibrium composition of the system. Since the number of kilomoles of each substance must necessarily be greater than zero, we find that the possible values of \( a \) and \( b \) are restricted to:

\[
\begin{align*}
    a &\geq 0 \\
    b &\geq 0 \\
    (a + b) &\leq 0.5
\end{align*}
\]

The two equilibrium equations are, assuming that the mixture behaves as an ideal gas,

\[
\begin{align*}
    K_1 &= \frac{y_{H_2}y_{O_2}}{y_{H_2O}} \left( \frac{P}{P_0} \right)^{2a + b} \\
    K_2 &= \frac{y_{H_2}y_{OH}}{y_{H_2O}} \left( \frac{P}{P_0} \right)^{2b}
\end{align*}
\]

Since the mole fraction of each component is the ratio of the number of kilomoles of the component to the total number of kilomoles of the mixture, these equations can be written in the form:

\[
\begin{align*}
    K_1 &= \frac{(2a + b)^2}{(1 - 2a - 2b)^2} \left( \frac{a}{1 + a + b} \right) \left( \frac{P}{P_0} \right)^{2a + b} \\
    K_2 &= \frac{(2b)^2}{(1 - 2a - 2b)^2} \left( \frac{b}{1 + a + b} \right) \left( \frac{P}{P_0} \right)^{2b}
\end{align*}
\]

and

\[
\begin{align*}
    K_1 &= \frac{(2a + b)^2}{(1 - 2a - 2b)^2} \left( \frac{a}{1 + a + b} \right) \left( \frac{P}{P_0} \right)^{2a + b} \\
    K_2 &= \frac{(2b)^2}{(1 - 2a - 2b)^2} \left( \frac{b}{1 + a + b} \right) \left( \frac{P}{P_0} \right)^{2b}
\end{align*}
\]

giving two equations in the two unknowns \( a \) and \( b \), since \( P = 0.1 \) M Pa and the values of \( K_1, K_2 \) are known. From Table A.11 at 3000 K, we find:

\[
\begin{align*}
    K_1 &= 0.002 \, 062 \\
    K_2 &= 0.002 \, 893
\end{align*}
\]

Therefore, the equations can be solved simultaneously for \( a \) and \( b \). The values satisfying the equations are:

\[
\begin{align*}
    a &= 0.0534 \\
    b &= 0.0551
\end{align*}
\]
Substituting these values into the expressions for the number of kilomoles of each component and of the mixture, we find the equilibrium mole fractions to be

\[
y_{\text{H}_2\text{O}} = 0.7063
\]
\[
y_{\text{H}_2} = 0.1461
\]
\[
y_{\text{O}_2} = 0.0482
\]
\[
y_{\text{OH}} = 0.0994
\]

The procedure followed in this section can readily be extended to equilibrium systems having more than two independent reactions. In each case, the number of simultaneous equilibrium equations is equal to the number of independent reactions. The expression and solution of the resulting large set of nonlinear equations require a formal mathematical iterative technique and are carried out on a computer. A different approach is typically followed in situations including a large number of chemical species. This involves the direct minimization of the system Gibbs function \( G \) with respect to variations in all of the species assumed to be present at the equilibrium state (for example, in Example 16.7 these would be \( \text{H}_2\text{O}, \text{H}_2, \text{O}_2 \), and \( \text{OH} \)). In general, this is \( G = \sum G_i \Delta n_i \), in which the \( G_i \) are each given by Eq. 16.10 and the \( \Delta n_i \) are the variations in moles. However, the number of changes in moles are not all independent, as they are subject to constraints on the total number of atoms of each element present (in Example 16.7 these would be \( \text{H} \) and \( \text{O} \)). This process then results in a set of nonlinear equations equal to the sum of the number of elements and the number of species. Again, this set of equations requires a formal iterative solution procedure, but this technique is more straightforward and simpler than that utilizing the equilibrium constants and equations in situations involving a large number of chemical species.

### 16.6 COAL GASIFICATION

The processes involved with the gasification of coal (or other biomass) begin with heating the solid material to around 300–400 °C such that pyrolysis results in a solid char (essentially carbon) plus volatile gases (\( \text{CO}_2, \text{CO}, \text{H}_2\text{O}, \text{H}_2 \), some light hydrocarbons) and tar. In the gasifier, the char reacts with a small amount of oxygen and steam in the reactions

\[
\text{C} + 0.5 \text{O}_2 \rightarrow \text{CO} \] (16.30)
\[
\text{C} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO} \] (16.31)

The resulting gas mixture of \( \text{H}_2 \) and \( \text{CO} \) is called syngas.

Then using appropriate catalysts, there is the water–gas shift equilibrium reaction

\[
\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO}_2 \] (16.32)

and the methanation equilibrium reaction

\[
\text{CO} + 3 \text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O} \] (16.33)

Solution of the two equilibrium equations, Eqs. 16.32 and 16.33, depends on the initial amounts of \( \text{O}_2 \) and \( \text{H}_2\text{O} \) that were used to react with char in Eqs. 16.30 and 16.31, and are, of course, strongly dependent on temperature and pressure. Relatively low \( T \) and high \( P \)
favor the formation of $\text{CH}_4$, while high $T$ and low $P$ favor $\text{H}_2$ and $\text{CO}$. Time is also a factor, as the mixture may not have time to come to equilibrium in the gasifier. The entire process is quite complex but is one that has been thoroughly studied over many years. Finally, it should be pointed out that there are several different processes by which syngas can be converted to liquid fuels; this is also an ongoing field of research and development.

16.7 IONIZATION

In this section, we consider the equilibrium of systems that are made up of ionized gases, or plasmas, a field that has been studied and applied increasingly in recent years. In previous sections, we discussed chemical equilibrium, with a particular emphasis on molecular dissociation, as for example the reaction

$$\text{N}_2 \rightleftharpoons 2\text{N}$$

which occurs to an appreciable extent for most molecules only at high temperature, of the order of magnitude 3000 to 10 000 K. At still higher temperatures, such as those found in electric arcs, the gas becomes ionized. That is, some of the atoms lose an electron, according to the reaction

$$\text{N} \rightleftharpoons \text{N}^+ + e^-$$

where $\text{N}^+$ denotes a singly ionized nitrogen atom, one that has lost one electron and consequently has a positive charge, and $e^-$ represents the free electron. As the temperature rises still higher, many of the ionized atoms lose another electron, according to the reaction

$$\text{N}^+ \rightleftharpoons \text{N}^{++} + e^-$$

and thus become doubly ionized. As the temperature continues to rise, the process continues until a temperature is reached at which all the electrons have been stripped from the nucleus.

Ionization generally is appreciable only at high temperature. However, dissociation and ionization both tend to occur to greater extents at low pressure; consequently, dissociation and ionization may be appreciable in such environments as the upper atmosphere, even at moderate temperature. Other effects, such as radiation, will also cause ionization, but these effects are not considered here.

The problems of analyzing the composition in a plasma become much more difficult than for an ordinary chemical reaction, for in an electric field the free electrons in the mixture do not exchange energy with the positive ions and neutral atoms at the same rate that they do with the field. Consequently, in a plasma in an electric field, the electron gas is not at exactly the same temperature as the heavy particles. However, for moderate fields, assuming a condition of thermal equilibrium in the plasma is a reasonable approximation, at least for preliminary calculations. Under this condition, we can treat the ionization equilibrium in exactly the same manner as an ordinary chemical equilibrium analysis.

At these extremely high temperatures, we may assume that the plasma behaves as an ideal-gas mixture of neutral atoms, positive ions, and electron gas. Thus, for the ionization of some atomic species A,

$$A \rightleftharpoons A^+ + e^- \quad (16.34)$$
we may write the ionization equilibrium equation in the form

\[ K = \frac{y_A y_e}{y_e - y_A} \left( \frac{P}{P_0} \right)^{1-1} \]  

(16.35)

The ionization-equilibrium constant \( K \) is defined in the ordinary manner

\[ \ln K = -\frac{\Delta G_0^0}{RT} \]  

(16.36)

and is a function of temperature only. The standard-state Gibbs function change for reaction 16.34 is found from

\[ \Delta G_0^0 = n_A^0 + n_e^0 - n_A^0 \]  

(16.37)

The standard-state Gibbs function for each component at the given plasma temperature can be calculated using the procedures of statistical thermodynamics, so that ionization-equilibrium constants can be tabulated as functions of temperature.

The ionization-equilibrium equation, Eq. 16.35, is then solved in the same manner as an ordinary chemical-reaction equilibrium.

**EXAMPLE 16.8**

Calculate the equilibrium composition if argon gas is heated in an arc to 10 000 K, 1 kPa, assuming the plasma to consist of \( \text{Ar, Ar}^+, \text{e}^- \). The ionization-equilibrium constant for the reaction

\[ \text{Ar} \rightleftharpoons \text{Ar}^+ + \text{e}^- \]

at this temperature is 0.000 42.

Control volume: Heating arc.
Exit state: \( P, T \) known.
Model: Ideal-gas mixture at equilibrium.

**Analysis and Solution**

Consider an initial composition of 1 kmol neutral argon, and let \( z \) be the number of kilomoles ionized during the heating process. Therefore,

\[ \text{Ar} \rightleftharpoons \text{Ar}^+ + \text{e}^- \]

Initial: \( 1 \ 0 \ 0 \)
Change: \( -z \ z \ z \)
Equilibrium: \( (1 - z) \ z \ z \)

and

\[ n = (1 - z) + z + z = 1 + z \]

Since the number of kilomoles of each component must be positive, the variable \( z \) is restricted to the range

\[ 0 \leq z \leq 1 \]
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The equilibrium mole fractions are

\[ y_{Ar} = \frac{n_{Ar}}{n} = \frac{1 - z}{1 + z} \]
\[ y_{Ar^+} = \frac{n_{Ar^+}}{n} = \frac{z}{1 + z} \]
\[ y_e = \frac{n_e}{n} = \frac{z}{1 + z} \]

The equilibrium equation is

\[ K = \frac{y_{Ar^+} y_e}{y_{Ar}} \left( \frac{P}{P_0} \right) ^{1+1-1} = \frac{\left( \frac{2}{1+z} \right) \left( \frac{2}{1+z} \right)}{\left( \frac{1+z}{1+z} \right)} \left( \frac{P}{P_0} \right) \]

so that, at 10 000 K, 1 kPa,

\[ 0.00042 = \left( \frac{2}{1+0.2} \right) (0.01) \]

Solving,

\[ z = 0.2008 \]

and the composition is found to be

\[ y_{Ar} = 0.6656 \]
\[ y_{Ar^+} = 0.1672 \]
\[ y_e = 0.1672 \]

16.8 APPLICATIONS

Chemical reactions and equilibrium conditions become important in many industrial processes that occur during energy conversion, like combustion. As the temperatures in the combustion products are high, a number of chemical reactions may take place that would not occur at lower temperatures. Typical examples of these are dissociations that require substantial energy to proceed and thus have a profound effect on the resulting mixture temperature. To promote chemical reactions in general, catalytic surfaces are used in many reactors, which could be platinum pellets, as in a three-way catalytic converter on a car exhaust system. We have previously shown some of the reactions that are important in coal gasification and some of the homework have a few reactions used in the production of synthetic fuels from biomass or coal. Production of hydrogen for fuel cell applications is part of this class of processes (recall Eqns.16.31-16.33), and for this it is important to examine the effect of both the temperature and the pressure on the final equilibrium mixture.

One of the chemical reactions that is important in the formation of atmospheric pollutants is the formation of NOₓ (nitrogen-oxygen combinations), which takes place in all combustion processes that utilize fuel and air. Formation of NOₓ happens at higher temperatures and consists of nitric oxide (NO) and nitrogen dioxide (NO₂); usually NO is
the major contributor. This forms from the nitrogen in the air through the following reactions called the extended Zeldovich mechanism:

1: \( O + N_2 \rightleftharpoons NO + N \)

2: \( N + O_2 \rightleftharpoons NO + O \)  

3: \( N + OH \rightleftharpoons NO + H \)  

Adding the first two reactions equals the elementary reaction listed in Table A.11 as

4: \( O_2 + N_2 \rightleftharpoons 2NO \)

In equilibrium the rate of the forward reaction equals the rate of the reverse reaction. However, in nonequilibrium that is not the case, which is what happens when NO is being formed. For smaller concentrations of NO the forward reaction rates are much larger than the reverse rates, and they are all sensitive to temperature and pressure. With a model for the reactions rates and the concentrations, the rate of formation of NO can be described as

\[
\frac{dy_{NO}}{dt} = \frac{y_{NO}}{\tau_{NO}}
\]

\[
\tau_{NO} = CT \left( \frac{P}{P_0} \right)^{-1/2} \exp \left( \frac{58300 K}{T} \right)
\]

where \( C = 8 \times 10^{-16} \text{ s K}^{-1} \), \( y_{NO_e} \) is the equilibrium NO concentration and \( \tau_{NO} \) is the time constant in seconds. For peak \( T \) and \( P \), as typical in an engine, the time scale becomes short (1 ms), so the equilibrium concentration is reached very quickly. As the gases expand and \( T \), \( P \) decrease, the time scale becomes large, typically for the reverse reactions that removes NO, and the concentration is frozen at the high level. The equilibrium concentration for NO is found from reaction 4 equilibrium constant \( K_4 \) (see Table A.11), according to Eq.16.16:

\[
y_{NO_e} = [K_4 y_{O_2} y_{N_2}]^{1/2}
\]

To model the total process, including the reverse reaction rates, a more detailed model of the combustion product mixture, including the water–gas reaction, is required.

This simple model does illustrate the importance of the chemical reactions and the high sensitivity of NO formation to peak temperature and pressure, which are the primary focus in any attempt to design low-emission combustion processes. One way of doing this is by steam injection, shown in Problems 13.178 and 15.144. Another way is a significant bypass flow, as in Problem 15.187. In both cases, the product temperature is reduced as much as possible without making the combustion unstable.

A final example of an application is simultaneous reactions, including dissociations and ionization in several steps. When ionization of a gas occurs it becomes a plasma, and to a first approximation we again make the assumption of thermal equilibrium and treat it as an ideal gas. The many simultaneous reactions are solved by minimizing the Gibbs function, as explained in the end of Section 16.5. Figure 16.11 shows the equilibrium composition of air at high temperature and very low density, and indicates the overlapping regions of the various dissociations and ionization processes. Notice, for instance, that beyond 3000 K there is virtually no diatomic oxygen left, and below that temperature only O and NO are formed.
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In-Text Concept Questions

d. When dissociations occur after combustion, does $T$ go up or down?
e. For nearly all the dissociations and ionization reactions, what happens to the composition when the pressure is raised?
f. How does the time scale for NO formation change when $P$ is lower at the same $T$?
g. Which atom in air ionizes first as $T$ increases? What is the explanation?

SUMMARY
A short introduction is given to equilibrium in general, with application to phase equilibrium and chemical equilibrium. From previous analysis with the second law, we have found the reversible shaft work as the change in Gibbs function. This is extended to give the equilibrium state as the one with minimum Gibbs function at a given $T$, $P$. This also applies to two phases in equilibrium, so each phase has the same Gibbs function.
Chemical equilibrium is formulated for a single equilibrium reaction, assuming the components are all ideal gases. This leads to an equilibrium equation tying together the mole fractions of the components, the pressure, and the reaction constant. The reaction constant is related to the shift in the Gibbs function from the reactants (LHS) to the products (RHS) at a temperature $T$. As $T$ or $P$ changes, the equilibrium composition will shift according to its sensitivity to $T$ and $P$. For very large equilibrium constants the reaction is shifted toward the RHS, and for very small ones it is shifted toward the LHS. We show how elementary reactions can be used in linear combinations and how to find the equilibrium constant for this new reaction.

In most real systems of interest, there are multiple reactions coming to equilibrium simultaneously with a fairly large number of species involved. Often species are present in the mixture without participating in the reactions, causing a dilution, so all mole fractions are lower than they otherwise would be. As a last example of a reaction, we show an ionization process where one or more electrons can be separated from an atom.

In the final sections, we show special reactions to consider for the gasification of coal, which also leads to the production of hydrogen and synthetic fuels. At higher temperatures, ionization is important and is shown to be similar to dissociations in the way the reactions are treated. Formation of NOx at high temperature is an example of reactions that are rate sensitive and of particular importance in all processes that involve combustion with air.

You should have learned a number of skills and acquired abilities from studying this chapter that will allow you to:

- Apply the principle of a minimum Gibbs function to a phase equilibrium.
- Understand that the concept of equilibrium can include other effects, such as elevation, surface tension, and electrical potentials, as well as the concept of metastable states.
- Understand that the chemical equilibrium is written for ideal-gas mixtures.
- Understand the meaning of the shift in Gibbs function due to the reaction.
- Know when the absolute pressure has an influence on the composition.
- Know the connection between the reaction scheme and the equilibrium constant.
- Understand that all species are present and influence the mole fractions.
- Know that a dilution with an inert gas has an effect.
- Understand the coupling between the chemical equilibrium and the energy equation.
- Intuitively know that most problems must be solved by iterations.
- Be able to treat a dissociation added to a combustion process.
- Be able to treat multiple simultaneous reactions.
- Know that syngas can be formed from an original fuel.
- Know what an ionization process is and how to treat it.
- Know that pollutants like NOx form in a combustion process.

### KEY CONCEPTS AND FORMULAS

<table>
<thead>
<tr>
<th>Gibbs function</th>
<th>$g = h - Ts$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibrium</td>
<td>$g_f = g$</td>
</tr>
<tr>
<td>Phase equilibrium</td>
<td>$g_f = g$</td>
</tr>
<tr>
<td>Equilibrium reaction</td>
<td>$v_a A + v_b B \leftrightarrow v_c C + v_d D$</td>
</tr>
</tbody>
</table>
| Change in Gibbs function | $\Delta G^\circ = v_a \gamma_a \pi_a^0 + v_b \gamma_b \pi_b^0 - v_c \gamma_c \pi_c^0 - v_d \gamma_d \pi_d^0$ | evaluate at $T$, $P^\circ$
CHAPTER SIXTEEN
INTRODUCTION TO PHASE AND CHEMICAL EQUILIBRIUM

Equilibrium constant
\[ K = e^{-\frac{\Delta G^0}{RT}} \]
\[ K = \frac{y_vC^n}{y_vD^m \cdot P^p} \]
Mole fractions \[ y_i = \frac{n_i}{n_{\text{tot}}} \] (\( n_{\text{tot}} \) includes nonreacting species)
Reaction scheme
Reaction scheme III \[ a + b \rightarrow K_{III} = K_a K_b \]
Dilution
Simultaneous reactions \[ K_1, K_2, \ldots \] and more \( y \)'s

CONCEPT-STUDY GUIDE PROBLEMS
16.1 Is the concept of equilibrium limited to thermodynamics?
16.2 How does the Gibbs function vary with quality as you move from liquid to vapor?
16.3 How is a chemical equilibrium process different from a combustion process?
16.4 Must \( P \) and \( T \) be held fixed to obtain chemical equilibrium?
16.5 The change in the Gibbs function \( \Delta G^0 \) for a reaction is a function of which property?
16.6 In a steady-flow burner, \( T \) is not controlled; which properties are?
16.7 In a closed rigid-combustion bomb, which properties are held fixed?
16.8 In a dissociation process, which properties are?
16.9 A1 298 K, \( K = \exp(-184) \) for the water dissociation; what does that imply?
16.10 If a reaction is insensitive to pressure, prove that it is also insensitive to dilution effects at a given \( T \).
16.11 For a pressure-sensitive reaction, an inert gas is added (dilution); how does the reaction shift?
16.12 In a combustion process, is the adiabatic flame temperature affected by reactions?
16.13 In equilirium, the Gibbs function of the reactants and products is the same; how about the energy?
16.14 Does a dissociation process require energy or does it give out energy?
16.15 If I consider the nonfrozen (composition can vary) heat capacity but still assume that all components are ideal gases, does that change temperature? Of pressure?
16.16 What is \( K \) for the water–gas reaction in Example 16.4 at 1200 K?
16.17 What would happen to the concentrations of the monatomic species like O and N if the pressure is higher in Fig. 16.17?

HOMEWORK PROBLEMS
Equilibrium and Phase Equilibrium
16.18 Carbon dioxide at 15 MPa is injected into the top of a 5-km-deep well in connection with an enhanced oil-recovery process. The fluid column standing in the well is at a uniform temperature of 40 C. What is the pressure at the bottom of the well, assuming ideal-gas behavior?
16.19 Consider a 2-km-deep gas well containing a gas mixture of methane and ethane at a uniform temperature of 30 C. The pressure at the top of the well is 14 M Pa, and the composition on a mole basis is 90% methane, 10% ethane. Each component is in equilibrium (top to bottom), with \( dG + g dZ = 0 \), and assume ideal gas, so, for each component, Eq.16.10 applies. Determine the pressure and composition at the bottom of the well.
16.20 A container has liquid water at 20 C, 100 kPa, in equilibrium with a mixture of water vapor and dry air also at 20 C, 100 kPa. What is the water vapor pressure and what is the saturated water vapor pressure?
16.21 Using the same assumptions as those in developing Eq. d in Example 16.1, develop an expression for pressure at the bottom of a deep column of
liquid in terms of the isothermal compressibility, \( \beta_T \). For liquid water at 20°C, we know that \( \beta_T = 0.0005 \) [1/MPa]. Use the answer to the first question to estimate the pressure in the Pacific Ocean at a depth of 3 km.

Chemical Equilibrium, Equilibrium Constant

16.22 Which of the reactions listed in Table A.11 are pressure sensitive?

16.23 Calculate the equilibrium constant for the reaction \( O_2 \rightleftharpoons 2O \) at temperatures of 298 K and 6000 K. Verify the result with Table A.11.

16.24 Calculate the equilibrium constant for the reaction \( H_2 \rightleftharpoons 2H \) at a temperature of 2000 K, using properties from Table A.9. Compare the result with the value listed in Table A.11.

16.25 For the dissociation of oxygen, \( O_2 \rightleftharpoons 2O \), we want a mathematical expression for the equilibrium constant \( K(T) \). Assume constant heat capacity, at 2000 K, for \( O_2 \) and \( O \) from Table A.9 and develop the expression from Eqs. 16.12 and 16.15.

16.26 Find \( K \) for \( CO_2 \rightleftharpoons CO + \frac{1}{2}O_2 \) at 3000 K using Table A.11.

16.27 Plot to scale the values of ln \( K \) versus 1/T for the reaction \( 2CO_2 \rightleftharpoons 2CO + O_2 \). Write an equation for ln \( K \) as a function of temperature.

16.28 Consider the reaction \( 2CO_2 \rightleftharpoons 2CO + O_2 \) obtained after heating 1 kmol \( CO_2 \) to 3000 K. Find the equilibrium constant from the shift in Gibbs function and verify its value with the entry in Table A.11. What is the mole fraction of \( CO \) at 3000 K, for \( O_2 \) and \( O \) from Table A.9 and compare the result to Table A.11.

16.29 Consider the dissociation of oxygen, \( O_2 \rightleftharpoons 2O \), starting with 1 kmol oxygen at 298 K and heating it at constant pressure 100 kPa. At which temperature will we reach a concentration of monatomic oxygen of 10%?

16.30 The combustion products from burning pentane, \( C_5H_{12} \), with pure oxygen in a stoichiometric ratio exit at 2400 K, 100 kPa. Consider the dissociation of only \( CO_2 \) and find the equilibrium mole fraction of \( CO \).

16.31 Pure oxygen is heated from 25°C to 3200 K in a steady-state process at a constant pressure of 200 kPa. Find the exit composition and the heat transfer.

16.32 Nitrogen gas, \( N_2 \), is heated to 4000 K, 10 kPa. What fraction of the \( N_2 \) is dissociated to \( N \) at this state?

16.33 Hydrogen gas is heated from room temperature to 4000 K, 500 kPa, at which state the diatomic species has partially dissociated to the monatomic form. Determine the equilibrium composition at this state.

16.34 Hydrogen gas is heated from 25°C to 3200 K in a steady-state process at a constant pressure of 200 kPa. Find the exit composition and the heat transfer.

16.35 Pure oxygen is heated from 25°C to 3200 K in a steady-state process at a constant pressure of 200 kPa. Find the exit composition and the heat transfer.

16.36 Find the equilibrium constant for \( CO + \frac{1}{2}O_2 \rightleftharpoons CO_2 \) at 2000 K using Table A.11.

16.37 Find the equilibrium constant for the reaction \( 2NO + O_2 \rightleftharpoons 2NO_2 \) from the elementary reactions in Table A.11 to answer the question: which of the nitrogen oxides, \( NO \) or \( NO_2 \), is more stable at ambient conditions? What about at 2000 K?

16.38 Helium is heated to 4000 K, 10 kPa. What fraction of the \( N_2 \) is dissociated to \( N \) at this state?
16.44 A mixture of 1 kmol CO\textsubscript{2}, 2 kmol CO, and 2 kmol O\textsubscript{2}, at 25 °C, 150 kPa, is heated in a constant-pressure steady-state process to 3000 K. Assuming that only these substances are present in the exiting chemical equilibrium mixture, determine the composition of that mixture.

16.45 Consider combustion of CH\textsubscript{4} with O forming CO\textsubscript{2} and H\textsubscript{2}O as the products. Find the equilibrium constant for the reaction at 1000 K. Use an average heat capacity of \(C_p = 52\) kJ/kmol K for the fuel and Table A.9 for the other components.

16.46 Repeat Problem 16.44 for an initial mixture that also includes 2 kmol N\textsubscript{2}, which does not dissociate during the process.

16.47 A mixture flows with 2 kmol/s CO\textsubscript{2}, 1 kmol/s argon, and 1 kmol/s CO at 298 K and it is heated to 3000 K at constant 100 kPa. Assume the dissociation of CO\textsubscript{2} is the only equilibrium process to be considered. Find the exit equilibrium composition and the heat transfer rate.

16.48 Catalytic gas generators are frequently used to decompose a liquid, providing a desired gas mixture (spacecraft control systems, fuel cell gas supply, and so forth). Consider feeding pure liquid hydrazine, N\textsubscript{2}H\textsubscript{4}, to a gas generator, from which exits a gas mixture of N\textsubscript{2}, H\textsubscript{2}, and NH\textsubscript{3} in chemical equilibrium at 100 °C, 350 kPa. Calculate the mole fractions of the species in the equilibrium mixture.

16.49 Water from the combustion of hydrogen and pure oxygen is at 3800 K and 50 kPa. Assume we only have H\textsubscript{2}O, O\textsubscript{2}, and H\textsubscript{2} as gases. Find the equilibrium composition.

16.50 Complete combustion of hydrogen and pure oxygen is at 3800 K and 50 kPa. Assume we only have H\textsubscript{2}O, O\textsubscript{2}, and H\textsubscript{2} as gases. Find the equilibrium composition.

16.51 The van’t Hoff equation relates the chemical equilibrium constant \(K\) to the enthalpy of reaction \(\Delta H^\circ\). From the value of \(K\) in Table A.11 for the dissociation of hydrogen at 2000 K and the value of \(\Delta H^\circ\) calculated from Table A.9 at 2000 K, use the van’t Hoff equation to predict the equilibrium constant at 2400 K.

16.52 Consider the water–gas reaction in Example 16.4. Find the equilibrium constant at 500, 1000, 1200, and 1400 K. What can you infer from the result?

16.53 A piston/cylinder contains 0.1 kmol H\textsubscript{2} and 0.1 kmol Ar gas at 25 °C, 200 kPa. It is heated in a constant-pressure process, so the mole fraction of atomic hydrogen, H, is 10%. Find the final temperature and the heat transfer needed.

16.54 A tank contains 0.1 kmol H\textsubscript{2} and 0.1 kmol Ar gas at 25 °C, 200 kPa, and the tank maintains constant volume. To what \(T\) should it be heated to have a mole fraction of atomic hydrogen, H, of 10%?

16.55 A gas mixture of 1 kmol CO, 1 kmol N\textsubscript{2}, and 1 kmol O\textsubscript{2} at 25 °C, 150 kPa, is heated in a constant-pressure steady-state process. The exit mixture can be assumed to be in chemical equilibrium with CO\textsubscript{2}, CO, O\textsubscript{2}, and N\textsubscript{2} present. The mole fraction of CO\textsubscript{2} at this point is 0.176. Calculate the heat transfer for the process.

16.56 A liquid fuel can be produced from a lighter fuel in a catalytic reactor according to

\[
\text{C}_2\text{H}_4 + \text{H}_2\text{O} \leftrightarrow \text{C}_2\text{H}_5\text{OH}
\]

Show that the equilibrium constant is ln \(K = -6.691\) at 700 K, using \(C_p = 63\) kJ/kmol K for ethylene and \(C_p = 115\) kJ/kmol K for ethanol at 500 K.

16.57 A step in the production of a synthetic liquid fuel from organic waste material is the following conversion process at 5 MPa: 1 kmol ethylene gas (converted from the waste) at 25 °C and 2 kmol steam at 390 °C enter a catalytic reactor. An ideal gas mixture of ethanol, ethylene, and water in equilibrium (see the previous problem.) leaves the reactor at 700 K, 5 MPa. Determine the composition of the mixture.

16.58 A rigid container initially contains 2 kmol CO and 2 kmol O\textsubscript{2} at 25 °C, 100 kPa. The content is then heated to 3000 K, at which point an equilibrium mixture of CO\textsubscript{2}, CO, and O\textsubscript{2} exists. Disregard other possible species and determine the
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**HOMEWORK PROBLEMS**

16.59 Use the information in Problem 16.81 to estimate the entropy of reaction, \( \Delta S^\circ \), at 700 K using the van't Hoff equation (see Problem 16.51) with finite differences for the derivatives.

16.60 A acetylene gas at 25°C is burned with 140% theoretical air, which enters the burner at 25°C, 100 kPa, 80% relative humidity. The combustion products form a mixture of CO₂, H₂O, N₂, and O₂ in chemical equilibrium at 2200 K, 100 kPa. This mixture is then cooled to 1000 K very rapidly, so that the composition does not change. Determine the mole fraction of NO in the products and the heat transfer for the overall process.

16.61 An important step in the manufacture of chemical fertilizer is the production of ammonia according to the reaction N₂ + 3H₂ ⇌ 2NH₃. Show that the equilibrium constant is

\[ K = 6.202 \]

at 150°C.

16.62 Consider the previous reaction in equilibrium at 150°C, 5 MPa. For an initial composition of 25% nitrogen, 75% hydrogen, on a mole basis, calculate the equilibrium composition.

16.63 Methane at 25°C, 100 kPa, is burned with 200% theoretical oxygen at 400 K, 100 kPa, in an adiabatic steady-state process, and the products of combustion exit at 100 kPa. Assume that the only significant dissociation reaction in the products is that of CO₂ going to CO and O₂. Determine the equilibrium composition of the products and also their temperature at the combustor exit.

16.64 Calculate the irreversibility for the adiabatic combustion process described in the previous problem.

16.65 One kilomole of CO₂ and 1 kilomol of H₂ at room temperature and 200 kPa is heated to 1200 K, 200 kPa. Use the water-gas reaction to determine the mole fraction of CO. Neglect dissociations of H₂ and O₂.

16.66 Hydrides are rare earth metals, M, that have the ability to react with hydrogen to form a different substance M₄H₄ with a release of energy. The hydrogen can then be released, the reaction reversed, by heat addition to the M₄H₄. In this reaction only the hydrogen is a gas, so the formula developed for the chemical equilibrium is inappropriate. Show that the proper expression to be used instead of Eq. 16.14 is

\[ \ln \left( \frac{P_{H2}}{P_0} \right) = \Delta G^\circ / RT \]

when the reaction is scaled to 1 kmol of H₂.

**Simultaneous Reactions**

16.67 For the process in Problem 16.47, should the dissociation of oxygen also be considered? Provide a verbal answer but one supported by number(s).

16.68 Which other reactions should be considered in Problem 16.50 and which components will be present in the final mixture?

16.69 Ethane is burned with 150% theoretical air in a gas-turbine combustor. The products exiting consist of a mixture of CO₂, H₂O, N₂, and NO in chemical equilibrium at 1800 K, 1 MPa. Determine the mole fraction of NO in the products. Is it reasonable to ignore CO in the products?

16.70 A mixture of 1 kmol H₂O and 1 kmol O₂ at 400 K is heated to 3000 K, 200 kPa, in a steady-state process. Determine the equilibrium composition at the outlet of the heat exchanger, assuming that the mixture consists of H₂O, H₂, O₂, and OH.

16.71 A assume dry air (79% N₂ and 21% O₂) is heated to 2000 K in a steady-flow process at 200 kPa and only the reactions listed in Table A.11 (and their linear combinations) are possible. Find the final composition (anything smaller than 1 ppm is neglected) and the heat transfer needed for 1 kmol of air in.

16.72 One kilomole of water vapor at 100 kPa, 400 K, is heated to 3000 K in a constant-pressure flow process. Determine the final composition, assuming that H₂O, H₂, O₂, and OH are present at equilibrium.

16.73 Water from the combustion of hydrogen and pure oxygen is at 3800 K, 50 kPa. A assume we only have H₂O, O₂, OH, and H₂ as gases with the two simple water dissociation reactions active. Find the equilibrium composition.

16.74 Methane is burned with theoretical oxygen in a steady-state process, and the products exit the combustion chamber at 3200 K, 700 kPa. Calculate the equilibrium composition at this state, assuming that only CO₂, CO, H₂O, H₂, O₂, and OH are present.
Gasification

16.75 Butane is burned with 200% theoretical air, and the products of combustion, an equilibrium mixture containing only CO, H₂O, O₂, N₂, NO, and NO₂, exits from the combustion chamber at 1400 K, 2 MPa. Determine the equilibrium composition at this state.

16.76 One kilomole of air (assumed to be 78% N₂, 21% O₂, and 1% Ar) at room temperature is heated to 4000 K, 200 kPa. Find the equilibrium composition at this state, assuming that only N₂, O₂, NO, and Ar are present.

16.77 A cryogenic gas and x times theoretical air (x > 1) at room temperature and 500 kPa are burned at constant pressure in an adiabatic flow process. The flame temperature is 2600 K, and the combustion products are assumed to consist of N₂, O₂, CO₂, H₂O, CO, and NO. Determine the value of x.

Gasification

16.78 One approach to using hydrocarbon fuels in a fuel cell is to "reform" the hydrocarbon to obtain hydrogen, which is then fed to the fuel cell. As a part of the analysis of such a procedure, consider the reaction CH₄ + H₂O ⇄ CO + 3H₂. One kilomole each of methane and water are fed to a catalytic reformer. A mixture of CH₄, H₂O, H₂, and CO exists in chemical equilibrium at 800 K, 100 kPa; determine the equilibrium composition of this mixture using an equilibrium constant of K = 0.0237.

16.82 One approach to using hydrocarbon fuels in a fuel cell is to "reform" the hydrocarbon to obtain hydrogen, which is then fed to the fuel cell. As a part of the analysis of such a procedure, consider the reaction CH₄ + H₂O ⇄ CO + 3H₂. One kilomole each of methane and water are fed to a catalytic reformer. A mixture of CH₄, H₂O, H₂, and CO exists in chemical equilibrium at 800 K, 100 kPa; determine the equilibrium composition of this mixture using an equilibrium constant of K = 0.0237.

16.83 Consider a gasifier that receives 4 kmol CO, 3 kmol H₂, and 3.76 kmol N₂ and brings the mixture to equilibrium at 900 K, 1 MPa, with the following reaction:

2CO + 2H₂ ⇄ CH₄ + CO₂

which is the sum of Eqs. 16.32 and 16.33. If the equilibrium constant is K = 2.679, find the exit flow composition.

16.84 Consider the production of a synthetic fuel (methanol) from coal. A gas mixture of 50% CO and 50% H₂ leaves a coal gasifier at 500 K, 1 MPa, enters a catalytic converter. A gas mixture of methanol, CO, and H₂ in chemical equilibrium with the reaction CO + 2H₂ ⇄ CH₃OH leaves the converter at the same temperature and pressure,

where it is known that ln K = -5.119.

16.85 At 10 000 K the ionization reaction for Ar as Ar ⇄ Ar⁺ + e⁻ has an equilibrium constant of K = 4.2 × 10⁻⁴. What should the pressure be for a mole concentration of argon ions (Ar⁺) of 10%?

16.86 Repeat the previous problem, assuming the argon constitutes 1% of a gas mixture where we neglect any reactions of other gases and find the pressure that will give a mole concentration of Ar⁺ of 0.1%.

16.87 Operation of an MHD converter requires an electrically conducting gas. A helium gas "seeded" with 1.0 mole percent cesium, as shown in Fig. P16.87, is used where the cesium is partly ionized (Cs⁺ = Cs⁺⁺ + e⁻) by heating the mixture to 1800 K, 1 MPa, in a nuclear reactor to provide free electrons. No helium is ionized in this process, so that the mixture entering the converter consists of...
He, Cs, Cs⁺, and e⁻. Determine the mole fraction of electrons in the mixture at 1800 K, where \( \ln K = 1.402 \) for the cesium ionization reaction described.

### Applications

16.91 Are the three reactions in the Zeldovich mechanism pressure sensitive if we look at equilibrium conditions?

16.92 Assume air is at 3000 K, 1 MPa. Find the time constant for NO formation. Repeat for 2000 K, 800 kPa.

16.93 Consider air at 2600 K, 1 MPa. Find the equilibrium concentration of NO, neglecting dissociations of oxygen and nitrogen.

16.94 Redo the previous problem but include the dissociation of oxygen and nitrogen.

16.95 Calculate the equilibrium constant for the first reaction in the Zeldovich mechanism at 2600 K, 500 kPa. Notice that this is not listed in Table A.11.

16.96 Find the equilibrium constant for the reaction 2NO + O₂ ⇌ 2NO₂ from the elementary reaction in Table A.11 to answer these two questions: Which nitrogen oxide, NO or NO₂, is more stable at 25° C, 100 kPa? At what T do we have an equal amount of each?

16.97 If air at 300 K is brought to 2600 K, 1 MPa, instantly, find the formation rate of NO.

16.98 Estimate the concentration of oxygen atoms in air at 3000 K, 100 kPa, and 0.0001 kPa. Compare this to the result in Fig. 16.11.

16.99 At what temperature range does air become a plasma?

### Review Problems

16.10 In a test of a gas-turbine combustor, saturated-liquid methane at 115 K is burned with excess air to hold the adiabatic flame temperature to 1600 K. It is assumed that the products consist of a mixture of CO₂, H₂O, N₂, O₂, and NO in chemical equilibrium. Determine the percent excess air used in the combustion and the percentage of NO in the products.

16.101 Find the equilibrium constant for the reaction in Problem 16.83.

16.102 A space heating unit in Alaska uses propane combustion as the heat supply. Liquid propane comes from an outside tank at -44° C, and the air supply is also taken in from the outside at -44° C. The air flow regulator is misadjusted, such that only 95% of the theoretical air enters the combustion chamber, resulting in incomplete combustion.
CHAPTER SIXTEEN
INTRODUCTION TO PHASE AND CHEMICAL EQUILIBRIUM

The products exit at 1000 K as a chemical equilibrium gas mixture, including only CO$_2$, CO, H$_2$O, H$_2$, and O. Find the composition of the products. 

Hint: Use the water gas reaction in Example 16.4.

16.103 Derive the van’t Hoff equation given in Problem 16.51, using Eqs. 16.12 and 16.15. Note: The d(g/T) at constant P is for each component can be expressed using the relations in Eqs. 14.18 and 14.19.

16.104 Repeat Problem 16.21 using the generalized charts, instead of ideal-gas behavior.

16.105 Find the equilibrium constant for Eq. 16.33 at 600 K (see Problem 16.79).

16.106 One kilomole of liquid oxygen, O$_2$, at 93 K, and x kilomoles of gaseous hydrogen, H$_2$, at 25°C, are fed to a combustion chamber (x is greater than 2) such that there is excess hydrogen for the combustion process. There is a heat loss from the chamber of 1000 kJ per kilomole of reactants. Products exit the chamber at chemical equilibrium at 3800 K, 400 kPa, and are assumed to include only H$_2$O, H$_2$, and O.

a. Determine the equilibrium composition of the products and x, the amount of H$_2$ entering the combustion chamber.

b. Should another substance(s) have been included in part (a) as being present in the products? Justify your answer.

16.107 Dry air is heated from 25°C to 4000 K in a 100-kPa constant-pressure process. List the possible reactions that may take place and determine the equilibrium composition. Find the required heat transfer.

16.108 Saturated liquid butane (note: use generalized charts) enters an insulated constant-pressure combustion chamber at 25°C, and x times theoretical oxygen gas enters at the same pressure and temperature. The combustion products exit at 3400 K. Assuming that the products are a chemical equilibrium gas mixture that includes CO, what is x?

ENGLISH UNIT PROBLEMS

16.109E CO$_2$ at 2200 lbf/in.$^2$ is injected into the top of a 3-mi-deep well in connection with an enhanced oil recovery process. The fluid column standing in the well is at a uniform temperature of 100°F. What is the pressure at the bottom of the well, assuming ideal-gas behavior?

16.110E Find the equilibrium constant for CO$_2$ ⇌ CO + $\frac{1}{2}$O$_2$ at 3960 R using Table A.11.

16.111E Calculate the equilibrium constant for the reaction O$_2$ ⇌ 2O at temperatures of 537 R and 10 800 R.

16.112E Consider the dissociation of oxygen, O$_2$ ⇌ 2O, starting with 1 lbmol oxygen at 77°F and heating it at constant pressure, 1 atm. At what temperature will we reach a concentration of monatomic oxygen of 10%?

16.113E Redo Problem 16.112, but start with 1 lbmol oxygen and 1 lbmol helium at 77°F, 1 atm.

16.114E Pure oxygen is heated from 77°F to 5300°F in a constant-volume container. Find the exit composition and the heat transfer.

16.115E Air (assumed to be 79% nitrogen and 21% oxygen) is heated in a steady-state process at a constant pressure of 14.7 lbf/in.$^2$, and some NO is formed. At what temperature will the mole fraction of NO be 0.001?

16.116E The combustion products from burning pentane, C$_5$H$_{12}$, with pure oxygen in a stoichiometric ratio exit at 4400 R. Consider the dissociation of only CO$_2$ and find the equilibrium mole fraction of CO.

16.117E Pure oxygen is heated from 77°F to 14.7 lbmol. Find the equilibrium mole fraction of NO at 5400 R, 75 psia, disregarding dissociations.

16.118E Assume the equilibrium mole fractions of oxygen and nitrogen are close to those in air. Find the equilibrium mole fraction for NO at 5400 R, 75 psia, disregarding dissociations.

16.119E Use the information in Problem 16.129E to estimate the enthalpy of reaction, $\Delta H^\circ$, at 1260 R using the van’t Hoff equation (see Problem 16.51) with finite differences for the derivatives.

16.120E A gas mixture of 1 lbmol CO, 1 lbmol N$_2$, and 1 lbmol O$_2$ at 77°F, 20 psia, is heated in a constant-pressure process. The exit mixture can
be assumed to be in chemical equilibrium with CO₂, CO, O₂, and N₂ present. The mole fraction of CO at this point is 0.176. Calculate the heat transfer for the process.

16.121E A acetylene gas at 77 F is burned with 140% theoretical air, which enters the burner at 77 F, 14.7 lbf/in.², 80% relative humidity. The combustion products form a mixture of CO₂, H₂O, N₂, O₂, and NO in chemical equilibrium at 3500 F, 14.7 lbf/in.². This mixture is then cooled to 1340 F very rapidly so that the composition does not change. Determine the mole fraction of NO in the products and the heat transfer for the overall process.

16.122E An important step in the manufacture of chemical fertilizer is the production of ammonia, according to the reaction

\[ \text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3 \]

Show that the equilibrium constant is

\[ K = 6.826 \] at 300 F.

16.123E Consider the previous reaction in equilibrium at 300 F, 750 psia. For an initial composition of 25% nitrogen, 75% hydrogen, on a mole basis, calculate the equilibrium composition.

16.124E Ethane is burned with 150% theoretical air in a gas-turbine combustor. The products exiting consist of a mixture of CO₂, H₂O, N₂, and NO in chemical equilibrium at 2800 F, 150 lbf/in.². Determine the mole fraction of NO in the products. Is it reasonable to ignore CO in the products?

16.125E One-pound mole of water vapor at 14.7 lbf/in.², 720 R, is heated to 5400 R in a constant-pressure adiabatic flow process. Determine the final composition, assuming that H₂O, H₂, H, O₂, and OH are present at equilibrium.

16.126E Methane is burned with theoretical oxygen in a steady-state process, and the products exit the combustion chamber at 5300 F, 100 lbf/in.². Calculate the equilibrium composition at this state, assuming that only CO₂, CO, H₂O, H₂, O₂, and OH are present.

16.127E One-pound mole of air (assumed to be 78% nitrogen, 21% oxygen, and 1% argon) at room temperature is heated to 7200 R, 30 lbf/in.². Find the equilibrium composition at this state, assuming that only N₂, O₂, NO, O, and Ar are present.

16.128E A acetylene gas and \( x \) times theoretical air (\( x > 1 \)) at room temperature, and 75 lbf/in.² are burned at constant pressure in an adiabatic flow process. The flame temperature is 4600 R, and the combustion products are assumed to consist of N₂, O₂, CO₂, H₂O, CO, and NO. Determine the value of \( x \).

16.129E The equilibrium reaction with methane as

\[ \text{CH}_4 \rightleftharpoons \text{C} + 2\text{H}_2 \]

has \( \ln K = -0.3362 \) at 1440 R and \( \ln K = -4.607 \) at 1080 R. By noting the relation of \( K \) to temperature, show how you would interpolate \( \ln K \) in \((1/\text{T})\) to find \( K \) at 1260 R and compare that to a linear interpolation.

16.130E In a test of a gas-turbine combustor, saturated-liquid methane at 210 R is to be burned with excess air to hold the adiabatic flame temperature to 2880 R. It is assumed that the products consist of a mixture of CO₂, H₂O, N₂, O₂, and NO in chemical equilibrium. Determine the percent excess air used in the combustion, and the percentage of NO in the products.

16.131E Dry air is heated from 77 F to 720 R in a 14.7 lbf/in.² constant-pressure process. List the possible reactions that may take place and determine the equilibrium composition. Find the required heat transfer.

COMPUTER, DESIGN, AND OPEN-ENDED PROBLEMS

16.132 Write a program to solve the general case of Problem 16.57, in which the relative amount of steam input and the reactor temperature and pressure are program input variables and use constant specific heats.

16.133 Write a program to solve the following problem. One kmol of carbon at 25 °C is burned with \( b \) kmol of oxygen in a constant-pressure adiabatic process. The products consist of an equilibrium mixture of CO₂, CO, and O₂. We wish to determine the flame temperature for various combinations of \( b \) and the pressure \( P \), assuming constant specific heat for the components from Table A.5.
16.134 Study the chemical reactions that take place when CFC-type refrigerants are released into the atmosphere. The chlorine may create compounds as HCl and ClONO2 that react with the ozone O3.

16.135 Examine the chemical equilibrium that takes place in an engine where CO and various nitrogen-oxygen compounds summarized as NOx may be formed. Study the processes for a range of air-fuel ratios and temperatures for typical fuels. Are there important reactions not listed in the book?

16.136 A number of products may be produced from the conversion of organic waste that can be used as fuel (see Problem 16.57). Study the subject and make a list of the major products that are formed and the conditions at which they are formed in desirable concentrations.

16.137 The hydrides as explained in Problem 16.66 can store large amounts of hydrogen. The penalty for the storage is that energy must be supplied when the hydrogen is released. Investigate the literature for quantitative information about the quantities and energy involved in such a hydrogen storage.

16.138 The hydrides explained in Problem 16.66 can be used in a chemical heat pump. The energy involved in the chemical reaction can be added and removed at different temperatures. For some hydrides, these temperatures are low enough to make them feasible for heat pumps for heat upgrade, refrigerators, and air conditioners. Investigate the literature for such applications and give some typical values for these systems.

16.139 Power plants and engines have high peak temperatures in the combustion products where NO is produced. The equilibrium NO level at the high temperature is frozen at that level during the rapid drop in temperature with the expansion. The final exhaust therefore contains NO at a level much higher than the equilibrium value at the exhaust temperature. Study the NO level at equilibrium when natural gas, CH4, is burned adiabatically with air (at T0) in various ratios.

16.140 Excess air or steam addition is often used to lower the peak temperature in combustion to limit formation of pollutants like NO. Study the steam addition to the combustion of natural gas as in the Cheng cycle (see Problem 13.174), assuming the steam is added before the combustion. How does this affect the peak temperature and the NO concentration?