Combustion and Energy

2.1 INTRODUCTION

Combustion engineering requires an ability to analyze energetics of chemically reactive mixtures. Most thermodynamics texts address the general subject of energy conversion and conservation as well as cover principles of mass conservation, property relationships, equations of state, and process relationships. Classical thermodynamics provides a useful overall energy balance bookkeeping technique for describing components and processes. The particular discipline termed thermochemistry deals with global energy analysis associated with combustion processes. In this chapter, a basic comprehension of thermodynamics will be assumed, and a general energy balance for a chemically reactive medium will be developed.

In most cases, the conservation of energy principle is stated for changes, or processes, that occur between some initial stable, i.e., equilibrium condition, or state, and some final equilibrium condition; see Figure 2.1. Since thermodynamics does not address the rate at which these processes occur, it will be necessary in later chapters to develop materials that will describe the dynamic nature of combustion.

2.2 THE CONSERVATION OF MASS

The conservation of mass principle is a fundamental engineering concept. Consider the case of a fixed total mass of a chemically reactive mixture, using a control mass or closed system reference. In general, the chemical composition of such a reactive mixture will undergo change with time. The initial condition is referred to as the reactant state, while the final condition is termed the product state.
A mathematical means expressing composition change and mass conservation for reactive systems is provided by the chemical reaction equation, written in general form as

$$\sum \nu_i R_i \rightarrow \sum \nu_j P_j$$

(2.1)

where

- $\nu_i$ = mass or moles of species $i$
- $R_i$ = reactant species $i$
- $\nu_j$ = mass or moles of species $j$
- $P_j$ = product species $j$

All initial reactants are placed on the left-hand side of the general reaction equation, while any final products appear on the right-hand side. Indication of the type of particular reaction process, i.e., $P = c$, $V = c$, $T = c$, is shown above the process arrow.

The general mass conservation principle for a chemical reaction can be stated in terms of an atomic mass balance, i.e., total number of atoms of an element in the final product state, such as for example hydrogen atom, must equal the initial number of atoms of the element in the reactant state. The conservation of atomic species will yield a set of equations equal to the unique number of elements in the reactant mixture. Chemical reactions involving species containing the atoms H, C, O, and N, for example, generate four distinct atomic mass balances.

![Figure 2.1](image) A generalized thermochemical process.
Often, it is convenient to describe chemically reactive mixtures on a molar basis. **Molar analysis** utilizes a relative chemical mass scale for compounds based on the periodic chart. Molar based quantities (recall the universal gas constant) will be recognized by having a bar placed over the quantity in question. For a mixture of \( k \) total chemical species, a mole fraction \( \xi_i \) for each \( i \) species can be expressed as

\[
\xi_i = \frac{N_i}{N_{\text{tot}}} = \frac{\text{kgmole}_i}{\text{kgmole}_{\text{tot}}}
\]

and the total moles \( N_{\text{tot}} \) is equal to

\[
\sum_{i=1}^{k} N_i = N_{\text{tot}} \text{ kgmole (lbmole)}
\]

and

\[
\sum_{i=1}^{k} \xi_i = 1.0
\]

A description based on mass or weight for a mixture of compounds, termed a **gravimetric analysis**, expresses the total mass of either reactant and/or product state in terms of each pure constituent. For a mixture of \( k \) total chemical species, a mass fraction \( mf_i \) for each \( i \) component species can be written as

\[
mf_i = \frac{m_i}{m_{\text{tot}}} = \frac{\text{kg}_i}{\text{kg}_{\text{tot}}} \left( \frac{\text{lbm}_i}{\text{lbm}_{\text{tot}}} \right)
\]

and the total mass \( m_{\text{tot}} \) is then equal to

\[
\sum_{i=1}^{k} m_i = m_{\text{tot}} \text{ kg (lbm)}
\]

and

\[
\sum_{i=1}^{k} mf_i = 1.0
\]

Even though the total mass of a combustion process may remain constant, concentration of individual constituents such as oxygen or carbon dioxide may change during a reaction. The mass fraction of a constituent as a reactant species \( i \) may be quite different from that as a product species \( j \).

In Chapter 1, the bridge between molar and mass analysis was shown to be molecular weight. The mole-mass relationship for species \( i \) is given as

\[
m_i = N_i \cdot MW_i
\]
where

\[ m_i \] = mass species \( i \), kg (lbm)

\[ N_i \] = moles species \( i \), kgmole (lbmole)

\[ MW_i \] = molecular weight species \( i \), kg/kgmole (lbm/lbmole)

For a mixture of \( k \) species, the total mass can be written

\[
m_{\text{tot}} = N_{\text{tot}} MW_{\text{tot}} = \sum_{i=1}^{k} N_i MW_i
\]

or

\[
MW_{\text{tot}} = \sum_{i=1}^{k} \left( \frac{N_i}{N_{\text{tot}}} \right) MW_i = \sum_{i=1}^{k} \bar{x}_i MW_i
\]

(EXAMPLE 2.1) Standard atmospheric conditions for many combustion calculations can be represented by the following mole fractions:

- N\(_2\) 78%
- O\(_2\) 21%
- Ar 1%

For these conditions, determine (a) the mass fractions of N\(_2\), O\(_2\), and Ar; (b) the mixture molecular weight, kg/kgmole; and (c) the specific gas constant \( R \) for air, J/kg K.

**Solution**

1. Mole fractions:
   \[ \bar{x}_{N_2} = 0.78 \quad x_{O_2} = 0.21 \quad \bar{x}_{Ar} = 0.01 \]

2. Mass fractions:

<table>
<thead>
<tr>
<th>( \bar{x}_i )</th>
<th>( MW_i )</th>
<th>( \bar{x}_i MW_i )</th>
<th>( mf_i^{*} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(_2)</td>
<td>0.21</td>
<td>32.0</td>
<td>6.72</td>
</tr>
<tr>
<td>N(_2)</td>
<td>0.78</td>
<td>28.0</td>
<td>21.84</td>
</tr>
<tr>
<td>Ar</td>
<td>0.01</td>
<td>40.0</td>
<td>0.40</td>
</tr>
</tbody>
</table>

\[
\frac{kgmole_i}{kgmole_{\text{tot}}} \quad \frac{kg_i}{kgmole_{i}} \quad \frac{kg_i}{kgmole_{\text{tot}}} \quad \frac{kg_i}{kg_{\text{tot}}}
\]
The most prominent chemical reaction associated with power production and heat transfer is the overall oxidation reaction, i.e.,

\[ \text{Fuel} + \text{oxidizer} \rightarrow \text{Products} \]

Reactants and/or products of combustion may exist as a solid, liquid, and/or vapor. In addition, the contributing species may be single species, pure compounds, complex mixtures, stable molecules, and/or radicals. Traditionally, most fuels of engineering relevance have been hydrocarbon compounds, represented symbolically as \( \text{CH}_x \).

Furthermore, the most commonly used oxidizing agent is air. In combustion calculations, air is often assumed to be approximately 21% \( \text{O}_2 \) and 79% \( \text{N}_2 \) by volume. This theoretical air, termed dry air, has a molecular weight of approximately 28.96 in this text. For every mole of \( \text{O}_2 \) in air there will be an additional 3.76 moles of \( \text{N}_2 \) or 4.76 total moles of air for each mole of \( \text{O}_2 \).

For any given fuel-oxidant reaction, the actual potential combining proportions can depend on (1) the fuel, (2) the oxidant, (3) the combustion process, and/or (4) the combustion device. Ideal complete combustion of a fuel assumes formation of the most fully oxidized products. The most stable oxidized product of carbon is carbon dioxide, \( \text{CO}_2 \), while the most stable oxidized product of hydrogen is water, \( \text{H}_2\text{O} \). Therefore, the most stable oxidized products formed from complete combustion of any hydrocarbon fuel would be only \( \text{CO}_2 \) and \( \text{H}_2\text{O} \).

Sufficient oxidant theoretically required to support complete combustion of a particular fuel and ideally to form its most stable products can be expressed in terms of the stoichiometric equation. For example, consider the two stoichiometric oxidation reactions below.

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

For a fuel-air mixture, stoichiometric conditions are often referred to as 100% theoretical air, TA. It is important to note that an actual reaction having stoichiometric fuel-air proportions will not ensure complete combustion. Since stoichiometric oxidation reactions do not achieve complete combustion, many combustion systems operate using excess air, EA, i.e., a percentage of air over and above stoichiometric proportions. For instance, 150% theoretical air is equivalent to 50% excess air. A fuel-air mixture having excess air is termed a fuel-lean mixture, whereas a mixture that has excess fuel is called a fuel-rich mixture.
\[ \text{C}_3\text{H}_8 + (5)(1.2)(\text{O}_2 + 3.76\text{N}_2) \xrightarrow{B} 3\text{CO}_2 + 4\text{H}_2\text{O} + \text{O}_2 + (6)(3.76)\text{N}_2 \]

Practical engineering considerations give rise to the use of a fuel-to-air ratio, \( FA \), or an air-to-fuel ratio, \( AF \). These ratios can be expressed on a mass or molar basis as follows:

**Mass basis:**

\[
AF = \frac{\text{mass of air}}{\text{mass of fuel}} = \frac{\text{kg air}}{\text{kg fuel}}, \quad FA = \frac{\text{mass of fuel}}{\text{mass of air}} = \frac{\text{lbm fuel}}{\text{lbm air}}
\]  

(2.5)

**Mole basis:**

\[
\frac{\text{moles of air}}{\text{moles of fuel}} = \frac{\text{kg mole air}}{\text{kg mole fuel}}, \quad \frac{\text{moles of fuel}}{\text{moles of air}} = \frac{\text{lbm mole fuel}}{\text{lbm mole air}}
\]  

(2.6)

A useful dimensionless fuel-oxidant ratio, or equivalence ratio \( \Phi \), can be defined as

\[
\Phi = \frac{\left( \frac{\text{moles fuel}}{\text{moles oxidant}} \right)_{\text{actual}}}{\left( \frac{\text{moles fuel}}{\text{moles oxidant}} \right)_{\text{stoichiometric}}}
\]  

(2.7)

where

\( \Phi < 1 \) fuel - lean mixture
\( \Phi = 1 \) stoichiometric mixture
\( \Phi > 1 \) fuel - rich mixture

**EXAMPLE 2.2** The reaction of gaseous hydrogen and oxygen to form water is well known. The combustion of carbon with oxygen forming carbon dioxide is also an important chemical reaction. Write the chemical reactions for these two oxidation reactions, and calculate (a) the reactant’s molar analysis, (b) the reactant’s gravimetric analysis, and (c) mass of oxygen required per mass of fuel.

**Solution:**

1. **Stoichiometric hydrogen combustion:**

   \[
   \text{H}_2 + a\text{O}_2 \rightarrow b\text{H}_2\text{O}
   \]

   Hydrogen atom balance \( 2 = 2b \) \( b = 1 \)

   Oxygen atom balance \( 2a = 1 \) \( a = 0.5 \)

   \[
   \text{H}_2 + 0.5\text{O}_2 \rightarrow \text{H}_2\text{O}
   \]
2. Mole fractions:
\[ \bar{x}_{H_2} = \frac{1}{1 + 0.5} = 0.667 \]
\[ x_{O_2} = \frac{0.5}{1.5} = 0.333 \]

3. Mass fractions:

<table>
<thead>
<tr>
<th>( \bar{x}_i )</th>
<th>( MW_i )</th>
<th>( x_i MW_i )</th>
<th>( mf_i^a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)</td>
<td>0.667</td>
<td>2.0</td>
<td>1.333</td>
</tr>
<tr>
<td>O(_2)</td>
<td>0.333</td>
<td>32.00</td>
<td>10.667</td>
</tr>
</tbody>
</table>

\[ MW = \sum \bar{x}_i MW_i = 1.333 + 10.667 = 12.00 \text{ lbm/lbmole} \]

\[ mf_{H_2} = \frac{1.333}{12.00} = 0.111, \quad mf_{O_2} = \frac{10.667}{12.00} = 0.889 \]

4. Mass O\(_2\)/H\(_2\):
\[ OF = \frac{Z \text{ lbm O}_2}{1.0 \text{ lbm H}_2} = \frac{88.9 \text{ lbm O}_2}{11.1 \text{ lbm H}_2} \quad Z = \frac{8.01 \text{ lbm O}_2}{\text{lbm H}_2} \]

5. Stoichiometric carbon combustion:
\[ C_5 + aO_2 \rightarrow bCO_2 \]
\[ \text{Carbon atom balance} \quad 1 = b \]
\[ \text{Oxygen atom balancer} \quad 2a = 2 \quad a = 1 \]

\[ C_5 + O_2 \rightarrow CO_2 \]

6. Mole fractions:
\[ \bar{x}_{C_5} = \frac{1}{1 + 1} = 0.50 \]
\[ x_{O_2} = 1 - 0.5 = 0.5 \]
7. Mass fractions:

<table>
<thead>
<tr>
<th>$x_i$</th>
<th>$MW_i$</th>
<th>$\bar{x}_i MW_i$</th>
<th>$mf^b_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_S$</td>
<td>0.50</td>
<td>12.00</td>
<td>6.00</td>
</tr>
<tr>
<td>$O_2$</td>
<td>0.50</td>
<td>32.00</td>
<td>16.00</td>
</tr>
</tbody>
</table>

\[
MW = \sum x_i MW_i = 6.00 + 16.00 = 22.00 \text{ lbm/lbmole}_{\text{tot}}
\]

\[
bmf_{C_S} = \frac{6.00}{22.00} = 0.273, \quad mf_{O_2} = \frac{16.00}{22.00} = 0.727
\]

8. Mass $O_2/C_S$:

\[
OF = \frac{Z \text{ lbm } O_2}{1.0 \text{ lbm } C} = \frac{72.7 \text{ lbm } O_2}{27.3 \text{ lbm } C} \quad Z = \frac{\text{lbm } O_2}{\text{lbm } C_S} = 2.663
\]

Comments: This problem illustrates the variations in air-fuel ratios for hydrocarbon compounds. Not only will the stoichiometric proportions vary with each particular fuel, but the ratio will differ depending on whether the results are based on a mass or molar analysis.

2.3 THERMODYNAMIC PROPERTIES

An energetic analysis of important combustion reactions will often require thermodynamic characteristics, or properties, of relevant constituents. Several of the more familiar include: temperature $T$, total pressure $P$, total volume $V$, moles $N$ (or $\bar{x}_i$), mass $M_i$ (or $mf_i$), total internal energy $U$, and/or total enthalpy $H$. The state of a simple pure homogeneous substance can be described by specifying two independent and substance-dependent, or intrinsic, properties. Internal energy and pressure are examples of intrinsic properties, while kinetic and potential energies are examples of nonintrinsic, or extrinsic, properties.

Combustion reactions involve multiphase, multicomponent mixtures that undergo chemical transformation in both time and space. Obviously, such a complex event as chemistry cannot be characterized using a single pure homogeneous constituent. Even for most nonreactive mixtures, two independent intrinsic properties, such as temperature and total pressure, plus the chemical composition, are necessary to define a state. Considering
the many possible thermodynamic property combinations needed for combustion analysis, simply tabulating or graphing needed data is prohibitive.

Thermochemical calculations can be based on fundamental relations expressed collectively in terms of pure component species properties. Furthermore, it will be convenient to think in terms of reactant and product conditions initially as being two distinct nonreactive equilibrium mixture states. Many product mixtures can furthermore be treated as ideal-gas mixtures in part because of the heat release and high product temperatures as well as the chemical composition of most major fuels being used today.

The Gibbs-Dalton law describes the thermodynamic nature of an ideal-gas mixture in terms of each pure component species. The rule states that, in an equilibrium mixture of ideal gases, each component acts as if it were alone in the system at \( V_{\text{tot}}, T \). By careful application of this law, thermodynamic state and useful thermochemical properties for a mixture can be developed.

For an equilibrium mixture of nonreactive gases \( A, B, C, \ldots \), and using the Gibbs-Dalton law, one can write the following facts:

\[
V_A = V_B = V_C = \cdots = V_i = V_{\text{tot}} \tag{2.8}\]
\[
T_A = T_B = T_C = \cdots = T_i = T \tag{2.9}\]

From the conservation of mass principle,

\[
N_{\text{tot}} = N_A + N_B + N_C + \cdots = \sum_{i=1}^{k} N_i \tag{2.2a}\]

From Chapter 1, the ideal-gas equation of state was given as

\[
P_{\text{tot}}V_{\text{tot}} = N_{\text{tot}}\bar{R}T \tag{1.4}\]

Combining Equations (1.4), (2.3), (2.8), and (2.9) yields

\[
P_{\text{tot}}V_{\text{tot}} = \left(N_A + N_B + N_C + \cdots\right)\bar{R}T = \sum N_i\bar{R}T
\]
or

\[
P_{\text{tot}} = \frac{N_A\bar{R}T}{V_A} + \frac{N_B\bar{R}T}{V_B} + \frac{N_C\bar{R}T}{V_C} + \cdots = \sum \frac{N_i\bar{R}T}{V_i} \tag{2.10}\]

The pressure exerted by a pure component species \( i \) if it were alone in a closed system at the total volume and mixture temperature is termed its partial pressure \( P_i \) or

\[
P_i = N_i\bar{R}T/V \tag{2.11a}\]

and

\[
P_i = \frac{N_i\bar{R}T/V}{N_{\text{tot}}\bar{R}T/V} = \frac{N_i}{N_{\text{tot}}} = \bar{x}_i
\]

\[
P_i = \bar{x}_iP_{\text{tot}} \tag{2.11b}\]

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where
\[
\sum P_i = \sum_{i=1}^{k} \bar{x}_i P_{tottot} = P_{tot}
\]  
(2.11c)

\( P \) = pressure

\( i \) = chemical species \( i \)

\( k \) = total number of species

The total pressure is equal to the sum of partial pressures where partial pressure of a species \( i \) is equal to total pressure multiplied by its mole fraction.

Additional thermodynamic properties, such as internal energy and enthalpy, can also be evaluated by applying the Gibbs-Dalton law.

Internal energy \( U \), for example, generally is expressed as a function of temperature, volume, and composition, i.e., \( U = U\{T, V, N_i\} \). Since, for ideal gases, \( U = U\{T, N_i\} \), the total internal energy of a mixture can be written as

Extensive:
\[
U_{tot} = m_{tot} u_{tot} = \sum m_i u_i \quad \text{kJ (Btu)}
\]  
(2.12a)

or
\[
U_{tot} = N_{tot} \bar{u}_{tot} = \sum N_i \bar{u}_i \quad \text{kJ (Btu)}
\]  
(2.12b)

Intensive:
\[
u_{tot} = \sum_{i=1}^{k} \left( \frac{m_i}{m_{tot}} \right) u_i = \sum_{i=1}^{k} \frac{m_f}{m_{mixt}} u_i \quad \text{kJ (Btu)}
\]  
(2.12c)

or
\[
\bar{u}_{tot} = \sum_{i=1}^{k} \left( \frac{N_i}{N_{tot}} \right) \bar{u}_i = \sum_{i=1}^{k} \frac{N_f}{N_{mole mixt}} \bar{u}_i \quad \text{kJ (Btu)}
\]  
(2.12d)

Enthalpy \( H \) is generally expressed as a function of temperature, pressure, and composition, i.e., \( H = H\{T, P, N_i\} \). Again, for ideal gases \( H = H\{T, N_i\} \), and the total enthalpy of a mixture is stated as

Extensive:
\[
H_{tot} = m_{tot} h_{tot} = \sum m_i h_i \quad \text{kJ (Btu)}
\]  
(2.13a)

or
\[
H_{tot} = N_{tot} \bar{h}_{tot} = \sum N_i \bar{h}_i \quad \text{kJ (Btu)}
\]  
(2.13b)

Intensive:
\[
h_{tot} = \sum_{i=1}^{k} \frac{m_f}{m_{mixt}} h_i \quad \text{kJ (Btu)}
\]  
(2.13c)
or
\[ \bar{h}_{tot} = \sum_{i=1}^{k} \bar{x}_i \bar{h}_i \frac{\text{kJ}}{\text{kg mole mixt}} \left( \frac{\text{Btu}}{\text{lb mole mixt}} \right) \]  \hspace{1cm} (2.13d)

A constant-volume specific heat \( C_v \) is defined as
\[ C_v \text{tot} = \frac{\partial u_{\text{tot}}}{\partial T} \right)_v \frac{\text{kJ}}{\text{kg mole mixt}} \left( \frac{\text{Btu}}{\text{lb mole mixt}} \right) \]  \hspace{1cm} (2.14)

or for a nonreactive ideal-gas mixture using Equation (2.12c),
\[ = \frac{\partial}{\partial T} \left( \frac{1}{m_{\text{tot}}} \sum_{i=1}^{k} m_i u_i \right)_v = \frac{1}{m_{\text{tot}}} \sum_{i=1}^{k} m_i \frac{\partial u_i}{\partial T} \right)_v = \Sigma m_i C_{v_i} \]
\[ C_v \text{tot} = \sum_{i=1}^{k} m_i C_{v_i} \frac{\text{kJ}}{\text{kg mole mixt}} \left( \frac{\text{Btu}}{\text{lb mole mixt}} \right) \]  \hspace{1cm} (2.14a)

or
\[ C_v \text{tot} = \sum_{i=1}^{k} \bar{x}_i C_{v_i} \frac{\text{kJ}}{\text{kg mole mixt}} \left( \frac{\text{Btu}}{\text{lb mole mixt}} \right) \]  \hspace{1cm} (2.14b)

A constant-pressure specific heat \( C_p \) can be defined in similar fashion for a nonreactive ideal-gas mixture as
\[ C_p \text{tot} = \frac{\partial h_{\text{tot}}}{\partial T} \right)_p \frac{\text{kJ}}{\text{kg mole mixt}} \left( \frac{\text{Btu}}{\text{lb mole mixt}} \right) \]  \hspace{1cm} (2.15)

or for a nonreactive ideal-gas mixture using Equation (2.12c),
\[ = \frac{\partial}{\partial T} \left( \frac{1}{m_{\text{tot}}} \sum_{i=1}^{k} m_i h_i \right)_p = \frac{1}{m_{\text{tot}}} \sum_{i=1}^{k} m_i \frac{\partial h_i}{\partial T} \right)_p = \Sigma m_i C_{p_i} \]
\[ C_p \text{tot} = \sum_{i=1}^{k} m_i C_{p_i} \frac{\text{kJ}}{\text{kg mole mixt}} \left( \frac{\text{Btu}}{\text{lb mole mixt}} \right) \]  \hspace{1cm} (2.15a)

or
\[ C_p \text{tot} = \sum_{i=1}^{k} \bar{x}_i C_{p_i} \frac{\text{kJ}}{\text{kg mole mixt}} \left( \frac{\text{Btu}}{\text{lb mole mixt}} \right) \]  \hspace{1cm} (2.15b)

Enthalpy and internal energy are related by the equation \( h = u + Pv \). For an ideal gas, this can be expressed as
\[ h = u + RT \]  \hspace{1cm} (2.16)
and

\[ dh = du + RdT \]  

(2.16a)

combining Equations (2.14), (2.15), and (2.16a) and noting that specific heats for an ideal gas depend only on temperature,

\[ C_p dT = C_v dT + RdT \]

or

\[ R_{tot} = C_{p_{tot}} - C_{v_{tot}} \]

(2.17)

and

\[ R_{tot} = \sum_{i=1}^{k} mf_i C_{p_i} - \sum_{i=1}^{k} mf_i C_{v_i} \]

\[ = \sum_{i=1}^{k} mf_i (C_{p_i} - C_{v_i}) \]

\[ R_{tot} = \sum_{i=1}^{k} mf_i R_i \]

The specific heat ratio \( \gamma \) is defined as

\[ \gamma \equiv \frac{C_p}{C_v} = \frac{\overline{C_p}}{\overline{C_v}} \]

(2.18)

Using Equations (2.17) and (2.18), one can also write

\[ C_p = \frac{R \gamma}{\gamma - 1} \quad \text{or} \quad \overline{C_p} = \frac{\overline{R \gamma}}{\gamma - 1} \]  

(2.19a)

and

\[ C_v = \frac{R}{\gamma - 1} \quad \text{or} \quad \overline{C_v} = \frac{\overline{R}}{\gamma - 1} \]  

(2.19b)

Substituting Equations (2.14b) and (2.15b) into (2.18) gives

\[ \gamma_{tot} = \frac{\sum_i \overline{C_{p_i}}}{\sum_i \overline{C_{v_i}}} = \frac{\sum mf_i C_{p_i}}{\sum mf_i C_{v_i}} \]  

(2.18a)
EXAMPLE 2.3 Consider a homogeneous mixture of ethylene, C₂H₄, and 130% theoretical air. Calculate as a function of temperature (a) the mixture gas constant $R$, kJ/kg; (b) the mixture constant-pressure specific heat $C_p$, kJ/kg-K; (c) the mixture constant-volume specific heat $C_v$, kJ/kg-K; and (d) the specific heat ratio $\gamma$.

**Solution**

1. Stoichiometric equation:
   
   \[
   C_2H_4 + aO_2 \rightarrow bCO_2 + cH_2O
   \]

   Carbon atom balance \( b = 2 \)
   
   Hydrogen atom balance \( c = 2 \)
   
   Oxygen atom balance \( 2a = 2(2) + 2 \)
   
   \( a = 3 \)

2. Actual reaction:
   
   \[
   C_2H_4 + (1.3)(3)[O_2 + 3.76N_2] \rightarrow 2CO_2 + 2H_2O + 0.9O_2 + (3.9)(3.76)N_2
   \]

3. Mixture molecular weight:
   
   \[
   x_{C_2H_4} = \frac{1.0}{1.0 + (3.9)(4.76)} = 0.0511
   \]
   
   \[
   x_{air} = 1.0000 - 0.0511 = 0.9489
   \]
   
   \[
   MW_{tot} = \sum x_i MW_i = (0.0511)(28) + (0.9489)(28.97)
   \]
   
   \[
   MW_{tot} = 28.92 \text{ kg/kgmole mixt}
   \]

4. Thermodynamic properties:
   
   a. \( R = \frac{\bar{R}}{MW} = \frac{8.314 \text{ kJ/kgmole} \cdot \text{K}}{28.92 \text{ kg/kgmole}} = 0.2875 \text{ kJ/kg} \cdot \text{K} \)

   and

   \[
   C_p = \frac{\bar{C}_p}{MW} = \frac{\bar{C}_p}{28.92} \quad C_p - C_v = R \quad C_p/C_v = \gamma
   \]
   
   \[
   \bar{C}_p = \sum x_i \bar{C}_p = 0.9489 \bar{C}_{p,air} + 0.0511 \bar{C}_{C_2H_4}
   \]
5. From Tables B.7 and B.25 in Appendix B,

<table>
<thead>
<tr>
<th></th>
<th>Air</th>
<th>C_2H_4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\overline{C}_p$</td>
<td>$\overline{C}_p$</td>
</tr>
<tr>
<td>298</td>
<td>6.947</td>
<td>29.087</td>
</tr>
<tr>
<td>400</td>
<td>7.010</td>
<td>12.679</td>
</tr>
<tr>
<td>600</td>
<td>7.268</td>
<td>16.889</td>
</tr>
<tr>
<td>800</td>
<td>7.598</td>
<td>20.039</td>
</tr>
<tr>
<td>1,000</td>
<td>7.893</td>
<td>22.443</td>
</tr>
<tr>
<td>1,200</td>
<td>8.109</td>
<td>24.290</td>
</tr>
<tr>
<td>1,400</td>
<td>8.289</td>
<td>25.706</td>
</tr>
<tr>
<td>1,600</td>
<td>8.437</td>
<td>26.794</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>K cal/gmole-K</th>
<th>kJ/kgmole-K</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>29.794</td>
<td>1.030</td>
</tr>
<tr>
<td>400</td>
<td>30.564</td>
<td>1.057</td>
</tr>
<tr>
<td>600</td>
<td>32.489</td>
<td>1.123</td>
</tr>
<tr>
<td>800</td>
<td>34.475</td>
<td>1.192</td>
</tr>
<tr>
<td>1,000</td>
<td>36.161</td>
<td>1.250</td>
</tr>
<tr>
<td>1,200</td>
<td>37.414</td>
<td>1.294</td>
</tr>
<tr>
<td>1,400</td>
<td>38.432</td>
<td>1.329</td>
</tr>
<tr>
<td>1,600</td>
<td>39.254</td>
<td>1.357</td>
</tr>
</tbody>
</table>

Comments: This problem illustrates that the assumption of constant specific heats and specific heat ratio may, in certain problems with a wide temperature variation, lead to serious error. Note that the specific heats $C_p$ and $C_v$ both increase with increasing temperature while $\gamma$ decreases with increasing temperature.

The enthalpy of a single compound on a unit mole basis can be expressed as a function of temperature and pressure or

$$\tilde{h}_i = \tilde{h}_i (T, P) \frac{\text{kJ}}{\text{kgmole}_i} \left(\frac{\text{Btu}}{\text{lbmole}_i}\right)$$

(2.20)

Differential changes in enthalpy are equal to

$$d\tilde{h}_i = \left(\frac{\partial \tilde{h}_i}{\partial T}\right)_P dT + \left(\frac{\partial \tilde{h}_i}{\partial P}\right)_T dP$$

(2.20a)
Since, for an ideal gas, enthalpy is independent of pressure
\[ \bar{h}_i = \bar{h}_i(T) \]  
(2.21)
and Equation (2.15) becomes
\[ d\bar{h}_i = \left( \frac{\partial \bar{h}_i}{\partial T} \right)_p dT = \bar{C}_p(T) dT \]  
(2.21a)
integrating Equation (2.21a) between limits
\[ \Delta \bar{h}_i = \int_{h_0}^{h} d\bar{h}_i = \int_{T_0}^{T} \bar{C}_p(T) dT \]  
(2.21b)
where
\[ T = \text{system temperature} \]
\[ T_0 = \text{reference datum temperature} = 25^\circ \text{C} (77^\circ \text{F}) \]
Values for \( \bar{C}_p \) versus \( T \) for several gases are found in Tables B.2–B.25 in Appendix B.

The temperature dependency of ideal-gas specific heats can be expressed in virial form. Consider, for example, the constant-pressure molar specific heat of a pure component \( i \), expressed as a fitted power series in temperature as
\[ \bar{C}_p(T) = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4 \]  
(2.22)
Substituting the virial form for \( \bar{C}_p \) into Equation (2.21b), Equation (2.22) yields an illustrative expression for changes in enthalpy for a compound as
\[ \bar{h}_i(T_2) - \bar{h}_i(T_0) = \int_{T_0}^{T} \left[ a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4 \right] dT \]  
(2.23)
\[ = \left[ a_1 T + \frac{a_2}{2} T^2 + \frac{a_3}{3} T^3 + \frac{a_4}{4} T^4 + \frac{a_5}{5} T^5 \right]_{T_0}^{T} \]  
(2.23a)
Values for \( \Delta \bar{h}_i(T) \) for several gases are also found in Tables B.2–B.25 in Appendix B.

Changes in internal energy for an ideal gas can be obtained from an appropriate expression in terms of enthalpy
\[ \bar{h}_i = \bar{u}_i + P_i \bar{v}_i = \bar{u}_i + \bar{R}T \]  
(2.24)
\[ \bar{u}_i = \bar{h}_i - \bar{R}T \frac{\text{kJ}}{\text{kgmole}} \left( \frac{\text{Btu}}{\text{lbmole}} \right) \]
and
\[ \Delta \bar{u}_i + \bar{u}_i(T) - \bar{u}_i(T_0) = \Delta \bar{h}_i - \bar{R} \Delta T = \Delta \bar{h}_i - \bar{R}(T - T_0) \]  
(2.24a)
EXAMPLE 2.4  A 10-kg mixture of 25% CO and 75% N₂ by weight is cooled from 1,800 to 800K. For these conditions, determine (a) $\Delta h$, kJ/kg mixture; (b) $\Delta \bar{h}$, kJ/kgmole; (c) $\Delta \bar{u}$, kJ/kgmole; and (d) $\Delta u$, kJ/kg.

**Solution:**

1. Mixture properties from Tables B.4 and B.18 in Appendix B:

<table>
<thead>
<tr>
<th></th>
<th>$\bar{h}(T) - \bar{h}(T_0)$</th>
<th>$\bar{h}(1,800) - \bar{h}(800)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1,800K</td>
<td>800K</td>
</tr>
<tr>
<td>N₂</td>
<td>49,017.2</td>
<td>15,056.5</td>
</tr>
<tr>
<td>CO</td>
<td>49,557.3</td>
<td>15,186.2</td>
</tr>
</tbody>
</table>

$kJ/kgmole$

Values are equal to $4.187 \times [\bar{h}(T) - \bar{h}(T_0)]$ from Appendix B.

where

$$
\Delta h_{N_2} = \frac{\Delta \bar{h}}{MW_{N_2}} = \frac{33,960.7 \text{ kJ/kgmole}}{28 \text{ kg/kgmole}} = 1,212.9 \text{ kJ/kg}
$$

$$
\Delta h_{CO} = \frac{\Delta \bar{h}}{MW_{CO}} = \frac{34,371.1 \text{ kJ/kgmole}}{28 \text{ kg/kgmole}} = 1,227.5 \text{ kJ/kg}
$$

2. Mixture enthalpy:

$$
\Delta h = \sum mf_i \Delta h_i = \left(0.25 \frac{\text{kg CO}}{\text{kg mixt}} \right) \left(1,227.5 \frac{\text{kJ}}{\text{kg CO}} \right) + \left(0.75 \frac{\text{kg N}_2}{\text{kg mixt}} \right) \left(1,212.9 \frac{\text{kJ}}{\text{kg N}_2} \right)
$$

a. $\Delta h = 1,216.6 \text{ kJ/kg mixt}$

3. Mixture molar enthalpy:

$$
\Delta \bar{h}_{tot} = \Delta h_{tot} \times MW_{tot} = (1,216.6 \text{ kJ/kg mixt})(28 \text{ kg/kgmole})
$$

b. $\Delta \bar{h} = 34,064.8 \text{ kJ/kgmole}$

4. Mixture molar internal energy:

$$
\bar{u}_i = \bar{h}_i - \bar{RT}_i
$$
Combustion and Energy

and

$$\Delta u_i = \Delta h_i - R \Delta T$$

or

$$\Delta u = 34,064.8 \text{ kJ/kg mole} - (8.314 \text{ kJ/kg mole} \cdot \text{K})(1,000 \text{ K})$$

c. $$\Delta u = 25,750.8 \text{ kJ/kg mole}$$

5. Mixture internal energy

$$\Delta u_{\text{tot}} = \Delta u_{\text{tot}} / MW_{\text{tot}}$$

$$\Delta u_{\text{tot}} = \frac{25,750.8 \text{ kJ/kg mole}}{28 \text{ kg/kg mole}}$$

d. $$\Delta u = 919.7 \text{ kJ/kg mixt}$$

Comments: This problem illustrates the methodology used in preparing thermodynamic tables for gas mixtures. Tables such as for air and for products of combustion of fuel with 200% theoretical air and 400% theoretical air, as well as those for particular water vapor-air mixtures, are familiar to the student of engineering thermodynamics. For complex calculations, it is convenient to store these procedures in computer codes for access and easy solution to many thermochemical problems.

Several additional properties, including entropy and Gibbs and Hemholtz functions, will be covered in Chapter 3.

2.4 HEATS OF REACTION

Thermodynamic processes will usually result in a change in temperature, pressure, and/or volume. Thermochemical processes produce additional effects, including compositional changes and release or absorption of additional energy due to chemical reactions. For the purposes of analysis, it will be convenient to model the actual energetics of combustion reactions in terms of an ideal hypothetical process.

Chemical processes can result in energy being liberated by a reaction, termed an exothermic reaction, or the process may require energy to be absorbed, termed an endothermic reaction; see Figure 2.2. Furthermore, any energy absorbed or released at the reference datum by reaction would cause temperature to change and, therefore, make it necessary to transfer energy, usually as heat, to return the final temperature to its datum value.

Consider, for example, a closed system in which a chemical reaction occurs at constant total pressure; see Figure 2.3. Experience indicates that the temperature and composition will change as reactants are converted to products. To analyze this problem, it will be assumed that all chemical reactions, i.e., mass conversions and energy release, will occur only at a datum state, i.e., conditions of constant temperature and total pressure: $$T_0, P_0$$. This idea is similar to boiling and/or condensation energy transfer, in

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which $T_{\text{sat}}$ and $P_{\text{sat}}$ do not change but rather the energy transfer results in phase changes from liquid $\leftrightarrow$ vapor.

**Figure 2.2**  Energy of reaction.

**Figure 2.3**  Heat of reaction.
This energy transfer is called the heat of reaction, \( \Delta H_R \), and is defined as the energy absorbed or liberated from a chemical reaction when products are brought back to the initial temperature of the reactants. Since chemical reactions involve rearrangement of chemical bonds and formation and destruction of species, it is necessary to develop a means of comparing the ideal chemical energetics of various compounds, i.e., a kind of a chemical potential energy of a species. Thus, for instance, certain compounds such as fuels have a greater capacity to react rapidly with oxygen, i.e., have high chemical potential energies, whereas product species such as \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) have low chemical potential energies. This new species property, an energy of formation, will be seen to have direct bearing on the heat of reaction.

Two standard states have been used to define the datum in thermochemistry: the gaseous monatomic species datum and the natural elemental species datum. In both standards, the datum pressure and temperature are

\[
\begin{align*}
P_0 &= 1 \text{ atm} = 101 \text{ kPa} = 14.7 \text{ psi} \\
T_0 &= 25^\circ \text{C} = 298 \text{ K} = 77^\circ \text{F} = 537^\circ \text{R}
\end{align*}
\]

Standard state compounds are selected compounds that are assigned zero chemical potential energy at standard temperature and pressure (STP). Since our datum is for a constant-pressure process, this energy of formation is termed the enthalpy of formation, \( h^0_f \).

In the monatomic standard at STP, all monatomic species, i.e., O, H, N, etc., have \( h^0_f = 0 \). In the natural elemental standard, all natural elemental compounds have \( h^0_f = 0 \). A natural elemental compound is a species in which only one element appears and in a form in which it occurs naturally at STP, i.e., \( \text{H}_2 \), \( \text{N}_2 \), \( \text{O}_2 \), and solid carbon. Note that, for example, CO is not a natural elemental species since it contains more than one atomic species and O is also not a natural elemental species since oxygen occurs naturally as \( \text{O}_2 \) at STP. The natural elemental standard will be used in this text.

Two important heats of reaction warrant special attention: the heat of formation and the heat of combustion. The heat of formation, \( \Delta H_f \), is the energy absorbed or liberated by a chemical reaction when the product (a single chemical compound) is brought back to the initial temperature of the reactants (only natural elemental species). The heat of formation reaction for several compounds is shown below.

<table>
<thead>
<tr>
<th>Elemental compounds</th>
<th>Single compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2 + \frac{1}{2}\text{O}_2 ) STP</td>
<td>H(_2\text{O})</td>
</tr>
<tr>
<td>( \text{CS} + 2\text{H}_2 ) STP</td>
<td>( \text{CH}_4 )</td>
</tr>
<tr>
<td>( \text{C}_8\text{S} + \text{O}_2 ) STP</td>
<td>( \text{CO}_2 )</td>
</tr>
<tr>
<td>( 8\text{CS} + 9\text{H}_2 ) STP</td>
<td>( \text{C}<em>8\text{H}</em>{18} )</td>
</tr>
</tbody>
</table>

Another useful heat of reaction is the heat of combustion, \( \Delta H_c \), which is the energy liberated when a compound reacts with an oxidant to form the most oxidized form of the reactants, and is brought back to the initial reactant temperature. Recall that, for
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hydrocarbon chemistry, the most common oxidant is $O_2$ and the most stable oxidized products are $CO_2$ and $H_2O$; i.e.,

$$\text{Fuel} + \text{oxidant} \xrightarrow{\text{STP}} a\text{CO}_2 + b\text{H}_2\text{O}$$

If the water formed exists in the vapor state, the heat of combustion is termed lower heating value. If the water in the product state exists as a liquid, the heat of combustion is termed higher heating value of the fuel. This implies that the product mixture gave up its additional latent heat in going from a vapor to a liquid state.

Obviously, actual combustion processes do not occur at STP, and real combustion processes may not go to completion. It is therefore necessary to develop a means of expressing the energetics of chemical reactions in the more general case of combustion, which will be done in the following sections.

### 2.5 FIRST LAW FOR REACTIVE SYSTEMS

The first law of thermodynamics leads directly to an energy conservation principle. An extensive development of this concept can be found in most undergraduate thermodynamics texts. This fundamental relationship provides a statement, in general terms, of conservation and conversion of various energy forms.

From classical thermodynamics and the first law, one can obtain a differential form of the general energy equation for an open system (also termed a fixed or control volume relationship) as

$$\frac{dE}{dt} = \dot{Q} - \dot{W} + \sum_{i_{\text{in}}} \dot{m}_i e_i - \sum_{i_{\text{out}}} \dot{m}_i e_i \quad \text{kW} \left( \frac{\text{Btu}}{\text{min}} \right)$$  \hspace{1cm} (2.25a)

or

$$\frac{dE}{dt} = \dot{Q} - \dot{W} + \sum_{i_{\text{in}}} \dot{N}_i e_i - \sum_{i_{\text{out}}} \dot{N}_i \bar{e}_i$$  \hspace{1cm} (2.25b)

where

- $E$ = total system energy in C.V.
- $\dot{Q}$ = rate of heat transfer to/from (+ in/– out) the C.V.
- $\dot{W}$ = rate of work transfer to/from (– in/+ out) the C.V.
- $\dot{m}_{i,j}$ = mass flow rate of material transferred across the C.V. boundaries
- $\dot{N}_{i,j}$ = molar flow rate of material transferred across the C.V. boundaries
- $e_{i,j}$ = intensive total energy per unit mass of material transferred across the C.V. boundaries
- $\bar{e}_{i,j}$ = intensive total energy per unit mole of material transferred across the C.V. boundaries

This relationship can be expressed on a mass or molar basis but, in this text, will most frequently be written on a molar basis.
Figure 2.4 Open-system energy transfers.

Table 2.1 General Energy Equation and Applications

<table>
<thead>
<tr>
<th>Heat exchangers</th>
<th>Turbines</th>
<th>K.E. (nozzles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boilers</td>
<td>Compressors</td>
<td>P.E. (hydroelectric)</td>
</tr>
<tr>
<td>Furnaces</td>
<td>Pump</td>
<td>U (steam vs. air)</td>
</tr>
<tr>
<td>Condensers</td>
<td>Fan</td>
<td>$h_f$ (combustion)</td>
</tr>
</tbody>
</table>

Equation (2.25) shows that the total energy $E$ of a control volume may change with time, i.e., increase, decrease, and/or remain constant. Furthermore, it indicates that the rate of change of total control volume energy can be the result of several influences, including heat and/or work transfer rates to and/or from an open system, as well as various energy fluxes associated with material transfer across the boundaries. Figure 2.4 and Table 2.1 illustrate the significance of this equation to certain applications.

Many specific forms of the energy equation can easily be obtained by a proper application of the general energy equation as expressed by Equation (2.25). To do so, one must: (1) understand the physics of a particular problem under consideration, (2) formulate the proper mathematical statement of the appropriate energy balance, and (3) obtain the necessary properties required for solution.

To illustrate a technique for reducing the general energy equation to a suitable specific form, consider the case in which all the properties within a C.V., as well as those transferring across the boundary, do not change with time, i.e., steady state and steady...
flow. Under these restrictions, the rate of change in total C.V. energy must remain constant or
\[
\frac{dE}{dt} = 0
\]

Thus, the net energy flux into C.V. must equal the net energy flux out of C.V. or, when one equates transient energy forms of heat transfer and power to energy as properties crossing the boundaries due to mass transfer,
\[
\dot{Q} - \dot{W} = \sum_{j_{out}} \dot{m}_j e_j - \sum_{i_{in}} \dot{m}_i e_i = \sum_{j_{out}} \dot{N}_j \overline{c}_j = \sum_{i_{in}} \dot{N}_i \overline{c}_i
\]  
(2.26)

Unsteady applications that allow mass transfer from an open system, such as in rocket propulsion systems (see Figure 2.5), are instances in which the rate of decrease in total C.V. energy is written as
\[
\frac{dE}{dt} = Q - \sum_{j_{out}} \dot{m}_j e_j = Q - \sum_{j_{out}} \dot{N}_j \overline{c}_j
\]  
(2.27)

Consider another illustrative case in which no material is transferred across the boundary, i.e., a closed system (often termed a fixed or control mass). In this instance,
\[
\dot{m}_i = \dot{m}_j = 0
\]

and
\[
\frac{dE}{dt} = \dot{Q} - \dot{W}
\]

Multiplying both sides by \(dt\),
\[
dE = \delta Q - \delta W
\]

In many engineering applications, closed systems can produce boundary expansion work, such as with a piston-cylinder geometry, as illustrated in Figure 2.6. In this instance, the force through a distance relationship for work takes the familiar form,
\[
\delta W = PdV
\]  
(2.28)

and
\[
\frac{dE}{dt} = \delta Q - PdV
\]  
(2.29)

For a device that operates on a thermodynamic cycle, the initial and final states must be identical, requiring that the system must function as a closed system and integrating around the cyclic loop
\[
\int dE = 0 = \int \delta Q - \int \delta W
\]
\[Q_{net} = W_{net}
\]  
(2.30)
The total energy $E$ of an ideal-gas mixture according to the Gibbs-Dalton law can be written as

$$E_{\text{tot}} = \sum m_i \bar{e}_i = \sum N_i \bar{e}_i \quad \text{kJ (Btu)}$$  \hspace{1cm} (2.31)
or

\[ e_{\text{tot}} = \sum mf_i e_i \quad \text{kJ/kg (Btu/lbm)} \quad (2.31a) \]

and

\[ e_{\text{tot}} = \sum \bar{e}_i \quad \text{kJ/kg mole (Btu/lbmole)} \quad (2.31b) \]

A component species \( i \) can store energy in several ways, including potential, kinetic, internal, and chemical potential energy or

\[ e_i = \frac{g}{g_0} z_i + \frac{V_i^2}{2g_0} + u_i + h_{f_i}^0 \quad (2.32) \]

Neglecting kinetic and potential energy terms for the moment, the total energy of a mixture of fixed total mass equals

\[ E_{\text{tot}} = U_{\text{tot}} = \sum \bar{e}_i \left( \bar{u}_i + \bar{h}_{f_i}^0 \right) \quad (2.33) \]

Since enthalpy data are available in this text, Equation (2.33) can also be written as

\[ E_{\text{tot}} = U_{\text{tot}} = \sum N_i \left[ \bar{h}_i \left( \bar{h}' \right) - \bar{RT} + \bar{h}_{f_i}^0 \right] \quad (2.34) \]

A plot of total mixture energy versus temperature for a fixed composition will yield a curve having a positive slope since both \( u \) and \( h \) increase with increasing temperature; see Figure 2.7. In addition, mixture lines representing reactants have a greater total energy value at a given temperature than corresponding curves for products because fuels have larger chemical potential energies.

In open-system applications, there is an additional energy flux term associated with pressure gradients in the flowfield termed flow work or flow energy. Flow work or energy per unit mass crossing the control volume as a result of mass transfer is equal to the local product \( P_Nv_i \). The total energy term associated with mass that can cross a control volume is then equal to

\[ e_i = \frac{g}{g_0} z_i + \frac{V_i^2}{2g_0} + u_i + h_{f_i}^0 + P_i v_i \quad (2.35) \]

Since \( h_i = u_i + p_i v_i \), Equation (2.35) becomes

\[ e_i = \frac{g}{g_0} z_i + \frac{v_i}{2g_0} + h_i + h_{f_i}^0 \quad (2.35a) \]

The general energy equation equates heat- and work-transfer rates to changes in energy levels of materials that undergo state changes or processes. Therefore, it is the difference between energy terms rather than their absolute values that is most important to the engineer. Since thermochemical reactants in this text assume all chemical changes occur at \( STP \), it will be convenient to express internal energy and enthalpy values referenced to the \( STP \) state as a datum (Figure 2.8).
Figure 2.7 Total mixture energy lines vs. temperature.

When this approach is used, the total molar enthalpy of a species $i$ may be expressed as

$$\bar{h}_i^{\text{tot}} = \bar{h}_i(T) - \bar{h}_i(T_0) + \bar{h}_i^0$$  \hspace{1cm} (2.36)

and the change in total enthalpy is equal to

$$\Delta H_{\text{tot}} = H_{\text{tot}}(T_2) - H_{\text{tot}}(T_1) = \Sigma N_j \left[ \bar{h}_j(T_2) - \bar{h}_j(T_0) + \bar{h}_j^0 \right]$$  \hspace{1cm} (2.37)

Consider the case of a nonreactive gas mixture undergoing a process, i.e., $N_i = N_j$, $T_2 \neq T_1$, and

$$\Delta H_{\text{tot}} = \Sigma N_i \left[ \bar{h}_i(T_2) - \bar{h}_i(T_0) + \bar{h}_i^0 \right] = \Sigma N_i \left[ \bar{h}_i(T_1) - \bar{h}_i(T_0) + \bar{h}_i^0 \right]$$  \hspace{1cm} (2.38)

Equation (2.38) is the familiar form found in most introductory thermodynamics texts.
Using the energy equation as developed in this chapter, an expression for various thermochemical processes pertinent to combustion can now be written. Consider the energy analysis for the heat of formation of a particular species occurring at STP. In this instance, $P = P_0 =$ const, $T = T_0 =$ const, the initial state constituents are standard elemental species, and the final state consists of a single product species. For a fixed total mass system analysis, the closed-system form of the energy equation is applicable, or

$$dE = dU_{\text{tot}} = \delta Q - PdV$$

(2.39)

$$\delta Q_{\text{STP}} = dU_{\text{tot}} + PdV + \Delta dP = dH_{\text{tot}}$$

(2.40)

Integrating Equation (2.40) yields

$$Q_{\text{STP}} = \Delta H_{\text{tot}} = \sum_{\text{prod}} N_j \left[ \overline{h}_j^0 + \Delta \overline{h}_j \right] - \sum_{\text{react}} N_i \left[ \overline{h}_i^0 + \Delta \overline{h}_i \right]$$

(2.40a)

where

$$\Delta \overline{h}_{i,j} = 0 \text{ (reaction at STP)}$$

i.e., $T_2 = T_1 + T_0$

and
The heat of formation $\Delta hf$ is therefore given as

$$Q_{\text{STP}} = 1.0 \overline{h}_f^0 \equiv \Delta H_f$$

(2.41)

Table B.1 in Appendix B lists the heat of formation at STP for various compounds.

Consider the energy analysis for heat of combustion of a stoichiometric hydrocarbon fuel and air mixture reaction at STP. Again, this process requires that $P = P_0 =$ const and $T = T_0 =$ const, with the initial state a stoichiometric fuel and air mixture and the final state consisting of most oxidized products, i.e., CO$_2$ and H$_2$O. Equation (2.40a) again applies and

\[ Q = \Delta H_{\text{tot}} = \sum_{\text{prod}} N_j \left[ \overline{h}_f^0 + \Delta \overline{h} \right]_j - \sum_{\text{react}} N_j \left[ \overline{h}_f^0 + \Delta \overline{h} \right]_j \]

(2.40a)

where

\[ N_{i,j} = \text{determined from the stoichiometric equation} \]

\[ \Delta \overline{h}_{i,j} = O \quad \text{(reaction at STP)} \]

\[ Q_{\text{STP}} = N_{\text{CO}_2} \overline{h}_f^0 \text{CO}_2 + N_{\text{H}_2\text{O}} \overline{h}_f^0 \text{H}_2\text{O} - N_{\text{fuel}} \overline{h}_f^0 \text{fuel} = \Delta H_c \]

(2.42)

EXAMPLE 2.5 Carbon monoxide, CO, is an important product, resulting from incomplete combustion of many hydrocarbon fuels. Consider the stoichiometric reaction of carbon monoxide with oxygen. Determine (a) the constant-pressure heat of combustion of carbon monoxide at STP, Btu/lbm CO; (b) the constant-volume heat of combustion, Btu/lbm CO; and (c) the constant-pressure heat of combustion at 1800°F and 14.7 psia, Btu/lbm CO.

Solution:

1. Stoichiometric equation:

\[ \text{CO} + a\text{O}_2 \xrightarrow{\text{STP}} b\text{CO}_2 \]

Carbon atom balance: $b = 1$

Oxygen atom balance: $1 + 2a = 2b$ \quad $a = 0.5$

CO + \frac{1}{2} O$_2$ \rightarrow CO$_2$

2. Energy equation: $P = c$ (STP) using Table B.1 in Appendix B.
\[ \Delta H = \delta Q - \delta H + \sum N_i \tilde{e}_i - \sum N_i \tilde{e}_i \]

\[ Q = \sum_{\text{prod}} N_i \left[ \tilde{h}_i^0 + \left[ \tilde{h}(T) - \tilde{h}(T_0) \right]_i \right] - \sum_{\text{react}} N_i \left[ \tilde{h}_i^0 + \left[ \tilde{h}(T) - \tilde{h}(T_0) \right]_i \right] \]

\[ Q = 1.0 \left[ \tilde{h}_f^0 + \tilde{h}_{CO_2} \right]_{CO_2} - 0.5 \left[ \tilde{h}_f^0 + \tilde{h}_{O_2} \right]_{O_2} - 1.0 \left[ \tilde{h}_f^0 + \tilde{h}_{CO} \right]_{CO} - 1.0 \left[ 94,054 + 26,416 \text{ cal/gmole} \right] \left[ 1.8001 \text{ Btu/lbmole} \right] \]

\[ = -121,755 \text{ Btu/lbmole CO} \]

or

\[ a. \ Q = \frac{-121,755 \text{ Btu/lbmole}}{28 \text{ lbm/lbmole}} = -4,348.4 \text{ Btu/lbm CO} \]

3. Energy equation: \( V = c \quad (STP) \)

\[ Q = \sum_{\text{prod}} N_i \left[ \tilde{h}_i^0 + \left[ \tilde{h}(T) - \tilde{h}(T_0) \right]_i \right] - \sum_{\text{react}} N_i \left[ \tilde{h}_i^0 + \left[ \tilde{h}(T) - \tilde{h}(T_0) \right]_i \right] \]

\[ Q = 1.0 \left[ \tilde{h}_f^0 + \tilde{h}_{CO_2} \right]_{CO_2} - 0.5 \left[ \tilde{h}_f^0 + \tilde{h}_{O_2} \right]_{O_2} - 1.0 \left[ \tilde{h}_f^0 + \tilde{h}_{CO} \right]_{CO} - (1.0 - 0.5 - 1.0) \tilde{R}T \]

\[ = -121,755 + (0.5)(1.987)(537) = -121,221 \text{ Btu/lbm CO} \]

b. \( Q = \frac{-121,221}{28} = -4,329.3 \text{ Btu/lbm CO} \)

4. Energy equation: \( P = c \quad T = 1800^\circ R \)

\[ Q = 1.0 \left[ -94,054 + 7,984 \right]_{CO_2} - 0.5 \left[ 0 + 5,427 \right]_{O_2} - 1.0 \left[ -26,416 + 5,183 \right]_{CO} \]

\[ = -67,550.5 \text{ cal/gmole CO} \]

\[ Q = \frac{-67,550.5(1.8001)}{28} \]

C. \( Q = -4,342.8 \text{ Btu/lbm CO} \)

Comments: This problem illustrates that the heating value of a fuel at \( STP \) in many engineering problems is a good approximation for the heat released by combustion at conditions other than at \( STP \).

Since the formation and combustion reactions both occur at \( STP \), one can simply add the appropriate heats of formation via stoichiometric equations to determine heats of combustion of important fuels. Note also that addition of \( N_2 \) or excess \( O_2 \) does not change the value of heat of combustion since both those compounds are elemental species. The heat of combustion \( \Delta H_c \) can be visualized on an \( H-T \) diagram as the vertical distance between the reactant mixture and product curves at \( T = T_0 \); see Figure 2.9. The heat of combustion at \( STP \) for various species is found in Appendix B.
EXAMPLE 2.6 A rigid vessel filled with diatomic hydrogen and air is initially at 25°C and 1 atm total pressure. Calculate the adiabatic flame temperature for ideal complete combustion for an equivalence ratio of (a) 1.0, (b) 1.4, (c) 1.8, (d) 0.6, and (e) 0.2.

Solution:

1. Stoichiometric equation:

   \[ H_2 + 0.5\left(\text{O}_2 + 3.76\text{N}_2\right) \xrightarrow{\text{L}} \text{H}_2\text{O} + 1.88\text{N}_2 \]

2. Equivalence ratio:

   \[ \phi = \frac{FA_{\text{actual}}}{FA_{\text{stoich}}} \]

   Assume that the moles of air remain constant and vary the moles of hydrogen, giving

   \[ \phi \ H_2 + 0.5\left(\text{O}_2 + 3.76 \text{N}_2\right) \xrightarrow{\text{L}} \text{products} \]
3. Rich combustion:

$$\Phi > 1.0 \quad \text{(excess H}_2)$$

$$\Phi \text{H}_2 + 0.5[\text{O}_2 + 3.76 \text{N}_2] \rightarrow a\text{H}_2 + b\text{H}_2\text{O} + 1.88 \text{N}_2$$

Hydrogen atom balance  \( \Phi = a + b \)

Oxygen atom balance  \( 1 = b \)

and

<table>
<thead>
<tr>
<th>( \Phi )</th>
<th>( a )</th>
<th>( b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>1.4</td>
<td>0.4</td>
<td>1.0</td>
</tr>
<tr>
<td>1.8</td>
<td>0.8</td>
<td>1.0</td>
</tr>
</tbody>
</table>

4. Energy balance:

$$\delta Q - \delta W = \delta \dot{\rho} - \rho \dot{\omega} = dU$$

or

$$U \langle T_2 \rangle = U \langle T_1 \rangle$$

$$\sum_{\text{prod}} N_i \left[ \tilde{h}_j^0 + \left[ \tilde{h} \langle T_2 \rangle - \tilde{h} \langle T_0 \rangle \right] - \tilde{R} T_2 \right]$$

$$= \sum_{\text{react}} N_j \left[ \tilde{h}_j^0 + \left[ \tilde{h} \langle T_1 \rangle - \tilde{h} \langle T_0 \rangle \right] - \tilde{R} T_1 \right]$$

5. Energy balance—rich combustion:

$$a \tilde{h}^0 + \Delta \tilde{h} \|_{\text{H}_2} + \left[ \tilde{h}^0 + \Delta \tilde{h} \|_{\text{H}_2\text{O}} + 1.88 \left[ \tilde{h}^0 + \Delta \tilde{h} \|_{\text{N}_2} - (2.88 + a) \tilde{R} T_2 \right.ight.$$

$$= \Phi \left[ \tilde{h}^0 + \Delta \tilde{h} \|_{\text{H}_2} + 2.38 \tilde{h} |_{\text{air}} - (\phi + 2.38) \tilde{R} T_1 \right.$$}

where \( \tilde{h}^0 \|_{\text{H}_2\text{O}} = -57,798 \text{ cal/gmole} \) (Appendix B)

6. For \( \Phi = 1.0 \), using values for \( \Delta \tilde{h} \|_{(j)} \) from Tables B.4 and B.18 in Appendix B;

$$\Delta \tilde{h} \|_{\text{H}_2\text{O}} + 1.88 \Delta \tilde{h} \|_{\text{N}_2} - 5.723 T_2 = 55,797$$

by trial and error,

$$T_2 \approx 3.045 \text{ K}$$

For \( \Phi = 1.4 \),

$$0.4 \Delta \tilde{h} \|_{\text{H}_2} + \Delta \tilde{h} \|_{\text{H}_2\text{O}} + 1.88 \Delta \tilde{h} \|_{\text{N}_2} - 6.517 T_2 = 55,560$$
by trial and error,

\[ T_2 \cong 2,805 \text{ K} \]

For \( \Phi = 1.8 \),

\[ 0.8\Delta h_{\text{H}_2} + \Delta h_{\text{H}_2\text{O}} + 1.88\Delta h_{\text{N}_2} - 7.312 T_2 = 55,320 \]

by trial and error

\[ T_2 \cong 2,605 \text{ K} \]

7. Lean combustion: \( \Phi < 1.0 \) (excess air)

\[ \Phi \text{H}_2 + 0.5[\text{O}_2 + 3.76 \text{N}_2] \xrightarrow{\text{f}} \text{cO}_2 + d\text{H}_2\text{O} + 1.88\text{N}_2 \]

Hydrogen atom balance \( \Phi = d \)
Oxygen atom balance \( 1 = 2c + d \)

<table>
<thead>
<tr>
<th>( \Phi )</th>
<th>( c )</th>
<th>( d )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>0.2</td>
<td>0.6</td>
</tr>
<tr>
<td>0.2</td>
<td>0.4</td>
<td>0.2</td>
</tr>
</tbody>
</table>

8. Energy balance—lean combustion:

\[ c\left[ h_f^0 + \Delta h\right]_{\text{O}_2} + d\left[ h_f^0 + \Delta h\right]_{\text{H}_2\text{O}} + 1.88\left[ h_f^0 + \Delta h\right]_{\text{N}_2} - (c + d + 1.88)RT_2 \]
\[ = \Phi\left[ h_f^0 + \Delta h\right]_{\text{H}_2} + 2.38\left[ h_f^0 + \Delta h\right]_{\text{air}} - (\Phi + 2.38)RT_1 \]

9. For \( \Phi = 0.6 \),

\[ 0.2\Delta h_{\text{O}_2} + 0.6\Delta h_{\text{H}_2\text{O}} + 1.88\Delta h_{\text{N}_2} - 5.325 T_2 = 32,914 \]

by trial and error,

\[ T_2 \cong 2,240 \text{ K} \]

For \( \Phi = 0.2 \),

\[ 0.4\Delta h_{\text{O}_2} + 0.2\Delta h_{\text{H}_2\text{O}} + 1.88\Delta h_{\text{N}_2} - 4.928 T_2 = 10,030 \]

by trial and error

\[ T_2 \cong 800 \text{ K} \]

Comments: This problem illustrates the fact that, for most oxidation reactions, the peak flame temperature occurs at or near stoichiometric conditions. In practice, the maximum...
adiabatic flame temperature may occur just on the rich side of stoichiometric proportions. This slight shift can be attributed to the reduction in specific heat of the rich combustion products with a corresponding increase in temperature. Also, in actual flame systems, incomplete combustion and heat loss to surroundings will reduce the temperature, but the above calculated trend of temperature versus $\Phi$ will still hold.

Finally, consider the control volume energy balance analysis for a burner; see Figure 2.10. For the purposes of analysis, it will be assumed that the burner system operates at steady-state, steady-flow conditions and that, in this case, no work or power transfer occurs. Also assuming negligible changes in kinetic and potential energy fluxes, one can write the energy balance for the burner as

$$\frac{d E}{dt} = \delta Q - \delta W + \sum_{i_e} \frac{d N_i}{dt} \left[ \bar{H}_{tot}(T_i) \right] - \sum_{j_{out}} \frac{d N_j}{dt} \left[ \bar{H}_{tot}(T_j) \right]$$

(2.43)

$$\dot{Q} = \sum_{j_{out}} \dot{N}_j \left[ \bar{h}_j^0 + \{ \bar{h}(T_j) - \bar{h}(T_0) \} \right] - \sum_{i_e} \dot{N}_i \left[ \bar{h}_i^0 + \{ \bar{h}(T_i) - \bar{h}(T_0) \} \right]$$

(2.44)

Energy transfer from the generated gases as heat to the surroundings due to combustion is influenced in part by (1) particular fuel burned $\left( h_j^0 \right)$, (2) particular reaction $AF$ ratio ($N_i$ and $N_j$), (3) reactant state (fuel and oxidant phase/temperatures), and (4) final product state (completeness of combustion and product temperature).

The general burner combustion process can also be visualized by use of the $H$–$T$ diagram; see Figure 2.11. The actual heat release, process $1 \rightarrow 2$, can be modeled using three fictitious processes. First, if reactant conditions are offset from $T_0$ on the reactant line, an amount of energy is needed to “cool” reactants to STP conditions, i.e., process $1 \rightarrow a$. Next, the vertical path $a \rightarrow b$ represents the heat of combustion in going from reactant to products. Finally, the product state 2 indicates that an additional amount of energy is needed to heat the product mixture from STP to the final state, process $b \rightarrow 2$.

![Figure 2.10 Combustor or burner schematic.](image)
EXAMPLE 2.7 Oxygen-gas combustion is being pursued for use as a supplement and/or replacement for conventional air-gas chemistry in a variety of applications. The first order design assessment in such instances is illustrated in part by the following thermochemical analysis of an acetylene cutting torch burning oxygen or air. Using ideal complete combustion of acetylene at equivalence ratio values of 1.0, 0.83333, 0.714285, 0.625, 0.55556, and 0.5, determine (a) the mass of oxidant consumed per mass of fuel burned for oxygen and air, kg oxidant/kJ fuel; (b) the adiabatic flame temperatures for acetylene in oxygen and air, K; and (c) the volume of product gas generated per mole of fuel for oxygen and air, m³ product/kgmole fuel.
Solution:
1. Stoichiometric equation for ideal combustion of acetylene in oxygen:
   \[ \text{C}_2\text{H}_2 + a\text{O}_2 \rightarrow b\text{CO}_2 + c\text{H}_2\text{O} \]
   carbon atom balance \[ b = 2 \]
   hydrogen atom balance \[ 2c = 2 \quad c = 1 \]
   oxygen atom balance \[ 2a = 4 + 1 \quad a = 2.5 \]

2. Stoichiometric equation for ideal combustion of acetylene in air:
   \[ \text{C}_2\text{H}_2 + 2.5[\text{O}_2 + 3.76\text{N}_2] \rightarrow 2\text{CO}_2 + \text{H}_2\text{O} + (2.5)(3.76)\text{N}_2 \]

3. Theoretical equation for ideal combustion of acetylene in oxygen and air:
   \[ \phi\text{C}_2\text{H}_2 + 2.5\text{O}_2 \rightarrow 2\phi\text{CO}_2 + \phi\text{H}_2\text{O} + 2.5(1 - \phi)\text{O}_2 \]
   \[ \phi\text{C}_2\text{H}_2 + 2.5[\text{O}_2 + 3.76\text{N}_2] \rightarrow 2\phi\text{CO}_2 + \phi\text{H}_2\text{O} + 2.5(1 - \phi)\text{O}_2 + (2.5)(3.76)(1 - \phi)\text{N}_2 \]
   or
   \[ \text{C}_2\text{H}_2 + (2.5/\phi)\text{O}_2 \rightarrow 2\text{CO}_2 + \text{H}_2\text{O} + 2.5((1 - \phi)/\phi)\text{O}_2 \]
   \[ \text{C}_2\text{H}_2 + (2.5/\phi)[\text{O}_2 + 3.76\text{N}_2] \rightarrow 2\text{CO}_2 + \text{H}_2\text{O} 2.5((1 - \phi)/\phi)\text{O}_2 + (2.5)(3.76)((1 - \phi)/\phi)\text{N}_2 \]

4. Recall the definition of equivalence ratio, \( \Phi \):
   \[ \Phi = \frac{\text{moles fuel/moles oxidant})_{\text{actual}}}{\text{moles fuel/moles oxidant})_{\text{stoichiometric}}} \]
   for equal moles of fuel the equivalence ratio, \( \Phi \), then becomes
   \[ \Phi = \frac{\text{moles oxidant})_{\text{stoichiometric}}}{\text{moles oxidant})_{\text{actual}}} \]
   or
   \[ (\text{moles oxidant})_{\text{actual}} = (\text{moles oxidant})_{\text{stoichiometric}}/\Phi \]

5. Now the concept of theoretical oxidant, \( TO \), can be described as
   \( (\text{moles oxidant})_{\text{actual}} = (\text{moles oxidant})_{\text{stoichiometric}} \times TO \)
   by relating the two concepts of equivalence ratio and theoretical oxidant, one obtains
   \[ TO = (1/\Phi)100 \]

<table>
<thead>
<tr>
<th>( \Phi )</th>
<th>( TO )</th>
<th>( \Phi )</th>
<th>( TO )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>100</td>
<td>0.625</td>
<td>160</td>
</tr>
<tr>
<td>0.83333</td>
<td>120</td>
<td>0.55556</td>
<td>180</td>
</tr>
<tr>
<td>0.714285</td>
<td>140</td>
<td>0.5</td>
<td>200</td>
</tr>
</tbody>
</table>
6. The mass of oxidant consumed per mass of fuel burned for oxygen and air can be determined from the moles of oxidant and fuel and their molecular weights:

<table>
<thead>
<tr>
<th>TO</th>
<th>Moles oxidant</th>
<th>$MW_O$ kg/kgmoles</th>
<th>$MW_f$ kg/kgmoles</th>
<th>OF kg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kgmoles</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>2.5</td>
<td>32.00</td>
<td>26.04</td>
<td>3.072a</td>
</tr>
<tr>
<td>120</td>
<td>3.0</td>
<td>32.00</td>
<td>26.04</td>
<td>3.687</td>
</tr>
<tr>
<td>140</td>
<td>3.5</td>
<td>32.00</td>
<td>26.04</td>
<td>4.301</td>
</tr>
<tr>
<td>160</td>
<td>4.0</td>
<td>32.00</td>
<td>26.04</td>
<td>4.916</td>
</tr>
<tr>
<td>180</td>
<td>4.5</td>
<td>32.00</td>
<td>26.04</td>
<td>5.530</td>
</tr>
<tr>
<td>200</td>
<td>5.0</td>
<td>32.00</td>
<td>26.04</td>
<td>6.144</td>
</tr>
</tbody>
</table>

$OF = N_O \times \frac{MW_O}{N_f} \times \frac{MW_f}{1.0} = 2.5 \times 32/1.0 \times 26.4 = 3.072$

7. The moles of product species generated per mole of fuel for oxygen and air can be determined from the combustion equation knowing the values of the equivalence ratio:

<table>
<thead>
<tr>
<th>TO</th>
<th>Moles CO₂</th>
<th>Moles H₂O</th>
<th>Moles O₂</th>
<th>Moles N₂</th>
<th>Moles total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kgmoles</td>
<td>kgmoles</td>
<td>kgmoles</td>
<td>kgmoles</td>
<td>kgmoles</td>
</tr>
<tr>
<td>100</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>3b</td>
</tr>
<tr>
<td>120</td>
<td>2</td>
<td>1</td>
<td>0.5</td>
<td>0</td>
<td>3.5</td>
</tr>
<tr>
<td>140</td>
<td>2</td>
<td>1</td>
<td>1.0</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>160</td>
<td>2</td>
<td>1</td>
<td>1.5</td>
<td>0</td>
<td>4.5</td>
</tr>
<tr>
<td>180</td>
<td>2</td>
<td>1</td>
<td>2.0</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>200</td>
<td>2</td>
<td>1</td>
<td>2.5</td>
<td>0</td>
<td>5.5</td>
</tr>
</tbody>
</table>

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The mole fractions of product species generated per mole of fuel for oxygen and air can be determined knowing the moles of product species generated per mole of fuel. The molecular weight of product generated per mole of fuel for oxygen and air can be determined knowing the mole fractions and molecular weight of product species generated per mole of fuel.

\[
\begin{array}{cccccc}
\text{TO} & \text{Moles CO}_2 & \text{Moles H}_2\text{O} & \text{Moles O}_2 & \text{Moles N}_2 & \text{Moles}_{\text{total}} \\
\text{kgmoles} & \text{kgmoles} & \text{kgmoles} & \text{kgmoles} & \text{kgmoles} & \\
\hline
\text{Air} & \hline
100 & 2 & 1 & 0 & 9.40 & 12.40 \\
120 & 2 & 1 & 0.5 & 11.28 & 14.78 \\
140 & 2 & 1 & 1.0 & 13.16 & 17.16 \\
160 & 2 & 1 & 1.5 & 15.04 & 19.54 \\
180 & 2 & 1 & 2.0 & 16.92 & 21.92 \\
200 & 2 & 1 & 2.5 & 18.80 & 24.30 \\
\end{array}
\]

\[b N_{\text{tot}} = N_{\text{CO}_2} + N_{\text{H}_2\text{O}} + N_{\text{O}_2} + N_{\text{N}_2} = 2 + 1 + 0 + 0 = 3\]

8. The mole fractions of product species generated per mole of fuel for oxygen and air can be determined knowing the moles of product species generated per mole of fuel. The molecular weight of product generated per mole of fuel for oxygen and air can be determined knowing the mole fractions and molecular weight of product species generated per mole of fuel.

\[
\begin{array}{cccccc}
\phi & \bar{x}_{\text{CO}_2} & \bar{x}_{\text{H}_2\text{O}} & \bar{x}_{\text{O}_2} & \bar{x}_{\text{N}_2} & MW_{\text{prod}} \\
\hline
\text{Oxygen} & \hline
100 & 0.66667 & 0.33333 & 0 & 0 & 35.333 \\
120 & 0.57143 & 0.28571 & 0.14286 & 0 & 34.857 \\
140 & 0.50000 & 0.25000 & 0.25000 & 0 & 34.500 \\
160 & 0.44444 & 0.22222 & 0.33333 & 0 & 34.222 \\
180 & 0.40000 & 0.20000 & 0.40000 & 0 & 34.000 \\
200 & 0.36363 & 0.18182 & 0.45455 & 0 & 33.818 \\
\end{array}
\]

\[
\text{Air}
\]

\[
\begin{array}{cccccc}
100 & 0.16129 & 0.08065 & 0 & 0.75807 & 29.774 \\
120 & 0.13532 & 0.06766 & 0.03383 & 0.76319 & 29.624 \\
140 & 0.11655 & 0.05828 & 0.05828 & 0.76690 & 29.515 \\
160 & 0.10235 & 0.05118 & 0.07677 & 0.76970 & 29.433 \\
180 & 0.09124 & 0.04562 & 0.09124 & 0.77190 & 29.369 \\
200 & 0.08231 & 0.04115 & 0.10288 & 0.77366 & 29.317 \\
\end{array}
\]

\[
x_{\text{prod}} = N_{\text{prod}}/N_{\text{tot}} = N_{\text{CO}_2}/N_{\text{tot}} = 2/3 = 0.66667
\]

\[
MW_{\text{prod}} = \sum x_i MW_i = (0.66667)(44) + (0.33333)(18) + (0)(32) + (0)(28)
\]

\[
= 35.333
\]

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9. Energy balance  \( P = c \)  \( H_{\text{prod}} = H_{\text{react}} \)

**oxygen**

\[
0 = \left\{ N_{\text{CO}_2} \left[ h_f^{0} + \Delta h \right]_{\text{CO}_2} + N_{\text{H}_2\text{O}} \left[ h_f^{0} + \Delta h \right]_{\text{H}_2\text{O}} + N_{\text{NO}_2} \left[ h_f^{0} + \Delta h \right]_{\text{NO}_2} \right. \\
+ N_{\text{N}_2} \left[ h_f^{0} + \Delta h \right]_{\text{N}_2} \left\} \right. \text{prod} - \left\{ N_{\text{fuel}} \left[ h_f^{0} + \Delta h \right]_{\text{fuel}} + N_{\text{O}_2} \left[ h_f^{0} + \Delta h \right]_{\text{O}_2} \right. \\
\]

or

\[
\left[ h_f^{0} \right]_{\text{C}_2\text{H}_2} + \left( \frac{2.5}{\phi} \right) \left[ h_f^{0} \right]_{\text{O}_2} = 2 \left[ h_f^{0} + \Delta h \right]_{\text{CO}_2} + \left[ h_f^{0} + \Delta h \right]_{\text{H}_2\text{O}} \\
+ 2.5 \left( \frac{1 - \phi}{\phi} \right) \left[ h_f^{0} + \Delta h \right]_{\text{O}_2} + (-54.194) + \left( \frac{2.5}{\phi} \right) [0] \\
= 2 \left[ -94.054 + \Delta h \right]_{\text{CO}_2} + \left[ -57.798 + \Delta h \right]_{\text{H}_2\text{O}} 2.5 \left( \frac{1 - \phi}{\phi} \right) [0 + \Delta h]_{\text{O}_2},
\]

**air**

\[
0 = \left\{ N_{\text{CO}_2} \left[ h_f^{0} + \Delta h \right]_{\text{CO}_2} + N_{\text{H}_2\text{O}} \left[ h_f^{0} + \Delta h \right]_{\text{H}_2\text{O}} + N_{\text{NO}_2} \left[ h_f^{0} + \Delta h \right]_{\text{NO}_2} \right. \\
+ N_{\text{N}_2} \left[ h_f^{0} + \Delta h \right]_{\text{N}_2} \left\} \right. \text{prod} \\
- \left\{ N_{\text{fuel}} \left[ h_f^{0} + \Delta h \right]_{\text{fuel}} + N_{\text{O}_2} \left[ h_f^{0} + \Delta h \right]_{\text{O}_2} + N_{\text{N}_2} \left[ h_f^{0} + \Delta h \right]_{\text{N}_2} \right. \\
\]

or

\[
\left[ h_f^{0} \right]_{\text{C}_2\text{H}_2} + \left( \frac{2.5}{\phi} \right) \left[ h_f^{0} \right]_{\text{O}_2} + 3.76 \left[ h_f^{0} \right]_{\text{N}_2} \left[ \right. \\
= 2 \left[ h_f^{0} + \Delta h \right]_{\text{CO}_2} + \left[ h_f^{0} + \Delta h \right]_{\text{H}_2\text{O}} 2.5 \left( \frac{1 - \phi}{\phi} \right) \left[ h_f^{0} + \Delta h \right]_{\text{O}_2} \\
+ (2.5)(3.76) \left( \frac{1 - \phi}{\phi} \right) \left[ h_f^{0} + \Delta h \right]_{\text{N}_2} - 54.194 + \left( \frac{2.5}{\phi} \right) [0 + (3.76)(0)] \\
= 2 \left[ -94.054 + \Delta h \right]_{\text{CO}_2} + \left[ -57.798 + \Delta h \right]_{\text{H}_2\text{O}} 2.5 \left( \frac{1 - \phi}{\phi} \right) [0 + \Delta h]_{\text{O}_2} \\
+ (2.5)(3.76) \left( \frac{1 - \phi}{\phi} \right) [0 + \Delta h]_{\text{N}_2},
\]

using the values for \( \Delta h \) from appropriate tables in Appendix B, by trial and error the values for \( T_2 \) can thus be determined for the oxygen and air cases as listed below.
<table>
<thead>
<tr>
<th>TO</th>
<th>$T_2$, K</th>
<th>$V_2$, $m^3$/kgmole fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>5,008.3</td>
<td>1,236.9</td>
</tr>
<tr>
<td>120</td>
<td>4,572.6</td>
<td>1,313.3</td>
</tr>
<tr>
<td>140</td>
<td>4,215.0</td>
<td>1,383.5</td>
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<tr>
<td>160</td>
<td>3,915.8</td>
<td>1,445.9</td>
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<tr>
<td>180</td>
<td>3,661.4</td>
<td>1,502.2</td>
</tr>
<tr>
<td>200</td>
<td>3,442.3</td>
<td>1,553.6</td>
</tr>
<tr>
<td>Air</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>2,036.7</td>
<td>2,072.4</td>
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<tr>
<td>120</td>
<td>1,803.7</td>
<td>2,187.6</td>
</tr>
<tr>
<td>140</td>
<td>1,627.4</td>
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<td>1,489.2</td>
<td>2,387.8</td>
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<td>180</td>
<td>1,377.6</td>
<td>2,477.9</td>
</tr>
<tr>
<td>200</td>
<td>1,285.6</td>
<td>2,563.5</td>
</tr>
</tbody>
</table>

ADIBATIC FLAME TEMPERATURE

![Graph showing adiabatic flame temperature vs. theoretical oxidant]
10. The final product volume $V_2$ can now be determined by applying the ideal gas law, Equation (1.3a), knowing the adiabatic temperature, $T_2$, and the total product moles $N_{\text{tot}}$:

$$P V = N_{\text{tot}} R T$$

Since $P_2 = P_1$

$$V_2 = N_{\text{tot}} \frac{2 R T_2}{P_1}$$

$$V_2 = (3 \text{ kgmol product} \cdot 8,314.34 \text{ N} \cdot \text{m/kgmolK}) \frac{(5,008.3 \text{ K})}{(101,000 \text{ N/m}^2)}$$

$$= 1,236.9 \text{ m}^3/\text{kgmole fuel}$$

Comments: This problem illustrates the fact that oxygen enrichment uses less oxidant, produces a higher theoretical adiabatic flame, and less product gas volume per mole of fuel as compared to air at equal equivalence ratios. With the appearance in recent years of improved air separation technologies, applications of oxygen and oxygen-enriched combustion of industrial burners, furnaces, and certain high temperature operations, including cutting torches, have occurred. Great care should be taken however to ensure that more than simply applying energy balances are undertaken when attempting to do any oxygen enrichment design work. Among some of the more noteworthy fuel-engine oxygen enrichment impact issues are flammability limits, flame speeds, incomplete combustion, emissions, and materials that can work in high oxygen concentration and high temperature environments. In addition, economics issues such as the cost for the generation of oxygen and costs for safety-related elements of the combustion process also need to be addressed.
A combustion efficiency $\eta_c$, in similar fashion to turbine and compressor efficiency concepts introduced in thermodynamics, can be utilized to characterize actual heat release knowing the heating value of the fuel being burned; see Figure 2.12.

$$\eta_c = \frac{\text{actual heat released}}{\text{ideal heat released}} = \frac{\Delta H}{\Delta H_c} \leq 1.0 \quad (2.45)$$

For heat-transfer applications, such as in furnaces, heaters, and boilers, high combustion efficiency requires that the combustion device results in a product temperature approaching $T_0$, i.e., large heat transfer from the product combustion gases; see Figure 2.12. In the limit, the ideal heat release by reaction would equal the heat of combustion. For high-power gas expansion output applications, such as internal combustion and turbine engines, the need to produce a maximum combustion temperature leads to the concept of adiabatic flame temperature, i.e., a combustion process in which there is no heat transfer, i.e., $\Delta H = 0$ and low combustion efficiency.

Figure 2.12  $H$-$T$ diagram and combustion efficiency.
PROBLEMS

2.1 Consider a stoichiometric mixture of hydrogen and air. Calculate for these conditions the (a) reactant mass fractions, \( mf \); (b) reactant mixture molecular weight, kg/kg mole; (c) molar \( \overline{AF} \) ratio, kg mole air/kg mole fuel; and (d) mass \( FA \) ratio, kg fuel/kg air.

2.2 Repeat Problem 2.1 for methane, \( \text{CH}_4 \).

2.3 Repeat Problem 2.1 for propane, \( \text{C}_3\text{H}_8 \).

2.4 Repeat Problem 2.1 for iso-octane, \( \text{C}_8\text{H}_{18} \).

2.5 Repeat Problem 2.1 for dodecane, \( \text{C}_{12}\text{H}_{26} \).

2.6 Repeat Problem 2.1 for ethanol, \( \text{C}_2\text{H}_5\text{OH} \).

2.7 An unknown hydrocarbon fuel is burned with air. The molar \( \overline{AF} \) ratio for the combustion process is equal to 21.43 lbmole air/lbmole fuel, while the corresponding mass \( FA \) ratio is given as 0.0451 lbm fuel/lbm air. Calculate (a) fuel molecular weight, lbm/lbmole; (b) fuel structure \( \text{C}_x\text{H}_y \), %; and (c) reaction excess air, % for the reaction.

2.8 A gaseous fuel having a volumetric analysis of 65% \( \text{CH}_4 \), 25% \( \text{C}_2\text{H}_6 \), 5% CO, and 5% \( \text{N}_2 \) is burned with 30% excess air. Determine (a) mass \( AF \) ratio, lbm air/lbm fuel; (b) mass of CO\(_2\) produced, lbm CO\(_2\)/lbm fuel; (c) mass of water formed, lbm H\(_2\)O/lbm fuel; and (d) mass of products formed, lbm products/lbm reactants.

2.9 The dry products of combustion have the following molar percentages:

\[
\begin{align*}
\text{CO} & \text{ 2.7\%} \\
\text{O}_2 & \text{ 5.3\%} \\
\text{H}_2 & \text{ 0.9\%} \\
\text{CO}_2 & \text{ 16.3\%} \\
\text{N}_2 & \text{ 74.8\%}
\end{align*}
\]

Find, for these conditions: (a) mixture gravimetric analysis; (b) mixture molecular weight, lbm/lbmole; and (c) mixture specific gas constant \( R \), ft lbf/ftm \(^2\)R.

2.10 For the product conditions in Problem 2.9, assuming 1 atmosphere total pressure and a gas temperature of 1,800K, calculate: (a) mixture constant pressure specific heat, kJ/kgmole\(K\); (b) mixture specific heat ratio; (c) mixture enthalpy, kJ/kgmole; and (d) mixture internal energy, kJ/kgmole.

2.11 A hydrocarbon fuel, \( \text{C}_x\text{H}_y \), is burned at constant pressure in air. The volumetric analysis of the products of combustion on a dry basis are:

\[
\begin{align*}
\text{CO} & \text{ 1.1\%} \\
\text{O}_2 & \text{ 8.3\%} \\
\text{CO}_2 & \text{ 7.8\%} \\
\text{N}_2 & \text{ 82.8\%}
\end{align*}
\]

Determine (a) the molar carbon to hydrogen ratio for the fuel; (b) fuel mass fraction composition, %C and %H; (c) theoretical air, %; (d) mass \( AF \) ratio, kg air/kg fuel; and (e) dew point temperature for 1 atmospheric combustion, \( ^\circ\text{C} \).

2.12 A homogeneous mixture of methane, \( \text{CH}_4 \), and air at \( \text{STP} \) has a specific heat ratio of 1.35. Obtain for this mixture (a) the reactant mixture mole fractions, %; (b) the reactant mixture molecular weight, kg/kgmole; (c) the mixture constant-pressure specific heat, kJ/kgmole\(K\); (d) the mixture constant volume specific heat, kJ/kg K; and (e) the mixture density, kg/m\(^3\).

2.13 Repeat Problem 2.12 except for enriched air using the JANAF data for \( \text{O}_2 \) and \( \text{N}_2 \) and assuming that enriched air consists of percentages of \( \text{O}_2 \) and \( \text{N}_2 \). Find, for the mixture as a function of enrichment: (a) molar specific heats \( \overline{C}_p \) and \( \overline{C}_v \), kJ/kg mole K; (b) mass specific heats, kJ/kg K; and (c) specific heat ratio \( \gamma \) for 1 atm and 300K.
2.14 Using the JANAF data for O$_2$ and N$_2$ and assuming that air consists of 1 kgmole O$_2$ and 3.76 kgmole N$_2$, find for the mixture: (a) molar specific heats $\overline{C}_p$ and $\overline{C}_v$, kJ/kgmole K; (b) mass specific heats, kJ/kg K; and (c) specific heat ratio $\gamma$ for 1 atm and 300K.

2.15 Repeat Problem 2.14 for a temperature of 1,000K.

2.16 A fuel composed of 50% C$_7$H$_{14}$ and 50% C$_8$H$_{18}$ by weight is burned using 10% excess air. For 100 lbm of fuel, determine: (a) the volume of STP air required for ideal combustion, ft$^3$; and (b) the mass $AF$ ratio, lbm air/lbm fuel.

2.17 One kg of Octane, C$_8$H$_{18}$, in gaseous state is combusted with 12 kg of air. For these proportions obtain: (a) the moles of air that react per moles of fuel, kgmole air/kgmole fuel; (b) moles of CO produced per mole of fuel, kgmole CO; (c) moles of CO$_2$ produced per mole of fuel, kgmole CO$_2$; and (d) product mole fractions.

2.18 Consider the reaction of propane, C$_3$H$_{18}$, and 120% theoretical air. Assuming ideal combustion, determine (a) product mole fractions, %; (b) product mass fractions, %; (c) product mixture molecular weight, kg/kgmole; and (d) product mixture specific gas constant, kJ/kg K.

2.19 An advanced turbine concept proposes the use of carbon dioxide as the working fluid. Inlet conditions for the turbine are 2,200K and 1,150 kPa abs. with exhaust conditions specified as 600K and 120 kPa abs. If the unit is to produce 50 kW of power output, calculate: (a) the mass flowrate, kg CO$_2$/sec; (b) the inlet volumetric flowrate, m$^3$ CO$_2$/sec; and (c) the turbine work, kJ/kJ CO$_2$.

2.20 For a reactive mixture, the dew point temperature is defined as the saturation temperature of water corresponding to the water vapor partial pressure. Calculate (a) product mole fractions, %; (b) product water vapor partial pressure; and (c) dew point temperature, K, for the ideal constant-volume combustion of acetylene, C$_2$H$_2$, and 20% excess air. Assume that the reactants are at 14.5 psi and 77° F, while the products are at 960°R.

2.21 The lower heating value of gaseous butene, C$_4$H$_8$, is 19,483 Btu/lbm. For reaction conditions at STP, calculate (a) molar enthalpy of formation of butene, Btu/lbmole; (b) mass enthalpy of formation, Btu/lbm; and (c) the enthalpy of hydrogenation associated with the reaction C$_4$H$_8$ + H$_2$ $\rightarrow$ C$_4$H$_{10}$, Btu/lbmole H$_2$.

2.22 A propane torch, C$_3$H$_8$, burns lean with 120% excess air. Temperature of the flame is 1,400°R. Find (a) molar $AF$ ratio, lbmole air/lbmmole fuel; (b) ideal combustion product mole fractions, %; (c) volume of exhaust gas to volume of combustion air, ft$^3$ gas/ft$^3$ air; and (d) heat released by an ideal combustion process, Btu/lbm fuel.

2.23 A unique underwater propulsion power plant uses hydrogen peroxide, H$_2$O$_2$, to oxidize gaseous hydrogen, H$_2$. For ideal stoichiometric gas phase thermochemistry determine (a) the reactant molecular weight, lbm/lbmole; (b) the reactant mass fractions, %; (c) the water produced, lbm H$_2$O/lbm reactants; and (d) the energy density at STP, Btu/lbm reactants.

2.24 A rigid vessel contains a mixture of one mole of methane, CH$_4$, and three moles of oxygen, O$_2$. The reactants initially are at 14.7 psia and 537°R. After complete combustion, the products are cooled to 1,080°R. Find (a) the vessel volume, ft$^3$; (b) the final pressure, psia; (c) the product dew point temperature, °F; (d) the heat transfer, Btu/ft$^2$; and (e) the product gravimetric analysis, %.

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2.25 Hydrazine, $\text{N}_2\text{H}_4$g, and hydrogen peroxide, $\text{H}_2\text{O}_2$g, comprise a hyperbolic (self-igniting on contact) mixture used in special applications such as torpedo and missile propulsion. If the hydrogen peroxide is supplied in a 90% $\text{H}_2\text{O}_2$–10% $\text{H}_2\text{O}$ gravimetric mixture, calculate for ideal complete combustion of the stoichiometric reaction (a) mole fractions of $\text{H}_2\text{O}_2$ and $\text{H}_2\text{O}$ in oxidizing solution, %; (b) FO ratio, kg fuel/kg oxidant; (c) product mole fractions, %; and (d) mixture lower heating value, kJ/kg mixture.

2.26 A furnace burns 2,500 ft$^3$/hr of a gas having the following volumetric analysis: 90% $\text{CH}_4$, 7% $\text{C}_2\text{H}_6$, and 3% $\text{C}_3\text{H}_8$. Both gas and air are supplied at 25°C and atmospheric pressure. The flue gas in the exhaust has a temperature of 1,300K and passes through a stack with an inside diameter of 30 cm. Calculate (a) volumetric analysis of the ideal dry flue gas, %; (b) velocity of stack gas, cm/sec; (c) heat release for ideal combustion, Btu/hr; and (d) combustion efficiency, %.

2.27 Ethylene, $\text{C}_2\text{H}_4$, is to be reacted in 18% excess air in an atmosphere with changing humidity. Calculate (a) product mole fraction for dry air, %; (b) dew point temperature for dry air combustion, °C; (c) product mole fraction for humid air with a humidity ratio $\omega = 18$ gm $\text{H}_2\text{O}$/kg dry air, %; and (d) dew point temperature for the humid air combustion, °C.

2.28 Calculate the (a) adiabatic flame temperature, K; (b) total moles of products; (c) final total pressure, kPa; and (d) product dew point temperature, °C, for the constant-volume combustion of methane, $\text{CH}_4$, and oxygen with a 0.75 equivalence ratio. Assume homogeneous gas-phase reactant conditions of 101 kPa and 298K.

2.29 A mixture of hydrogen and air initially at 25°C and 1 atm pressure is burned in a constant-pressure adiabatic process in which the adiabatic flame temperature is 2,800K. Assuming complete combustion in all calculations determine (a) volume of products to the volume of reactants; (b) molar $AF$ ratio, kg mole air/kg mole fuel; (c) excess air required, %; and (d) equivalence ratio for the process.

2.30 Propane, $\text{C}_3\text{H}_8$, is burned in 130% theoretical air. The dry products of combustion consist of CO, CO$_2$, O$_2$, and N$_2$ with the oxygen percentage equal to 6.444%. For these percentages determine: (a) the Orsat combustion analysis, %; (b) the product molecular weight, kg/kg mole; (c) the mass of water produced per mass of fuel burned, kg $\text{H}_2\text{O}$/kg fuel; and (d) the percentage of fuel carbon converted to CO, %.

2.31 A hydrocarbon fuel $\text{C}_x\text{H}_y$ is burned in enriched air, i.e. $[\text{O}_2 + n_{\text{air}} \text{N}_2]$ where $0 < n_{\text{air}} < 3.76$ is the moles of nitrogen in the synthetic atmosphere. Determine an expression in terms of neair for (a) the molecular weight of the enriched air, kg enriched air/kg mole enriched air; (b) the generalized stoichiometric equation for the combustion of one mole of fuel; (c) the molar $AF$ ratio, kg mole enriched air/kg mole fuel; and (d) the mass $AF$ ratio, kg enriched air/kg fuel.

2.32 An equimolar mixture of hydrogen and carbon monoxide is mixed with a stoichiometric quantity of air in a closed well-insulated vessel. The total initial pressure of the mixture is 5 atm and total initial temperature is 25°C. The mixture is ignited by an electric spark. Assuming the oxidation reaction to have gone to completion, determine (a) the total moles of product, kg mole products; (b) the maximum temperature, °C; and (c) the peak pressure, atm.

2.33 Reconsider Problem 2.29. Determine an expression in terms of neair for (a) the total moles of product, kg mole products; (b) the molecular weight of the products, kg
products/kgmole products; (c) the mole fractions of product species; and (d) the mass fractions of product species.

2.34 Gaseous propane, \( \text{C}_3\text{H}_8 \), and air are burned in a steady flow constant pressure process. The fuel and air are supplied at \( \text{STP} \) while the products are at 1,260°R. Assuming a lean adiabatic process calculate (a) the equivalence ratio required for these conditions; (b) the molar air-fuel ratio, for the reaction, lbmole air/lbmole fuel; and (c) moles of CO\(_2\) formed per moles of propane burned.

2.35 Gaseous hydrogen and oxygen are pre-mixed in the proportion 10 parts O\(_2\) to 1 part H\(_2\) by weight. The mixture’s initial state is at \( \text{STP} \). For these reactant proportions calculate: (a) the mixture equivalence ratio; (b) the reactant mixture molecular weight, kg/kgmole; (c) the reactant mixture specific gravity; and (d) the reactant mixture lower heating value, kJ/kgfuel.

2.36 Propylene is burned in 30% excess air to provide waste heat. The combustion efficiency for the process is 80% with 60% of the carbon yield being CO\(_2\) and 30% producing CO. Reactants are supplied to the burner at \( \text{STP} \). For this process find: the HHV, kJ/kg fuel; (b) heat transfer, kJ/kgmole fuel; (c) moles of product, %; and (d) product temperature, K.

2.37 Methane undergoes a reaction in a constant volume combustion vessel. Complete reaction for a stoichiometric reactive mixture, initially at \( \text{STP} \), results in a final reaction peak temperature of 1,200K. For these constraints find: (a) the stoichiometric reaction coefficients; (b) the peak pressure, kPa; and (c) the heat transferred during the combustion process, kJ/kgmole CH\(_4\).