CHAPTER 2

Fundamental Concepts in Engineering Thermodynamics

2.1 Introduction

Engineering thermodynamics provides the foundation in mass and energy balances essential to understanding bioenergy and biobased products. Accounting for these balances is more complicated than for energy conversion processes that do not include chemical reaction because chemical constituents change and energy is released from the rearrangement of chemical bonds.

This chapter is designed to introduce or reacquaint readers, as appropriate, to fundamental concepts in engineering thermodynamics. The treatment does not pretend to be exhaustive; readers requiring additional background are directed to the list of reference materials at the end of this chapter.

2.2 General Concepts in Mass and Molar Balances

In the absence of chemical reaction, the change in mass of a particular constituent within a control volume is equal to the difference in net mass flow of the constituent entering and exiting the control volume. Figure 2.1 illustrates mass balance for a system consisting of five inlets and five exits. In general, the mass balance for a given chemical constituent can be written in the form:

$$\frac{\mathrm{d}m_{\mathrm{CV}}}{\mathrm{d}t} = \sum_i \dot{m}_i - \sum_e \dot{m}_e \tag{2.1}$$

where m_{CV} is the amount of mass contained within the control volume; $\dot{m}_i$ and $\dot{m}_e$ are, respectively, the rates at which mass enters at i and exists at e, where we allow for the possibility of several inlets and exits. For steady flow conditions, the net

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Biorenewable Resources: Engineering New Products from Agriculture, Second Edition. Robert C. Brown and Tristan R. Brown.

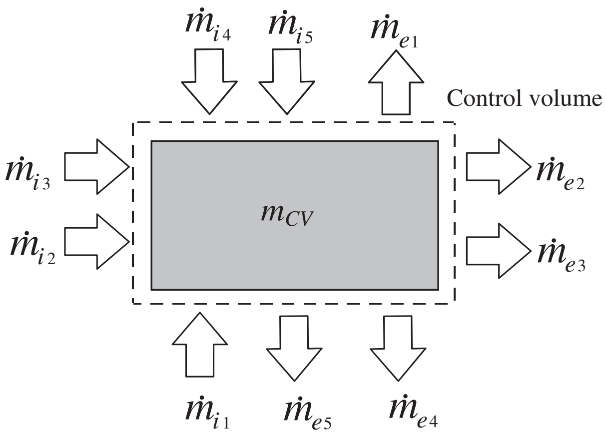

FIG. 2.1 Mass balance on steady-flow control volume with five inlets and five exits.

quantity of mass in the control volume is unchanging with time, and Equation 2.1 can be written as:

$$\sum_i \dot{m}_i = \sum_e \dot{m}_e \tag{2.2}$$

However, when chemical reaction occurs, chemical compounds are not conserved as they flow through the system. For example, methane (CH_4) and oxygen (O_2) entering a combustor are consumed and replaced by carbon dioxide (CO_2) and water (H_2O):

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{2.3}$$

Accordingly, mass balances cannot be written for methane and oxygen using either Equation 2.1 (unsteady flow) or Equation 2.2 (steady flow). Although chemical compounds are not conserved, the chemical elements making up these compounds are conserved; thus, elemental mass balances can be written.

In the case of the reaction of CH_4 with O_2, mass balances can be written for the chemical elements carbon (C), hydrogen (H), and oxygen (O). However, because chemical compounds react in distinct molar proportions, it is usually more convenient to write *molar* balances on the elements.

Recall that a mole of any substance is the amount of mass of that substance that contains as many individual entities (whether atoms, molecules, or other particles), as there are atoms in 12 mass units of carbon-12. For engineering systems, it is usually more convenient to work with kilograms as the unit of mass; thus, for this measure kilomole (kmol) will be employed instead of the gram-mole (gmol) that often appears in chemistry books. The number of kilomoles of a substance, n, is related to the number of kilograms of a substance, m, by its molecular weight, M (kg/kmol):

$$n = \frac{m}{M} \tag{2.4}$$

On a molar basis, it is straightforward to account for the mass changes that occur during chemical reactions: an overall chemical reaction is written that is supported by molar balances on the elements appearing in the reactant and product chemical compounds.

Example: One kilogram of methane reacts with air. (a) If all of the methane is to be consumed, how many kilograms of air will be required? (b) How many kilograms of carbon dioxide, water, and nitrogen will appear in the products?

One kilogram of methane, with a molecular weight of 16, is calculated to be 1/16 kmol using Equation 2.4. Air is approximated as 79% nitrogen and 21% oxygen on a molar basis. The overall chemical reaction can be written as:

$$\left(\frac{1}{16}\right) CH_4 + a\left(O_2 + \frac{0.79}{0.21}N_2\right) \rightarrow x\,CO_2 + y\,H_2O + z\,N_2$$

where a is the number of kilomoles of oxygen required to consume 1/16 kilomole of CH_4 and x, y, and z are the kilomoles of CO_2, H_2O, and N_2, respectively, in the products. The unknowns in this equation can be found from molar balances on the elements C, H, O, and N:

$$\text{carbon: } \frac{1}{16} = x \text{ (kmol)}$$

$$\therefore m_{CO_2} = n_{CO_2} \times M_{CO_2} = \frac{1}{16} \times 44 = 2.75 \text{ kg}$$

$$\text{hydrogen: } \frac{1}{16} \times 4 = 2y$$

$$y = \frac{1}{8}\text{(kmol)}$$

$$\therefore m_{H_2O} = n_{H_2O} \times M_{H_2O} = \frac{1}{8} \times 18 = 2.25 \text{ kg}$$

$$\text{oxygen: } 2a = 2x + y = 2 \times \frac{1}{16} + \frac{1}{8} = \frac{1}{4}$$

$$a = \frac{1}{8}(\text{kmol})$$

$$\therefore m_{O_2} = n_{O_2} \times M_{O_2} = \frac{1}{8} \times 32 = 4 \text{ kg}$$

$$\text{nitrogen: } \frac{0.79}{0.21}a = \frac{0.79}{0.21} \times \frac{1}{8} = 0.47 = z \text{ (kmol)}$$

$$\therefore m_{N_2} = n_{N_2} \times M_{N_2} = 0.47 \times 28 = 13.2 \text{ kg}$$

A check shows that 18.2 kg of methane and air are converted into 18.2 kg of products in the form of carbon dioxide, water, and nitrogen, as expected from mass conservation.

Mixtures of reactants or products are conveniently described on the basis of either mass fractions or mole fractions. If a mixture consists of N constituents, then the total mass, m, and total number of moles, n, are given by:

$$m = m_1 + m_2 + \cdots + m_N = \sum_{i=1}^{N} m_i \tag{2.5}$$

$$n = n_1 + n_2 + \cdots + n_N = \sum_{i=1}^{N} n_i \tag{2.6}$$

The mass fraction, y_i, of the ith constituent of a mixture is equal to:

$$y_i = \frac{m_i}{m} \tag{2.7}$$

Mass fractions are sometimes presented as percentages by multiplying by 100 and assigning units of weight percent (wt%). The mole fraction, x_i, of the ith constituent of a mixture is equal to:

$$x_i = \frac{n_i}{n} \tag{2.8}$$

Mole fractions are sometimes presented as percentages by multiplying by 100 and assigning units of mole percent (mol%).

Mole fractions are useful in calculating partial pressures, p_i, of the constituents of a gas mixture:

$$p_i = x_i p$$

where p is the total pressure of the mixture:

$$\sum_i^N p_i = \sum_i^N x_i p = p \sum_i^N x_i = p$$

The apparent molecular weight of a mixture, M, can be calculated from the molecular weights of each of the constituents, M_i:

$$M = \frac{m}{n} = \frac{\sum_{i=1}^N m_i}{n} = \frac{\sum_{i=1}^N n_i M_i}{n} = \sum_{i=1}^N \frac{n_i}{n} M_i = \sum_{i=1}^N x_i M_i \tag{2.9}$$

It is often useful to convert from mass fractions to mole fractions and vice versa:

$$x_i = \frac{n_i}{n} = \frac{\frac{m_i}{M_i}}{\sum_{i=1}^N \frac{m_i}{M_i}} = \frac{\frac{m_i/m}{M_i}}{\sum_{i=1}^N \frac{m_i/m}{M_i}} = \frac{\frac{y_i}{M_i}}{\sum_{i=1}^N \frac{y_i}{M_i}} \tag{2.10}$$

$$y_i = \frac{m_i}{m} = \frac{n_i M_i}{\sum_{i=1}^N n_i M_i} = \frac{(n_i/n) M_i}{\sum_{i=1}^N (n_i/n) M_i} = \frac{x_i M_i}{\sum_{i=1}^N x_i M_i} \tag{2.11}$$

Example: The combustion of 1 kg of methane requires 17.2 kg of air (4 kg of oxygen and 13.2 kg of nitrogen). As shown in the previous example, the products of combustion are 2.75 kg of carbon dioxide, 2.25 kg of water, and 13.2 kg of nitrogen. Calculate the mass fractions of products. From the mass fractions, calculate the mole fractions. Use the mole fractions to calculate the apparent molecular weight of the product mixture.

Mass of products:

$$m = \sum_{i=1}^N m_i = m_{CO_2} + m_{H_2O} + m_{N_2} = 2.75 \text{ kg} + 2.25 \text{ kg} + 13.2 \text{ kg} = 18.2 \text{ kg}$$

Mass fractions of products:

$$y_{CO_2} = \frac{m_{CO_2}}{m} = \frac{2.75}{18.2} = 0.151; y_{H_2O} = \frac{m_{H_2O}}{m} = \frac{2.25}{18.2} = 0.124;$$

$$y_{N_2} = \frac{m_{N_2}}{m} = \frac{13.2}{18.2} = 0.725$$

Mole fractions of products from the mass fractions calculated above:

$$x_{CO_2} = \frac{\dfrac{y_{CO_2}}{M_{CO_2}}}{\sum_{i=1}^{N} \dfrac{y_i}{M_i}} = \frac{\dfrac{0.151}{44}}{\dfrac{0.151}{44} + \dfrac{0.124}{18} + \dfrac{0.725}{28}} = \frac{0.00343}{0.0362} = 0.0947$$

$$x_{H_2O} = \frac{\dfrac{y_{H_2O}}{M_{H_2O}}}{\sum_{i=1}^{N} \dfrac{y_i}{M_i}} = \frac{\dfrac{0.124}{18}}{0.0362} = 0.190; \; x_{N_2} = \frac{\dfrac{y_{N_2}}{M_{N_2}}}{\sum_{i=1}^{N} \dfrac{y_i}{M_i}} = \frac{\dfrac{0.725}{28}}{0.0362} = 0.715$$

Apparent molecular weight from the mole fractions calculated above:

$$M = \sum_{i=1}^{N} x_i M_i = x_{CO_2} M_{CO_2} + x_{H_2O} M_{H_2O} + x_{N_2} M_{N_2} = 0.0947 \times 44$$
$$+ 0.190 \times 18 + 0.715 \times 28 = 27.6\,\text{kg/kmol}$$

Mass and molar balances are extremely important in evaluating the progress of chemical reactions and in designing chemical reactors. A number of different measures have been devised for evaluating reactant ratios and the extent of chemical reactions.

2.2.1 Mass and Molar Balances Applied to Combustion and Gasification

For combustion and gasification processes, it is useful to compare the actual oxygen provided to the fuel to the amount theoretically required for complete oxidation (the stoichiometric requirement). The fuel–oxygen ratio, *F*/*O*, is defined as the mass of fuel per the mass of oxygen consumed (a molar fuel–oxygen ratio is also sometimes defined). Another frequently used ratio is the equivalence ratio, ϕ:

$$\varphi = \frac{(F/O)_{\text{actual}}}{(F/O)_{\text{stoichiometric}}} \tag{2.12}$$

This ratio is less than unity for fuel-lean conditions and greater than unity for fuel-rich conditions. For combustion reactions, two other relationships are also useful, which can be calculated on either mass or molar bases:

$$\text{Theoretical air (\%)} = \left(\frac{\text{actual air}}{\text{stoichiometric air}}\right) \times 100 \tag{2.13}$$

$$\text{Excess air (\%)} = \frac{(\text{actual air} - \text{stoichiometric air}) \times 100}{\text{stoichiometric air}} \tag{2.14}$$

2.2.2 Mass and Molar Balances Applied to Reaction Conversion, Yield, and Selectivity

In evaluating the changes that actually take place during chemical reaction, three quantities are particularly useful: conversion, yield, and selectivity. Conversion is the amount of reactant that is transformed into products during a reaction. The relative conversion, X (not to be confused with mole fractions x_i), is the ratio of the change in the amount of reactant to the initial amount of reactant. It is readily calculated by comparing the initial mass of reactant ($m_{\text{r initial}}$) to the final mass of reactant ($m_{\text{r final}}$):

$$X = \frac{m_{\text{r initial}} - m_{\text{r final}}}{m_{\text{r initial}}} \tag{2.15}$$

Notice that both the numerator and the denominator of Equation 2.15 are based on amounts of reactant, which means it could also be calculated from the initial moles of reactant ($n_{\text{r initial}}$) and the final moles of reactant ($n_{\text{r final}}$):

$$X = \frac{n_{\text{r initial}} - n_{\text{r final}}}{n_{\text{r initial}}} \tag{2.16}$$

Conversion is often presented on a percentage basis by multiplying by 100. Of course, a reaction may involve more than one reactant, in which case the reactant which limits the extent of reaction is considered in calculating conversion.

Yield is the amount of a particular product formed from a reaction. The relative yield Y (not to be confused with mass fractions y_i) can be calculated on either a mass or molar basis, but different operational definitions are required in these two cases, because they involve both reactants and products in their calculation. Relative *mass* yield is calculated as the ratio of the mass of product, m_p, to the mass of reactant, m_r:

$$Y(\text{mass basis}) = \frac{m_\text{p}}{m_\text{r}} \tag{2.17}$$

This ratio is often presented as a percentage by multiplying by 100 and assigning dimensions of wt% to make clear that it is on a mass basis. Mass yields are straightforward to calculate from gravimetric yield data. They are also frequently preferred when calculating processing costs.

The relative *molar* yield is also written as a ratio of the amount of product to the amount of reactant, but since moles are not conserved in a reaction, the expression must be adjusted to account for the stoichiometric requirement of reactant to produce a mole of product:

$$Y(\text{molar basis}) = \left(\frac{n_\text{p}}{n_\text{r}}\right)\phi \tag{2.18}$$

where ϕ, the stoichiometric factor, is the moles of reactant required stoichiometrically to produce the observed moles of product:

$$\phi = \frac{n_\text{r stoich}}{n_\text{p}} \tag{2.19}$$

Substituting Equation 2.19 into Equation 2.18 reveals that relative molar yield can be equivalently stated as the moles of reactant required stoichiometrically to produce the observed products divided by the actual moles of reactant:

$$Y(\text{molar basis}) = \left(\frac{n_\text{p}}{n_\text{r}}\right)\phi = \left(\frac{n_\text{p}}{n_\text{r}}\right) \times \left(\frac{n_\text{r stoich}}{n_\text{p}}\right) = \frac{n_\text{r stoich}}{n_\text{r}} \tag{2.20}$$

The relative molar yield is also commonly presented as a percentage by multiplying by 100 and assigning a unit of mol% to make clear that it is on a molar basis. Molar yields are frequently preferred to mass yields when evaluating chemical pathways for reactions.

Often the relative molar yield is defined in terms of the actual moles of product formed compared to the theoretically expected moles of product as determined from the stoichiometric formula for the reaction:

$$Y(\text{molar basis}) = \frac{n_\text{p}}{n_\text{p stoic}} \tag{2.21}$$

Equations 2.20 and 2.21 are functionally equivalent.

Example: One kilomole of glucose ($C_6H_{12}O_6$) is fermented to produce 1.75 kmol of ethanol (C_2H_5OH). Calculate both mass and molar relative yields of ethanol. Show that Equations 2.18 and 2.19 give the same relative molar yield.

Relative mass yield:

$$m_{\text{glucose}} = 1 \text{ kmol} \times (180 \text{ kg/kmol}) = 180 \text{ kg};$$

$$m_{\text{ethanol}} = 1.75 \text{ kmol} \times (46 \text{ kg/kmol}) = 80.5 \text{ kg}$$

$$Y_{\text{ethanol}}(\text{mass basis}) = \frac{m_{\text{p}}}{m_{\text{r}}} = \frac{m_{\text{ethanol}}}{m_{\text{glucose}}} = \frac{80.5 \text{ kg}}{180 \text{ kg}} \times 100 = 44.7\text{wt\%}$$

From stoichiometrically balanced reaction for ethanol fermentation, we can see that as much as 2 kmol of ethanol could have been produced:

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$

Complete conversion to ethanol would have given a mass yield of 51.1%, the remaining mass having been converted to CO_2.

Relative molar yield:
One kilomole of glucose is required to produce 2 kmol of ethanol; thus, the stoichiometric factor is:

$$\phi = \frac{\text{stoichiometric requirement for moles of reactant}}{\text{moles of product}} = \frac{1}{2}$$

Substituting into Equation 2.20 yields:

$$Y(\text{molar basis}) = \left(\frac{n_{\text{p}}}{n_{\text{r}}}\right)\phi = \left(\frac{1.75}{1}\right) \times \frac{1}{2} \times 100 = 87.5\%$$

The relative molar yield given by Equation 2.21 gives the same result as above:

$$Y(\text{molar basis}) = \frac{n_{\text{p}}}{n_{\text{p stoic}}} = \left(\frac{1.75}{2}\right) \times 100 = 87.5\%$$

In contrast to mass yield, notice that molar relative yield would have reached 100% if the glucose had been completely converted to ethanol. The fact that this was not achieved indicates that other metabolic reactions produced additional products, such as acetic acid.

Selectivity, S, can be defined two different ways. Sometimes it is useful to define selectivity as the ratio of moles of desired product to moles of undesired products. Alternatively, selectivity can be written as the ratio of moles of desired product to the moles of the reactant converted. For mass selectivities, this is simply the ratio of the mass of specific product to the mass of the reactant converted:

$$S_{\mathrm{p}_i}(\text{mass basis}) = \left(\frac{m_{\mathrm{p}_i}}{m_{\mathrm{r\ converted}}}\right) \tag{2.22}$$

where $m_{\mathrm{p}i}$ is the mass of the ith product and $m_{\mathrm{r\ converted}}$ is the mass of the reactant converted. For molar selectivities, because both reactants and products are involved in the calculation, the definition must be adjusted to account for the stoichiometric amount of the reactant required to produce a mole of product:

$$S_{\mathrm{p}_i}(\text{molar basis}) = \left(\frac{n_{\mathrm{p}_i}}{n_{\mathrm{r\ converted}}}\right)\phi_{\mathrm{p}_i} \tag{2.23}$$

where $n_{\mathrm{p}i}$ is the moles of the ith product and $\phi_{\mathrm{p}i}$ is the stoichiometric amount of the reactant required to produce $n_{\mathrm{p}i}$:

$$\phi_{\mathrm{p}_i} = \frac{n_{\mathrm{r\ stoich}}}{n_{\mathrm{p}i}} \tag{2.24}$$

This ratio is often presented as a percentage by multiplying by 100 and assigning a unit of mol% to make clear that it is on a molar basis. Occasionally, selectivity is defined in terms of a certain class of products, in which case the denominator of Equation 2.23 refers to only that amount of the reactant that is converted to the specified class of products.

Given the conversion of a reactant and the selectivity of the products, the yields of specific products can be calculated by combining Equation 2.16 with Equation 2.23:

$$\begin{aligned} Y_{\mathrm{p}_i}(\text{molar basis}) &= X \cdot S_{\mathrm{p}_i} = \left(\frac{n_{\mathrm{r\ initial}} - n_{\mathrm{r\ final}}}{n_{\mathrm{r\ initial}}}\right)\left(\frac{n_{\mathrm{p}_i}}{n_{\mathrm{r\ initial}} - n_{\mathrm{r\ final}}}\right)\phi_{\mathrm{p}_i} \\ &= \frac{n_{\mathrm{p}_i}}{n_{\mathrm{r\ initial}}}\phi_{\mathrm{p}_i} \end{aligned} \tag{2.25}$$

Example: One hundred kilograms of cellulose are mixed with water and a catalyst and heated to a high temperature and pressure in a closed vessel (a process called hydrothermal processing) and undergoes a combination of hydrolysis (water adding) and dehydrating (water removing) reactions. At the end of the experiment, 10 kg of unreacted cellulose ($C_6H_{10}O_5$) and 8.9 kg of char (solid carbon) are filtered from the aqueous solution, which is found to contain 44.4 kg of glucose ($C_6H_{12}O_6$), 23.3 kg of hydroxymethyl furfural (HMF) ($C_6H_6O_3$), and 13.3 kg of water. Calculate the conversion of cellulose, the selectivity of glucose, HMF, and char products, and the yield of glucose for this process.

Cellulose conversion:

$$X = \frac{m_{\text{r initial}} - m_{\text{r final}}}{m_{\text{r initial}}} = \frac{100\ \text{kg} - 10\ \text{kg}}{100\ \text{kg}} x 100 = 90\%$$

To calculate selectivities on a molar basis, products must first be converted from mass to moles:

Glucose ($C_6H_{12}O_6$): $M_{\text{glucose}} = 6 \times 12 + 12 \times 1 + 6 \times 16 = 180\ \text{kg/kmol}$

$$n_{\text{glucose}} = \frac{44.4\ \text{kg}}{180\,\text{kg/kmol}} = 0.247\ \text{kmol}$$

HMF ($C_6H_6O_3$): $M_{\text{HMF}} = 6 \times 12 + 6 \times 1 + 3 \times 16 = 126\,\text{kg/kmol}$

$$n_{\text{HMF}} = \frac{23.3\ \text{kg}}{126\,\text{kg/kmol}} = 0.185\ \text{kmol}$$

Char (carbon): $M_{\text{char}} = 12\,\text{kg/kmol}$

$$n_{\text{char}} = \frac{8.9\ \text{kg}}{12\,\text{kg/kmol}} = 0.742\ \text{kmol}$$

Also, the initial and final moles of cellulose must be determined:

Initial cellulose ($C_6H_{10}O_5$): $M_{\text{cellulose}} = 6 \times 12 + 10 \times 1 + 5 \times 16 = 162\,\text{kg/kmol}$

$$n_{\text{cellulose initial}} = \frac{100\ \text{kg}}{162\,\text{kg/kmol}} = 0.617\ \text{kmol}$$

Final cellulose ($C_6H_{10}O_5$): $n_{\text{cellulose final}} = \frac{10\ \text{kg}}{162\,\text{kg/kmol}} = 0.0617\ \text{kmol}$

Next, the stoichiometric factors for each of the products must be calculated, which requires identification of the reactions of cellulose that produce each of the products:

Hydrolysis of cellulose to glucose: $C_6H_{10}O_5 + H_2O \rightarrow C_6H_{12}O_6$

Dehydration of cellulose to HMF: $C_6H_{10}O_5 \rightarrow C_6H_6O_3 + 3H_2O$

Dehydration of cellulose to char: $C_6H_{10}O_5 \rightarrow 6C + 5H_2O$

From these, the stoichiometric factors can be calculated:

$$\phi_{\text{glucose}} = \frac{n_{\text{cellulose stoich}}}{n_{\text{glucose}}} = \frac{1}{1} = 1$$

$$\phi_{\text{HMF}} = \frac{n_{\text{cellulose stoich}}}{n_{\text{HMF}}} = \frac{1}{1} = 1$$

$$\phi_{\text{char}} = \frac{n_{\text{cellulose stoich}}}{n_{\text{char}}} = \frac{1}{6} = 0.167$$

Selectivities for products on a molar basis can then be calculated:

$$S_{\text{glucose}} = \left(\frac{n_{\text{glucose}}}{n_{\text{cellulose initial}} - n_{\text{cellulose final}}}\right)\phi_{\text{glucose}} = \frac{0.247\ \text{kmol}}{0.617\ \text{kmol} - 0.0617\ \text{kmol}} \times 1 \times 100 = 44.5\%$$

$$S_{\text{HMF}} = \left(\frac{n_{\text{HMF}}}{n_{\text{cellulose initial}} - n_{\text{cellulose final}}}\right)\phi_{\text{HMF}} = \left(\frac{0.185\ \text{kmol}}{0.617\ \text{kmol} - 0.0617\ \text{kmol}}\right) \times 1 \times 100 = 33.3\%$$

$$S_{\text{char}} = \left(\frac{n_{\text{char}}}{n_{\text{cellulose initial}} - n_{\text{cellulose final}}}\right)\phi_{\text{char}} = \left(\frac{0.742\ \text{kmol}}{0.617\ \text{kmol} - 0.0617\ \text{kmol}}\right) \times 0.167 \times 100 = 22.3\%$$

Notice that the selectivities on a molar basis sum to 100%, which should be the case if all products are accounted for. The yield of glucose is calculated from the relative conversion of cellulose, X, and the selectivity for glucose, S_{glucose}:

$$Y_{\text{glucose}}(\text{molar basis}) = X \cdot S_{\text{glucose}} = 0.90 \times 0.445 \times 100 = 40.05\ \text{mole\%}$$

In reactions of organic compounds, it is often desirable to determine how much carbon in the reactants is converted to particular products. Thus, carbon yield, Y_C, is defined as the amount of carbon in a specific product to the carbon in the reactant. Since moles of elements are conserved during a reaction, this quantity can be calculated using either mass or molar quantities:

$$Y_{C,pi} = \frac{n_{C,p_i}}{n_{C,r}} = \frac{n_{C,p_i} M_C}{n_{C,r} M_C} = \frac{m_{C,p_i}}{m_{C,r}} \tag{2.26}$$

where the subscript C on the molar and mass terms refers to carbon. Furthermore, the carbon yield can be related to the relative mass yield Y_i:

$$Y_{C,p_i} = \frac{m_{C,p_i}}{m_{C,r}} = \left(\frac{m_{C,p_i}/m_{p_i}}{m_{C,r}/m_r}\right)\left(\frac{m_{p_i}}{m_r}\right) = \left(\frac{f_{C,p_i}}{f_{C,r}}\right) Y_i(\text{mass basis}) \tag{2.27}$$

where $f_{C,pi}$ is the mass fraction of the carbon in the ith product and $f_{C,r}$ is the mass fraction of the carbon in the reactant.

A similar relationship exists between the carbon selectivity and the mass selectivity:

$$\begin{aligned} S_{C,p_i} &= \frac{n_{C,p_i}}{n_{C,\text{r converted}}} = \frac{m_{C,p_i}/M_C}{m_{C,\text{r converted}}/M_C} = \frac{m_{C,p_i}}{m_{C,\text{r converted}}} \\ &= \left(\frac{m_{C,p_i}/m_{p_i}}{m_{C,\text{r converted}}/m_{\text{r converted}}}\right)\left(\frac{m_{p_i}}{m_{\text{r converted}}}\right) \\ &= \left(\frac{f_{C,\,p_i}}{f_{C,\,r}}\right) S_{p_i}(\text{mass basis}) \end{aligned} \tag{2.28}$$

where $m_{C,\text{r converted}}$ is the mass of the carbon converted in the reactant.

Carbon yield can be calculated from the reactant conversion and the carbon selectivity:

$$Y_{C,p_i} = X \cdot S_{C,p_i} = \left(\frac{n_{C,\text{r converted}}}{n_{C,r}}\right)\left(\frac{n_{C,p_i}}{n_{C,\text{r converted}}}\right) = \frac{n_{C,p_i}}{n_{C,r}} \tag{2.29}$$

Example: Calculate the carbon selectivity and the carbon yield for each of the products (glucose, HMF, and char) for the previous example of hydrothermally processing of cellulose.

The relative conversion of cellulose was stated in the previous problem to be 90%. Mass selectivities are first calculated using Equation 2.22, which recognizes that only 90% of the 100 kg of cellulose is converted to products:

$$S_{\text{glucose}}(\text{mass basis}) = \left(\frac{m_{\text{glucose}}}{m_{\text{cellulose converted}}}\right) = \left(\frac{44.4\ \text{kg}}{90\ \text{kg}}\right) \times 100 = 49.3\%$$

$$S_{\text{HMF}}(\text{mass basis}) = \left(\frac{m_{\text{HMF}}}{m_{\text{cellulose converted}}}\right) = \left(\frac{23.3\ \text{kg}}{90\ \text{kg}}\right) \times 100 = 25.9\%$$

$$S_{\text{carbon}}(\text{mass basis}) = \left(\frac{m_{\text{carbon}}}{m_{\text{cellulose converted}}}\right) = \left(\frac{8.9\ \text{kg}}{90\ \text{kg}}\right) \times 100 = 9.9\%$$

Notice that selectivities based on mass do not sum to 100%, because product water is not included in the calculation.

To calculate selectivities on a molar basis, the mass fractions of the carbon in the reactant and the products must first be determined:

$$\text{Cellulose } (C_6H_{10}O_5){:}\quad f_{\text{C,cellulose}} = \frac{6 \times 12}{(6 \times 12 + 10 \times 1 + 5 \times 16)} = 0.44$$

$$\text{Glucose } (C_6H_{12}O_6){:}\quad f_{\text{C,glucose}} = \frac{6 \times 12}{(6 \times 12 + 12 \times 1 + 6 \times 16)} = 0.40$$

$$\text{HMF } (C_6H_6O_3){:}\quad f_{\text{C,HMF}} = \frac{6 \times 12}{(6 \times 12 + 6 \times 1 + 3 \times 16)} = 0.57$$

$$\text{Char (C)}{:}\quad f_{\text{C,Char}} = \frac{1 \times 12}{1 \times 12} = 1.00$$

These carbon mass fractions can be combined with the previously determined mass selectivities of the products using Equation 2.28:

$$S_{\text{C,glucose}} = \left(\frac{f_{\text{C, glucose}}}{f_{\text{C, cellulose}}}\right) S_{\text{glucose}}(\text{mass basis}) = \left(\frac{0.40}{0.44}\right) \times 49.3 \times 100 = 44.8\%$$

$$S_{\text{C,HMF}} = \left(\frac{f_{\text{C, HMF}}}{f_{\text{C, cellulose}}}\right) S_{\text{HMF}}(\text{mass basis}) = \left(\frac{0.57}{0.44}\right) \times 25.9\% = 33.5\%$$

$$S_{\text{C,Char}} = \left(\frac{f_{\text{C, Char}}}{f_{\text{C, cellulose}}}\right) S_{\text{Char}}(\text{mass basis}) = \left(\frac{1.00}{0.44}\right) \times 9.9\% = 22.5\%$$

Molar carbon yields are then calculated from Equation 2.29:

$$Y_{\mathrm{C,glucose}} = X \cdot S_{\mathrm{C,glucose}} = 0.9 \times 44.8 = 40.3\%$$

$$Y_{\mathrm{C,HMF}} = X \cdot S_{\mathrm{C,HMF}} = 0.9 \times 33.5 = 30.2\%$$

$$Y_{\mathrm{C,Char}} = X \cdot S_{\mathrm{C,Char}} = 0.9 \times 22.5 = 20.3\%$$

These do not sum to 100% because only 90% of the cellulose is converted into products.

2.3 General Concepts in Energy Balances

In the absence of chemical reaction, the net change in the stored energy within a control volume is given by the net flow of the energy into the control volume in the form of heat and work as well as kinetic energy, potential energy, and enthalpy associated with mass flowing into and out of the control volume. Figure 2.2 illustrates the energy balance for a control volume with two inlets and one outlet and with work transferred in and heat transferred out. More generally, a system undergoing steady flow processes can be described by an energy balance of the form:

$$\frac{\mathrm{d}E_{\mathrm{CV}}}{\mathrm{d}t} = \dot{Q}_{\mathrm{CV}} - \dot{W}_{\mathrm{CV}} + \sum_{i} \dot{m}_{\mathrm{i}} \left(h_{\mathrm{i}} + \tfrac{1}{2}V_{\mathrm{i}}^2 + gz_{\mathrm{i}}\right) - \sum_{e} \dot{m}_{\mathrm{e}} \left(h_{\mathrm{e}} + \tfrac{1}{2}V_{\mathrm{e}}^2 + gz_{\mathrm{e}}\right) \tag{2.30}$$

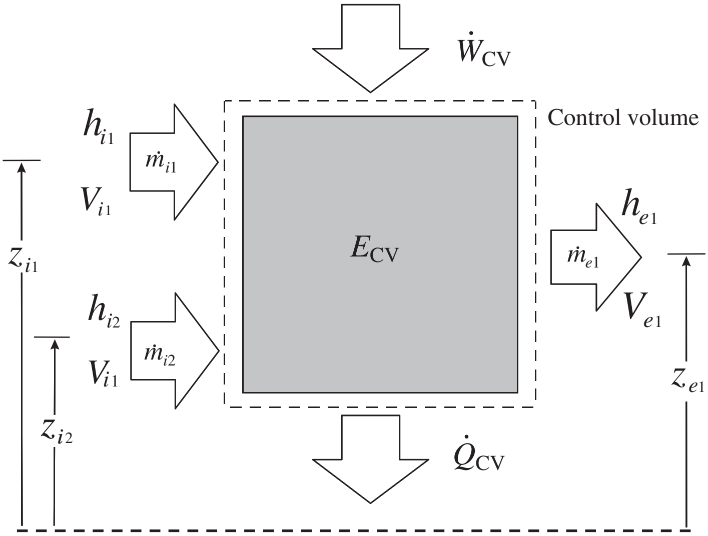

FIG. 2.2 Energy balance on steady-flow control volume with two inlets and one exit.

where E_{CV} is the stored energy in the control volume, $\dot{Q}_{\mathrm{CV}}$ and $\dot{W}_{\mathrm{CV}}$ are the rates at which heat and work cross the control volume boundary, h is enthalpy, V is velocity, and z is elevation with respect to an arbitrary datum for the mass flows at the inlet, i, and outlet, e. In steady flow, with a single inlet and single outlet and no velocity or elevation changes in the system, Equation 2.30 simplifies to:

$$\dot{Q}_{\mathrm{CV}} - \dot{W}_{\mathrm{CV}} = \dot{m}\,(h_{\mathrm{e}} - h_{\mathrm{i}}) \tag{2.31}$$

However, for a chemically reacting system, this formulation of an energy balance does not take into account changes in the chemical composition of the system nor the chemical energy absorbed or released during these reactions. Like mass conservation, it is more convenient to present energy conservation in a molar formulation rather than a mass formulation when chemical reaction occurs. The intensive property enthalpy, h, with units of kJ/kg, is replaced by the intensive property molar enthalpy, $\bar{h}$, with units of kJ/kmol. Enthalpy, like other properties, can be evaluated as a function of two other independent properties, usually taken to be temperature and pressure. In the case of ideal gases, enthalpy is independent of pressure and can be expressed solely as a function of temperature. Table 2.1 includes an abbreviated collection of molar enthalpies of selected ideal gases as a function of temperature. More extensive collections are available in thermodynamics textbooks.

Energy conservation on a molar basis for a steady flow system consisting of one inlet for reactants r and one outlet for products p (and neglecting velocity or elevation changes) is of the form:

$$\dot{Q}_{\mathrm{CV}} - \dot{W}_{\mathrm{CV}} = \sum_{\mathrm{p}} \dot{n}_{\mathrm{p}}\bar{h}_{\mathrm{p}} - \sum_{\mathrm{r}} \dot{n}_{\mathrm{r}}\bar{h}_{\mathrm{r}} \tag{2.32}$$

where $\dot{n}$ specifies the molar flow rate of a chemical constituent and the summation is over all the products p at the exit or all the reactants r at the inlet. Integrated over a finite time interval, this equation takes the form:

$$Q_{\mathrm{CV}} - W_{\mathrm{CV}} = \sum_{\mathrm{p}} n_{\mathrm{p}}\bar{h}_{\mathrm{p}} - \sum_{\mathrm{r}} n_{\mathrm{r}}\bar{h}_{\mathrm{r}} \tag{2.33}$$

where Q_{CV} and W_{CV} are the amounts of heat and work done over a designated time interval and n_{r} and n_{p} are the moles of the reactants and the products, respectively, crossing the control surface in the time interval. A convenient shorthand is to designate H_{p} and H_{r} as the mixture enthalpies (kJ) of the products and the reactants, respectively, and ΔH as the change in enthalpy between the products and the reactants:

$$\Delta H = H_{\mathrm{p}} - H_{\mathrm{r}} = \sum_{\mathrm{p}} n_{\mathrm{p}}\bar{h}_{\mathrm{p}} - \sum_{\mathrm{r}} n_{\mathrm{r}}\bar{h}_{\mathrm{r}} \tag{2.34}$$

Table 2.1 Thermodynamic properties for selected gases

T (K), $\bar{h}$ (kJ/kmol), $\bar{S}_0$ (kJ/kmol-K)

	N_2		O_2		H_2O (g)		CO		CO_2		H_2	
T	$\bar{h}$	$\bar{S}_0$	$\bar{h}$	$\bar{S}_0$	$\bar{h}$	$\bar{S}_0$	$\bar{h}$	$\bar{S}_0$	$\bar{h}$	$\bar{S}_0$	$\bar{h}$	$\bar{S}_0$
0	0	0	0	0	0	0	0	0	0	0	0	0
298	8 669	191.50	8 682	205.03	9 904	188.72	8 669	197.54	9 364	213.69	8 468	130.57
500	14 581	206.63	14 770	220.59	16 828	206.41	14 600	212.72	17 678	234.81	14 350	145.63
1000	30 129	228.06	31 389	243.47	35 882	232.60	30 355	234.42	42 769	269.22	29 154	166.11
1500	47 073	241.77	49 292	257.97	57 999	250.45	47 517	248.31	71 078	292.11	44 738	178.72
2000	64 810	251.97	67 881	268.66	82 593	264.57	65 408	258.60	100 804	309.21	61 400	188.30
2500	82 981	260.07	87 057	277.21	108 868	276.29	83 692	266.76	131 290	322.81	78 960	196.13
3000	101 407	266.79	106 780	284.40	136 264	286.27	102 210	273.51	162 226	334.08	97 211	202.78
3250	110 690	269.76	116 827	287.61	150 272	290.76	111 534	276.49	177 822	339.07	106 545	205.77

Substance	Formula	h_f^0 (kJ/kmol)
Carbon	C(s)	0
Hydrogen	H_2	0
Nitrogen	N_2	0
Oxygen	O_2	0
Carbon monoxide	CO	–110 530
Carbon dioxide	CO_2	−393 520
Water (liquid)	H_2O (l)	−285 830
Water (vapor)	H_2O (g)	−241 820
Methane	CH_4	−74 850
Methanol (liquid)	CH_3OH (l)	−238,810
Methanol (vapor)	CH_3OH (g)	−200 890
Ethanol (liquid)	C_2H_5OH (l)	−277 690
Ethanol (vapor)	C_2H_5OH (g)	−235 310

Source: Excerpted from Cengel, Y. and Boles, M. (2010) *Thermodynamics: An Engineering Approach*, 7th edn. McGraw-Hill.

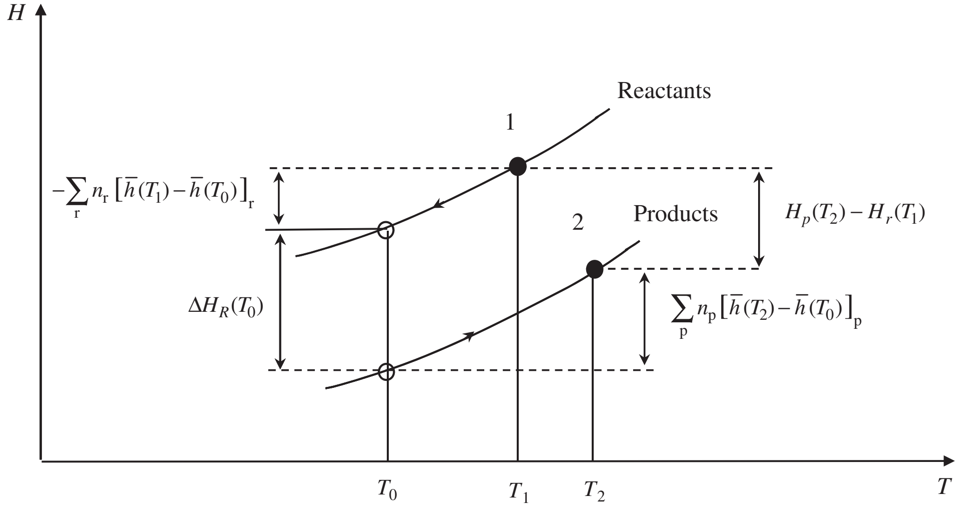

FIG. 2.3 Relationship between mixture enthalpy and temperature for a chemically reacting system.

An enthalpy–temperature diagram, shown in Figure 2.3, is useful in understanding the change in enthalpy that occurs in the presence of a chemical reaction. For a given mixture of reactants, say methane and oxygen, there is a unique enthalpy–temperature relationship. Similarly, a unique enthalpy relationship exists for the products of methane oxidation (carbon dioxide and water). It is also easy to understand the enthalpy change that occurs for a constant temperature chemical reaction: reactants at T_o are converted to products at T_o with a release or absorption of energy known as the enthalpy of reaction $\Delta H_R(T_o)$ at temperature T_o. Reactions that release energy (exothermic reactions) have negative enthalpies of reaction, whereas reactions that absorb energy (endothermic reactions) have positive enthalpies of reaction. This situation becomes obvious by inspecting Equation 2.33 and recalling the convention that Q_{cv} is negative for heat flow out of a system.

However, the typical chemical reaction is not isothermal; indeed, many combustion reactions are accompanied by temperature increases of over 1000 K. Thus, enthalpy changes must account for sensible enthalpy changes of the reactants, sensible enthalpy changes for the products, and the release or absorption of heat as a result of the chemical reaction. One way to handle this potentially complicated situation is to visualize the reaction as following the reaction pathway illustrated in Figure 2.3: reactants initially at temperature T_1 are cooled to temperature T_o at which point the reactants undergo isothermal chemical reaction to form the products that are then heated to the final temperature T_2. Thus, the enthalpy change for non-isothermal chemical reactions can be calculated from the relationship:

$$H_p(T_2) - H_r(T_1) = \sum_p n_p \left[\bar{h}(T_2) - \bar{h}(T_o)\right]_p + \Delta H_R(T_o) - \sum_r n_r \left[\bar{h}(T_1) - \bar{h}(T_o)\right]_r \tag{2.35}$$

where sensible enthalpies, $\bar{h}(T)$, for a variety of chemical substances are available as tabulations of thermodynamic properties of substances. Likewise, enthalpies of reaction at a specified reference temperature, T_o, have been compiled for a number of chemical reactions. In the SI system, T_o is chosen as 298 K for the purpose of tabulating data. Using Equation 2.35, tabulations of sensible enthalpies and enthalpies of reaction can be used to calculate enthalpy changes for reactions under a wide variety of conditions.

Example: One kilomole of biogas produced by anaerobic digestion of animal waste consists of 60% methane and 40% carbon dioxide by volume (i.e., molar basis). The biogas reacts with 1.2 kilomoles of oxygen to form carbon dioxide and water. The enthalpy of reaction for methane is –890 330 kJ/kmol at 298 K. Calculate the enthalpy change if the reactants are at 298 K and the products are at 1500 K.

The complete reaction is:

$$(0.6CH_4 + 0.4CO_2) + 1.2O_2 \rightarrow CO_2 + 1.2H_2O$$

From Table 2.1 the following sensible enthalpies are found:

Temperature (K)	$h_{CH4}(T)$ (kJ/kmol)	$h_{O2}(T)$ (kJ/kmol)	$h_{CO2}(T)$ (kJ/kmol)	$h_{H2O}(T)$ (kJ/kmol)
298	–	8 682	9 364	9 904
1500	–	–	71 078	57 999

Substituting values into Equation 2.35:

$$[1(71\,078 - 9364) + 1.2(57\,999 - 9904)] + 0.6(-890\,330) - [0.6(0) + 0.4(0) + 1.2(0)]$$
$$= -414\,770$$

Thus, 414 770 kJ is released by the combustion of 1 kilomole of biogas under these conditions.

For some well-characterized fuels, such as hydrogen, methane, and ethanol, enthalpies of reaction can be calculated from tabulations of specific enthalpies of formation, $\bar{h}_f^o$, of chemical compounds from their elements at a standard state:

$$\Delta H_R^o = \sum_p n_p \bar{h}_f^o)_p - \sum_r n_r \bar{h}_f^o)_r \tag{2.36}$$

where n_r and n_p are the number of moles of reactants and products for the chemical reaction. Selected values of enthalpies of formation are found in Table 2.1.

Example: Use standard enthalpies of formation to calculate the enthalpy of reaction of liquid ethanol (C_2H_5OH) with oxygen to form carbon dioxide and water vapor.

The stoichiometric reaction is expressed by:

$$C_2H_5OH\,(l) + 3O_2 \rightarrow 2CO_2 + 3H_2O\,(g)$$

From Table 2.1:

Compound	C_2H_5OH (l)	O_2	CO_2	H_2O (g)
$\bar{h}_f^o$ (kJ/kmol)	–277 690	0	–393 520	–241 820
Kilomoles	1	3	2	3

Substituting into Equation 2.36 yields:

$$\Delta H_R^o = 2(-393\,520) + 3(-241\,820) - (-277\,690) - 3(0) = -1\,234\,800\,\text{kJ}$$

Enthalpies of formation are very useful in thermodynamic calculations, but this data is rarely tabulated for biomass because of the wide variability in its composition. However, if higher heating value for a biomass fuel has been determined in a bomb calorimeter, its enthalpy of formation can be determined by summing the enthalpies of formation for the products of combustion and subtracting from this sum the higher heating value.

Example: A sample of switchgrass has an elemental analysis that gives a generic molecular formula of $CH_{1.4}O_{0.8}$ (apparent molecular weight of 26.2 kg/kmol) and its higher heating value is measured to be 18.1 MJ/kg. The combustion of 1 kmol of switchgrass can be represented by:

$$CH_{1.4}O_{0.8} + 0.95O_2 \rightarrow CO_2 + 0.7H_2O\ (\text{liq})$$

The enthalpy of reaction is calculated from the various enthalpies of formation using Equation 2.36:

$$\Delta H_R = h^o_{f\ CO_2} + 0.7h^o_{f\ H_2O(\text{liq})} - \left(h^o_{f\ CH_{1.4}O_{0.8}} + 0.95h^o_{fO_2}\right)$$

$$-18.1\frac{\text{MJ}}{\text{kg}}\left(26.2\ \frac{\text{kg}}{\text{kmol}}\right) = -393.5\frac{\text{MJ}}{\text{kmol}} + 0.7\left(-285.8\frac{\text{MJ}}{\text{kmol}}\right)$$

$$-\left(\Delta h^o_{fCH_{1.4}O_{0.8}} + 0\right)$$

Solving for the enthalpy of formation for $CH_{1.4}O_{0.8}$ yields:

$$h^{o}_{fCH_{1.4}O_{0.8}} = -119.3\frac{MJ}{kmol}$$

This value can be used in various thermodynamic calculations for this switchgrass sample, whether gasification to hydrogen or combustion to flue gas.

Commonly Equations 2.35 and 2.36 are combined to allow calculation of enthalpy changes purely in terms of tabulated sensible enthalpies and enthalpies of formation:

$$\begin{aligned} H_p(T_2) - H_r(T_1) &= \sum_p n_p\left[\bar{h}(T_2) - \bar{h}(T_o)\right]_p + \sum_p n_p \bar{h}^{o}_{f})_p - \sum_r n_r \bar{h}^{o}_{f})_r \\ &- \sum_r n_r\left[\bar{h}(T_1) - \bar{h}(T_o)\right]_r = \sum_p n_p\left\{\bar{h}^{o}_{f} + \left[\bar{h}(T_2) - \bar{h}(T_o)\right]\right\}_p \qquad (2.37) \\ &- \sum_r n_r\left\{\bar{h}^{o}_{f} + \left[\bar{h}(T_1) - \bar{h}(T_o)\right]\right\}_r \end{aligned}$$

Thus, the molar enthalpy for a chemical compound participating in a chemical reaction must include both the enthalpy of formation and the sensible enthalpy change with respect to the reference temperature T_o. Sometimes it is convenient to express changes in enthalpy with Equation 2.34 as long as it is recognized that the molar enthalpies $\bar{h}_p$ and $\bar{h}_r$ in this expression include both the enthalpy of formation and the sensible enthalpy change:

$$\bar{h}_i = \left\{\bar{h}^{o}_{f} + \left[\bar{h}(T) - \bar{h}(T_o)\right]\right\}_i \qquad (2.38)$$

Example: One kilomole of hydrogen reacts with one-half kilomole of oxygen at 298 K to form 1 kilomole of water vapor at 1500 K. What is the change in enthalpy for the reaction?

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

Compound	H_2	O_2	H_2O (g)
$\bar{h}^{o}_{f}$ (kJ/kmol)	0	0	–241 820
$\bar{h}$(298 K)	8468	8682	9904
$\bar{h}$(1500 K)	–	–	57 999
Kilomoles	1	1/2	1

$$
\begin{aligned}
H_\mathrm{p}(T_2) - H_\mathrm{r}(T_1) &= \sum_\mathrm{p} n_\mathrm{p}\bar{h}_\mathrm{p} - \sum_\mathrm{r} n_\mathrm{r}\bar{h}_\mathrm{r} = \sum_\mathrm{p} n_\mathrm{p}\left\{\bar{h}_\mathrm{f}^\mathrm{o} + \left[\bar{h}(T_2) - \bar{h}(T_\mathrm{o})\right]\right\}_\mathrm{p} \\
&\quad - \sum_\mathrm{r} n_\mathrm{r}\left\{\bar{h}_\mathrm{f}^\mathrm{o} + \left[\bar{h}(T_1) - \bar{h}(T_\mathrm{o})\right]\right\}_\mathrm{r} \\
&= 1 \times \{-241\,820 + [57\,999 - 9904]\} - 1 \\
&\quad \times \{0 + [8468 - 8468]\} - \tfrac{1}{2}\{0 + [8682 - 8682]\} \\
&= -193\,730\,\mathrm{kJ}
\end{aligned}
$$

2.3.1 Thermodynamic Efficiency

The conversion of the chemical energy stored in biomass into more useful forms, such as gaseous and liquid fuels or electrical power, is accompanied by loss of energy to forms that are not easily recovered or utilized. There are many reasons for such losses. Separation processes can inadvertently reject valuable fractions of a feedstock to waste streams. Heat losses can reduce the amount of energy available to energy conversion processes. Entropy production inherent in even ideal processes limits the amount of energy that can be converted into useful forms. Every energy conversion process can be characterized by thermodynamic (or energy) efficiency defined as:

$$\eta = \frac{E_\mathrm{useful}}{E_\mathrm{in}} \tag{2.39}$$

where E_in = all forms of energy entering the conversion process; E_useful = useful energy leaving the conversion process.

Energy entering the process includes the chemical enthalpy of the feedstock (E_feed) and the heat and power required to process the feedstock (E_process). The useful energy leaving the process includes chemical energy of gaseous and liquid fuels, electric power, and heat that can be used external to the process, such as district heating of buildings. If all the input energy was converted into useful energy, energy efficiency would be 1. However, most energy conversion processes have efficiencies substantially less than unity indicating that some energy leaves the process as waste energy (i.e., incompletely converted feedstock or waste heat).

When applied to the thermodynamic performance of heat engines, E_in is the heat energy entering the engine, Q_in, and E_useful is the net mechanical work generated by the engine, W_net:

$$\eta = \frac{W_\mathrm{net}}{Q_\mathrm{in}} \tag{2.40}$$

In the case of electrical power plants, Q_{in} is calculated as the enthalpy of reaction (MJ/kg) multiplied by the mass flow rate of fuel (kg/s), while W_{net} is the net electric power generated measured in megawatts (MJ/s).

In the electric power industry, energy efficiency is frequently expressed as heat rate, HR, defined as:

$$\text{HR} = \frac{\dot{Q}}{P} \quad \text{(Btu/kW-h)} \tag{2.41}$$

where $\dot{Q}$ is the thermal energy input measured in English units (Btu/h) and P is the net electrical power output measured in SI units (kW). Heat rate is the reciprocal of thermodynamic efficiency except that it is expressed in mixed systems of units. Notice that low heat rates correspond to high thermodynamic efficiencies.

2.3.2 Energy Return on Energy Invested

Another way of tracking energy borrows from the economic concept of return on investment (ROI), which considers the amount of money invested in a project to the net amount of money returned over the course of the project (see Chapter 12). Applied to extractive energy resources, such as petroleum, natural gas, or coal, the so-called energy return on energy invested (EROEI) is the ratio of useful energy, E_{useful}, to the process energy expended in extracting the resource, E_{process}:

$$\text{EROEI} = \frac{E_{\text{useful}}}{E_{\text{process}}} \tag{2.42}$$

Of course, the amount of energy contained in fossil resources is much greater than the amount of energy required to pump it or dig it out of the ground and EROEI in this case is much greater than unity, ranging as high as 50 but more typically on the order of 5–20. Much the same can be said of harvesting biomass resources.

EROEI is less useful when considering the conversion of fossil or renewable resources into finished energy products. This is particularly true in comparing transportation fuels derived from petroleum and biomass, where EROEI may be greater than 10 for petroleum-derived gasoline and less than 2 for biofuels. Sometimes it is argued that this large disparity is a barrier to the use of biomass in the production of fuels. Certainly, it is true that biomass requires more extensive processing than petroleum to produce fuels, as described in subsequent chapters. Petroleum is the product of natural "geothermal processing" of biomass deposited into geological deposits many millions of years ago to produce hydrocarbons, much of which requires relatively little additional processing to yield transportation fuels.

However, the main reason for the large difference in EROEI is that the operational definition of EROEI is mathematically unbounded. Since the denominator of Equation 2.42 (E_{process}) excludes the chemical enthalpy of the feedstock, it can become very small compared to the numerator (E_{useful}). Since dividing a very large number by a very small number can exaggerate comparisons, EROEI can give an exaggerated impression of the relative amounts of energy that can be extracted from different resources. Although EROEI can be useful for comparing energy costs for extracting different kinds of energy resources, energy efficiency should be employed when comparing the fraction of an energy resource that can be converted to finished energy products.

This becomes clear upon inspecting the simplified energy balance on the fuel production facility illustrated in Figure 2.4. Energy entering the facility is of two kinds: $E_{\text{feedstock}}$ is the chemical enthalpy of the feedstock, while E_{process} is the heat and power used to process the feedstock. Energy exiting the plant is of two kinds as well: E_{useful} is the useful energy produced, while E_{waste} is the incompletely converted feedstock and waste heat. As indicated in Table 2.2, the conversion of petroleum to gasoline has an EROEI of 10–20, while energy efficiency is 0.69–0.72. The conversion of corn grain to ethanol has an EROEI of 1.3, while energy efficiency is 0.35. Petroleum to gasoline is more favorable by both energy metrics, but EROEI greatly exaggerates this advantage. The EROEI simply indicates that eight times more energy must be expended to produce ethanol than gasoline, but the amount of energy recovered from petroleum compared to corn grain by these two processes differs by a more modest factor of 2.

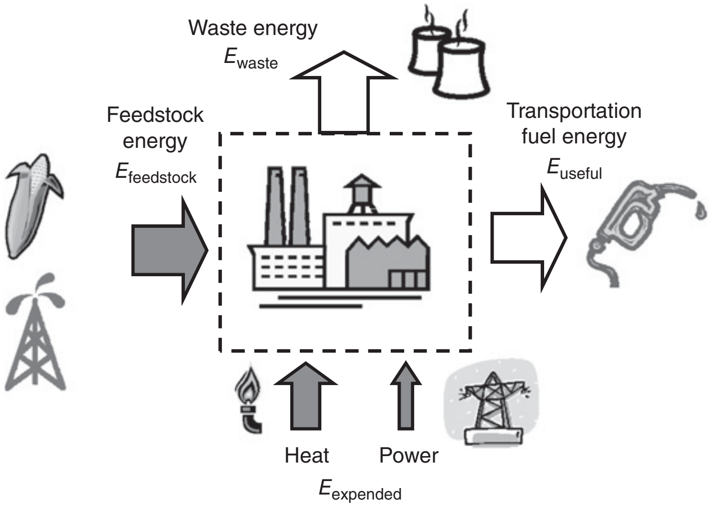

FIG. 2.4 Energy balance comparing conversion of petroleum to gasoline and corn grain to ethanol.

Table 2.2 Comparison of EROEI and energy efficiency for conversion of petroleum into gasoline and corn grain into ethanol

	Formula	Petroleum to Gasoline	Corn Grain to Ethanol
EROEI	$\text{EROEI} = \dfrac{E_{\text{useful}}}{E_{\text{expended}}}$	10–20	1.3
Energy efficiency	$\eta = \dfrac{E_{\text{useful}}}{E_{\text{expended}} + E_{\text{feedstock}}}$	0.69–0.72	0.35

The frequent misuse of EROEI may be responsible for the common misperception among many people that "you should get more energy out than you put in to fuels production." Certainly, we should expect the useful energy produced to be greater than the process energy input (EROEI $>$ 1). However, when considering the total energy into a process ($E_{\text{feedstock}}+E_{\text{process}}$), one should expect to get less energy out in the form of fuels than one puts in. This is because for all real energy conversion processes, some energy is dissipated as heat or diverted to co-products other than the desired energy products with the result that the useful energy out is less than the total energy into the process.

2.3.3 Exothermic vs Endothermic Reactions in the Manufacture of Energy Products

The useful energy obtained from a process is always smaller than the energy expended, which is a consequence of the First and Second Laws of Thermodynamics. By way of analogy, a dropped rubber ball may be expected to recover some of its original elevation (gravitational potential energy) on the rebound, but no one seriously expects it to bounce higher than the height from which it was dropped. Similarly, the energy in fuel products will always be less than the energy inputs to the process.

What matters is preserving within the energy products as much as possible of the feedstock and processing energy used to manufacture the energy products, subject to the constraints of the laws of thermodynamics and the cost of accomplishing this purpose. Success in this endeavor is strongly dependent upon the nature of the energy source, the quality of the energy products, and the capital investment that can be economically justified. Figure 2.5 illustrates the efficiency of various energy conversion processes as the rebound of a dropped ball.

If a molecule is to serve as an energy product, clearly it must be able to undergo an energy releasing (exothermic) reaction within an engine or fuel cell. Conversely, we might expect that an energy absorbing (endothermic) reaction is required to manufacture an energy product. For example, the decomposition of water to produce hydrogen (along with oxygen) is an endothermic reaction. The energy to produce this energy product comes from an energy resource; for example, solar

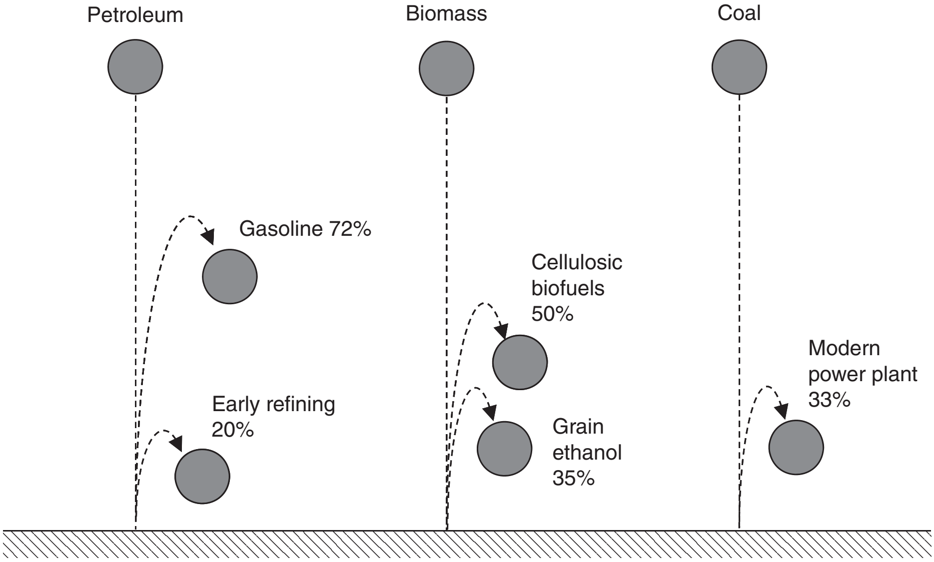

FIG. 2.5 Rebound of a dropped ball as an analogy for energy efficiency.

energy converted to electricity can then power an electrolysis unit to decompose water into hydrogen and oxygen.

In fact, both endothermic and exothermic reactions can be used to generate energy products. Consider an energy source that stores a large amount of chemical energy but in a form not convenient as transportation fuel. An exothermic reaction that rearranges chemical bonds to yield molecules more useful as transportation fuel might be employed despite the loss of part of the original energy. An example is fermentation of glucose to ethanol by yeast, an exothermic process that consumes about 3% of the chemical energy of the sugar to support the metabolism of the microorganism. From the standpoint of meeting the energy needs of the microorganism, fermentation is an appallingly inefficient process. However, the rejected energy is in the form of ethanol, an energy-dense liquid that is more convenient as transportation fuel than the sugar or starch granules from which it was produced.

Although exothermic reactions are commonly employed to convert energy resources into energy products, they are inherently less efficient than endothermic reactions for the production of energy products. This is because the energy released during the manufacture of energy products is frequently dissipated as waste heat. Nevertheless, many people have the misconception that the addition of energy to manufacture an energy product inevitably translates into low energy efficiency, which overlooks the fact that often this added energy is incorporated into the energy product. Fuel manufacture is usually a combination of exothermic and endothermic processes, which are ideally balanced to achieve the highest energy efficiency (i.e., very little waste energy is rejected from the process).

2.4 Chemical Equilibrium

A reaction is in chemical equilibrium when the reverse reaction rate balances the forward reaction rate. The two thermodynamic properties important in understanding chemical equilibrium are entropy $\bar{s}(T, p)$ and the Gibbs function $\bar{g}(T, p)$, also known as the Gibbs free energy. These properties are functions of both temperature and pressure. For an ideal gas, entropy is calculated by the expression:

$$\bar{s}_i(T, p) = \bar{s}_i^o(T) - \bar{R}\ln\frac{p_i}{p_{\mathrm{REF}}} \tag{2.43}$$

where $\bar{s}_i^o(T)$ is the entropy of chemical species i at temperature T and reference pressure p_{REF} and $\bar{R}$ is the ideal gas constant. The Gibbs function can be calculated from its enthalpy and entropy:

$$\begin{aligned}\bar{g}_i(T, p) &= \bar{h}_i(T) - T\bar{s}_i(T, p) = \bar{h}_i(T) - T\left[\bar{s}_i^o(T) - \bar{R}\ln\left(\frac{p_i}{p_{\mathrm{REF}}}\right)\right] \\ &= \left[\bar{h}_i(T) - T\bar{s}_i^o(T)\right] - \bar{R}\ln\left(\frac{p_i}{p_{\mathrm{REF}}}\right) = \bar{g}_i^o - \bar{R}\ln\left(\frac{p_i}{p_{\mathrm{REF}}}\right)\end{aligned} \tag{2.44}$$

When calculating the Gibb's function of chemically reacting systems, recall that the molar enthalpy $\bar{h}_i(T)$ includes both enthalpy of formation and sensible enthalpy change with respect to temperature (see Equation 2.38). Values of $\bar{s}_i^o(T)$ are tabulated in Table 2.1 for various gases with the reference pressure taken to be 1 atm. Notice that $\bar{g}_i^o(T)$ is the Gibb's function at temperature T and the reference pressure p_{REF}. It also sometimes tabulated but has not been included in Table 2.1, because it can be calculated from tabulations of $\bar{h}_i(T)$ and $\bar{s}_i^o(T)$.

Changes in these properties for a chemical reaction can be calculated in a manner similar to calculating changes in enthalpy:

$$\Delta S = \sum_{\mathrm{p}} n_{\mathrm{p}}\bar{s}_{\mathrm{p}} - \sum_{\mathrm{r}} n_{\mathrm{r}}\bar{s}_{\mathrm{r}} \tag{2.45}$$

$$\Delta G = \sum_{\mathrm{p}} n_{\mathrm{p}}\bar{g}_{\mathrm{p}} - \sum_{\mathrm{r}} n_{\mathrm{r}}\bar{g}_{\mathrm{r}} \tag{2.46}$$

These two properties are related by the following equation:

$$\Delta G = \Delta H - T\Delta S \tag{2.47}$$

where the temperature T is evaluated in Kelvin.

The Gibbs function is particularly useful in chemical thermodynamics. For example, the change in Gibbs function represents the maximum work that could be produced from a chemically reacting system. As evident from Equation 2.47, the Gibbs function represents some fraction of the chemical enthalpy associated with a chemical reaction, dependent on the entropy and the temperature of the reaction, an important consideration in the discussion of fuel cells in Chapter 6.

The Gibbs function is also useful in calculating the equilibrium composition of a chemically reacting system. From the Second Law of Thermodynamics, it can be shown that chemical equilibrium for a constant pressure, constant temperature process corresponds to a minimum in the Gibbs function for the reaction. Although numerical methods are often employed to find this minimum for complex chemical reaction systems, the concept of equilibrium constant was developed for simpler reaction systems.

We consider the calculation of chemical equilibrium from equilibrium coefficients for a single reaction described by the stoichiometrically balanced equation:

$$\sum_{\mathrm{r}} \nu_{\mathrm{r}} A_{\mathrm{r}} = \sum_{\mathrm{p}} \nu_{\mathrm{p}} A_{\mathrm{p}} \tag{2.48}$$

where A_r and A_p are the symbols for the p-th chemical product and r-th chemical reactant, respectively, and ν_r and ν_p are their corresponding stoichiometric coefficients. For example, the stoichiometrically balanced reaction of hydrogen and oxygen to produce water is:

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O$$

The stoichiometric coefficients for the reactants hydrogen and oxygen are 1 and $\frac{1}{2}$, respectively, and the stoichiometric coefficient for the product water is 1.

It can be shown that for ideal gas mixtures, products and reactants at chemical equilibrium conform to the relationship:

$$K_p(T) = \frac{\prod_{\mathrm{p}} \left(\frac{p_\mathrm{p}}{p_\mathrm{ref}}\right)^{\nu_\mathrm{p}}}{\prod_{\mathrm{r}} \left(\frac{p_\mathrm{r}}{p_\mathrm{ref}}\right)^{\nu_\mathrm{r}}} \tag{2.49}$$

where p_p and p_r are the partial pressure and stoichiometric coefficient of the p-th chemical product and r-th chemical reactant, respectively, and $K_p(T)$ is the equilibrium constant in terms of partial pressure as a function of temperature T. The symbol Π is mathematical shorthand that indicates the calculation of the product among the partial pressure terms of the chemical products or reactants.

The equilibrium constant is defined by the expression:

$$\ln\ K_p(T) = -\frac{\Delta G^\mathrm{o}}{\bar{R}T} \tag{2.50}$$

where ΔG^{o} is the Gibb's function for the stoichiometrically balanced chemical reaction of Equation 2.48:

$$\Delta G^{o} = \sum_{p} \nu_{p}\bar{g}_{p}^{o} - \sum_{r} \nu_{r}\bar{g}_{r}^{o} \tag{2.51}$$

The superscripts on the Gibbs functions indicate that they are evaluated at the reference pressure and the indicated temperature. However, the Gibb's function can also be calculated from the enthalpies and entropies at the reference pressure:

$$\Delta G^{o} = \sum_{p} \nu_{p}\left(\bar{h}_{p} - T\bar{s}_{p}^{o}\right) - \sum_{r} \nu_{r}\left(\bar{h}_{r} - T\bar{s}_{r}^{o}\right) \tag{2.52}$$

Example: The water–gas shift reaction is important during gasification, influencing the relative proportions of carbon monoxide (CO) and hydrogen (H_2) in the product gas:

$$CO + H_2O \rightarrow CO_2 + H_2$$

Assuming that the starting composition of a gas stream contains 1 kilomole each of CO, CO_2, H_2, and steam (H_2O) reacting at 10 atm pressure and 727°C (1000 K), what is the expected equilibrium composition of the gas mixture?

The first step is to write the overall molar balance for the conversion of the gases making up the initial gas mixture into an equilibrium mixture of the gases:

$$CO + CO_2 + H_2 + H_2O \rightarrow wCO + xCO_2 + yH_2 + zH_2O$$

From the above equation, molar balances on carbon, oxygen, and hydrogen can be performed:

carbon: $1 + 1 = w + x$

hydrogen: $2(1) + 2(1) = 2y + 2z$

oxygen: $1 + 2(1) + 1 = w + 2x + z$

These three equations are solved simultaneously in terms of one of the four variables, which is arbitrarily chosen here to be x. Substituting the solutions into the overall molar balance:

$$CO + CO_2 + H_2 + H_2O \rightarrow (2 - x)CO + xCO_2 + xH_2 + (2 - x)H_2O$$

Notice that for this particular reaction, the total number of moles is conserved (moles of reactants equal moles of products), although that is not necessarily the case for other reactions:

$$\sum_{\mathrm{r}} n_{\mathrm{r}} = n_{\mathrm{CO}} + n_{\mathrm{CO_2}} + n_{\mathrm{H_2}} + n_{\mathrm{H_2O}} = 1 + 1 + 1 + 1 = 4$$

$$\sum_{\mathrm{p}} n_{\mathrm{p}} = n_{\mathrm{CO}} + n_{\mathrm{CO_2}} + n_{\mathrm{H_2}} + n_{\mathrm{H_2O}} = (2 - x) + x + x + (2 - x) = 4$$

From the molar balances, the partial pressures of the products and reactants needed to solve Equation 2.49 can be calculated (in atmospheres of pressure):

$$p_{\mathrm{CO}} = x_{\mathrm{CO}}p = \frac{n_{\mathrm{CO}}}{n}p = \frac{(2-x)}{4}10; \quad p_{\mathrm{CO_2}} = x_{\mathrm{CO_2}}p = \frac{n_{\mathrm{CO_2}}}{n}p = \left(\frac{x}{4}\right)10$$

$$p_{\mathrm{H_2}} = x_{\mathrm{H_2}}p = \frac{n_{\mathrm{H_2}}}{n}p = \left(\frac{x}{4}\right)10; \quad p_{\mathrm{H_2O}} = x_{\mathrm{H_2O}}p = \frac{n_{\mathrm{H_2O}}}{n}p = \frac{2-x}{4}10$$

Note that total moles, *n*, of chemical compounds are conserved in this example, although this is not generally the case. If moles are not conserved, then *n* in the above denominators would not be a constant but rather a function of *x*.

Substituting these partial pressures into Equation 2.49 and using the appropriate stoichiometric coefficient for each of the chemical species (where reference pressure is 1 atm):

$$K_p(T) = \frac{\prod_{\mathrm{p}}\left(\frac{p_{\mathrm{p}}}{p_{\mathrm{REF}}}\right)^{\nu_{\mathrm{p}}}}{\prod_{\mathrm{r}}\left(\frac{p_{\mathrm{r}}}{p_{\mathrm{REF}}}\right)^{\nu_{\mathrm{r}}}} = \frac{\left(\frac{x}{4}10\right)^1\left(\frac{x}{4}10\right)^1}{\left(\frac{2-x}{4}10\right)^1\left(\frac{2-x}{4}10\right)^1} = \frac{x^2}{(2-x)^2}$$

Notice that pressure does not affect this equi-molar reaction. This expression can be simplified:

$$\left(K_{\mathrm{p}} - 1\right)x^2 - 4K_{\mathrm{p}}x + 4K_{\mathrm{p}} = 0$$

All that remains is to determine the value of the equilibrium coefficient K_p at 1000 K. From Equation 2.50, this requires the calculation of the Gibb's function for the stoichiometrically balanced equation:

$$\mathrm{CO + H_2O \rightarrow CO_2 + H_2}$$

Some tabulations of thermodynamic properties include the Gibb's functions for chemical species although more commonly only enthalpy and entropy are tabulated. Substituting appropriate values from Table 2.1 into Equation 2.52:

$$\begin{aligned}
\Delta G^{\mathrm{o}} &= \sum_{\mathrm{p}} \nu_{\mathrm{p}} \left(\bar{h}_{\mathrm{p}} - T\bar{s}^{\mathrm{o}}_{\mathrm{p}}\right) - \sum_{\mathrm{r}} \nu_{\mathrm{r}} \left(\bar{h}_{\mathrm{r}} - T\bar{s}^{\mathrm{o}}_{\mathrm{r}}\right) \\
&= \nu_{\mathrm{CO_2}} \left\{\left[\bar{h}_{\mathrm{f}} + \left(\bar{h}(T) - \bar{h}(T_{\mathrm{ref}})\right)\right]_{\mathrm{CO_2}} - T\bar{s}^{\mathrm{o}}_{\mathrm{CO_2}}\right\} \\
&\quad + \nu_{\mathrm{H_2}} \left\{\left[\bar{h}_{\mathrm{f}} + \left(\bar{h}(T) - \bar{h}(T_{\mathrm{ref}})\right)\right]_{\mathrm{H_2}} - T\bar{s}^{\mathrm{o}}_{\mathrm{H_2}}\right\} \\
&\quad - \nu_{\mathrm{CO}} \left\{\left[\bar{h}_{\mathrm{f}} + \left(\bar{h}(T) - \bar{h}(T_{\mathrm{ref}})\right)\right]_{\mathrm{CO}} - T\bar{s}^{\mathrm{o}}_{\mathrm{CO}}\right\} \\
&\quad - \nu_{\mathrm{H_2O}} \left\{\left[\bar{h}_{\mathrm{f}} + \left(\bar{h}(T) - \bar{h}(T_{\mathrm{ref}})\right)\right]_{\mathrm{H_2O}} - T\bar{s}^{\mathrm{o}}_{\mathrm{H_2O}}\right\} \\
&= 1\,\{[-393\,520 + (42\,769 - 9364)] - 1000 \times 269.22\} \\
&\quad + 1\,\{[0 + (29\,154 - 8468)] - 1000 \times 166.11\} \\
&\quad - 1\,\{[-110\,530 + (30\,355 - 8669)] - 1000 \times 234.42\} \\
&\quad - 1\,\{[-241\,820 + (35\,882 - 9904)] - 1000 \times 232.60\} \\
&= -629\,335 - 145\,424 + 323\,264 + 448\,442 \\
&= -3053\,\mathrm{kJ/kmol}
\end{aligned}$$

Substituting into Equation 2.50:

$$\ln\ K_p = -\frac{\Delta G^{\mathrm{o}}}{\bar{R}T} = -\left(\frac{-3053\,\mathrm{kJ/kmol}}{8.314\,\mathrm{kJ/kmol\,K} \cdot 1000\,\mathrm{K}}\right) = 0.367$$

$$K_p = \exp(0.367) = 1.444$$

Substituting this into the previously developed equilibrium expression in terms of variable x:

$$\begin{aligned}
&\left(K_p - 1\right) x^2 - 4K_p x + 4K_p = 0 \\
&(1.444 - 1)x^2 - 4(1.444)x + 4(1.444) = 0 \\
&0.444x^2 - 5.776x + 5.776 = 0 \\
&x = 1.092\ \mathrm{kmol}
\end{aligned}$$

Thus, the final molar product distribution is:

$$0.908\ \mathrm{kmol\ CO} + 1.092\ \mathrm{kmol\ CO_2} + 1.092\ \mathrm{kmol\ H_2} + 0.908\ \mathrm{kmol\ H_2O}$$

Further Reading

Engineering Thermodynamics

Moran, M., and Shapiro, H. (2010) *Fundamentals of Engineering Thermodynamics*, 7th edn. New York: John Wiley & Sons, Inc.

Chemical Reaction Mass Balances

Schmidt, L.D., (ed.) (2005) *The Engineering of Chemical Reactions*, 2nd edn. Oxford: Oxford University Press.

Energy Return on Energy Invested

Hall, A.S. and Hansen, D., (eds) (2011) *Special Issue on New Studies in EROI (Energy Return on Investment) Sustainability,* Vol. 3.