CHAPTER 2

FUEL CELL THERMODYNAMICS

Thermodynamics is the study of energetics; the study of the transformation of energy from one form to another. Since fuel cells are energy conversion devices, fuel cell thermodynamics is key to understanding the conversion of chemical energy into electrical energy. For fuel cells, thermodynamics can predict whether a candidate fuel cell reaction is energetically spontaneous. Furthermore, thermodynamics places upper bound limits on the maximum electrical potential that can be generated in a reaction. Thus, thermodynamics yields the theoretical boundaries of what is possible with a fuel cell; it gives the "ideal case."

Any real fuel cell will perform at or below its thermodynamic limit. Understanding real fuel cell performance requires a knowledge of kinetics in addition to thermodynamics. This chapter covers the thermodynamics of fuel cells. Subsequent chapters will cover the major kinetic limitations on fuel cell performance, defining practical performance.

2.1 THERMODYNAMICS REVIEW

This section presents a brief review of the main tenets of thermodynamics. These basic theories are typically taught in an introductory thermodynamics course. Next, these concepts are extended to include parameters that are needed to understand fuel cell behavior. Readers are advised to consult a thermodynamics book if additional review is required.

2.1.1 What Is Thermodynamics?

It is no secret that no one really understands the meaning of popular thermodynamic quantities. For example, Nobel Prize–winning physicist Richard Feynman wrote in his *Lectures*

on Physics: "It is important to realize that in modern physics today, we have no knowledge of what energy is" [1]. We have even less intuition about terms such as *enthalpy* and *free energy*. The fundamental assumptions of thermodynamics are based on human experience. Assumptions are the best we can do. We *assume* that energy can never be created or destroyed (first law of thermodynamics) only because it fits with everything experienced in human existence. Nevertheless, no one knows why it should be so.

If we accept a few of these fundamental assumptions, however, we can develop a self-consistent mathematical description that tells us how important quantities such as energy, temperature, pressure, and volume are related. This is really all that thermodynamics is; it is an elaborate bookkeeping scheme that allows us to track the properties of systems in a self-consistent manner, starting from a few basic assumptions or "laws."

2.1.2   Internal Energy

A fuel cell converts energy stored within a fuel into other, more useful forms of energy. The total intrinsic energy of a fuel (or of any substance) is quantified by a property known as internal energy (U). Internal energy is the energy associated with microscopic movement and interaction between particles on the atomic and molecular scales. It is separated in scale from the macroscopic ordered energy associated with moving objects. For example, a tank of H_2 gas sitting on a table has no apparent energy. However, the H_2 gas actually has significant internal energy (see Figure 2.1); on the microscopic scale it is a whirlwind of molecules traveling hundreds of meters per second. Internal energy is also associated with the *chemical bonds* between the hydrogen atoms. A fuel cell can convert *only a portion* of the internal energy associated with a tank of H_2 gas into electrical energy. The limits on
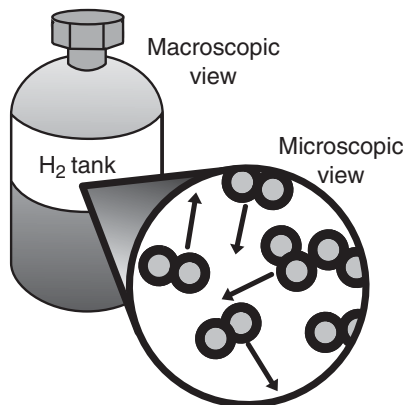

Figure 2.1. Although this tank of H_2 gas has no apparent macroscopic energy, it has significant internal energy. Internal energy is associated with microscopic movement (kinetic energy) and interactions between particles (chemical/potential energy) on the atomic scale.

how much of the internal energy of the H_2 gas can be transformed into electrical energy are established by the first and second laws of thermodynamics.

2.1.3   First Law

The first law of thermodynamics is also known as the law of conservation of energy—energy can never be created or destroyed—as expressed by the equation

$$d(\text{Energy})_{\text{univ}} = d(\text{Energy})_{\text{system}} + d(\text{Energy})_{\text{surroundings}} = 0 \qquad (2.1)$$

Viewed another way, this equation states that any change in the energy of a system must be fully accounted for by energy transfer to the surroundings:

$$d(\text{Energy})_{\text{system}} = -d(\text{Energy})_{\text{surroundings}} \qquad (2.2)$$

There are two ways that energy can be transferred between a closed system and its surroundings: via *heat* (Q) or *work* (W). This allows us to write the first law in its more familiar form:

$$dU = dQ - dW \qquad (2.3)$$

This expression states that the change in the internal energy of a closed system (dU) must be equal to the heat transferred to the system (dQ) minus the work done by the system (dW). To develop this expression from Equation 2.2, we have substituted dU for $d(\text{Energy})_{\text{system}}$; if we choose the proper reference frame, then all energy changes in a system are manifested as internal energy changes. Note that we define positive work as work done *by* the system on the surroundings.

For now, we will assume that only mechanical work is done by a system. Mechanical work is accomplished by the expansion of a system against a pressure. It is given by

$$(dW)_{\text{mech}} = p\,dV \qquad (2.4)$$

where p is the pressure and dV is the volume change. Later, when we talk about fuel cell thermodynamics, we will consider the electrical work done by a system. For now, however, we ignore electrical work. Considering only mechanical work, we can rewrite the expression for the internal energy change of a system as

$$dU = dQ - p\,dV \qquad (2.5)$$

2.1.4   Second Law

The second law of thermodynamics introduces the concept of *entropy*. Entropy is determined by the number of possible microstates accessible to a system, or, in other words, the number of possible ways of configuring a system. For this reason, entropy can be thought

of as a measure of "disorder," since an increasing entropy indicates an increasing number of ways of configuring a system. For an isolated system (the simplest case)

$$S = k \log \Omega \qquad (2.6)$$

where S is the total entropy of the system, k is Boltzmann's constant, and Ω denotes the number of possible microstates accessible to the system.

WORK AND HEAT

In contrast to internal energy, work and heat are not properties of matter or of any particular system (e.g., substance or body). They represent *energy in transit*, in other words, energy that is transferred between substances or bodies.

In the case of work, this transfer of energy is accomplished by the application of a force over a distance. Heat, on the other hand, is transferred between substances whenever they have different thermal energies, as manifested by differences in their temperature.

Due to repercussions of the second law (which we will discuss momentarily), work is often called the most "noble" form of energy; it is the universal donor. Energy, in the form of work, can be converted into any other form of energy at 100% theoretical efficiency. In contrast, heat is the most "ignoble" form of energy; it is the universal acceptor. Any form of energy can eventually be 100% dissipated to the environment as heat, but heat can never be 100% converted back to more noble forms of energy such as work.

The nobility of work versus heat illustrates one of the central differences between fuel cells and combustion engines. A combustion engine burns fuel to produce heat and then converts some of this heat into work. Because it first converts energy into heat, the combustion engine destroys some of the work potential of the fuel. This unfortunate destruction of work potential is called the "thermal bottleneck." Because a fuel cell bypasses the heat step, it avoids the thermal bottleneck.

Microstates can best be understood with an example. Consider the "perfect" system of 100 identical atoms shown in Figure 2.2*a*. There is only one possible microstate, or *configuration*, for this system. This is because the 100 atoms are exactly identical and indistinguishable from one another. If we were to "switch" the first and the second atoms, the system would look exactly the same. The entropy of this perfect 100-atom crystal is therefore zero ($S = k \log 1 = 0$). Now consider Figure 2.2*b*, where three atoms have been removed from their original locations and placed on the surface of the crystal. Any three atoms could have been removed from the crystal, and depending on which atoms were removed, the final configuration of the system would be different. In this case, there are many microstates available to the system. (Figure 2.2*b* represents just one of them.) We can calculate the number of microstates available to the system by evaluating the number of possible ways there are to take N atoms from a total of Z atoms:

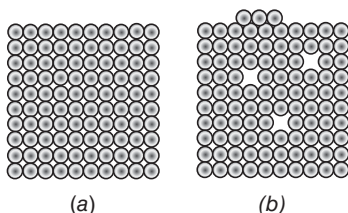$$\Omega \equiv \frac{Z(Z-1)(Z-2)\cdots(Z-N+1)}{N!} = \frac{Z!}{(Z-N)!(N!)} \qquad (2.7)$$

Figure 2.2. (*a*) The entropy of this 100-atom perfect crystal is zero because there is only one possible way to arrange the atoms to produce this configuration. (*b*) When three atoms are removed from the crystal and placed on the surface, the entropy increases. This is because there are many possible ways to configure a system of 100 atoms where 3 have been removed.

In Figure 2.2*b*, there are 100 atoms. The number of ways to take 3 atoms from 100 is

$$\Omega = \frac{100!}{97!3!} == 1.62 \times 10^5 \tag{2.8}$$

This yields $S = 7.19 \times 10^{-23}$ J/K.

Except for extremely simple systems like the one in this example, it is impossible to calculate entropy exactly. Instead, a system's entropy is usually *inferred* based on how heat transfer causes the entropy of the system to change. For a reversible transfer of heat at constant pressure, the entropy of a system will change as

$$dS = \frac{dQ_{\text{rev}}}{T} \tag{2.9}$$

where dS is the entropy change in the system associated with a reversible transfer of heat (dQ_{rev}) at a constant temperature (T). In other words, "dumping" energy, including heat, into a system causes its entropy to increase. Essentially, by providing additional energy to the system, we enable it to access additional microstates, causing its entropy to increase. For an irreversible transfer of heat, the entropy increase will be even larger than that dictated by Equation 2.9. This is a key statement of the second law of thermodynamics.

The most widely known form of the second law acknowledges that the entropy of a system and its surroundings must increase or at least remain zero for any process:

$$dS_{\text{univ}} \geq 0 \tag{2.10}$$

This inequality, when combined with the first law of thermodynamics, allows us to separate thermodynamically "spontaneous" processes from "nonspontaneous" processes.

2.1.5 Thermodynamic Potentials

Based on the first and second laws of thermodynamics, we can write down "rules" to specify how energy can be transferred from one form to another. These rules are called *thermodynamic potentials*. You are already familiar with one thermodynamic potential: the internal

energy of a system. We can combine results from the first and the second laws of thermo-dynamics (Equations 2.3 and 2.9) to arrive at an equation for internal energy that is based on the variation of two independent variables, entropy S and volume V:

$$dU = T\,dS - p\,dV \tag{2.11}$$

Remember, $T\,dS$ represents the reversible heat transfer and $p\,dV$ is the mechanical work. As mentioned above, from this equation we can conclude that U, the internal energy of a system, is a function of entropy and volume:

$$U = U(S, V) \tag{2.12}$$

We can also derive the following useful relations, which show how the *dependent* vari-ables T and p are related to variations in the *independent* variables (S and V):

$$\left(\frac{dU}{dS}\right)_V = T \tag{2.13}$$

$$\left(\frac{dU}{dV}\right)_S = -p \tag{2.14}$$

Unfortunately, S and V are not easily measurable in most experiments. (There is no such thing as an "entropy meter.") Therefore, a new thermodynamic potential is needed equivalent to U but depending on quantities that are more readily measured than S and V. Temperature T and pressure p fall into this category. Happily, there is a simple math-ematical way to accomplish this conversion using a *Legendre transform*. A step-by-step transformation of U begins by defining a new thermodynamic potential $G(T,\ p)$ as follows:

$$G = U - \left(\frac{dU}{dS}\right)_V S - \left(\frac{dU}{dV}\right)_S V \tag{2.15}$$

Since we know that $(dU/dS)_V = T$ and $(dU/dV)_S = -p$, we obtain

$$G = U - TS + pV \tag{2.16}$$

This function is called the Gibbs free energy. Let us show that G is indeed a function of the temperature and the pressure. The variation of G (mathematically dG) results in

$$dG = dU - T\,dS - S\,dT + p\,dV + V\,dp \tag{2.17}$$

Since we know that $dU = T\,dS - p\,dV$, we can see that

$$dG = -S\,dT + V\,dp \tag{2.18}$$

So, the Gibbs free energy is nothing more than a thermodynamic description of a system that depends on T and p instead of S and V.

What if we want a potential that depends on S and p? No problem! Remember that U is a function of S and V. To get a thermodynamic potential that is a function of S and p, we need only to transform U with respect to V this time. Analogously to Equation 2.15, we define this new thermodynamic potential H as

$$H = U - \left(\frac{dU}{dV}\right)_S V \tag{2.19}$$

Again, since $(dU/dV)_S = -p$, we obtain

$$H = U + pV \tag{2.20}$$

where H is called enthalpy. Through differentiation, we can show that H is a function of S and p:

$$dH = dU + p\,dV + V\,dp \tag{2.21}$$

Again, $dU = T\,dS - p\,dV$; so

$$dH = T\,dS + V\,dp \tag{2.22}$$

Thus far, we have defined three thermodynamic potentials: $U(S, V)$, $H(S, p)$, and $G(T, p)$. Defining a fourth and final thermodynamic potential that depends on temperature and volume, $F(T, V)$, completes the symmetry:

$$F = U - TS \tag{2.23}$$

where F is the Helmholtz free energy. We leave it to the reader to show that

$$dF = -S\,dT - p\,dV \tag{2.24}$$

A summary of these four thermodynamic potentials is provided in Figure 2.3. This mnemonic diagram, originally suggested by Schroeder [2], can help you keep track of the relationships between the thermodynamic potentials. Loosely, the four potentials are defined as follows:

- *Internal Energy* (U). The energy needed to create a system in the absence of changes in temperature or volume.
- *Enthalpy* (H). The energy needed to create a system plus the work needed to make room for it (from zero volume).
- *Helmholtz Free Energy* (F). The energy needed to create a system minus the energy that you can get from the system's environment due to spontaneous heat transfer (at constant temperature).
- *Gibbs Free Energy* (G). The energy needed to create a system and make room for it minus the energy that you can get from the environment due to heat transfer. In other words, G represents the net energy cost for a system created at a constant environmental temperature T from a negligible initial volume after subtracting what the environment automatically supplied.
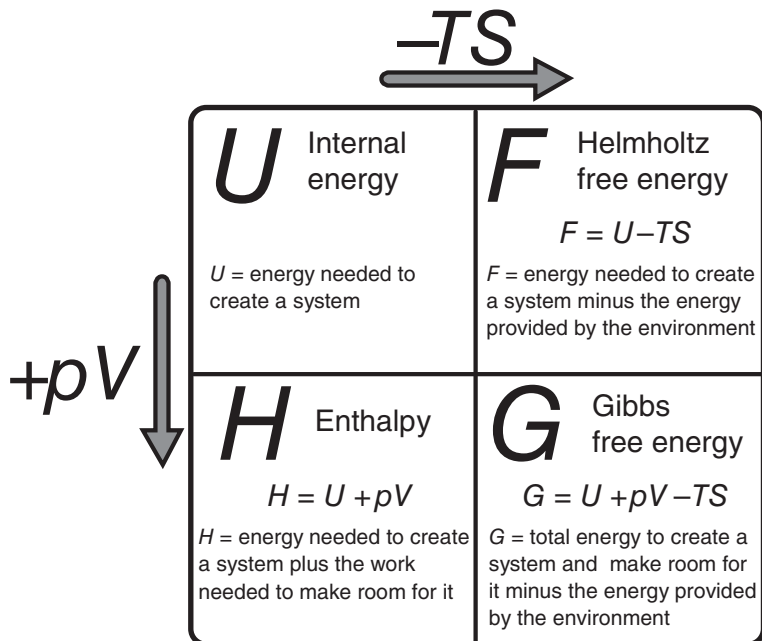
Figure 2.3. Pictorial summary of the four thermodynamic potentials. They relate to one another by offsets of the "energy from the environment" term *TS* and the "expansion work" term *pV*. Use this diagram to help remember the relationships. Copyright © 2000 by Addison Wesley Longman. Reprinted by permission of Pearson Education, Inc. (Figure 5.2, p. 151, from *An Introduction to Thermal Physics* by Daniele V. Schroeder [2]).

2.1.6   Molar Quantities

Typical notation distinguishes between intrinsic and extrinsic variables. Intrinsic quantities such as temperature and pressure do not scale with the system size; extrinsic quantities such as internal energy and entropy do scale with system size. For example, if the size of a box of gas molecules is doubled and the number of molecules in the box doubles, then the internal energy and entropy double, while the temperature and pressure remain constant. It is conventional to denote intrinsic quantities with a lowercase letter (p) and extrinsic quantities with an uppercase letter (U).

Molar quantities such as $\hat{u}$, the internal energy per mole of gas (units of kilojoules per mole), are intrinsic. It is often useful to calculate energy changes due to a reaction on a per-mole basis:

$$\Delta\hat{g}_{rxn}, \Delta\hat{s}_{rxn}, \Delta\hat{v}_{rxn}$$

The Δ symbol denotes a change during a thermodynamic process (such as a reaction), calculated as final state–initial state. Therefore, a negative energy change means energy is released during a process: A negative volume change means the volume decreases during

a process. For example, the overall reaction in a H_2–O_2 fuel cell,

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \tag{2.25}$$

has $\Delta\hat{g}_{rxn} = -237$ kJ/mol H_2 at room temperature and pressure. For every mole of H_2 gas consumed (or every 1/2 mol of O_2 gas consumed or mole of H_2O produced), the Gibbs free-energy change is –237 kJ. If 5 mol of O_2 gas is reacted, the extrinsic Gibbs free-energy change (ΔG_{rxn}) would be

$$5 \text{ mol } O_2 \times \left(\frac{1 \text{ mol } H_2}{(1/2) \text{ mol } O_2} \right) \times \left(\frac{-237 \text{ kJ}}{\text{mol } H_2} \right) = -2370 \text{ kJ} \tag{2.26}$$

Of course the *intrinsic* (per-mole) Gibbs free energy of this reaction is still $\Delta\hat{g}_{rxn} = -237$ kJ/mol H_2.

2.1.7 Standard State

Because most thermodynamic quantities depend on temperature and pressure, it is convenient to reference everything to a standard set of conditions. This set of conditions is called the standard state. There are two common types of standard conditions:

The thermodynamic standard state describes the standard set of conditions under which reference values of thermodynamic quantities are typically given. Standard-state conditions specify that all reactant and product species are present in their pure, most stable forms at unit activity. (Activity is discussed in Section 2.4.3.) Standard-state conditions are designated by a superscript zero. For example, $\Delta\hat{h}^0$ represents an enthalpy change under standard-state thermodynamic conditions. Importantly, there is no "standard temperature" in the definition of thermodynamic standard-state conditions. However, since most tables list standard-state thermodynamic quantities at 25°C (298.15 K), this temperature is usually implied. At temperatures other than 25°C, it is sometimes necessary to apply temperature corrections to $\Delta\hat{h}^0$ and $\Delta\hat{s}^0$ values obtained at 25°C, although it is frequently approximated that these values change only slightly with temperature, and hence this issue can be ignored. For temperatures far from 25°C, however, this approximation should not be made. You will have the opportunity to explore this issue in Example 2.1 and problem 2.9.

It should be noted that $\Delta\hat{g}^0$ changes much more strongly with temperature (as shown in Equation 2.39) and therefore $\Delta\hat{g}^0$ values should always be adjusted by temperature using at least the linear dependence predicted by Equation 2.39. The use of this linear temperature dependence is shown in Example 2.2.

Standard temperature and pressure, or STP, is the standard condition most typically associated with gas law calculations. STP conditions are taken as room temperature (298.15 K) and atmospheric pressure. (Standard-state pressure is actually defined as 1 bar = 100 kPa. Atmospheric pressure is taken as 1 atm = 101.325 kPa. These slight differences are usually ignored.)

2.1.8 Reversibility

We frequently use the term "reversible" when talking about the thermodynamics of fuel cells. Reversible implies equilibrium. A reversible fuel cell voltage is the voltage produced by a fuel cell at thermodynamic equilibrium. A process is thermodynamically reversible when an infinitesimal reversal in the driving force causes it to reverse direction; such a system is always at equilibrium.

Equations relating to reversible fuel cell voltages only apply to equilibrium conditions. As soon as current is drawn from a fuel cell, equilibrium is lost and reversible fuel cell voltage equations no longer apply. To distinguish between reversible and nonreversible fuel cell voltages in this book, we will use the symbols E and V, where E represents a reversible (thermodynamically predicted) fuel cell voltage and V represents an operational (nonreversible) fuel cell voltage.

2.2 HEAT POTENTIAL OF A FUEL: ENTHALPY OF REACTION

Now that we have reviewed general thermodynamics, the exciting work begins. We will now apply what we know about thermodynamics to fuel cells. Remember, the goal of a fuel cell is to extract the internal energy from a fuel and convert it into more useful forms of energy. What is the maximum amount of energy that we can extract from a fuel? The maximum depends on whether we extract energy from the fuel in the form of heat or work. As is shown in this section, the maximum heat energy that can be extracted from a fuel is given by the fuel's enthalpy of reaction (for a constant-pressure process).

Recall the differential expression for enthalpy (Equation 2.22):

$$dH = T\,dS + V\,dp \tag{2.27}$$

For a constant-pressure process ($dp = 0$), Equation 2.27 reduces to

$$dH = T\,dS \tag{2.28}$$

Here, dH is the same as the heat transferred (dQ) in a reversible process. For this reason, we can think of enthalpy as a measure of the heat potential of a system under constant-pressure conditions. In other words, for a constant-pressure reaction, the enthalpy change expresses the amount of heat that could be evolved by the reaction. From where does this heat originate? Expressing dH in terms of dU at constant pressure provides the answer:

$$dH = T\,dS = dU + dW \tag{2.29}$$

From this expression, we see that the heat evolved by a reaction is due to changes in the internal energy of the system, after accounting for any energy that goes toward work. The

internal energy change in the system is largely due to the reconfiguration of chemical bonds. For example, as discussed in the previous chapter, burning hydrogen releases heat due to molecular bonding reconfigurations. The product water rests at a lower internal energy state than the initial hydrogen and oxygen reactants. After accounting for the energy that goes toward work, the rest of the internal energy difference is transformed into heat during the reaction. The situation is analogous to a ball rolling down a hill; the potential energy of the ball is converted into kinetic energy as it rolls from the high-potential-energy initial state to the low-potential-energy final state.

The enthalpy change associated with a combustion reaction is called the *heat of combustion*. The name *heat* of combustion indicates the close tie between enthalpy and heat potential for constant-pressure chemical reactions. More generally, the enthalpy change associated with any chemical reaction is called the *enthalpy of reaction* or *heat of reaction*. We use the more general term *enthalpy of reaction* (ΔH_{rxn} or $\Delta \hat{h}_{rxn}$) in this text.

2.2.1   Calculating Reaction Enthalpies

Since reaction enthalpies are associated mainly with the reconfiguration of chemical bonds during a reaction, they can be calculated by considering the bond enthalpy differences between the reactants and products. For example, in problem 1.7, we *approximated* how much heat is released in the H_2 combustion reaction by comparing the enthalpies of the reactant O–O and H–H bonds to the product H–O bonds.

Bond enthalpy calculations are somewhat awkward and give only rudimentary approximations. Therefore, enthalpy-of-reaction values are normally calculated by computing the *formation enthalpy* differences between reactants and products. A standard-state formation enthalpy $\Delta \hat{h}_f^0(i)$ tells how much enthalpy is required to form 1 mol of chemical species i at STP from the reference species. For a general reaction
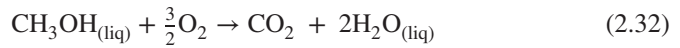
$$aA + bB \rightarrow mM + nN \tag{2.30}$$

where A and B are reactants; M and N are products; and a, b, m, n represent the number of moles of A, B, M, and N, respectively; $\Delta \hat{h}_{rxn}^0$ may be calculated as

$$\Delta \hat{h}_{rxn}^0 = \left[m \, \Delta \hat{h}_f^0(M) + n \, \Delta \hat{h}_f^0(N) \right] - \left[a \, \Delta \hat{h}_f^0(A) + b \, \Delta \hat{h}_f^0(B) \right] \tag{2.31}$$

Thus, the enthalpy of reaction is computed from the difference between the *molar weighted* reactant and product formation enthalpies. Note that enthalpy changes (like all energy changes) are computed in the form of *final state–initial state*, or in other words, *products–reactants*.

An expression analogous to Equation 2.31 may be written for the standard-state entropy of a reaction, $\Delta \hat{s}_{rxn}^0$, using *standard entropy* values $\hat{s}^0$ for the species taking part in the reaction. See Example 2.1 for details.

Example 2.1 A direct methanol fuel cell uses methanol as fuel instead of hydrogen. Calculate the $\Delta\hat{h}^0_{rxn}$ and $\Delta\hat{s}^0_{rxn}$ for the methanol combustion reaction:

$$CH_3OH_{(liq)} + \tfrac{3}{2}O_2 \rightarrow CO_2 + 2H_2O_{(liq)} \tag{2.32}$$

Solution: From Appendix B, the $\Delta\hat{h}^0_f$ and $\hat{s}^0$ values for CH_3OH, O_2, CO_2, and H_2O are given in the following table.

Chemical Species	$\Delta\hat{h}^0_f$ (kJ/mol)	$\hat{s}^0$ [J/(mol·K)]
$CH_3OH_{(liq)}$	–238.5	127.19
O_2	0	205.00
CO_2	–393.51	213.79
$H_2O_{(liq)}$	–285.83	69.95

Following Equation 2.31, the $\Delta\hat{h}^0_{rxn}$ for methanol combustion is calculated as

$$\Delta\hat{h}^0_{rxn} = \left[2\,\Delta\hat{h}^0_f(H_2O_{(liq)}) + \Delta\hat{h}^0_f(CO_2)\right] - \left[\tfrac{3}{2}\,\Delta\hat{h}^0_f(O_2) + \Delta\hat{h}^0_f(CH_3OH_{(liq)})\right]$$

$$= [2(-285.83) + (-393.51)] - \left[\tfrac{3}{2}(0) + (-238.5)\right]$$

$$= -726.67 \text{ kJ/mol} \tag{2.33}$$

Similarly, $\Delta\hat{s}^0_{rxn}$ is calculated as

$$\Delta\hat{s}^0_{rxn} = \left[2\hat{s}^0(H_2O_{(liq)}) + \hat{s}^0(CO_2)\right] - \left[\tfrac{3}{2}\hat{s}^0(O_2) + \hat{s}^0(CH_3OH_{(liq)})\right]$$

$$= [2(69.95) + (213.79)] - \left[\tfrac{3}{2}(205.00) + (127.19)\right]$$

$$= -81.00 \text{ J/(mol} \cdot \text{K)} \tag{2.34}$$

2.2.2 Temperature Dependence of Enthalpy

The amount of heat energy that a substance can absorb changes with temperature. It follows that a substance's formation enthalpy also changes with temperature. The variation of enthalpy with temperature is described by a substance's heat *capacity*:

$$\Delta\hat{h}_f = \Delta\hat{h}^0_f + \int_{T_0}^{T} c_p(T)\,dT \tag{2.35}$$

where $\Delta\hat{h}_f$ is the formation enthalpy of the substance at an arbitrary temperature T, $\Delta\hat{h}^0_f$ is the reference formation enthalpy of the substance at $T_0 = 298.15$ K, and $c_p(T)$ is the

constant-pressure heat capacity of the substance (which itself may be a function of temperature). If phase changes occur along the path between T_0 and T, extra caution must be taken to make sure that the enthalpy changes associated with these phase changes are also included.

In a similar manner, the entropy of a substance also varies with temperature. Again, this variation is described by the substance's heat capacity:

$$\hat{s} = \hat{s}^0 + \int_{T_0}^{T} \frac{c_p(T)}{T} dT \tag{2.36}$$

From Equations 2.31, 2.35, and 2.36, $\Delta\hat{h}_{rxn}$ and $\Delta\hat{s}_{rxn}$ for any reaction at any temperature can be calculated as long as the basic thermodynamic data ($\Delta\hat{h}_f^0$, $\hat{s}^0$, c_p) are provided. Appendix B provides a collection of basic thermodynamic data for a variety of chemical species relevant to fuel cells.

Since heat capacity effects are generally minor, $\Delta\hat{h}_f^0$ and $\hat{s}^0$ values are usually assumed to be independent of temperature, simplifying thermodynamic calculations. See Example 2.2 for an illustration.

In a perfect world, we could harness all of the enthalpy released by a chemical reaction to do useful work. Unfortunately, thermodynamics tells us that this is not possible. Only a portion of the energy evolved by a chemical reaction can be converted into useful work. For electrochemical systems (i.e., fuel cells), the Gibbs free energy gives the maximum amount of energy that is available to do electrical work.

2.3   WORK POTENTIAL OF A FUEL: GIBBS FREE ENERGY

Recall from Section 2.1.5 that the Gibbs free energy can be considered to be the net energy required to create a system and make room for it minus the energy received from the environment due to spontaneous heat transfer. Thus, G represents the energy that *you* had to transfer to create the system. (The environment also transferred some energy via heat, but G subtracts this contribution out.) If G represents the net energy you had to transfer to create the system, then G should also represent the maximum energy that you could ever get back out of the system. In other words, the Gibbs free energy represents the exploitable energy potential, or *work potential*, of the system.

2.3.1   Calculating Gibbs Free Energies

Since the Gibbs free energy is the key to the work potential of a reaction, it is necessary to calculate $\Delta\hat{g}_{rxn}$ values as we calculated $\Delta\hat{h}_{rxn}$ and $\Delta\hat{s}_{rxn}$ values. In fact, we can calculate $\Delta\hat{g}_{rxn}$ values *directly* from $\Delta\hat{h}_{rxn}$ and $\Delta\hat{s}_{rxn}$ values. Recalling how G is defined, it is apparent that G already contains H, since $G = U + PV - TS$ and $H = U + PV$. We can therefore define the Gibbs free energy as

$$G = H - TS \tag{2.37}$$

Differentiating this expression gives

$$dG = dH - T\,dS - S\,dT \tag{2.38}$$

Holding temperature constant (isothermal process, $dT = 0$) and writing this relationship in terms of molar quantities give

$$\Delta\hat{g} = \Delta\hat{h} - T\,\Delta\hat{s} \tag{2.39}$$

Thus, for an isothermal reaction, we can compute $\Delta\hat{g}$ in terms of $\Delta\hat{h}$ and $\Delta\hat{s}$. The isothermal reaction assumption means that temperature is constant *during* the reaction. However, it is important to realize that we can still use Equation 2.39 to calculate $\Delta\hat{g}$ values at different reaction temperatures.

Example 2.2 Determine the approximate temperature at which the following reaction is no longer spontaneous:

$$CO + H_2O_{(g)} \rightarrow CO_2 + H_2 \tag{2.40}$$
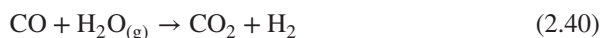
Solution: To answer this question, we need to calculate the Gibbs free energy for this reaction as a function of temperature and then solve for the temperature at which the Gibbs free energy for this reaction goes to zero:

$$\Delta\hat{g}_{rxn}(T) = \Delta\hat{h}_{rxn}(T) - T\,\Delta\hat{s}_{rxn}(T) = 0 \tag{2.41}$$

To get an approximate answer, we can assume that $\Delta\hat{h}_{rxn}$ and $\Delta\hat{s}_{rxn}$ are independent of temperature (heat capacity effects are ignored). In this case, the temperature dependence of $\Delta\hat{g}_{rxn}$ is approximated as

$$\Delta\hat{g}_{rxn}(T) = \Delta\hat{h}_{rxn}^0 - T\,\Delta\hat{s}_{rxn}^0 \tag{2.42}$$

From Appendix B, the $\Delta\hat{h}_f^0$ and $\hat{s}^0$ values for CO, CO_2, H_2, and H_2O are given in the table below.

Chemical Species	$\Delta\hat{h}_f^0$ (kJ/mol)	$\hat{s}^0$ [J/(mol·K)]
CO	−110.53	197.66
CO_2	−393.51	213.79
H_2	0	130.68
$H_2O(g)$	−241.83	188.84

Following Equation 2.31, $\Delta\hat{h}^0_{rxn}$ is calculated as

$$\Delta\hat{h}^0_{rxn} = \left[\Delta\hat{h}^0_f(CO_2) + \Delta\hat{h}^0_f(H_2)\right] - \left[\Delta\hat{h}^0_f(CO) + \Delta\hat{h}^0_f(H_2O)\right]$$
$$= [(-393.51) + (0)] - [(-110.53) + (-241.83)]$$
$$= -41.15 \text{ kJ/mol} \tag{2.43}$$

Similarly, $\Delta\hat{s}^0_{rxn}$ is calculated as

$$\Delta\hat{s}^0_{rxn} = \left[\hat{s}^0(CO_2) + \hat{s}^0(H_2)\right] - \left[\hat{s}^0(CO) + \hat{s}^0(H_2O)\right]$$
$$= [(213.79) + (130.68)] - [(197.66) + (188.84)]$$
$$= -42.03 \text{ J/(mol} \cdot \text{K)} \tag{2.44}$$

This gives

$$\Delta\hat{g}_{rxn}(T) = -41.15 \text{ kJ/mol} - T[-0.04203 \text{ kJ/(mol} \cdot \text{K)}] \tag{2.45}$$

Examining this expression, it is apparent that at low temperatures the enthalpy term will dominate over the entropy term, and the free energy will be negative. However, as the temperature increases, entropy eventually wins and the reaction ceases to be spontaneous. Setting this equation equal to zero and solving for T give us the temperature where the reaction ceases to be spontaneous:

$$-41.15 \text{ kJ/mol} + T[0.04203 \text{ kJ/(mol} \cdot \text{K)}] = 0 \quad T \approx 979 \text{ K} \approx 706°\text{C} \tag{2.46}$$

This reaction is known as the water gas shift reaction. It is important for high-temperature internal reforming of direct hydrocarbon fuel cells. These fuel cells run on simple hydrocarbon fuels (such as methane) in addition to hydrogen gas. Since these fuels contain carbon, carbon monoxide is often produced. The water gas shift reaction allows additional H_2 fuel to be created from the CO stream. However, if the fuel cell is run above 700°C, the water gas shift reaction is thermodynamically unfavorable. Therefore, operating a high-temperature direct hydrocarbon fuel cell requires a delicate balance between the thermodynamics of the reactions (which are more favorable at lower temperatures) and the kinetics of the reactions (which improve at higher temperatures). This balance is discussed in greater detail in Chapter 11.

2.3.2 Relationship between Gibbs Free Energy and Electrical Work

Now that we know how to calculate Δg, we can determine the work potential of a fuel cell. For fuel cells, recall that we are specifically interested in electrical work. Let us find the maximum amount of electrical work that we can extract from a fuel cell reaction.

From Equation 2.17, remember that we define a change in Gibbs free energy as

$$dG = dU - T\,dS - S\,dT + p\,dV + V\,dp \tag{2.47}$$

As we have done previously, we can insert the expression for dU based on the first law of thermodynamics (Equation 2.3) into this equation. However, this time we expand the work term in dU to include both mechanical work and electrical work:

$$\begin{aligned} dU &= T\,dS - dW \\ &= T\,dS - (p\,dV + dW_{\text{elec}}) \end{aligned} \tag{2.48}$$

which yields

$$dG = -S\,dT + V\,dp - dW_{\text{elec}} \tag{2.49}$$

For a constant-temperature, constant-pressure process ($dT,\ dp = 0$) this reduces to

$$dG = -dW_{\text{elec}} \tag{2.50}$$

Thus, the maximum electrical work that a system can perform in a constant-temperature, constant-pressure process is given by the negative of the Gibbs free-energy difference for the process. For a reaction using molar quantities, this equation can be written as

$$W_{\text{elec}} = -\Delta g_{\text{rxn}} \tag{2.51}$$

Again, remember that the constant-temperature, constant-pressure assumption used here is not really as restrictive as it seems. The only limitation is that the temperature and pressure do not vary *during* the reaction process. Since fuel cells usually operate at constant temperature and pressure, this assumption is reasonable. *It is important to realize that the expression derived above is valid for different values of temperature and pressure as long as these values are not changing during the reaction*. We could apply this equation for $T = 200$ K and $p = 1$ atm or just as validly for $T = 400$ K and $p = 5$ atm. Later, we will examine how such steps in temperature and pressure (think of them as changes in the operating conditions from one fixed state to a new fixed state) affect the maximum electrical work available from the fuel cell.

OPERATION OF A THERMODYNAMIC ENGINE AT CONSTANT TEMPERATURE AND PRESSURE (OPTIONAL)

The thermodynamics of fuel cell operation can be analyzed just like any other thermodynamic (or heat) engine. In the case of a fuel cell, steady-state operation typically occurs under constant-pressure (isobaric) and constant-temperature (isothermal) environments. Figure 2.4 describes the operation of this heat engine.
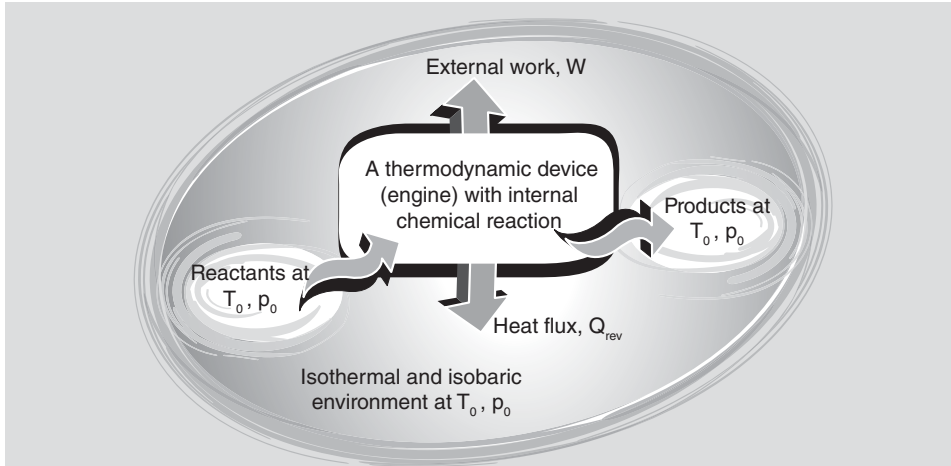
Figure 2.4. Diagram of a reversible thermodynamic engine (or heat engine) operating under constant pressure and temperature. Reactants and products enter and exit from the engine at constant pressure and temperature, respectively. The engine generates external work using the chemical (heat) energy of reactants. Also, the engine releases unused chemical energy to the isothermal and isobaric environment.

Reactants at ambient temperature and pressure T_0 and p_0 enter the engine. At this time, the reactants carry a total chemical (heat) energy or enthalpy of $H_{\text{Reactant}}(T_0, p_0)$. After the chemical reactions take place in the engine, products exit from the engine at ambient temperature and pressure T_0 and p_0 carrying $H_{\text{Product}}(T_0, p_0)$. The engine generates external work, W, using the heat energy from the chemical reaction. At the same time, the engine releases unused heat, $Q(= -Q_{\text{rev}})$, to the environment at ambient temperature T_0.

Assuming no accumulation of energy in the device in steady state, we can write an equation for the heat and energy balance of the system using the first law of thermodynamics:

$$H_{\text{Reactants}}(T_0, p_0) = H_{\text{Products}}(T_0, p_0) - Q_{\text{rev}} + W \tag{2.52}$$

After rearranging the equation for W, we obtain

$$\begin{aligned} W &= H_{\text{Reactants}}(T_0, p_0) - H_{\text{Products}}(T_0, p_0) + Q_{\text{rev}} \\ &= -\Delta H(T_0, p_0) + Q_{\text{rev}} \end{aligned} \tag{2.53}$$

Since the engine is thermodynamically reversible, we obtain the following equation from the second law of thermodynamics:

$$dS(T_0, p_0) = \frac{dQ_{\text{rev}}}{T_0} \tag{2.54}$$

Integrating both sides and solving for Q_{rev}, we have

$$\int dS(T_0, p_0) = S_{\text{Products}}(T_0, p_0) - S_{\text{Reactants}}(T_0, p_0) = \Delta S(T_0, p_0)$$

$$= \int \frac{dQ_{rev}}{T_0} = \frac{Q_{rev}}{T_0} \qquad (2.55)$$

$$Q_{rev} = T_0 \, \Delta S(T_0, p_0)$$

Plugging Equation 2.55 into 2.53 and solving for W, we have

$$W = -\Delta H(T_0, p_0) + Q_{rev}$$

$$= -\Delta H(T_0, p_0) + T_0 \, \Delta S(T_0, p_0) \qquad (2.56)$$

$$= -\Delta G(T_0, p_0)$$

Thus, any thermodynamic engine at steady state can generate a maximum amount of work equivalent to the Gibbs free energy if it operates under isobaric (constant-pressure) and isothermal (constant-temperature) conditions. The fuel cell is one type of thermodynamic engine that can generate work, W, in electrical form under this condition. This result is not surprising, since we have already learned that maximum available thermodynamic work potential under this condition is equal to the Gibbs energy in the system.

2.3.3 Relationship between Gibbs Free Energy and Reaction Spontaneity

In addition to determining the maximum amount of electrical work that can be extracted from a reaction, the Gibbs free energy is also useful in determining the spontaneity of a reaction. Obviously, if ΔG is zero, then no electrical work can be extracted from a reaction. Worse yet, if ΔG is greater than zero, then work must be input for a reaction to occur. Therefore, the sign of ΔG indicates whether or not a reaction is spontaneous:

$\Delta G > 0$ Nonspontaneous (energetically unfavorable)

$\Delta G = 0$ Equilibrium

$\Delta G < 0$ Spontaneous (energetically favorable)

A spontaneous reaction is energetically favorable; it is a "downhill" process. Although spontaneous reactions are energetically favorable, spontaneity is no guarantee that a reaction will occur, nor does it indicate how fast a reaction will occur. Many spontaneous reactions do not occur because they are impeded by kinetic barriers. For example, at STP, the conversion of diamond to graphite is energetically favorable ($\Delta G < 0$). Fortunately for diamond lovers, kinetic barriers prevent this conversion from occurring. Fuel cells, too, are constrained by kinetics. The rate at which electricity can be produced from a fuel cell is limited by several kinetic phenomena. These phenomena are covered in Chapters 3–5. Before

we get to kinetics, however, you need to understand how the electrical work capacity of a fuel cell is translated into a cell *voltage*.

2.3.4 Relationship between Gibbs Free Energy and Voltage

The potential of a system to perform electrical work is measured by voltage (also called *electrical potential*). The electrical work done by moving a charge Q, measured in coulombs, through an electrical potential difference E in volts is

$$W_{elec} = EQ \tag{2.57}$$

If the charge is assumed to be carried by electrons, then

$$Q = nF \tag{2.58}$$

where n is number of moles of electrons transferred and F is Faraday's constant. Combining Equations 2.51, 2.57, and 2.58 yields

$$\Delta \hat{g} = -nFE \tag{2.59}$$

Thus, the Gibbs free energy sets the magnitude of the reversible voltage for an electrochemical reaction. For example, in a hydrogen–oxygen fuel cell, the reaction

$$H_2 + \tfrac{1}{2}O_2 \rightleftharpoons H_2O \tag{2.60}$$

has a Gibbs free-energy change of –237 kJ/mol under standard-state conditions for liquid water product. The reversible voltage generated by a hydrogen–oxygen fuel cell under standard-state conditions is thus

$$
\begin{aligned}
E^0 &= -\frac{\Delta \hat{g}^0_{rxn}}{nF} \\
&= -\frac{-237,000 \text{ J/mol}}{(2 \text{ mol e}^-/\text{mol reactant})(96,485 \text{ C/mol})} \\
&= +1.23 \text{ V}
\end{aligned}
\tag{2.61}
$$

where E^0 is the standard-state reversible voltage and $\Delta \hat{g}^0_{rxn}$ is the standard-state free-energy change for the reaction.

At STP, thermodynamics dictates that the highest voltage attainable from a H_2–O_2 fuel cell is 1.23 V. If we need 10 V, forget about it. In other words, the chemistry of the fuel cell sets the reversible cell voltage. By picking a different fuel cell chemistry, we could establish a different reversible cell voltage. However, most feasible fuel cell reactions have reversible cell voltages in the range of 0.8–1.5 V. To get 10 V from fuel cells, we usually have to stack several cells together in series.

TABLE 2.1. Selected List of Standard Electrode Potentials

Electrode Reaction	E^0 (V)
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	−0.440
$CO_2 + 2H^+ + 2e^- \rightleftharpoons CHOOH_{(aq)}$	−0.196
$2H^+ + 2e^- \rightleftharpoons H_2$	+0.000
$CO_2 + 6H^+ + 6e^- \rightleftharpoons CH_3OH + H_2O$	+0.03
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.229

2.3.5 Standard Electrode Potentials: Computing Reversible Voltages

Although we learned how to calculate cell voltage using Equation 2.59, the cell potentials of many reactions have already been calculated for us in *standard electrode potential* tables. It is often easier to determine reversible voltages using these electrode potential tables. Standard electrode potential tables compare the standard-state reversible voltages of various electrochemical half reactions relative to the hydrogen reduction reaction. In these tables, the standard-state potential of the hydrogen reduction reaction is defined as zero, thus making it easy to compare other reactions.

To illustrate the concept of electrode potentials, a brief list is presented in Table 2.1. A more complete set of electrode potentials is provided in Appendix C.

To find the standard-state voltage produced by a complete electrochemical system, we simply sum all the potentials in the circuit:

$$E^0_{cell} = \sum E^0_{half\ reactions} \tag{2.62}$$

THE QUANTITY *nF*

When studying fuel cells or other electrochemical systems, we will frequently encounter expressions containing the quantity nF. This quantity is our bridge from the world of thermodynamics (where we talk about moles of chemical species) to the world of electrochemistry (where we talk about current and voltage). In fact, the quantity nF expresses one of the most fundamental aspects of electrochemistry: the quantized transfer of electrons, in the form of an electrical current, between reacting chemical species. In any electrochemical reaction, there exists an integer correspondence between the moles of chemical species reacting and the moles of electrons transferred. For example, in the H_2–O_2 fuel cell reaction, 2 mol of electrons is transferred for every mole of H_2 gas reacted. In this case, $n = 2$. To convert this molar quantity of electrons to a quantity of charge, we must multiply n by Avogadro's number ($N_A = 6.022 \times 10^{23}$ electrons/mol) to get the number of electrons and then multiply by the charge per electron ($q = 1.60 \times 10^{-19}$ C/electron) to get the total charge. Thus we have

$$Q = nN_Aq = nF \tag{2.63}$$

What we call Faraday's constant is really the quantity $N_A \times q$:

$$F = N_A \times q = (6.022 \times 10^{23} \text{electrons/mol}) \times (1.60 \times 10^{-19} \text{C/electron})$$

$$= 96,485 \text{ C/mol}$$

Interestingly, the fact that Faraday's constant is a large number has important techno-logical repercussions. Because F is large, a little chemistry produces a lot of electricity. This relationship is one of the factors that make fuel cells technologically feasible.

Students are often confused whether they should base the number of moles of elec-trons transferred (n) in a reaction on a per-mole reactant basis, per-mole product basis, or so on. The answer is that it does not matter as long as you are consistent. For example, consider the reaction
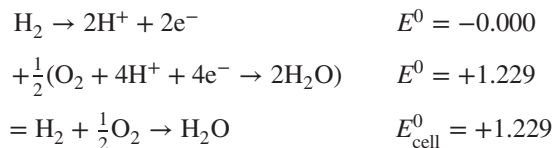
$$A + 2B \rightarrow C + 2e^- \quad \Delta G_{rxn} \tag{2.64}$$
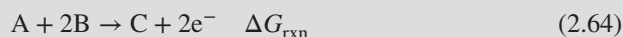
In this reaction, $n = 2$ per mole of A reacted, or per mole of C produced, or per 2 mol of B reacted. If instead n is desired per mole of B reacted, then the reaction stoichiometry must be adjusted as

$$\tfrac{1}{2}A + B \rightarrow \tfrac{1}{2}C + e^- \quad \tfrac{1}{2}\Delta G_{rxn} \tag{2.65}$$

Now, per mole of B reacted, $n = 1$. Also $n = 1$ per 1/2 mol of A reacted or per 1/2 mol of C produced. However, keep in mind that the Gibbs free energy for reaction 2.65 is now $\tfrac{1}{2}\Delta G$ of the original reaction. As long as n and ΔG are kept consistent with the reaction stoichiometry, you should not suffer any confusion.

For example, the standard-state potential of the hydrogen–oxygen fuel cell is deter-mined by
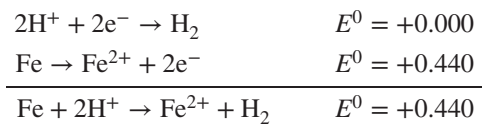
$$H_2 \rightarrow 2H^+ + 2e^- \qquad\qquad E^0 = -0.000$$

$$+\tfrac{1}{2}(O_2 + 4H^+ + 4e^- \rightarrow 2H_2O) \qquad E^0 = +1.229$$

$$= H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \qquad\qquad E^0_{cell} = +1.229$$

Note that we multiply the O_2 reaction by 1/2 to get the correct stoichiometry. However, do not multiply the E^0 values by 1/2. The E^0 values are independent of reaction amounts. Note also that in this calculation we reverse the direction of the hydrogen reaction (in a hydrogen–oxygen fuel cell, hydrogen is oxidized, not reduced). When we reverse the direc-tion of a reaction, we reverse the sign of its potential. For the hydrogen reaction, this makes no difference, since +0.000 V = –0.000 V. However, the standard-state potential of the iron *oxidation* reaction, for example,

$$Fe \rightleftharpoons Fe^{2+} + 2e^- \tag{2.66}$$
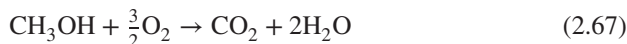
would be +0.440 V.

A complete electrochemical reaction generally consists of two half reactions, a reduction reaction *and* an oxidation reaction. However, electrode potential tables list all reactions as

reduction reactions. For a set of coupled half reactions, how do we know which reaction will spontaneously proceed as the reduction reaction and which reaction will proceed as the oxidation reaction? The answer is found by comparing the *size* of the electrode potentials for the reactions. Because electrode potentials really represent free energies, increasing potential indicates increasing "reaction strength." For a matched pair of electrochemical half reactions, the reaction with the larger electrode potential will occur as written, while the reaction with the smaller electrode potential will occur opposite as written. For example, consider the Fe^{2+}–H^+ reaction couple from the list above. Because the hydrogen reduction reaction has a larger electrode potential compared to the iron reduction reaction (0 V > –0.440 V), the hydrogen reduction reaction will occur as written. The iron reaction will proceed in the opposite direction as written:

$$2H^+ + 2e^- \rightarrow H_2 \qquad E^0 = +0.000$$
$$\underline{Fe \rightarrow Fe^{2+} + 2e^- \qquad E^0 = +0.440}$$
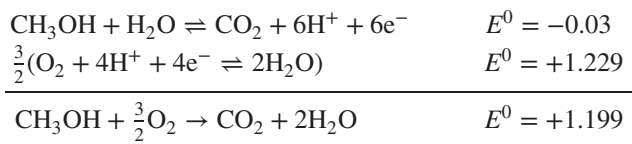$$Fe + 2H^+ \rightarrow Fe^{2+} + H_2 \qquad E^0 = +0.440$$

Thus, thermodynamics predicts that in this system iron will be spontaneously oxidized to Fe^{2+} and hydrogen gas will be evolved, with a net cell potential of +0.440 V. This is the thermodynamically spontaneous reaction direction under standard-state conditions. Any thermodynamically spontaneous electrochemical reaction will have a positive cell potential. Of course, the reaction could be made to occur in the reverse direction if an external voltage greater than 0.440 V is applied to the cell. In this case, a power supply would be doing work to the cell in order to overcome the thermodynamics of the system.

> **Example 2.3** A direct methanol fuel cell uses methanol (CH_3OH) as fuel instead of hydrogen:
>
> $$CH_3OH + \tfrac{3}{2}O_2 \rightarrow CO_2 + 2H_2O \tag{2.67}$$
>
> Calculate the standard-state reversible potential for a direct methanol fuel cell.
>
> *Solution:* We break this overall reaction into two electrochemical half reactions:
>
> $$CH_3OH + H_2O \rightleftharpoons CO_2 + 6H^+ + 6e^- \qquad E^0 = -0.03$$
> $$\underline{\tfrac{3}{2}(O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O) \qquad E^0 = +1.229}$$
> $$CH_3OH + \tfrac{3}{2}O_2 \rightarrow CO_2 + 2H_2O \qquad E^0 = +1.199$$
>
> Thus, the net cell potential for a methanol fuel cell is +1.199 V—almost the same as for a H_2–O_2 fuel cell. Note that although we multiplied the oxygen reduction reaction by $\tfrac{3}{2}$ to get a balanced reaction, we did not multiply the E^0 value by $\tfrac{3}{2}$. The E^0 values are *independent* of reaction amounts.

2.4   PREDICTING REVERSIBLE VOLTAGE OF A FUEL CELL UNDER NON-STANDARD-STATE CONDITIONS

Standard-state reversible fuel cell voltages (E^0 values) are only useful under standard-state conditions (room temperature, atmospheric pressure, unit activities of all species). Fuel cells are frequently operated under conditions that vary greatly from the standard state. For example, high-temperature fuel cells operate at 700–1000°C, automotive fuel cells often operate under 3–5 atm of pressure, and almost all fuel cells cope with variations in the concentration (and therefore activity) of reactant species.

In the following sections, we systematically define how reversible fuel cell voltages are affected by departures from the standard state. First, the influence of temperature on the reversible fuel cell voltage will be explored, then the influence of pressure. Finally, contributions from species activity (concentration) will be delineated, which will result in the formulation of the Nernst equation. In the end, we will have thermodynamic tools to predict the reversible voltage of a fuel cell under any arbitrary set of conditions.

2.4.1   Reversible Voltage Variation with Temperature

To understand how the reversible voltage varies with temperature, we need to go back to our original differential expression for the Gibbs free energy:

$$dG = -S\,dT + V\,dp \tag{2.68}$$

from which we can write

$$\left(\frac{dG}{dT}\right)_p = -S \tag{2.69}$$

For molar reaction quantities, this becomes

$$\left(\frac{d(\Delta\hat{g})}{dT}\right)_p = -\Delta\hat{s} \tag{2.70}$$

We have previously shown that the Gibbs free energy is related to the reversible cell voltage by

$$\Delta\hat{g} = -nFE \tag{2.71}$$

Combining Equations 2.70 and 2.71 allows us to express how the reversible cell voltage varies as a function of temperature:

$$\left(\frac{dE}{dT}\right)_p = \frac{\Delta\hat{s}}{nF} \tag{2.72}$$

We define E_T as the reversible cell voltage at an arbitrary temperature T. At constant pressure, E_T can be calculated by

$$E_T = E^0 + \frac{\Delta\hat{s}}{nF}(T - T_0) \tag{2.73}$$

Generally, we assume $\Delta\hat{s}$ to be independent of temperature. If a more accurate value of E_T is required, it may be calculated by integrating the heat-capacity-related temperature dependence of $\Delta\hat{s}$.

As Equation 2.73 indicates, if $\Delta\hat{s}$ for a chemical reaction is positive, then E_T will increase with temperature. If $\Delta\hat{s}$ is negative, then E_T will decrease with temperature. For most fuel cell reactions $\Delta\hat{s}$ is negative; therefore reversible fuel cell voltages tend to *decrease* with increasing temperature.

For example, consider our familiar H_2–O_2 fuel cell. As can be calculated from the data in Appendix B, $\Delta\hat{s}_{rxn} = -44.34$ J/(mol·K) (for $H_2O_{(g)}$ as product). The variation of cell voltage with temperature is approximated as

$$\begin{aligned} E_T &= E^0 + \frac{-44.34\,\text{J/(mol}\cdot\text{K)}}{(2)(96,485)}(T - T_0) \\ &= E^0 - (2.298 \times 10^{-4}\,\text{V/K})(T - T_0) \end{aligned} \tag{2.74}$$

Thus, for every 100 degrees increase in cell temperature, there is an approximate 23-mV decrease in cell voltage. A H_2–O_2 SOFC operating at 1000 K would have a reversible voltage of around 1.07 V. The temperature variation for the electrochemical oxidation of a number of different fuels is given in Figure 2.5.

Since most reversible fuel cell voltages decrease with increasing temperature, should we operate a fuel cell at the lowest temperature possible? The answer is NO! As you will learn in Chapters 3 and 4, kinetic losses tend to decrease with increasing temperature. Therefore, real fuel cell performance typically *increases* with increasing temperature even though the thermodynamically reversible voltage decreases.

2.4.2   Reversible Voltage Variation with Pressure

Like temperature effects, the pressure effects on cell voltage may also be calculated starting from the differential expression for the Gibbs free energy:

$$dG = -S\,dT + V\,dp \tag{2.75}$$

This time, we note

$$\left(\frac{dG}{dp}\right)_T = V \tag{2.76}$$

Written for molar reaction quantities, this becomes

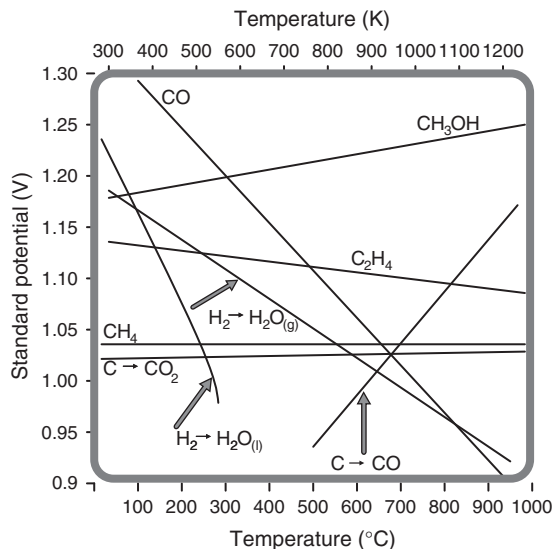$$\left(\frac{d(\Delta\hat{g})}{dp}\right)_T = \Delta\hat{v} \tag{2.77}$$

Figure 2.5. Reversible voltage (E_T) versus temperature for electrochemical oxidation of a variety of fuels. (After Broers and Ketelaar [3].)

We have previously shown that the Gibbs free energy is related to the reversible cell voltage by

$$\Delta\hat{g} = -nFE \tag{2.78}$$

Substituting this equation into Equation 2.77 allows us to express how the reversible cell voltage varies as a function of pressure:

$$\left(\frac{dE}{dp}\right)_T = -\frac{\Delta\hat{v}}{nF} \tag{2.79}$$

In other words, the variation of the reversible cell voltage with pressure is related to the volume change of the reaction. If the volume change of the reaction is negative (if fewer moles of gas are generated by the reaction than consumed, for instance), then the cell voltage will increase with increasing pressure. This is an example of *Le Chatelier's principle*: Increasing the pressure of the system favors the reaction direction that relieves the stress on the system.

Usually, only gas species produce an appreciable volume change. Assuming that the ideal gas law applies, we can write Equation 2.79 as

$$\left(\frac{dE}{dp}\right)_T = -\frac{\Delta n_g RT}{nFp} \tag{2.80}$$

where Δn_g represents the change in the total number of moles of gas upon reaction. If n_p is the number of product moles of gas and n_r is the number of reactant moles of gas, then $\Delta n_g = n_p - n_r$.

Pressure, like temperature, turns out to have a minimal effect on reversible voltage. As you will see in a forthcoming example, pressurizing a H_2–O_2 fuel cell to 3 atm H_2 and 5 atm O_2 increases the reversible voltage by only 15 mV.

2.4.3 Reversible Voltage Variation with Concentration: Nernst Equation

To understand how the reversible voltage varies with concentration, we need to introduce the concept of *chemical potential*. Chemical potential measures how the Gibbs free energy of a system changes as the chemistry of the system changes. Each chemical species in a system is assigned a chemical potential. Formally

$$\mu_i^\alpha = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j\neq i}} \tag{2.81}$$

where μ_i^α is the chemical potential of species i in phase α and $(\partial G/\partial n_i)_{T,p,n_{j\neq i}}$ expresses how much the Gibbs free energy of the system changes for an infinitesimal increase in the quantity of species i (while temperature, pressure, and the quantities of all other species in the system are held constant). When we change the amounts (concentrations) of chemical species in a fuel cell, we are changing the free energy of the system. This change in free energy in turn changes the reversible voltage of the fuel cell. Understanding chemical potential is key to understanding how changes in concentration affect the reversible voltage.

Chemical potential is related to concentration through *activity a*:

$$\mu_i = \mu_i^0 + RT \ln a_i \tag{2.82}$$

where μ_i^0 is the reference chemical potential of species i at standard-state conditions and a_i is the activity of species i. The activity of a species depends on its chemical nature:

- *For an ideal gas*, $a_i = p_i/p^0$, where p_i is the partial pressure of the gas and p^0 is the standard-state pressure (1 atm). For example, the activity of oxygen in air at 1 atm is approximately 0.21. The activity of oxygen in air pressurized to 2 atm would be 0.42. Since we accept $p^0 = 1$ atm, we are often lazy and write $a_i = p_i$, recognizing that p_i is a *unitless* gas partial pressure.
- *For a nonideal gas*, $a_i = \gamma(p_i/p^0)$, where γ is an activity coefficient describing the departure from ideality ($0 < \gamma_i < 1$).
- *For a dilute (ideal) solution*, $a_i = c_i/c^0$, where c_i is the molar concentration of the species and c^0 is the standard-state concentration (1 M = 1 mol/L). For example, the activity of Na^+ ions in 0.1 M NaCl is 0.10.
- *For nonideal solutions*, $a_i = \gamma(c_i/c^0)$. Again, we use γ to describe departures from ideality ($0 < \gamma < 1$).
- *For pure components*, $a_i = 1$. For example, the activity of gold in a chunk of pure gold is 1. The activity of platinum in a platinum electrode is 1. The activity of liquid water is usually taken as 1.
- *For electrons in metals*, $a_i = 1$.

Combining Equations 2.81 and 2.82, it is possible to calculate changes in the Gibbs free energy for a system of i chemical species by

$$dG = \sum_i \mu_i \, dn_i = \sum_i (\mu_i^0 + RT \ln a_i) \, dn_i \tag{2.83}$$

WHAT IS CHEMICAL POTENTIAL?

Recall from Section 2.1.5 that U, F, H, and G are extrinsic quantities and therefore scale with the size or number of atoms in the system. In our initial discussions of these thermodynamic potentials, however, this explicit composition dependence was not included. Initially, we defined each thermodynamic potential using two independent variables only. In order to accommodate the thermodynamic dependence on the number of atoms in a system, we must explicitly add n_i (the number of atoms or molecules of species i) as a third variable. Thus, the four thermodynamic potentials actually depend on three independent variables as $U = U(S, V, n_i)$, $G = G(T, p, n_i)$, $H = H(S, p, n_i)$, and $F = F(T, V, n_i)$.

The quantity that describes how U, F, H, and G depend on n_i is called the chemical potential, μ_i. The chemical potential has a logarithmic dependence on the concentration (number per volume) or the activity (normalized concentration) of species i in a system:

$$\mu_i = \mu_i^0 + RT \ln a_i$$

This logarithmic dependence can be understood based on the relative impact of adding atoms when a system is small compared to when a system is large. When a thermodynamic system is very small, that is, the number of species in the system is low, adding or subtracting a few particles will have a big impact on the activity and hence the chemical potential. Conversely, if the number of species in the system is very large, a small change in the number of species will not have a big impact on the activity or the chemical potential. In other words, the magnitude of change in chemical potential depends on how many atoms or molecules of species i are present. This "size sensitivity" is captured by the mathematical form of the chemical potential, which incorporates the composition dependence inside a natural logarithm.

As will be discussed soon in Section 2.4.4, the concept of the chemical potential needs to be further expanded when dealing with charged particles. Charged particles are sensitive not only to chemical composition but also to electric fields. In this situation, we can formally expand the concept of chemical potential into *electrochemical* potential by adding the electrostatic potential of the charged particles to the chemical potential. In its most basic definition, the electrochemical potential represents the work required to assemble 1 mol of ions from some standard state and bring it to a defined chemical concentration and electrical potential.

Consider an arbitrary chemical reaction placed on a molar basis for species A in the form

$$1A + bB \rightleftharpoons mM + nN \tag{2.84}$$

where A and B are reactants, M and N are products, and 1, b, m, and n represent the number of moles of A, B, M, and N, respectively. On a molar basis for species A, $\Delta \hat{g}$ for this reaction may be calculated from the chemical potentials of the various species participating in the reaction (assuming a single phase):

$$\Delta \hat{g} = (m\mu_M^0 + n\mu_N^0) - (\mu_A^0 + b\mu_B^0) + RT \ln \frac{a_M^m a_N^n}{a_A^1 a_B^b} \tag{2.85}$$

Recognizing that the lumped standard-state chemical potential terms represent the standard-state molar free-energy change for the reaction, $\Delta \hat{g}^0$, the equation can be simplified to a final form:

$$\Delta \hat{g} = \Delta \hat{g}^\circ + RT \ln \frac{a_M^m a_N^n}{a_A^1 a_B^b} \tag{2.86}$$

This equation, called the van't Hoff isotherm, tells how the Gibbs free energy of a system changes as a function of the activities (read concentrations or gas pressures) of the reactant and product species.

From previous thermodynamic explorations (Section 2.3.4), we know that the Gibbs free energy and the reversible cell voltage are related:

$$\Delta \hat{g} = -nFE \tag{2.87}$$

Combining Equations 2.86 and 2.87 allows us to see how the reversible cell voltage varies as a function of chemical activity:

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_M^m a_N^n}{a_A^1 a_B^b} \tag{2.88}$$

For a system with an arbitrary number of product and reactant species, this equation takes the general form

$$E = E^0 - \frac{RT}{nF} \ln \frac{\prod a_{products}^{v_i}}{\prod a_{reactants}^{v_i}} \tag{2.89}$$

Always take care to raise the activity of each species by its corresponding stoichiometric coefficient (v_i). For example, if a reaction involves $2Na^+$, the activity of Na^+ must be raised to the power of 2 (e.g., $a_{Na^+}^2$). Importantly, only chemical species that are actually participating as reactants or products in the electrochemical reaction appear in the Nernst equation (e.g., O_2, H_2, and H_2O for a H_2 fuel cell). The activities or partial pressures of unreactive, inert, or diluent species (such as N_2 in air) should not be included.

This important result is known as the Nernst equation. The Nernst equation outlines how reversible electrochemical cell voltages vary as a function of species concentration, gas pressure, and so on. This equation is the centerpiece of fuel cell thermodynamics. Remember it forever.

As an example of the utility of this equation, we will apply it to the familiar hydrogen–oxygen fuel cell reaction:

$$H_2 + \tfrac{1}{2}O_2 \rightleftharpoons H_2O \tag{2.90}$$

We write the Nernst equation for this reaction as

$$E = E^0 - \frac{RT}{2F} \ln \frac{a_{H_2O}}{a_{H_2} a_{O_2}^{1/2}} \tag{2.91}$$

Following our activity guidelines, we replace the activities of hydrogen and oxygen gases by their unitless partial pressures ($a_{H_2} = p_{H_2}, a_{O_2} = p_{O_2}$). If the fuel cell is operated below 100°C, so that liquid water is produced, we set the activity of water to unity ($a_{H_2O} = 1$). This yields

$$E = E^0 - \frac{RT}{2F} \ln \frac{1}{p_{H_2} p_{O_2}^{1/2}} \tag{2.92}$$

From this equation, it is apparent that pressurizing the fuel cell in order to increase the reactant gas partial pressures will increase the reversible voltage. However, because the pressure terms appear within a natural logarithm, the voltage improvements are slight. For example, if we operate a room temperature H_2–O_2 fuel cell on 3 atm pure H_2 and 5 atm air, thermodynamics predicts a reversible cell voltage of 1.254 V:

$$E = 1.229 - \frac{(8.314)(298.15)}{(2)(96,485)} \ln \frac{1}{(3)(5 \times 0.21)^{1/2}} \tag{2.93}$$

$$= 1.254 \text{ V}$$

PRESSURE, TEMPERATURE, AND NERNST EQUATION

The Nernst equation accounts for the same pressure effects that were previously discussed in Section 2.4.2. Either Equation 2.89 or Equation 2.79 can be used to determine how the reversible voltage varies with pressure. If you use one, do not also use the other. The Nernst equation allows you to calculate voltage effects directly in terms of reactant and product pressures, while Equation 2.79 requires the volume change for the reaction (which you will have to express in terms of reactant gas pressures using the ideal gas law). The Nernst equation is generally more convenient.

Although temperature enters into the Nernst equation as a variable, the Nernst equation *does not* fully account for how the reversible voltage varies with temperature.

At an arbitrary temperature $T \neq T_0$, the Nernst equation must be modified as

$$E = E_T - \frac{RT}{nF} \ln \frac{\prod a_{products}^{v_i}}{\prod a_{reactants}^{v_i}} \tag{2.94}$$

where E_T is given from Equation 2.73 as

$$E_T = E^0 + \frac{\Delta \hat{s}}{nF}(T - T_0) \tag{2.95}$$

Thus, the full expression describing how the reversible cell voltage varies with temperature, pressure, and activity can be written as

$$E = E^0 + \frac{\Delta \hat{s}}{nF}(T - T_0) - \frac{RT}{nF} \ln \frac{\prod a_{products}^{v_i}}{\prod a_{reactants}^{v_i}} \tag{2.96}$$

In summary, to properly account for both temperature and pressure changes, make sure to use Equation 2.96 or Equations 2.73 and 2.79.

This is not much of an increase for all the extra work of pressurizing the fuel cell stack! From a thermodynamic perspective it is not worth the trouble; however, as you will learn in Chapters 3 and 5, there may be kinetic reasons to pressurize a fuel cell.

In contrast, what does the Nernst equation indicate about low-pressure operation? Perhaps we are worried that almost all fuel cells operate on air instead of pure oxygen. Air is only about 21% oxygen, so at 1 atm, the partial pressure of oxygen in air is only 0.21. How much does this affect the reversible voltage of a room temperature H_2–O_2 fuel cell?

$$
\begin{aligned}
E &= 1.229 - \frac{(8.314)(298.15)}{(2)(96,485)} \ln \frac{1}{(1)(0.21)^{1/2}} \\
&= 1.219\,\text{V}
\end{aligned}
\tag{2.97}
$$

Operation in air drops the reversible voltage by only 10 mV. Again, kinetic factors can introduce more deleterious penalties for air operation. However, as far as thermodynamics is concerned, air operation is not a problem.

2.4.4 Concentration Cells

The curious phenomenon of the concentration cell highlights some of the most fascinating implications of the Nernst equation. In a concentration cell, the *same* chemical species is present at both electrodes but at different concentrations. Amazingly, such a cell will develop a voltage because the concentration (activity) of the chemical species is different
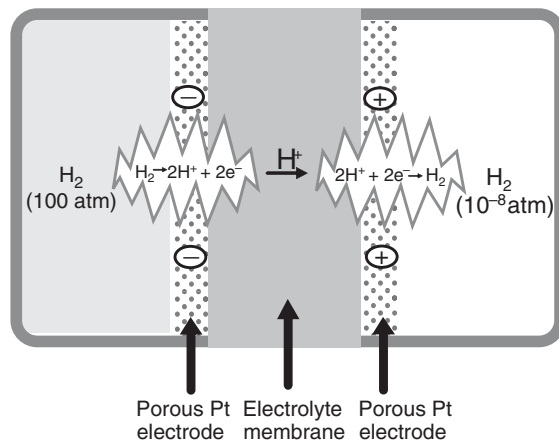
Figure 2.6. Hydrogen concentration cell. A high-pressure hydrogen compartment and a low-pressure hydrogen compartment are separated by a platinum–electrolyte–platinum membrane structure. This device will develop a voltage due to the difference in the chemical potential of hydrogen between the two compartments.

at one electrode versus the other electrode. For example, *a salt water battery* consisting of salt water at one electrode and freshwater at the other will produce a voltage because the concentration of salt differs at the two electrodes.

As a second example, consider the *hydrogen concentration cell* shown in Figure 2.6, which consists of a pressurized hydrogen fuel compartment and an evacuated ultra-low-pressure vacuum compartment separated by a composite platinum–electrolyte–platinum membrane structure. This "hydrogen fuel cell" contains no oxygen to react with the hydrogen, yet it will still produce a significant voltage. Thus, you could even use this fuel cell in outer space, where oxygen is unavailable. The thermodynamic voltage produced by the cell is related to the concentration of hydrogen in the fuel compartment relative to the vacuum compartment. For example, if the hydrogen fuel compartment is pressurized to 100 atm H_2 and the vacuum compartment is evacuated to 10^{-8} atm (presumably what remains will be mostly H_2), then this device will exhibit a voltage as determined by the Nernst equation:

$$E = 0 - \frac{(8.314)(298.15)}{(2)(96,485)} \ln \frac{10^{-8}}{100}$$

$$= 0.296 \, \text{V}$$

(2.98)

At room temperature, we can extract almost 0.3 V just by exploiting a difference in hydrogen concentration. How is this possible? A voltage develops because the chemical potential of the hydrogen on one side of the membrane is dramatically different from the chemical potential of the hydrogen on the other side of the membrane. Driven by the chemical potential gradient, some of the hydrogen in the fuel compartment decomposes on the platinum catalyst electrode to protons and electrons. The protons flow through the

electrolyte to the vacuum compartment, where they react with electrons in the second plat-inum catalyst electrode to reproduce hydrogen gas. If the two platinum electrodes are not connected, then very quickly excess electrons will accumulate on the fuel side, while elec-trons will be depleted on the vacuum side, setting up an electrical potential gradient. This electrical potential gradient retards further movement of hydrogen from the fuel compart-ment to the vacuum compartment. Equilibrium is established when this electrical potential gradient builds up sufficiently to exactly balance the chemical potential gradient. (This is very similar to the "built-in voltage" that occurs at semiconductor p–n junctions.) The chem-ical potential difference created by the vastly different hydrogen concentrations at the two electrodes is offset by the development of an electrical potential, which is equal but opposite in magnitude. The concept of chemical and electrical potentials offsetting one another to maintain thermodynamic equilibrium is summarized by a quantity called the *electrochem-ical potential*:

$$\tilde{\mu} = \mu_i + z_i F\phi_i = \mu_i^0 + RT \ln a_i + z_i F\phi_i \tag{2.99}$$

where $\tilde{\mu}_i$ is the electrochemical potential of species i, μ_i is the chemical potential of species i, z_i is the charge number on the species (e.g., $z_{e^-} = -1$, $z_{Cu^{2+}} = +2$), F is Faraday's constant, and ϕ_i is the electrical potential experienced by species i. At equilibrium, the net change in the electrochemical potential for the species taking part in the system must be zero; in other words, the chemical and electrical potentials offset one another. For a reaction

$$\left(\sum_i v_i \tilde{\mu}_i\right)_{\text{products}} - \left(\sum_i v_i \tilde{\mu}_i\right)_{\text{reactants}} = 0$$

$$\left(\sum_i v_i \mu_i\right)_{\text{products}} - \left(\sum_i v_i \mu_i\right)_{\text{reactants}} = -z_i F \Delta\phi_i \qquad \text{(at equilibrium)} \tag{2.100}$$

Compare this to Equation 2.59. Do you see how these two equations are really expressing the same thing? Following procedures analogous to Equations 2.82, 2.83, 2.84–2.86, we can rederive the Nernst equation from the basis of the electrochemical potential:

$$\tilde{\mu}_i = \mu_i^0 + RT \ln a_i + z_i F\phi_i = 0 \tag{2.101}$$

The trick to rederiving the Nernst equation is to write out the change in electrochemical potential for the reactants being converted into products while also including the change in electrochemical potential for the electrons as they move from the anode to the cathode. Solving for the difference in the electrical potential for the electrons at the cathode versus the anode ($\Delta\phi_{e^-}$) gives the cell potential E. If n moles of electrons move from the anode to the cathode per mole of chemical reaction, then

$$\Delta\phi_{e^-} = E = -\frac{\Delta\hat{g}^0}{nF} - \frac{RT}{nF} \ln \frac{\prod a_{\text{products}}^{v_i}}{\prod a_{\text{reactants}}^{v_i}} \tag{2.102}$$

which gives

$$E = E^0 - \frac{RT}{nF} \ln \frac{\prod a_{\text{products}}^{v_i}}{\prod a_{\text{reactants}}^{v_i}} \tag{2.103}$$

The details of this derivation are left as a homework problem at the end of this chapter.

Based on this discussion of concentration cells, you should see that it is possible to think of an H_2–O_2 fuel cell as simply a hydrogen concentration cell. Oxygen is used at the cathode merely as a convenient way to chemically "tie up" hydrogen. The O_2 gas keeps the cathode concentration of hydrogen to extremely low effective levels, allowing a significant thermodynamic voltage to be produced.

ELECTROCHEMICAL EQUILIBRIUM

This dialogue box provides additional details on the calculation of electrochemical equilibria. As an example, we will derive the Nernst equation for the Cu^{2+} concentration cell illustrated in Figure 2.7.
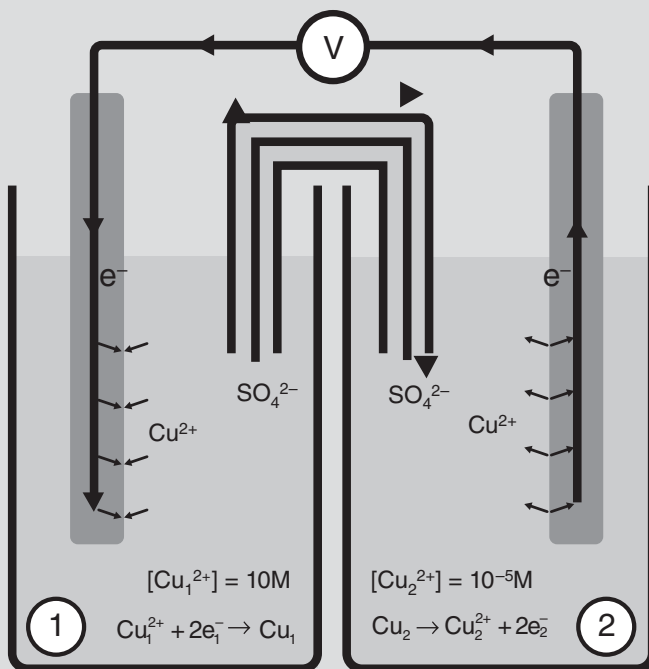

Figure 2.7. Copper concentration cell.

In this concentration cell, we have two electrolyte baths containing different concentrations of Cu^{2+} ions (with counterbalancing SO_4^{2-} ions for ionic charge balance),

connected by an SO_4^{2-} conducting salt bridge. Copper electrodes are placed in both baths, and a voltage potential difference is established between the two electrodes, which exactly counterbalances the chemical potential difference caused by the Cu^{2+} concentration difference between the two baths. Because of the high concentration of Cu^{2+} ions in bath 1, we have the reaction

$$Cu_1^{2+} + 2e_1^- \rightarrow Cu_1 \tag{2.104}$$
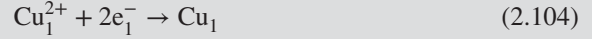
Copper ions precipitate from solution, consuming electrons in the process and leaving the electrode positively charged. In bath 2, the opposite reaction occurs due to the low concentration of Cu^{2+} ions:

$$Cu_2 \rightarrow Cu_2^{2+} + 2e_2^- \tag{2.105}$$
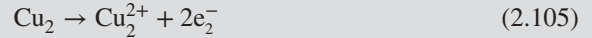
Copper dissolves from electrode 2, which therefore builds up a negative charge. The buildup of charge between electrodes 1 and 2 proceeds until the voltage is sufficiently large to exactly offset the chemical potential difference due to the Cu^{2+} ion imbalance between baths 1 and 2. At this point, electrochemical equilibrium has been established.

In order to mathematically describe this electrochemical equilibrium, we must employ Equation 2.100. The overall reaction occurring in this concentration cell is

$$Cu_2 + Cu_1^{2+} + 2e_1^- \rightarrow Cu_2^{2+} + 2e_2^- + Cu_1 \tag{2.106}$$
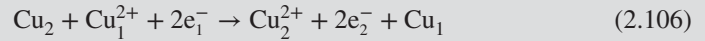
This is simply the sum of the two half-cell reactions above. The next step is to write the electrochemical potentials for each of the species in this overall reaction (following Equation 2.99):

$$\tilde{\mu}_{Cu^{2+}}^1 = \mu_{Cu^{2+}}^0 + RT \ln a_{Cu^{2+}}^1 + 2F\varphi_{Cu^{2+}}^1$$
$$\tilde{\mu}_{Cu^{2+}}^2 = \mu_{Cu^{2+}}^0 + RT \ln a_{Cu^{2+}}^2 + 2F\varphi_{Cu^{2+}}^2$$
$$\tilde{\mu}_{e^-}^1 = \mu_{e^-}^0 + RT \ln a_{e^-}^1 - 1F\varphi_{e^-}^1 = \mu_{e^-}^0 - 1F\varphi_{e^-}^1$$
$$\tilde{\mu}_{e^-}^2 = \mu_{e^-}^0 + RT \ln a_{e^-}^2 - 1F\varphi_{e^-}^2 = \mu_{e^-}^0 - 1F\varphi_{e^-}^2$$
$$\tilde{\mu}_{Cu}^1 = \mu_{Cu}^0 + RT \ln a_{Cu}^1 = \mu_{Cu}^0$$
$$\tilde{\mu}_{Cu}^2 = \mu_{Cu}^0 + RT \ln a_{Cu}^2 = \mu_{Cu}^0 \tag{2.107}$$

In writing these equations, we've used $z = +2$ for Cu^{2+} ions, and $z = -1$ for e^-. The activity of electrons in metals is defined as 1, as is the activity of a pure component (Cu), so these terms vanish from the equations. We now apply Equations 2.113 to the overall reaction 2.106, yielding

$$(\mu_{Cu}^0 + \mu_{Cu^{2+}}^0 + RT \ln a_{Cu^{2+}}^2 + 2F\varphi_{Cu^{2+}}^2 + 2\mu_{e^-}^0 - 2F\varphi_{e^-}^2)$$
$$- (\mu_{Cu}^0 + \mu_{Cu^{2+}}^0 + RT \ln a_{Cu^{2+}}^1 + 2F\varphi_{Cu^{2+}}^1 + 2\mu_{e^-}^0 - 2F\varphi_{e^-}^1) = 0 \tag{2.108}$$

Note that we have multiplied the electrochemical potentials of the electron terms by 2 since in each case the stoichiometric coefficient for electrons is 2. Canceling terms and rearranging the equation yields

$$RT \ln a^1_{Cu^{2+}} + 2F\varphi^1_{Cu^{2+}} - RT \ln a^2_{Cu^{2+}} - 2F\varphi^2_{Cu^{2+}} = 2F(\varphi^1_{e-} - \varphi^2_{e-}) \qquad (2.109)$$

Now comes an important point: The salt bridge connecting the two baths maintains ionic charge equilibrium. In other words, when Cu^{2+} ions are consumed in bath 1 and created in bath 2, the ion bridge allows counterbalancing SO_4^{2-} ions to move from bath 1 to bath 2, thereby maintaining zero net ionic charge in both baths. Mathematically, this means $\varphi^1_{Cu^{2+}} = \varphi^2_{Cu^{2+}}$. Applying this final simplification yields

$$RT \ln \frac{a^1_{Cu^{2+}}}{a^2_{Cu^{2+}}} = 2F(\varphi^1_{e-} - \varphi^2_{e-}) = 2FE \qquad (2.110)$$

where $(\varphi^1_{e-} - \varphi^2_{e-})$ represents the equilibrium electrical potential (voltage) difference established between the two electrodes due to the Cu^{2+} ion concentration difference between the two baths. This final equation result is the Nernst equation for this concentration cell.

2.4.5 Summary

Let us briefly summarize the effects of non-standard-state conditions on reversible electrochemical cell voltages. In the past few pages, we have used classical thermodynamics to predict how changes in temperature, pressure, and chemical composition affect the reversible voltages of fuel cells. (Incidentally, these relations are equally applicable to all electrochemical systems, not just fuel cells.)

- The variation of the reversible cell voltage with temperature is

$$\left(\frac{dE}{dT} \right)_p = \frac{\Delta \hat{s}}{nF} \qquad (2.111)$$

- The variation of the reversible cell voltage with pressure is

$$\left(\frac{dE}{dp} \right)_T = -\frac{\Delta n_g RT}{nFp} = -\frac{\Delta \hat{v}}{nF} \qquad (2.112)$$

- The variation of the reversible cell voltage with chemical activity (chemical composition, concentration, etc.) is given by the Nernst equation:

$$E = E^0 - \frac{RT}{nF} \ln \frac{\prod a^{v_i}_{products}}{\prod a^{v_i}_{reactants}} \qquad (2.113)$$

The Nernst equation accounts for the pressure effects on reversible cell voltage (it supersedes Equation 2.112) but does not fully account for the temperature effects. When $T \neq T_0$, E^0 in the Nernst equation should be replaced by E_T. *Importantly, only electrochemically active species appear in the Nernst equation (e.g., O_2, H_2, and H_2O for a H_2 fuel cell). The activities or partial pressures of unreactive, inert, or diluent species (such as N_2 in air) should not be included.*

These equations give us the ability to predict the reversible voltage of a fuel cell under an arbitrary set of conditions.

2.5   FUEL CELL EFFICIENCY

For any energy conversion device, efficiency is of great importance. Central to a discussion of efficiency are the concepts of "ideal" (or reversible) efficiency and "real" (or practical) efficiency. Although you might be tempted to think that the ideal efficiency of a fuel cell should be 100%, this is not true. Just as thermodynamics tells us that the electrical work available from a fuel cell is limited by ΔG, the ideal efficiency of a fuel cell is also limited by ΔG. The story for real fuel cell efficiency is even worse. A real fuel cell must always be less efficient than an ideal fuel cell because real fuel cells incur nonideal irreversible losses during operation. A discussion of real fuel cell efficiency motivates forthcoming chapters, where these non-thermodynamic losses are discussed.

2.5.1   Ideal Reversible Fuel Cell Efficiency

We define the *efficiency*, ε, of a conversion process as the amount of useful energy that can be extracted from the process relative to the total energy evolved by that process:

$$\varepsilon = \frac{\text{useful energy}}{\text{total energy}} \tag{2.114}$$

If we wish to extract work from a chemical reaction, the efficiency is

$$\varepsilon = \frac{\text{work}}{\Delta \hat{h}} \tag{2.115}$$

For a fuel cell, recall that the maximum amount of energy available to do work is given by the Gibbs free energy. Thus, the reversible efficiency of a fuel cell can be written as

$$\varepsilon_{\text{thermo, fc}} = \frac{\Delta \hat{g}}{\Delta \hat{h}} \tag{2.116}$$

At room temperature and pressure, the H_2–O_2 fuel cell has $\Delta \hat{g}^0 = -237.17$ kJ/mol and $\Delta \hat{h}^0_{\text{HHV}} = -285.83$ kJ/mol. This yields a 83% reversible HHV efficiency for the H_2–O_2 fuel cell at STP:

$$\varepsilon_{\text{thermo, fc}} = \frac{-237.17}{-285.83} = 0.83 \tag{2.117}$$

In contrast to a fuel cell, the maximum theoretical efficiency of a conventional heat/expansion engine is described by the Carnot cycle. This efficiency may be derived from classical thermodynamics. We do not repeat the derivation here, but we provide the result:

$$\varepsilon_{\text{Carnot}} = \frac{T_H - T_L}{T_H} \tag{2.118}$$

HIGHER HEATING VALUE EFFICIENCY

To convert water from the liquid to the vapor state requires heat input. The quantity of heat required is called the latent heat of vaporization. Due to this latent heat of vaporization, the $\Delta \hat{h}_{\text{rxn}}$ for a hydrogen–oxygen fuel cell is significantly different, depending on whether vapor or liquid water product is assumed. When liquid water is produced, $\Delta \hat{h}_{\text{rxn}}^0 = -286$ kJ/mol; when water vapor is produced, $\Delta \hat{h}_{\text{rxn}}^0 = -241$ kJ/mol. Basically, the difference between these two numbers tells us that more total heat is recoverable if the product water can be condensed to the liquid form. The extra heat recovered by condensing steam to liquid water is precisely the latent heat of vaporization. Because condensation to liquid water results in more heat recovery, the $\Delta \hat{h}_{\text{rxn}}^0$ involving liquid water is called the higher heating value (HHV), while the $\Delta \hat{h}_{\text{rxn}}^0$ involving water vapor is called the lower heating value (LHV).

Which of these values should be used in computing a fuel cell's efficiency? The most equitable calculations of fuel cell efficiency use the HHV. Using the HHV instead of the LHV is appropriate because it acknowledges the true total heat that could theoretically be recovered from the hydrogen combustion reaction. Use of the LHV will result in higher, but perhaps misleading, efficiency numbers.

All calculations and examples in this book will make use of the HHV. Thus, we should rewrite Equation 2.116 to explicitly reflect this fact:

$$\varepsilon_{\text{thermo, fc}} = \frac{\Delta \hat{g}}{\Delta \hat{h}_{\text{HHV}}} \tag{2.119}$$

In these efficiency calculations, it is important to note that $\Delta \hat{g}$ should still be calculated by properly accounting for phase transitions. Thus, for a hydrogen–oxygen fuel cell operating above 100°C, the calculation of $\Delta \hat{g}$ should use formation enthalpies and entropies for water vapor. Below 100°C, the calculation of $\Delta \hat{h}_{\text{HHV}}$ should use the formation enthalpies and entropies for liquid water. You should recognize that calculating $\Delta \hat{g}$ based on water vapor above 100°C, while simultaneously using $\Delta \hat{h}_{\text{HHV}}$ (based on liquid water) for efficiency calculations, does not represent a contradiction. What this calculation says is that, in a fuel cell operating above 100°C, we are losing the ability to convert the latent heat of vaporization of the product water into useful work.

In this expression, T_H is the maximum temperature of the heat engine and T_L is the rejection temperature of the heat engine. For a heat engine that operates at 400°C (673 K) and rejects heat at 50°C (323 K), the reversible efficiency is 52%.
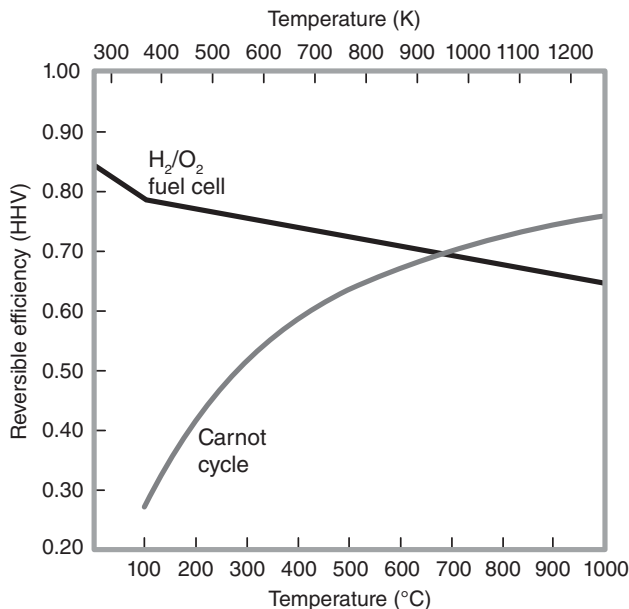
Figure 2.8. Reversible HHV efficiency of H_2–O_2 fuel cell compared to reversible efficiency of heat engine (Carnot cycle, rejection temperature 273.15 K). Fuel cells hold a significant thermodynamic efficiency advantage at low temperature but lose this advantage at higher temperatures. The kink in the fuel cell efficiency curve at 100°C arises from the entropy difference between liquid water and water vapor (consider the $H_2O_{(l)}$ vs. $H_2O_{(g)}$ curves from Figure 2.5).

From the Carnot equation, it is apparent that the reversible efficiency of a heat engine *improves* as the operating temperature increases. In contrast, the reversible efficiency of a fuel cell tends to *decrease* as the operating temperature increases.

As an example, the reversible HHV efficiency of an H_2–O_2 fuel cell is compared to the reversible efficiency of a heat engine as a function of temperature in Figure 2.8. Fuel cells hold a significant thermodynamic efficiency advantage at low temperature but lose this advantage at higher temperatures. Note the kink in the fuel cell efficiency curve at 100°C. This change in slope arises from the entropy difference between liquid water and water vapor.

2.5.2   Real (Practical) Fuel Cell Efficiency

As mentioned previously, the real efficiency of a fuel cell must always be less than the reversible thermodynamic efficiency. The two major reasons are:

1. Voltage losses
2. Fuel utilization losses

The real efficiency of a fuel cell, ε_{real}, may be calculated as

$$\varepsilon_{real} = (\varepsilon_{thermo}) \times (\varepsilon_{voltage}) \times (\varepsilon_{fuel}) \qquad (2.120)$$

where ε_{thermo} is the reversible thermodynamic efficiency of the fuel cell, $\varepsilon_{voltage}$ is the voltage efficiency of the fuel cell, and ε_{fuel} is the fuel utilization efficiency of the fuel cell. Each of these terms is briefly discussed:

- The *reversible thermodynamic efficiency*, ε_{thermo}, was described in the previous section. It reflects how, even under ideal conditions, not all the enthalpy contained in the fuel can be exploited to perform useful work.
- The *voltage efficiency of the fuel cell*, $\varepsilon_{voltage}$, incorporates the losses due to irreversible kinetic effects in the fuel cell. Recall from Section 1.7 that these losses are captured in the operational i–V curve of the fuel cell. The voltage efficiency of a fuel cell is the ratio of the real operating voltage of the fuel cell (V) to the thermodynamically reversible voltage of the fuel cell (E):

$$\varepsilon_{voltage} = \frac{V}{E} \qquad (2.121)$$

  Note that the operating voltage of a fuel cell depends on the current (i) drawn from the fuel cell, as given by the i–V curve. Therefore, $\varepsilon_{voltage}$ will change depending on the current drawn from the cell. The higher the current load, the lower the voltage efficiency. Therefore, fuel cells are *most efficient at low load*. This is in direct contrast to combustion engines, which are generally most efficient at maximum load.

- The *fuel utilization efficiency*, ε_{fuel}, accounts for the fact that not all of the fuel provided to a fuel cell will participate in the electrochemical reaction. Some of the fuel may undergo side reactions that do not produce electric power. Some of the fuel will simply flow through the fuel cell without ever reacting. The fuel utilization efficiency, then, is the ratio of the fuel used by the cell to generate electric current versus the total fuel provided to the fuel cell. If i is the current generated by the fuel cell (A) and v_{fuel} is the rate at which fuel is supplied to the fuel cell (mol/s), then

$$\varepsilon_{fuel} = \frac{i/nF}{v_{fuel}} \qquad (2.122)$$

  If an overabundance of fuel is supplied to a fuel cell, it will be wasted, as reflected in ε_{fuel}. Fuel cells are typically operated in either a *constant-flow-rate* condition, or a *constant-stoichiometry* condition. In the constant-flow-rate condition, a constant amount of fuel is supplied to the cell regardless of how much it actually needs at a particular current density. Typically, sufficient fuel is provided to ensure that the cell is not starved at maximum current density. However, this means that significant amounts of fuel will be wasted when the fuel cell is operating at lower current densities.
  More often, the supply of fuel to a fuel cell is adjusted according to the current so that the fuel cell is always supplied with just a bit more fuel than it needs at any load. Fuel cells operated in this manner are at *constant stoichiometry*. For example, a fuel

cell supplied with 1.5 times more fuel than would be required for 100% fuel utilization is operating at 1.5 times stoichiometric. (The stoichiometric factor λ for this fuel cell is 1.5.) For fuel cells operating under a stoichiometric condition, fuel utilization is independent of current, and we can write the fuel utilization efficiency as

$$\varepsilon_{\text{fuel}} = \frac{1}{\lambda} \quad \text{where } \lambda = \left(\frac{v_{\text{fuel}}}{i/nF}\right) \tag{2.123}$$

Combining effects of thermodynamics, irreversible kinetic losses, and fuel utilization losses, we can write the practical efficiency of a real fuel cell as

$$\varepsilon_{\text{real}} = \left(\frac{\Delta\hat{g}}{\Delta\hat{h}_{\text{HHV}}}\right)\left(\frac{V}{E}\right)\left(\frac{i/nF}{v_{\text{fuel}}}\right) \tag{2.124}$$

For a fuel cell operating under a constant-stoichiometry condition, this equation simplifies to

$$\varepsilon_{\text{real}} = \left(\frac{\Delta\hat{g}}{\Delta\hat{h}_{\text{HHV}}}\right)\left(\frac{V}{E}\right)\left(\frac{1}{\lambda}\right) \tag{2.125}$$

As illustrated in Figure 2.9, operation under a constant-stoichiometry condition versus a constant-flow-rate condition has significant repercussions on fuel cell efficiency. Under a
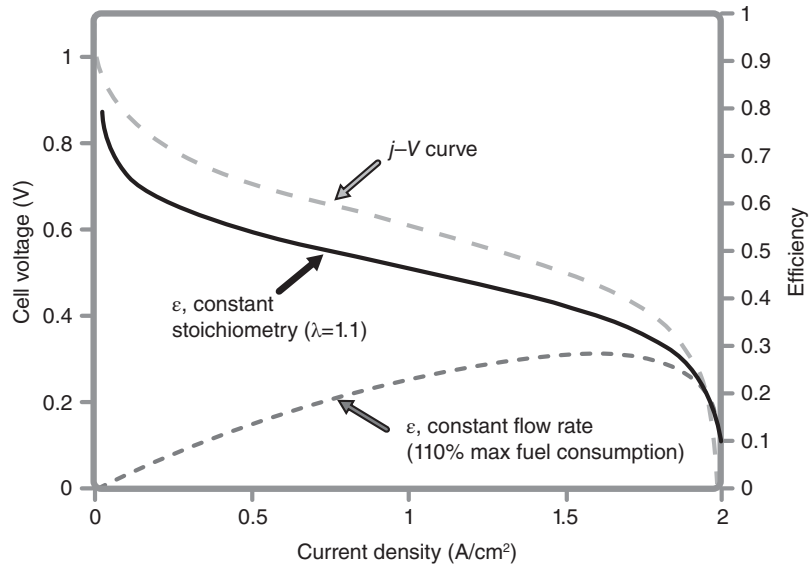

Figure 2.9. Fuel cell efficiency under constant-stoichiometry versus constant-flow-rate conditions. Under a constant-stoichiometry condition ($\lambda = 1.1$), the fuel cell efficiency curve follows the fuel cell j–V curve, and efficiency is highest at low current density. Under a constant-flow-rate condition (in this case, 110% of the rate required at maximum current), fuel cell efficiency is poor at low current densities (because most of the fuel is wasted) and reaches a maximum at high current densities when most of the fuel is used.

constant-stoichiometry condition, the fuel cell efficiency curve follows the shape of the fuel cell j–V curve (because the fuel flow rate is constantly adjusted to match the fuel cell current), and therefore *efficiency is highest at low current density*. In contrast, under a constant-flow condition, *efficiency is lowest at low current density* because most of the fuel is wasted. In general, then, constant-stoichiometry operation is preferred under most circumstances, but this requires a system control scheme so that the fuel flow rate can be continuously adjusted to match the fuel cell current.

2.6 THERMAL AND MASS BALANCES IN FUEL CELLS

A fuel cell is an energy *conversion* device, not an energy *creation* device (energy creation would violate the first law of thermodynamics). A fuel cell converts chemical energy into electrical energy (with some inevitable waste heat, dictated, as we have learned, by entropy and the second law of thermodynamics). A hydrogen fuel cell, for example, consumes hydrogen and oxygen to generate water, heat, and electricity. Although hydrogen and oxygen are consumed during operation, water, heat, and electricity are produced in correspondingly proportionate quantities such that the laws of energy and mass conservation are maintained. It is important to be able to account for the exact quantities of fuel, oxidant, water, heat, and electricity entering and/or leaving a fuel cell. Fortunately, this thermal and mass balance accounting can be straightforwardly conducted by applying the laws of mass and energy conservation.

From Equation 2.63, the rate of consumption of reactant, v (mol/s), in a fuel cell is related to the current, i, via

$$i = Q/s = nFv \tag{2.126}$$

If we know the enthalpy of the reactant fuel, $\Delta \hat{h}$ (J/mol), the rate of energy input, P_{in} (J/s), into the fuel cell is

$$P_{\text{in}} = |\Delta \hat{h}|v = P_h + P_e = P_h + V \times i \tag{2.127}$$

Here P_h (J/s), P_e (J/s), V (V), and i (A) stand for the heat production rate, output electrical power, operating voltage, and operating current of the fuel cell, respectively. Equation 2.127 is a simple but important energy balance equation that describes how the input fuel energy into a fuel cell is converted into a mixture of electrical energy and heat. Combining Equations 2.126 and 2.127, we have

$$P_h = P_{\text{in}} - P_e = |\Delta \hat{h}|v - V \times i$$
$$= \left(\frac{\lambda \left| \Delta \hat{h} \right|}{nF} - V \right) \times i = (\lambda E^H - V) \times i \tag{2.128}$$

where λ is the stoichiometry factor. Recall from the previous section of this chapter that λ describes how much fuel is delivered to the fuel cell compared to the stoichiometric amount required for operation at current i ($\lambda = nFv/i$). From this equation, we can determine how much heat a fuel cell generates when it produces electricity at a specified

voltage, V, and current, i. The term $E^H = \frac{|\Delta \hat{h}|}{nF}$ in Equation 2 is known as the "thermoneu-tral voltage." E^H represents an "ideal" voltage calculated from the enthalpy of reaction, similarly to how the ideal reversible voltage of a fuel cell ($E^0 = \frac{|\Delta \hat{g}|}{nF}$) is calculated from the Gibbs free energy of reaction. Even though E^H does not have any direct physical meaning in a fuel cell, it is extremely useful for calculating the magnitude of heat release from a fuel cell. The difference between reaction enthalpy input into the fuel cell and electrical power output from the fuel cell must be dissipated as heat. By converting the reaction enthalpy term into a "hypothetical" voltage, this heat loss can then be schematically represented on the fuel cell j–V curve as shown in Figure 2.10.

As an example, for a hydrogen fuel cell at STP, we can calculate

$$E^H = \frac{|\Delta \hat{h}|}{nF} = \frac{286,000 \ \text{J/mol}}{2 \times 96,485 \ \text{C/mol}} = 1.48 \ \text{V}$$

If this fuel cell is operating at 0.7 V and 10 A under STP conditions with 100% fuel utiliza-tion ($\lambda = 1$), it generates 7 W of electrical power ($P_e = 0.7 \ \text{V} \times 10 \ \text{A} = 7 \ \text{W}$) and 7.8 W of heat [$P_h = (1.48 \ \text{V} - 0.7 \ \text{V}) \times 10 \ \text{A} = 7.8 \ \text{W}$ using Equation 2.128]. As is the case with many practical fuel cells, this fuel cell actually generates more heat than power!

Because heat generation in fuel cells is significant, heat removal must almost always be designed into fuel cell systems. Heat can be removed from a fuel cell by (1) coolant flowing through the fuel cell, (2) unused but heated fuel and oxidant exiting the fuel cell, and/or (3) heat conduction or radiation from the fuel cell to the environment. Heat management in fuel cells is discussed in more detail in Chapter 12.
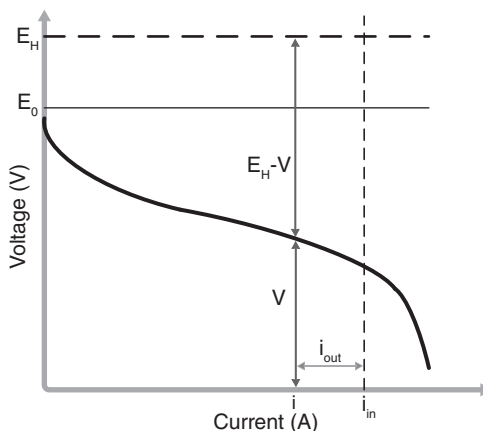

Figure 2.10. Thermal balance in a fuel cell. The difference between the operation voltage V and an "imaginary" thermoneutral voltage calculated from the enthalpy of reaction ($E^H = \frac{|\Delta \hat{h}|}{nF}$) represents the total energy loss in a fuel cell. This energy is converted to heat. The input, consumption, and output fluxes of reactants can be converted to equivalent currents to satisfy mass balance.

Most fuel cells are supplied with more fuel and oxidant than they consume. Excess fuel and oxidant are provided to the cell because depletion effects inside a fuel cell can degrade performance or even permanently damage fuel cell structures. Unused reactants simply exit the fuel cell, carrying some of the fuel cell's heat with them. For a given species, overall mass balance requires that the amount coming out of the fuel cell must be equal to the amount going into the fuel cell plus or minus any amount which is produced/consumed within the fuel cell:

$$v_{out} = v_{in} \pm \frac{i}{nF} \tag{2.129}$$

Here, v_{in} (mol/s) and v_{out} (mol/s) represent the molar input flow rate and output flow rate of a species, respectively, and the i/nF term accounts for production/consumption of that species within the fuel cell; the negative sign applies if the species is consumed in the fuel cell, while the positive sign applies if the species is produced within the fuel cell.

For example, consider a H_2/air fuel cell that generates 1000 kA and is supplied with air at 20 mol/s. Using Equation 2.129, we can find the oxygen output flux from the fuel cell:

$$
\begin{aligned}
v_{O_2,out} &= v_{O_2,in} - \frac{i}{nF} = v_{Air,in} \times w_{O_2} - \frac{i}{nF} \\
&= 20\,\text{mol/s} \times 0.21 - \frac{1,000,000\,\text{A}}{4 \times 96,485\,\text{C/mol}} = 1.6\,\text{mol/s}
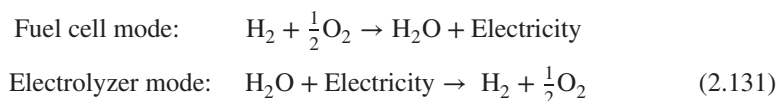\end{aligned}
\tag{2.130}
$$

Here, w_{O_2} represents the molar fraction of oxygen in air (=0.21). Please note that $n = 4$ in this calculation since one O_2 molecule accepts four electrons. In comparison, the water generation rate (or hydrogen consumption rate) for this fuel cell would be

$$\left(v_{H_2O} = v_{H_2} = \frac{i}{nF} = \frac{1000\ \text{kA}}{2 \times 96485\ \text{C/mol}} \right) = 5.18\ \text{mol/s}$$

The input and output flow rate of reactants can be converted to equivalent current using Equation 2.126 and plotted in the polarization curve (see Figure 2.10). For example, air supply at 20 mol/s would be sufficient to generate up to 1621 kA ($nFv_{O_2} = nFv_{air}w_{O_2} = 4 \times 96,485\ \text{C/s} \times 20\ \text{mol/s} \times 0.21 = 1621\ \text{kA}$) for a hydrogen fuel cell. Since the fuel cell generates 1000 kA with this supply of oxygen but could generate as much as 1621 kA, the air stoichiometric factor must be 1.62 (1621 kA/1000 kA = 1.62).

2.7 THERMODYNAMICS OF REVERSIBLE FUEL CELLS

Certain fuel cells can be designed to operate in either the forward or reverse direction. In other words, they can operate under the "fuel cell" mode, converting hydrogen and oxygen to water and electricity, or under the "electrolyzer mode," converting water and electricity to hydrogen and oxygen. The two modes are contrasted in Equation 2.131 below:

$$
\begin{aligned}
\text{Fuel cell mode:} &\quad H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O + \text{Electricity} \\
\text{Electrolyzer mode:} &\quad H_2O + \text{Electricity} \rightarrow H_2 + \tfrac{1}{2}O_2
\end{aligned}
\tag{2.131}
$$

A fuel cell that can run in both directions is known as a *reversible fuel cell*. Under the electrolysis mode, efficiency is calculated as the chemical energy (enthalpy) of the fuel produced by the system divided by the electrical energy supplied to the system. Thus the maximum ideal (thermodynamic) limit for electrolyzer efficiency is given by

$$\eta_{\text{thermo,electrolyzer}} = \frac{\Delta\hat{h}}{\Delta\hat{g}} \tag{2.132}$$

For water electrolysis at room temperature and pressure, we have $\Delta\hat{g}^0 = 237.17$ kJ/mol and $\Delta\hat{h}^0_{\text{HHV}} = 286$ kJ/mol, respectively (these are simply the reverse of the values for the fuel cell mode of operation). This implies a 120% reversible HHV efficiency for water electrolysis at STP!

$$\varepsilon_{\text{thermo,electrolyzer}} = \frac{286}{237} = 1.2 \tag{2.133}$$

How is it possible that the ideal thermodynamic efficiency for water electrolysis is greater than 100%? The answer comes from the direction of the irreversible entropic heat flow under the electrolyzer mode as compared to the fuel cell mode (i.e., the $T\Delta s$ term). Under H_2–O_2 fuel cell operation, the amount of electricity produced (as given by Δg) is less than the amount of chemical energy supplied (as given by Δh) due to irreversible entropic heat *losses to the environment* (quantified by $T\Delta s$). However, in the electrolyzer mode, the situation is reversed. The amount of electricity required for electrolysis (as given by Δg) is less than the amount of chemical energy produced (as given by Δh) due to irreversible entropic heat *contributions from the environment* (quantified by $T\Delta s$). Thus, electrolysis has the potential to achieve greater than 100% efficiency (based on our definition of efficiency) because heat from the environment is used in the process of splitting water into hydrogen. This can be quantified if we substitute the relationship $\Delta g = \Delta h - T\Delta s$ into Equation 2.132:

$$\eta_{\text{thermo,electrolyzer}} = \frac{\Delta\hat{h}}{\Delta\hat{g}} = \frac{\Delta\hat{h}}{\Delta\hat{h} - T\Delta s} \tag{2.134}$$

It should be noted that the >100% thermodynamic efficiency for water electrolysis is not in violation of thermodynamic principles. In a reversible fuel cell, the entropic losses incurred under the fuel cell mode of operation exactly offset the entropic gains associated with the electrolyzer mode of operation, such that the overall ideal thermodynamic round-trip efficiency involved in splitting water with electricity and then making electricity with the produced hydrogen is exactly 100%. In other words,

$$\varepsilon_{\text{thermo,electrolyzer}} \times \varepsilon_{\text{thermo, fc}} = 1.2 \times 0.83 = 1.0 \tag{2.135}$$

In reality, the actual efficiency of even very good electrolyzers is generally less than 100% for many of the same reasons that the practical efficiency of fuel cells is less than the thermodynamic limit. These idealities cause the operating voltage of a practical electrolyzer to be *higher* than the ideal STP thermodynamic voltage of 1.23 V (typically 1.4 V or higher is applied for electrolysis), indicating that more electricity is required to split water than the ideal thermodynamic prediction. Meanwhile, the voltage that is produced when this

hydrogen is consumed in the fuel cell mode is inevitably less than the ideal STP thermody-namic voltage of 1.23 V (typically less than 1 V). Thus, the practical round-trip efficiency of combined electrolysis + fuel cell operation is inevitably far less than 100%.

2.7.1   Heat Balance in Reversible Fuel Cells

In Section 2.6, we discussed fuel cell heat and mass balance. However, for a reversible fuel cell operating under the electrolysis mode operation, there are subtle heat balance differ-ences. Figure 2.11 illustrates these differences.

As discussed in Section 2.6, the heat balance of a fuel cell can be directly visualized on the j–V curve by comparing the operating voltage, V, versus the thermoneutral voltage, $E^H = \frac{|\Delta \hat{h}|}{nF}$. In the fuel cell mode, there is a net production of heat given by the difference between E^H and V. However, upon switching from the fuel cell mode to the electrolyzer mode, the situation reverses. At low electrolyzer current densities, there is a net heat *con-sumption* by the electrolyzer. The heat consumption of the electrolyzer can be visualized by the difference between electrical power supplied to the electrolyzer (as given by the oper-ating voltage V and current i) versus the chemical "power" produced by the electrolyzer (as given by E^H and i):

$$P_{h,\text{electrolysis}} = P_{e,\text{ in}} - P_{\text{chem, out}} = V \times i - |\Delta \hat{h}| \frac{i}{nF}$$

$$= \left(V - \frac{|\Delta \hat{h}|}{nF} \right) \times i = (V - E^H) \times i \tag{2.136}$$

In this analysis, the Faradaic efficiency of the electrolyzer is assumed to be 100%. This means that 100% of the current supplied to the electrolyzer is assumed to produce hydro-gen fuel.

As can be seen in this equation, and also in Figure 2.11, there is a net *consumption* of heat at low current densities when the operating voltage of the electrolyzer, V, is below the thermoneutral voltage, E^H. However, above the thermoneutral voltage, net heat is pro-duced in the electrolysis mode because entropic heat consumption is more than offset by irreversible heat production due to activation, ohmic, and mass transport losses in the elec-trolyzer. Maintaining system temperature during electrolysis under endothermic (net heat consumption) conditions can be difficult. Thus, most electrolyzers are designed to operate at or above the thermoneutral voltage.

Figure 2.12 illustrates a final key difference between fuel cell and electrolysis modes of operation. As was illustrated in Figure 2.8, the ideal thermodynamic efficiency of a H_2–O_2 fuel cell decreases with increasing temperature due to increasing irreversible entropic losses ($T \Delta s$ losses). As shown in Figure 2.12, the situation is reversed for an electrolyzer. Thus, the ideal thermodynamic efficiency of an electrolyzer *increases* with increasing temperature. At the same time, kinetic and mass transport losses tend to decrease at high temperatures (just as in fuel cell operation). Thus, for situations where high-quality waste heat is available, high-temperature electrolysis is an interesting option as it can provide the opportunity for high-efficiency operation.
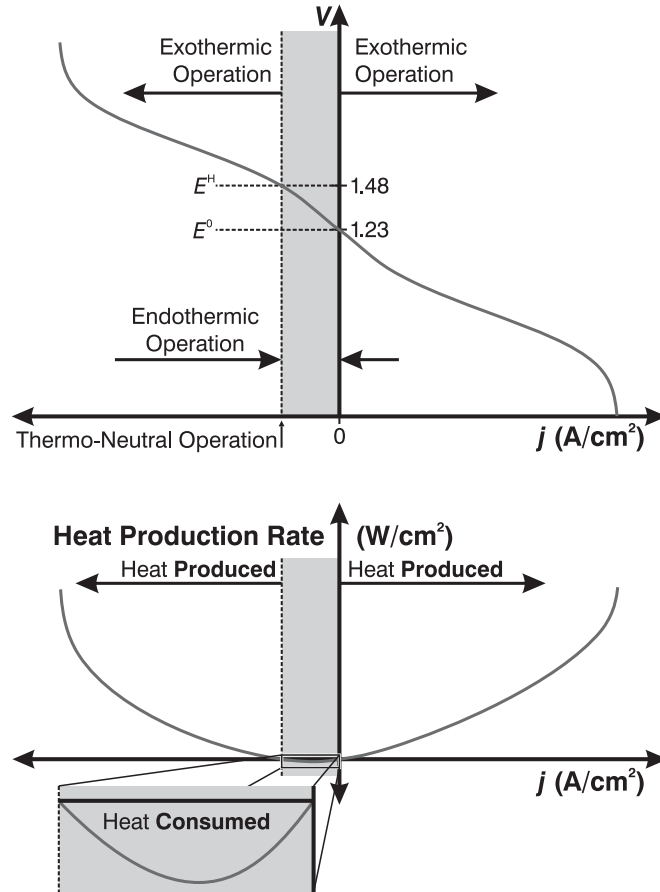
Figure 2.11. Thermal balance in a reversible fuel cell illustrating both the fuel cell and electrolyzer domains of operation. Under fuel cell operation, the difference between the operation voltage V and the thermoneutral voltage E^H ($E^H = \frac{|\Delta \hat{h}|}{nF}$) represents the heat loss in the fuel cell. Under the electrolyzer mode of operation, there is a net *consumption* of heat at low current densities when the operating voltage of the electrolyzer, V, is below the thermoneutral voltage, E^H. However, above the thermoneutral voltage, net heat is produced in the electrolysis mode because entropic heat consumption is fully offset by irreversible heat production due to activation, ohmic, and mass transport losses in the electrolyzer. Maintaining system temperature during electrolysis under endothermic (net heat consumption) conditions can be difficult. Thus, most electrolyzers are designed to operate at or above the thermoneutral voltage.
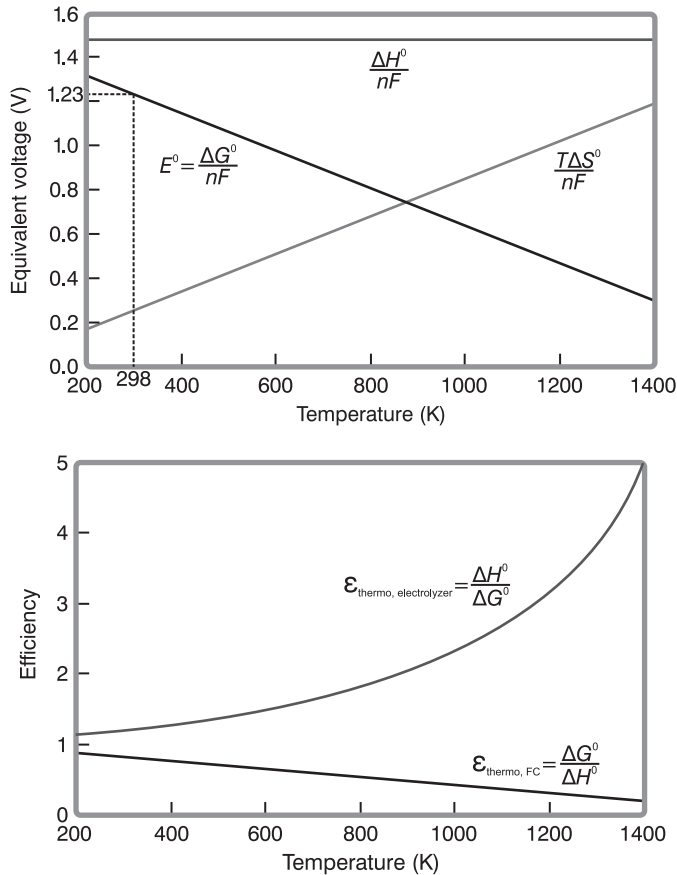
Figure 2.12. Reversible HHV efficiency of H_2O electrolysis compared to an H_2–O_2 fuel cell. The thermodynamic efficiency of electrolysis increases with increasing temperature, while thermodynamic fuel cell efficiency decreases with increasing temperature.

2.8 CHAPTER SUMMARY

The purpose of this chapter is to understand the theoretical limits to fuel cell performance by applying the principles of thermodynamics. The main points introduced in this chapter include the following:

- Thermodynamics provides the theoretical limits or ideal case for fuel cell performance.
- The heat potential of a fuel is given by the fuel's heat of combustion or, more generally, the enthalpy of reaction.
- Not all of the heat potential of a fuel can be utilized to perform useful work. The work potential of the fuel is given by the Gibbs free energy, ΔG.

- Electrical energy can only be extracted from a spontaneous ("downhill") chemical reaction. The magnitude of ΔG gives the amount of energy that is available ("free") to do electrical work. Thus, the sign of ΔG indicates whether or not electrical work can be done, and the size of ΔG indicates how much electrical work can be done.
- The reversible voltage of a fuel cell, E, is related to the molar Gibbs free energy by $\Delta \hat{g} = -nFE$.
- ΔG scales with reaction amount whereas $\Delta \hat{g}$ and E do not scale with reaction amount.
- E varies with temperature as $dE/dT = \Delta \hat{s}/nF$. For fuel cells, $\Delta \hat{s}$ is generally negative; therefore, reversible fuel cell voltages tend to decrease with increasing temperature. E varies with pressure as $dE/dp = -\Delta n_g RT/(nFp) = -\Delta \hat{v}/nF$
- The Nernst equation describes how E varies with reactant/product activities:

$$E = E^0 - \frac{RT}{nF} \ln \frac{\prod a_{\text{products}}^{v_i}}{\prod a_{\text{reactants}}^{v_i}}$$

- The Nernst equation intrinsically includes the pressure effects on reversible cell voltage but does not fully account for the temperature effects.
- Ideal HHV fuel cell efficiency $\varepsilon_{\text{thermo}} = \Delta \hat{g}/\Delta \hat{h}_{\text{HHV}}$.
- Thermodynamic fuel cell efficiency generally decreases as temperature increases. Contrast this to heat engines, for which thermodynamic efficiency generally increases as temperature increases.
- Real fuel cell efficiency is always less than the ideal thermodynamic efficiency. Major reasons are irreversible kinetic losses and fuel utilization losses. Total overall efficiency is given by the product of individual efficiencies.
- A fuel cell satisfies the laws of energy and mass conservation. Accordingly, the thermal and mass balance of a fuel cell can be obtained from input, output, and conversion fluxes of energy and mass in the fuel cell.

CHAPTER EXERCISES

Review Questions

2.1 If an isothermal reaction involving gases exhibits a large negative volume change, will the entropy change for the same reaction likely be negative or positive? Why?

2.2 (a) If $\Delta \hat{h}$ for a reaction is negative and $\Delta \hat{s}$ is positive, can you say anything about the spontaneity of the reaction? (b) What if $\Delta \hat{h}$ is negative and $\Delta \hat{s}$ is negative? (c) What if $\Delta \hat{h}$ is positive and $\Delta \hat{s}$ is negative? (d) What if $\Delta \hat{h}$ is positive and $\Delta \hat{s}$ is positive?

2.3 Reaction A has $\Delta \hat{g}_{\text{rxn}} = -100$ kJ/mol. Reaction B has $\Delta \hat{g}_{\text{rxn}} = -200$ kJ/mol. Can you say anything about the relative speeds (reaction rates) for these two reactions?

2.4 Why does ΔG for a reaction scale with reaction quantity but E does not? For example, ΔG_{rxn}^0 for the combustion of 1 mol of hydrogen is 1×-237 kJ/mol $= -237$ kJ,

while ΔG_{rxn}^0 for the combustion of 2 mol of hydrogen is $2 \times -237 \text{ kJ/mol} = -474 \text{ kJ}$. In both cases, however, the reversible cell voltage produced by the reaction, E^0, is 1.23 V.

2.5 In general, will increasing the concentration (activity) of reactants increase or decrease the reversible cell voltage of an electrochemical system?

2.6 Derive the Nernst equation starting from Equation 2.101 for a general chemical reaction of the form

$$ze_{\overline{A}} + 1A + bB \rightleftharpoons mM + nN + ze_{\overline{C}} \qquad (2.137)$$

2.7 Can the thermodynamic efficiency of a fuel cell, as defined by $\varepsilon = \Delta \hat{g}/\Delta \hat{h}$, ever be greater than unity? Explain why or why not. Consider all fuel cell chemistries, not just H_2–O_2 fuel cells.

2.8 Assume x moles per second of methanol and y moles per second of air are supplied to a direct methanol fuel cell (DMFC) generating a current of i amperes at a voltage V (volts). (a) Write expressions for the output mass flux (mol/s) of methanol ($v_{\text{MeOH, out}}$), air ($v_{\text{air, out}}$), water ($v_{H_2O, \text{out}}$), and carbon dioxide ($v_{CO_2, \text{out}}$) using the given variables. (b) Write expressions for the stoichiometric factors for methanol (λ_{MeOH}) and air (λ_{air}) using the given variables. (Clearly indicate numeric values for n in all cases.)

Calculations

2.9 In Example 2.2, we assumed that $\Delta \hat{h}_{rxn}$ and $\Delta \hat{s}_{rxn}$ were independent of temperature. We are now interested in determining how much of an error this assumption introduced into our solution. Rework Example 2.2 assuming constant-heat-capacity values for all species involved in the reaction. Heat capacity values are provided in the following table.

Chemical Species	c_p (J/mol·K)
CO	29.2
CO_2	37.2
H_2	28.8
$H_2O_{(g)}$	33.6

Note that a more accurate calculation is made by using temperature-dependent heat capacity equations. These equations generally use polynomial series to reflect how the heat capacity changes with temperature. Such calculations are tedious and are now mostly done via computer programs.

2.10 (a) If a fuel cell has a reversible voltage of E_1 at $p = p_1$ and $T = T_1$, write an expression for the temperature T_2 that would be required to maintain the fuel cell voltage at E_1 if the cell pressure is adjusted to p_2. (b) For a H_2–O_2 fuel cell operating at room

temperature and atmospheric pressure (on pure oxygen), what temperature would be required to maintain the original reversible voltage if the operating pressure is reduced by one order of magnitude?

2.11 In Section 2.4.4, it was mentioned that you could think of a hydrogen–oxygen fuel cell as simply a hydrogen concentration cell, where oxygen is used to chemically "tie up" hydrogen at the cathode. Oxygen's ability to chemically tie up hydrogen is measured by the Gibbs free energy of the hydrogen–oxygen reaction. At STP (assuming air at the cathode), what is the effective hydrogen pressure that oxygen is able to chemically maintain at the cathode of a hydrogen–oxygen (air) fuel cell?

2.12 A typical H_2–O_2 PEMFC might operate at a voltage of 0.75 V and $\lambda = 1.10$. At STP, what is the efficiency of such a fuel cell (use HHV and assume pure oxygen at the cathode)?

2.13 A direct methanol fuel cell generates 1000 A at 0.3 V at STP. Methanol and air are supplied to the fuel cell at 0.003 and 0.03 mol/s, respectively. Calculate (a) the output mass flux (mol/s) of methanol ($v_{MeOH, \, out}$), air ($v_{air, \, out}$), water ($v_{H_2O, out}$), and carbon dioxide ($v_{CO_2, out}$); (b) the stoichiometric factors for methanol (λ_{MeOH}) and air (λ_{air}); and (c) the heat generation rate (J/s) for this fuel cell assuming $\Delta \hat{h}_{rxn} = -719.19$ kJ/mol for methanol combustion at STP.

2.14 You are provided with a fuel cell that is designed to operate at $j = 3$ A/cm^2 and $P = 1.5$ W/cm^2. How much fuel cell active area (in cm^2) is required to deliver 2 kW of electrical power? (This is approximately enough to provide power to the average American home.)

(a) 296.3 cm^2

(b) 1333.3 cm^2

(c) 444.4cm^2

(d) 666.6 cm^2

2.15 For the fuel cell described above in problem 2.14, assuming operation on pure hydrogen fuel, how much water would be produced during 24 hours of operation at $P = 2$ kW? (Recall: molar mass of water = 18 g/mol, density of water = 1 g/cm^3.)

(a) 0.49 L

(b) 10.7 L

(c) 32.2 L

(d) 66.3 L

2.16 Given a fuel cell with the following overall reaction: $3A(g) + 2B(g) \rightarrow 2C(g)$, how will uniformly increasing the cell pressure affect the thermodynamic voltage?

(a) E decreases.

(b) E increases.

(c) E is constant.

(d) This cannot be determined.

2.17 Given the following half-cell reactions:

1. $O^{2-} + CO(g) \rightarrow CO_2(g) + 2e^-$
2. $2O^{2-} \rightarrow 4e^- + O_2(g)$
3. $8e^- + 2H_2O(g) + CO_2(g) \rightarrow 4O^{2-} + CH_4(g)$
4. $\frac{1}{2}O_2(g) + H_2O(g) + 2e^- \rightarrow 2(OH)^-$

(a) Using two of these half reactions, write a balanced full-cell reaction for a *fuel cell* (consumes fuel and oxygen). Identify which reaction is occurring at the anode and which at the cathode.

(b) Using two of these half reactions, write a balanced full-cell reaction for an *electrolysis cell* (makes fuel and oxygen). Identify which reaction is occurring at the anode and which at the cathode.

2.18 A residential solid-oxide fuel cell is operated on methane (CH_4) and is designed to provide the household with both heat and electricity.

(a) Assuming that the fuel cell is operated at $j = 1$ A/cm^2 and $V = 0.6$ V, how much fuel cell active area (in cm^2) would be required to deliver 3 kW of electrical power? (This is approximately enough to provide power to the average American home.)

(b) At the fuel cell's standard operating condition (750°C, 1 atm), Δh and Δg for methane combustion are –802 and –801 kJ/mol, respectively. (Note: This is not a typo; Δh and Δg are almost equal for this reaction.) Assuming 100% fuel utilization, what is the rate of heat generation by the fuel cell (P_{heat}, in kW) when operated at $j = 1$ A/cm^2 and $V = 0.6$ V?

(c) Assuming 100% fuel utilization, how much water (in liters) would be produced during 24 hours of operation at $P_{elec} = 3$ kW? (Recall: molar mass of water $= 18$ g/mol, density of water $= 1$ g/cm^3.)

(d) Given that the average American household water consumption is ~200 gal/day (~ 750 L/day), would this fuel cell be able to supply the average American household's entire daily water requirements in addition to its electrical power requirements? (Provide support for your answer.)