

## Chapter 15: Spontaneity

The hydrolysis of adenosine triphosphate, ATP, is the primary energy source for most cellular processes:



This reaction must be spontaneous to be useful. Cells must have a supply of ATP available for use as an energy source. ATP is produced through the respiration of sugars in the diet or through photosynthesis in plants and photosynthetic bacteria. To produce ATP, the reverse of the above reaction must become spontaneous. This example shows that it is possible to control the spontaneous direction for a reaction by adjusting the reaction conditions. Chemical synthesis is, in general, the manipulation of conditions to achieve spontaneous processes for the production of the substances of interest. What changes in reaction conditions are necessary to reverse the spontaneous direction of the hydrolysis of ATP?

We wish to predict the direction for spontaneous change for a process and the position of equilibrium. Many spontaneous processes are exothermic, so a first guess for a good spontaneity criterion might be the internal energy or enthalpy. However, many spontaneous processes are endothermic, Eqs. 10.1.1-10.1.2, so internal energy or enthalpy alone will not tell us what we want to know. The internal energy change for a process is not always useful as a spontaneity criterion since all processes conserve energy, whether they are spontaneous or not. The Second Law of thermodynamics gives us a powerful tool for predicting the spontaneous direction for processes. Using the Second Law and the state of the system, we can determine if the system is at equilibrium and if not, the spontaneous direction for change as the system attains equilibrium. The Second Law states that entropy always increases for spontaneous processes in an isolated system. So entropy is the key to determining how far a reaction or other process will run.

### 15.1 Isolated Systems

The composite First and Second Laws tell us that the change in internal energy for a closed system with PV work and chemical work is given by Eq. 14.1.4:

$$dU = TdS - PdV + \sum_{i=1}^{n_s} v_i \mu_i d\xi \quad (\text{closed, PV \& chemical work}) \quad 15.1.1$$

where the sum is over all chemical constituents. At equilibrium,  $\xi$  is constrained to give the equilibrium extent of the reaction. This last equation can be solved to obtain the change in entropy for a closed system for any process involving PV work and chemical reactions:

$$dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{1}{T} \sum_{i=1}^{n_s} v_i \mu_i d\xi \quad (\text{closed, PV \& chemical work}) \quad 15.1.2$$

To apply the Second Law, we must work with an isolated system, Figure 15.1.1. For an isolated system,  $dU$  and  $dV$  are zero. Then, according to the Second Law,  $dS \geq 0$  and from Eq. 15.1.2:

$$dS = -\frac{1}{T} \sum_{i=1}^{n_s} v_i \mu_i d\xi \geq 0 \quad (\text{isolated}) \quad 15.1.3$$

where the  $>$  sign applies to a spontaneous process and the equality to a reversible, equilibrium process. Often as we think of processes, we think of minimizing a function to tell us the spontaneous direction for the process. In classical mechanics, for example, we think of minimizing the total energy of the system. Entropy, on the other hand is maximized. For convenience, to develop a criterion that is minimized for a spontaneous process, we multiply both sides of Eq. 15.1.3 by  $-T$ , which also changes the direction of the inequality:

$$\sum_{i=1}^{n_s} v_i \mu_i d\xi < 0 \quad (\text{isolated, spontaneous}) \quad 15.1.4$$

For a reversible, equilibrium process:

$$\sum_{i=1}^{n_s} v_i \mu_i d\xi = 0 \quad (\text{isolated, reversible}) \quad 15.1.5$$

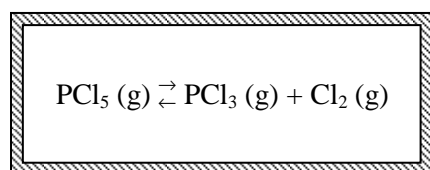


Figure 15.1.1: A chemical reaction in an isolated system is governed by the Second Law of thermodynamics,  $dS \geq 0$ .

The direction for spontaneous change is the direction that increases the entropy of an isolated system, and equilibrium is achieved when the entropy is at a maximum. The form of Eqs. 15.1.2-15.1.5 are quite central, so we should look at several examples. First, take a reaction such as a *cis-trans* isomerization:



The isomerization of naturally occurring *cis*-linkages in vegetable oils to *trans*-linkages in the production of margarine is a health concern. At equilibrium, from Eq. 15.1.5, the sum is simply

$$\sum_{i=1}^{n_s} v_i \mu_i d\xi = \mu_{\text{trans}} d\xi - \mu_{\text{cis}} d\xi = 0 \quad (\text{equilibrium}) \quad 15.1.7$$

Because of the sign convention for  $v_i$ , the result is always  $[\Sigma \text{products}] - [\Sigma \text{reactants}]$  as usual in thermochemistry. Dividing by  $d\xi$  and adding  $\mu_{\text{cis}}$  to both sides of this equation gives:

$$\mu_{\text{trans}} = \mu_{\text{cis}} \quad (\text{equilibrium}) \quad 15.1.8$$

In other words, at equilibrium the chemical potentials of the reactants and products are equal. If  $\mu_{\text{trans}} < \mu_{\text{cis}}$  then  $\mu_{\text{trans}} d\xi - \mu_{\text{cis}} d\xi < 0$  if  $d\xi$  is positive. If  $d\xi$  is positive, the reaction is

spontaneous in the direction as written. If  $\mu_{\text{trans}} > \mu_{\text{cis}}$  to get  $\mu_{\text{trans}} d\xi - \mu_{\text{cis}} d\xi < 0$  then  $d\xi$  must be negative and the spontaneous direction is in the reverse direction. Any reaction with stoichiometry  $A \rightleftharpoons B$  will give the same result, Figure 15.1.2. The spontaneous direction is the direction that decreases the overall chemical potential.

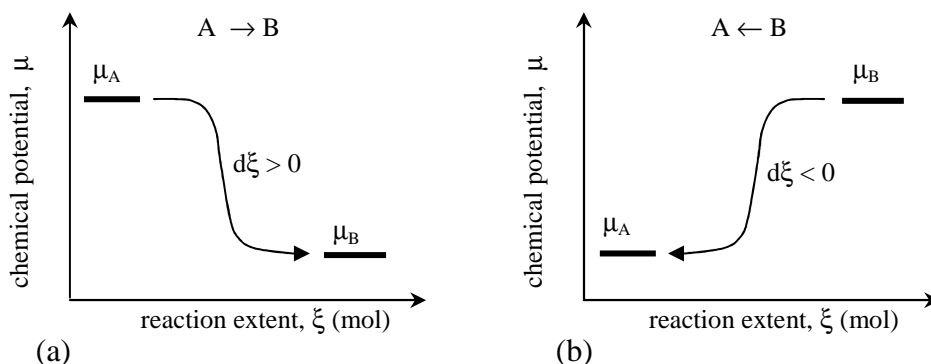


Figure 15.1.2: The spontaneous direction is from high chemical potential to low chemical potential.

Consider dissociation as a second example:



At equilibrium:

$$\mu_{\text{PCl}_3} d\xi + \mu_{\text{Cl}_2} d\xi - \mu_{\text{PCl}_5} d\xi = 0 \quad (\text{equilibrium}) \quad 15.1.10$$

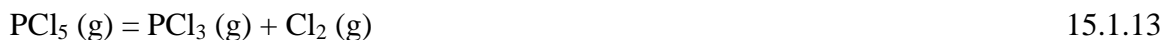
or equivalently:

$$\mu_{\text{PCl}_3} + \mu_{\text{Cl}_2} = \mu_{\text{PCl}_5} \quad (\text{equilibrium}) \quad 15.1.11$$

Once again, the equilibrium state is characterized by equivalence of the chemical potentials of the products and reactants. For the general reaction  $aA + bB \rightleftharpoons cC + dD$  the chemical potentials are related by

$$c \mu_C + d \mu_D = a \mu_A + b \mu_B \quad (\text{equilibrium}) \quad 15.1.12$$

which is the generalization of the idea that the chemical potentials of the reactants and products are equal at equilibrium. Because of this equality, an equilibrium reaction such as Eq. 15.1.9 is often written with an equal sign, instead of a double arrow:



You can use “ $\rightleftharpoons$ ” and “=” interchangeably to help remember the equivalence of the chemical potentials at equilibrium.

## 15.2. Free Energy

*The Spontaneity Criterion at Constant Temperature and Volume is the Helmholtz Energy:* Eq. 15.1.3 is specific for an isolated system, which applies when the internal energy and volume are constant. However, we often work with a system at constant temperature and volume, such as a

constant volume calorimeter bomb or a molecular dynamics simulation at constant volume. How can we recast the expressions for spontaneity for isothermal circumstances? Consider a closed, constant volume system and its surroundings taken together as an isolated composite-system, Figure 15.2.3a. The system can exchange energy with the surroundings. The surroundings are considered to be large in extent so that the surroundings act as a constant temperature reservoir. Contact with the surroundings keeps the system at constant temperature. The entropy change of the system and surroundings add to give the total entropy of the isolated composite-system,

$$dS_{\text{tot}} = dS + dS_{\text{surr}} \geq 0 \quad (\text{composite isolated}) \quad 15.2.1$$

For the special case where the isolated system is considered to be the universe,  $dS_{\text{tot}} = dS_{\text{univ}}$ . We can use  $dS_{\text{tot}}$  and  $dS_{\text{univ}}$  interchangeably, depending on the example.

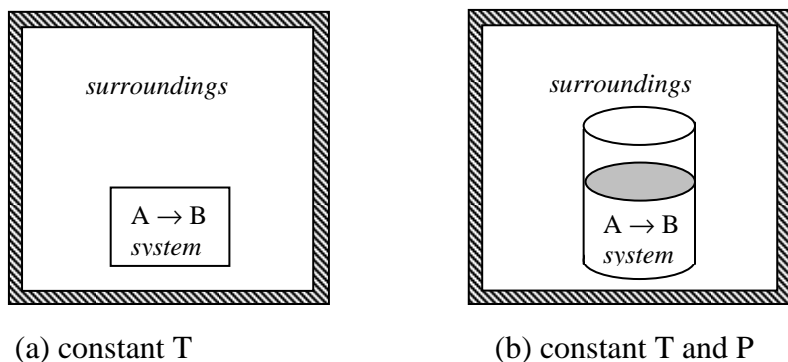


Figure 15.2.3 The system and surroundings, taken together as a composite, are isolated. (a) The surroundings act as a constant temperature reservoir to keep the system temperature constant,  $T = T_{\text{surr}}$ . (b) The surroundings also act as a constant pressure reservoir to keep the system pressure constant,  $P = P_{\text{ext}}$ . Many kinds of processes can occur in such systems; a simple chemical reaction is shown as one specific example.

The entropy change of the surroundings for a constant volume process is easy to calculate using Eq. 13.5.3. Substituting Eq. 13.5.3 into Eq. 15.2.1 gives the total entropy for the isolated composite-system as:

$$dS - \frac{dU}{T} \geq 0 \quad (\text{closed, cst. T\&V}) \quad 15.2.2$$

We wish to develop a criterion that is minimized for a spontaneous process and also has units of energy, as we did for Eq. 15.1.4. Multiplying both sides of Eq. 15.2.2 by  $-T$ , which also changes the direction of the inequality gives:

$$dU - T dS \leq 0 \quad (\text{closed, cst. T\&V}) \quad 15.2.3$$

The  $<$  applies to a spontaneous process, and the equality to a reversible, equilibrium process. Since we suspect that this combination of terms will arise often, it is convenient to define a new thermodynamic potential energy function  $A$  as:

$$A \equiv U - TS \quad 15.2.4$$

In general:

$$dA = dU - TdS - SdT \quad 15.2.5$$

This function, as we have seen from Eq. 15.2.3, is particularly useful for isothermal processes where at constant T:

$$dA = dU - T dS \quad (\text{isothermal}) \quad 15.2.6$$

and for an isothermal, constant volume process, the Second Law gives, from Eq. 15.2.3:

$$dA = dU - T dS \leq 0 \quad (\text{cst. T\&V}) \quad 15.2.7$$

This new function is a state function, since U, T, and S are all state functions. A is called the **Helmholtz free energy** or just **Helmholtz energy**, after Hermann Ludwig Ferdinand von Helmholtz (1821-1894). The spontaneous direction for a process at constant T and V is one that minimizes the Helmholtz energy. A process is at equilibrium at constant T and V when the change in the Helmholtz energy is zero for the process,  $dA = 0$ . Notice that, even though the variables in this equation only apply to the system, that from Eq. 13.5.3,  $dU = -T dS_{\text{surr}}$ . So this equation automatically keeps track of the entropy change of the system,  $dS$ , and the entropy change of the surroundings:

$$dA = \underset{\substack{\uparrow \\ -TdS_{\text{surr}}}}{dU} - \underset{\substack{\uparrow \\ TdS \text{ for system}}}{T dS} \quad (\text{isothermal}) \quad (\text{isothermal, cst. V}) \quad 15.2.8$$

The result is that by minimizing A, we automatically maximize the total entropy.

We can explore the usefulness of the Helmholtz energy by substituting for  $dU$  in Eq. 15.2.5 using Eq. 15.1.1:

$$dA = TdS - PdV + \sum_{i=1}^{n_s} v_i \mu_i d\xi - T dS - SdT \quad (\text{closed, PV \& chemical work}) \quad 15.2.9$$

The  $TdS$  terms cancel to give:

$$dA = -SdT - PdV + \sum_{i=1}^{n_s} v_i \mu_i d\xi \quad (\text{closed, PV \& chemical work}) \quad 15.2.10$$

For an isothermal process,  $-SdT = 0$ . For a reversible process,  $P = P_{\text{ext}}$ , therefore  $-PdV$  is the maximum expansion work for the system. At constant temperature, the right hand side of Eq. 15.2.10 is the total maximum work available from a reversible process:

$$dA = dw_{\text{max}} \quad (\text{closed, isothermal}) \quad 15.2.11$$

Even though we have only included PV and chemical work at this point, this result is quite general for all forms of work. Other forms of work add terms of the form  $Fdx$  to the right side of Eq. 15.2.10. The Helmholtz energy is, then, particularly useful in predicting the amount of useful work that a process can provide. This ability explains the use of the term “free energy;” no energy is available without cost, but the energy is free for use, that is available for use, for our purposes.

Helmholtz energy is a good spontaneity criterion at constant T and V, Eq. 15.2.7. At constant temperature and volume,  $dT = dV = 0$  and then Eq. 15.2.10 simplifies to:

$$dA = \sum_{i=1}^{n_s} \nu_i \mu_i d\xi \leq 0 \quad (\text{closed, cst. T\&V, chemical work}) \quad 15.2.12$$

Therefore, at constant T and V, the Helmholtz energy focuses just on our specific area of interest. The < applies to a spontaneous process and the equality to a reversible, equilibrium process, giving that at constant T and V, the spontaneous direction for a chemical reaction is to minimize the Helmholtz energy and at equilibrium the chemical potentials of the reactants and products are equal. These results at constant T and V are parallel to Eq. 15.1.4-15.1.5, which apply to isolated systems.

*The Spontaneity Criterion at Constant Temperature and Pressure is the Gibbs Energy:*

Processes at constant temperature and pressure are more common than those at constant volume. Systems open to the atmosphere on the bench top or in a living cell are at constant T and P. Consider a closed, constant pressure system and its surroundings taken together as an isolated composite, Figure 15.2.3b. Contact with the surroundings act as a constant temperature and pressure reservoir. The entropy change of the surroundings is easy to calculate since the heat transfer at constant pressure is the enthalpy change,  $dq_p = dH$ , and substituting Eq. 13.5.4 into  $dS_{\text{tot}} = dS + dS_{\text{surr}} \geq 0$  gives:

$$dS - \frac{dH}{T} \geq 0 \quad (\text{closed, cst. T\&P}) \quad 15.2.13$$

To develop a criterion that is minimized for a spontaneous process and also has units of energy, we multiply both sides of Eq. 15.2.13 by  $-T$ , which once again changes the direction of the inequality:

$$dH - T dS \leq 0 \quad (\text{closed, cst. T\&P}) \quad 15.2.14$$

The < applies to a spontaneous process, and the equality to a reversible, equilibrium process. Since we suspect that this combination of terms will arise often, it is convenient to define a new thermodynamic potential energy function G as:

$$G \equiv H - TS \quad 15.2.15$$

In general:

$$dG = dH - TdS - SdT \quad 15.2.16$$

This function, as we have seen from Eq. 15.2.14, is particularly useful for isothermal processes so that:

$$dG = dH - T dS \quad (\text{isothermal}) \quad 15.2.17$$

and for an isothermal, constant pressure process, the Second Law gives from Eq. 15.2.14:

$$dG = dH - T dS \leq 0 \quad (\text{isothermal, cst. P}) \quad 15.2.18$$

This new function is a state function, since H, T, and S are all state functions. G is called the **Gibbs free energy** or just **Gibbs energy**, after Josiah Willard Gibbs (1839-1903) who proposed the definition in 1876. The spontaneous direction for a process at constant T and P is one that minimizes the Gibbs energy. A process is at equilibrium at constant T and P when the change in the Gibbs energy is zero for the process,  $dG = 0$ . Notice that, even though the variables in this

equation only apply to the system, from Eq. 13.5.4,  $dH = -T dS_{\text{surr}}$ . So this equation automatically keeps track of the entropy change of the system,  $dS$ , and the entropy change of the surroundings:

$$dG = \underset{\substack{\uparrow \\ -TdS_{\text{surr}}}}{dH} - \underset{\substack{\uparrow \\ TdS \text{ for system}}}{T dS} \quad \text{(isothermal)} \quad \text{(cst. T\&P)} \quad 15.2.19$$

The result is that by minimizing  $G$ , we automatically maximize the total entropy.

We can explore the usefulness of the Gibbs energy by substituting for  $dH$  in Eq. 15.2.16 to get the total differential:

$$dG = dU + PdV + VdP - TdS - SdT \quad 15.2.20$$

and then substituting for  $dU$  from Eq. 15.1.1 for a closed system, as we did for the Helmholtz energy:

$$dG = TdS - PdV + \sum_{i=1}^{n_s} v_i \mu_i d\xi + PdV + VdP - T dS - SdT \quad \text{(closed, PV \& chemical work)} \quad 15.2.21$$

Cancelling terms gives:

$$dG = -SdT + VdP + \sum_{i=1}^{n_s} v_i \mu_i d\xi \quad \text{(closed, PV \& chemical work)} \quad 15.2.22$$

At constant temperature and pressure the equation simplifies to:

$$dG = \sum_{i=1}^{n_s} v_i \mu_i d\xi \leq 0 \quad \text{(closed, cst. T\&P, PV \& chemical work)} \quad 15.2.23$$

Our general conclusions about the spontaneity of chemical reactions follow directly, just as they did for the Helmholtz energy. For a spontaneous process:

$$dG = \sum_{i=1}^{n_s} v_i \mu_i d\xi < 0 \quad \text{(spontaneous, closed, cst. T\&P, PV \& chemical work)} \quad 15.2.24$$

and for a reversible, equilibrium process:

$$dG = \sum_{i=1}^{n_s} v_i \mu_i d\xi = 0 \quad \text{(equilibrium, closed, cst. T\&P, PV \& chemical work)} \quad 15.2.25$$

Once again, we reach the conclusion that the chemical potentials of the products and reactants are equal at equilibrium. But we have now shown this equality to hold at equilibrium for any isolated system and for closed systems for isothermal processes at constant volume or pressure. This result is one of the most powerful and central ideas in understanding chemical reactivity. We also write Eq. 15.2.24 in the equivalent form (see Section 14.3):

$$dG = \sum_{i=1}^{n_s} \mu_i dn_i \leq 0 \quad (\text{closed, cst. T\&P, PV \& chemical work}) \quad 15.2.26$$

If chemical reactions occur, it is very important to remember, however, that the  $dn_i$  are dependent variables.

Notice that this simple conclusion results from the application of constraints on the intensive and extensive variables so that the number of independent variables is decreased, see Chapter 14. The intensive variables T and P are constrained by contact with reservoirs. The extensive constraints are the specification of a closed system in an isolated composite with the surroundings. The constraints simplify the problem so that we can focus on the central issue of chemical reactivity and non-PV work.

Even though we have only included PV and chemical work at this point, this result is quite general for all forms of work. Other forms of work add additional terms in the form  $Fdx$  to the right side of this last equation. The Gibbs energy gives the maximum non-PV work for a process. The non-PV work is often defined as the **net work**,  $dw_{\text{net}}$ , with  $dw = -P_{\text{ext}}dV + dw_{\text{net}}$  and:

$$dG = dw_{\text{net,max}} \quad (\text{closed}) \quad 15.2.27$$

The interplay between  $dA$  and  $dG$  is important. If we are burning ethanol in an internal combustion engine, the work is all PV work, and  $dA$  gives the maximum work available. On the other hand, if we use ethanol as the fuel in a fuel cell, the electrical work is important, and  $dG$  gives us the maximum electrical work available. Since the combustion of ethanol creates a gas, the process necessarily does PV work, which diminishes the work available for generating an electrical current:



Which is more efficient, internal combustion or a fuel cell? Fuel cells are not governed by the Carnot efficiency, so fuel cells are much more efficient than internal combustion engines overall even though some energy is lost as PV work. In living cells, glucose and other sugars are “burned” to produce chemical or electrical work. The chemical work is primarily the synthesis of ATP. The combustion of glucose also produces  $\text{CO}_2$  gas, which does PV work against the atmosphere and diminishes the useful work available to run the cell. Gibbs energy is the important state function to describe biochemical energetics.

### 15.3 Gibbs Energy and Other Forms of Work

In the analysis above we used chemical work as an example of non-PV work. Any other form of work follows the same pattern. Remember that non-PV work can be cast in the form of a force multiplied by a displacement,  $dw = F dx$ . The total PV and non-PV work is then:

$$dw = -P_{\text{ext}}dV + F dx \quad 15.3.1$$

To study this system we need to simplify by setting up a constraint for the total displacement as in Chapter 14.3 and 14.4, Figures 14.3.1 and 14.4.1. The internal energy is then given as:

$$dU = TdS - PdV + F_A dx_A + F_B dx_B \quad (\text{constant } x_{\text{tot}}) \quad 15.3.2$$

Using Eq. 15.2.20 for a closed system at constant temperature and pressure with  $Fx$  work only:



$$dG = TdS - PdV + F_A dx_A + F_B dx_B + PdV - T dS \quad (\text{constant } x_{\text{tot}}, \text{ cst. T\&P}) \quad 15.3.3$$

Cancelling terms gives:

$$dG = F_A dx_A + F_B dx_B \leq 0 \quad (\text{constant } x_{\text{tot}}, \text{ cst. T\&P, Fx work}) \quad 15.3.4$$

The displacements,  $dx_A = -dx_B$ , will change to decrease the Gibbs energy of the system, as we have seen before. Gibbs energy is a very general spontaneity criterion for processes at constant temperature and pressure.

One particularly important form of work is electrical work. As we saw in Section 14.4, membrane potentials are an important specific example and so are electrochemical cells. The internal energy for a set of  $n_s$  ions is given from Eq. 7.9.9-7.9.10 as:

$$dU = dq - P_{\text{ext}}dV + \sum_{i=1}^{n_s} z_i F \phi_i dn_i \quad (\text{PV \& electrical work}) \quad 15.3.5$$

and from the combined First and Second Laws of thermodynamics:

$$dU = TdS - PdV + \sum_{i=1}^{n_s} z_i F \phi_i dn_i \quad 15.3.6$$

for an ion  $i$  with charge  $z_i$  in electric field  $\phi_i$ . If chemical reactions can also occur then:

$$dU = TdS - PdV + \sum_{i=1}^{n_s} \mu_i dn_i + \sum_{i=1}^{n_s} z_i F \phi_i dn_i \quad 15.3.7$$

The change in Gibbs energy for ions in the presence of an electrical field at constant temperature and pressure is:

$$dG = \sum_{i=1}^{n_s} \mu_i dn_i + \sum_{i=1}^{n_s} z_i F \phi_i dn_i \quad (\text{cst. T\&P}) \quad 15.3.8$$

Since each sum is over the same set of mole amounts, we can define the **electrochemical potential** as:

$$\bar{\mu}_i \equiv \mu_i + z_i F \phi_i \quad 15.3.9$$

Then the change in Gibbs energy is

$$dG = \sum_{i=1}^{n_s} \bar{\mu}_i dn_i \quad 15.3.10$$

and in a closed system at constant temperature and pressure taking into account differences in concentration, chemical reactions, and electric fields:

$$dG = \sum_{i=1}^{n_s} \bar{\mu}_i dn_i \leq 0 \quad (\text{closed; cst. T\&P; PV, electric, \& chemical work}) \quad 15.3.11$$

if we note that the  $dn_i$  are dependent if chemical reactions take place. In terms of the extent of the reaction:

$$dG = \sum_{i=1}^{n_s} \nu_i \bar{\mu}_i d\xi \leq 0 \quad (\text{closed, cst. T\&P; PV, electric, \& chemical work}) \quad 15.3.12$$

From this last expression, we find at equilibrium the electrochemical potentials of the products and reactants are equal as given by:

$$\sum_{i=1}^{n_s} \nu_i \bar{\mu}_i = 0 \quad (\text{equilibrium, closed, cst. T\&P; PV, electric, \& chemical work}) \quad 15.3.13$$

We will use this equation when we study electrochemistry and also membrane potentials. For one specific example, consider the example from Figure 14.4.2, where an ion experiences a difference in concentration and electric potential across a semi-permeable membrane for that ion. The difference in Gibbs energy for the transfer of one mole of ions is:



$\Delta G$  is given by the difference in electrochemical potential across the membrane, Figure 15.3.4:

$$\Delta G = \bar{\mu}_{\text{in}} - \bar{\mu}_{\text{out}} = (\mu_{\text{in}} + z_+ F \phi_{\text{in}}) - (\mu_{\text{out}} + z_+ F \phi_{\text{out}}) \quad 15.3.15$$

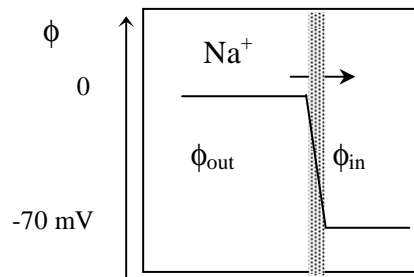


Figure 15.3.4: The Gibbs energy for transfer across a semi-permeable membrane. The membrane potential is  $\Delta\phi = \phi_{\text{in}} - \phi_{\text{out}}$ .

The spontaneous direction for the transfer is from the side with the higher electrochemical potential to the side with the lower electrochemical potential. At equilibrium,  $\Delta G = 0$  and  $\bar{\mu}_{\text{in}} = \bar{\mu}_{\text{out}}$ . Generating the membrane potential is responsible for much of the energy consumption of your brain. (Your brain feeds on Gibbs energy.)

#### 15.4 Applications of Helmholtz and Gibbs Energies

In this section we give some beginning examples using the Helmholtz and Gibbs energies and show how to relate the thermodynamic potentials to each other. The thermodynamic potentials can be easily related to each other through their definitions. The “thermodynamic cube” shows these relationships at constant temperature and pressure in an easy to remember form, Figure 15.4.1. For example, to convert  $\Delta U$  to  $\Delta A$ , just add  $-T\Delta S$ ; that is  $\Delta A = \Delta U - T\Delta S$ . To convert  $\Delta U$  to  $\Delta H$ , just add  $P\Delta V$ ; that is  $\Delta H = \Delta U + P\Delta V$ . You can also work along the diagonal:  $\Delta G = \Delta U + P\Delta V - T\Delta S$ .

$$\begin{array}{ccc}
 \Delta U & \xrightarrow{-T\Delta S} & \Delta A \\
 | & & | \\
 +P\Delta V & & +P\Delta V \\
 \downarrow & & \downarrow \\
 \Delta H & \xrightarrow{-T\Delta S} & \Delta G
 \end{array}$$

Figure 15.4.1: Thermodynamic relationships at constant temperature and pressure.

*Isothermal Processes:* Helmholtz and Gibbs energies were designed to be useful for constant temperature processes. For a closed system with no chemical reactions for an isothermal process, Eq. 15.2.10 reduces to:

$$dA = -P dV \quad (\text{closed, cst. T, PV work only}) \quad 15.4.1$$

For an ideal gas  $P = nRT/V$  and Eq. 15.4.1 integrates to:

$$\Delta A = -nRT \ln \frac{V_2}{V_1} \quad (\text{ideal gas, closed, cst. T, PV work only}) \quad 15.4.2^\circ$$

which is also the work for an isothermal reversible process, Eq. 7.3.6. This result should not be surprising since  $\Delta A = w_{\max}$  and for maximum work you must choose a reversible process. Another equivalent approach is to start with Eq. 15.2.6,  $dA = dU - TdS$ , but for an isothermal process for an ideal gas  $dU = C_v dT = 0$ . Then using the change in entropy for an isothermal process of ideal gas,  $\Delta S = nR \ln(V_2/V_1)$ , gives the same result.

Now consider  $\Delta G$ . For a closed system with no chemical reactions for an isothermal process, Eq. 15.2.22 reduces to:

$$dG = VdP \quad (\text{closed, cst. T, PV work only}) \quad 15.4.3$$

Using the ideal gas law,  $V = nRT/P$ , integrates to:

$$\Delta G = nRT \ln \frac{P_2}{P_1} \quad (\text{ideal gas, cst. T, closed, PV work only}) \quad 15.4.4^\circ$$

We can compare  $\Delta A$  to  $\Delta G$ , Eq. 15.4.2<sup>o</sup> to Eq. 15.4.4<sup>o</sup>, using that for an isothermal process in an ideal gas  $P_2V_2 = P_1V_1$ , or rearranging:

$$\frac{P_2}{P_1} = \frac{V_1}{V_2} \quad (\text{ideal gas, cst. T}) \quad 15.4.5^\circ$$

Substitution of this last equation into Eq. 15.4.4<sup>o</sup> gives the net result:

$$\Delta G = nRT \ln \frac{P_2}{P_1} = nRT \ln \frac{V_1}{V_2} = -nRT \ln \frac{V_2}{V_1} \quad (\text{ideal gas, cst. T}) \quad 15.4.6^\circ$$

So,  $\Delta A = \Delta G$  for this process. Eq. 15.4.4 is one of the most commonly used equations in thermodynamics, and we will use it to explore chemical equilibrium and solutions. Simply stated the Gibbs energy for a substance increases with pressure.

For a liquid or a solid, Eq. 15.4.3 can be easily integrated knowing  $V$  as a function of  $P$ . For small changes in pressure, the volume of a condensed phase doesn't change much, and we can consider  $V$  as constant with  $V \approx V_o$ , the initial volume:

$$\Delta G = V_o \Delta P \quad (\text{closed, cst. } T, \text{ small } \Delta P) \quad 15.4.7$$

This approximation is at the "good" level (review Section 7.6). At the "better" level for moderate changes in pressure, we use Eq. 7.6.28,  $V = V_o - V_o \kappa_T (P - P_o)$ , with  $P_o$  the initial pressure and integrate Eq. 15.4.3 to give:

$$\Delta G = V_o (P - P_o) - \frac{1}{2} V_o \kappa_T (P - P_o)^2 \quad (\text{closed, cst. } T, \text{ moderate } \Delta P) \quad 15.4.8$$

You will prove this equation in your homework. We will work with other example processes for  $\Delta A$  and  $\Delta G$  in the next chapter.

#### Example 15.4.1:

Calculate the change in Gibbs energy for one mole of an ideal gas for a pressure change from 1.00 bar to 2.00 bar at 298.2 K:

$$\text{Answer: } \Delta G = nRT \ln \frac{P_2}{P_1} = 1.00 \text{ mol} (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \ln \frac{2.00}{1.00} = 1.72 \text{ kJ mol}^{-1}$$

The important part of this example is to note that as the gas pressure increases, the Gibbs energy increases. At the higher pressure the gas has the ability to do more useful work. Note also the units of pressure don't affect the final result. Any doubling of the pressure gives the same  $\Delta G$ : 1 torr  $\rightarrow$  2 torr, or 10 atm  $\rightarrow$  20 atm.

*The Change in Helmholtz Energy with Temperature at Constant Volume:* We will return to this problem in the next chapter, but for now for a closed, constant volume process for  $\Delta A$  we need to integrate Eq. 15.2.10. At constant  $V$ :

$$dA = -SdT \quad (\text{closed, cst. } V) \quad 15.4.9$$

If the temperature range is quite narrow so that the entropy can be considered essentially constant, then Eq. 15.4.9 integrates to:

$$\Delta A = -S\Delta T \quad (\text{closed, cst. } V, \text{ small } \Delta T) \quad 15.4.10$$

However, entropy is a strong function of temperature. Eq. 13.2.29 gives the change in entropy for a constant volume process with an initial entropy of  $S_o$  at reference temperature  $T_o$  as:

$$S = S_o + C_v \ln \frac{T}{T_o} \quad (\text{closed, cst. } V \& C_v) \quad 15.4.11$$

Integrating using  $\int \ln x \, dx = x \ln x - x$  and assuming a constant heat capacity:

$$\Delta A = -S_o (T - T_o) + C_v (T - T_o) - C_v (T \ln T - T \ln T_o) \quad (\text{closed, cst. } V \& C_v) \quad 15.4.12$$

Combining the ln terms:

$$\Delta A = -S_o (T - T_o) + C_v (T - T_o) - C_v T \ln \frac{T}{T_o} \quad (\text{closed, cst. } V \& C_v) \quad 15.4.13$$

This result is a bit complicated, but straightforward. The last two terms tend to cancel, so you need to keep both.

*The Change in Gibbs Energy with Temperature at Constant Pressure:* For a closed, constant pressure process with no chemical reactions, Eq. 15.2.22 reduces to  $dG = -SdT$ . If the temperature range is quite narrow so that the entropy can be considered essentially constant, then:

$$\Delta G = -S\Delta T \quad (\text{closed, cst. } P, \text{ small } \Delta T) \quad 15.4.14$$

For broader temperature ranges, integrating Eq. 15.2.22 starting from a reference temperature  $T_o$  proceeds in the same fashion as Eq. 15.4.13:

$$\Delta G = -S_o (T - T_o) + C_p (T - T_o) - C_p T \ln \frac{T}{T_o} \quad (\text{closed, cst. } P \& C_p) \quad 15.4.15$$

This full equation is used by geochemists, oceanographers, chemical engineers, and others working under extreme conditions. We will find an alternate form for the temperature dependence of the Gibbs energy for chemical reactions in the next chapter.

**Example 15.4.2:**

Calculate the change in Gibbs energy for one mole of  $H_2$  gas for an increase in temperature from 298.2 K to 398.2 K at 1 bar pressure. Is  $H_2$  a better fuel in a fuel cell at room temperature or at higher temperature?

*Answer:* The standard entropy at 298.2 K for  $H_2$  is  $130.574 \text{ J K}^{-1} \text{ mol}^{-1}$ , and  $C_p$  is  $28.824 \text{ J K}^{-1} \text{ mol}^{-1}$ . First use the most approximate formula, Eq. 15.4.14:

$$\Delta G = -S\Delta T = -130.574 \text{ J K}^{-1} \text{ mol}^{-1} (100.0 \text{ K}) = -13.06 \text{ kJ mol}^{-1}$$

Now compare with the more accurate formula, Eq. 15.4.15, that takes into account the temperature dependence of the entropy. Notice the first term of the more accurate formula is the same as we just calculated:

$$\begin{aligned} \Delta G &= -S_o (T - T_o) + C_p (T - T_o) - C_p T_o \ln \frac{T}{T_o} \\ &= -13.06 \text{ kJ mol}^{-1} + 28.824 \text{ J K}^{-1} \text{ mol}^{-1} (100.0 \text{ K}) - 28.824 \text{ J K}^{-1} \text{ mol}^{-1} (398.2 \text{ K}) \ln \frac{398.2}{298.2} \\ &= -13.06 \text{ kJ mol}^{-1} + 2.88 \text{ J K}^{-1} \text{ mol}^{-1} - 3.32 \text{ kJ mol}^{-1} \\ &= -13.50 \text{ kJ mol}^{-1} \end{aligned}$$

Notice that the last two terms tend to cancel making  $\Delta G = -S\Delta T$  a better approximation than you might suspect. The error for the simpler formula is only 3% with a 100 K temperature range. Note that both formulas assume  $C_p$  is a constant. The temperature dependence of the heat

capacities must be taken into account for very large temperature ranges. The result for this problem shows numerically that the Gibbs energy for a pure substance decreases with temperature, since the absolute entropy for a substance is always positive. Therefore,  $H_2$  is a poorer fuel at the higher temperature. Another way to look at this is to remember that  $\Delta G = \Delta H - T\Delta S$ ; when the temperature increases, the weighting of the entropy term increases. The large favorable entropy of a gas makes the Gibbs energy more negative, increasingly so with temperature. A more favorable  $\Delta G$  is more negative and the substance is more stable.

*Phase Transitions at Equilibrium:* Consider the Helmholtz and Gibbs energies for phase transitions. At the equilibrium phase transition temperature, the process is reversible and at constant pressure and temperature. The entropy for the phase transition, Eq. 13.3.2, is then:

$$\Delta_{tr}S = \frac{\Delta_{tr}H}{T_{tr}} \quad (\text{equilibrium}) \quad 15.4.16$$

and from the definition  $G \equiv H - TS$  for constant temperature:  $\Delta G = \Delta H - T\Delta S$ . The change in Gibbs energy is easy for this equilibrium phase transition. But, before we use Eq. 15.4.16, think about the final result. What should  $\Delta G$  be for a reversible, constant temperature and pressure process? Now substituting Eq. 15.4.16 into  $\Delta G$  gives:

$$\Delta_{tr}G = \Delta_{tr}H - T_{tr}\Delta_{tr}S = \Delta_{tr}H - T_{tr}\frac{\Delta_{tr}H}{T_{tr}} = 0 \quad (\text{equilibrium}) \quad 15.4.17$$

As expected, the change in Gibbs energy for a reversible, equilibrium process is zero at constant temperature and pressure. For  $\Delta_{tr}A$ , the calculation is through  $\Delta_{tr}A = \Delta_{tr}U - T_{tr}\Delta_{tr}S$ , and assuming an ideal vapor  $\Delta_{tr}H = \Delta_{tr}U + \Delta n_{gas}RT_{tr}$ :

$$\Delta_{tr}A = \Delta_{tr}U - T_{tr}\Delta_{tr}S = \Delta_{tr}H - \Delta n_{gas}RT_{tr} - T_{tr}\frac{\Delta_{tr}H}{T_{tr}} = -\Delta n_{gas}RT_{tr} \quad (\text{equilibrium, ideal vapor}) \quad 15.4.18^\circ$$

Once again, this result shouldn't be too surprising, since  $dA = dw_{max}$ , which for  $\Delta n_{gas}$  moles of an ideal gas expanding against a constant pressure gives  $w = -P\Delta V = -\Delta n_{gas}RT_{tr}$ . So  $\Delta_{tr}A$  is just the work of expansion for the vapor produced in the phase transition. The vapor does work against the surroundings, which decreases the Helmholtz energy of the system.

*Chemical Reactions and Gibbs Energy:* The change in Gibbs energy is the appropriate spontaneity criterion for chemical reactions at constant temperature and pressure. Also note that  $\Delta_rG = w_{net}$ , which shows that the Gibbs energy is the work available for any non-PV process, including pumping ions across membranes, electrochemical cells, and the work of chemical synthesis. Figure 15.4.1 is useful for visualizing the relationships among the thermodynamic potentials for chemical reactions. The key concept is that since  $G$  is a state function, Hess's Law holds for Gibbs energies just as it does for enthalpies and entropies. The Gibbs energy of formation for a substance,  $\Delta_fG$ , is the Gibbs energy for the formation of one mole of product from the constituent elements in their standard states. For example,  $\Delta_fG^\circ$  for water at 298.15 K is:



This convention for the formation reaction gives the  $\Delta_f G^\circ$  for any element in its standard state as zero. The standard state for species in solution is an activity of 1 m. Also,  $\Delta_f G^\circ \equiv 0$  and  $\Delta_f H^\circ \equiv 0$  for  $\text{H}^+$  ion by definition. In general from *General Pattern* **¶7**,  $\Delta_r G^\circ = [\Sigma \text{products}] - [\Sigma \text{reactants}]$ , as we found for the for the reaction enthalpy:

$$\Delta_r G = \sum_{i=1}^{n_s} \nu_i \Delta_f G_i \quad 15.4.20$$

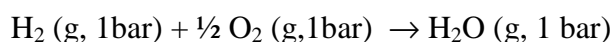
A few example problems are given next. The standard state thermodynamic properties for several biochemicals are given in Table 15.4.1. Additional  $\Delta_f G^\circ$  values are given in the Appendix Data Section.

Table 15.4.1 Standard Gibbs Energies of Formation and Enthalpies of Formation at 298.15 K and Zero Ionic Strength.<sup>1</sup>

Species	$\Delta_f H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta_f G^\circ$ (kJ mol <sup>-1</sup> )
$\text{H}^+$	0	0
$\text{ATP}^{4-}$	-3619.21	-2768.10
$\text{HATP}^{3-}$	-3612.91	-2811.48
$\text{ADP}^{3-}$	-2626.54	-1906.13
$\text{HADP}^{2-}$	-2620.94	-1947.10
$\text{HPO}_4^{2-}$	-1299.00	-1096.10
$\text{H}_2\text{PO}_4^-$	-1302.60	-1137.3
$\text{H}_2\text{O}$	-285.83	-237.19
Glucose-6-Phosphate <sup>2-</sup>	-2276.44	-1763.94
Glucose	-1262.19	-915.9

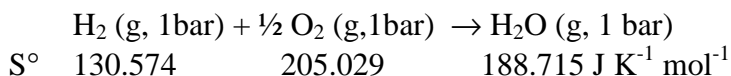
### Example 15.4.3:

Hydrogen is a clean burning alternative to fossil fuels. The reaction for the formation of gaseous water is:



This reaction has a standard enthalpy change of  $-241.82 \text{ kJ mol}^{-1}$ . Calculate  $\Delta_r G^\circ$  at 298.15 K for the reaction as written.

*Answer:* From Appendix Table 8.4.1, the absolute entropies for the reactants and products are:



$$\begin{aligned} \text{Giving } \Delta_r S^\circ &= [\Sigma \text{products}] - [\Sigma \text{reactants}] = \\ &= [1 (188.715 \text{ J K}^{-1} \text{ mol}^{-1})] - [1 (130.574 \text{ J K}^{-1} \text{ mol}^{-1}) + \frac{1}{2} (205.029 \text{ J K}^{-1} \text{ mol}^{-1})] \\ \Delta_r S^\circ &= -44.37 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned}\text{Then } \Delta_r G^\circ &= \Delta_r H^\circ - T \Delta_r S^\circ = -241.82 \text{ kJ mol}^{-1} - 298.15 \text{ K} (-44.37 \text{ J K}^{-1})(1 \text{ kJ}/1000 \text{ J}) \\ &= -228.6 \text{ kJ mol}^{-1}\end{aligned}$$

Hydrogen is a very good fuel. However, notice that  $\Delta_r G^\circ$  provides less energy than  $\Delta_r H^\circ$ , because the process decreases the entropy of the system. The entropy of the surroundings must compensate to make the process overall favorable. Another way of saying this is less energy is available for use in a fuel cell for making electricity than is available in an internal combustion engine where gas expansion is the driving force. The other problem with  $\text{H}_2$  is that energy is required to make it,  $-\Delta_f G^\circ = 237.19 \text{ kJ mol}^{-1}$ , starting from liquid water.

#### Example 15.4.4:

Is the hydrolysis of ATP spontaneous under standard conditions and 298.2 K? Is the reaction favored or disfavored by the enthalpy or entropy? (a) Calculate  $\Delta_r G^\circ$ ,  $\Delta_r H^\circ$  and  $\Delta_r S^\circ$ . The reaction is:



*Answer:* The standard state thermodynamic properties are given in Table 15.4.1:

	ATP <sup>4-</sup>	+ H <sub>2</sub> O	→	ADP <sup>3-</sup>	+ HPO <sub>4</sub> <sup>2-</sup>	+ H <sup>+</sup>	units
$\Delta_f H^\circ$	-3619.21	-285.83		-2626.54	-1299	0	kJ mol <sup>-1</sup>
$\Delta_f G^\circ$	-2768.10	-237.19		-1906.13	-1096.1	0	kJ mol <sup>-1</sup>

$$\begin{aligned}\text{(a) } \Delta_r H^\circ &= [\Sigma \text{products}] - [\Sigma \text{reactants}] = -20.5 \text{ kJ mol}^{-1} \\ \Delta_r G^\circ &= \Delta_r H^\circ - T \Delta_r S^\circ = -20.5 \text{ kJ mol}^{-1} - 298.2 \text{ K} (-79.02 \text{ J K}^{-1} \text{ mol}^{-1})(1 \text{ kJ}/1000 \text{ J}) \\ \Delta_r G^\circ &= 3.06 \text{ kJ mol}^{-1}\end{aligned}$$

$$\Delta_r S^\circ = \frac{\Delta_r H^\circ - \Delta_r G^\circ}{T} = \frac{(-20.5 \text{ kJ mol}^{-1} - 3.06 \text{ kJ mol}^{-1})(1000 \text{ J}/1\text{kJ})}{298.15 \text{ K}}$$

$$\Delta_r S^\circ = -79.02 \text{ J K}^{-1} \text{ mol}^{-1}$$

Surprisingly, the reaction is not spontaneous under these conditions. The reverse reaction, which is the production of ATP, is spontaneous. However, these are standard state conditions. At pH 7 in the cell, this reaction must be spontaneous; otherwise, ATP wouldn't be a good energy source. We will determine the effect of the concentration on  $\Delta_r G$  in Chapter 17. Then, we will more carefully consider the effect of pH on this reaction. The reaction as written, under standard conditions, is enthalpically favored and entropically disfavored.

#### Example 15.4.5:

This example explores the issue of the arbitrary reference we apply to Gibbs energy and enthalpies of formation as opposed to the absolute reference for entropy. Consider the hydrogenation of ethylene:  $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$ .

Assume all reactants and products are at 1 bar and 298.15 K. The  $\Delta_f G^\circ$  and  $\Delta_f H^\circ$  of  $\text{H}_2$  is defined as zero, but the standard state absolute entropy for  $\text{H}_2$  is  $130.59 \text{ J K}^{-1} \text{ mol}^{-1}$ . Does the change in reference state make a difference? (a) Calculate  $\Delta_r H^\circ$  and  $\Delta_r S^\circ$ . From  $\Delta_r H^\circ$  and  $\Delta_r S^\circ$ ,



calculate  $\Delta_r G^\circ$ . (b) Calculate  $\Delta_r G^\circ$  directly from tabulated  $\Delta_f G^\circ$  values and compare with part (a). (c) Does the choice of reference for Gibbs energy and entropy make a difference?

*Answer:* The standard state thermodynamic properties are given in the Appendix Data Section:

	$\text{C}_2\text{H}_4(\text{g})$	$+$	$\text{H}_2(\text{g})$	$\rightarrow$	$\text{C}_2\text{H}_6(\text{g})$	Change for reaction
$\Delta_f H^\circ$	52.26		0		-84.68 kJ mol <sup>-1</sup>	$\Delta_r H^\circ = -136.94 \text{ kJ mol}^{-1}$
$S^\circ$	219.56		130.574		229.49 J K <sup>-1</sup> mol <sup>-1</sup>	$\Delta_r S^\circ = -120.64 \text{ J K}^{-1} \text{ mol}^{-1}$
$\Delta_f G^\circ$	68.15		0		-32.89 kJ mol <sup>-1</sup>	$\Delta_r G^\circ = -101.04 \text{ kJ mol}^{-1}$

where the reaction changes are as usual  $[\Sigma \text{products}] - [\Sigma \text{reactants}]$ . (a). Using the calculated values for  $\Delta_r H^\circ$  and  $\Delta_r S^\circ$ :

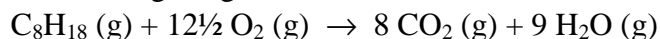
$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ = -136.94 \text{ kJ mol}^{-1} - 298.15 \text{ K} (-120.64 \text{ J K}^{-1} \text{ mol}^{-1})(1 \text{ kJ}/1000 \text{ J})$$

$$\Delta_r G^\circ = -100.97 \text{ kJ mol}^{-1}$$

(b). Using tabulated Gibbs energies of formation,  $\Delta_f G^\circ = -101.04 \text{ kJ mol}^{-1}$ , as shown in the table. The value using  $\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ$  and the direct value in the table agree to within experimental and round-off error. (c). As long as we always calculate differences, the reference point is arbitrary and can be different for  $\Delta_f H$ ,  $\Delta_f G$ , and  $S$ .

#### Example 15.4.6:

The “octane” rating for gasoline is based on the combustion of isooctane, 2,2,4-trimethylpentane:



The  $\Delta_r U^\circ(298 \text{ K}) = -5109. \text{ kJ mol}^{-1}$ . Calculate  $\Delta_r S^\circ$  and  $\Delta_r A^\circ$  for this reaction at 298.15 K. The absolute entropy for iso-octane is 423.2 J K<sup>-1</sup> mol<sup>-1</sup> (Table 8.4.2).

*Answer:* The standard state thermodynamic properties are given in Tables 8.4.1-8.4.2 in the Appendix Data Section.

	$\text{C}_8\text{H}_{18}(\text{g})$	$+$	$12\frac{1}{2} \text{O}_2(\text{g})$	$\rightarrow$	$8 \text{CO}_2(\text{g})$	$+$	$9 \text{H}_2\text{O}(\text{g})$
$S^\circ$	423.2		205.029		213.74		188.715 J K <sup>-1</sup> mol <sup>-1</sup>

$$\Delta_r S^\circ = [\Sigma \text{products}] - [\Sigma \text{reactants}]$$

$$\Delta_r S^\circ = [8 (213.74 \text{ J K}^{-1} \text{ mol}^{-1}) + 9 (188.715 \text{ J K}^{-1} \text{ mol}^{-1})] - [1 (423.2 \text{ J K}^{-1} \text{ mol}^{-1}) + 12.5 (205.029 \text{ J K}^{-1} \text{ mol}^{-1})] = 422.29 \text{ J K}^{-1} \text{ mol}^{-1}$$

Then  $\Delta_r A^\circ = \Delta_r U^\circ - T \Delta_r S^\circ = -5109. \text{ kJ mol}^{-1} - 298.15 \text{ K}(422.29 \text{ J K}^{-1} \text{ mol}^{-1})(1 \text{ kJ}/1000 \text{ J})$

$$\Delta_r A^\circ = -5235. \text{ kJ mol}^{-1}$$

Notice that  $\Delta_r A^\circ$  gives the maximum total work available, which in this case is more work available from the reaction than  $\Delta_r U^\circ$ . The reason that more work is available than the internal energy change is that the reaction has a favorable entropy change, which adds to the total work that can be done by the system. The entropy change is favorable because of the larger number of moles of gaseous products.

## 15.5 Summary – Looking Ahead

The thermodynamic potential energy functions each play an important role in accounting for energy transfers in chemical processes and in the environment.

Internal energy change gives the heat transfer at constant volume.

Enthalpy change gives the heat transfer at constant pressure.

Internal energy change gives the work for an adiabatic process.

Enthalpy change gives the maximum non-PV work for an adiabatic constant pressure process.

Helmholtz energy change gives the maximum work at constant temperature.

Gibbs energy change gives the maximum non-PV work at constant temperature and pressure.

The spontaneity criterion for an isolated system is an increase in entropy. To apply the Second Law to a non-isolated system, we form an isolated composite combining the system and the surroundings. The entropy increases for a spontaneous process in the isolated composite. The surroundings act as a constant temperature and pressure reservoir. The spontaneity criterion at constant temperature and volume is the Helmholtz energy. The spontaneity criterion at constant temperature and pressure is the Gibbs energy. The thermodynamic potentials can also be used to determine if a system is at equilibrium. At constant temperature and volume, the Helmholtz energy is minimized for a system at equilibrium, and  $dA = 0$  for an equilibrium process. At constant temperature and pressure, the Gibbs energy is minimized for a system at equilibrium, and  $dG = 0$  for an equilibrium process. At equilibrium the electrochemical potentials of the products and reactants are equal as given by  $\sum v_i \bar{\mu}_i = 0$ . The changes in  $U$ ,  $H$ ,  $A$ , and  $G$  can be calculated for any process; however, each has a useful interpretation under specific conditions.

The things we wish to do involve transfers of heat and work. Thermodynamics shows the interrelationships that govern all physical macroscopic processes for transfers of heat and work. Spontaneous processes are required for useful purposes. Spontaneity is governed by an increase in entropy for an isolated system. The universe can be considered as an isolated system for many purposes. Thermodynamics provides a powerful framework that can be applied to any macroscopic process. The power of thermodynamics is its complete generality and the ability to highlight interrelationships of a system to its surroundings. In the next chapter we combine the concepts concerning spontaneity and equilibrium with the mathematical techniques that are necessary to completely characterize any thermodynamic process. In the subsequent chapters we apply the formalism to phase transitions, processes in solution, chemical equilibria, and electrochemistry. The result will be a unified and general framework for solving problems and for understanding the intricacies of nature.

## Chapter Summary

1. The change in entropy for a closed system for any process involving PV work and chemical reactions:

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{1}{T} \sum_{i=1}^{n_s} v_i \mu_i d\xi$$

2. For an isolated system, entropy is a good spontaneity criterion:

$$dS = -\frac{1}{T} \sum_{i=1}^{n_s} v_i \mu_i d\xi \geq 0 \quad \text{or} \quad \sum_{i=1}^{n_s} v_i \mu_i d\xi \geq 0 \quad (= \text{reversible})$$

3. The Helmholtz energy is defined as  $A \equiv U - TS$ , giving  $dA = dU - TdS - SdT$ .

4. From the combined First and Second Laws of thermodynamics for a closed system with PV and chemical work:

$$dA = -SdT - PdV + \sum_{i=1}^{n_s} v_i \mu_i d\xi$$

5. For a closed system at constant temperature and volume, Helmholtz energy is a good

$$\text{spontaneity criterion: } dA = \sum_{i=1}^{n_s} v_i \mu_i d\xi \leq 0. \quad (= \text{reversible})$$

6. For a closed system in an isothermal process the Helmholtz energy gives the maximum work available:  $dA = dw_{\text{max}}$ .

7. The Gibbs energy is defined as  $G \equiv H - TS$ , giving:

$$dG = dH - TdS - SdT = dU + PdV + VdP - TdS - SdT$$

8. From the combined First and Second Laws of thermodynamics for a closed system with PV and chemical work:

$$dG = -SdT + VdP + \sum_{i=1}^{n_s} v_i \mu_i d\xi$$

9. For a closed system at constant temperature and pressure, Gibbs energy is a good spontaneity

$$\text{criterion: } dG = \sum_{i=1}^{n_s} v_i \mu_i d\xi \leq 0. \quad (= \text{reversible})$$

10. The Gibbs energy gives the maximum non-PV work for a closed, isothermal process:

$$dG = dw_{\text{net,max}}$$

11. Non-PV work can be cast in the form  $dw = F dx$ . The total PV and non-PV work is then:

$$dw = -P_{\text{ext}}dV + F dx. \quad \text{For a closed system at constant temperature and pressure with } Fx \text{ work only: } dG = F_A dx_A + F_B dx_B \leq 0, \text{ with constant } x_{\text{tot}} = x_A + x_B.$$

12. For chemical and electrical work,  $dU = TdS - PdV + \sum_{i=1}^{n_s} \mu_i dn_i + \sum_{i=1}^{n_s} z_i F \phi_i dn_i$

13. The change in Gibbs energy for ions in the presence of an electrical field at constant

$$\text{temperature and pressure is: } dG = \sum_{i=1}^{n_s} \mu_i dn_i + \sum_{i=1}^{n_s} z_i F \phi_i dn_i$$

14. The electrochemical potential is defined as:  $\bar{\mu}_i = \mu_i + z_i F \phi_i$

15. For a closed system at constant temperature and pressure in the presence of an electric potential, the change in Gibbs energy is:

$$dG = \sum_{i=1}^{n_s} \bar{\mu}_i dn_i$$

16. For a closed system at constant temperature and pressure taking into account differences in concentration, chemical reactions, and electric fields:

$$dG = \sum_{i=1}^{n_s} \bar{\mu}_i dn_i \leq 0 \quad \text{or equivalently} \quad dG = \sum_{i=1}^{n_s} v_i \bar{\mu}_i d\xi \leq 0$$

17. For a closed system for an isothermal expansion of an ideal gas:

$$\Delta A = -nRT \ln \frac{V_2}{V_1} \quad \Delta G = nRT \ln \frac{P_2}{P_1}$$

18. For an isothermal process in a liquid or a solid for small changes in pressure:  $\Delta G = V_o \Delta P$ .  
For moderate changes in pressure:  $\Delta G = V_o (P - P_o) - \frac{1}{2} V_o \kappa_T (P - P_o)^2$ .

19. For small changes in temperature for a constant volume process,  $\Delta A = -S\Delta T$  and for a constant pressure process:  $\Delta G = -S\Delta T$ .

20. Assuming a constant heat capacity, at constant volume:

$$\Delta A = -S_o (T - T_o) + C_v (T - T_o) - C_v T \ln \frac{T}{T_o}$$

$$\text{and at constant pressure: } \Delta G = -S_o (T - T_o) + C_p (T - T_o) - C_p T \ln \frac{T}{T_o}$$

21. For a phase transition at the equilibrium transition temperature:  $\Delta_{tr}A = -\Delta n_{gas}RT_{tr}$ .

22. For a chemical reaction at constant temperature and pressure:  $\Delta_r G = \sum_{i=1}^{n_s} v_i \Delta_f G_i$ .

### Literature Cited:

1. R. A. Alberty, *Thermodynamics of Biochemical Reactions*, Wiley, Hoboken, NJ, 2003.

### Further Reading:

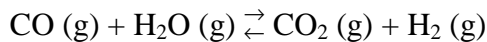
F. C. Andrews, *Thermodynamics: Principles and Applications*, Wiley-Interscience, New York, NY, 1971.  
Chapt. 30.

*Gibbs Energy and Biochemical Reactions:*

R. A. Alberty, *Thermodynamics of Biochemical Reactions*, Wiley, Hoboken, NJ, 2003.

### Problems: Spontaneity

1. The water gas shift reaction is an important process in the gasification of coal or biomass to produce transportation fuels:



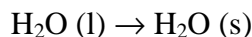
What is the relationship among the chemical potentials for the reaction at equilibrium?

2. Some authors use “=” instead of “ $\rightleftharpoons$ ” for chemical equations at equilibrium. For example:



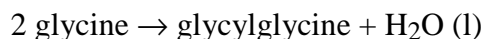
Why is the use of the equals sign a good idea?

3. Calculate  $\Delta_{\text{fus}}H^\circ$ ,  $\Delta_{\text{fus}}S^\circ$ , and  $\Delta_{\text{fus}}G^\circ$  for freezing one mole of supercooled water at  $-10.0^\circ\text{C}$  and 1.00 bar pressure:



At 273.15 K,  $\Delta_{\text{fus}}H^\circ = 6.008 \text{ kJ mol}^{-1}$ . Assume the heat capacities are constant over the temperature range with  $C_{\text{p,m}}(\text{s}) = 37.66 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $C_{\text{p,m}}(\text{l}) = 75.29 \text{ J K}^{-1} \text{ mol}^{-1}$ .

4. Determine the energy necessary to form a peptide bond by determining  $\Delta_rG^\circ$  for the following reaction at 298.15 K:



Use the data table below.

Substance	$\Delta_f H_m^\circ$ (kJ mol <sup>-1</sup> )	$S_m^\circ$ (J K <sup>-1</sup> mol <sup>-1</sup> )
glycine	-528.5	103.5
glycylglycine	-747.7	190.0
H <sub>2</sub> O (l)	-285.830	69.92

5. The enzyme pyruvate decarboxylase catalyzes the following reaction:



Calculate  $\Delta_rH^\circ$ ,  $\Delta_rS^\circ$ , and  $\Delta_rG^\circ$  for this reaction at 298.15 K given the following data. Is this process enthalpy or entropy driven?

substance	$\Delta_f H_m^\circ$ (kJ mol <sup>-1</sup> )	$\Delta_f G_m^\circ$ (kJ mol <sup>-1</sup> )
acetaldehyde (g)	-166.19	-128.86
CO <sub>2</sub> (g)	-393.509	-394.359
pyruvic acid (l)	-584.5	-463.4

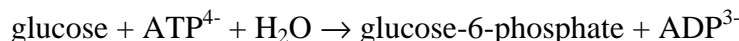
6. Before glucose can be used as an energy source in your body, it must first be phosphorylated:



the energy for this process is supplied by the hydrolysis of ATP:

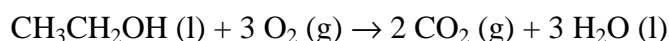


at pH 7. The overall reaction is then:

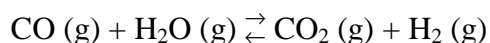


Calculate the entropy change for the overall reaction at 298.2 K from the given values of  $\Delta_rG^\circ$  and  $\Delta_rH^\circ$ . Is the phosphorylation of glucose enthalpy or entropy driven?

7. Ethanol is used as an additive in gasoline to increase the octane rating and to help decrease air pollution. Calculate  $\Delta_rH^\circ$ ,  $\Delta_rS^\circ$ , and  $\Delta_rG^\circ$  for the combustion of ethanol at 298.2 K using standard data tabulations:

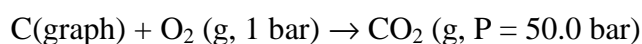


8. Why can we choose the Gibbs energy of formation of an element, in its most stable state at 1 bar pressure, as equal to zero?
9. The enthalpy change for a reaction can be endothermic or exothermic. The entropy change for a chemical reaction can be positive or negative. Consider the temperature dependence of the spontaneity of a chemical reaction at constant pressure. Assume that the sign of the reaction enthalpy and entropy don't change with temperature. Under what cases, for the signs of the enthalpy and the entropy, is a reaction always spontaneous? Under what cases is a reaction never spontaneous?
10. The water gas shift reaction is an important process in the gasification of coal or biomass to produce transportation fuels:



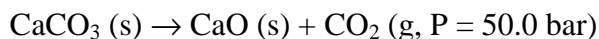
What is the relationship between the Gibbs and Helmholtz reaction energy changes at constant pressure? Why?

11. The internal energy of combustion of iso-propyl alcohol is  $-2003.2 \text{ kJ mol}^{-1}$  at 298.2 K and 1.000 bar. The absolute entropy of iso-propyl alcohol is  $181.1 \text{ J K}^{-1} \text{ mol}^{-1}$  at 298.2 K and 1.000 bar. Calculate the enthalpy, Helmholtz energy, and Gibbs energy of combustion of iso-propyl alcohol. Treat all gases as ideal.
12. Calculate the change in Gibbs energy when one mole of an ideal gas expands isothermally from an initial volume of 1.00 L to a final volume of 10.0 L at 298.15 K.
13. Calculate the changes in Gibbs energy and Helmholtz energy when one mole of an ideal gas expands isothermally from an initial pressure of 2.00 bar to a final pressure of 1.00 bar at 298.15 K.
14. General Chemistry texts often use a standard state pressure of 1 atm instead of 1 bar. Does the change in standard state make a significant difference in the tabulated values? Calculate the standard state Gibbs energy of formation for  $\text{CO}_2$  at  $P^\circ = 1 \text{ atm}$ , given that the 1 bar standard state is  $\Delta_f G^\circ(\text{CO}_2) = -394.36 \text{ kJ mol}^{-1}$  at 298.15 K.
15. General Chemistry texts often use a standard state pressure of 1 atm instead of 1 bar. Does the change in standard state make a significant difference in the tabulated values for Gibbs energies of formation? Calculate the standard state Gibbs energy of formation for  $\text{SO}_3$  at  $P^\circ = 1 \text{ atm}$  assuming ideal gas behavior, given that the 1 bar standard state is  $\Delta_f G^\circ(\text{SO}_3, P^\circ = 1 \text{ bar}) = -371.06 \text{ kJ mol}^{-1}$  at 298.15 K.
16. Carbon dioxide plays an important role in many geochemical processes, which often occur at high pressure. Calculate the Gibbs energy of formation for  $\text{CO}_2$  at 50.0 bar and 298.15 K, relative to the constituent elements in their standard states:



Assume ideal gas behavior and  $\Delta_f G^\circ(\text{CO}_2) = -394.359 \text{ kJ mol}^{-1}$  at 298.15 K.

17. Carbon dioxide plays an important role in many geochemical processes, which often occur at high pressure. Calculate the reaction Gibbs energy at 50.0 bar and 298.2 K for:



One crystalline form of  $\text{CaCO}_3$  is the mineral calcite. Neglect the effect of the pressure on the solids and assume ideal gas behavior.

18. Derive Eq. 15.4.8,  $\Delta G = V_o (P - P_o) - \frac{1}{2} V_o \kappa_T (P - P_o)^2$ , from  $dG = V dP$  for an isothermal process, from an initial pressure  $P_o$  and a final pressure  $P$ .

19. Calculate the change in Gibbs energy for one mole of liquid benzene at 298.2 K for a change in pressure from 1.00 bar to 600.0 bar. The isothermal compressibility of benzene is  $90.9 \times 10^{-6} \text{ bar}^{-1}$  and the density is  $0.8765 \text{ g/cm}^3$ . Compare the results using Eqs. 15.4.7 and 15.4.8

20. Calculate the Gibbs energy difference for one mole of water at the bottom of the Mariana Trench compared to 1 bar pressure, given  $\kappa_T = 4.587 \times 10^{-10} \text{ Pa}^{-1}$  at  $20^\circ\text{C}$ . The maximum depth of the trench is 10911 m (35798 ft) and the pressure is 1,086. bar (15,750 psi). Use the density of pure water,  $0.9982 \text{ g mL}^{-1}$  at 1 bar, for this problem, instead of the density of sea water.

21. Starting from  $\Delta A = -nRT \ln V_2/V_1$  and the definition of  $G$ , in the form  $G \equiv A + PV$ , show that  $\Delta G = nRT \ln P_2/P_1$  for an ideal gas in an isothermal process.

22. Reverse osmosis is the most cost effective method for seawater desalination. However, reverse osmosis is energy intensive. In reverse osmosis, seawater is pressurized to 60-70 bar to force water to flow through a semi-permeable membrane. The work in reverse osmosis can be estimated using  $w = -P\Delta V$ , where  $P$  is the constant high pressure of the process and  $\Delta V$  is the volume of water pushed through the membrane. Calculate the change in Helmholtz energy for purifying  $1.00 \text{ m}^3$  of water using reverse osmosis with an applied pressure of 65.0 bar. Give your results in joules and kWh ( $1 \text{ kWh} = 3.6 \times 10^6 \text{ J}$ ). Why is the change in Helmholtz energy salient for water desalination?

23. How big of an effect does an electric field have on the electrochemical potential of an ion? Consider a simple electrochemical cell,  $\text{Zn}|\text{Zn}^{2+}||\text{Cu}^{2+}|\text{Cu}$ . Assume the electric potential is 0.500 V at the cathode. Calculate the electrochemical potential for one mole of  $\text{Cu}^{2+}$  ions, at standard state concentration, in the cathode (right-hand) compartment. In the absence of a field,  $\Delta_f G_m^\circ$  for  $\text{Cu}^{2+}$  from standard tables is  $65.49 \text{ kJ mol}^{-1}$ .

24. Two solutions containing  $\text{K}^+$  ions are separated by a  $\text{K}^+$  ion-selective membrane. Electrodes are placed in both solutions and the flow of  $\text{K}^+$  ions is monitored as a function of applied potential,  $\Delta\phi = \phi_{\text{in}} - \phi_{\text{out}}$ . The  $\text{K}^+$  ions cease migration across the membrane for an applied potential of -70.0 mV. Calculate the difference in chemical potential of the  $\text{K}^+$  ions in the two solutions.

25. Coastal communities may exploit the  $\text{Na}^+$  gradient between seawater and fresh river water to generate electricity. Calculate the electric potential available from a seawater-fresh water cell with a  $\text{Na}^+$  ion selectively-permeable membrane. Assume the difference in chemical potential, in the absence of electric fields, between seawater and fresh water is  $10.5 \text{ kJ mol}^{-1}$  (roughly a factor of 100 difference in concentration with an activity coefficient for 0.5 m NaCl of 0.680).

26. The standard state Gibbs energy of formation of liquid water at 298.15 K is  $-237.13 \text{ kJ mol}^{-1}$ . Normally, we ignore any changes of  $\Delta_f G^\circ$  with pressure for liquids and solids if the specific reaction is run near 1 bar of pressure. How big of an error does this make? Calculate the change in Gibbs energy for one mole of liquid water for a pressure change from 1.00 bar to 50.0 bar.

27. Calculate the change in Helmholtz and Gibbs energies for the vaporization of 1.00 mol of liquid water at 372.76 K and 1.00 bar. The enthalpy of vaporization at 372.76 K is  $40.7 \text{ kJ mol}^{-1}$ . Treat water vapor as ideal. What does the difference between the Helmholtz and Gibbs energies tell you about the process? (The standard boiling point of water is  $99.61^\circ\text{C}$  or 372.76 K.)

28. Calculate the change in Gibbs energy for the vaporization of 2.00 mol of liquid water at 372.76 K and 1.000 bar to give water vapor at 0.500 bar and the same temperature. Assume the vapor is ideal. (The standard boiling point of water is  $99.61^\circ\text{C}$  or 372.76 K.)

29. Show that for small changes in temperature the last two terms cancel in Eq. 15.4.15:

$$\Delta G = -S_o (T - T_o) + C_p (T - T_o) - C_p T \ln \frac{T}{T_o} \approx -S_o (T - T_o)$$

To prove this relationship, expand the logarithmic term in a Taylor series and keep just the first non-zero term. (Note: the Taylor series expansion for  $\ln(x_2/x_1) \approx x_2/x_1 - 1$ , for  $x_2/x_1 \approx 1$ .)

30. Prove Eq. 15.4.15, that is  $\Delta G = -S_o (T - T_o) + C_p (T - T_o) - C_p T \ln \frac{T}{T_o}$ .

31. Calculate the standard state Gibbs energy of formation for  $\text{H}_2\text{S}$  (g) at 500.0 K. Remember that the Gibbs energy of formation is for a chemical reaction and not just a pure substance. The relevant data are given in the table below.

Substance at 298.15 K	$\Delta_f G^\circ$ ( $\text{kJ mol}^{-1}$ )	$S^\circ$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )	$C_p^\circ$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )
$\text{H}_2\text{S}$ (g)	-33.4	205.8	34.23
$\text{H}_2$ (g)	0	130.574	28.824
S (s, rhombic)	0	32.054	22.64

32. Calculate the standard state Gibbs energy of formation for  $\text{SO}_2$  (g) at 500.0 K.

33. Determine if the following statements are true or false. If the statement is false, describe the changes that are necessary to make the statement true, if possible. If the statement is true but too restrictive, give the more general statement.

- When a change in state occurs at constant pressure, the increase in the Gibbs energy of the system must equal the decrease in the Gibbs energy of the surroundings.
- The entropy change of the universe is a spontaneity criterion only for isolated systems.
- Gibbs energy is minimized for processes at constant temperature and pressure and no electrical work.
- For a chemical reaction at constant pressure, the changes in Helmholtz and Gibbs energies are identical if the volume of the products is identical to the volume of the reactants.
- For phase transitions, the Gibbs energy change is zero.

34. Show that the internal energy change gives the work for an adiabatic process and the enthalpy change gives the maximum non-PV work for an adiabatic constant pressure process.