1.6: The Gibbs and Helmholtz Energy

In this chapter we introduce two additional state properties: the Gibbs energy and the Helmholtz energy. These additional variables are useful for allowing us to determine the direction of spontaneous change without having to directly calculate the change in entropy of the universe from the second law. The Gibbs energy has particular importance in biochemistry. We next introduce the (intensive) molar Gibbs and the chemical potential. Emphasis is placed on the thermodynamics of mixtures and phase separations.

> **Learning Objectives**
>
> - Know the thermodynamic definitions of the Gibbs energy and Helmholtz energy and why these two properties are important.
> - Understand that the change in Gibbs energy has both an enthalpic and entropic contribution.
> - Know that at constant pressure and temperature the Gibbs energy decreases for a spontaneous process, and at constant volume and temperature the Helmholtz energy decreases for a spontaneous process.
> - Be able to identify the fundamental differentials for dU, dH, dG, and dA and how these can be used to arrive at thermodynamic relationships.

The Gibbs and Helmholtz energy

The first law of thermodynamics (Chapter I.2) accounts for the conservation of energy and the second law of thermodynamics (Chapter I.4) determines the spontaneity. Together, these laws should allow us to deal with any biophysical problem, but their direct application is not always convenient. In addition to our current set of state properties it is useful to define two additional state properties: the **Gibbs energy** and the **Helmholtz energy**.

Recall that we have already define the **total internal energy U** and the **enthalpy $\mathbf{H = U + PV}$**. Similarly, we now define the **Gibbs energy:**

$$G = H - TS \tag{1.6.1}$$

The Gibbs energy ($\mathbf{G}$) is the enthalpy minus the product of the temperature and the entropy.

We also define the **Helmholtz energy:**

$$A = U - TS \tag{1.6.2}$$

The Helmholtz energy ($\mathbf{A}$) is the total internal energy minus the product of the temperature and the entropy.

If we are interested in infinitesimal changes in the Gibbs or Helmholtz energies we can consider the differential form of Equation 1.6.1 and Equation 1.6.2

$$dG = dH - TdS - SdT \tag{1.6.3}$$

$$dA = dU - TdS - SdT \tag{1.6.4}$$

> **📌 Note**
>
> <u>Note</u>: In the differential form of Equation 1.6.4 we have made use of the product rule for derivatives: $d(AB) = BdA + AdB$

The Significance of the Gibbs and Helmholtz energy

In order to understand why the Gibbs and Helmholtz energies are important, we need to recall the second law of thermodynamics which states:

$$dS_{sys} + dS_{surr} \geq 0 \tag{1.6.5}$$

Recalling that for the surroundings:

$$dS_{surr} = \frac{\delta q_{surr}}{T}$$

$$= -\frac{\delta q_{sys}}{T} \tag{1.6.6}$$

We can substitute Equation 1.6.6 into Equation 1.6.5 to obtain an alternative expression for the second law in terms of only the system variables:

$$dS - \frac{\delta q_{sys}}{T} \geq 0$$

$$TdS - \delta q_{sys} \geq 0 \tag{1.6.7}$$

Equation 1.6.7 follows from the second law of thermodynamics. We will now consider two particular cases.

Case 1: Constant T and P Conditions

At constant P, the heat transfer is equivalent to the enthalpy (see Chapter I.2):

$$\delta q_p = dH \tag{1.6.8}$$

Substitution of Equation 1.6.8 into Equation 1.6.7 gives:

$$TdS - dH \geq 0 \tag{1.6.9}$$

Substituting the differential form of the Gibbs energy (Equation 1.6.4) into Equation 1.6.9 gives:

$$dG + SdT \leq 0 \tag{1.6.10}$$

At constant T, the second term $SdT = 0$ because T is not changing, giving the final result:

$$dG \leq 0 \tag{1.6.11}$$

or upon integrating both sides from an initial to final state:

$$\Delta G \leq 0 \tag{1.6.12}$$

The equality holds for a reversible (equilibrium) process, and the inequality holds for any spontaneous process at constant T and P.

> Key Result: At constant T and P conditions $\Delta G < 0$ for a spontaneous process and $\Delta G = 0$ for a reversible process.

Since we are at constant T, the differential form of dG from Equation 1.6.4 simplifies to:

$$dG = dH - TdS \tag{1.6.13}$$

Integrating both sides at constant T and P from an initial state to a final state gives:

$$\Delta G = \Delta H - T\Delta S \tag{1.6.14}$$

from which we see that the Gibbs energy has an enthalpic term and an entropic term.

> Key Result: $\Delta G = \Delta H - T\Delta S$
>
> The expression is valid at constant T and P.

Case 2: Constant T and V Conditions

For the case of constant volume, the heat transfer is equivalent to the total internal energy (see Chapter I.2):

$$\delta q_v = dU \tag{1.6.15}$$

Substitution of Equation 1.6.15 into Equation 1.6.7 gives:

$$TdS - dU \geq 0 \tag{1.6.16}$$

Substituting the differential form of the Helmholtz energy (Equation 1.6.4) into Equation 1.6.16 gives:

$$dA + SdT \leq 0 \tag{1.6.17}$$

Again at constant T, the second term $SdT = 0$ because T is not changing, giving the final result:

$$dA \leq 0 \tag{1.6.18}$$

or upon integrating both sides from an initial to final state:

$$\Delta A \leq 0 \tag{1.6.19}$$

The equality holds for a reversible (equilibrium) process, and the inequality holds for any spontaneous process at constant T and V.

> Key Result: At constant T and V conditions $\Delta A < 0$ for a spontaneous process and $\Delta A = 0$ for a reversible process.

Since we are at constant T, the differential form of dA from Equation 1.6.4 simplifies to:

$$dA = dU - TdS \tag{1.6.20}$$

Integrating both sides at constant T and V from an initial state to a final state gives:

$$\Delta A = \Delta U - T\Delta S \tag{1.6.21}$$

> Key Result: $\Delta A = \Delta U - T\Delta S$
>
> The expression is valid at constant T and V.

Four Fundamental differentials of thermodynamics

The first law of thermodynamics in differential form is:

$$dU = \delta q + \delta w \tag{1.6.22}$$

For a reversible process we have defined the entropy as $dS = \delta q_{rev}/T$ and the reversible work as $\delta w = -P \cdot dV$. Substituting these identities into Equation 1.6.22 gives the following differential form of the first law:

$$dU = TdS - PdV \tag{1.6.23}$$

Note that Equation 1.6.23 is valid for a reversible process in which the only work is due to compression/expansion.

The enthalpy was defined in Chapter I.2 as:

$$H = U + PV \tag{1.6.24}$$

From Equation 1.6.24 we can write a differential form of the enthalpy as:

$$dH = dU + PdV + VdP \tag{1.6.25}$$

where we have again used the product rule from calculus on the PV term. Substituting Equation 1.6.23 into Equation 1.6.25 for the dU term gives another differential relation for dH:

$$dH = TdS - PdV + PdV + VdP$$
$$dH = TdS + VdP \tag{1.6.26}$$

Similarly, substitution of Equation 1.6.23 into the dU term in the differential form for dA in Equation 1.6.4 gives another differential for dA:

$$dA = TdS - PdV - TdS - SdT$$
$$dA = -PdV - SdT \tag{1.6.27}$$

Finally, substitution of Equation 1.6.26 into the dH term differential form for dG in Equation 1.6.4 gives another differential for dG:

$$dG = TdS + VdP - TdS - SdT$$
$$dG = VdP - SdT \tag{1.6.28}$$

Table I.6.i summarizes the four fundamental differential relations for dU, dH, dG, and dA:

Table I.6.i

$dU = TdS - PdV$	(Equation 1.6.23)
$dH = TdS - VdP$	(Equation 1.6.26)
$dA = -PdV - SdT$	(Equation 1.6.27)
$dG = VdP - SdT$	(Equation 1.6.28)

Pressure dependence of ΔG

The fundamental differentials from **Table I.6.i** are useful for deriving various thermodynamic relationships. As an example, we can use Equation 1.6.28 to derive the pressure dependence of ΔG. Starting from Equation 1.6.28, at **constant T** the second term $SdT = 0$, giving:

$$dG = VdP \qquad (1.6.29)$$

or

$$\left(\frac{\partial G}{\partial P}\right)_T = V \qquad (1.6.30)$$

Integrating both sides of Equation 1.6.29 from an initial pressure $\mathbf{P_i}$ to a final pressure $\mathbf{P_f}$ gives:

$$\Delta G = \int_{P_i}^{P_f} VdP \qquad (1.6.31)$$

Solids and liquids are nearly incompressible, so the volume does not change significantly with changes in the pressure. Therefore, for **solids and liquids** the volume can be treated as constant in Equation 1.6.31, and upon integration gives:

$$\Delta G = V\Delta P \qquad (1.6.32)$$

Note that Equation 1.6.32 is valid for solids and liquids. For an ideal gas we can substitute $V = nRT/P$ for the volume in Equation 1.6.31:

$$\Delta G = \int_{P_i}^{P_f} \frac{nRT}{P} dP$$

$$\Delta G = nRT \int_{P_i}^{P_f} \frac{dP}{P}$$

$$\Delta G = nRT \ln\left(\frac{P_f}{P_i}\right) \qquad (1.6.33)$$

If we set the initial pressure to 1 bar (standard pressure), and replace the initial Gibbs energy $\mathbf{G_i}$ with the symbol for G at the standard state $\mathbf{G^\circ}$, then Equation 1.6.33 becomes:

$$G = G^\circ + nRT \ln\left(\frac{P}{1\,\text{bar}}\right)$$

$$\bar{G} = \bar{G}^\circ + RT \ln\left(\frac{P}{1\,\text{bar}}\right) \qquad (1.6.34)$$

where in the last line we have use the expression for the **molar Gibbs, $\bar{\mathbf{G}}$**.

See Practice Problem 1

Examples

✔ **Example 1.6.1**

Show that at constant pressure, the entropy is given by:

$$S = -\left(\frac{\partial G}{\partial T}\right)_P$$

Solution

Starting with Equation 1.6.28:

$$dG = V\,dP - S\,dT$$
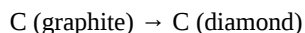
At constant pressure ($dP = 0$), we have:

$$dG = -S\,dT$$

or, solving for S:

$$S = -\left(\frac{\partial G}{\partial T}\right)_P$$

Practice Problems

Problem 1. At high pressure, graphite (density $\rho = 2.25$ g/cm^3) can be spontaneously converted into diamond (density $\rho = 3.51$ g/cm^3) through a solid-to-solid phase transition:

C (graphite) → C (diamond)

At 1 atm of pressure the standard molar Gibbs energy of this reaction is $\Delta\bar{G}^\circ = 2.84$ kJ/mol. At what pressure does the reaction become spontaneous (i.e. at what pressure does $\Delta\bar{G} = 0$)?

Problem 2. Consider the *reversible* freezing of liquid water into ice at a constant temperature of 0 °C and constant pressure of 1 atm.

H$_2$O (l) ↔ H$_2$O (g) 0 °C
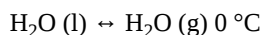
Show that ΔG for this process is 0. (Hint: use the relation $\Delta G = \Delta H - T\Delta S$).