In this chapter we introduce a few new functions and derive a large number of very useful equations relating one thermodynamic property to another. The basis throughout is a constant amount of a single substance† in internal equilibrium. Often we will also consider cases where the only type of work is that of volume changes against an external pressure. The basic equation for this type of system was derived above:

\[ dU = TdS - PdV \]  

(2-26)

This is the appropriate equation to use if entropy and volume are the independent variables of the problem, but this is rarely the case. More often, pressure is the appropriate variable instead of volume and temperature instead of entropy. In order to deal conveniently with these situations, Gibbs¹ in 1875 defined three new functions as follows:

\[ H = U + PV \]  

(3-1)

\[ A = U - TS \]  

(3-2)

\[ G = U - TS + PV = H - TS = A + PV \]  

(3-3)

Note that \( H, A, \) and \( G \) are state functions or properties since all of the quantities entering their definitions have that characteristic. The process of their formation is sometimes called a Legendre transform.

It should be noted that Massieu² had already in 1869 defined two functions, which are \(-A/T\) and \(-G/T\) in terms of those defined above, and had developed some of the relationships of the type given below for \( A \) and \( G \). Also Helmholtz³ proposed in 1882 the function \( U - TS \) and applied it to certain chemical processes; this work was published after that of Gibbs and Massieu but was presumably independent. It was Gibbs,⁴ however, who demonstrated the great utility of all of these functions in the interpretation of diverse physical-chemical phenomena and, in particular, for multicomponent systems.

Gibbs used the Greek letters \( \varepsilon, \chi, \psi, \) and \( \Omega \), respectively, for \( U, H, A, \) and \( G \), but these symbols have not been in general use for many years. After some differences concerning \( A \) and \( G \), with accompanying confusion, the symbols shown above have been widely agreed upon and are recommended by IUPAC.⁵† We also follow the IUPAC⁶ recommendations for names: enthalpy for \( H \), Helmholtz energy for \( A \), Gibbs energy for \( G \). Alternates in the literature are heat content for \( H \); Helmholtz function, Helmholtz free energy, or work content for \( A \); and Gibbs function or Gibbs free energy for \( G \). The reader should always take care to ascertain the names and symbols in use for \( U - TS \) and \( H - TS \) in a particular book, article, or table.

We now take the differential of \( H \),

\[ dH = dU + PdV + VdP \]

and substitute Eq. (2-24) to obtain

\[ dH = TdS + VdP \]  

(3-4)

Similarly, one obtains

\[ dA = -SdT - PdV \]  

(3-5)

\[ dG = -SdT + VdP \]  

(3-6)

† The principal difference has been the use of \( F \) instead of either \( A \) or \( G \). The literature in physics commonly used and sometimes still uses \( F \) instead of \( A \) for \( U - TS \). The use of \( F \) instead of \( G \) for \( H - TS \) was common among American physical chemists until recently; that choice was adopted by Lewis and Randall in 1923. In our revision in 1961, we retained \( F \) for \( H - TS \) but recognized the need for some change. We also advocated the abandonment of \( F \) for either \( U - TS \) or \( H - TS \), and urged the adoption of \( A \) and \( G \), respectively. We are pleased that this was the decision of IUPAC.

¹ Relationships when there is more than one component with variation of composition will be considered in Chapter 10.
A number of very useful relationships now follow directly. At constant \( T \) or \( S \),

\[
\left( \frac{\partial A}{\partial V} \right)_T = -P = \left( \frac{\partial U}{\partial V} \right)_S \tag{3-7}
\]

\[
\left( \frac{\partial G}{\partial P} \right)_T = V = \left( \frac{\partial H}{\partial P} \right)_S \tag{3-8}
\]

while at constant \( V \) or \( P \),

\[
\left( \frac{\partial A}{\partial T} \right)_V = -S = \left( \frac{\partial G}{\partial T} \right)_P \tag{3-9}
\]

\[
\left( \frac{\partial U}{\partial S} \right)_V = T = \left( \frac{\partial H}{\partial S} \right)_P \tag{3-10}
\]

From further differentiation, we obtain

\[
\frac{\partial^2 A}{\partial T \partial V} = \left( \frac{\partial S}{\partial V} \right)_T \left( \frac{\partial P}{\partial T} \right)_V
\]

hence,

\[
\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V \tag{3-11}
\]

and, similarly, from \( \partial^2 G/\partial T \partial P \),

\[
\left( \frac{\partial S}{\partial P} \right)_T = -\left( \frac{\partial V}{\partial T} \right)_P \tag{3-12}
\]

from \( \partial^2 H/\partial S \partial P \)

\[
\left( \frac{\partial T}{\partial P} \right)_S = \left( \frac{\partial V}{\partial S} \right)_P \tag{3-13}
\]

and from \( \partial^2 U/\partial S \partial V \)

\[
\left( \frac{\partial T}{\partial V} \right)_S = \left( \frac{\partial P}{\partial S} \right)_V \tag{3-14}
\]

The last four equations are known as the Maxwell relations.

For the effect of change in pressure on enthalpy at constant temperature, one combines Eqs. (3-3), (3-8), and (3-12) to obtain

\[
\left( \frac{\partial H}{\partial P} \right)_T = \left( \frac{\partial G}{\partial P} \right)_T + T \left( \frac{\partial S}{\partial P} \right)_T = V - T \left( \frac{\partial T}{\partial P} \right)_P \tag{3-15}
\]

If we now combine Eq. (3-9) with the original definitions (3-2) and (3-3) we obtain valuable relationships that are appropriately known as the Gibbs–Helmholtz equations:

\[
A = U + T \left( \frac{\partial A}{\partial T} \right)_V \tag{3-16a}
\]

\[
G = H + T \left( \frac{\partial G}{\partial T} \right)_P \tag{3-16b}
\]

These equations can be rearranged to more compact and useful forms as follows:

\[
\left[ \frac{\partial (A/T)}{\partial T} \right]_V = -\frac{U}{T^2} \tag{3-17}
\]

\[
\left[ \frac{\partial (G/T)}{\partial T} \right]_P = -\frac{H}{T^2} \tag{3-18}
\]

Alternate forms are sometimes more convenient:

\[
\left[ \frac{\partial (A/T)}{\partial (1/T)} \right]_V = U \tag{3-19}
\]

\[
\left[ \frac{\partial (G/T)}{\partial (1/T)} \right]_P = H \tag{3-20}
\]

Equations (3-18) and (3-20) are particularly important in the treatment of the temperature dependency of chemical equilibria under constant pressure.

**Change of Variable**

In a number of problems it is necessary to transform an expression from one set of independent variables to another. The most frequent case in thermodynamics is a change from \( T \) and \( V \) to \( T \) and \( P \). We will use that transformation as an example, but the mathematics is general, of course. Suppose that the property \( Y \) is a function of \( T \) and \( V \). Its differential is

\[
dY = \left( \frac{\partial Y}{\partial T} \right)_V dT + \left( \frac{\partial Y}{\partial V} \right)_T dV
\]

Therefore, along a constant-pressure path the temperature derivative is

\[
\left( \frac{\partial Y}{\partial T} \right)_P = \left( \frac{\partial Y}{\partial T} \right)_V + \frac{\partial Y}{\partial V} \left( \frac{\partial V}{\partial T} \right)_P \tag{3-21}
\]

It is also useful to consider an increment in \( T \) along the path of constant \( Y \), i.e., \( dY = 0 \):

\[
0 = \left( \frac{\partial Y}{\partial T} \right)_V + \left( \frac{\partial Y}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_T \tag{3-22}
\]
This may be arranged to
\[ \left( \frac{\partial V}{\partial T} \right)_T = \frac{(\partial V/\partial T)_V}{(\partial V/\partial T)_T} \]  
(3-23)

Another rearrangement has an interesting symmetry:
\[ \left( \frac{\partial V}{\partial T} \right)_T \left( \frac{\partial V}{\partial T} \right)_T \frac{\partial T}{\partial Y} = -1 \]  
(3-24)

Note the cyclic order of the three variables; each occurs once "above," once "below," and once "outside."

**Thermal Processes at Constant Pressure**

In many calorimetric measurements and other processes involving heat transfer, the pressure rather than the volume is held constant. Then there is a work term \(-P \Delta V\) and the first law yields
\[ \Delta U = q - P \Delta V \]

But at constant pressure,
\[ \Delta H = \Delta U + P \Delta V = q \]  
(3-25)

Hence for any constant-pressure process with no work other than that of volume change, the enthalpy increase is exactly the heat absorbed. For this reason \(H\) is sometimes called the heat content.

**Heat Capacity**

In the previous chapter we obtained for the heat capacity at constant volume
\[ C_V = \left( \frac{\partial U}{\partial T} \right)_V \]  
(2-7)

From the definition of entropy, we now have for a process of heating at constant volume,
\[ dS = \frac{C_V}{T} dT = C_V d\ln T \]  
(3-26)

For a constant-pressure process, we showed in Eq. (3-25) that the heat absorbed is just \(\Delta H\); hence, the heat capacity at constant pressure is
\[ C_P = \left( \frac{\partial H}{\partial T} \right)_p \]  
(3-27)

and the entropy change with temperature at constant pressure is
\[ dS = \frac{C_P}{T} dT = C_P d\ln T \]  
(3-28)

It is often of interest to relate \(C_P\) to \(C_V\). From the general relationship for a change of variable, Eq. (3-21), one has
\[ \left( \frac{\partial S}{\partial T} \right)_P = \left( \frac{\partial S}{\partial T} \right)_V + \left( \frac{\partial S}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P \]

Then, from (3-11), (3-26), and (3-28), one obtains
\[ \frac{C_P}{T} = \frac{C_V}{T} + \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P \]

and
\[ C_P = C_V + T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P \]  
(3-29)

If, as is usually the case, one is using \(P\) and \(T\) as the independent variables, one uses the transformation, Eq. (3-23),
\[ \left( \frac{\partial P}{\partial T} \right)_V = \frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T} \]

to obtain
\[ C_P = C_V - T \left( \frac{\partial P}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P \]  
(3-30)

Finally, one may prefer an expression in terms of the coefficient of expansion
\[ \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \]  
(3-31)

and the compressibility
\[ \kappa = \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \]  
(3-32)

The result is
\[ C_P = C_V + \frac{TV\alpha^2}{\kappa} \]  
(3-33)

Occasionally, one prefers to use the pair \(V, T\) as independent variables. Then a different transformation,
\[ \left( \frac{\partial V}{\partial T} \right)_P = \frac{(\partial P/\partial T)_V}{(\partial P/\partial V)_T} \]
is inserted into (3-29) to obtain
\[ C_P = C_V - T \left( \frac{\partial P/\partial T}_V \right) \]  
(3-34)
Also of interest is the effect on \( C_P \) of a change in pressure; from Eqs. (3-15) and (3-27) one obtains

\[
\left( \frac{\partial C_P}{\partial P} \right)_T = \frac{\partial^2 H}{\partial P \partial T} = -T \left( \frac{\partial^2 V}{\partial T^2} \right)_P
\]  

(3-35)

If the substance is an ideal gas with \( P = nRT/V \), one has

\[
\left( \frac{\partial P}{\partial T} \right)_V = \frac{nR}{V}
\]

and

\[
\left( \frac{\partial P}{\partial V} \right)_T = \frac{nRT}{V^2}
\]

whereupon

\[
C_P = C_V + nR
\]  

(3-36)*

**Maximum Work**

In order to more fully understand the meaning of the Helmholtz energy, \( A \), let us consider the maximum work that can be obtained from a change at constant temperature. The work done by the system is, from the first law and the definition of \( A \),

\[
-w = q - \Delta U
\]

\[
= q - \Delta A - T\Delta S
\]  

(3-37)

We know, however, from the second law, Eq. (2-23), that

\[
q \leq T\Delta S
\]

where the equality corresponds to a reversible process and the inequality to a dissipative process. Then

\[
-w \leq -\Delta A
\]  

(3-38)

which shows that the decrease in \( A \) gives the maximum limit to the amount of work done by the system. Also, if the process is reversible, the equality sign applies and the work done is \(-\Delta A\).

In view of these relationships \( A \) can be called the "isothermal work content." It has, less precisely, been called the "work content" and first received the symbol \( A \) after the German word Arbeit.

**Maximum Net (non-PV) Work**

Let us now separate the work term into the work done against a constant-pressure atmosphere, \( P\Delta V \), and any other work, which we designate \( w' \). This quantity is sometimes called the useful work, but that is misleading because \( P\Delta V \) can in some circumstances be useful work. It is only expansion against the natural atmosphere that is intrinsically useless; expansion against an artificial high-pressure system can be useful work of compression. Thus, we prefer the terms "net work" or "non-PV work" for \( w' \).

From Eq. (3-38) and the definitions of \( A \) and \( G \), we have

\[
-w' = -w - P\Delta V
\]

\[
\leq -\Delta A - P\Delta V
\]

and

\[
-w' \leq -\Delta G
\]  

(3-39)

Thus, the change in Gibbs energy gives the maximum for the "net work" that can be obtained from an isothermal process. Again, the equality sign applies if the process is reversible.

If no work is involved other than \( PV \) work, then one has the very simple and important result

\[
\Delta G \leq 0
\]  

(3-40)

for an isothermal process. And the condition for equilibrium at constant \( T \) and \( P \) (and with no work other than \( P\Delta V \)) is

\[
\Delta G = 0
\]  

(3-41)

**Example with Net Work**

As an example where there is work of a type other than \( PV \), consider an electrochemical system. Specifically, take a system in which zinc acts upon aqueous sulfuric acid to form aqueous zinc sulfate and hydrogen, under constant atmospheric pressure, and in a thermostat. Evidently this process can occur in such a way as to perform no work except the small amount done against the atmosphere by the evolved hydrogen. This, in fact, is just what will occur if impure zinc is added directly to the acid. This process is highly irreversible. On the other hand, if we place in the thermostat the same substances arranged as a galvanic cell, with zinc as one electrode and another electrode of hydrogen in contact with a platinum electrode, and if these two electrodes are connected to a motor or other electrical system in such a way as to utilize the electrical energy that is now available, an amount of work will be done that will depend upon the efficiency of our arrangements.

The maximum work would be obtained if at every instant the external electrical system were arranged to exert so large a counter emf that, when infinitesimally increased, it would force the current in the opposite direction, thus causing hydrogen to be consumed and zinc to precipitate. The process would then be reversible and the net work equal to \(-\Delta G\).

In both the processes we have described, the system passes from the same initial to the same final states. Therefore \(-\Delta G\) is the same in both cases. This difference \(-\Delta G\) is, in the reversible process, the work that the system has performed, while in the irreversible process it is the maximum work that might have been performed.