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Thermodynamic Potentials

Nobody knows why, but the only theories which work are the mathematical ones.

Michael Holt, in *Mathematics in Art*

Although the fundamental relation in either the entropy, $S = S(U, V, N)$, or energy, $U = U(S, V, N)$ (for monotonic entropy functions), representations contains all thermodynamic information about the system of interest, it is not always easy to use that information for practical calculations.

For example, many experiments are done at constant temperature, with the system in contact with a thermal reservoir. It would be very convenient to have the fundamental relation expressed in terms of the intensive parameters T and P , instead of the extensive parameters S and V . It turns out that this can be done, but it requires us to introduce new functions that are generally known as thermodynamic potentials. The mathematics required involves Legendre transforms (named after the French mathematician Adrien-Marie Legendre (1752–1833)), which will be developed in the next section. The rest of the chapter is devoted to investigating the properties and advantages of various thermodynamic potentials.

Of particular interest are Massieu functions (Section 12.6), which are Legendre transforms of the entropy.

12.1 Mathematical Digression: The Legendre Transform

Before we go through the details of the Legendre transform, it might be useful to discuss why we need it and what problems it solves.

12.1.1 The Problem of Loss of Information

The basic reason for representing the fundamental relation in terms of T, P , or μ , instead of U, V , or N , is that we want to use the derivative of a function as the independent variable. For simplicity, consider some function

$$y = y(x) \tag{12.1}$$

and its derivative

$$p = \frac{dy}{dx} = p(x). \quad (12.2)$$

We could, of course, invert eq. (12.2) to find $x = x(p)$, and then find $y = y(x(p)) = y(p)$. Unfortunately, this procedure results in a loss of information. The reason is illustrated in Fig. 12.1, which shows that all functions of the form $y(x - x_0)$ give exactly the same function $y(p)$. If we only have $y(p)$, we have lost all information about the value of x_0 .

12.1.2 Point Representations and Line Representation

To solve the problem of lost information, we can turn to an alternative representation of functions.

When we write $y = y(x)$, we are using a ‘point’ representation of the function; for each value of x , $y(x)$ specifies a value of y , and the two together specify a point in the x, y -plane. The set of all such points specifies the function.

However, we could also specify a function by drawing tangent lines at points along the curve, as illustrated in Fig. 12.2. The envelope of the tangent lines also reveals the function. This is known as a ‘line’ representation of a function.

12.1.3 Direct Legendre Transforms

The idea of a Legendre transform is to calculate the equations of the tangent lines that carry the full information about the function. The information we need for each tangent line is clearly the slope, which we want to be our new variable, and the y -intercept.

Consider a function, $y = y(x)$, which is plotted as a curve in Fig. 12.3. We can construct a straight-line tangent to any point (x, y) along the curve, which is also shown in Fig. 12.3.

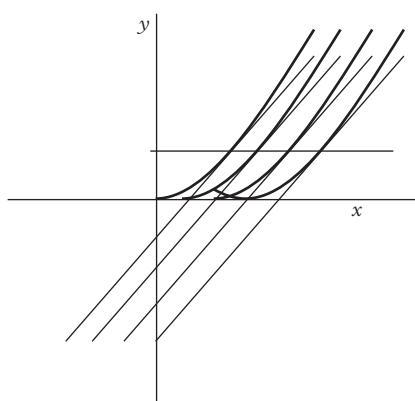


Fig. 12.1 Illustration of distinct functions $y = y(x)$ that have the same slope at a given value of y .

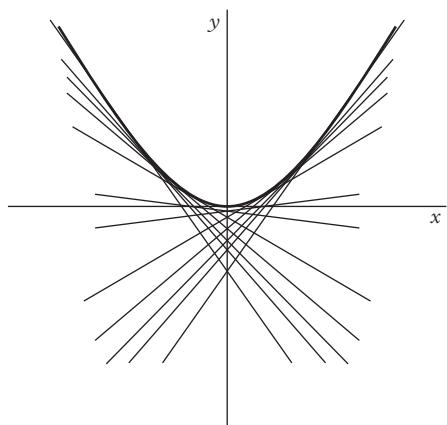


Fig. 12.2 Illustration of how to represent a function by the envelope of tangent lines.

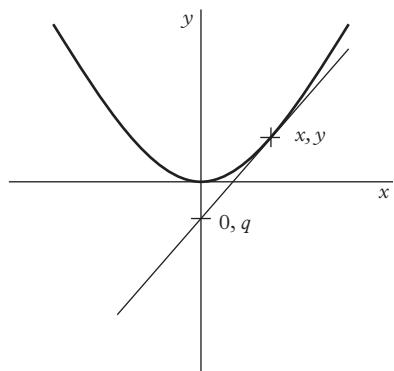


Fig. 12.3 Graphical representation of a general Legendre transform. The straight line is tangent to the curve $y = y(x)$. The y -intercept of the tangent line is located at $(0, q)$.

If the y -intercept is located at $(0, q)$, we can calculate the slope of the tangent line,

$$p = \frac{dy}{dx} = \frac{y - q}{x - 0} = p(x). \quad (12.3)$$

Assuming that $p = p(x)$ is monotonic, we can invert it to obtain $x = x(p)$. We can then eliminate x in favor of p in eq. (12.3) and solve for $q = q(p)$,

$$q = y - px = q(p) \equiv y[p]. \quad (12.4)$$

The square brackets in $y[p]$ indicate that $y[p] = y - px$ is the Legendre transform of $y(x)$, with p as the new independent variable.

12.1.4 Inverse Transformations

The inverse Legendre transformation proceeds in the same way. In this case,

$$x = -\frac{dq}{dp} = x(p). \quad (12.5)$$

Assuming that $x = x(p)$ is monotonic, we can invert it to obtain $p = p(x)$. Eq. (12.4) can be solved for y ,

$$y = q - (-x)p = q + xp. \quad (12.6)$$

We can then eliminate p in favor of x in eq. (12.3) and solve for $y = y(x)$. There is no loss of information in either the direct or inverse Legendre transform.

The Legendre transform and its inverse are summarized in Table 12.1.

12.1.5 Legendre Transform of Infinitesimals

It will be very useful to write the information in eqs. (12.3) and (12.5) using infinitesimals,

$$dy = p dx \quad (12.7)$$

$$dq = -x dp. \quad (12.8)$$

Note that going between the original infinitesimal and the Legendre transform merely involves switching x and p and changing the sign. This simple observation will make life much easier when working with the thermodynamic potentials discussed in the rest of this chapter—assuming that you have memorized eq. (10.27).

Table 12.1 General form of a Legendre transform.

Direct transform	Inverse transform
$y = y(x)$	$q = q(p)$
$dy = p dx$	$dq = -x dp$
$p = \frac{dy}{dx}$	$-x = \frac{dq}{dp}$
$q = y - px$	$y = q + xp$
$q = q(p) = y[p]$	$y = y(x)$
$dq = -x dp$	$dy = p dx$

12.2 Helmholtz Free Energy

Many experiments are carried out at constant temperature, and we have thermometers to measure the temperature. However, we do not have an easy way of measuring entropy, so it would be very useful to express the fundamental relation, which contains all thermodynamic information about a system, in terms of the temperature.

We begin with the fundamental relation in the energy representation, $U = U(S, V, N)$. We wish to replace the entropy S with the temperature T as the independent variable

$$T = \left(\frac{\partial U}{\partial S} \right)_{V, N}. \quad (12.9)$$

We follow exactly the same procedure as in Section 12.1, except that we use partial derivatives and hold V and N constant. The Legendre transform of the energy with respect to temperature is called the Helmholtz free energy, and is denoted by the symbol F in this book, although you will also see it called A in some other texts,

$$F(T, V, N) \equiv U[T] = U - TS. \quad (12.10)$$

Since you have memorized the differential form of the fundamental relation in the energy representation, eq. (10.27),

$$dU = TdS - PdV + \mu dN \quad (12.11)$$

you can easily find the differential form of the fundamental relation in the Helmholtz free energy representation by exchanging S and T in the first term and reversing the sign:

$$dF = -SdT - PdV + \mu dN. \quad (12.12)$$

From eq. (12.12) we can read off the partial derivative of F with respect to the new independent variable T ,

$$S = -\left(\frac{\partial F}{\partial T} \right)_{V, N}. \quad (12.13)$$

The other partial derivatives look much the same as before, but it is important to keep track of what is being held constant. For example, in the energy representation, the pressure is found from the partial derivative

$$P = -\left(\frac{\partial U}{\partial V} \right)_{S, N} \quad (12.14)$$

Table 12.2 Helmholtz free energy.

Direct transform	Inverse transform
$U = U(S, V, N)$	$F = F(T, V, N)$
$dU = TdS - PdV + \mu dN$	$dF = -SdT - PdV + \mu dN$
$T = \left(\frac{\partial U}{\partial S}\right)_{V,N}$	$-S = \left(\frac{\partial F}{\partial T}\right)_{V,N}$
$F = U - TS$	$U = F + TS$
$F = F(T, V, N) = U[T]$	$U = U(S, V, N)$
$dF = -SdT - PdV + \mu dN$	$dU = TdS - PdV + \mu dN$

where the entropy is held constant. In the Helmholtz free energy representation, the pressure is found from a similar partial derivative

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \quad (12.15)$$

but now the temperature is held constant.

The Legendre transforms, direct and inverse, for the Helmholtz free energy are summarized in Table 12.2.

12.3 Enthalpy

The Legendre transform of the energy with respect to pressure is called the enthalpy, and is denoted by the symbol $H = U[p]$. It is often convenient because it takes the pressure as one of the independent variables. It is very widely used in chemistry for that reason, since most chemical experiments are carried out at atmospheric pressure.

We again begin with the fundamental relation in the energy representation, $U = U(S, V, N)$. This time we will replace the volume V with the pressure P as the independent variable,

$$P = -\left(\frac{\partial U}{\partial V}\right)_{S,N}. \quad (12.16)$$

To find the enthalpy we follow exactly the same procedure as in the previous section,

$$H(S, P, N) \equiv U[p] = U + PV. \quad (12.17)$$

The differential form for the enthalpy is found from the differential form of the fundamental relation in the energy representation, eq. (12.11), but we now exchange V and P and change the sign of that term,

$$dH = TdS + VdP + \mu dN. \quad (12.18)$$

From eq. (12.18) we can read off the partial derivative of H with respect to the new independent variable P ,

$$V = \left(\frac{\partial H}{\partial P} \right)_{S,N}. \quad (12.19)$$

The Legendre transforms, direct and inverse, for the enthalpy are summarized in Table 12.3.

In some chemistry texts, the enthalpy is also referred to as the ‘heat content’, even though dQ is not an exact differential, and we cannot properly speak of the amount of ‘heat’ in a system. The reason for this usage can be seen by referring to eq. (12.18). Most chemical experiments are carried out under conditions of constant pressure, with a fixed number of particles. If we recall the relationship between heat transfer and entropy change in eq. (10.24), we find that the change in enthalpy is equal to the heat transferred into the system under these conditions:

$$\begin{aligned} dH &= TdS + VdP + \mu dN \\ &= TdS + 0 + 0 \\ &= dQ. \end{aligned} \quad (12.20)$$

This equation is a bit peculiar in that it sets an exact differential equal to an inexact differential. This came about by specifying the path of integration with the conditions

Table 12.3 *Enthalpy.*

Direct transform	Inverse transform
$U = U(S, V, N)$	$H = H(S, P, N)$
$dU = TdS - PdV + \mu dN$	$dH = TdS + VdP + \mu dN$
$P = - \left(\frac{\partial U}{\partial V} \right)_{S,N}$	$V = \left(\frac{\partial H}{\partial P} \right)_{S,N}$
$H = U + PV$	$U = H - PV$
$H = H(S, V, N) = U[p]$	$U = U(S, V, N)$
$dH = TdS + VdP + \mu dN$	$dU = TdS - PdV + \mu dN$

$dP = 0$ and $dN = 0$, which made the path one-dimensional. Since one-dimensional differentials are always exact, $dH = dQ$ along the specified path.

12.4 Gibbs Free Energy

The Gibbs free energy is the Legendre transform of the energy with respect to both the temperature and the pressure. It is denoted with the letter G , which seems remarkably logical after seeing the standard choices for the Helmholtz free energy (F or A) and the enthalpy (H). There are three ways to calculate it:

1. Find the Legendre transform of the Helmholtz free energy with respect to pressure.
2. Find the Legendre transform of the enthalpy with respect to temperature.
3. Start with the energy and carry out both Legendre transforms at the same time.

Since the first two possibilities should be self-evident, I will just give the third option in the form of Table 12.4.

Table 12.4 Gibbs free energy.

Direct transform	Inverse transform
$U = U(S, V, N)$	$G = G(T, P, N)$
$dU = TdS - PdV + \mu dN$	$dG = -SdT + VdP + \mu dN$
$T = \left(\frac{\partial U}{\partial S}\right)_{V,N}$	$-S = \left(\frac{\partial G}{\partial T}\right)_{P,N}$
$P = -\left(\frac{\partial U}{\partial V}\right)_{S,N}$	$V = \left(\frac{\partial G}{\partial P}\right)_{T,N}$
$G = U - TS + PV$	$U = G + TS - PV$
$G = G(T, P, N) = U[T, P]$	$U = U(S, V, N)$
$dG = -SdT + VdP + \mu dN$	$dU = TdS - PdV + \mu dN$

12.5 Other Thermodynamic Potentials

Since there are three thermodynamic variables for even the simplest system (U , V , and N), and we can construct a Legendre transform from any combination of the corresponding partial derivatives, there are $2^3 = 8$ different thermodynamic potentials. Each of these potentials provides a representation of the fundamental relation. They can all be derived by the same procedures that we used for F , H , and G .

12.6 Massieu Functions

In addition to those discussed previously, there is another class of thermodynamic potentials, known as Massieu functions, which are generated from the fundamental relation in the entropy representation, $S = S(U, V, N)$. The differential form for the fundamental relation in the entropy representation was found in eq. (10.26),

$$dS = \left(\frac{1}{T}\right)dU + \left(\frac{P}{T}\right)dV - \left(\frac{\mu}{T}\right)dN. \quad (12.21)$$

As can be seen from eq. (12.21), the natural variables for a Legendre transform are $1/T$, P/T , and μ/T . Although these variables appear rather strange, working with them is essentially the same as for the more usual thermodynamic potentials.

It is easier to use a different notation. If we use the inverse temperature $\beta = 1/k_B T$ and a dimensionless entropy $\tilde{S} = S/k_B$, as we did in Section 11.8, the differential form for the fundamental relation in the dimensionless entropy representation becomes

$$d\tilde{S} = \beta dU + (\beta P)dV - (\beta \mu)dN. \quad (12.22)$$

In this equation, we have put parentheses around (βP) and $(\beta \mu)$ to emphasize that each of these products is to be regarded as a single variable.

The Legendre transform of the dimensionless entropy with respect to β is then $\tilde{S}[\beta]$, with the differential form given as

$$d\tilde{S}[\beta] = -Ud\beta + (\beta P)dV - (\beta \mu)dN. \quad (12.23)$$

Similarly, the Legendre transform with respect to both β and (βP) is given by

$$d\tilde{S}[\beta, (\beta P)] = -Ud\beta - Vd(\beta P) - (\beta \mu)dN. \quad (12.24)$$

We will find that both of these Massieu functions are quite useful when we discuss partition functions in Chapters 19, 20, 21, 23, and 24.

12.7 Summary of Legendre Transforms

The usefulness of Legendre transforms and thermodynamic potentials is not limited to providing alternative representations of the fundamental relation, although that is very important. We will see in Chapter 14 that they also play a crucial role in deriving thermodynamic identities; that is, equations relating measurable quantities that are true for *all* thermodynamic systems. In Chapter 15 we will see that thermodynamic potentials can be used to determine equilibrium conditions from extremum principles similar to the maximization principle for the entropy. Finally, in Chapter 16 we will find that they are essential to deriving stability criteria that are also valid for all systems.

12.8 Problems

PROBLEM 12.1

Legendre transform of the energy with respect to temperature for the classical ideal gas

Starting with the fundamental equation in the entropy representation (that is, the entropy of the classical ideal gas—which you have memorized):

$$S = S(U, V, N) = k_B N \left(\frac{3}{2} \ln \left(\frac{U}{N} \right) + \ln \left(\frac{V}{N} \right) + \ln X \right).$$

- Derive the fundamental relation in the energy representation ($U = U(S, V, N)$).
- Derive the temperature as a function of entropy, volume, and number of particles (one of the three equations of state).
- Find the entropy as a function of temperature, volume, and number of particles. Is this an equation of state or a fundamental relation?
- Derive the Helmholtz free energy of the classical ideal gas, $F(T, V, N) = U - TS$.

PROBLEM 12.2

More Legendre transforms

- Starting with the fundamental equation in the Helmholtz free energy representation ($F = F(T, V, N)$) that you derived for the previous assignment, derive the fundamental relation in the Gibbs free energy representation ($G = G(T, P, N)$).
- Find the volume of the ideal gas as a function of temperature, pressure, and number of particles by taking a derivative of the Gibbs free energy.

PROBLEM 12.3

General thermodynamic function

Suppose we know some terms in a series expansion of the Gibbs free energy as a function of T and P for some region near the point (T_0, P_0) ,

$$G = AT + BT^2 + CP + DP^2 + ETP$$

where A, B, C, D , and E are constants.

- Find the volume of the system as a function of T and P .
- The isothermal compressibility is defined as

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{T, N}.$$

- Find κ_T for this system.
3. Find the entropy as a function of T and P for this system.

PROBLEM 12.4**Enthalpy**

The enthalpy of a material in a certain range of temperature and pressure is well approximated by the expression:

$$H = A + BT + CP + DT^2 + EP^2 + FTP.$$

1. Is this expression for H an approximation to the fundamental relation, or is it an equation of state? Explain your answer for credit.
 2. Calculate the specific heat at constant pressure, c_P , within the approximation for H given previously.
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