15.6: Appendix F- Mathematical Properties of State Functions

A state function is a property of a thermodynamic system whose value at any given instant depends only on the state of the system at that instant (Sec. 2.4).

F.1 Differentials

The **differential** $\mathrm{d}f$ of a state function f is an infinitesimal change of f. Since the value of a state function by definition depends only on the state of the system, integrating $\mathrm{d}f$ between an initial state 1 and a final state 2 yields the change in f, and this change is independent of the path:

$$\int_{f_1}^{f_2} \mathrm{d}f = f_2 - f_1 = \Delta f \tag{F.1.1}$$

A differential with this property is called an *exact* differential. The differential of a state function is always exact.

F.2 Total Differential

A state function f treated as a dependent variable is a function of a certain number of independent variables that are also state functions. The **total differential** of f is $\mathrm{d}f$ expressed in terms of the differentials of the independent variables and has the form

$$\mathrm{d}f = \left(\frac{\partial f}{\partial x}\right)\mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)\mathrm{d}y + \left(\frac{\partial f}{\partial z}\right)\mathrm{d}z + \ldots \tag{F.2.1}$$

There are as many terms in the expression on the right side as there are independent variables. Each partial derivative in the expression has all independent variables held constant except the variable shown in the denominator.

Figure F.1 interprets this expression for a function f of the two independent variables x and y. The shaded plane represents a small element of the surface $f = f(x, y)$.

Consider a system with three independent variables. If we choose these independent variables to be x, y, and z, the total differential of the dependent state function f takes the form

$$\mathrm{d}f = a\,\mathrm{d}x + b\,\mathrm{d}y + c\,\mathrm{d}z \tag{F.2.2}$$

where we can identify the coefficients as

$$a = \left(\frac{\partial f}{\partial x}\right)_{y,z} \qquad b = \left(\frac{\partial f}{\partial y}\right)_{x,z} \qquad c = \left(\frac{\partial f}{\partial z}\right)_{x,y} \tag{F.2.3}$$

These coefficients are themselves, in general, functions of the independent variables and may be differentiated to give mixed second partial derivatives; for example:

$$\left(\frac{\partial a}{\partial y}\right)_{x,z} = \frac{\partial^2 f}{\partial y \partial x} \qquad \left(\frac{\partial b}{\partial x}\right)_{y,z} = \frac{\partial^2 f}{\partial x \partial y} \tag{F.2.4}$$

The second partial derivative $\partial^2 f/\partial y \partial x$, for instance, is the partial derivative with respect to y of the partial derivative of f with respect to x. It is a theorem of calculus that if a function f is single valued and has continuous derivatives, the order of differentiation in a mixed derivative is immaterial. Therefore the mixed derivatives $\partial^2 f/\partial y \partial x$ and $\partial^2 f/\partial x \partial y$, evaluated for the system in any given state, are equal:

$$\left(\frac{\partial a}{\partial y}\right)_{x,z} = \left(\frac{\partial b}{\partial x}\right)_{y,z} \tag{F.2.5}$$

The general relation that applies to a function of any number of independent variables is

$$\left(\frac{\partial X}{\partial y}\right) = \left(\frac{\partial Y}{\partial x}\right) \tag{F.2.6}$$

where x and y are *any* two of the independent variables, X is $\partial f/\partial x$, Y is $\partial_\mathrm{f}/\partial y$, and each partial derivative has all independent variables held constant except the variable shown in the denominator. This general relation is the Euler reciprocity relation, or

reciprocity relation for short. A necessary and sufficient condition for df to be an exact differential is that the reciprocity relation is satisfied for each pair of independent variables.

F.3 Integration of a Total Differential

If the coefficients of the total differential of a dependent variable are known as functions of the independent variables, the expression for the total differential may be integrated to obtain an expression for the dependent variable as a function of the independent variables.

For example, suppose the total differential of the state function $f(x, y, z)$ is given by Eq. F.2.2 and the coefficients are known functions $a(x, y, z)$, $b(x, y, z)$, and $c(x, y, z)$. Because f is a state function, its change between $f(0, 0, 0)$ and $f(x', y', z')$ is independent of the integration path taken between these two states. A convenient path would be one with the following three segments:

1. The expression for $f(x, y, z)$ is then the sum of the three integrals and a constant of integration.

   Here is an example of this procedure applied to the total differential

   $$\mathrm{d}f = (2xy)\,\mathrm{d}x + (x^2 + z)\,\mathrm{d}y + (y - 9z^2)\,\mathrm{d}z \tag{F.3.1}$$

   An expression for the function f in this example is given by the sum

   $$\begin{aligned} f &= \int_0^{x'} (2x \cdot 0)\,\mathrm{d}x + \int_0^{y'} [(x')^2 + 0]\,\mathrm{d}y + \int_0^{z'} (y' - 9z^2)\,\mathrm{d}z + C \\ &= 0 + x^2y + (yz - 9z^3/3) + C \\ &= x^2y + yz - 3z^3 + C \end{aligned} \tag{F.3.2}$$

   where primes are omitted on the second and third lines because the expressions are supposed to apply to any values of x, y, and z. C is an integration constant. You can verify that the third line of Eq. F.3.2 gives the correct expression for f by taking partial derivatives with respect to x, y, and z and comparing with Eq. F.3.1.

   A different kind of integration can be used to express a dependent extensive property in terms of independent extensive properties. An *extensive* property of a thermodynamic system is one that is additive, and an *intensive* property is one that is not additive and has the same value everywhere in a homogeneous region (Sec. 2.1.1). Suppose we have a state function f that is an extensive property with the total differential

   $$\mathrm{d}f = a\,\mathrm{d}x + b\,\mathrm{d}y + c\,\mathrm{d}z + \ldots \tag{F.3.3}$$

   where the independent variables $x, y, z, \ldots$ are extensive and the coefficients $a, b, c, \ldots$ are intensive. If the independent variables include those needed to describe an open system (for example, the amounts of the substances), then it is possible to integrate both sides of the equation from a lower limit of zero for each of the extensive functions while holding the intensive functions constant:

   $$\int_0^{f'} \mathrm{d}f = a\int_0^{x'} \mathrm{d}x + b\int_0^{y'} \mathrm{d}y + c\int_0^{z'} \mathrm{d}z + \ldots \tag{F.3.4}$$

   $$f' = ax' + by' + cz' + \ldots \tag{F.3.5}$$

   Note that a term of the form $c\,\mathrm{d}u$ where u is *intensive* becomes *zero* when integrated with intensive functions held constant, because $\mathrm{d}u$ is this case is zero.

F.4 Legendre Transforms

A **Legendre transform** of a state function is a linear change of one or more of the independent variables made by subtracting products of conjugate variables.

To understand how this works, consider a state function f whose total differential is given by

$$\mathrm{d}f = a\,\mathrm{d}x + b\,\mathrm{d}y + c\,\mathrm{d}z \tag{F.4.1}$$

In the expression on the right side, x, y, and z are being treated as the independent variables. The pairs a and x, b and y, and c and z are *conjugate pairs*. That is, a and x are conjugates, b and y are conjugates, and c and z are conjugates.

For the first example of a Legendre transform, we define a new state function f_1 by subtracting the product of the conjugate variables a and x:

$$f_1 \stackrel{\text{def}}{=} f - ax \tag{F.4.2}$$

The function f_1 is a Legendre transform of f. We take the differential of Eq. F.4.2

$$\mathrm{d}f_1 = \mathrm{d}f - a\,\mathrm{d}x - x\,\mathrm{d}a \tag{F.4.3}$$

and substitute for $\mathrm{d}f$ from Eq. F.4.1:

$$\begin{aligned} \mathrm{d}f_1 &= (a\,\mathrm{d}x + b\,\mathrm{d}y + c\,\mathrm{d}z) - a\,\mathrm{d}x - x\,\mathrm{d}a \\ &= -x\,\mathrm{d}a + b\,\mathrm{d}y + c\,\mathrm{d}z \end{aligned} \tag{F.4.4}$$

Equation F.4.4 gives the total differential of f_1 with a, y, and z as the independent variables. The functions x and a have switched places as independent variables. What we did in order to let a replace x as an independent variable was to subtract from f the product of the conjugate variables a and x.

Because the right side of Eq. F.4.4 is an expression for the total differential of the state function f_1, we can use the expression to identify the coefficients as partial derivatives of f_1 with respect to the new set of independent variables:

$$-x = \left(\frac{\partial f_1}{\partial a}\right)_{y,z} \qquad b = \left(\frac{\partial f_1}{\partial y}\right)_{a,z} \qquad c = \left(\frac{\partial f_1}{\partial z}\right)_{a,y} \tag{F.4.5}$$

We can also use Eq. F.4.4 to write new reciprocity relations, such as

$$-\left(\frac{\partial x}{\partial y}\right)_{a,z} = \left(\frac{\partial b}{\partial a}\right)_{y,z} \tag{F.4.6}$$

We can make other Legendre transforms of f by subtracting one or more products of conjugate variables. A second example of a Legendre transform is

$$f_2 \stackrel{\text{def}}{=} f - by - cz \tag{F.4.7}$$

whose total differential is

$$\begin{aligned} \mathrm{d}f_2 &= \mathrm{d}f - b\,\mathrm{d}y - y\,\mathrm{d}b - c\,\mathrm{d}z - z\,\mathrm{d}c \\ &= a\,\mathrm{d}x - y\,\mathrm{d}b - z\,\mathrm{d}c \end{aligned} \tag{F.4.8}$$

Here b has replaced y and c has replaced z as independent variables. Again, we can identify the coefficients as partial derivatives and write new reciprocity relations.

If we have an algebraic expression for a state function as a function of independent variables, then a Legendre transform preserves all the information contained in that expression. To illustrate this, we can use the state function f and its Legendre transform f_2 described above. Suppose we have an expression for $f(x,y,z)$—this is f expressed as a function of the independent variables x, y, and z. Then by taking partial derivatives of this expression, we can find according to Eq. F.2.3 expressions for the functions $a(x,y,z)$, $b(x,y,z)$, and $c(x,y,z)$.

Now we perform the Legendre transform of Eq. F.4.7: $f_2 = f - by - cz$ with total differential $\mathrm{d}f_2 = a\,\mathrm{d}x - y\,\mathrm{d}b - z\,\mathrm{d}c$ (Eq. F.4.8). The independent variables have been changed from x, y, and z to x, b, and c.

We want to find an expression for f_2 as a function of these new variables, using the information available from the original function $f(x,y,z)$. To do this, we eliminate z from the known functions $b(x,y,z)$ and $c(x,y,z)$ and solve for y as a function of x, b, and c. We also eliminate y from $b(x,y,z)$ and $c(x,y,z)$ and solve for z as a function of x, b, and c. This gives us expressions for $y(x,b,c)$ and $z(x,b,c)$ which we substitute into the expression for $f(x,y,z)$, turning it into the function $f(x,b,c)$. Finally, we use the functions of the new variables to obtain an expression for $f_2(x,b,c) = f(x,b,c) - by(x,b,c) - cz(x,b,c)$.

The original expression for $f(x,y,z)$ and the new expression for $f_2(x,b,c)$ contain the same information. We could take the expression for $f_2(x,b,c)$ and, by following the same procedure with the Legendre transform $f = f_2 + by + cz$, retrieve the expression for $f(x,y,z)$. Thus no information is lost during a Legendre transform.