

3.3: Natural Variables and Legendre Transforms

It is more than just happenstance that $\partial U = \partial q$ and $\partial H = \partial q$ at constant V and P , respectively. To understand more of the fundamentals we introduce here the concept of “natural variables” in thermodynamics. Natural variables are revealed when we examine how thermodynamic variables change, i.e. we derive their differentials. For example, in an adiabatic system $\partial U = \partial w = -P\partial V$, and we see that the expression relates ∂U to ∂V but not ∂P . This makes internal energy U connected with volume in a fundamental way that it is not with pressure; as a result, we state that V is a natural variable of U . Note that when U ’s natural variable volume is held constant, then an important relationship emerges, which is that $\partial U = \partial q$ (i.e. the change in internal energy is the heat transaction).

Here we formalize the definition of a natural variable using calculus. Recall that the change of a function $f(x)$ is:

$$\partial f(x) = \frac{\partial f}{\partial x} \partial x \quad (3.3.1)$$

We say that x is the natural variable of function f , and $\frac{\partial f}{\partial x}$ is the conjugate of x . Let’s define a new function called g using f , x , and x ’s conjugate:

$$g = f - \left(\frac{\partial f}{\partial x} \right) \cdot x \quad (3.3.2)$$

What is the natural variable of g ? To find out, we must determine ∂g and see what makes it change; note the use of the product rule and the color coding to help you see how equations 3.9 and 3.10 are combined:

$$\partial g = \partial f - \partial \left\{ \left(\frac{\partial f}{\partial x} \right) \cdot x \right\} = \frac{\partial f}{\partial x} \partial x - \frac{\partial f}{\partial x} \cdot \partial x - x \cdot \partial \left(\frac{\partial f}{\partial x} \right) = -x \cdot \partial \left(\frac{\partial f}{\partial x} \right)$$

Thus $\partial g = -x \cdot \partial \left(\frac{\partial f}{\partial x} \right)$, and we conclude that $\left(\frac{\partial f}{\partial x} \right)$ is the natural variable of function g . To summarize, what we did was take a function and subtract its natural variable times the natural variable’s conjugate. This is called a Legendre transform, and it takes an old function with a natural variable and creates a new function with a different natural variable (that being the conjugate of the old natural variable).

You might be asking, in the example above how can the derivative $\left(\frac{\partial f}{\partial x} \right)$ also be variable? Also, is the partial of a derivative $\partial \left(\frac{\partial f}{\partial x} \right)$ meaningful, or is it mathematical gibberish? To address this, let’s examine a function like internal energy under adiabatic, reversible conditions: $\partial U = -P\partial V$. To equate this to $\partial f(x) = \frac{\partial f}{\partial x} \partial x$, we see that $U = f(x)$ and $V = x$, then we can also see that: $\partial U = \frac{\partial U}{\partial V} \partial V = -P\partial V$ which means $\frac{\partial U}{\partial V} = -P$. Thus, negative pressure is conjugate to internal energy’s natural variable volume.

Let’s now explore the use of a Legendre transform on U , whereby we create a new function that has a natural variable of pressure. Starting with the definition of a Legendre transform, Equation 3.10: $g = f - \left(\frac{\partial f}{\partial x} \right) \cdot x$, we recognize that $f(x) = U$, $x = V$, and $\frac{\partial f}{\partial x} = -P$:

$$g = U - \left(\frac{\partial U}{\partial V} \right) \cdot V = U - (-P)V = U + PV$$

And now we see that this Legendre transform of U is the enthalpy H . To determine enthalpy’s natural variables, we differentiate it under adiabatic conditions:

$$\partial H = \partial U + \partial(PV) = -P\partial V + P\partial V + V\partial P = V\partial P$$

Hence pressure is a natural variable of H , and $\frac{\partial H}{\partial P} = V$ is conjugate to pressure. Although we have performed this derivation by invoking adiabatic reversible conditions, it is true that $H = U + PV$ for any transition since U and H are state variables.

3.3.1 Inexactness of q . As all this talk of natural variables and conjugates may be overwhelming and too abstract, we will slow down and work an example to solidify your understanding. Recall in Chapter 2 we were able to demonstrate that work (∂w) is inexact due to the fact that reversible and irreversible work are not the same. Here we show that heat (∂q) is also inexact, facilitated by the fact that we know more about heat capacity and have had a lot of practice with partials. First, we start with the familiar relation: $\partial U = \partial q + \partial w$, and following the reversible path ($-\partial w = P\partial V$) means $\partial q = \partial U - \partial w = \partial U + P\partial V$. Next we substitute $\partial U = C_V \partial T$, and as a result $\partial q = C_V \partial T + P\partial V$. Now we need to make sure that we understand what our function is, what are the natural variables and those variables’ conjugates. We do so by lining up ∂q above with the expression for the change in a function $\partial f(x, y) = \left(\frac{\partial f}{\partial x} \right)_y \partial x + \left(\frac{\partial f}{\partial y} \right)_x \partial y$ as follows:

It is clear that $f=q$, $x=T$, and $y=V$, and $\left(\frac{\partial f}{\partial y} \right)_x = \left(\frac{\partial q}{\partial V} \right)_T = C_V$ and $\left(\frac{\partial f}{\partial x} \right)_y = \left(\frac{\partial q}{\partial T} \right)_V = P$. Let us now define what it means to be inexact using Equation 2.9, the Euler test (an inexact partial fails the Euler test, hence the \neq):

$$\left(\frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right)_y \right)_x \neq \left(\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y} \right)_x \right)_y \quad \text{nonnumber}$$

Making the proper substitutions defined above yields:

$$\left(\frac{\partial}{\partial V} \left(\frac{\partial q}{\partial T} \right)_V \right)_T \neq \left(\frac{\partial}{\partial T} \left(\frac{\partial q}{\partial V} \right)_T \right)_V \quad \text{nonnumber}$$

The right-hand double derivative is: $\left(\frac{\partial}{\partial V} \left(\frac{\partial q}{\partial T} \right)_V \right)_T = \left(\frac{\partial}{\partial V} \left(\frac{\partial P}{\partial T} \right)_V \right)_T = \left(\frac{\partial^2 P}{\partial T \partial V} \right)_T$. We assume perfect gas conditions, i.e. $P = \frac{nRT}{V}$, leaving us with: $\left(\frac{\partial P}{\partial T} \right)_V = \frac{\partial nRT/V}{\partial T} = \frac{nR}{V}$. The left-hand side is:

$$\left(\frac{\partial}{\partial T} \left(\frac{\partial q}{\partial V} \right)_T \right)_V = \left(\frac{\partial}{\partial T} C_V \right)_V \quad \text{since } \partial q = C_V \partial T. \quad \text{Unfortunately, } \left(\frac{\partial C_V}{\partial V} \right)_T \text{ requires}$$

some effort. Recall that the heat capacity at constant volume is related to the internal energy via: $C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{1}{2} nR \cdot (\text{degrees of freedom})$ as we demonstrated in Chapter 2, Equation 2.11. There is no volume dependence to the degrees of freedom, at least for a perfect gas since they don’t interact with each other. As a result, there is no reason to believe that there is any volume dependence to the heat capacity, which makes the derivative with respect to volume $\left(\frac{\partial C_V}{\partial V} \right)_T = 0 \text{ J/m}^3$. Thus, heat is not exact because it fails the Euler test:

$$\left(\frac{\partial}{\partial V} \left(\frac{\partial q}{\partial T} \right)_V \right)_T = 0 \text{ J/m}^3 \neq \left(\frac{\partial}{\partial T} \left(\frac{\partial q}{\partial V} \right)_T \right)_V = \frac{nR}{V} \quad \text{nonnumber}$$

