1 The Fundamental Equation of Thermodynamics

We can write:

$$\underline{U} = f_U(\underline{S}, \underline{V}, N_1, ..., N_n) \tag{1}$$

This function completely describes all of the stable equilibrium states of a system system of n components. By solving for the entropy $\underline{S}$:

$$\underline{S} = f_S(\underline{U}, \underline{V}, N_1, ..., N_n) \tag{2}$$

We say that equation 1 is the *energy representation*, while equation 2 is known as the *entropy representation* of the fundamental equation of thermodynamics.

- **NOTE:** Intensive properties are only a function of $n+1$ other independent intensive properties.

Some useful derivatives of the fundamental equation:

$$\left(\frac{\partial \underline{U}}{\partial \underline{S}}\right)_{\underline{V},N_i} = T \qquad \left(\frac{\partial \underline{U}}{\partial \underline{V}}\right)_{\underline{S},N_i} = -P \qquad \left(\frac{\partial \underline{U}}{\partial \underline{N}}\right)_{\underline{S},\underline{V},N_{j[i]}} = \mu_i \tag{3}$$

1.1 Euler's Theorem for Homogeneous Functions of Degree h

Below is a brief description of Euler's Theorem, for a most complete discussion, please see Appendix C of Tester and Modell.

$$f(a, b, kx, ky) = k^h \cdot f(a, b, x, y) \tag{4}$$

$$h \cdot f(a, b, x, y) = x\left(\frac{\partial f}{\partial x}\right)_{a,b,y} + y\left(\frac{\partial f}{\partial y}\right)_{a,b,x} \tag{5}$$

We can now apply this to the fundamental equation for a 1 component system. Given:

$$\underline{U} = f(\underline{S}, \underline{V}, N) \tag{6}$$

We also know that $\underline{U}$ is first order in mass (or moles) and that $\underline{S}, \underline{V}$ and N are proportional to the mass. Remember that $\underline{V} = NV$, $\underline{S} = NS$, etc.

$$\underline{U}(k\underline{S}, k\underline{V}, kN = k\underline{U}(\underline{S}, \underline{V}, N) \tag{7}$$

Since our function is first order in mass, $h = 1$ in equation 5. Also set $x = \underline{S}$, $y = \underline{V}$, $z = N$. When we plug these values into equation 5, the result is:

$$\underline{U} = \underline{S}\left(\frac{\partial \underline{U}}{\partial \underline{S}}\right)_{\underline{V},N_i} + \underline{V}\left(\frac{\partial \underline{U}}{\partial \underline{V}}\right)_{\underline{S},N_i} + N\left(\frac{\partial \underline{U}}{\partial \underline{N}}\right)_{\underline{S},\underline{V},N_{j[i]}} \tag{8}$$

or

$$\underline{U} = \underline{S}T - \underline{V}P + N\mu \tag{9}$$

For an n-component system we can write the integral

$$\underline{U} = \underline{S}T - \underline{V}P + \sum_{i=1}^{n} N_i\mu_i \tag{10}$$

and derivative

$$d\underline{U} = Td\underline{S} - Pd\underline{V} + \sum_{i=1}^{n} \mu_i dN_i \tag{11}$$

forms of the fundamental equation of thermodynamics.

- Now that we have the fundamental equation, an important question arises. How can we work with functions of variables other than $\underline{S}, \underline{V}$ and N?

Operations that combine integration and taking of derivatives can be problematic. For example, suppose we have the following function:

$$y(x) = x^2 + 5 \tag{12}$$

and wish to convert $y(x)$ to $y(\xi)$, where $\xi = \dfrac{dy}{dx}$.

$$\xi = 2x \qquad x = \xi/2 \tag{13}$$

Therefore

$$y(\xi) = \xi^2/4 + 5 \tag{14}$$

Note: if we integrate $\dfrac{dy}{dx}$:

$$\int \frac{dy}{dx}dx = \int 2x dx = x^2 + \mathrm{c} \tag{15}$$

there is a constant of integration that appears. Information is lost when we take the derivative. Consider the case of $y(x) = (x + 3)^2 + 5$.

$$\xi = 2(x + 3) \qquad x + 3 = \xi/2 \tag{16}$$

and

$$y(\xi) = \xi^2/4 + 5 \tag{17}$$

which is identical to the case in which $y(x) = x^2 + 5$! This shows us that our transformation is not unique. This is why we turn to *Legendre Transforms* when manipulating thermodynamic variables.

2 Legendre Transforms

Legendre Transforms are a powerful and relatively simple way of relating thermodynamic variables. Before proceeding, we must define the **basis function:**

$$y^{(0)}(x_1, x_2, ..., x_n) \tag{18}$$

$$dy^{(0)} = \xi_1 x_1 \qquad \xi_i = \left(\frac{\partial y^{(0)}}{\partial x_i}\right)_{x_{j[i]}} \tag{19}$$

One can transform from $y^{(0)}$ to $y^{(1)}$ in the following way:

$$y^{(0)}(\xi_1, x_2, ..., x_n) = y^{(0)} - x_1\xi_1 \tag{20}$$

- **NOTE:** both the forward and reverse transformations are unique since only differentiations are involved. Also, $(y^{(1)})^{(1)} = y^{(0)}$. For the generic case, we can write:

$$y^{(k)} = y^{(0)} - \sum_{j=1}^{k} x_j \xi_j \tag{21}$$

and

$$dy^{(k)} = -x_1 d\xi_1 - x_2 d\xi_2 - ... - x_k d\xi_k + \xi_{k+1} dx_{k+1} + ... + \xi_n dx_n \tag{22}$$

for

$$y^{(k)}(\xi_1, \xi_2, ..., \xi_k, x_{k+1}, ..., x_n) \tag{23}$$

- **NOTE:** Trasform depends on the ordering of variables

2.1 Examples

At this point we should also discuss *conjugate variables.* If you look at the fundamental equation, you will notice certain variables grouped together. These pairings are $(T, \underline{S})$, $(-P, \underline{V})$, and (μ_i, N_i). Each pair contains an intensive and an extensive quantity, respectively Suppose we start with the fundamental equation, $\underline{U} = \underline{U}(\underline{S}, \underline{V}, N_1, ..., N_n)$

$$y^{(0)} = \underline{U}(\underline{S}, \underline{V}, N_1, ..., N_n) \tag{24}$$

where n is the number of components and we wish to perform the first transform. Let's start with a table. Things may be clearer if we look at the full version of the fundamental equation in integral

$$\underline{U} = \underline{S}T - \underline{V}P + \sum_{i=1}^{n} N_i \mu_i \tag{25}$$

and differential forms.

$$d\underline{U} = Td\underline{S} - Pd\underline{V} + \sum_{i=1}^{n} \mu_i dN_i \tag{26}$$

Now let's make a table, remembering:

$$y^{(0)}(x_1, x_2, ..., x_n) \qquad \xi_i = \left(\frac{\partial y^{(0)}}{\partial x_i}\right)_{x_{j[i]}} \tag{27}$$

Therefore $x_1 = \underline{S}$, $x_2 = \underline{V}$, $x_3 = N_1$, etc, while

$$\xi_1 = \left(\frac{\partial \underline{U}}{\partial \underline{S}}\right)_{\underline{V}, N_i} = T \qquad \xi_2 = \left(\frac{\partial \underline{U}}{\partial \underline{V}}\right)_{\underline{S}, N_i} = -P \qquad \xi_3 = \left(\frac{\partial \underline{U}}{\partial \underline{N}}\right)_{\underline{S}, \underline{V}, N_{j[1]}} = \mu_1 \tag{28}$$

Table 1: $y^{(0)} = \underline{U}$

x_i	ξ_i
$\underline{S}$	T
$\underline{V}$	$-P$
N_1	μ_1
|	|
N_n	μ_n

Table 2: $y^{(1)} = \underline{U} - T\underline{S}$

x_i	ξ_i
T	$-\underline{S}$
$\underline{V}$	$-P$
N_1	μ_1
|	|
N_n	μ_n

Table 3: $y^{(2)} = \underline{U} - T\underline{S} + P\underline{V}$

x_i	ξ_i
$\underline{S}$	T
$-P$	$-\underline{V}$
N_1	μ_1
|	|
N_n	μ_n

Notice the following relationships:

- **Helmholtz Energy:** $y^{(1)} = \underline{A} = \underline{U} - T\underline{S}$
  - $\underline{A} = f(T, \underline{V}, N)$
- **Gibbs Free Energy:** $y^{(2)} = \underline{G} = \underline{U} - T\underline{S} + P\underline{V}$
  - $\underline{G} = f(T, P, N)$
- **Total Transform:** $y^{(n+2)} = \underline{U} - T\underline{S} - \sum_{i=1}^{n} \mu_i N_i + P\underline{V} = 0$
  - Rearrange to form the Gibbs-Duhem equation: $\underline{U} = T\underline{S} - P\underline{V} + \sum_{i=1}^{n} \mu_i N_i$

Suppose we reorder the fundamental equation such that:

$$y^{(0)} = \underline{U}(\underline{V}, \underline{S}, N_1, ...N_n) \quad (29)$$

and perform the first transform: Suppose we wish to get from $\underline{G}$ to $\underline{A}$.

Table 4: $y^{(0)} = \underline{U}$

x_i	ξ_i
$\underline{V}$	$-P$
$-\underline{S}$	T
N_1	μ_1
|	|
N_n	μ_n

Table 5: $y^{(1)} = \underline{U} + P\underline{V} = \underline{H}$

x_i	ξ_i
$-P$	$-\underline{V}$
$\underline{S}$	T
N_1	μ_1
|	|
N_n	μ_n

$$\underline{G} = y^{(0)}(P, T, N_i) \tag{30}$$

$$d\underline{G} = -\underline{S}dT + \underline{V}dP + \sum_{i=1}^{n} \mu_i dN_i \tag{31}$$

Table 6: $y^{(0)} = \underline{G}$

x_i	ξ_i
P	$\underline{V}$
T	$-\underline{S}$
N_1	μ_1
$\vert$	$\vert$
N_n	μ_n

Table 7: $y^{(1)} = \underline{G} - P\underline{V} = \underline{A}$

x_i	ξ_i
$\underline{V}$	$-P$
T	$-\underline{S}$
N_1	μ_1
$\vert$	$\vert$
N_n	μ_n

2.2 Maxwell Relations

Consider:

$$\left(\frac{\partial S}{\partial V}\right)_{T,n} \tag{32}$$

which implies we are looking at S as a function of V, T, and n. It is instructive to analyze this derivative in the context of the differential that is a natural function of T, V, and n:

$$dA = -SdT - pdV + \mu dn \tag{33}$$

We note that if $df = a\,dx + b\,dy$, then:

$$\left(\frac{\partial a}{\partial y}\right)_x = \left(\frac{\partial b}{\partial x}\right)_y \tag{34}$$

By analogy, our differential for A implies

$$\left(\frac{\partial S}{\partial V}\right)_{T,n} = \left(\frac{\partial p}{\partial T}\right)_{V.n} \tag{35}$$

In Tester and Model, a different (albeit more confusing) notation is used.

$$\left(\frac{\partial(\partial F/\partial x)_y}{\partial y}\right)_x = \left(\frac{\partial(\partial F/\partial y)_x}{\partial x}\right)_y \tag{36}$$

which can be expressed in abbreviated form as: $F_{xy} = F_{yx}$

- For example, $\underline{U}_{12} = \underline{U}_{21}$ and $y^{(0)} = \underline{U}(\underline{V}, \underline{S}N)$

$$\underline{U}_{\underline{V},\underline{S}} = \left(\frac{\partial^2 \underline{U}}{\partial \underline{V} \partial \underline{S}}\right) = \left(\frac{\partial^2 \underline{U}}{\partial \underline{S} \partial \underline{V}}\right) = \underline{U}_{\underline{S},\underline{V}} \tag{37}$$

which becomes

$$-\left(\frac{\partial P}{\partial \underline{S}}\right)_{\underline{V},N} = \left(\frac{\partial T}{\partial \underline{V}}\right)_{\underline{S},N} \tag{38}$$

2.3 2nd Derivatives

$$y_{11}^{(1)} = \frac{-1}{y_{11}^{(0)}} \tag{39}$$

where

$$y_{ij}^{(k)} = \frac{\partial y^{(k)}}{\partial x_i \partial x_j} \tag{40}$$

Example

$$y^{(0)} = \underline{U}(\underline{S}, \underline{V}, N) \qquad y^{(1)} = \underline{A}(T, \underline{V}, N) \tag{41}$$

Plug into the above formulas:

$$y_{11}^{(1)} = \left(\frac{\partial^2 \underline{A}}{\partial T^2}\right)_{\underline{V},N} \qquad y_{11}^{(0)} = \left(\frac{\partial^2 \underline{U}}{\partial \underline{S}^2}\right)_{\underline{V},N} \tag{42}$$

The result:

$$\left(\frac{\partial^2 \underline{U}}{\partial \underline{S}^2}\right)_{\underline{V},N} = -\frac{1}{\left(\frac{\partial^2 \underline{A}}{\partial T^2}\right)_{\underline{V},N}} \tag{43}$$

For $i \neq 1$

$$y_{1i}^{(1)} = \frac{y_{1i}^{(0)}}{y_{11}^{(0)}} \tag{44}$$

An example: Determine $y_{12}^{(1)}$

$$y_{12}^{(1)} = \frac{y_{12}^{(0)}}{y_{11}^{(0)}} \tag{45}$$

if we choose $y^{(0)} = \underline{U}(\underline{V}, \underline{S}N)$ then $y^{(1)} = \underline{H}(P, \underline{S}N)$

$$y_{11}^{(0)} = \left(\frac{\partial^2 \underline{U}}{\partial \underline{V}^2}\right)_{\underline{S},N} \qquad y_{12}^{(0)} = \left(\frac{\partial^2 \underline{U}}{\partial \underline{V} \partial \underline{S}}\right)_{\underline{N}} \tag{46}$$

$$\left(\frac{\partial^2 \underline{U}}{\partial \underline{V} \partial \underline{S}}\right)_{\underline{N}} = -\left(\frac{\partial \underline{P}}{\partial \underline{S}}\right) \qquad \text{since} \qquad \left(\frac{\partial \underline{U}}{\partial \underline{V}}\right) = -P \tag{47}$$

Therefore:

$$y_{12}^{(1)} = \frac{\left(\frac{\partial^2 \underline{U}}{\partial \underline{V}^2}\right)}{\left(\frac{\partial^2 \underline{U}}{\partial \underline{V} \partial \underline{S}}\right)} = \frac{-\left(\frac{\partial P}{\partial \underline{S}}\right)}{-\left(\frac{\partial P}{\partial \underline{V}}\right)} = \left(\frac{\partial \underline{V}}{\partial \underline{S}}\right) \tag{48}$$

For $i, j, > 1$

$$y_{ij}^{(1)} = y_{ij}^{(0)} - \frac{y_{1i}^{(0)} y_{1j}^{(0)}}{y_{11}^{(0)}} \tag{49}$$

2.4 Other useful relationships:

- **XYZ-1 Rule**

$$\left(\frac{\partial a}{\partial b}\right)_c \left(\frac{\partial b}{\partial c}\right)_a \left(\frac{\partial c}{\partial a}\right)_b = -1 \tag{50}$$

- **Chain Rule**

$$\left(\frac{\partial a}{\partial b}\right)_c = \left(\frac{\partial a}{\partial d}\right)_c \left(\frac{\partial d}{\partial b}\right)_c \tag{51}$$

2.5 The usefulness of 2nd Derivatives

- The 2nd derivatives of $\underline{G}$ are experimentally measureable.

For $y^{(0)} = \underline{G}(T, -P, N)$

$$\underline{G}_{11} = \left(\frac{\partial^2 \underline{G}}{\partial T^2}\right)_{P,N} = -\left(\frac{\partial \underline{S}}{\partial T}\right)_{P,N} = \frac{-C_p}{T} \tag{52}$$

$$\underline{G}_{12} = \left(\frac{\partial^2 \underline{G}}{\partial T \partial P}\right)_{P,N} = \underline{V}\alpha_p \tag{53}$$

$$\underline{G}_{22} = \left(\frac{\partial^2 \underline{G}}{\partial P^2}\right)_{P,N} = -\left(\frac{\partial \underline{V}}{\partial P}\right) = K_T \tag{54}$$

where α_P is the coefficient of thermal expansion, and K_T is the isothermal compressibility.

- Example: Express $\left(\frac{\partial \underline{S}}{\partial \underline{V}}\right)_P$ in terms of experimentally measurable quantities.
  - Start by applying the chain rule

$$\left(\frac{\partial \underline{S}}{\partial \underline{V}}\right)_P = \left(\frac{\partial \underline{S}}{\partial \underline{T}}\right)_P \left(\frac{\partial T}{\partial \underline{V}}\right)_P \tag{55}$$

$$\left(\frac{\partial \underline{S}}{\partial T}\right)_P = \frac{C_p}{T} \qquad \left(\frac{\partial T}{\partial \underline{V}}\right)_P = \frac{1}{\underline{V}\alpha_p} \tag{56}$$

Therefore:

$$\left(\frac{\partial \underline{S}}{\partial \underline{V}}\right)_P = \frac{C_p}{T\underline{V}\alpha_p} \tag{57}$$