Objectives of Chapter 5

1. to understand the framework of the Fundamental Equation – including the geometric and mathematical relationships among derived properties (\( U, S, H, A, \) and \( G \))
2. to describe methods of derivative manipulation that are useful for computing changes in derived property values using measurable, experimentally accessible properties like \( T, P, V, N, x_i, \) and \( \rho \).
3. to introduce the use of Legendre Transformations as a way of alternating the Fundamental Equation without losing information content

Starting with the combined 1\(^{st}\) and 2\(^{nd}\) Laws and Euler’s theorem we can generate the Fundamental Equation:

Recall for the combined 1\(^{st}\) and 2\(^{nd}\) Laws:

- Reversible, quasi-static
- Only \( PdV \) work
- Simple, open system (no KE, PE effects)
- For an \( n \) component system

\[
\begin{align*}
    dU &= T dS - P dV + \sum_{i=1}^{n} (H - TS) dN_i \\
    dU &= T dS - P dV + \sum_{i=1}^{n} \mu_i dN_i
\end{align*}
\]

and Euler’s Theorem:

- Applies to all smoothly-varying homogeneous functions \( f \):

\[
f(a, b, ..., x, y, ...)\]

where \( a, b, ... \) intensive variables are homogenous to zero order in mass and \( x, y \), extensive variables are homogeneous to the 1\(^{st}\) degree in mass or moles \( (N) \).  

- \( df \) is an exact differential (not path dependent) and can be integrated directly

\[
\text{if } Y = ky \text{ and } X = kx \text{ then}
\]
\[ f(a, b, \ldots, X, Y, \ldots) = k f(a, b, \ldots, x, y, \ldots) \]

and

\[ x \left( \frac{\partial f}{\partial x} \right)_{a, b, \ldots, x, \ldots} + y \left( \frac{\partial f}{\partial y} \right)_{a, b, \ldots, x, \ldots} + \ldots = (1) f(a, b, \ldots x, y, \ldots) \]

**Fundamental Equation:**

- Can be obtained via Euler integration of combined 1\(^{st}\) and 2\(^{nd}\) Laws

- Expressed in Energy \((U)\) or Entropy \((S)\) representation

\[
U = f_u [S, V, N_1, N_2, \ldots, N_n] = TS - PV + \sum_{i=1}^{n} \mu_i N_i
\]

or

\[
S = f_s [U, V, N_1, N_2, \ldots, N_n] = \frac{U}{T} + \frac{P}{T} V - \sum_{i=1}^{n} \frac{\mu_i}{T} N_i
\]

The following section summarizes a number of useful techniques for manipulating thermodynamic derivative relationships

Consider a general function of \(n + 2\) variables

\[
F(x, y, z_1, \ldots, z_{n+2})
\]

where \(x \equiv z_1, y \equiv z_2\). Then expanding via the rules of multivariable calculus:

\[
dF = \sum_{i=1}^{n+2} \left( \frac{\partial F}{\partial z_i} \right) dz_i
\]

Now consider a process occurring at constant \(F\) with \(z_3, \ldots, z_{n+2}\) all held constant. Then

\[
dF = 0 = \left( \frac{\partial F}{\partial x} \right)_{y, z_3, \ldots} dx + \left( \frac{\partial F}{\partial y} \right)_{x, z_4, \ldots} dy
\]
Rearranging, we get:

**Triple product “x-y-z-(1) rule” for** $F(x,y)$:

\[
(\partial F / \partial x)_y (\partial x / \partial y)_F (\partial y / \partial F)_x = -1
\]

example:

\[
(\partial H / \partial T)_P (\partial T / \partial P)_H (\partial P / \partial H)_T = -1
\]

**Add another variable to** $F(x,y)$:

\[
(\partial F / \partial y)_x = \left( \frac{\partial F / \partial \phi}{\partial y / \partial \phi} \right)_x
\]

example: $F(x,y) = S(P,H)$ and $\phi = T$ then

\[
\left( \frac{\partial S}{\partial H} \right)_P = \left( \frac{\partial S / \partial T}{\partial H / \partial T} \right)_P = \frac{C_P / T}{C_p} = 1 / T
\]

**Derivative inversion for** $F(x,y)$:

\[
(\partial F / \partial y)_x = 1 / (\partial y / \partial F)_x
\]

example:

\[
(\partial T / \partial S)_P = 1 / (\partial S / \partial T)_P = T / C_P
\]

**Maxwell’s reciprocity theorem:**

Applies to all homogeneous functions, e.g. $F(x,y,..)$

\[
\left[ \frac{\partial(\partial F / \partial x)_{y,..}}{dy} \right]_{x,..} = \left[ \frac{\partial(\partial F / \partial y)_{x,..}}{\partial x} \right]_{y,..} \text{ or } F_{xy} = F_{yx}
\]

example:

\[
dU_\Sigma = TdS - PdV + \sum_{i=1}^{n} \mu_i dN_i
\]

\[
(\partial T / \partial V)_{S,N} = U_{SV} = U_{SV} = -(\partial P / \partial S)_{V,N} = U_{VS} = U_{VS}
\]
Legendre Transforms:

\[
\begin{align*}
(x_i, \xi_i) \\
(S, T) \\
(V_i, -P) \\
(N_i, \mu_i) \\
(x_i, F_i) \\
(\rho, \sigma)
\end{align*}
\]

Conjugate coordinates

( extensive, intensive)

<table>
<thead>
<tr>
<th>General relationship</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>( y^{(0)} = f[x_1, \ldots, x_m] ) (basis function)</td>
<td>( U = f[S, V, N_1, \ldots, N_n] )</td>
</tr>
<tr>
<td>( y^{(k)} = y^{(0)} - \sum_{i=1}^{k} \xi_i x_i ) ((k^{th}) transform)</td>
<td>( y^{(1)} = A = U - T S )</td>
</tr>
<tr>
<td>or by changing variable order to ( U = f(V, S, N_1, \ldots, N_n) ),</td>
<td>( y^{(1)} = H = U + PV )</td>
</tr>
</tbody>
</table>
### General relationship

\[
d y^{(k)} = - \sum_{i=1}^{k} x_i d\xi_i + \sum_{i=k+1}^{m} \xi_i dx_i
\]

\[
d y^{(l)} \equiv dA = -SdT - PdV + \sum_{i=1}^{n} \mu_i dN_i
\]

or

\[
d y^{(l)} \equiv dH = TdS + VdP + \sum_{i=1}^{n} \mu_i dN_i
\]

\[
y^{(m)} = y^{(0)} - \sum_{i=1}^{m} \xi_i x_i = 0
\]

\[
y^{(n+2)} = 0 \quad \text{(total transform with } m = n + 2)\]

\[
d y^{(m)} = - \sum_{i=1}^{m} x_i d\xi_i = 0
\]

\[
d y^{(n+2)} = -SdT + VdP - \sum_{i=1}^{n} N_i d\mu_i = 0
\]

(Gibbs-Duhem Equation)

### Examples

### Relationships among Partial Derivatives of Legendre Transforms

\[
y_{ij}^{(k)} = y_{ji}^{(k)} = \frac{\partial^2 y^{(k)}}{\partial x_i \partial x_j}
\]

\(\text{(Maxwell relation)}\)

\[
\xi_i \equiv y_i^{(0)} = \left( \frac{\partial y^{(0)}}{\partial x_i} \right)_{x_i=0}
\]

\[
y_{ii}^{(0)} = \frac{\partial^2 y^{(0)}}{\partial x_i \partial x_i} \quad y_{11}^{(0)} = \frac{\partial^2 y^{(0)}}{\partial x_1^2}
\]

\[
y_i^{(1)} = \begin{cases} -x_i & i = 1 \\ \xi_i & i > 1 \end{cases}
\]

[NB: \( \xi_i = y_i^{(0)} \) as well for \( i > 1 \)]
Reordering and Use of Tables 5.3-5.5

Table 5.3 – 2nd & 3rd order derivatives of \([ y^{(1)}_{ij} \text{ and } y^{(1)}_{ijk} ] \) in terms of \( y^{(0)}_{ii} \), etc

Table 5.4 – Relations between 2nd order derivatives of \( j^{th} \) Legendre transform \( y^{(j)}_{ik} \) and the basis function \( y^{(0)}_{ik} \)

Table 5.5 – Relationships among 2nd order derivatives of \( j^{th} \) Legendre transform \( y^{(j)}_{ik} \) to \((j-q)\) transform \( y^{(j-q)}_{ik} \)