Supplementary Notes for Chapter 5
The Calculus of Thermodynamics

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_i, x_i, and ρ .
3. to introduce the use of Legendre Transformations as a way of alternating the Fundamental Equation without losing information content

Starting with the combined 1st and 2nd Laws and Euler's theorem we can generate the Fundamental Equation:

Recall for the combined 1st and 2nd Laws:

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

$$d\underline{U} = Td\underline{S} - Pd\underline{V} + \sum_{i=1}^{n} \left(H - TS\right)_i \, dN_i$$

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

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 1st degree in mass or moles (*N*).

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

  if $Y = ky$ and $X = kx$ then

$$f(a,b,\ldots,X,Y,\ldots) = k\, f(a,b,\ldots,x,y,\ldots)$$

and

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

Fundamental Equation:

- Can be obtained via Euler integration of combined 1st and 2nd Laws
- Expressed in Energy ($\underline{U}$) or Entropy ($\underline{S}$) representation

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

or

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

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

Consider a general function of $n + 2$ variables

$$F\left(x,y,z_3,\ldots,z_{n+2}\right)$$

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, .., z_{n+2} all held constant. Then

$$dF = 0 = \left(\frac{\partial F}{\partial x}\right)_{y,z_3,\ldots} dx + \left(\frac{\partial F}{\partial y}\right)_{x,z_3,\ldots} dy$$

Rearranging, we get:

Triple product "*x*-*y*-*z*-(-1) rule" for *F*(*x,y*):

$$\left(\partial F/\partial x\right)_y\left(\partial x/\partial y\right)_F\left(\partial y/\partial F\right)_x = -1$$

example: $$\left(\partial H/\partial T\right)_P\left(\partial T/\partial P\right)_H\left(\partial P/\partial H\right)_T = -1$$

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

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

example: $F(x,y) = S(P,H)$ and $\phi = T$ then $$\left(\frac{\partial S}{\partial H}\right)_P = \frac{\left(\partial S/\partial T\right)_P}{\left(\partial H/\partial T\right)_P} = \frac{C_p/T}{C_p} = 1/T$$

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

$$\left(\partial F/\partial y\right)_x = 1/\left(\partial y/\partial F\right)_x$$

example: $$\left(\partial T/\partial S\right)_P = 1/\left(\partial S/\partial T\right)_P = T/C_p$$

Maxwell's reciprocity theorem:

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

$$\left\lfloor \frac{\partial(\partial F/\partial x)_{y,\ldots}}{dy} \right\rfloor_{x,..} = \left\lfloor \frac{\partial(\partial F/\partial y)_{x,\ldots}}{\partial x} \right\rfloor_{y,..} \quad or\ F_{xy} = F_{yx}$$

example:

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

$$(\partial T/\partial \underline{V})_{\underline{S},N} = \underline{U}_{\underline{S}\underline{V}} = \underline{U}_{SV} = -(\partial P/\partial \underline{S})_{\underline{V},N} = \underline{U}_{\underline{V}\underline{S}} = \underline{U}_{VS}$$

Legendre Transforms:

$$\left.\begin{array}{l}(x_i\,,\xi_i)\\(\underline{S}\,,T)\\(\underline{V}\,,-P)\\(N_i\,,\mu_i)\\(\underline{x}_i\,,F_i)\\(\underline{a}\,,\sigma)\end{array}\right\}\quad \textit{Conjugate coordinates}$$

(extensive, intensive)

General relationship	***Examples***
$y^{(0)} = f[x_1,...,x_m]$ (*basis function*)	$\underline{U} = f[\underline{S},\underline{V},N_1,...N_n]$
$y^{(k)} = y^{(0)} - \sum_{i=1}^{k} \xi_i x_i$ (k^{th} *transform*)	$y^{(1)} = \underline{A} = \underline{U} - T\underline{S}$ or by changing variable order to $U = f(\underline{V}, \underline{S}, N_1,\ldots,N_n)$, $y^{(1)} = \underline{H} = \underline{U} + P\underline{V}$

General relationship	***Examples***
$dy^{(k)} = -\sum_{i=1}^{k} x_i d\xi_i + \sum_{i=k+1}^{m} \xi_i dx_i$	$dy^{(1)} \equiv d\underline{A} = -\underline{S}dT - Pd\underline{V} + \sum_{i=1}^{n} \mu_i dN_i$ *or* $dy^{(1)} \equiv d\underline{H} = Td\underline{S} + \underline{V}dP + \sum_{i=1}^{n} \mu_i dN_i$
$y^{(m)} = y^{(0)} - \sum_{i=1}^{m} \xi_i x_i = 0$	$y^{(n+2)} = 0 \quad (\textit{total transform with } m = n+2)$
$dy^{(m)} = -\sum_{i=1}^{m} x_i d\xi_i = 0$	$dy^{(n+2)} = -\underline{S}dT + \underline{V}dP - \sum_{i=1}^{n} N_i d\mu_i = 0$ (Gibbs-Duhem Equation)

Relationships among Partial Derivatives of Legendre Transforms

$$y_{ij}^{(k)} = y_{ji}^{(k)} = \frac{\partial^2 y^{(k)}}{\partial x_i \partial x_j} \qquad (\textit{Maxwell relation}) \qquad \xi_i \equiv y_i^{(0)} = \left(\frac{\partial y^{(0)}}{\partial x_i}\right)_{x_j[i]}$$

$$y_{1i}^{(0)} = \frac{\partial^2 y^{(0)}}{\partial x_1 \partial x_i} \qquad y_{11}^{(0)} = \frac{\partial^2 y^{(0)}}{\partial x_1^2} \qquad y_i^{(1)} = \begin{cases} -x_i & i = 1 \\ \xi_i & i > 1 \end{cases}$$

$[\text{NB}: \quad \xi_i = y_i^{(0)}$ as well for $i > 1]$

Reordering and Use of Tables 5.3-5.5

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

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

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

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