Mathematical Relations and Changing Variables

Last Time

Reaction Equilibria

Exact Differentials

Legendre Transformations

Lechatelier’s Principle
Maxwell’s Relations

\[ df = \left( \frac{\partial f}{\partial x} \right)_y \ dx + \left( \frac{\partial f}{\partial y} \right)_x \ dy \]  \hspace{1cm} (22-1)

A property of a perfect differential is:

\[ \frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \]  \hspace{1cm} (22-2)

If Equation 22-2 is applied to \( dU = TdS - PdV \):

\[ \frac{\partial^2 U}{\partial V \partial S} = - \left( \frac{\partial P}{\partial S} \right)_V \quad \frac{\partial^2 U}{\partial S \partial V} = \left( \frac{\partial T}{\partial V} \right)_S \]  \hspace{1cm} (22-3)

This can be summarized in the following tables (you should be able to derive these tables on your own):

<table>
<thead>
<tr>
<th>Internal Energy ( U )</th>
<th>Second Law Formulation</th>
<th>Independent Variables</th>
<th>Conjugate Variables</th>
<th>Maxwell Relations</th>
</tr>
</thead>
<tbody>
<tr>
<td>( dU = TdS )</td>
<td>( S )</td>
<td>( T = \left( \frac{\partial U}{\partial S} \right)_{V,N_i} )</td>
<td>( (\frac{\partial U}{\partial V})<em>{S,N_i} = - (\frac{\partial T}{\partial S})</em>{V,N_i} )</td>
<td></td>
</tr>
<tr>
<td>( -PdV )</td>
<td>( V )</td>
<td>( -P = \left( \frac{\partial U}{\partial V} \right)_{S,N_i} )</td>
<td>( (\frac{\partial P}{\partial V})<em>{S,N_i} = - (\frac{\partial P}{\partial N_i})</em>{S,V,N_j \neq N_i} )</td>
<td></td>
</tr>
<tr>
<td>( + \sum_{i=1}^C \mu_i dN_i )</td>
<td>( N_i )</td>
<td>( \mu_i = \left( \frac{\partial U}{\partial N_i} \right)_{S,V,N_j \neq N_i} )</td>
<td>( (\frac{\partial \mu_i}{\partial V})<em>{S,N_i} = - (\frac{\partial \mu_i}{\partial N_i})</em>{S,V,N_j \neq N_i} )</td>
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</tr>
</tbody>
</table>
### Enthalpy $H$

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<tbody>
<tr>
<td>$dH = TdS + VdP + \sum_{i=1}^{C} \mu_i dN_i$</td>
<td>$S$</td>
<td>$T = \left( \frac{\partial H}{\partial S} \right)_{V,N_i}$</td>
<td>$(\frac{\partial H}{\partial S})<em>{V,N_i} = \left( \frac{\partial V}{\partial S} \right)</em>{P,N_i}$</td>
</tr>
<tr>
<td></td>
<td>$P$</td>
<td>$V = \left( \frac{\partial H}{\partial P} \right)_{S,N_i}$</td>
<td>$(\frac{\partial H}{\partial P})<em>{S,N_i} = \left( \frac{\partial V}{\partial N_i} \right)</em>{S,P,N_i \neq N_i}$</td>
</tr>
<tr>
<td></td>
<td>$N_i$</td>
<td>$\mu_i = \left( \frac{\partial H}{\partial N_i} \right)_{S,P,N_i \neq N_i}$</td>
<td>$(\frac{\partial H}{\partial N_i})_{S,P,N_i \neq N_i}$</td>
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</tbody>
</table>

### Helmholtz Free Energy $F$

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</tr>
</thead>
<tbody>
<tr>
<td>$dF = -SdT - PdV + \sum_{i=1}^{C} \mu_i dN_i$</td>
<td>$T$</td>
<td>$-S = \left( \frac{\partial F}{\partial T} \right)_{V,N_i}$</td>
<td>$(\frac{\partial F}{\partial T})<em>{V,N_i} = \left( \frac{\partial H}{\partial T} \right)</em>{V,N_i}$</td>
</tr>
<tr>
<td></td>
<td>$V$</td>
<td>$-P = \left( \frac{\partial F}{\partial V} \right)_{T,N_i}$</td>
<td>$(\frac{\partial F}{\partial V})<em>{T,N_i} = - \left( \frac{\partial H}{\partial V} \right)</em>{T,V,N_i \neq N_i}$</td>
</tr>
<tr>
<td></td>
<td>$N_i$</td>
<td>$\mu_i = \left( \frac{\partial F}{\partial N_i} \right)_{T,V,N_i \neq N_i}$</td>
<td>$(\frac{\partial F}{\partial N_i})_{T,V,N_i \neq N_i}$</td>
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### Gibbs Free Energy $G$

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</tr>
</thead>
<tbody>
<tr>
<td>$dG = -SdT + VdP + \sum_{i=1}^{C} \mu_i dN_i$</td>
<td>$T$</td>
<td>$-S = \left( \frac{\partial G}{\partial T} \right)_{P,N_i}$</td>
<td>$(\frac{\partial G}{\partial T})<em>{P,N_i} = \left( \frac{\partial H}{\partial T} \right)</em>{P,N_i}$</td>
</tr>
<tr>
<td></td>
<td>$P$</td>
<td>$V = \left( \frac{\partial G}{\partial V} \right)_{T,N_i}$</td>
<td>$(\frac{\partial G}{\partial V})<em>{T,N_i} = - \left( \frac{\partial H}{\partial V} \right)</em>{T,P,N_i \neq N_i}$</td>
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<td>$N_i$</td>
<td>$\mu_i = \left( \frac{\partial G}{\partial N_i} \right)_{T,P,N_i \neq N_i}$</td>
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</tbody>
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### Change of Variable

Sometimes it is more useful to be able to measure some quantity, such as

\[
C_P = T \left( \frac{\partial S}{\partial T} \right)_P = f_1(T, P)
\]  

(22-4)

or

\[
C_V = T \left( \frac{\partial S}{\partial T} \right)_V = f_2(T, V)
\]  

(22-5)

under different conditions than those indicated by their natural variables.

It would be easier to measure $C_V$ at constant $P$, $T$, so a change of variable would be useful.
To change variables, a useful scheme using Jacobians can be employed:  

\[
\frac{\partial(u, v)}{\partial(x, y)} \equiv \det \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} \end{vmatrix} = \frac{\partial u \partial v}{\partial x \partial y} - \frac{\partial u \partial v}{\partial y \partial x} \\
= \left( \frac{\partial u}{\partial x} \right)_y \left( \frac{\partial v}{\partial y} \right)_x - \left( \frac{\partial u}{\partial y} \right)_x \left( \frac{\partial v}{\partial x} \right)_y \\
= \frac{\partial u(x, y)}{\partial x} \frac{\partial v(x, y)}{\partial y} - \frac{\partial u(x, y)}{\partial y} \frac{\partial v(x, y)}{\partial x} 
\]

(22-6)

To see where the last rule comes from:

For example,

\[
C_V = T \left( \frac{\partial S}{\partial T} \right)_V = T \frac{\partial(S, V)}{\partial(T, V)} 
\]

(22-8)

23 An alternative scheme is presented in Denbigh, Sec. 2.10(c)
Using the Maxwell relation: \( \left( \frac{\partial S}{\partial P} \right)_T = - \left( \frac{\partial V}{\partial T} \right)_P \):

\[
C_P - C_V = -T \left[ \frac{\left( \frac{\partial V}{\partial T} \right)_P}{\left( \frac{\partial V}{\partial P} \right)_T} \right]^2
\]  \( (22-9) \)