Lecture 22

Mathematical Relations and Changing Variables

Last Time

Reaction Equilibria

Exact Differentials

Legendre Transformations

Lechatelier's Principle

Maxwell's Relations

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy \tag{22-1}$$

A property of a perfect differential is:

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \tag{22-2}$$

If Equation 22-2 is applied to $dU = TdS - PdV$:

$$\frac{\partial^2 U}{\partial V \partial S} = -\left(\frac{\partial P}{\partial S}\right)_V \qquad \frac{\partial^2 U}{\partial S \partial V} = \left(\frac{\partial T}{\partial V}\right)_S \tag{22-3}$$

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

Internal Energy U				
Second Law Formulation		Independent Variables	Conjugate Variables	Maxwell Relations
$dU =$	TdS	S	$T = \left(\frac{\partial U}{\partial S}\right)_{V,N_i}$	$\left(\frac{\partial T}{\partial V}\right)_{S,N_i} = -\left(\frac{\partial P}{\partial S}\right)_{V,N_i}$
	$-PdV$	V	$-P = \left(\frac{\partial U}{\partial V}\right)_{S,N_i}$	$\left(\frac{\partial \mu_i}{\partial V}\right)_{S,N_i} = -\left(\frac{\partial P}{\partial N_i}\right)_{S,V,N_j \neq N_i}$
	$+\sum_{i=1}^{C} \mu_i dN_i$	N_i	$\mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_j \neq N_i}$	$\left(\frac{\partial \mu_i}{\partial V}\right)_{S,N_i} = -\left(\frac{\partial P}{\partial N_i}\right)_{S,V,N_j \neq N_i}$

Enthalpy H			
$H = U + PV$ $\quad H = G + TS$ $\quad H = F + PV - TS$			
Second Law Formulation	Independent Variables	Conjugate Variables	Maxwell Relations
$dH = \quad TdS$	S	$T = \left(\frac{\partial H}{\partial S}\right)_{V,N_i}$	$\left(\frac{\partial T}{\partial P}\right)_{S,N_i} = \left(\frac{\partial V}{\partial S}\right)_{P,N_i}$
$+VdP$	P	$V = \left(\frac{\partial H}{\partial P}\right)_{S,N_i}$	$\left(\frac{\partial \mu_i}{\partial P}\right)_{S,N_i} = \left(\frac{\partial V}{\partial N_i}\right)_{S,P,N_j \neq N_i}$
$+\sum_{i=1}^{C} \mu_i dN_i$	N_i	$\mu_i = \left(\frac{\partial H}{\partial N_i}\right)_{S,P,N_j \neq N_i}$	$\left(\frac{\partial \mu_i}{\partial S}\right)_{P,N_i} = \left(\frac{\partial T}{\partial N_i}\right)_{S,P,N_j \neq N_i}$

Helmholtz Free Energy F			
$F = U - TS$ $\quad F = H - PV - TS$ $\quad F = G + PV$			
Second Law Formulation	Independent Variables	Conjugate Variables	Maxwell Relations
$dF = \quad -SdT$	T	$-S = \left(\frac{\partial F}{\partial T}\right)_{V,N_i}$	$\left(\frac{\partial S}{\partial V}\right)_{T,N_i} = \left(\frac{\partial P}{\partial T}\right)_{V,N_i}$
$-PdV$	V	$-P = \left(\frac{\partial F}{\partial V}\right)_{T,N_i}$	$\left(\frac{\partial \mu_i}{\partial V}\right)_{T,N_i} = -\left(\frac{\partial P}{\partial N_i}\right)_{T,V,N_j \neq N_i}$
$+\sum_{i=1}^{C} \mu_i dN_i$	N_i	$\mu_i = \left(\frac{\partial F}{\partial N_i}\right)_{T,V,N_j \neq N_i}$	$\left(\frac{\partial \mu_i}{\partial T}\right)_{V,N_i} = -\left(\frac{\partial S}{\partial N_i}\right)_{T,V,N_j \neq N_i}$

Gibbs Free Energy G			
$G = U - TS + PV$ $\quad G = F + PV$ $\quad G = H - TS$			
Second Law Formulation	Independent Variables	Conjugate Variables	Maxwell Relations
$dG = \quad -SdT$	T	$-S = \left(\frac{\partial G}{\partial T}\right)_{P,N_i}$	$\left(\frac{\partial S}{\partial P}\right)_{T,N_i} = -\left(\frac{\partial V}{\partial T}\right)_{P,N_i}$
$+VdP$	P	$V = \left(\frac{\partial G}{\partial V}\right)_{T,N_i}$	$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,N_i} = -\left(\frac{\partial S}{\partial N_i}\right)_{T,P,N_j \neq N_i}$
$+\sum_{i=1}^{C} \mu_i dN_i$	N_i	$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_j \neq N_i}$	$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,N_i} = \left(\frac{\partial V}{\partial N_i}\right)_{T,P,N_j \neq N_i}$

Change of Variable

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

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P = f_1(T,P) \tag{22-4}$$

or

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V = f_2(T,V) \tag{22-5}$$

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:[23]

$$
\begin{aligned}
\frac{\partial(u,v)}{\partial(x,y)} &\equiv \det \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} \end{vmatrix} \\
&= \frac{\partial u}{\partial x}\frac{\partial v}{\partial y} - \frac{\partial u}{\partial y}\frac{\partial v}{\partial x} \\
&= \left(\frac{\partial u}{\partial x}\right)_y \left(\frac{\partial v}{\partial y}\right)_x - \left(\frac{\partial u}{\partial y}\right)_x \left(\frac{\partial v}{\partial x}\right)_y \\
&= \frac{\partial u(x,y)}{\partial x}\frac{\partial v(x,y)}{\partial y} - \frac{\partial u(x,y)}{\partial y}\frac{\partial v(x,y)}{\partial x}
\end{aligned}
\tag{22-6}
$$

$$
\begin{aligned}
\frac{\partial(u,v)}{\partial(x,y)} = -\frac{\partial(v,u)}{\partial(x,y)} &= \frac{\partial(v,u)}{\partial(y,x)} \\
\frac{\partial(u,v)}{\partial(x,v)} &= \left(\frac{\partial u}{\partial x}\right)_v \\
\frac{\partial(u,v)}{\partial(x,y)} &= \frac{\partial(u,v)}{\partial(r,s)}\frac{\partial(r,s)}{\partial(x,y)}
\end{aligned}
\tag{22-7}
$$

To see where the last rule comes from:

For example,

$$
C_V = T\left(\frac{\partial S}{\partial T}\right)_V = T\frac{\partial(S,V)}{\partial(T,V)} \tag{22-8}
$$

[23] An alternative scheme is presented in Denbigh, Sec. 2.10(c)

Using the Maxwell relation: $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$:

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