

Nov. 4 2002: Lecture 22:

Mathematical Relations and Changing Variables

Last Time

Reaction Equilibria

Exact Differentials

Legendre Transformations

Lechatelier's Principle

Maxwell's Relations

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

A property of a perfect differential is:

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \quad (22-2)$$

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

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

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
$dU = TdS - PdV + \sum_{i=1}^C \mu_i dN_i$	S V N_i	$T = \left(\frac{\partial U}{\partial S}\right)_{V, N_i}$ $-P = \left(\frac{\partial U}{\partial V}\right)_{S, N_i}$ $\mu_i = \left(\frac{\partial U}{\partial N_i}\right)_{S, V, N_j \neq N_i}$	$\left(\frac{\partial T}{\partial V}\right)_{S, N_i} = - \left(\frac{\partial P}{\partial S}\right)_{V, N_i}$ $\left(\frac{\partial \mu_i}{\partial V}\right)_{S, N_i} = - \left(\frac{\partial P}{\partial N_i}\right)_{S, V, N_j \neq N_i}$ $\left(\frac{\partial \mu_i}{\partial V}\right)_{S, N_i} = - \left(\frac{\partial P}{\partial N_i}\right)_{S, V, N_j \neq N_i}$

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

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

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

Change of Variable

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

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

or

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

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,

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

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

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

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