Lecture 21: Natural Variables

Maxwell Relations Part 2

Natural Variables

Set of variables that make taking partials easier

State Function	Differential	Maxwell Relation
$U(S,V)$	$dU = T\,dS - P\,dV$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$
$H(S,P) = U + PV$	$dH = T\,dS + V\,dP$	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$
$A(T,V) = U - TS$	$dA = -S\,dT - P\,dV$	$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$
$G(T,P) = U - TS + PV$	$dG = -S\,dT + V\,dP$	$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

Using Natural Variables

Starting from:

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

Show that:

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

Maxwell Relations:

$$dH = T\,dS + V\,dP$$

$$T = \left(\frac{\partial H}{\partial S}\right)_P \quad V = \left(\frac{\partial H}{\partial P}\right)_S$$

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial H}{\partial S}\right)_P \left(\frac{\partial S}{\partial T}\right)_P$$

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P \implies \boxed{\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}}$$

Without Natural Variables

Starting from the Gibbs free energy:

$$dG = -S\,dT + V\,dP$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_P = -\left(\frac{\partial S}{\partial T}\right)_P$$

From definition of Gibbs:

$$G = H - TS \implies H = G + TS$$

$$H = G - T\left(\frac{\partial G}{\partial T}\right)_P$$

Substitute and use product rule:

$$H = G - T\left(\frac{\partial G}{\partial T}\right)_P$$

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial G}{\partial T}\right)_P - \left[\left(\frac{\partial G}{\partial T}\right)_P + T\left(\frac{\partial^2 G}{\partial T^2}\right)_P\right]$$

$$= -T\left(\frac{\partial^2 G}{\partial T^2}\right)_P$$

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P \implies \boxed{\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}}$$

Triple Product Rule

Total differential of $z(x, y)$:

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

Consider constant z, $dz = 0$, $dy = \left(\frac{\partial y}{\partial x}\right)_z dx$:

$$0 = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z dx$$

$$\left(\frac{\partial z}{\partial x}\right)_y = -\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z$$

Dividing both sides by $\left(\frac{\partial z}{\partial x}\right)_y$:

Triple Product Rule

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$