Callen : Thermodynamics (App A)

— Implicit functions

1. $\Phi(x, y, z) = \text{const}$

$\Rightarrow z = z(x,y)$, or $x = x(y,z)$, or $y = y(x,z)$

2. $d\Phi$

$= \left(\frac{\partial \Phi}{\partial x}\right)_{y,z} dx + \left(\frac{\partial \Phi}{\partial y}\right)_{x,z} dy + \left(\frac{\partial \Phi}{\partial z}\right)_{x,y} dz = 0$

put $dz = 0$ (i.e. let z = const) and divide through by dx,

$$0 = \left(\frac{\partial \Phi}{\partial x}\right)_{y,z} + \left(\frac{\partial \Phi}{\partial y}\right)_{x,z} \left(\frac{\partial y}{\partial x}\right)_z = 0$$

$$\boxed{\left(\frac{\partial y}{\partial x}\right)_z = - \frac{\left(\frac{\partial \Phi}{\partial x}\right)_{y,z}}{\left(\frac{\partial \Phi}{\partial y}\right)_{x,z}}}$$

3. put $dy = 0$ in (1)

$$\left(\frac{\partial x}{\partial z}\right)_y = -\frac{\left(\frac{\partial \Phi}{\partial z}\right)_{x y}}{\left(\frac{\partial \Phi}{\partial x}\right)_{y, z}}$$

put $dx = 0$

$$\left(\frac{\partial z}{\partial y}\right)_x = -\frac{\left(\frac{\partial \Phi}{\partial y}\right)_{x, z}}{\left(\frac{\partial \Phi}{\partial z}\right)_{x, y}}$$

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

4.

二.

1.

$$U = U(S, V)$$

$$dU = T\,dS - p\,dV$$

$$\begin{cases} \left(\frac{\partial U}{\partial S}\right)_V \equiv T = T(S, V) \\ \left(\frac{\partial U}{\partial V}\right)_S = -p \end{cases}$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad (M1)$$

2. F

$$\left(\frac{\partial U}{\partial S}\right)_V = T \Rightarrow T = T(S, V)$$
$$\Rightarrow S = S(T, V)$$

$$U = U(S, V)$$
$$= U(S(T, V), V)$$

$$dU = T\,dS - p\,dV$$
$$= T\left[\left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV\right]$$
$$- p\,dV$$
$$= T\left(\frac{\partial S}{\partial T}\right)_V dT + \left[T\left(\frac{\partial S}{\partial V}\right)_T - p\right] dV$$

Define

$$F = F(T, V) \equiv U - TS \qquad L(1)$$

$$dF = TdS - pdV - TdS - SdT$$

$$= -SdT - pdV$$

$$\begin{cases} \left(\frac{\partial F}{\partial T}\right)_V = -S \\ \left(\frac{\partial F}{\partial V}\right)_T = -p \end{cases}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \qquad (M2)$$

3. $H = H(S, p) \equiv U + pV \qquad L(2)$

$\cancel{dU}$

$$dH = TdS - pdV + pdV + Vdp$$

$$= TdS + Vdp$$

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

$$\left(\frac{\partial H}{\partial p}\right)_S = V$$

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \qquad (M3)$$

4. $G = G(T, p) \equiv G + TS - pV \quad L(3)$

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

$$\begin{cases} \left(\frac{\partial G}{\partial T}\right)_p = -S \\ \left(\frac{\partial G}{\partial p}\right)_T = V \end{cases}$$

$$-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p \qquad (M4)$$

Maxwell relations (M1)(M2)(M3)M(4)

Legendre transformation (L1)(L2)(L3)