Study Problems, Chapter 3

(1) Derive $\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p$

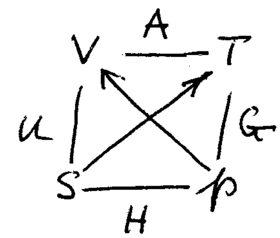
$H = H(S, p)$ natural variables of H are S + p

$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dp$$

divide by ∂p and impose constant T:

$$\left(\frac{\partial H}{\partial p}\right)_T = \left(\frac{\partial H}{\partial S}\right)_p \left(\frac{\partial S}{\partial p}\right)_T + \left(\frac{\partial H}{\partial p}\right)_S$$

now $\left(\frac{\partial H}{\partial S}\right)_p = T$ and $\left(\frac{\partial H}{\partial p}\right)_S = V$ from



$$\therefore \left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T + V$$

Use the Maxwell Relation $\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$

substitute into previous equation:

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

For a perfect gas $V = \frac{nRT}{p}$ and $\left(\frac{\partial V}{\partial T}\right)_p = \frac{nR}{p}$

$$\therefore \left(\frac{\partial H}{\partial p}\right)_T = \frac{nRT}{p} - T\left(\frac{nR}{p}\right) = 0$$

(2) For 1 mol $V = V_m = \frac{RT}{p} = f(T,p)$

$$\therefore dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp$$

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{p} \qquad \left(\frac{\partial V}{\partial p}\right)_T = -\frac{RT}{p^2}$$

$$\therefore dV \quad \frac{R}{p}\,dT - \frac{RT}{p^2}\,dp = M(T,p)\,dT + N(T,p)\,dp$$

$$\left(\frac{\partial}{\partial p}\left(\frac{R}{p}\right)\right)_T = -\frac{R}{p^2} \text{ and } \left(\frac{\partial}{\partial T}\left(-\frac{RT}{p^2}\right)\right)_p = -\frac{R}{p^2}$$

$$\therefore \left(\frac{\partial M}{\partial p}\right)_T = \left(\frac{\partial N}{\partial T}\right)_p$$ and dV is exact

(3) $p = \frac{nRT}{V}$ $\qquad V = \frac{nRT}{p}$ $\qquad T = \frac{pV}{nR}$

$(\partial P/\partial V)_T = -nRT/V^2$; $(\partial V/\partial T)_p = nR/p$; $(\partial T/\partial P)_V = V/nR$

$$\therefore \left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_V = \left(-\frac{nRT}{V^2}\right)\left(\frac{nR}{p}\right)\left(\frac{V}{nR}\right) = -\frac{nRT}{pV} = -1$$

since $pV = nRT$

(4) Since U is a state function, the test for exactness says that $\left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right)_V$; by definition, $C_V = \left(\frac{\partial U}{\partial T}\right)_V$ and for an ideal gas $\left(\frac{\partial U}{\partial V}\right)_T = 0$

$$\therefore \left(\frac{\partial C_V}{\partial V}\right)_T = 0 \text{ since } \left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right)_V = 0$$

(5) $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ for an ideal gas $V = \frac{nRT}{p}$ and $\left(\frac{\partial V}{\partial T}\right)_p = \frac{nR}{p}$

$\therefore \alpha = \frac{1}{V}\left(\frac{nR}{p}\right) = \frac{1}{T}$

$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$ and $\left(\frac{\partial V}{\partial p}\right)_T = -\frac{nRT}{p^2}$

$\therefore \kappa = -\frac{1}{V}\left(-\frac{nRT}{p^2}\right) = \frac{nRT}{Vp^2} = \frac{1}{p}$

(6) $dz = \frac{3}{2}x^2y^2\,dx + x^3y\,dy = M\,dx + N\,dy$

$\left(\frac{\partial M}{\partial y}\right)_x = 3x^2y \quad \left(\frac{\partial N}{\partial x}\right)_y = 3x^2y$

$\therefore \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$ and dz is exact

(7)

$dp = \left(\frac{\partial p}{\partial T}\right)_V dT + \left(\frac{\partial p}{\partial V}\right)_T dV$ and $p = \frac{nRT}{V}$

$(\partial p/\partial T)_V = nR/V \qquad (\partial p/\partial V)_T = -nRT/V^2$

$dp = \frac{nR}{V}\,dT - \frac{nRT}{V^2}\,dV = M\,dT + N\,dV$

$\left(\frac{\partial}{\partial V}\left(\frac{nR}{V}\right)\right)_T = -\frac{nR}{V^2}$ and $\left(\frac{\partial}{\partial T}\left(-\frac{nRT}{V^2}\right)\right)_V = -\frac{nR}{V^2}$

$\therefore \left(\frac{\partial M}{\partial V}\right)_T = \left(\frac{\partial N}{\partial T}\right)_V$ and dp is exact.