Thermo

Recitation #10

- Maxwell's relations & mixed derivatives
- Derivations

I Maxwell's relations

These are a set of equations in thermodynamics which are derivable from symmetry of second derivatives and from the definitions of the thermodynamic potentials.

Maxwell's equations

		derived from:
1	$-\left.\dfrac{\partial P}{\partial S}\right\|_V = \left.\dfrac{\partial T}{\partial V}\right\|_S$	$dU = -PdV + TdS$
2	$\left.\dfrac{\partial V}{\partial T}\right\|_P = -\left.\dfrac{\partial S}{\partial P}\right\|_T$	$dG = VdP - SdT$
3	$\left.\dfrac{\partial P}{\partial T}\right\|_V = \left.\dfrac{\partial S}{\partial V}\right\|_T$	$dA = -PdV - SdT$
4	$\left.\dfrac{\partial V}{\partial S}\right\|_P = \left.\dfrac{\partial T}{\partial P}\right\|_S$	$dH = TdS + VdP$

derivation

(1) 1^{st} law

$$dU = Q + W$$

$$\therefore dU = TdS - PdV \quad \text{———} \quad (1)$$

differentiating w.r.t V at const. S

$$\therefore \left.\frac{\partial U}{\partial V}\right|_S = T \cancel{\left.\frac{\partial S}{\partial V}\right|_S}^{\,0} - P \cancel{\left.\frac{\partial V}{\partial V}\right|_S}^{\,1}$$

$$\therefore \left.\frac{\partial U}{\partial V}\right|_S = -P$$

Now, $$-\left.\frac{\partial P}{\partial S}\right|_V = \frac{\partial}{\partial S}\left(\left.\frac{\partial U}{\partial V}\right|_S\right) = \frac{\partial^2 U}{\partial S \cdot \partial V} \quad \text{— } (2)$$

differentiating (1) w.r.t S at const. V

$$\left.\frac{\partial U}{\partial S}\right|_V = T \cancel{\left.\frac{\partial S}{\partial S}\right|_V}^{\,1} - P \cancel{\left.\frac{\partial V}{\partial S}\right|_V}^{\,0}$$

$$\left.\frac{\partial U}{\partial S}\right|_V = T$$

Now, $$\left.\frac{\partial T}{\partial V}\right|_S = \frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right) = \frac{\partial^2 U}{\partial V \cdot \partial S} \quad \text{— } (3)$$

For a continuous differential function (or intensive Property)

we can equate the second derivatives by symmetry

$\therefore$ from (2) & (3)

$$\frac{\partial^2 U}{\partial V \cdot \partial S} = \frac{\partial^2 U}{\partial S \cdot \partial V}$$

$$\therefore \quad \boxed{-\left.\frac{\partial P}{\partial S}\right|_V = \left.\frac{\partial T}{\partial V}\right|_S}$$

II Mixed derivatives

for a function $f(x,y)$ we can write:

$$df(x,y) = \left.\frac{\partial f}{\partial x}\right|_y dx + \left.\frac{\partial f}{\partial y}\right|_x dy$$

eg we can say entropy is a function of Temp & volume / pressure.

$\therefore$ $$\underline{\underline{f = S(T,P)}} \quad \text{or} \quad f = S(T,V)$$

$\therefore$ $$\boxed{dS = \left.\frac{\partial S}{\partial T}\right|_P \cdot dT + \left.\frac{\partial S}{\partial P}\right|_T \cdot dP}$$

Q1 (a) $\left.\frac{\partial H}{\partial P}\right|_T = ?$

Measurable properties : T, P, V, c_p, c_V

we know, $dH = TdS + V\,dP$

$$\left.\frac{\partial H}{\partial p}\right|_T = T\left.\frac{\partial S}{\partial p}\right|_T + V\left.\frac{\partial p}{\partial p}\right|_T \xrightarrow{} 1$$

$$\therefore \left.\frac{\partial H}{\partial p}\right|_T = T\cdot\left.\frac{\partial S}{\partial p}\right|_T + V$$

from maxwell's eqn : $\left.\frac{\partial S}{\partial P}\right|_T = -\left.\frac{\partial V}{\partial T}\right|_P$

$$\therefore \boxed{\left.\frac{\partial H}{\partial P}\right|_T = -T \cdot \left.\frac{\partial V}{\partial T}\right|_P + V}$$

(b) $$\left.\frac{\partial U}{\partial P}\right|_T$$

$$\because \quad dU = T\,dS - P\,dV$$

$$\therefore \quad \left.\frac{\partial U}{\partial P}\right|_T = T \left.\frac{\partial S}{\partial P}\right|_T - P \left.\frac{\partial V}{\partial P}\right|_T$$

from maxwell's eq: $$\left.\frac{\partial S}{\partial P}\right|_T = -\left.\frac{\partial V}{\partial T}\right|_P$$

$$\therefore \quad \boxed{\left.\frac{\partial u}{\partial p}\right|_T = -T\left.\frac{\partial V}{\partial T}\right|_p - p\left.\frac{\partial V}{\partial p}\right|_T}$$

Q2

Comparing the two derivatives

$$\rightarrow \left.\frac{\partial H}{\partial P}\right|_T - \left.\frac{\partial U}{\partial P}\right|_T = \cancel{-T\left.\frac{\partial V}{\partial T}\right|_P} + V - \left[\cancel{-T\left.\frac{\partial V}{\partial T}\right|_P} - P\left.\frac{\partial V}{\partial P}\right|_T\right]$$

$$\boxed{\left.\frac{\partial H}{\partial P}\right|_T - \left.\frac{\partial U}{\partial P}\right|_T = V + P\left.\frac{\partial V}{\partial P}\right|_T} \quad — \quad 4$$

starting from $dH = dU + d(PV)$

$\because \; dH = dU + d(PV)$

$$\therefore \quad \left.\frac{\partial H}{\partial p}\right|_T = \left.\frac{\partial U}{\partial p}\right|_T + \left.\frac{\partial (pV)}{\partial p}\right|_T$$

$$\therefore \quad \left.\frac{\partial H}{\partial p}\right|_T = \left.\frac{\partial U}{\partial p}\right|_T + p\left.\frac{\partial V}{\partial p}\right|_T + V\left.\cancelto{1}{\frac{\partial p}{\partial p}}\right|_T$$

$$\boxed{\therefore \quad \left.\frac{\partial H}{\partial p}\right|_T - \left.\frac{\partial U}{\partial p}\right|_T = p\left.\frac{\partial V}{\partial p}\right|_T + V} \quad — (5)$$

eq. (4) = (5)

Hence we get the same difference when starting from $dH = dU + d(pV)$

Q3

$$\left.\frac{\partial s}{\partial T}\right|_p$$

$$\because \quad dH = T\,ds + v\,dP$$

$$\left.\frac{\partial H}{\partial T}\right|_p = T \left.\frac{\partial s}{\partial T}\right|_p + v \cancel{\left.\frac{\partial P}{\partial T}\right|_p}^{\,0}$$

$$\because \quad \left.\frac{\partial H}{\partial T}\right|_p = c_p \cdot \cancel{\left.\frac{\partial T}{\partial T}\right|_p}^{\,1} = c_p$$

$$\therefore \quad c_p = T \left.\frac{\partial s}{\partial T}\right|_p$$

$$\therefore \quad \boxed{\left.\frac{\partial S}{\partial T}\right|_P = \frac{C_P}{T}} \quad — (6)$$

Q4 we can say entropy is a function of Temp & volume / pressure.

$$\therefore \quad f = S(T, P) \quad \text{or} \quad f = S(T, V)$$

$$\therefore \quad dS = \left.\frac{\partial S}{\partial T}\right|_P \cdot dT + \left.\frac{\partial S}{\partial P}\right|_T \cdot dP \quad — (7)$$

since, $\quad dS = \frac{Q}{T}$

from 6 $\rightarrow$ $$\left.\frac{\partial s}{\partial T}\right|_P = \frac{C_P}{T}$$

by maxwell eq:

$$\left.\frac{\partial s}{\partial P}\right|_T = -\left.\frac{\partial V}{\partial T}\right|_P \quad — 8$$

substituting 8 & 6 in 7

$$\therefore \boxed{ds = \frac{C_P}{T} \cdot dT - \left.\frac{\partial V}{\partial T}\right|_P \cdot dP} \quad — 9$$

This is the generalised relation for entropy changes of any fluid w.r.t T & P in terms of C_P, T, P & V.

Q 5

Evaluate (9) for ideal gas.

$\because \quad V = \frac{RT}{P}$

$\therefore \quad \left.\frac{\partial V}{\partial T}\right|_P = \frac{R}{P} \left.\cancel{\frac{\partial T}{\partial T}}\right|_P^{\,1} = \frac{R}{P}$

Substituting in (9)

$\therefore \quad ds = \frac{C_P}{T} \cdot dT - \frac{R}{P} \cdot dP$

integrating

$$\therefore \int_{S_1}^{S_2} dS = C_p \int_{T_1}^{T_2} \frac{dT}{T} - R \int_{P_1}^{P_2} \frac{dP}{P}$$

$$\therefore S_2 - S_1 = C_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

$$\therefore \boxed{\Delta S = C_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}}$$

* for ideal gas.

Q6

Equation of state (EOS):

$$V = \frac{RT}{P} + (a + bT)$$

$$\therefore \left.\frac{\partial V}{\partial T}\right|_P = \frac{R}{P}\left.\frac{\partial T}{\partial T}\right|_P^{\,1} + \left.\frac{\partial a}{\partial T}\right|_P^{\,0} + b\left.\frac{\partial T}{\partial T}\right|_P^{\,1}$$

$$\therefore \left.\frac{\partial V}{\partial T}\right|_P = \frac{R}{P} + b$$

substituting in 9

$$\therefore \quad dS = \frac{C_p}{T}\, dT - \frac{R}{P}\, dP - b\, dP$$

integrating

$$\therefore \quad \boxed{\Delta S = C_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} - b\, \Delta P}$$