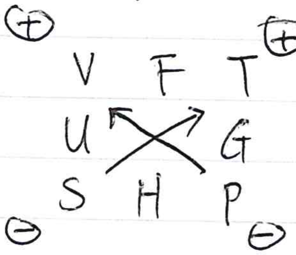
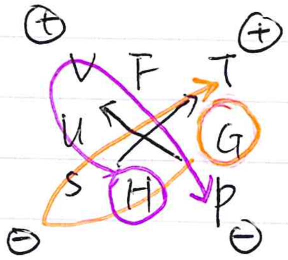
Use of Thermodynamic squares



Great Physicists Have Studied Under Very Fine Teachers

(each side has a pair of conjugate variables sandwiching a thermodynamic energy)

1) We can obtain thermodynamic energy expressions



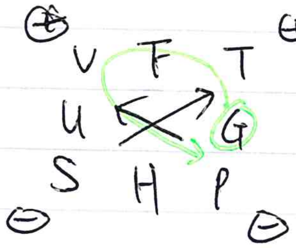
$\boxed{G = H - TS}$

$\boxed{H = U + pV}$

Similarly, we have, $U = F + TS$ and $F = G - pV$

~~or $F = U - TS$~~

we could do it ~~do~~ anticlockwise as well.



$\boxed{G = F + pV}$

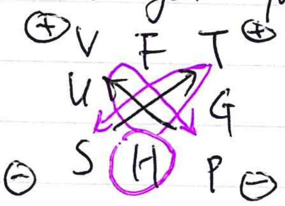
and $F = U - TS$

and $U = H - pV$

and $H = G + TS$

these are equivalent.

2) We can get fundamental equations (thermodynamic differentials)



$dH = Vdp + TdS$

$dG = -SdT + Vdp$

and similarly, $dF = -SdT - pdV$

$dU = TdS - pdV$

3) From the fundamental equations above, can get Maxwell relations.

a) Suppose we want to relate change of S to change of V, we will need these variables that are not the differentials, so that a second partial derivative of them can be taken, ie, we need,

$$dG = -SdT + Vdp$$

Then, since dG is an exact differential, we have,

$$\left[\frac{\partial(-S)}{\partial p}\right]_T = \left(\frac{\partial V}{\partial T}\right)_p \qquad \boxed{\because \ \frac{\partial^2 G}{\partial T \partial p} = \frac{\partial^2 G}{\partial p \partial T}}$$

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

b) if instead, we need to relate S and p, we need

$$dF = -SdT - pdV$$

then, we have

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

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

4) Now, Let's try to prove that the change in internal energy for an isothermal expansion for a perfect gas is zero, ie.,

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \quad \text{for perfect gases}$$

We start from

$$dU = TdS - pdV \qquad -(4.1)$$

since we want $\left(\frac{\partial U}{\partial V}\right)_T$, we need $U = U(V,T)$, therefore need to ~~change Eq. (4.1)~~ replace dS in Eq (4.1)

~~We know that any~~ We can write $S = S(V,T)$, then,

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \qquad -(4.2)$$

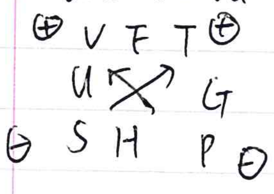
sub (4.2) into (4.1), we have

$$\begin{aligned} dU &= T\left(\frac{\partial S}{\partial T}\right)_V dT + T\left(\frac{\partial S}{\partial V}\right)_T dV - pdV \\ &= \underbrace{T\left(\frac{\partial S}{\partial T}\right)_V}_{} dT + \underbrace{\left[T\left(\frac{\partial S}{\partial V}\right)_T - p\right]}_{} dV \\ &= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \end{aligned}$$

$$\Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p \qquad (4.3)$$

Now, we need to replace $\left(\frac{\partial S}{\partial V}\right)_T$ in (4.3).

We could do this using Maxwell relation.



Since we want to relate S, and the conjugate variables used are (V,T), we need

$$dF = -SdT - pdV \Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad (4.$$

Sub. (4.4) into (4.3)

$$\Rightarrow \left(\frac{\partial u}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \qquad (4.5)$$

Now ~~I~~ for a perfect gas, equation of state is given by

$$p = \frac{nRT}{V}$$

$$\Rightarrow \left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V} \qquad (4.6)$$

Substituting (4.6) into (4.5), we arrive at

$$\left(\frac{\partial u}{\partial V}\right)_T = T\left(\frac{nR}{V}\right) - p = p - p = 0$$

//

Q.E.D.