

①. From the first law,  $du = \delta w + \delta q$ .

Consider an infinitesimal reversible process, so that  $\delta q = Tds$  and such that  $\delta w = -pdv$ .

Then,  $Tds = du + pdv$ .

Now, let  $u = u(T, p)$ . Then

$$du = \left. \frac{\partial u}{\partial T} \right|_p dT + \left. \frac{\partial u}{\partial p} \right|_T dp.$$

Hence  $Tds = \left. \frac{\partial u}{\partial T} \right|_p dT + \left. \frac{\partial u}{\partial p} \right|_T dp + pdv$ .

But we should think of  $v = v(T, p)$  also. Hence

$$dv = \left. \frac{\partial v}{\partial T} \right|_p dT + \left. \frac{\partial v}{\partial p} \right|_T dp.$$

and so

$$Tds = \left. \frac{\partial u}{\partial T} \right|_p dT + \left. \frac{\partial u}{\partial p} \right|_T dp + p \left[ \left. \frac{\partial v}{\partial T} \right|_p dT + \left. \frac{\partial v}{\partial p} \right|_T dp \right]$$

$$Tds = \left[ \left. \frac{\partial u}{\partial T} \right|_p + p \left. \frac{\partial v}{\partial T} \right|_p \right] dT + \left[ \left. \frac{\partial u}{\partial p} \right|_T + p \left. \frac{\partial v}{\partial p} \right|_T \right] dp \quad (*)$$

Notice that  $\delta q = Tds$

and that  $\delta q|_p \equiv C_p dT$ . So, setting  $dp = 0$  in the above expression,

$$C_p = \left. \frac{\partial u}{\partial T} \right|_p + p \left. \frac{\partial v}{\partial T} \right|_p \quad (1)$$

Also notice that (\*) is

$$dS = \frac{1}{T} \left[ \left. \frac{\partial u}{\partial T} \right|_P + P \left. \frac{\partial V}{\partial T} \right|_P \right] dT + \frac{1}{T} \left[ \left. \frac{\partial u}{\partial P} \right|_T + P \left. \frac{\partial V}{\partial P} \right|_T \right] dP.$$

Since  $dS$  is an exact differential,

$$\frac{\partial}{\partial P} \left\{ \frac{1}{T} \left[ \left. \frac{\partial u}{\partial T} \right|_P + P \left. \frac{\partial V}{\partial T} \right|_P \right] \right\}_T = \frac{\partial}{\partial T} \left\{ \frac{1}{T} \underbrace{\left[ \left. \frac{\partial u}{\partial P} \right|_T + P \left. \frac{\partial V}{\partial P} \right|_T \right]}_{[*]} \right\}_P$$

use this to solve for a nice expression for [\*].

After a fair amount of manipulation, one obtains

$$[*] = \left. \frac{\partial u}{\partial P} \right|_T + P \left. \frac{\partial V}{\partial P} \right|_T = -T \left. \frac{\partial V}{\partial T} \right|_P. \quad (2)$$

So, finally, combine (1) and (2) with (\*):

$$dS = C_p dT - T \left. \frac{\partial V}{\partial T} \right|_P dP.$$

②. An easier way:

$$\text{First, } \delta Q|_p \equiv C_p dT$$

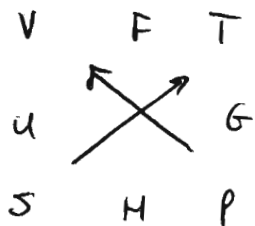
$$T dS|_p = C_p dT \quad \rightarrow \quad C_p = T \left. \frac{\partial S}{\partial T} \right|_p.$$

So, with  $S = S(T, p)$ ,

$$dS = \left. \frac{\partial S}{\partial T} \right|_p dT + \left. \frac{\partial S}{\partial p} \right|_T dp$$

$$dS = \frac{C_p}{T} dT + \left( \left. \frac{\partial S}{\partial p} \right|_T \right) dp.$$

From the Maxwell chart, you can read off:



$$\left. \frac{\partial S}{\partial p} \right|_T = - \left. \frac{\partial V}{\partial T} \right|_p$$

Hence

$$T dS = C_p dT - T \left. \frac{\partial V}{\partial T} \right|_p dp.$$