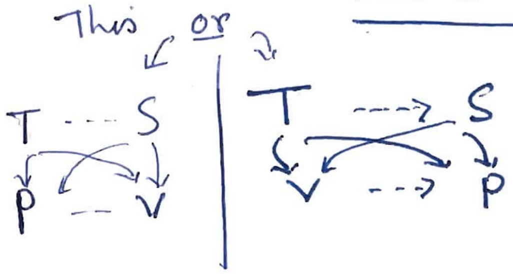
How to remember Maxwell's relations



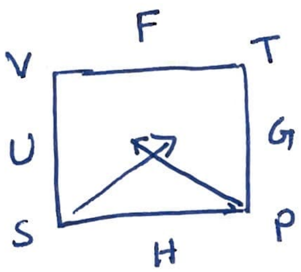
$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

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

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

Four Maxwell's relation.



T-ds equations:

I $S = S(T, V)$

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

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_V dT + T\left(\frac{\partial S}{\partial V}\right)_T dV$$

Since $TdS = dq$ for a reversible isochoric (i.e., const. Volume) process,

$$\therefore\ T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{dq}{dT}\right)_V = C_V$$

Also from Maxwell's relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

$$\therefore\ \boxed{TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV}$$

First T-dS equation.

II $S = S(T, P)$

$$\boxed{\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P}$$ Maxwell's relation

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP$$

$$\boxed{TdS = C_P dT - T\left(\frac{\partial T}{\partial V}\right)_P dP}$$

Second T-dS equation.

Applications of T-ds equations.

1st T-ds equations: $TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$

Q. 1 mole of a van der Waals gas undergoes a reversible iso-thermal expansion from an initial molar volume v_i to final molar volume v_f. How much heat has been transferred?

$\cdot$ T = const.

$$Tds = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dv$$

For vdW gas : $P = \frac{RT}{v-b} - \frac{a}{v^2}$

$$\therefore \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{v-b}$$

$$\therefore Tds = \frac{RT}{v-b} dv$$

$$\therefore dq = Tds = \frac{RT}{v-b} dv$$

$$\therefore q = \int_{v_i}^{v_f} \frac{RT}{v-b} dv = RT \ln\left(\frac{v_f - b}{v_i - b}\right)$$

2nd T-ds equation : $Tds = C_p dT - T\left(\frac{\partial V}{\partial T}\right)_p dp$

Q. What is the heat transferred in reversible iso-thermal change in pressure?

T = const.

$$\therefore dq = Tds = -T\left(\frac{\partial V}{\partial T}\right)_P dp$$

$$\therefore q = -\int T\left(\frac{\partial V}{\partial T}\right)_p dp$$

$$= -T\int_{P_i}^{P_f} V\alpha \, dp$$

$$= -TV\alpha[P_f - P_i]$$

$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

Change in V is assumed to be negligible and hence constant.

Internal energy equations

Change in internal energy in an reversible process:

$$du = Tds - Pdv \;; \Rightarrow \text{Divide this equation by } \cancel{dp}\ dv$$

$$\therefore \frac{du}{dv} = T\frac{ds}{dv} - P$$

$$\therefore \left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial s}{\partial v}\right)_T - P \Leftarrow$$

If T remains constant, then total derivative becomes partial derivative.

Using Maxwell's relation:

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$$

$$\boxed{\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v - P}$$

First internal-energy relation.

$$du = Tds - Pdv \;; \Rightarrow \text{Divide this equation by } dP$$

$$\therefore \frac{du}{dP} = T\frac{ds}{dP} - P\frac{dv}{dP}$$

$$\left(\frac{\partial u}{\partial P}\right)_T = T\left(\frac{\partial s}{\partial P}\right)_T - P\left(\frac{\partial v}{\partial P}\right)_T \Leftarrow$$

If T remains constant, then total derivative becomes partial derivative.

Utilizing Maxwell's relation:

$$\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P$$

$$\boxed{\left(\frac{\partial u}{\partial P}\right)_T = -T\left(\frac{\partial v}{\partial T}\right)_P - P\left(\frac{\partial v}{\partial P}\right)_T}$$

Second internal-energy relation.

Heat-capacity equations.

1st Tds equation: $Tds = C_v dT + T\left(\frac{\partial P}{\partial T}\right)_v dv$

2nd T-ds equation: $Tds = C_p dT - T\left(\frac{\partial v}{\partial T}\right)_P dP$

$$\therefore C_v dT + T\left(\frac{\partial P}{\partial T}\right)_v dv = C_p dT - T\left(\frac{\partial v}{\partial T}\right)_P dP$$

$$\Rightarrow dT = \frac{T\left(\frac{\partial P}{\partial T}\right)_v}{C_p - C_v} dv + \frac{T\left(\frac{\partial v}{\partial T}\right)_P}{C_p - C_v} dP$$

We know that $T = T(v, P)$

$$\therefore dT = \left(\frac{\partial T}{\partial v}\right)_P dv + \left(\frac{\partial T}{\partial P}\right)_v dP$$

$$\therefore \left(\frac{\partial T}{\partial v}\right)_P = \frac{T\left(\frac{\partial P}{\partial T}\right)_v}{C_p - C_v}$$

We know that if $f(P, v, T) = 0$ then

$$\left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_v = -1$$

$$\therefore \left(\frac{\partial P}{\partial T}\right)_v = -\left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P$$

$$\Rightarrow C_p - C_v = T\left(\frac{\partial v}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_v$$

$$= -T\left(\frac{\partial v}{\partial T}\right)_P \left(\frac{\partial v}{\partial T}\right)_P \left(\frac{\partial P}{\partial v}\right)_T$$

$$= -T\left(\frac{\partial v}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial v}\right)_T$$

- Since $\left(\frac{\partial P}{\partial V}\right)_T$ is almost always negative for all known materials, and $\left(\frac{\partial V}{\partial T}\right)_P^2$ is positive for <u>most</u> materials, $C_P - C_V \geq 0$

- As $T \to 0$, $C_P = C_V$