Table 3.5 The Maxwell relations

From U:	$\left(\dfrac{\partial T}{\partial V}\right)_S = -\left(\dfrac{\partial p}{\partial S}\right)_V$
From H:	$\left(\dfrac{\partial T}{\partial p}\right)_S = \left(\dfrac{\partial V}{\partial S}\right)_p$
From $\cancel{A}$ F:	$\left(\dfrac{\partial p}{\partial T}\right)_V = \left(\dfrac{\partial S}{\partial V}\right)_T$
From G:	$\left(\dfrac{\partial V}{\partial T}\right)_p = -\left(\dfrac{\partial S}{\partial p}\right)_T$

Table 3-5
Atkins Physical Chemistry, Eighth Edition

Tds equations

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

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

Consider reversible isochoric change

$TdS = (đQ)_{V=\text{const}}$ $\quad T\left(\frac{\partial S}{\partial T}\right)_V = C_V$.

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

; Maxwell's reln

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

→ 1st TdS eqn.

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

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

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

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

$\hookrightarrow$ 2nd TdS eqn.

Internal Energy eqn.s

$$dU = TdS - pdV$$

$$\frac{dU}{dP} = T\frac{dS}{dP} - p\frac{dV}{dP}.$$

Holding T const

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

Maxwell

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

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

$\longrightarrow$ 2nd internal energy identity

$$dU = T\,dS - p\,dV$$

$$\frac{dU}{dV} = T\frac{\partial S}{dV} - P$$

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

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

Maxwell

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

Heat Capacity Equation

$$T\,dS = C_p\,dT - T\left(\frac{\partial V}{\partial T}\right)_P dP \quad \text{— (1)}$$

$$T\,dS = C_v\,dT + T\left(\frac{\partial P}{\partial T}\right)_V dV \quad \text{— (2)}$$

Equating (1) & (2)

$$C_p\,dT - T\left(\frac{\partial V}{\partial T}\right)_P dP = C_v\,dT + T\left(\frac{\partial P}{\partial T}\right)_V dV.$$

$$dT = \frac{T\left(\frac{\partial P}{\partial T}\right)_V dV}{C_p - C_v} + \frac{T\left(\frac{\partial V}{\partial T}\right)_P}{C_p - C_v} dP \quad \text{— (3)}$$

But

$$dT = \left(\frac{\partial T}{\partial V}\right)_P dT + \left(\frac{\partial T}{\partial P}\right)_V dT \quad \text{— (4)}$$

$$\Rightarrow \left(\frac{\partial T}{\partial V}\right)_P = \frac{T\left(\frac{\partial P}{\partial T}\right)_V}{C_p - C_V} \quad ; \quad \left(\frac{\partial T}{\partial P}\right)_V = \frac{T\left(\frac{\partial V}{\partial T}\right)_P}{C_p - C_v}.$$

$$\boxed{C_p - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P}$$

But $\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T \longrightarrow$ chain rule

$$\boxed{C_p - C_V = -T\left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T}$$

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

- $\left(\frac{\partial P}{\partial V}\right)_T < 0$ for all known substances.

$\left(\frac{\partial V}{\partial T}\right)^2 > 0$ $\quad \therefore \boxed{C_p - C_v > 0}$

- $T \to 0$ $\quad C_p \to C_v$ $\quad$ at absolute zero $C_p = C_v$

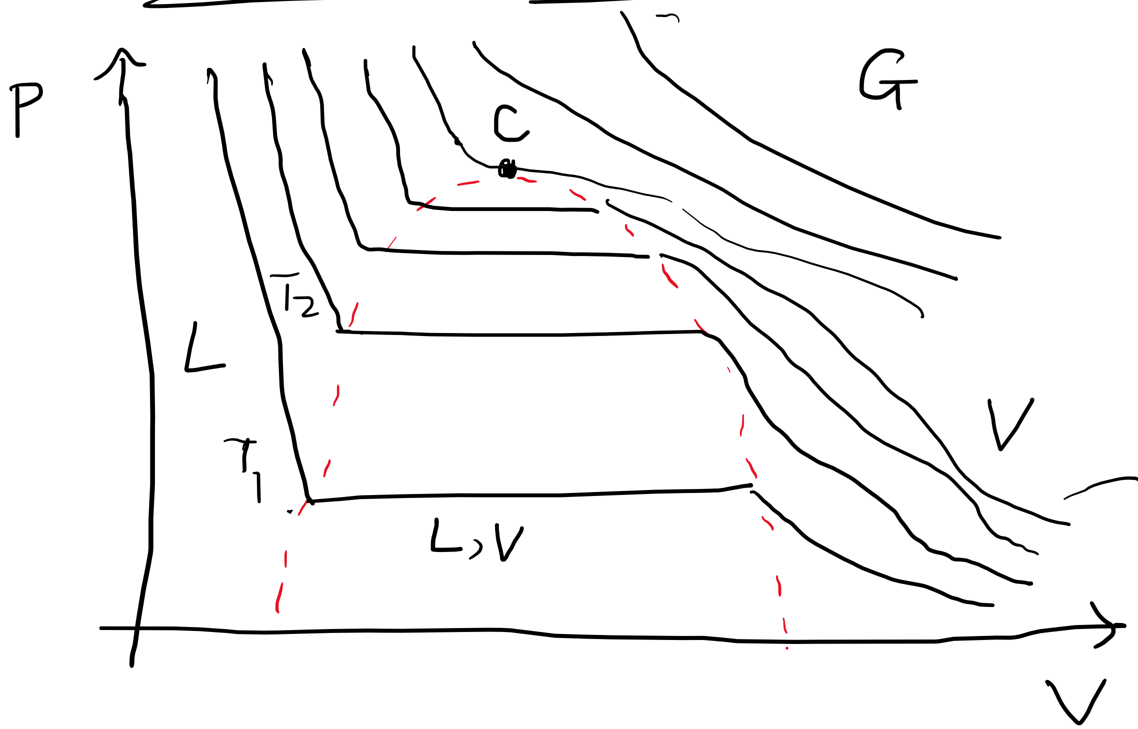
- $C_p = C_v$ when $\left(\frac{\partial V}{\partial T}\right)_P = 0$ at $4^\circ C$ ρ_w max

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

$$\boxed{C_p - C_v = \frac{T v \beta^2}{\kappa}}$$

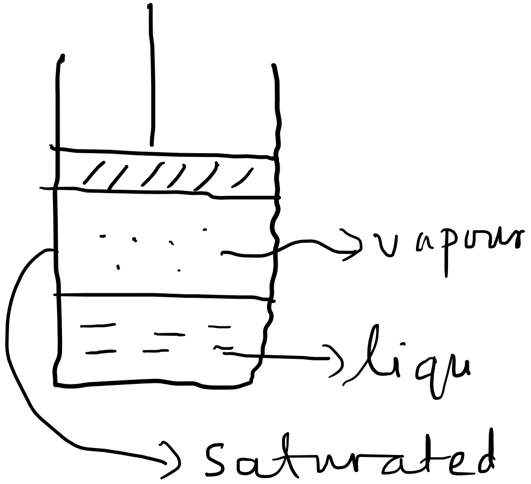
v : specific volume.

Gibbs potential application



at C
T_c, P_c, V_c

isotherms



Saturated vapour in equilibrium with liquid.

We will focus on flat region

$$m = m_1 + m_2$$

1 subscript liq.
2 " vapour

$$V = m_1 v_1(T) + m_2 v_2(T)$$ v : specific volume.

$$U = m_1 u_1(T) + m_2 u_2(T).$$

$$\left.\begin{aligned} U &= U_1 + U_2 \\ S &= S_1 + S_2 \\ V &= V_1 + V_2 \end{aligned}\right\} \rightarrow$$

$$G = U - TS + PV$$

T, P const region

$$G = G_1 + G_2.$$

$$\left.\begin{aligned} G_1 &= m_1 g_1 \\ G_2 &= m_2 g_2. \end{aligned}\right\}$$

P, T const

m_1, m_2 can vary.

$$m_1 \rightarrow m + dm$$

$$m_2 \rightarrow m - dm$$

$$(m_1 + dm)\, g_1 + (m_2 - dm)\, g_2 = G + dG$$

$$dG = dm(g_1 - g_2)$$ In equilibrium

$$\Rightarrow dG = 0 \Rightarrow \boxed{g_1 = g_2}$$

$$u_1 - Ts_1 + Pv_1 = u_2 - Ts_2 + Pv_2$$

$$(u_2 - u_1) - T(s_2 - s_1) + p(v_2 - v_1) = 0$$

$$\frac{d}{dT}(u_2 - u_1) - T\frac{d}{dT}(s_2 - s_1) - (s_2 - s_1) + \frac{dp}{dT}(v_2 - v_1)$$

$$+ p\frac{d}{dT}(v_2 - v_1) = 0$$

But 1st Law

$$T\frac{dS}{dT} = \frac{du}{dT} + P\frac{dV}{dT}.$$

$$\frac{d}{dT}(u_2-u_1) - T\frac{d}{dT}(s_2-s_1) - (s_2-s_1) + \frac{dp}{dT}(v_2-v_1) + P\frac{d}{dT}(v_2-v_1) = 0$$

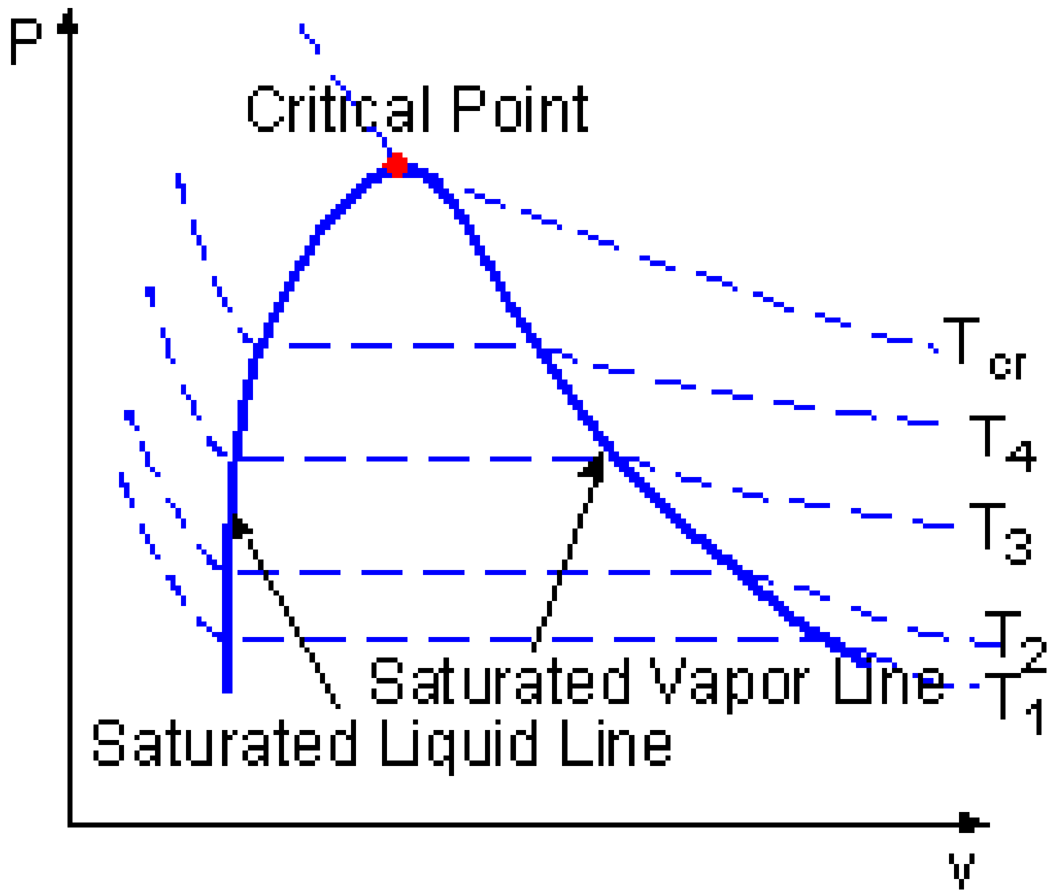
$$-(s_2-s_1) + \frac{dp}{dT}(v_2-v_1) = 0$$

; But $(s_2-s_1) = \frac{\lambda}{T}$

latent heat.

$$\boxed{\left(\frac{dP}{dT}\right) = \frac{\lambda}{T(v_2-v_1)}}$$

Clausius-Clapeyron eqn.


P
Critical Point
Tcr
T4
T3
T2
T1
Saturated Vapor Line
Saturated Liquid Line
v