Maxwell & other TD Relations, Clapeyron Equation

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Previously: What is controlled in experiments determines the relevant TD extremum fxn

$- TS$ →

+PV ↓

U (or E)	A (or F) $= U - TS$
H $= U + PV$	G $= U + PV - TS$

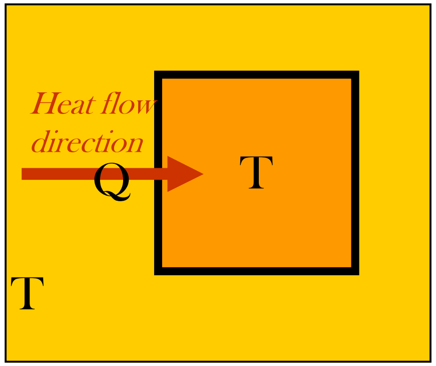
	Constant V	Constant P
Constant S	U	H
Constant T	F	G

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dA = -SdT - PdV$$

$$dG = -SdT + VdP$$



$$\Delta S - \frac{Q_{rev}}{T} \geq 0$$

$$\Delta A = \Delta U - (T\Delta S) \leq 0$$

- **δS (U,V,N)≥ 0; δU (S,V,N) ≤ 0; δH (S,P,N) ≤ 0;**
- **δA (T,V,N) ≤ 0; δG (T,P,N) ≤ 0;**

Maxwell Relations

$$du = T\,ds - P\,dv$$

$$dh = T\,ds + v\,dP$$

$$da = -s\,dT - P\,dv$$

$$dg = -s\,dT + v\,dP$$

$$dz = M\,dx + N\,dy$$

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

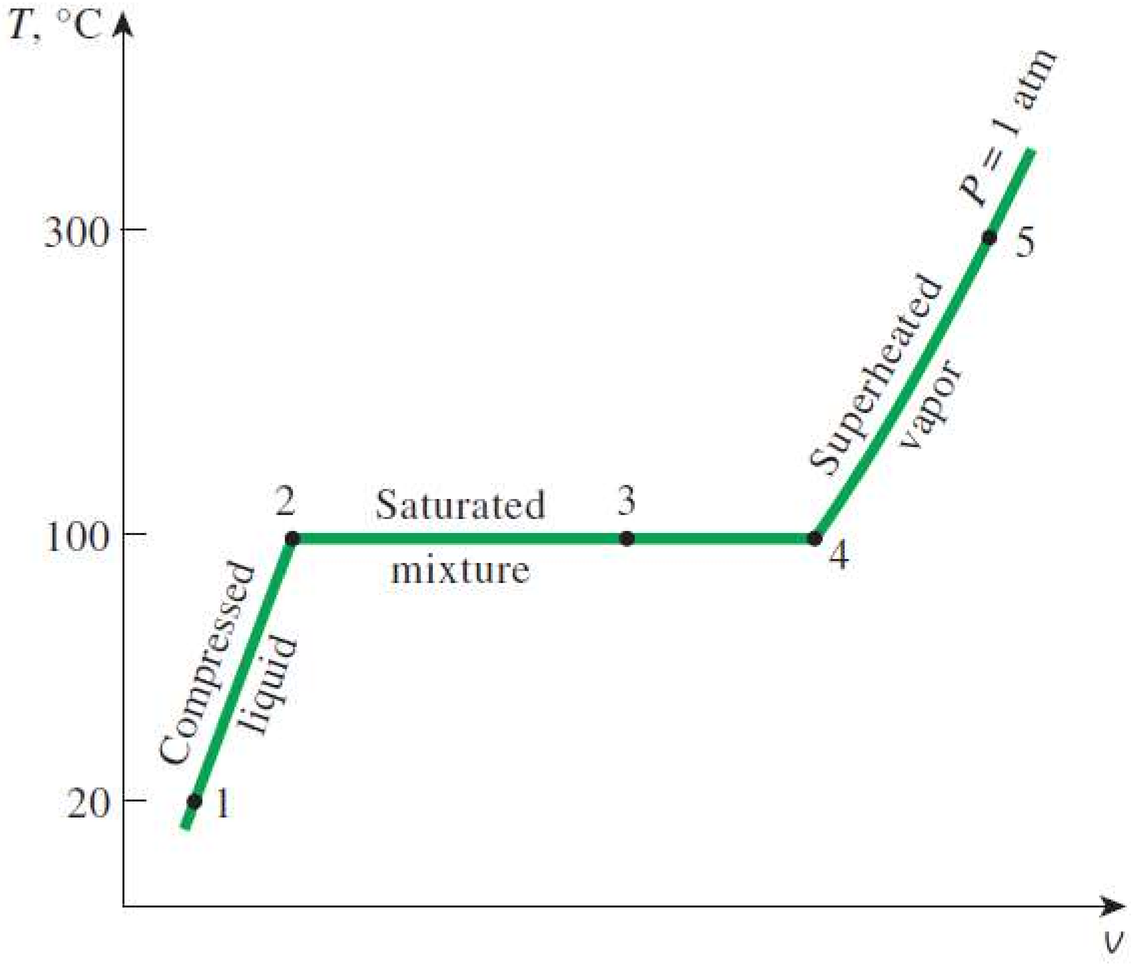
$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v$$

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

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

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

Liquid-Vapor Transition & Clapeyron equation



$$dh = Tds + vdp$$

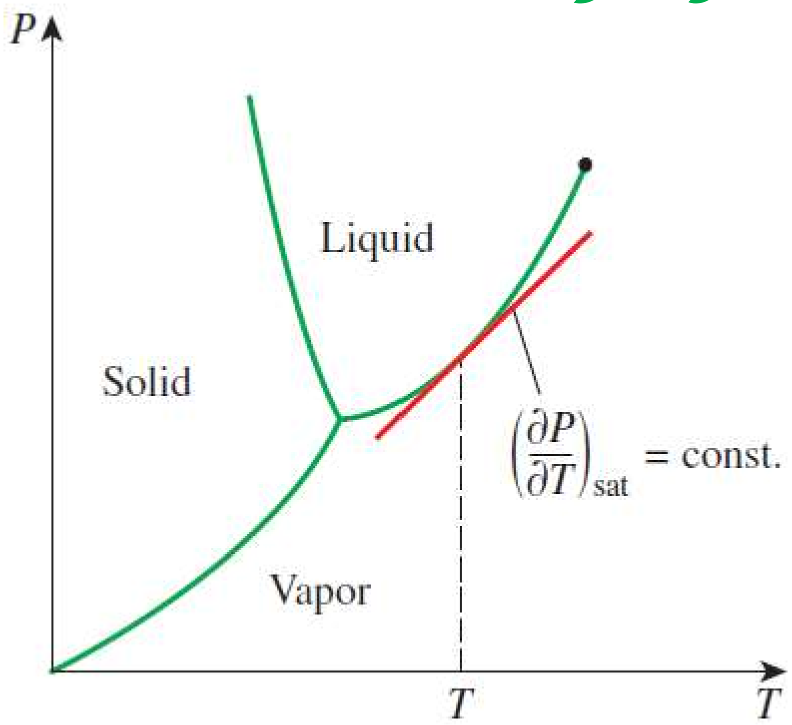
$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T$$

$$s_g - s_f = \left(\frac{dp}{dT}\right)_{sat}\left(v_g - v_f\right)$$

$$\left(\frac{dp}{dT}\right)_{sat} = \frac{h_g - h_f}{T\left(v_g - v_f\right)}$$

Figs: TD-Cengel & Boles; Moran, Shapiro, Boettner & Bailey

Clausius-Clapeyron equation & ideal gas



$$\left(\frac{dp}{dT}\right)_{sat} = \frac{h_g - h_f}{T\left(v_g - v_f\right)}$$

For an Ideal Gas, where $v_g >> v_f$, and $p << p_c$ such that $v_g = RT/p$:

$$\left(\frac{d\ln p}{dT}\right)_{sat} = \frac{h_g - h_f}{RT^2}$$

$$\ln\left(\frac{P_2}{P_1}\right)_{sat} \cong \frac{h_{fg}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)_{sat}$$

Figs: TD-Cengel & Boles; Moran, Shapiro, Boettner & Bailey

ΔU *in the single-phase regions*

$$du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv$$

$$du = c_v\, dT + \left(\frac{\partial u}{\partial v}\right)_T dv$$

$$du = T\, ds - P\, dv$$

$$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv$$

$$du = T\left(\frac{\partial s}{\partial T}\right)_v dT + \left[T\left(\frac{\partial s}{\partial v}\right)_T - P\right] dv$$

$$\left(\frac{\partial s}{\partial T}\right)_v = \frac{c_v}{T}$$

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

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

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

$$du = c_v\, dT + \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right] dv$$

$$u_2 - u_1 = \int_{T_1}^{T_2} c_v\, dT + \int_{v_1}^{v_2} \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right] dv$$

ΔH *in the single-phase regions*

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

$$dh = c_p\, dT + \left(\frac{\partial h}{\partial P}\right)_T dP$$

$$dh = T\, ds + v\, dP$$

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

$$dh = T\left(\frac{\partial s}{\partial T}\right)_P dT + \left[v + T\left(\frac{\partial s}{\partial P}\right)_T\right] dP$$

$$\left(\frac{\partial s}{\partial T}\right)_P = \frac{c_p}{T}$$

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

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

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

$$dh = c_p\, dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right] dP$$

$$h_2 - h_1 = \int_{T_1}^{T_2} c_p\, dT + \int_{P_1}^{P_2} \left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right] dP$$

$$h_2 - h_1 = u_2 - u_1 + (P_2 v_2 - P_1 v_1)$$

Δs *in the single-phase regions*

$$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv$$

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

$$ds = \frac{c_v}{T} dT + \left(\frac{\partial P}{\partial T}\right)_v dv$$

$$s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_v}{T} dT + \int_{v_1}^{v_2} \left(\frac{\partial P}{\partial T}\right)_v dv$$

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

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

$$ds = \frac{c_P}{T} dT - \left(\frac{\partial v}{\partial T}\right)_P dP$$

$$s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_p}{T} dT - \int_{P_1}^{P_2} \left(\frac{\partial v}{\partial T}\right)_P dP$$

Specific heat relationships

$$ds = \frac{c_v}{T}\,dT + \left(\frac{\partial P}{\partial T}\right)_v dv$$

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

$$ds = \frac{c_p}{T}\,dT - \left(\frac{\partial v}{\partial T}\right)_P dP$$

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

$$(c_p - c_{p0})_T = -T\int_0^P \left(\frac{\partial^2 v}{\partial T^2}\right)_P dP$$

$$dT = \frac{T(\partial P/\partial T)_v}{c_p - c_v}\,dv + \frac{T(\partial v/\partial T)_P}{c_p - c_v}\,dP$$

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

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

Specific heat relationships-2

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

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

$$\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P$$

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

$$c_p - c_v = \frac{vT\beta^2}{\alpha}$$

What's next?

- Joule-Thompson coefficient & relationships for real gases