QUIZ 4 :

$\underline{S}, P, N \longrightarrow H(\cancel{T}, P, N)$

$H(S, P, N)$

$$H = U - (-pV)$$

$$dH = T\,dS + V\,dp + \mu\,dN$$

CHANGES IN $\Delta S, \Delta V$, WITH N CONSTANT

$$\Delta U = \underbrace{\frac{\partial^2 U}{\partial S^2}\bigg|_{V,N,X}}_{a} \Delta S^2 + 2 \underbrace{\frac{\partial^2 U}{\partial S \partial V}\bigg|_{N,X}}_{\frac{b}{2}} \Delta S \Delta V + \underbrace{\frac{\partial^2 U}{\partial V^2}\bigg|_{S,N,X}}_{c} \Delta V^2 \geq 0$$

X : ANY OTHER EXTENSIVE STATE VARIABLE

$$\frac{1}{\Delta V^2} \qquad x = \frac{\Delta S}{\Delta V}$$

$$\Delta U = a x^2 + b x + C$$

CONSERVATION OF ENERGY : ΔU IS UNIQUE $\Rightarrow$ ax^2+bx+c CAN'T HAVE 2 SOLUTIONS

$$\Rightarrow b^2 \leq 4ac$$

$$\left(\frac{\partial^2 U}{\partial S \partial V}\bigg|_{N,X}\right)^2 \leq \frac{\partial^2 U}{\partial S^2}\bigg|_{V,N,X} \cdot \frac{\partial^2 U}{\partial V^2}\bigg|_{S,N,X}$$

$$\left(\frac{\partial T}{\partial V}\bigg|_{N,X}\right)^2 \qquad = \frac{T}{C_V} \qquad = \frac{1}{V \kappa_S}$$

$T(S(V))$

$$\to -\underbrace{\frac{\partial T}{\partial S}\bigg|_{V,N,X}}_{=\frac{T}{C_V}} \cdot \frac{\partial S}{\partial V}\bigg|_{T,N,X}$$

$\hookrightarrow$ MAXWELL $= \frac{\partial P}{\partial T}\bigg|_{V,N,X}$

$P(V(T))$

$$\to \frac{\partial P}{\partial T}\bigg|_{V,N,X} = \frac{\partial P}{\partial V}\bigg|_{T,N,X} \frac{\partial V}{\partial T}\bigg|_{P,N,X} = \frac{-1}{V\kappa_T} V \cdot \alpha$$

$$\left(\frac{T}{C_V}\frac{\alpha}{\kappa_T}\right)^2 \leq \frac{T}{C_V}\frac{1}{V\kappa_S}$$

$$\frac{V\alpha^2 T}{\kappa_T^2} \leq \frac{C_V}{\kappa_S}$$

USE

$$C_P - C_V = \frac{VT\alpha^2}{\kappa_T}$$

$$\frac{C_V}{\kappa_S} \geq \frac{C_P - C_V}{\kappa_T}$$

$$\kappa_T \geq 0$$

USE

$$\frac{C_P}{C_V} = \frac{\kappa_T}{\kappa_S}$$

$$C_V\frac{\kappa_T}{\kappa_S} \geq C_P - C_V$$

$$C_P \geq C_P - C_V$$

$$C_V \geq 0$$

$$C_P \geq C_V \geq 0$$

$$\kappa_T \geq \kappa_S \geq 0$$

GIBBS PHASE RULE

K, c DIFFERENT COMPONENTS (MOLECULES)

ϕ, φ DISTINCT PHASES IN EQUILIBRIUM WITH EACH OTHER (gas, liquid, solid)

VARIABLES TO DESCRIBE SYSTEM

$T, P = 2$ $\qquad$ $N+1$ for N WAYS TO DO WORK

FOR EACH PHASE

$$\frac{N_c^\varphi}{N^\varphi} = x_c^\varphi$$ CONCENTRATION OF EACH COMPONENT IN EACH PHASE

$$\sum_{c=1}^{K} x_c^\varphi = 1 \rightarrow K-1$$ INDEPENDENT CONCENTRATIONS

TOTAL NUMBER OF VARIABLES

$$2+\phi(K-1) \qquad N-1+\phi(K-1)$$

CONSTRAINTS

$$\mu_c^1 = \mu_c^2 = \dots = \mu_c^\phi \qquad \phi-1 \text{ IND EQUATIONS}$$

K components $\rightarrow K(\phi-1)$ CONSTRAINTS

NUMBER OF INDEPENDENT VARIABLES (DEGREES OF FREEDOM) f

$$f = \text{VARIABLES} - \text{CONSTRAINTS}$$

$$= 2 + \phi(k-1) - k(\phi-1)$$

$$f = 2 + k - \phi$$

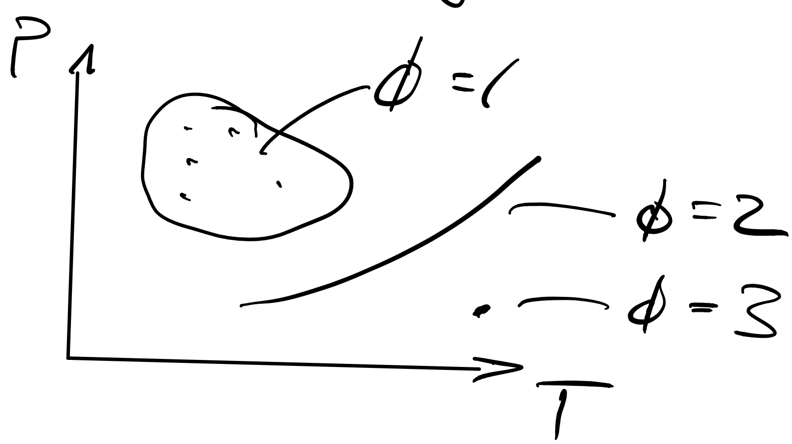
N WAYS OF WORK: $f = N + k + 1 - \phi$

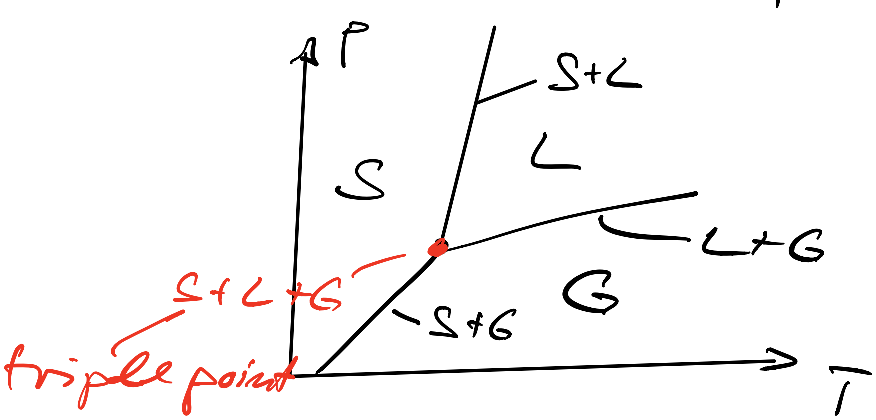
EXAMPLE: $k = 1$

$\to \phi = 1 \quad f = 2$

$\phi = 2 \quad f = 1$

$\phi = 3 \quad f = 0$





PHASE TRANSITIONS

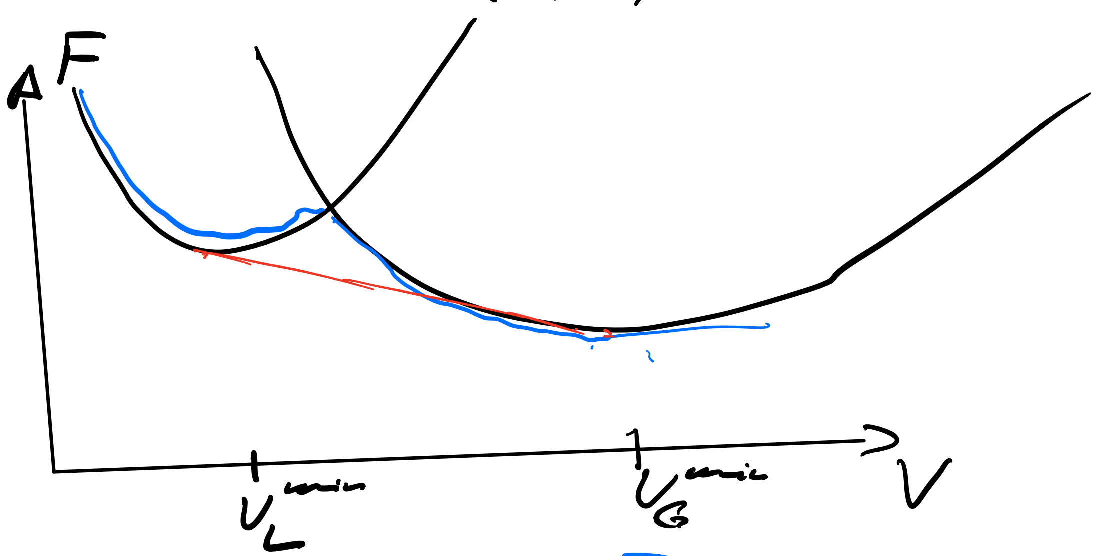
READ EOPC 11.1

2 TYPES:

- ABRUPT: DISCONTINUITIES IN MOST PHYSICAL PROPERTIES
- CONTINUOUS: ALL OTHER

CONSIDER 2 PHASES AS FUNCTION OF V (T, N fixed)

→ LOOK AT $F(T, V, N)$



– choose min F

CONSIDER LIQUID–GAS MIXTURE

$$V = \lambda V_g^{min} + (1-\lambda) V_L^{min}$$

$$F_{mix} = \lambda F_g + (1-\lambda) F_L$$

$$F_{mix} \leq F_{min}^{simple}$$

$$P_{mix} = -\left.\frac{\partial F}{\partial V}\right|_{T,N} = \text{CONST}$$