

01-1

(a) Law of corresponding states

→ There exist atleast semi-quantitatively a universal equation of state, containing no arbitrary constant, if expressed in terms of reduced variables

$$P_r = \frac{P}{P_c} ; T_r = \frac{T}{T_c} \text{ \& } V_r = \frac{V}{V_c} .$$

This law is known as law of corresponding state. (2)

(b)

(i) stability criterion in Helmholtz free energy representation.

$$\left(\frac{\partial^2 A}{\partial V^2} \right)_T \geq 0$$

$$\Rightarrow \left(\frac{\partial}{\partial V} \left(\frac{\partial A}{\partial V} \right)_T \right)_T \geq 0$$

$$\Rightarrow \left(\frac{\partial}{\partial V} (-P) \right)_T \geq 0$$

$$\Rightarrow - \left(\frac{\partial P}{\partial V} \right)_T \geq 0$$

$$- \frac{1}{\left(\frac{\partial V}{\partial P} \right)_T} \geq 0$$

$$\frac{-1}{-\chi_{KT}} \geq 0$$

$$\Rightarrow \frac{1}{V K_T} \geq 0$$

$$V > 0$$

$$\Rightarrow \boxed{K_T \geq 0} \quad (\text{for stability})$$

(3)

(ii) stability criterion in entropy representation

$$\left(\frac{\partial^2 S}{\partial U^2} \right)_{V,N} \leq 0$$

$$\left(\frac{\partial}{\partial U} \left(\frac{\partial S}{\partial U} \right)_{V,N} \right)_{V,N} \leq 0$$

$$\left(\frac{\partial}{\partial U} \left(\frac{1}{T} \right) \right)_{V,N} \leq 0$$

$$-\frac{1}{T^2} \left(\frac{\partial T}{\partial U} \right)_{V,N} \leq 0$$

$$= \frac{1}{T^2 \left(\frac{\partial U}{\partial T} \right)_{V,N}} \leq 0$$

$$= \frac{1}{N T^2 C_V} \leq 0$$

$$N > 0, T > 0$$

(3)

$$\Rightarrow \boxed{C_V \geq 0} \quad (\text{for stability})$$

(c) Gibb's phase rule

consider a system with.

Number of components = r

Number of phases = m

Then for the ' r ' components, there will be

$r+2$ independent extensive variables
& $r+1$ independent intensive variables

So, for total m phases

Total number of independent intensive variables = $2 + m(r-1)$

at equilibrium,

$$\mu_{1,1} = \mu_{1,2} = \dots = \mu_{1,m} \quad (\text{for component 1})$$

The above relationship for 1 component & ' m ' phases will give $(m-1)$ equations.

Now, for ' r ' components

$$\text{Total number of equations} = r(m-1)$$

Now, Degree of freedom (F) = $\frac{\text{Total number of independent intensive variables}}{\text{Total number of independent equations}}$

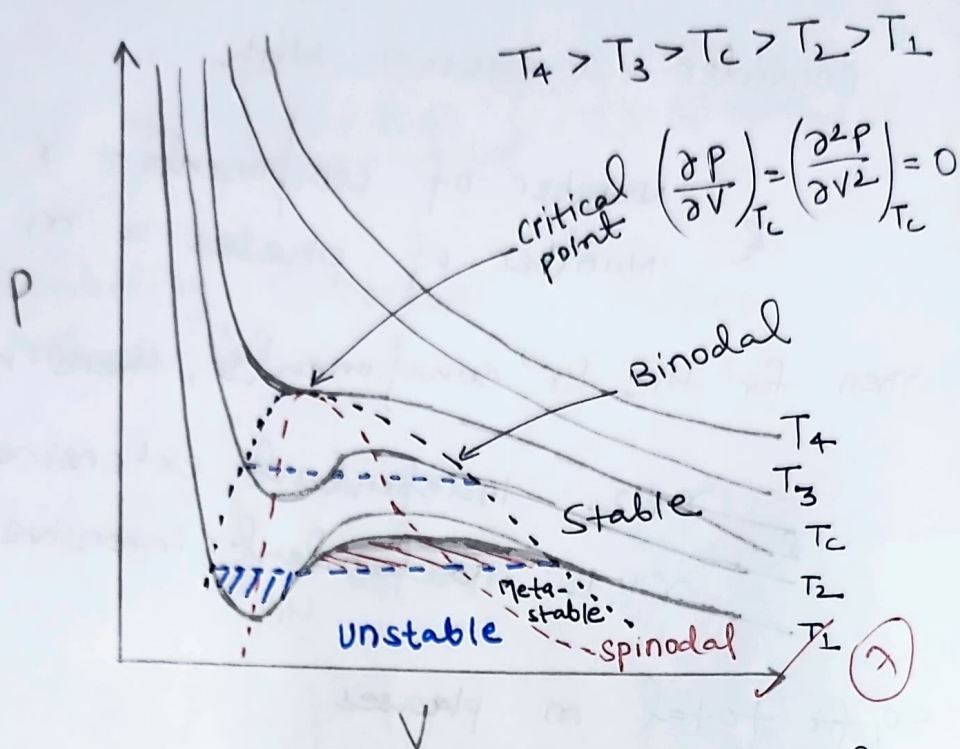
(6)

$$= 2 + m(r-1) - r(m-1)$$

$$\boxed{F = r - m + 2} \quad \left\{ \begin{array}{l} \text{Gibb's phase} \\ \text{Rule} \end{array} \right\}$$

(d)

(ii)



(iii) Thermodynamic characteristics of critical point in terms of Helmholtz Free energy, pressure, Volume, temperature & their derivatives/

At critical point

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0$$

Since,

$$\left(\frac{\partial A}{\partial V}\right)_{T_c} = -P$$

$$\left(\frac{\partial^3 A}{\partial V^3}\right)_{T_c} = -\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0$$

The stability criteria is,

$$dA = 0$$

$$d^2A \geq 0$$

$$\text{if } d^2A = 0$$

$$d^3A \geq 0$$

$$\text{if } d^3A = 0$$

$$d^4A \geq 0$$

Since,

$$\left(\frac{d^3 A}{dv^3} \right)_{T_c} = 0 ;$$

since,

$$A = A(T, v)$$

on an isotherm,

$$d^3 A = \left(\frac{\partial^3 A}{\partial v^3} \right)_{T_c} (dv)^3 = 0$$

Therefore for critical point to be stable,

$$\boxed{d^4 A \geq 0}$$

However, since

$$d^4 A = \left(\frac{\partial^4 A}{\partial v^4} \right)_{T_c} (dv)^4 \quad \left(\text{constant } T \right)$$

$$\boxed{\frac{\partial^4 A}{\partial v^4} \geq 0}$$

$$\Rightarrow - \left(\frac{\partial^3 P}{\partial v^3} \right)_{T_c} \geq 0$$

$$\Rightarrow \cancel{\left(\frac{\partial^3 P}{\partial v^3} \right)_{T_c} \leq 0}$$

$$\boxed{\left(\frac{\partial^3 P}{\partial v^3} \right)_{T_c} \leq 0}$$

(on critical point)

④

2) Given,

$$\xi = \left(\frac{\partial T}{\partial V} \right)_U$$

→ Rewriting in Jacobian representation,

$$\left(\frac{\partial T}{\partial V} \right)_U = \frac{[T, U]}{[V, U]} = - \frac{[U, T]}{[U, V]}$$

$$\therefore \frac{[T, U]}{[V, U]} = \frac{T[S, T] - P[V, T]}{T[S, V] - P[V, V]}$$

$$= \frac{[S, T]}{[S, V]} - \frac{P}{T} \frac{[V, T]}{[S, V]}$$

$$\left\{ \because [V, V] = 0 \right\}$$

$$= \frac{[T, S]}{[V, S]} + \frac{P}{T} \frac{[T, V]}{[S, V]} \Rightarrow$$

→ Using, Maxwell relationship

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

$$\therefore \frac{[T, V]}{[V, V]} = - \frac{[P, V]}{[S, V]} + \frac{P}{T} \left(\frac{[T, V]}{[S, V]} \right)$$

$$\left\{ \because C_V = T \frac{[S, V]}{[T, V]} \right\}$$

$$= \frac{[V, P]}{C_V [T, V]} + \frac{P}{T}$$

$$= \frac{1}{C_V} \left\{ - \frac{[V, P] \cdot T}{[V, T]} + P \right\}$$

$$\xi = \frac{1}{C_V} \left\{ \frac{-T\alpha}{k_T} + P \right\}$$

$$\left\{ \therefore \frac{\alpha}{k_T} = \frac{[V, P]}{[V, T]} \right\}$$

As we know;

$$C_V = C_P - \frac{V\alpha^2 T}{k_T}$$

$$\xi = \frac{1}{\left(C_P - \frac{V\alpha^2 T}{k_T} \right)} \left[P - \frac{\alpha T}{k_T} \right] \rightarrow \textcircled{3}$$

(3) For van der Waals gas,

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad \text{--- (1)}$$

$$(i) \quad K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad \text{--- (2)}$$

$$\left(\frac{\partial P}{\partial V} \right)_T = \left[\frac{\partial}{\partial V} \left\{ \frac{RT}{V-b} - \frac{a}{V^2} \right\} \right]_T$$

$$\left(\frac{\partial P}{\partial V} \right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3}$$

$$\Rightarrow \left(\frac{\partial V}{\partial P} \right)_T = \frac{1}{\frac{2a}{V^3} - \frac{RT}{(V-b)^2}}$$

from eqⁿ (2)

$$K_T = -\frac{1}{V} \left\{ \frac{1}{\frac{2a}{V^3} - \frac{RT}{(V-b)^2}} \right\}$$

$$K_T = \frac{1}{\frac{RTV}{(V-b)^2} - \frac{2a}{V^2}}$$

$$K_T = \frac{V^2(V-b)^2}{RTV^3 - 2a(V-b)^2}$$

(ii)

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

$$P = \frac{RT}{\underline{V}-b} - \frac{a}{\underline{V}^2}$$

$$\left(\frac{\partial P}{\partial T} \right)_P = \left(\frac{\partial}{\partial T} \left\{ \frac{RT}{\underline{V}-b} - \frac{a}{\underline{V}^2} \right\} \right)_P$$

$$0 = \frac{R}{\underline{V}-b} \times \frac{\partial T}{\partial T} + RT \left(\frac{\partial}{\partial T} \left(\frac{1}{\underline{V}-b} \right) \right)_P - a \left(\frac{\partial}{\partial T} \left(\frac{1}{\underline{V}^2} \right) \right)_P$$

$$0 = \frac{R}{\underline{V}-b} - \frac{RT}{(\underline{V}-b)^2} \left(\frac{\partial \underline{V}}{\partial T} \right)_P + \frac{2a}{\underline{V}^3} \left(\frac{\partial \underline{V}}{\partial T} \right)_P$$

$$\left\{ \frac{2a}{\underline{V}^3} - \frac{RT}{(\underline{V}-b)^2} \right\} \left(\frac{\partial \underline{V}}{\partial T} \right)_P = -\frac{R}{\underline{V}-b}$$

~~2/19/14~~

$$\left(\frac{RT}{(\underline{V}-b)^2} - \frac{2a}{\underline{V}^3} \right) \left(\frac{\partial \underline{V}}{\partial T} \right)_P = \frac{R}{\underline{V}-b}$$

$$\left\{ \frac{RT}{(\underline{V}-b)} - \frac{2a(\underline{V}-b)}{\underline{V}^3} \right\} \left(\frac{\partial \underline{V}}{\partial T} \right)_P = R$$

$$\left(\frac{\partial \underline{V}}{\partial T} \right)_P = \frac{R}{\frac{RT}{\underline{V}-b} - \frac{2a(\underline{V}-b)}{\underline{V}^3}}$$

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

$$\alpha = \frac{1}{\underline{V}} \left\{ \frac{R}{\frac{RT}{\underline{V}-b} - \frac{2a(\underline{V}-b)}{\underline{V}^3}} \right\}$$

$$\alpha = \frac{R}{\frac{RT\underline{V}}{\underline{V}-b} - \frac{2a(\underline{V}-b)}{\underline{V}^2}}$$

$$\alpha = \frac{R\underline{V}^2(\underline{V}-b)}{RT\underline{V}^3 - 2a(\underline{V}-b)^2}$$

④ Given, $\frac{1}{T_a} = \frac{3}{2} N_a \frac{R}{U_a}$ — (1)

$\frac{1}{T_b} = \frac{5}{2} N_b \frac{R}{U_b}$ — (2)

$N_a = 3 \text{ kmole}$

$N_b = 2 \text{ kmole}$

Initially,

$T_a^i = 400 \text{ K}$

$T_b^i = 700 \text{ K}$

from equation (1) & (2)

$U_a^i = \frac{3}{2} N_a R T_a^i$

$= \frac{3}{2} \times 3 \times 8.314 \times 400$

$U_a^i = 14965.2 \text{ KJ}$

$U_b^i = \frac{5}{2} N_b R T_b^i$

$= \frac{5}{2} \times 2 \times 8.314 \times 700$

$U_b^i = 29099 \text{ KJ}$

Total internal energy of the system (U)

$U = U_a^i + U_b^i$

$= 14965.2 + 29099$

$$U = 44064.2 \text{ kJ}$$

Finally,

$T_a =$
Wall is made diathermal & both the systems are allowed to reach the state of thermal equilibrium.

$$\Rightarrow \frac{1}{T_a} = \frac{1}{T_b} \quad (3)$$

from (1) & (2)

$$\frac{3}{2} N_a \frac{R}{U_a} = \frac{5}{2} N_b \frac{R}{U_b}$$

$$U_a = \frac{5}{3} N_b$$

$$U_a = \frac{3}{5} \left(\frac{N_a}{N_b} \right) U_b$$

$$U_a = \frac{3}{5} \times \frac{3}{2} \times U_b$$

$$U_a = 0.9 U_b$$

$$U_a + U_b = U = 0.9 U_b + U_b$$

$$1.9 U_b = U = 44064.2$$

$$U_b = 23191.68 \text{ kJ}$$

$$U_a = 20872.52 \text{ kJ}$$

from eqn ①

$$T_a = \frac{2}{3} \times \frac{1}{N_a} \times \frac{U_a}{R}$$

$$T_a = \frac{2}{3} \times \frac{1}{3} \times \frac{20872.52}{8.314}$$

$$T_a = 557.895 \text{ K}$$

✓ 1.5

from eqn ②

$$T_b = \frac{2}{5} \times \frac{1}{N_b} \times \frac{U_b}{R}$$

$$= \frac{2}{5} \times \frac{1}{2} \times \frac{23191.68}{8.314}$$

✓ 1.5

$$T_b = T_a = 557.895 \text{ K}$$

⑤ for van der Waals fluid

$$P = \frac{NRT}{V-Nb} - \frac{aN^2}{V^2} \quad \text{--- (1)}$$

$$\left(\frac{\partial P}{\partial N}\right)_{T,V} = \frac{RT}{V-Nb} + \frac{NbRT}{(V-Nb)^2} - \frac{2aN}{V^2}$$

for $\left(\frac{\partial P}{\partial N}\right)_{T,V} < 0$

$$\frac{RT}{V-Nb} + \frac{NbRT}{(V-Nb)^2} - \frac{2aN}{V^2} < 0$$

$$\frac{RTV^2}{aN(V-Nb)} + \frac{NbV^2RT}{aN(V-Nb)^2} - 2 < 0 \quad \text{--- (2)}$$

~~RT~~ $\underline{V}^* = \frac{V}{Nb} \Rightarrow V = Nb\underline{V}^*$

$$T^* = \frac{RTb}{a} \Rightarrow T = \frac{aT^*}{bR}$$

from (2)

$$\frac{R\left(\frac{aT^*}{bR}\right)\left(\frac{Nb\underline{V}^*}{Nb\underline{V}^*}\right)^2}{aN(Nb\underline{V}^* - Nb)} + \frac{Nb(\underline{V}^*Nb)^2 R\left(\frac{aT^*}{bR}\right)}{aN(\underline{V}^*Nb - Nb)^2} < 2$$

$$\frac{\frac{aR}{bR} \cancel{Nb^2} T^* \underline{V}^{*2}}{\cancel{aN} \cancel{b} (\underline{V}^* - 1)} + \frac{\cancel{aN} \cancel{b^2} \underline{V}^{*2} T^*}{\cancel{aN} \cancel{b^2} (\underline{V}^* - 1)^2} < 2$$

$$\frac{T^* \underline{V}^{*2}}{\underline{V}^* - 1} + \frac{T^* \underline{V}^{*2}}{(\underline{V}^* - 1)^2} < 2$$

$$\frac{T^* \underline{V}^{*2}}{\underline{V}^* - 1} \left(1 + \frac{1}{\underline{V}^* - 1} \right) < 2$$

$$\frac{T^* \underline{V}^{*2}}{(\underline{V}^* - 1)} \left(\frac{\underline{V}^*}{\underline{V}^* - 1} \right) < 2$$

$$\left(\frac{T^* \underline{V}^{*3}}{\underline{V}^* - 1} \right) \frac{1}{\underline{V}^* - 1} < 2 \quad (2)$$

for $\left(\frac{\partial P}{\partial N} \right)_{T,N} < 0$
 \Rightarrow

$$\boxed{\alpha = \frac{T^* \underline{V}^{*3}}{\underline{V}^* - 1}} \quad (1)$$