


Ch.7

Equilibrium and Stability (of One-component Systems)



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Outline

1. Criteria for Equilibrium and for Stability

2. Phase Equilibrium

3. Fugacity

4. Phase Transition Phenomena

5. Properties of Small Systems

The criteria for equilibrium

- For a closed system without shaft work,

$$\frac{dU}{dt} = \dot{Q} - P \frac{dV}{dt}$$

$$\frac{dS}{dt} = \frac{\dot{Q}}{T} + \dot{S}_{gen} \quad \& \quad \dot{S}_{gen} \geq 0$$

- If this system kept constant V and no heat transfer ($Q=0$) with its surroundings,

$$\frac{dU}{dt} = 0 \Rightarrow U = \text{constant or } \underline{U} = \text{constant}$$

$$\frac{dS}{dt} = \dot{S}_{gen} \geq 0 \Rightarrow \text{Approach to equilibrium} \Rightarrow \text{entropy increase}$$

- [S or $\underline{S} = \text{Maximum}$] at equilibrium in a closed system at constant U and V .

The criteria for equilibrium

- For a closed system at constant T and V approaching equilibrium,

$$\frac{dM}{dt} = 0 \quad \frac{dU}{dt} = \dot{Q} \quad \frac{dS}{dt} = \frac{\dot{Q}}{T} + \dot{S}_{gen}$$
$$\therefore \frac{d(U - TS)}{dt} = \frac{dA}{dt} = -T\dot{S}_{gen} \leq 0$$

- Therefore, at equilibrium A reaches its minimum.
- Similar discussions can lead to that G, H and U reaches their minimum at equilibrium.

Equilibrium

constant N, U, V

N^I S^I U^I V^I	N^{II} S^{II} U^{II} V^{II}
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$$N = N^I + N^{II}$$

$$U = U^I + U^{II}$$

$$V = V^I + V^{II}$$

$$S = S^I + S^{II}$$

$$S = f(U, V, N)$$

$$dU = TdS - PdV + GdN \Rightarrow dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{G}{T}dN$$

$$dS^I = \frac{1}{T^I}dU^I + \frac{P^I}{T^I}dV^I - \frac{G^I}{T^I}dN^I$$

$$dS = dS^I + dS^{II} = \frac{1}{T^I}dU^I + \frac{1}{T^{II}}dU^{II} + \frac{P^I}{T^I}dV^I + \frac{P^{II}}{T^{II}}dV^{II} - \frac{G^I}{T^I}dN^I - \frac{G^{II}}{T^{II}}dN^{II}$$

$$\text{However, } dN = dN^I + dN^{II} = 0 \Rightarrow dN^I = -dN^{II}, dU^I = -dU^{II}, dV^I = -dV^{II}$$

$$\therefore dS = \left(\frac{1}{T^I} - \frac{1}{T^{II}} \right) dU^I + \left(\frac{P^I}{T^I} - \frac{P^{II}}{T^{II}} \right) dV^I - \left(\frac{G^I}{T^I} - \frac{G^{II}}{T^{II}} \right) dN^I$$

- At equilibrium, $S = \text{maximum}$ or $dS = 0$. Since dU^I , dV^I , and dN^I are independent variables, thus

$$T^I = T^{II}, \quad P^I = P^{II}, \quad G^I = G^{II}$$

The composite system is uniform when the system is equilibrium.

Thermodynamic Equilibrium

❖ Closed System at Constant T and V

$$\frac{dU}{dt} = \dot{Q} \quad \& \quad \frac{dS}{dt} = \frac{\dot{Q}}{T} + \dot{S}_{gen} \Rightarrow \frac{d(U - TS)}{dt} = \frac{dA}{dt} = -T\dot{S}_{gen} \leq 0$$

A or A = minimum at equilibrium in a closed system at constant T & V

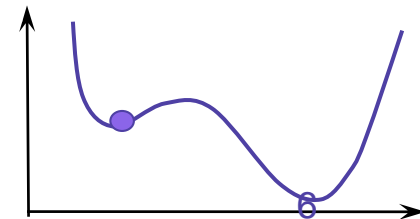
❖ Closed System at Constant T and P

$$\frac{dU}{dt} = \dot{Q} - P \frac{dV}{dt} = \dot{Q} - \frac{d(PV)}{dt} \quad \& \quad \frac{dS}{dt} = \frac{\dot{Q}}{T} + \dot{S}_{gen} \Rightarrow \frac{d(U + PV - TS)}{dt} = \frac{dG}{dt} = -T\dot{S}_{gen} \leq 0$$

G or G = minimum at equilibrium in a closed system at constant T & P

❖ Equilibrium & Stability Criteria

System	Constraint	Equilibrium criteria	Stability criteria
Isolated, adiabatic fixed-boundary system	U & V = constant	S = max. dS = 0	d ² S < 0
Constant T closed system with fixed boundary	T & V = constant	A = min. dA = 0	d ² A > 0
Constant T & P, closed system	T & P = constant	G = min. dG = 0	d ² G > 0
Constant T & P, open system moving with fluid velocity	T, P & M = constant	G = min dG = 0	d ² G > 0



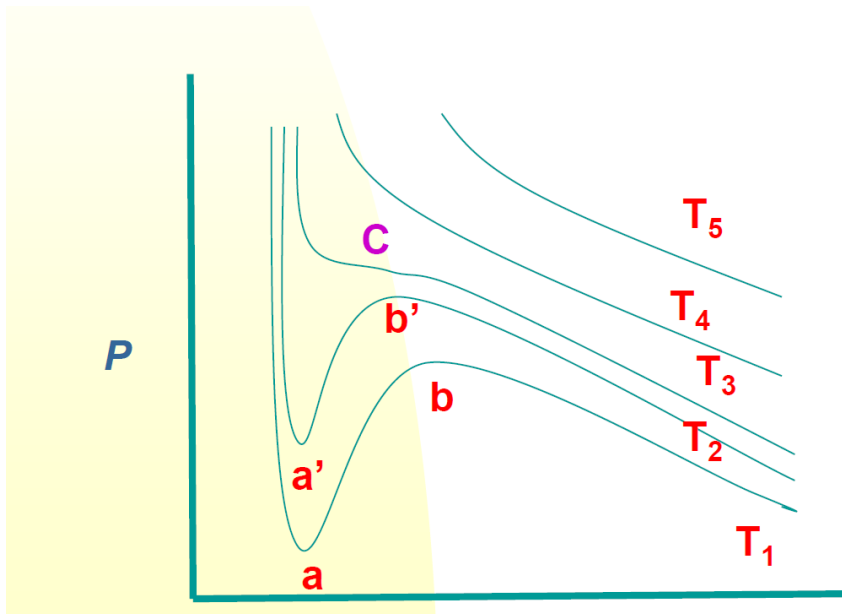
Phase equilibria

Stability of Thermodynamic Systems

❖ **Stable state: $d^2S < 0$**

$$C_V > 0$$

$$\left(\frac{\partial P}{\partial V}\right)_T < 0 \Rightarrow k_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T > 0 \text{ (isothermal compressibility)}$$



T_5, T_4 : All points are $\left(\frac{\partial P}{\partial V}\right)_T < 0$

T_3 : At point C, $\left(\frac{\partial P}{\partial V}\right)_T = 0$

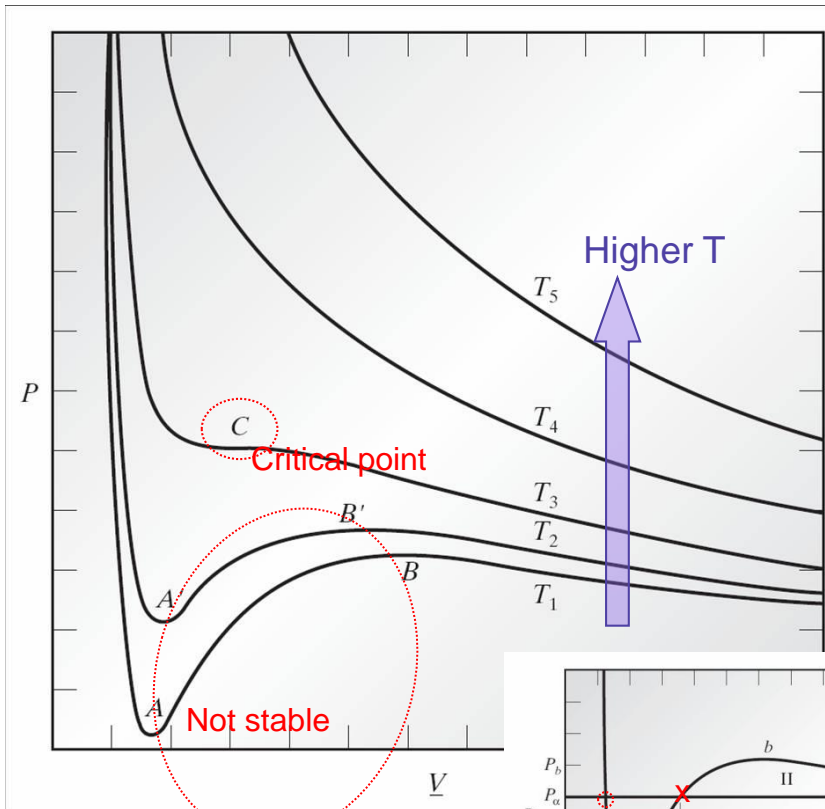
T_2 : Region a' to b' , $\left(\frac{\partial P}{\partial V}\right)_T > 0$, unstable

T_1 : Region a to b , $\left(\frac{\partial P}{\partial V}\right)_T > 0$, unstable

Fig. 7.3-1

Phase Equilibrium

- Plot van der Waal eqn. on P- \underline{V} diagram



$$\left(\frac{\partial P}{\partial \underline{V}}\right)_T < 0 \quad (\text{The stability criteria})$$

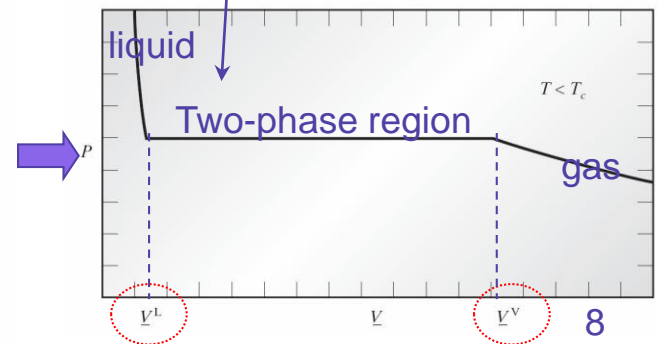
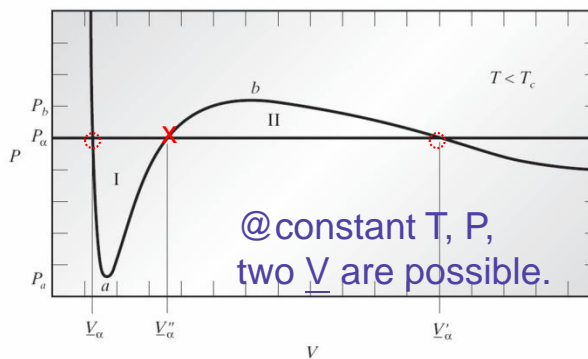
$$\underline{V} = x^V \underline{V}^V + x^L \underline{V}^L = x^V \underline{V}^V + (1 - x^V) \underline{V}^L$$

$$\therefore x^V = \frac{\underline{V} - \underline{V}^L}{\underline{V}^V - \underline{V}^L}$$

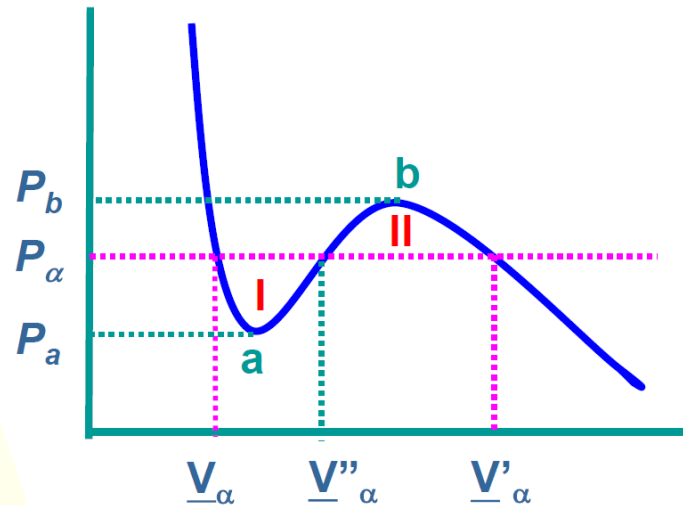
or

$$\frac{x^V}{1 - x^V} = \frac{\underline{V} - \underline{V}^L}{\underline{V}^V - \underline{V}}$$

(Maxwell's rule or lever rules)

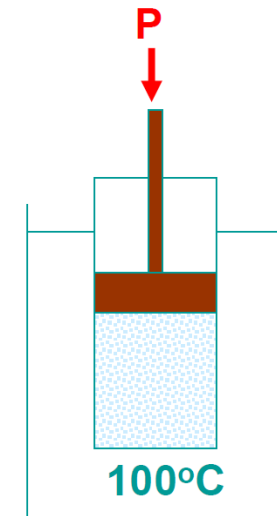
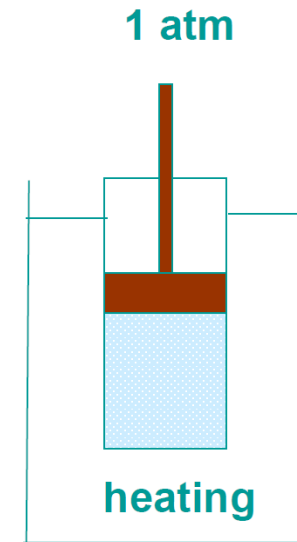
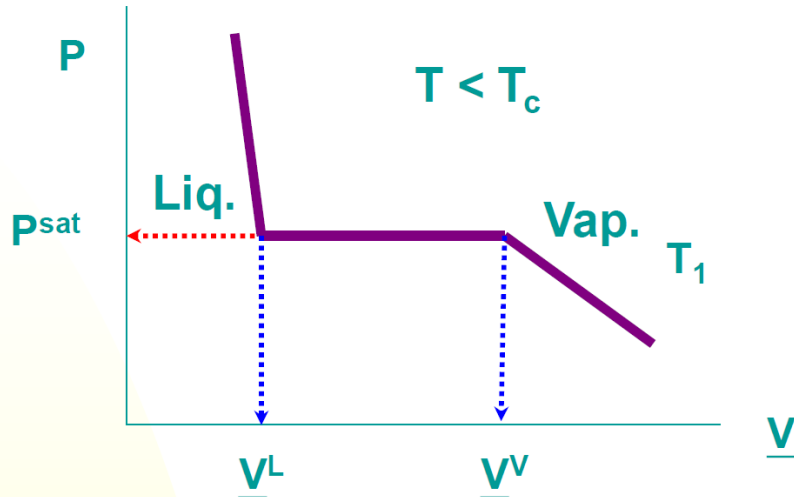


- ❖ T_1 and T_2 isotherms ($T < T_c$)
- ❖ Fig. 7.3-2 (van der Waals loops)



- ❖ $P_a < P_\alpha < P_b \Leftrightarrow$ three intersections between isobaric line P_α and EOS at T_1
 - ❖ V''_α is unattainable by the stability criterion.
 - ❖ V_α and V'_α are physically attainable.
 - ❖ V_α and V'_α are two-phase coexists at T_1 and P_α .
 - ❖ V_α : liquid phase
 - ❖ V'_α : vapor phase
- VLE for pure fluids

For real fluids



- ❖ Water
- ❖ VLE, $100^{\circ}\text{C} \rightleftharpoons 1 \text{ atm}$
- ❖ at 1 atm, $T < 100^{\circ}\text{C}$ (liquid)
 $T = 100^{\circ}\text{C}$ (boiling, VLE)
 $T > 100^{\circ}\text{C}$ (vapor)
- ❖ at 100°C , $P > 1 \text{ atm}$ (liquid)
 $P = 1 \text{ atm}$ (boiling, VLE)
 $P < 1 \text{ atm}$ (vapor)

Properties of two-phase mixtures

$$\underline{V} = \omega^V \underline{V}^V + (1 - \omega^V) \underline{V}^L$$

$$\Rightarrow \omega^V = \frac{\underline{V} - \underline{V}^L}{\underline{V}^V - \underline{V}^L} \quad (\text{quality})$$

$$\text{or } \frac{\omega^V}{1 - \omega^V} = \frac{\underline{V} - \underline{V}^L}{\underline{V}^V - \underline{V}} \quad (\text{Maxwell's rule or Lever rule})$$

❖ Similarly, H, U, G, A, S,

❖ Illustration 7.3-1

- ❖ Computing the properties of a two-phase mixture
- ❖ Compute the total volume, total enthalpy, and total entropy of 1 kg of water at 100°C, half by weight of which is steam and the remainder liquid water.

<sol>

$$\hat{V} = 0.5 \times 0.001004 + 0.5 \times 1.6729 = 0.83645 \text{ m}^3 / \text{kg}$$

$$\hat{H} = 0.5 \times 419.04 + 0.5 \times 2676.1 = 1547.6 \text{ kJ/kg}$$

$$\hat{S} = 0.5 \times 1.3069 + 0.5 \times 7.3549 = 4.3309 \text{ kJ/kgK}$$

Determine the vapor pressure at given temp

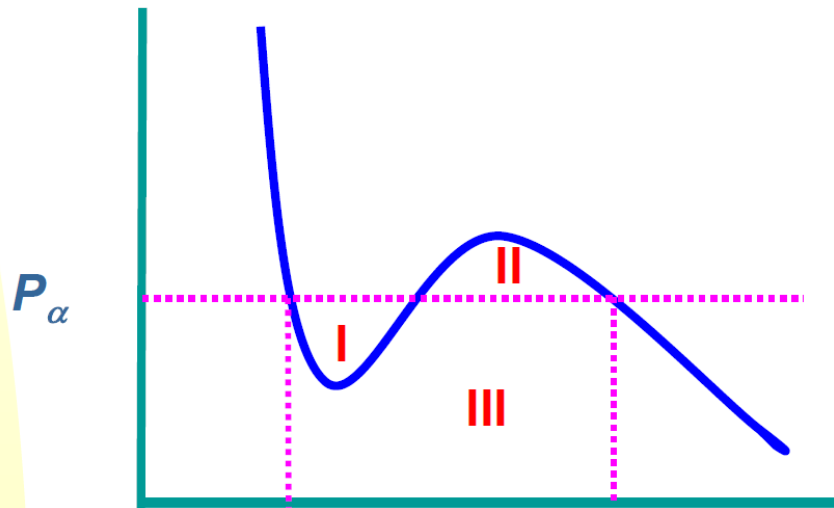
At vapor-liquid equilibrium, $\underline{G}^V = \underline{G}^L$

Since $d\underline{G} = \underline{V} dP - \underline{S} dT$, integrate along the isotherm,

$$\int_{\underline{G}^L}^{\underline{G}^V} d\underline{G} = \int_{P_\alpha}^{P_\alpha} \underline{V} dP \quad \& \quad dP \equiv \frac{1}{\underline{V}} d(P\underline{V}) - \frac{P}{\underline{V}} d\underline{V}$$

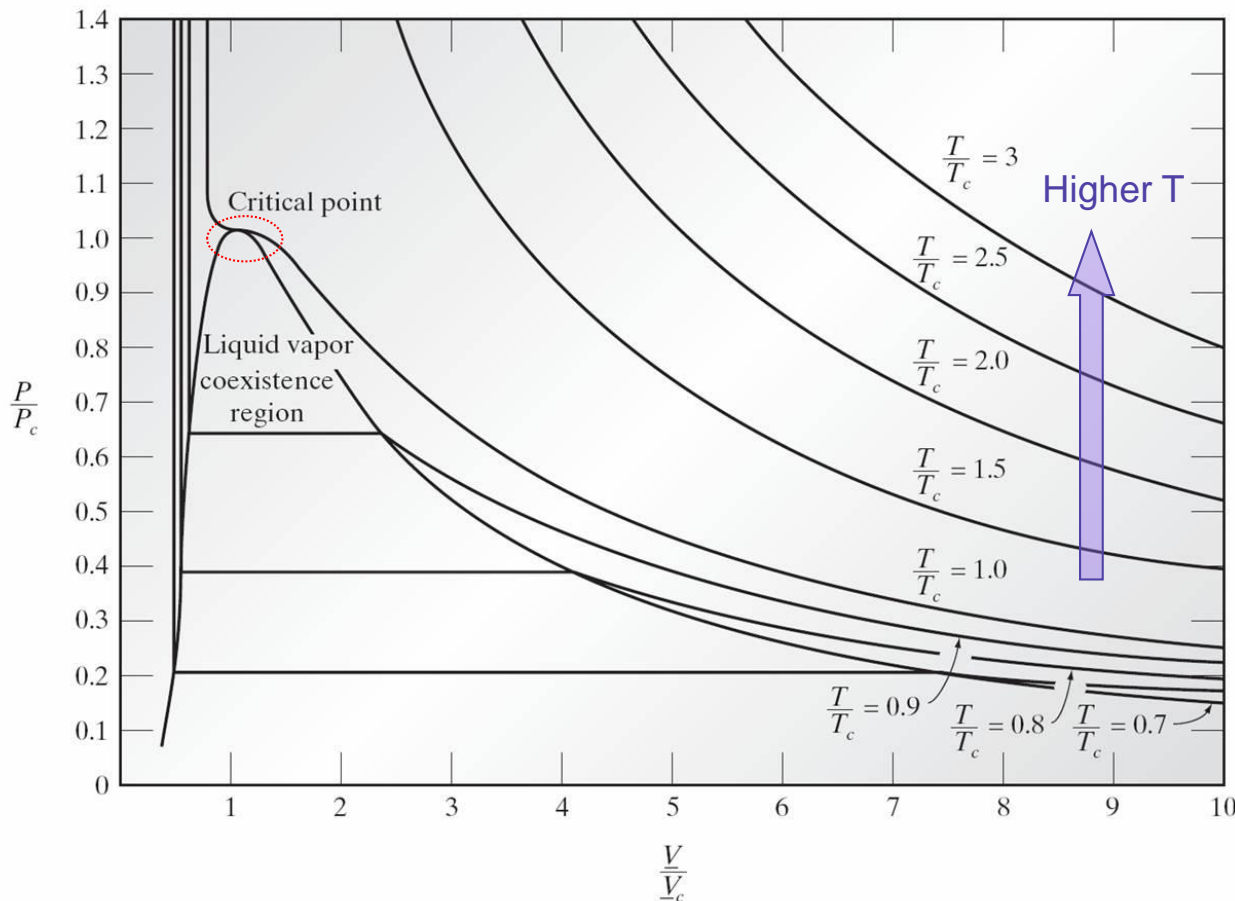
$$\begin{aligned} \Rightarrow \underline{G}^V - \underline{G}^L = 0 &= \int_{P_\alpha}^{P_\alpha} \underline{V} dP = \int_{P_\alpha}^{P_\alpha} \underline{V} d(P\underline{V}) - \int_{V^L}^{V^V} P d\underline{V} = P_\alpha (\underline{V}^V - \underline{V}^L) - \int_{V^L}^{V^V} P d\underline{V} \\ &= \text{area I} + \text{area III} - (\text{area III} + \text{area II}) = \text{area I} - \text{area II} \end{aligned}$$

$$\Rightarrow \text{area I} = \text{area II}$$



Phase Equilibrium

- replot van der Waal fluid with V-L coexistence region on P - V diagram



The equilibrium conditions for V-L coexistence:

$$T^V = T^L \quad P^V = P^L$$

$$\underline{G}^V = \underline{G}^L$$

P-V-T phase diagram with single solid phase

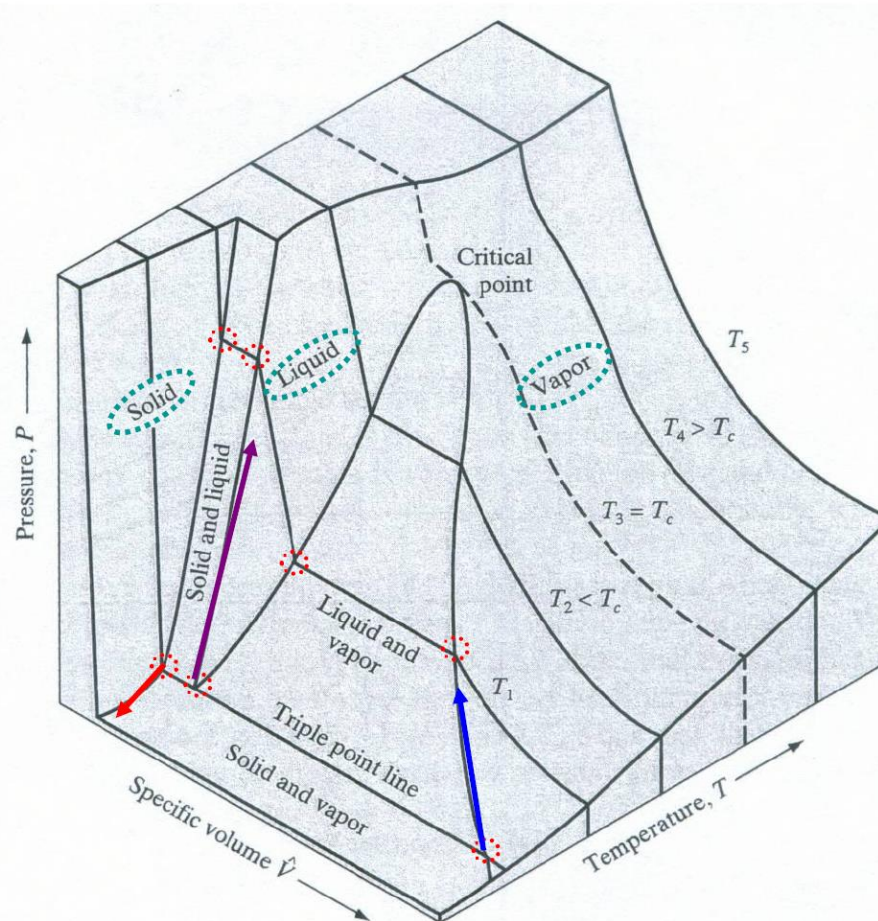
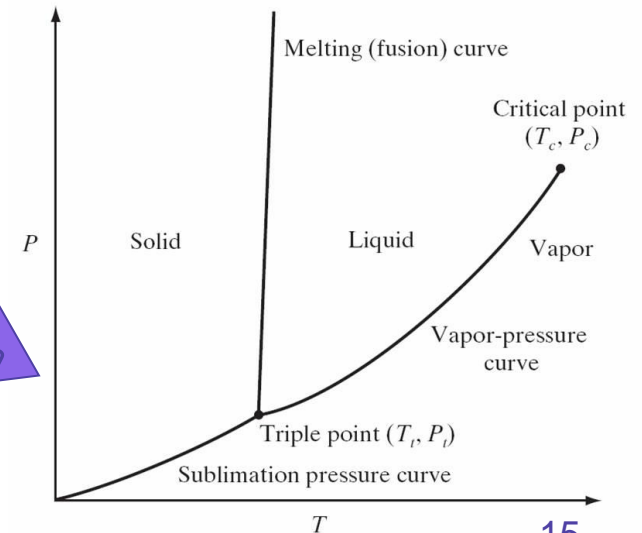
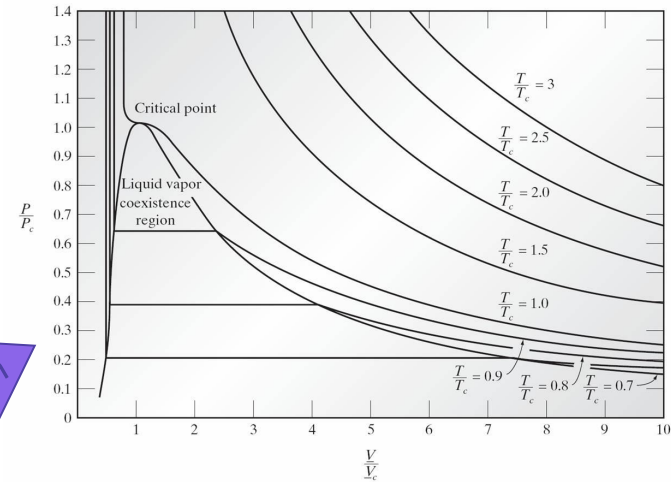
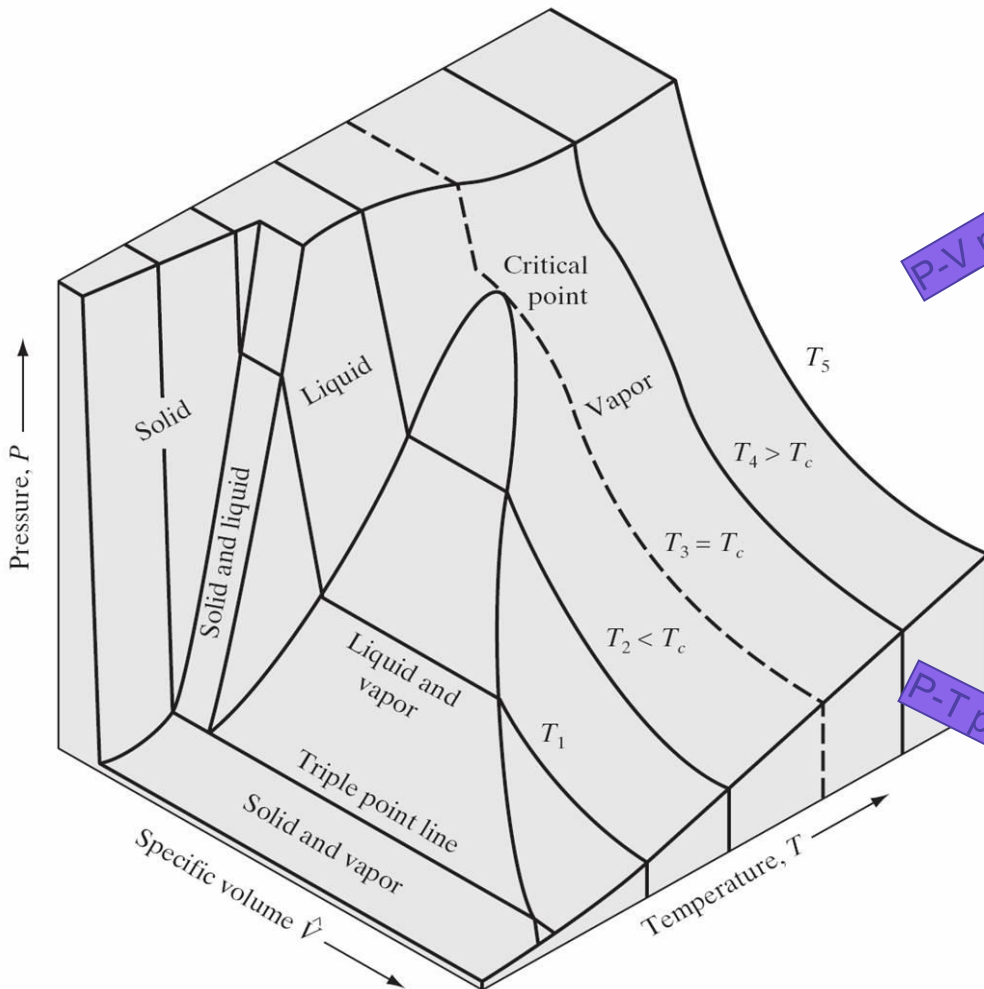


Figure 7.3-5 The PVT phase diagram for a substance with a single solid phase. [Adapted from J. Kestin, *A Course in Thermodynamics*, vol. 1. © 1966 by Blaisdell Publishing Co. (John Wiley & Sons, Inc.) Used with permission of John Wiley & Sons, Inc.]

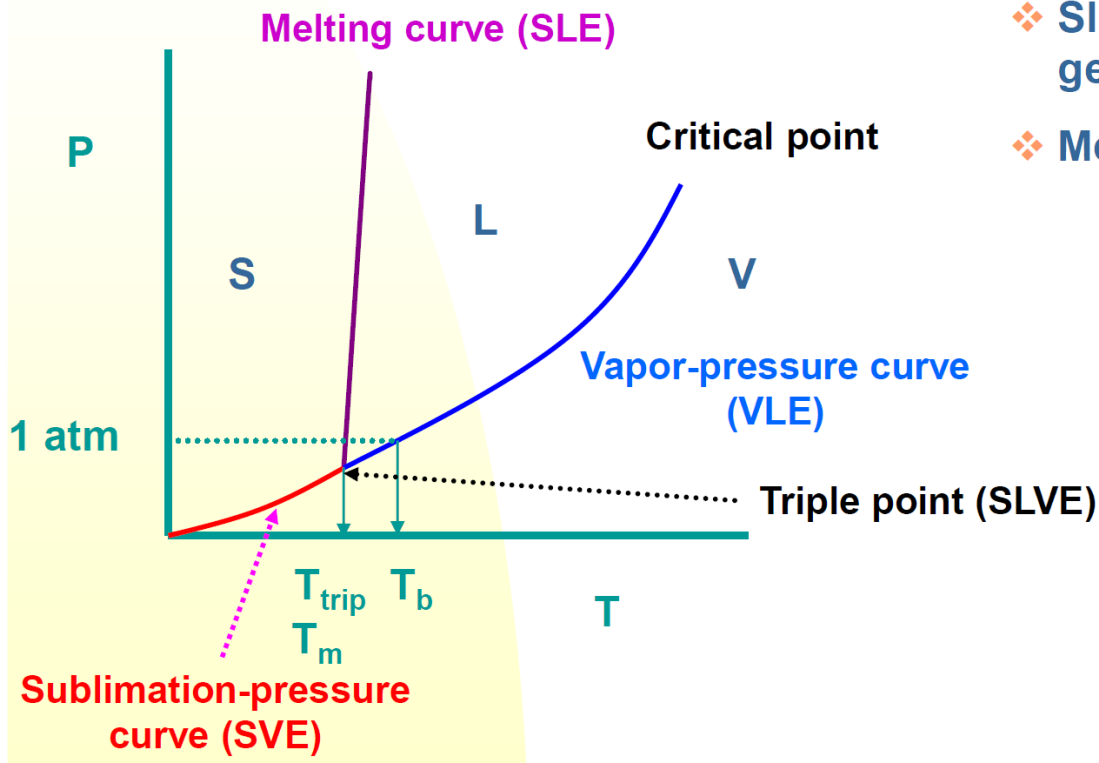
Phase Equilibrium

- The P-V-T phase diagram



P-T phase diagram

❖ Fig. 7.3-6 Phase diagram in the P-T plane



❖ Slope of melting curve is generally steep $\Rightarrow T_{trip} = T_m$

❖ Meta stable:

- ❖ Superheated liquid
- ❖ subcooled vapor
- ❖ subcooled liquid

Thermodynamic Stability

Stability Criterion:
 $d^2S < 0$

$$d^2S = \frac{N^I + N^{II}}{N^I N^{II}} [\theta_1 (dX_1)^2 + \theta_2 (dX_2)^2 + \theta_3 (dX_3)^2] < 0$$

- First Stability Criterion: thermal stability

$$\theta_1 = \underline{S}_{U,U}^\alpha \leq 0$$

$$\underline{S}_{U,U}^\alpha = N \frac{\partial}{\partial U} \left(\left(\frac{\partial S}{\partial U} \right)_{V,N} \right)_{V,N} = N \left(\frac{\partial(1/T)}{\partial U} \right)_{V,N} = -\frac{N}{T^2} \left(\frac{\partial T}{\partial U} \right)_{V,N} = -\frac{1}{T^2 C_V} \leq 0$$

$$\text{i.e., } C_V > 0$$

- Second Stability Criterion: mechanical stability

$$\theta_2 = (\underline{S}_{U,U}^\alpha \underline{S}_{V,V}^\alpha - \underline{S}_{U,V}^\alpha{}^2) / \underline{S}_{U,U}^\alpha \leq 0$$

$$\underline{S}_{U,V}^\alpha = N \frac{\partial}{\partial U} \left(\left(\frac{\partial S}{\partial V} \right)_{U,N} \right)_{V,N} = N \frac{\partial}{\partial V} \left(\left(\frac{\partial S}{\partial U} \right)_{V,N} \right)_{U,N} = N \left(\frac{\partial(1/T)}{\partial V} \right)_{U,N} = -\frac{N}{T^2} \left(\frac{\partial T}{\partial V} \right)_{U,N} = \frac{\left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right]}{C_V T^2}$$

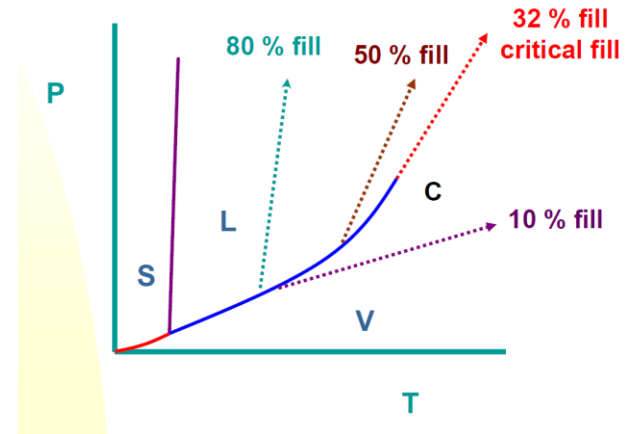
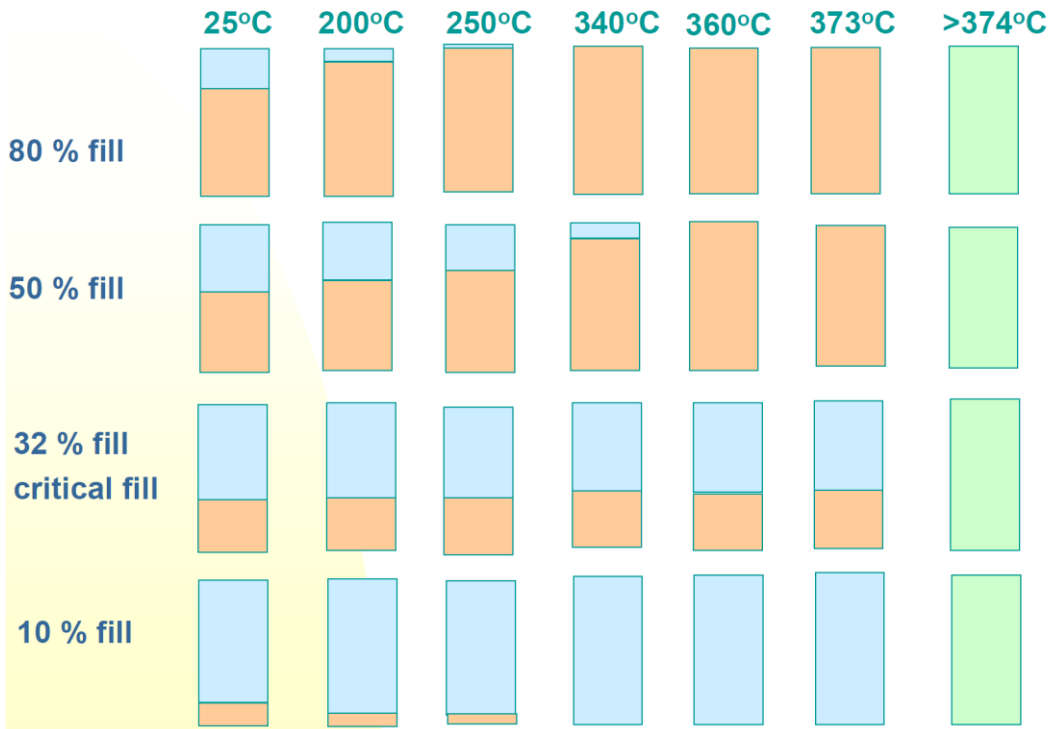
$$\underline{S}_{V,V}^\alpha = \dots = \frac{1}{T} \left(\frac{\partial P}{\partial V} \right)_T - \frac{\left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right]^2}{C_V T^2}$$

$$\theta_2 = \frac{1}{T} \left(\frac{\partial P}{\partial V} \right)_T < 0$$

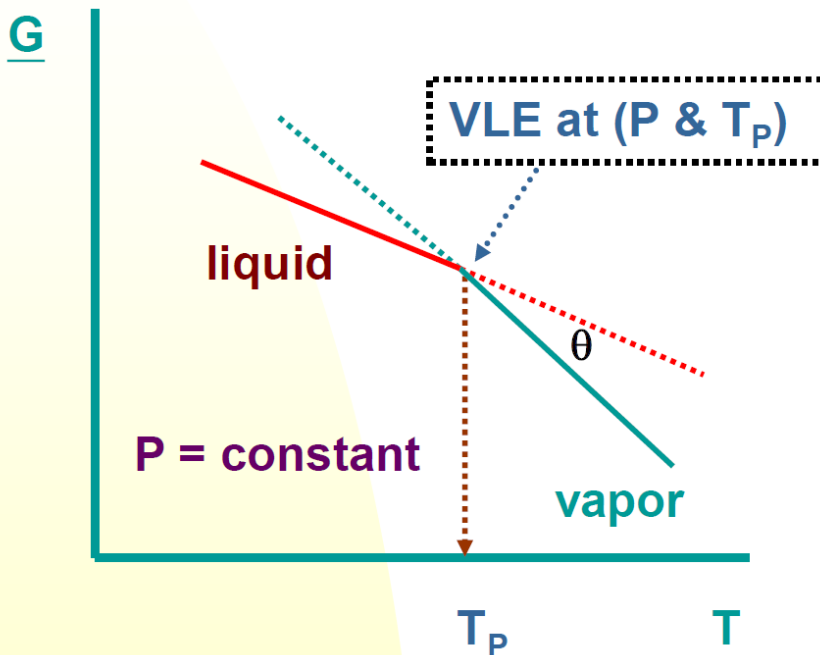
$$\text{or } \kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T > 0$$

NOTE: The stability criteria must be satisfied in each stable system (phase)

P-T diagram of the critical fill



G-T diagram



At VLE, $\underline{G}^L = \underline{G}^V$

At equilibrium, $\underline{G} = \text{min.}$

\Rightarrow liquid phase at P & $T < T_p$

\Rightarrow vapor phase at P & $T > T_p$

At critical point, $\theta = 0$; i.e.,

$$\left(\frac{\partial \underline{G}^L}{\partial T} \right)_P = \left(\frac{\partial \underline{G}^V}{\partial T} \right)_P$$

or

$$\underline{S}^L(T_c, P_c) = \underline{S}^V(T_c, P_c)$$

also

$$\underline{G}^L(T_c, P_c) = \underline{G}^V(T_c, P_c)$$

Fugacity and Gibbs Free Energy

- The departure function of \underline{G} :

$$\underline{G}^{departure}(T, P) = \underline{G}(T, P) - \underline{G}^{IG}(T, P) = \int_{P \rightarrow 0}^P \left(\underline{V} - \frac{RT}{P} \right) dP$$

- Define “fugacity”, f , as: $\ln \frac{f}{P} = \frac{\underline{G}(T, P) - \underline{G}^{IG}(T, P)}{RT} = \frac{1}{RT} \int_0^P \left(\underline{V} - \frac{RT}{P} \right) dP$

– Thus, “fugacity coefficient” is $\ln \phi = \ln \frac{f}{P} = \frac{\underline{G}(T, P) - \underline{G}^{IG}(T, P)}{RT}$

as $P \rightarrow 0$, $\underline{G} \rightarrow \underline{G}^{IG}$, $f \rightarrow P$, and $\phi \rightarrow 1$.

- Fugacity deviates from P when the “material” behave less like an ideal gas.
- Fugacity can be viewed as an indication of non-ideality.

- In the case of two-phase coexistence, $\underline{G}^I = \underline{G}^{II}$ (and also $T^I = T^{II}$, $P^I = P^{II}$).

$$\underline{G}^{IG}(T, P) + RT \ln \frac{f^I}{P} = \underline{G}^{IG}(T, P) + RT \ln \frac{f^{II}}{P}$$

$$\therefore f^I(T, P) = f^{II}(T, P) \quad \text{and} \quad \phi^I(T, P) = \phi^{II}(T, P)$$

- Fugacity is related to molar Gibbs free energy and, therefore, can be applied in situations involving molar Gibbs free energy.

Fugacity and Gibbs Free Energy

- The “fugacity coefficient”:

- Relation with departure function: $\ln \phi = \ln \frac{f}{P} = \frac{\underline{G}(T, P) - \underline{G}^{IG}(T, P)}{RT} = \frac{\underline{G}^{Departure}(T, P)}{RT}$
- P-dependency / T-dependency:

$$d \ln \phi = d \ln f - d \ln P$$

$$d(\ln \phi) = - \left[\frac{(H - H^{IG})}{RT^2} \right] dT + \left(\frac{V}{RT} - \frac{1}{P} \right) dP$$

$$d(\ln \phi) = - \left[\frac{(H - H^{IG})}{RT^2} \right] dT + \left(\frac{V - V^{IG}}{RT} \right) dP$$

$$d(\ln f) = \left(\frac{\partial \ln f}{\partial T} \right)_P dT + \left(\frac{\partial \ln f}{\partial P} \right)_T dP$$

$$d(\ln f) = - \left[\frac{(H - H^{IG})}{RT^2} \right] dT + \left(\frac{V}{RT} \right) dP$$

$$RT \left(\frac{\partial \ln f}{\partial P} \right)_T = \underline{V} = \left(\frac{\partial \underline{G}}{\partial P} \right)_T$$

- In terms of T, P: $\ln \frac{f}{P} = \frac{\underline{G}(T, P) - \underline{G}^{IG}(T, P)}{RT} = \frac{1}{RT} \int_0^P \left(\underline{V} - \frac{RT}{P} \right) dP$

- In terms of T, \underline{V} : $\ln \phi = \ln \frac{f}{P} = \frac{1}{RT} \int_{\underline{V} \rightarrow \infty}^{\underline{V}} \left(\frac{RT}{\underline{V}} - P \right) d\underline{V} - \ln Z + (Z - 1)$

NOTE: Fugacity calculation will provide info on $\underline{G}^{Departure}$ and, therefore, \underline{G} which is important for the equilibrium between two phases (systems)

Molar Gibbs Free Energy & Fugacity of a Pure Component

❖ At VLE, $\underline{G}^L(T,P) = \underline{G}^V(T,P)$

Note that $d\underline{G} = -\underline{S} dT + \underline{V} dP$ and $d\underline{G} = \underline{V} dP$ at constant T.

Integrate

$$\underline{G}(T_1, P_2) - \underline{G}(T_1, P_1) = \int_{P_1}^{P_2} \underline{V} dP \quad (a)$$

If the fluid is an ideal gas

$$\underline{G}^{IG}(T_1, P_2) - \underline{G}^{IG}(T_1, P_1) = \int_{P_1}^{P_2} \frac{RT}{P} dP \quad (b)$$

eq.(a) - eq.(b) \Rightarrow

$$\left[\underline{G}(T_1, P_2) - \underline{G}^{IG}(T_1, P_2) \right] - \left[\underline{G}(T_1, P_1) - \underline{G}^{IG}(T_1, P_1) \right] = \int_{P_1}^{P_2} \left(\underline{V} - \frac{RT}{P} \right) dP$$

Set $P_1 \rightarrow 0$, all fluids are ideal gases as $P = 0$

$$\Rightarrow \underline{G}(T_1, P = 0) = \underline{G}^{IG}(T_1, P = 0)$$

Let $T = T_1$ & $P = P_2$, then

Departure \underline{G}

$$\left[\underline{G}(T, P) - \underline{G}^{IG}(T, P) \right] = \int_0^P \left(\underline{V} - \frac{RT}{P} \right) dP$$

Fugacity and Gibbs Free Energy

- Fugacity can be considered as an evaluation of material characteristic using the ideal gas state as the reference.
- For fugacity (and fugacity coefficient) analysis for materials other than gas phase, we can apply the

following concept: $RT \ln \frac{f^L}{P} = \underline{G}^L(T, P) - \underline{G}^{IG}(T, P)$

$$= \underline{G}^L(T, P) - \underline{G}^L(T, P^{sat}) + \underline{G}^L(T, P^{sat}) - \underline{G}(T, P^{sat}) + \underline{G}(T, P^{sat}) - \underline{G}^{IG}(T, P)$$

$$= \Delta \underline{G}_{T, P \rightarrow T, P^{sat}}^L + \Delta \underline{G}_{T, P^{sat}}^{L \rightarrow G} + \Delta \underline{G}_{T, P^{sat} \rightarrow T, P}$$

– Therefore, $RT \ln \frac{f^L}{P} = \Delta \underline{G}_{T, P \rightarrow T, P^{sat}}^L + \Delta \underline{G}_{T, P^{sat}}^{L \rightarrow G} + \Delta \underline{G}_{T, P^{sat} \rightarrow T, P}$

$$= \int_{P^{sat}}^P \left(\underline{V}^L - \frac{RT}{P} \right) dP + \int_0^{P^{sat}} \left(\underline{V} - \frac{RT}{P} \right) dP$$

$$= \int_{P^{sat}}^P \left(\underline{V}^L - \frac{RT}{P} \right) dP + RT \ln \left(\frac{f}{P} \right)_{sat, T}$$

$$= \int_{P^{sat}}^P \underline{V}^L dP - RT \ln \frac{P}{P^{sat}} + RT \ln \left(\frac{f}{P} \right)_{sat, T}$$

$$\therefore \frac{f^L(T, P)}{P^{sat}} = \left(\frac{f}{P} \right)_{sat, T} \exp \left(\frac{1}{RT} \int_{P^{sat}}^P \underline{V}^L dP \right)$$

Poynting pressure correction, important only at high P or very low T

Fugacity and Gibbs Free Energy

- Fugacity of a liquid: $f^L(T,P) = P^{sat} \left(\frac{f}{P} \right)_{sat,T} \exp \left(\frac{1}{RT} \int_{P^{sat}}^P \underline{V}^L dP \right)$
 - At low P, nonassociative liquid $f^L(T,P) = P^{sat}(T)$
 - At low P, associative liquid $f^L(T,P) = P^{sat}(T) \left(\frac{f}{P} \right)_{sat,T}$
 - Assuming incompressible, $f^L(T,P) = P^{sat} \left(\frac{f}{P} \right)_{sat,T} \exp \left(\frac{V^L(P - P^{sat})}{RT} \right)$
 - Alternatively, if ϕ can be evaluated using corresponding states (Fig.7.4-1), $f^L(T,P) = P(T) \left(\frac{f}{P} \right)_{T,P}$
- Fugacity of a solid: $f^S(T,P) = P^{sat} \left(\frac{f}{P} \right)_{sat,T} \exp \left(\frac{1}{RT} \sum_{J=1}^{P^{J+1}} \int_{P^J} \underline{V}^J dP \right)$
 - In general, P^{sat} of solid is low and $f^S(T,P) = P^{sat}(T)$
 - Pressure correction with incompressibility, $f^S(T,P) = P^{sat} \exp \left(\frac{V^S(P - P^{sat})}{RT} \right)$

Fugacity and Fugacity coefficient

- ❖ For convenience, Lewis defined a new thermodynamic function, fugacity, by

$$f \equiv P \exp \left[\frac{\underline{G}(T, P) - \underline{G}^{IG}(T, P)}{RT} \right] = P \exp \left[\frac{1}{RT} \int_0^P \left(\underline{V} - \frac{RT}{P} \right) dP \right]$$

- ❖ Fugacity coefficient

$$\phi \equiv \frac{f}{P} = \exp \left[\frac{\underline{G}(T, P) - \underline{G}^{IG}(T, P)}{RT} \right] = \exp \left[\frac{1}{RT} \int_0^P \left(\underline{V} - \frac{RT}{P} \right) dP \right]$$

As $P \rightarrow 0$, $\underline{G}(T, P) \approx \underline{G}^{IG}(T, P) \Rightarrow f \rightarrow P$ & $\phi \rightarrow 1$

- ❖ Criterion of equilibrium,

$$\underline{G}^I(T, P) = \underline{G}^{II}(T, P)$$

$$RT \ln \left(\frac{f^I}{P} \right) + \underline{G}^{IG}(T, P) = RT \ln \left(\frac{f^{II}}{P} \right) + \underline{G}^{IG}(T, P)$$

$$f^I(T, P) = f^{II}(T, P)$$

Calculation of fugacity from EOS

$$\ln \phi = \frac{1}{RT} \int_0^P \left(\underline{V} - \frac{RT}{P} \right) dP \quad \& \quad dP \equiv \frac{1}{\underline{V}} d(P\underline{V}) - \frac{P}{\underline{V}} d\underline{V} = \frac{P}{Z} dZ - \frac{P}{\underline{V}} d\underline{V}$$

$$\therefore \ln \left(\frac{f}{P} \right) = \ln \phi = \frac{1}{RT} \int_{\underline{V}=\infty}^{\underline{V}} \left(\frac{RT}{\underline{V}} - P \right) d\underline{V} - \ln Z + (Z - 1)$$

EOS, P = f (T, V)

where $Z = PV/(RT)$, $Z \rightarrow 1$ as $P \rightarrow 0$ (ideal gas)

❖ Pressure dependence of fugacity

$$RT \left(\frac{\partial \ln f}{\partial P} \right)_T = RT \frac{\partial}{\partial P} \left[\ln P + \frac{1}{RT} \int_0^P \left(\underline{V} - \frac{RT}{P} \right) dP \right] = RT \left[\frac{1}{P} + \frac{1}{RT} \left(\underline{V} - \frac{RT}{P} \right) \right] = \underline{V}$$

❖ Temperature dependence of fugacity

$$\left(\frac{\partial \ln \phi}{\partial T} \right)_P = \frac{-1}{RT^2} (\underline{H} - \underline{H}^{IG})$$

Fugacity of a pure gaseous species

$$\ln\left(\frac{f^V(T,P)}{P}\right) = \frac{1}{RT} \int_{\underline{V}=\infty}^{\underline{V}=Z^V RT/P} \left(\frac{RT}{\underline{V}} - P\right) d\underline{V} - \ln Z^V + (Z^V - 1)$$

EOS, $P = f(T, \underline{V})$

- ❖ At given T & P, \underline{V}^V (or Z^V) solve from the EOS
- ❖ At very low P => ideal gas assumption

$$P\underline{V} = RT \quad \& \quad Z^V = 1$$

$$\Rightarrow \ln\left[\frac{f^V(T,P)}{P}\right] = 0 \Rightarrow \phi = 1 \quad \& \quad f^V(T,P) = P$$

- ❖ At low to moderate pressures, two-term virial equation may be used,

$$\frac{P\underline{V}}{RT} = Z = 1 + \frac{B(T)}{\underline{V}}$$

$$\Rightarrow \ln\left[\frac{f^V(T,P)}{P}\right] = \ln \phi^V = \frac{2B(T)}{\underline{V}^V} - \ln Z^V, \quad \text{where } Z^V = \frac{1}{2} \left[1 + \sqrt{1 + \frac{4B(T)P}{RT}} \right]$$

- ❖ At higher pressures, the PR EOS provides a more accurate description for hydrocarbons and simple gases,

$$P = \frac{RT}{\underline{V} - b} - \frac{a(T)}{\underline{V}(\underline{V} + b) + b(\underline{V} - b)}$$

$$\Rightarrow \ln\left[\frac{f^V(T,P)}{P}\right] = \ln \phi^V = (Z^V - 1) - \ln(Z^V - B) - \frac{A}{2\sqrt{2}B} \ln\left[\frac{Z^V + (1 + \sqrt{2})B}{Z^V + (1 - \sqrt{2})B}\right]$$

$$\text{where } A = aP/(RT)^2 \quad \& \quad B = Pb/(RT)$$

Fugacity calculation (I)

❖ Illustration 7.4-1

- ❖ Use the volumetric information in the steam tables of Appendix A.III to compute the fugacity of superheated steam at 300°C and 8 MPa

<sol>

$$f = P \exp \left[\frac{1}{RT} \int_0^P \left(\underline{V} - \frac{RT}{P} \right) dP \right]$$

⇒ From superheated steam tables at $T = 300^\circ\text{C}$, we have \hat{V} at P from 0.01 MPa to 8.0 MPa.

⇒ Calculate the integral numerically

$$\int_0^{8\text{MPa}} \left(\underline{V} - \frac{RT}{P} \right) dP \approx -1.093 \times 10^{-3} \frac{\text{m}^3 \text{MPa}}{\text{mol}}$$

$$f = 8 \text{ MPa} \times \exp \left(\frac{-1.093 \times 10^{-3} \frac{\text{m}^3 \text{MPa}}{\text{mol}}}{573.15 \text{ K} \times 8.314 \times 10^{-6} \frac{\text{MPa m}^3}{\text{mol K}}} \right) = 6.397 \text{ MPa}$$

$$\phi = f/P = 0.7996$$

- ❖ Fugacity coefficient of the superheated steam at 300°C and 8 MPa is about 0.7996. Its behavior is closer to an ideal gas.

Fugacity calculation (II)

❖ Illustration 7.4-2

- ❖ Use other data in the superheated steam tables to calculate the fugacity of steam at 300°C and 8 MPa

<sol>

$$f(T = 300^\circ\text{C}, P = 8\text{ MPa}) = P \exp\left[\frac{\underline{G}(300^\circ\text{C}, 8\text{ MPa}) - \underline{G}^{IG}(300^\circ\text{C}, 8\text{ MPa})}{RT}\right]$$

$$\hat{G} = \hat{H} - T\hat{S}$$

$$\hat{H}(300^\circ\text{C}, 8\text{ MPa}) = 2785.0\text{ kJ/kg}, \quad \hat{S}(300^\circ\text{C}, 8\text{ MPa}) = 5.7906\text{ kJ/kg K}$$

$$\hat{G}(300^\circ\text{C}, 8\text{ MPa}) = 2785.0 - 573.15 \times 5.7906 = -533.88\text{ kJ/kg} \Rightarrow \underline{G}(300^\circ\text{C}, 8\text{ MPa}) = -9617.9\text{ J/mol}$$

$$\underline{G}^{IG}(300^\circ\text{C}, 8\text{ MPa}) = \underline{G}^{IG}(300^\circ\text{C}, 0.01\text{ MPa}) + \int_{0.01\text{ MPa}}^{8\text{ MPa}} \underline{V}^{IG} dP$$

$$\hat{G}^{IG}(300^\circ\text{C}, 0.01\text{ MPa}) = \hat{H}(300^\circ\text{C}, 0.01\text{ MPa}) - T\hat{S}(300^\circ\text{C}, 0.01\text{ MPa}) = 3076.5 - 573.15 \times 9.2813 = -2243.1\text{ kJ/kg}$$

$$\Rightarrow \underline{G}^{IG}(300^\circ\text{C}, 0.01\text{ MPa}) = -2243.1 \times 18.015 = -40409\text{ J/mol}$$

$$\underline{G}^{IG}(300^\circ\text{C}, 8\text{ MPa}) = -40409 + \int_{0.01\text{ MPa}}^{8\text{ MPa}} \frac{RT}{P} dP = -40409 + 8.314 \times 573.15 \times \ln(8/0.01) = -8555.7\text{ J/mol}$$

$$f = 8\text{ MPa} \times \exp\left(\frac{-9617.9 - (-8555.7)}{573.15 \times 8.314}\right) = 6.402\text{ MPa}$$

$$\phi = f/P = 6.402/8 = 0.80$$

- ❖ Excellent agreement with the results obtained in Illustration 7.4-1

Fugacity calculation (III)

❖ Illustration 7.4-3

- ❖ Calculate the fugacity of saturated steam at 300°C

<sol>

$$f^V(T = 300^\circ\text{C}, P = 8.581\text{ MPa}) = P \exp\left[\frac{G(300^\circ\text{C}, 8.581\text{ MPa}) - G^{IG}(300^\circ\text{C}, 8.581\text{ MPa})}{RT}\right]$$

$$= 8.581 \exp\left[\frac{-9376.8 - (-8221.6)}{8.314 \times 573.15}\right] = 6.7337\text{ MPa}$$

$$\text{At VLE, } f^V = f^L(300^\circ\text{C}, 8.581\text{ MPa}) = 6.7337\text{ MPa}$$

❖ Illustration 7.4-4 & 7.4-5

- ❖ Calculate the fugacity of pure ethane and pure butane at 373.15 K and 1, 10, 15 bar from virial equation and the Peng-Robinson EOS. $B_{\text{ET}}(373.15\text{ K}) = -1.15 \times 10^{-4}\text{ m}^3/\text{mol}$, $B_{\text{BU}}(373.15\text{ K}) = -4.22 \times 10^{-4}\text{ m}^3/\text{mol}$; T_c , P_c , ω

<sol>

- ❖ Two-term virial equation is applicable up to about 10 - 15 bar.
- ❖ The results from two models are only slightly different.
- ❖ The differences would become larger as the pressure increases or the temperature decrease.

Fugacity coefficient from principle of corresponding states

$$\phi^V = \exp \left[\frac{1}{RT} \int_0^P (\underline{V} - \underline{V}^{IG}) dP \right] = \exp \left[\int_0^P \left(\frac{P\underline{V}}{RT} - 1 \right) \frac{dP}{P} \right] = \exp \left\{ \int_0^{P_r} [Z(T_r, P_r) - 1] d \ln P_r \right\} \quad \text{or}$$

$$\ln \phi^V = \int_0^{P_r} [Z(T_r, P_r) - 1] d \ln P_r$$

Fig. 7.4-1 Generalized fugacity coefficients of pure gases and liquids

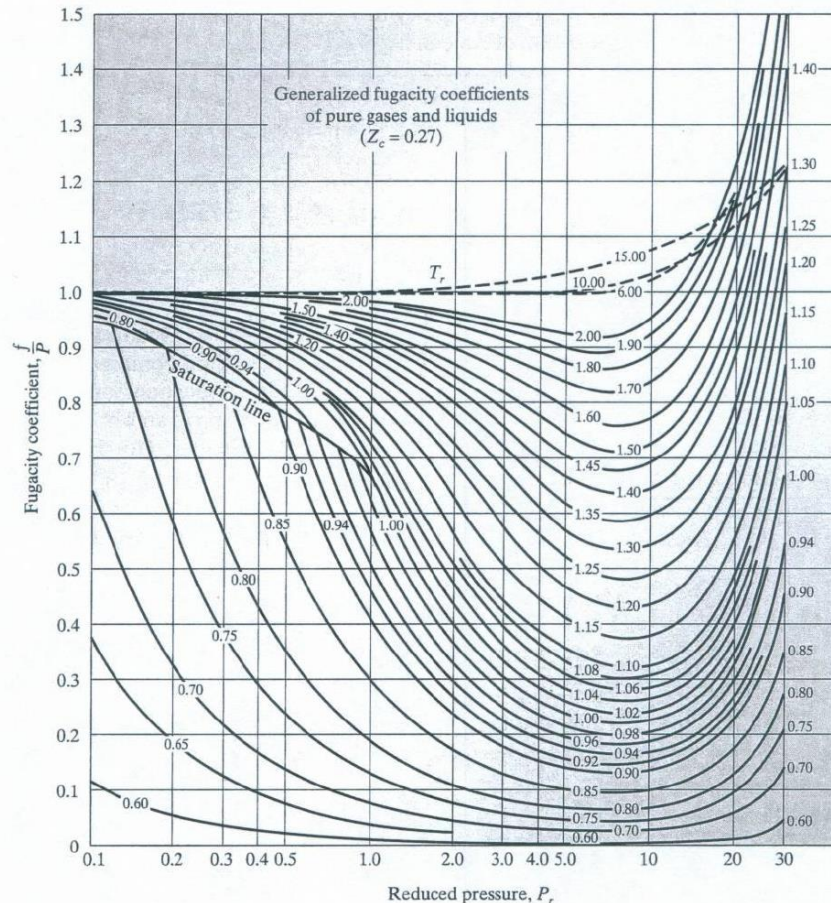


Figure 7.4-1 (Reprinted with permission from O. A. Hougen, K. M. Watson, and R. A. Ragatz, *Chemical Process Principles Charts*, 2nd ed., John Wiley & Sons, New York, 1960.)

Fugacity of a pure liquid

$$\ln\left(\frac{f^L(T,P)}{P}\right) = \frac{1}{RT} \int_{V=\infty}^{V=Z^L RT/P} \left(\frac{RT}{V} - P\right) dV - \ln Z^L + (Z^L - 1)$$

$$\ln \phi^L = (Z^L - 1) - \ln(Z^L - B) - \frac{A}{2\sqrt{2}B} \ln \left[\frac{Z^L + (1 + \sqrt{2})B}{Z^L + (1 - \sqrt{2})B} \right]$$

❖ Fugacity calculation for liquids from some available data

$$\begin{aligned} RT \ln \phi^L &= RT \ln\left(\frac{f^L}{P}\right) = \int_0^P \left(\underline{V} - \frac{RT}{P}\right) dP = \underline{G} - \underline{G}^{IG} \\ &= \int_0^{P^{vap}} \left(\underline{V} - \frac{RT}{P}\right) dP + RT \Delta(\ln \phi)_{\text{phase change}} + \int_{P^{vap}}^P \left(\underline{V} - \frac{RT}{P}\right) dP \\ &= RT \ln \phi_{sat,T} + \int_{P^{vap}}^P \left(\underline{V} - \frac{RT}{P}\right) dP = RT \ln \phi_{sat,T} + \int_{P^{vap}}^P \underline{V} dP - RT \int_{P^{vap}}^P \frac{dP}{P} \\ &= RT \ln \left(\frac{f_{sat}}{P^{vap}} \times \frac{P^{vap}}{P} \right) + \int_{P^{vap}}^P \underline{V} dP \\ f^L(T,P) &= P^{vap} \left(\frac{f}{P} \right)_{sat,T} \exp \left[\frac{1}{RT} \int_{P^{vap}}^P \underline{V} dP \right] = f_{sat}(T) \exp \left[\frac{1}{RT} \int_{P^{vap}}^P \underline{V} dP \right] \end{aligned}$$

- Poynting pressure correction
- Only important at high pressures

Fugacity of liquids and solids

- If neglect the Poynting term

$$f^L(T, P) = f_{sat}(T) = P^{vap}(\phi)_{sat, T}$$

- If total pressure and vapor pressure are sufficiently low.

$$\phi_{sat, T} \approx 1 \Rightarrow f^L(T, P) = P^{vap}(T)$$

except for associated fluids, e.g., acetic acid, which may form dimers

- If liquid is incompressible,

$$f^L(T, P) = P^{vap} \phi_{sat, T} \exp\left[\frac{V(P - P^{vap})}{RT}\right]$$

- Fugacity of a pure solid

$$f^S(T, P) = (P^{sat} \phi_{sat, T}) \exp\left[\frac{1}{RT} \int_{P^{sat}}^P \underline{V}^S dP\right] \approx P^{sat} \exp\left[\frac{1}{RT} \int_{P^{sat}}^P \underline{V}^S dP\right]$$

- Solid at low total pressures

$$f^S(T, P) = P^{sat}(T)$$

- Solid at moderate or high total pressures

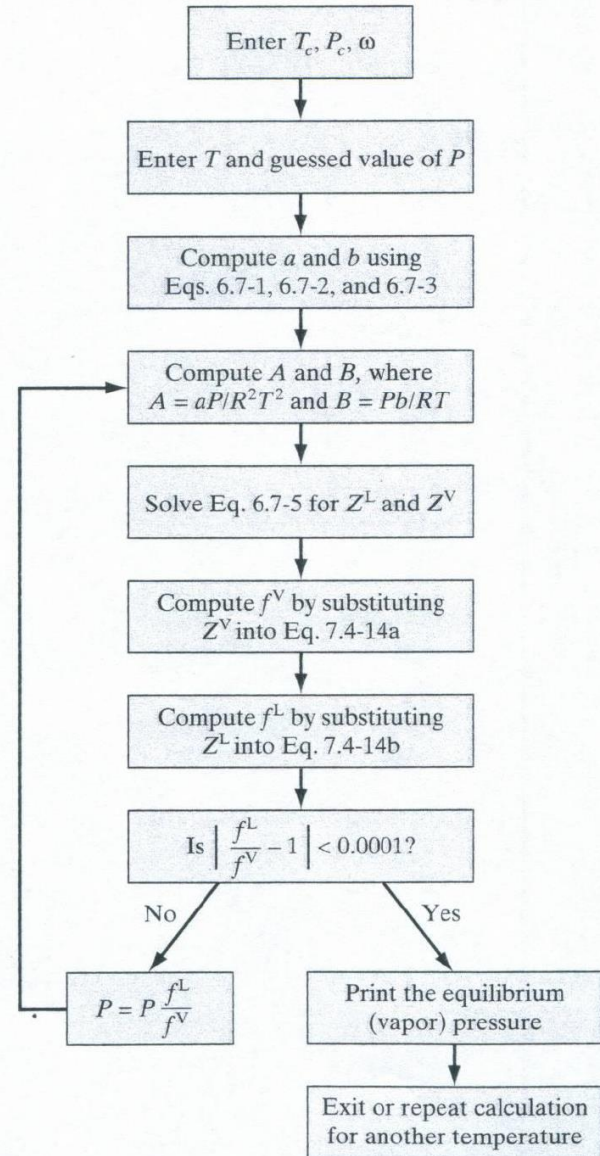
$$f^S(T, P) = P^{sat}(T) \phi_{sat, T} \exp\left[\frac{V^S(P - P^{sat})}{RT}\right] \approx P^{sat}(T) \exp\left[\frac{V^S(P - P^{sat})}{RT}\right]$$

Calculation of Pure Fluid Phase Equilibrium

- Computation of vapor pressure from an EOS
 - ◆ Pure fluid at VLE, $F = 3 - P = 3 - 2 = 1$
 - ◆ Given T , calculate P^{vap} for $\underline{G}^{\text{V}} = \underline{G}^{\text{L}}$ or $f^{\text{V}} = f^{\text{L}}$
 - ◆ Calculation procedure
 - given $T_{\text{C}}, P_{\text{C}}, \omega$
 - given T & guess P
 - solve EOS to find \underline{V}^{L} & \underline{V}^{V} (or Z^{L} & Z^{V})
 - calculate f^{L} and f^{V}
 - check $f^{\text{L}} = f^{\text{V}}$?
 - No, adjust $P^{\text{new}} = P^{\text{old}} \times (f^{\text{L}}/f^{\text{V}})$, then go to step 3
 - Yes, $P^{\text{vap}} = P, \underline{V}^{\text{L}}$ & \underline{V}^{V}

❖ Flow sheet of a computer program for calculation of the P^{vap} using the PR EOS

■ Fig. 7.5-1



❖ Illustration 7.5-1

Compute the **vapor pressure** of oxygen over the temperature range of -200°C to the critical temperature. Also compute specific volume, enthalpy, and entropy along the VLE phase envelope.

Fig. 7.5-3 P^{vap} of O_2 calculated using the PR EOS

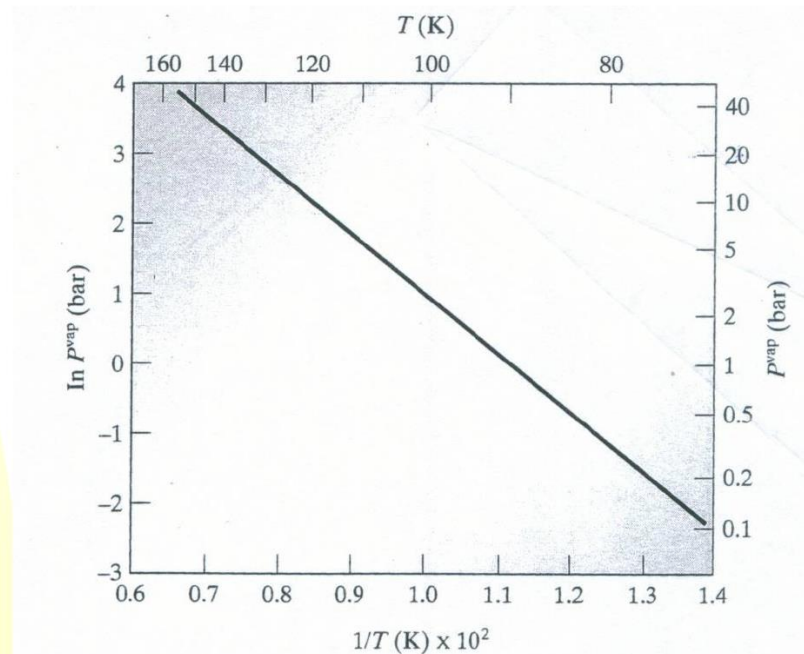


Figure 7.5-3 The vapor pressure of oxygen calculated using the Peng-Robinson equation of state.

Phase Equilibrium: Gibbs Phase Rule

- For a **single-component, single-phase system**, the state (and thermodynamic properties) can be specified by specifying two state variables.
 - Thus, we say a one-component, one-phase system has **2 degrees of freedom**.
 - In order to fix the total size (and total properties), we also need to specify its mass or one of its extensive properties.
- The degree of freedom, $\mathcal{F} = (\text{No. of variables}) - (\text{No. of equations})$
 - Variables, needed to specify the state of a system.
 - Equations, already implied by thermodynamic rules.
- For a **single-component system** with the presence of **more than one phase**, Gibbs phase rule gives the number of degrees of freedom.
 - Let \mathcal{P} = number of phases,
It needs 2 state variable for each phase, total number of variables = $2\mathcal{P}$
Equilibrium conditions ($T^I=T^{II}$, $P^I=P^{II}$, $\overline{G}^I=\overline{G}^{II}$) for every two coexistence phases, total number of independent equations = $3(\mathcal{P}-1)$
$$\mathcal{F} = 2\mathcal{P} - 3(\mathcal{P} - 1) = 3 - \mathcal{P}$$
 (for single-component system)
 - When $\mathcal{P} = 1$, $\mathcal{F} = 2$ (need two state variables to specify the state).
 - When $\mathcal{P} = 2$, $\mathcal{F} = 1$ (need one state variable to specify the state).
 - When $\mathcal{P} = 3$, $\mathcal{F} = 0$ (need no state variables to specify the state).

Phase Equilibrium: Gibbs Phase Rule

- For a single-component system with more than one phase,
 - We need \mathcal{F} ($= 3 - \mathcal{P}$) variables to specify the state of each phase.
 - In addition, we need $\mathcal{P} - 1$ thermodynamic properties to specify the mass distribution among phases in the system, e.g., in the form as

$$\hat{V} = \sum_{i=1}^{\mathcal{P}} x^i \hat{V}^i \qquad x^I + x^{II} + \dots = \sum_{i=1}^{\mathcal{P}} x^i = 1$$

$$\text{or } \hat{\theta} = \sum_{i=1}^{\mathcal{P}} x^i \hat{\theta}^i$$

- For multi-component system with more than one phase

$$\mathcal{F} = \mathcal{P}(C + 1) - (C + 2)(\mathcal{P} - 1) = C + 2 - \mathcal{P} \quad (\text{Gibbs Phase Rule})$$

- C: total number of components in the system.
- For each phase, we need to specify the *composition for C-1 components* and two state variables of each phase of a system. Therefore, there are $(C+1)\mathcal{P}$ variables.
- Equilibrium conditions give C+2 equations between two coexistence phases.

Specification of the Equilibrium Thermodynamic State of a System of Several Phases

❖ The Gibbs Phase Rule for a One-Component System

For one-phase & one-component system, the degree of freedom (d.o.f.) is 2.

For p-phase & one-component system, there are

- ❖ **2P** of independent state variables

- ❖ **3 (P-1)** relationships

$(T^I = T^{II}, T^I = T^{III}, \dots); (P^I = P^{II}, P^I = P^{III}, \dots); (G^I = G^{II}, G^I = G^{III}, \dots)$

- ❖ **F = 2P - 3 (P-1) = 3 - P**

- ❖ The character of the variable to be specified as d.o.f is not completely arbitrary.

e.g., VLE for one-component system, $F = 3 - 2 = 1$

- ❖ Specify either \underline{V}^L or $\underline{V}^V \Rightarrow$ Fix the thermodynamic state of both phases.

- ❖ Specify either \underline{V} or any other molar property of the two phases combined is not suitable for d.o.f. specification.

- ❖ To fix the thermodynamic state of each of p phase in equilibrium, we should specify **(3 - P)** properties of the **individual phases**.

$$\underline{V} = x^V \underline{V}^V + (1 - x^V) \underline{V}^L$$

Determine the distribution of mass or number of moles between the phases for a one-component system

❖ **Variables:** x^I, x^{II}, \dots, x^P (P variables)

❖ **Relation:** $\sum_{i=1}^P x^i = 1$ (1 relation)

❖ **Need (P – 1) additional specific properties of the multiphase system**

❖ $\Rightarrow \sum_{i=1}^P x^i \hat{\theta}^i = \hat{\theta}$ (*thermodynamic property per unit mass for whole system*)

❖ **e.g., VLE for one-component system (3 – P = 1; P-1 = 1)**

Given T \Rightarrow $P^{\text{vap}}, \underline{V}^L, \underline{V}^V, \underline{H}^L, \underline{H}^V, \underline{S}^L, \underline{S}^V, \dots$

If we know any one thermodynamic property of the two phases mixture (e.g., \underline{V}), we can calculate the distribution of mass or no. of moles, then calculate $\underline{H}, \underline{S}, \dots$

$$\underline{V} = x^V \underline{V}^V + (1 - x^V) \underline{V}^L \Rightarrow \text{solve } x^V, \text{ and thus } x^L.$$

❖ **To determine the total size of the system, we need one extensive property, e.g., V, then $N^V = (V/\underline{V}) x^V$ and $N^L = (V/\underline{V}) x^L$**

Example: Triple point of a pure substance

- ❖ $F = 3 - P = 0$
 - ❖ d.o.f. = 0, no state properties of the individual phases should be specified.
 - ❖ Calculate T_{tr} , P_{tr} , from $f^S = f^L$ and $f^L = f^V$, then \underline{V}^S , \underline{V}^L , \underline{V}^V , \underline{H}^S , \underline{H}^L , \underline{H}^V ,
- ❖ $P - 1 = 2$
 - ❖ Two additional variables should be specified to determine the distribution of mass between vapor, liquid, solid.
 - ❖ e.g., \underline{V} and $\underline{H} \Rightarrow x^V, x^L$, thus x^S and then \underline{S} , \underline{G} .,
- ❖ 1 extensive property
 - ❖ e.g., V is given, then total number of mole $N = V/\underline{V}$ and
 - ❖ $N^V = (V/\underline{V}) x^V$; $N^L = (V/\underline{V}) x^L$; $N^S = (V/\underline{V}) x^S$

❖ **Duhem's Theorem:** For a closed system at given masses of each species, the no. of independent variables is **2**

$$\text{❖ } [2 + (C-1)P + P] - [(P-1)C + C] = [(C+1)P + P] - [(C+2)(P-1) + C] = 2$$

Thermodynamic Properties of Phase Transitions

- ❖ In a P-T diagram
 - ❖ Slope of the VLE line => Rate of change of the vapor pressure of the liquid with temperature
 - ❖ Slope of the VSE line => Rate of change of the sublimation pressure of the solid with temperature
 - ❖ Inverse of the slope of the SLE line => The change of the melting temperature of the solid with pressure.
- ❖ At phase equilibrium,

$$\underline{G}^I(T, P) = \underline{G}^{II}(T, P)$$

or

$$d\underline{G}^I = d\underline{G}^{II}$$

$$\Rightarrow \underline{V}^I dP - \underline{S}^I dT = \underline{V}^{II} dP - \underline{S}^{II} dT$$

Since P and T are the same in both phases,

$$\left(\frac{\partial P^{sat}}{\partial T} \right)_{\underline{G}^I = \underline{G}^{II}} = \frac{\underline{S}^I - \underline{S}^{II}}{\underline{V}^I - \underline{V}^{II}} = \frac{\underline{\Delta S}}{\underline{\Delta V}} = \frac{\underline{\Delta H} / T}{\underline{\Delta V}}$$

Clapeyron equation

Note that

$$\left(\frac{\partial P}{\partial T} \right)_{\underline{G}^I = \underline{G}^{II}} \neq 0 \text{ (not horizontal) due to } \underline{\Delta S} \neq 0 \text{ \& } \underline{\Delta H} \neq 0$$

$$\left(\frac{\partial P}{\partial T} \right)_{\underline{G}^I = \underline{G}^{II}} \neq \infty \text{ (not vertical) due to } \underline{\Delta V} \neq 0$$

Generally,

$$\underline{\Delta}_{fus} \underline{H} > 0 \text{ and } \underline{\Delta}_{fus} \underline{V} > 0 \Rightarrow \left(\frac{\partial P}{\partial T} \right)_{\underline{G}^I = \underline{G}^{II}} > 0$$

$\Rightarrow T_m$ increases as P increase

Water is an exception,

$$\underline{\Delta}_{fus} \underline{H} > 0 \text{ and } \underline{\Delta}_{fus} \underline{V} < 0 \Rightarrow \left(\frac{\partial P}{\partial T} \right)_{\underline{G}^I = \underline{G}^{II}} < 0$$

$\Rightarrow T_m$ decreases as P increase

Clausius – Clapeyron Equation

Since $\underline{V}^V \gg \underline{V}^L \Rightarrow \Delta\underline{V} \approx \underline{V}^V$

Assuming that vapor phase is ideal $\Rightarrow \underline{V}^V = RT / P$

$$\Rightarrow \frac{dP^{\text{vap}}}{dT} = \frac{P^{\text{vap}} \Delta \underline{H}^{\text{vap}}}{RT^2} \text{ where } \Delta \underline{H}^{\text{vap}} = \underline{H}^V - \underline{H}^L$$

or

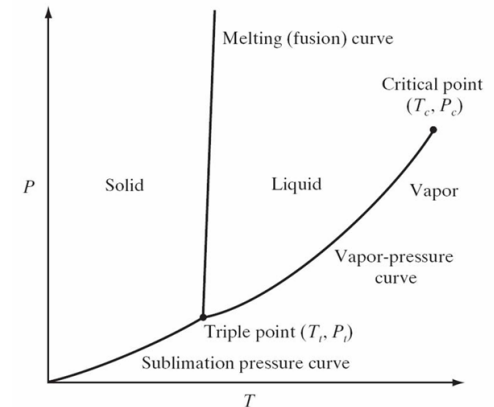
$$\Rightarrow \frac{d \ln P^{\text{vap}}}{dT} = \frac{\Delta \underline{H}^{\text{vap}}}{RT^2}$$

Clausius-Clapeyron equation

$$\Rightarrow \ln \frac{P^{\text{vap}}(T_2)}{P^{\text{vap}}(T_1)} = \int_{T_1}^{T_2} \frac{\Delta \underline{H}^{\text{vap}}}{RT^2} dT$$

Assuming that $\Delta \underline{H}^{\text{vap}} \neq f(T)$

$$\ln \frac{P^{\text{vap}}(T_2)}{P^{\text{vap}}(T_1)} = \frac{-\Delta \underline{H}^{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$



❖ Illustration 7.7-1: Use of the Clausius-Clapeyron Equation

Correlations of Vapor Pressures

Integrate the Clausius - Clapeyron Equation

$$\Rightarrow \ln P^{\text{vap}} = \frac{-\Delta H^{\text{vap}}}{RT} + C \Rightarrow \ln P^{\text{vap}} = A - \frac{B}{T} \text{ where } B = \Delta H^{\text{vap}} / R$$

Antoine equation

$$\Rightarrow \ln P^{\text{vap}} = A - \frac{B}{T + C} \quad (1 - 200 \text{ kPa})$$

Other vapor pressure correlations

Riedel Equation: $\ln P^{\text{vap}} = A + \frac{B}{T} + C \ln T + DT^6$

Harlecher - Braun Equation: $\ln P^{\text{vap}} = A + \frac{B}{T} + C \ln T + \frac{DP^{\text{vap}}}{T^2}$ (from low P up to critical P)

Illustration 7.7-2: Interrelating the Thermodynamics of Properties of Phase Changes

- Estimate **heat of sublimation** of ice, **heat of vaporization** of water, **heat of fusion** of ice, the **triple point** of water from the Clausius-Clapeyron equation with the sublimation pressure and vapor pressure data of water.

ice	T (°C)	P ^{vap} (mmHg)	water	T (°C)	P ^{vap} (mmHg)
	-4	3.28		2	5.294
	-2	3.88		4	6.101

<sol> (a)

$$\frac{\Delta_{sub}H}{R} = -\frac{\ln\left(\frac{3.88}{3.28}\right)}{\frac{1}{271.15} - \frac{1}{269.15}} = 6130 \Rightarrow \Delta_{sub}H = 50.97 \text{ kJ/mol}$$

(b)

$$\frac{\Delta_{vap}H}{R} = -\frac{\ln\left(\frac{6.101}{5.294}\right)}{\frac{1}{277.15} - \frac{1}{275.15}} = 5410 \Rightarrow \Delta_{vap}H = 44.98 \text{ kJ/mol}$$

(c)

$$\Delta_{fus}H = H_{liquid} - H_{solid} = (H_{vapor} - H_{solid}) - (H_{vapor} - H_{liquid}) = \Delta_{sub}H - \Delta_{vap}H = 5.99 \text{ kJ/mol}$$

(d)

At triple point temperature (T_t), $P^{sub} = P^{vap} = P_t$.

Solve T_t & P_t from the following simultaneous equations:

$$\frac{\Delta_{sub}H}{R} = 6130 = -\frac{\ln(P_t / 3.88)}{\frac{1}{T_t} - \frac{1}{271.15}}$$

$$\frac{\Delta_{vap}H}{R} = 5410 = -\frac{\ln(P_t / 5.294)}{\frac{1}{T_t} - \frac{1}{275.15}}$$

$$\Rightarrow T_t = 273.279 \text{ K} \ \& \ P_t = 4.627 \text{ mmHg}$$

$$\Rightarrow \text{Experimental values: } T_t = 273.16 \text{ K} \ \& \ P_t = 4.579 \text{ mmHg}$$

Estimate sublimation pressures and vapor pressures from the Clausius-Clapeyron equation

$$\ln\left(\frac{P^{sub}}{3.88}\right) = -6130\left(\frac{1}{T} - \frac{1}{271.15}\right)$$

$$\ln\left(\frac{P^{vap}}{5.294}\right) = -5410\left(\frac{1}{T} - \frac{1}{275.15}\right)$$

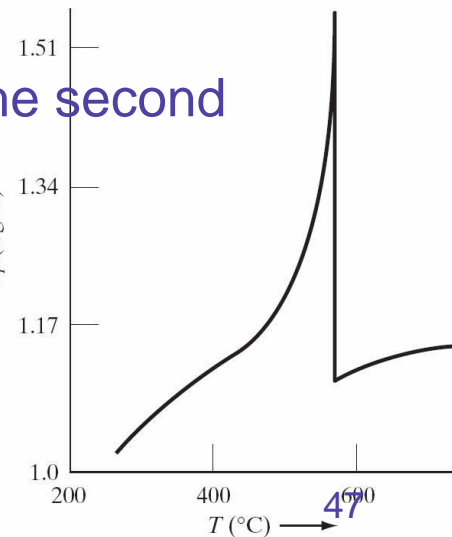
$$\text{e.g., } P^{sub}(-10^\circ \text{C}) = 1.951 \text{ mmHg} \ (\text{Expt'l: } 1.950 \text{ mmHg})$$

$$P^{vap}(10^\circ \text{C}) = 9.227 \text{ mmHg} \ (\text{Expt'l: } 9.209 \text{ mmHg})$$

Phase Transition Properties

- First-order phase transition, e.g., V-L transition
 - $\underline{G}^V = \underline{G}^L$, \underline{G} is continuous during transition.
 - $\underline{V}^V \neq \underline{V}^L$, $\underline{S}^V \neq \underline{S}^L$, $\underline{H}^V \neq \underline{H}^L$, \underline{V} , \underline{S} , \underline{H} are discontinuous during transition.
 - C_V , C_P are infinite during phase transition. $\left(\frac{\partial \underline{G}}{\partial T}\right)_P = -\underline{S}$ and $\left(\frac{\partial \underline{G}}{\partial P}\right)_T = \underline{V}$
- Second-order transition, e.g., structural rearrangement of quartz
 - \underline{V} , \underline{S} , \underline{G} , are continuous during transition.
 - Discontinuous during phase transition occurs at the second order derivatives of \underline{G} , e.g., C_P .
- Third-order transition
 - ... (no expt observation yet)

$$\left(\frac{\partial^2 \underline{G}}{\partial T^2}\right)_P = -\left(\frac{\partial \underline{S}}{\partial T}\right)_P = -\frac{C_P}{T}$$



Thermodynamic Properties of Small System

- For small systems, surface phenomena contribute more significantly to the properties of a system.
 - Surface tension contribution to work (force-displacement) cannot be neglected. Work due the effect of surface tension = σdA .

E-balance for a closed system (no W_S),

$$\frac{dU}{dt} = \dot{Q} - P \frac{dV}{dt} - \sigma \frac{dA}{dt}$$

For spherical drops, $V = 4\pi r^3/3$, $A = 4\pi r^2$.

$$\frac{dU}{dt} = \dot{Q} - \left(P + \frac{2\sigma}{r} \right) \frac{dr}{dt}$$

$$\text{or } \frac{dU}{dt} = \dot{Q} - P_{\text{int}} \frac{dr}{dt}$$

$$r \rightarrow 0, P_{\text{int}} \gg P$$

$$r \rightarrow \infty, P_{\text{int}} \rightarrow P$$

- Surface charge contribution, if any, and others.

Thermodynamic Properties of Small System

Table 7.8-1 Surface Tension at a Liquid-Vapor Interface

Liquid	Temperature (°C)	σ (dyne/cm)*
Water	20	72.9
	25	72.1
Methanol	20	22.7
Ethanol	20	22.1
1-Octanol	20	27.6
Benzene	20	28.9
Aniline	20	43.4
Glycerol	20	64.0
Perfluorohexane	20	11.9
<i>n</i> -Heptane	20	20.4
<i>n</i> -Octane	20	21.6
Propionic acid	20	26.7
Mercury	20	487
Sodium	139	198
Sodium chloride	1073	115

*Divide by 1000 for J/m².

Table 7.8-2 Interfacial Tension at a Liquid-Liquid Interface

Liquid	Temperature (°C)	σ (dyne/cm)*
Water/ <i>n</i> -butyl alcohol	20	1.8
Water/mercury	20	415
Water/benzaldehyde	20	15.5
Water/diethylene glycol	25	57
Mercury/ <i>n</i> -hexane	20	378

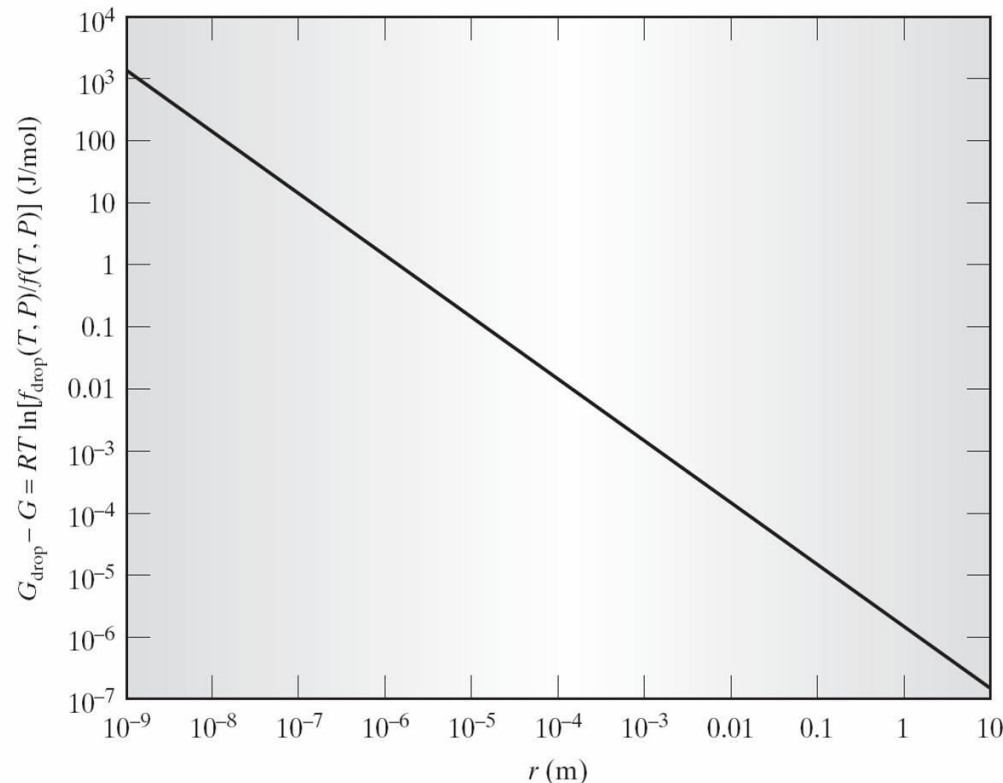
*Divide by 1000 for J/m².

Thermodynamic Properties of Small System

- For the calculation of fugacity of small droplets

$$f_{drop}^L(T, P) = f^L(T, P_{int}) = f^L\left(T, P + \frac{2\sigma}{r}\right) = f^L(T, P) \exp\left(\frac{2\sigma V^L}{rRT}\right)$$

- The fugacity of the drop is always larger than the fugacity of the bulk liquid at the same T and P.



Thermodynamic Properties of Small System

- Effect of the larger fugacity of the drop than that of the bulk liquid at the same T and P:
 - The boiling point of small drops will be lower than that of the bulk liquid.
 - Or, small drops vaporize more easily. The vaporization process is accelerated due to gradual decrease in droplet size.
 - Condensation of vapor into drops will not be as easy as that of the bulk liquid. A lower T will be needed which is the subcooling.
 - Superheating of boiling liquid can also occur.
 - Similar phenomena occur in other phase transitions, e.g., crystallization, solidification.
 - Ostwald ripening.