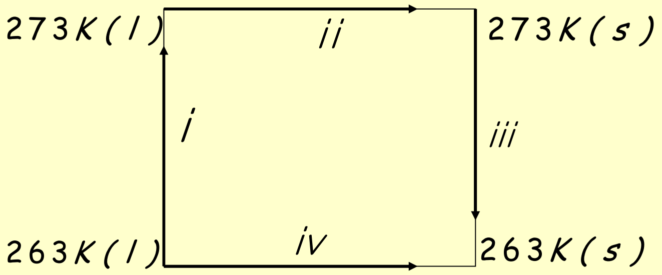
Thermodynamics of Materials

12th Lecture

2008. 4. 21 (Monday)

Freezing of Supercooled Water

$-10^\circ C$ water (l) $\rightarrow -10^\circ C$ ice (s)



For H_2O

at 273 K, $\Delta H_m = \Delta H_{(s\to l)} = 6008\ J/mol$

$S_{H2O(l),298K} = 70.08\ J/K$

$S_{H2O(s),298K} = 44.77\ J/K$

$C_{p,H_2O(l)} = 75.44\ J/K$

$C_{p,H_2O(s)} = 38\ J/K$

$$\Delta G_{(l\to s)} = \Delta H_{(l\to s)} - T\Delta S_{(l\to s)}$$

$$\Delta H_{i} = \int_{263}^{273} 75.44 dT = 754.4$$

$$\Delta H_{ii} = -\Delta H_m = -6008\ J$$

$$\Delta H_{iii} = \int_{273}^{263} 38 dT = -380$$

$$\therefore\ \Delta H_{(l\to s)} = \Delta H_i + \Delta H_{ii} + \Delta H_{iii} = -5633.6\ J$$

$$\Delta S_{i} = S_{273(l)} - S_{263(l)}$$

$$= (S_{298(l)} + \int_{298}^{273} C_{p(l)} d \ln T)$$

$$-(S_{298(l)} + \int_{298}^{263} C_{p(l)} d \ln T) = 75.44 \ln \frac{273}{263}$$

$$\Delta S_{ii} = \frac{-6008}{273} = -22.007$$

$$\Delta S_{iii} = S_{263(s)} - S_{273(s)} = 38 \ln \frac{263}{273}$$

$$\therefore \Delta S_{(l \to s)} = \Delta S_{i} + \Delta S_{ii} + \Delta S_{iii} = -20.61 \ J/K$$

$$\Delta G_{(l \to s)} = \Delta H_{(l \to s)} - T\Delta S_{(l \to s)}$$

$$\therefore \Delta H_{(l \to s)} = \Delta H_{i} + \Delta H_{ii} + \Delta H_{iii} = -5633.6 \ J$$

$$\therefore \Delta S_{(l \to s)} = \Delta S_{i} + \Delta S_{ii} + \Delta S_{iii} = -20.61 \ J/K$$

$$\therefore \Delta G = -5633.6 + 263 \times 20.61 = -213 \ J / \text{mole}$$

$$dG = -SdT + VdP$$

$$\text{at constant } P \rightarrow dG = -SdT$$

$$\Delta G_{273k \rightarrow 263k} = \int -SdT$$

$$S = S_{298k} + \int_{298}^{T} \frac{C_p}{T} dT = 70.08 + 75.44 \ln \frac{T}{298}$$

$$\Delta G_{273 \rightarrow 263K}^{water} = -\int_{273}^{263} \left[70.08 + 75.44 \ln \left(\frac{T}{298} \right) \right] dT$$

$$= 700.8 + 75.44[(273 \ln 273 - 273) -$$
$$(263 \ln 263 - 263)] - 754.4 \ln 298$$
$$= 620.7$$

$$\Delta G_{273k \rightarrow 263k}^{water} = 620.7 \ J / \text{mole}$$

$$\Delta G_{273 \rightarrow 263K}^{ice} = -\int_{273}^{263} \left[44.77 + 38 \ln \left(\frac{T}{298} \right) \right] dT$$

$$= 447.7 - 380 \ln 298$$
$$-38[(263 \ln 263 - 263) - 273 \ln 273 - 273)]$$
$$= 407.4$$

$$\Delta G_{273 \rightarrow 263K}^{ice} = 407.4 \ J / \text{mole}$$

$$\therefore \Delta G_{263k}^{water\to ice} = \Delta G_{273\to 263K}^{ice} - \Delta G_{273k\to 263k}^{water}$$

$$= 407.4 - 620.7 = -213.3 \ J/mole$$

$$\therefore \Delta G = -213 \ J/mole$$

i), ii) 결과 동일

i)의 경우 상전이시 ΔH를 알아야 하고

ii)의 경우 S_{298}또는 특정 온도에서 S를 알아야 한다.

What would be the driving force for precipitation ($\Delta G_{290K}^{vapor\to water}$) when the water vapor saturated at 300K is supercooled to 290K?

What would be the driving force for precipitation ($\Delta G_{290K}^{vapor \rightarrow water}$) when the water vapor saturated at 300K is supercooled to 290K?

$$\Delta G = \Delta H - T\Delta S$$

$$dG = VdP - SdT \rightarrow \Delta G = \int -SdT$$

$$\Delta G_{300 \rightarrow 290K} = -RT\ln\left(\frac{P}{P_{290}^{eq}}\right) = -RT\ln\left(\frac{P_{300}^{eq}}{P_{290}^{eq}}\right)$$

Why is the critical nucleus defined by the condition of $\left(\frac{\partial G}{\partial r}\right)_{P,T} = 0$ instead of the condition of $\Delta G_{P,T}=0$?

Open System

$$dU = TdS - PdV + dU_{matter}$$

$$dG = VdP - SdT + dG_{matter}$$

dU_{matter} or $dG_{matter} \propto$?

$$dG_{matter} \propto dn \rightarrow dG_{matter} = \mu dn$$

$$dG = VdP - SdT + \Sigma \mu_i dn_i$$

Chemical Potential

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} = \mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j} = \left(\frac{\partial F}{\partial n_i}\right)_{T,V,n_j}$$

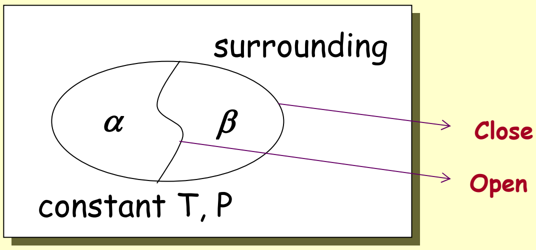
$$dU = TdS - PdV + \sum \mu_i dn_i$$

$$dH = TdS + VdP + \sum \mu_i dn_i$$

$$dF = -SdT - PdV + \sum \mu_i dn_i$$

$$dG = -SdT + VdP + \sum \mu_i dn_i$$

Equilibrium between α and β for one component system



What is the G of α and β system ?

$$G = G^{\alpha}n^{\alpha} + G^{\beta}n^{\beta} = \mu^{\alpha}n^{\alpha} + \mu^{\beta}n^{\beta}$$

$G^{\alpha}, G^{\beta} \rightarrow$ molar free energy of α and β

$$\mu = \left(\frac{\partial G'}{\partial n}\right)_{T,P} = \left[\frac{\partial (nG)}{\partial n}\right]_{T,P} = G\left(\frac{\partial n}{\partial n}\right)_{T,P} = G$$

For one component system

$$n = n^{\alpha} + n^{\beta} = \text{const} \rightarrow dn^{\beta} = -dn^{\alpha}$$

$$dG = G^{\alpha}dn^{\alpha} + G^{\beta}dn^{\beta} = \mu^{\alpha}dn^{\alpha} + \mu^{\beta}dn^{\beta}$$

$$= \left(G^{\alpha} - G^{\beta}\right)dn^{\alpha} < 0 \quad \text{for an irreversible process}$$

$$= \left(\mu^{\alpha} - \mu^{\beta}\right)dn^{\alpha} < 0$$

if $G^{\alpha} > G^{\beta},\ dn^{\alpha} < 0 \quad \left(\text{if } \mu^{\alpha} > \mu^{\beta},\ dn^{\alpha} < 0\right)$

if $G^{\alpha} < G^{\beta},\ dn^{\alpha} > 0 \quad \left(\text{if } \mu^{\alpha} < \mu^{\beta},\ dn^{\alpha} > 0\right)$

$\mu^{\alpha} = G^{\alpha} \rightarrow$ for one component system

Equilibrium between α and β for multi-component system

$\mu_A^{\alpha} = G_A^{\alpha} \leftarrow$ multicomponent system

chemical potential of A in α

= partial molar Gibbs free energy of A in α

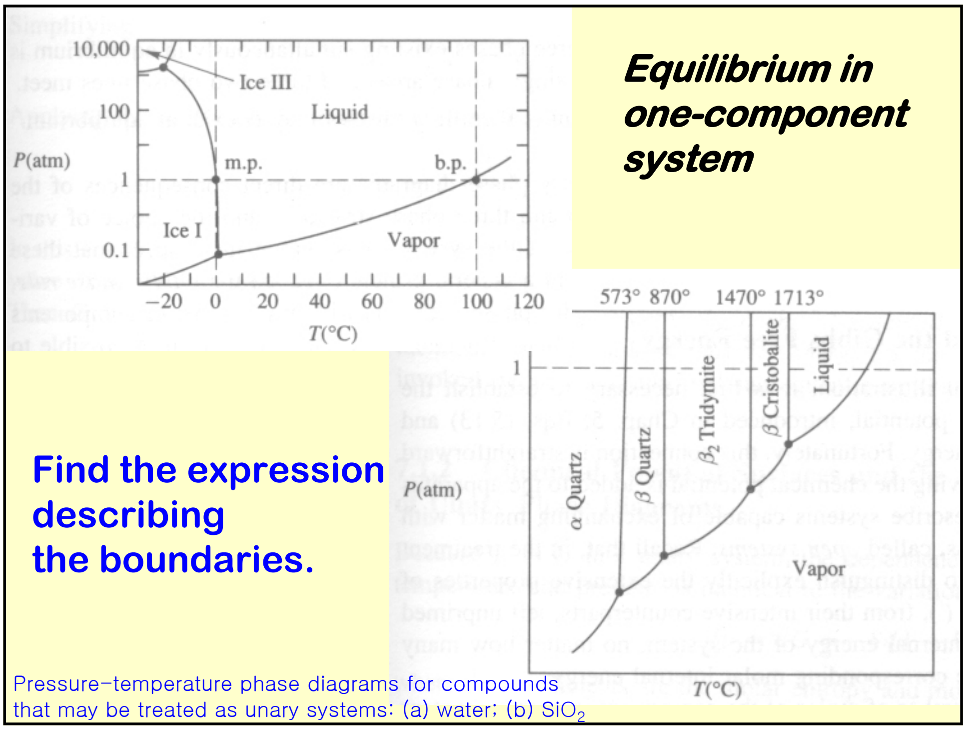
$\mu_A^{\alpha} = \mu_A^{\beta}$

→ Equilibrium condition for the transfer of A between α and β

$\Delta\mu_A^{\alpha\rightarrow\beta} = \mu_A^{\beta} - \mu_A^{\alpha} < 0$

→ Irreversible transfer of A from α to β

Equilibrium in one-component system



Find the expression describing the boundaries.

Pressure-temperature phase diagrams for compounds that may be treated as unary systems: (a) water; (b) SiO_2

Equilibrium between α and β for one component system

Chemical potential or molar Gibbs free energy should be the same.

$$\mu^{\alpha} = \mu^{\beta} \qquad G^{\alpha} = G^{\beta} \rightarrow dG^{\alpha} = dG^{\beta}$$

$$dG = -SdT + VdP$$

→ G, S, V : molar quantity

$$d\mu^{\alpha} = -S^{\alpha}dT^{\alpha} + V^{\alpha}dP^{\alpha}$$

$$d\mu^{\beta} = -S^{\beta}dT^{\beta} + V^{\beta}dP^{\beta}$$

$$-S^{\alpha}dT^{\alpha} + V^{\alpha}dP^{\alpha} = -S^{\beta}dT^{\beta} + V^{\beta}dP^{\beta}$$

$$(S^{\beta} - S^{\alpha})dT = (V^{\beta} - V^{\alpha})dP$$

$$\Delta S^{\alpha\rightarrow\beta}dT = \Delta V^{\alpha\rightarrow\beta}dP$$

$$\frac{dP}{dT} = \frac{\Delta S^{\alpha\rightarrow\beta}}{\Delta V^{\alpha\rightarrow\beta}} \quad \rightarrow \quad \frac{dP}{dT} = \frac{\Delta H^{\alpha\rightarrow\beta}}{T\Delta V^{\alpha\rightarrow\beta}}$$

note conjugates of P, V and S, T

⇒ Clausius-Clapeyron equation

$$\frac{dP}{dT} = \frac{\Delta H^{\alpha\rightarrow\beta}}{T\Delta V^{\alpha\rightarrow\beta}}$$

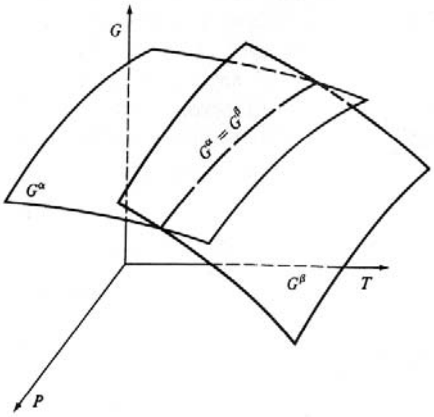


Figure 14. Illustration of the condition for the coexistence of two phases α and β. The intersection of the two free energy surfaces is a line $G^\alpha = G^\beta$ along which α and β coexist.

$$\frac{dP}{dT} = \frac{\Delta H^{l\to s}}{T\Delta V^{l\to s}}$$

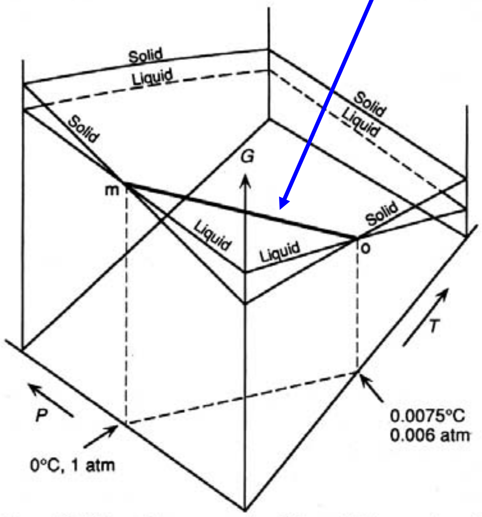
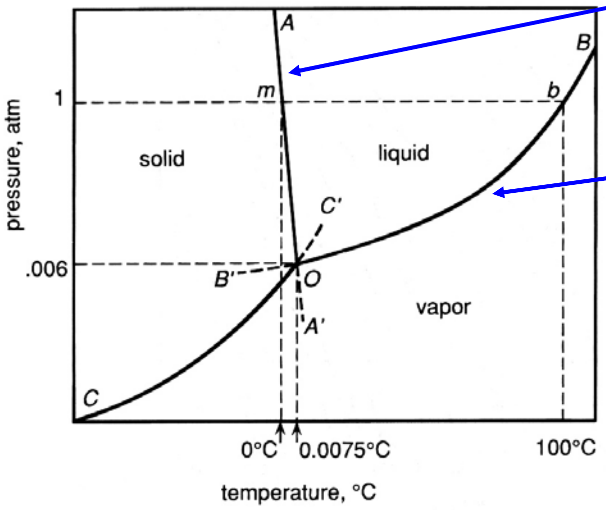


Figure 7.8 Schematic representation of the equilibrium surfaces of the solid and liquid phases of water in *G-T-P* space.

$$\frac{dP}{dT} = \frac{\Delta H^{l\to s}}{T\Delta V^{l\to s}}$$



equilibrium vapor pressure

Figure 7.11 Schematic representation of part of the phase diagram for H_2O.

Equilibrium Vapor Pressure

$$\frac{dP}{dT} = \frac{\Delta H^{l\to s}}{T\Delta V^{l\to s}} \qquad \Delta V^{\alpha\to G} = V^G - V^\alpha \cong V^G = \frac{RT}{P}$$

$$\frac{dP}{dT} = \frac{\Delta H}{TV} = \frac{\Delta H}{T\left(\frac{RT}{P}\right)} = \frac{P\Delta H}{RT^2}$$

$$\frac{dP}{P} = \frac{\Delta H}{RT^2}dT \quad \to \quad \ln\left(\frac{P}{P_0}\right) = \frac{\Delta H}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)$$

$$\ln\left(\frac{P}{P_0}\right) = \frac{\Delta H}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)$$

$$P = P_0 \exp\left(\frac{\Delta H}{RT_0}\right)\exp\left(-\frac{\Delta H}{RT}\right) = A\exp\left(-\frac{\Delta H}{RT}\right)$$

$$P = A\exp\left(-\frac{\Delta H}{RT}\right)$$

Equilibrium Vapor Pressure
→ Boltzman distribution

$$\ln\left(\frac{P}{P_0}\right) = \frac{\Delta H}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)$$

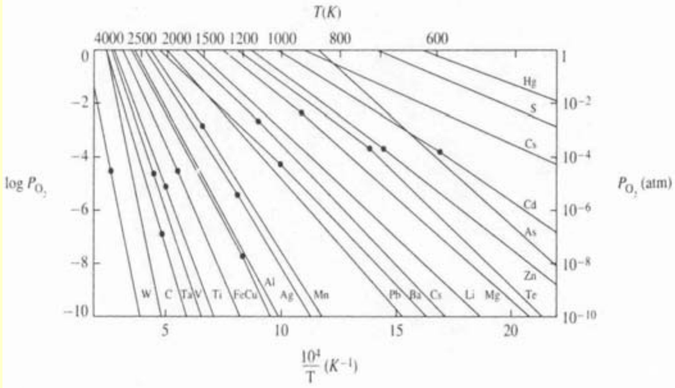


FIGURE 7.6

Compilation of vapor pressure curves for common elements, plotting the logarithm of the vapor pressure versus $1/T$. A change in slope corresponds to the melting point [7.5].

$$\ln\left(\frac{P}{P_0}\right) = \frac{\Delta H}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)$$

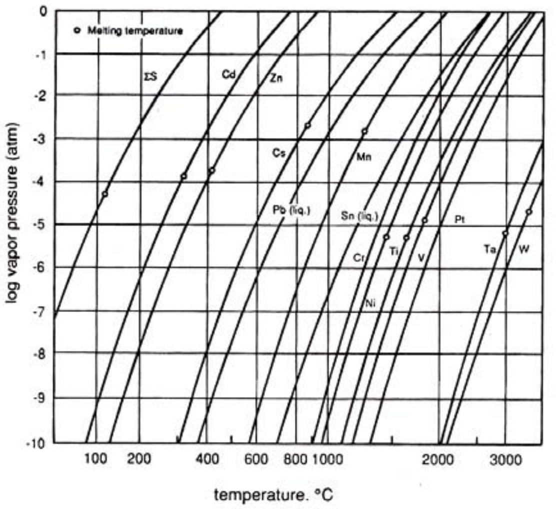


Figure 7.10 The vapor pressures of several elements as functions of temperature.

Why is P-T diagram different from P-V or T-X diagram?

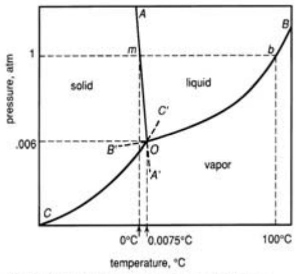


Figure 7.11 Schematic representation of part of the phase diagram for H_2O.

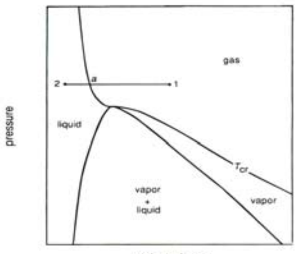
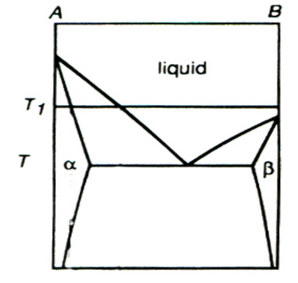


Figure 8.2 The fields of phase stability of a typical real gas



Intensive parameters of P, T, and μ are the same at equilibrium.

→ Equilibrium along the phase boundary

P-T diagram

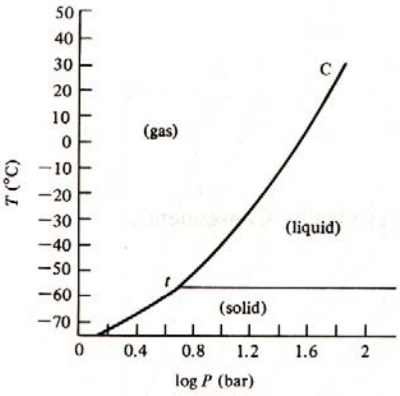


Figure 18. Pressure–temperature phase diagram for CO_2. (*From Gas Encyclopaedia* [*15*].)

P : intensive parameter
T : intensive parameter

P-V diagram

V : extensive parameter

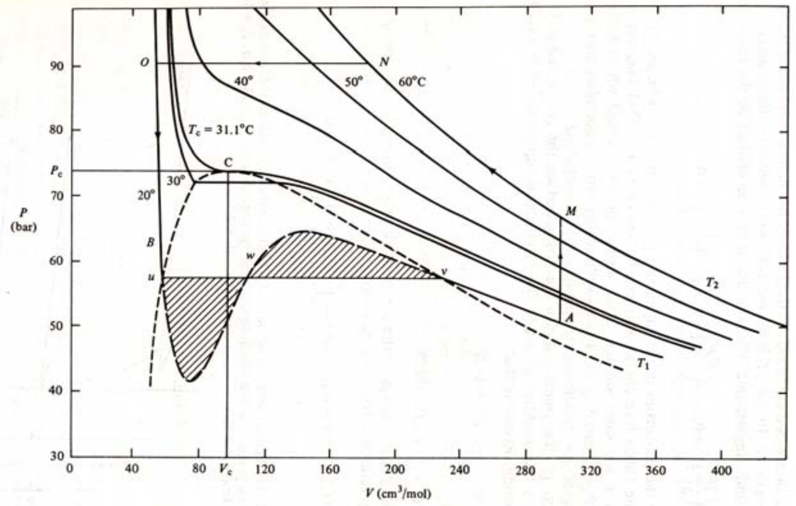
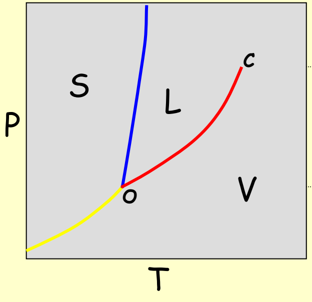


Figure 19. Pressure–volume diagram for CO$_2$. The coordinates of the critical point are $V_c = 94.9$ cm^3/mol and $P_c = 73.8$ bar [15] (1 bar = 0.987 atm). The liquid *u* being in equilibrium with the gas *v*, the two shaded areas must be equal. It is possible to pass from the gas *A* to the liquid *B* either by compression and condensation (*AvuB*), or by the process *AMNOB* in which CO$_2$ remains always homogeneous.

Alternative Representations of Unary Phase Diagrams

$P^{\alpha} = P^{L}$ $T^{\alpha} = T^{L}$

In two phase equilibrium

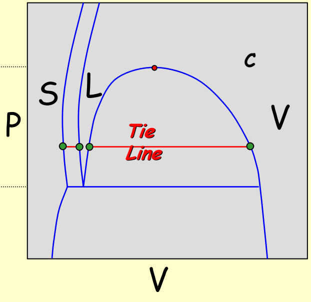


No tie-line

Intensive-Intensive

$P^{\alpha} = P^{L}$ $V^{\alpha} \neq V^{L}$

In two phase equilibrium

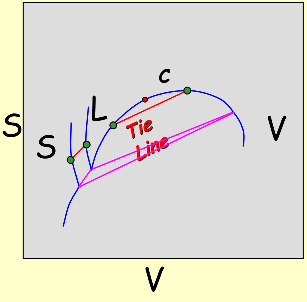


Horizontal tie-line

Intensive-Extensive

$S^{\alpha} \neq S^{L}$ $V^{\alpha} \neq V^{L}$

In two phase equilibrium



Inclined tie-line

Extensive-Extensive

Compare with T-X and Ternary diagrams.

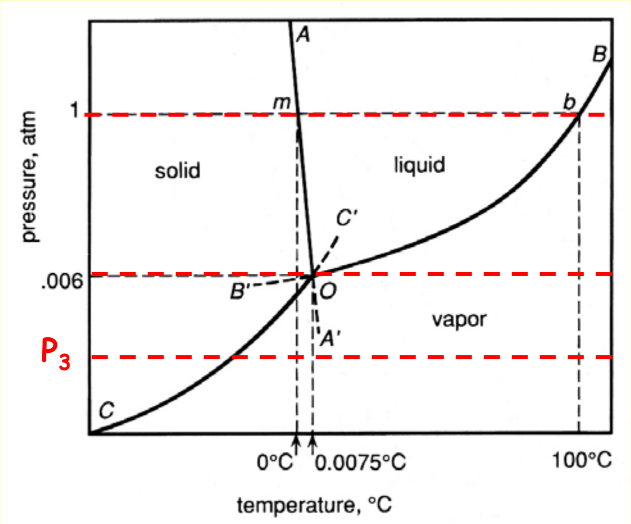


Figure 7.11 Schematic representation of part of the phase diagram for H_2O.

Draw G-T diagram at P = 1, 0.006 and P_3.

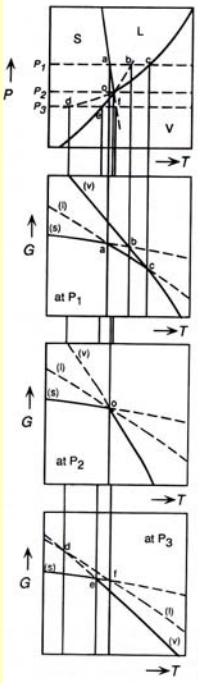


Figure 7.12 *(a)* Schematic representation of the constant-pressure variations of the molar Gibbs free energies of solid, liquid, and vapor H_2O at pressures above, at, and below the triple-point pressure.

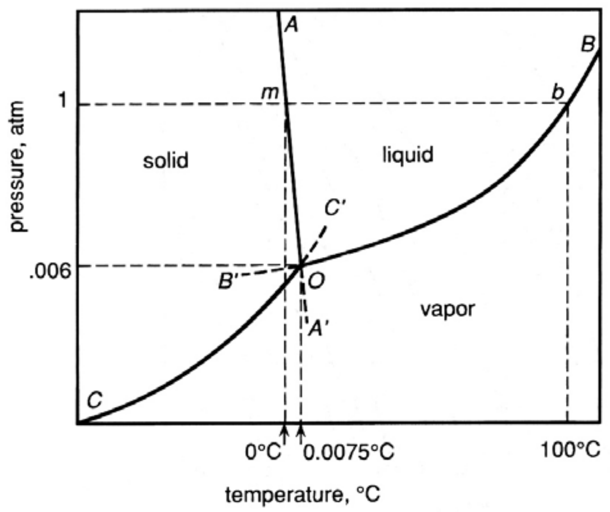


Figure 7.11 Schematic representation of part of the phase diagram for H_2O.

Draw G-P diagram at temperatures above, at and below the triple point.

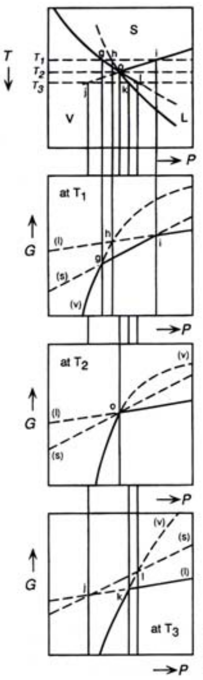
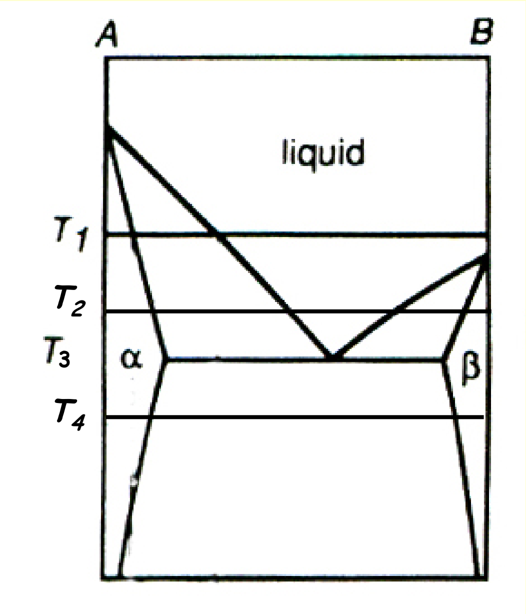


Figure 7.12 *(b)* Schematic representation of the constant-temperature variations of the molar Gibbs free energies of solid, liquid, and vapor H_2O at temperatures above, at, and below the triple-point temperature.

Draw G-X and a-X diagrams at T_1, T_2, T_3 and T_4.



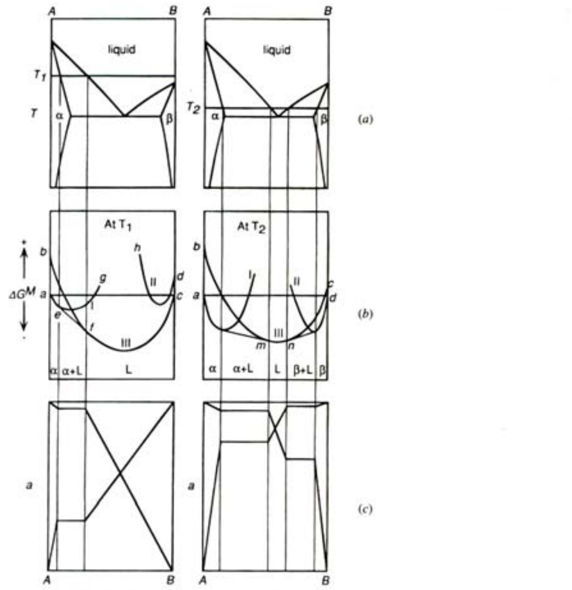


Fig. 10.11 Fig. 10.12

Figures 10.11–10.14 The effect of temperature on the molar Gibbs free energies of mixing and the activities of the components of the system A–B

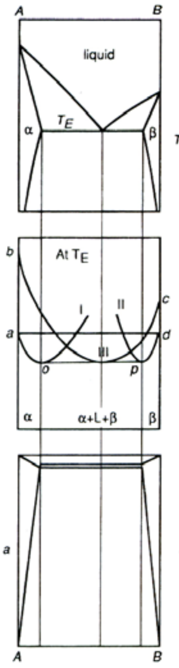


Fig. 10.13

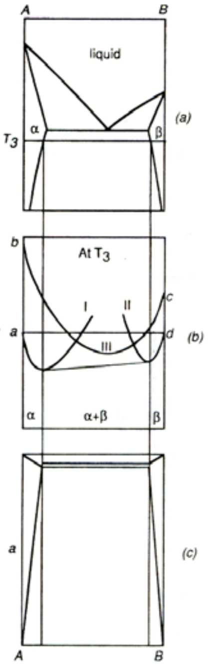


Fig. 10.14

How do we handle a non-ideal mixture?

The volume per one mole of pure water : 18 cm^3
The volume per one mole of pure ethanol : 58 cm^3

What would be the volume of the mixture if half a mole of each is mixed?

9 + 29 = 38 cm^3 → *if it is ideal.*

However, experimentally 37.1 cm^3

How do we handle gas mixture or solution (solid or liquid)? ex) volume of mixture

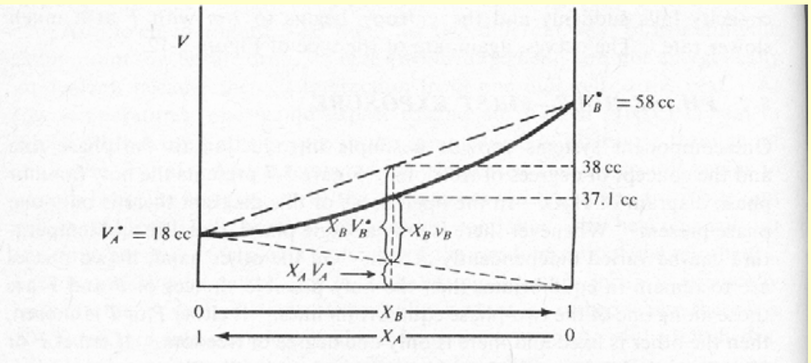


FIGURE 5-14. *Total volume of a binary liquid mixture of water (A) and ethanol (B) as a function of the mole fraction composition of the solution. If all of the observed shrinkage upon mixing were to be ascribed to a component B, then it would have an* apparent *molar volume under these conditions of* v_B. *Volumes for an ideal solution, with no shrinkage or expansion, are shown by a dashed line.*

ideal gas, ideal solution

Dickerson

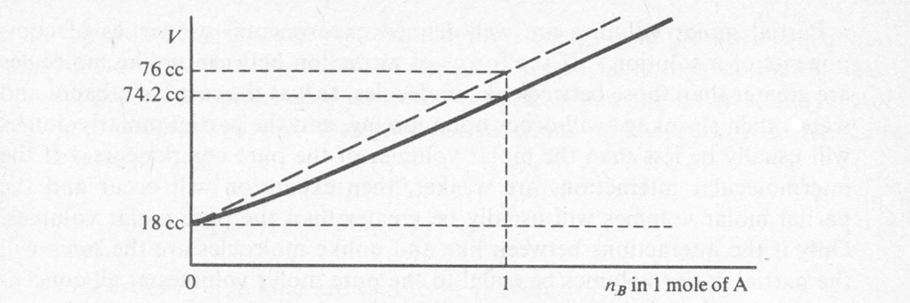


FIGURE 5-15. *If the total volume of a mixture is plotted against the number of moles of component B in 1 mole of A, then the slope of the curve at any point is the partial molar volume of component B. In this diagram, A is water and B is ethanol.*

$$\bar{V}_B = \left(\frac{\partial V}{\partial n_B}\right)_{P,T,n_A} \qquad \bar{V}_A = \left(\frac{\partial V}{\partial n_A}\right)_{P,T,n_B}$$

Dickerson

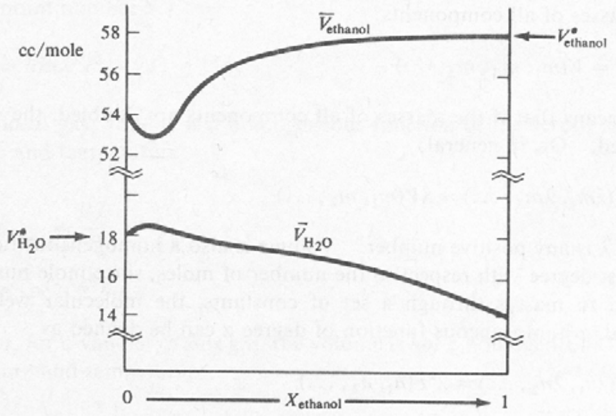


FIGURE 5-16. *Partial molar volumes of water and ethanol in solutions of varying concentrations.*

Dickerson

Gas mixture or Solution (solid or liquid)

partial pressure (ideal gas) $p_i = X_i P$

partial volume (ideal solution) $V_i = X_i V$

partial volume (real solution) $V_i \neq X_i V$

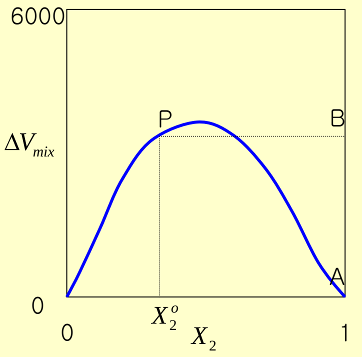
$$V_{mixture} \neq V_A^o X_A + V_B^o X_B$$

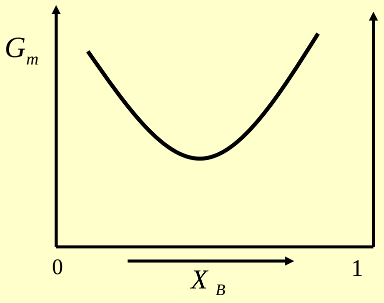
partial Gibbs free energy $G_i \neq X_i G$

$$G_{mixture} \neq G_A^o X_A + G_B^o X_B$$

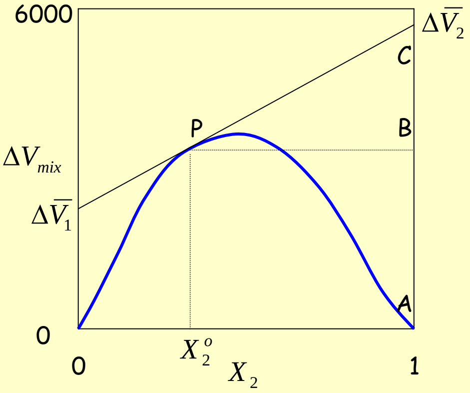
Rule of mixture does not hold!

How should we handle the mixture?





Express ΔV_{mix} at X_2^o in terms of $\Delta\overline{V}_1$ and $\Delta\overline{V}_2$.



partial molar quantity

partial molar volume $\bar{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{P,T,n_j}$

partial molar Gibbs free energy

$$\bar{G}_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j}$$

partial molar operator $\left(\frac{\partial}{\partial n_i}\right)_{P,T,n_j}$