Polyphase Equilibria

- All reactions governed by equilibrium between reactants and products e.g.

$$Ag^{+}(aq) + Cl^{-}(aq) \leftrightarrow AgCl(s)$$

- Equilibrium governed by an equilibrium constant that indicates the extent of reaction.

- Solid phase equilibria behave in the same manner.
  - Another phase develops when the concentration of one component in the original phase is too large.
  - Surface between two phases which can control the rate at which equilibrium is obtained.

- Most commercial alloys are composed of different phases.
  - Thermodynamics of these phases in the solid phase important to help understand when and how new solid state phases behave.

- We start by discussing single phase solutions.

Ideal Solutions

- Ideal solution occurs when no heat generated upon mixing. I.e. $\Delta H_m = 0$.
- Random combination of solution components occurs.
- All interactions between components are equal in energy – no matter what it interacts with.
- In Ideal solutions components having similar physical and chemical properties in pure state for ideal solutions with each other. (E.g. Benzene and toluene).
- Energy changes from an ideal solution due only to changes in the entropy.
- Free Energy is usually written as a function of T, and P:

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

- Free Energy varies upon mixing so that the composition must also be included in the total differential. Thus,

  $G = f(T, P, n_1, n_2)$
- The total differential equation becomes:

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2,\ldots} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2,\ldots} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2,\ldots} dn_1 + \left(\frac{\partial G}{\partial n2}\right)_{T,P,n_1,\ldots} dn_2$$

Chemical Potential

- Chemical potential defined as $m_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}$
- The total differential becomes:

$$dG = -SdT + VdP + m_1 \cdot dn_1 + m_2 \cdot dn_2$$

- At constant T and P, the total differential is:

$$dG = \left(\frac{\partial G}{\partial n_1}\right) dn_1 + \left(\frac{\partial G}{\partial n_2}\right) dn_2 = m_1 \cdot dn_1 + m_2 \cdot dn_2$$

- Euler's theorem: if f(x,y) is a homogeneous function of degree n then

$$n \cdot f(x,y) = x\left(\frac{\partial f}{\partial x}\right)_y + y\left(\frac{\partial f}{\partial y}\right)_x$$

- Extensive thermodynamic properties at constant temperature and pressure are homogeneous functions of degree 1.
- G(n_1, n_2): $G = n_1\left(\frac{\partial G}{\partial n_1}\right)_{n_2} + n_2\left(\frac{\partial G}{\partial n_2}\right)_{n_1} = n_1 m_1 + n_2 m_2$
- Differentiate:

$$dG = n_1 dm_1 + m_1 dn_1 + n_2 dm_2 + m_2 dn_2$$
$$= m_1 dn_1 + m_2 dn_2 + n_1 dm_1 + n_2 dm_2$$

- But from the total derivative we showed:

$$dG = m_1 \cdot dn_1 + m_2 \cdot dn_2$$

- These two equations cannot be simultaneously correct unless (***Gibbs-Duhem equation***):

$$n_1 dm_1 + n_2 dm_2 = 0$$

Free Energy of Mixing

- Free Energy of mixing obtained by: $\Delta G = G_{final} - G_{initial}$
  where $G_{initial}$ is the free energy of pure components.
- Leads to: $\Delta G = n_1 m_1 + n_2 m_2 - n_1 m_1^o - n_2 m_2^o$
- But from other courses we know that $G_A = G_A^o + RT \ln P$
- In ideal mixture of two components: $m_A = m_A^o + RT \ln p_A$
  where p_A is the partial pressure of A in the mixture.
- Remember that fugacity is often used instead of pressure to describe changes in free energy:

$$\lim_{p \to 0} \frac{f}{P} = 1$$

- Remember this tells us that pressure and fugacity equal each other as the pressure is reduced to zero.
- Chemical potential then expressed as:

$$m_A = RT \ln f + B(T)$$

- where B(T) is a material dependent function of temperature.
- Substitute:

$$\Delta G = n_1[RT \ln f_1 + B(T) - RT \ln f_1^o - B(T)] +$$

$$n_2[RT \ln f_2 + B(T) - RT \ln f_2^o - B(T)]$$

$$= n_1 RT \ln \frac{f_1}{f_1^0} + n_2 RT \ln \frac{f_2}{f_2^0}$$

Free Energy of Mixing (cont)

- In Ideal solutions: f = Xf^o, substitute:

$$\Delta G_m = X_1 RT \ln X_1 + X_2 RT \ln X_2$$

  where X_i replaced n_i since we describe this in terms of one mole.

- For more than a two component system:

$$\Delta G_m = RT \sum_i X_i \ln X_i$$

- $X_i < 1 \Rightarrow \Delta G \leq 0$ (at T = 0)
- Recall $\Delta H_m = 0$ for ideal solutions; $\Delta G_m = -T\,\Delta S_m$ or

$$\Delta S_m = -R \sum_i X_i \ln X_i$$

- Notice $\Delta S_m \geq 0$
- Free energy minimum value and entropy change (see Fig.) at maximum when mole fraction is 0.5.
- When $\Delta H_m \neq 0$, it must be included for nonideal solutions. Then $\Delta G_m = \Delta H_m - T\Delta S_m$
- Entropy term is still often dominant. E.g. 50-50 CuNi Alloy, ΔH_m = 1779 J when T ΔS_m = 5567 J at 973 K.
- ΔH_m varies with temperature since heat capacities of reactants and products have weak temperature dependence.

Phase Diagram for Ideal Binary Solutions

- Solubility rules of liquid solutions are familiar to us:
  - "like dissolves like"
    - NaCl in C_6H_6 does not dissolve
    - NaCl in H_2O dissolves
    - Organic alcohols in H_2O polar side of molecule helps low MW alcohols dissolve.
- Solubility rules for solids (similar concept); one metal dissolves in the other when they:
  - Are within 15% of the same size
  - Have similar crystal structure,
  - Have similar electronegativity,
  - Have same # of valence electrons,
  - Or else at least when valence electrons are not the same, element with largest # of valence electrons dissolves in the one with fewer; not the reverse.
- Solubility will be limited if these requirements are not met.
- Ni-Cu alloys satisfy these requirements and form nearly ideal solutions.
  - Liquidus upper portion of curve
  - Solidus lower portion.
  - Composition of each phase in equilibrium is often different. E.g. X_{Ni}(solid) = 0.60 mp = 1300°C; X_{Ni}(liquid) $\approx$ 0.47

Calculation of Equilibrium Cencentrations in Liquid Phase

- Equilibrium exists when $\Delta G = 0 \Rightarrow$ Chemical potential of each component in each phase must also be the same in each phase.
- The ΔG for the formation of liquid phase under reversible conditions will be the sum of the free energy to convert the pure component into the liquid phase plus the free energy of mixing.

$$\Delta G_l = X_{B,l} \cdot \Delta G_{B,me} + \Delta G_{B,mix}$$

- But, $\Delta G_{B,mix} = RT\left[X_{A,l} \ln X_{A,l} + X_{B,l} \ln X_{B,l}\right]$
- So that $\Delta G_l = X_{B,l} \cdot \Delta G_{B,mel} + RT\left[X_{A,l} \ln X_{A,l} + X_{B,l} \ln X_{B,l}\right]$
- At equilibrium chemical potentials for each component in each phase must be equal. $m_{B,l} = m_{B,s}$
- Remember for ideal solutions:

$$m_{B,l} = m^o_{B,l} + RT \ln X_{B,l} \wedge m_{B,s} = m^o_{B,s} + RT \ln X_{B,s}$$

- Equating the two: $m^o_{B,l} + RT \ln X_{B,l} = m^o_{B,s} + RT \ln X_{B,s}$

$$m^o_{B,l} - m^o_{B,s} = RT \ln \frac{X_{B,s}}{X_{B,l}}$$

- Below the melting point $m^o_{B,l} - m^o_{B,s} > 0$

  and $X_{B,s}/X_{B,l} > 1$, otherwise reaction would proceed spontaneously.

Free Energy of Melting

- Recall $$\left(\frac{\partial G/T}{\partial T^{-1}}\right)_P = \Delta H_{B,melt}$$
- Integrate: $\int_{T_{B,mel}}^{T} d\left(\frac{\Delta G}{T}\right) = \int_{T_B,mel}^{T} \Delta H_{B,M}\, d(T^{-1})$
- At $T_{B,mel}$: $\Delta G_{B,mel} = 0$ which leads to $\Delta G_{B,mel}(T)$

$$\Delta G_{B,mel} = \Delta H_{B,mel}\left(\frac{1}{T} - \frac{1}{T_{B,mel}}\right)$$

which is the free energy of melting at temperatures other than the melting temperature at equilibrium.

- Free Energy Change for the solid can be obtained as above for the liquid phase:

$$\Delta G_s = X_{A,s} \cdot \Delta G_{A,f} + RT\left[X_{A,s} \ln X_{A,s} + X_{B,s} \ln X_{B,s}\right]$$

- Free Energy of Freezing negative in front of equation:

$$\Delta G_{A,f} = -\Delta H_{A,mel}\left(\frac{1}{T} - \frac{1}{T_{A,mel}}\right)$$

- Combine these 4 equations gives:

$$\Delta G_s = -X_{A,s} \cdot \Delta H_{A,mel}\left(\frac{1}{T} - \frac{1}{T_{A,mel}}\right) + RT\left[X_{A,s} \ln X_{A,s} + X_{B,s} \ln X_{B,s}\right]$$

$$\Delta G_l = X_{B,l} \cdot \Delta H_{B,mel}\left(\frac{1}{T} - \frac{1}{T_{B,mel}}\right) + RT\left[X_{A,s} \ln X_{A,s} + X_{B,s} \ln X_{B,s}\right]$$

Chemical Potentials

- Express each equation in terms of Chemical Potential by taking the derivative of each. For the solid phase one gets:

$$\mu_{B,l} = \frac{\partial \Delta G_l}{\Delta X_{B,l}} \wedge \mu_{B,s} = \frac{\partial \Delta G_s}{\Delta X_{B,s}}$$

$$\mu_{B,s} = \frac{\partial \Delta G_s}{\partial X_{B,s}} = \frac{\partial}{\partial X_{B,s}}\left(- X_{A,s} \cdot \Delta H_{A,mel}\left(\frac{1}{T} - \frac{1}{T_{A,mel}}\right) + RT\left[X_{A,s} \ln X_{A,s} + X_{B,s} \ln X_{B,s}\right]\right)$$

$$= -RT\left[\ln X_{B,s} + \frac{X_{B,s}}{X_{B,s}}\right]$$

$$= -RT\left[\ln X_{B,s} + 1\right]$$

- For the liquid phase component B:

$$\mu_{B,l} = \frac{\partial \Delta G_l}{\partial X_{B,l}} = \frac{\partial}{\partial X_{B,l}}\left(X_{B,l} \cdot \Delta H_{B,mel}\left(\frac{1}{T} - \frac{1}{T_{B,mel}}\right) + RT\left[X_{A,s} \ln X_{A,s} + X_{B,l} \ln X_{B,l}\right]\right)$$

$$= \Delta H_{B,mel}\left(\frac{1}{T} - \frac{1}{T_{B,mel}}\right) + RT\left[\ln X_{B,l} + \frac{X_{B,l}}{X_{B,l}}\right]$$

$$= \Delta H_{B,mel}\left(\frac{1}{T} - \frac{1}{T_{B,mel}}\right) + RT\left[\ln X_{B,l} + 1\right]$$

- Setting the two chemical potentials equal to each other:

$$\mu_{B,l} = \mu_{B,s}$$

$$-RT\left[\ln X_{B,s} + 1\right] = \Delta H_{B,mel}\left(\frac{1}{T} - \frac{1}{T_{B,mel}}\right) + RT\left[\ln X_{B,l} + 1\right]$$

$$\ln \frac{X_{B,s}}{X_{B,l}} = \frac{\Delta H_{B,mel}}{R}\left(\frac{1}{T} - \frac{1}{T_{B,mel}}\right)$$

Chemical Potential of A

- As with B we take the derivative with respect to X_A to determine the Chemical potential, μ_A,

$$\mu_{A,s} = \frac{\partial \Delta G_s}{\partial X_{A,s}} = \frac{\partial}{\partial X_{A,s}}\left(-X_{A,s}\cdot \Delta H_{A,mel}\left(\frac{1}{T}-\frac{1}{T_{A,mel}}\right)+RT\left[X_{A,s}\ln X_{A,s}+X_{B,s}\ln X_{B,s}\right]\right)$$

$$= -\Delta H_{A,mel}\left(\frac{1}{T}-\frac{1}{T_{A,mel}}\right)+RT\left[\ln X_{A,s}+\frac{X_{A,s}}{X_{A,s}}\right]$$

$$= -\Delta H_{A,mel}\left(\frac{1}{T}-\frac{1}{T_{A,mel}}\right)+RT\left[\ln X_{A,s}+1\right]$$

- And for the liquid:

$$\mu_{A,l} = \frac{\partial \Delta G_l}{\partial X_{A,l}} = \frac{\partial}{\partial X_{A,l}}\left(X_{B,l}\cdot \Delta H_{B,mel}\left(\frac{1}{T}-\frac{1}{T_{B,mel}}\right)+RT\left[X_{A,l}\ln X_{A,l}+X_{B,l}\ln X_{B,l}\right]\right)$$

$$= RT\left[\ln X_{A,l}+\frac{X_{A,l}}{X_{A,l}}\right]$$

$$= RT\left[\ln X_{A,l}+1\right]$$

- Setting them equal

$$m_{A,s} = m_{A,l}$$

$$RT\left[\ln X_{A,l}+1\right] = -\Delta H_{A,mel}\left(\frac{1}{T}-\frac{1}{T_{A,mel}}\right)+RT\left[\ln X_{A,s}+1\right]$$

$$\ln\frac{X_{A,s}}{X_{A,l}} = \frac{\Delta H_{A,mel}}{R}\left(\frac{1}{T}-\frac{1}{T_{A,mel}}\right)$$

$$X_{A,s} = X_{A,l}\exp\left[\frac{\Delta H_{A,mel}}{R}\left(\frac{1}{T}-\frac{1}{T_{A,mel}}\right)\right]$$

- Thus, $X_{B,s} = X_{B,l}\exp\left[\frac{\Delta H_{B,mel}}{R}\left(\frac{1}{T}-\frac{1}{T_{B,mel}}\right)\right]$

$$X_{A,s} = X_{A,l}\exp\left[\frac{\Delta H_{A,mel}}{R}\left(\frac{1}{T}-\frac{1}{T_{A,mel}}\right)\right]$$

Calculation of Liquidus and Solidus Curves

- Using

$$X_{B,s} = X_{B,l} \exp\left[\frac{\Delta H_{B,mel}}{R}\left(\frac{1}{T} - \frac{1}{T_{B,mel}}\right)\right]$$

$$X_{A,s} = X_{A,l} \exp\left[\frac{\Delta H_{A,mel}}{R}\left(\frac{1}{T} - \frac{1}{T_{A,mel}}\right)\right]$$

$$X_{B,s} + X_{A,s} = 1 \wedge X_{B,l} + X_{A,l} = 1$$

- We perform algabraic manipulations

$$X_{B,s} = X_{B,l} \exp\left[\frac{\Delta H_{B,mel}}{R}\left(\frac{1}{T} - \frac{1}{T_{B,mel}}\right)\right]$$

$$1 - X_{B,l} \exp\left[\frac{\Delta H_{B,mel}}{R}\left(\frac{1}{T} - \frac{1}{T_{B,mel}}\right)\right] = \left(1 - X_{B,l}\right)\exp\left[\frac{\Delta H_{A,mel}}{R}\left(\frac{1}{T} - \frac{1}{T_{A,mel}}\right)\right]$$

$$= \exp\left[\frac{\Delta H_{A,mel}}{R}\left(\frac{1}{T} - \frac{1}{T_{A,mel}}\right)\right] - X_{B,l} \exp\left[\frac{\Delta H_{A,mel}}{R}\left(\frac{1}{T} - \frac{1}{T_{A,mel}}\right)\right]$$

$$X_{B,l}\left(\exp\left[\frac{\Delta H_{B,mel}}{R}\left(\frac{1}{T} - \frac{1}{T_{B,mel}}\right)\right] - \exp\left[\frac{\Delta H_{A,mel}}{R}\left(\frac{1}{T} - \frac{1}{T_{A,mel}}\right)\right]\right) = 1 - \exp\left[\frac{\Delta H_{A,mel}}{R}\left(\frac{1}{T} - \frac{1}{T_{A,mel}}\right)\right]$$

- To obtain

$$X_{B,l} = \frac{1 - \exp\left[\frac{\Delta H_{A,mel}}{R}\left(\frac{1}{T} - \frac{1}{T_{A,mel}}\right)\right]}{\exp\left[\frac{\Delta H_{B,mel}}{R}\left(\frac{1}{T} - \frac{1}{T_{B,mel}}\right)\right] - \exp\left[\frac{\Delta H_{A,mel}}{R}\left(\frac{1}{T} - \frac{1}{T_{A,mel}}\right)\right]}$$

- Complete liquidus and solidus curves are then calculated from the melting points and heats of fusion (see Fig. 9.3).

REAL SOLID SOLUTIONS

- Solutions not obeying Raoult's law call ***real (nonideal) solutions***.
- Instead of mole fraction a correction must be added to account for the deviation from ideality. Chemical potential becomes:

$$m_A = m_A^o + RT \ln a_A$$

$$a = g \cdot X$$

where γ = the activity coefficient.

- Substitute for a_i to get:

$$m_A = m_A^o + RT \ln g_A \cdot X_A \wedge m_B = m_B^o + RT \ln g_B \cdot X_B$$

- $\gamma(T, X)$.
- Excess free energy compared with ideal solution determined and related to the activity coefficient.

$$\Delta G_{f,e} = \Delta G_{f,real} - \Delta G_{f,ideal}$$
$$= \left(X_A \Delta m_A + X_B \Delta m_B\right) - \left(X_A \Delta m_{A,i} + X_B \Delta m_{B,i}\right)$$

- But we know that $\Delta m_{A,i} = RT \ln X_A \wedge \Delta m_{B,i} = RT \ln X_B$
- Substitute:

$$\Delta G_{f,e} = RT\left(X_A \ln g_A X_A + X_B \ln g_B X_B\right) - RT\left(X_A \ln X_A + X_B \ln X_B\right)$$
$$= RT\left(X_A \ln g_A + X_B \ln g_B\right)$$

- As stated earlier, heat of mixing of ideal solution is zero.
- Bragg-Williams model assumes all $\Delta G_{f,e}$ is due to a heat of mixing. $\Delta G_{f,e} = \Delta H_{f,e}$
- $\Delta H_{f,e}$ can be determined from average bond energy, ε, and the number of nearest neighbors. Gives the overall energy associated with the bonding in the phase.

Requirements for Equilibrium Among Phases

- To explore necessary requirements for equilibrium to exist, write total differential with respect to T, P, composition.
- Free energy of an isolated system must be at a minimum for equilibrium to exist, i.e. dG = 0

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_i} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_j} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_j} dn_2$$

$$= -SdT + VdP + \sum_i m_i dn_i$$

- Examine the way each variable changes at equilibrium to keep dG = 0.
- Entropy: total entropy change

$$\partial S = \sum_i dS_i = \frac{dq_1}{dT_1} + \frac{dq_2}{dT_2} + \cdots + \frac{dq_i}{dT_i} = 0$$

where i refers to the different phases able to transfer heat.

- Heat is only transferred from hotter to colder regions (Zeroeth law of Thermo.)

$$\left(\frac{dq_1}{dT_1} + \frac{dq_2}{dT_2} + \cdots + \frac{dq_j}{dT_j}\right) - \left(\frac{dq_{j+1}}{dT_{j+1}} + \frac{dq_{j+2}}{dT_{j+2}} + \cdots + \frac{dq_i}{dT_i}\right) = 0$$

- Heat lost by one part of the system ($dq_{j+1} \ldots dq_i$) must equal the heat gained by some other part of it ($dq_1 \ldots dq_j$).
- $T_i < T_j$
- Heat gain and lost can be thought of as coming in pairs;
- Difference should always be positive since division by T_i gives a smaller number than division by T_j

$$\frac{dq_j}{dT_j} - \frac{dq_i}{dT_i} > 0$$

- This cannot be true since the sum of these must be equal.
- Conclusion:heat must be transferred isothermally; no temperature gradients.

Pressure gradients when systems are at equilibrium

- Examine the existence of pressure gradients when a system. Second term in the total differential gives information on the mechanical stability of phases under isothermal conditions.
- Total volume must be kept constant, although the volume of certain regions may vary.
- Varying volumes in some regions means it is possible to do PdV work within the system.
- Since dG = 0 and V = constant: $\delta V_\alpha + \delta V_\beta + \delta V_\gamma + \cdots = 0$
- Work would be: $P_\alpha \delta V_\alpha + P_\beta \delta V_\beta + P_\gamma \delta V_\gamma + \cdots = 0$
- Rearrange: $P_\alpha \delta V_\alpha = -\left(P_\beta \delta V_\beta + P_\gamma \delta V_\gamma + \cdots\right)$
- But: $\delta V_\alpha = -\left(\delta V_\beta + \delta V_\gamma + \cdots\right)$
- And $-P_\alpha\left(\delta V_\beta + \delta V_\gamma + \cdots\right) = -\left(P_\beta \delta V_\beta + P_\gamma \delta V_\gamma + \cdots\right)$
- For the two sides to be equal, $P_\alpha = P_\beta = P_\gamma = \cdots$
- Thus, there can be *no pressure gradients in the system, if it is at equilibrium*.

Chemical Potential Changes

- At equilibrium,

$$dG = 0 = \mu_1^\alpha \delta n_1^\alpha + \mu_1^\beta \delta n_1^\beta + \mu_1^\gamma \delta n_1^\gamma + \cdots + \mu_2^\alpha \delta n_2^\alpha + \mu_2^\beta \delta n_2^\beta + \mu_2^\gamma \delta n_2^\gamma + \cdots + \mu_n^\alpha \delta n_n^\alpha + \mu_n^\beta \delta n_n^\beta + \mu_n^\gamma \delta n_n^\gamma + \cdots$$

- But in an isolated system matter is conserved $\Rightarrow$

$$\Sigma \delta n_1 = 0; \Sigma \delta n_2 = 0; \text{etc.}$$

- As with work (pressure) we can show this equation can only be true when

$$\mu_1^\alpha = \mu_1^\beta = \mu_1^\gamma + \cdots; \mu_2^\alpha = \mu_2^\beta = \mu_2^\gamma = \cdots; \mu_n^\alpha = \mu_n^\beta = \mu_n^\gamma = \cdot\cdot$$

The Phase Rule

- Gives us the total number of experimental parameters required to totally describe an equilibrium between multiple component systems in equilibrium with several phases.
- Tells us how many variables can be changed without changing the composition or number of phases (degrees of freedom).
- Let c = # of components; p = # of phases; there are pc composition variables.
- Add T and P for the system (only one of each since same for all phases (see earlier overhead).
- There are now pc + 2 variables possible.
- Reduce that number by using relationships between the components:

$$X_1^a + X_2^a + \cdots + X_n^a = 1; X_1^b + X_2^b + \cdots + X_n^b = 1; X_1^w + X_2^w + \cdots + X_n^w = 1$$

- Composition of all of components can be determined, from the composition of c-1 components for each phase. We need to know *p* fewer compositions.
- Degrees of freedom are then: f = pc – p + 2 = p(c – 1) + 2
- Chemical potentials in each phase must be the same:

$$m_1^a = m_1^b = m_1^g = \cdots; m_2^a = m_2^b = m_2^g = \cdots; m_n^a = m_n^b = m_n^g = \cdots$$

- Each equivalency reduces the number of independent variables. For p phases and c components the total number of constraints is c(p – 1); subtract from other degrees of freedom:

$$f = p(c-1) + 2 + c(p-1)$$
$$= c - p + 2$$

Phase Rule and Phase Diagram

See Fig. 9.4; pressure held constant in constructing phase diagram $\Rightarrow$ eliminates one variable.

- It is two component system, c = 2.
- *Solidus* region: c = 2; p = 1 $\Rightarrow$ f = 2 – 1 + 1 = 2.
  - –Two variables can change independently with no change in the number of phases.
- *Liquidus* region: c= 2; p = 1 $\Rightarrow$ f = 2. Same behavior.
- Two phase in equilibrium: f = 2 – 2 + 1 = 1. Only one variable can be changed independently and maintain two phases.
  - –E.g. temperature variation, the composition in the particular phase changes to a new place on the graph.

Some Phase Diagrams

- Single component system:
  - One phase present:

    c = 1, p = 1 ⇒

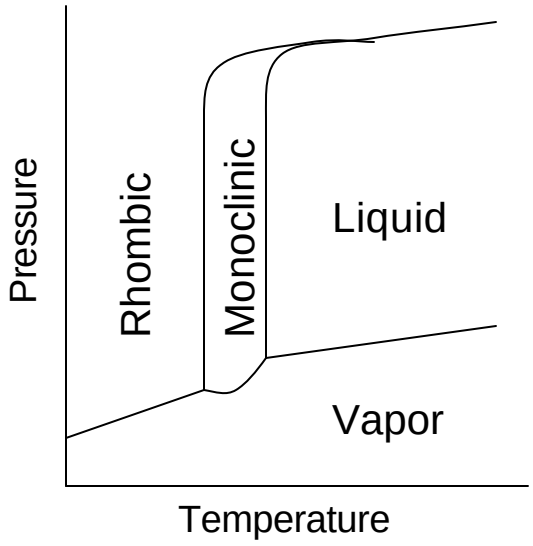
    f = 1 – 1 + 2 = 2

    Pressure and temperature can be varied independently to maintain a single phase.
  - Two phase present:

    c = 1, p = 2

    f = 1 – 2 + 2 = 1

    Only one independent variable; changes in one variable affect the dependent variable.



Phase Diagram of Sulfur

  - Three phases present (triple point) c = 1; p = 3 ⇒

    f = 1 – 3 +2

    A change in any variable changes the number of phases; note that S has three triple points.

Two component Phase Diagram (Binary phase Diagram)

- c = 2, $f = 2 - 2 + 2$
  $= 2$
- Phase diagram plotted (Fig. 9.9) with either pressure or temperature constant.
- Liquidus = negative deviation from ideality
- Solidus = positive deviation from ideality.
- Minimum (or maximum) = point where composition of each phase is same.
- Solidus has two components that are not the same in composition and coexist over some temperature range.
- Composition of each determined by the ***lever law***.
- Run an isothermal tie line between two phase lines (dashed line in bottom portion of phase diagram.
- Conservation of matter gives

$$X_B(n_a + n_{a'}) = X_{B,a}\, n_a + X_{B,a'} n_{a'}$$

  where X_B = overall mole fraction of B; n_α, $n_{\alpha'}$ are the number of moles in each phase.
- Rearrange to get:

$$\frac{n_a}{n_{a'}} = \frac{X_{B,a'} - X_B}{X_B - X_{B,a}}$$

Ternary Systems

- Often represented using planar graphs under isothermal and isobaric conditions.
- Triangular graphical representation used to describe composition of a solution.
- Composition determined using parallel lines on the appropriate side of the graph (see Fig. 9.19).
  - Point x: 0.3 A, 0.5 B, and 0.2 C;
  - Point y: 0.1 A, 0.35 B, and 0.55 C;
  - Point z: 0.6 A, 0.1 B, and 0.3 C;
- A point on any of the sides has only two components.
- The line from one apex to any point on the opposite end of the triangle gives constant ratio of components any where along the line.
- E.g. Consider dotted line from B to other end of triangle:
  - At 0.9B: we have 0.05 A and 0.05 C; A/C = 1.0
  - At 0.5B: we have 0.25 A and 0.25 C; A/C = 1.0, etc.

$H_2O/CHCl_3/CH_3COOH$

- Binary solutions of $CHCl_3$/ CH_3COOH (left) and H_2O/ CH_3COOH (right) form single phases at all concentrations.
- $CHCl_3/H_2O$ mixtures form single phases at the two extremes in relative concentration, but a 2 phase region exists at intermediate concentrations.
- Follow the line $a_1a_2a_3a_4$ to see what happens when acetic acid added to a two phase mixture of $CHCl_3/H_2O$.
- Note from our earlier discussion the relative proportions of $CHCl_3/H_2O$ do not change as we add CH_3COOH to the solution.
  - $\underline{a_2}$: composition of aqueous and chloroform phases given by a_2'' and a_2', respectively. The relative amount in the aqueous phase is given by the lever rule (the ratio of the lengths of the two tie line segments.
  - $\underline{a_3}$: two phases, although the chloroform layer is only a trace.
  - a_4: only one phase exist at any point on the line beyond a_3, i.e. after addition of any more acetic acid.

$NH_4Cl/(NH_4)_2SO_4/H_2O$

- b: solubility of ammonium chloride in water; Solid ammonium chloride in equilibrium with the saturated solution.
- c: solubility of ammonium sulfate: solid ammonium sulfate in equilibrium with saturated solution.
- Let's analyze the line $a_1a_2a_3a_4$. The relative amounts of two salts the same all of the way down the line. Only the relative amount of water is varying. Moving down line is like evaporating water.
- a_1: single phase between two salts and water.
- a_2: small amount of solid ammonium chloride and an aqueous solution of the salts in equilibrium.
- a_3: more water has evaporated; more ammonium chloride precipitated; solution composition given by point d.
- After a_3 both salts start to precipitate.