



## Outline

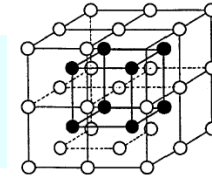
- Review – Sublattice Model
- Example – Sublattice Model
- Thermodynamic Modeling – Introduction
- Example – Alloy Design
- Ternary Phase Diagrams
- Gibbs Phase Rule
- Thermodynamics of Multicomponent Systems



## Review: Sublattice Model

- For ordered intermediate solid solutions, it is better to use a model that can describe the structure more specifically.
- In the sublattice model the elements of the phase are divided into separate lattices according to the crystallographic structure of the phase.

For example, in a simple BCC structure sites at the body's centre and in corner positions can be described as different sublattices, as illustrated in the accompanied figure.



BCC structure

- In the sublattice model, instead of the overall composition  $x_i$ , the site-fraction  $y_i^S$  is used as a coefficient when defining the Gibbs energy of the phase.

The site-fraction is defined as the fractional site occupation of each of the components on the specific sublattice.

$$y_i^S = \frac{n_i^S}{\sum_j n_j^S}$$



## Review: Sublattice Model

$$y_i^S = \frac{n_i^S}{\sum_j n_j^S}$$

where  $n_i^S$  is the number of atoms of component  $i$  on sublattice  $S$

$\sum_j$  is performed for all components on sublattice  $S$

- If there are vacancies on the sublattice they are taken into account as components.
- The overall composition given in mole fractions is directly related to site fractions by the following relationship:

where  $N^S$  is the total number of sites on sublattice  $S$  and  $y_{va}^S$  is the number of vacancies on sublattice  $S$

$$x_i = \frac{\sum_s N^s y_i^s}{\sum_s N^s (1 - y_{va}^s)}$$

The ideal entropy of mixing is made up of the configurational contributions by components mixing on each of the sublattices. The number of permutations that are possible, assuming ideal interchanges within each sublattice, is given by:

$$W_p = \prod_s \frac{N^s!}{\prod_i n_i^s!}$$

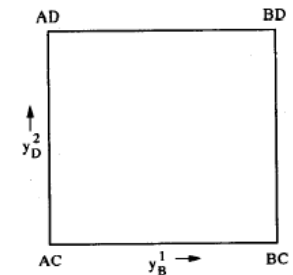


## Example: Sublattice Model

And the molar Gibbs energy of ideal mixing is:

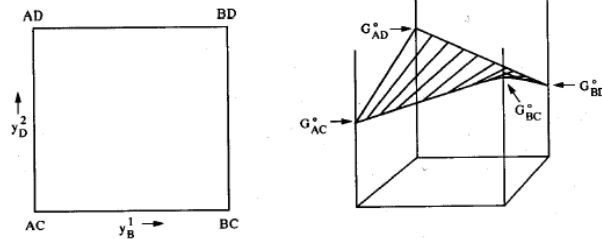
$${}^{id}G = -T \times {}^{id}S = RT \sum_s N^s \sum_i y_i^s \ln y_i^s$$

- The end members generated when only **pure components** exist on the sublattice, effectively define the Gibbs energy reference state.
- For a sublattice phase with the following formula  $(A,B)_1(C,D)_1$ , it is possible for four points of complete occupation to exist where pure A exists on sublattice 1 and either pure C or D on sublattice 2 or, conversely, pure B exists on sublattice 1 with either C or D on sublattice 2.





### Example: Sublattice Model



- The composition space of the phase can then be considered in the figure above as consisting of four compounds, the so-called ..... (at the corners of the square).
- The composition of the phase is then encompassed in the space between the four end-member compounds and the ..... will look as shown in the above figure.

This surface can be represented by:

$$^{\text{ref}}G = y_A y_C {}^{\circ}G_{AC} + y_B y_C {}^{\circ}G_{BC} + y_A y_D {}^{\circ}G_{AD} + y_B y_D {}^{\circ}G_{BD}$$

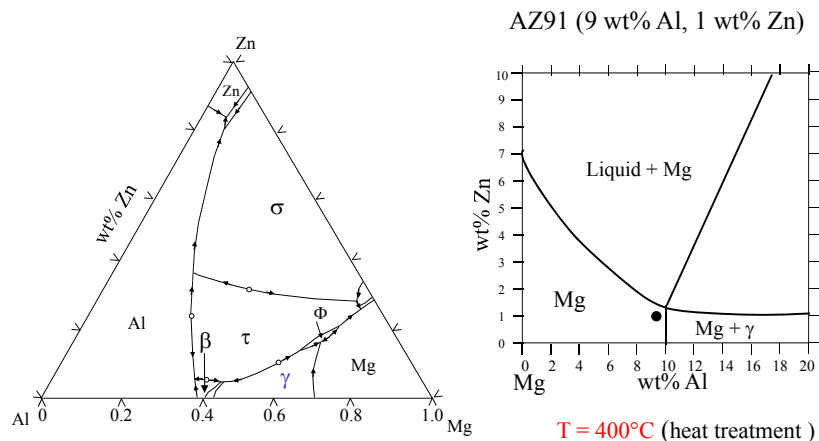


### Why Thermodynamic Modelling?

- As we all know so far, thermodynamics provide relations between many different materials properties like amount of phases and their compositions, heat of transformation, partial pressures etc.
- Experimental thermodynamics has proved its value for materials research for more than 100 years.
- Modern **multicomponent** materials would require very extensive experimental work in order to establish the relevant data for phase equilibria and thermodynamic properties.
- Modelling is the **only** possible technique to reduce experimental work and to increase the value of each new experiment by allowing accurate extrapolation.
- Thermodynamics provide the most important information for a phase transformation: *the final equilibrium state*



### Example: Alloy Design Using Thermodynamic Modeling

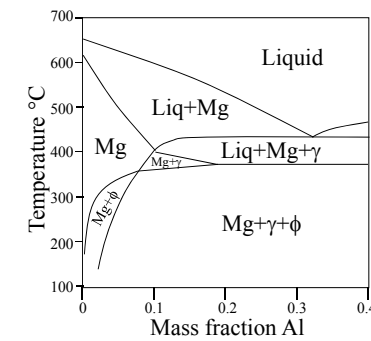


Mg-Al-Zn exp. Phase diagram, after H. Liang *et. al.*



### Alloy Design Cont'd

AZ91 (9 wt% Al, 1 wt% Zn)

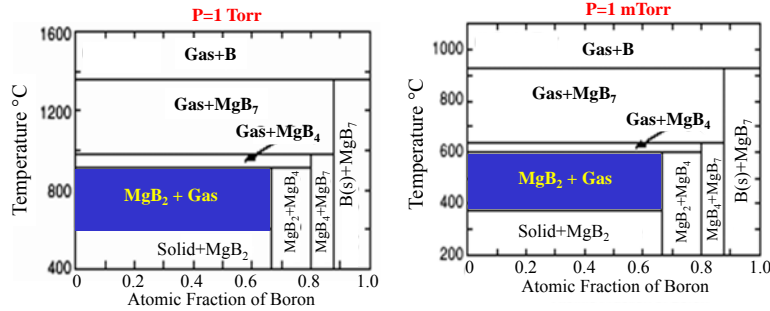




## Example: Process Development By Thermodynamic Modeling

### Mg-B System

- MgB<sub>2</sub> superconductivity at 39 K (highest T<sub>c</sub> for non-oxide)
- Thermodynamics provide helpful insight into the appropriate processing conditions for MgB<sub>2</sub>



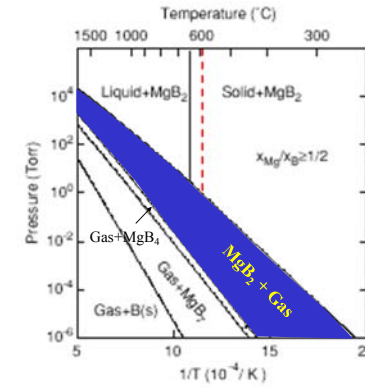
Mg-B calculated phase diagram, after X. Xi *et al.* (2002)

- Insufficient Mg supply will lead to MgB<sub>4</sub>, MgB<sub>7</sub> or solid B phases.



## Process Development Cont'd

### Mg-B System

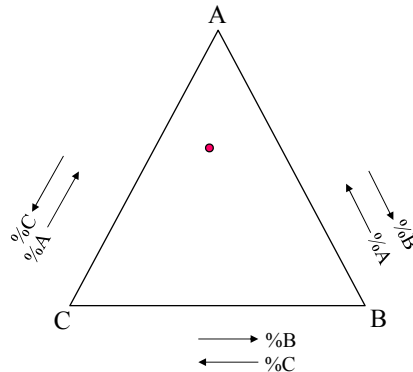


- Building a thermodynamic database for this system helps to develop a process to deposit the superconducting phase MgB<sub>2</sub>

The pressure-temperature phase diagram for the Mg-B, after Z.-K. Liu *et al.* (2002)



## Ternary Phase Diagrams

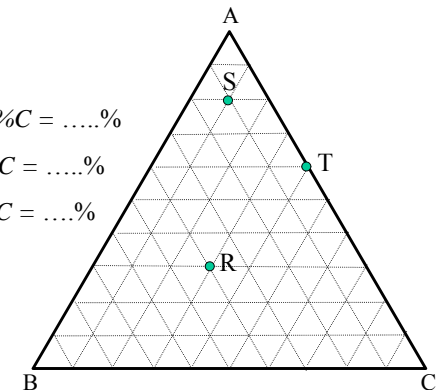


$$X_A + X_B + X_C = 100$$



## Ternary PD cont'd

- T: %A = .....%; %B = .....%; %C = .....%
- R: %A = .....%; %B = .....%; %C = .....%
- S: %A = .....%; %B = .....%; %C = .....%





### Ternary PD cont'd

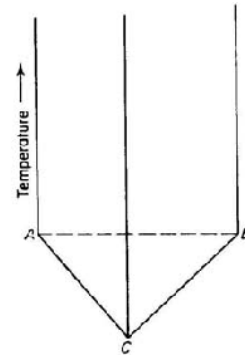
- In order to have the same information that we had for binary diagrams (*composition plus T*), we would need a 3D representation with the composition triangle as basis.

- However, except for relatively simple cases, it is difficult to depict clearly by means of perspective diagrams the complete ternary space model with its constituent spaces, curves, and points.

- Therefore, it is convenient to use:

**projected views** (e.g., a projection of the liquidus or the solidus surface on to the base of the space model)

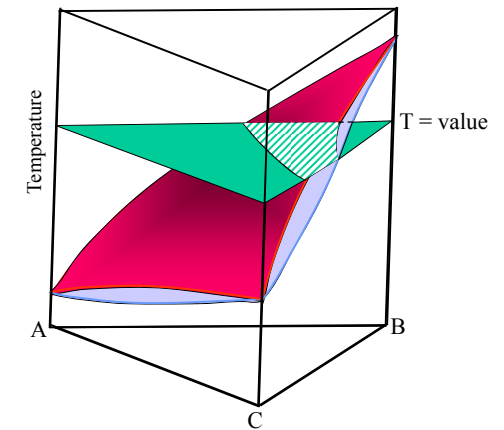
**plane sections**, taken horizontally (i.e. isothermally) or vertically (similar to the binary diagrams) through the 3D space model.



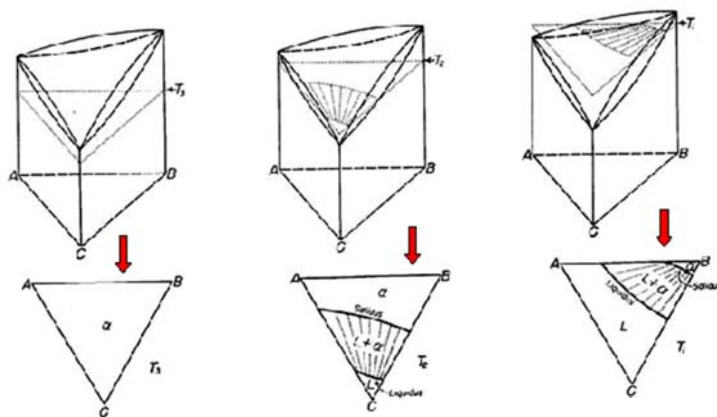
### Ternary PD cont'd

- In contrast to binaries, it is impossible to make a convenient graphical representation of the complete ternary phase diagram that can be utilized in all practically important cases.

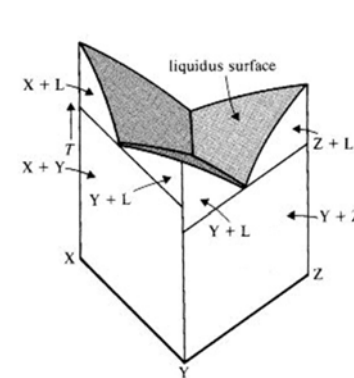
- Solution: employing a computer program which will compute the equilibrium composition in the ternary system at any given temperature and composition.



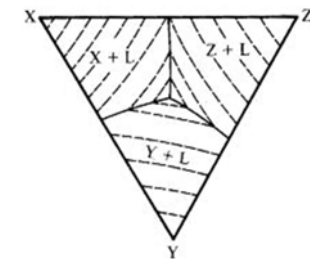
### Ternary Isothermal Sections



### Ternary Eutectic

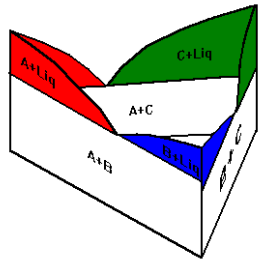


Liquidus projection

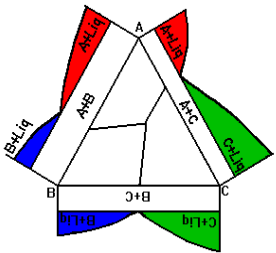




## Ternary Eutectic



- Consider the three binary systems ....., ....., and .....
- We can arrange the three diagrams in three dimensions as shown here.



- The space inside the triangular prism represents systems with all three components present.
- There will be a field where A crystallizes first, a field where B crystallizes first, and one where C crystallizes first.

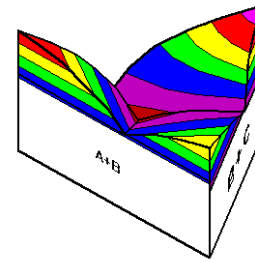
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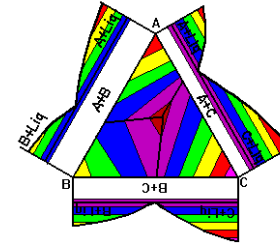
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## Ternary Eutectic



In reality, there is a liquidus surface covering the triangle and as the system cools, it will slide down the surface



- This diagram shows the relationship between temperature in the binary systems and temperature on the triangle diagram.
- Very often, temperature contours are omitted. If the system is simple, this is not a problem. However, if there are maxima or minima on the liquidus surface, the diagram becomes less useful without contours

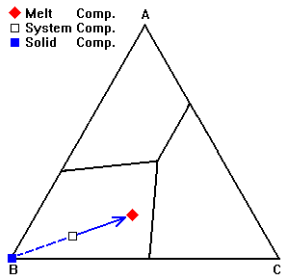
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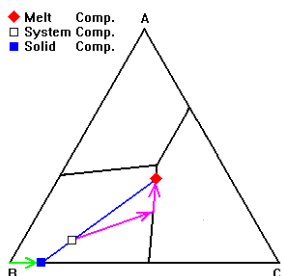
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## Phase Evolution of Ternary Eutectics



- The first thing that will happen is that one component will begin to crystallize. In this case, it is B. As we remove B from the melt, the melt composition will migrate straight away from the B corner as shown.



- Eventually the melt will hit a field boundary and then a second component will begin to form. In this case, it is C. The composition of the melt will migrate away from both B and C in the general direction of A. The path of the melt is shown in magenta.
- Since C is now forming along with B, the solid composition migrates in the direction of C.
- The melt, system, and solid compositions always lie on a straight line as shown.

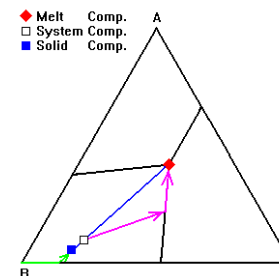
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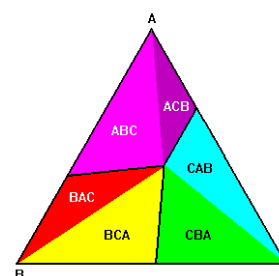
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## Phase Evolution of Ternary Eutectics



- Finally the melt reaches the ternary eutectic and all three components begin to form. The eutectic is usually a temperature minimum so the melt does not move once it reaches the eutectic.
- Since all three components are now forming, the solid composition moves into the interior of the triangle.
- The melt, system, and solid compositions always lie on a straight line as shown. Since the melt stays at the eutectic, the solid migrates toward the system composition as shown in green. Once it reaches the system composition, the entire system is solidified.



Given the rules above, we can divide the triangle into six fields with crystallization orders as shown. Note that any order is .....

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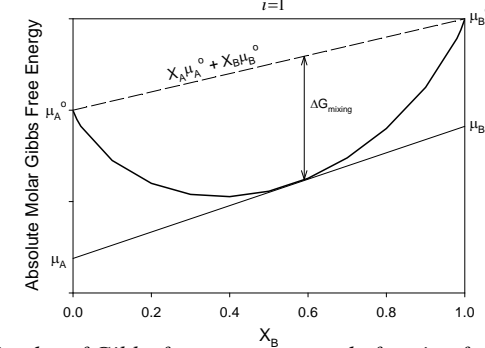
10 minutes Break



## Review: Partial Molar Free Energy

$$\bar{G}_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,P,n_j} \equiv \mu_i \quad \text{Partial Gibbs energy or } \dots\dots\dots$$

$$\text{Also: } G = \sum_{i=1}^n n_i \mu_i \quad X_i = \frac{n_i}{\sum_{i=1}^n n_i} \quad \text{and} \quad \bar{G} = \sum_{i=1}^n X_i \mu_i$$



Schematic plot of Gibbs free energy vs. mole fraction for a binary system



## Review: Thermodynamics with Compositional Changes

The Master equations that we developed previously are:

$$dU = TdS - PdV + \sum_{i=1}^n \mu_i dn_i$$

$$dH = TdS + VdP + \sum_{i=1}^n \mu_i dn_i$$

$$dG = -SdT + VdP + \sum_{i=1}^n \mu_i dn_i$$

$$dA = -SdT - PdV + \sum_{i=1}^n \mu_i dn_i$$

It can also be shown that:

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



## Thermodynamics of Multicomponent Systems

Consider a system with components  $i, j, k, l, \dots$  distributed among phases  $\alpha, \beta, \gamma, \delta, \dots$ . At equilibrium it must be true that:

$$\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma = \mu_i^\delta = \dots$$

$$\mu_j^\alpha = \mu_j^\beta = \mu_j^\gamma = \mu_j^\delta = \dots$$

$$\mu_k^\alpha = \mu_k^\beta = \mu_k^\gamma = \mu_k^\delta = \dots$$

$$\mu_l^\alpha = \mu_l^\beta = \mu_l^\gamma = \mu_l^\delta = \dots$$

etc.

Chemical potentials represent the **slope** of the Gibbs free energy surface in compositional space. Thus, a component will move from a phase in which it has a ..... chemical potential, to one in which it has a ..... chemical potential, until its chemical potential in all phases is **the** .....

Specific example: Consider a Mg-Al-Ca melt in equilibrium with two solids  $\alpha$  and  $\beta$ . At equilibrium:

$$\mu_{\text{Mg}}^{\text{melt}} = \mu_{\text{Mg}}^\alpha = \mu_{\text{Mg}}^\beta$$

$$\mu_{\text{Al}}^{\text{melt}} = \mu_{\text{Al}}^\alpha = \mu_{\text{Al}}^\beta$$

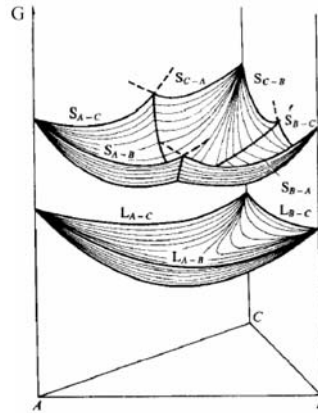
$$\mu_{\text{Ca}}^{\text{melt}} = \mu_{\text{Ca}}^\alpha = \mu_{\text{Ca}}^\beta$$





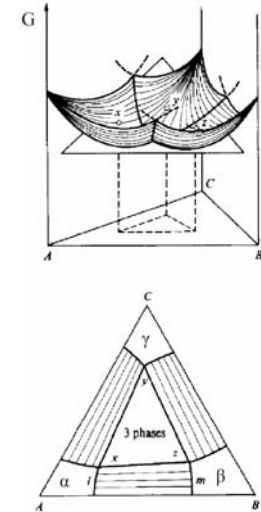
## Ternary Systems

- Instead of **curves** for a binary system, in the case of a ternary system, Gibbs free energy **surfaces** can be plotted for all the possible phases as functions of temp and composition.
- The chemical potentials of A, B, and C of any phase in this system are given by the points where the **tangential plane** to the free energy surfaces **intersects** the A, B, and C axis.
- A three-phase **equilibrium** in the ternary system for a given temperature can be derived by means of the **tangential plane** construction.



## Ternary Systems

- Eutectic point: four-phase equilibrium between  $\alpha$ ,  $\beta$ ,  $\gamma$ , and liquid
- For two phases to be in equilibrium, the chemical potentials should be **.....**, that is the compositions of the two phases in equilibrium must be given by points connected by a common tangential plane (e.g. *l* and *m*).
- The relative amounts of phases are given by the **..... rule**.
- A three phase triangle can result from a common tangential plane simultaneously touching the Gibbs free energies of three phases (e.g. *points x, y, and z*).



## Thermodynamics of Multicomponent Systems

$$G^\varphi = G^o + G^{ideal} + G^{Excess}$$

For binary systems:

$$G^\varphi = x_A G_A^o + x_B G_B^o + RT \{ x_A \ln x_A + x_B \ln x_B \} + x_A x_B \sum_{k=0}^n {}^k L_{AB} (x_A - x_B)^k$$

Partial excess  
Gibbs energy

$$\begin{cases} {}^{ex}G_A = RT \ln \gamma_A = x_B^2 \left[ {}^0 L_{AB} + \sum_{k=1}^n {}^k L_{AB} (x_A - x_B)^{k-1} ((2k+1)x_A - x_B) \right] \\ {}^{ex}G_B = RT \ln \gamma_B = x_A^2 \left[ {}^0 L_{AB} + \sum_{k=1}^n {}^k L_{AB} (x_A - x_B)^{k-1} (x_A - (2k+1)x_B) \right] \end{cases}$$

For ternary systems:

$$G^\varphi = x_A G_A^o + x_B G_B^o + x_C G_C^o + RT \{ x_A \ln x_A + x_B \ln x_B + x_C \ln x_C \} + x_A x_B \sum_{k=0}^{n_{AB}} {}^k L_{AB} (x_A - x_B)^k + x_A x_C \sum_{k=0}^{n_{AC}} {}^k L_{AC} (x_A - x_C)^k + x_B x_C \sum_{k=0}^{n_{BC}} {}^k L_{BC} (x_B - x_C)^k$$

where the parameters  ${}^k L$  have the same values as in each of the binary systems



## Thermodynamics of Multicomponent Systems

If necessary, a ternary term  $x_A x_B x_C G^{ABC}(T, X)$  can be added in order to describe the contribution of three element interactions to the Gibbs energy.

$${}^{ex}G^\varphi = \sum_i^m \sum_{j>i}^m x_i x_j L_{ij} + x_i x_j x_k L_{ijk}$$

Where  $L_{ijk} = x_i {}^0 L_{ijk} + x_j {}^1 L_{ijk} + x_k {}^2 L_{ijk}$

and

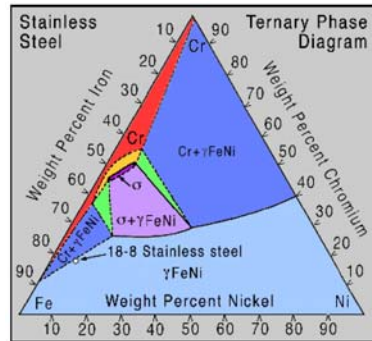
$$x_i + x_j + x_k = 1$$

$L_{ijk}$  is a **ternary interaction parameter**

Higher order interaction parameters can be usually omitted (*a few exceptions in quaternary systems*)



## Example: Fe-Ni-Cr System



The ternary diagram of Ni-Cr-Fe includes Stainless Steel (wt.% of Cr > 11.5 %, wt.% of Fe > 50 %) and Inconel (Nickel based superalloys).

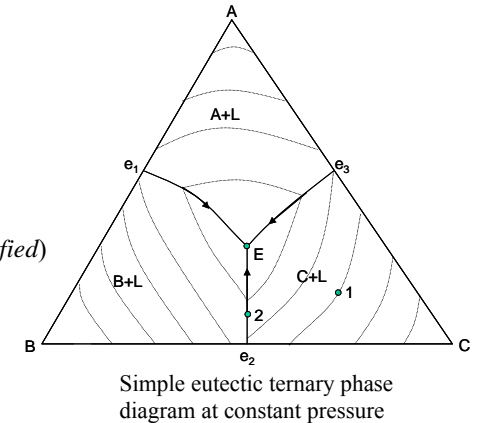


## The Gibbs Phase Rule: Example - Ternary Systems

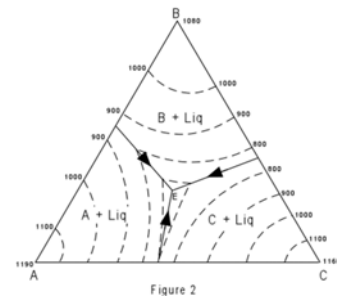
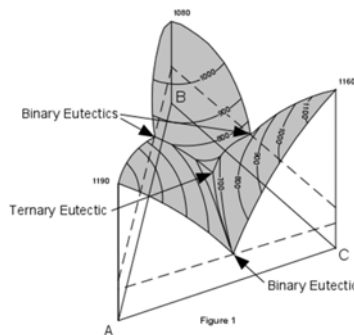
- At point 1  
 $Ph = 2$  (solid C & L)  
 $C = 3$   
 $F = 3 - Ph + 2$   
as pressure is constant  
 $\Rightarrow F = 4 - Ph$   
 $F = \dots\dots$   
*(T and  $X_A$ ,  $X_B$  or  $X_C$  should be specified)*

- At point 2,  
 $Ph = 3$  (solid A, C & L)  
 $C = 3$   
 $F = 4 - Ph = \dots\dots$   
*(T only should be specified)*

- At E the eutectic where all three phase fields meet:  
 $P = 4$  (solid A, B, C and L)  
 $C = 3$   
 $F = 4 - Ph = \dots\dots$  (T and comp are fixed)



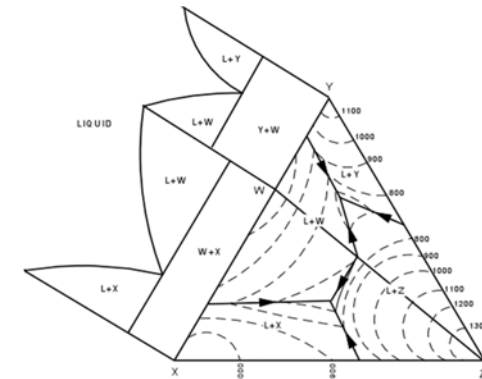
## Ternary Systems



- Note that the eutectic points in each of the binary systems project into the ternary systems as lines. These lines are called **boundary curves**, and any composition on one of these curves will crystallize the two phases on either side of the curve.



## Ternary Systems with Binary Congruent Compounds

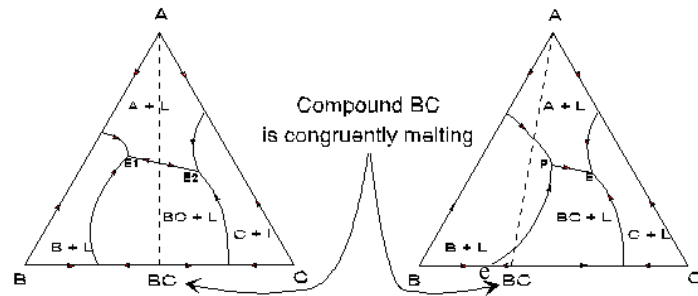


A ternary system that has a binary sub-system with a compound that shows congruent melting (*melts to a liquid of its own composition*). The result of the addition of this intermediate compound is essentially that the ternary system XYZ is divided into two smaller ternary systems represented by triangles WYZ and XWZ





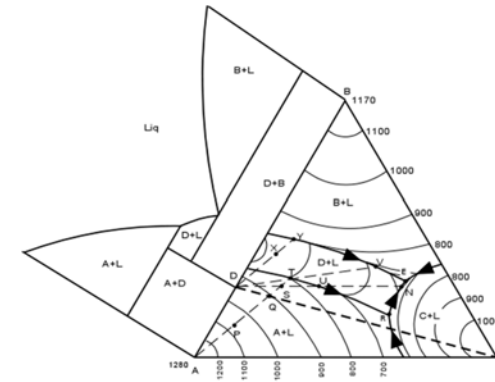
## Ternary Systems with Binary Congruent Compounds



- The intermediate compounds BC are congruently melting.
- It is characteristic of the congruently melting binary compound that its composition point always **falls** ..... its primary field of stability in the ternary system.
- In these two cases, this primary phase field is described by the lines  $E_1-E_2$  and  $P-e$ .



## Ternary Systems with Binary Incongruent Compounds

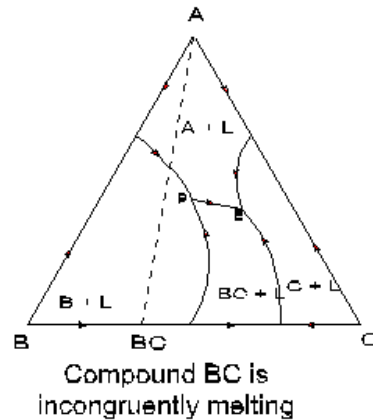


A ternary system ABC and one of the binary systems AB that contains a compound, D, that melts incongruently.



## Ternary Systems with Binary Incongruent Compounds

- The intermediate compound BC in this diagram is incongruently melting because it is not in the primary phase field of the compound. **Congruent** melting is important in determining the Alkamade lines and the crystallization path.



Next time:  
**Continue Ternary Systems**

