



## Outline

- Utility of phase diagrams
- Construction of phase diagram
- Phase diagram calculation using Gibbs energy minimization
- Phase diagram with intermediate phases
  - solid solutions
  - compounds
- Fe-Fe<sub>3</sub>C phase diagram
- Classifications of Fe-C alloys
- Microstructure of Fe-C alloys
- The phase rule



## Utility of Phase Diagrams

- Soldering
- Brazing
- Diffusion Problems
- Kirkendahl Voiding: *If there is a major difference in solid solubility limits, voiding can be expected to occur in the phase that permits less solid solubility (e.g., the Al-Au system)*
- Corrosion
- Electrical Resistivity – *dependence of resistivity on composition*
- Mechanical Properties
- Processing – *Casting, molding, high temp deformation ..etc.*
- Glass forming systems
- Ceramic processing – *transient liquid phase sintering*
- ... etc.



## Construction of Phase Diagram

The data for the construction of equilibrium diagrams are determined experimentally by a variety of methods, the most common methods are:

- **Metallographic Methods**
- **Diffraction Technique (X-ray)**
- **Thermal Analysis**

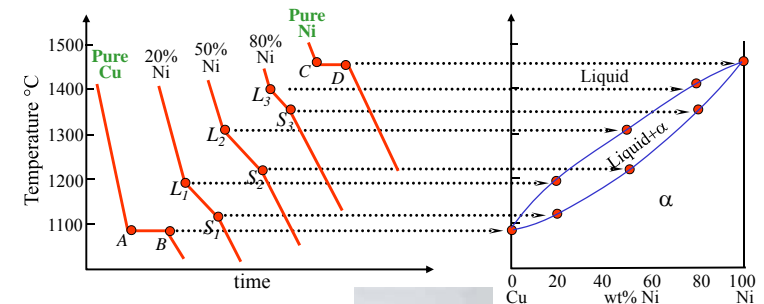
Some of the techniques used for this purpose:

- ✓ Cooling Curves
- ✓ Differential Scanning Calorimetry
- ✓ Differential Thermal Analysis
- ✓ Energy Dispersive X-ray Spectroscopy
- ✓ Electron Microprobe Analyzer
- ✓ X-ray Diffraction also Neutron Diffraction
- ✓ Transmission Electron Microscopy
- ✓ Inductive Coupled Plasma
- ✓ Phase Transformation using Electrical Resistivity Measurements



## How to construct a phase diagram using cooling curves

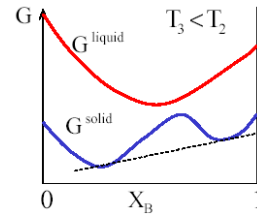
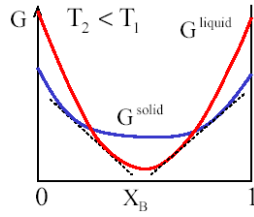
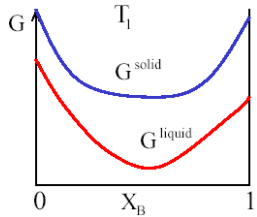
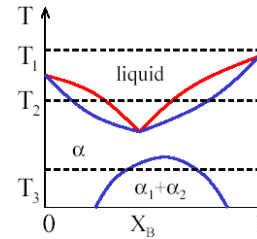
Example: Cu-Ni phase diagram





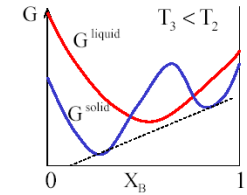
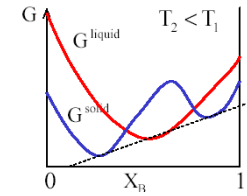
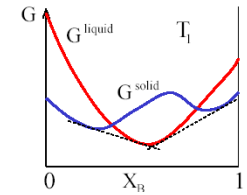
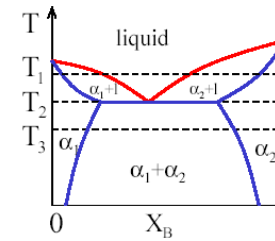
## Binary Solutions with a Miscibility Gap

Let us consider a system in which the liquid phase is approximately ideal, but for the solid phase we have  $\Delta H_{\text{mix}} > 0$



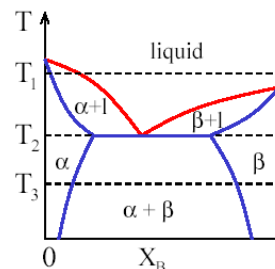
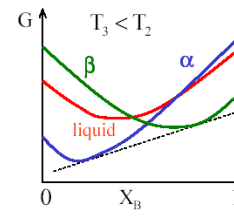
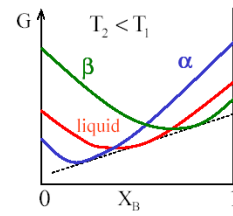
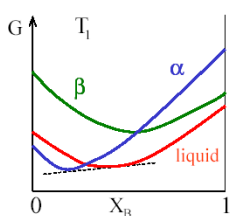
## Eutectic Phase Diagram

For an even larger  $\Delta H_{\text{mix}}$  the miscibility gap can extend into the liquid phase region. In this case we have eutectic phase diagram.



## Eutectic Phase Diagram

Now, let us consider that the pure solids, in the previous eutectic system, have different crystal structures.



A similar eutectic phase diagram can result if pure A and B have different crystal structures.



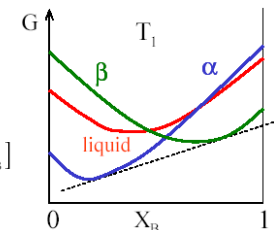
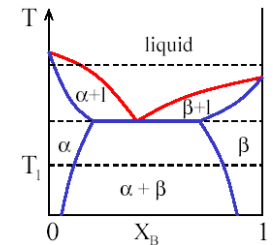
## Temperature Dependence of Solubility

Let us consider, again, a regular binary solution with limited solubilities of A in B and B in A.

The closer is the minimum of the Gibbs free energy curve  $G^{\alpha}(X_B)$  to the axes  $X_B = 0$ , the **smaller** is the *maximum possible* concentration of B in **phase  $\alpha$** . Therefore, to discuss the temperature dependence of solubility we need to find the minimum of  $G^{\alpha}(X_B)$ .

$$G^{\text{reg}} = X_A G_A + X_B G_B + \Omega X_A X_B + RT[X_A \ln X_A + X_B \ln X_B]$$

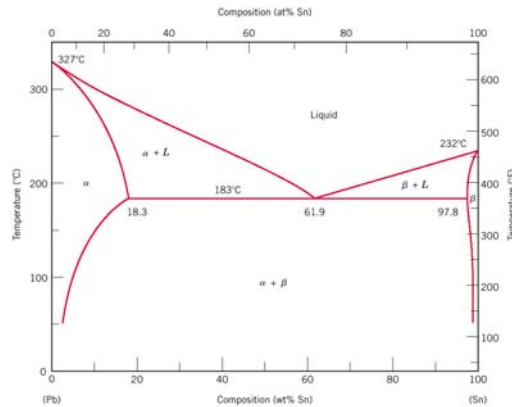
$$\frac{dG}{dX_B} = 0 \rightarrow \text{Minimum of } G(X_B)$$





## Phase Diagrams with Intermediate Phases

- Eutectic systems that we have studied so far have only two solid phases ( $\alpha$  and  $\beta$ ) that exist near the ends of phase diagrams. These phases are called ..... solid solutions.



- Some binary alloy systems have ..... **solid solution** phases. In phase diagrams, these phases are separated from the composition extremes (0% and 100%).

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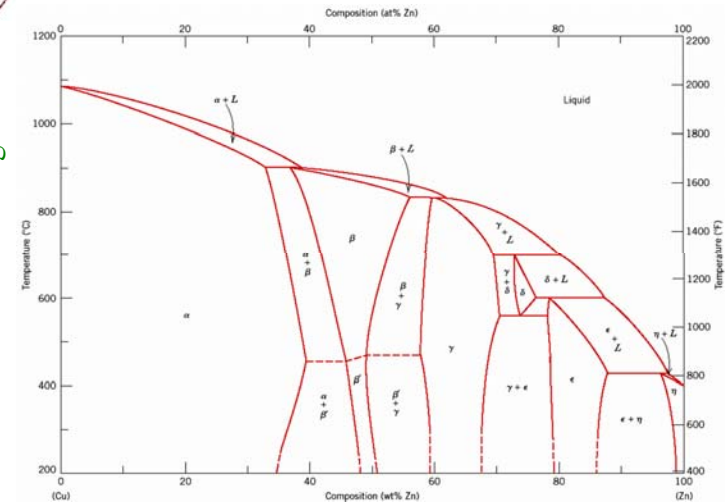
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## Phase Diagrams with Intermediate Phases

Cu-Zn Phase Diagram



- $\alpha$  and  $\eta$  are terminal solid solutions
- $\beta$ ,  $\beta'$ ,  $\gamma$ ,  $\delta$  and  $\epsilon$  are intermediate solid solutions.
- new phenomena exist: - ..... reaction — ..... reaction

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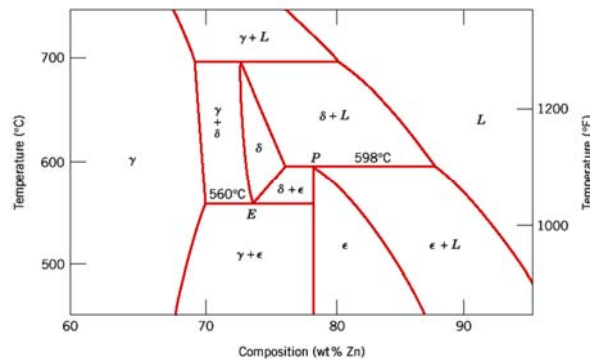
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## Cu-Zn Phase Diagram

### Eutectoid and Peritectic Reactions



**Eutectoid:** one solid phase transforms into two other solid phases upon cooling

**Peritectic:** one solid and one liquid phase transform into another solid phase upon cooling

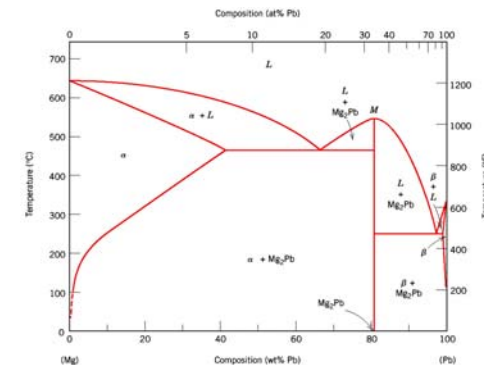
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## Phase Diagrams with Intermediate Phases



- $\alpha$  and  $\beta$  are the terminal solid solutions
- $\text{Mg}_2\text{Pb}$  is an intermetallic compound
  - ratio (2:1) (Mg:Pb)
  - 67 mol% Mg and 33 mol% Pb
  - 19 wt% Mg and 81 wt% Pb
- melts at a fixed temperature M
- Intermetallic compounds are very common in metal alloy systems.

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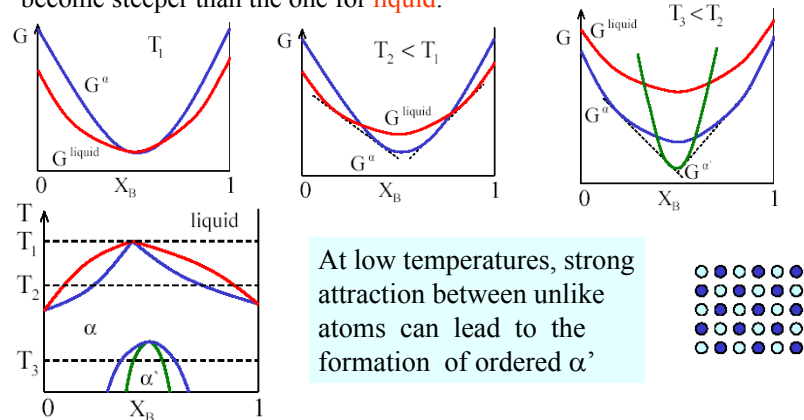
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## Binary Systems with an Ordered Solid Solution

If  $\Delta H_{\text{mix}} < 0$  (of the solid solution), bonding becomes stronger upon mixing. Hence melting point of the solid solution will be higher than the ones of the pure components. For the solid phase, strong interaction between unlike atoms can lead to (*partial*) ordering  $\rightarrow |\Delta H_{\text{mix}}|$  can become larger than  $|\Omega X_A X_B|$  and the Gibbs free energy curve for the **solid** can become steeper than the one for **liquid**.



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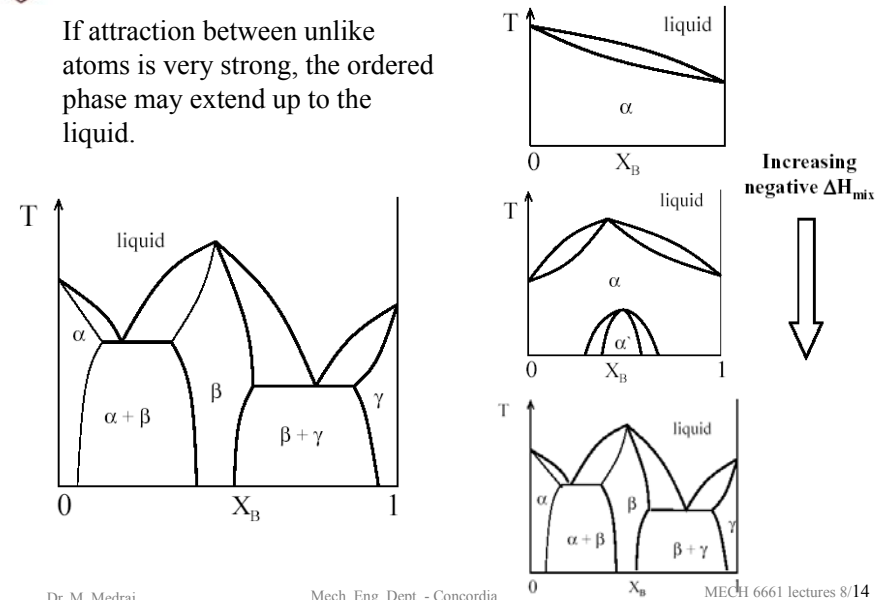
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## Binary Systems with an Ordered Intermediate Solid Solution

If attraction between unlike atoms is very strong, the ordered phase may extend up to the liquid.



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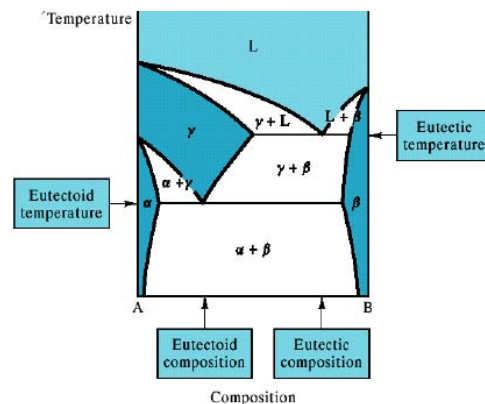
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## Eutectoid Reactions

The **eutectoid** (*eutectic-like* in Greek) reaction is similar to the eutectic reaction but occurs from **one solid** phase to two new solid phases.



This phase diagram contains both an *eutectic* reaction and (its solid-state analog) an *eutectoid* reaction

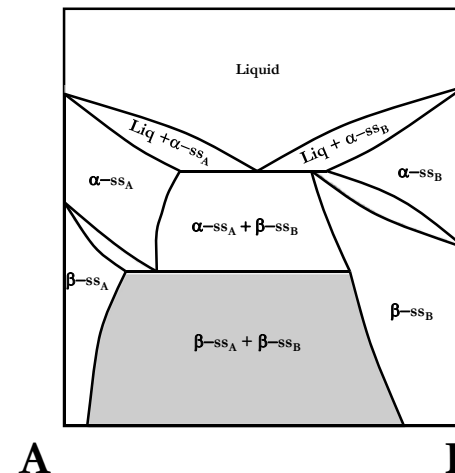
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## Phase Diagrams with Complex Solid Solutions



- Two Phase Regions
  - $\alpha\text{-ss}_A + \beta\text{-ss}_B$  and  $\beta\text{-ss}_A + \beta\text{-ss}_B$

- Polymorphism of Components
  - Represents a change in crystal structure within the end members

- Two Phase Mixture of an End Member
  - ✓ Represents a Mixture of polymorphs for an end member

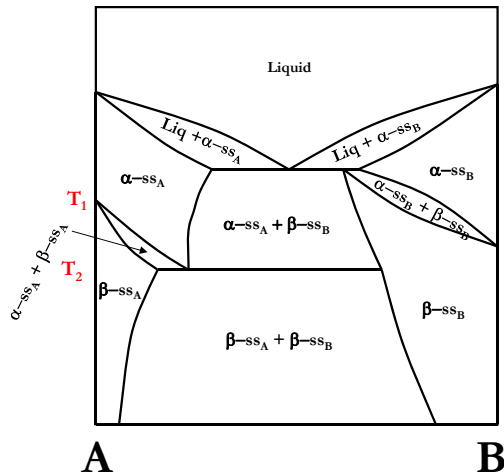
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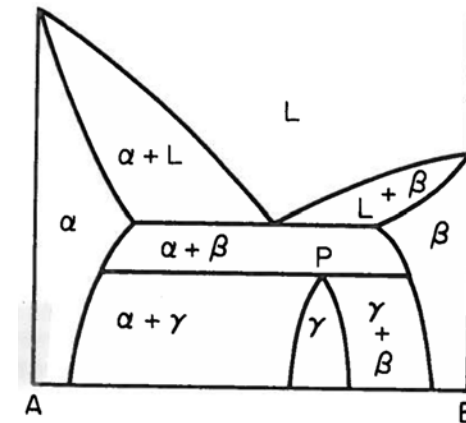
## Phase Diagrams with Complex Solid Solutions



- High Temperature Phase Stabilization Region
  - region normally associated with higher temperatures stable at a lower temperature
  - original polymorph stable to  $T_1$  → stable to a lower temp.  $T_2$
- **Eutectic Point**  
 $\alpha\text{-ss}_A + \beta\text{-ss}_B \rightarrow \text{Liquid}$
- **Eutectoid Point**  
 $\beta\text{-ss}_A + \beta\text{-ss}_B \rightarrow \alpha\text{-ss}_A$
- **Peritectic Point**  
 $\beta\text{-ss}_B \rightarrow \alpha\text{-ss}_B + \text{Liquid}$



## Phase Diagrams with Peritectoid Point

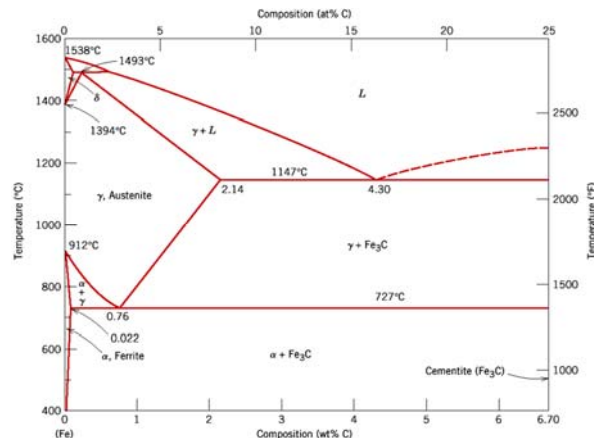


- Point P is a **peritectoid point**.
- The peritectoid reaction is  $\alpha + \beta \rightarrow \gamma$



## The Iron–Iron Carbide (Fe–Fe<sub>3</sub>C) Phase Diagram

In their simplest form, steels are alloys of Iron (Fe) and Carbon (C). The Fe–C phase diagram is a fairly complex one, but we will only consider the part up to around 7% carbon of the diagram.



912°C 1394°C 1538°C  
 $\alpha$  (BCC)  $\leftrightarrow$   $\gamma$  (FCC)  $\leftrightarrow$   $\delta$  (BCC)  $\leftrightarrow$  liquid



## Phases in Fe–Fe<sub>3</sub>C Phase Diagram

### $\alpha$ -ferrite - solid solution of C in ..... Fe

- Stable form of iron at room temperature.
- The maximum solubility of C is 0.022 wt% (**interstitial solubility**)
- Soft and relatively easy to deform

### $\gamma$ -austenite - solid solution of C in ..... Fe

- The maximum solubility of C is 2.14 wt % at 1147°C.
- Interstitial lattice positions are much larger than ferrite (**higher C%**)
- Is not stable below the eutectoid temperature (727°C) unless cooled rapidly (*Chapter 10*).

### $\delta$ -ferrite solid solution of C in ..... Fe

- The same structure as  $\alpha$ -ferrite
- Stable only at high T, above 1394°C
- Also has low solubility for carbon (BCC)

### Fe<sub>3</sub>C (iron carbide or cementite)

- This intermetallic compound is metastable, it remains as a compound indefinitely at room T, but decomposes (very slowly, within several years) into  $\alpha$  -Fe and C (graphite) at 650 - 700 °C

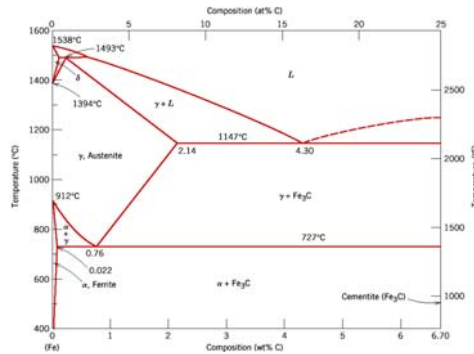
### Fe-C liquid solution





## Classifications of Fe-C alloys

- $< 0.008 \text{ wt\% Carbon}$  → .....
  - $\alpha$ -ferrite at room T
- $0.008 - 2.14 \text{ wt\% C}$  → .....
  - usually  $< 1 \text{ wt\%}$
  - $\alpha$ -ferrite +  $\text{Fe}_3\text{C}$  at room T
- $2.14 - 6.7 \text{ wt\% C}$  → .....
  - usually  $< 4.5 \text{ wt\%}$



- Magnetic properties:  $\alpha$ -ferrite is magnetic (below  $768^\circ\text{C}$ ), austenite is non-magnetic.
- Mechanical properties: Cementite is very **hard** and **brittle** thus it can strengthen steels.
- Mechanical properties also depend on ....., that is, how ferrite and cementite are mixed.

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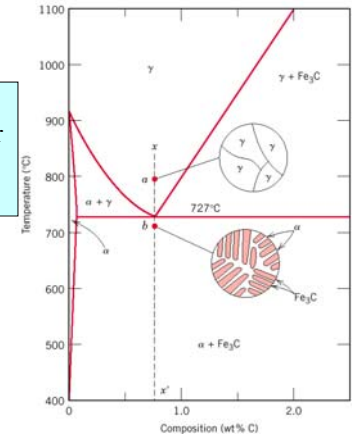
## Development of Microstructure in Iron - Carbon alloys

- Microstructure depends on composition (carbon content) and heat treatment.
- In the discussion below we consider slow cooling in which equilibrium is maintained.

### Eutectoid steel

When alloy of eutectoid composition ( $0.76 \text{ wt\% C}$ ) is cooled slowly it forms a lamellar or layered structure of  $\alpha$  and cementite ( $\text{Fe}_3\text{C}$ ). This structure is called .....

Mechanically, pearlite has properties intermediate to soft, ductile ferrite and hard, brittle cementite.



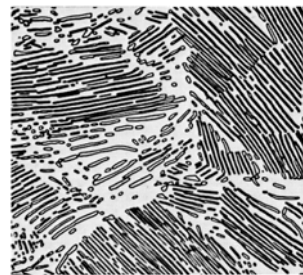
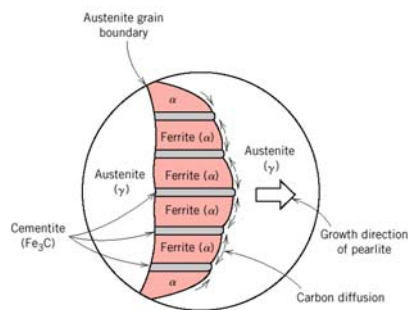
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## Development of Microstructure in Iron - Carbon alloys



the dark areas are  $\text{Fe}_3\text{C}$  layers, the light phase is  $\alpha$ -ferrite

The layers of alternating phases in pearlite are formed for the same reason as layered structure of eutectic phases: that is, redistribution of C atoms between ferrite ( $0.022 \text{ wt\%}$ ) and cementite ( $6.7 \text{ wt\%}$ ) by .....

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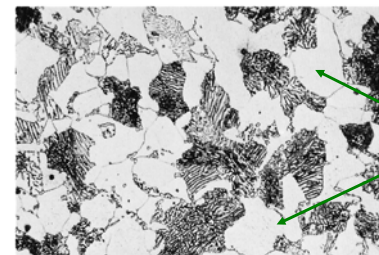
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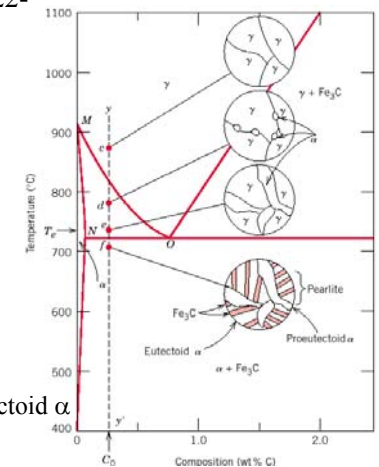
## Microstructure of hypoeutectoid steel

Compositions to the left of eutectoid ( $0.022 - 0.76 \text{ wt\% C}$ ) **hypoeutectoid** alloys  
- less than eutectoid (Greek)

Hypoeutectoid alloys contain **proeutectoid ferrite** (formed above the eutectoid temperature) plus the **eutectoid pearlite** that contains **eutectoid ferrite** and **cementite**.



Proeutectoid  $\alpha$



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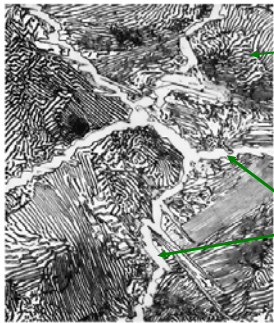
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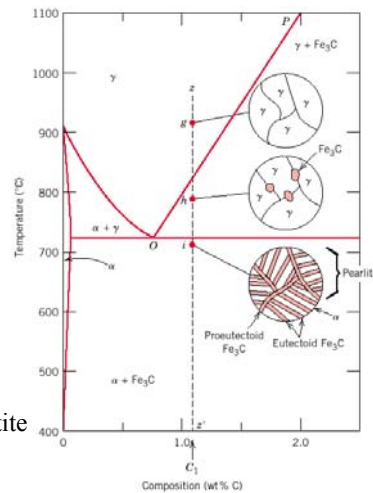
## Microstructure of hypereutectoid steel

Compositions to the right of eutectoid (0.76 - 2.14 wt % C) **hypereutectoid** alloys.  
- more than eutectoid (Greek)



pearlite

Pre-eutectoid cementite



## Phase Rule

- ✓ Are we free to vary the **temperature**? .....
- ✓ Are we free to vary both **temperature** and **pressure** independently? .....
- ✓ Are we free to vary both **temperature**, **pressure** and **volume** independently? .....

1 mole & ideal gas

As you know, we must specify only two variables (i.e. T and P, P and V, or V and T.) and the third variable is uniquely determined by the equation of state.

This means that the equilibrium condition of the system is fully defined by specifying two variables.

= We have two variables under our control

We can also say: Number of **degrees of freedom** = 2

What if the gas phase is a mixture of ideal gases A and B? Is the number of DOF still the same? .....

- Specifying T and P will determine V but the composition of the gas phase is left undetermined until the concentration of either A or B is fixed.
- Even after fixing T and P, we can freely vary the composition of either A or B, but not both, because  $X_A + X_B = 1 \rightarrow$  we have only one additional DOF

Number of **degrees of freedom** = 3



## Phase Rule

- ✓ What if a liquid phase coexist with the gas phase?
- ✓ What if a solid phase coexist as well?
- ✓ Is it possible thermodynamically to have another solid phase at equilibrium?

How can we answer these questions systematically?

J. W. Gibbs developed the thermodynamic methods for the characterization of equilibrium states of heterogeneous systems involving any number of substances.

• Recall that phase is a physically distinct, homogeneous and mechanically separable part of a system.

- Ice, water and steam are three distinct phases.
- Vapors and gases (*pure or mixed*) constitute a single phase because the component gases are miscible.
- Solutions (*liquid or solid*) are single phases
- Immiscible liquids constitute separate phases



## Equilibrium and Chemical Potential

Recall that:  $G = f(T, P) \rightarrow dG = -SdT + VdP$  For a **closed** system

And for an **open** system  $G = f(T, P, n_1, n_2, \dots) \rightarrow dG = -SdT + VdP + \mu_1 dn_1 + \mu_2 dn_2 + \dots$

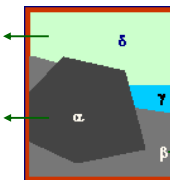
At constant pressure and temperature:  $dG = \mu_1 dn_1 + \mu_2 dn_2 + \dots$

This equation applies to all phases in a system!

$$dG^\delta = \mu_1^\delta dn_1^\delta + \mu_2^\delta dn_2^\delta + \dots$$

$$dG^\alpha = \mu_1^\alpha dn_1^\alpha + \mu_2^\alpha dn_2^\alpha + \dots$$

$$dG^\beta = \mu_1^\beta dn_1^\beta + \mu_2^\beta dn_2^\beta + \dots$$



For simplicity, let's consider two-component (1 and 2) and two-phase ( $\alpha$  and  $\beta$ ) system

$$dG = dG^\alpha + dG^\beta = \mu_1^\alpha dn_1^\alpha + \mu_2^\alpha dn_2^\alpha + \mu_1^\beta dn_1^\beta + \mu_2^\beta dn_2^\beta$$

$$\text{From mass balance: } dn_1^\alpha + dn_1^\beta = 0 \text{ and } dn_2^\alpha + dn_2^\beta = 0$$

$$\rightarrow dG = (\mu_1^\alpha - \mu_1^\beta) dn_1^\alpha + (\mu_2^\alpha - \mu_2^\beta) dn_2^\alpha$$

At equilibrium  $dG = 0$ , since  $dn_1^\alpha$  and  $dn_2^\alpha$  are not zero

$$\rightarrow \mu_1^\alpha = \mu_1^\beta \text{ and } \mu_2^\alpha = \mu_2^\beta$$



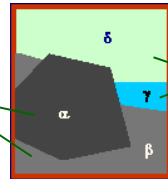
## Equilibrium and Chemical Potential

$$\mu_1^\alpha = \mu_1^\beta$$

$$\mu_2^\alpha = \mu_2^\beta$$

This applies for all phases

This means that the chemical potential of component 1 in phase  $\alpha$  is the same as that in phase  $\beta$ .



The same applies to  $\gamma$  and  $\delta$  phases

$$\text{In general: } \mu_1^\alpha = \mu_1^\beta = \mu_1^\delta = \mu_1^\gamma$$

At equilibrium, the chemical potential of each component is constant throughout the entire system.



## Phase Rule

Consider a system composed of  $c$  components that are distributed between  $p$  phases

- There are  $(c-1)$  component variables in each phase, because by knowing the concentrations of  $(c-1)$  components the last one can be found from:

$$X_1 + X_2 + \dots + X_c = 1$$

- Since there are  $p$  phases, the total number of component variables of the system is  $p(c-1)$ .
- Two additional variables are temperature and pressure.

→ The total number of variables is:  $p(c-1) + 2$



- Since the chemical potential of component  $i$  is constant throughout the system:

$$\mu_i^\alpha = \mu_i^\beta = \dots = \mu_i^p$$

→ The number of independent equations for each component is:  $(p-1)$

- Since there are  $c$  components, the total number of restricting equations is:  $c(p-1)$

Therefore, the number of undetermined variables =  $p(c-1) + 2 - c(p-1)$

$$\rightarrow \text{Number of DOF} = f = c - p + 2$$



## Phase Rule

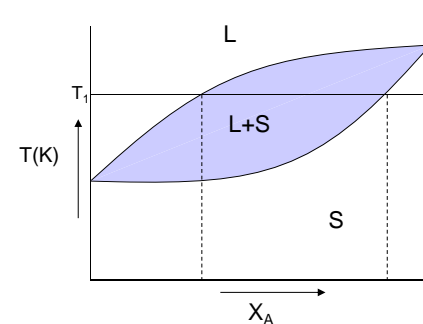
$$f = c - p + 2$$

- This equation is called **Gibbs Phase Rule** or the **Phase Rule**.
- This rule applies to both homogeneous and heterogeneous systems at equilibrium.
- It offers a simple means of determining the minimum number of intensive variables that have to be specified in order to unambiguously determine the thermodynamic state of the system.
- The application of the phase rule does not require a knowledge of the actual constituents of a phase.
- The phase rule applies only to systems that are at equilibrium.

**Algebraic Analogy:** It is commonly known that a system of two equations can be used to solve a maximum of two unknowns. However, if the system contains three unknowns yet only two equations, one of these independent variables must be defined in order to solve for the other two variables. In this case the system has one **Degree of Freedom**. In other words, the **Degrees of Freedom** equals the number of variables minus the number of equations.



## Application of the Phase Rule to Binary PD



Binary system at const. pressure (1 atm.)

### P=1 (solid or liquid)

$$F = C - P + 2 = 2 - 1 + 2$$

$$F = 3$$

As pressure is constant,  $F=2$

→ temp and comp vary independently

The region is thus called .....

### P=2 (Solid+Liquid)

$$F = C - P + 2 = 2 - 2 + 2$$

$$F = 2$$

Again because pressure is constant,  $F=1$

→ Here only temp varies independently for which comp is fixed

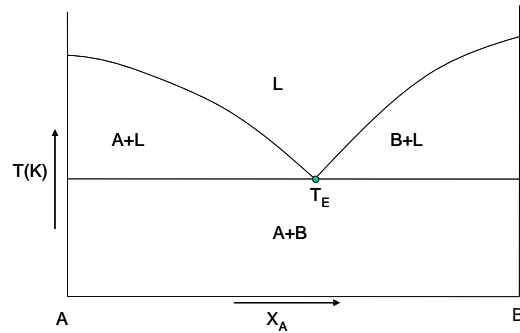
The two phase region is thus called .....





## Application of the Phase Rule to Binary PD

What is the number of DOF at the eutectic point?



**P=3 (liquid, solid A, B)**

$$F = C - P + 2 = 2 - 3 + 2$$

$$F = 1$$

As pressure is constant,  $F=0$

Eutectic point is an ..... point.

Next time:

**Multicomponent Systems**