Motivation

Phase diagram (Ch 9)

Temperature

A

B

Kinematics (Ch 10)

Time

A

B

New structure, concentration (mixing level)
(at what temperature? for how long?)
Goals for this unit

- Learn definitions and basic concepts of phase equilibria and phase diagrams
- Interpret equilibrium phase diagrams
  - binary isomorphous (complete ss)
  - binary eutectic (limited ss or no ss)
  - Intermediate compounds/phases
  - phases present
- their compositions and amounts (i.e., the “phase assemblage” of the system)

ss: solid solution

Phase Diagrams - Introduction

- Many materials systems can exist in a variety of forms depending on the temperature, pressure and overall composition (allotropy)
- A "phase diagram" is a graphical representation which details the form(s) the material takes under specific conditions
- Assumes the system has achieved chemical equilibrium (“equilibrium diagrams”)

Material Sciences and Engineering
MatE271
Week 7
Definitions and Basic Concepts

- **Equilibrium**
  - thermodynamic definition: a system is at equilibrium if its free energy is at a minimum
  - characteristics of the system do not change with time, i.e., the system is stable
  - If you change the temperature, pressure, or composition, the free energy will change
    - the specific phase(s) present may (or may not) change but the “phase assemblage” will!

Definitions

- **Component** (elements or compounds)
  - pure substance(s) required to express composition of phases in the system
- **Phase** (solid, liquid, gas)
  - Homogeneous portion of a system
  - uniform chemical and physical properties
  - several phases may be present simultaneously
  - in principal, phases are recognizable and separable
- **System variables**
  - Composition (in terms of components), temperature “T” and pressure “p”
Phase Equilibria

- Most systems we work with are solid systems:
- Sometimes (usually) the kinetics (rate of reaction) of the system will not allow a phase change to take place completely, or instantly, under certain conditions
  - example: glass of ice water in the sun when it’s 75°F outside (stays at 32°F until all ice is melted)
- Consider glass, stable form is quartz
  - This is a metastable state - persists indefinitely
  - Same with diamond and graphite

Definitions & Basic Concepts: Solubility

- Solubility limit - Sugar in Water

![Phase Diagram]

Material Sciences and Engineering
MatE271
Week 7
Phase composition

- A particular phase can have variable composition (i.e., can be a solution)
- Solute and solvent
  - Solvent (component present in greatest amount)
  - Solute (present in minor concentration)
- Solubility Limit
  - maximum allowed concentration of solute in solvent
  - depends on species, temperature and pressure

Definition – Phases

- This phase diagram is a two-component system, sugar (dextrose) and water.
- Q. What are the phases in this system?
- A. liquid ("syrup" or sugar -in-water sol’n) and a solid (pure crystalline sugar)
- Note: Solution vs. Mixture!
  - A mixture is heterogeneous (more than one phase present)
  - A solution is a single homogeneous phase of variable composition.
A two-phase mixture is present in the system ("syrup"+sugar)
Phases

Phase Characteristics:
A phase does not have to be BOTH physically and chemically distinct

Q. What is an example of a physically, but not chemically distinct phase?
- A. Water, ice, steam or Diamond, graphite

Q. What is an example of a chemically, but not physically distinct phase?
- A. Oil and water (both are liquids)

Equilibrium Diagrams

• Represents phase relationships as a function of temperature, pressure and composition (equilibrium phases and microstructure)

  - But many useful diagrams are constructed for constant pressure of 1 atmosphere, so only composition and temperature are variables

• Phase diagrams provides us with information needed for the control of phase and microstructure in the materials we make
Single Component Systems (fixed composition)

Variables:  - Pressure “p”
            - Temperature “T”

Note: polymorphism
      triple point

Two Component Systems (P=1 atm)

- Melting temp of ice changes with % salt
- Four phase fields
  - Liquid (Brine)
  - Solid and Liquid (Ice & Brine)
  - Solid and Liquid (Salt & Brine)
  - Solids (Ice and Salt)
- Composition of brine changes
- Questions
  - What is min temp at which salt works?
  - At any given temp is there an optimal amount of salt?
The Phase Rule

- Gibbs Phase Rule
  - After J. W. Gibbs - 19th century physicist
- Based on thermodynamics
- Predicts the number of phases that will coexist within a system at EQUILIBRIUM
- Does not apply in non-equilibrium situations!

\[ P + F = C + N \]

- \( P = \) number of phases present
- \( C = \) the number of components
  (minimum # needed to describe system)
- \( N = \) number of noncompositional variables
- \( N = 1 \) or \( 2 \) for \( T \) (\textit{temperature}) and \( p \) (\textit{pressure})
  \[ N = 1 \text{ if } p=\text{const or } T=\text{const} \]
  (HINT: \( p \) is usually constant so \( N \) is usually 1)
The Phase Rule

\[ P + F = C + N \]

- \( P \) = Phases
- \( C \) = Number of components
- \( N \) = 1 (usually for temperature)

\( F \) = number of degrees of freedom

No. of externally controllable variables (e.g. \( T \), \( p \), and composition of a phase), which can be changed independently without altering the number and kinds of phases which coexist at equilibrium.

Phase Rule - Example

Point: \( \Delta \)

\[ P + F = C + 1 \] (\( N = 1 \), \( p = \text{const.} \))

\( C = 2 \) (A and B) \( P = 1 \) (liquid) \( \Rightarrow F = C + 1 - P = 2 + 1 - 1 = 2 \)

To completely describe the characteristics of this alloy:
- you must describe 2 parameters \( T \) and composition
- you can change 2 variables without changing the # of phases at equilibrium
Phase Rule - Example

Point: B  \[ P + F = C + 1 \]  (N = 1, p = const.)

C = 2 (A and B)  P = 2 (liquid and \( \alpha \))  \[ F = C + 1 - P = 2 + 1 - 2 = 1 \]

To completely describe the characteristics of this alloy:
- you must describe 1 parameter (T or composition of one of the phases)
- you can change 1 variable without changing the # of phases at equilibrium

(note only the nature of the phases is important - not relative amount)

Phase Rule - Example

Point: C  \[ P + F = C + 1 \]  (N = 1, p = const.)

C = 2 (A and B)  P = 3 (liquid and \( \alpha \) and \( \beta \))  \[ F = C + 1 - P = 2 + 1 - 3 = 0 \]

To completely describe the characteristics of this alloy:
- you do not need to describe T or composition
- you cannot change any variables without changing the number of phases present
Equilibrium phase diagrams - binary systems

I. Binary isomorphous (complete ss)
II. Binary eutectic with no ss
III. Binary eutectic with limited ss
IV. Eutectoid
V. Peritectic
VI. Intermediate Phase
VII. General

I. Binary Isomorphous Systems “complete ss”

• Complete liquid and solid solubility of both components
• Common in some alloy systems
e.g. Ni-Cu
• Seen in some salt systems
  KCl- KBr
• Solid phase is a “solid solution”
  • it’s like a liquid solution e.g. water and alcohol
  • not like a liquid mixture e.g. oil and water
Solid Solutions

- How do they form:
  - Usually by introducing solute atoms into the solvent lattice
- Why are solid solutions important?
  - tailor mechanical, electrical, magnetic properties
- Complete solid solution sometimes occurs when solute and solvent have:
  - same crystal structure and similar atomic radii

Solid Solution Phase Diagram

- Complete Solid Solubility
  - note that solid and liquid are each homogenous
- Q: Number of phases in each phase field

What is this point?

Liquid: AB
SS: AB
Solid Solution Phase Diagram

- Note solid solution phase is called $\alpha$
- Liquidus line - First solid appears on cooling
- Solidus line - Last liquid disappears on cooling

Interpretation of Phase Diagrams

To determine phases present:

1. Locate
   - Temperature
   - Composition

2. Phase Field is labeled
   - Liquid and S.S. ($\alpha$)
   - Solid Solution, $\alpha$ "Only"
What is the phase assemblage
For a composition of 35% B
at a temperature of $T_1$?

- Phases present (by inspection)
- solid solution $\alpha$ and liquid
- Phase compositions (ends of the tie line)
  $\alpha$ -- 45% B, 55% A
  liquid -- 10% B, 90% A

How much liquid and how much solid?

- Valid for two phase region only

Fraction of liquid = $\frac{C_L - C_\alpha}{C_L - C_\alpha}$
Fraction of solid = $\frac{C_k - C_\alpha}{C_L - C_\alpha}$
Phase Amounts - Inverse Lever law

\[ C_o = 35\% \text{ B} \]
\[ C_L = 10\% \text{ B} \]
\[ C_\alpha = 45\% \text{ B} \]

Phase Amount

- Calculate length of tie line and length of each segment
- e.g. For an overall composition of 35\% AB at T_1
  liquid amount =\((45-35)/(45-10)\) = 0.286 (28.6%)  
solid amount =\((35-10)/(45-10)\) = 0.714 (71.4%)

Common Mistakes

- Mixing up phase composition and phase amount
- Taking the fraction of the tie line for the wrong phase (take the length opposite the phase you are interested in)
- Weight fraction vs. mole fraction
- note how the composition axis is labeled!
- you may have to convert from weight to mole fraction or even to volume fraction
Example

50-50 w% Cu-Ni
Cooling from 1400°C
- What T does 1st solid form?
- What is the comp. of the solid phase?
- At what T does the last liquid solidify?
- What is the composition of the liquid phase?

Example

- 1st solid at 1320°C
- Composition of solid: 62w% Ni, 38w% Cu
- Last liquid at 1275°C
- Composition of liquid: 37% Ni, 63% Cu
- Ni rich solid forms leaving Cu rich liquid
Microstructure Development

Cu-Ni phase diagram
Microstructure Development

- Notice that composition of solid changes continuously as it forms
- Adjustments in composition is often limited by diffusion (dependent on rate of cooling)
- Most cooling processes are fast
  - nonequilibrium solidification
  - “segregation”
  - “cored” structures

“Cored” Microstructure

- Interior is rich in higher melting component
- Exterior is rich in lower melting component
II. Simple Binary Eutectic: *No Solid Solubility*

- **Liquidus** - first solid appears on cooling
- **Eutectic Line** - line of 3 phase equilibrium
- **Invariant Point** - where 2 liquidus lines and eutectic line meet

\[ T_{m(eutectic)} < T_{m(A)} \text{ or } T_{m(B)} \]

III. Simple Binary Eutectic: *Limited Solid Solubility*

- **Limited Solid Solubility**
  - \( \alpha \) is solid A with small amount of solid B dissolved in it
  - \( \beta \) is solid B with small amount of solid A dissolved in it
- Components have different solid solubilities
**Binary Eutectic**

- **Eutectic (occurs at eutectic temperature)**
  - Line of three-phase equilibrium
- **Limit of solid solubility**
  - solidus (between solid and liquid and solid solution)
  - solvus (between single solid solution and mixture of solid solutions)

**Interpretation of Phase Diagrams**

To determine phases present

- Locate
  - Temperature
  - Composition
- Phase field is labeled

At $T_1$ and $C_o$ (approx. 35%B)

- Composition of liquid is $C_L$ (approx. = 45% B), amount (~ 20%)
- Composition of solid is $\alpha$ - (approx. = 10%B), amount (~ 80%)
Microstructure

- Close to end-member
- Liquid above liquidus
- Solid $\alpha$ precipitates crossing two phase boundary
- Solid $\alpha$ forms completely in solid solution region
- No other phase forms

Microstructure

- First solid ($\alpha$) forms at liquidus
- Solid grows - changes in composition
- Crosses solvus - becomes pure $\alpha$
- Crosses two-phase boundary - ($\beta$ precipitates)
Eutectic Microstructure

(forms when eutectic liquid freezes)

Lamellae

Alternating Pb-rich $\alpha$-phase (dark layers)
and a Sn-rich $\beta$-phase (light layers)

Chk textbook P. 317

IV. Eutectoid Binary Diagram ($\gamma$–Fe $\rightarrow$ $\alpha$-Fe)

- Eutectoid Reaction
  - Invariant point with three phases
  - Upon cooling, a solid phase transforms into two other solid phases
    - e.g. $\gamma$ (eutectoid) $\leftrightarrow$ $\alpha+\beta$
    - It's like a eutectic only involving solids
      
      \[ L \text{ (eutectic)} \Leftrightarrow \alpha+\beta \]
Unit Review

• Explain basic concepts of phase equilibria and phase diagrams
  • Solubility limit, phases, microstructure
  • Equilibrium phase diagram topics:
    • binary isomorphous, binary invariant points
    • phases present - their composition and amounts
    • microstructural development
• The phase rule is \( p + f = c + n \)
• READ Class Notes & Shackelford, 2001, Ch 9, pp 304-321, 331-348