Phase equilibria and Phase diagram

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Development of materials

- We have seen metals, metalloids and non metals in the periodic table
- Humans were using metals even before the periodic table was established
- Copper awl from 5000 BC
- Metals like gold in pure form
- Copper age to Bronze age to Iron and steels
- Alloying is the greatest gift of metallurgy to mankind

https://journals.plos.org/plosone/article?id=10.1371/journal.pone.0092591

- Aim is to improve properties
- Copper is good but can we get a lustre like gold so bronze
- Iron is good but can I make my sword stronger than that of my enemy
- Damascus or Wootz steel (iron carbon alloy)
- 24 carat gold is actually an alloy of gold and copper
- **An alloy is mixture or solid-solution of two or more elements where at least one of them is a metal. The final mixture is metallic in nature.**

Alloys

- From simple alloys lime Fe-C, Al-Cu, Cu-Zn, Cu-Sn to FeNiCr, AlMgSi, TiAlV, TiZrNb
- Superalloys contain 12 elements
- One major element other minor
- Multimetallic cocktails
- Bulk metallic glasses: Confusion principle
- High entropy alloys or complex concentrated alloys
- Thermodynamic and kinetic modelling

Phase and Phase diagram

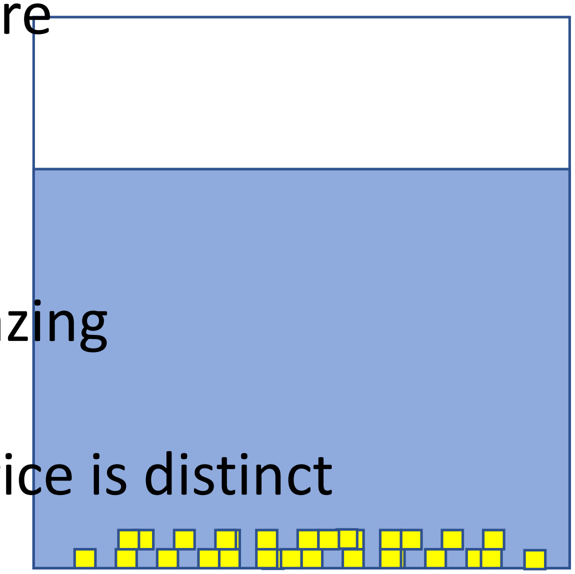
- Alloying for improvement in properties of metallic materials
- High strength, ductility, corrosion resistance
- Important to understand the effect of chemistry and microstructure
- This is captured using phase diagram
- Let us try to understand "Phase"

- Ice, water and steam
- Same chemical composition but distinct physical arrangement
- 3 different phases of water
- Crystalline ice has 18 known forms that is different crystal structures
- 18 forms of crystalline ice, water and steam are different phases of H_2O
- Iron: alpha iron (BCC); gamma iron (FCC); delta iron (BCC) are phases of iron

- A phase is defined as a homogeneous portion of a system that has uniform physical and chemical characteristics
- Every pure material is considered to be a phase; so also is every solid, liquid, and gaseous solution
- For example: ice, water, water vapour are phases
- Similarly; water, salt and solution of salt in water is a phase
- Ferrite is a phase of interstitial carbon in BCC alpha iron

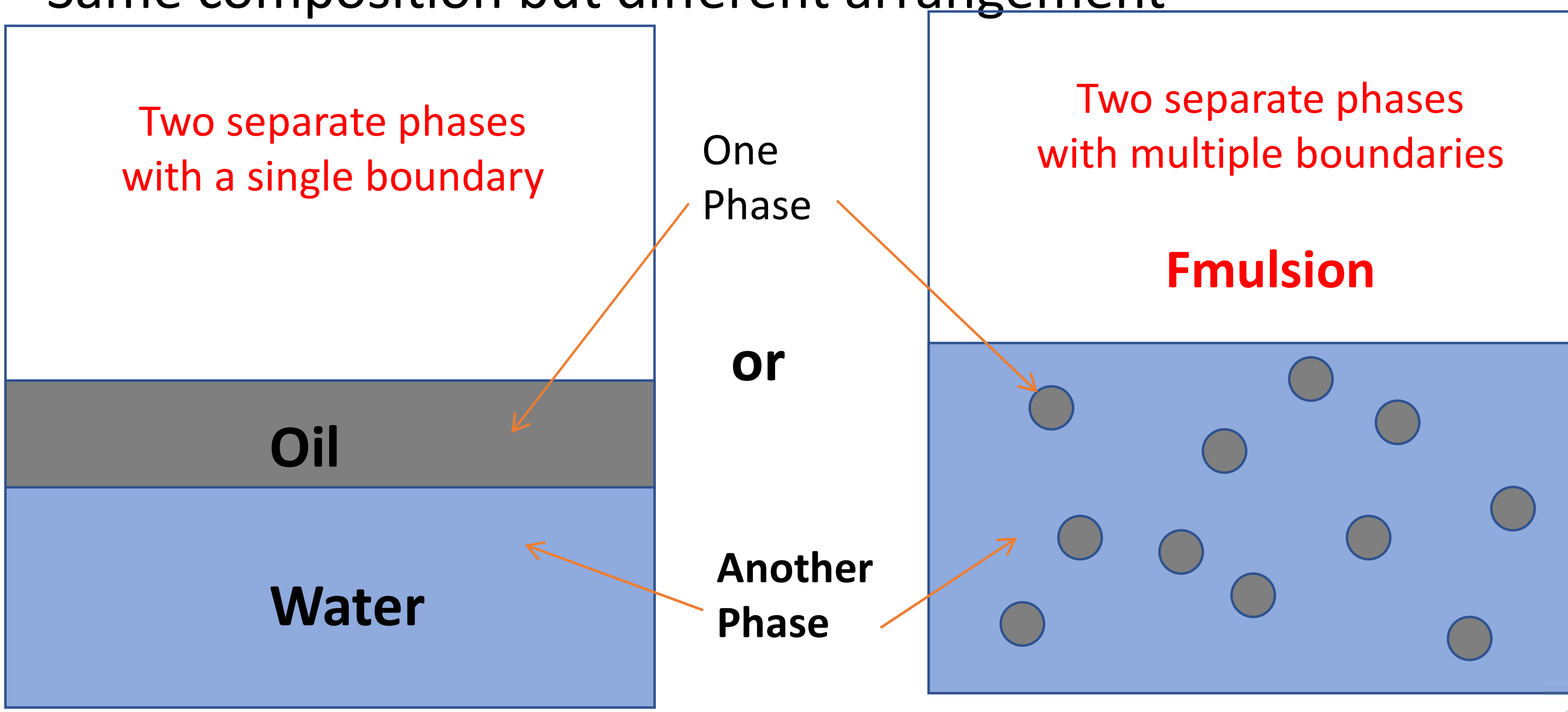
Examples

- Solution of salt in water
- Water and table salt NaCl are liquid and solid phase
- Solution has a concentration of salt in water and is a phase
- More salt dissolves at higher temperature
- Used to cook rice in biryani with spices
- Jackfruit biryani of Biryani by kilo is amazing
- Add oil so that each and every grain of rice is distinct



- For the ones with a sweet tooth
- Jalebi, gulab jamun, rasogulla include sugar solution
- Different concentration, different taste

- Salt, sugar water like each other
- Oil and water do not mix
- Same composition but different arrangement



- Making alloys is similar to cooking
- Trial and error or Serendipity
- Computational tools are the new cookbook for alloy making
  - Atomistic
  - First principles
  - Thermodynamic and kinetic modelling
  - Increasing use of ML
  - High throughput experiments
  - Advanced characterization
  - Rapid alloy prototyping

Advertisement

Journal of Alloys and Compounds

Volume 697, 15 March 2017, Pages 434-442

In the quest of single phase multi-component multiprincipal high entropy alloys

Tazuddin, N.P. Gurao, Krishanu Biswas

Tazuddin made us believe in Thermocalc

Journal of Alloys and Compounds

Volume 806, 25 October 2019, Pages 587-595

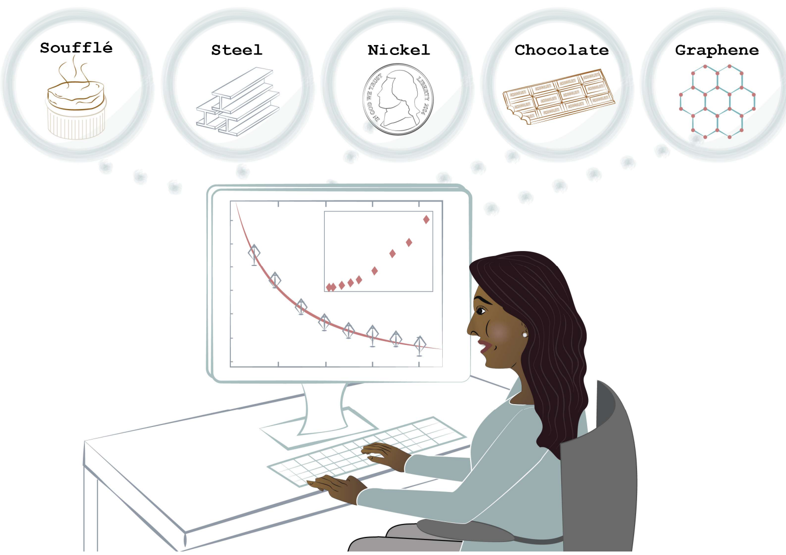
ICME approach to explore equiatomic and non-equiatomic single phase BCC refractory high entropy alloys

Abheepsit Raturi, Jaya Aditya C, N.P. Gurao, Krishanu Biswas

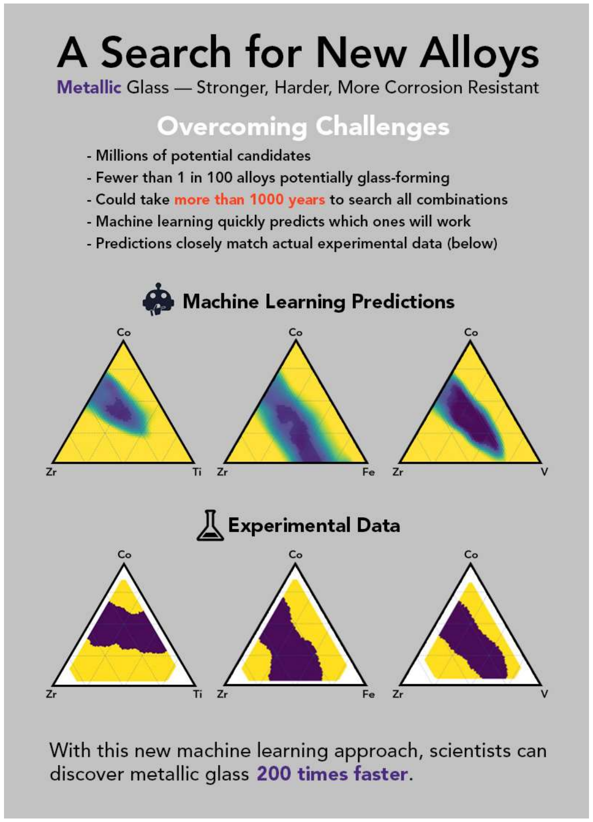
Abheepsit and Jaya Aditya took it to another level

MGI and ICME

Materials Genomics Initiative
and
Integrated Computational Materials Engineering



https://www.nist.gov/featured-stories/materials-design



Terminology

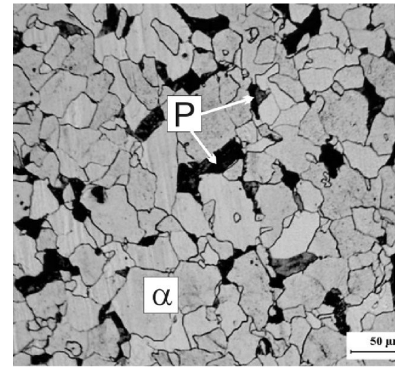
- **System:** water-salt or water-oil system
- **Phase:** salt, salt solution, water, ice, water vapour
- **Component:** water, salt, oil distinct chemistry
  Ice, water and water vapour are phases of H_2O
  H_2O is a component
- **Boundary:** interface between phases or components or system and environment
- **Phase boundary**: A boundary separating the phases in a system across which there will be a discontinuous and abrupt change in physical and/or chemical characteristics.

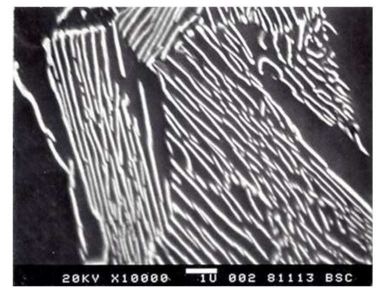
- Two regions of a system could be said to be representing two different phases, when:
  a) They are chemically different or
  b) They are structurally (physically) different, or
  c) both of the above

- Salt and water or melting ice that is ice and water are two phases

- Two and one component system respectively

- Remember this image Ferrite and pearlite
- Polish and etch
- Different response so we get contrast
- Are they two phases ?
- SEM shows pearlite has lamellar structure of ferrite and cementite
- Pearlite is a mixture of two phases





- Ferrite is solid solution of carbon in iron
- C occupies octahedral sites in BCC iron
- Cementite has Fe_3C composition
- Compound of metallic iron and metalloid carbon
- Orthorhombic crystal structure
- Pearlite appears lamellar in 2D but is wavy in 3D

- Equilibrium is state of balance
- Phase equilibrium refers to stability of phases for given components and external conditions like temperature and pressure
- Boiling of water and melting of ice
- For more than one component, composition is also important along with temperature and pressure to decide stability of a phase

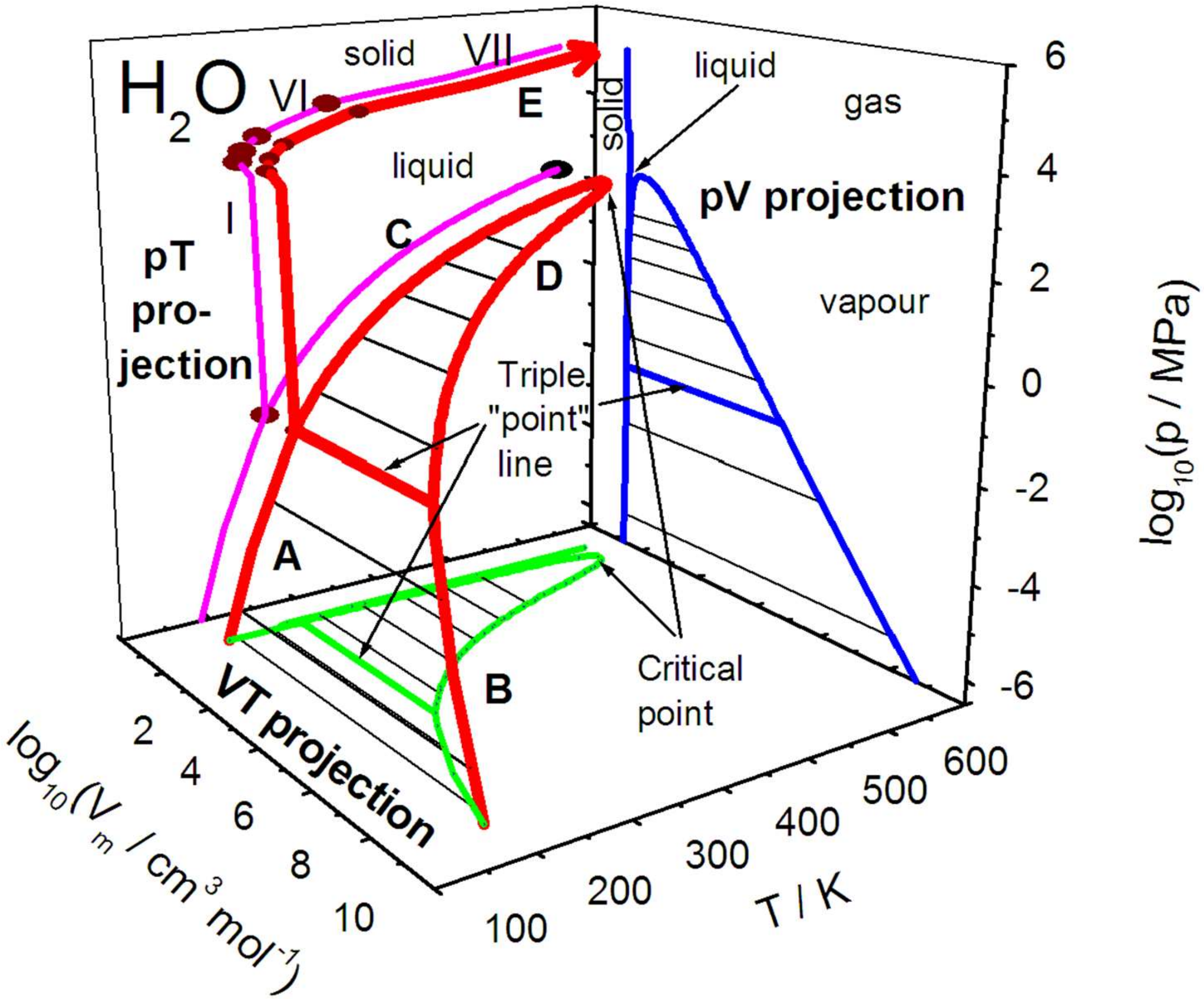
- Phase diagram is a graphical representation of phases present at equilibrium for given composition, temperature or pressure (c, T, P)

- Different sub-spaces like P-T or T-c are also used

- Temperature composition sub space at constant (normal) pressure is common in metallurgical operation

- 2D representation is common

PVT space for H_2O



http://biomodel.uah.es/Jmol/plots/phase-diagrams/

Pressure-Temperature phase diagram of water

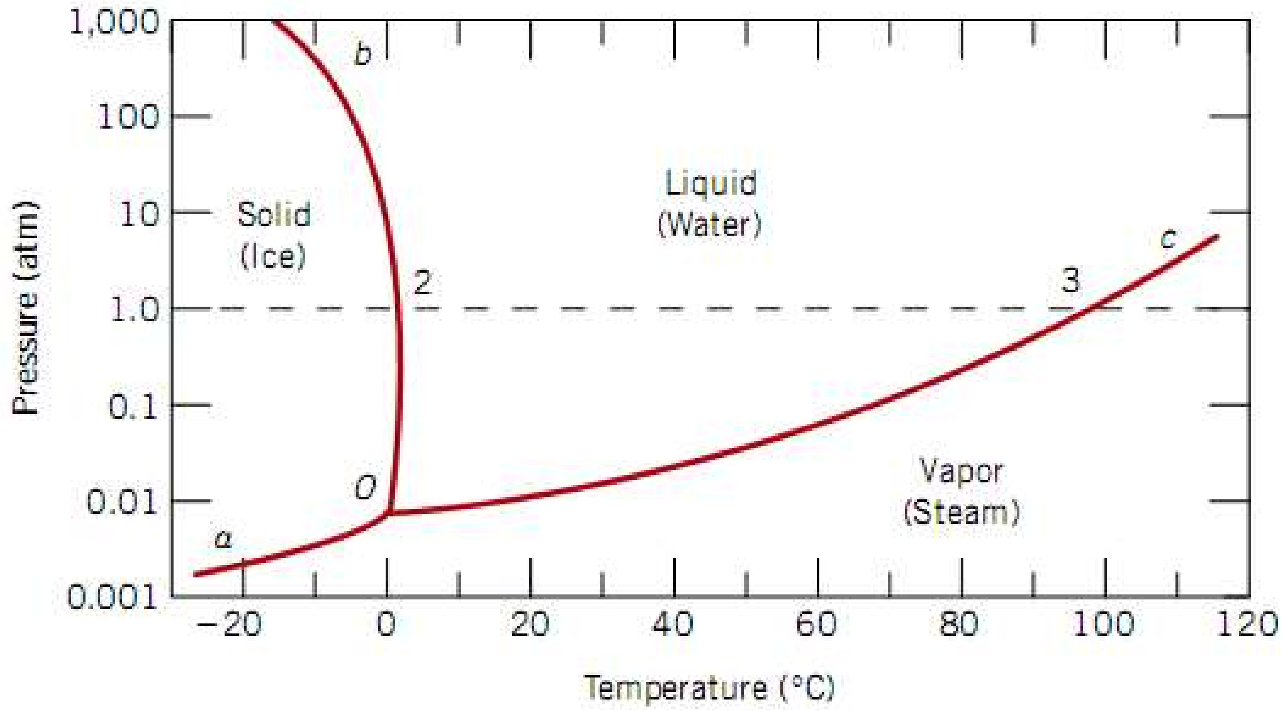
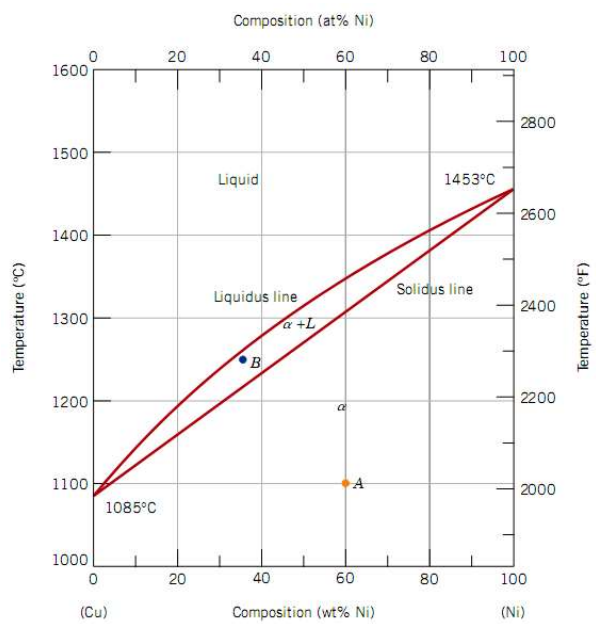


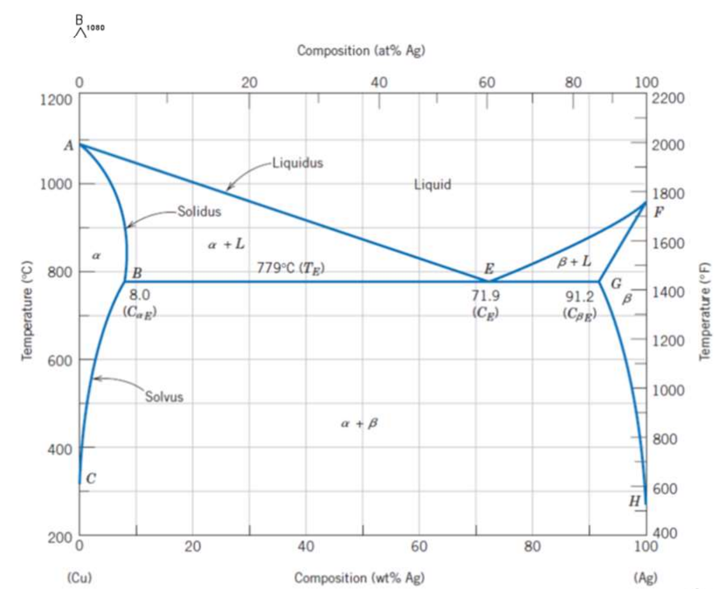
Figure 9.2 Pressure–temperature phase diagram for H_2O. Intersection of the dashed horizontal line at 1 atm pressure with the solid–liquid phase boundary (point 2) corresponds to the melting point at this pressure (T = 0°C). Similarly, point 3, the intersection with the liquid–vapor boundary, represents the boiling point (T = 100°C).

Phase diagram in materials science

- Materials processes at atmospheric pressure
- Composition vs temperature
- Binary linear scale in weight or atomic percentage



Callister



Phase diagram in materials science

- Ternary in 3D
- Ternary is combination of 3 binaries and 3 unaries

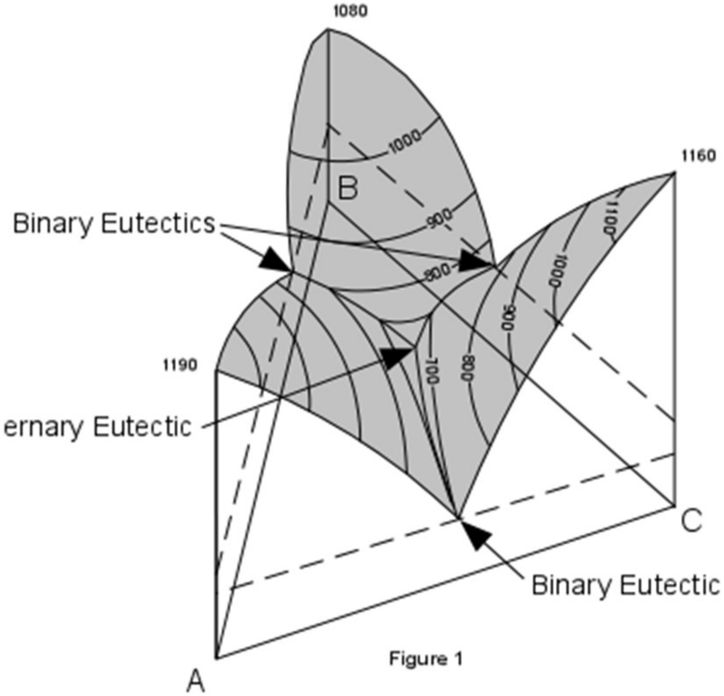


Figure 1

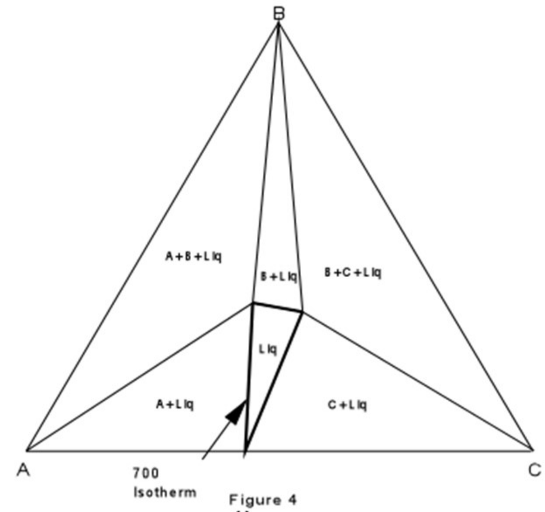


Figure 4

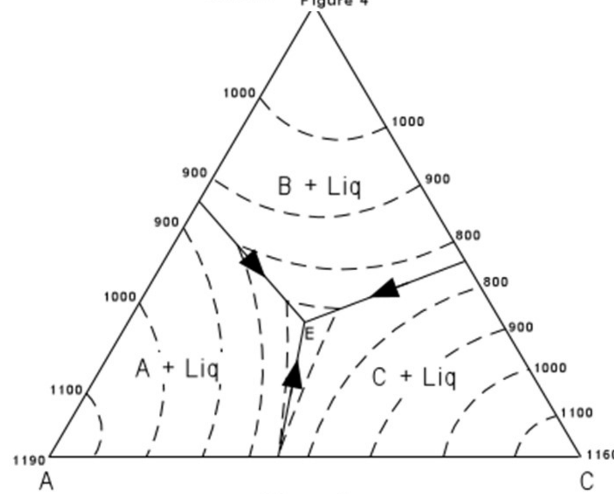
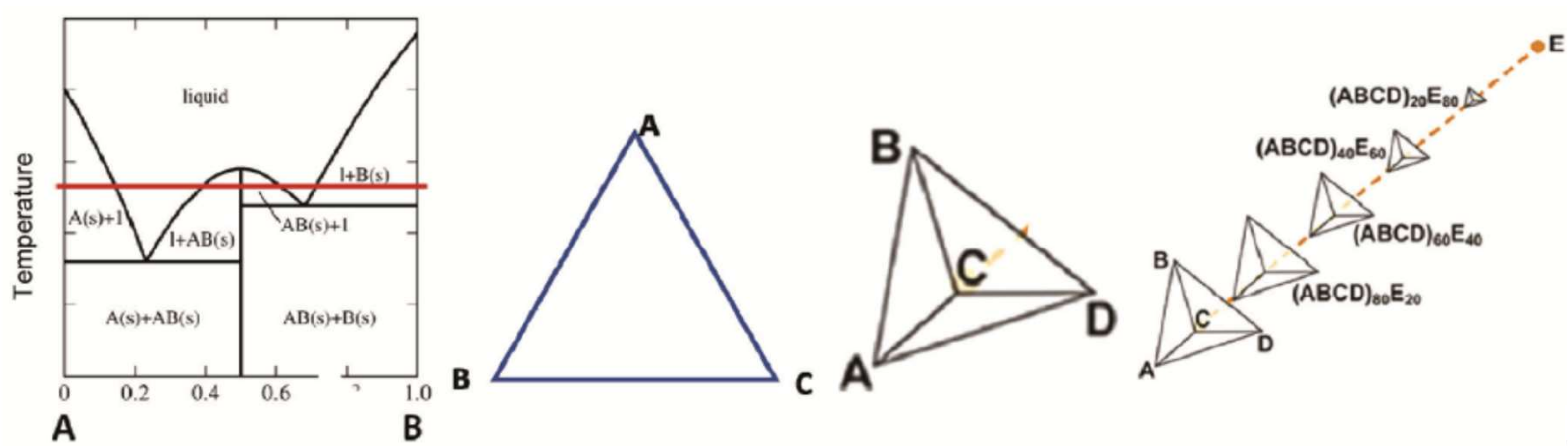


Figure 2

https://www.tulane.edu/~sanelson/eens212/ternaryphdiag.htm

Phase diagram in materials science

- Can go to higher dimensions for more components
- An isotherm is a point in unary, line in binary, equilateral triangle in ternary and tetrahedron in quaternary systems



Isomorphous phase diagram

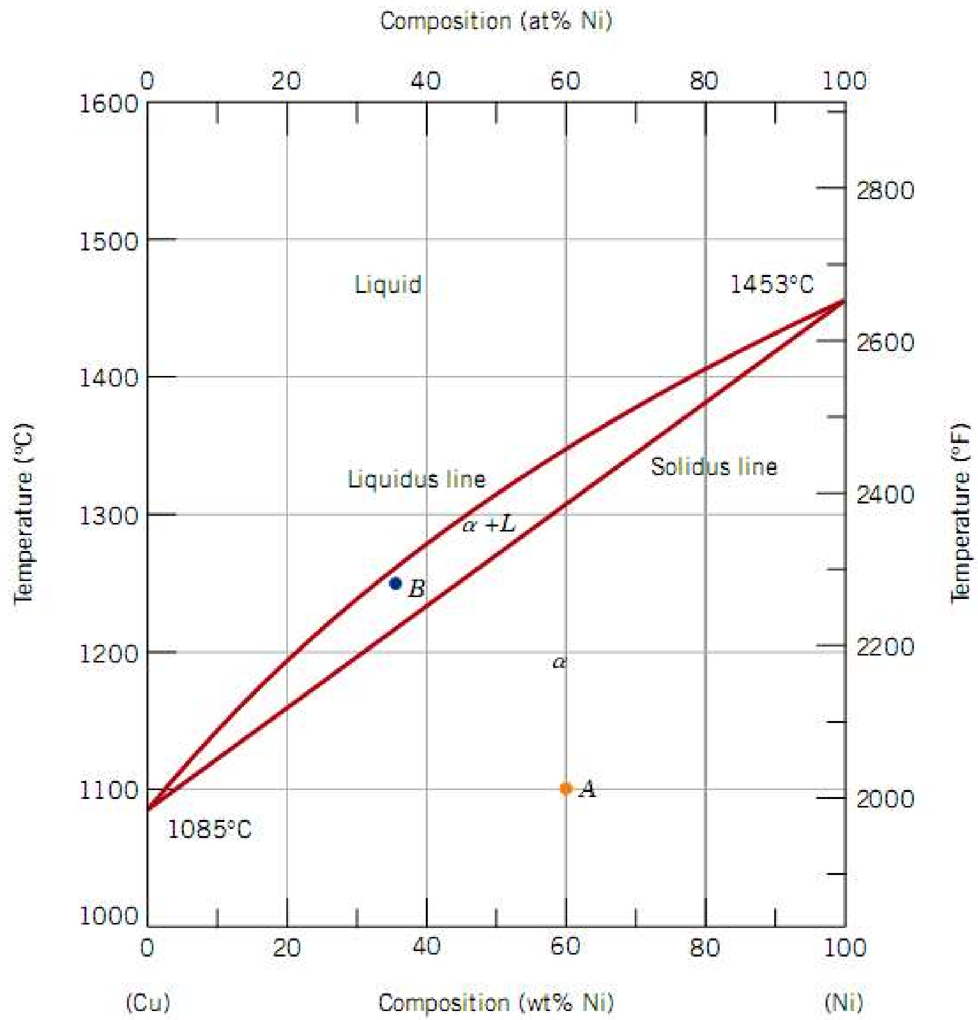
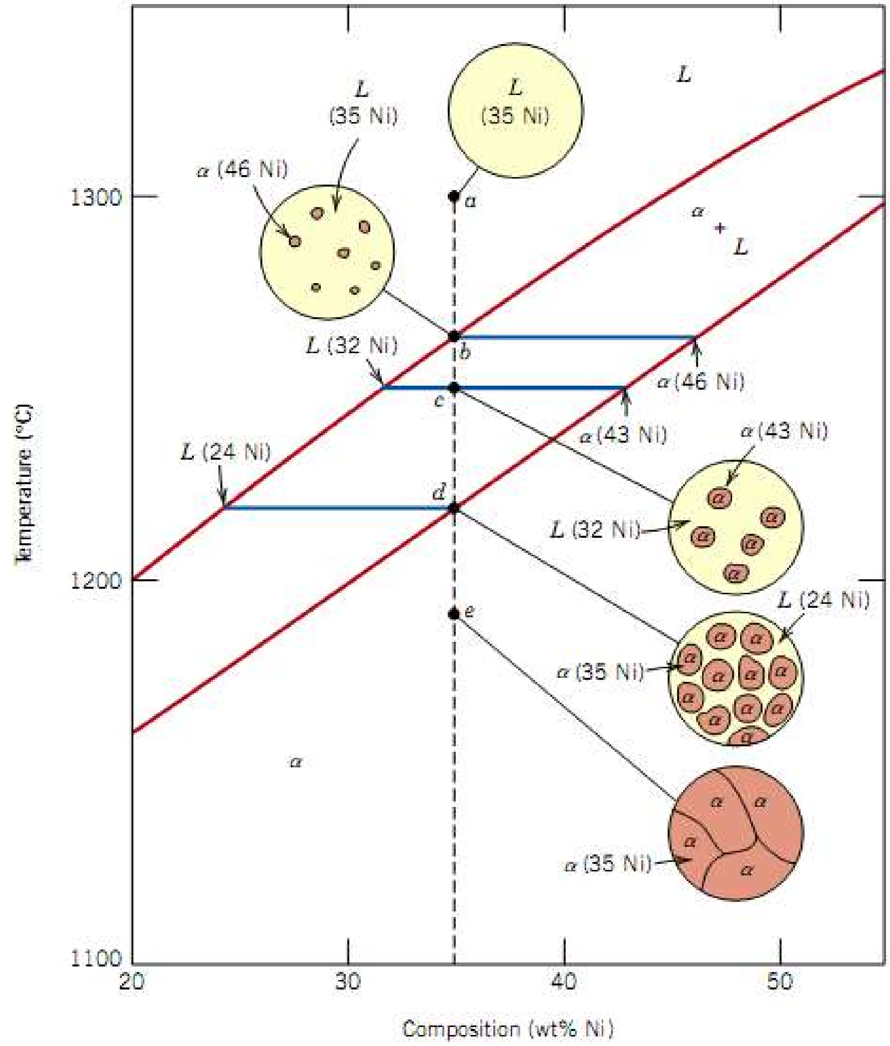


Figure 9.4 Schematic representation of the development of microstructure during the equilibrium solidification of a 35 wt% Ni–65 wt% Cu alloy.



Quasi-equilibrium

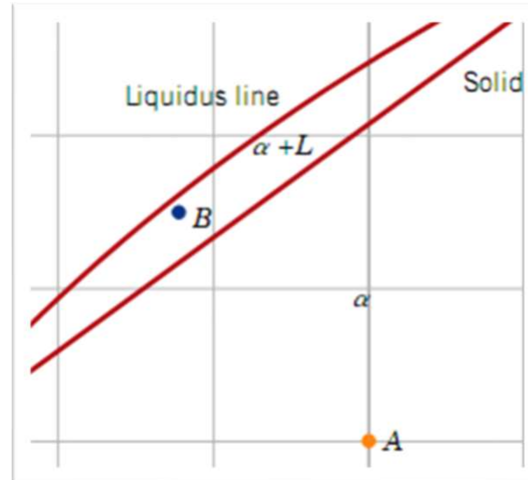
Phases present

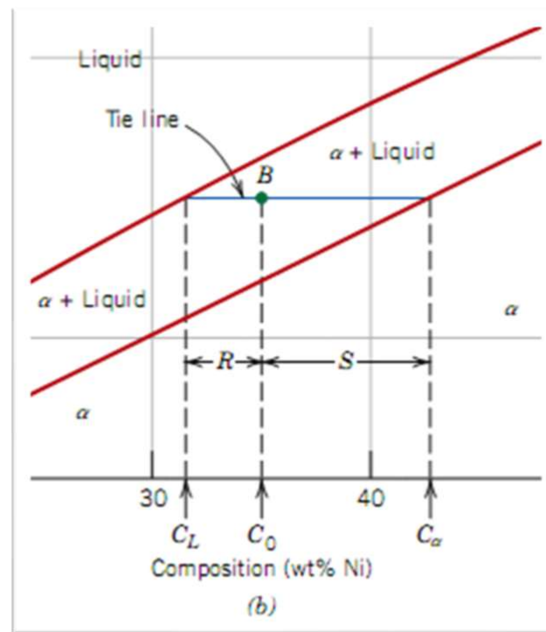
Composition of

Phases present

(a) In a single phase Region

(b) Multiple phase region





(3) Amount of

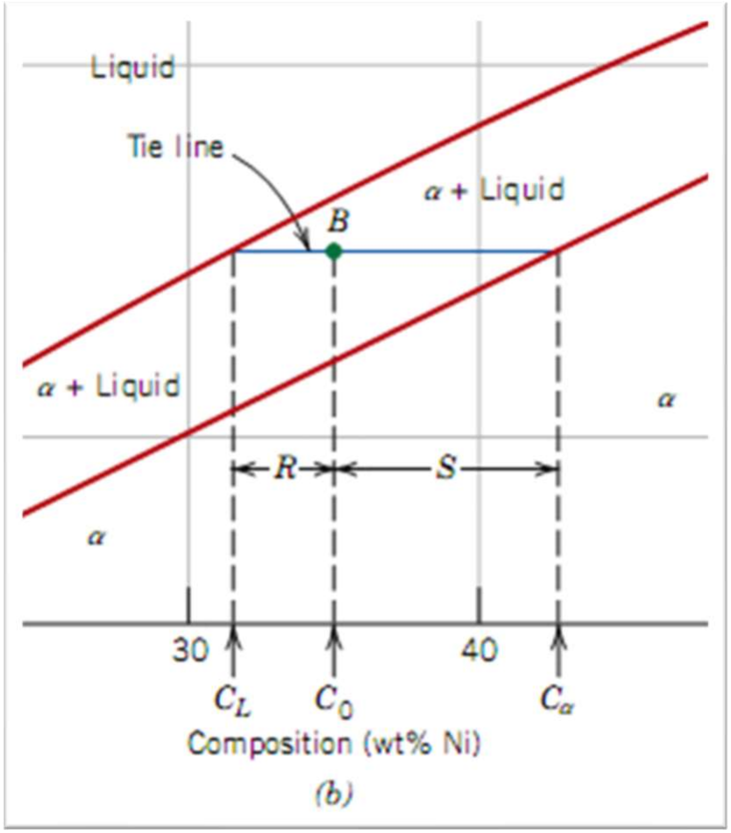
each phase present :

Lever rule

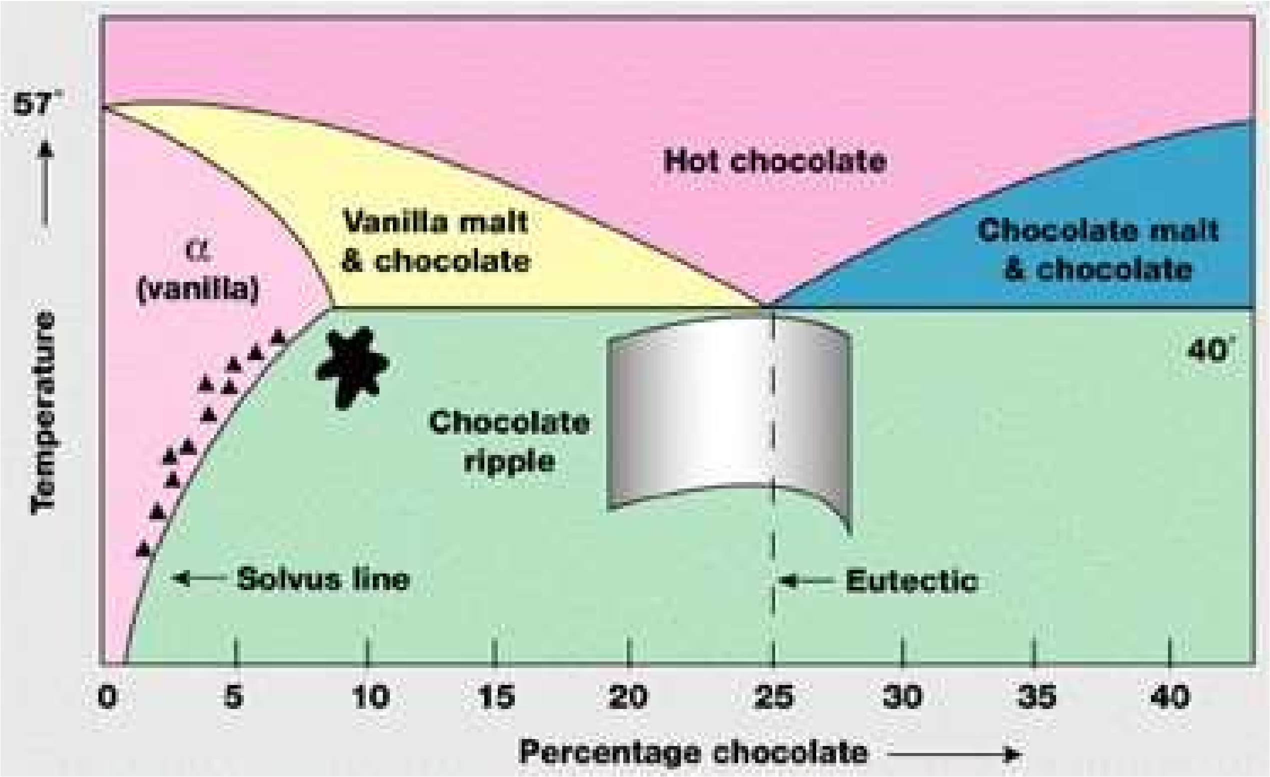
$$W_L = \frac{S}{R + S}$$

$$W_L = \frac{C_\alpha - C_0}{C_\alpha - C_L}$$

$$W_\alpha = \frac{R}{R + S} = \frac{C_0 - C_L}{C_\alpha - C_L}$$



Eutectic Chocolate vanilla



$$L(C_E) \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \alpha(C_{\alpha E}) + \beta(C_{\beta E})$$

Eutectic reaction

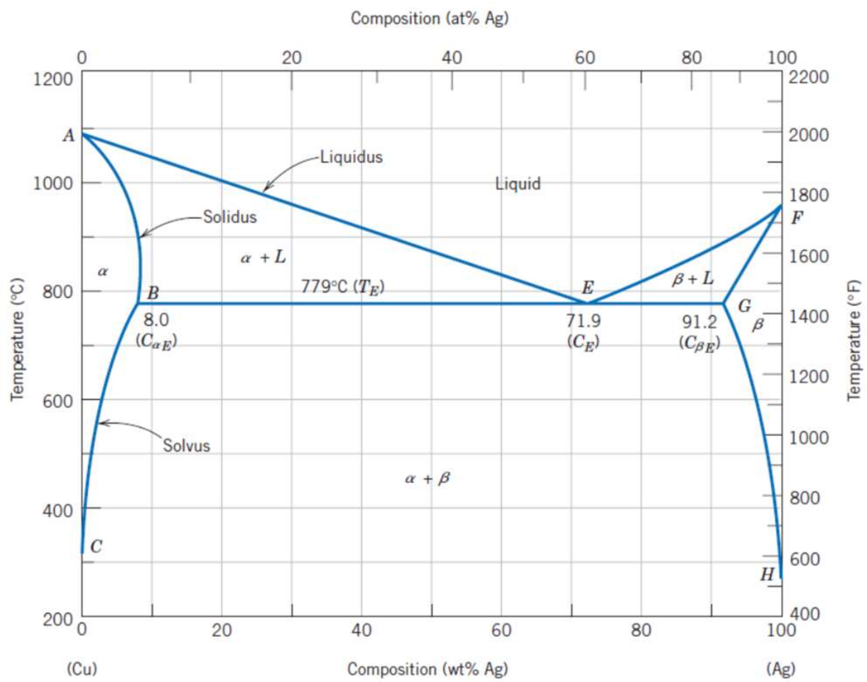
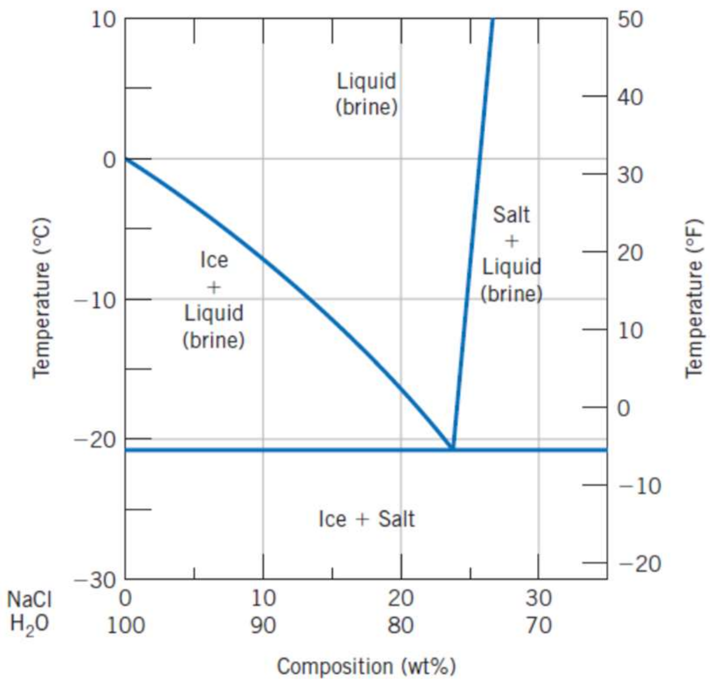


Figure 9.7 The copper–silver phase diagram. [Adapted from *Binary Alloy Phase Diagrams,* 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

$$L(71.9\text{ wt\% Ag}) \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \alpha(8.0\text{ wt\% Ag}) + \beta(91.2\text{ wt\% Ag})$$

Clearing ice and making solders



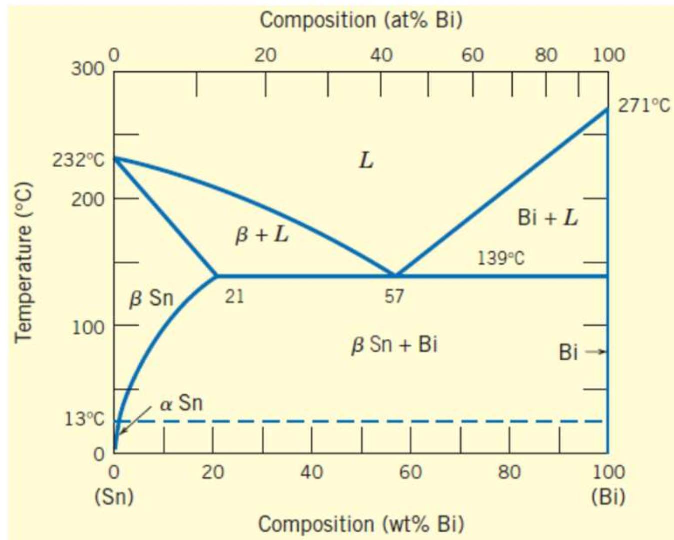
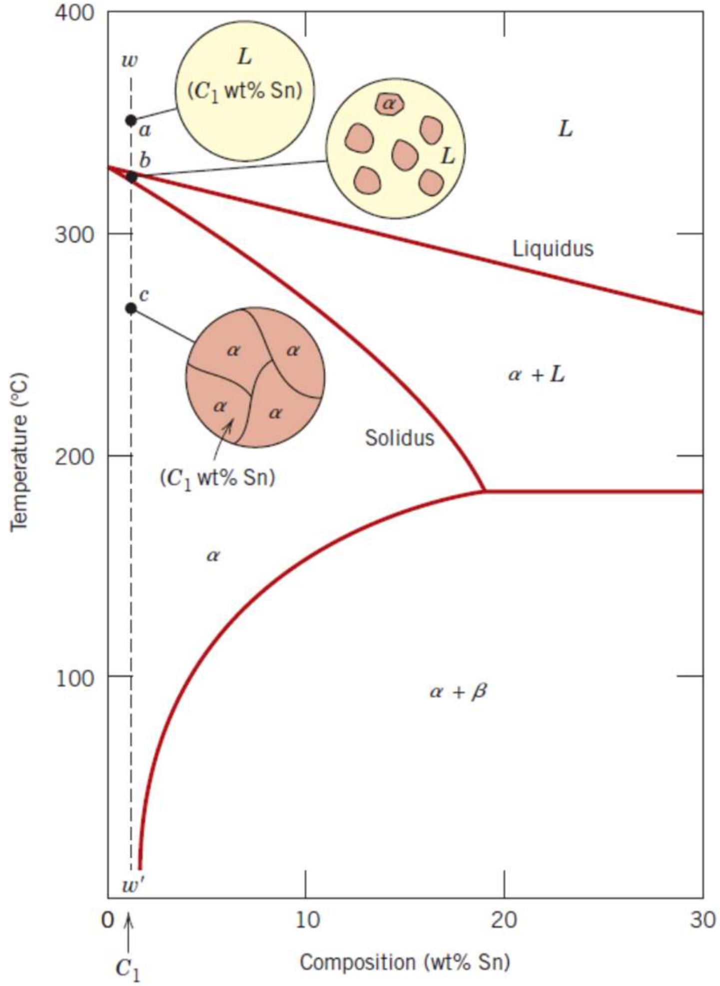


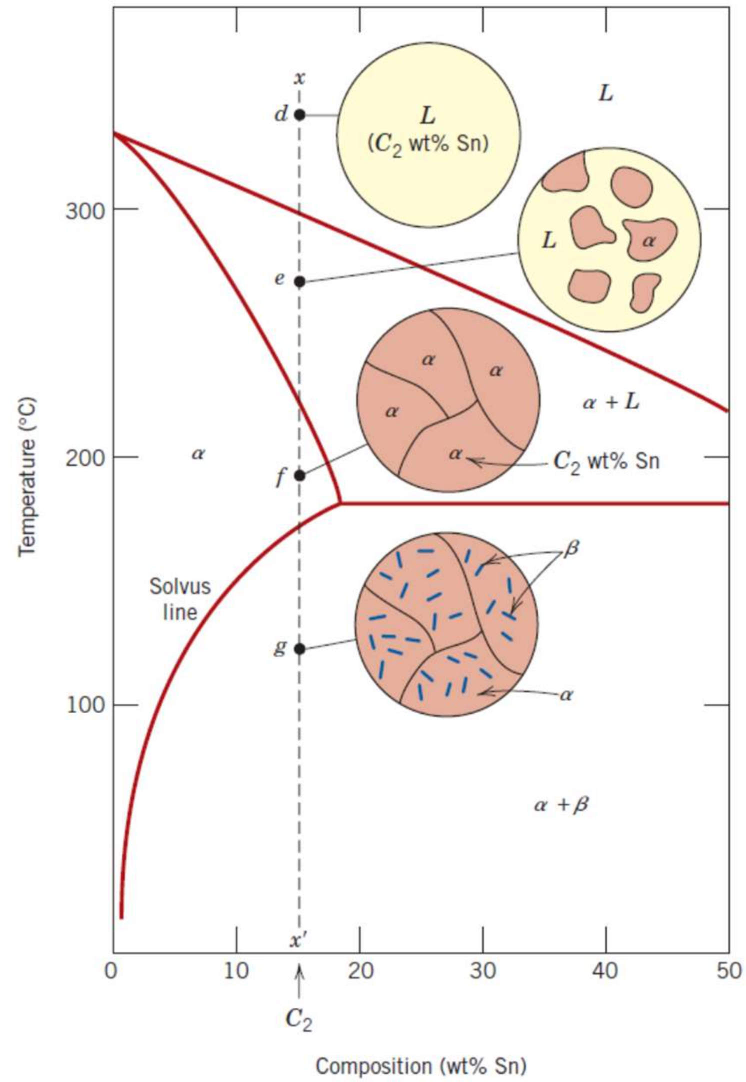
Figure 9.10 The tin–bismuth phase diagram. [Adapted from *ASM Handbook*, Vol. 3, *Alloy Phase Diagrams*, H. Baker (Editor), ASM International, 1992, p. 2.106. Reprinted by permission of ASM International, Materials Park, OH.]

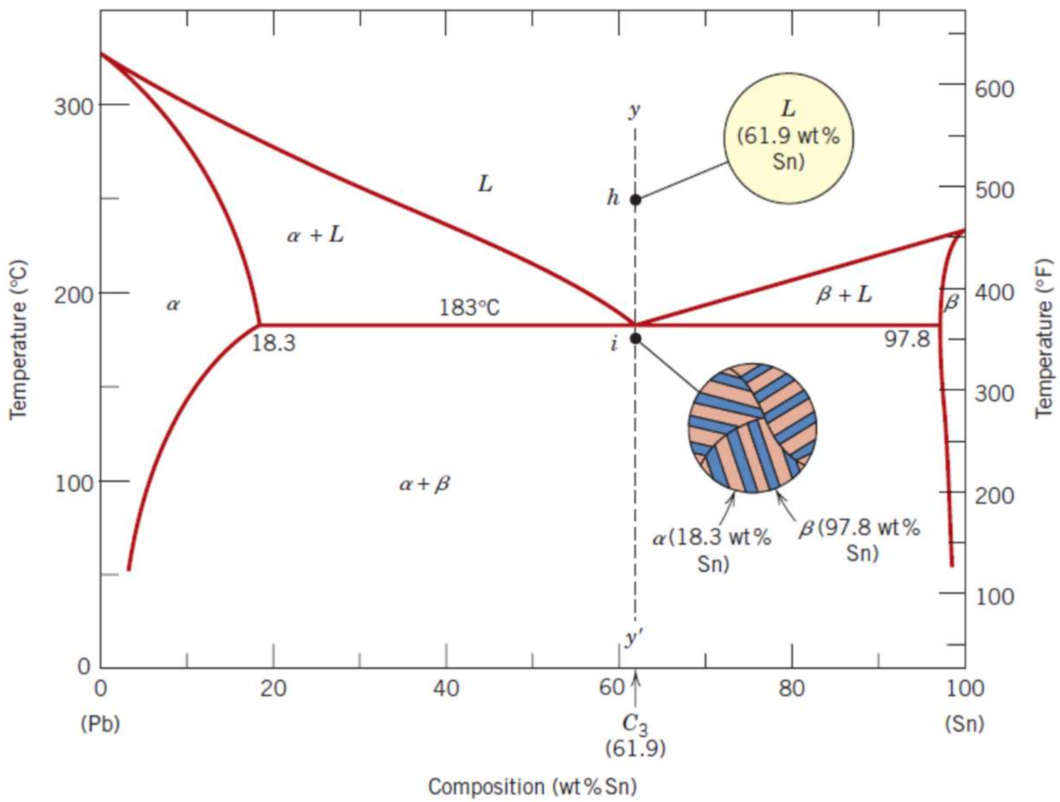
Salt is added on roads to melt ice

Soldering has lower melting point Lead free solders

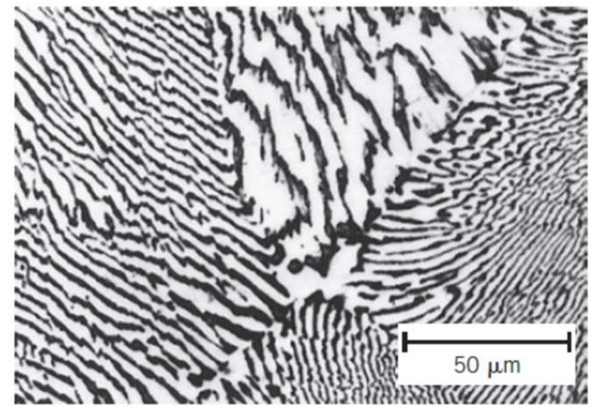
Microstructures



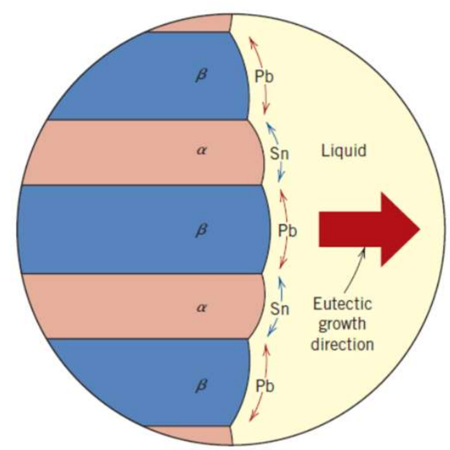




Temperature (°C)
Temperature (°F)
300
200
100
0
600
500
400
300
200
100
L
α + L
α
183°C
18.3
97.8
β + L
β
α + β
y
h
i
y′
L
(61.9 wt% Sn)
α(18.3 wt% Sn)
β(97.8 wt% Sn)
0
20
40
60
80
100
(Pb)
(Sn)
C_3
(61.9)
Composition (wt% Sn)

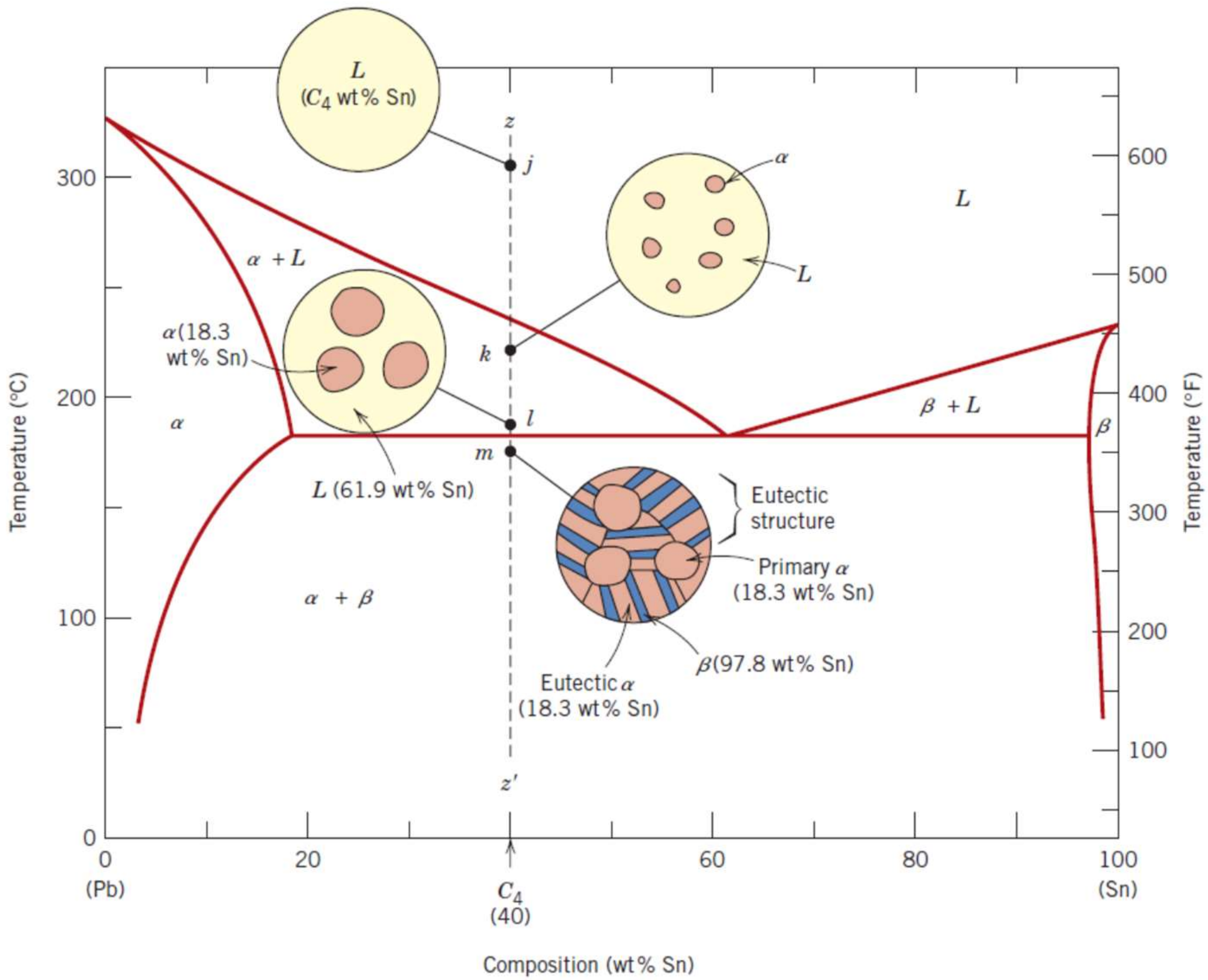


50 μm

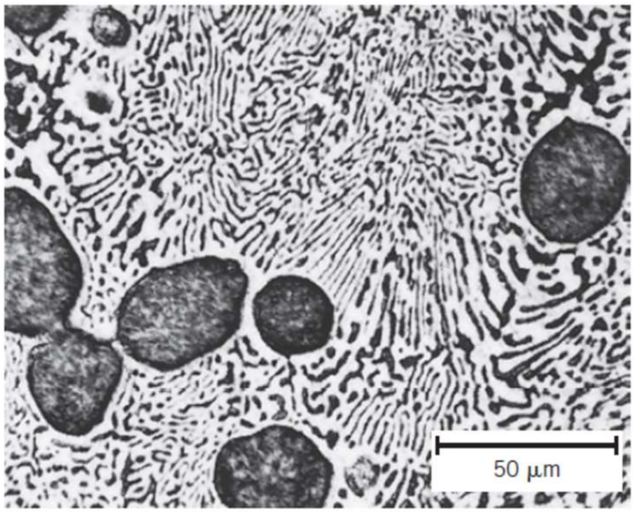


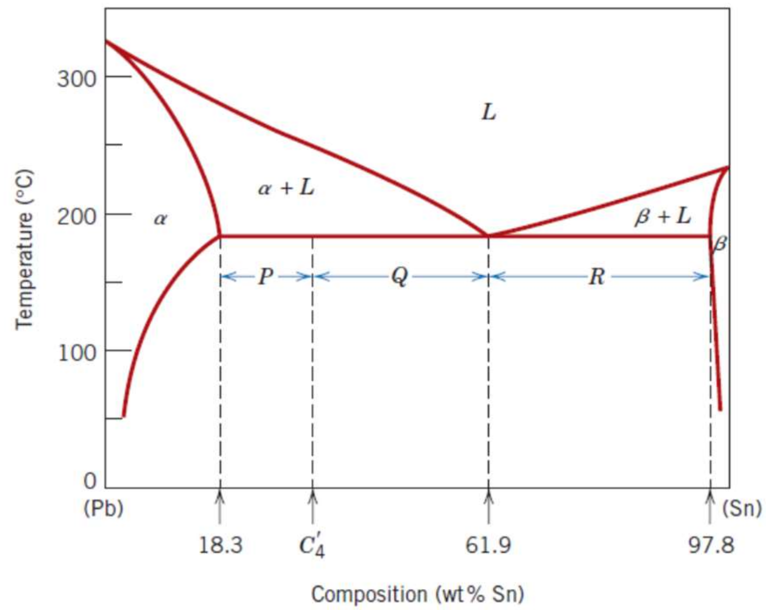
β
α
β
α
β
Pb
Sn
Pb
Sn
Pb
Liquid
Eutectic
growth
direction

Primary and Eutectuc phase



Primary solid solution and Eutectic phase





$$W_{\alpha'} = \frac{Q}{P + Q}$$

Primary alpha

$$W_{\alpha} = \frac{Q + R}{P + Q + R}$$

Total alpha

Imtermetallic phases and compounds in PD

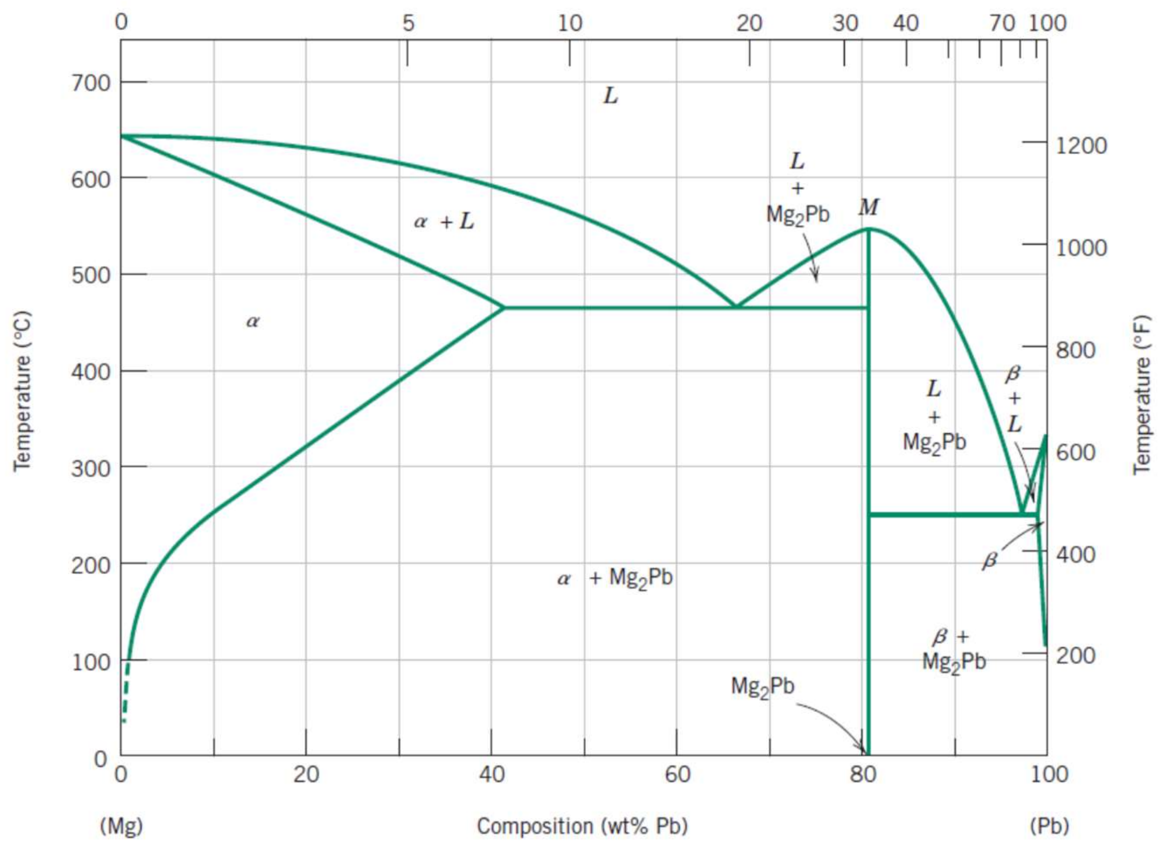
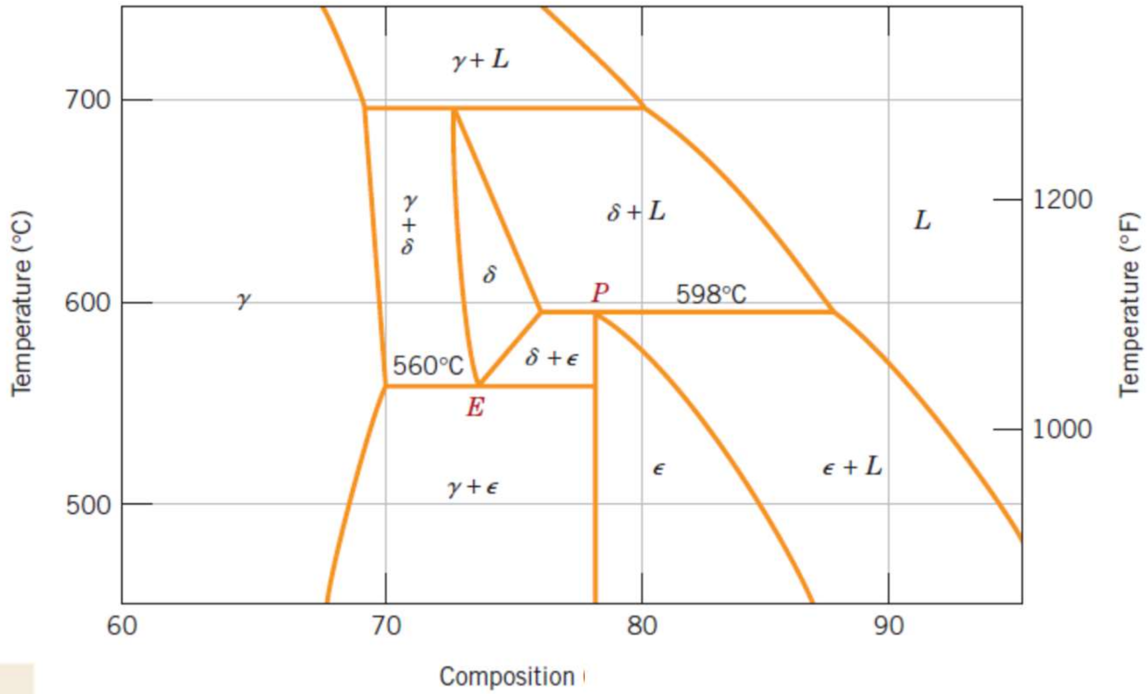


Figure 9.20 The magnesium–lead phase diagram. [Adapted from *Phase Diagrams of Binary Magnesium Alloys,* A. A. Nayeb-Hashemi and J. B. Clark (Editors), 1988. Reprinted by permission of ASM International, Materials Park, OH.]

Eutectoid and Peritectic reaction

Figure 9.21 A region of the copper–zinc phase diagram that has been enlarged to show eutectoid and peritectic invariant points, labeled *E* (560°C, 74 wt% Zn) and *P* (598°C, 78.6 wt% Zn), respectively. [Adapted from *Binary Alloy Phase Diagrams*, 2nd edition, Vol. 2, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]



$$\delta \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \gamma + \epsilon$$

$$\delta + L \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \epsilon$$

Eutectoid

Peritectic

Gibbs phase rule

- Prof. J. W. Gibbs

- Phase rule describes the number of intensive variables that must be defined to determine the state of the system.

- Relation between F, P, and C at equilibrium

- $F + P = C + 2$

- F: number of degrees of freedom P: number of phases, C: number of components, pressure and temperature constitute the two degrees of freedom for a system in equilibrium

- No chemical reaction

Gibbs phase rule

- The 'degrees of freedom' of the system (at chemical equilibrium) refer to the number of conditions or variables that can be altered, independent of each other, without effecting the number of phases in the system.

- Essentially, the degrees of freedom of a system describe the dependency of parameters such as temperature and pressure on each other.

- Temperature and pressure are intensive parameters or variables while mass, volume number of moles.

- Independent variables and dependent variables (restrictive conditions)

- System at equilibrium: temperature, pressure, concentration of each component in each and every phase

- C components in P phases, so total number of concentration in mol fraction are CP

- Total variables = CP +2

- Summation of concentration of all components in one phase is 1 so we have P equations

- Total variables = CP + 2 - P

- Now chemical potential of one component in all the phases is same

- If we know chemical potential of one component on one phase, we need not know the chemical potential in rest that is P-1 phases

- This is a restrictive condition so total chemical potentials that need not be determined are P-1

- $F = CP + 2 - P - (C(P-1))$

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

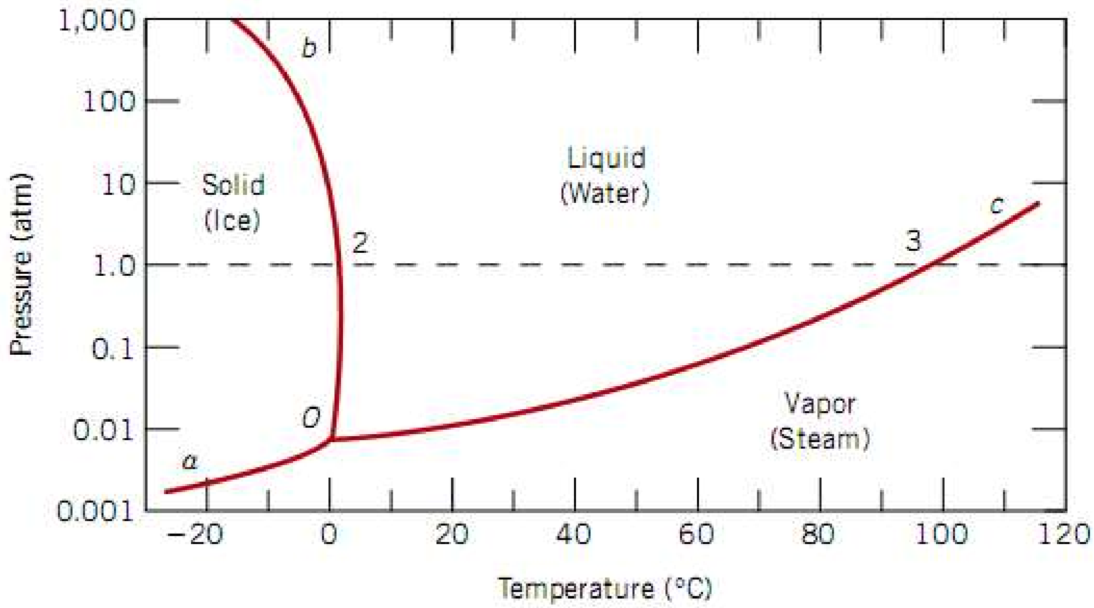
- $F + P = C + 2$

- For reactive C = C_s - r – s, r is independent reactions and s is species, C_s is no. of substances

- Beyond the scope

- Let us keep it simple

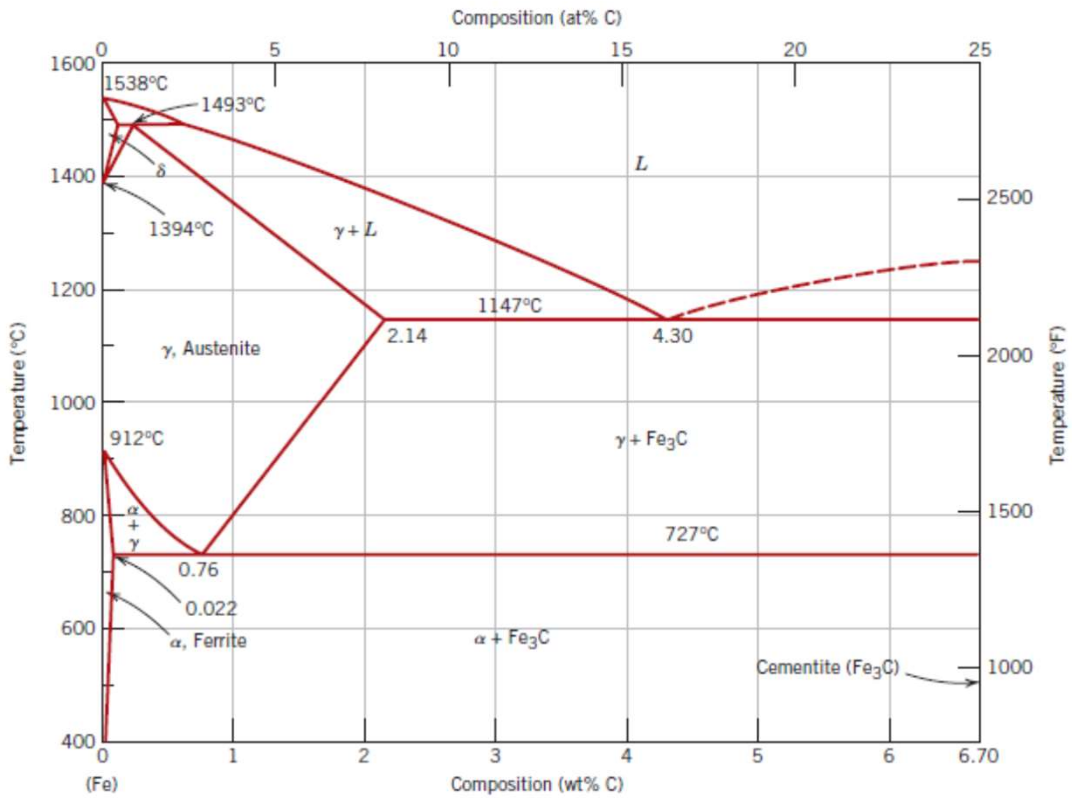
DOF in unary



- F + P = C + 2 = 1 + 2 = 3
- F = 2 for single phase region, one can independently vary intensive temperature ot pressure
- F = 1 for two phase, for pressure of 1 atmosphere, get the temperature and vice versa
- F = 0 at triple point

DOF in binary

- For binary systems, C = 2 and pressure is constant for metallurgical processes
- F + P = C +2 becomes
- F + P = 3 or F = 3 - P



- Single phase field, F = 2
- Two phase region F = 1
- Three phase region F = 0