Reading: West 11-12

Phase Diagram

- Also called equilibrium or constitutional diagram
- Represent the relationships between temperature and composition and quantities of phase at equilibrium
- Pressure also influences phase structure
  - Remains virtually constant in most applications
  - Most phase diagrams at 1 atm

Phases

- Homogeneous portion of the system with uniform physical and chemical characteristics
  - Salt – water
  - Salt NaCl
- A difference in either physical or chemical properties constitutes a phase
  - Water and ice
  - FCC and BCC polymorphic forms of an element

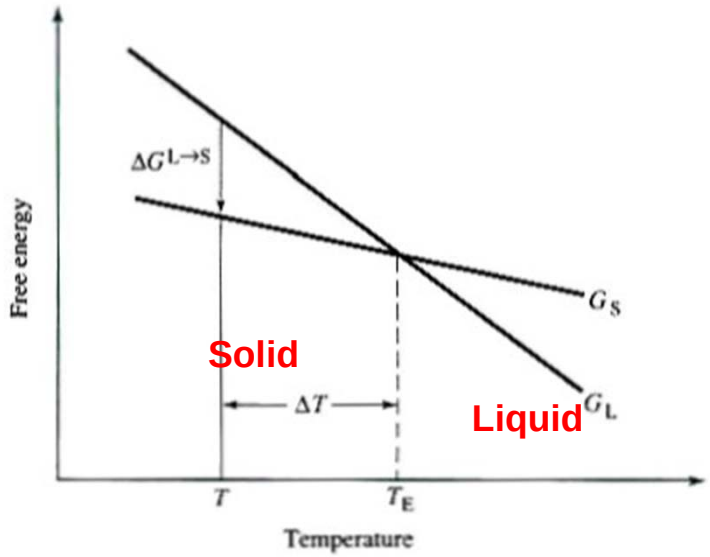
Phase Equilibria

- Free energy
  - Function of internal energy and randomness
  - Equilibrium → free energy is at a minimum under some specified combination of ***temperature, pressure, and composition***
  - spontaneous change to lower energy state

    $\Delta G = \Delta H - T\Delta S$
- Reaction occurs only if it results in a reduction in total energy of the system

Driving Force for Phase Changes

- Depends on change in free energy
- If free energy of solid < free energy of liquid at a particular temperature, solid forms, or vice versa
- Both may coexist at T_E as they have the same free energy ($G_L = G_S$)



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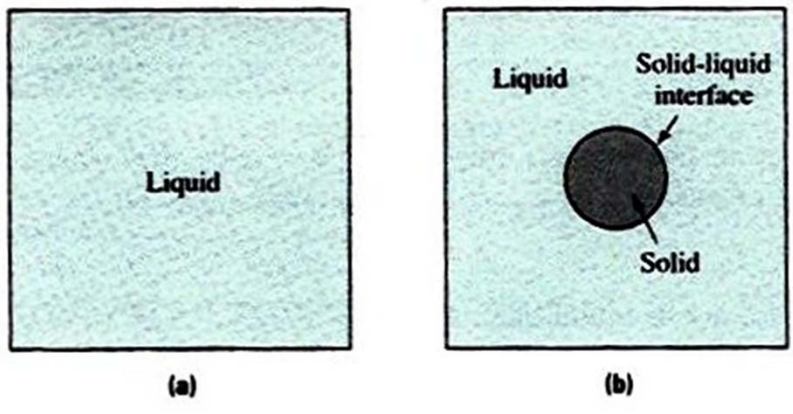
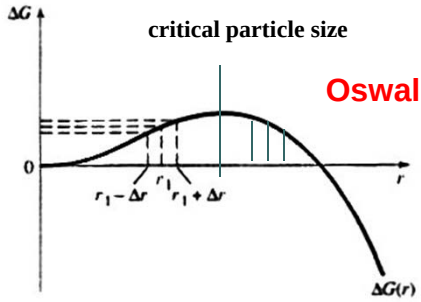


Crystal Nucleation and Growth



All particles with r<r are unstable. For a particle of size r_1 to grow an amount Δr represents an increase in Free energy, not a spontaneous process.*

The spontaneous process would be the dissolution of a particle of radius r_1, which lower the energy (subcrtical nuclei).

R = r* is a critical particle size since either growth or dissolution decreases the free energy. Beyond r*, only growth reduces free energy.

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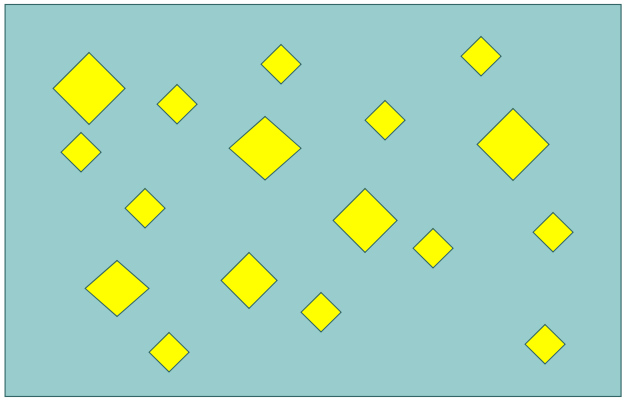
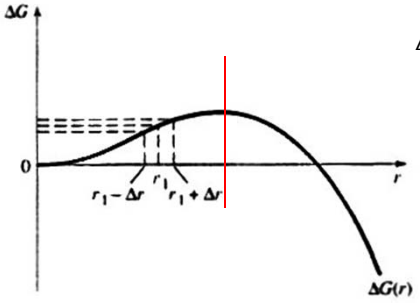
Oswald Ripening



Critical size of nuclei



ΔG_v The free energy per unit volume of the Nucleus relative to the parent phase

ΔG_s The surface free energy per unit area of the nucleus.

$$\Delta G_n = 4\pi r^2 \Delta G_s - \frac{4}{3}\pi r^3 \Delta G_v$$

$$\frac{d\Delta G}{dr} = 8\pi r \Delta G_s - 4\pi r^2 \Delta G_v$$

$$r_c = \frac{2\Delta G_s}{\Delta G_v}$$

$$\Delta G_c = \frac{16}{3}\frac{\pi \Delta G_s^{\,3}}{\Delta G_v^{\,2}}$$

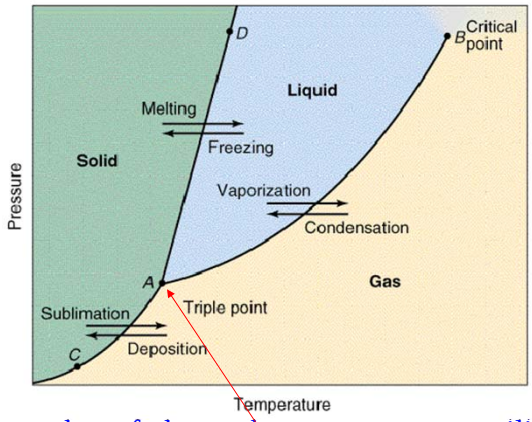
Nucleation is difficult at temperature close to T_E

Phase Rule

$$\mathbf{P + F = C + 2}$$

P: number of phases present in equilibrium
C: number of components need to describe the system
F: number of degrees of freedom, e.g. T, P, composition

One component phase diagram



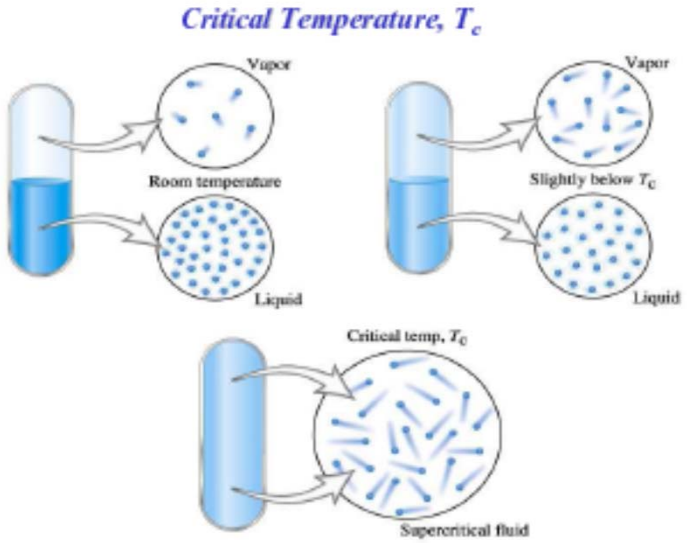
Largest number of phases that can occur at equilibrium:

P + 0 =1+2=3

Two phase: (lines)

One phase region.

Critical Temperature



Supercritical fluid

A **supercritical fluid** is any substance at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist. It can effuse through solids like a gas, and dissolve materials like a liquid.

Solvent	Molecular weight	Critical temperature	Critical pressure	Critical density
	g/mol	K	Mpa (atm)	g/cm^3
Carbon dioxide (CO_2)	44.01	304.1	7.38 (72.8)	0.469
Water (H_2O)	18.015	647.096	22.064 (217.755)	0.322

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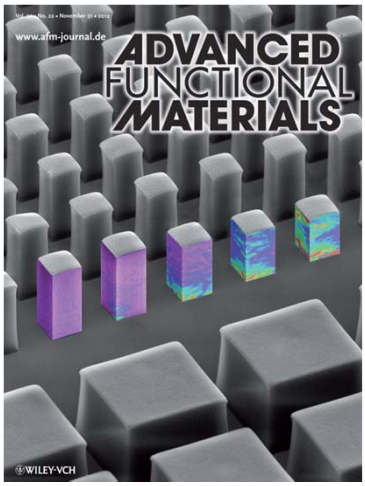
Supercritical fluid

- There is no surface tension in a supercritical fluid, as there is no liquid/gas phase boundary.
- Supercritical drying is a method of removing solvent without surface tension effects. As a liquid dries, the surface tension drags on small structures within a solid, causing distortion and shrinkage. Under supercritical conditions there is no surface tension, and the supercritical fluid can be removed without distortion. Supercritical drying is used for manufacture of aerogels.

Supercritical drying



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Example: a system of boiling water

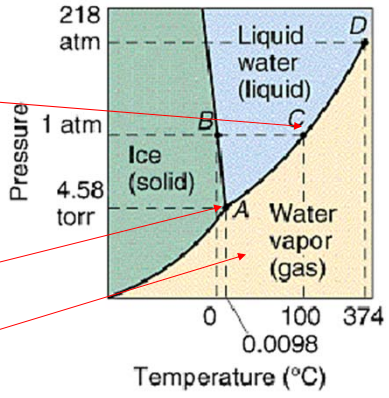
P+F =C+2

C=1 (water)
P=2 (Vapor + Liquid)

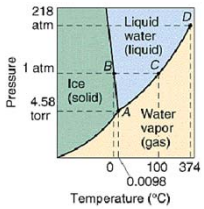
F=1 (either T or P, but not both)

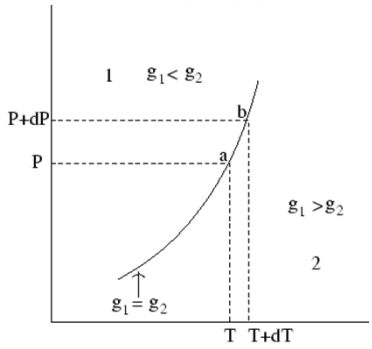
F=0

F=2



Clausius-Clapeyron Equation





From a to b:

$$dg_1 = -s_1 dT + v_1 dP$$

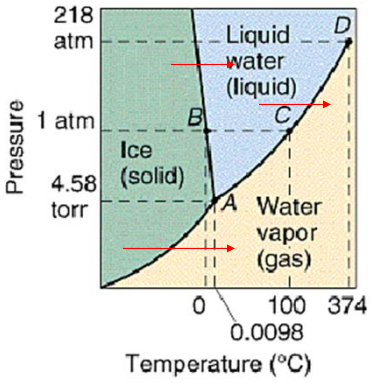
$$dg_2 = -s_2 dT + v_2 dP$$

$$dg_1 = dg_2$$

$$\frac{dP}{dT} = \frac{s_2 - s_1}{v_2 - v_1} \qquad \Delta S = \frac{\Delta H}{T}$$

$$\boxed{\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}}$$

One component phase diagram



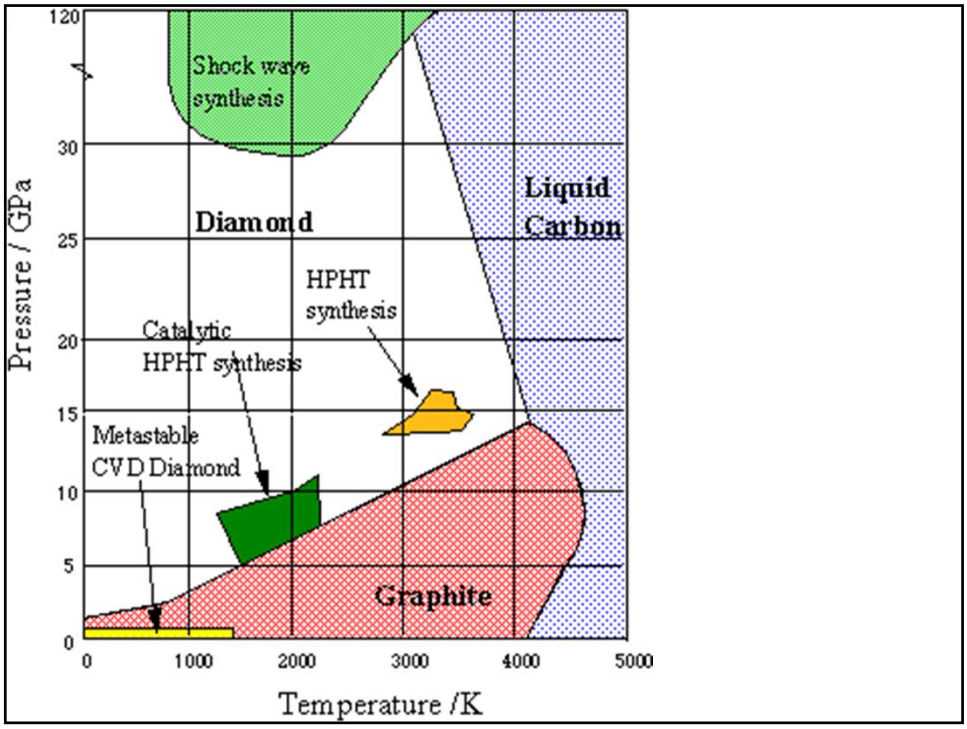
Slope of the phase-boundary Curves:

Clausius-Clapeyron Equation

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$

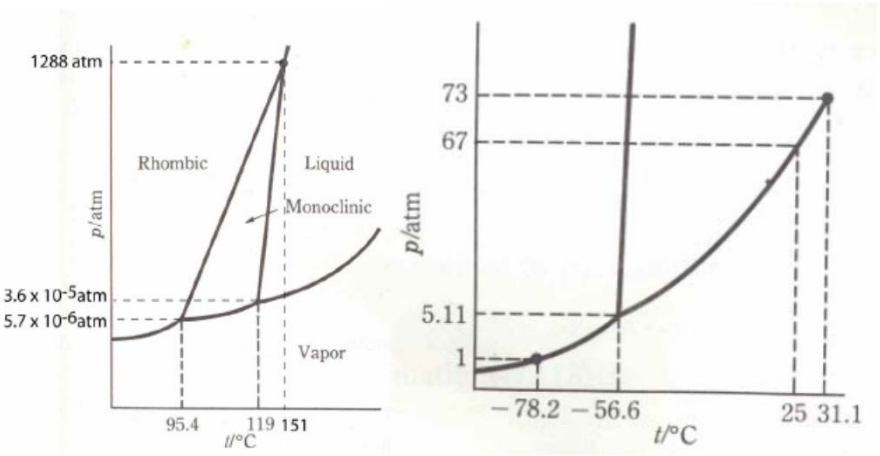
ΔH always positive

ΔV



More than 100 tons of the stones is produced annually worldwide by firms like Diamond Innovations (previously part of General Electric), Sumitomo Electric, and De Beers.

Gemesis, GE, Sumitomo Electric, and De Beers



Sulfur CO_2

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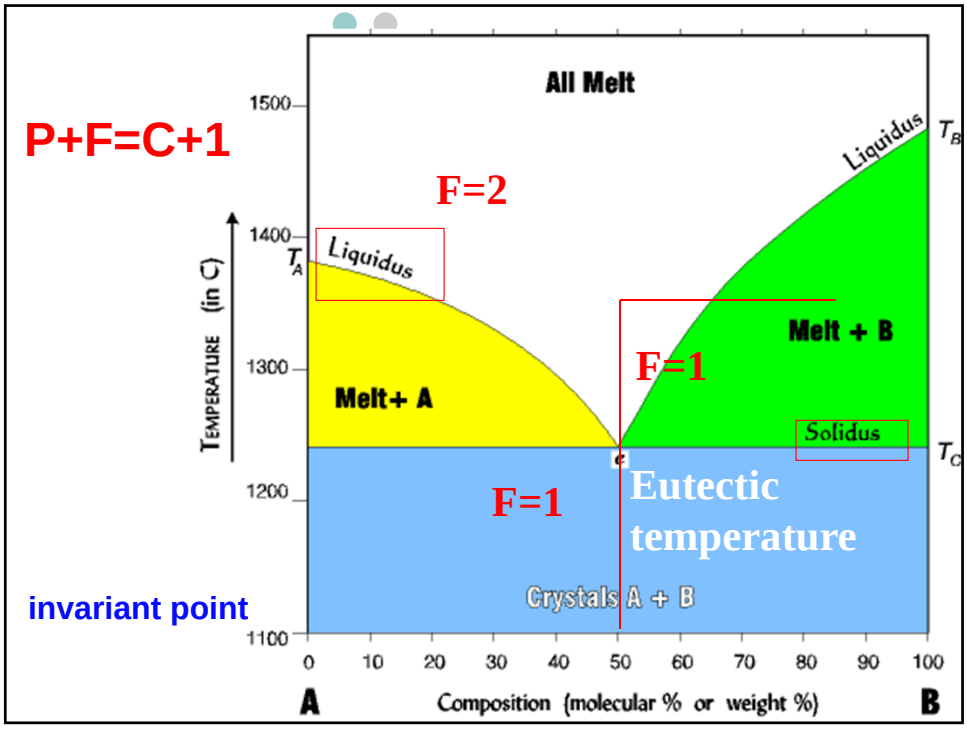
Two Components System

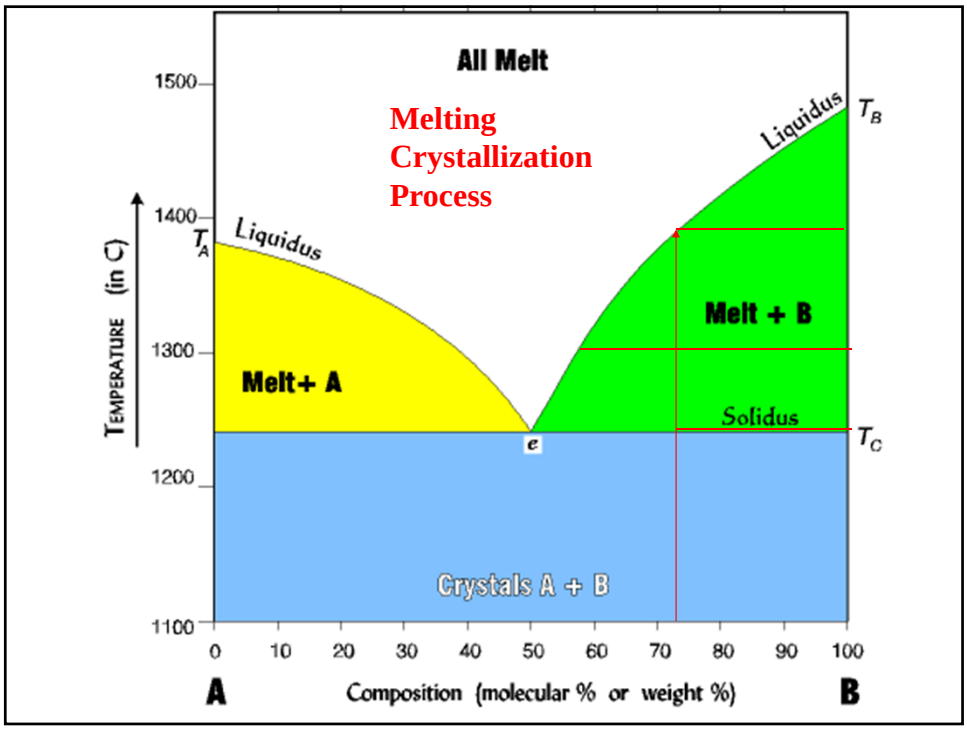
Three independent variables: T, P, compositions
In general, constant pressure (fixed parameter).

$$P+F=C+1$$

Simple Eutectic System

The binary eutectic phase diagram explains the chemical behavior of two immiscible (unmixable) crystals form a completely miscible (mixable) melt.

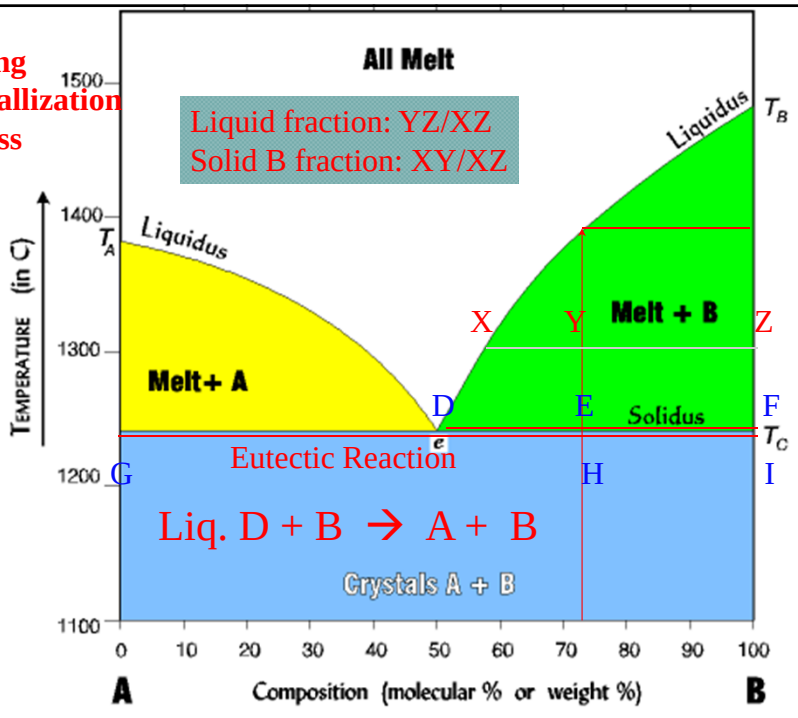

P+F=C+1
All Melt
F=2
Liquidus
T_B
1500
1400
T_A
Liquidus
Melt + B
F=1
Melt+ A
Solidus
T_C
1300
TEMPERATURE (in C)
e
1200
F=1
Eutectic temperature
invariant point
Crystals A + B
1100
0 10 20 30 40 50 60 70 80 90 100
A
Composition (molecular % or weight %)
B

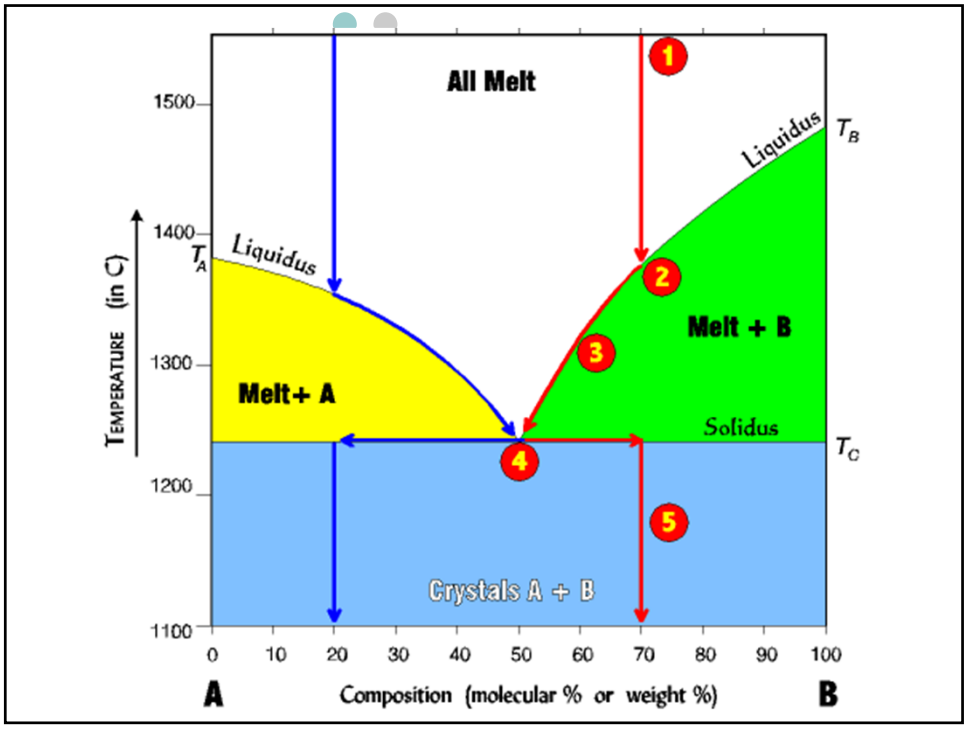

All Melt
Melting
Crystallization
Process
1500
Liquidus
T_B
1400
T_A
Liquidus
Melt + B
Melt+ A
Solidus
T_C
1300
TEMPERATURE (in C)
e
1200
Crystals A + B
1100
0 10 20 30 40 50 60 70 80 90 100
A
Composition (molecular % or weight %)
B

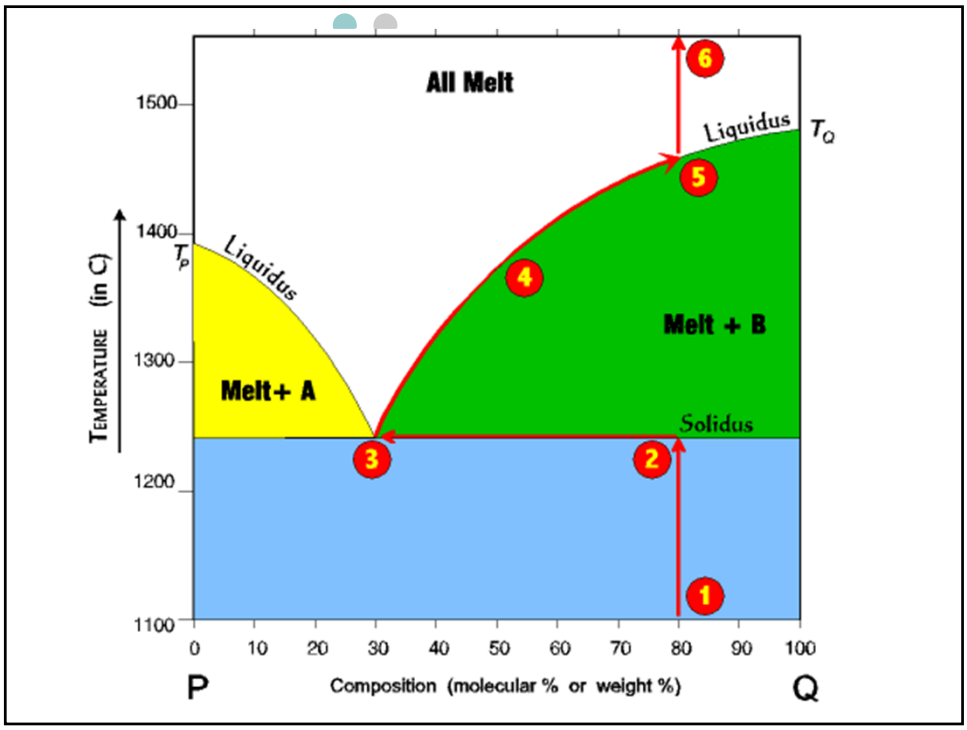
Lever Rule

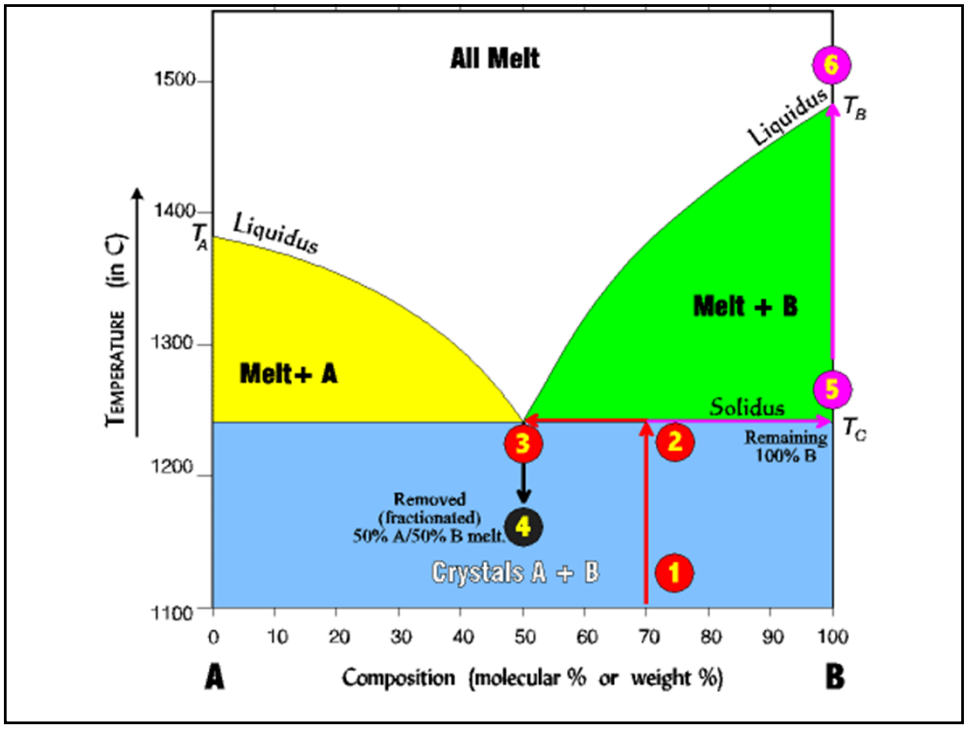
- Connect tie line across two – phase region at the temperature of the alloy
- Locate overall alloy composition on tie line
- Calculate fraction of each phase using lever rule

Melting Crystallization Process




All Melt
Liquidus
T_B
Liquidus
T_A
Melt + B
Melt+ A
Solidus
T_C
Crystals A + B
1500
1400
1300
1200
1100
Temperature (in C)
0 10 20 30 40 50 60 70 80 90 100
A
Composition (molecular % or weight %)
B
1
2
3
4
5


All Melt
Liquidus
T_Q
Liquidus
T_P
Melt + B
Melt+ A
Solidus
1500
1400
1300
1200
1100
Temperature (in C)
0 10 20 30 40 50 60 70 80 90 100
P
Composition (molecular % or weight %)
Q
6
5
4
3
2
1



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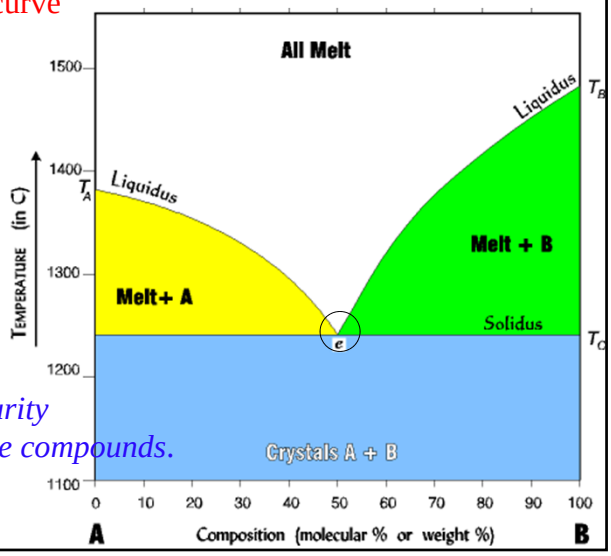
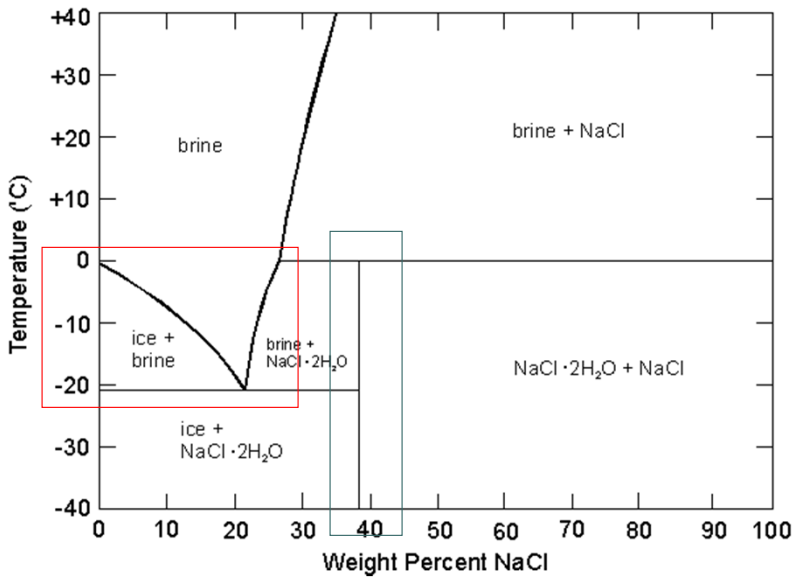
Liquidus Line:

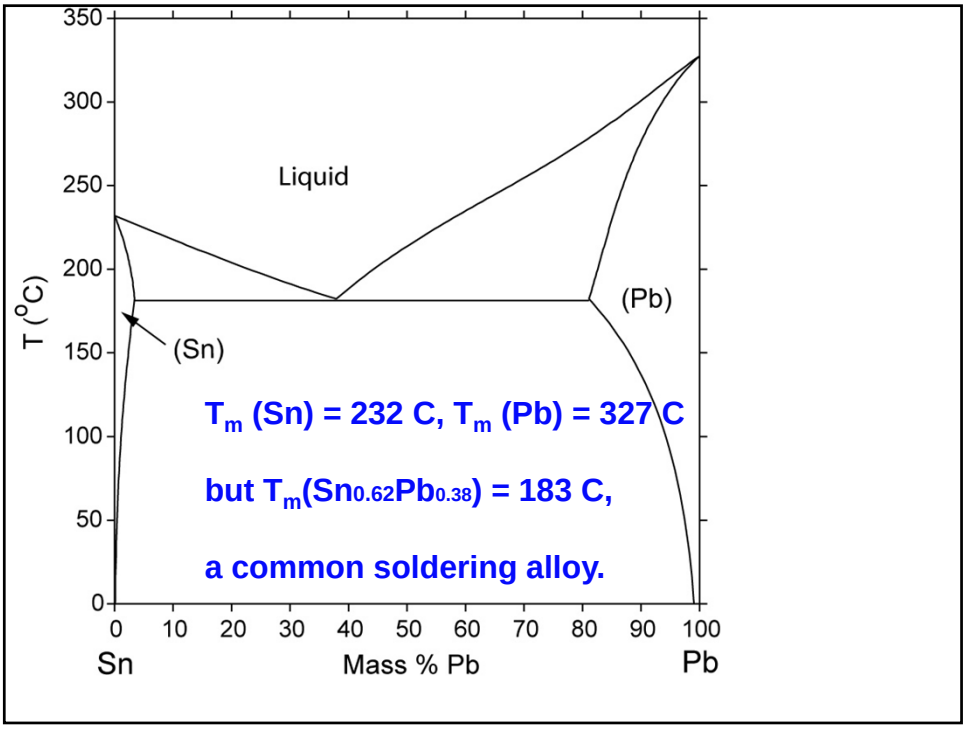
Maximum T at which crystals can exist.

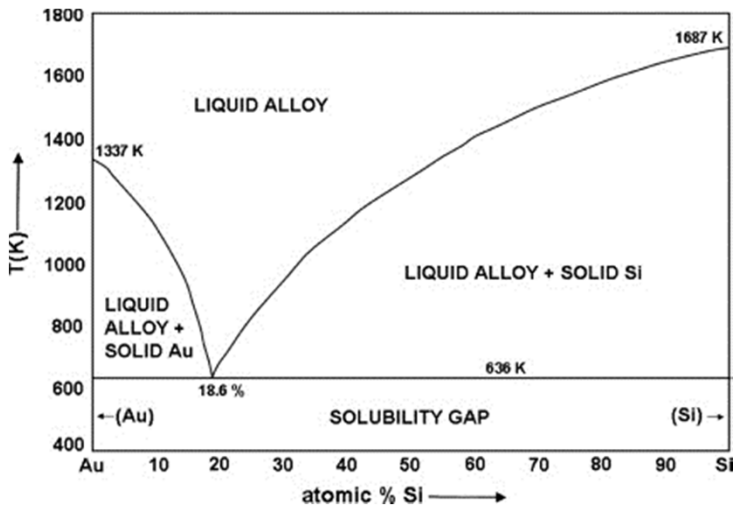
Saturation solubility curve



The effect of soluable impurity on the melting point of pure compounds.


+40
+30
+20
+10
0
-10
-20
-30
-40
Temperature (°C)
brine
brine + NaCl
ice +
brine
brine +
NaCl·2H2O
NaCl·2H2O + NaCl
ice +
NaCl·2H2O
0
10
20
30
40
50
60
70
80
90
100
Weight Percent NaCl


350
300
250
200
150
100
50
0
T (°C)
Liquid
(Pb)
(Sn)
Tm (Sn) = 232 C, Tm (Pb) = 327 C
but Tm(Sn0.62Pb0.38) = 183 C,
a common soldering alloy.
0
10
20
30
40
50
60
70
80
90
100
Sn
Mass % Pb
Pb



T_m (Au) = 1064 C, T_m (Si) = 2550 C……
but $T_m(Au_{0.97}Si_{0.03})$ = 363 C, so thin layer of gold is used to attach Si chip to a ceramic substrate (shock protection)