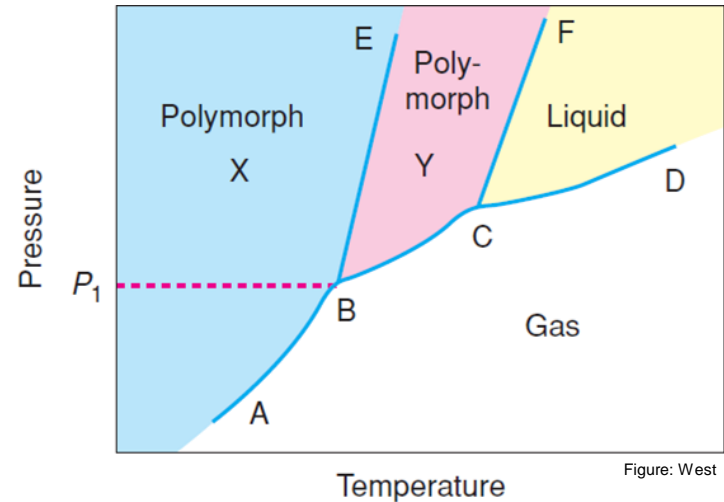


Lecture 5: Phase Diagrams and crystal growth

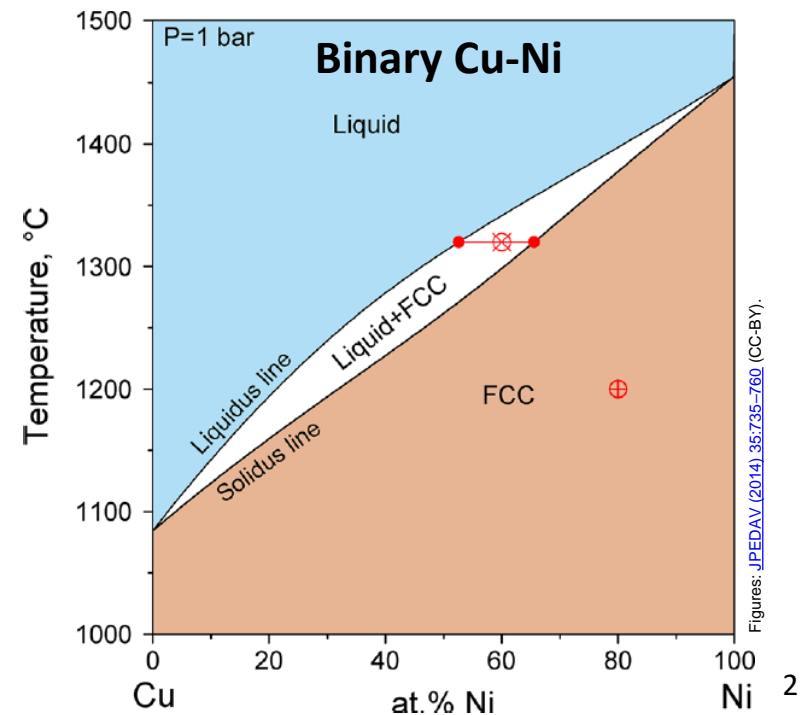
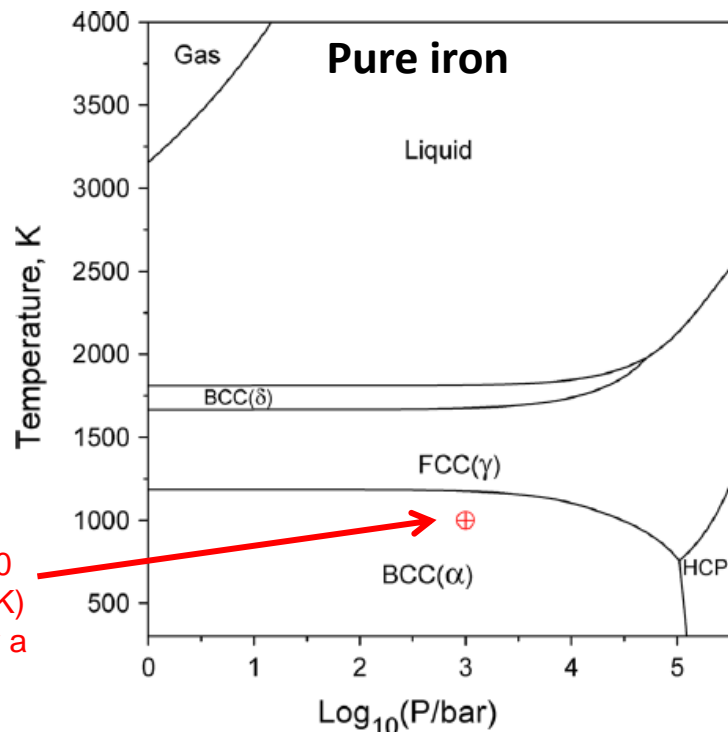
- Phase diagrams
 - Phase rule
 - One-component systems (unary)
 - Two-component systems (binary)
 - Three-component systems (ternary)
- Single crystal growth (*extra material*)
 - Czochralski method
 - Bridgman and Stockbarger methods
 - Zone melt methods
 - Flux methods



13 gram single crystal of $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ (Christensen et al. *Nature Mater.* **2008**, 7, 811)

Phase diagrams

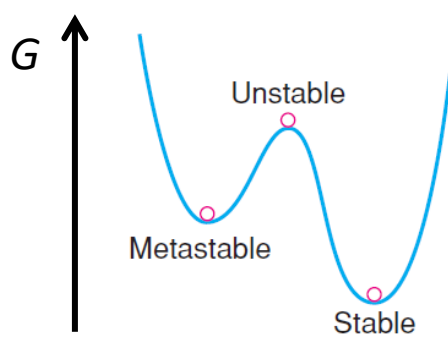
- “Phase diagrams are the beginning of wisdom - not the end of it” - [William Hume-Rothery](#) (English metallurgist and materials scientist)
- For a comprehensive introduction to phase diagrams: MyCourses -> Materials -> Scientific papers -> Schmid-Fetzer 2014 Phase Diagrams
- Phase diagrams are a **roadmap** for understanding the conditions for phase formation or transformation in any material system
- Phase diagrams are a starting point for materials design and process optimization



Figures: JFEDAV (2014), 35:735-760 (CC-BY).

Equilibrium

- In using phase diagrams, it is important to understand what is meant by **thermodynamic equilibrium**.
- The equilibrium state is always the state with the lowest Gibbs free energy G .
 - Other minima may exist, but they are not as deep as the equilibrium well.
 - If there is a considerable energy barrier involved in moving from a **metastable** state to the stable state, the reaction product may stay in its metastable state.
- **Important:** phase diagrams give no information concerning **kinetics** of reactions or transformations!
- A good example of a thermodynamically metastable but kinetically stable state is the metastability of diamond (C) relative to graphite (C) at room temperature.



Schematic diagram showing stable, unstable, and metastable conditions

Definitions

- **Phase** is a physically separable part of a system with distinct physical and chemical properties.
- A **system** consists of one or more phases
- For example, NaCl–H₂O system:
 - If all salt is dissolved: one phase (salt solution).
 - If all salt is not dissolved: two phases, solid NaCl and solution.
 - If system is heated under sealed conditions: three phases (solid + solution + gas)
- Each phase in the system is composed of one or more **components**.
 - The NaCl–H₂O system has two components: NaCl and H₂O (**binary** system).
 - All other combinations can be described with these formula.
- Pure water would be a **unary** (one-component) system.
- Three components -> **ternary** system.
- Four components -> **quaternary** system.

Gibbs Phase Rule

- Applies to non-reactive multi-component heterogeneous systems in **thermodynamic equilibrium**.
 - Pressure p and temperature T are constant in the system.
 - The chemical potentials of the components are the same in each phase.
- $F = C - P + 2$
 - P is the number of phases present in equilibrium
 - C is the number of components needed to describe the system
 - F is the number of degrees of freedom or independent variables taken from temperature, pressure, and composition of the phases present
- In many cases, pressure is constant, and the *condensed phase rule* is used:
 - $F = C - P + 1$

Simple examples of phase rule

1. A partially melted solid (ice) in a **one-component** system (H_2O), in equilibrium at its melting point (ignoring pressure, condensed phase rule):

- $F = C - P + 1$
= $1 - 2 + 1$
= 0

- If the temperature changes, the number of phases must change

2. Boiling water: H_2O (l) and H_2O (g) in equilibrium ($C = 1$).

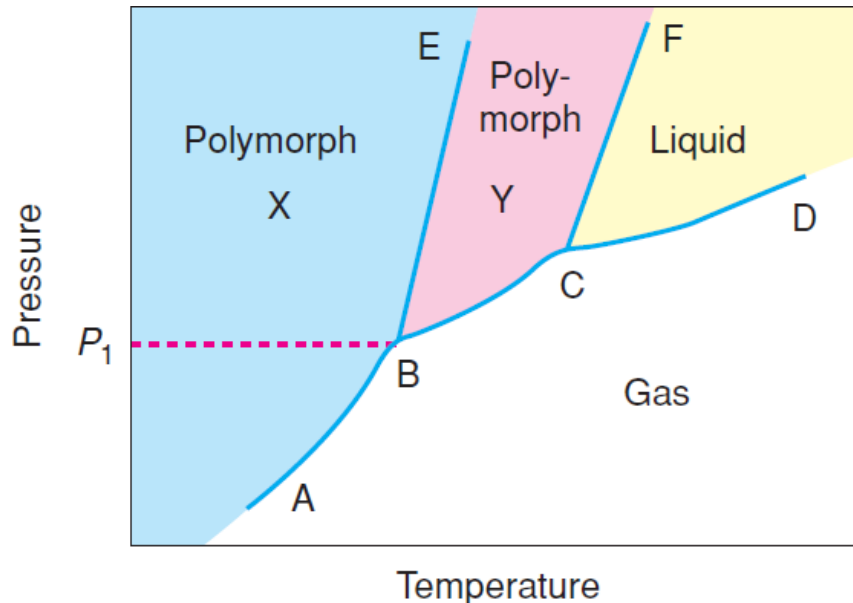
- $F = C - P + 2$
= $1 - 2 + 2$
= 1

- Boiling point depends on vapor pressure (only one degree of freedom).

- For example, Mount Everest: 8848 m; $p = 34 \text{ kPa}$ -> boiling point of $\text{H}_2\text{O} = 71 \text{ }^\circ\text{C}$

One-component systems (1)

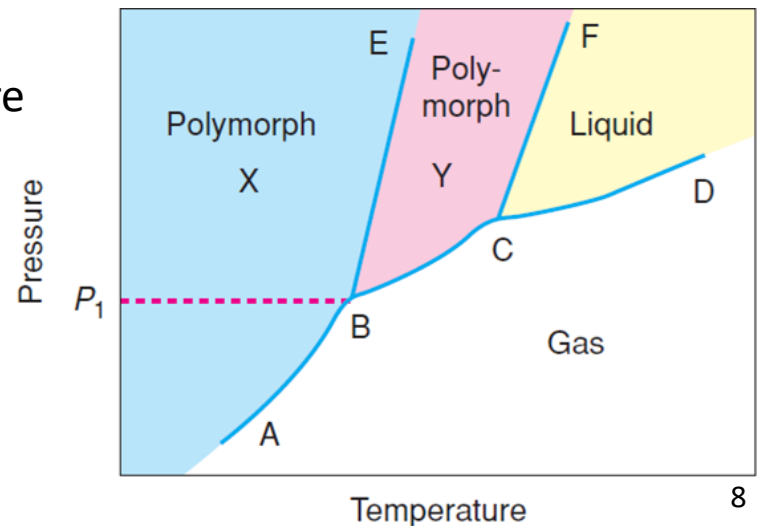
- The composition is fixed at $C = 1$ and the independent variables are T and p .
 - $F = C - P + 2 \Leftrightarrow F + P = 3$
 - The system is **bivariant** ($F = 2$) if one phase is present, **univariant** ($F = 1$) if two are present and **invariant** ($F = 0$) if three are present
- In the schematic example below, the possible phases are two solid-state polymorphs (X and Y), liquid, and gas
- If $P = 1$: $F = 2$ and each phase occupies an area or **field** on the diagram
 - Both p and T are needed to describe a point in one of these fields.



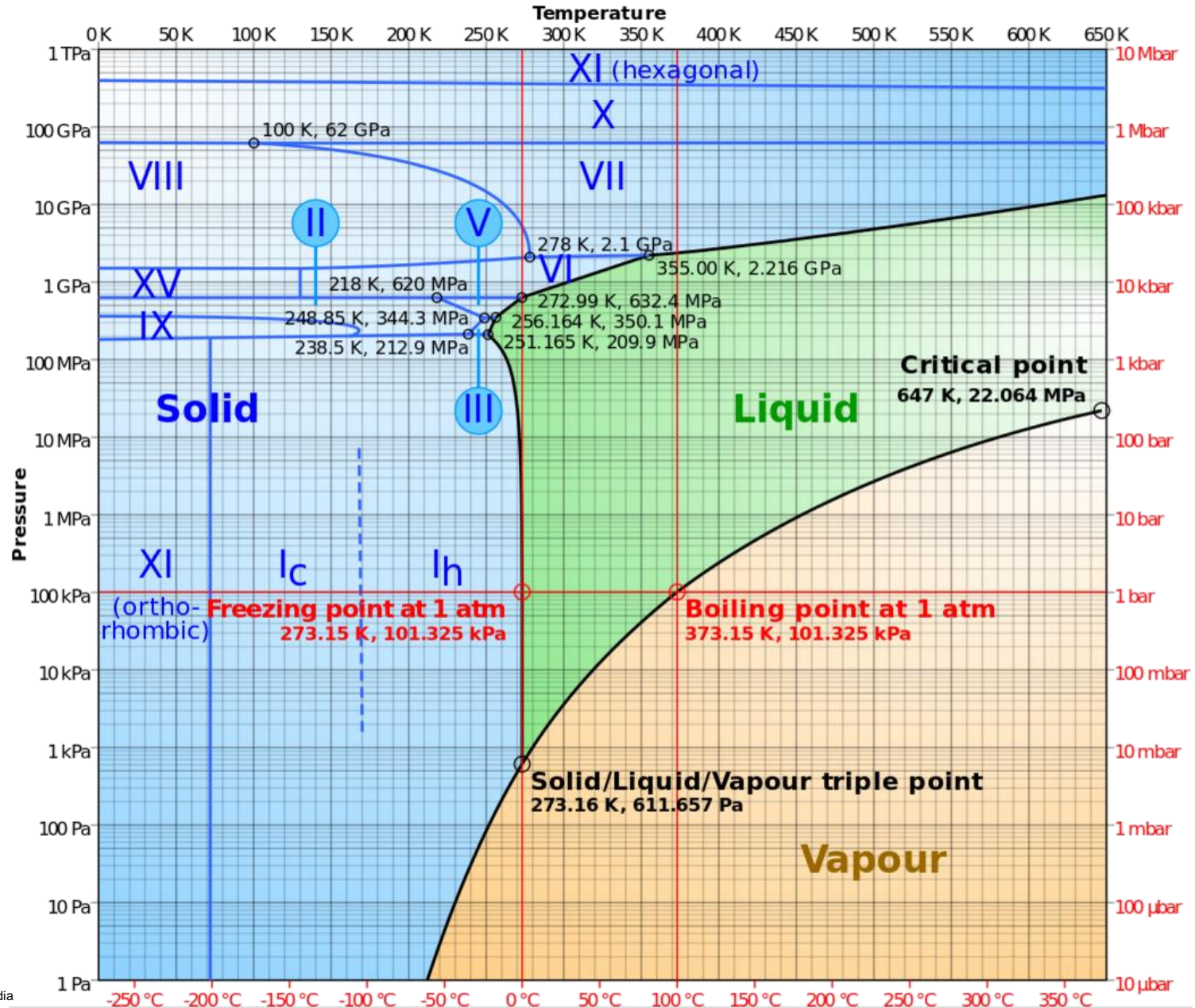
Schematic pressure vs. temperature phase diagram for a **one-component system**.

One-component systems (2)

- One-component system: $F + P = 3$
- Each single-phase region is separated from neighboring single-phase regions by **univariant** curves ($P = 2$ and $F = 1$): If p is fixed then T is fixed and vice versa
- The univariant curves on the diagram represent the following equilibria:
 - BE – transition temperature between polymorphs X and Y (the change of transition temperature with pressure)
 - FC – change of melting point of polymorph Y with pressure
 - AB, BC – sublimation curves for X and Y, respectively
 - CD – change of boiling point of liquid with pressure
- On heating, X can either sublime at a pressure below P_1 or transform to polymorph Y at pressures above. It **cannot** melt directly.
- B and C are **invariant** points ($P = 3$ and $F = 0$)
- They are also called *triple points*.



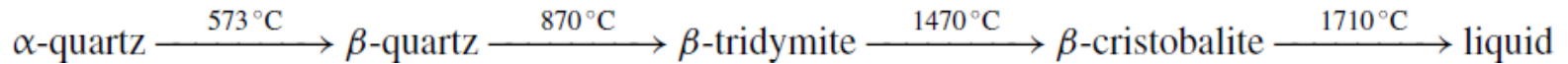
One-component systems: phase diagram of H₂O



One-component systems: SiO₂

- Silica (SiO₂) is the most common oxide in the Earth's crust and the main component of many ceramic materials

- It shows complex polymorphism at atmospheric pressure:



- With increasing pressure, the polymorphs with higher density are favored

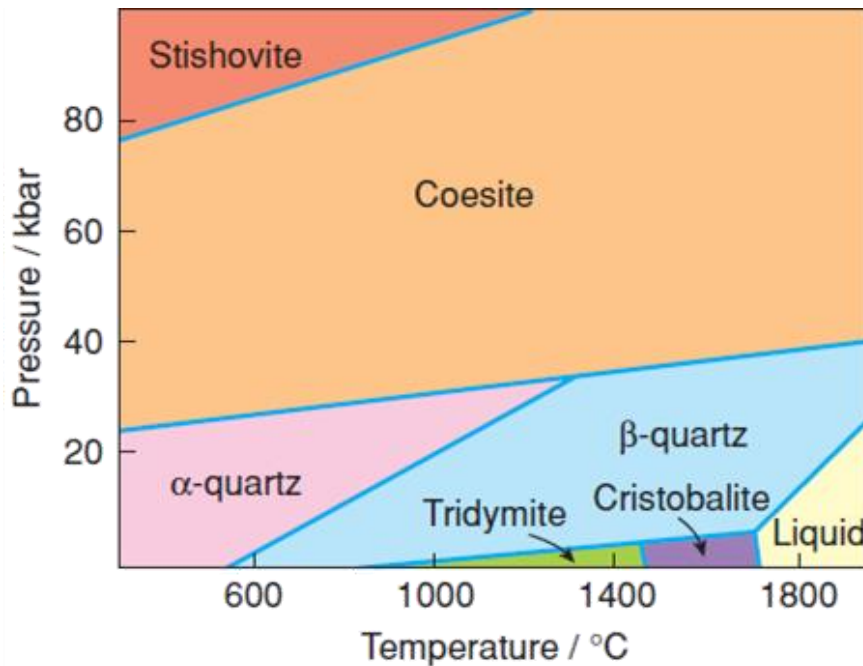
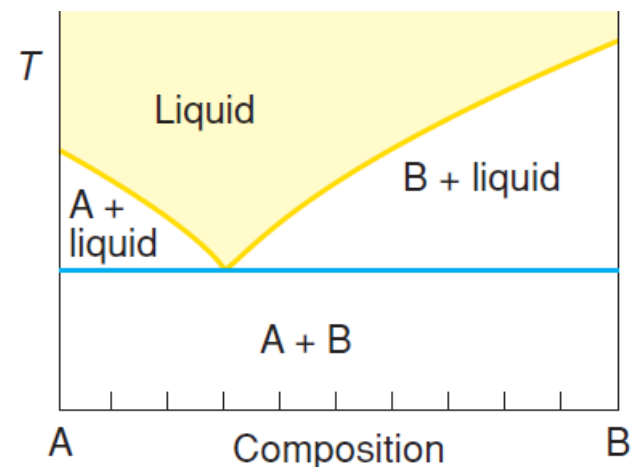


Table 7.1 Densities of SiO₂ polymorphs

Polymorph	Density/g cm ⁻³
Low tridymite	2.265
Low cristobalite	2.334
Low quartz	2.647
Coesite	3.00
Stishovite	4.40

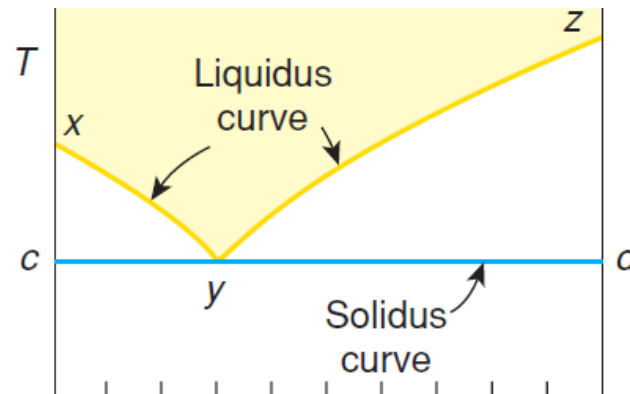
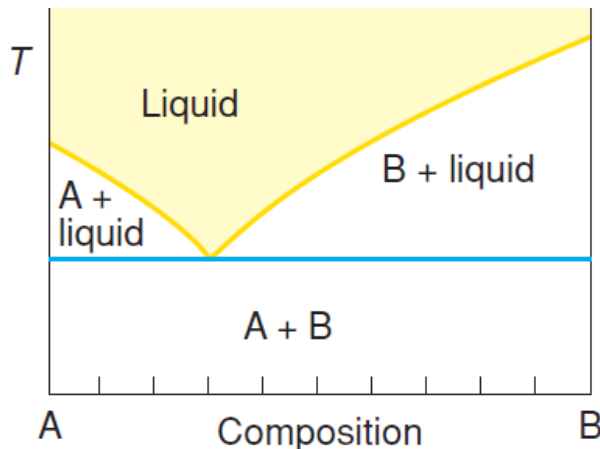
Binary eutectic system (1)

- Binary systems ($C = 2$) have three independent variables: p , T , and composition.
- Let's consider condensed phases (ignoring pressure): $F = C - P + 1 = 3 - P$.
 - Invariant point occurs when three phases coexist ($F = 0$), a univariant curve for two phases ($F = 1$), and a bivariant condition for one phase ($F = 2$).
- Conventionally, temperature is the vertical axis and composition is the horizontal axis in binary phase diagrams.
- The simplest two-component condensed system is the **eutectic** system below.
 - Occurs whenever two non-interacting solids, A and B, that can melt without decomposition, are mixed.
 - No compounds or solid solutions are formed but the mixtures melt at lower temperatures than pure A or B.



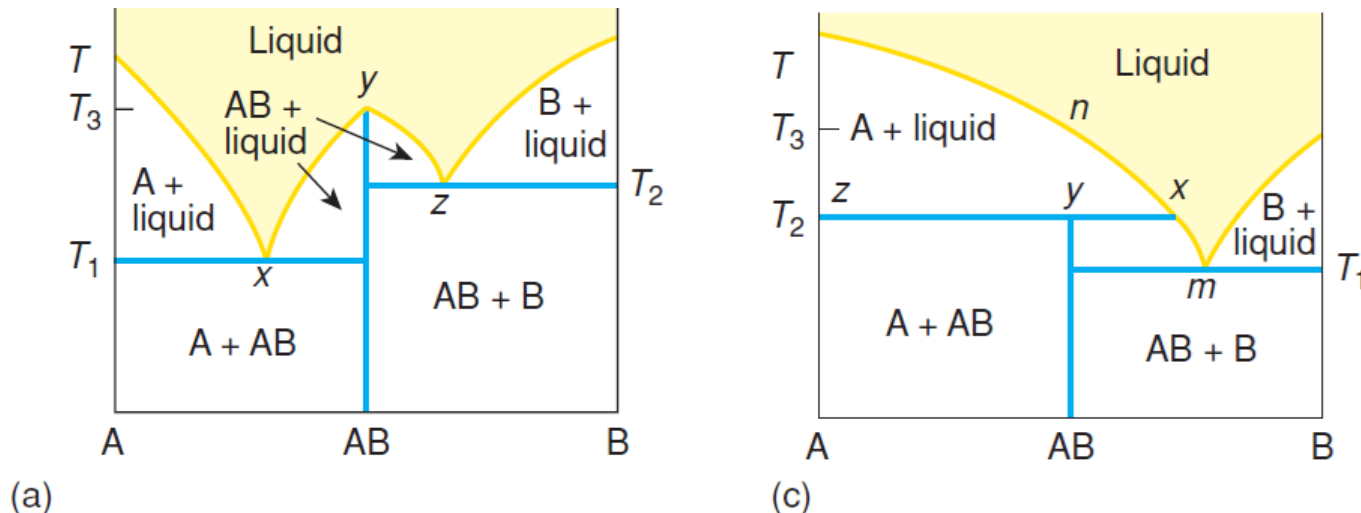
Binary eutectic system (2)

- The **liquidus** curve (*xyz*) gives the highest temperatures at which crystals can exist.
 - Shows the effect of soluble impurities on the melting points of pure compounds.
 - Practical example: In the binary system H₂O–NaCl, addition of NaCl lowers the melting point of ice.
- The **solidus** curve (*cyd*) gives the lowest temperatures at which liquids can exist.
- Point *y* is an **invariant point** at which three phases, A, B and liquid, coexist.
 - $F = C - P + 1 = 2 - 3 + 1 = 0$
 - Called the **eutectic point** (H₂O–NaCl system: –21°C and 23.3% NaCl by mass).
 - The lowest temperature at which a composition can be completely liquid.



Binary system with a compound (1)

- A stoichiometric binary compound such as AB is represented by a vertical line. This shows the range of temperatures over which it is stable
- Compound AB melts **congruently** in Fig. 7.8(a) because it changes directly from solid AB to liquid of the same composition at temperature T_3 .
 - Important for understanding **crystallization paths**
- In Fig. 7.8(c), compound AB melts **incongruently** at T_2 to give a mixture of A and liquid of composition x



Ref: West p. 338

Figure 7.8 Binary systems showing a compound AB melting congruently (a) and incongruently (c)

Binary system with a compound (2)

- Sometimes, compounds decompose before melting, as shown for AB in Fig. 7.9(a)
 - In this case, compound AB has an **upper limit of stability**
 - At temperature T_1 it disproportionates into a mixture of A and B;
 - At higher temperatures the system is simple eutectic in character
- There are also systems containing compounds with a **lower limit of stability**.
 - In Figure 7.9(b), compound AB decomposes into a mixture of A and B below T_l .

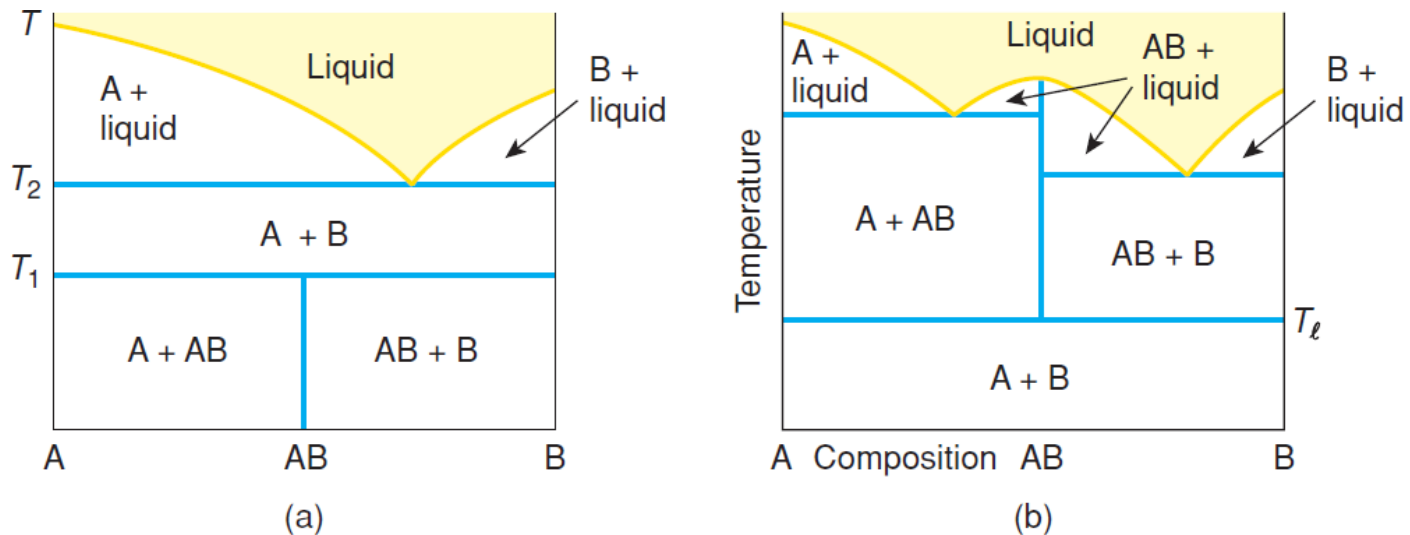
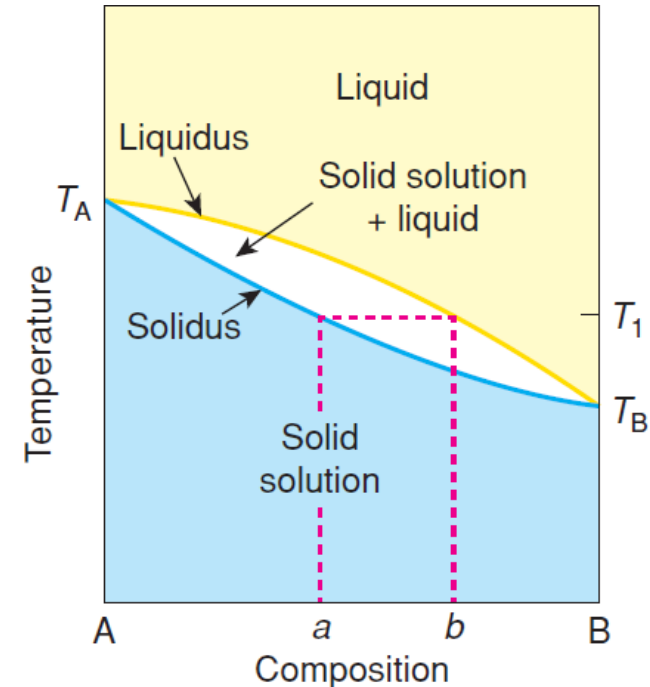


Figure 7.9 Binary system showing compound AB with (a) an upper limit of stability and (b) a lower limit of stability.

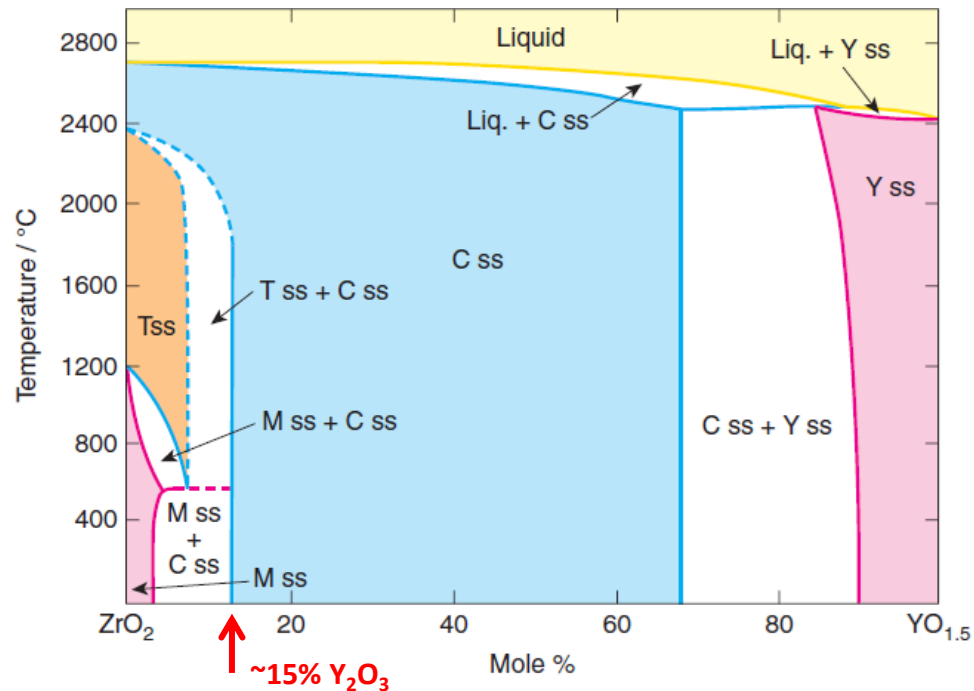
Binary systems with solid solutions

- The simplest **solid solution** system is one that shows complete miscibility in both solid and liquid states
- The melting point of end member A is depressed by addition of the other end member B.
- The liquidus and solidus are smooth curves which meet only at the end-member compositions A and B.
- At low temperatures, a single-phase, bivariant solid solution exists:
- $C = 2$, $P = 1$, and $F = C - P + 1 = 2$
- At high temperatures, a single-phase bivariant liquid solution exists.
- At intermediate temperatures, a two-phase region of solid solution + liquid exists



Yttria-stabilized Zirconia (YSZ)

- Zirconia, ZrO_2 , is potentially a very useful ceramic material with a high melting point of $\sim 2700\text{ }^\circ\text{C}$, but on cooling it undergoes a series of phase transitions:
cubic (fluorite) $\xrightarrow{2400\text{ }^\circ\text{C}}$ tetragonal $\xrightarrow{1050\text{ }^\circ\text{C}}$ monoclinic (baddeleyite)
- The tetragonal to monoclinic transition is associated with an increase in unit cell volume by $\sim 9\%$ \rightarrow ceramic bodies fabricated at high T shatter on cooling
- The transitions can be avoided by creating a solid solution $ZrO_2\text{-}Y_2O_3$:

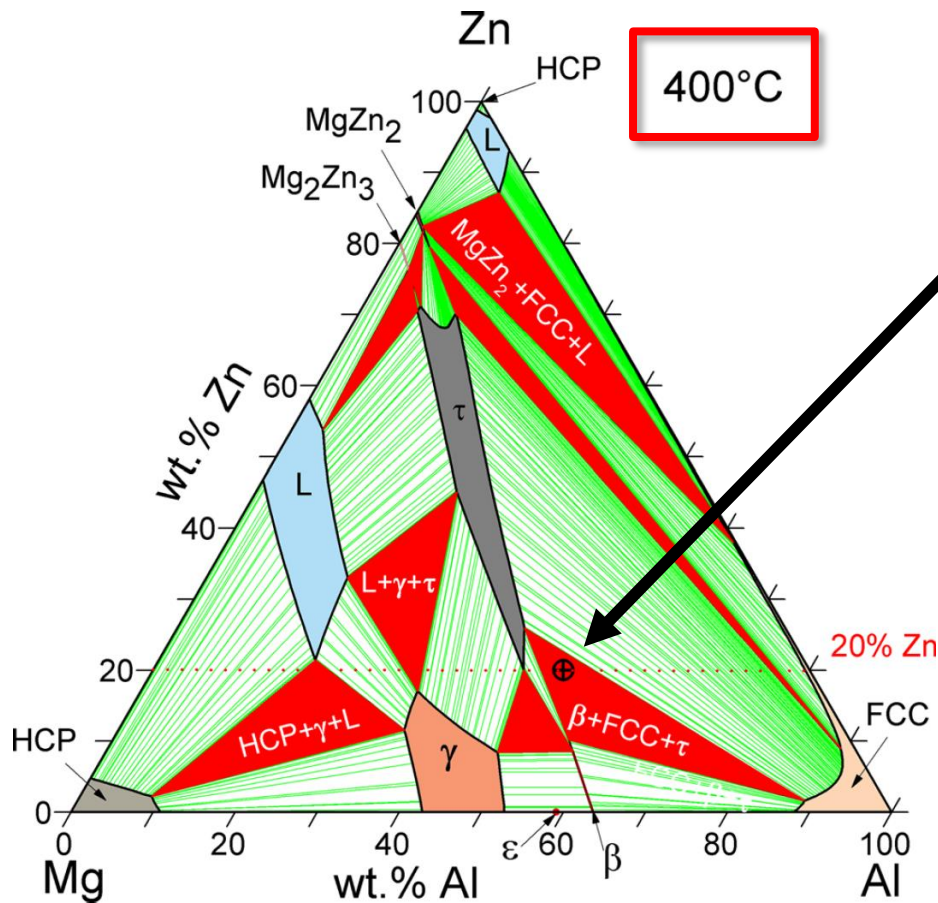


Ref: West p. 355

Figure 7.28 $ZrO_2\text{-}Y_2O_3$ phase diagram. M, T and C refer to the monoclinic, tetragonal and cubic polymorphs of zirconia, and their solid solutions, ss. Y = yttria, Y_2O_3 .

Ternary phase diagrams

- Ternary phase diagrams are much more complicated than binary diagrams
- One reasonable visualization is to show the diagram just for one temperature

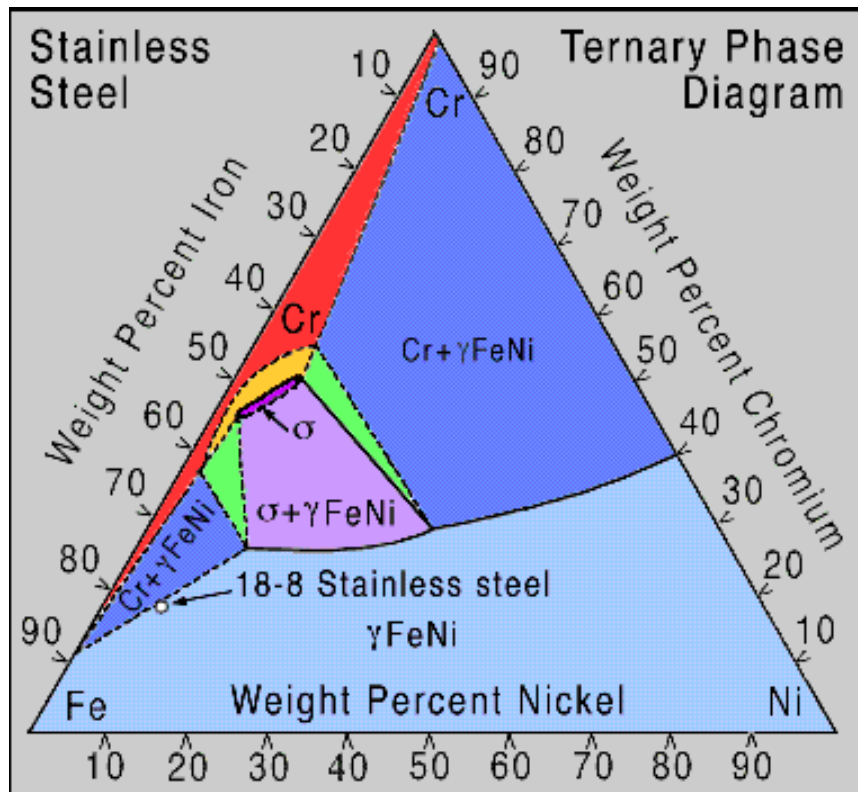


Isothermal section of the **Mg-Al-Zn** phase diagram at **400 °C**.

⊕ is a state point of the alloy “Mg₃₀Al₅₀Zn₂₀” (weight-%), located in the three-phase region β + FCC + τ

Phase diagram resources

- Resources for phase diagrams (require subscription):
 - <https://phaseonline.ceramics.org>
 - <https://www.asminternational.org/materials-resources/online-databases>
- [Journal of Physical and Chemical Reference Data](#) is a very good resource.
 - MyCourses -> Materials -> Phase diagrams includes few papers used in exercises.



Stainless steel phase diagram at 900°C (ASM 1-27)

Figure: ASM Handbook of Alloy Phase Diagrams

Extra slides

“Nice-to-know”-type material that is not needed for completing the exercises

[Methods for obtaining single crystals](#) (SSC Wiki)

Crystal Growth

- Crystals may be grown from vapor, liquid, or solid phases
 - Usually, only the vapor and liquid routes give crystals of sufficient size for applications or physical property measurements
 - The concepts of congruent and incongruent melting are important for understanding crystallization pathways (see the slide “Binary system with a compound (1)” above)
- Czochralski method
- Bridgman and Stockbarger methods
- Zone melting method
- Precipitation from solution or melt: flux method
- [Single crystal growth in gel medium](#) (SSC Wiki)



13 gram single crystal of $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ (Christensen et al. *Nature Mater.* **2008**, 7, 811)

Czochralski method

- <https://wiki.aalto.fi/display/SSC/Czochralski+method>
- A crystal is grown from a melt of the same composition by starting with a seed crystal in contact with the melt, whose temperature is maintained slightly above its melting point
- As the seed is gradually pulled out of the melt, the melt solidifies on the surface of the seed to give a rod-shaped crystal in the same crystallographic orientation as the original seed
- The melt and growing crystal are usually rotated counter-clockwise during pulling
- Widely used for semiconducting materials: Si, Ge, GaAs, etc.

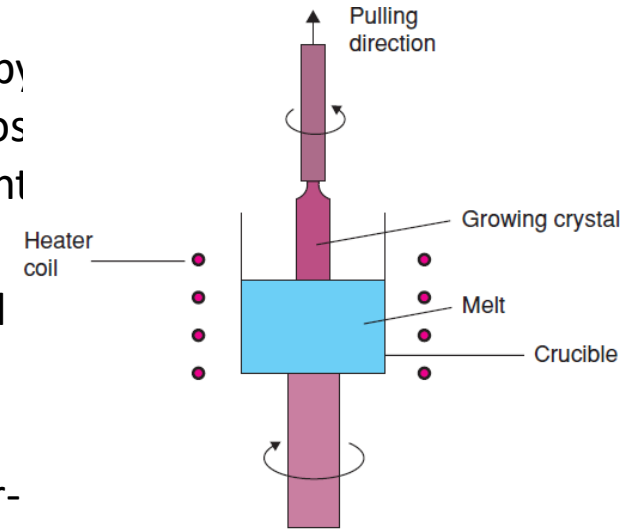


Figure 4.22 Czochralski method for crystal growth.

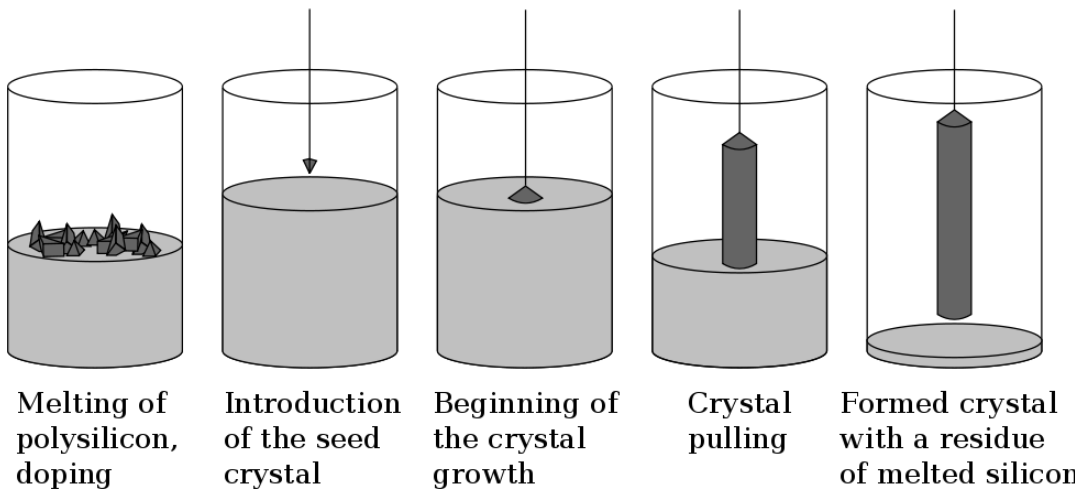


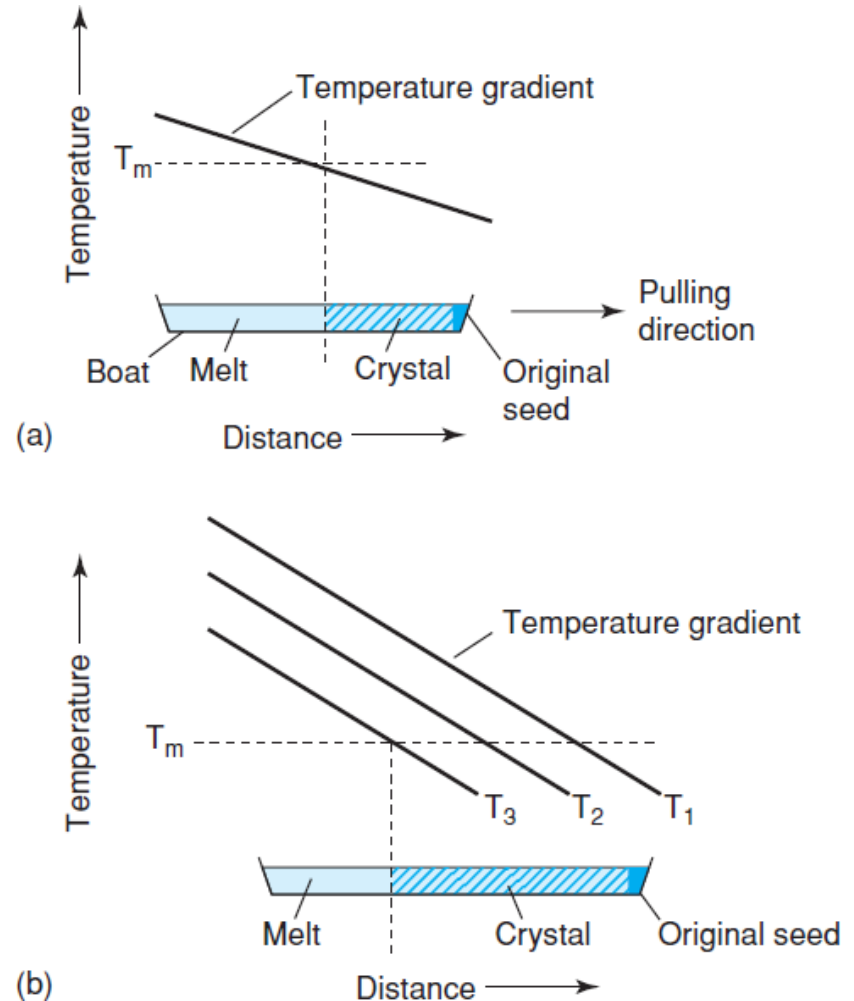
Figure: Wikipedia

Ref: West p. 226

Bridgman and Stockbarger methods

<https://wiki.aalto.fi/display/SSC/Bridgman+and+Stockbarger+methods>

- Based on the solidification of a stoichiometric melt
- Crystallisation is controlled by passing the melt through a temperature gradient such that crystallization occurs at the cooler end
- This is achieved in the Stockbarger method by arranging displacement of the melt within a temperature gradient
- In the Bridgman method, the melt is inside a temperature gradient furnace and the furnace is gradually cooled so that solidification begins at the cooler end
- In both methods, it is advantageous to use a seed crystal



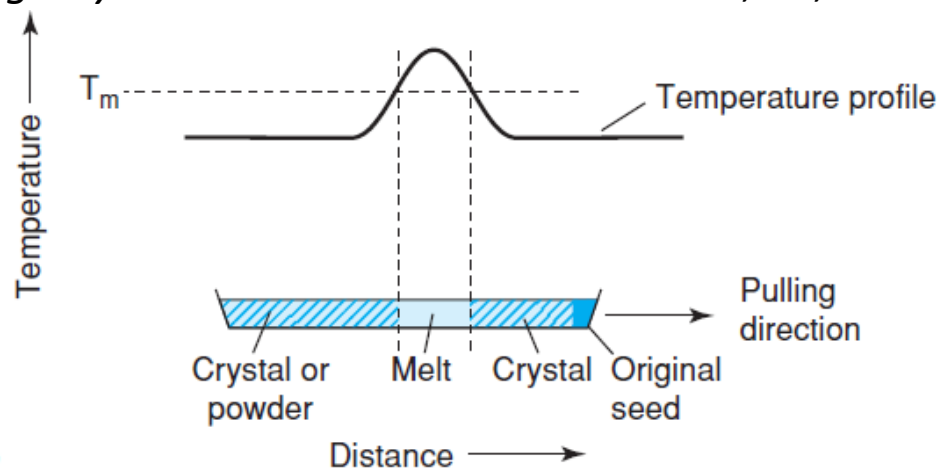
(a) Stockbarger method. T_m = crystal melting point.

(b) Bridgman method

Zone melting method

<https://wiki.aalto.fi/display/SSC/Zone+melt+methods>

- Related to the Stockbarger method but the thermal profile through the furnace is such that only a small part of the charge is molten at any one time
- Initially that part of the material in contact with the seed crystal is melted
- As the boat is pulled through the furnace, oriented solidification onto the seed occurs and, at the same time, more of the charge melts
- A well-known method for purification of solids, the zone-refining technique
- Makes use of the principle that impurities usually concentrate in the liquid rather than in the solid phase
- Impurities are “swept out” of the crystal by the moving molten zone
- State-of-the-art techniques: **Optical floating zone** (see e.g. S. M. Koohpayeh, D. Fort, J. S. Abell, *Prog. Cryst. Growth Charact. Mater.* **2008**, 54, 121-137 ([DOI](#)))



Precipitation from solution or melt: Flux method

- <https://wiki.aalto.fi/display/SSC/Flux+methods>
- In contrast to the above methods in which crystals have the same composition as the melt, precipitation methods involve the growth of crystals from a solvent of different composition
- The solvent may be one of the constituents of the desired crystal,
 - e.g. crystallization of salt hydrate crystals from water,
 - or the solvent may be an entirely separate liquid in which the crystals of interest are partially soluble, e.g. various high-melting silicates may be precipitated from low-melting borate or halide melts
- In these cases, the solvent melts are often referred to as **fluxes** since they effectively reduce the melting point of the crystals by a considerable amount.

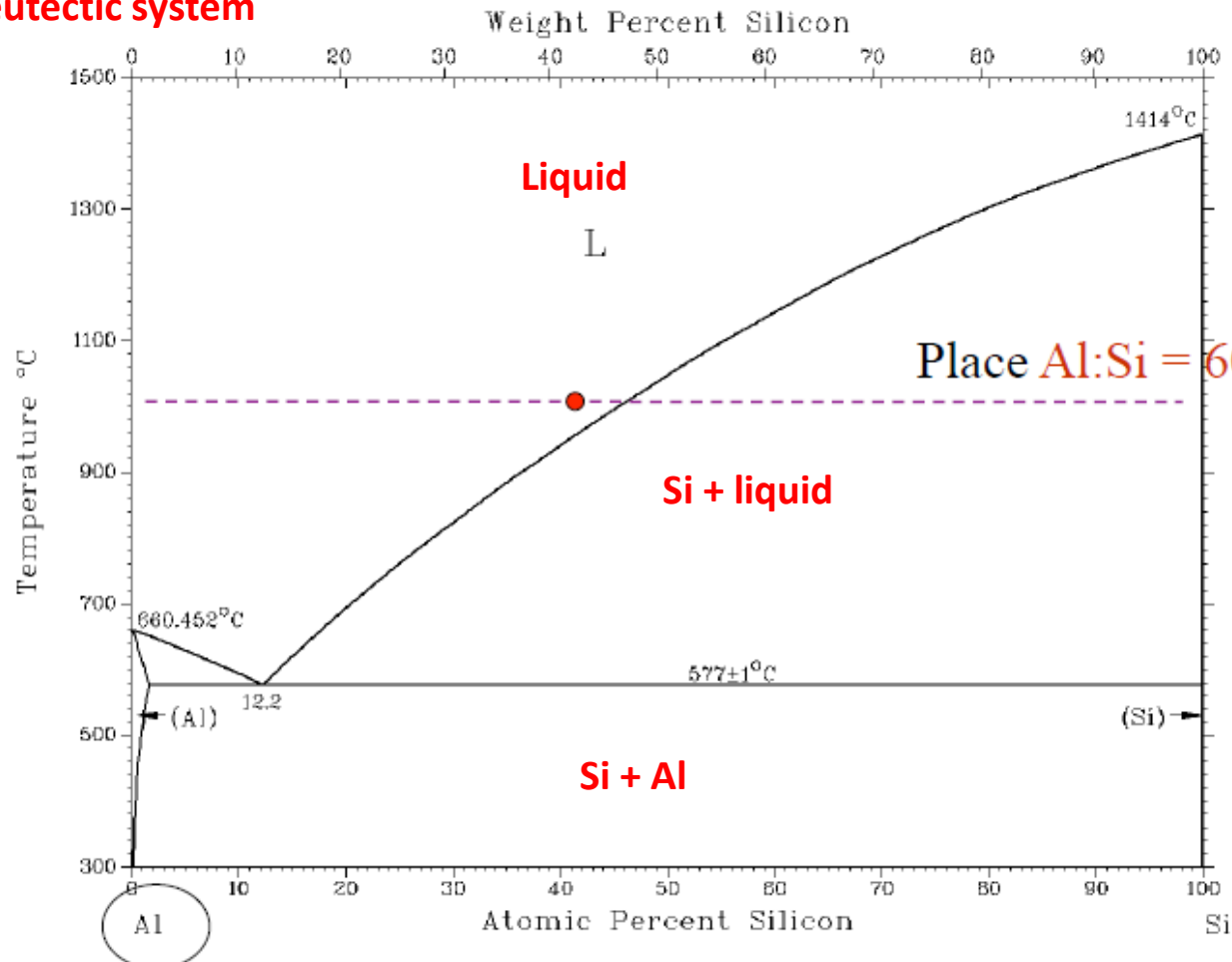
(1) How to make Si? ($T_{\text{melt}} = 1412\text{ }^{\circ}\text{C}$)

Let's aim for max temperature of our furnace of $\sim 1000\text{ }^{\circ}\text{C}$

Look up solvents that are low melting: Bi, Sn, Zn, Ga, **Al**

Best solvent

Binary eutectic system



Place Al:Si = 60:40 into Al_2O_3

Growing Si single crystals at lower temperature with the help of Al flux