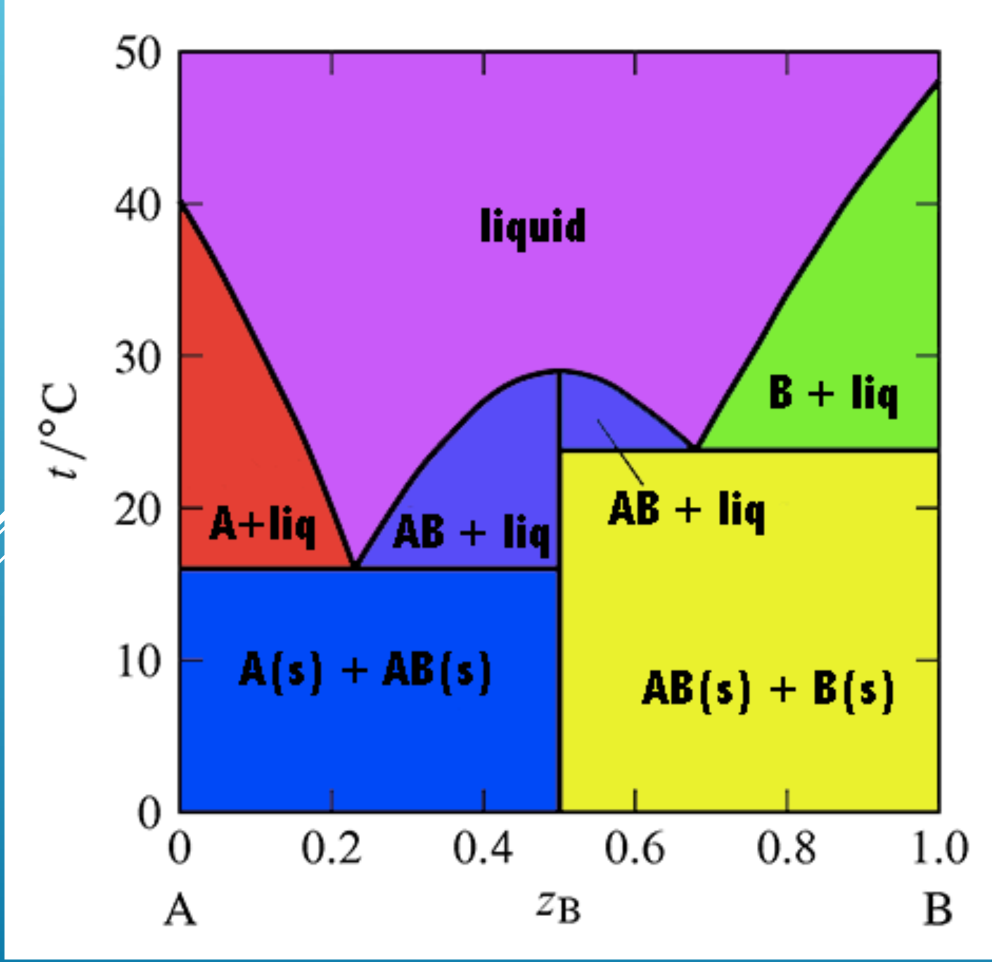
CHAPTER 11: TWO COMPONENT SYSTEM

Sarah Lambart



RECAP CHAP 10

- **Processes** by which minerals form:
  - From a fluid: precipitation or crystallization
  - From a vapor: deposition
  - From a solid-solid reaction
- **System**: a portion of the universe that you wish to study
  Ex: salt + water in a beaker: **isolated, closed or open**
- **Phase** = a physically separable part of the system with distinct **physical** and **chemical** properties. A system must consist of one or more phases.
- ***Component:*** Each phase in the system may be considered to be composed of one or more components. The number of components in the system must be **the minimum required to define all of the phases**.

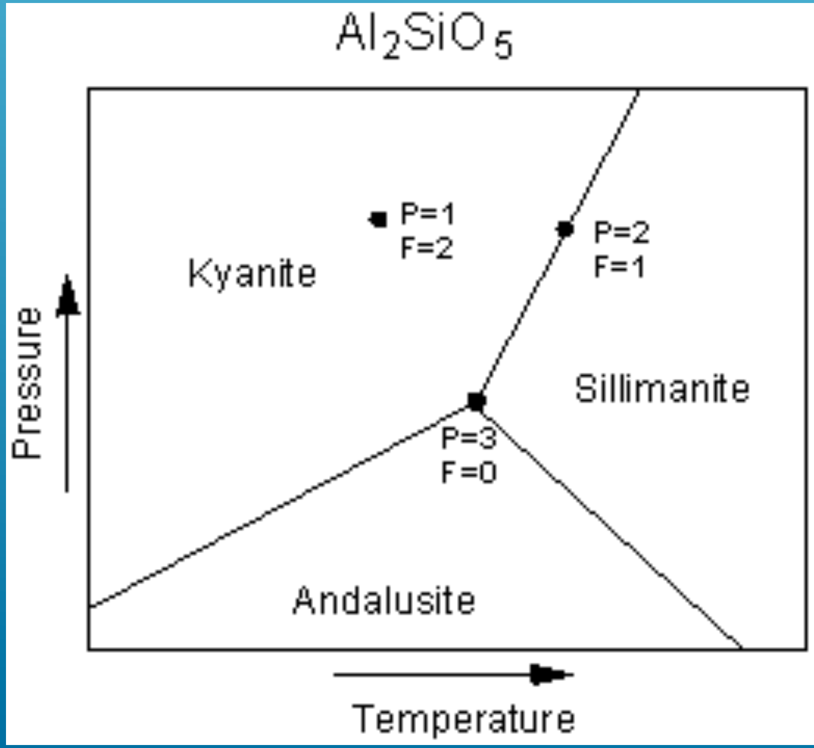
RECAP CHAP 10

- **Phase diagram**: projection of the mineral with the lowest free energy for each Pressure, Temperature and/or composition
- **Variables:**
  - **Intensive variables:** do not depend on the size of the system or the amount of material present - ex.: P and T
  - **Extensive variables:** depend on the size of the system or the amount of material present – ex.: G, V, S, E and H

RECAP CHAP 10

$f = c + 2 - \Phi$ (+n)

- **Phase rule:** relation between the minimum number of components (c) in a chemical system, the number of phases present (Φ), and the number of variables that can be independently varied while maintaining equilibrium, i.e the variance or the degrees of freedom (f)

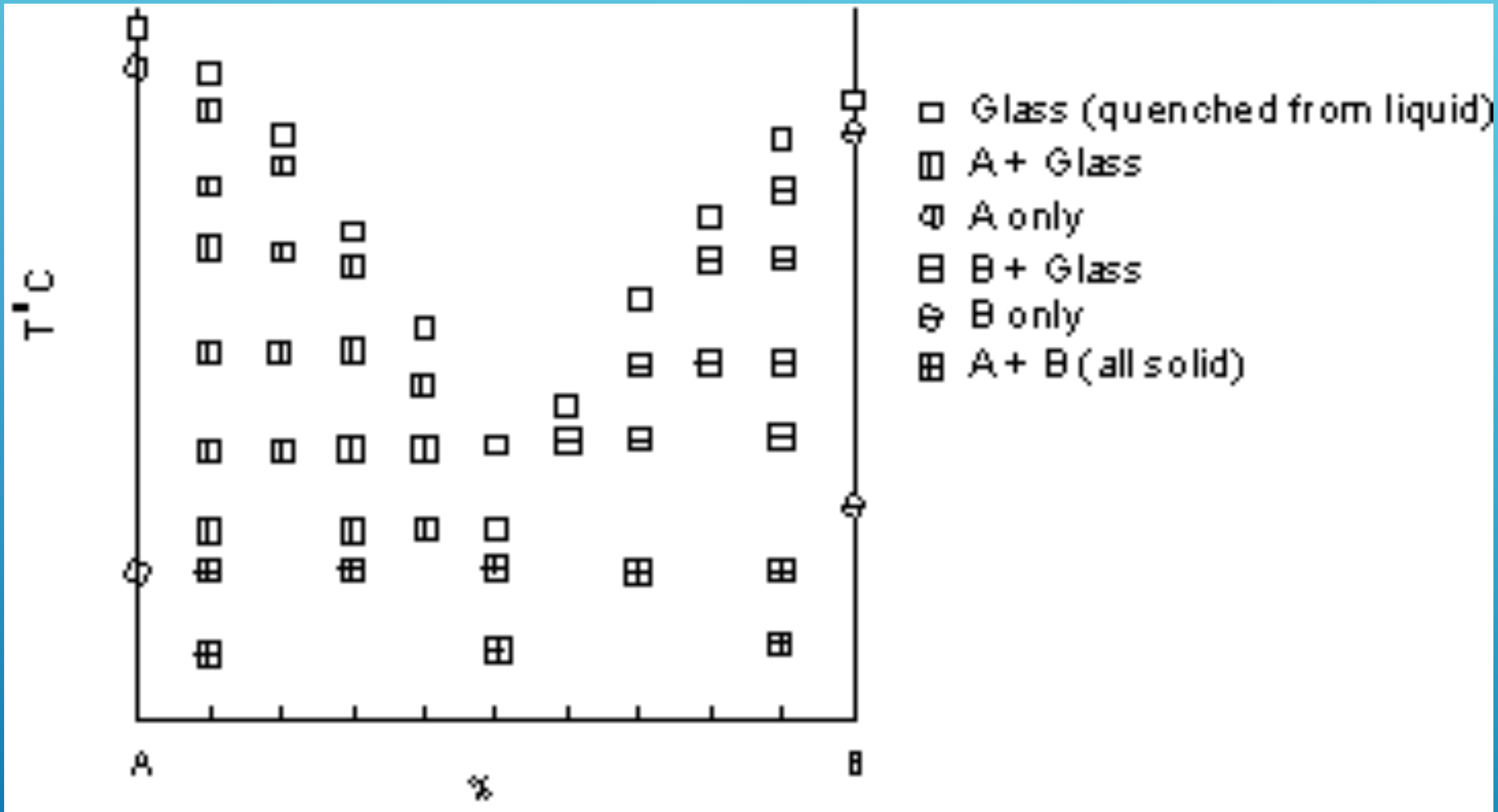


- **c: Al_2SiO_5 – c = 1**
- **P_1: Φ = 1 ⇒ f = 2 : this field stability is divariant =** I can change P independently of T and I keep the same mineralogical assemblage
- **P_2: Φ = 2 ⇒ f = 1 : the phase assemblage is univariant =** If I change P, I need to change T to keep the same mineralogical assemblage
- **P_3: Φ = 3 ⇒ f = 0 : the point is invariant =** I can't change the P, T condition without changing the mineralogical assemblage

TWO COMPONENT SYSTEM (C = 2)

- **Experimental determination:** how to determine the stability of a mixture between 2 minerals A and B?
- 2 end-members (pure A and pure B) + all the intermediates compositions (ex.: 35% A ⇔ 65% B)
- 3 variables: P, T and X ⇒ 2D-plot: P= constant (ex.: P = 1 bar)
- Experiments: in controlled atmosphere furnace.
  - Quench: rapid decrease in temperature ⇒ High T phase assemblage is preserved at room temperature – liquid is converted into glass

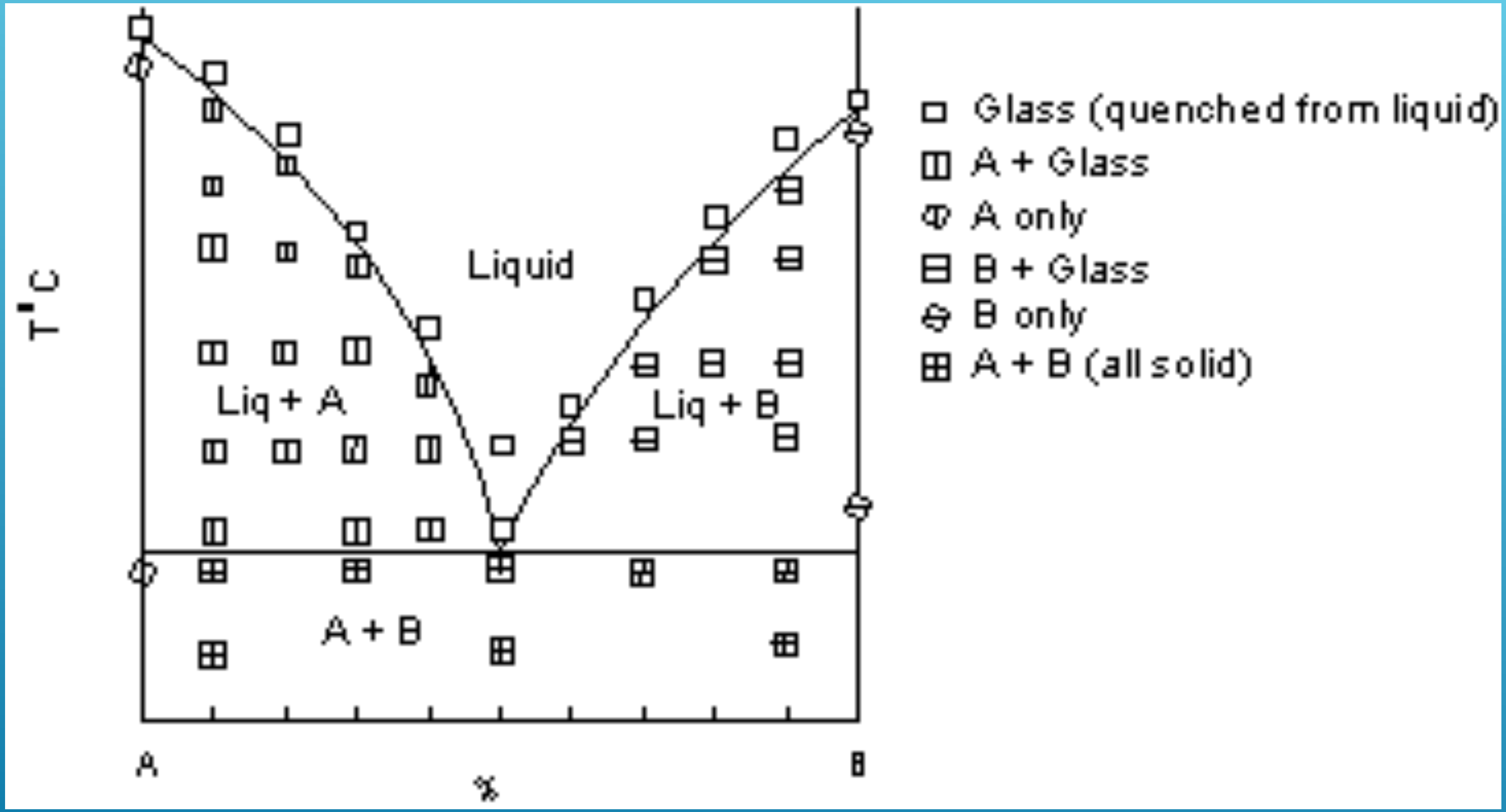
TWO COMPONENT SYSTEM (C = 2)



http://www.tulane.edu/~sanelson/eens211/2compphasdiag.html

- **Question I problem set IV**
- **With Excel:** use different series for different phase assemblages

TWO COMPONENT SYSTEM (C = 2)



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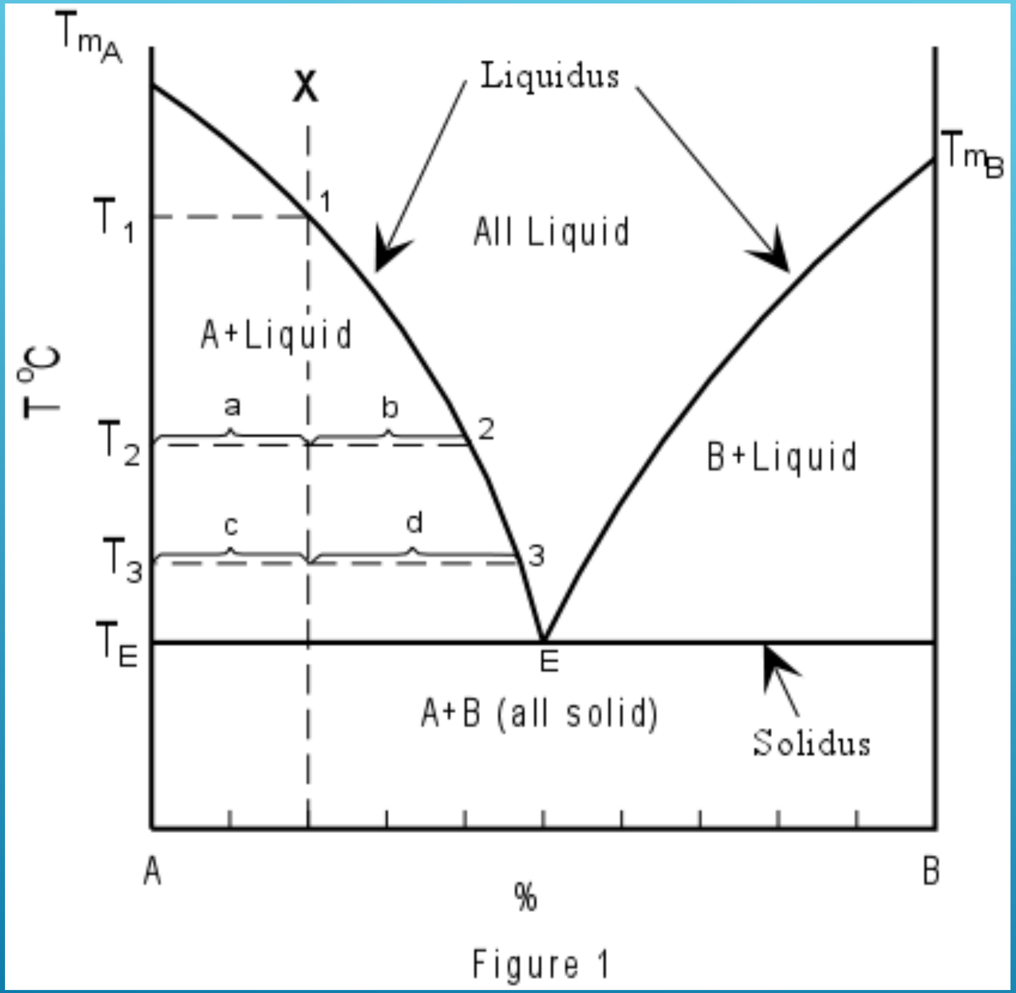
- Extrapolation of the experimental data: **determination of the phase stability fields.**

- **Binary eutectic diagram**

TWO COMPONENT EUTECTIC SYSTEM



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- X axis: composition: % B (or mol of B from 0 to 1).
- Y axis: T
- Above the liquidus: liquid phase only
- Below the solidus: solid phase(s) only
- E; where liquidus and solidus curves intersect = **eutectic point: all three phases (liquid, crystal of A, and crystal of B) coexist in equilibrium**

TWO COMPONENT EUTECTIC SYSTEM

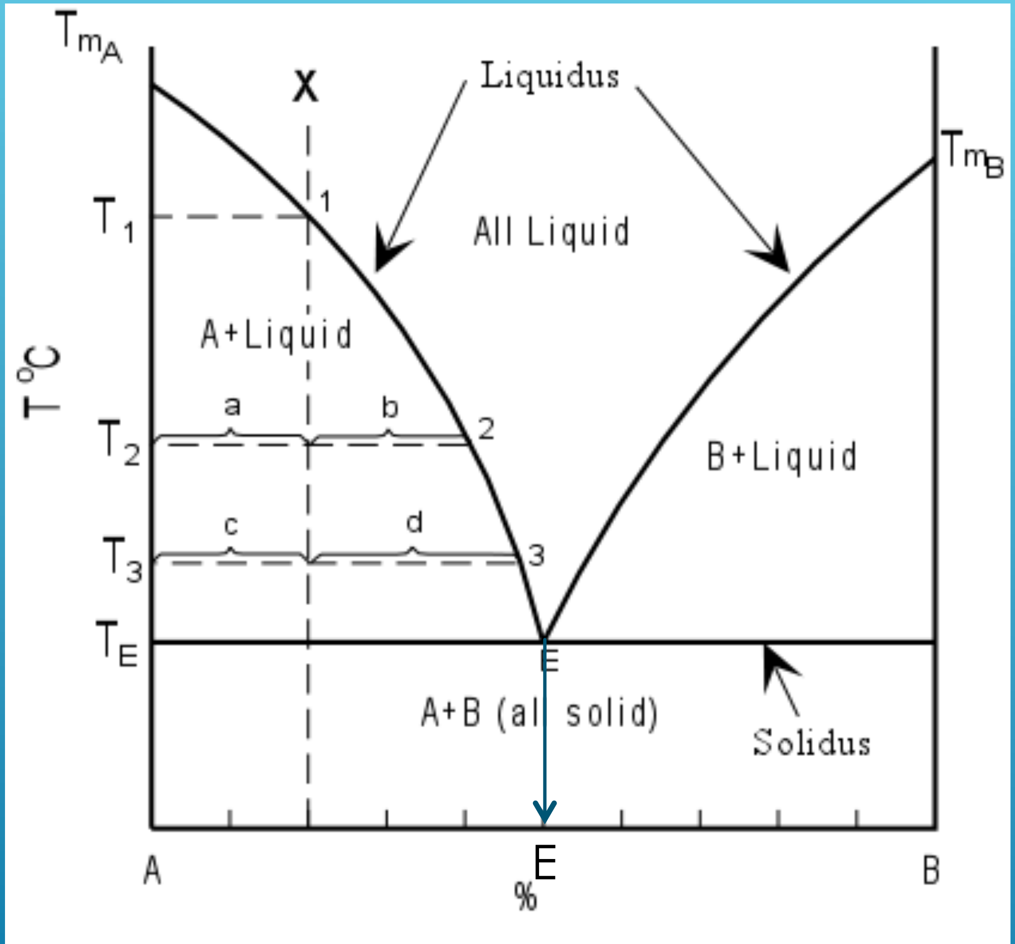
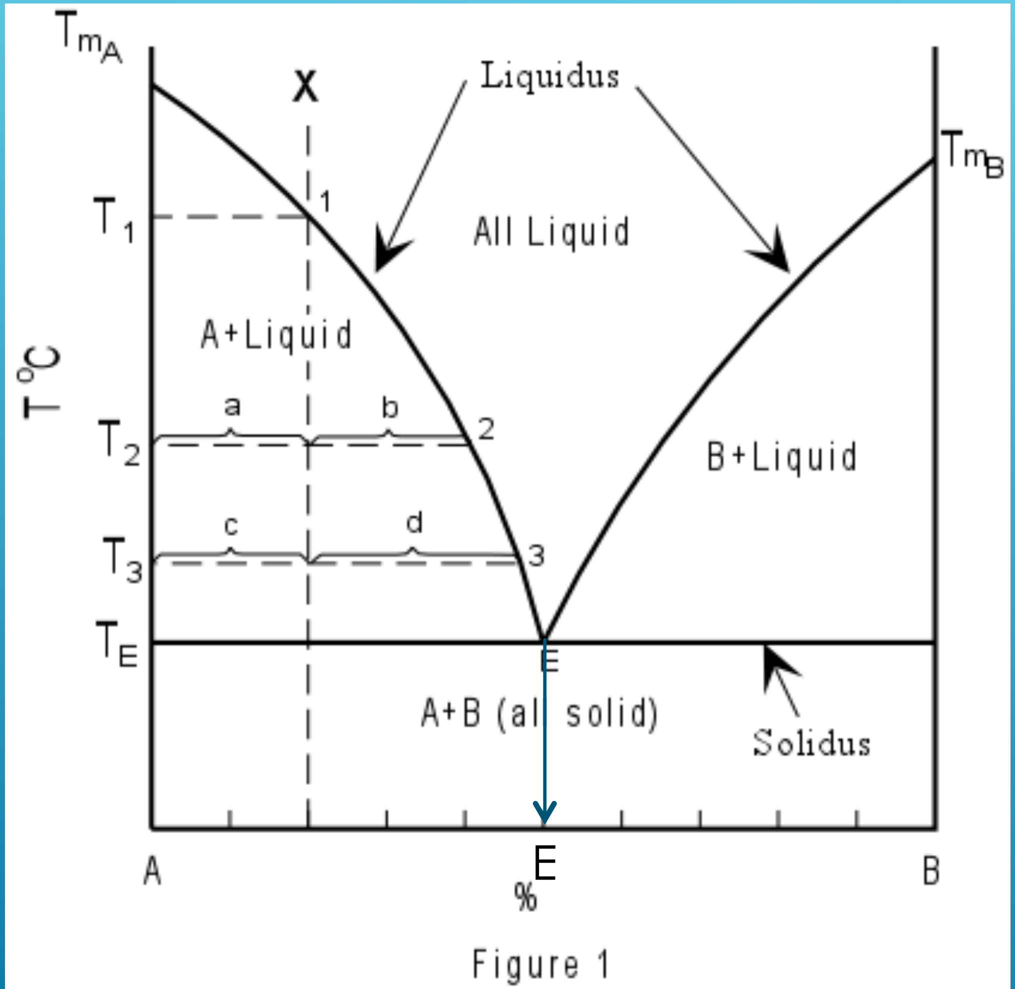


Figure 1

http://www.tulane.edu/~sanelson/eens211/2compphasdiag.html

- Phase rule: $f = c + 2 - p$ (2 for P and T variables)
- **P = constant ⇒ $f = c + 1 - p$**
- **E: p = 3 ⇒ f = 0**
- **If X = 100% A: one component system : A melts at one temperature (TmA)**
  if X = 100%B: one component system : A melts at one temperature (TmB)
- **All other compositions: melting start at T_E.**
  If X ≠ E: melting ⇔ range of T
  If X = E: melting ⇔ one T = T_E

TWO COMPONENT EUTECTIC SYSTEM



http://www.tulane.edu/~sanelson/eens211/2compphasdiag.html

- Crystallization of a liquid with the composition X.
- Rule#1: In equilibrium crystallization or melting in a closed system, the final composition of the system will be identical to the initial composition of the system
- X: 20%B and 80%A: rule #1 ⇒ final product is a mixture of 20% crystal B and 80% crystal A

TWO COMPONENT EUTECTIC SYSTEM

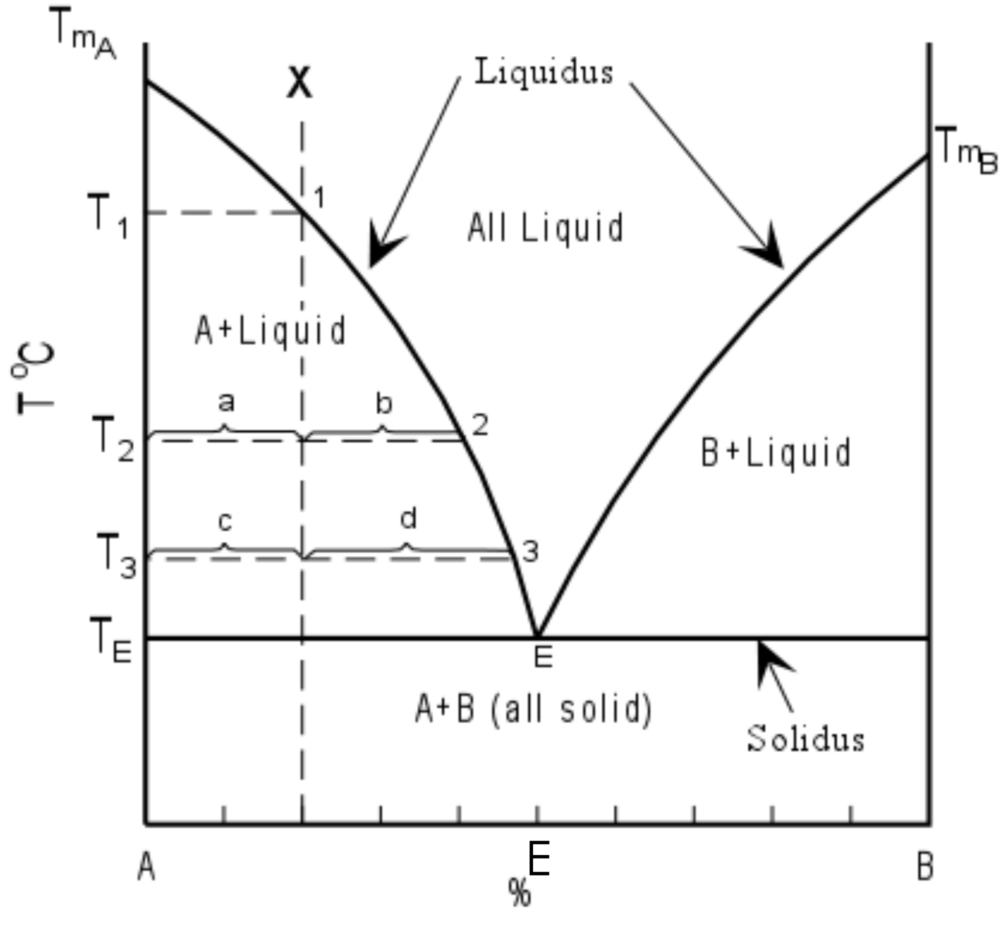
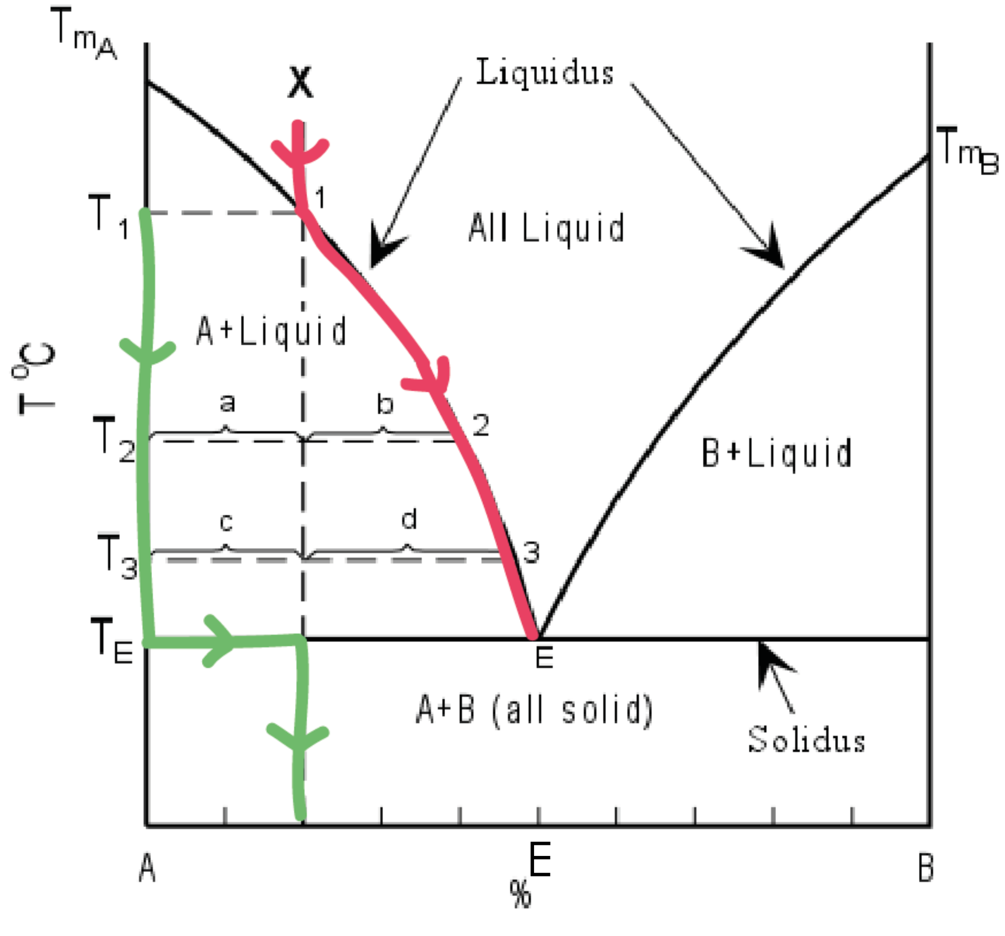


Figure 1

http://www.tulane.edu/~sanelson/eens211/2compphasdiag.html

- **If $T > T_1$: all liquid**
- **At T_1: first crystal of A**
- **At $T_E < T < T_1$:** more crystals of A ⇒ the liquid becomes more enriched in B (so the bulk composition stay constant) : **1→ 2 → 3 → E: 2 phases: liquid and crystals of A.**
- **At $T = T_E$: crystal of B begin to form, the 3 phases coexist. T = TE until one phase disappears.**
- **At $T < T_E$: A + B solid**

TWO COMPONENT EUTECTIC SYSTEM



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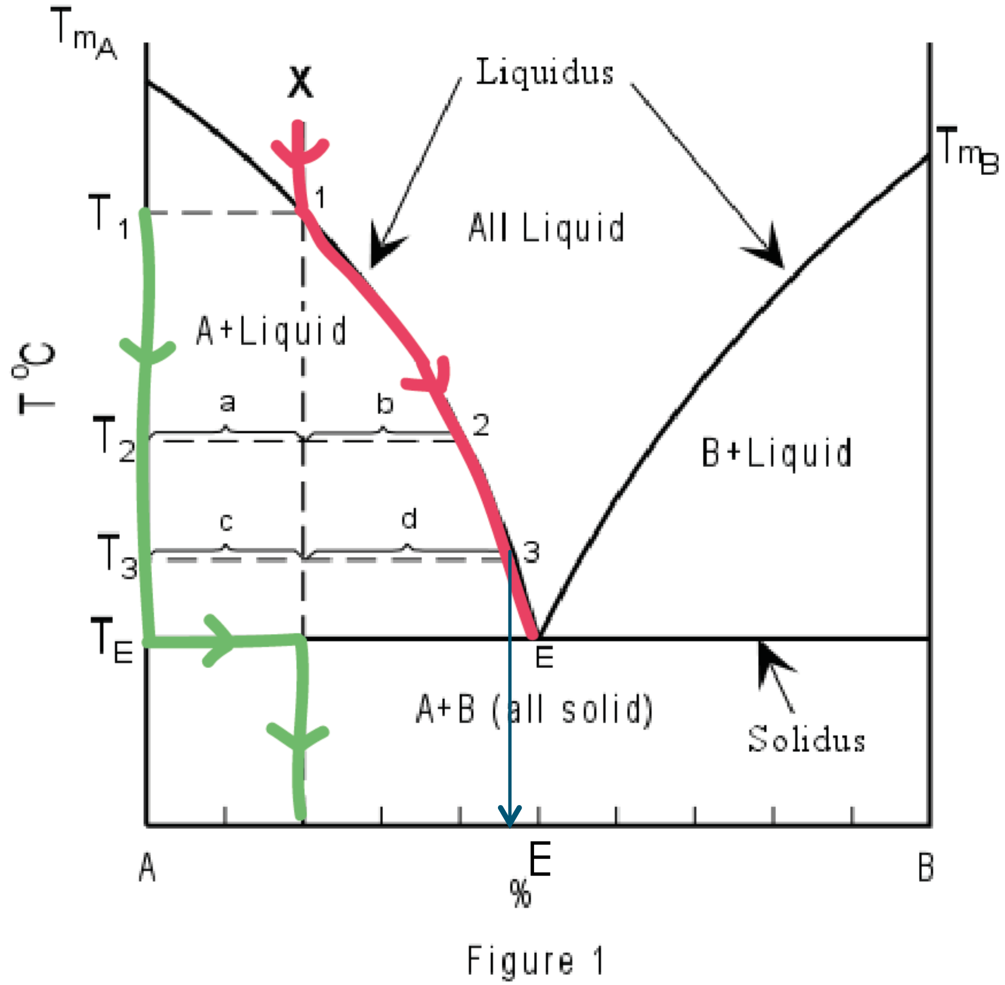
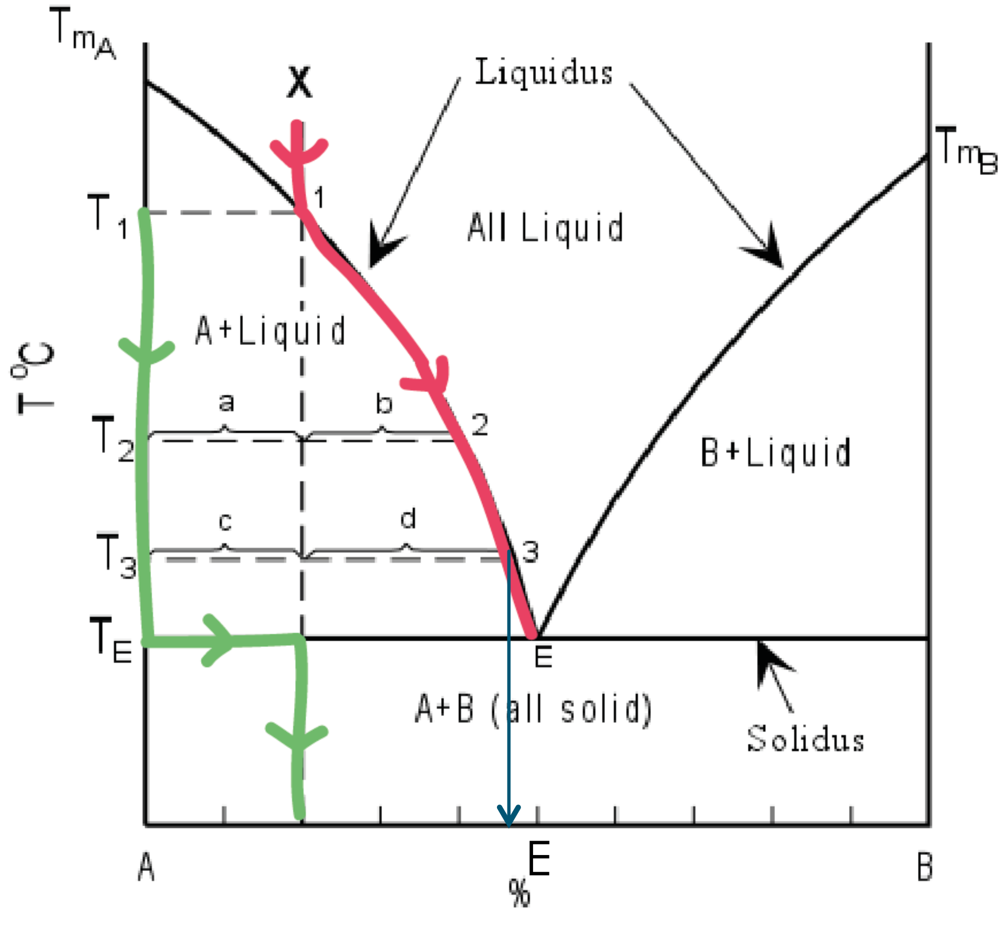


http://www.tulane.edu/~sanelson/eens211/2compphasdiag.html

- **Lever principle: to determine the amount of each phase present at a given temperature:**
- Ex. : amounts of crystal A and liquid at T3
  % crystal A = d/(c+d) * 100
  % liquid = c/(c+d) * 100

TWO COMPONENT EUTECTIC SYSTEM



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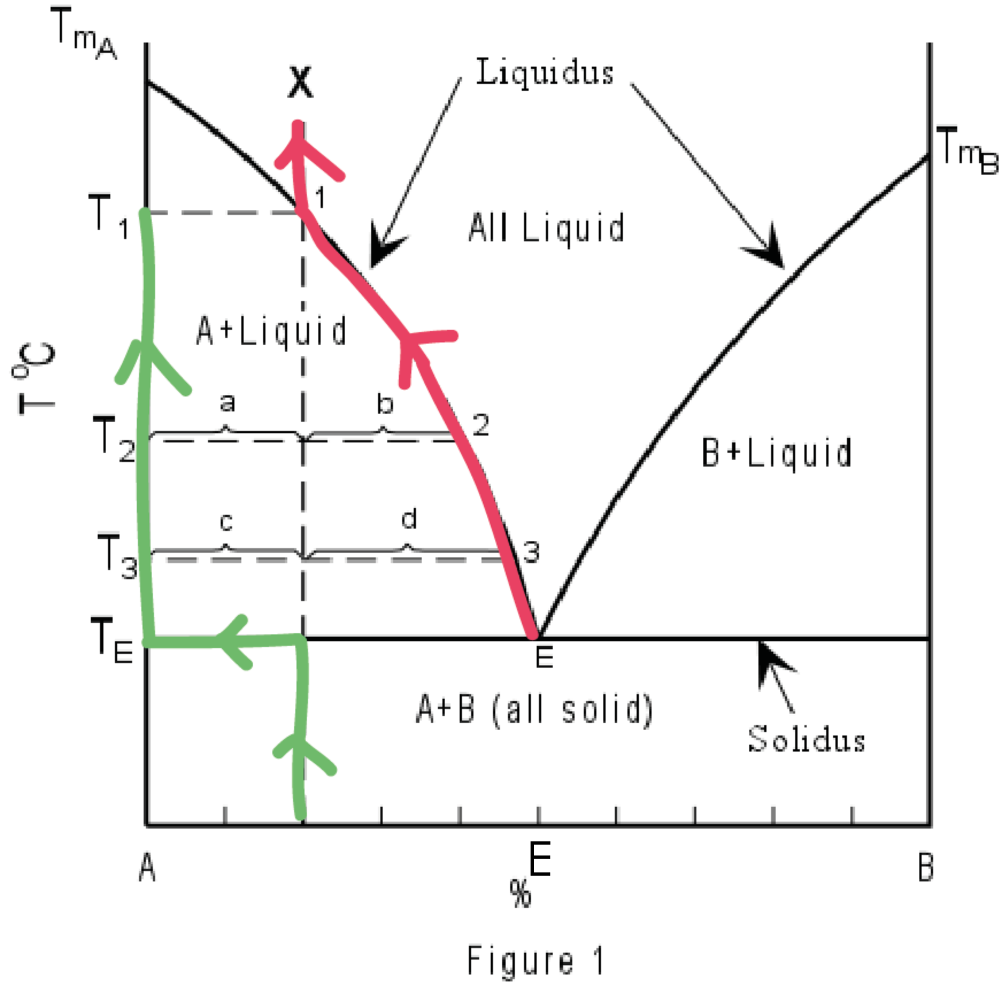
- **Lever principle: to determine the amount of each phase present at a given temperature:**
- Ex. : amounts of crystal A and liquid at T3
  % crystal A = d/(c+d) * 100
  % liquid = c/(c+d) * 100
- **Liquid composition at T_3: 47%B**
  Solid composition at T_3: 100%A (or 0%B)
  Bulk composition (at T_3): 20%B (or 80% A)
- **%crystal A = (0.47-0.2)/0.47*100= 57.45%**
  %liquid = (0.2-0)/0.47*100= 42.55%
  %crystal A + % liquid = 100%

TWO COMPONENT EUTECTIC SYSTEM



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- In equilibrium, the melting process is exactly the opposite of the crystallization process
- Melting story:
  - T<TE : all solid: crystal of A + crystal of B
  - T = TE: crystal of A + Crystal of B + liquid
  - TE < T < T1: Crystal of A + liquid
  - T> T1: all liquid

INCONGRUENT MELTING

- **Definitions:**
- **Liquidus:** The line separating the field of all liquid from that of liquid plus crystals.
- **Solidus:** The line separating the field of all solid from that of liquid plus crystals.
- **Eutectic point:** the point on a phase diagram where the maximum number of allowable phases are in equilibrium. When this point is reached, the temperature must remain constant until one of the phases disappears. A eutectic is an invariant point.
- **Congruent melting** - melting wherein a phase melts to a liquid with the same composition as the solid.

INCONGRUENT MELTING

- **Definitions:**
- **Peritectic point:** The point on a phase diagram where a reaction takes place between a previously precipitated phase and the liquid to produce a new solid phase. When this point is reached, the temperature must remain constant until the reaction has run to completion. A peritectic is also an invariant point.
- **Intermediate compound:** - A phase that has a composition intermediate between two other phases.
- **Incongruent melting:** melting wherein a phase melts to a liquid with a composition different from the solid and produces a solid of different composition to the original solid.

INCONGRUENT MELTING

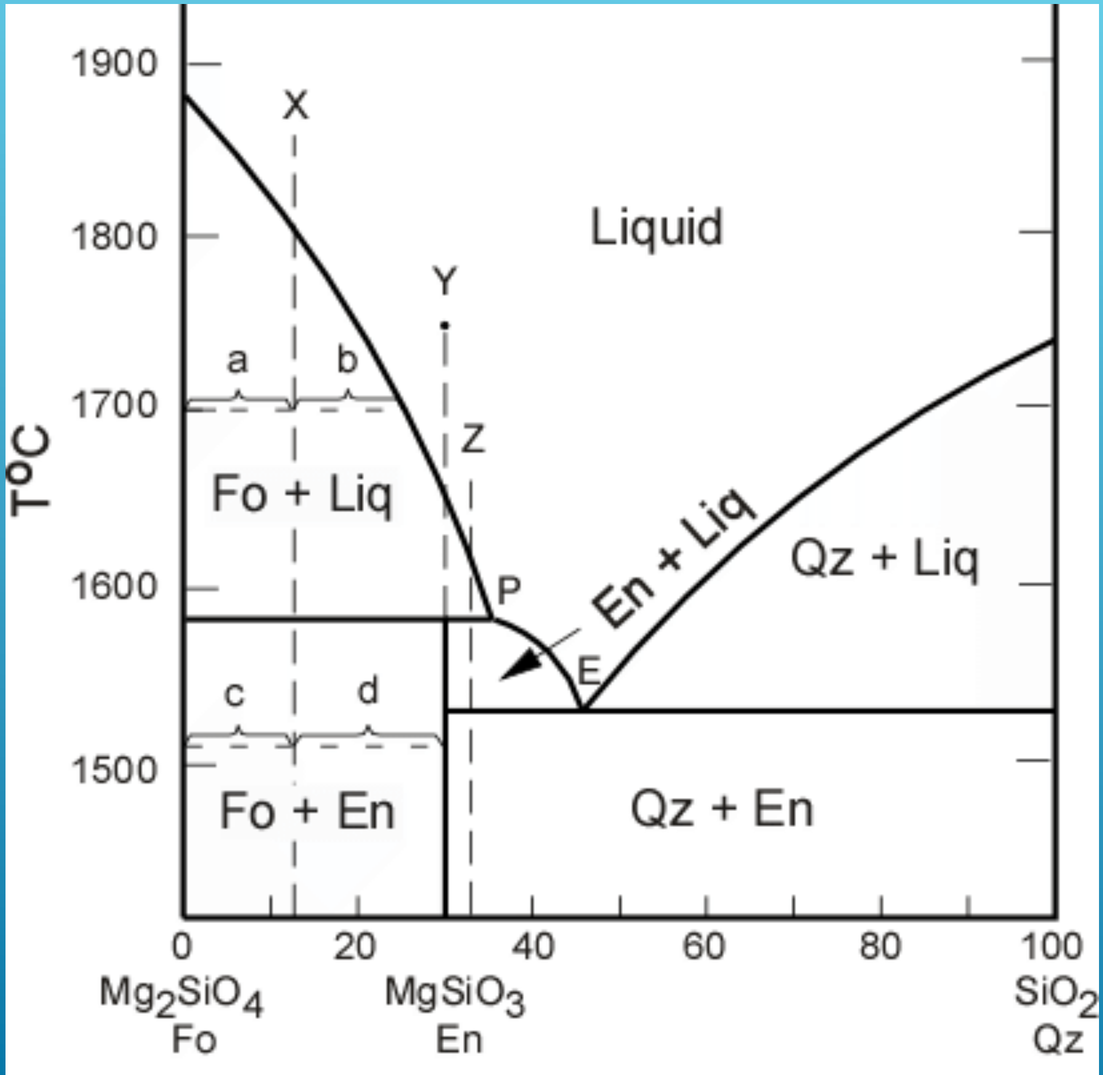

Figure 2

- Crystallization of a liquid with the composition X: 13% SiO_2, 87% Mg_2SiO_4
  - X: intermediate between pure forsterite and pure enstatite ⇒ final product = mixture of pure forsterite and pure enstatite.
- Peritectic point P: Fo + liquid → En ⇔ both forsterite and liquid are consumed to form enstatite

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- Eutectic point E: Liquid → En (or Qz) ⇔ only the liquid is consumed

INCONGRUENT MELTING

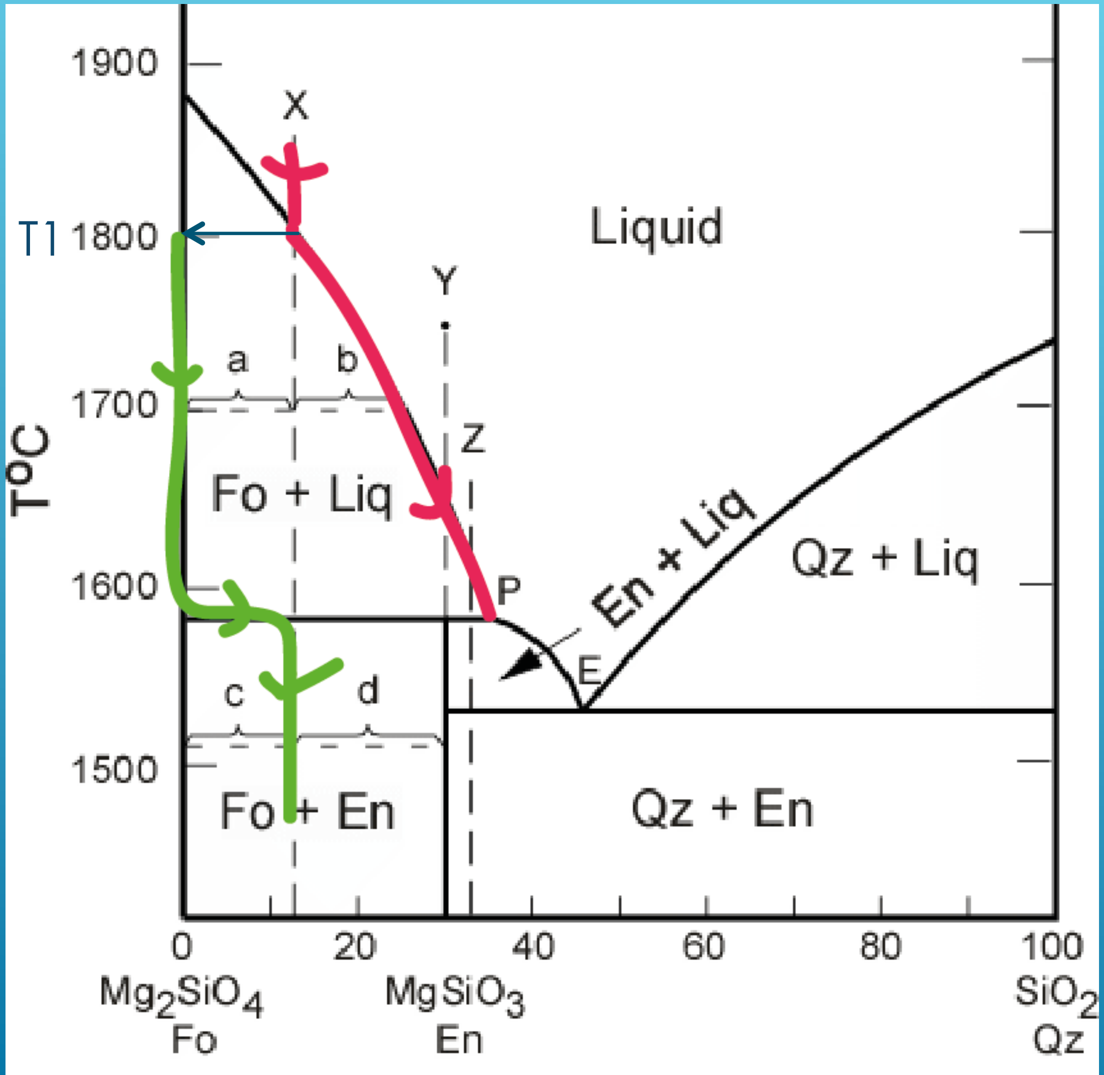
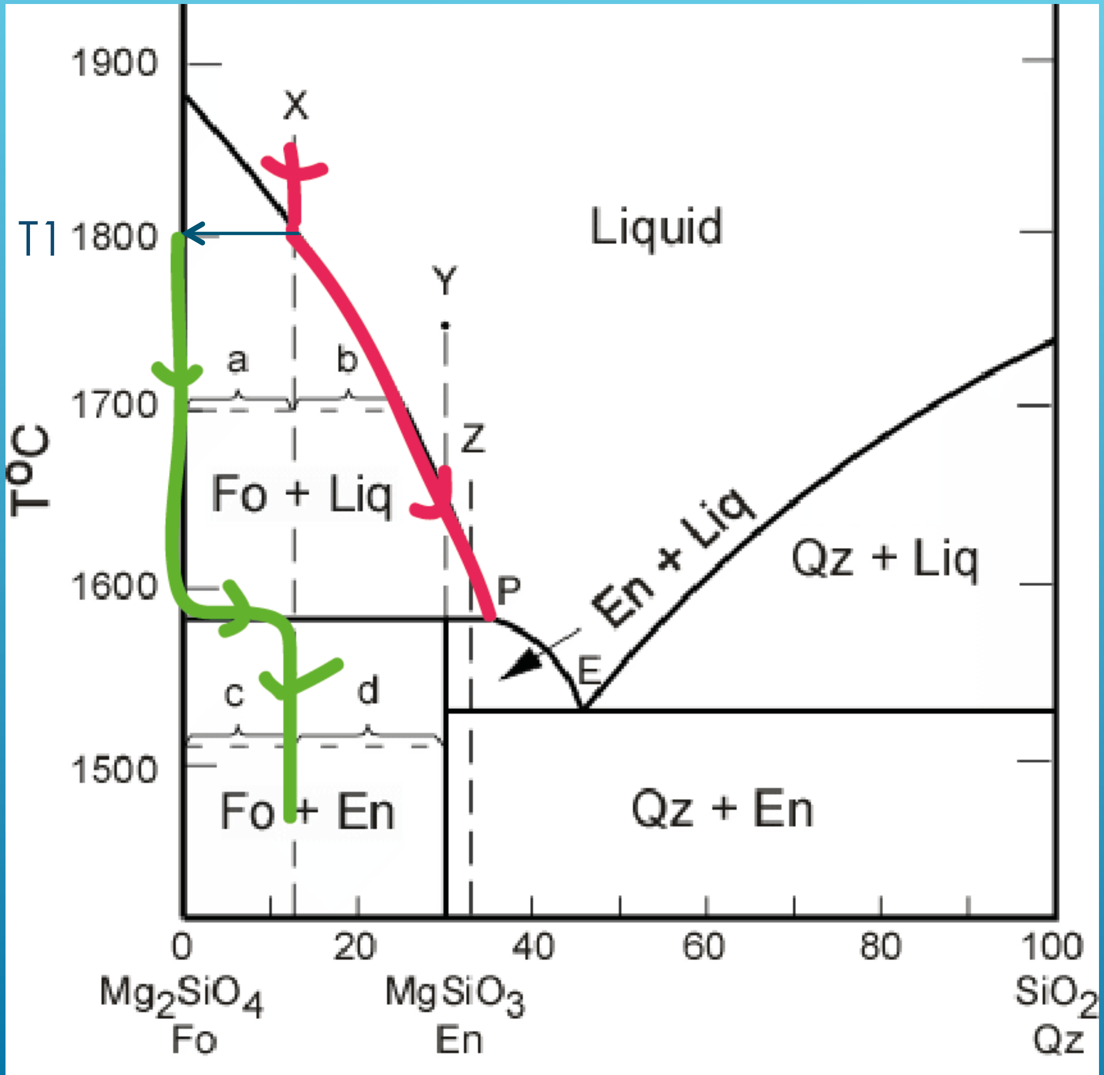


Figure 2

- Crystallization history:
  - T > T1 : all liquid
  - T = T1 first crystals of forsterite forms
  - TP < T < T1: proportion of forsterite increases
  - T = TP: 3 phase in equilibrium (Fo, En, Liq): Fo + Liq → En until all the liquid is consumed
  - T< TP: mixture of solid Fo and solid En

INCONGRUENT MELTING



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- **Crystallization history:**
  - **T > T1 : all liquid**
  - **T = T1 first crystals of forsterite forms**
  - **TP < T < T1: proportion of forsterite increases**
  - **T = TP: 3 phase in equilibrium (Fo, En, Liq): Fo + Liq → En until all the liquid is consumed**
  - **T< TP: mixture of solid Fo and solid En**
    - **Use of the lever principle to determine the proportion of Fo and En:**
    - **%Fo = d/(c+d)*100 = (30-13)/30*100 = 56.7%**
      %En = 100-56.7 = 43.3%

INCONGRUENT MELTING

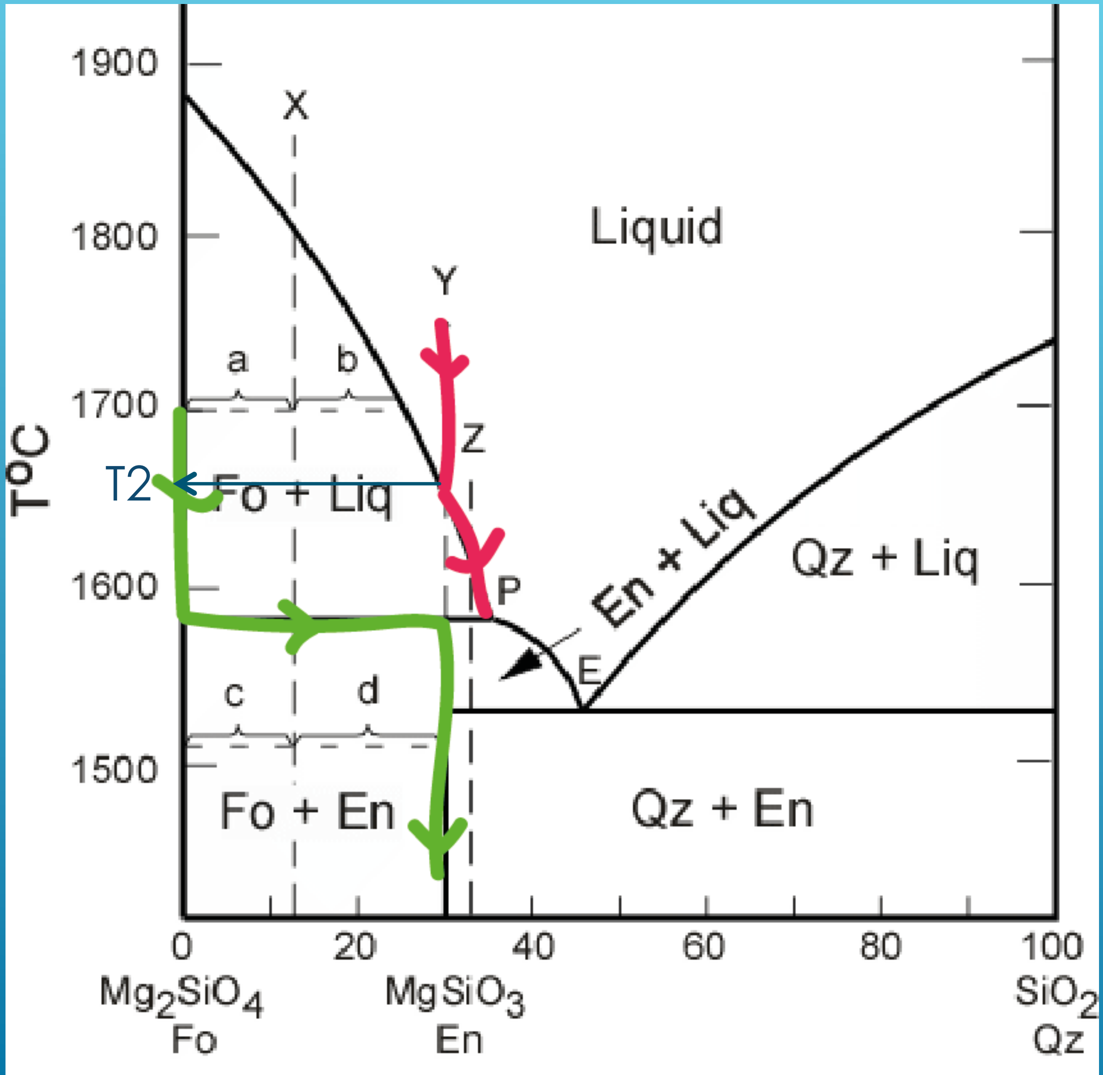


Figure 2

- **Crystallization of a liquid with the composition Y: 30% SiO_2, 70% Mg_2SiO_4 = pure En ($MgSiO_3$)**
  - **Final product: crystal of En and crystal if Qz**
- **Crystallization history:**
  - **T> T2: all liquid**
  - **TP < T < T2 : liquid + Fo**
  - **TP: Liquid + Fo = En: liquid and forsterite are consumed to produced En**
  - **T<TP : all En**

INCONGRUENT MELTING

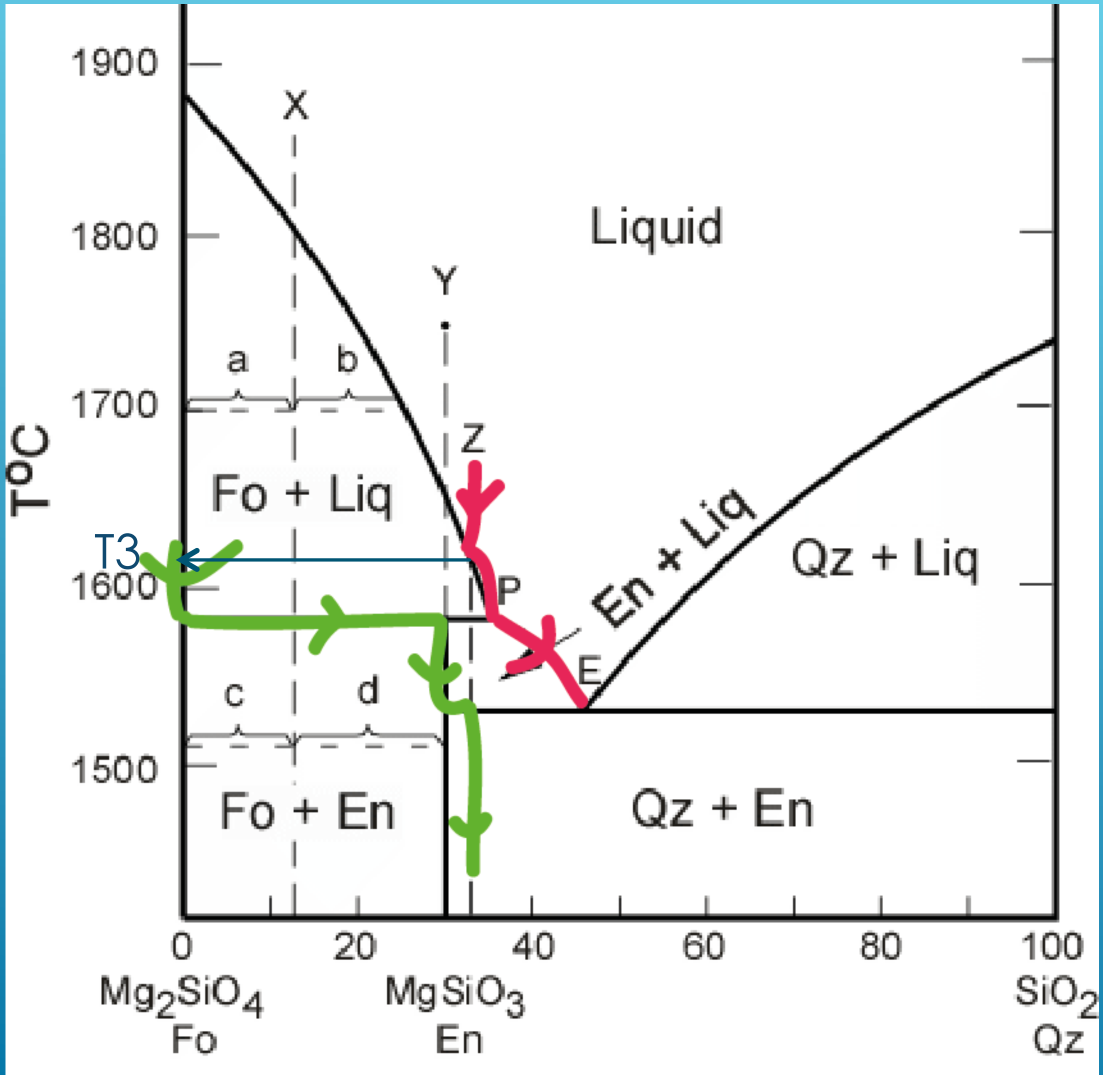
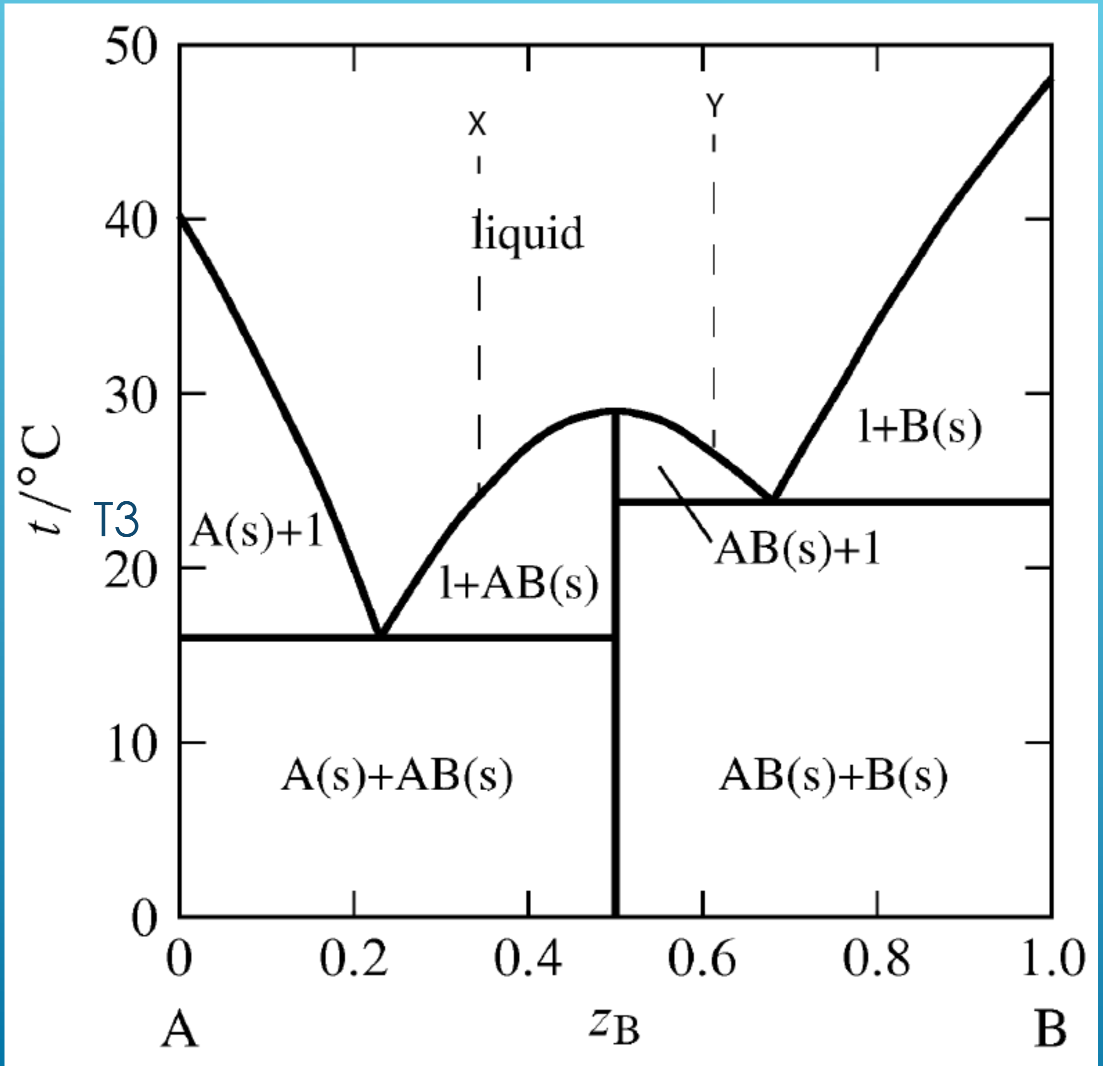


Figure 2

- Crystallization of a liquid with the composition Z: 33% SiO_2, 67% Mg_2SiO_4
  - Final product: pure enstatite.
- Crystallization history:
  - T> T3: all liquid
  - TP < T < T2 : liquid + Fo
  - TP: Liquid + Fo = En: all the Fo is consumed but liquid still present
  - TE < T < TP: Liquid + En
  - TE: Liquid + En + Qz until all the liquid is consumed
  - T < TE: Quartz + En

INCONGRUENT MELTING



- **Melting history of the composition X and Y**

SOLID SOLUTIONS SYSTEMS

- **So far:** solid phase are pure end-member phase (ex.: forsterite)
- **In nature:** substitutions in minerals ⇒ solid solution
  - When all the intermediate compositions are possible between 2 end-members = **complete solid solution**

SOLID SOLUTIONS SYSTEMS

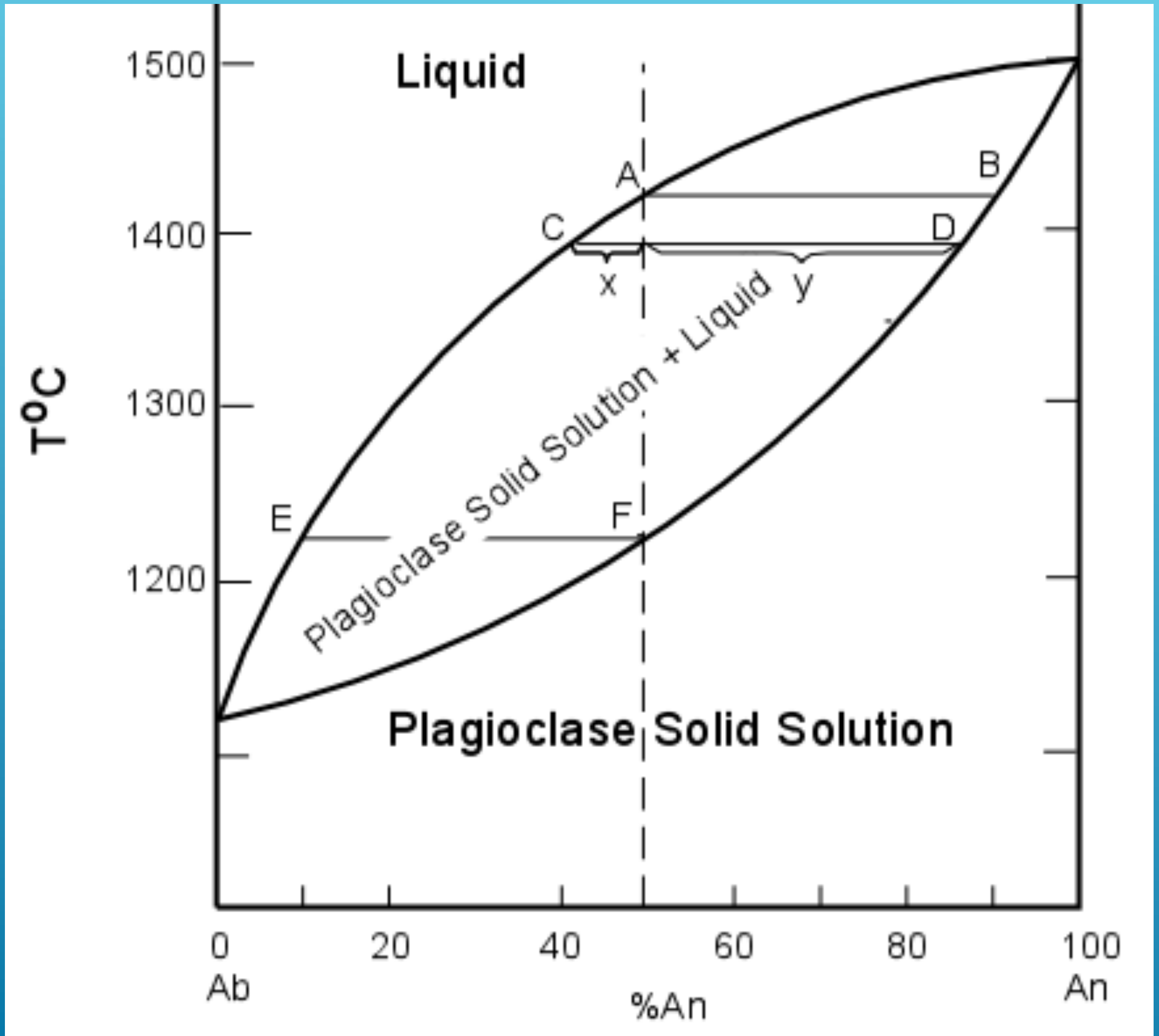


Figure 3

- **Pure albite: crystallizes (or melts) at 1118°C vs. pure anorthite: 1500°C (one temperature)**
- **All other compositions crystallize of melt on a range of T**
  Ex: a plagioclase with a composition of 50% albite and 50% anorthite starts to melt at 1220°C (F) and is totally melted at 1410°C (A)

SOLID SOLUTIONS SYSTEMS

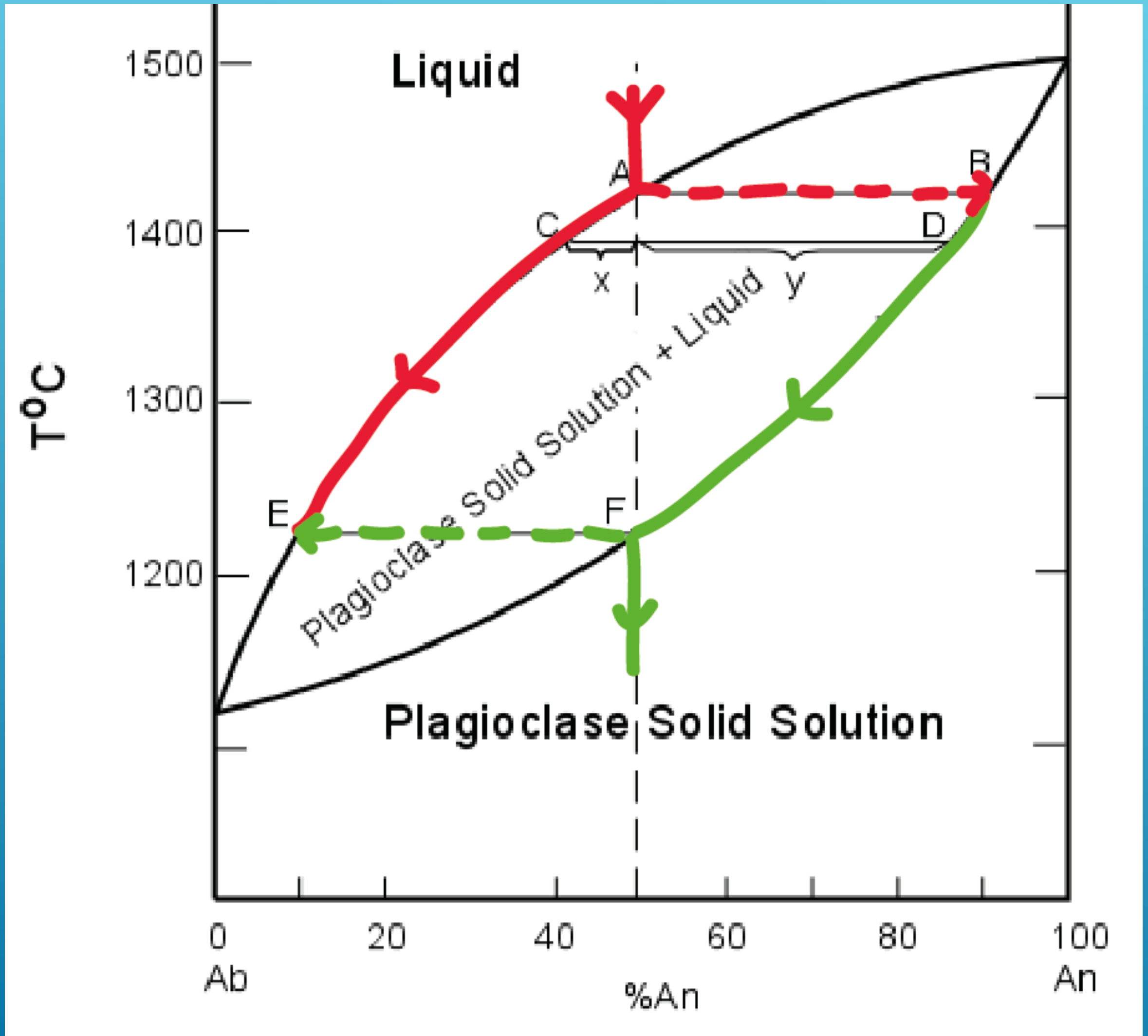


Figure 3

- Crystallization history of $An_{50}Ab_{50}$
- T> TA : all liquid
- T = TA (liquidus): formation of the first crystal of plagioclase: composition of the first crystal = B (on the solidus): $An_{90}Ab_{10}$
- TE < T < TA: the liquid evolves along the liquidus and the plagioclase evolves along the solidus.
- T = TE (or TF): the solid has the composition of the initial liquid ($An_{50}Ab_{50}$). The last liquid is $An^{10}Ab90$

SOLID SOLUTIONS SYSTEMS

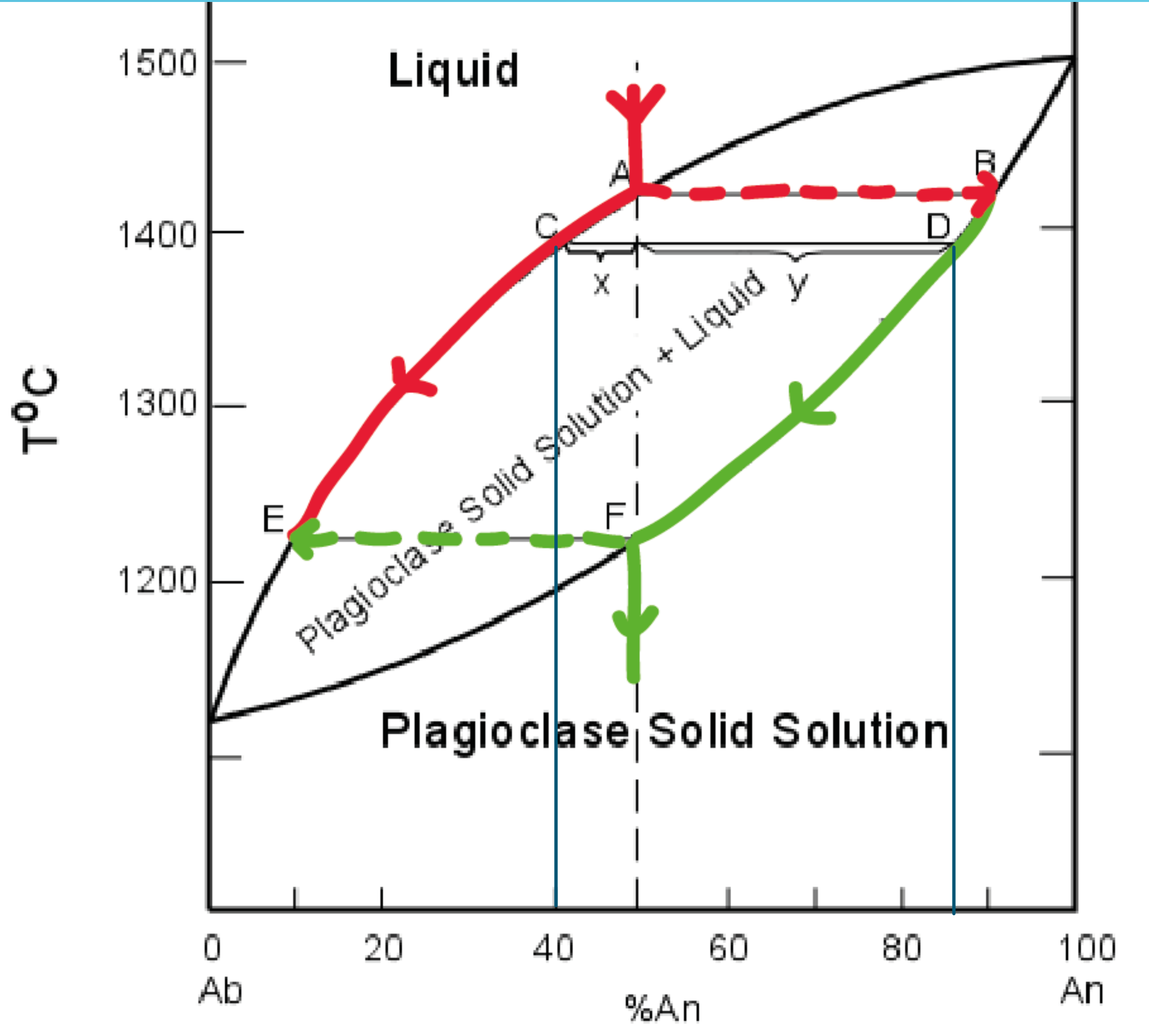


Figure 3

- Amount of liquid and solid at 1400°C:
- %liquid = y/(c+y)*100
  = (87-50)/(87-40)*100=78.7%
- %plagioclase=100-78.7=21.3%

EXSOLUTION

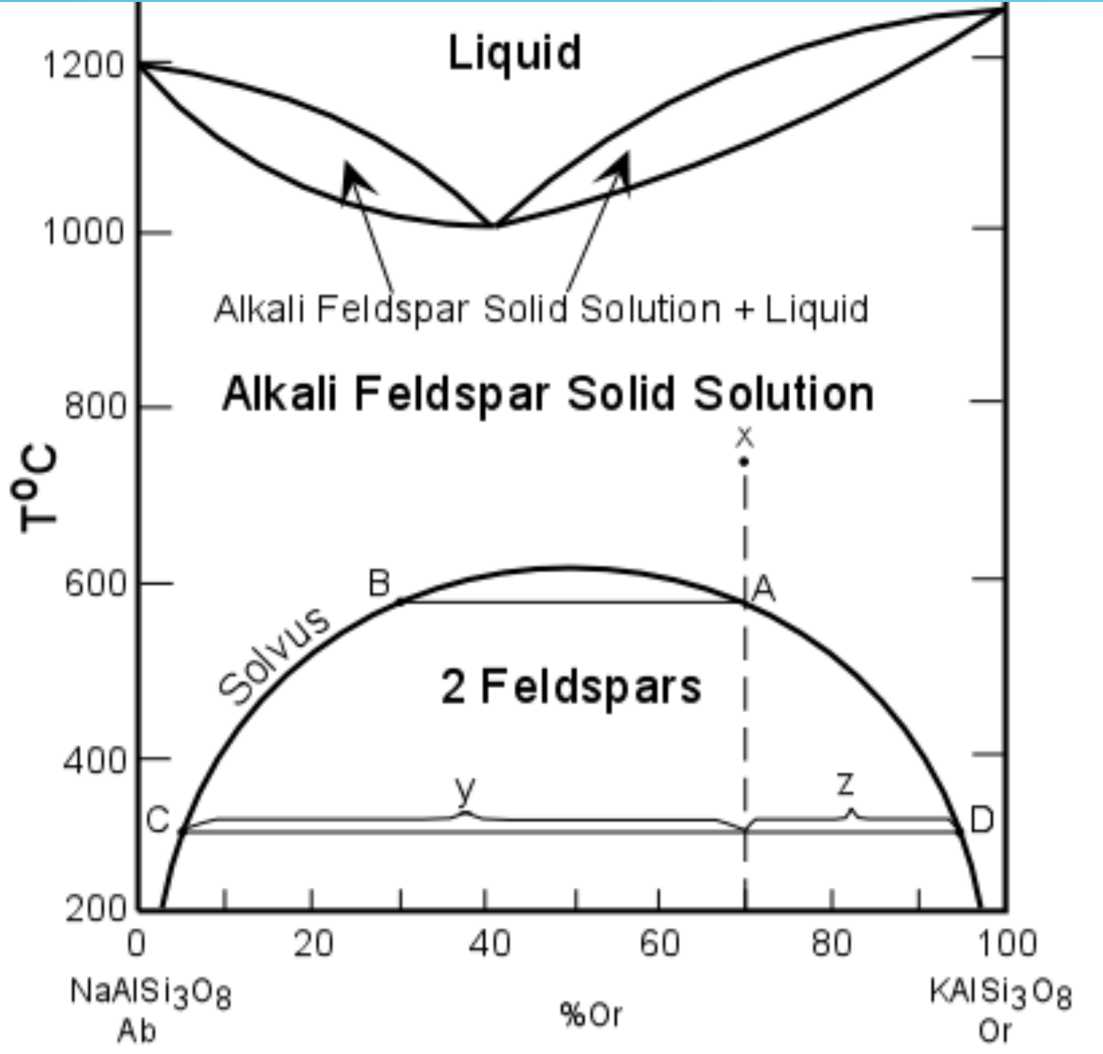


Figure 4

- **Exsolution : the solid solution stable at high temperature is no longer stable at lower temperature**
- **Exsolution phenomena below the solidus temperature = subsolidus reaction**

EXSOLUTION

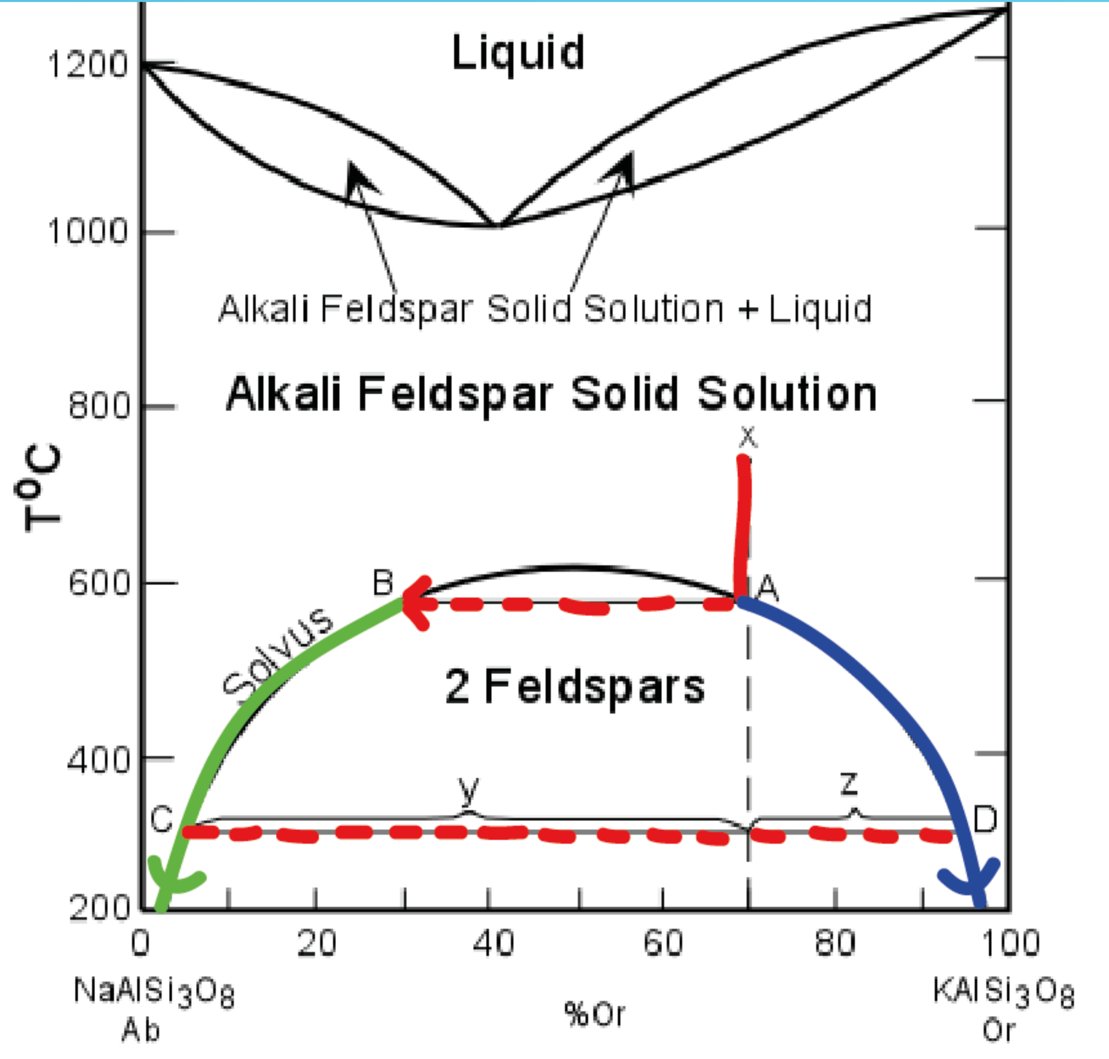


Figure 4

- Ex.: cooling of the composition X from 750°C
  - At 750°C: solid solution $Ab_{30}Or_{70}$ $(Na_{.3}K_{.7})AlSi_3O_8$
  - At 590°C: solid-solution no longer stable – starts to exsolve: solid solution with a composition of B ($Ab_{70}Or_{30}$) coexist with solid solution with a composition of A ($Ab_{32}Or_{68}$)
  - At T < 590°C: the two solid solutions evolve along the solvus. The coexisting feldspars can be find by drawing the isotherms.
  - At 300°C: 2 alkali feldspars:
    $Ab_{95}or_5$ and Ab_5Or_{95}
    Amount of $Ab_{95}An_5$: z/(y+z)*100