Solid Solutions and Vegard's Law

Learning Objectives

- Define a **solid solution** and compare to liquid solutions.
- State **Vegard's law**: unit cell dimensions (and some properties) vary linearly with composition.
- Apply Vegard's law to calculate lattice parameters and band gaps of intermediate compositions.
- Recognize and explain **deviations** from Vegard's law:
  - Charge transfer (e.g., Mn^{3+}/Ru^{5+} in Ca-based perovskites).
  - Ordering of different-size ions → more efficient packing.
- Appreciate the importance of solid solutions in **semiconductors** (epitaxy, heterojunction lasers, LEDs).
- Use Vegard's law to estimate **composition from property measurements** (e.g., lattice constant, band gap).

Vegard's Law

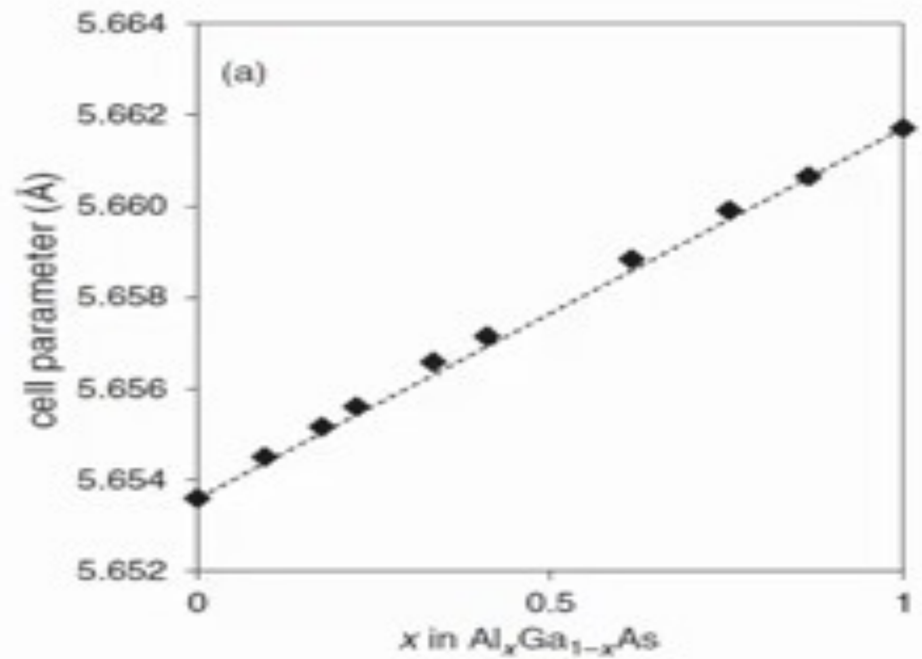
The unit cell parameters (and unit cell volume) vary linearly from one end member to the other as a function of composition.

$$a(x) = xa_{BX} + (1 - x)a_{AX}$$

a for solid solution

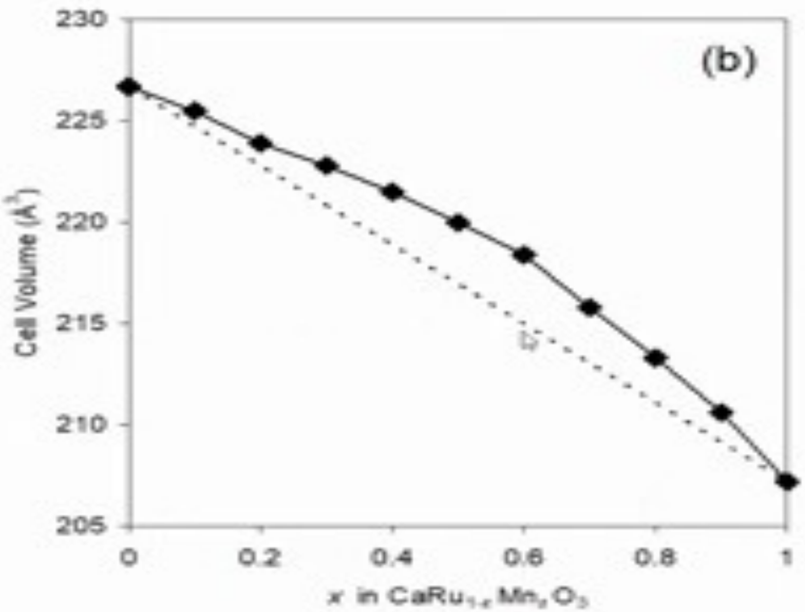
a for AlAs

a for GaAs



Deviations from Vegard's Law

Deviations from Vegard's Law can be either positive (as shown below) or negative.



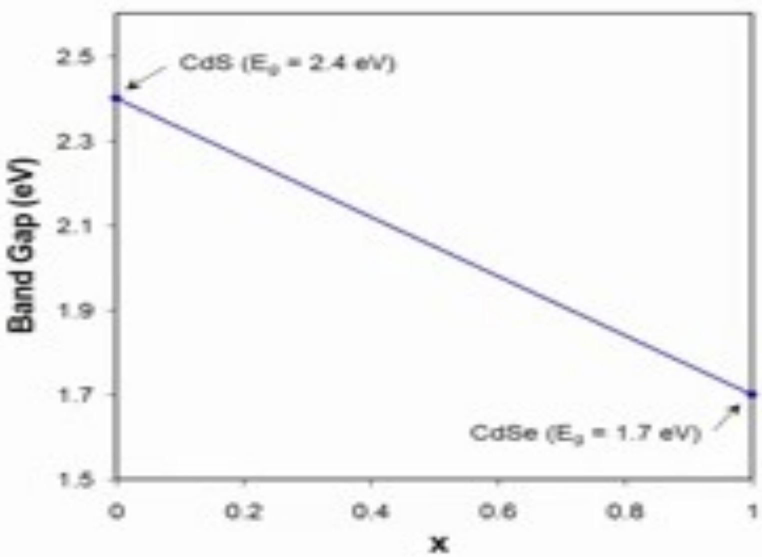
$CaRu^{+4}O_3$ $CaMn^{+4}O_3$

Causes for deviations from V-L

- Site ordering
- Inhomogeneities
- Changes in oxidation state

Band Gap Engineering

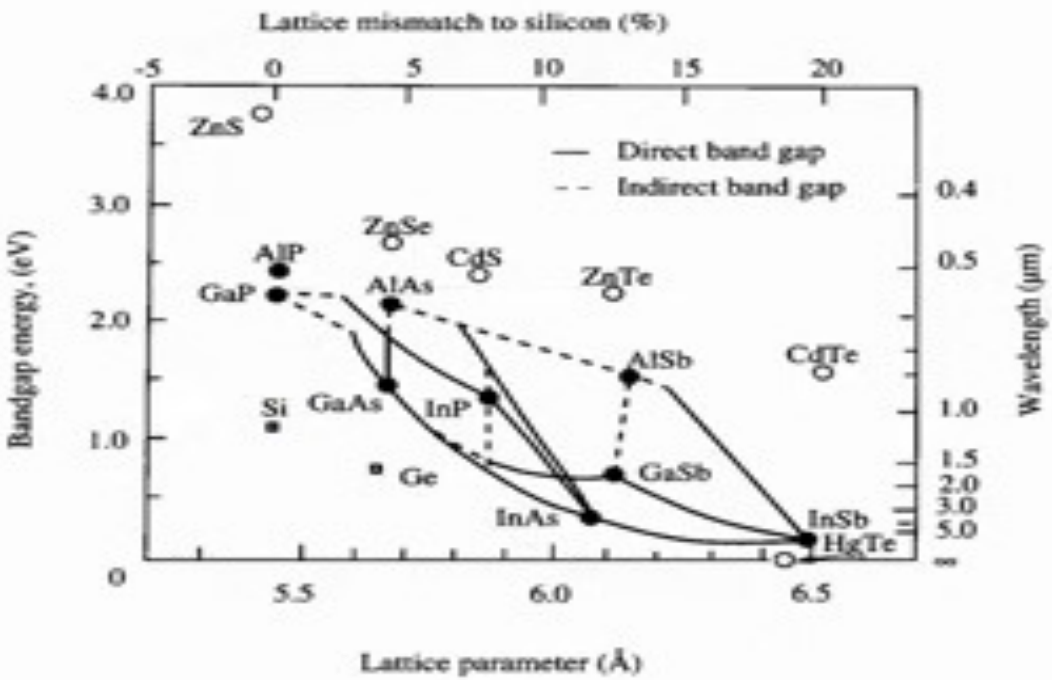
For semiconductors it is not unusual that the band gap will follow Vegard's Law.

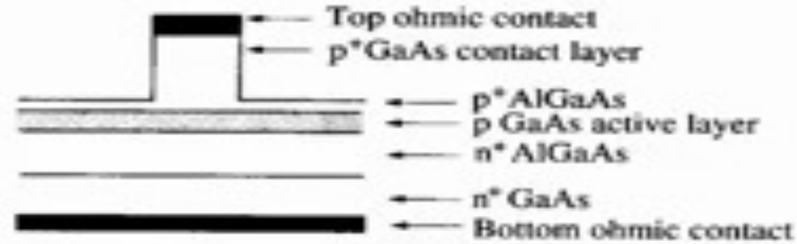


$$E_g(x) = xE_g(\mathrm{B}) + (1-x)E_g(\mathrm{A})$$

$$x = \frac{E_g(x) - E_g(\mathrm{A})}{E_g(\mathrm{B}) - E_g(\mathrm{A})}$$

Semiconductor Solid Solutions





Heterojunction laser

Figures taken from "Semiconductor Optoelectronic Devices", by P. Bhattacharya

The solid solution between GaAs (E_g=1.4 eV, a=5.65 Å) and AlAs (E_g=2.1 eV, a=5.66 Å) is among the most important for optoelectronic devices.

CdS-CdSe Solid Solutions

$CdS_{1-x}Se_x$ solid solutions are excellent pigments (cadmium yellow, cadmium orange). By controlling the composition, we can control the band gap and hence the color.

CdS (E_g = 2.4 eV)

$CdS_{1-x}Se_x$ compositions

CdSe (E_g = 1.7 eV)

Cadmium pigments

Example

What composition in the $CdS_{1-x}Se_x$ solid solution will have a band gap of 2.25 eV?

CdS (E_g = 2.4 eV)

$$x = \frac{E_g(x) - E_g(\mathrm{A})}{E_g(\mathrm{B}) - E_g(\mathrm{A})}$$

CdSe (E_g = 1.7 eV)

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CdSe (E_g = 1.7 eV)

$$x = \frac{2.25 - 2.40}{1.70 - 2.40} = 0.21$$

→ $CdS_{0.79}Se_{0.21}$

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What composition in the $CdS_{1-x}Se_x$ solid solution will have a band gap of 2.25 eV?

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CdSe (E_g = 1.7 eV)

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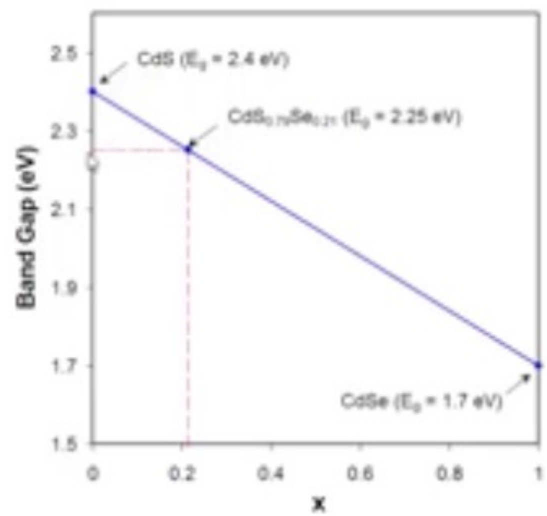


Summary

- **Solid solutions**: homogeneous crystals spanning compositions between two end members.
- **Vegard's law**: lattice constant (and sometimes other properties) varies linearly with composition.
- Deviations occur due to **charge transfer** or **cation/anion ordering**, leading to positive or negative curvature.
- Many **semiconductor properties** (e.g., band gap) also approximate Vegard's law, enabling band gap engineering.
- **Applications**:
  - GaAs–AlAs: nearly constant lattice parameter but tunable band gap → key for epitaxial devices (lasers, LEDs).
  - CdS–CdSe: tunable band gap controls pigment color (yellow → red → black).
- **Practical use**: Vegard's law lets us **predict composition from structure or property measurements**.

Homework

2.5 A sample of nonstoichiometric nickel oxide (**A**) was found to contain 77.70% Ni by mass. (a) Calculate the empirical formula of **A** and state the two alternatives for the intrinsic defect that would on its own give rise to this formula. (b) **A** has the NaCl-type structure and an experimental density of 6526 kg/m^3. Assuming a cell parameter of 4.180 Å, state which of the two defects is present. (c) State how the cell parameter of **A** could be determined experimentally and suggest how it would compare to that of stoichiometric NiO.

2.12 $GaAs_{1-x}P_x$ has a unit-cell parameter of 5.59 Å. Calculate x and estimate the band gap (E_g) of the material, given a_{GaAs} = 5.65 Å, E_g = 1.42 eV; a_{GaP} = 5.45 Å, E_g = 2.24 eV.

Phase Diagrams

Learning Objectives

By the end of this lecture, you should be able to:

- Explain the **Gibbs Phase Rule** and apply it to one- and two-component systems.
- Interpret **phase diagrams** with no compound formation (eutectic-type systems).
- Distinguish key regions: **liquidus, solidus, eutectic point, and miscibility gap**.
- Use the **lever rule** to calculate phase fractions in two-phase regions.
- Recognize real-world examples of eutectic and solid-solution systems (e.g., water, salt–water, diopside–anorthite, MgO–CaO).

Phase Rule

Gibbs Phase Rule

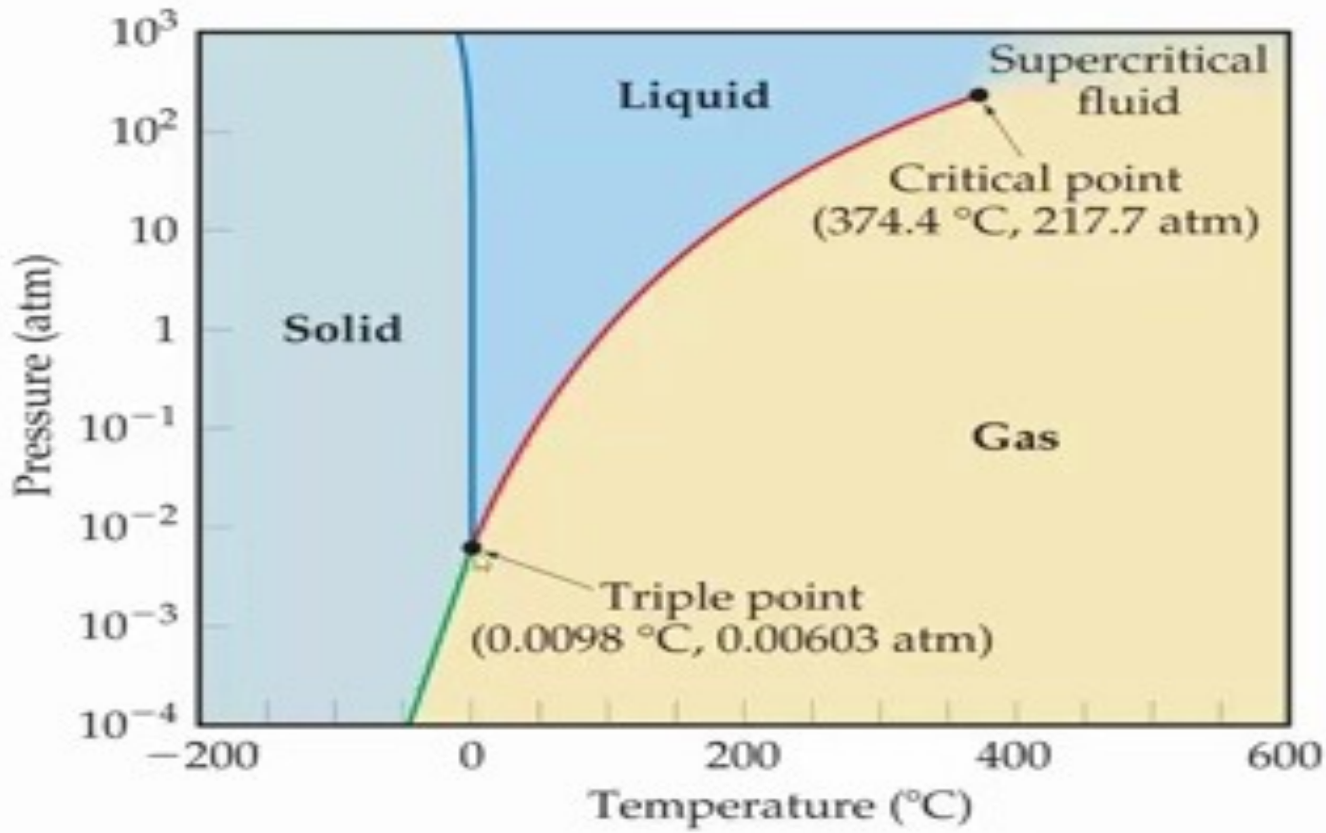
$$F = C + 2 - P$$

Where F = degrees of freedom, C = number of components, and P = number of phases

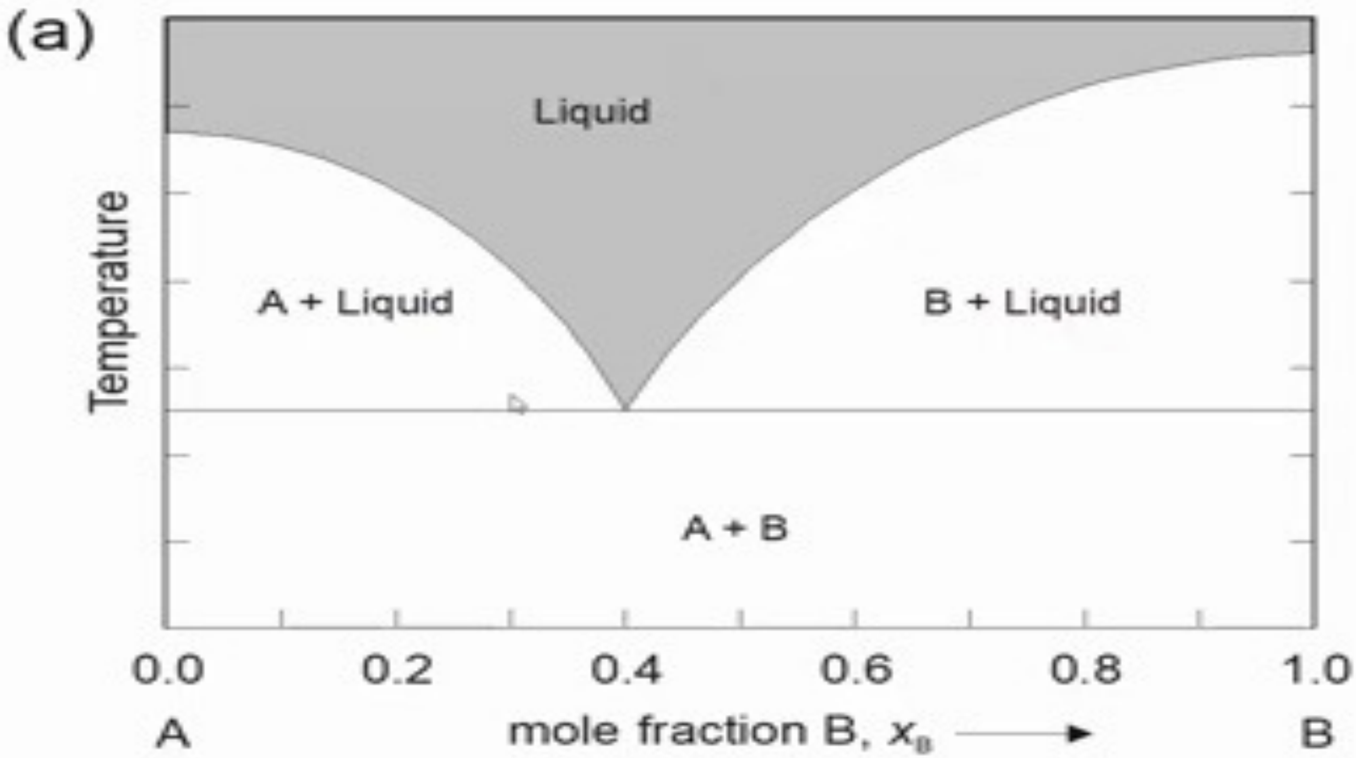
For condensed phase systems where the pressure is constant this reduces to

$$F = C + 1 - P$$

Phase Diagram of Water

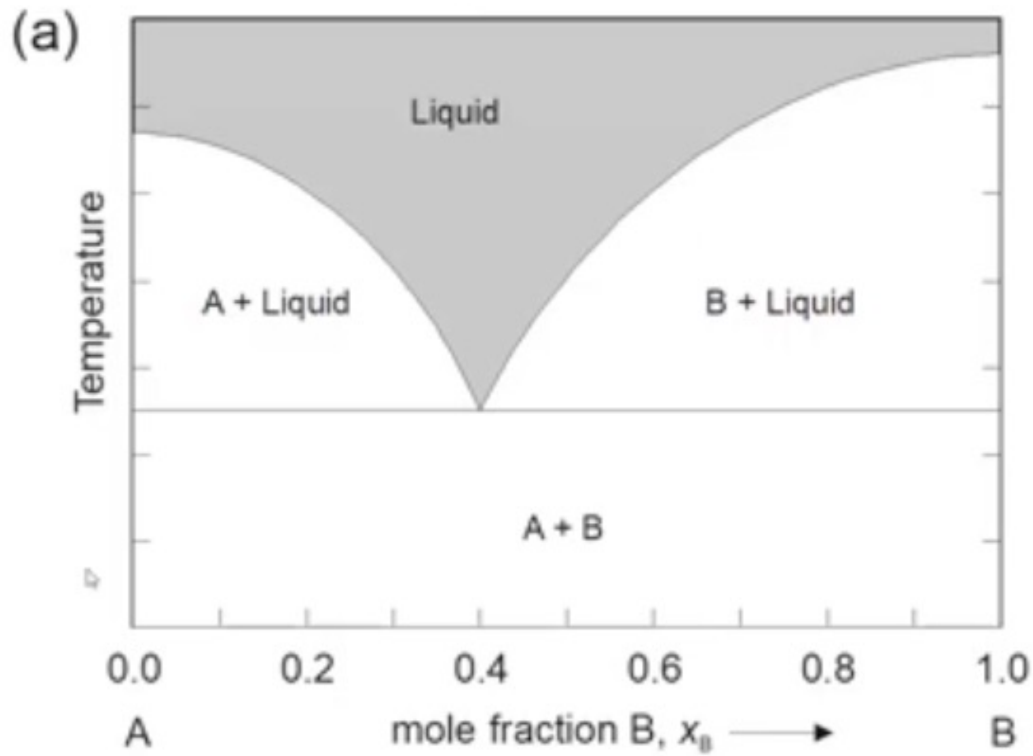


Binary system with no compounds or solid solutions



Binary system with no compounds or solid solutions

$$F = C + 1 - P$$
$$F = 3 - P$$



For more details see https://www.youtube.com/watch?v=L0-3WEokrWA

Binary system with no compounds or solid solutions

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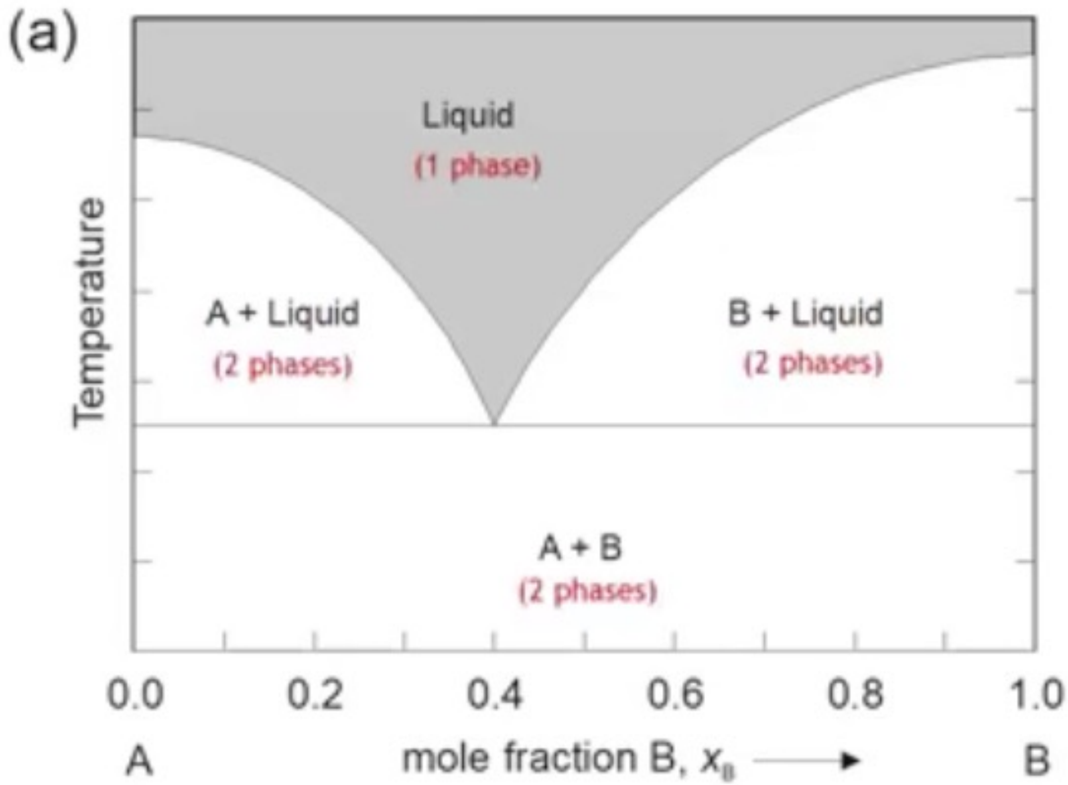

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Binary system with no compounds or solid solutions

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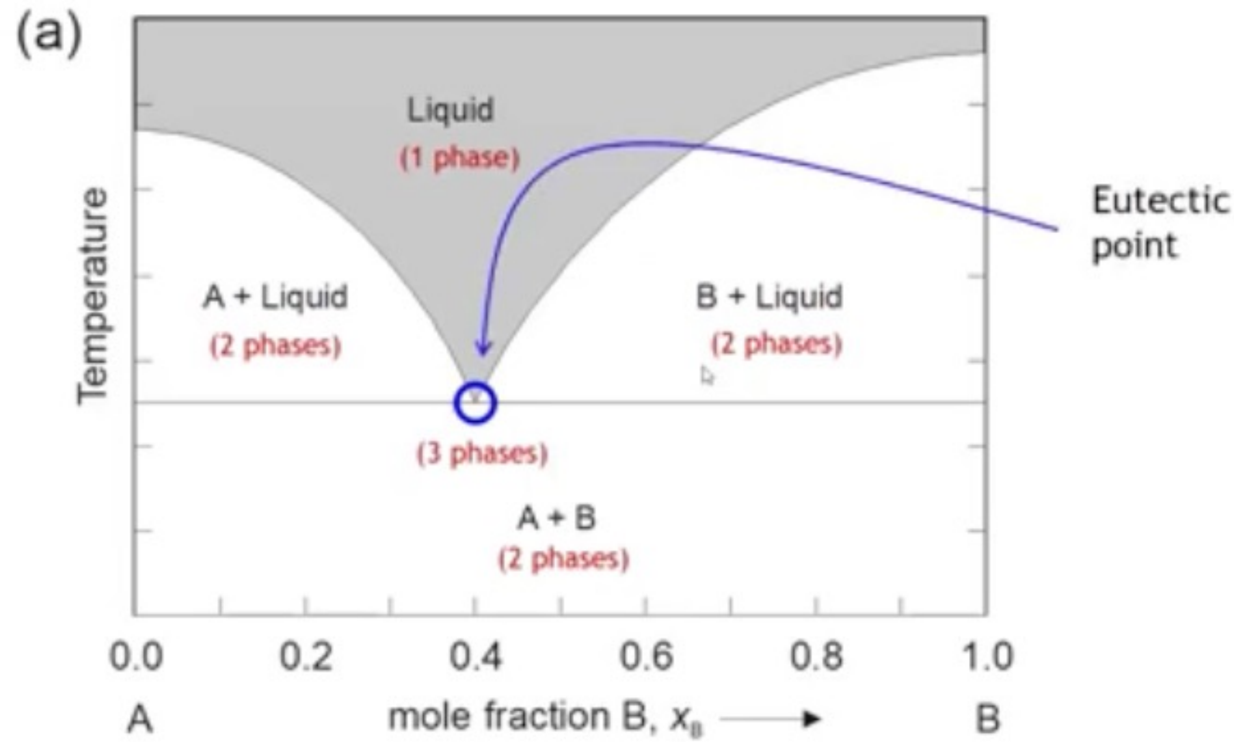

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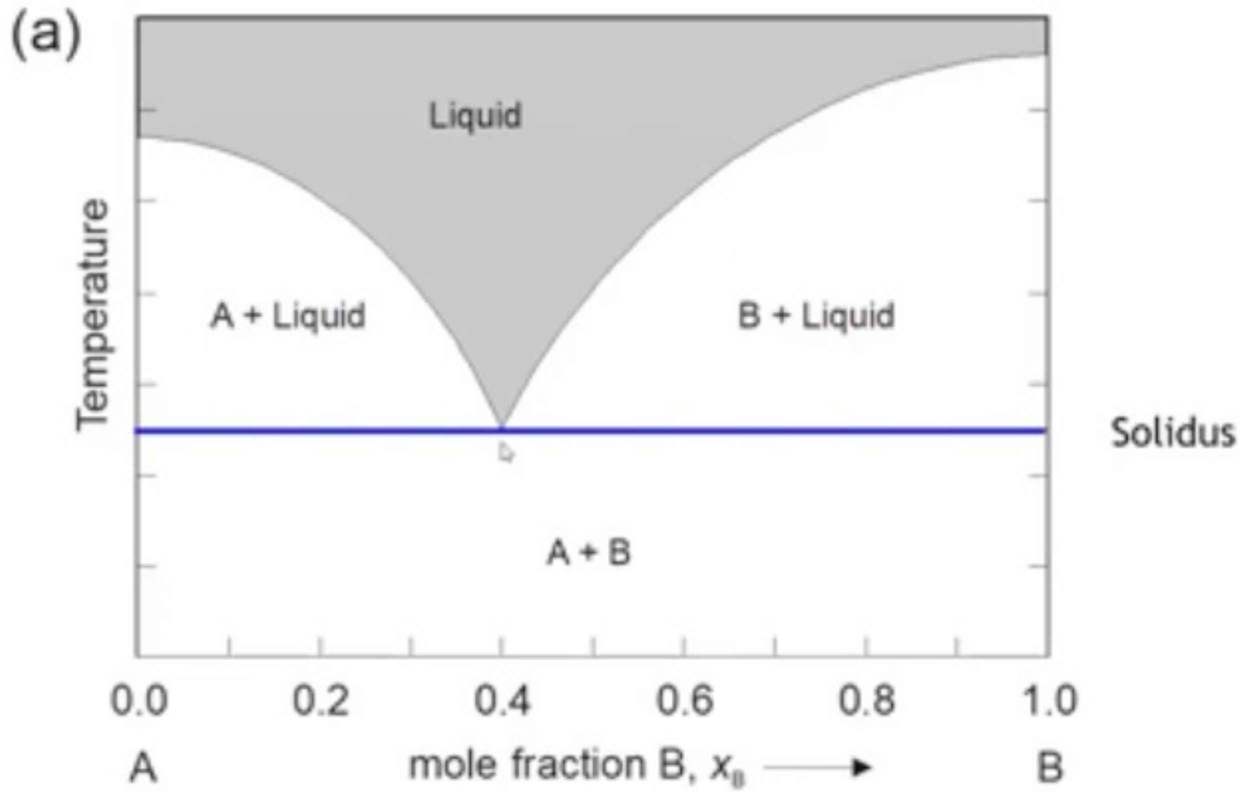

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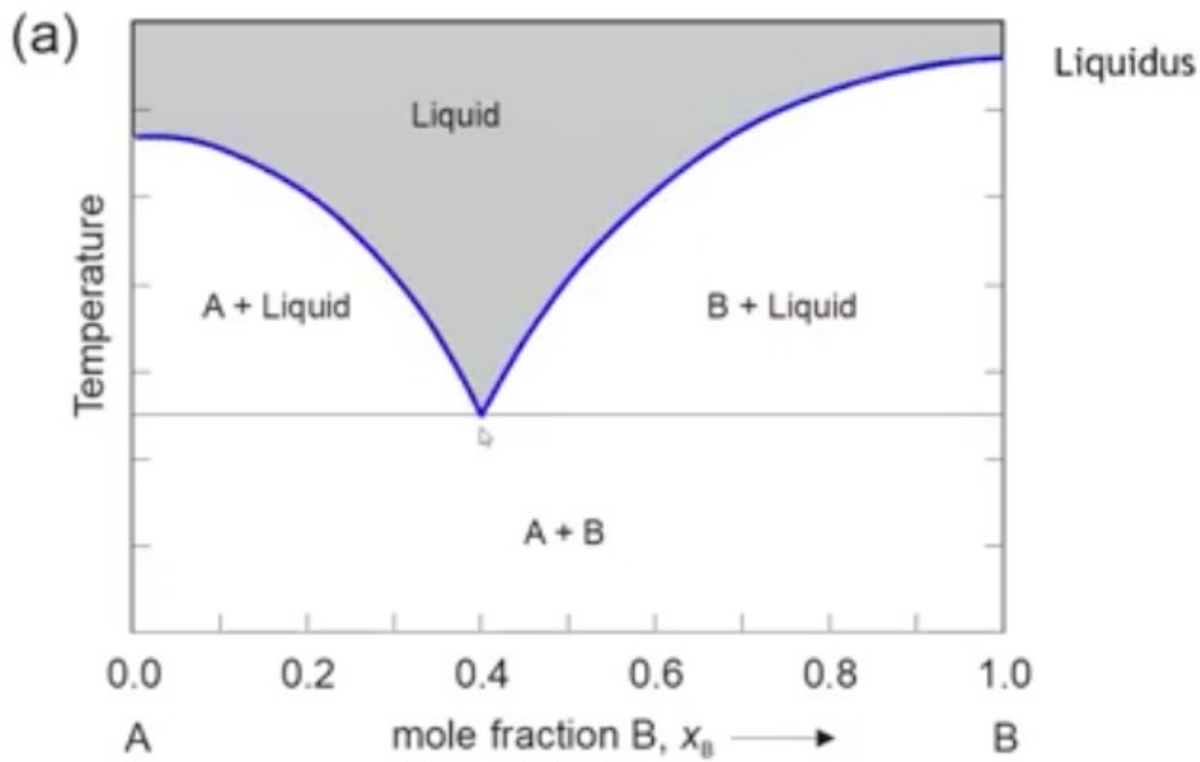

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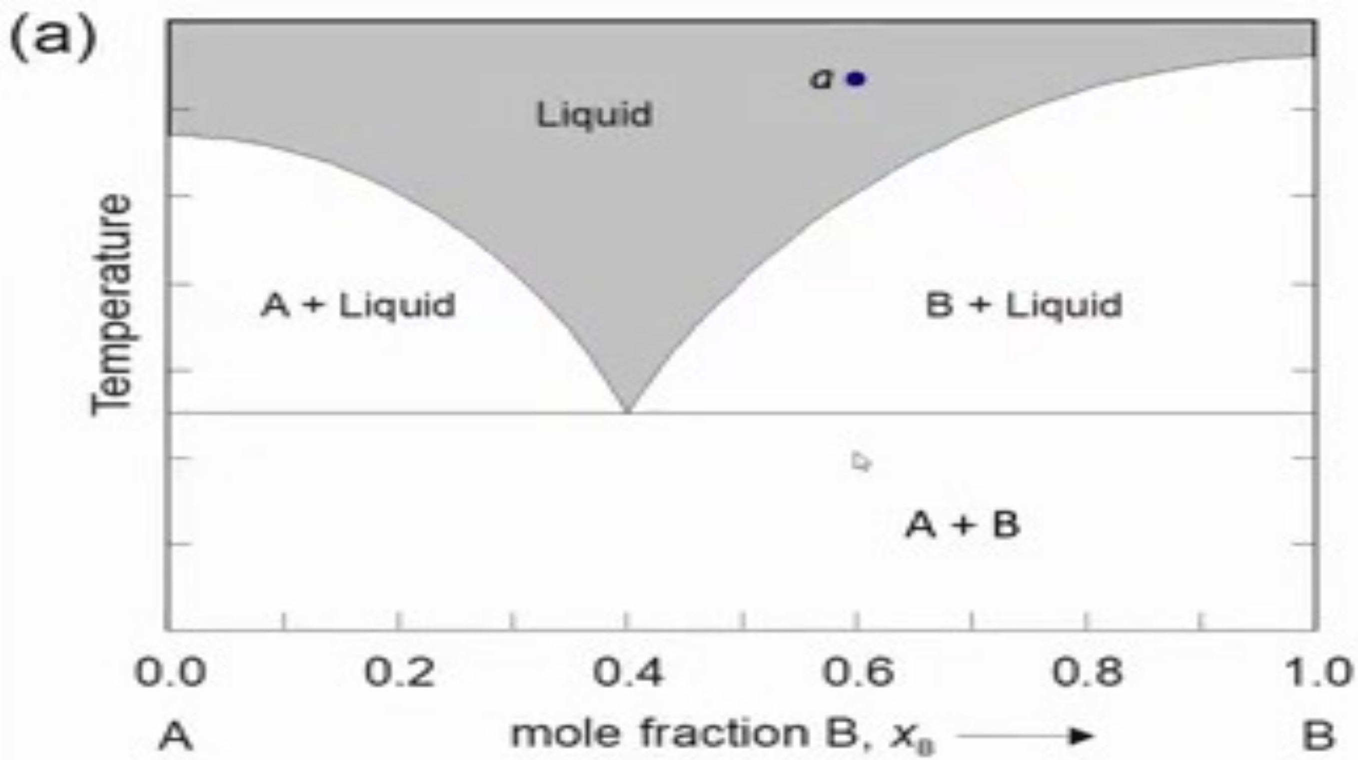
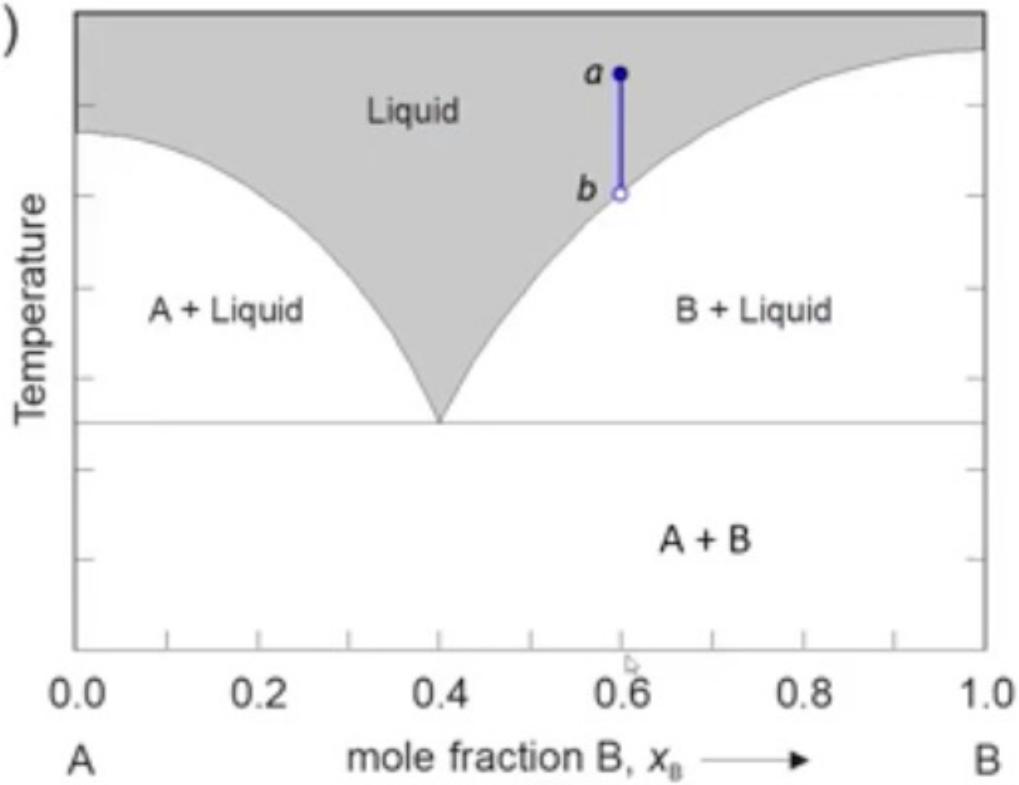


Point a
homogeneous liquid, $A_{0.4}B_{0.6}$

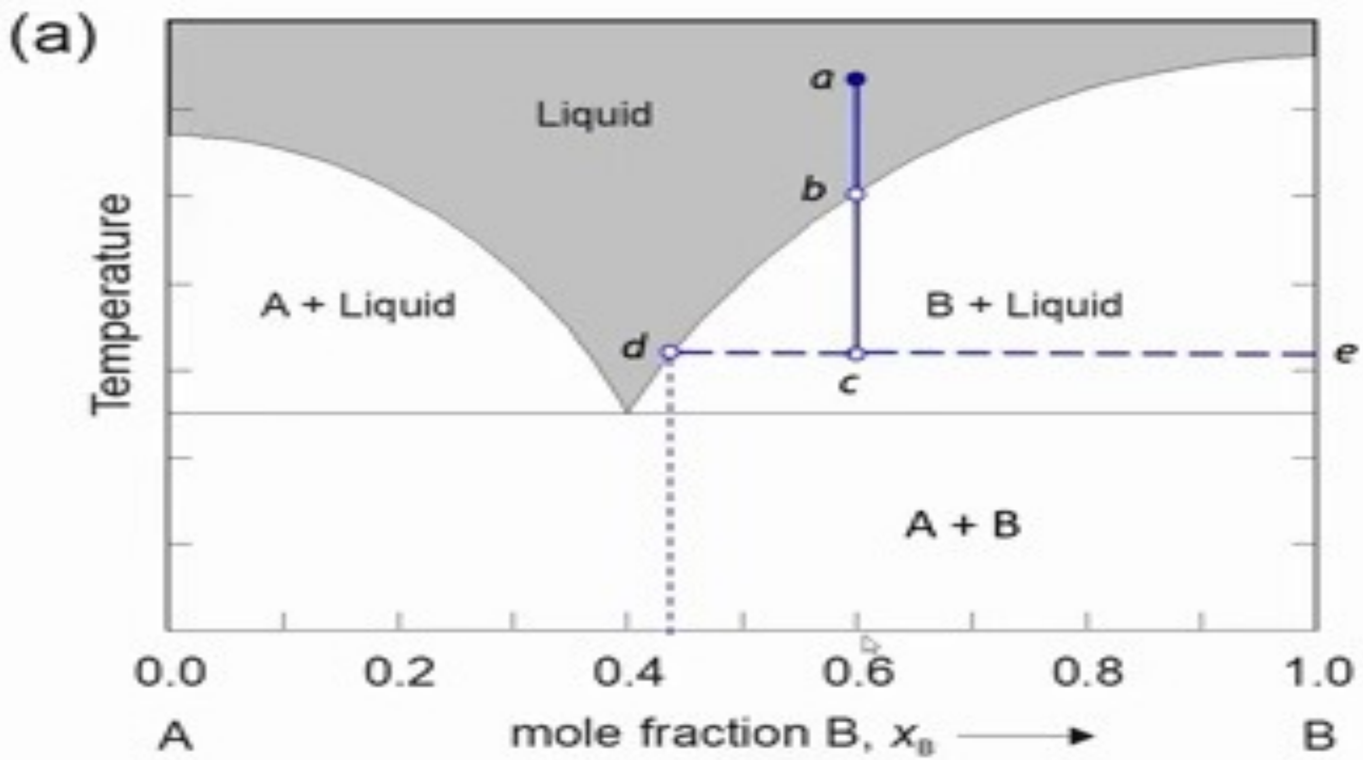
Binary system with no compounds or solid solutions

(a)



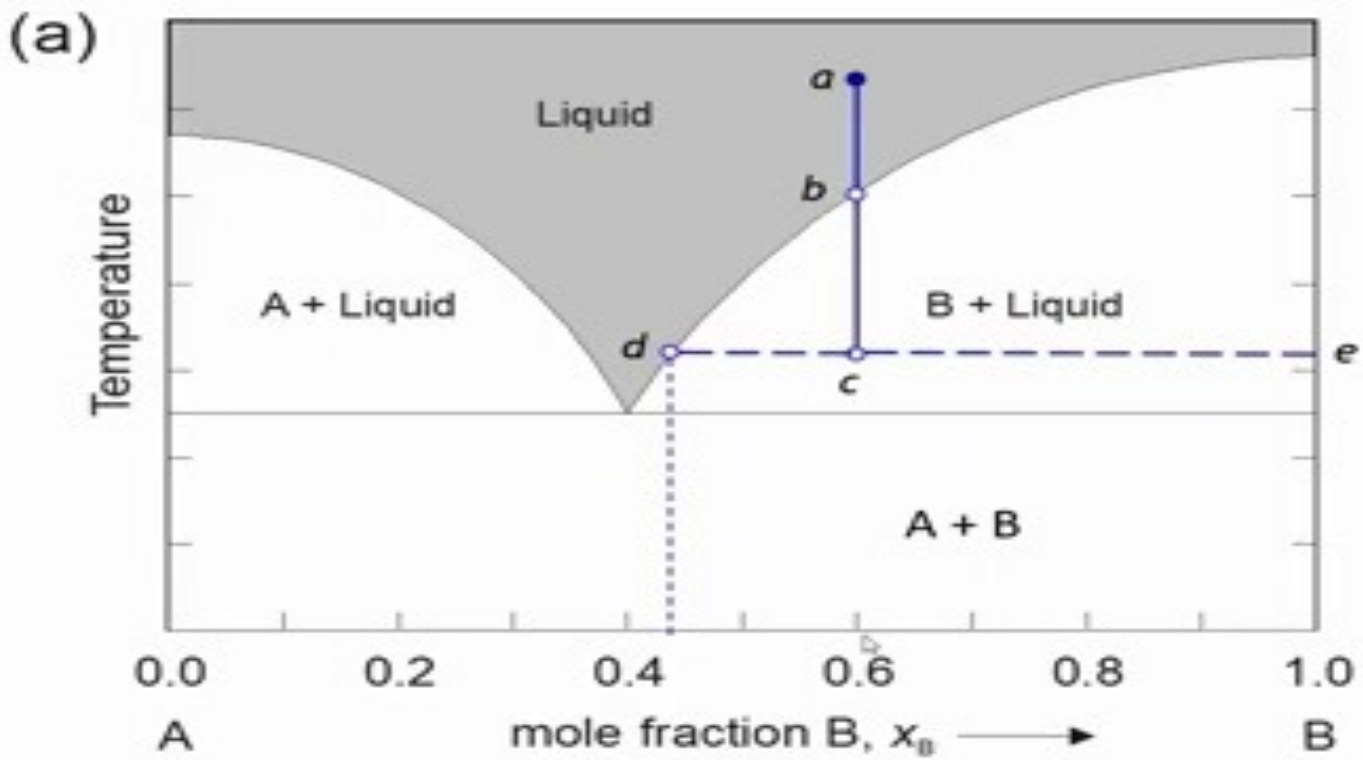
Point a
homogeneous liquid, $A_{0.4}B_{0.6}$

Point b
liquid $A_{0.4}B_{0.6}$
in equilibrium with solid B



Point c
liquid $A_{0.57}B_{0.43}$
in equilibrium with
solid B

Lever Rule



Point c
liquid $A_{0.57}B_{0.43}$
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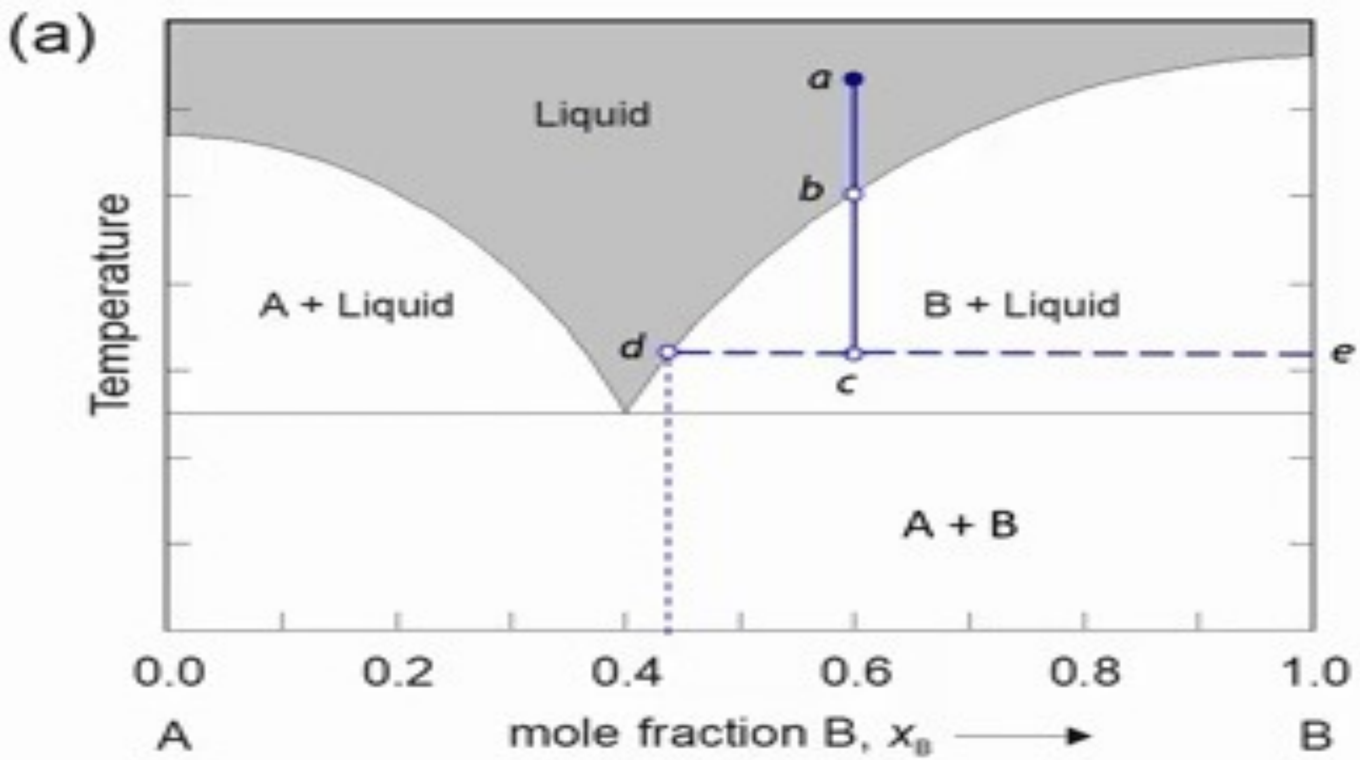
Mole fraction B (x_B)

$$x_B = \frac{l_{dc}}{l_{de}}$$

Lever Rule



Point c
liquid $A_{0.57}B_{0.43}$
in equilibrium with
solid B

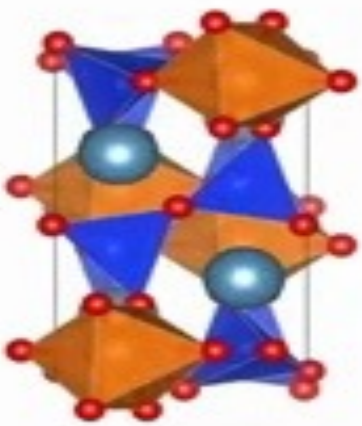
Mole fraction B (x_B)

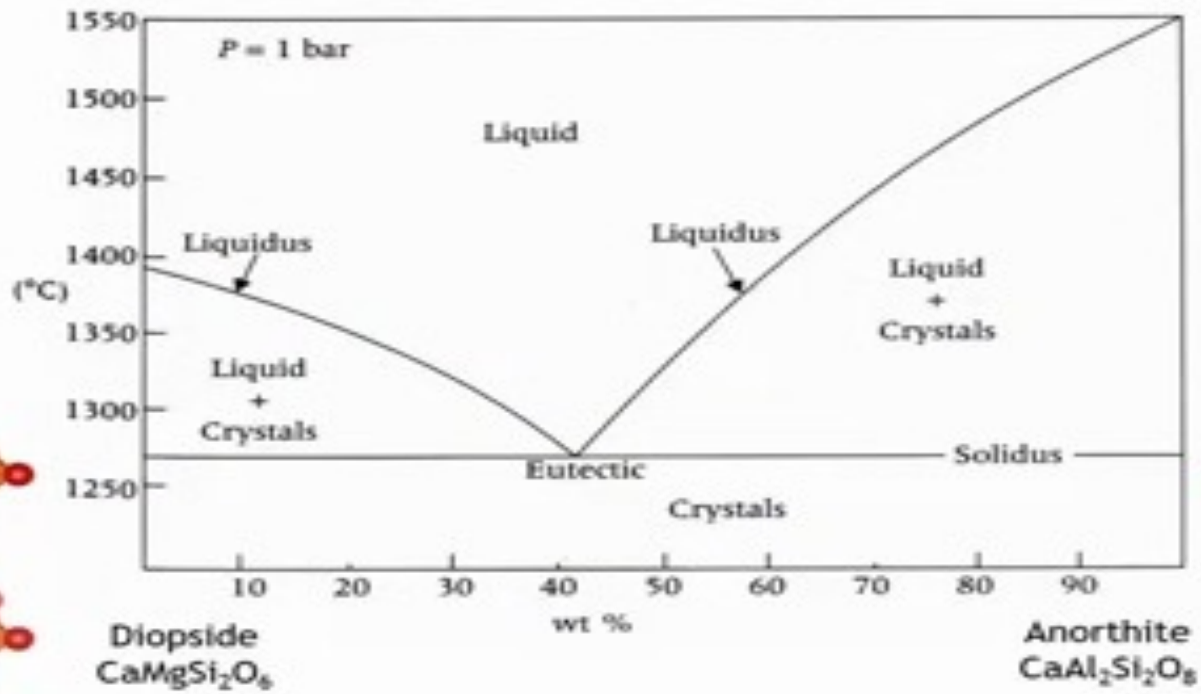
$$x_B = \frac{l_{dc}}{l_{de}}$$

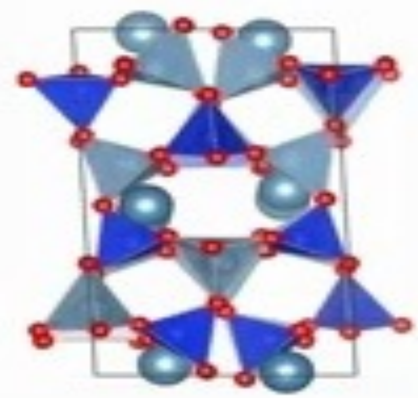
$$x_B = \frac{0.6 - 0.43}{1.0 - 0.43}$$

$$x_B = 0.30$$

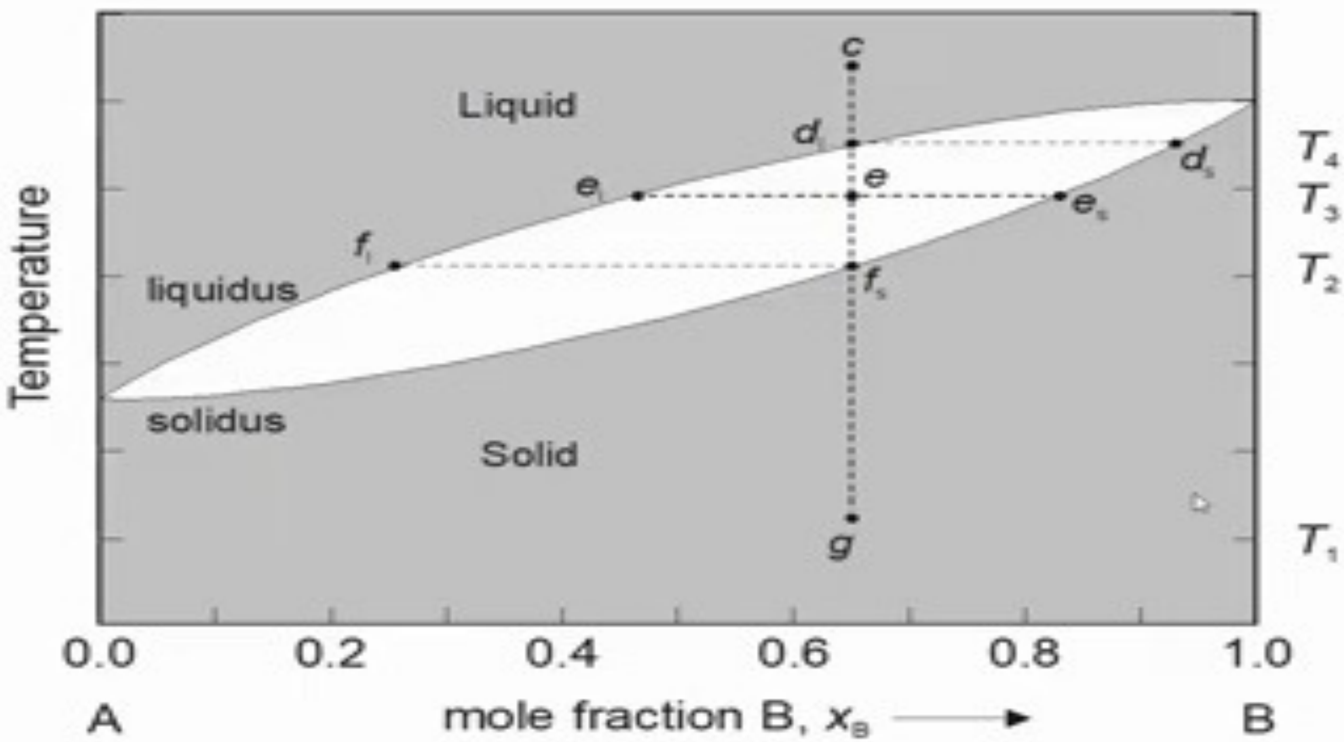
Diopside ($CaMgSi_2O_6$) - Anorthite ($CaAl_2Si_2O_8$) Phase Diagram



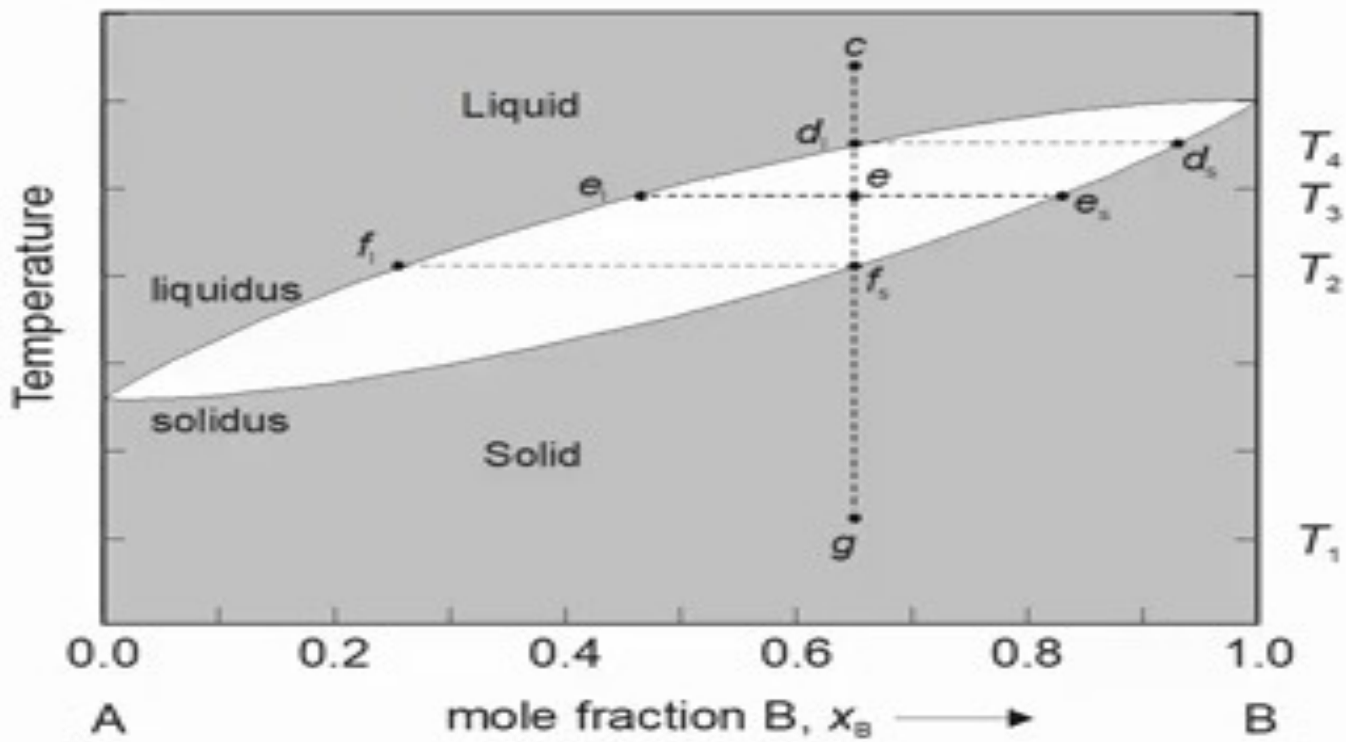




Binary system with complete solid solution formation



Binary system with complete solid solution formation



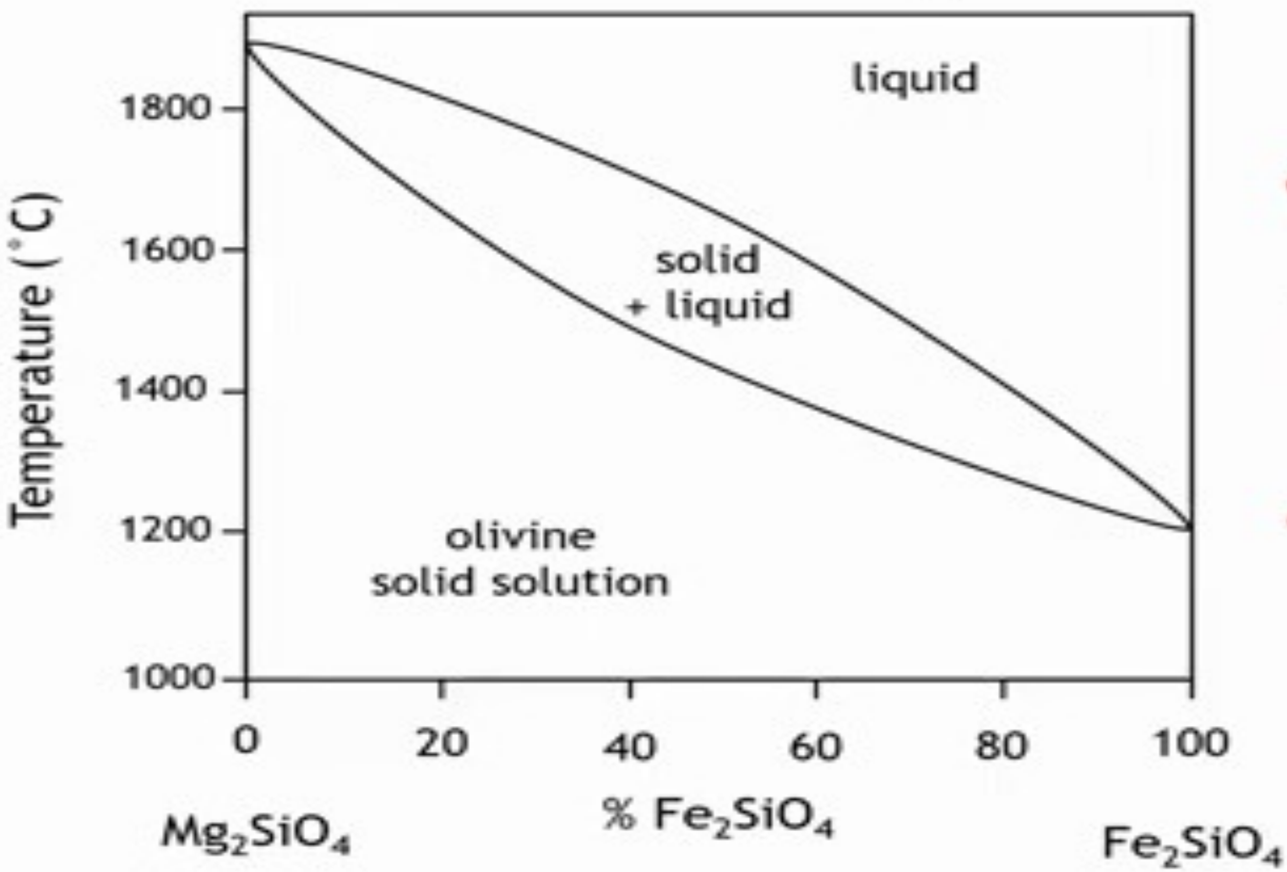
T_4 sample completely melts, composition $A_{0.35}B_{0.65}$

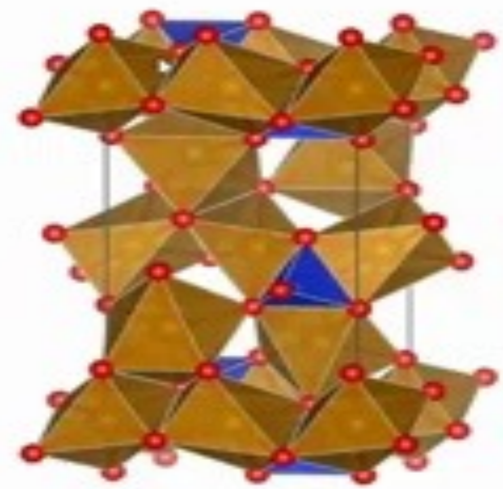
T_3 equilibrium mixture of liquid rich in A and solid rich in B

T_2 sample begins to melt

T_1 homogeneous solid, composition $A_{0.35}B_{0.65}$

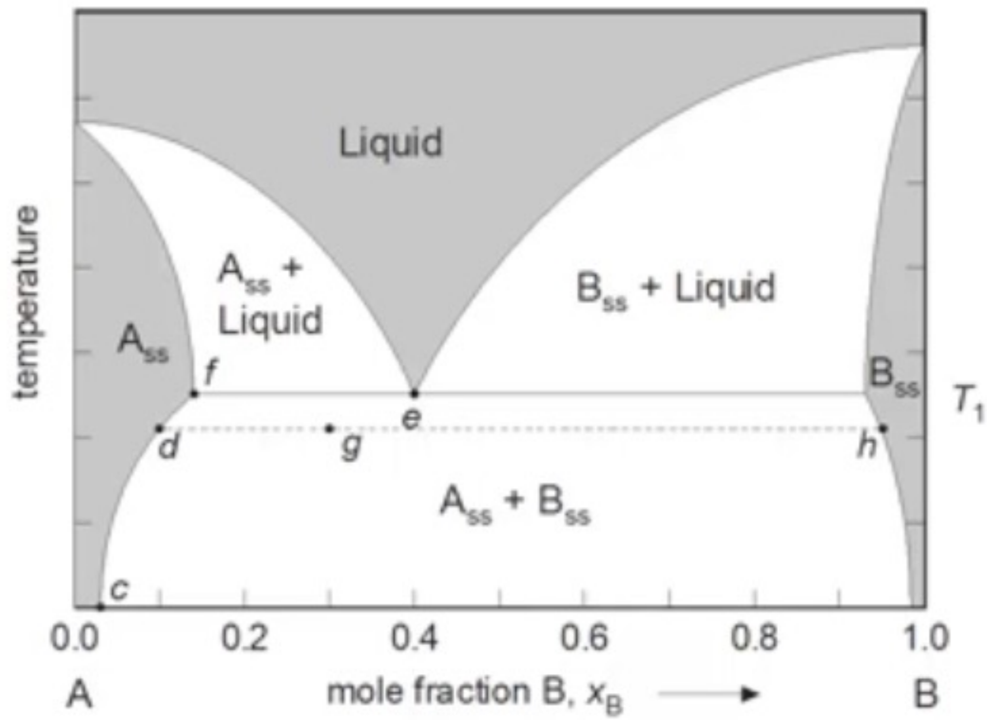
Forsterite (Mg_2SiO_4) - Fayalite (Fe_2SiO_4) Phase Diagram





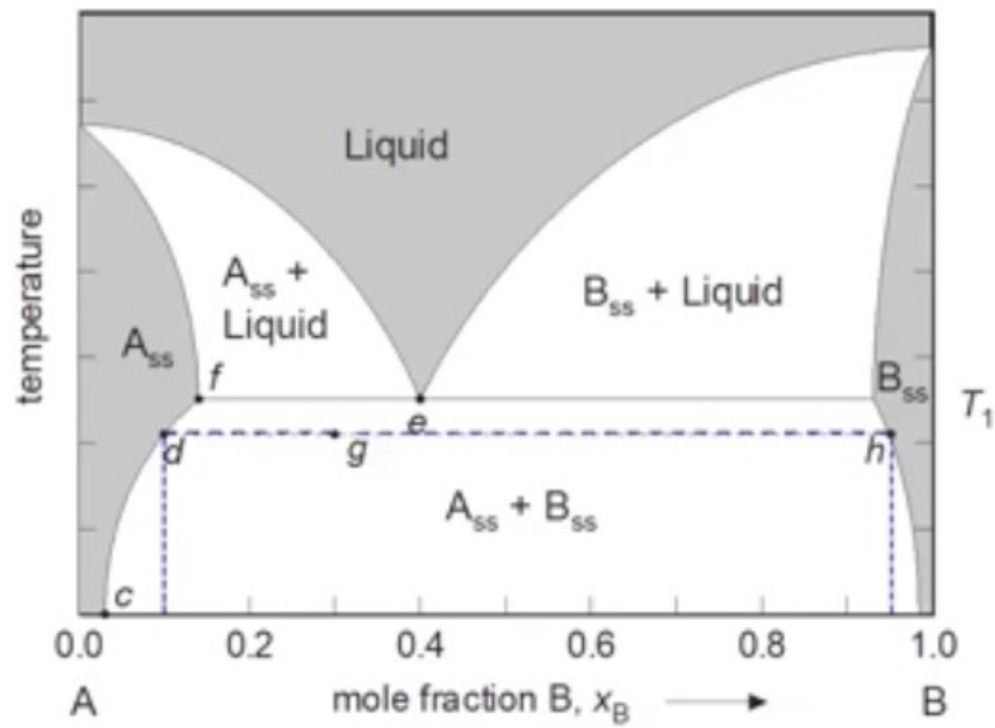
olivine structure

Binary system with partial solid solution formation



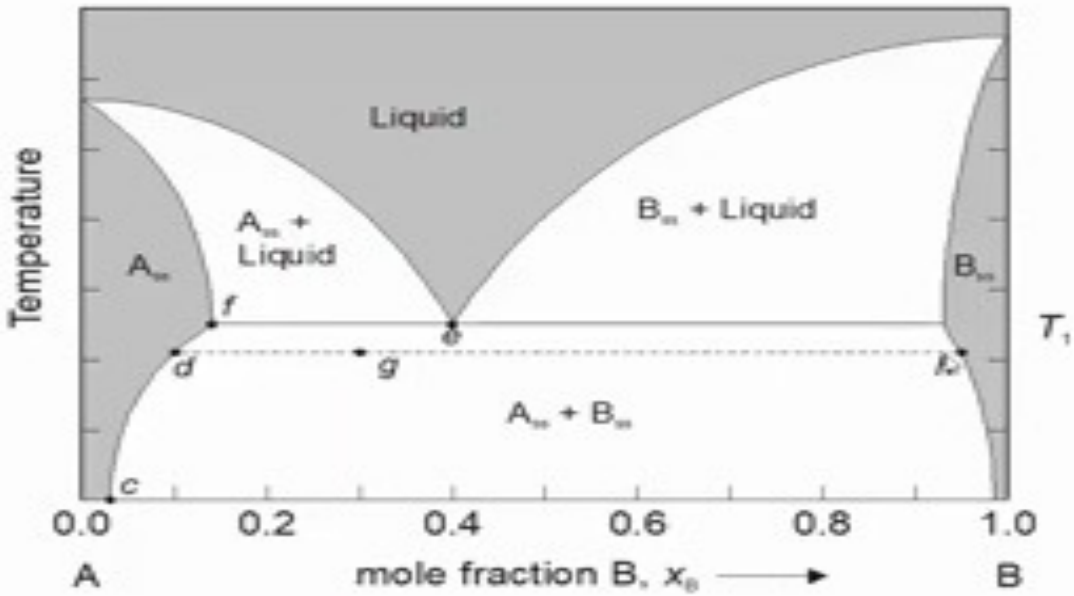
Considering the coordinates of points *d* (x_B = 0.1), *g* (x_B = 0.3) and *h* (x_B = 0.95) what phases are present at *g*? In what ratio?

Binary system with partial solid solution formation



$A_{0.9}B_{0.1}$ + $A_{0.05}B_{0.95}$

Binary system with partial solid solution formation



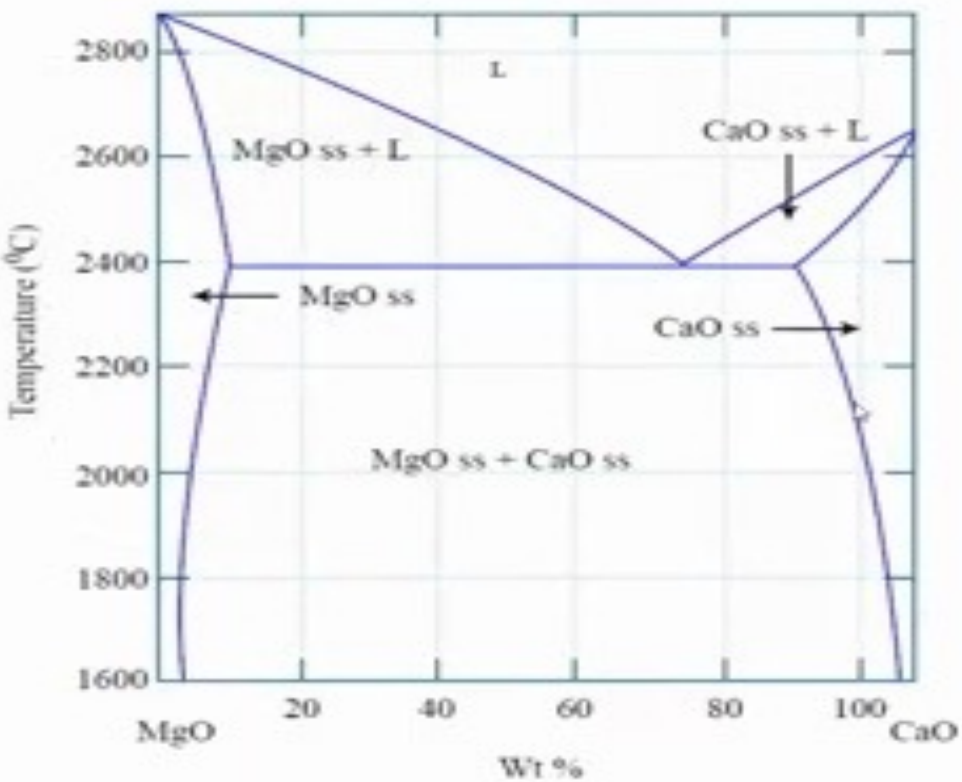
Mole fraction $A_{0.05}B_{0.95}$

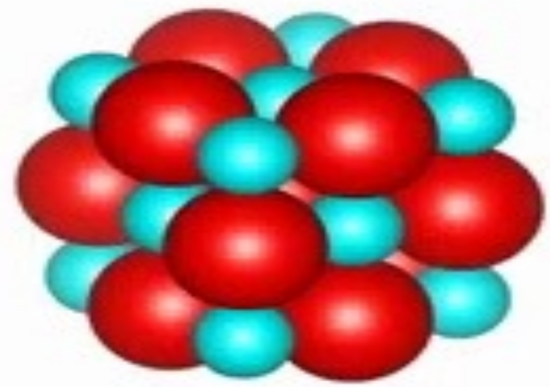
$$f = \frac{l_{gd}}{l_{dh}}$$

$$f = \frac{0.30 - 0.10}{0.95 - 0.10}$$

$$f = 0.24$$

MgO-CaO Phase Diagram





Rock salt structure

Taken from: https://ocw.mit.edu/courses/materials-science-and-engineering/3-012-fundamentals-of-materials-science-fall-2005/lecture-notes/lec19t.pdf

Summary

- **Phase diagrams** are critical tools for planning synthesis, crystal growth, and understanding equilibrium in solid-state systems.
- The **Gibbs Phase Rule** links components, phases, and degrees of freedom, simplifying under constant pressure.
- **Single-component diagrams** (e.g., water) illustrate triple points, phase boundaries, and constraints on degrees of freedom.
- **Binary diagrams** reveal liquidus/solidus lines, eutectic behavior, and solid solutions.
- The **lever rule** quantifies phase proportions in two-phase regions.
- Real materials (minerals, oxides, alloys) demonstrate **complete** and **incomplete solid solutions**, as well as **miscibility gaps**.

Homework

4.1 Give a brief definition of the terms *phase* (P), *component* (C), and *degrees of freedom* (F) in the condensed matter phase rule $P + F = C + 1$.

4.6 Use the phase rule to explain how a mixture of Ni and NiO can be used to provide a controlled low oxygen partial pressure in a closed system.