CHEM 548: MATERIALS CHEMISTRY

LECTURE 9: SOLID SOLUTIONS AND VEGARD'S LAW

Wed 09/23/2026

Solid solutions, Vegard's law and its deviations, and band-gap engineering

Reading: Woodward, Karen, Evans, and Vogt, *Solid State Materials Chemistry*
Ch. 2 §2.5 · Ch. 4 §§4.1–4.2

SOLID SOLUTIONS AND VEGARD'S LAW

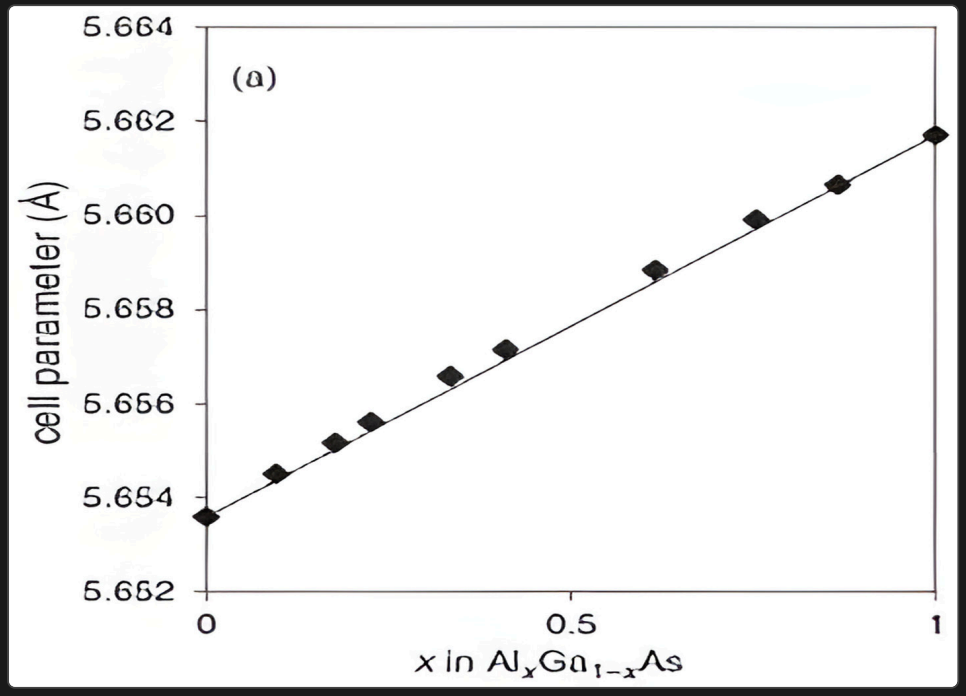
Solid solution	Define a solid solution and compare it to a liquid solution.
Vegard's law	Unit cell dimensions (and some properties) vary linearly with composition.
Apply it	Calculate lattice parameters and band gaps of intermediate compositions.
Deviations	Charge transfer (Mn^{3+}/Ru^{5+} in Ca-based perovskites), and ordering of different-size ions into more efficient packing.
Semiconductors	Solid solutions matter in semiconductors: epitaxy, heterojunction lasers, LEDs.
Composition from measurement	Estimate composition from a property measurement such as a lattice constant or a 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.

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

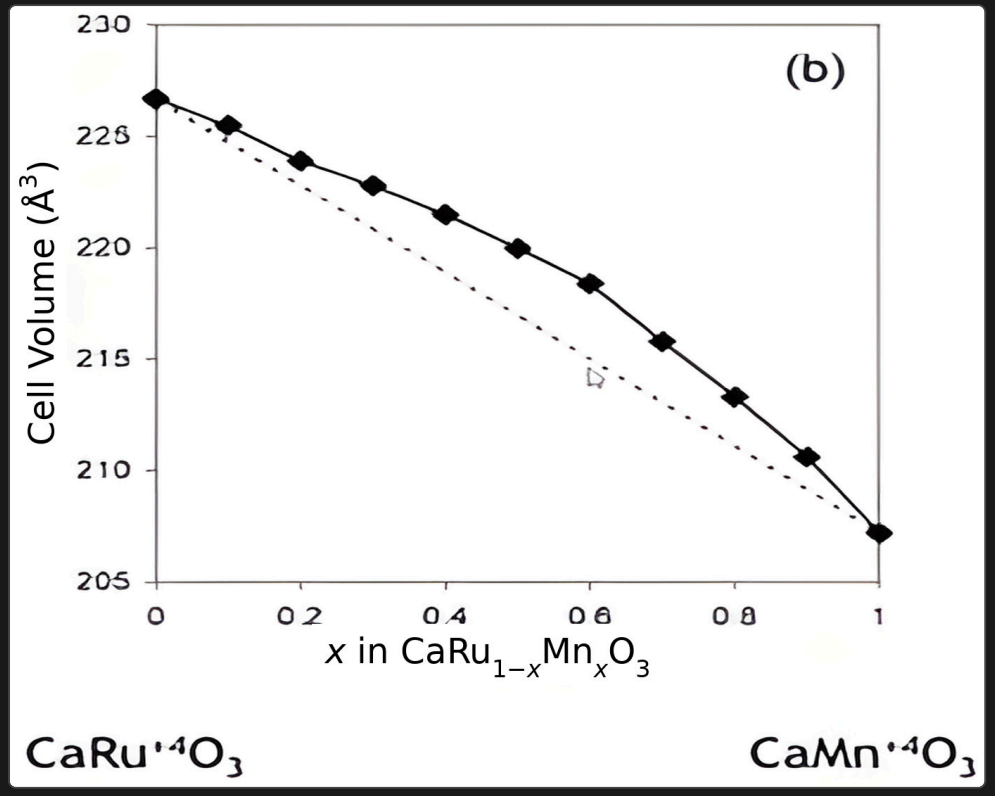
$a(x)$ for solid solution · a_{BX} for AlAs · a_{AX} for GaAs



Per *Solid State Materials Chemistry*, Figure 2.5a, section 2.5

DEVIATIONS FROM VEGARD'S LAW

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



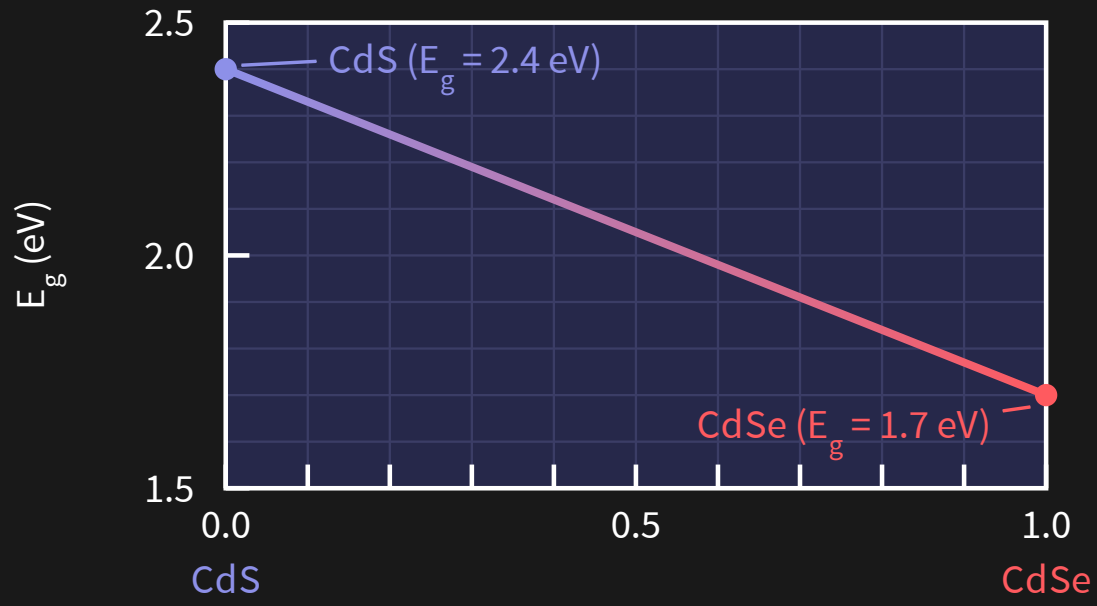
Causes for deviations from Vegard's law

Site ordering	Different-size ions order onto distinct sites.
Inhomogeneities	The sample is not a single homogeneous phase.
Changes in oxidation state	Charge transfer between the two cations.

Per *Solid State Materials Chemistry*, Figure 2.5b, section 2.5

BAND GAP ENGINEERING

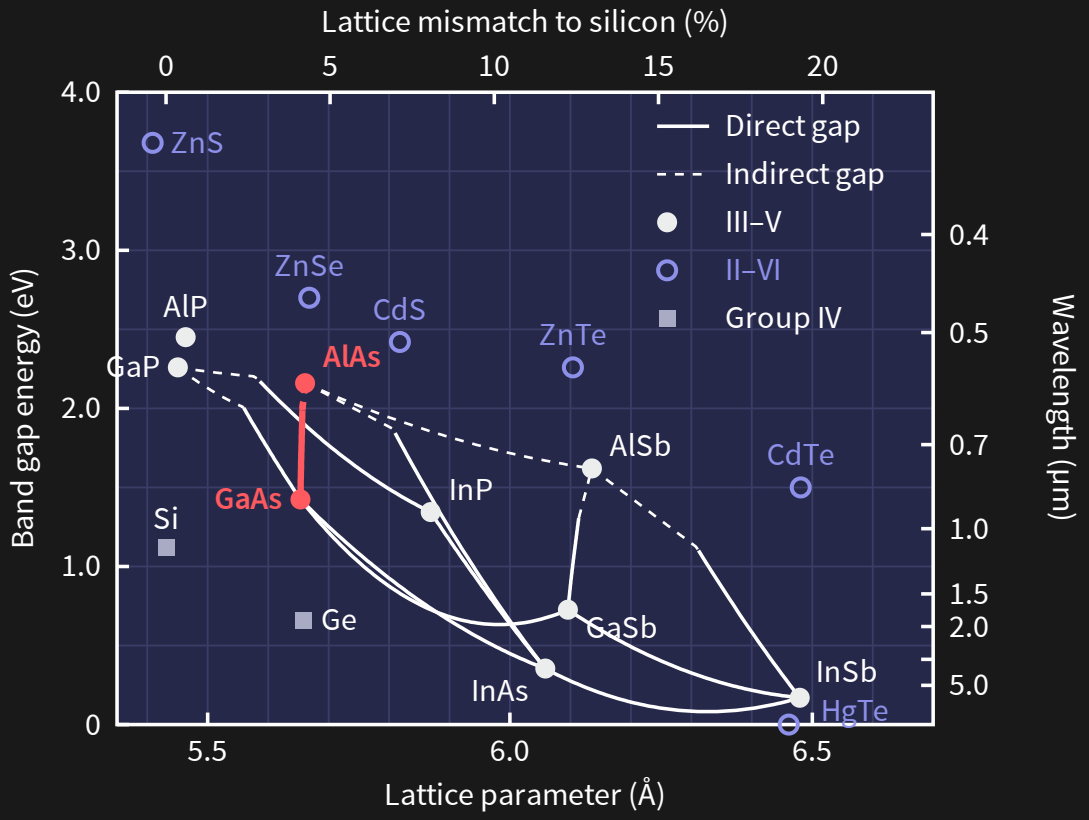
For semiconductors it is not unusual that the band gap will follow Vegard's law.

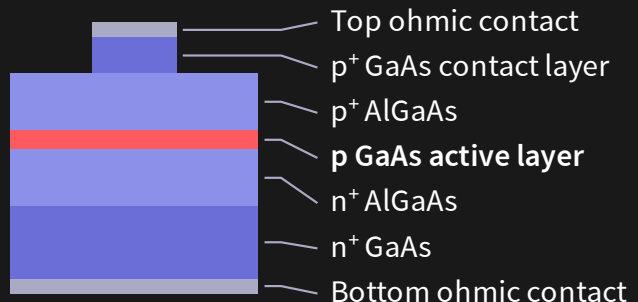


$$E_g(x) = xE_g(\mathrm{B}) + (1-x)E_g(\mathrm{A})$$

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

SEMICONDUCTOR SOLID SOLUTIONS





Heterojunction laser

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.

Adapted from P. Bhattacharya, *Semiconductor Optoelectronic Devices*; alloy curves after Vurgaftman *et al.* (2001)

CdS-CdSe SOLID SOLUTIONS

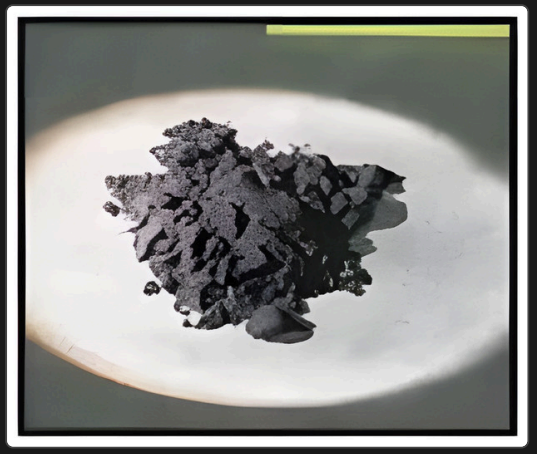
$CdS_{1-x}Se_x$ solid solutions are excellent pigments (cadmium yellow, cadmium orange). By controlling the composition, we can control the band gap and hence the color.



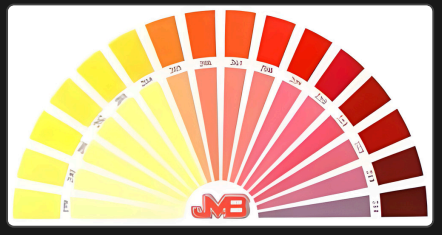
CdS (E_g = 2.4 eV)



$CdS_{1-x}Se_x$ compositions



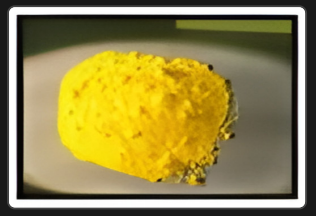
CdSe (E_g = 1.7 eV)

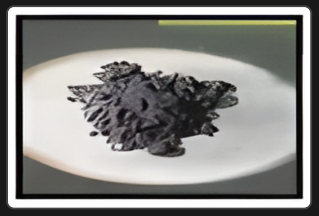


Cadmium pigments

EXAMPLE: ORANGE CdS-CdSe

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



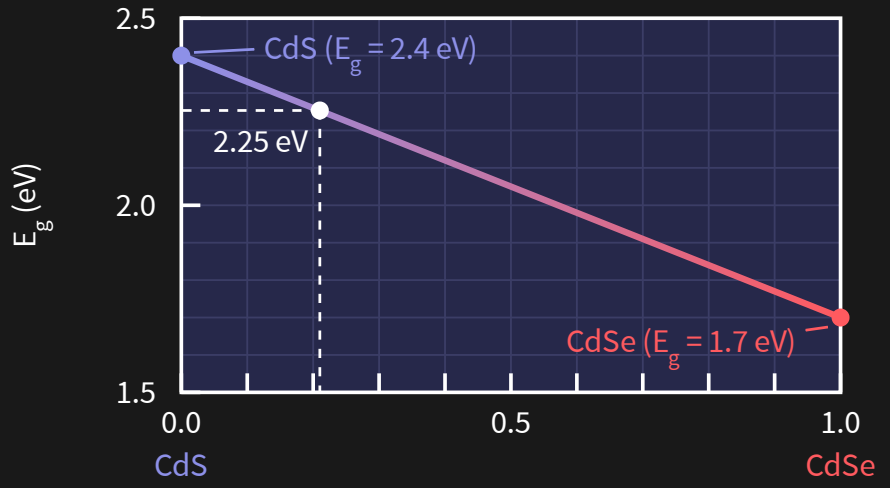


CdS (E_g = 2.4 eV) CdSe (E_g = 1.7 eV)

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

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

$CdS_{0.79}Se_{0.21}$



SUMMARY

Vegard's law lets us predict composition from structure or property measurements.

Solid solutions	Homogeneous crystals spanning the compositions between two end members
Vegard's law	The lattice constant, and sometimes other properties, varies linearly with composition
Deviations	Charge transfer or cation/anion ordering, giving positive or negative curvature
Semiconductor properties	The band gap also approximates Vegard's law, which is what makes band gap engineering possible
GaAs–AlAs	Nearly constant lattice parameter but tunable band gap, the key to epitaxial devices such as lasers and LEDs
CdS–CdSe	Tunable band gap controls the pigment color, yellow to red to black

WHY PHASE DIAGRAMS

Gibbs phase rule	Explain it and apply it to one- and two-component systems.
Phase diagrams	Interpret diagrams with no compound formation, the eutectic-type systems.
Key regions	Distinguish the liquidus, the solidus, the eutectic point, and the miscibility gap.
Lever rule	Calculate phase fractions in the two-phase regions.
Real systems	Recognize eutectic and solid-solution examples: diopside–anorthite, forsterite–fayalite, MgO–CaO.

THE GIBBS PHASE RULE

$$F = C + 2 - P$$

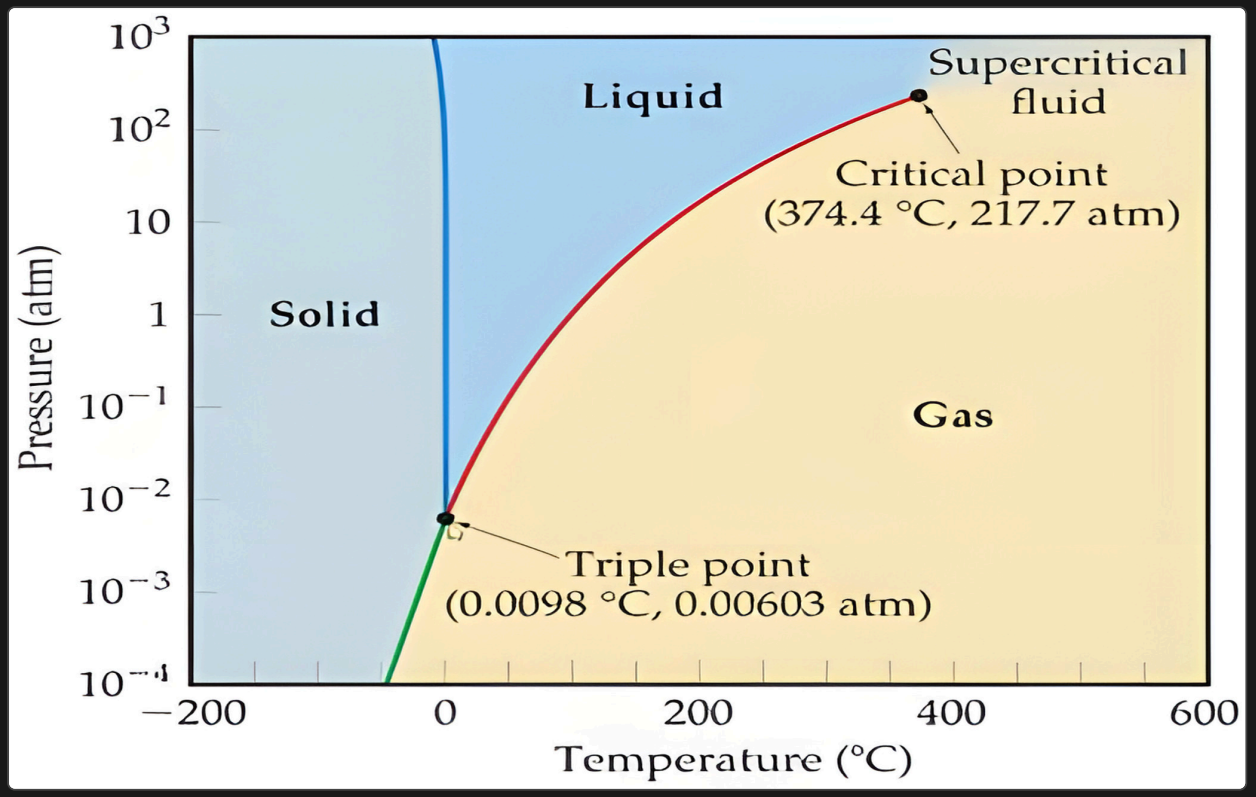
F	degrees of freedom: variables we can change without a phase appearing or disappearing (temperature, pressure, composition of each phase)
C	minimum number of independent species (elements or compounds) needed to express every phase's composition. Water: H_2O (C = 1). MgO–CaO: MgO, CaO (C = 2). Cu/Cu_2O/O_2(g): Cu, O_2 (C = 2).
P	number of phases

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

$$F = C + 1 - P$$

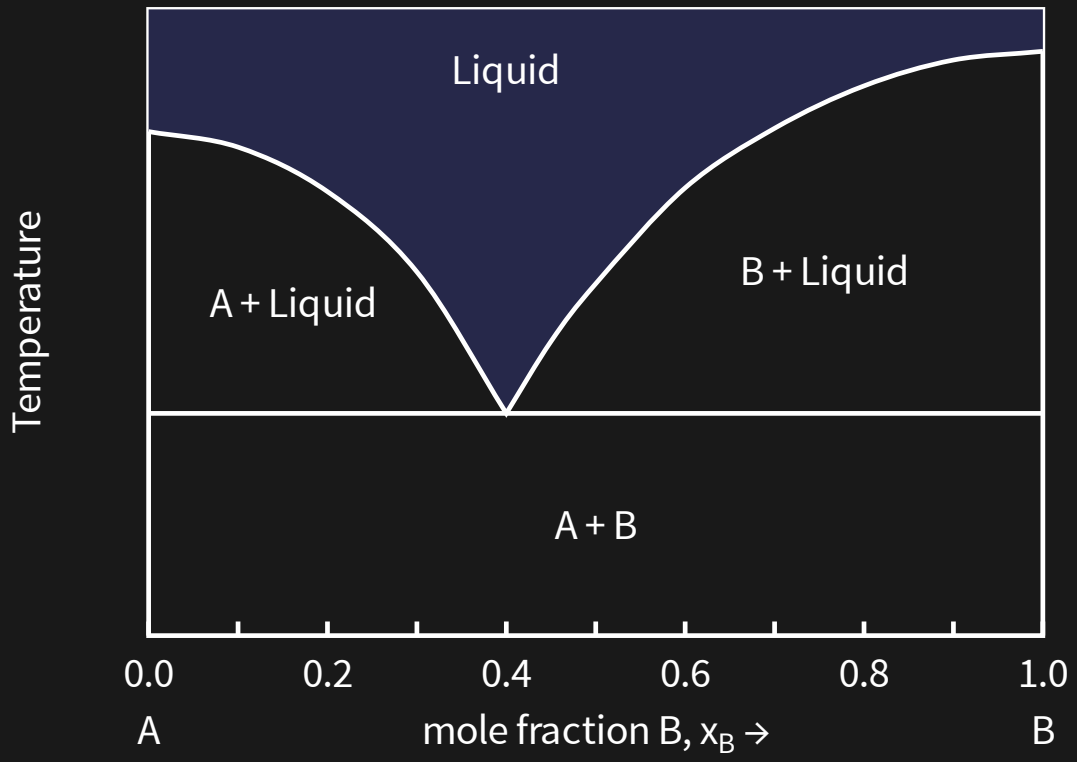
For more details: Gibbs Phase Rule for Material Science (LearnChemE)

ONE COMPONENT: WATER



Per *Solid State Materials Chemistry*, Figure 4.1, section 4.1

A BINARY DIAGRAM: THE AXES

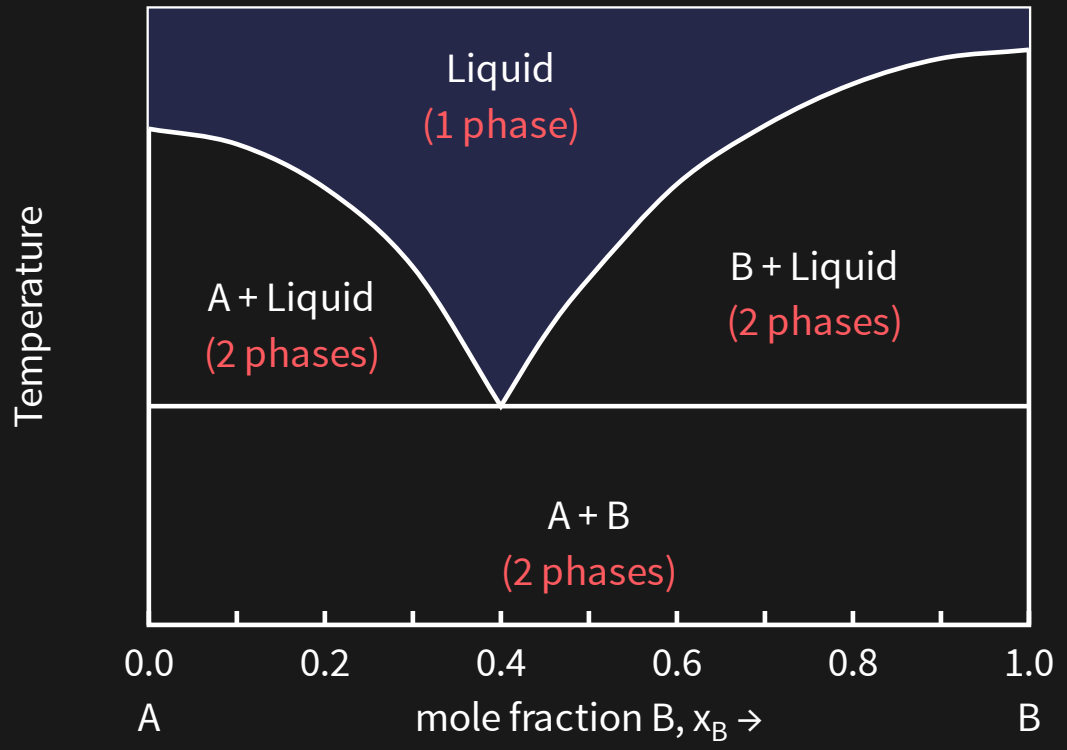


Per *Solid State Materials Chemistry*, Figure 4.2, section 4.2.1

BINARY SYSTEM WITH NO COMPOUNDS OR SOLID SOLUTIONS

$$F = C + 1 - P$$

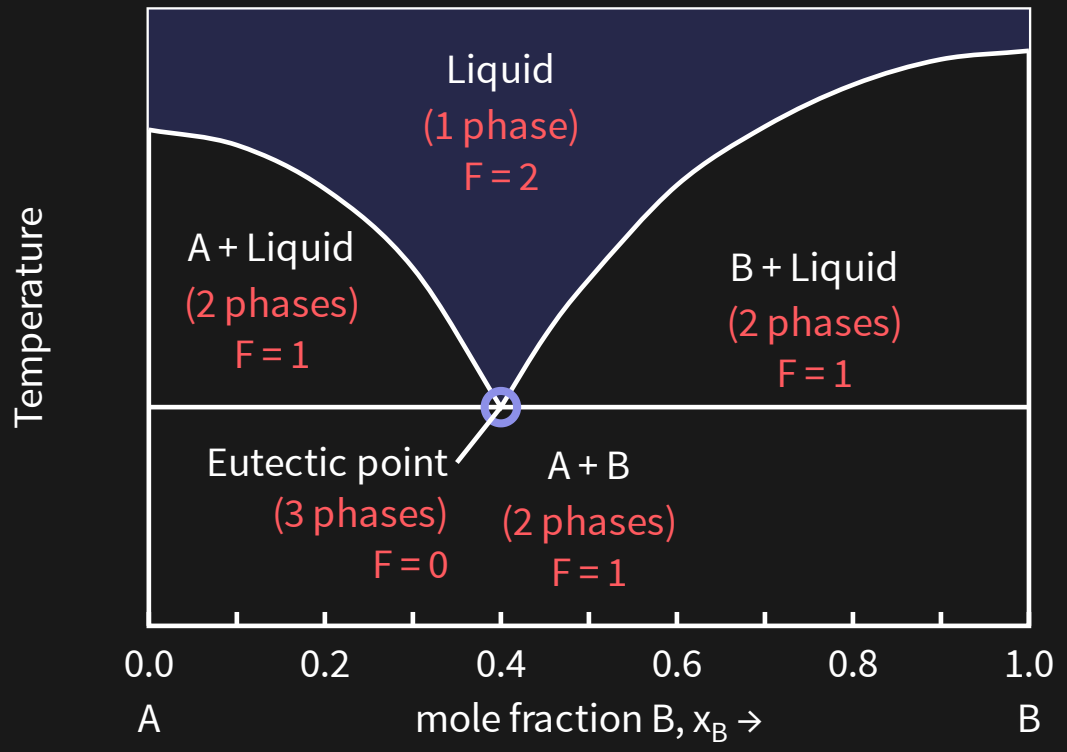
$$F = 3 - P$$



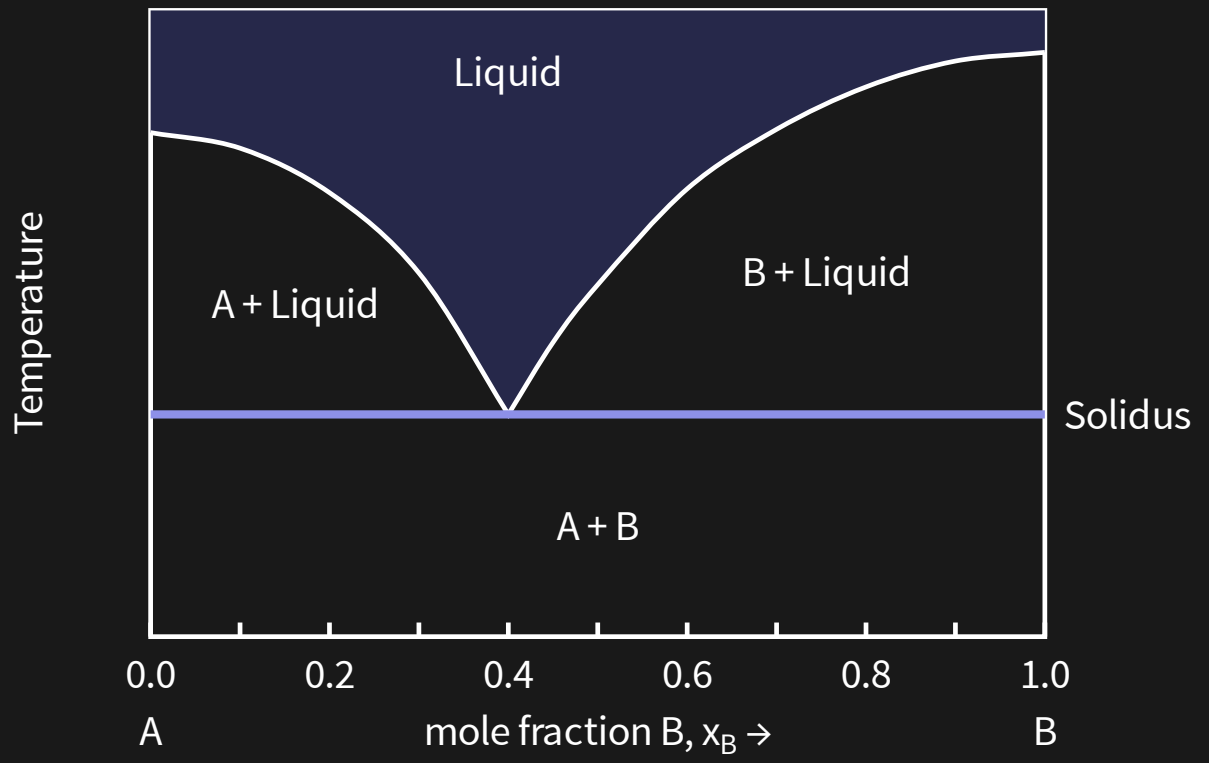
LIQUID, TWO-PHASE FIELDS, EUTECTIC POINT

$$F = C + 1 - P$$

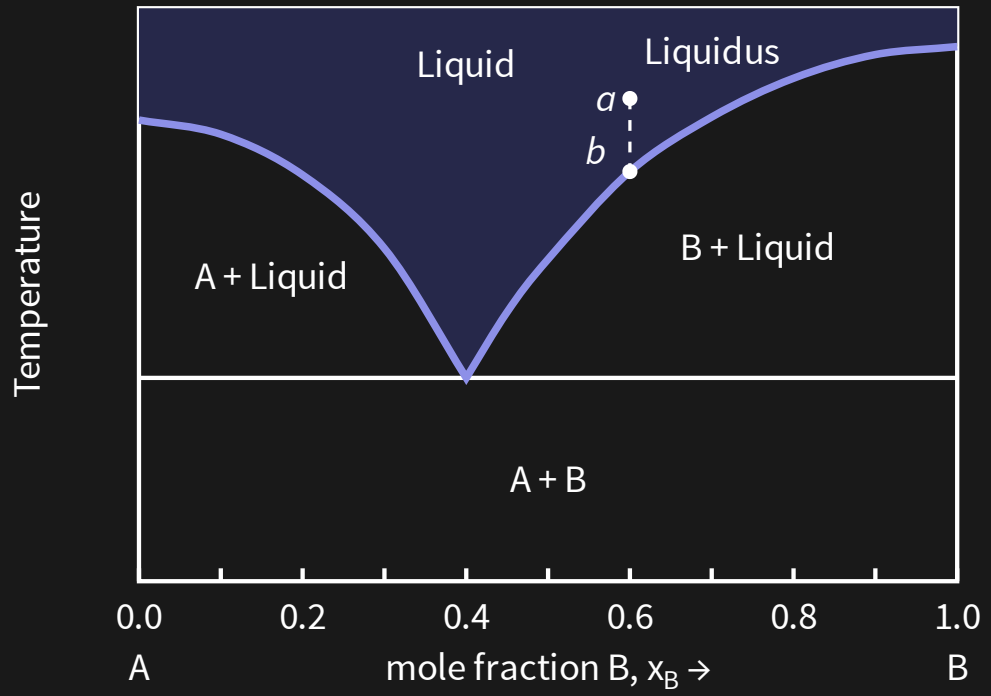
$$F = 3 - P$$



THE SOLIDUS


Liquid
A + Liquid
B + Liquid
Solidus
A + B
Temperature
0.0
0.2
0.4
0.6
0.8
1.0
A
mole fraction B, x_B →
B

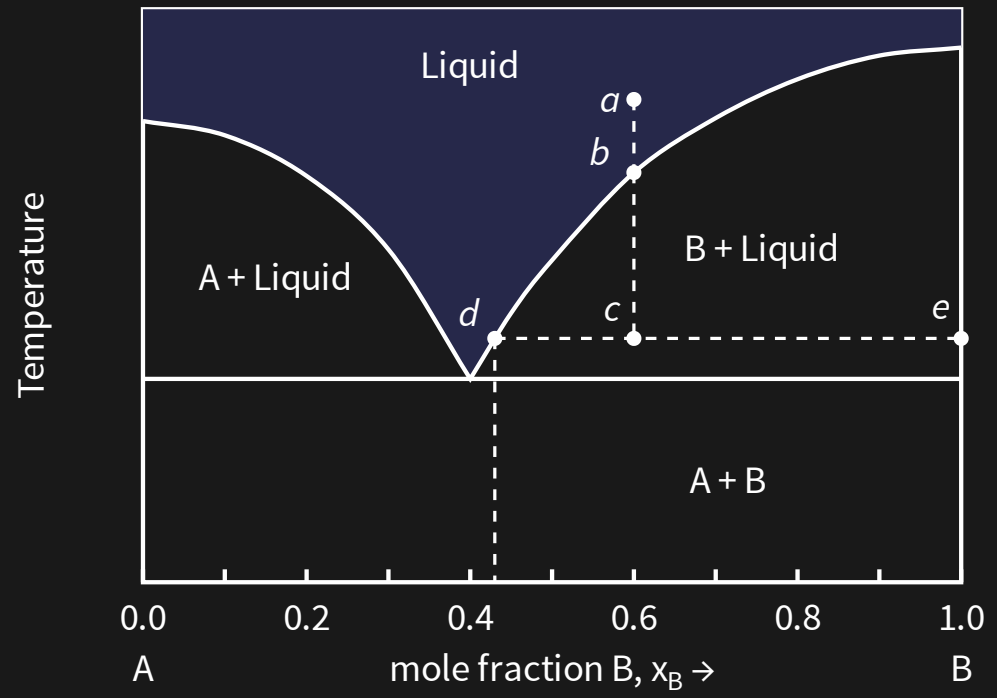
THE LIQUIDUS, THEN COOLING FROM POINT A



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

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

TIE LINE AT POINT C, THEN THE LEVER RULE



Point c

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

$F = 1$

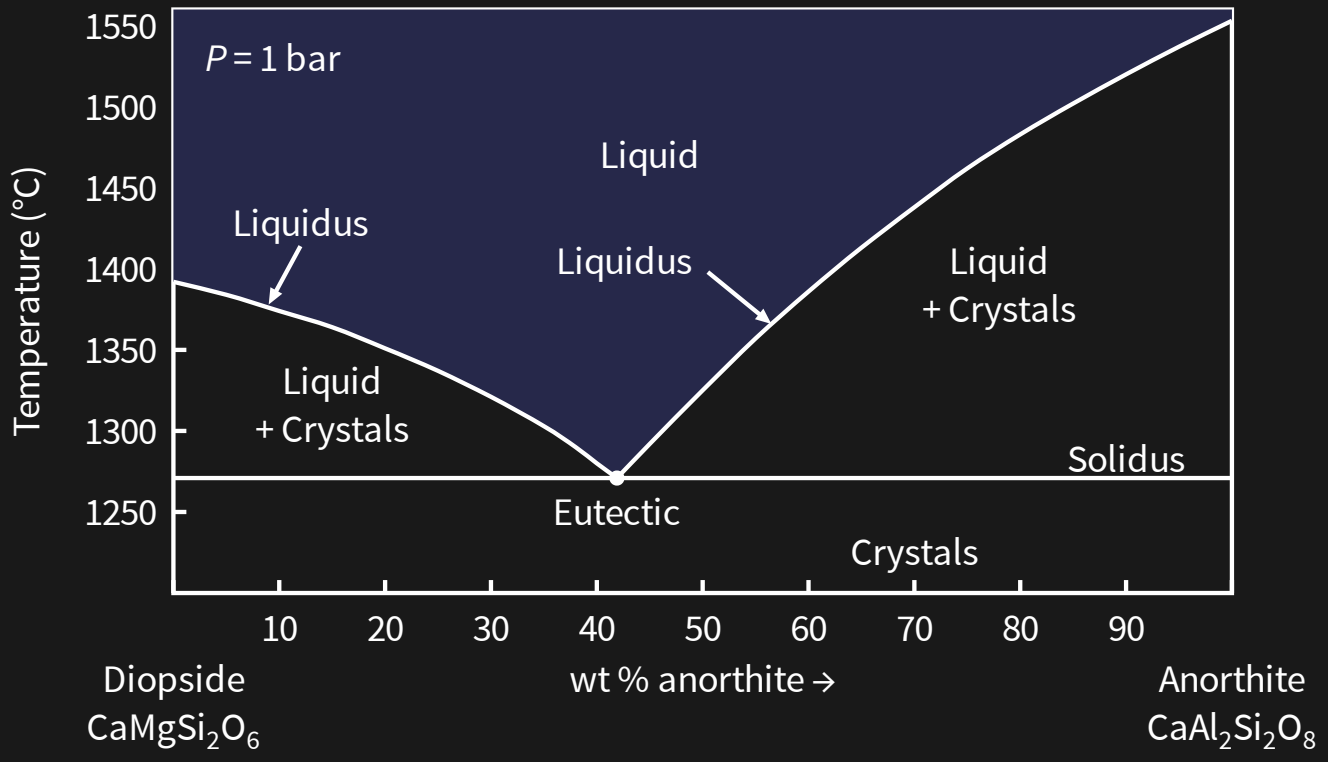
fix T and both phase compositions are set; moving c changes only the amounts

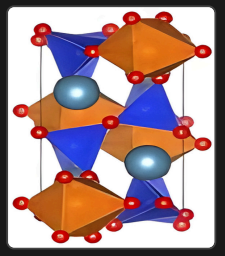
Fraction of solid B (f)

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

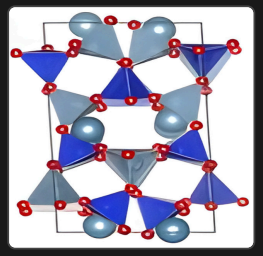
$$f = \frac{0.6 - 0.43}{1.0 - 0.43} = 0.30$$

A REAL EUTECTIC: DIOPSIDE AND ANORTHITE



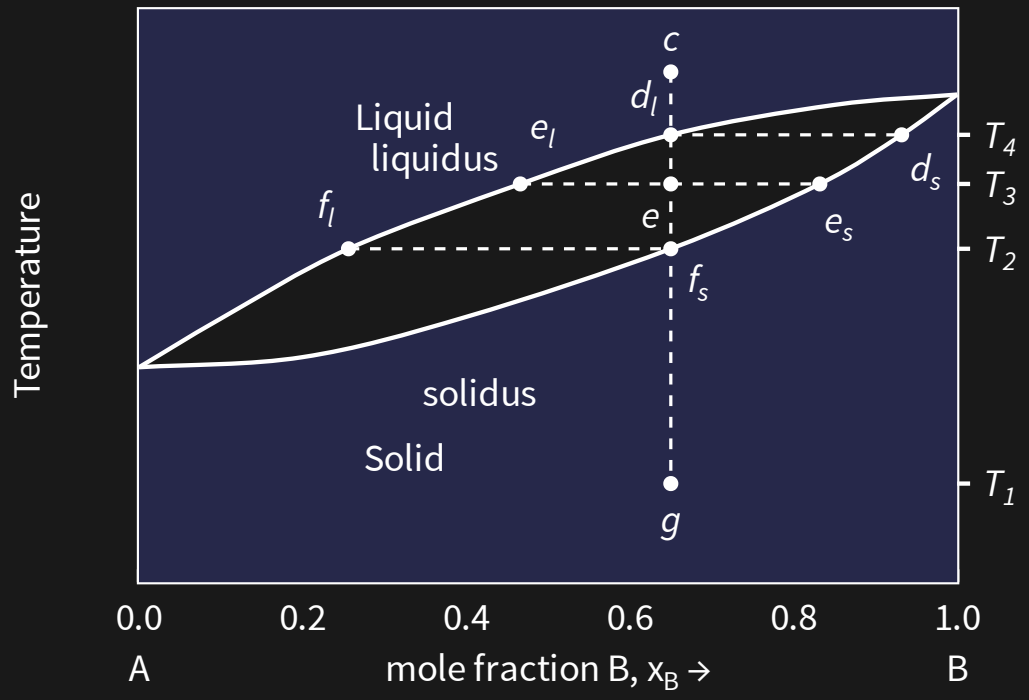


Diopside
$CaMgSi_2O_6$



Anorthite
$CaAl_2Si_2O_8$

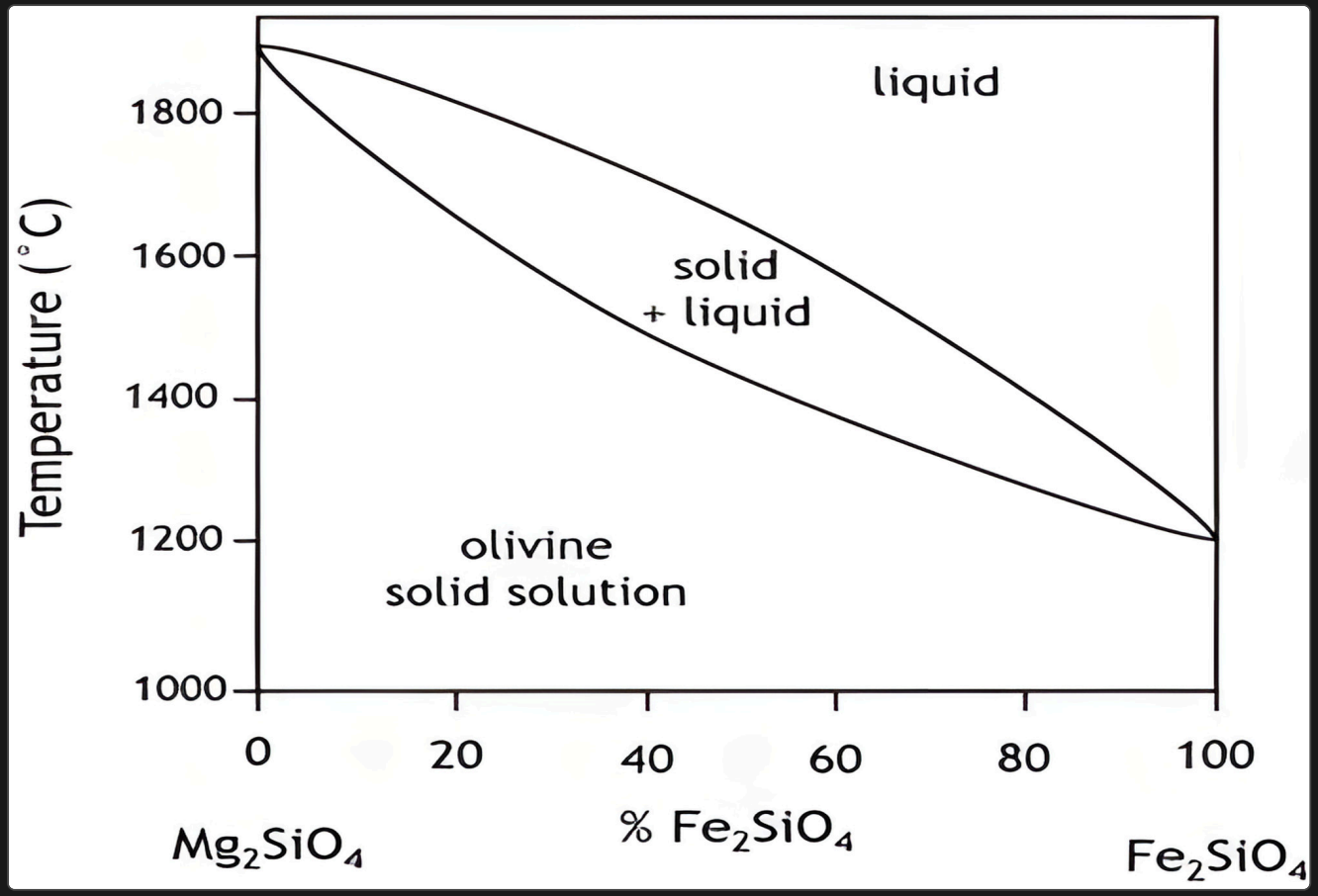
BINARY SYSTEM WITH COMPLETE SOLID SOLUTION FORMATION

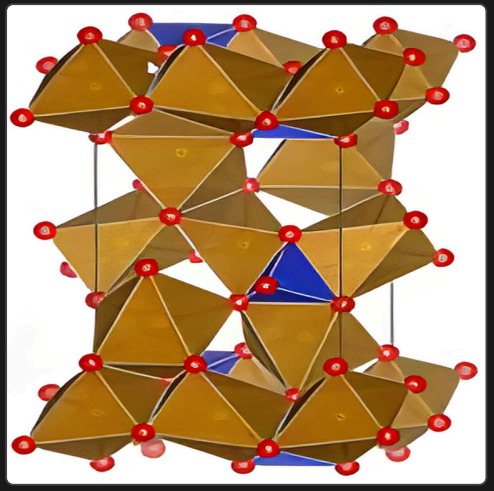


T_4	sample completely melts, composition $A_{0.35}B_{0.65}$
T_3	equilibrium mixture of liquid rich in A and solid rich in B
T_2	sample begins to melt
T_1	homogeneous solid, composition $A_{0.35}B_{0.65}$

Per *Solid State Materials Chemistry*, Figure 4.4, section 4.2.3

A REAL SOLID SOLUTION: FORSTERITE AND FAYALITE

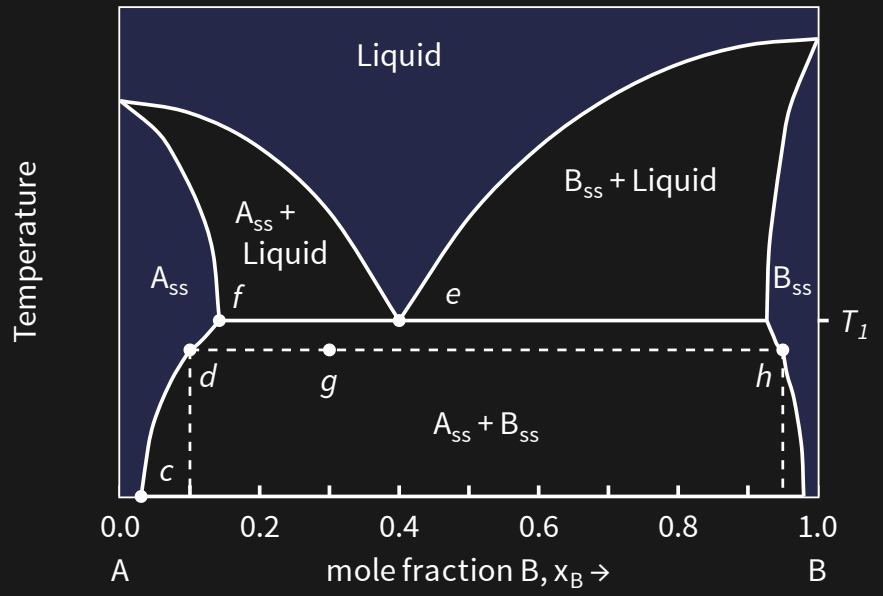




olivine structure

PARTIAL SOLID SOLUTIONS, LEVER RULE AT POINT G

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?



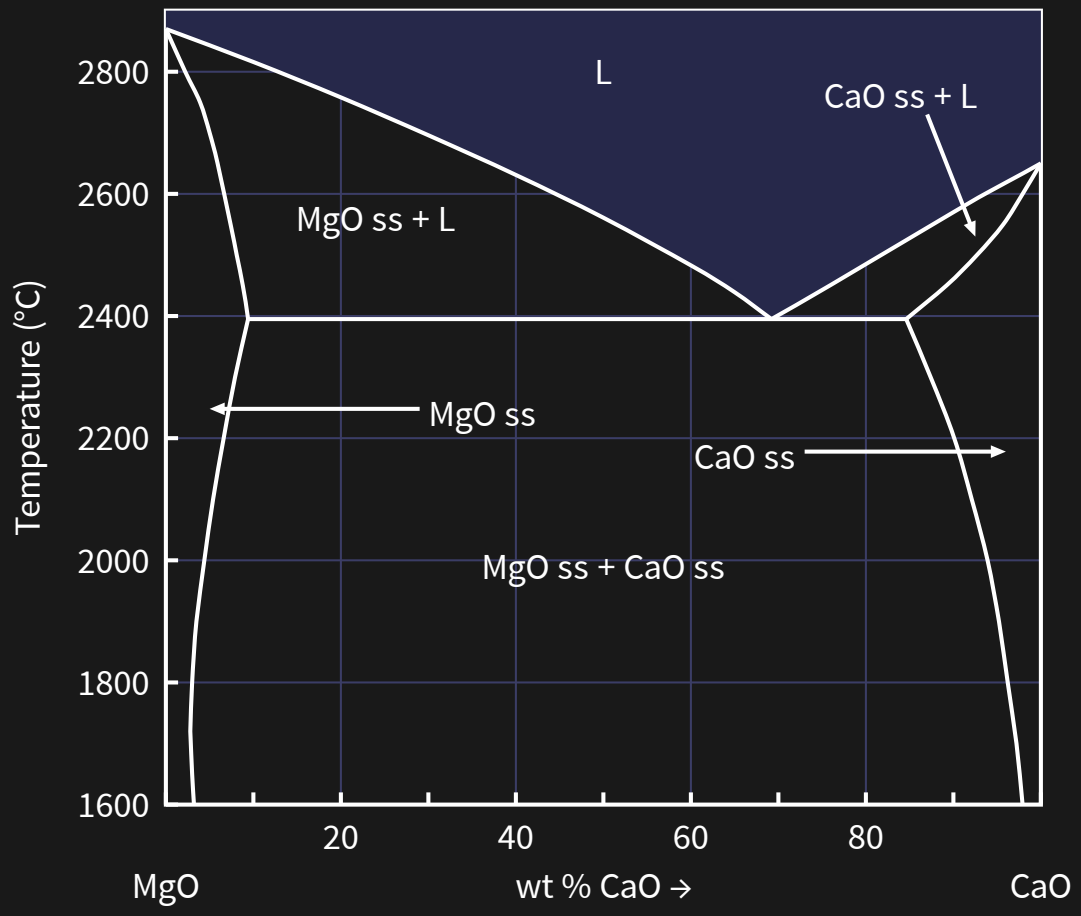
Phases at g $A_{0.9}B_{0.1}$ + $A_{0.05}B_{0.95}$

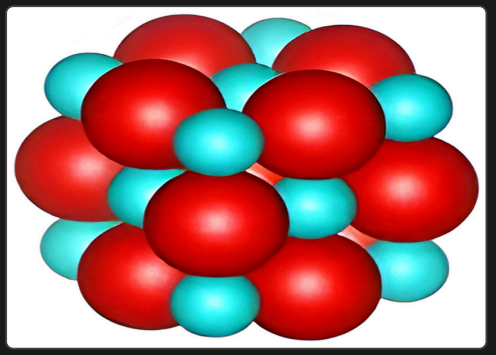
Fraction of $A_{0.05}B_{0.95}$

$$f = \frac{l_{gd}}{l_{dh}} = \frac{0.30 - 0.10}{0.95 - 0.10} = 0.24$$

Per *Solid State Materials Chemistry*, Figure 4.5, section 4.2.3

A REAL MISCIBILITY GAP: MgO AND CaO





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

Phase diagrams are the tools for planning synthesis, growing crystals, and reading what is at equilibrium.

Gibbs phase rule	Links components, phases and degrees of freedom, and simplifies under constant pressure
Single-component diagrams	Water shows the triple point, the phase boundaries, and the constraints on the degrees of freedom
Binary diagrams	The liquidus and the solidus, eutectic behavior, and solid solutions
Lever rule	Turns a tie line into the proportion of each phase in a two-phase region
Real materials	Minerals, oxides and alloys give complete and incomplete solid solutions, and the miscibility gaps between them

PRACTICE QUESTIONS

Work the Lecture 9 practice questions before the next class.

Open the Lecture 9 practice questions