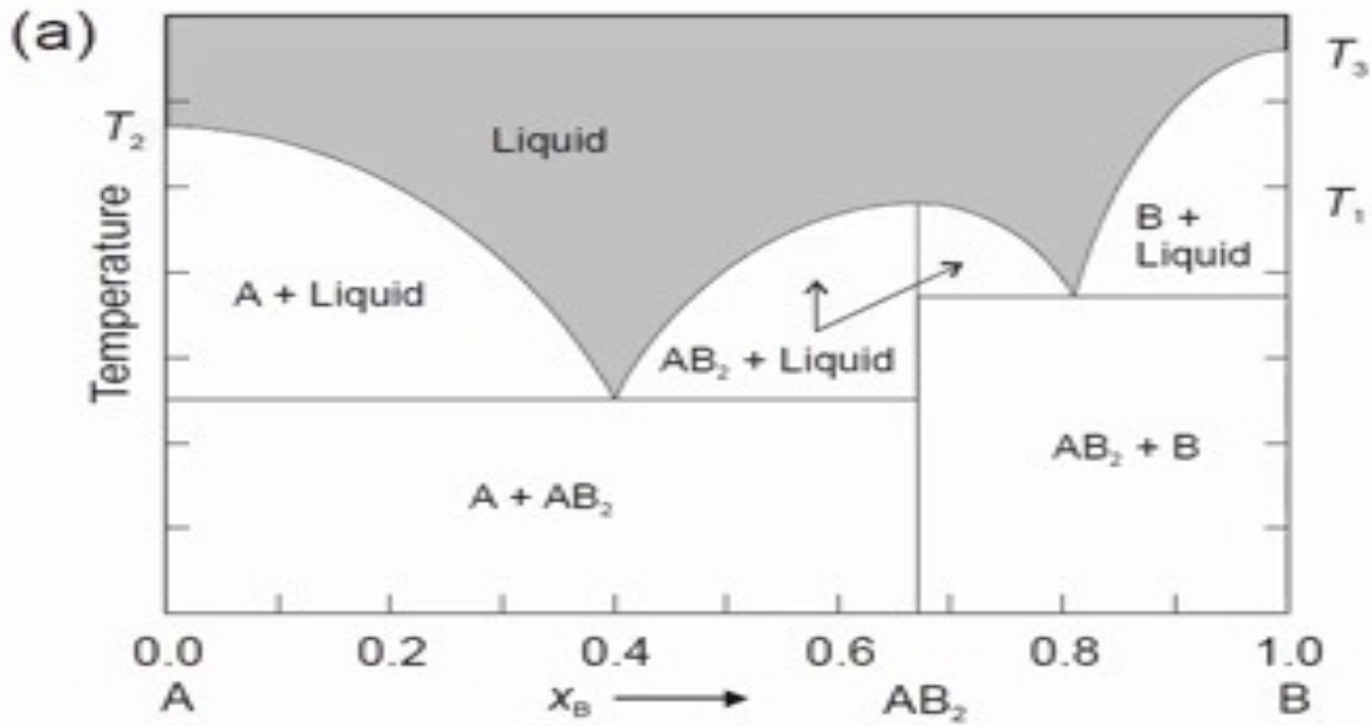
Binary Phase Diagrams Part 2

Learning Objectives

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

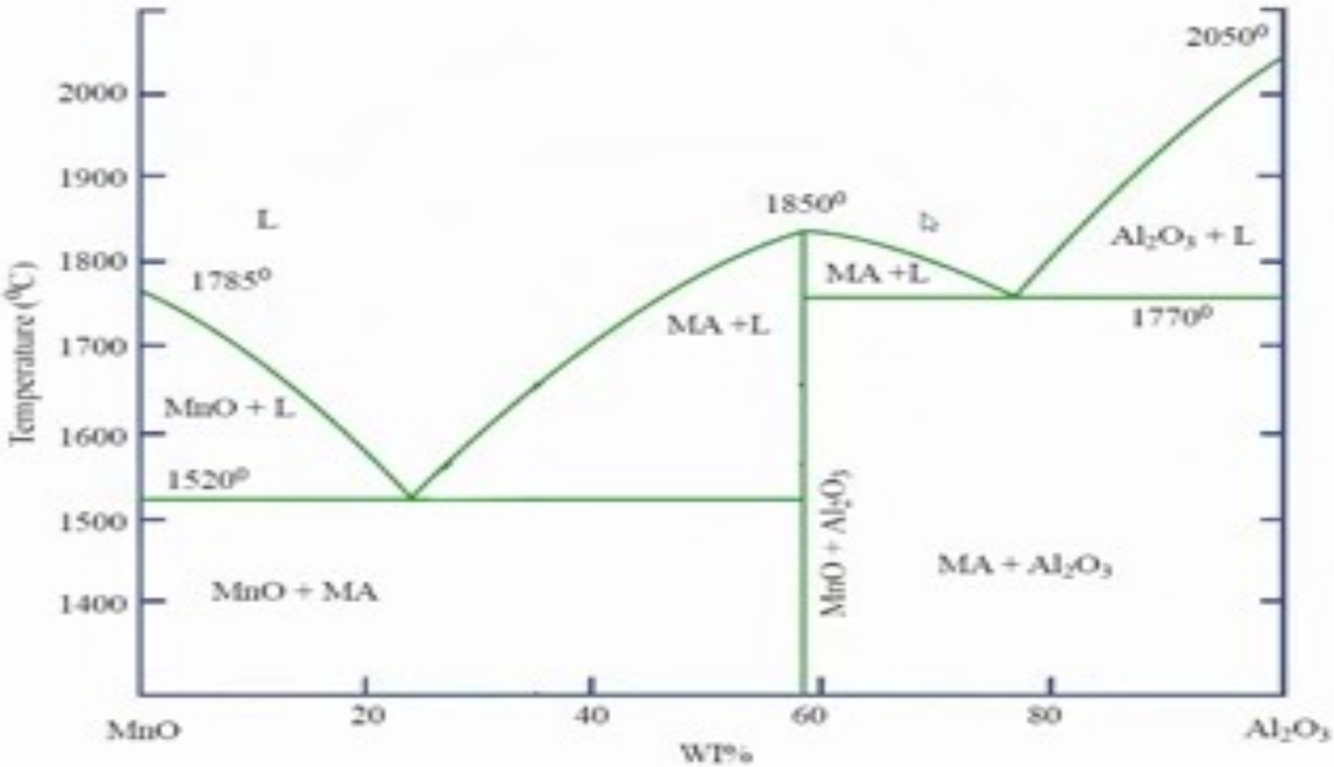
- Interpret binary phase diagrams that include an intermediate compound.
- Distinguish between **congruent** and **incongruent** melting behaviors.
- Identify **eutectic** and **peritectic** points and explain their significance.
- Predict which phases are in equilibrium at given regions of a diagram.
- Assess strategies for **growing single crystals** of intermediate compounds.

Binary system with a congruently melting binary compound



A congruently melting compound is one that forms a liquid of the same composition upon melting.

MnO-Al_2O_3 Phase Diagram

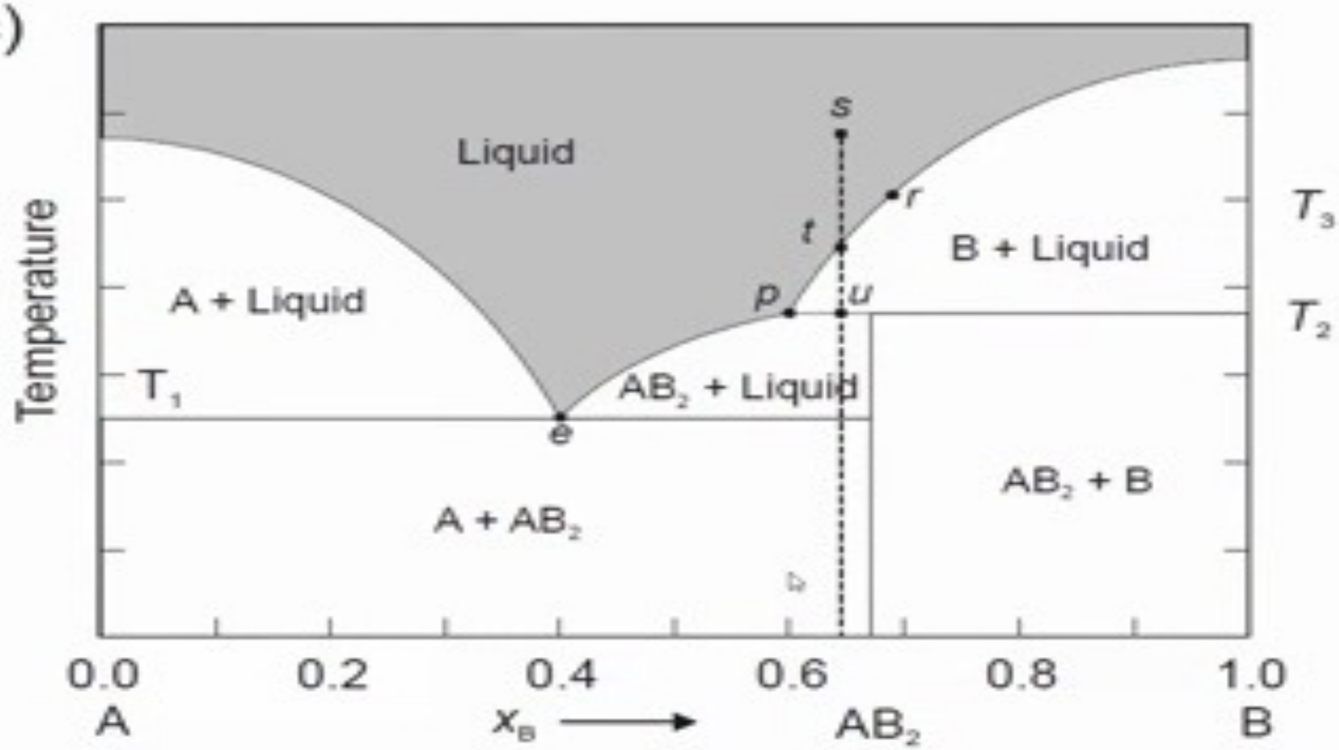


System MnO + Al_2O_3 (MA = MnO + Al_2O_3)

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

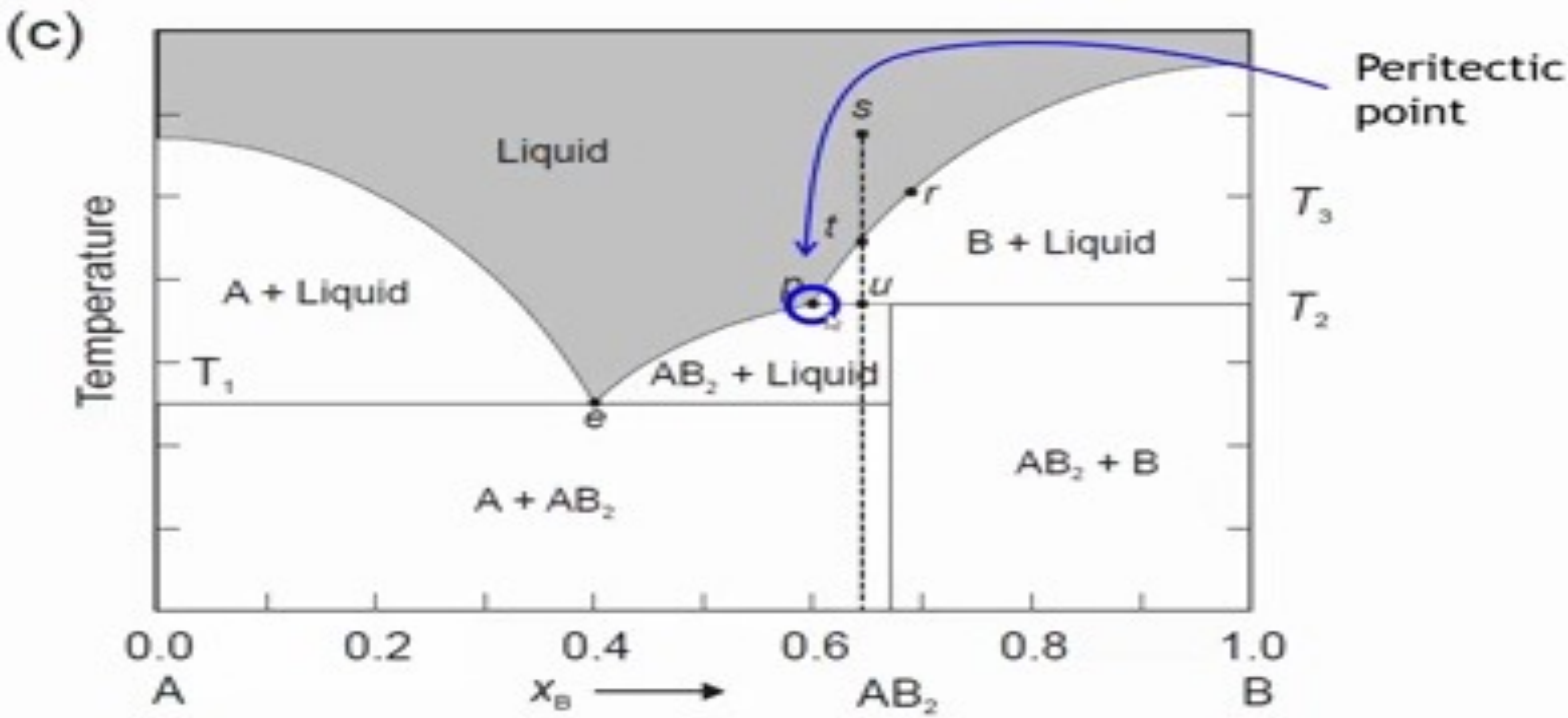
Binary system with an incongruently melting binary compound

(c)



An incongruently melting compound is one that forms a liquid and a solid of different compositions upon melting.

Binary system with an incongruently melting binary compound



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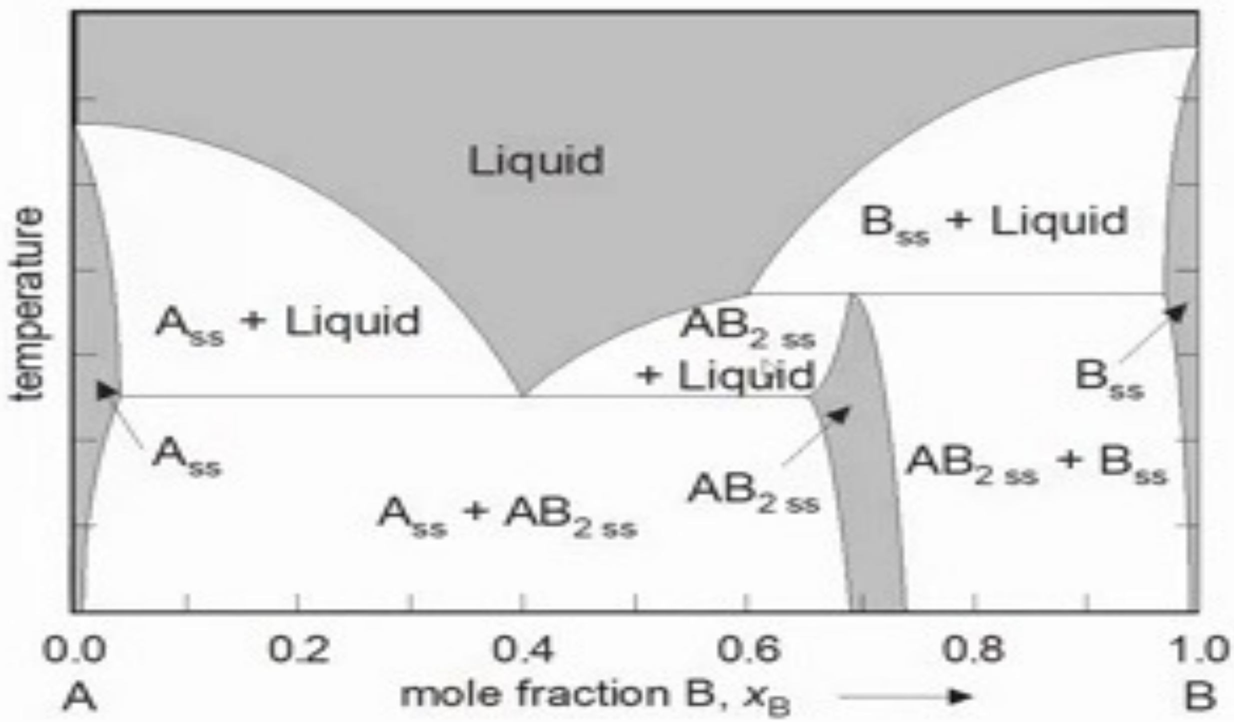
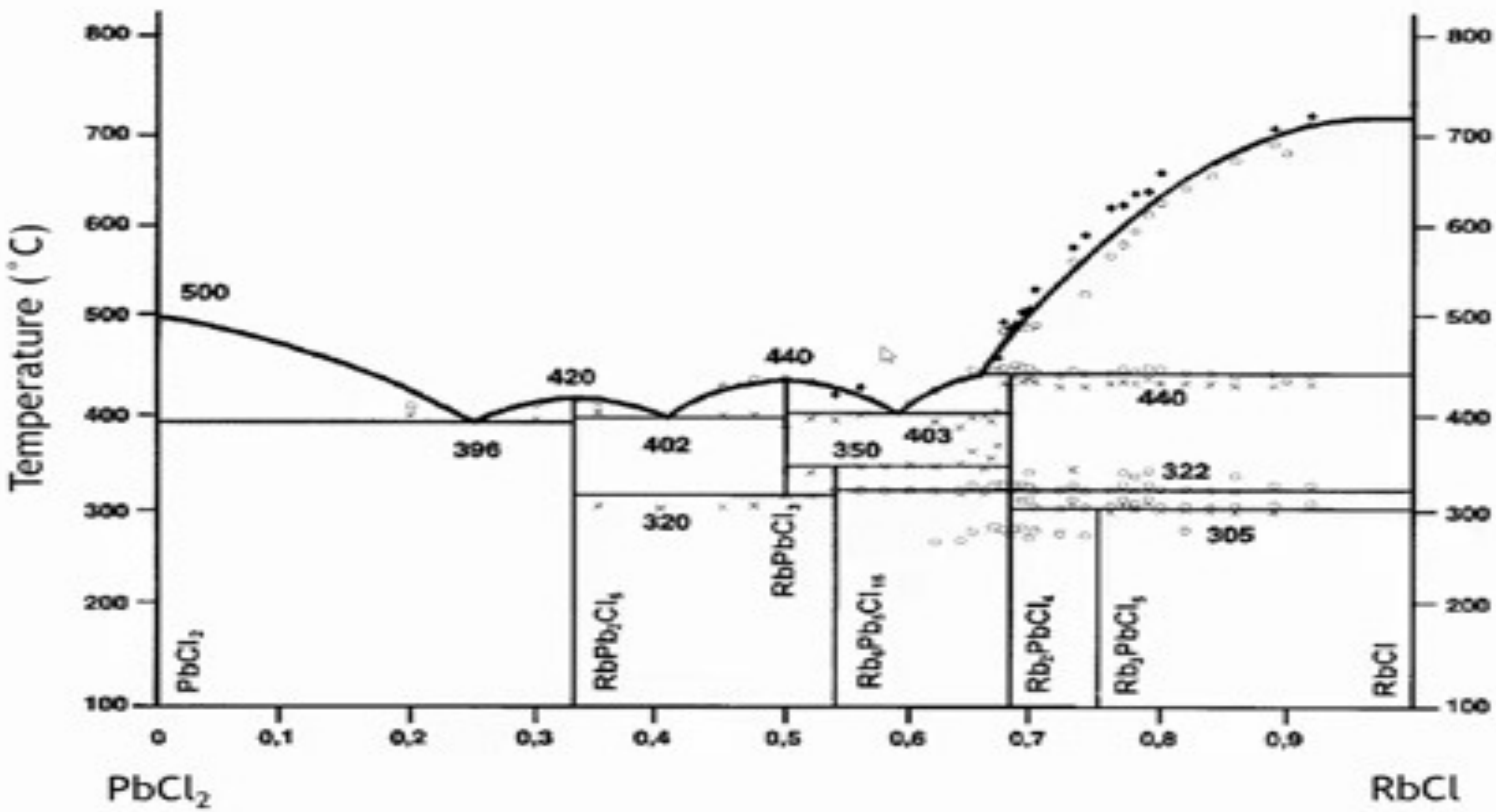
Typical two component phase diagram



$PbCl_2$ – RbCl Phase Diagram



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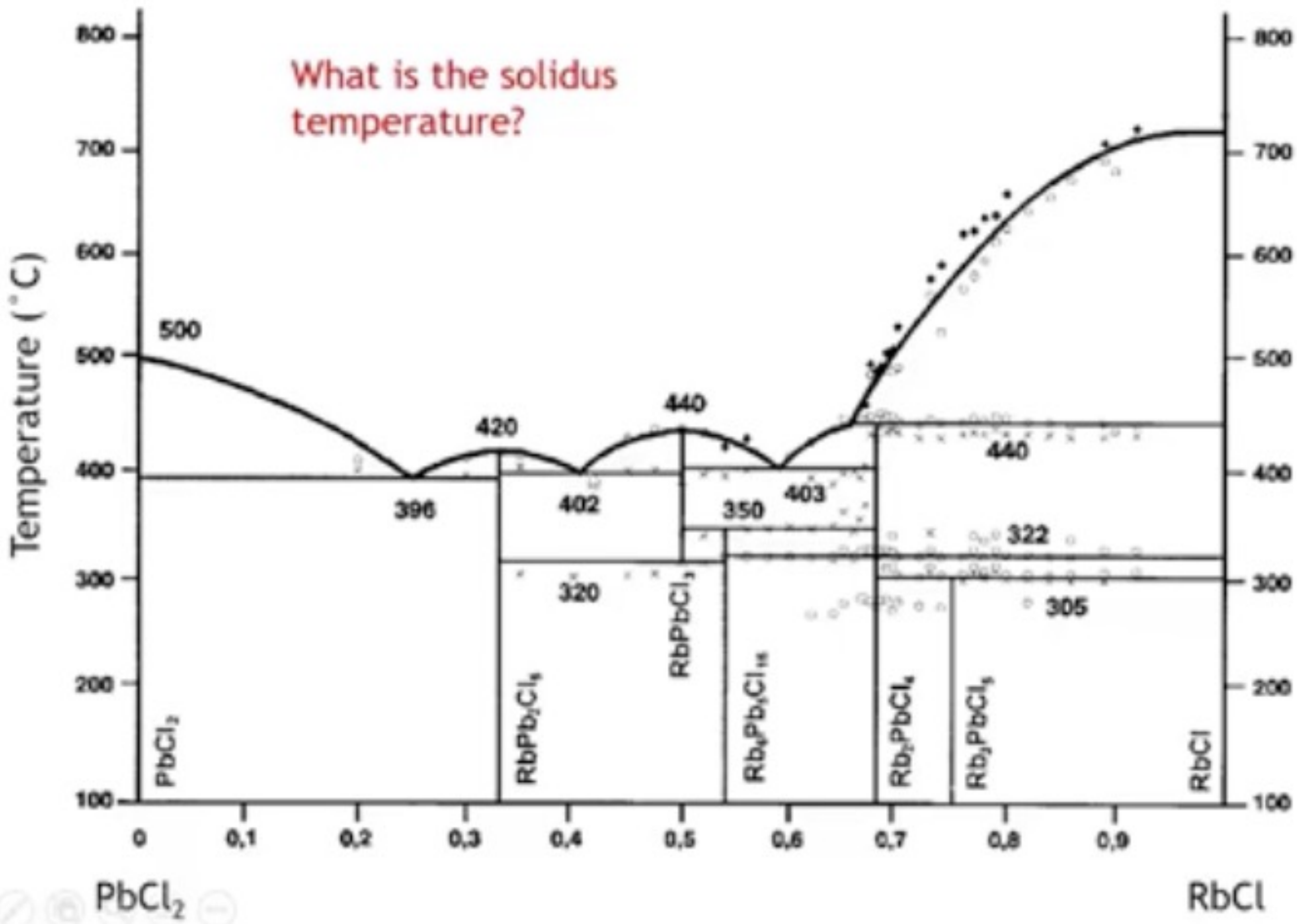

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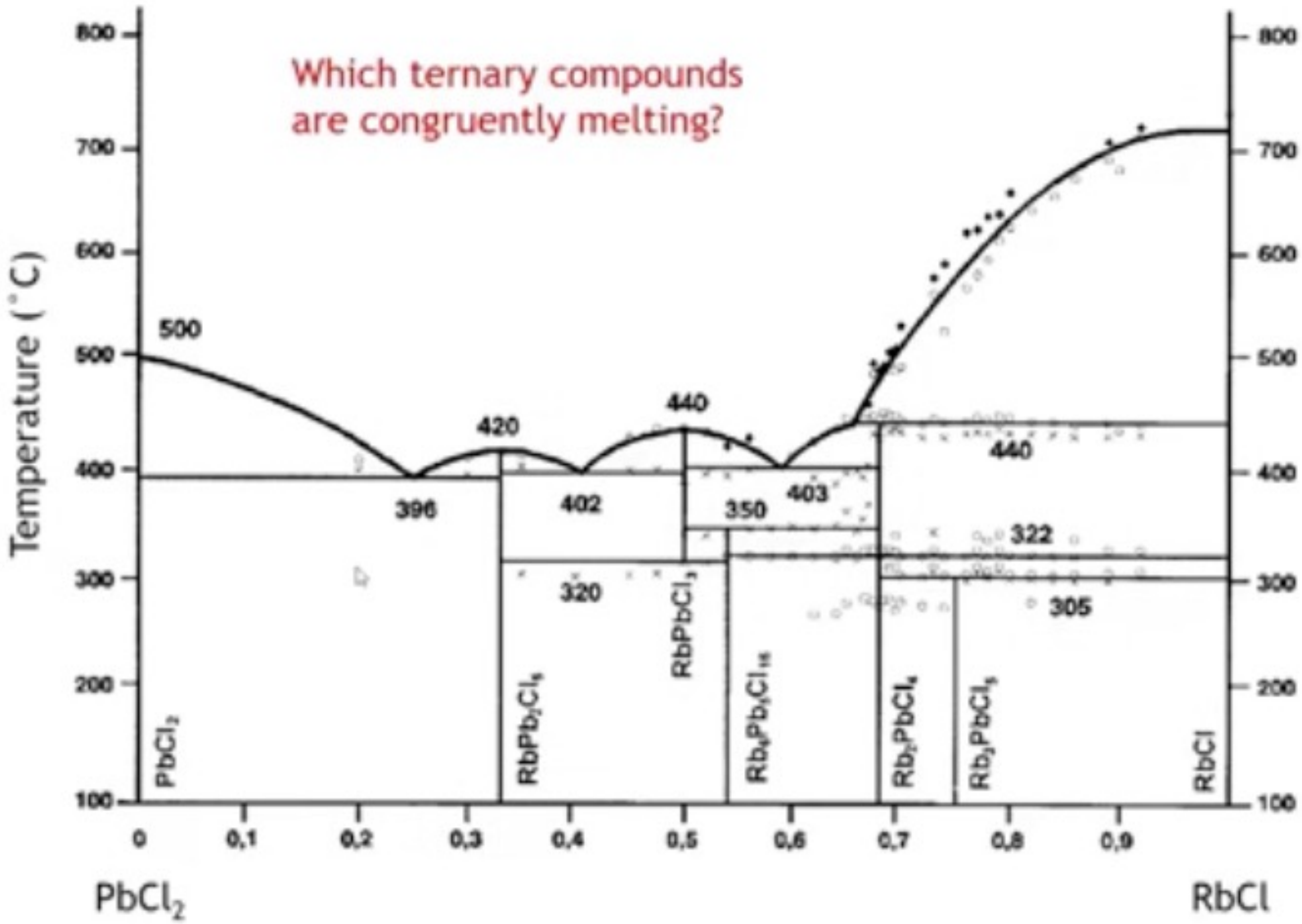
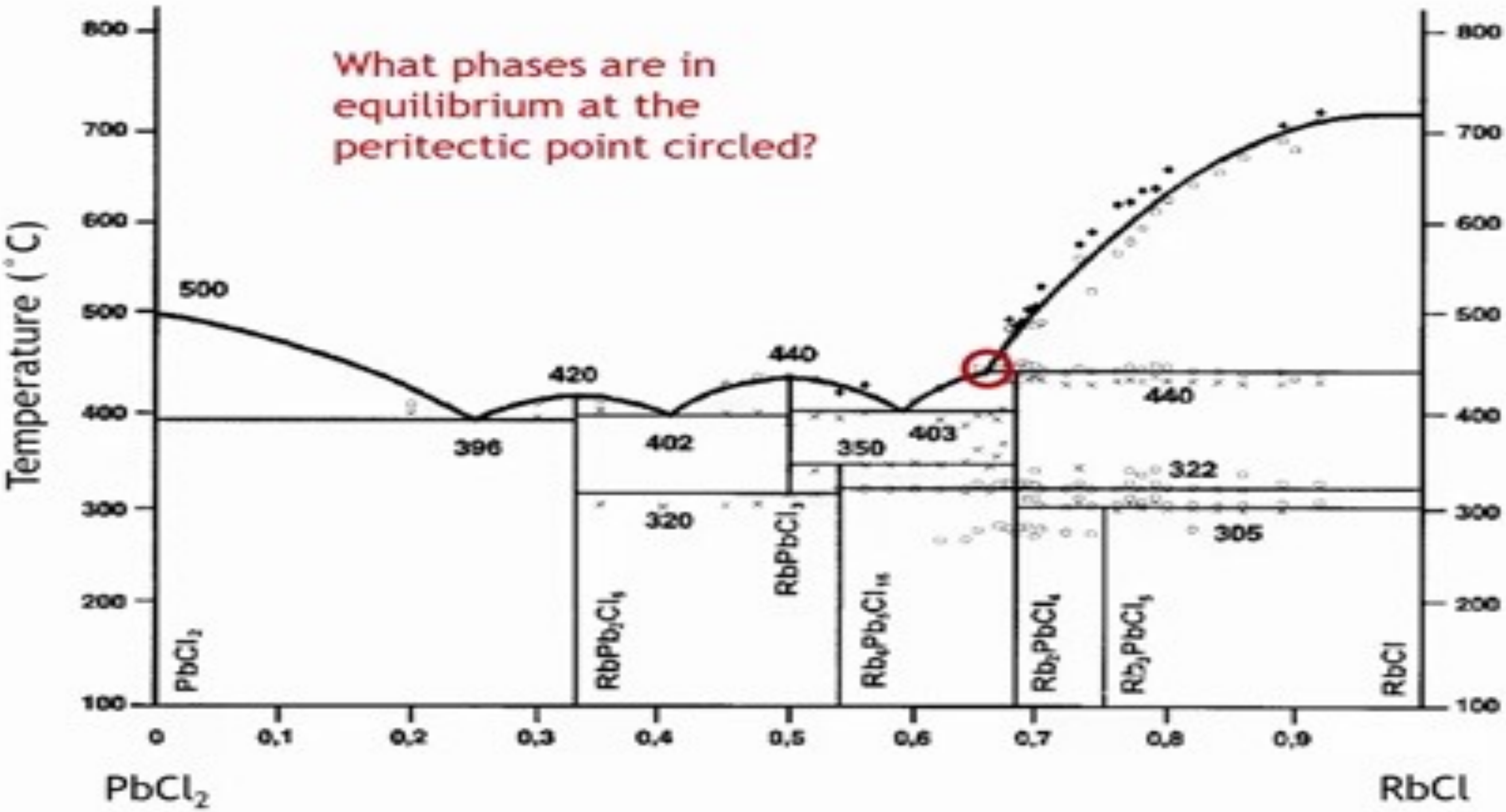
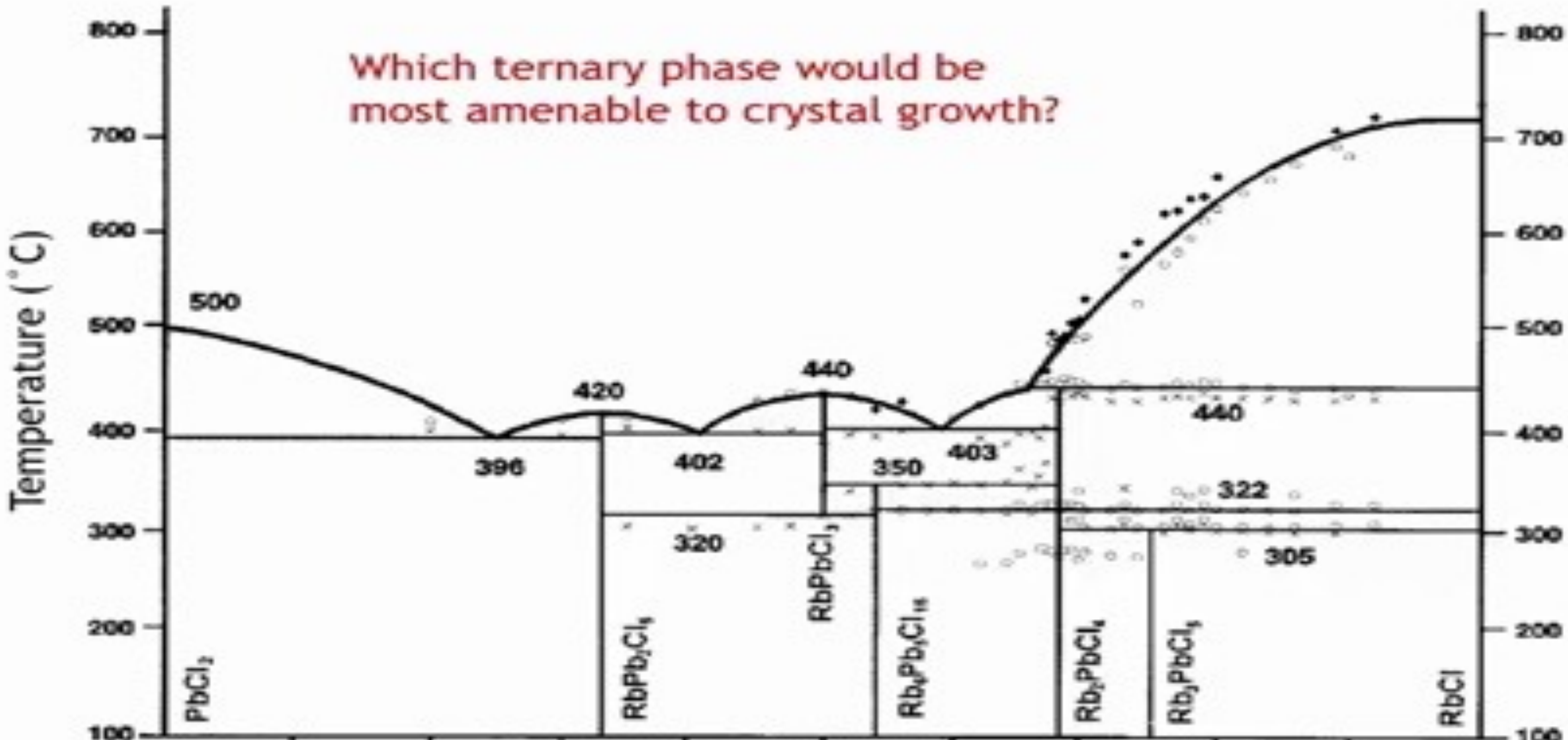


$PbCl_2$ – RbCl Phase Diagram



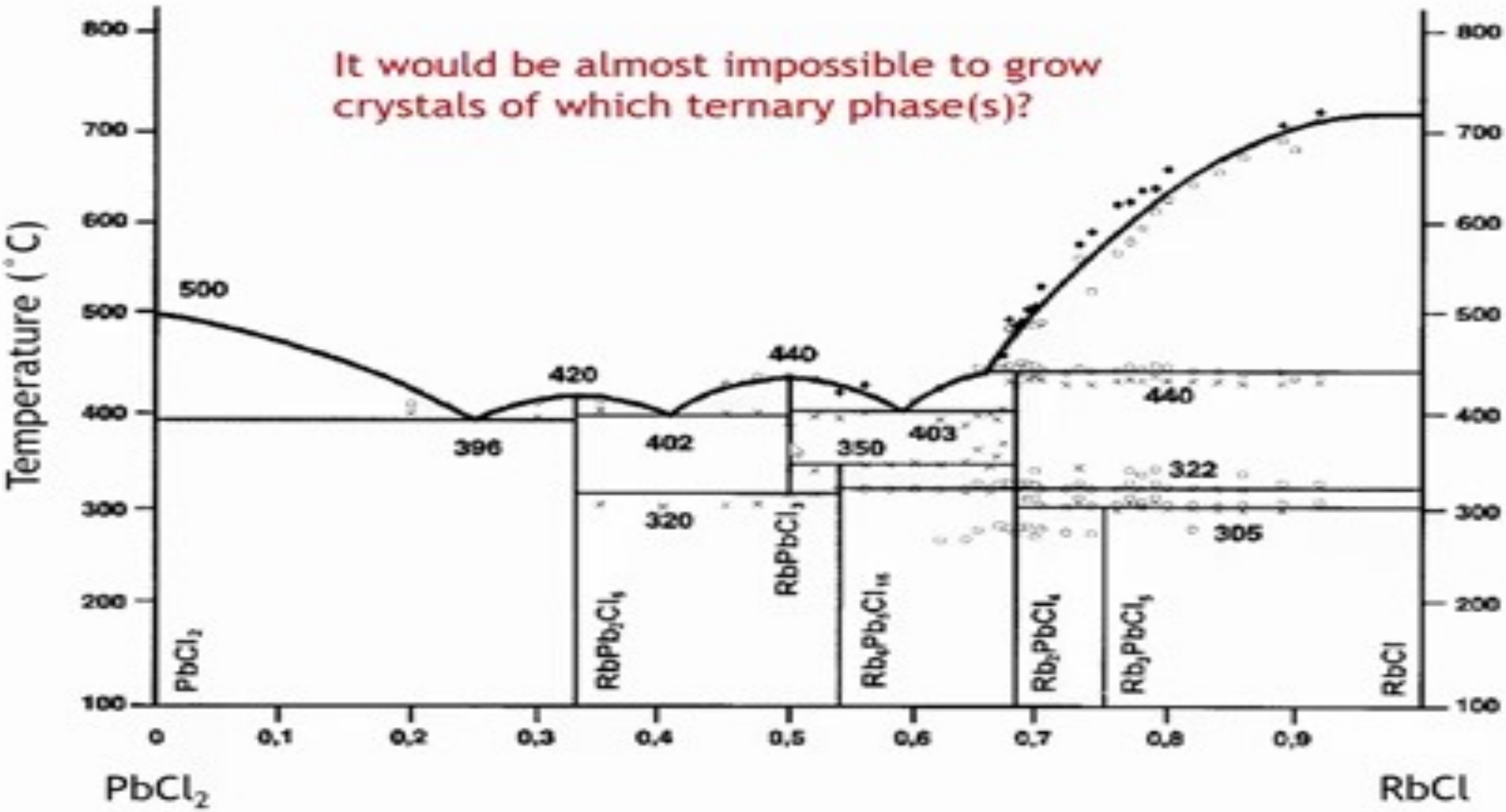
$PbCl_2$ – RbCl Phase Diagram

Which ternary phase would be most amenable to crystal growth?

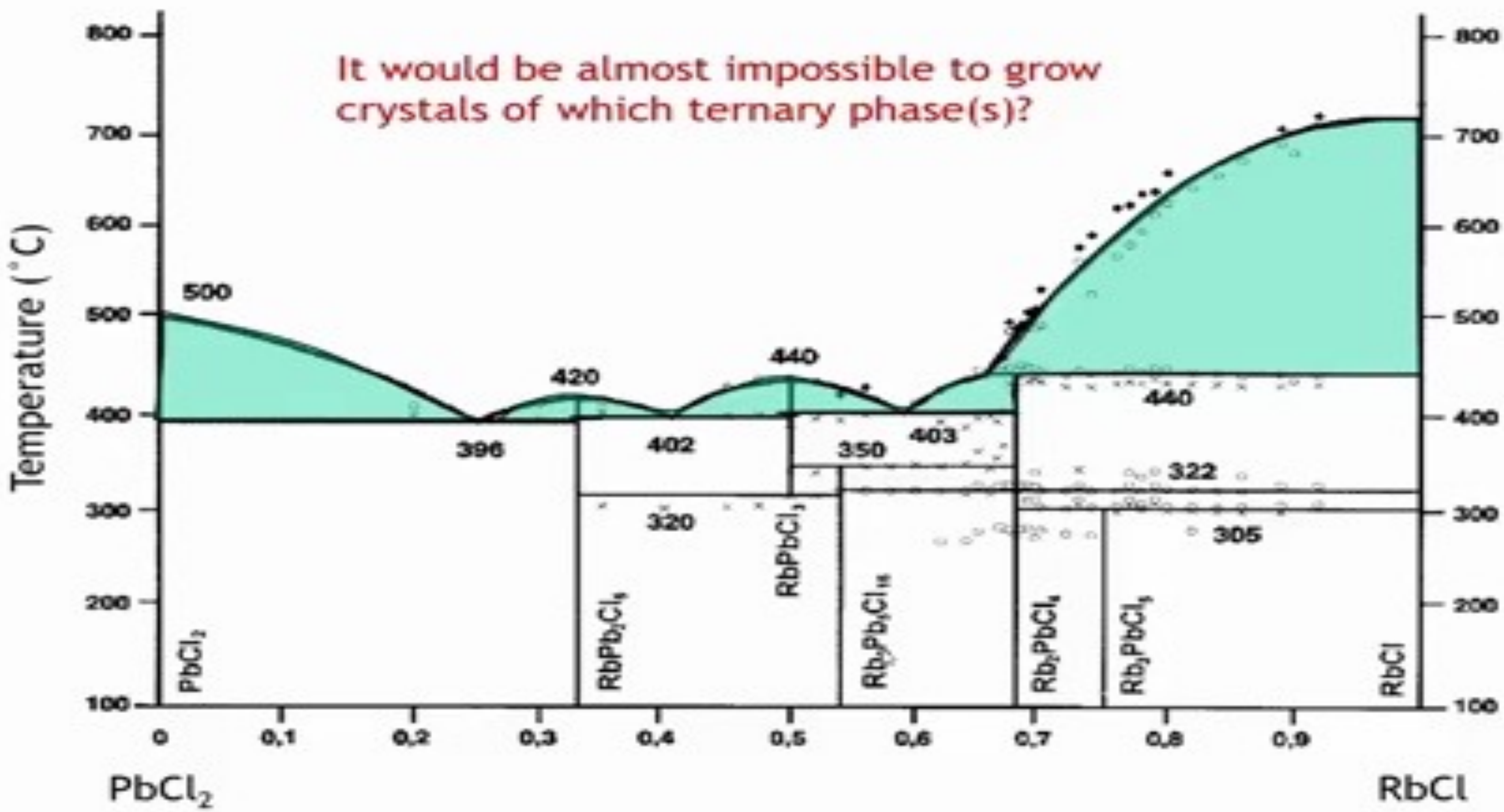


$PbCl_2$ RbCl

$PbCl_2$ – RbCl Phase Diagram

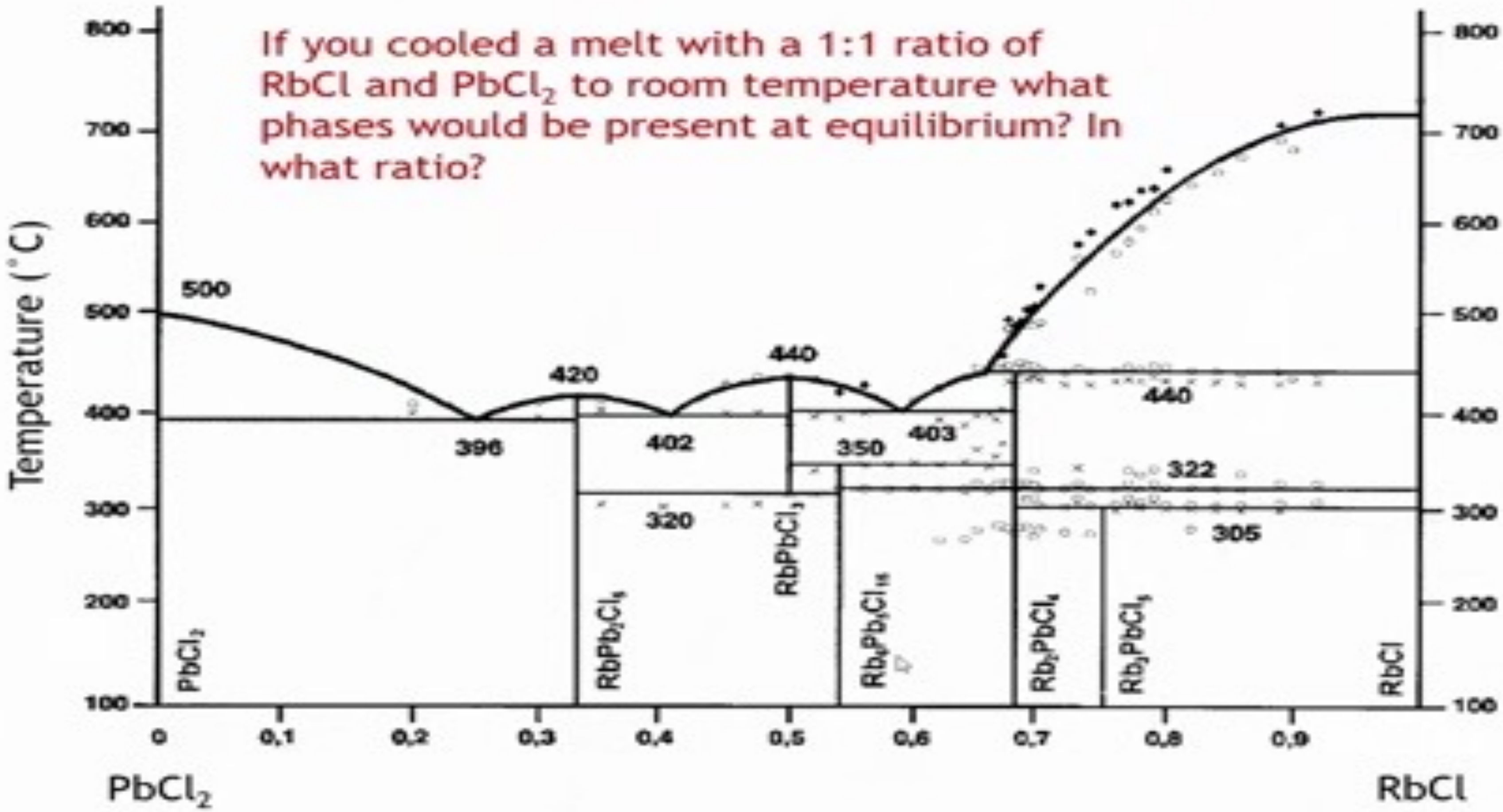


$PbCl_2$ – RbCl Phase Diagram



$PbCl_2$ – RbCl Phase Diagram

If you cooled a melt with a 1:1 ratio of RbCl and $PbCl_2$ to room temperature what phases would be present at equilibrium? In what ratio?



Summary

- Binary diagrams with intermediate compounds can be treated as two **eutectic diagrams side-by-side**.
- Intermediate compounds may be **line phases** with fixed stoichiometry (e.g., AB_2).
- **Congruently melting compounds**: melt to a liquid of the same composition.
- **Incongruently melting compounds**: melt to a liquid of different composition + another solid → introduces the **peritectic point.**
- Crystal growth:
  - Easier for congruently melting compounds.
  - Incongruent compounds require controlled growth between eutectic and peritectic compositions, often followed by **quenching.**
- Real systems often include **solid solutions** as well as intermediate line phases.

Homework

4.2 Refer to the phase diagram depicted below. (a) State which four phases are stable at 100 °C. (b) What is the name given to the horizontal line separating region 2 from 1 and 3? (c) What are the approximate melting points of A, AB, and B? (d) What happens if you try and melt

4.3 Using the phase diagram of Figure 4.8: (a) State how you would attempt to prepare a solid polycrystalline sample of ZrW_2O_8. (b) State how you would attempt to grow single crystals of ZrW_2O_8.

4.4 In the system Al_2O_3–BaO, five phases stable above 1300 °C were identified: Al_2O_3, $Al_{12}BaO_{19}$, Al_2BaO_4, $Al_2Ba_3O_6$, and BaO. Each was found to melt congruently at 2072 °C, 1900 °C, 1811 °C, 1616 °C, and 1918 °C, respectively. Eutectics form at $x_{BaO} = 0.11, 0.32,$

4.5 Perovskite chemists searching in the CaO–TiO_2 system initially found four phases stable above 1300 °C: CaO, $Ca_3Ti_2O_7$, $CaTiO_3$, and TiO_2. CaO, $CaTiO_3$, and TiO_2 were reported to melt congruently at 2600 °C, 1970 °C, and 1830 °C and $Ca_3Ti_2O_7$ to melt incongruently at 1750 °C. Eutectics were reported at $x_{TiO_2} = 0.29$ and 0.76 with melting points of 1695 °C and 1460 °C. Sketch and fully label a phase diagram for this system.

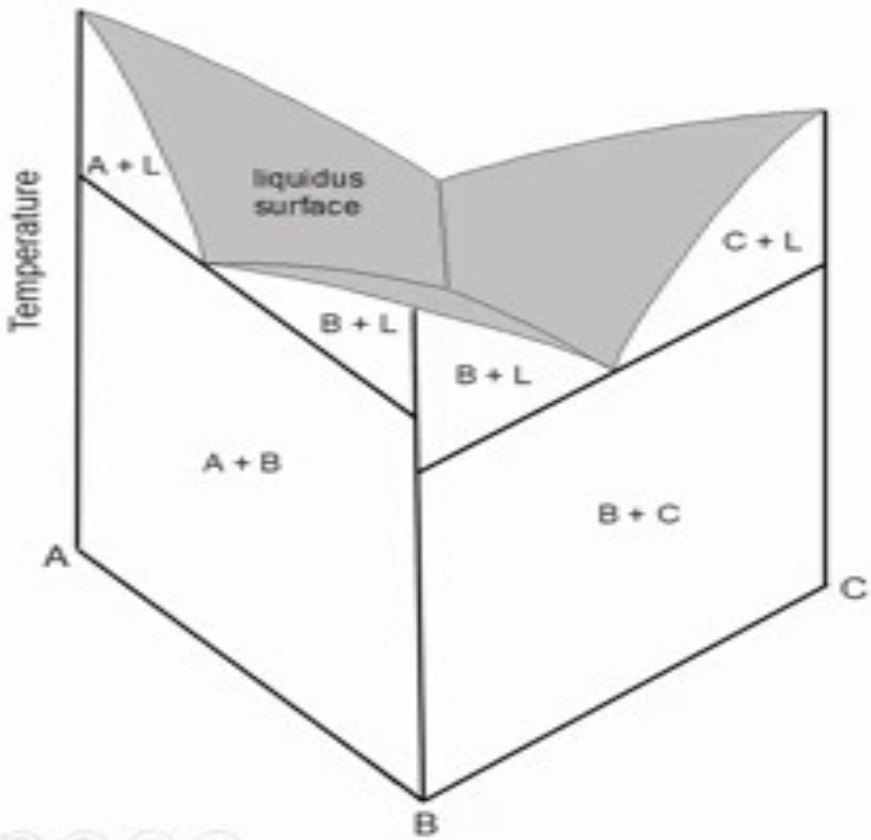
Ternary Phase Diagrams

Learning Objectives

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

- Explain the difference between binary and ternary phase diagrams.
- Describe how ternary phase diagrams are represented and why simplifications (isothermal cuts) are used.
- Locate a composition within a ternary diagram using the line/triangle method.
- Identify which phases are present at a given point, line, or region of a ternary diagram.
- Apply the triangle (lever) rule conceptually to determine phase fractions.
- Interpret real ternary phase diagrams (e.g., TiO_2–ZrO_2–Al_2O_3, Y_2O_3–BaO–CuO systems).

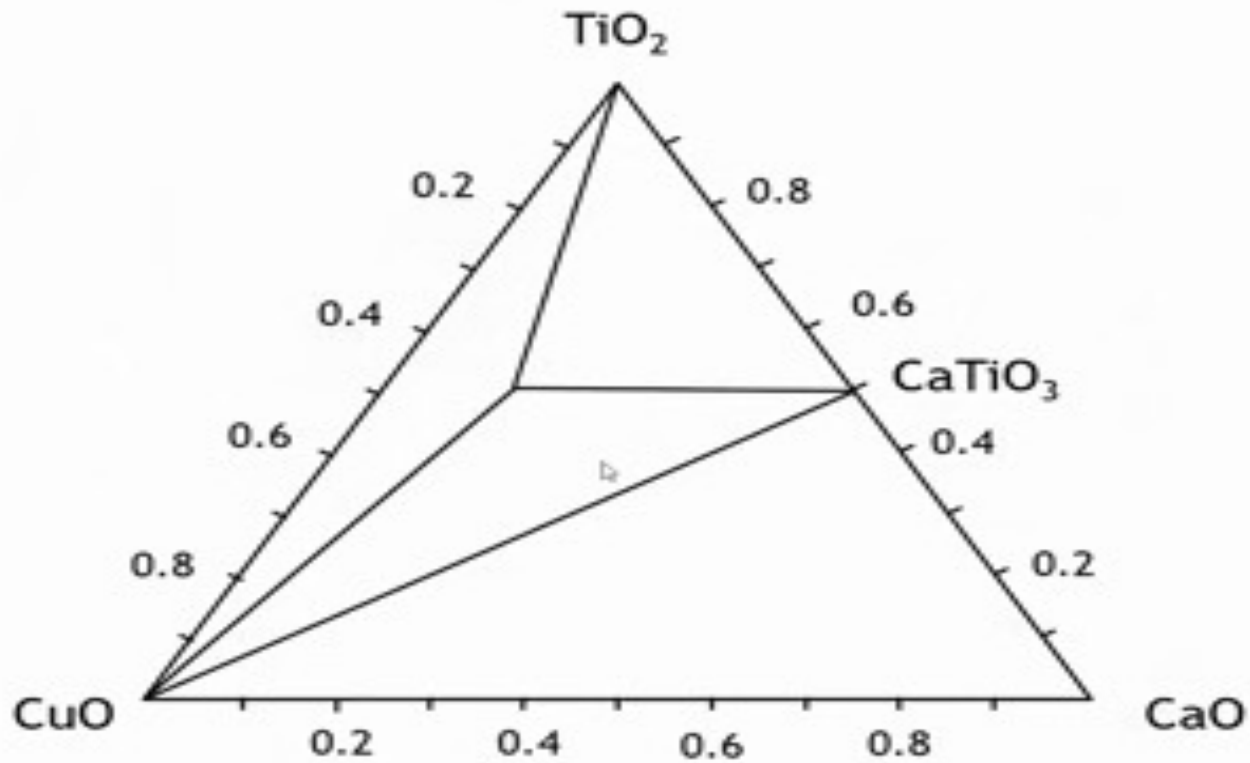
Ternary Phase Diagram
(Constant Pressure)



For a phase diagram with three components (a ternary phase diagram) we need four axes to plot the phase diagram at constant pressure.

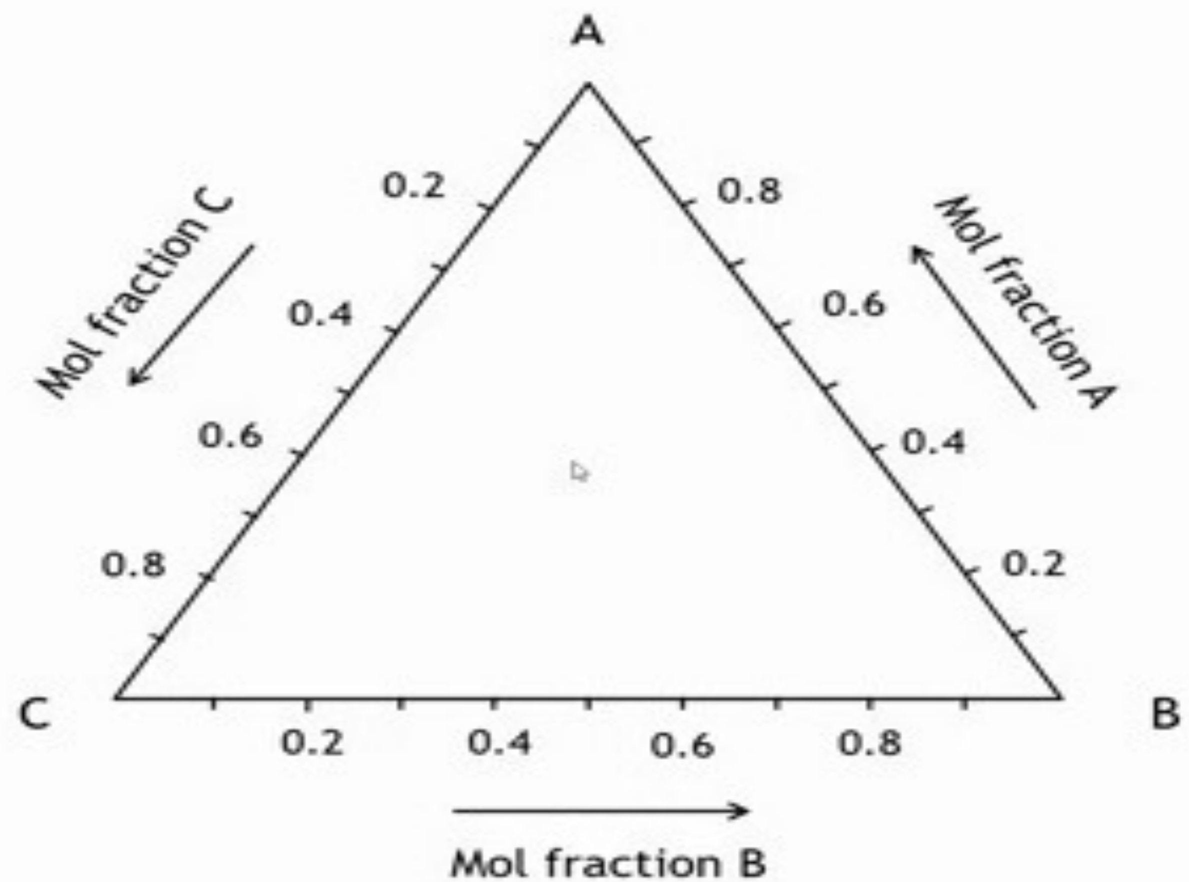
An equilateral triangle for the base and a vertical axis for temperature

Isothermal (sub-solidus) cut through a three-component phase diagram



This represents a 2D cut from the five-dimensional phase diagram at constant temperature and pressure

Determining the composition of a point



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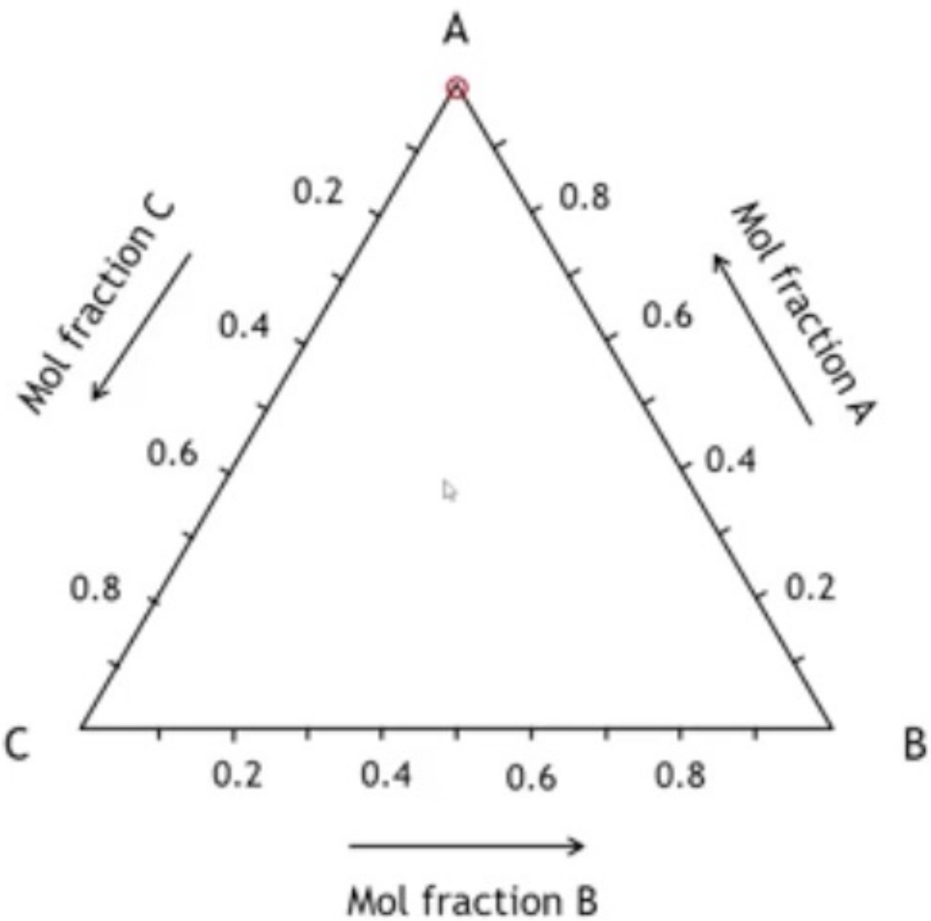

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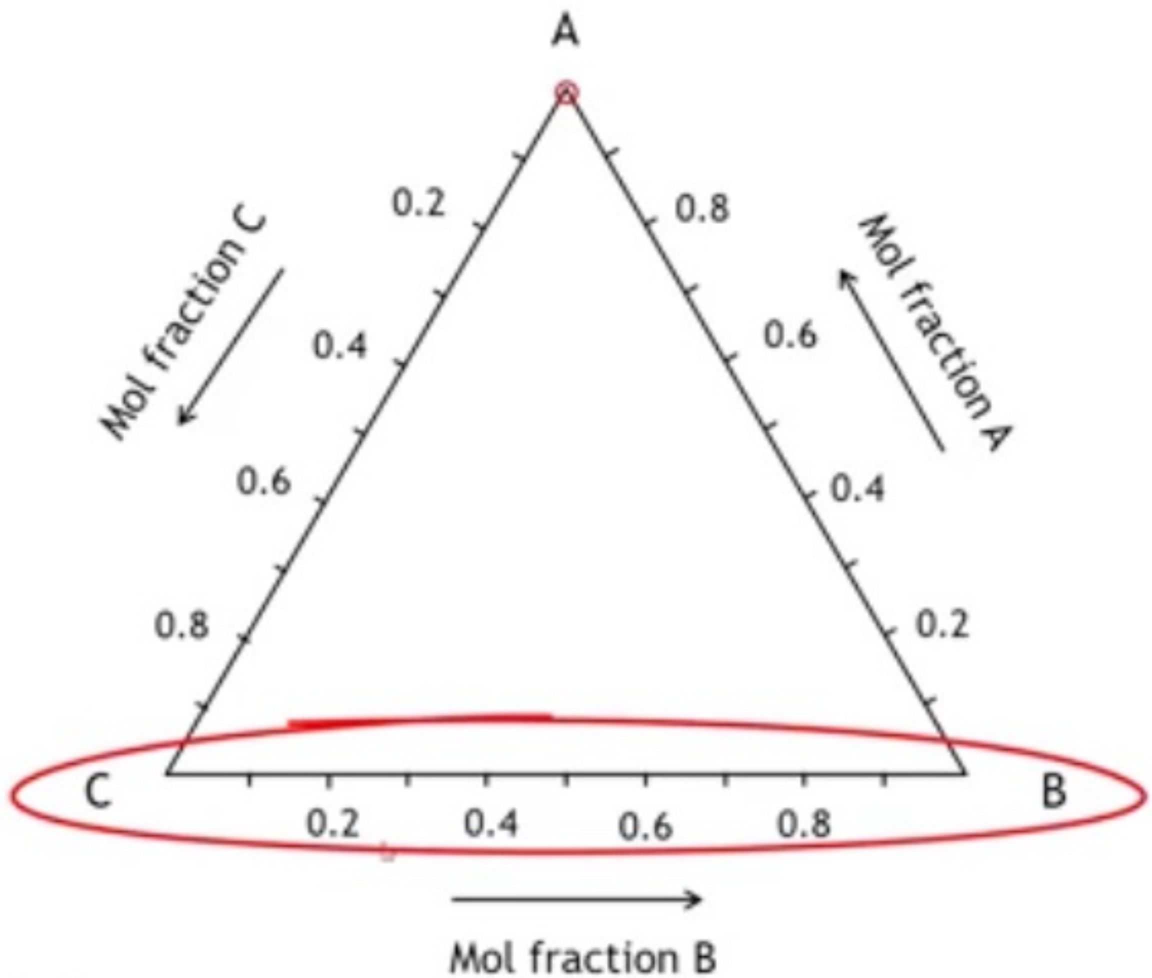

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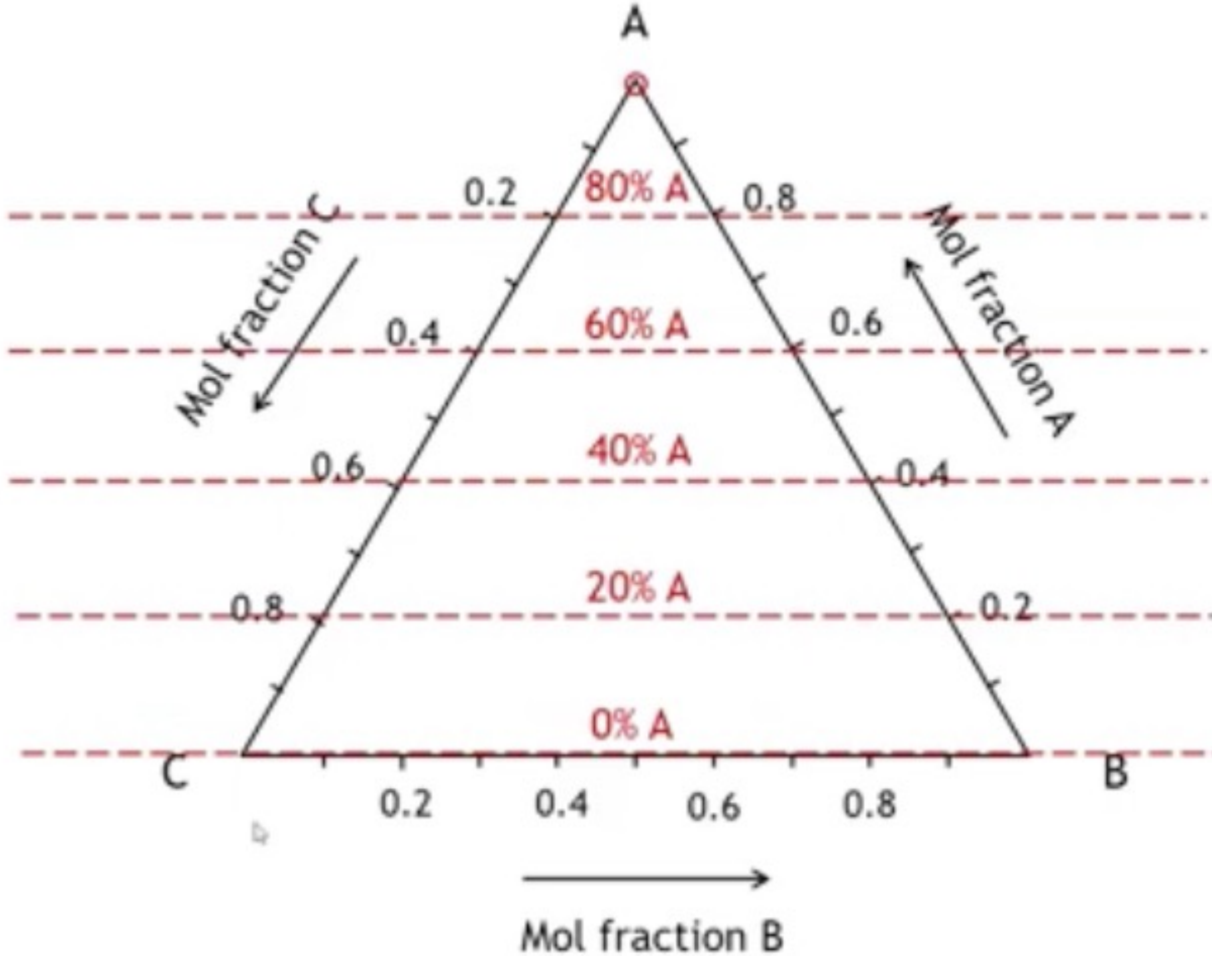
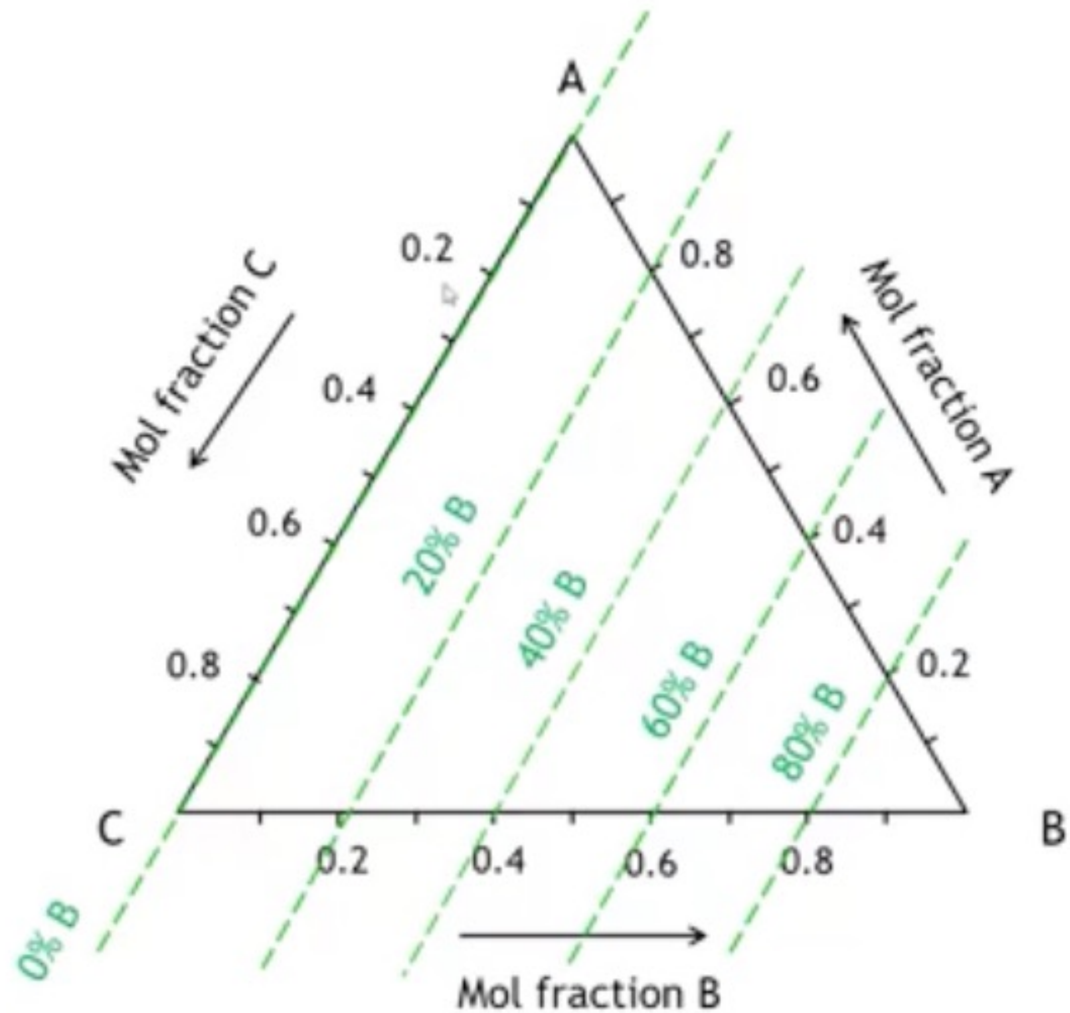
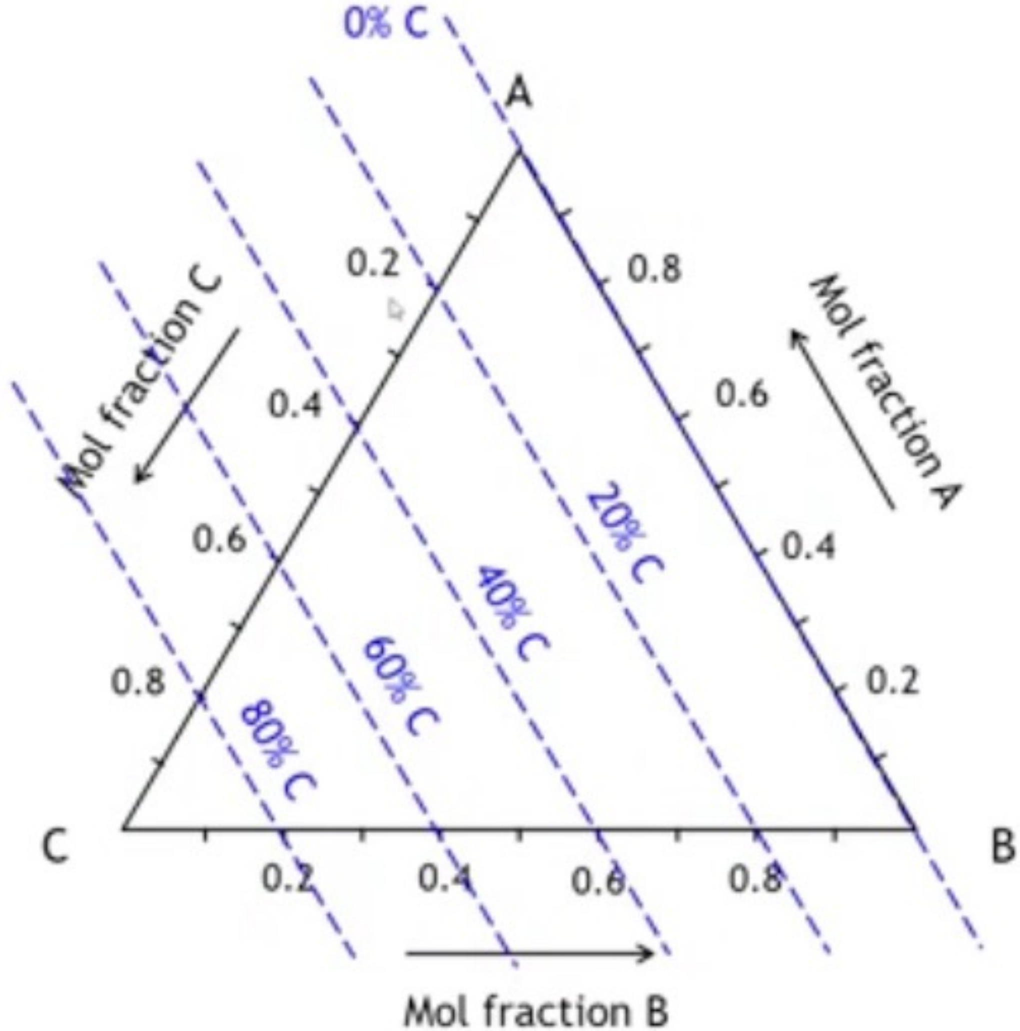


Determining the composition of a point

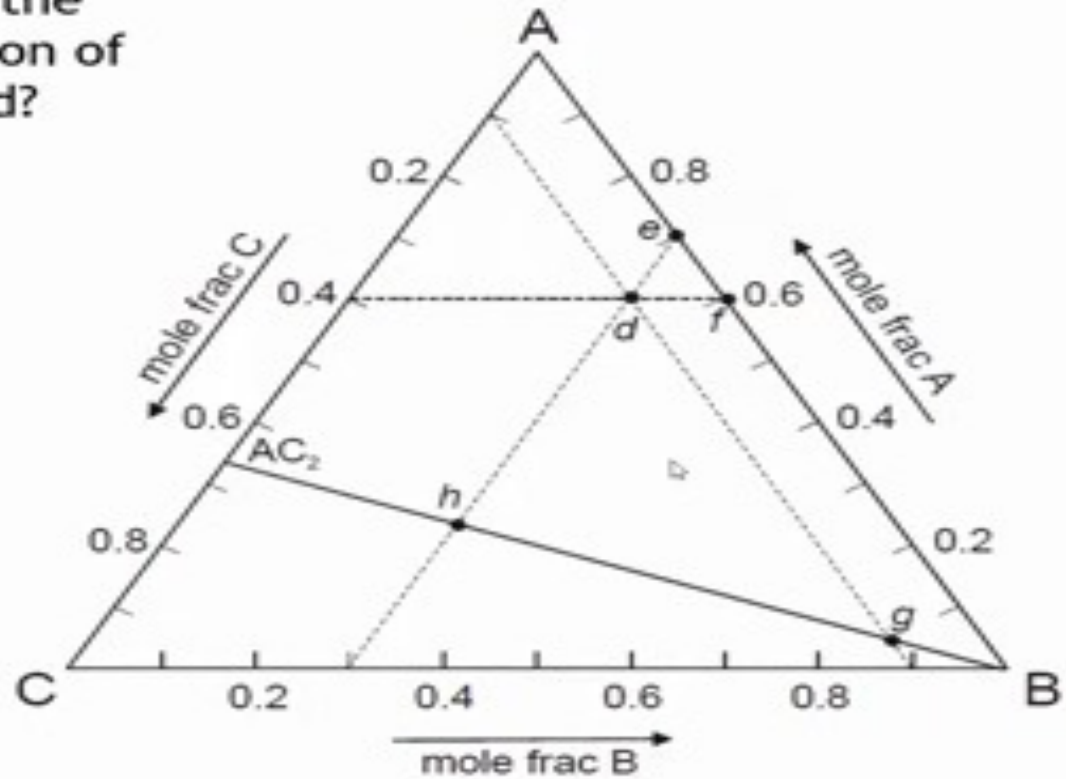


Determining the composition of a point



Determining the composition of a point

What is the composition of point d?



Determining the composition of a point

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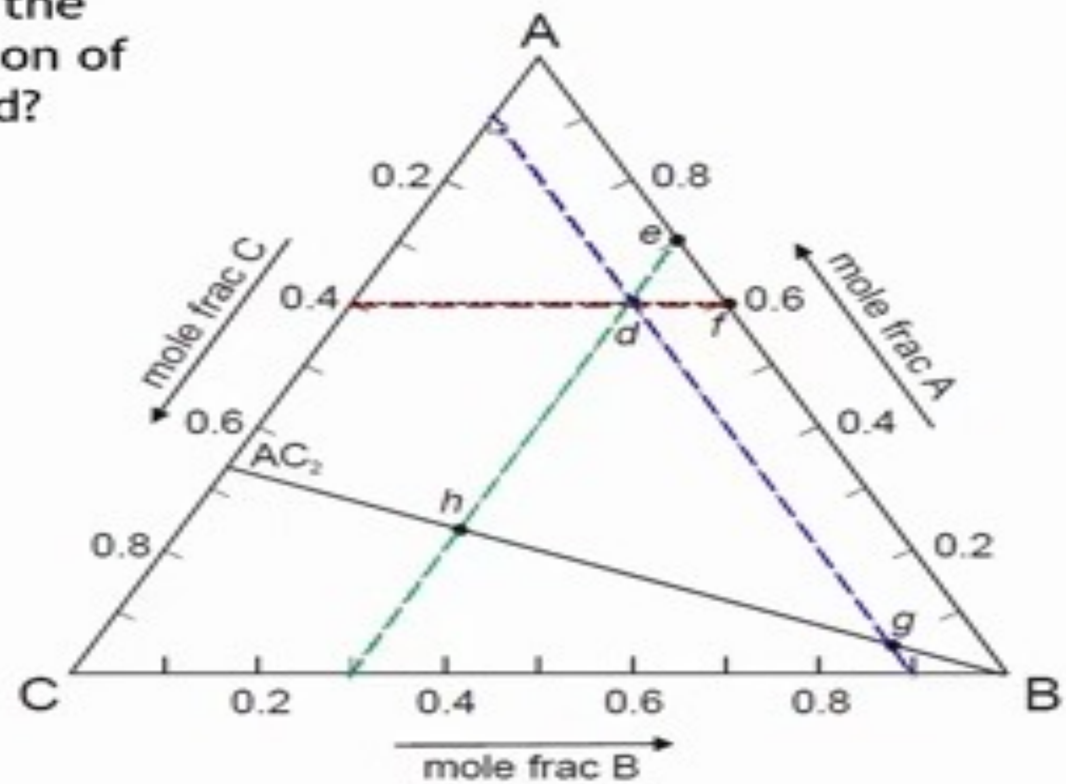


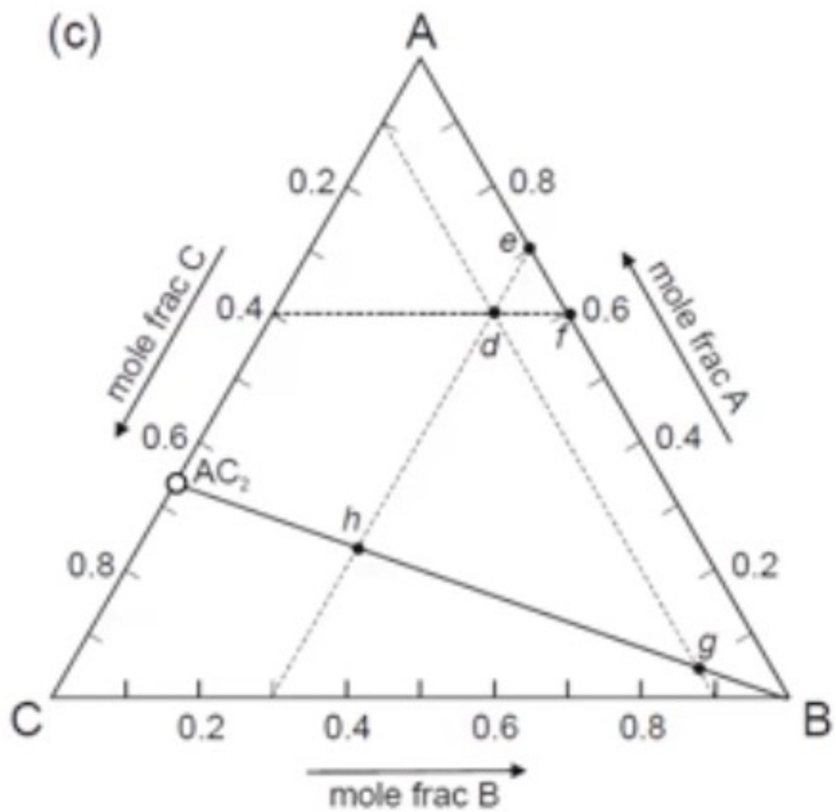
60% A

30% B

10% C

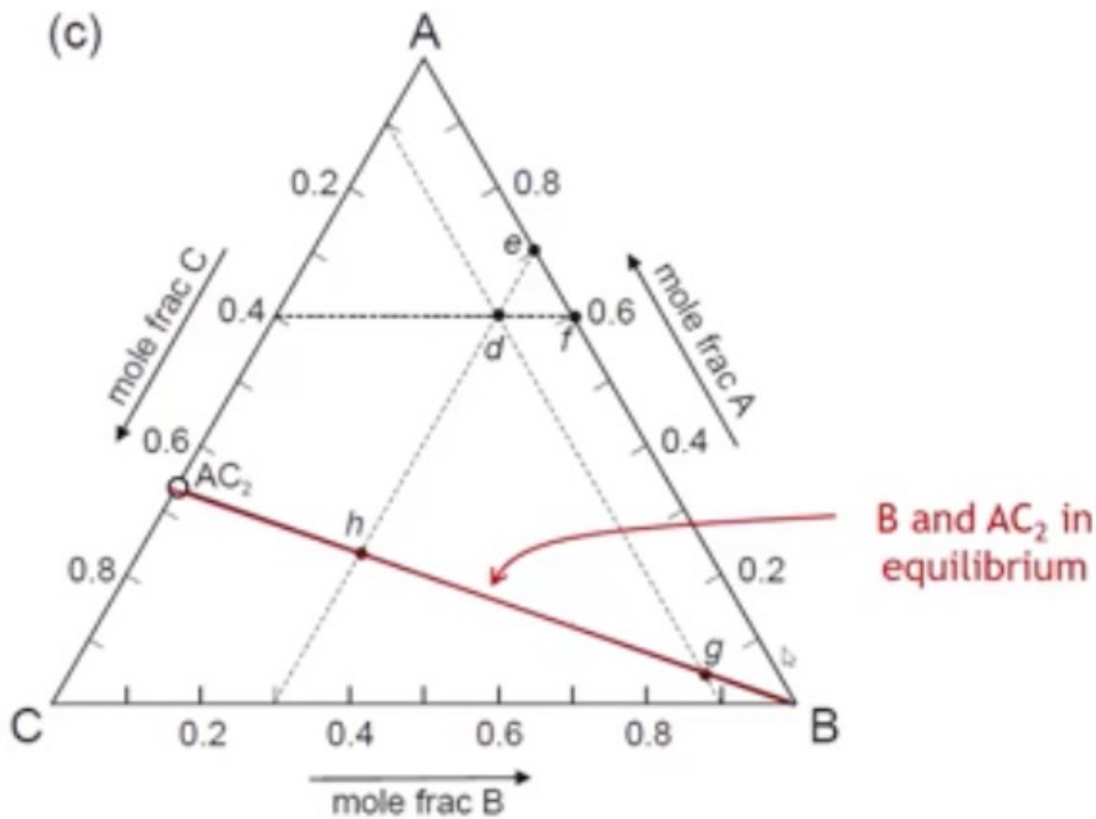
$A_{0.6}B_{0.3}C_{0.1}$

Reading a Ternary Phase Diagram



point = 1 phase

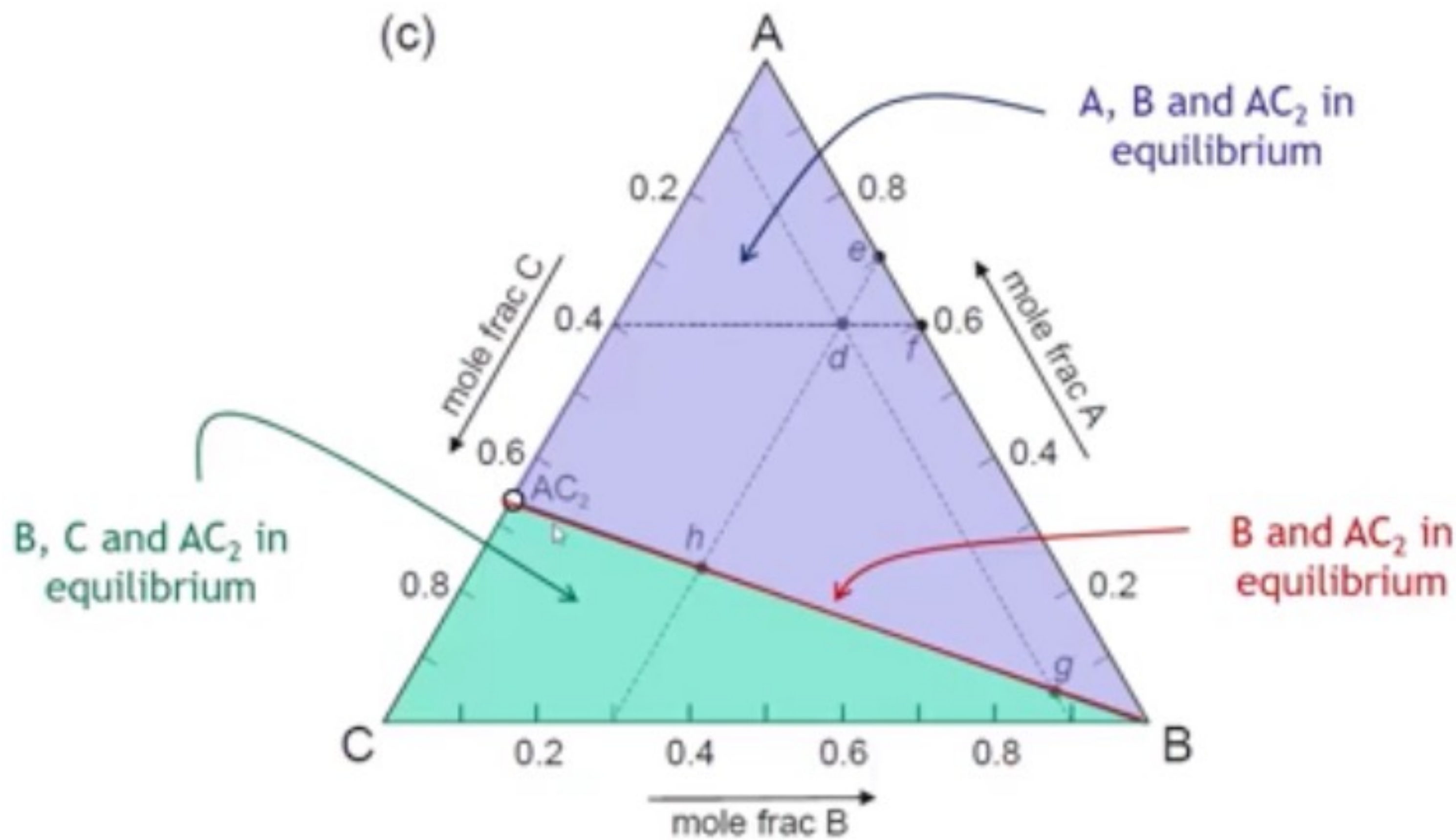
Reading a Ternary Phase Diagram



point = 1 phase

line = 2 phases

Reading a Ternary Phase Diagram

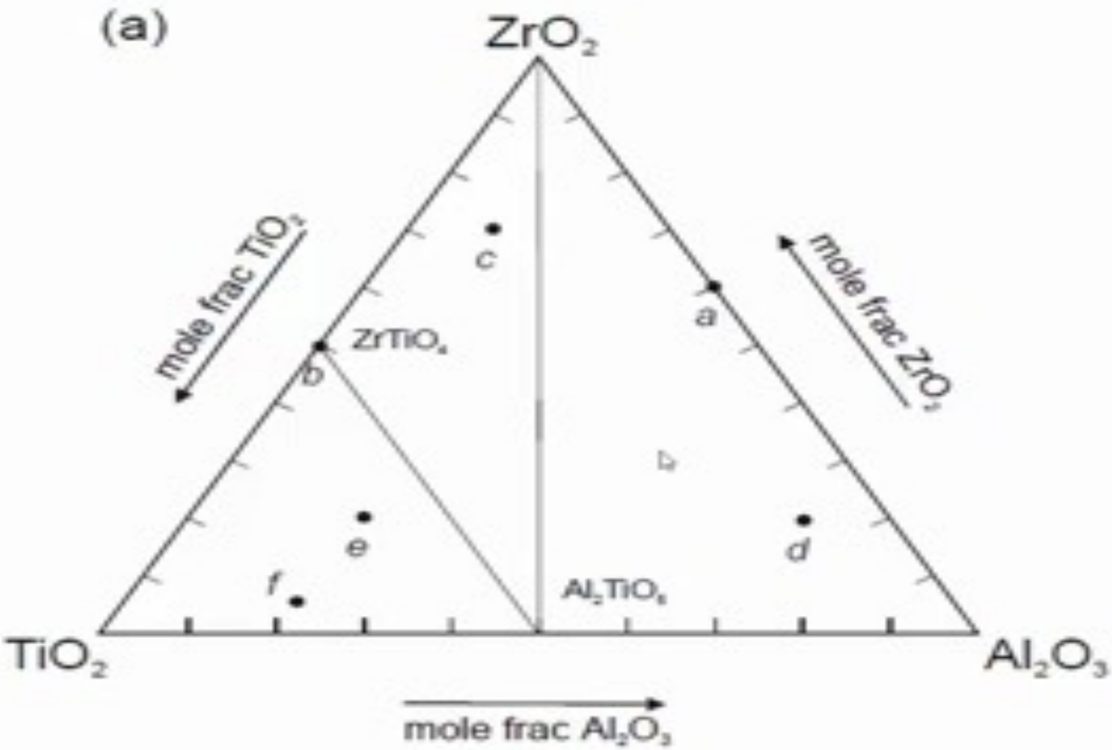


point = 1 phase

line = 2 phases

area = 3 phases

TiO_2 – ZrO_2 – Al_2O_3 phase diagram



What phases are present at each point?

a

b

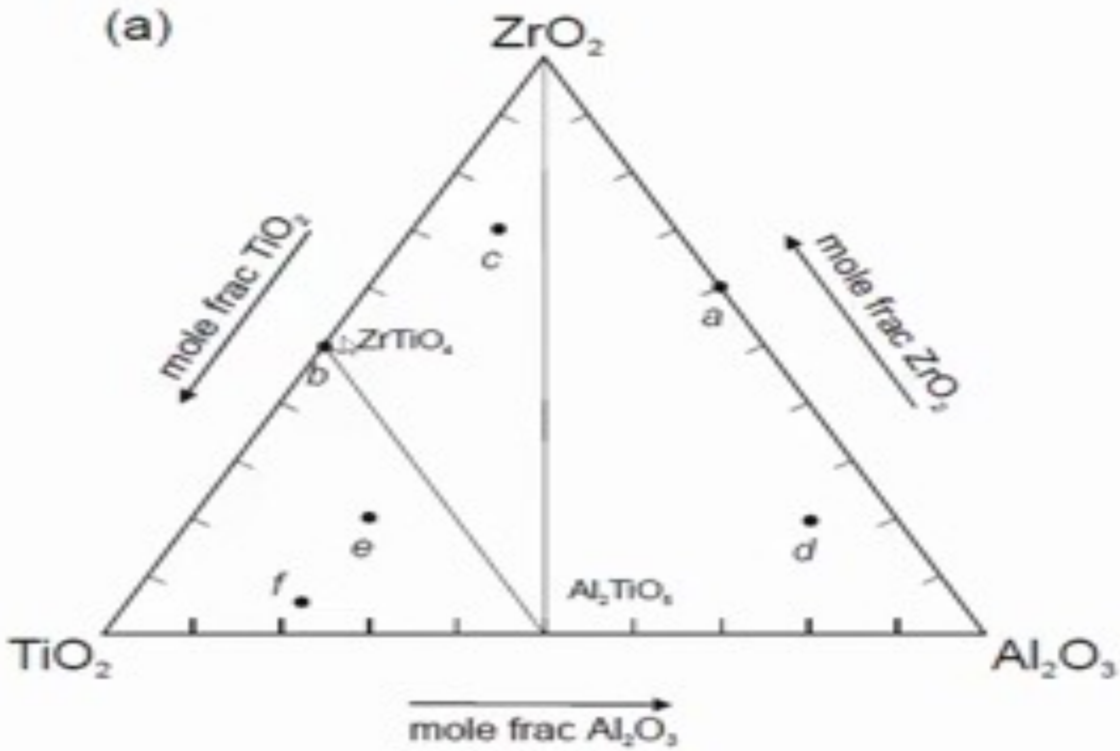
c

d

e

f

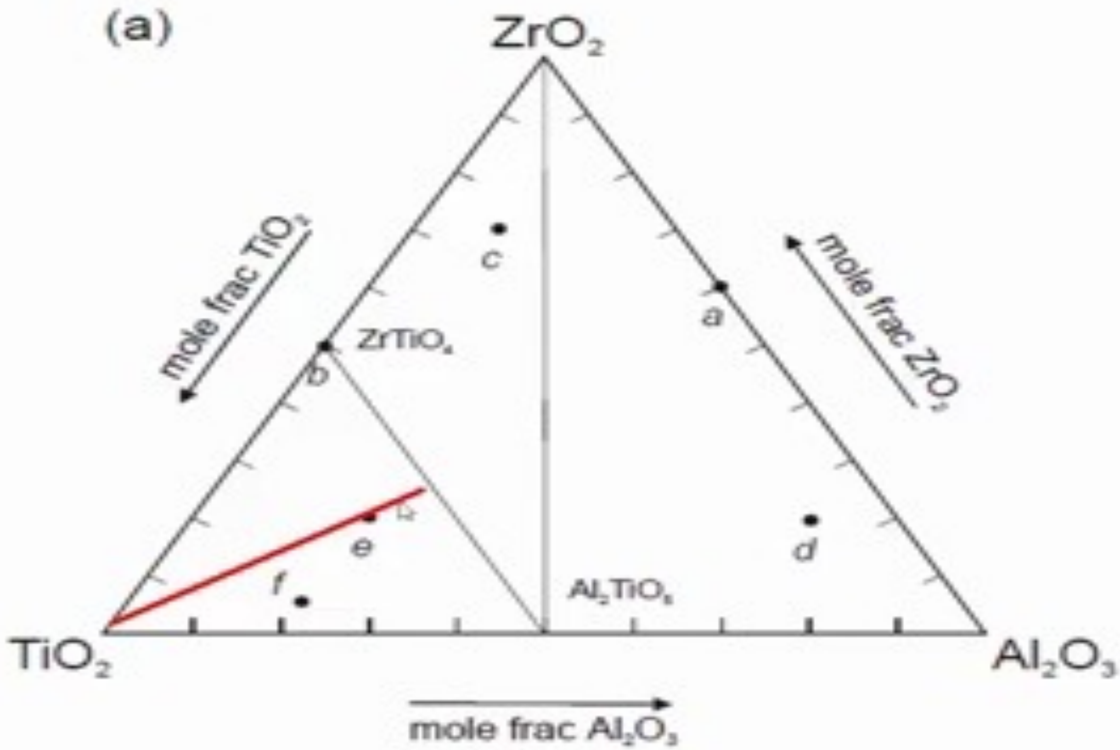
TiO_2 - ZrO_2 - Al_2O_3 phase diagram



What phases are present at each point?

- a ZrO_2 (60%), Al_2O_3 (40%)
- b $ZrTiO_4$
- c ZrO_2, $ZrTiO_4$, Al_2TiO_5
- d ZrO_2, Al_2TiO_5, Al_2O_3
- e $ZrTiO_4$, Al_2TiO_5, TiO_2
- f $ZrTiO_4$, Al_2TiO_5, TiO_2

TiO_2 – ZrO_2 – Al_2O_3 phase diagram



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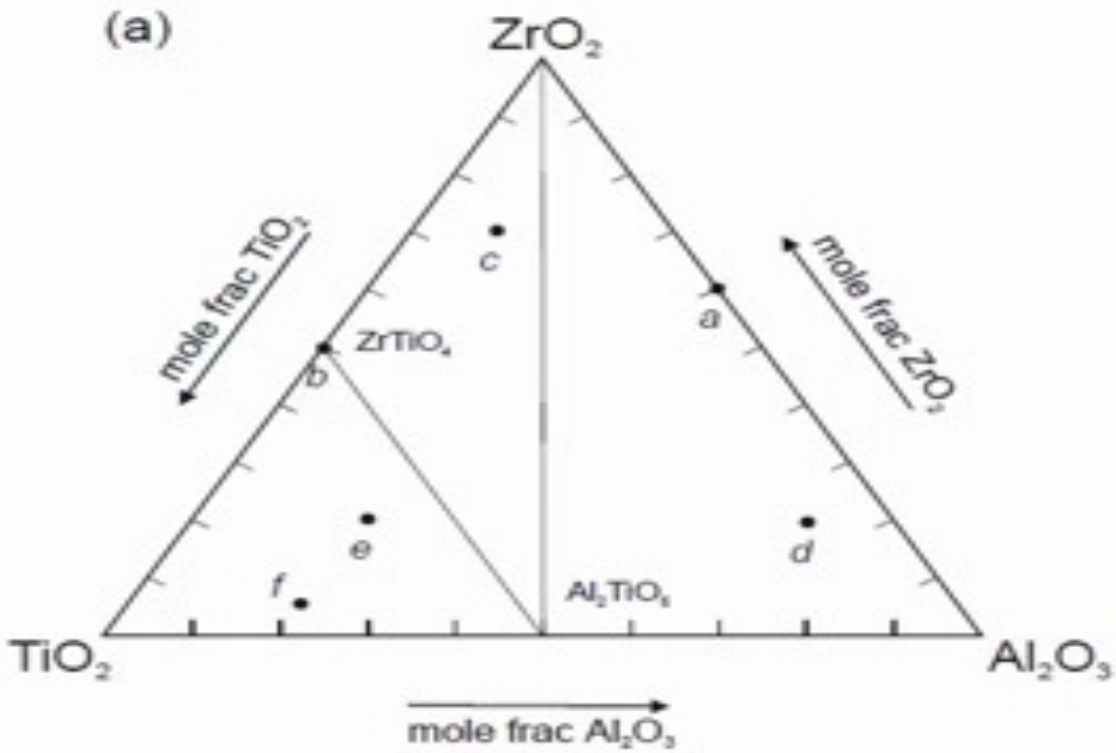
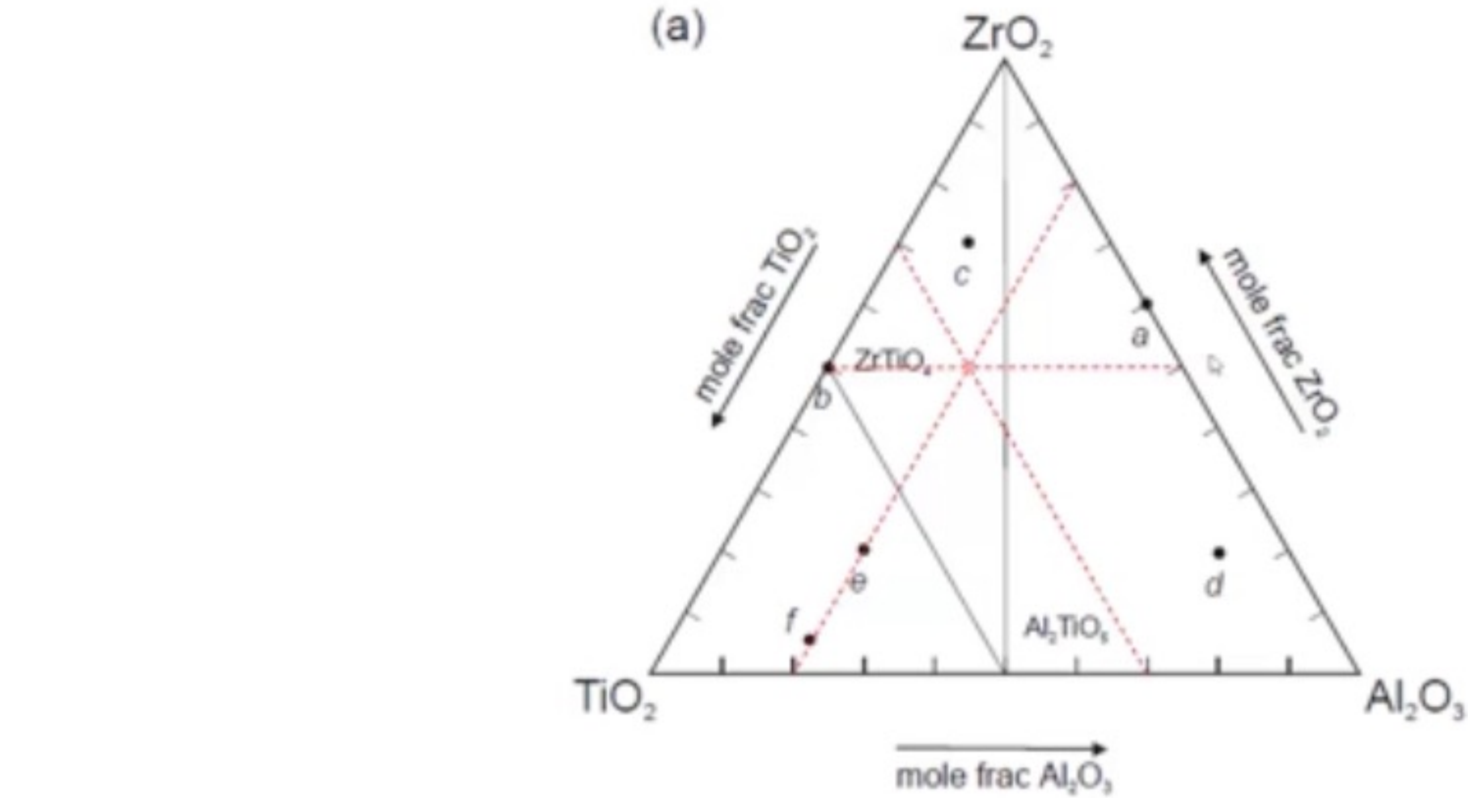
TiO_2 - ZrO_2 - Al_2O_3 phase diagram



Which phase(s) would be present if the overall composition was 50 mol% ZrO_2, 30 mol% TiO_2 and 20 mol% Al_2O_3?

TiO_2 - ZrO_2 - Al_2O_3 phase diagram



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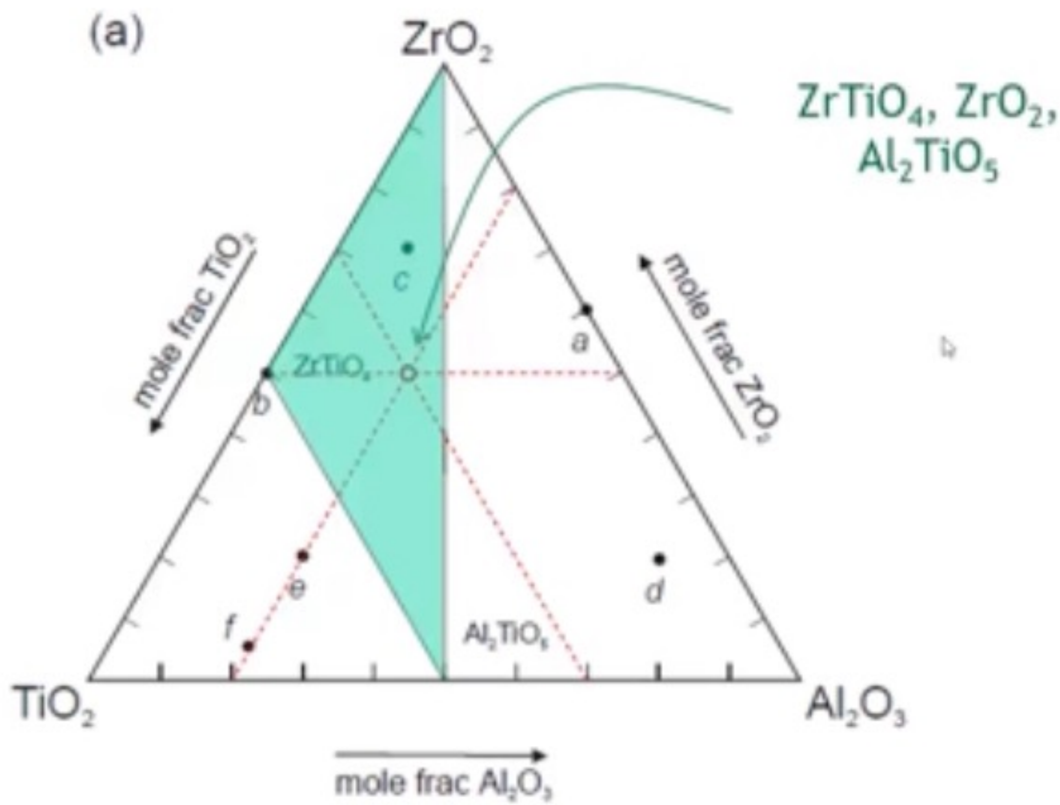
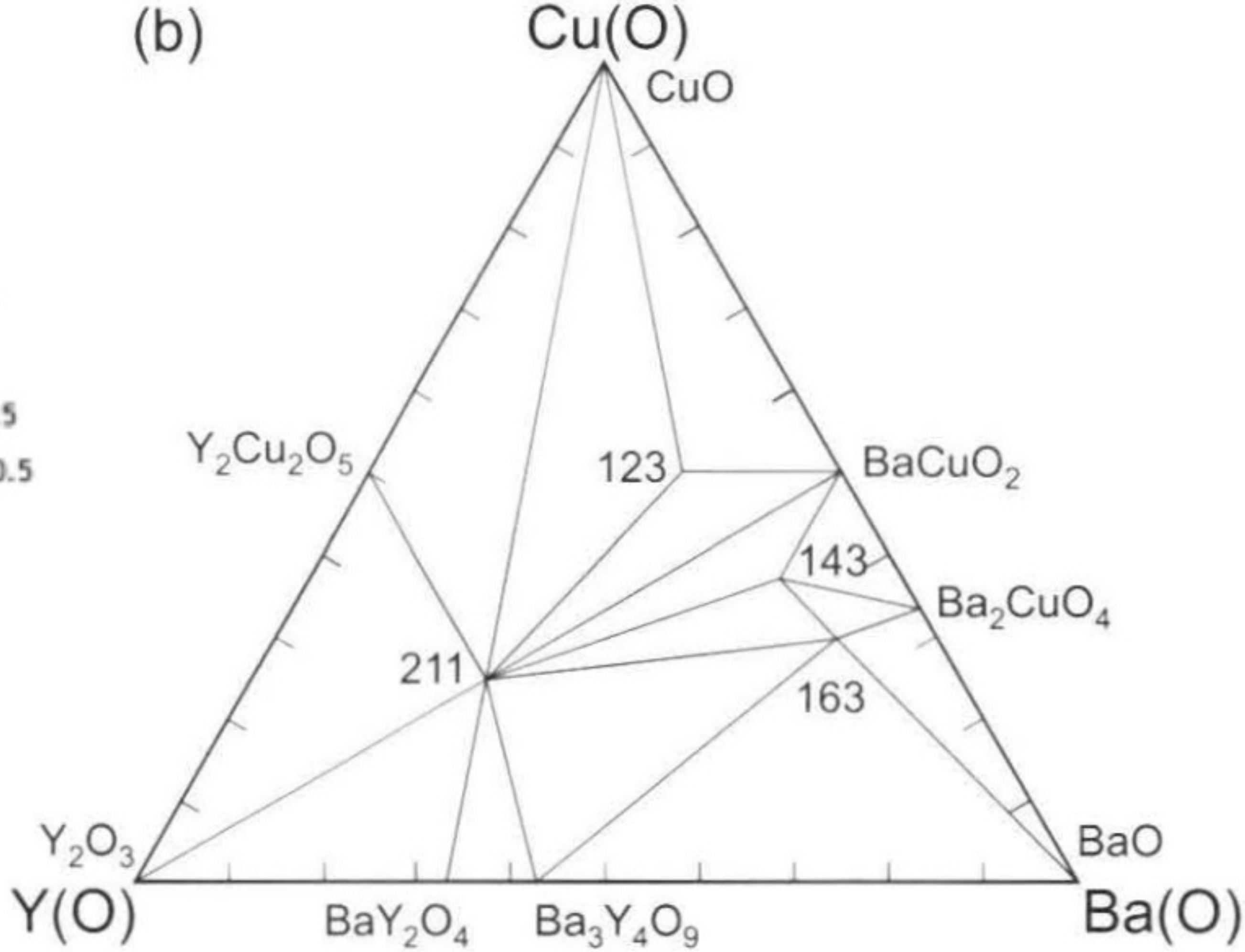


Which phase(s) would be present if the overall composition was 50 mol% ZrO_2, 30 mol% TiO_2 and 20 mol% Al_2O_3?

123 = $YBa_2Cu_3O_7$
211 = Y_2BaCuO_5
143 = $YBa_4Cu_3O_{8.5}$
163 = $YBa_6Cu_3O_{10.5}$

(b)



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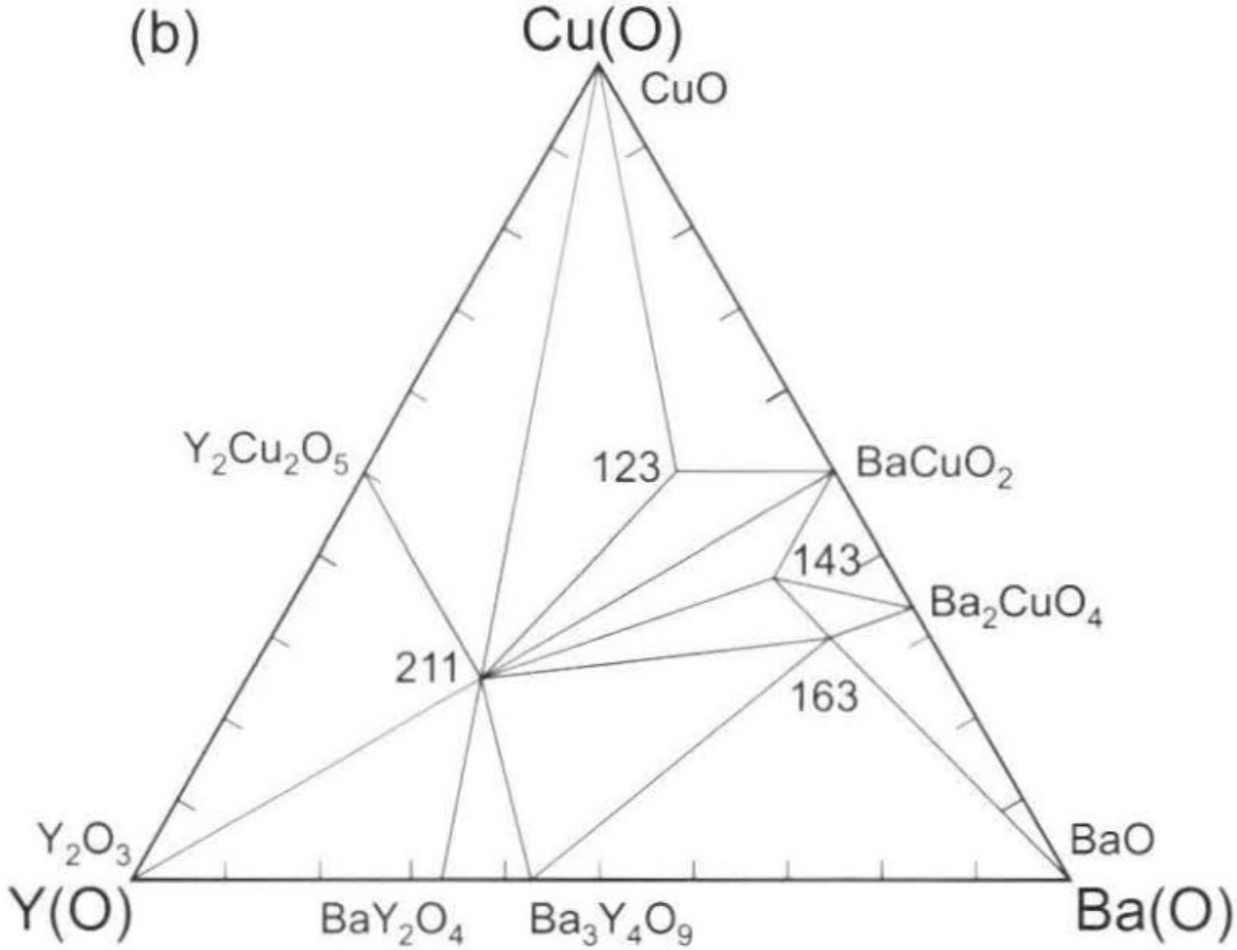

Which phase(s) would be present if the overall composition was $Y_2Ba_2Cu_4O_9$?

Y(O) - Ba(O) - Cu(O) phase diagram

123 = $YBa_2Cu_3O_7$
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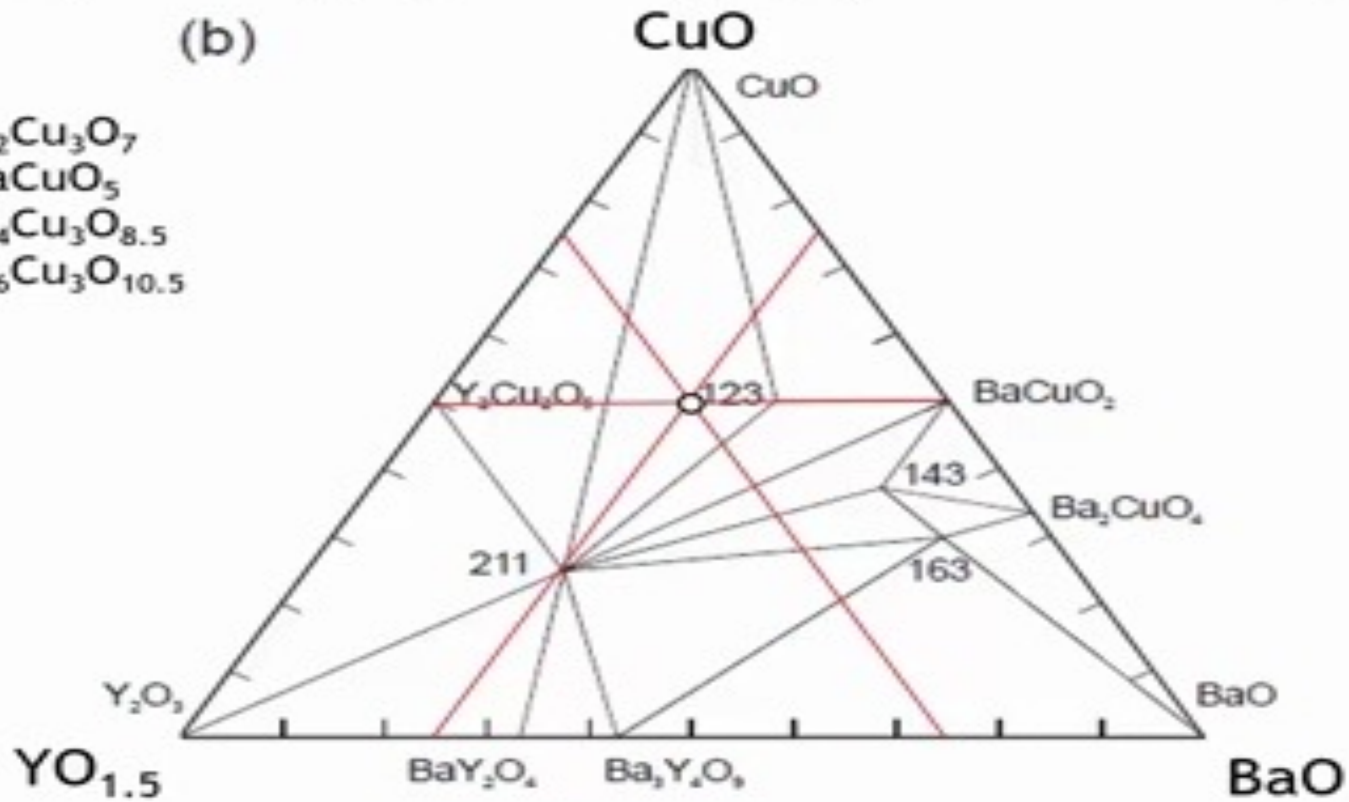
163 = $YBa_6Cu_3O_{10.5}$



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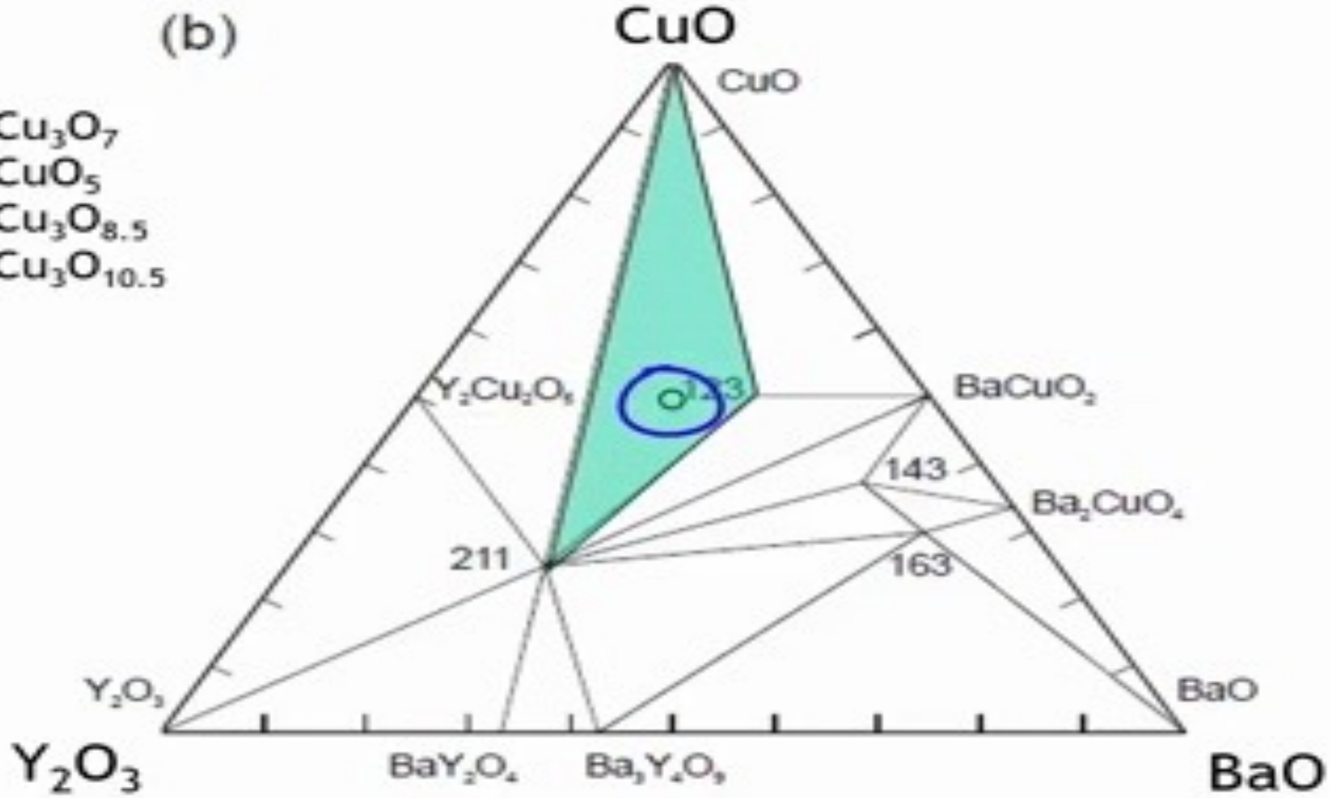

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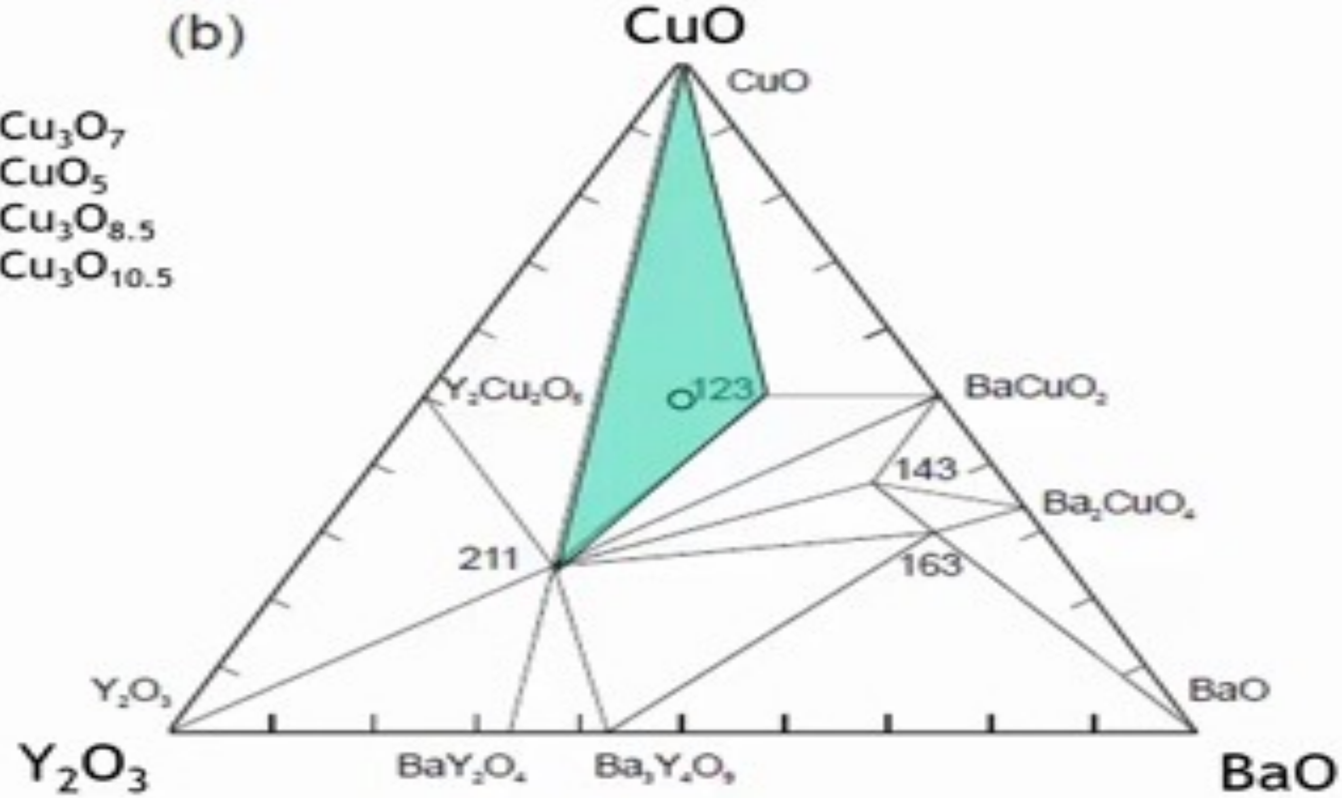

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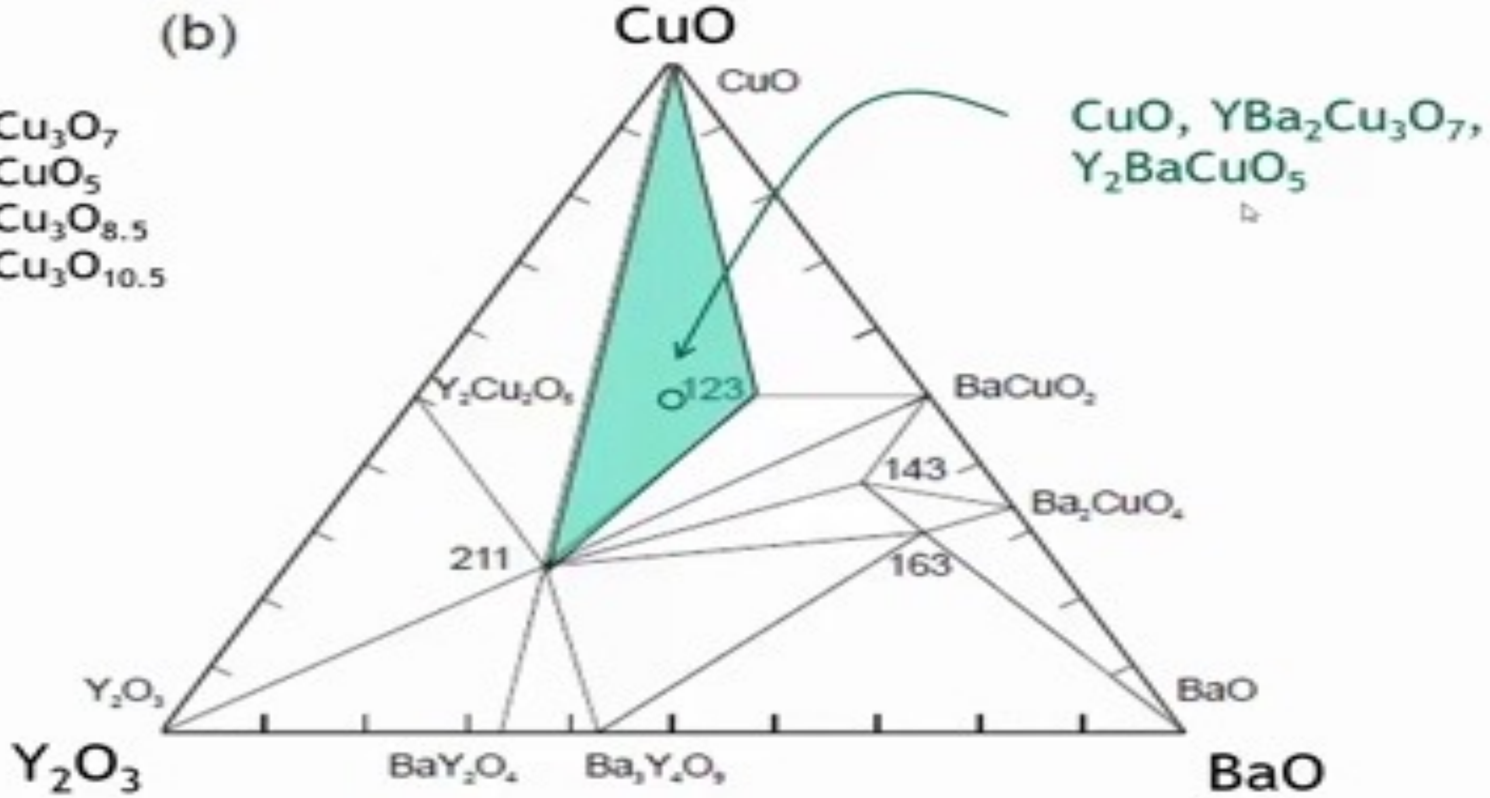


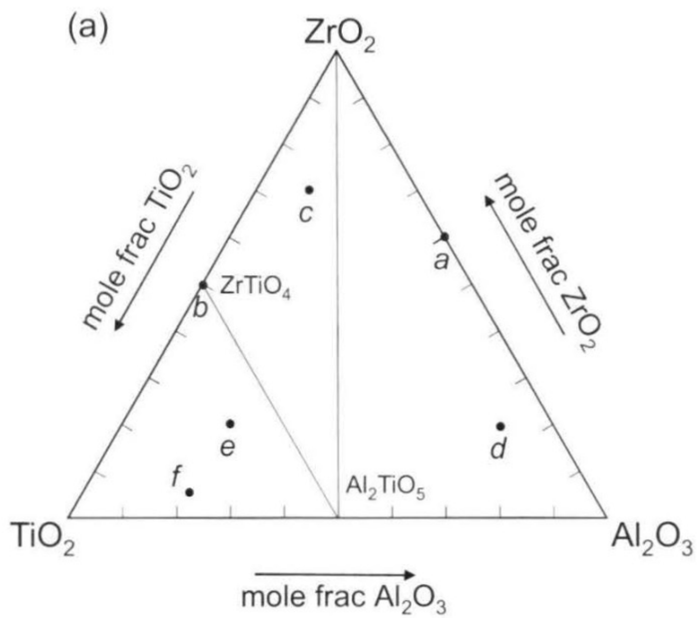
Which phase(s) would be present if the overall composition was $Y_2Ba_2Cu_4O_9$?

Summary: Ternary Phase Diagrams

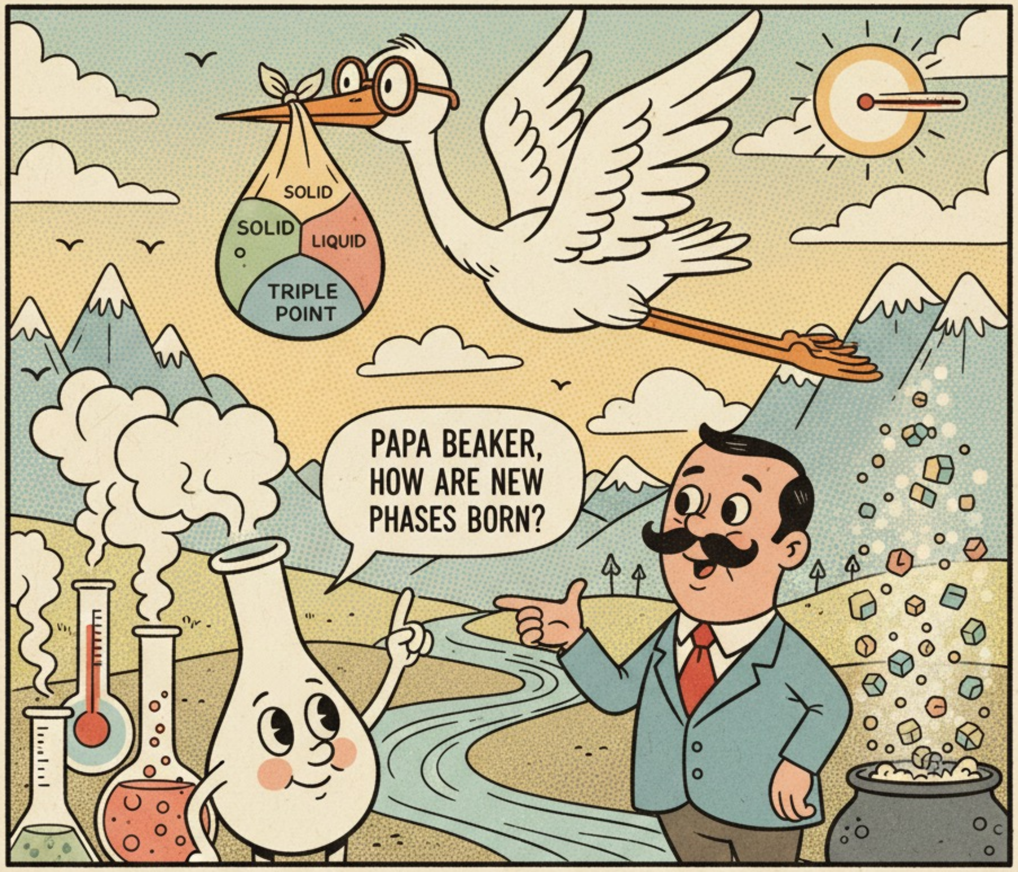
- Phase diagrams represent **thermodynamic stability** of phases as a function of composition, T, and P.
- A **full ternary system** requires 5D (3 compositions + T + P) → simplified by fixing pressure, often slicing at constant T.
- **2D triangular diagrams** represent isothermal sections below the liquidus.
- Each point in the triangle = a unique composition (relative fractions of A–B–C).
- **Tie-lines** connect coexisting phases; **tie-triangles** define three-phase equilibria.
- Lever rule applies inside two-phase and three-phase regions.

Homework

4.9 State the compounds you would expect to form and their relative phase fractions when oxide mixtures corresponding to points *a–f* in Figure 4.11 are reacted under equilibrium conditions.

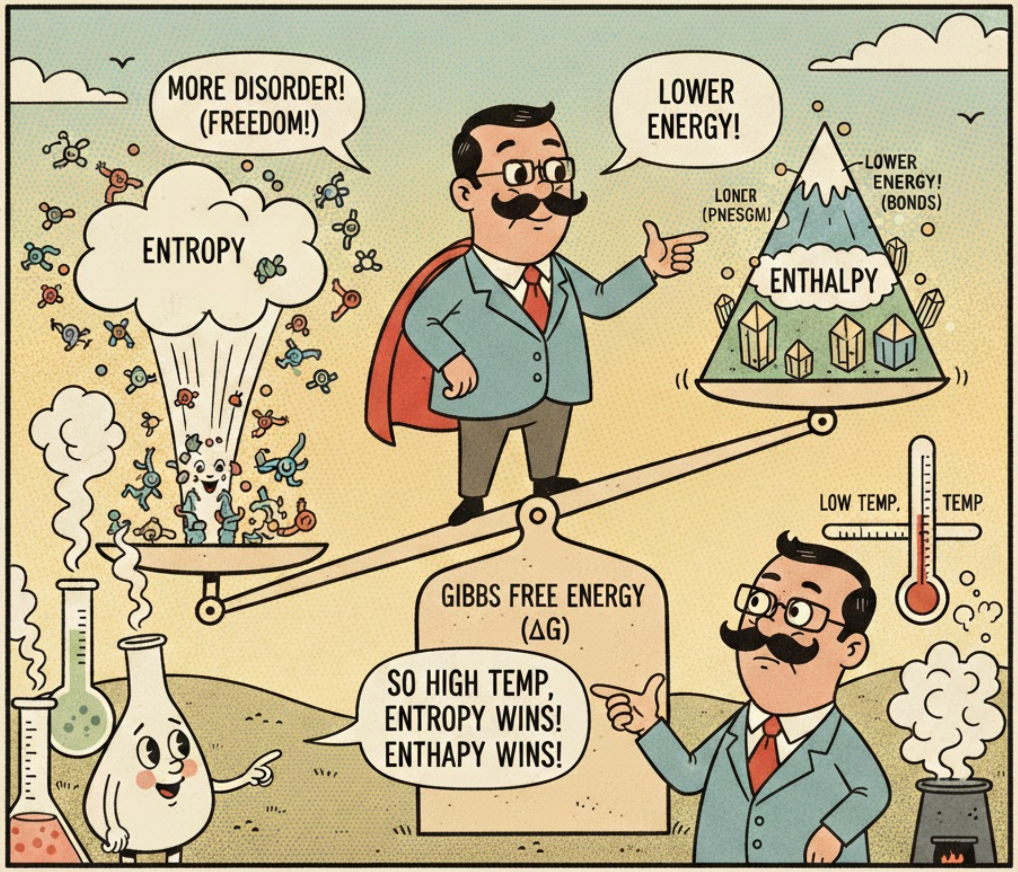


WHERE DO PHASE DIAGRAMS COME FROM?



A JOURNEY OF TEMPERATURE, PRESSURE & MOLEUCLAR LOVE

ENTROPY & ENTHAL Y: A LOVE-HATE STORY



PHASE TRANSITIONS: IT ALL DEPENDS ON THE TEMPERATURE!

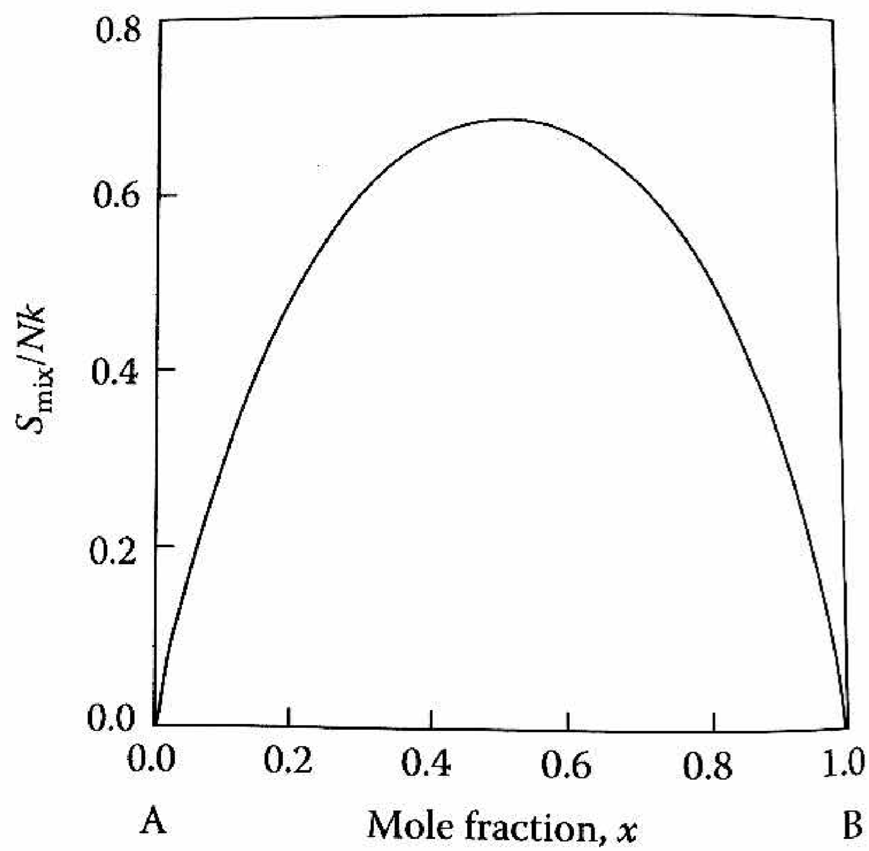
Where do Phase Diagrams Come From?

$F = U - TS$

Matter seeks to minimize the Helmoltz free energy at constant temp and Volume

$$S_{\text{mix}} = -Nk\left[\ln(1-x) + x\ln\left(\frac{1-x}{x}\right)\right]$$

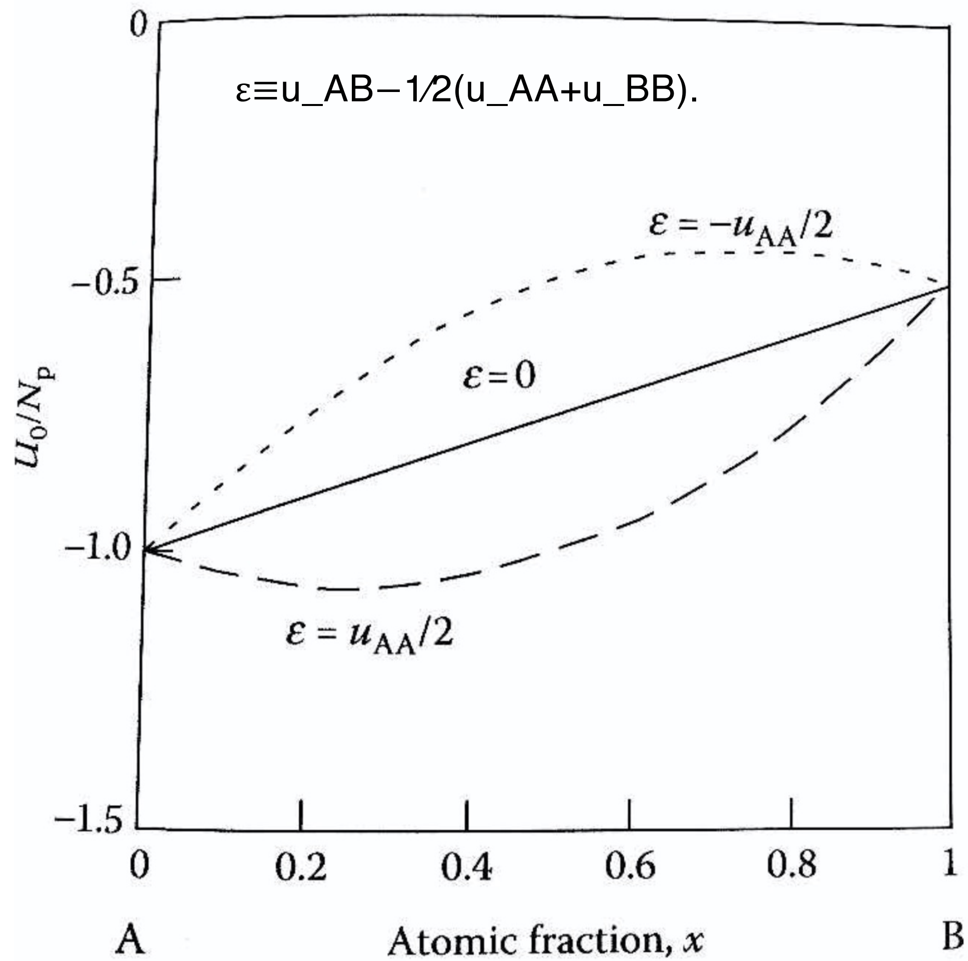
Entropy term is positive because there are more ways of rearranging 2 atoms in space then 1. Maximum at x=0.5.



$$U_{\text{tot}} = N\frac{p}{2}[(1-x)u_{AA} + xu_{BB} + 2x(1-x)\varepsilon]$$

Internal energy term is from bonding, which can be energetically favorable or unfavorable.

P is number of nearest neighbors.



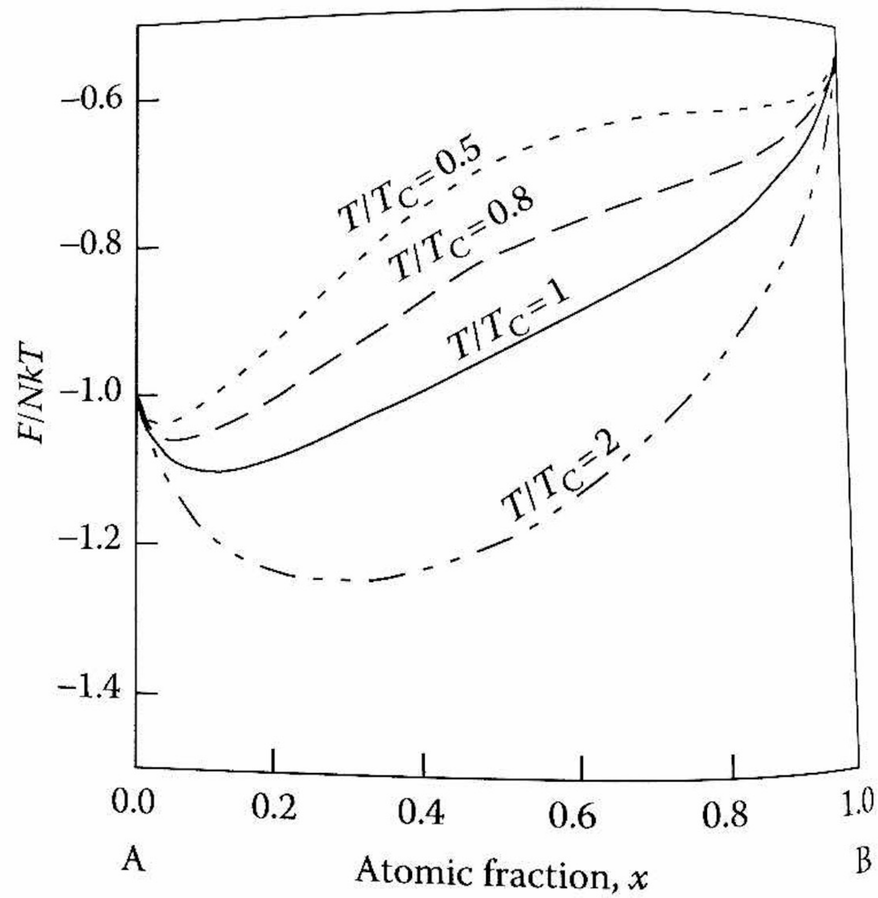
F(x,T)=ΔU(x)−T S_mix(x)

$$F(x,T) = \frac{Np}{2}\left[(1-x)\mu_{AA} + x\mu_{BB} + 2x(1-x)\varepsilon\right] + NkT\left[(1-x)\ln(1-x) + x\ln(x)\right]$$

At High T, Entropy Term dominates and mixing is favorable.

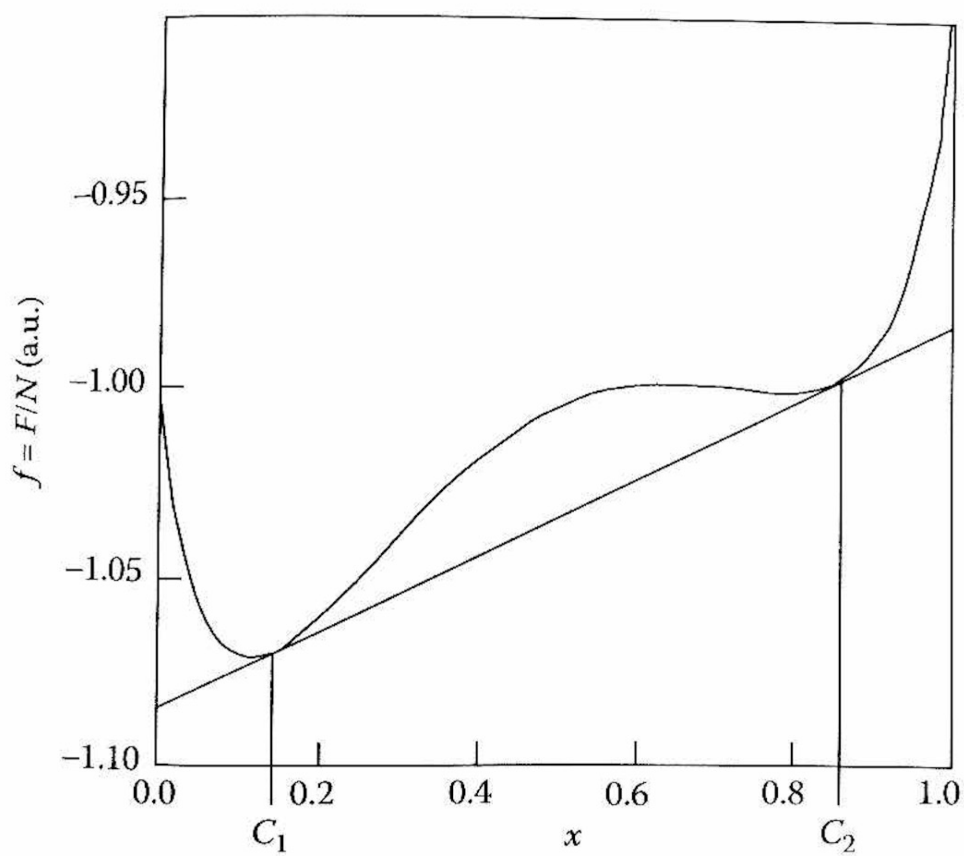
At low T, local minima appear, leading to phase segregation.

$T_c = p\varepsilon/2k$
p = #nearest neighbors
ε= energy penalty per unlike bond
k= Boltzmann constant

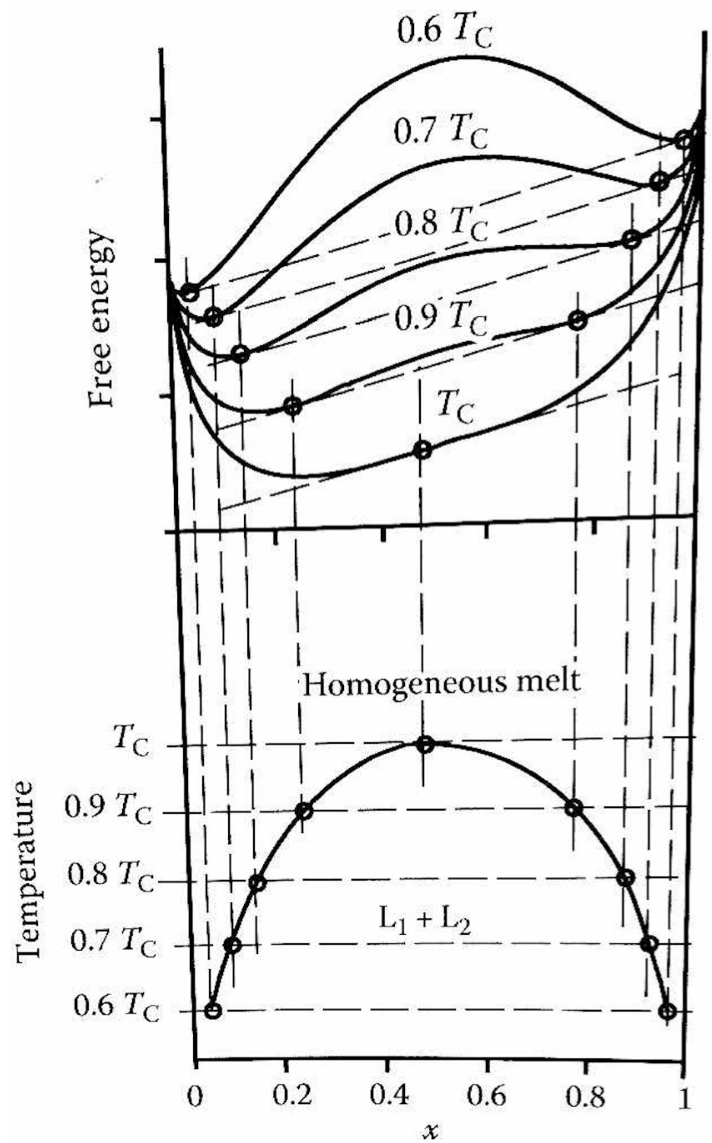


Method of Tangents

Method of Tangents can be used to find the compositions of each phase that are in equilibrium, in this case 13.2 % for alpha and 85.9 % for beta.



Applying the method of Tangents to free energy curves at different temperatures can be used to create a phase diagram.



Example of real ideal system (no heat of mixing)

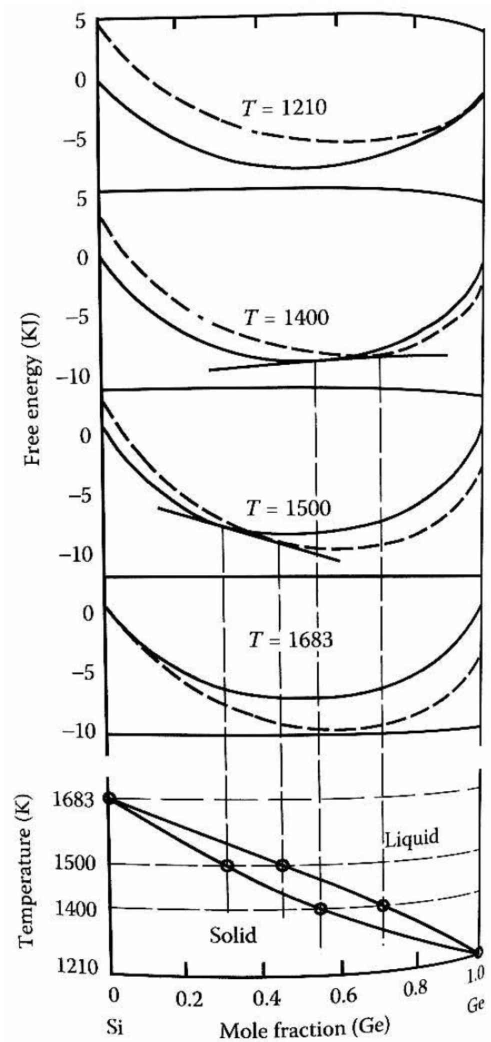


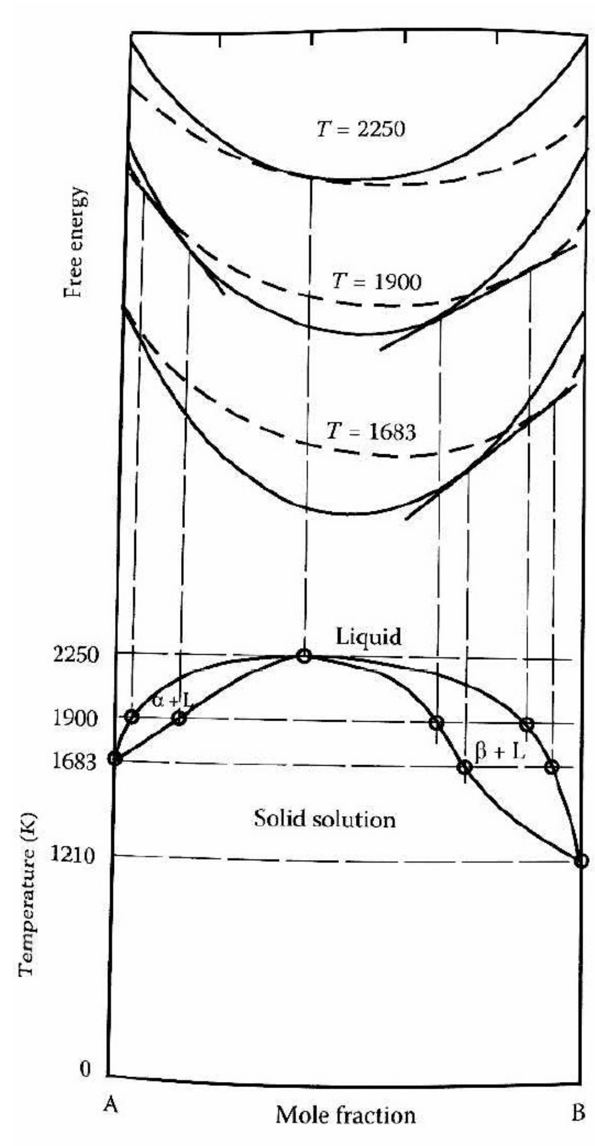
FIGURE 12.7
Construction of a phase diagram for the Si–Ge system, which is assumed to be isomorphic with no excess energy of mixing in either phase. The solid lines represent the free energy of the solid phase and the dashed line represent the free energies of the liquid phase. In the phase diagram, the line above which everything is liquid is the liquidus line. The line below which everything is solid is the solidus line. Liquid and solid coexist in the region between these two lines.

$$F_S(x \cdot T) = RT(x\ln(x) + (1-x)\ln(1-x))$$

$$F_L(x \cdot T) = RT(x\ln(x) + (1-x)\ln(1-x)) + \Delta S[x(T_B - T) + (1-x)(T_A - T)].$$

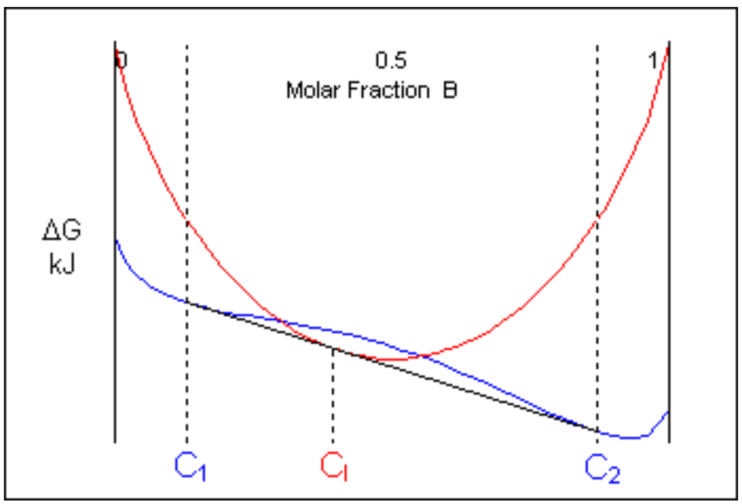
Example of system with heat of mixing of -30 kJ/mol

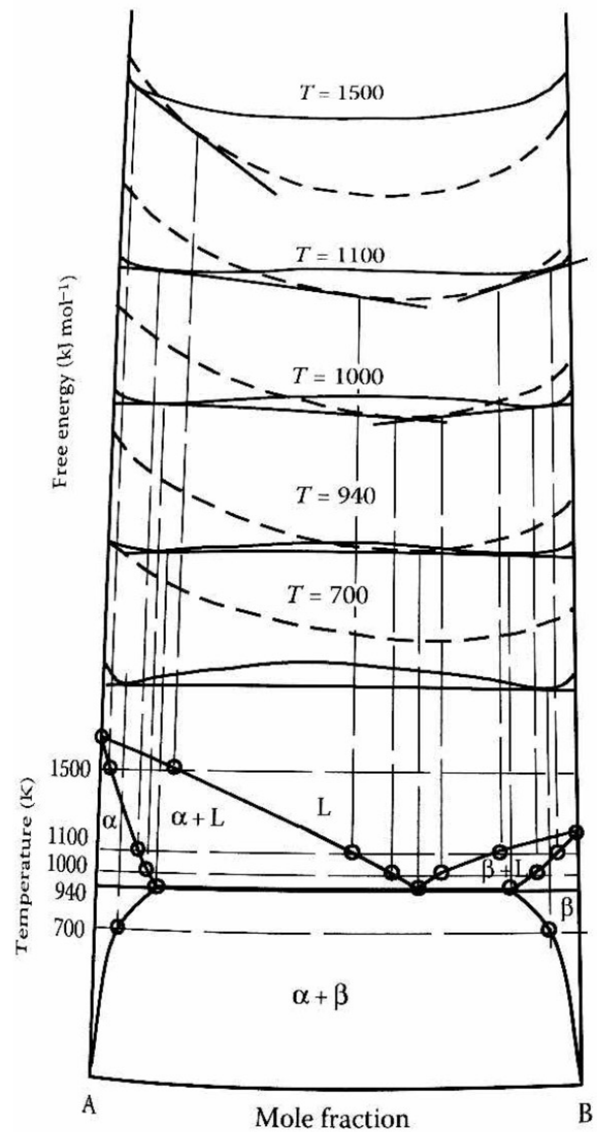
Positive heat of mixing means the melting point of the alloy is not higher than the melting point of the pure phases.



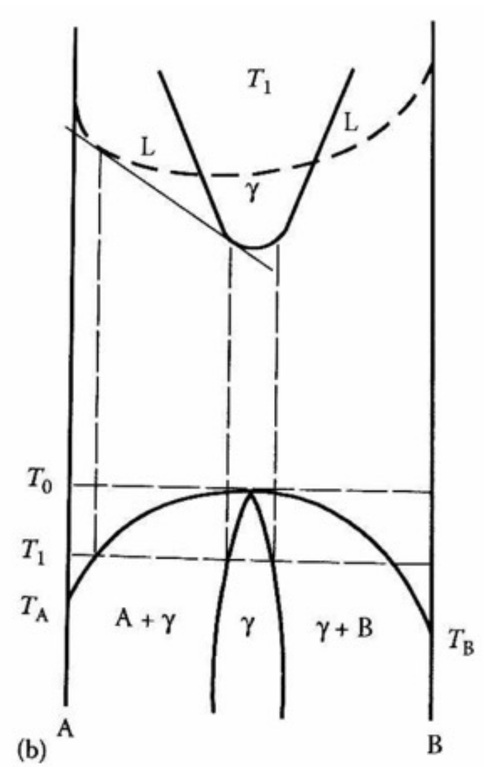
Example of system with
Positive heat of mixing.

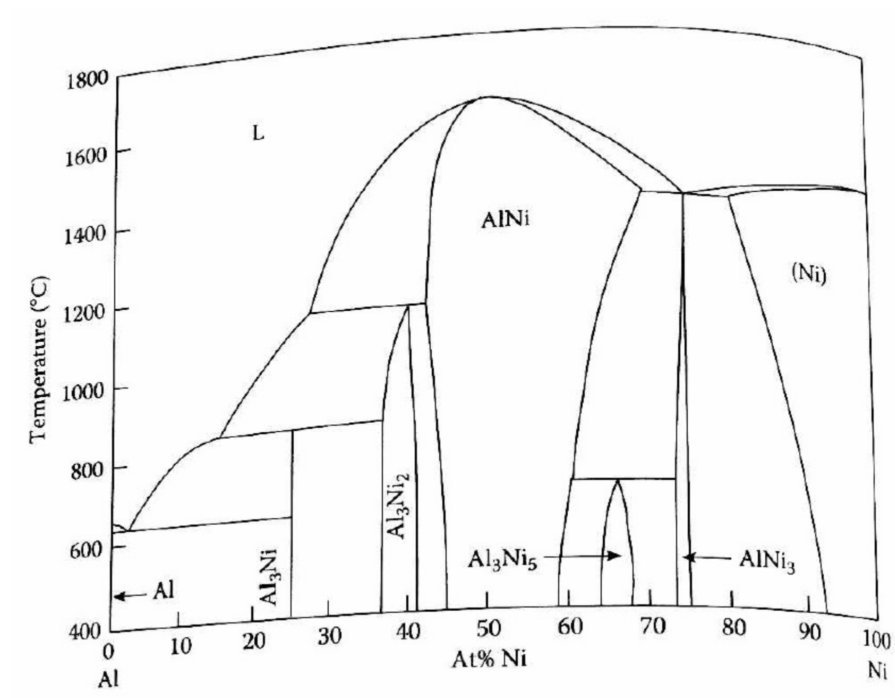
The point where the liquid line minima meets the tangents of the two solid phase minima leads to a lower melting point eutectic.



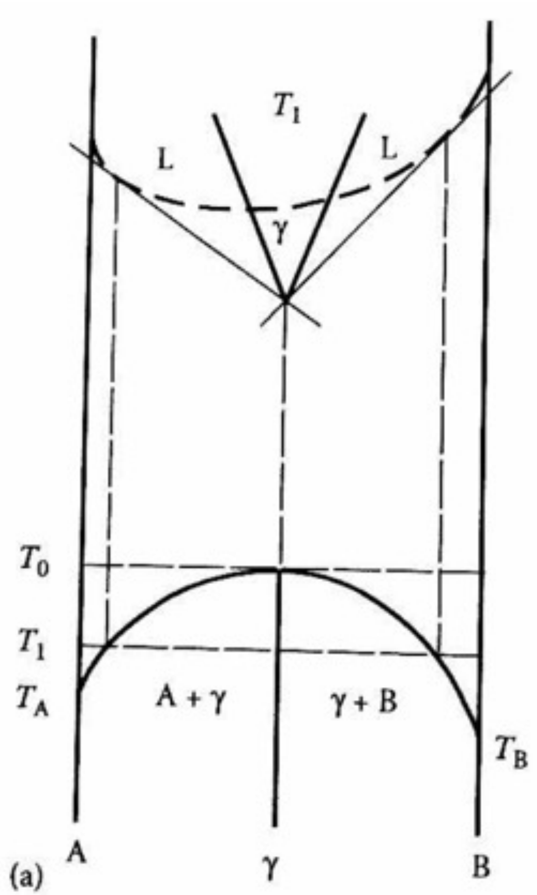


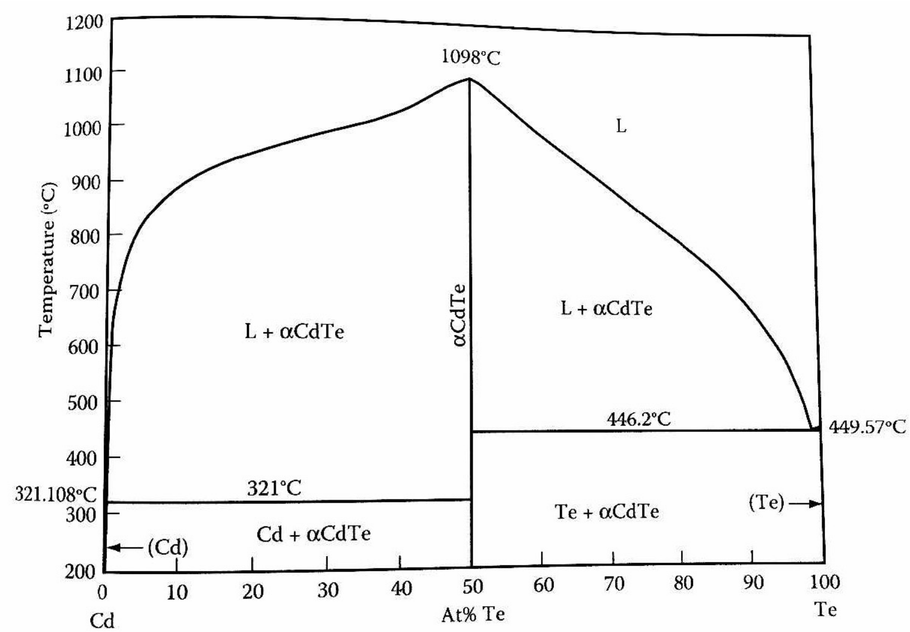
Example of solid solution intermediate phase





Example of Line compound.





Homework Questions

1. Define the parameter ε in the mean-field model of mixing. Physically, what does it mean if $\varepsilon < 0$? What about $\varepsilon > 0$?
2. Contrast the phase diagram topologies of an isomorphous alloy (Si–Ge) and an endothermically mixing alloy (with a eutectic). What underlying free-energy features produce the differences?
3. Calculate the entropy of mixing (per mole, in J/mol·K) for a binary solution with mole fraction $x_A = 0.25$, $x_B = 0.75$. Use $R = 8.314\ \text{J/molK}$.
4. Using the regular solution model with $p = 12$, $\varepsilon = 12\ \text{meV}$, compute the critical temperature T_c. Express your answer in Kelvin. (Constants: $1\ \text{eV} = 1.602 \times 10^{-19}\ \text{J},\ k_B = 8.617 \times 10^{-5}\ \text{eV/K}$).