CHEM 548: MATERIALS CHEMISTRY

PHASE DIAGRAMS: BINARY, TERNARY, AND FREE ENERGY

Mon 09/28/2026 | Meeting 10

Ternary phase diagrams, the ternary lever rule, and phase-diagram construction from free energy

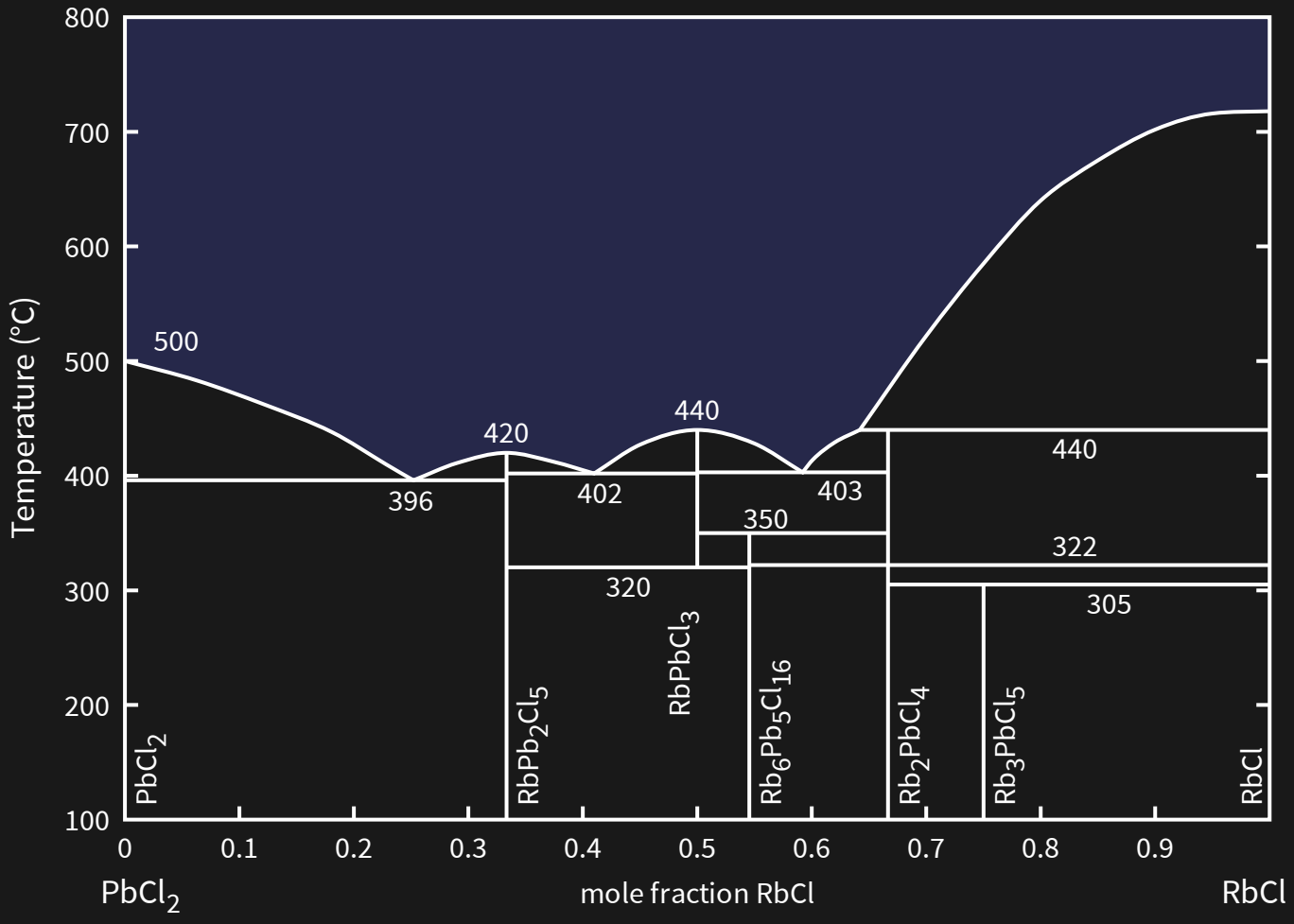
Reading: Woodward, Karen, Evans, and Vogt, *Solid State Materials Chemistry* Ch. 4 §§4.2–4.3

BINARY PHASE DIAGRAMS PART 2

Learning objectives — by the end of this lecture, you should be able to:

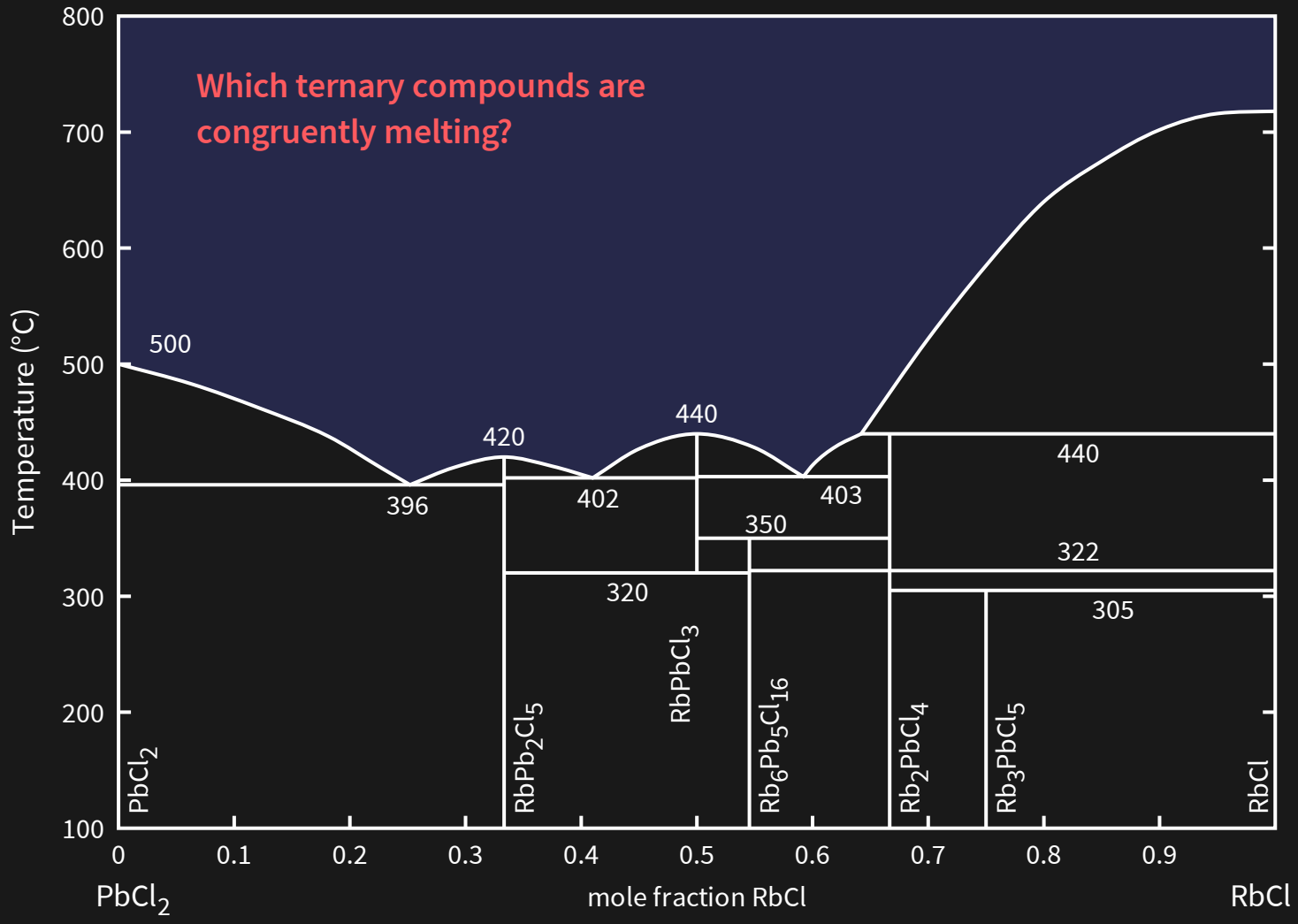
Intermediate compound	Interpret binary phase diagrams that include one.
Melting behaviour	Distinguish congruent from incongruent melting.
Invariant points	Identify eutectic and peritectic points and explain their significance.
Phase fields	Predict which phases are in equilibrium in a given region of a diagram.
Crystal growth	Assess strategies for growing single crystals of intermediate compounds.

$PBCL_2$–RBCL PHASE DIAGRAM

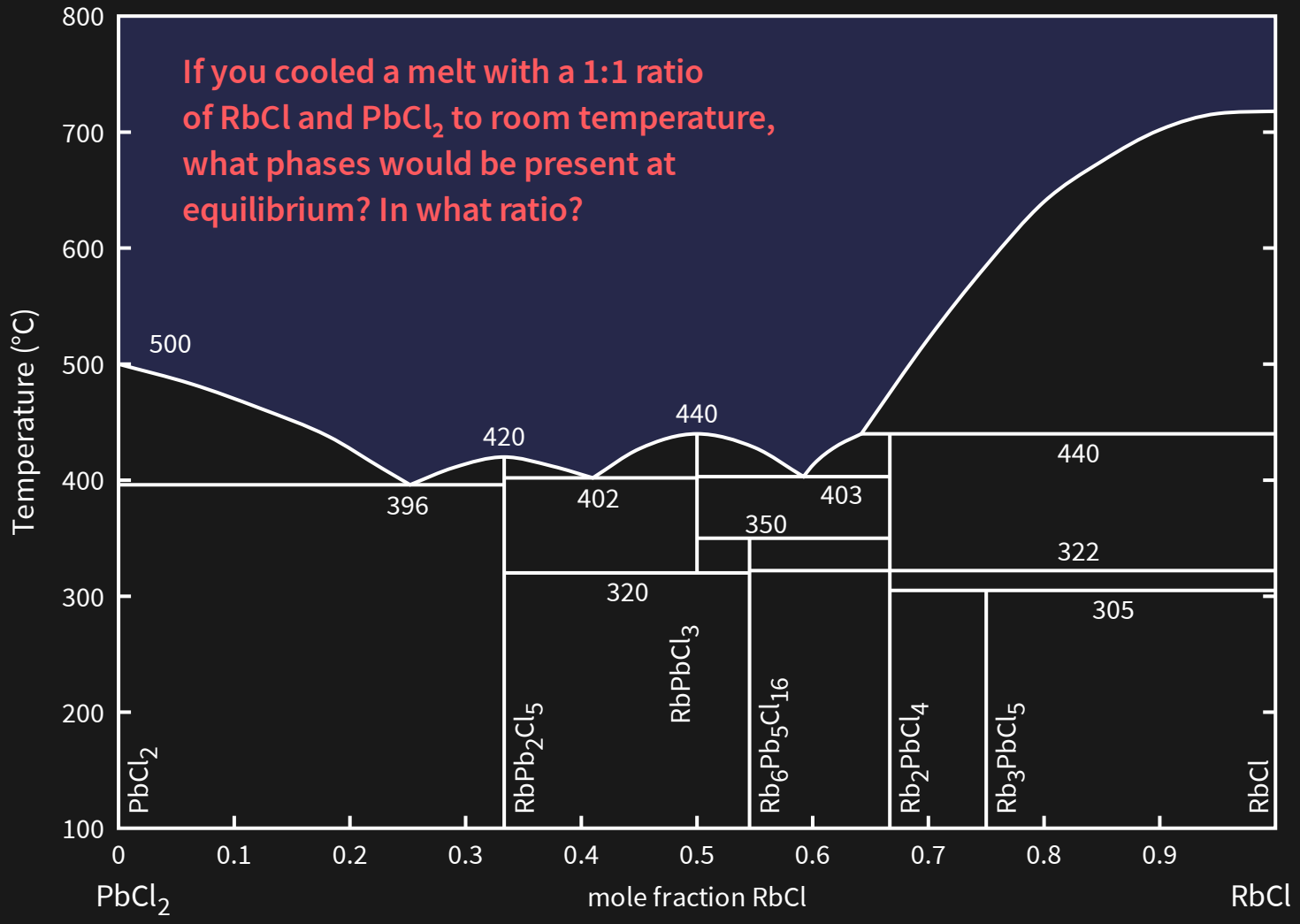


Five intermediate compounds and a eutectic at 396 °C, with the interpretation questions on the slides that follow.

A REAL BINARY DIAGRAM: $PBCL_2$–RBCL



EQUILIBRIA AND GROWTH IN $PBCL_2$–RBCL



SUMMARY

An intermediate compound splits a binary diagram into two eutectic diagrams side by side, and how that compound melts decides everything that follows.

Feature	On the diagram	Consequence for growth
Line phase (AB_2)	A vertical line at fixed stoichiometry	No composition range to work with
Congruent melting	That line runs all the way up to the liquidus	Cool a melt of the same composition slowly
Incongruent melting	The line stops short; a peritectic point appears	Cool from between the eutectic and the peritectic, then quench
Solid solution	A field of finite width instead of a line	Real systems show one around many compositions

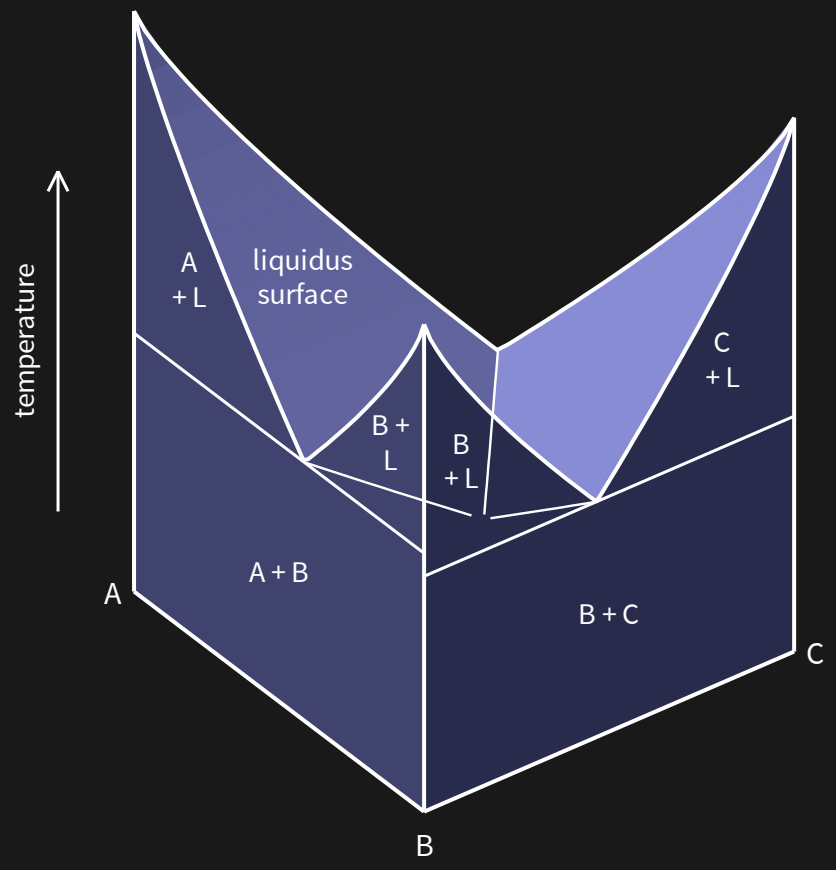
Melt to a liquid of the same composition and growth is easy; melt to a different liquid plus another solid and it is not.

TERNARY PHASE DIAGRAMS

Learning objectives — by the end of this lecture, you should be able to:

Two components or three	Explain the difference between binary and ternary phase diagrams.
Representation	Describe how ternary diagrams are drawn and why isothermal cuts are used.
Locating a composition	Place a composition in the triangle by the line method.
Phases present	Identify the phases at a given point, line, or region.
Triangle (lever) rule	Apply it to determine phase fractions.
Real systems	Interpret TiO_2–ZrO_2–Al_2O_3 and Y_2O_3–BaO–CuO diagrams.

TERNARY PHASE DIAGRAM



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

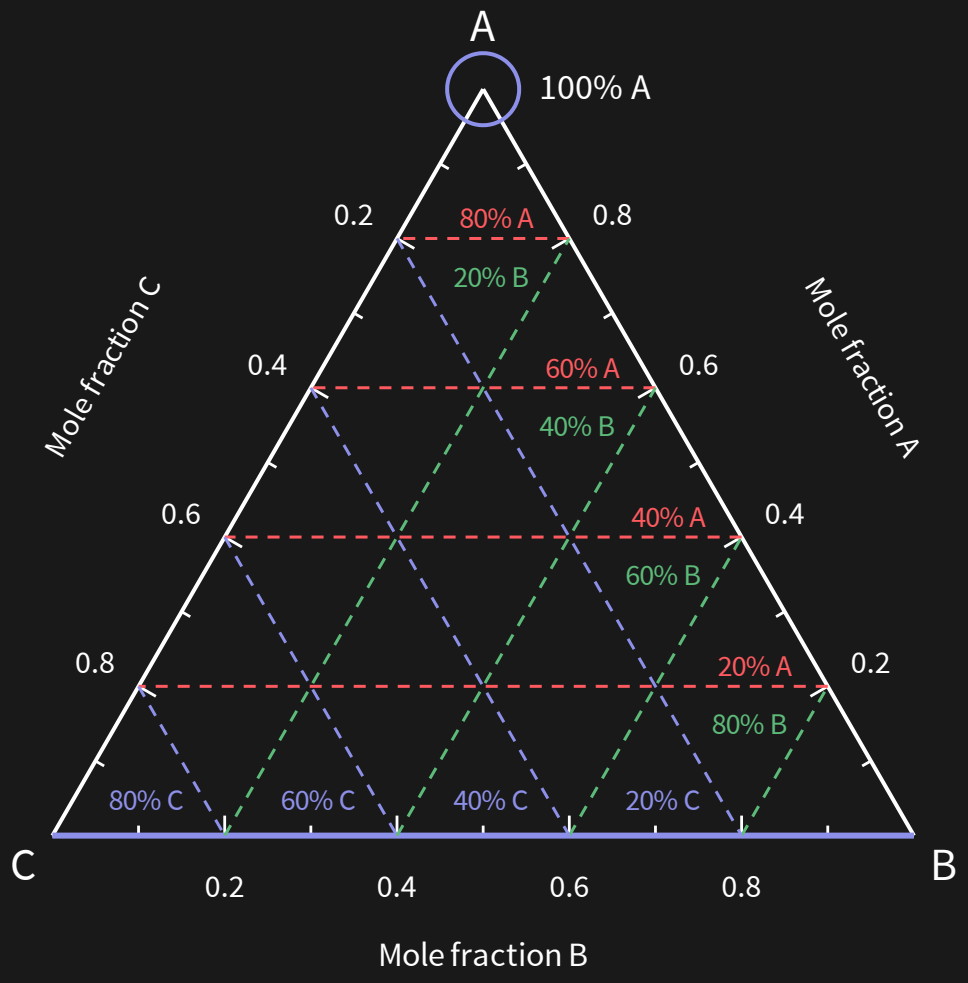
An equilateral triangle for the base, and a vertical axis for temperature.

Each vertical face of the prism is one of the three binary diagrams; the draped surface across the top is the liquidus.

Ternary phase diagrams at constant pressure.

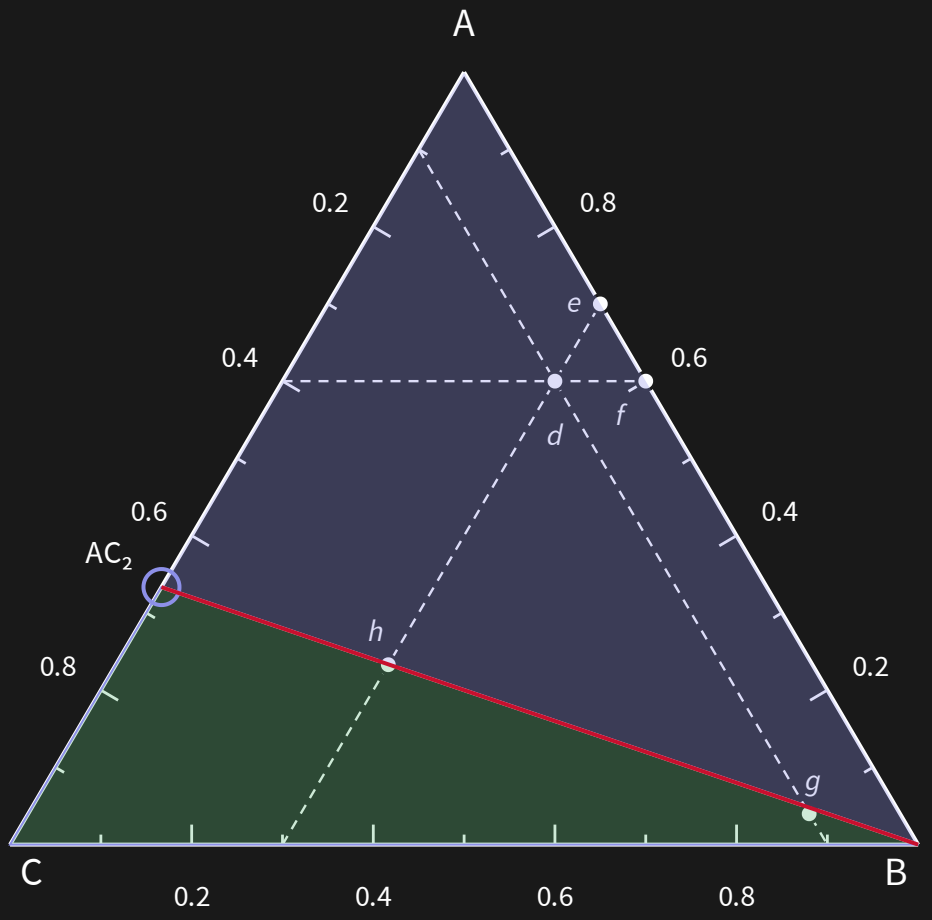
Woodward, Karen, Evans, and Vogt, *Solid State Materials Chemistry*, §4.3, Fig. 4.9.

DETERMINING THE COMPOSITION OF A POINT



Each family of dashed lines is parallel to the edge opposite the component it measures; the three fractions read off them sum to 100%.

READING A TERNARY PHASE DIAGRAM



A, B and AC_2 in equilibrium

B, C and AC_2 in equilibrium

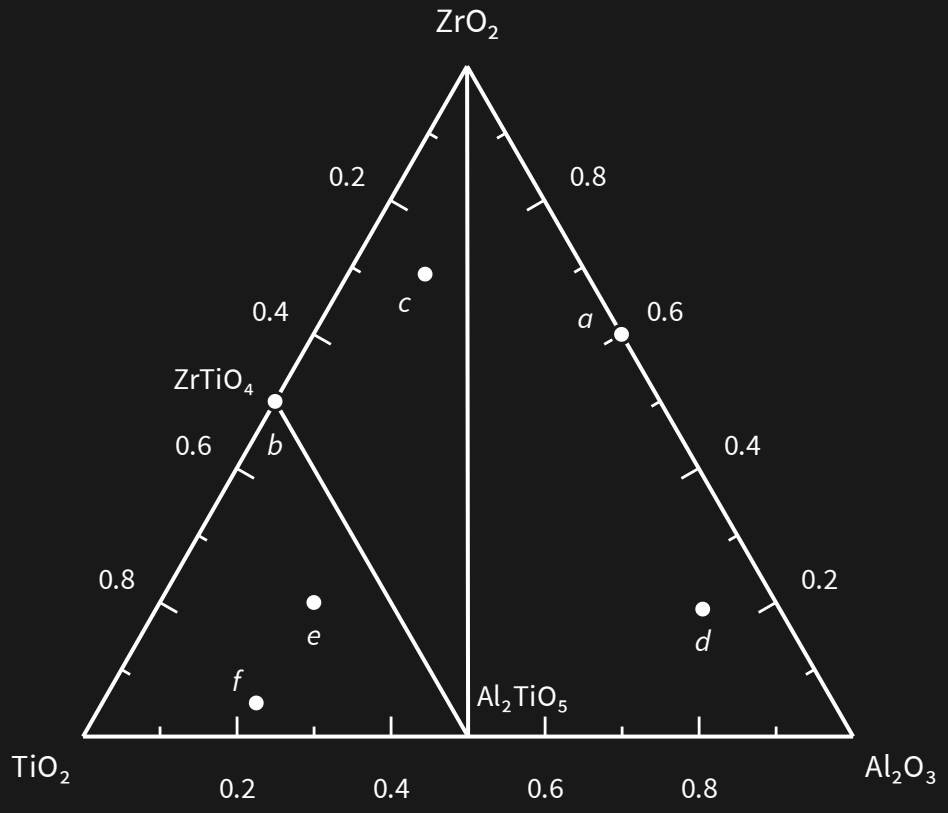
point = 1 phase

line = 2 phases

area = 3 phases

Woodward, Karen, Evans, and Vogt, *Solid State Materials Chemistry*, §4.3, Fig. 4.10c.

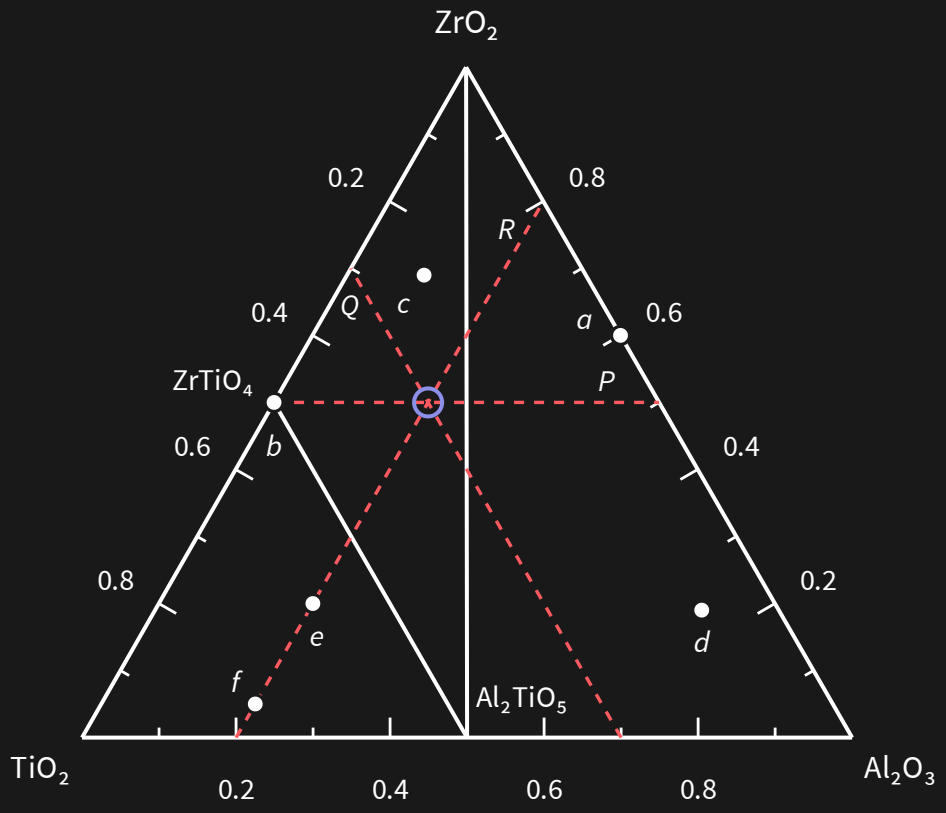
PHASES AT EACH POINT



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?

Woodward, Karen, Evans, and Vogt, *Solid State Materials Chemistry*, §4.3, Fig. 4.11a.

LOCATING THE 50/30/20 COMPOSITION



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?

P — 50% ZrO_2: halfway up, parallel to the TiO_2–Al_2O_3 base.

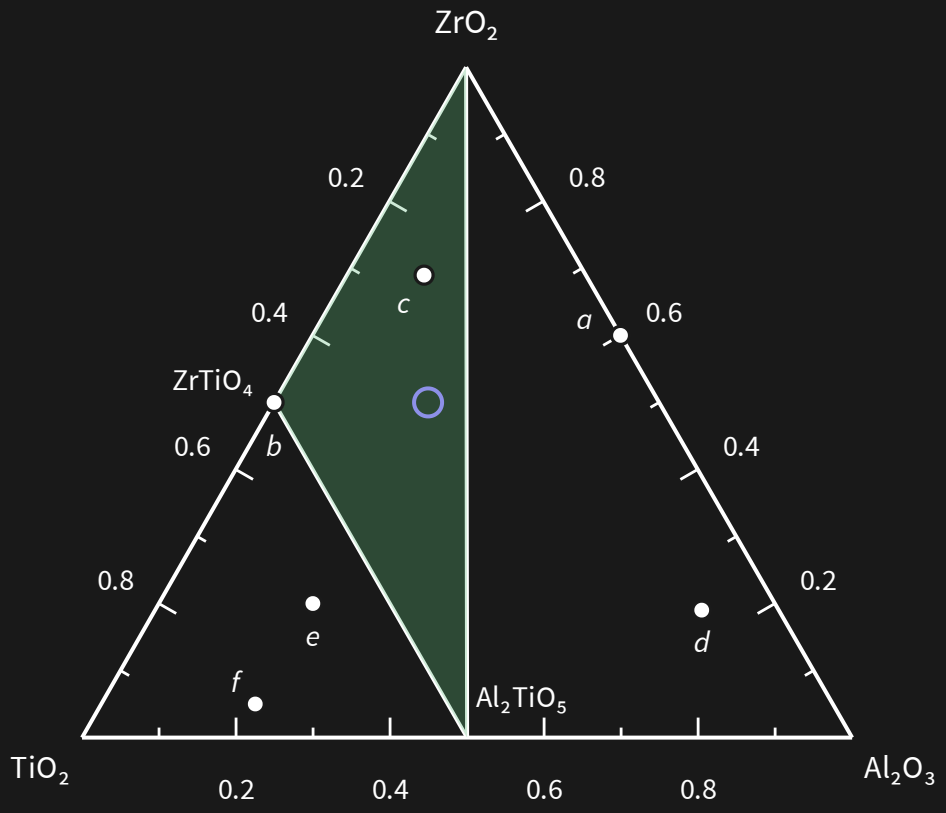
Q — 30% TiO_2: parallel to the ZrO_2–Al_2O_3 edge opposite TiO_2.

R — 20% Al_2O_3: parallel to the TiO_2–ZrO_2 edge opposite Al_2O_3.

All three lines meet at one point, which is the 50/30/20 composition.

Woodward, Karen, Evans, and Vogt, *Solid State Materials Chemistry*, §4.3, Fig. 4.11a.

THE SUB-TRIANGLE NAMES THE PHASES



The 50/30/20 point falls inside the sub-triangle whose vertices are $ZrTiO_4$, ZrO_2 and Al_2TiO_5.

Three phases in equilibrium: **$ZrTiO_4$, ZrO_2 and Al_2TiO_5.**

Every region of a correctly drawn sub-solidus section is a triangle, and the three phases present are the three compounds at its corners.

Woodward, Karen, Evans, and Vogt, *Solid State Materials Chemistry*, §4.3, Fig. 4.11a.

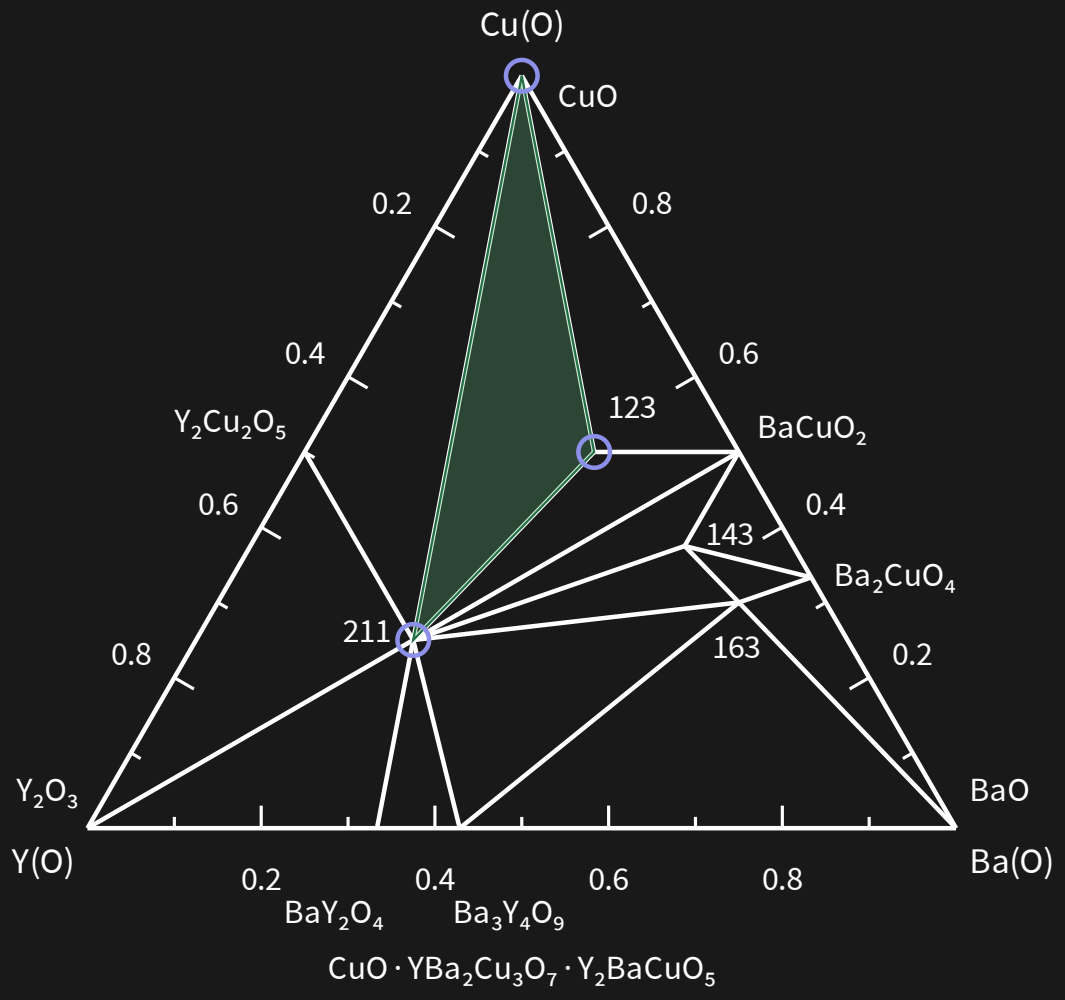
A REAL TERNARY SYSTEM: Y–BA–CU–O

123 = $YBa_2Cu_3O_7$

211 = Y_2BaCuO_5

143 = $YBa_4Cu_3O_{8.5}$

163 = $YBa_6Cu_3O_{10.5}$



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

Woodward, Karen, Evans, and Vogt, *Solid State Materials Chemistry*, §4.3, Fig. 4.11b.

SUMMARY: TERNARY PHASE DIAGRAMS

Phase diagrams represent the **thermodynamic stability** of phases as a function of composition, T, and P.

A full ternary system needs five dimensions — three compositions, T and P — so we fix the pressure and slice at one temperature, and what is left is a triangle of compositions below the liquidus.

Where the composition lands	Phases	How to read it
On a vertex or a compound	1	That phase alone
On a tie-line	2	The two phases the line joins; lever rule along the line
Inside a tie-triangle	3	The three phases at its vertices; triangle (lever) rule

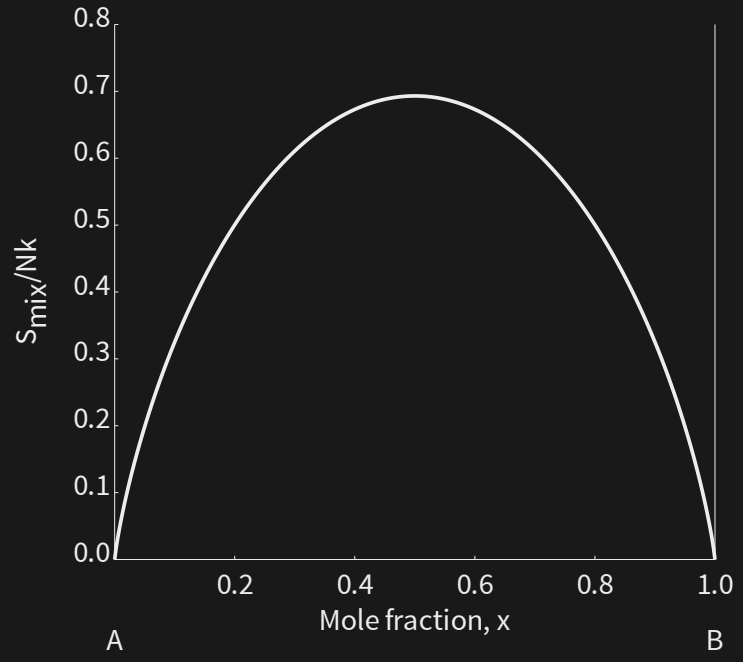
Every point in the triangle is one composition, so the phase count follows from the geometry alone.

WHERE DO PHASE DIAGRAMS COME FROM?

$$F = U - TS$$

Matter seeks to minimize the Helmholtz free energy at constant temperature and volume.

ENTROPY OF MIXING



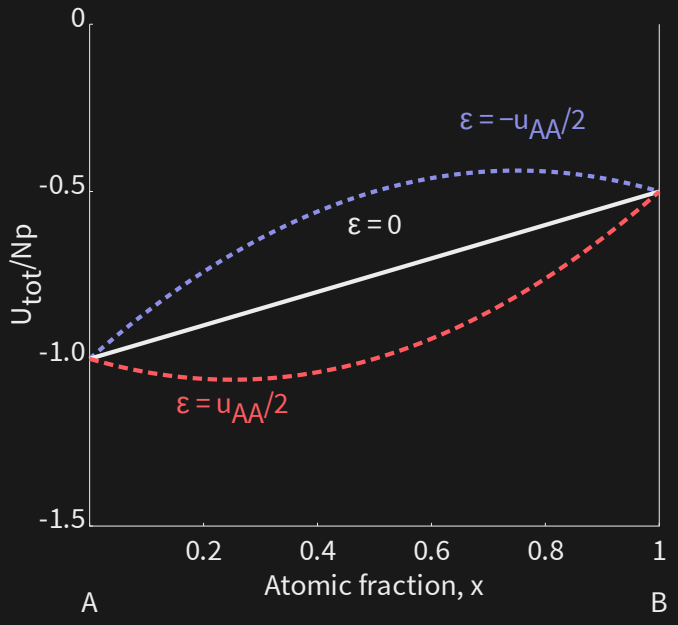
$$S_{\text{mix}} = -Nk \left[\ln(1-x) + x \ln\left(\frac{x}{1-x} \right) \right]$$

$N = N_A + N_B$ is the total number of atoms, x is the mole fraction of B, and k is Boltzmann's constant.

Entropy term is positive because there are more ways of rearranging 2 atoms in space than 1.

Maximum at $x = 0.5$, where $S_{\text{mix}}/Nk = \ln 2 \approx 0.693$; it falls to zero at both pure ends.

INTERNAL ENERGY OF MIXING



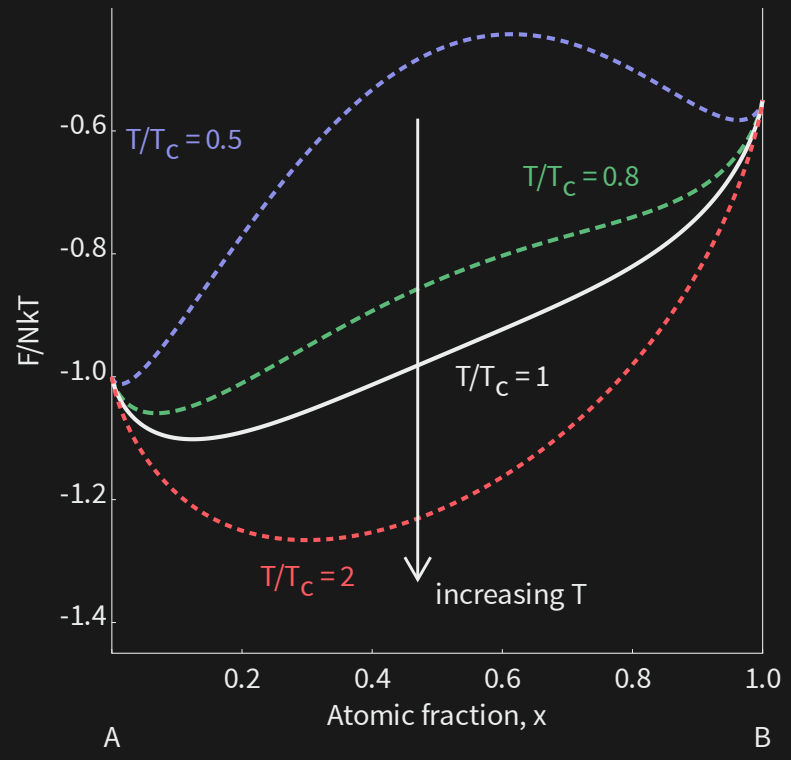
$$U_{\text{tot}} = N\frac{p}{2}\left[(1-x)\,u_{AA} + x\,u_{BB} + 2x(1-x)\,\varepsilon\right]$$

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

p is the number of nearest neighbors around each atom, so the N atoms share $Np/2$ bonds; u_{AA} and u_{BB} are the A–A and B–B bond energies, and the interaction parameter is $\varepsilon = u_{AB} - \frac{1}{2}(u_{AA} + u_{BB})$.

$\varepsilon < 0$ bows the curve below the straight mixing line; $\varepsilon > 0$ bows it above.

FREE ENERGY OF MIXING



$$F(x,T) = \Delta U(x) - T\,S_{\text{mix}}(x)$$

At high T the entropy term dominates and mixing is favorable.

At low T local minima appear, leading to phase segregation. They first split apart at $T_c = p\varepsilon/2k$.

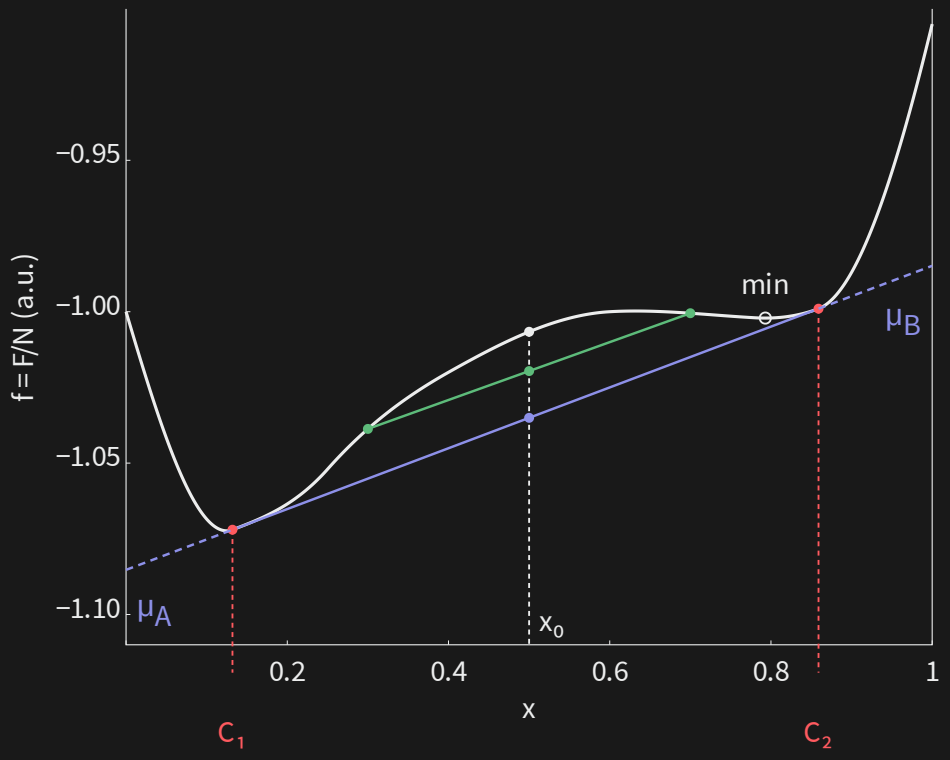
p = number of nearest neighbors per atom

ε = energy penalty per unlike bond

k = Boltzmann constant

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

METHOD OF TANGENTS



Method of tangents can be used to find the compositions of each phase that are in equilibrium.

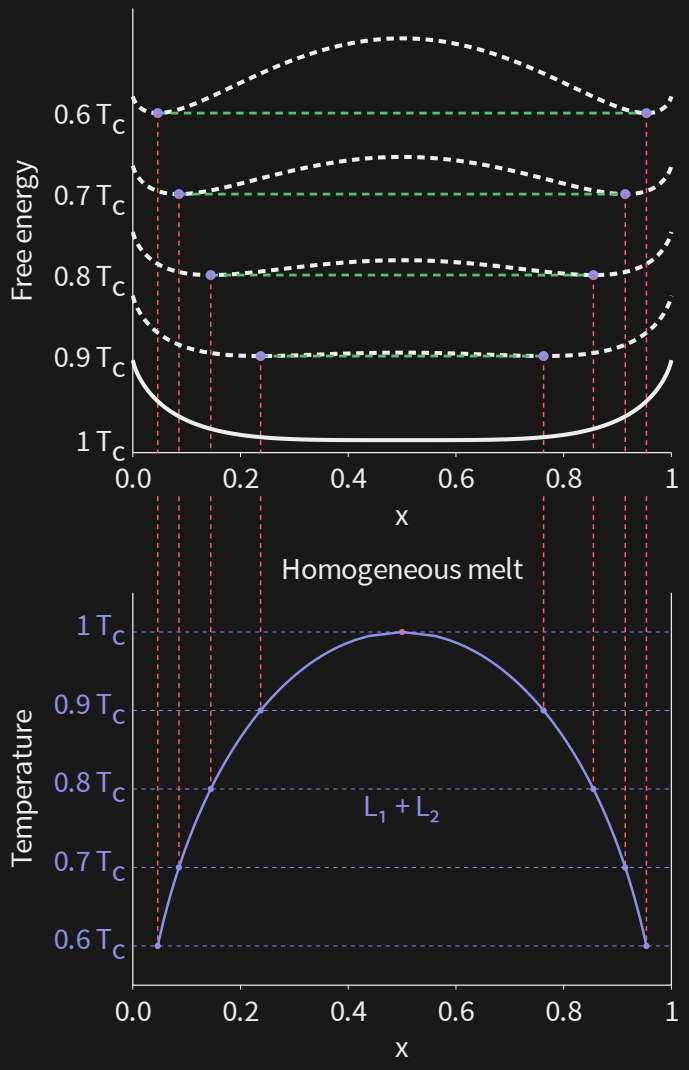
The atom count is fixed, so any split must average back to the overall composition x_0.

A two-phase mixture's free energy lies on the line joining the two phases, read at x_0.

The lowest such line is the common tangent: it touches the curve at $C_1 = 0.132$ and $C_2 = 0.859$, **13.2 % for alpha and 85.9 % for beta**.

One shared line: μ_A **and** μ_B **are the same in both phases**.

TANGENTS BUILD THE PHASE DIAGRAM

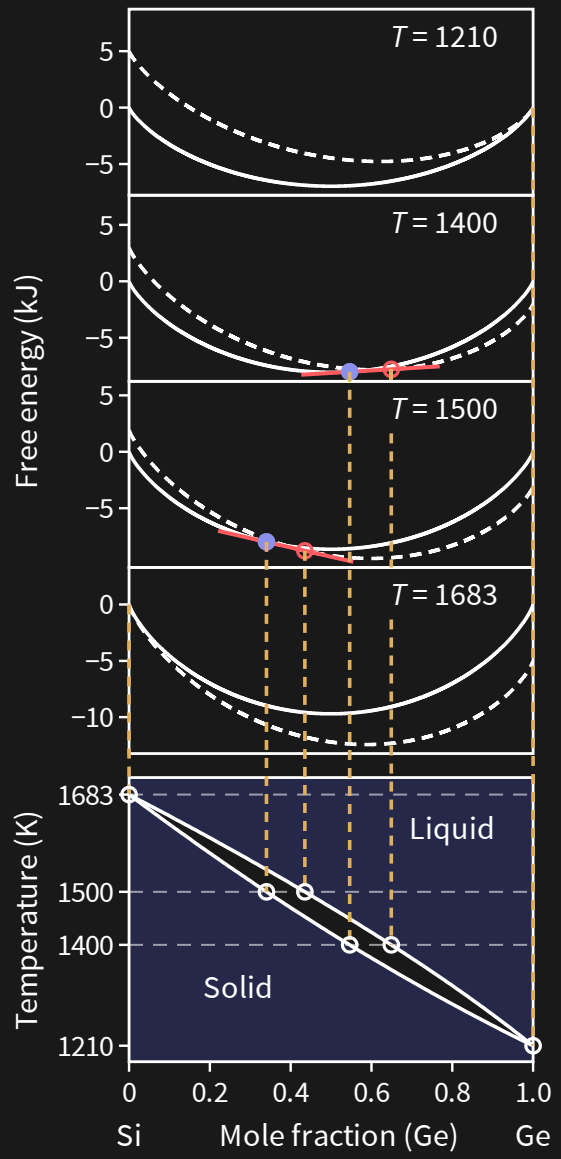


Applying the method of tangents to free energy curves at different temperatures can be used to create a phase diagram.

Drop each pair of tangent points onto the temperature–composition plane and the pairs trace the miscibility dome, from $0.6\,T_c$ up to T_c at its peak.

Above T_c there is one minimum and one phase; below it, two minima and two coexisting compositions.

EXAMPLE OF A REAL IDEAL SYSTEM (NO HEAT OF MIXING)



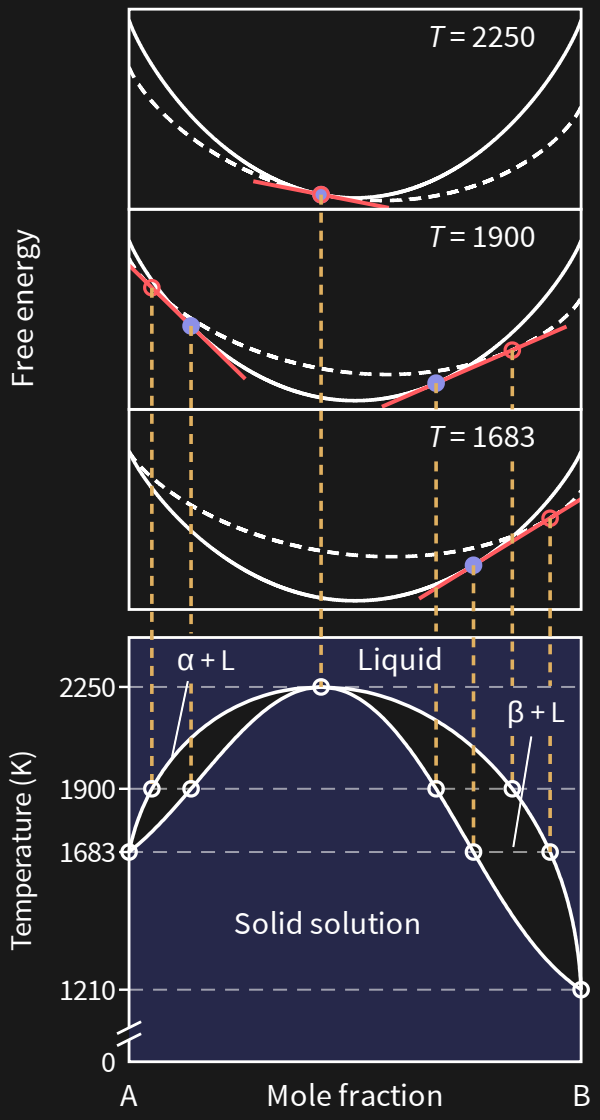
$$F_S(x,T) = RT\left(x\ln x + (1-x)\ln(1-x)\right)$$

$$F_L(x,T) = RT\left(x\ln x + (1-x)\ln(1-x)\right) + \Delta S\left[x(T_B - T) + (1-x)(T_A - T)\right]$$

F_S, F_L	Molar free energy of the solid (solid line) and the liquid (dashed line)
x	Mole fraction of Ge
T_A, T_B	Melting points of Si (1683 K) and Ge (1210 K)
$\Delta S, R$	Entropy of fusion per mole; gas constant
Model	Si–Ge is isomorphous, with no excess energy of mixing in either phase
Lens	All liquid above the liquidus, all solid below the solidus; the two coexist between

Nauman, Figure 12.7.

NEGATIVE HEAT OF MIXING

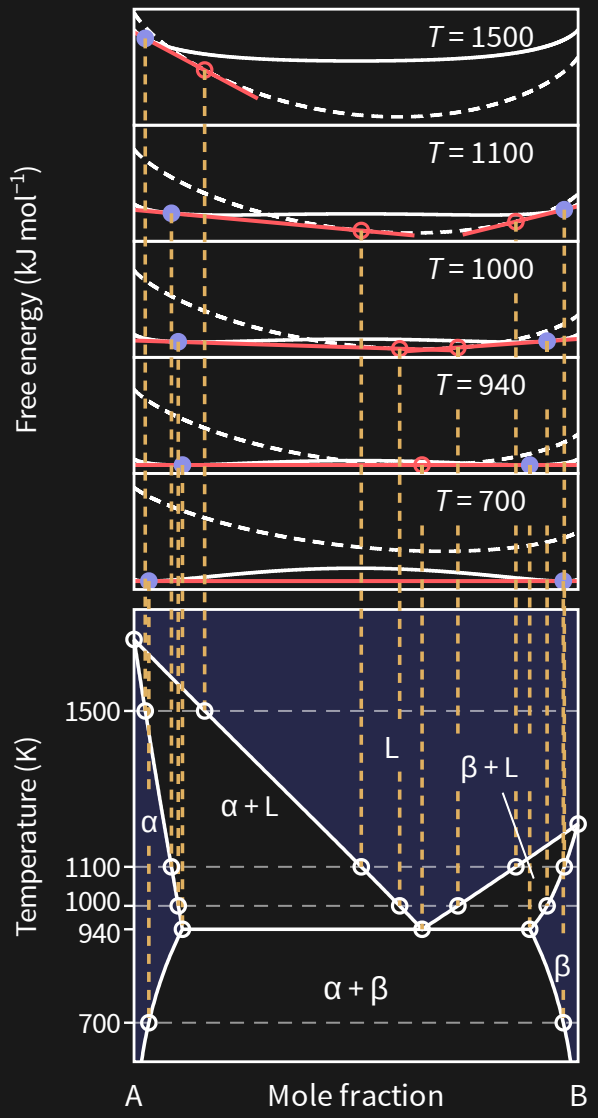


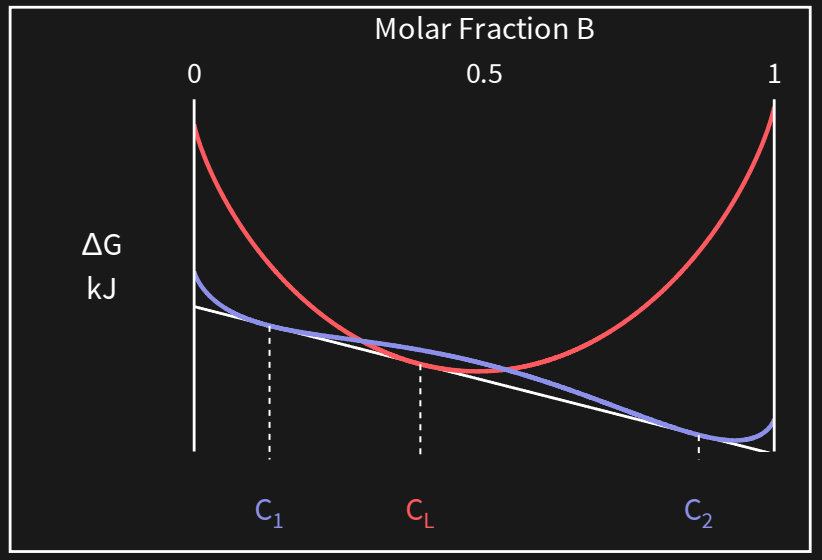
Example of system with heat of mixing of −30 kJ/mol.

Unlike neighbours are preferred, so the solid free-energy curve bows well below the straight mixing line and the alloy melts above either pure component: a continuous solid solution with a congruent maximum.

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

POSITIVE HEAT OF MIXING

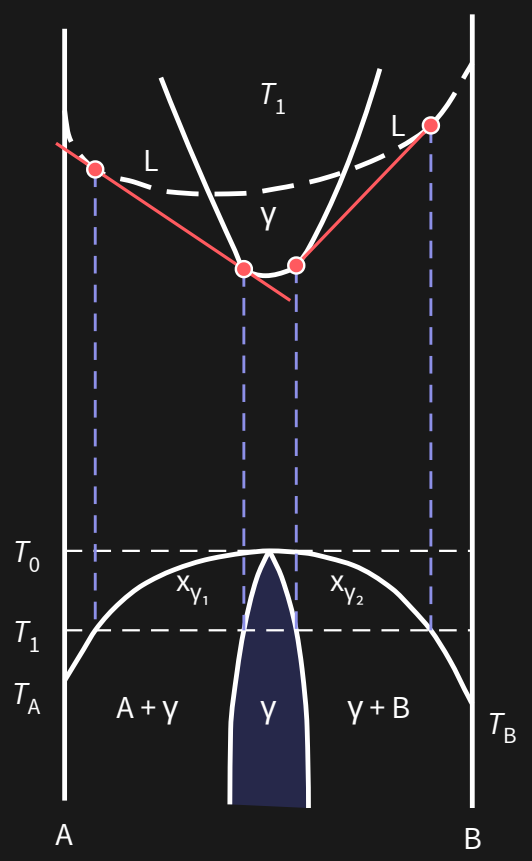


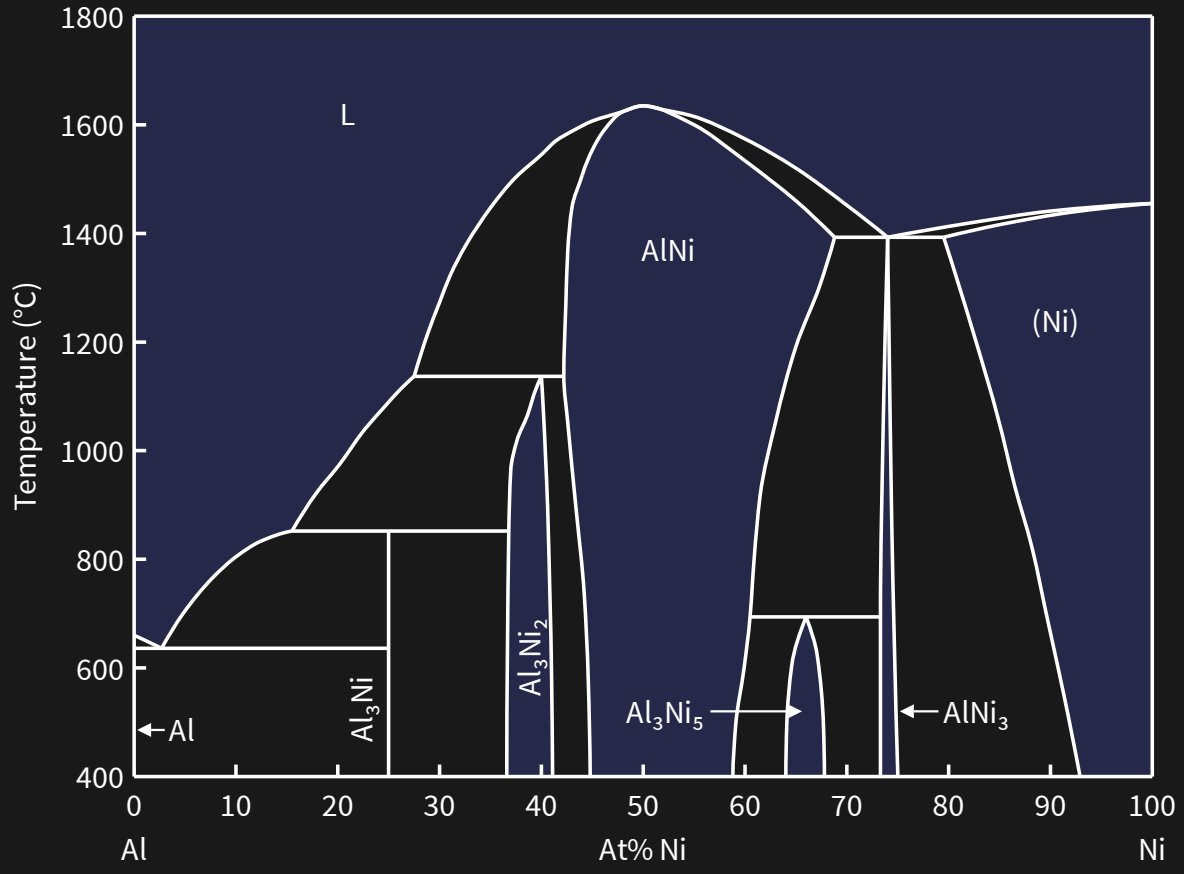


Example of system with positive heat of mixing.

The point where the liquid line minimum meets the tangents of the two solid phase minima leads to a lower melting point eutectic. The inset picks out C_1 and C_2 either side of the eutectic composition.

EXAMPLE OF SOLID SOLUTION INTERMEDIATE PHASE

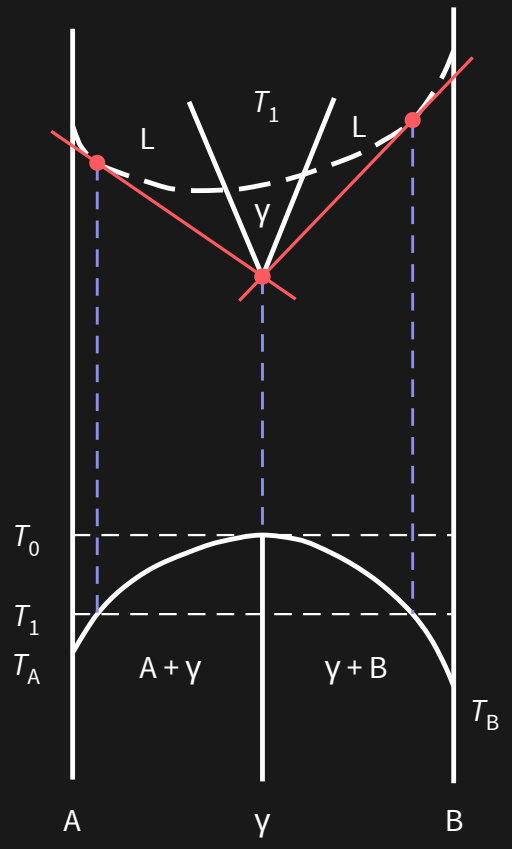


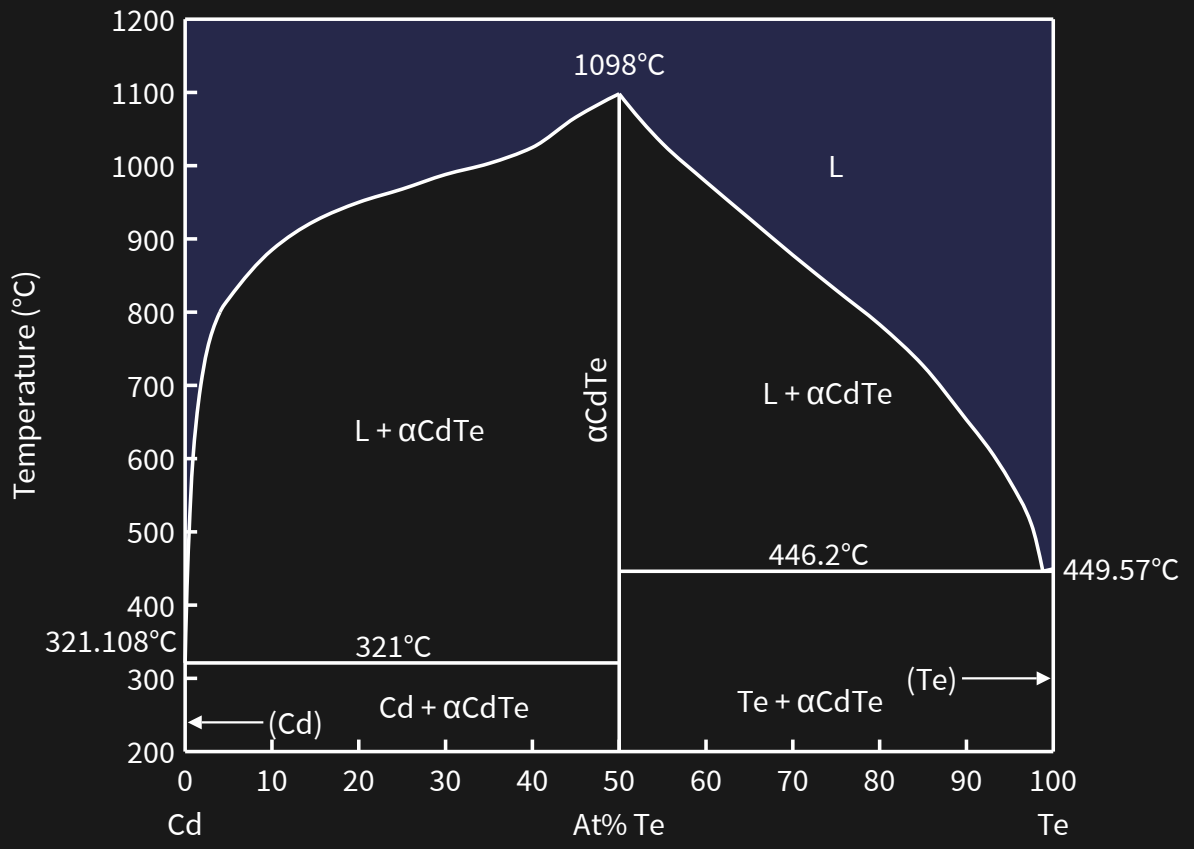


The free-energy curve of γ has a rounded nose, so the tangents from either side meet it at two compositions and γ occupies a band rather than a line.

In Al–Ni that phase is **AlNi**, stable from about 45 to 58 at% Ni and melting above both pure metals, while Al_3Ni and Al_3Ni_5 stay narrow.

EXAMPLE OF LINE COMPOUND





A line compound exists at one exact stoichiometry only, so it is drawn as a vertical line and its free-energy well is a single point.

In Cd–Te that compound is **αCdTe** at 50 at% Te, melting congruently at 1098 °C with a eutectic on each side.

PRACTICE QUESTIONS

Work the Lecture 10 practice questions before the next class.

Open the Lecture 10 practice questions