Mapping Stability: Binary Phase Diagrams

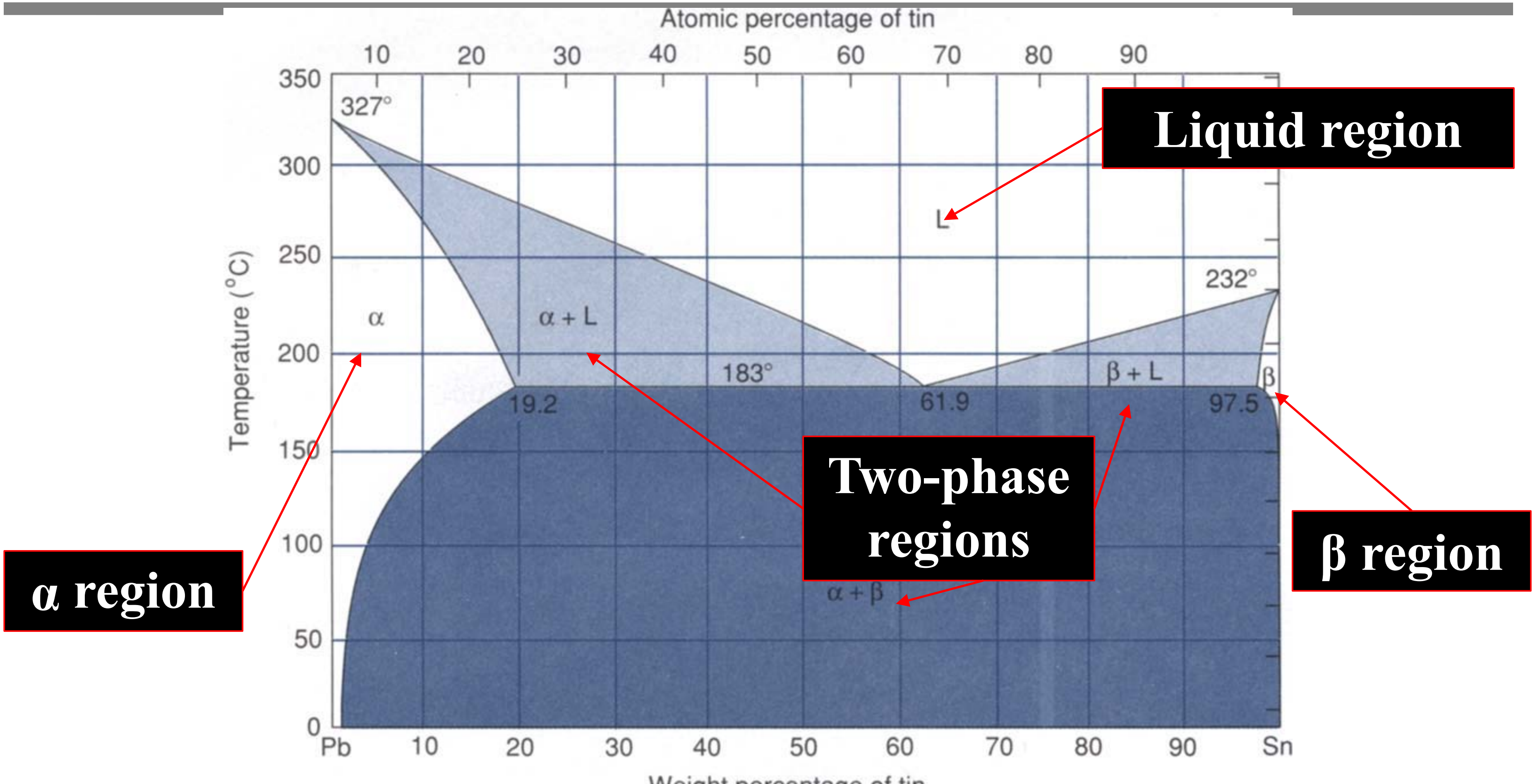
22.14 – Intro to Nuclear Materials
February 19 & 24, 2015

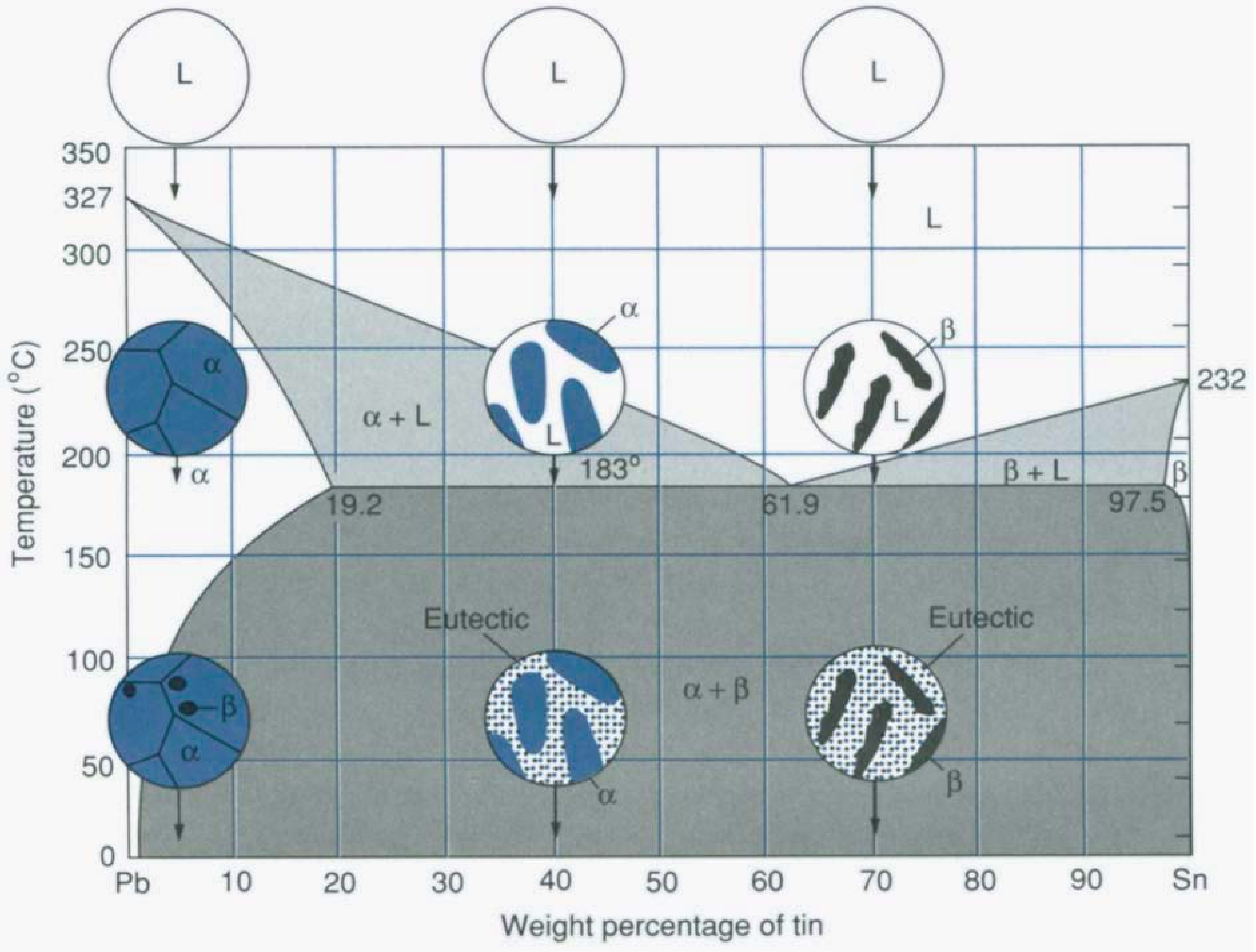
Images from **Engineering Materials Science,**
Milton Ohring unless otherwise noted

Major Steps

- Phase diagrams
- Reading phase diagrams
- Thermodynamics
- Free energy
- Free energy diagrams
- Constructing phase diagrams from free energy diagrams

Phase Diagram: Example

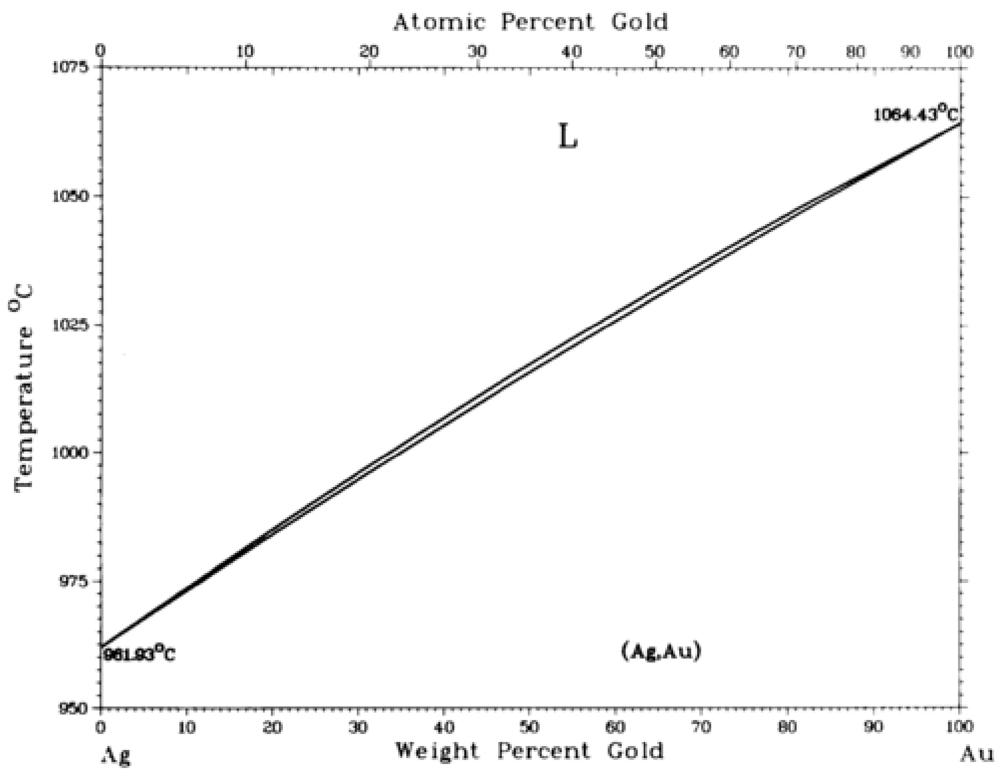



L
L
L
350
327
300
250
200
150
100
50
0
Temperature (°C)
L
α
α
β
α + L
L
183°
β
L
232
β + L
β
19.2
61.9
97.5
α
Eutectic
Eutectic
α + β
β
α
α
β
Pb
10
20
30
40
50
60
70
80
90
Sn
Weight percentage of tin

Phase Separation in Real Life

Image removed due to copyright restrictions. See Fig. 1 from http://cave.auburn.edu/rsrch-thrusts/lead-free.html for further details.

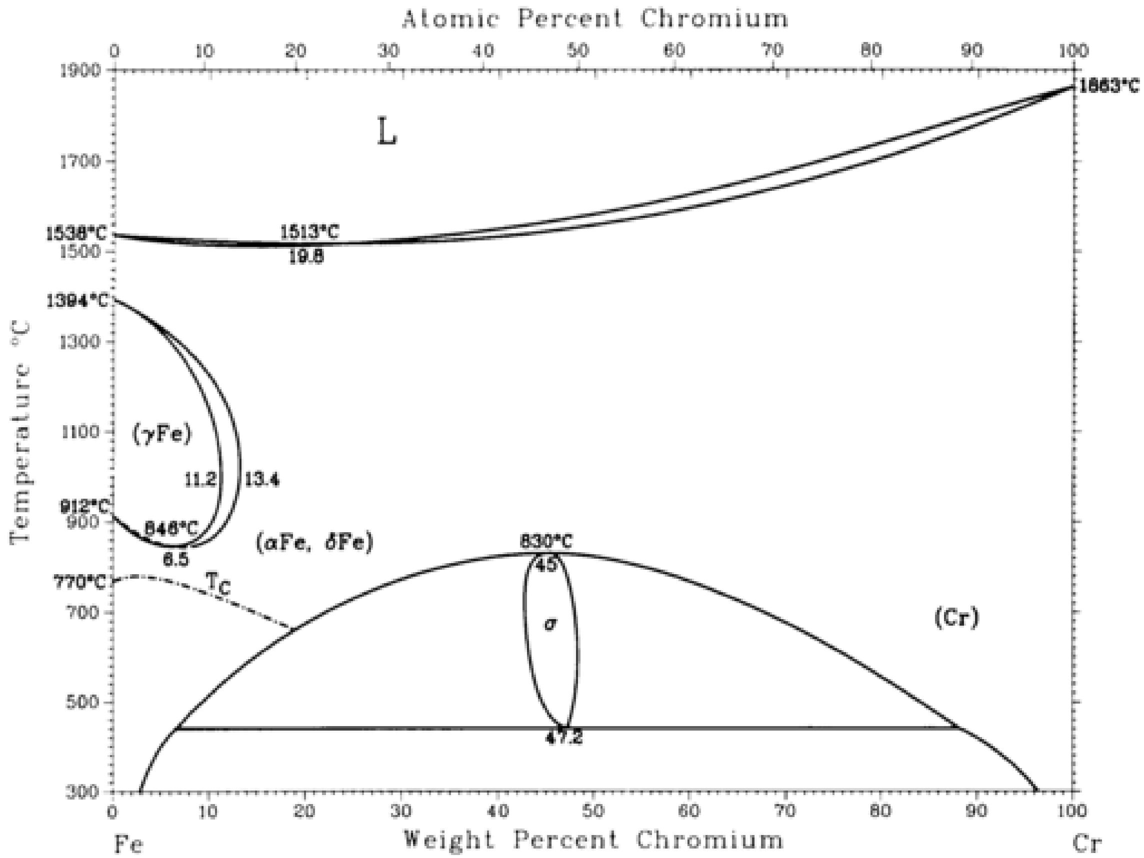
Examples: Complete Solubility



Source: ASM Handbook, Volume 3: Alloy Phase Diagrams. Reprinted with permission of ASM International®.

Binary phase diagrams from ASM Handbooks, Vol. 3 (available at vera.mit.edu)

Examples: Miscibility Gap



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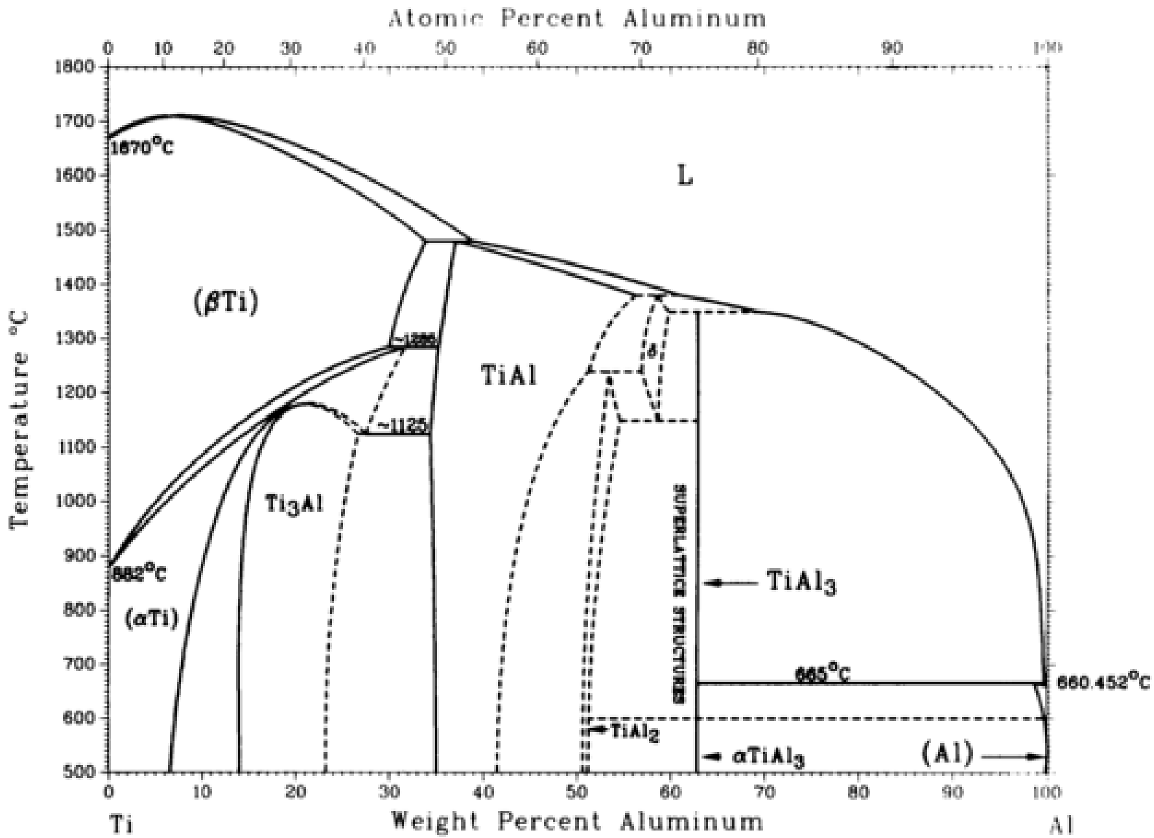
Examples: Intermetallics



Phase	Composition, wt% Al	Pearson symbol	Space group
(βTi)	0 to 33.8	$cI2$	$Im\overline{3}m$
(αTi)	0 to 32	$hP2$	$P6_3/mmc$
Ti_3Al	14 to 26	$hP8$	$P6_3/mmc$
TiAl	34 to 56.2	$tP4$	$P4/mmm$
Ti_3Al_5 [(a)]	44 to 49	$tP32$	$I4/mbm$
$TiAl_2$	51 to 54	$tI24$	$I4_1/amd$
$\alpha TiAl_2$ [(b)]	...	$oC12$	$Cmmm$
δ	57 to 59.8	(c)	...
$TiAl_3$	63	$tI8$	$I4/mmm$
$\alpha TiAl_2$	63	(d)	...
(Al)	98.8 to 100	$cF4$	$Fm\overline{3}m$

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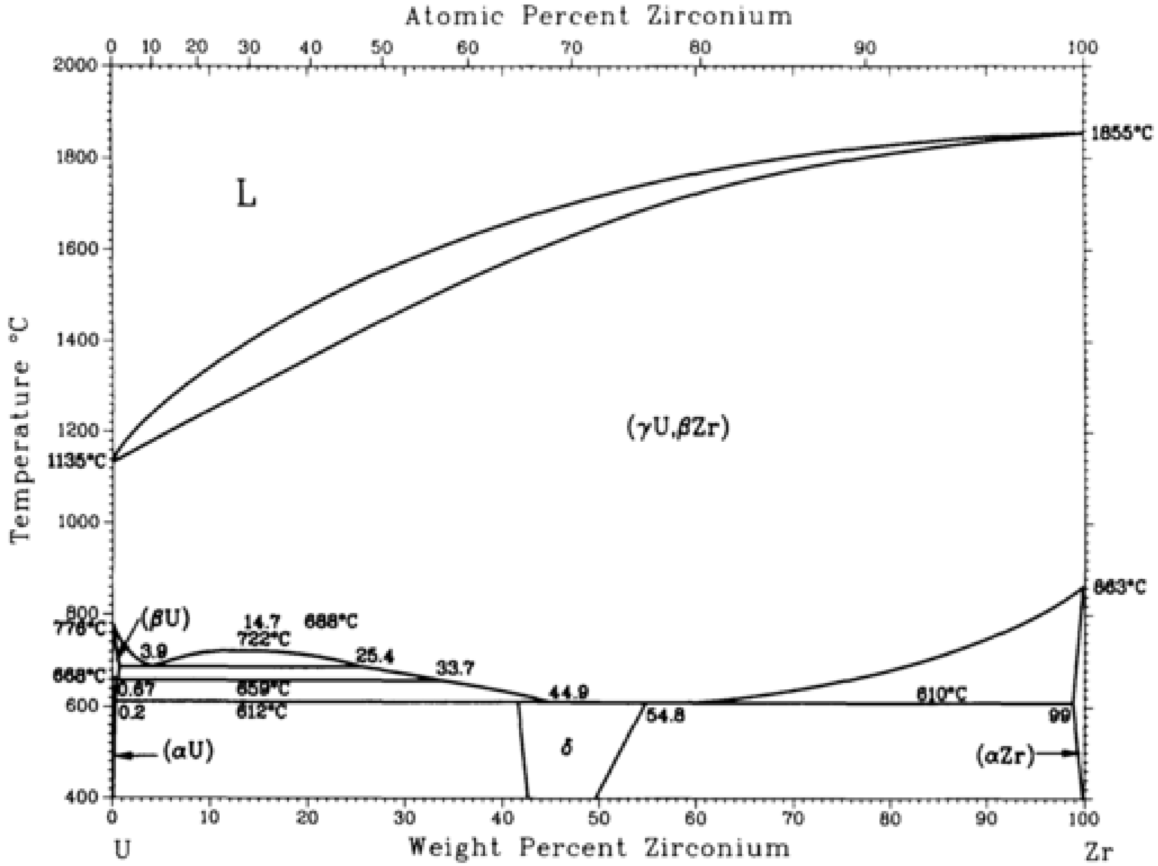
Example Phase Diagrams



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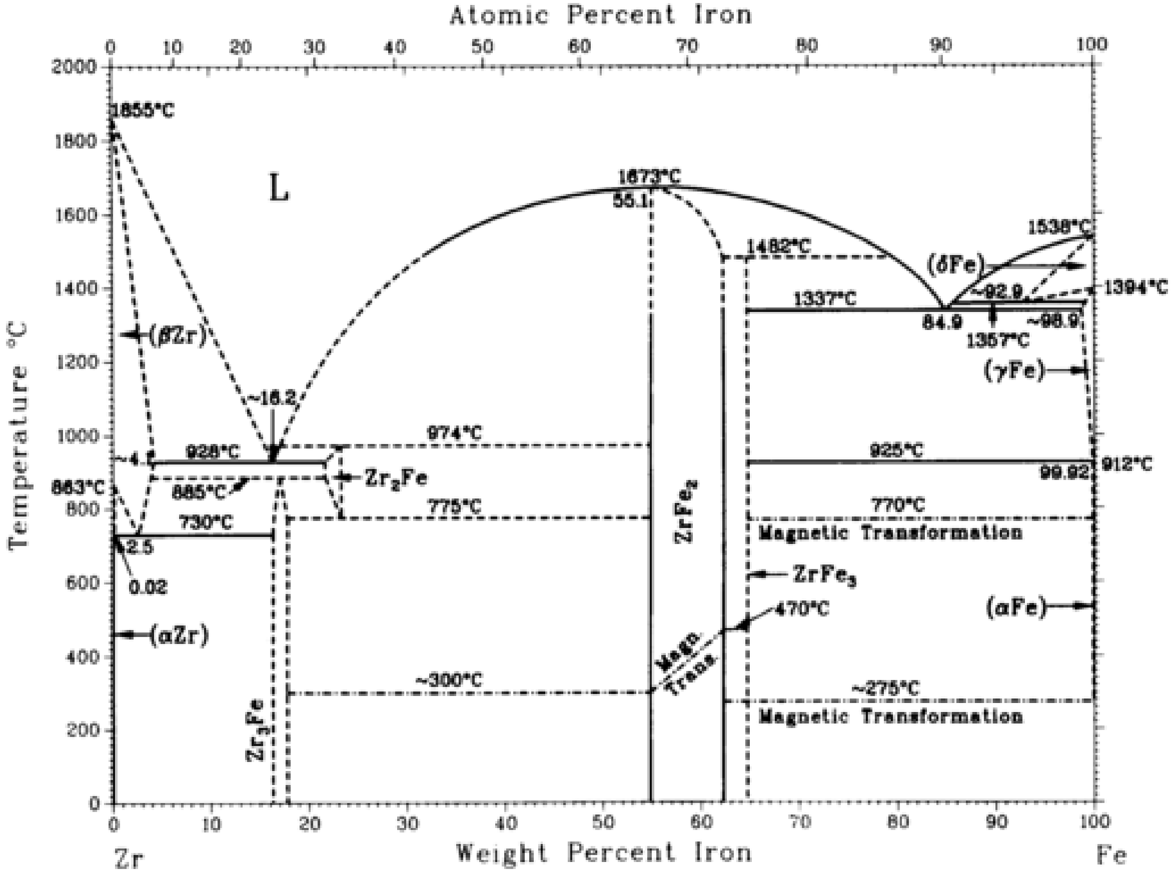
Examples: Eutectic, Everything!



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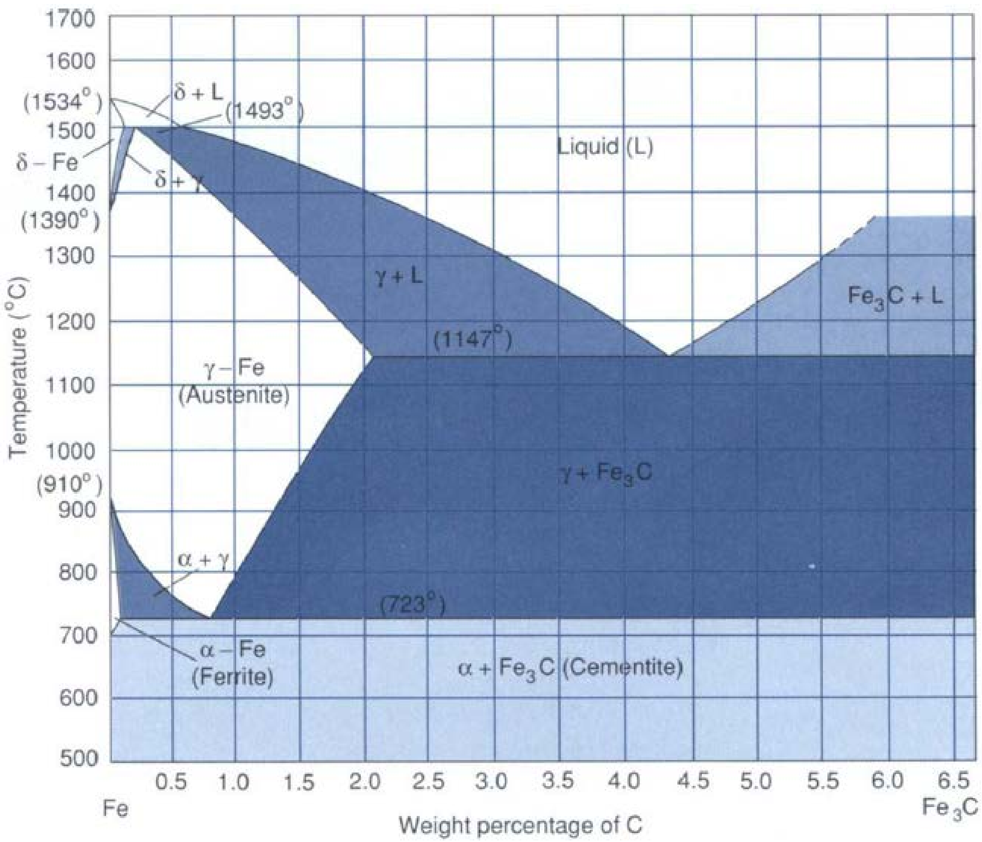
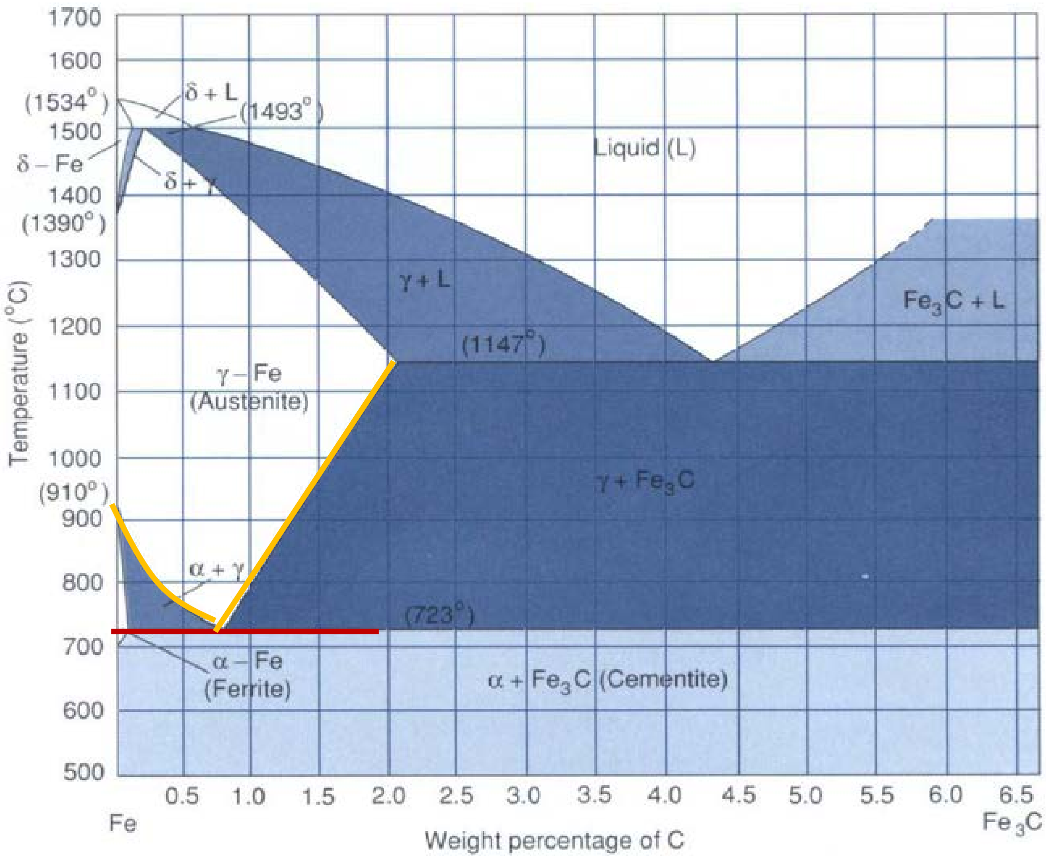
Fe-C Phase Diagram



Basis for steelmaking

Most important one to remember & understand!

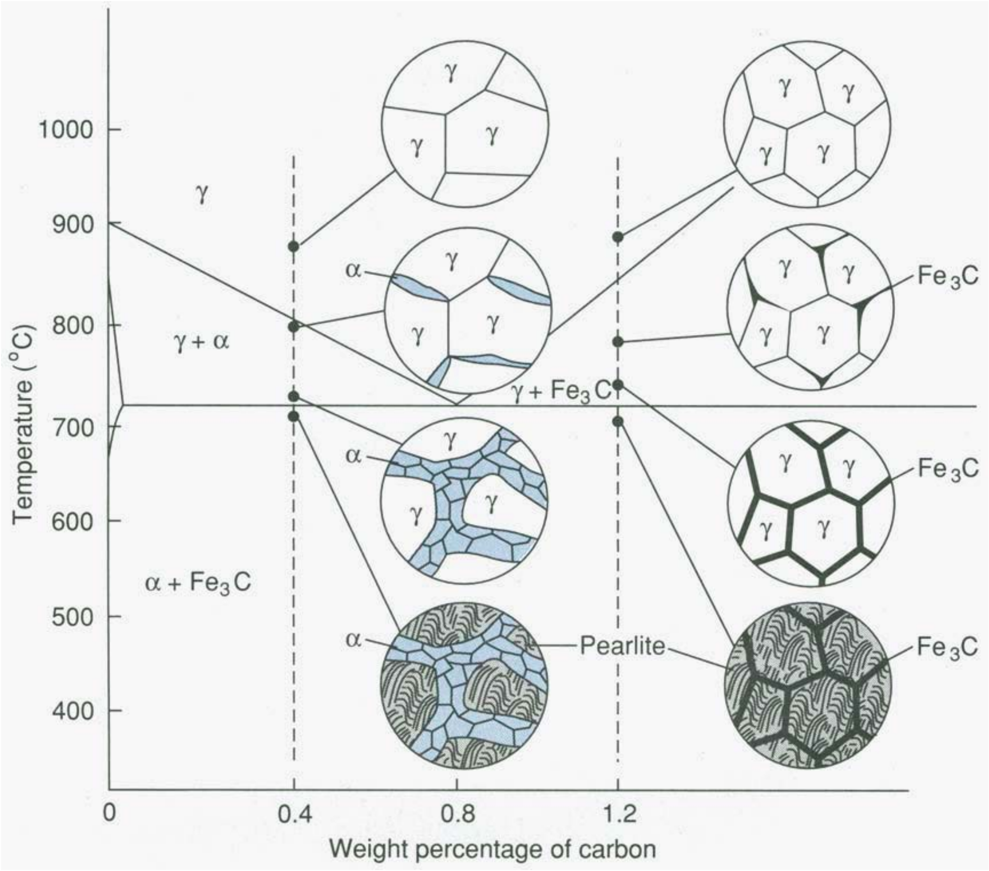
Fe-C Phase Diagram



A1: Temperature at which phase transformation from α-γ begins

A3: Temperature at which it ends

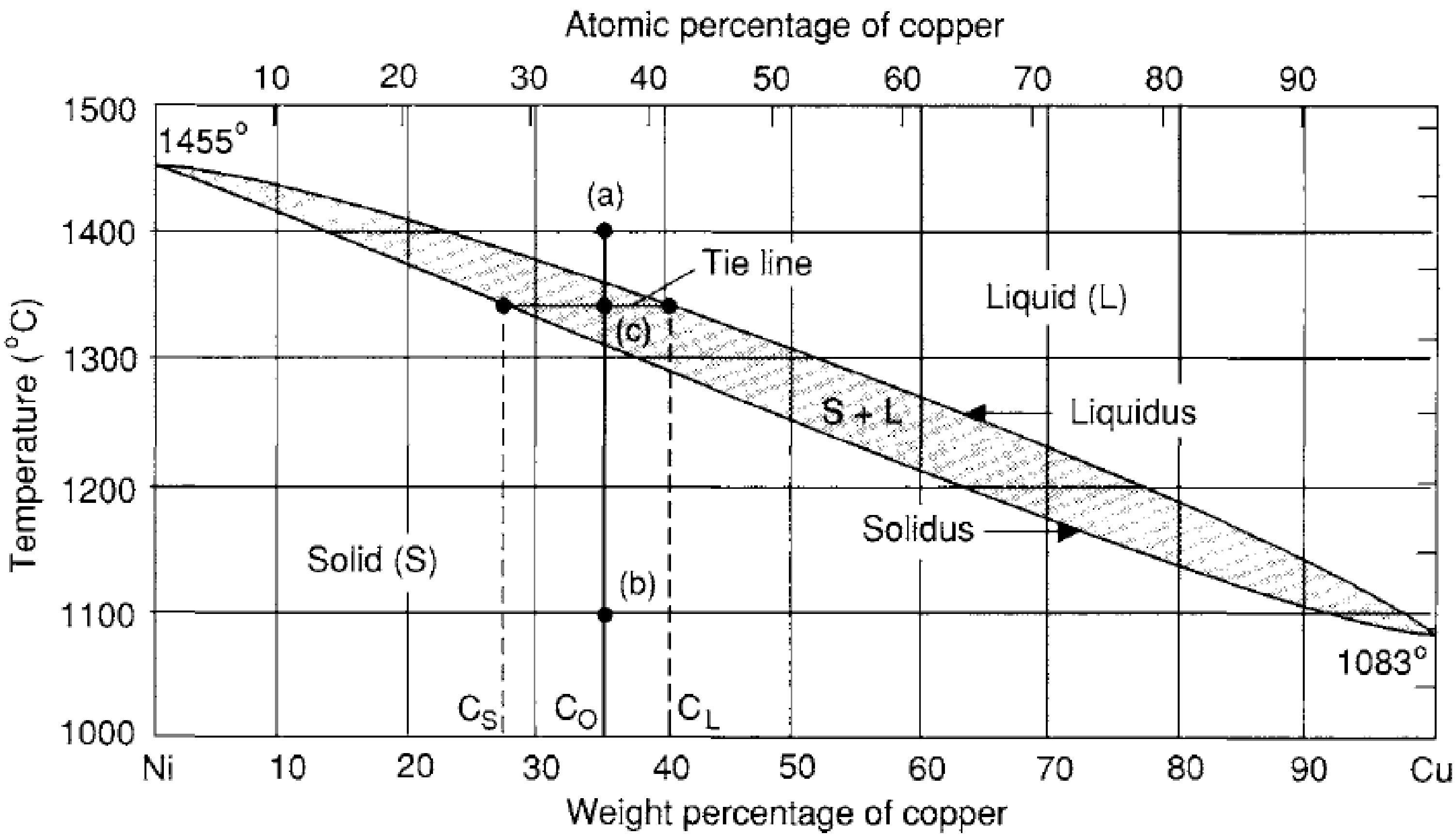
Fe-C Phase Diagram



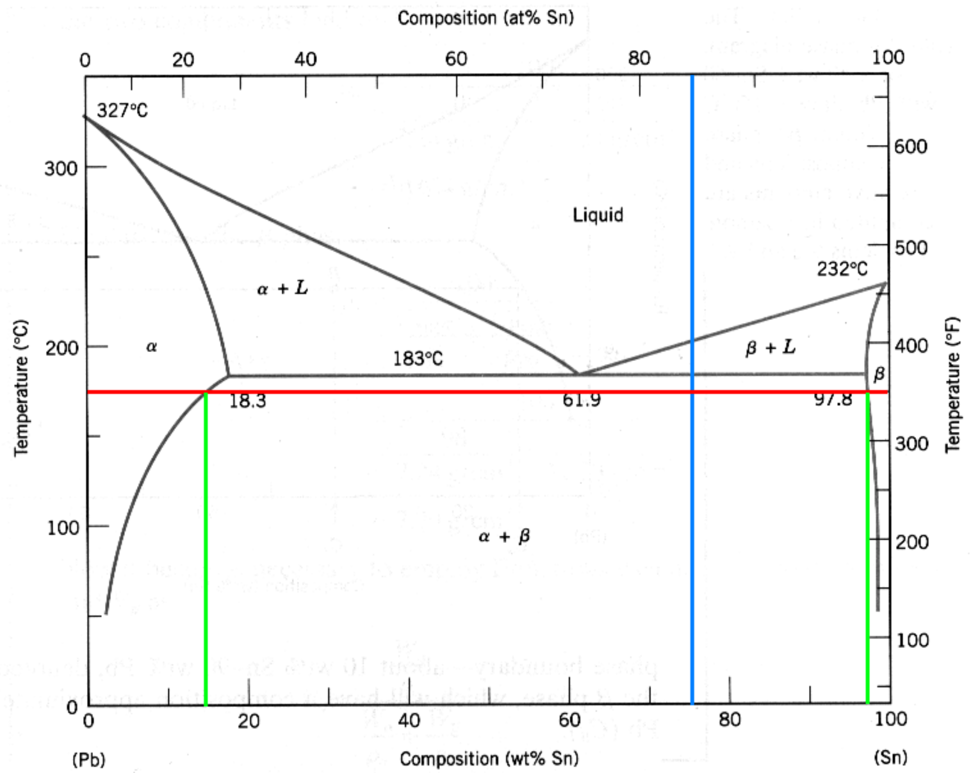
Composition determines ending microstructure

Microstructure determines steel properties

Reading Phase Diagrams



Reading Phase Diagrams: The Lever Rule



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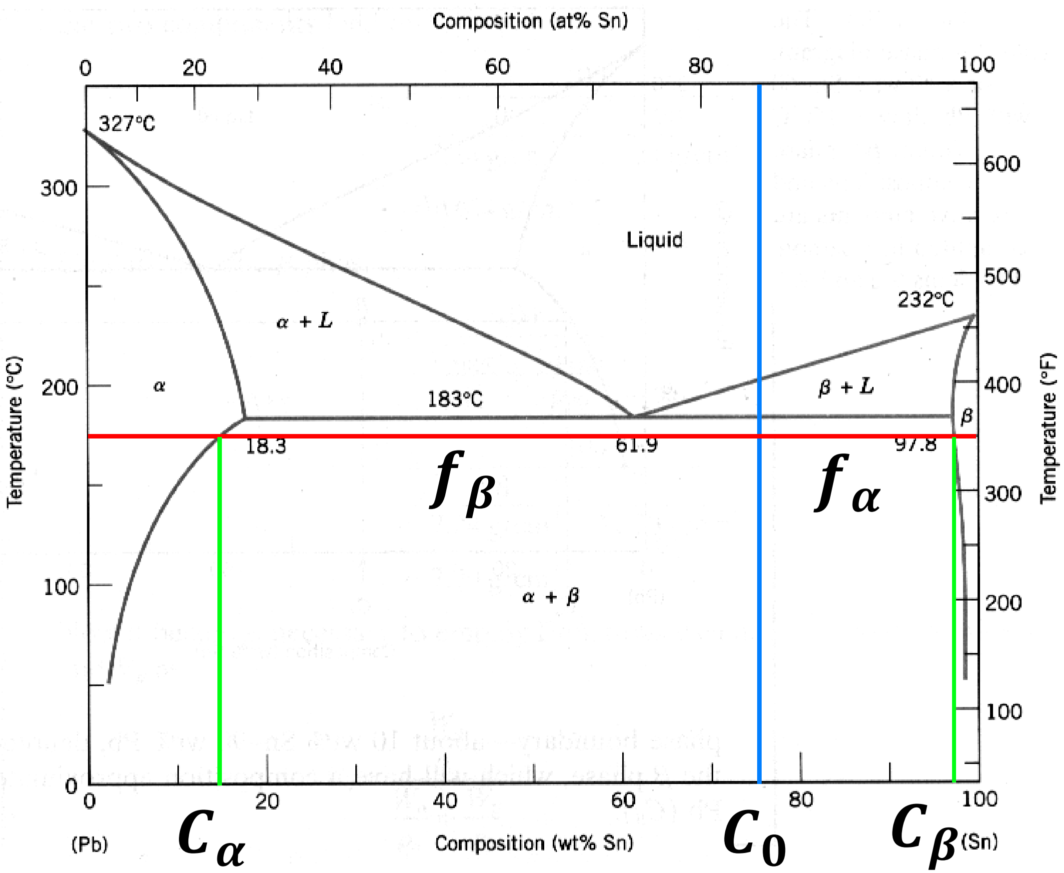
Reading Phase Diagrams: The Lever Rule



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$C_0 = Overall\ Composition$

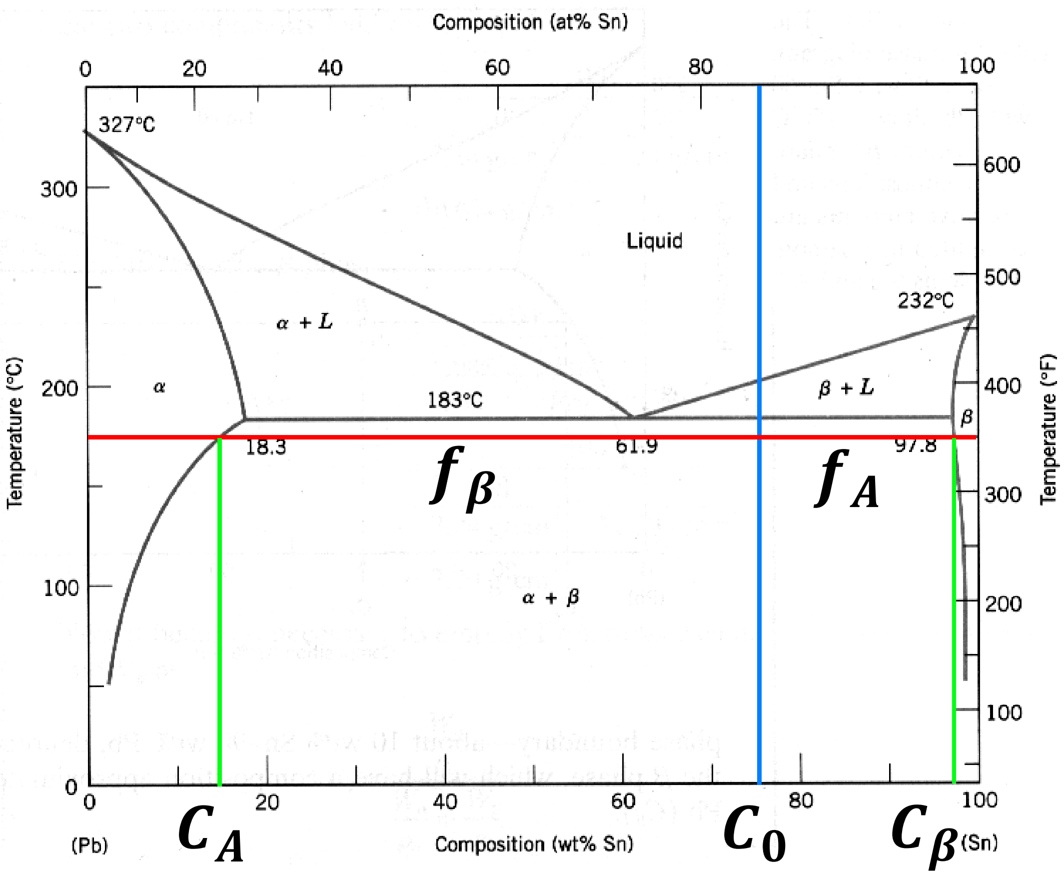
$C_\alpha = Composition\ of\ \alpha$

$C_\beta = Composition\ of\ \beta$

$$f_\alpha = Phase\ fraction\ of\ \alpha = \frac{C_\beta - C_0}{C_\beta - C_\alpha}$$

$$f_\beta = Phase\ fraction\ of\ \beta = \frac{C_0 - C_\alpha}{C_\beta - C_\alpha}$$

Reading Phase Diagrams: The Lever Rule

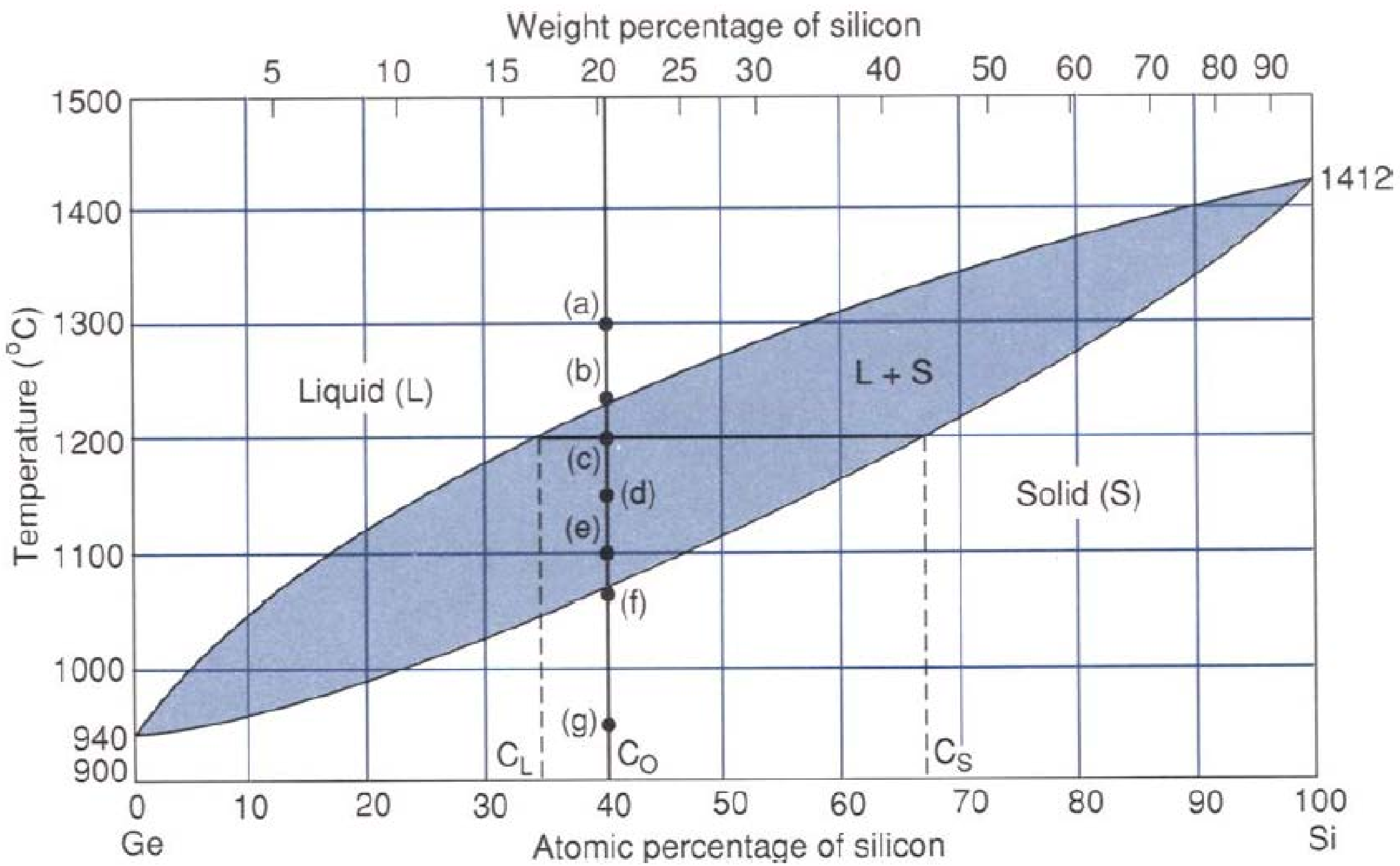


$$C_0 = f_\alpha C_\alpha + (1 - f_\alpha) C_{\boldsymbol{\beta}}$$

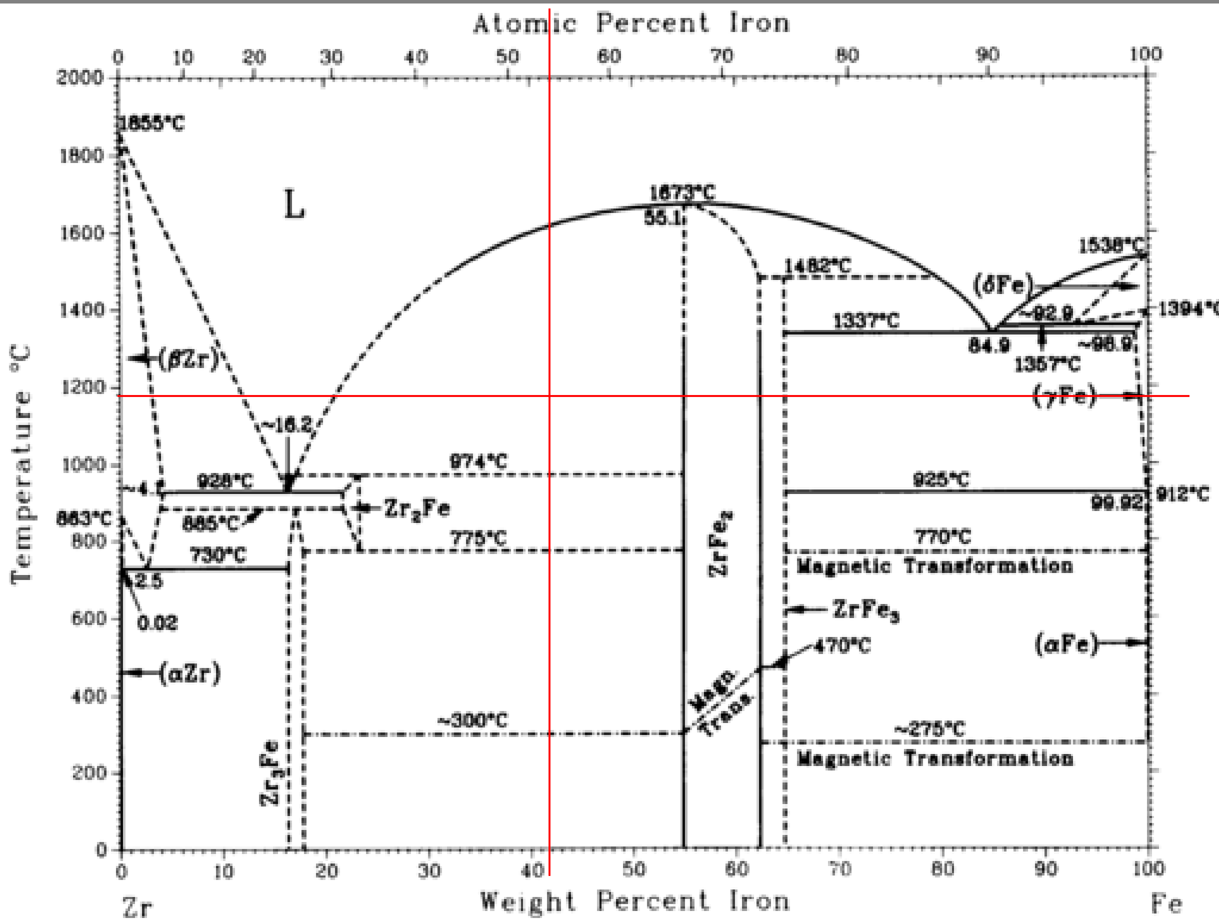
How much of each phase exists at the specified temperature?

What are the compositions of each phase?

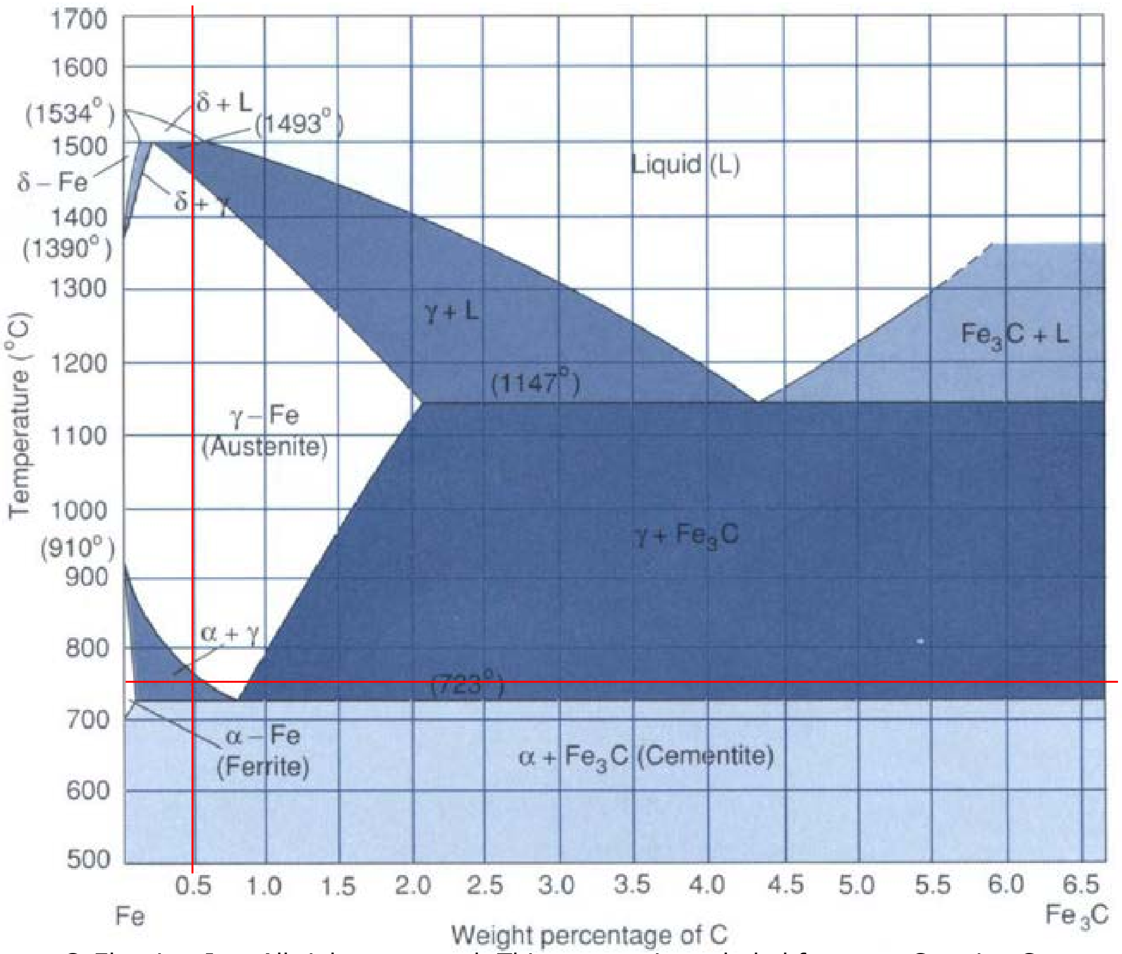
Reading Phase Diagrams



Reading Phase Diagrams



Reading Phase Diagrams



Thermodynamics Review

Pressure

Gibbs Free Energy

Temperature

$$G\left(p, V\right) = \boxed{U + pV} - TS$$

Entropy

Internal Energy

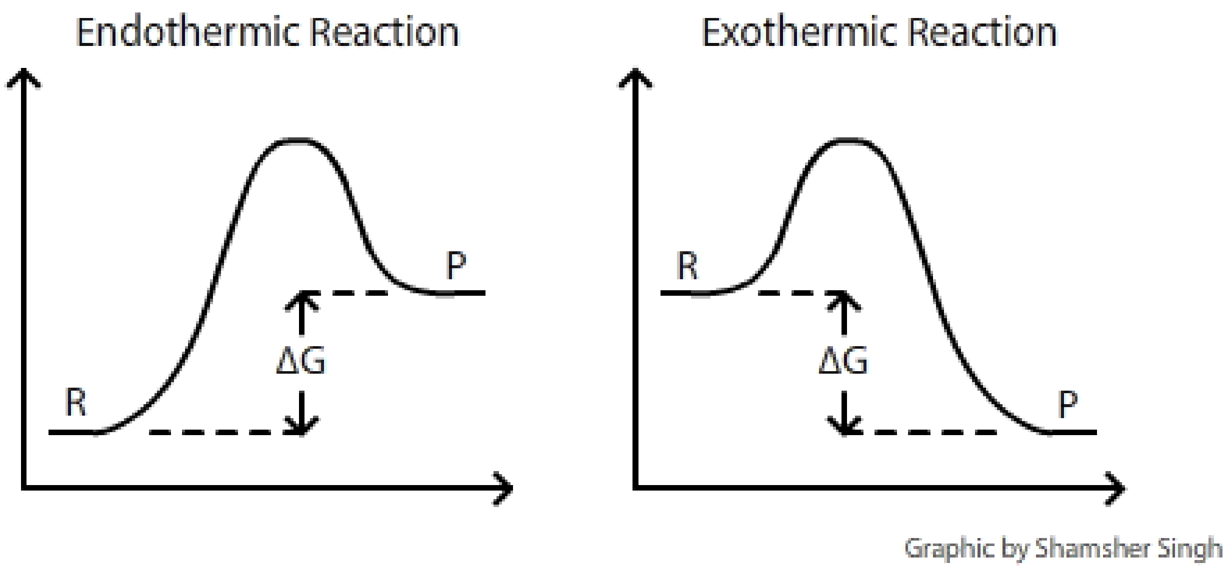
Volume

???

Free Energy

Each component *i* has a tabulated, specific Gibbs free energy (ΔG_i)

– Lower ΔG_i indicates higher stability



http://chemwiki.ucdavis.edu/Analytical_Chemistry/Electrochemistry/Electrochemistry_and_Thermodynamics

Free Energy of Mixtures

Two parts:

– Atomic (mole) fractions of free energies

– Free energy from mixing

$$G_{tot} = X_A G_A + X_B G_B + \Delta G_{mix}$$

Mole fraction of component A

Gibbs free energy of component B

Obtaining ΔG_{mix}

$$G(p, V) = U + pV - TS$$

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

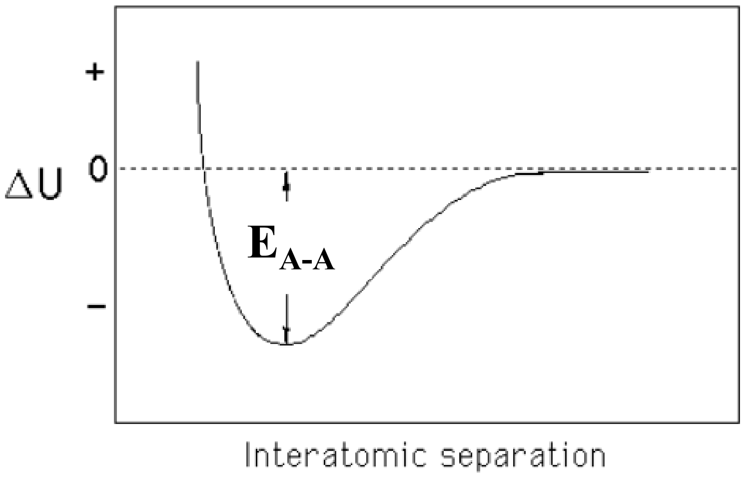
Obtaining ΔH_{mix}

Let's take a system of atoms (A & B) which totals one mole (N_{av}), with mole fractions X_A & X_B:

Energy of an A-A bond = $E_{A\text{-}A}$

Energy of an B-B bond = $E_{B\text{-}B}$

Energy of an A-B bond = $E_{A\text{-}B}$



Obtaining ΔH_{mix}

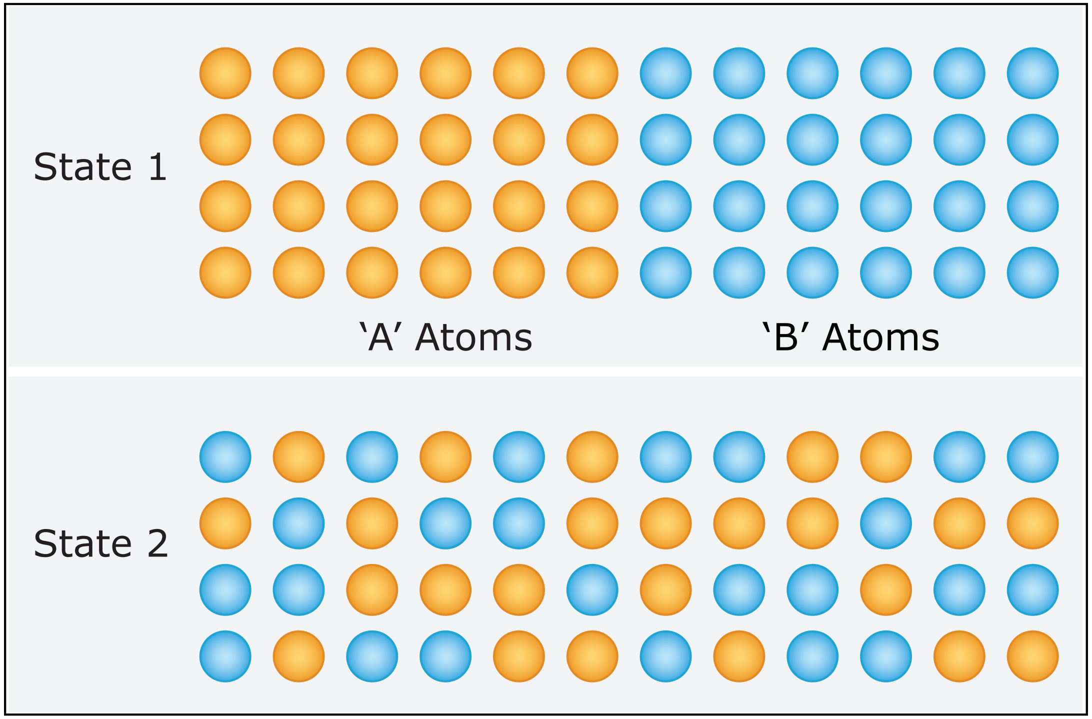
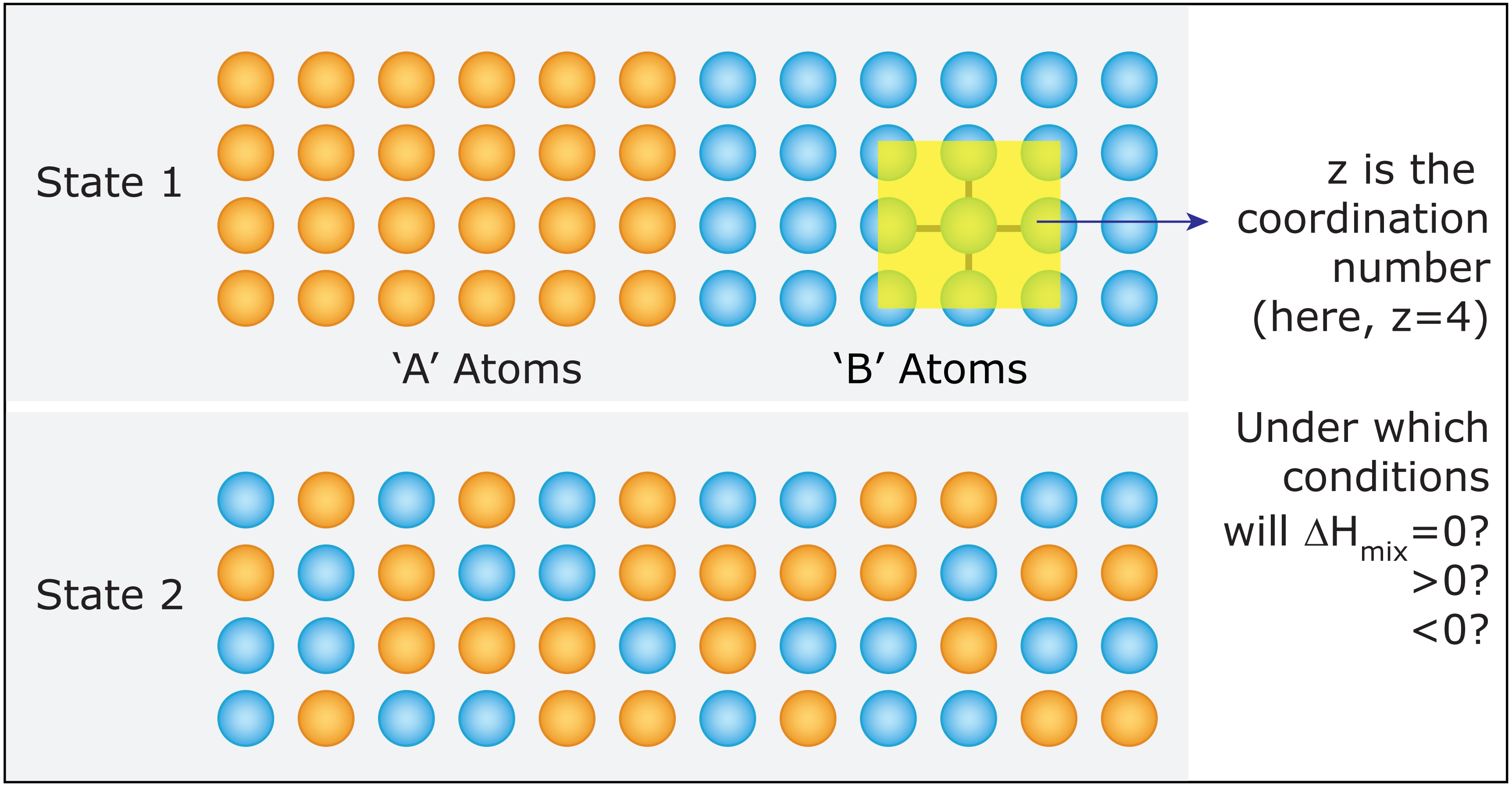


Image by MIT OpenCourseWare.

Only A-A and B-B bonds

A-A, B-B, and A-B bonds

Obtaining ΔH_{mix}



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Obtaining ΔH$_{mix}$

Bond numbers before mixing:

$$\#_{A-A} = \frac{zN_{av}X_A}{2} \qquad \#_{B-B} = \frac{zN_{av}X_B}{2}$$

Bond numbers after mixing:

$$\#_{A-A} = \frac{zN_{av}(X_A)^2}{2} \qquad \#_{B-B} = \frac{zN_{av}(X_B)^2}{2} \qquad \#_{A-B} = zN_{av}X_AX_B$$

z = coordination number (# bonds / atom)

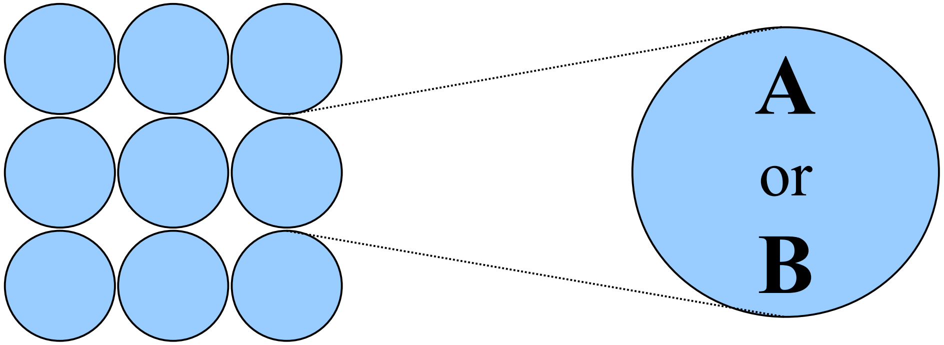
Obtaining ΔH_{mix}

Next steps:

- Obtain energy before & after mixing
- Subtract to get change in mixing enthalpy

Obtaining ΔS_{mix}

Examine available number of microstates...



Use the Boltzmann equation:

$$S = k_B \, ln \left(\Omega \right)$$

Obtaining ΔG$_{mix}$

$$G(p,V) = U + pV - TS$$

$$\Delta G_{mix} = \boxed{\Delta H_{mix}} - T\boxed{\Delta S_{mix}}$$

$$\boxed{\Delta H_{mix}} = zN_{av}X_A X_B\left(E_{A-B} - \frac{E_{A-A} + E_{B-B}}{2}\right)$$

$$\boxed{\Delta S_{mix}} = -R\left[X_A\,ln\left(X_A\right) + X_B\,ln\left(X_B\right)\right]$$

Drawing Free Energy Diagrams of One *Phase*

What happens to the free energy when...

$\Delta H_{mix} < 0$ $\Delta S_{mix} < 0$	$\Delta H_{mix} < 0$ $\Delta S_{mix} = 0$	$\Delta H_{mix} < 0$ $\Delta S_{mix} > 0$
$\Delta H_{mix} = 0$ $\Delta S_{mix} < 0$	$\Delta H_{mix} = 0$ $\Delta S_{mix} = 0$	$\Delta H_{mix} = 0$ $\Delta S_{mix} > 0$
$\Delta H_{mix} > 0$ $\Delta S_{mix} < 0$	$\Delta H_{mix} < 0$ $\Delta S_{mix} = 0$	$\Delta H_{mix} > 0$ $\Delta S_{mix} > 0$

Drawing Free Energy Diagrams of One *Phase*

What about...

$$\Delta H_{mix} > 0; \quad |\Delta H_{mix}| > |\Delta S_{mix}|$$

Drawing Free Energy Diagrams of One *Phase*

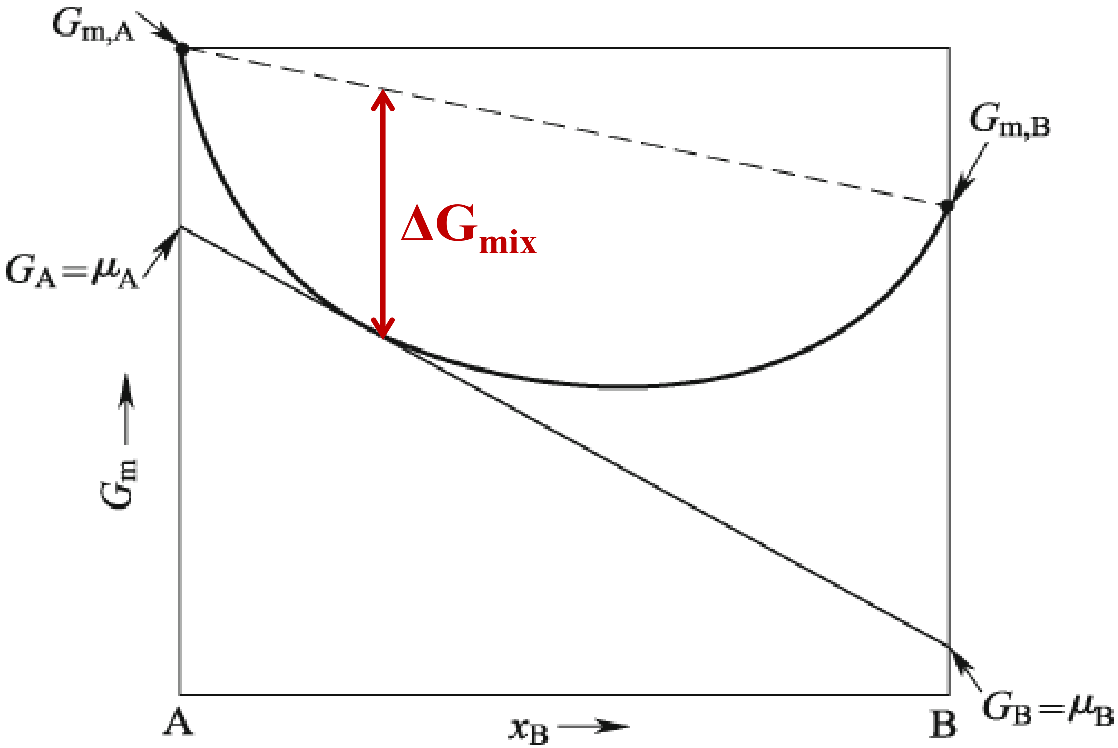
Start with the free energy of the two separate components in one phase...

Add in the free energy of mixing...

Then superimpose all possible phases.

Drawing Free Energy Diagrams

Image: Q. Jiang, Z. Wen. "Thermodynamics Of Materials." Available through MIT Libraries at http://link.springer.com/book/10.1007/978-3-642-14718-0/page/1.



Plot G_A and G_B, show how H_{mix} and $T\Delta S_{mix}$ change G_{tot}

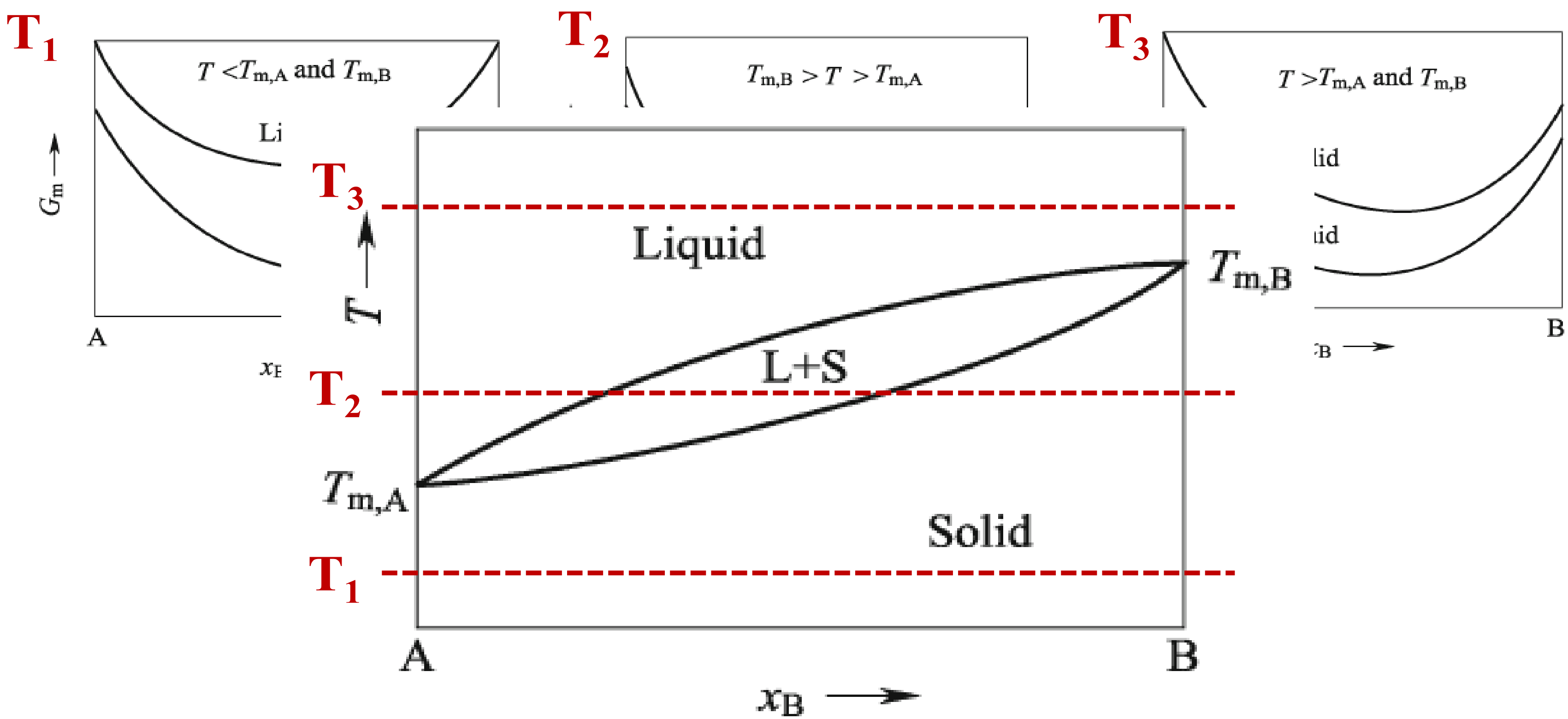
Drawing Free Energy Diagrams of *Multiple Phases*

Examples:

- Solid/liquid solution
- Miscibility gap
- Eutectic (zero solubility)
- Eutectic (some solubility)
- Intermetallic (ordered) compound

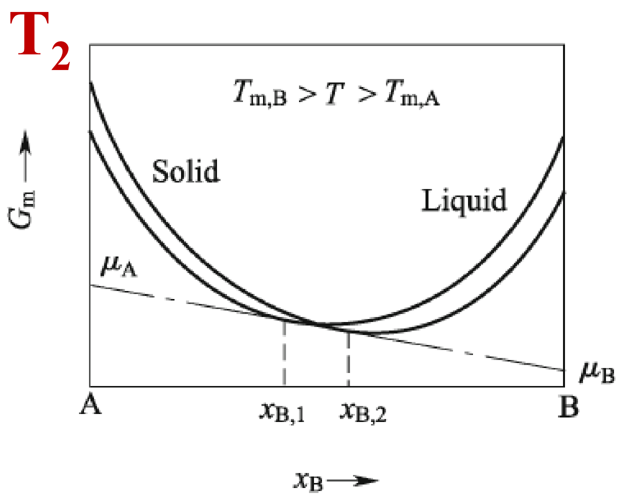
Free Energy Diagrams to Phase Diagrams

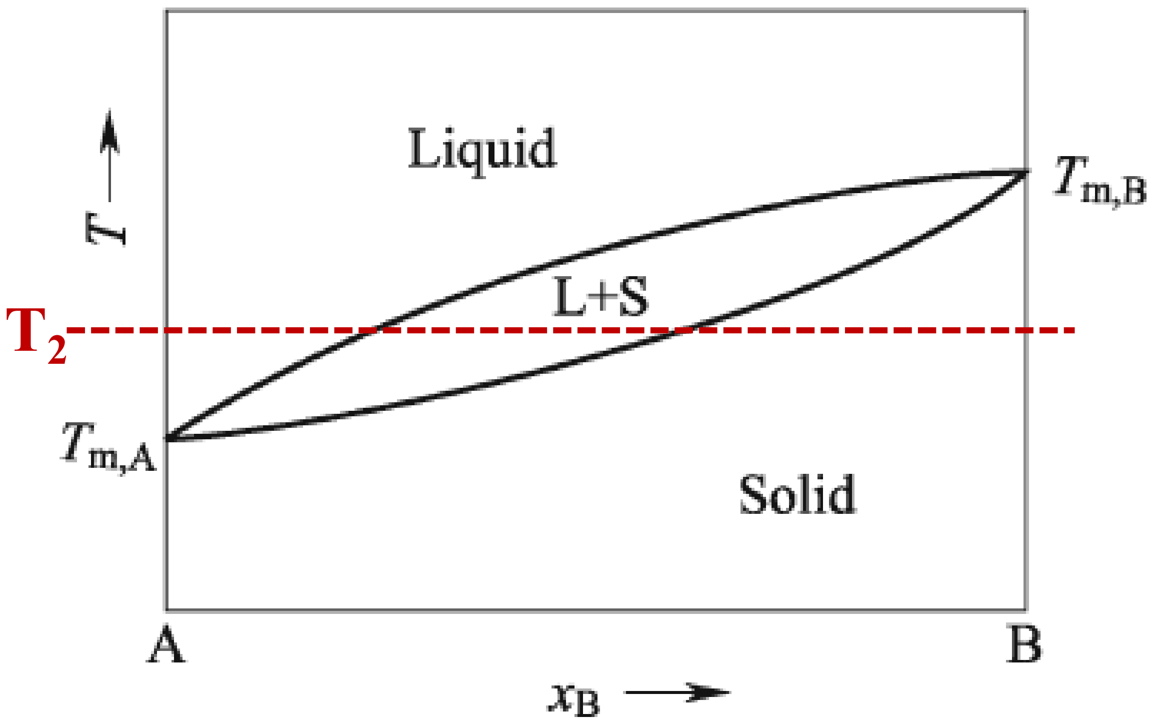
Image: Q. Jiang, Z. Wen. "Thermodynamics Of Materials." Available through MIT Libraries at http://link.springer.com/book/10.1007/978-3-642-14718-0/page/1.



Two-Phase Region Criterion

Image: Q. Jiang, Z. Wen. "Thermodynamics Of Materials." Available through MIT Libraries at http://link.springer.com/book/10.1007/978-3-642-14718-0/page/1.



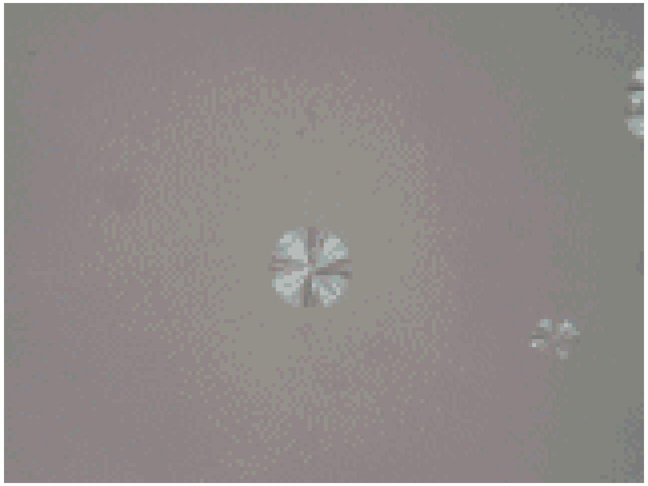


$$\frac{\partial \mu_A}{\partial n} = \frac{\partial \mu_B}{\partial n}$$

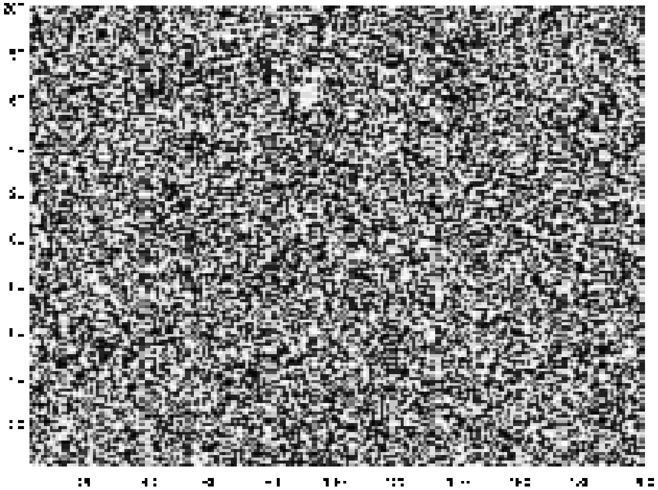
Chemical potential change is the same at mixture(s)

How will the phases form?

Nucleation & Growth



Spinodal Decomposition

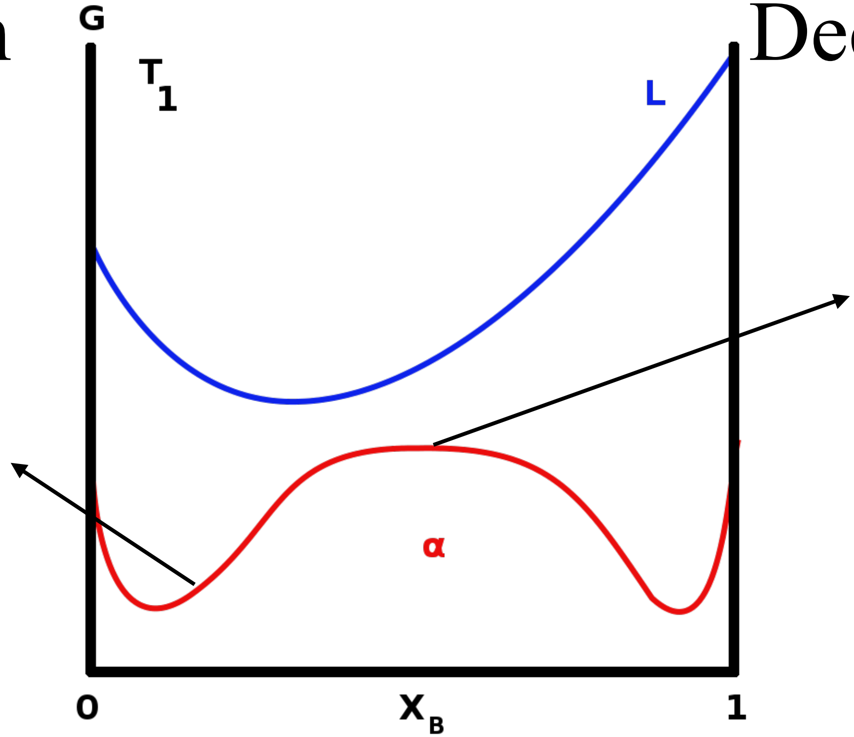


How will the phases form?

Nucleation & Growth

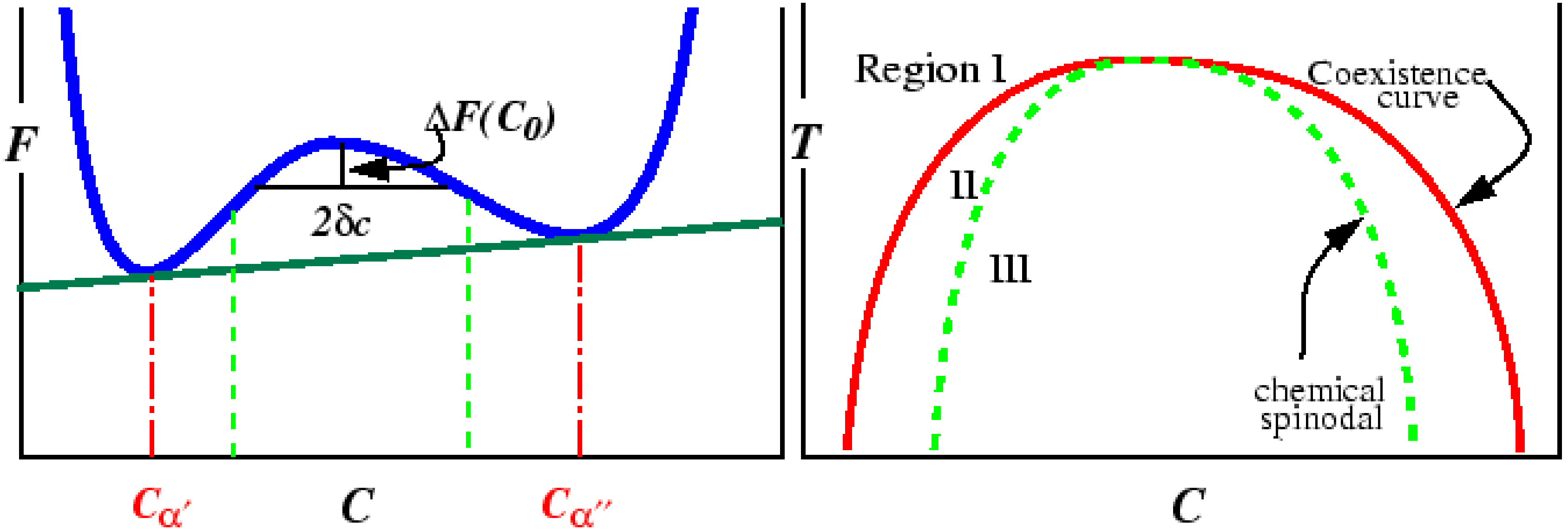
Spinodal Decomposition

$$\frac{\partial^2 G}{\partial c^2} > 0$$



$$\frac{\partial^2 G}{\partial c^2} < 0$$

Phase Diagram: Spinodal Region



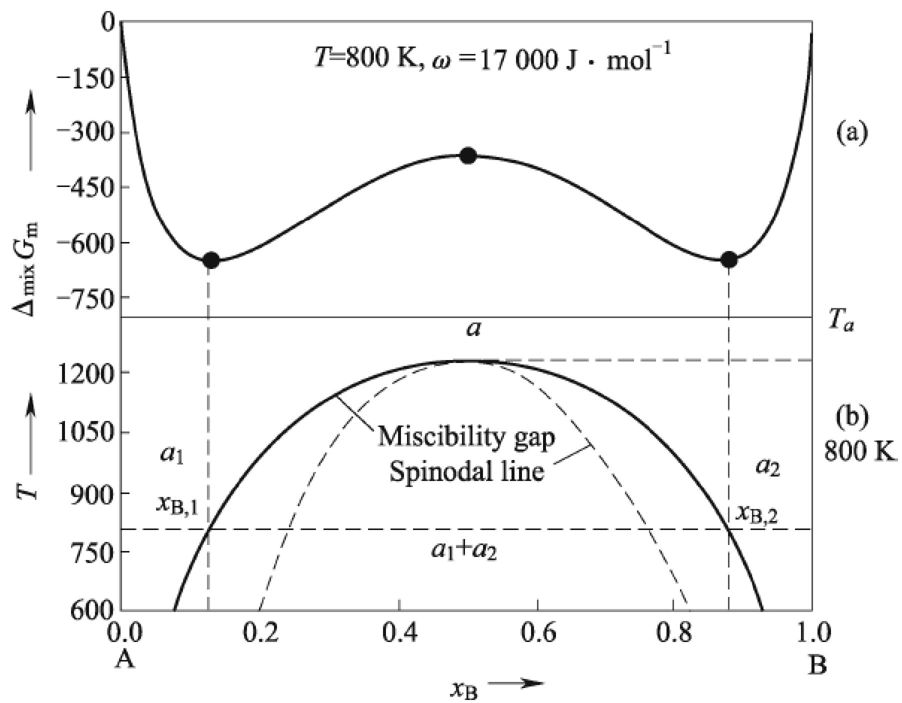
Courtesy of W. Craig Carter. Used with permission.

http://pruffle.mit.edu/~ccarter/3.21/Lecture_27/

Spinodal Decomposition Energy

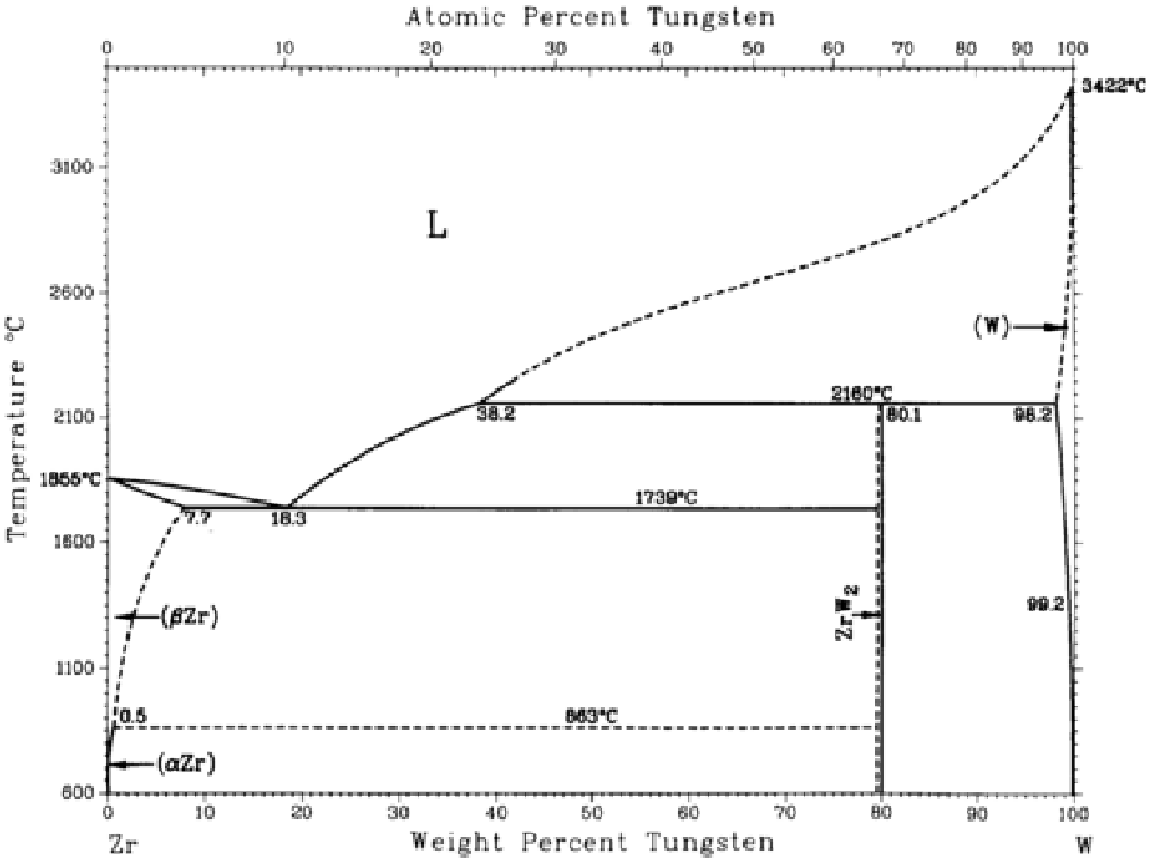
Image: Q. Jiang, Z. Wen. "Thermodynamics Of Materials." Available through MIT Libraries at http://link.springer.com/book/10.1007/978-3-642-14718-0/page/1.

$$\frac{\partial^2 \Delta_{\mathrm{mix}} G_{\mathrm{m}}}{\partial x_{\mathrm{B}}^2} = RT \left\{ \frac{1}{x_{\mathrm{B}}} + \frac{1}{(1 - x_{\mathrm{B}})} \right\} - 2\omega = 0.$$



In-Class Example: W-Zr

Draw the Gibbs free energy diagram at 1000C



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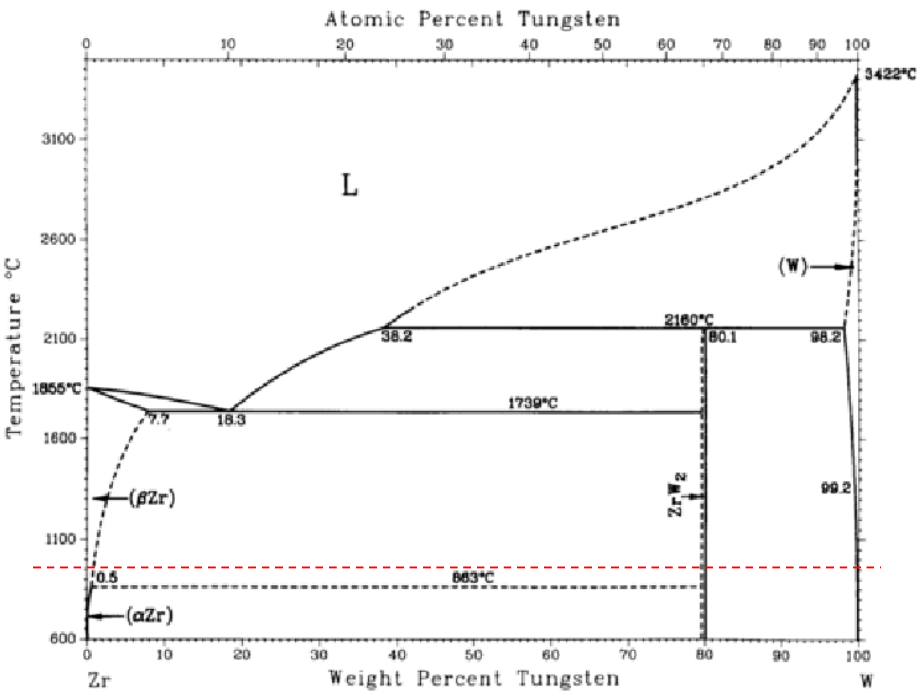
In-Class Example: W-Zr



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