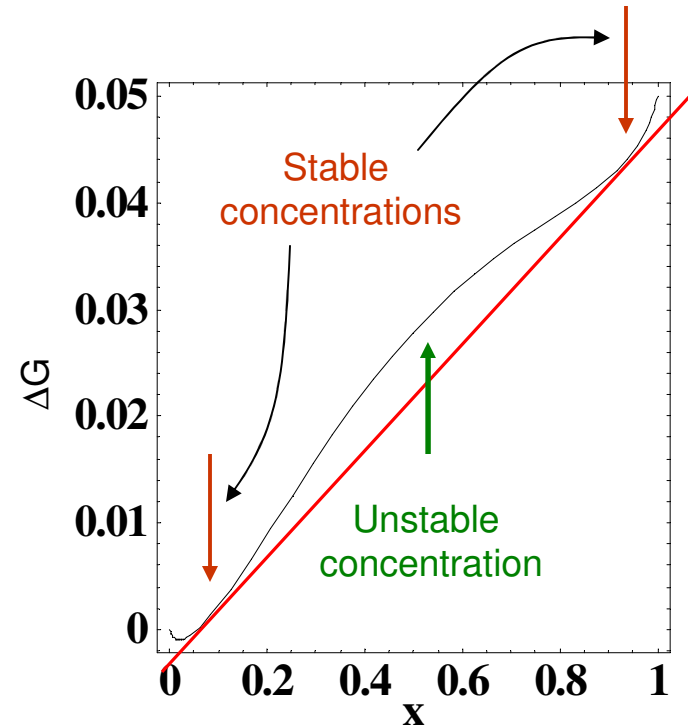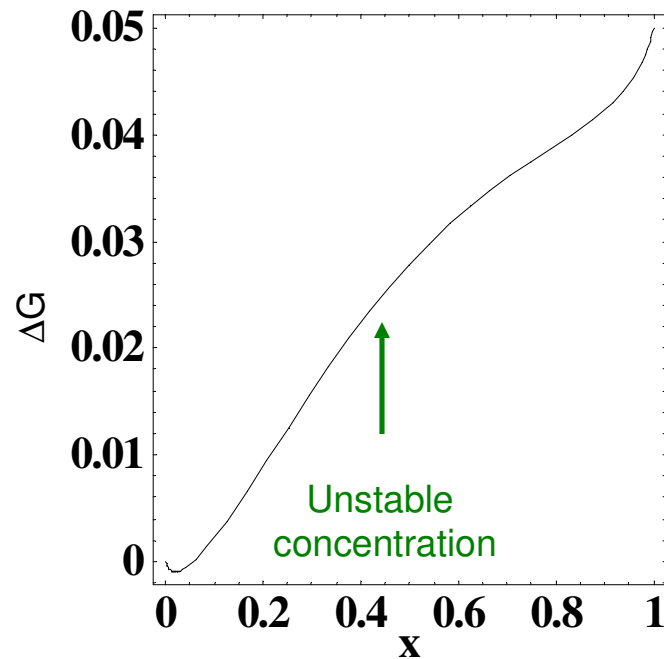# Phase Separation in Mixtures

Separation onto phases will lower the average Gibbs energy and thus the equilibrium state is phase separated

Phase Separation versus Temperature

Note that at higher temperatures the region of concentrations where phase separation takes place shrinks and eventually disappears

$$\Delta G = \Delta U - T\Delta S$$

This is because the term - TΔS becomes large at high temperatures. You can say that entropy "wins" over the potential energy cost at high temperatures

Microscopically, the kinetic energy becomes much larger than potential at high T, and the molecules randomly "run around" without noticing potential energy and thus intermix
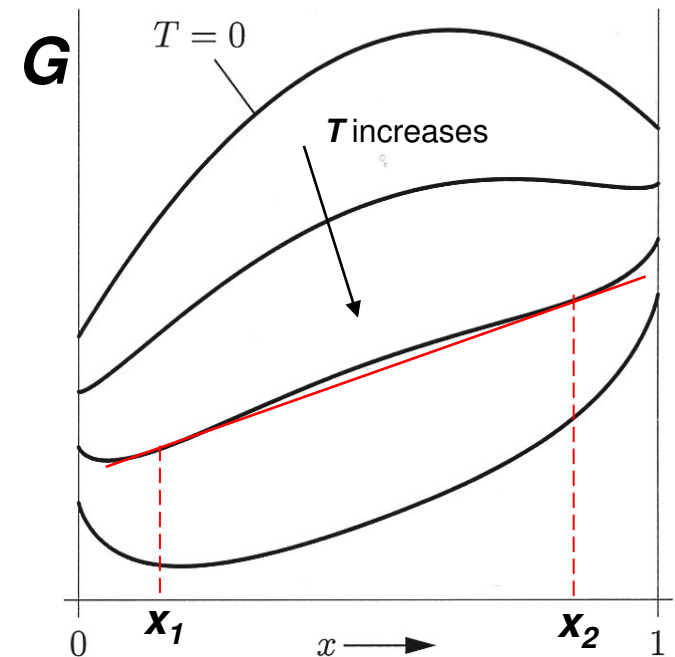
Oil and water mix at high temperature

Liquid-Gas Phase Separation in a Mixture

A binary mixture can exist in liquid or gas phases.

The liquid and gas phases have different Gibbs potentials as a function of mole fraction of one of the components of the mixture
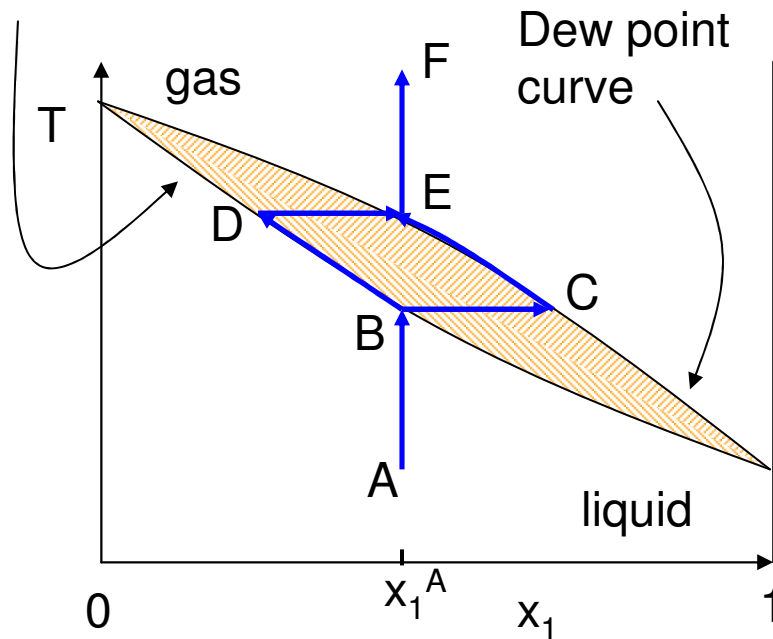
At high temperatures the $G_{gas} < G_{liquid}$ because the entropy of gas is greater than that of liquid

At lower temperatures, the two Gibbs potentials intersect and separation onto gas and liquid takes place.

Boiling of a binary mixture

Bubble point
curve

gas

Dew point
curve

liquid

T

F

E

D

C

B

A

0

x_1^A

x_1

1
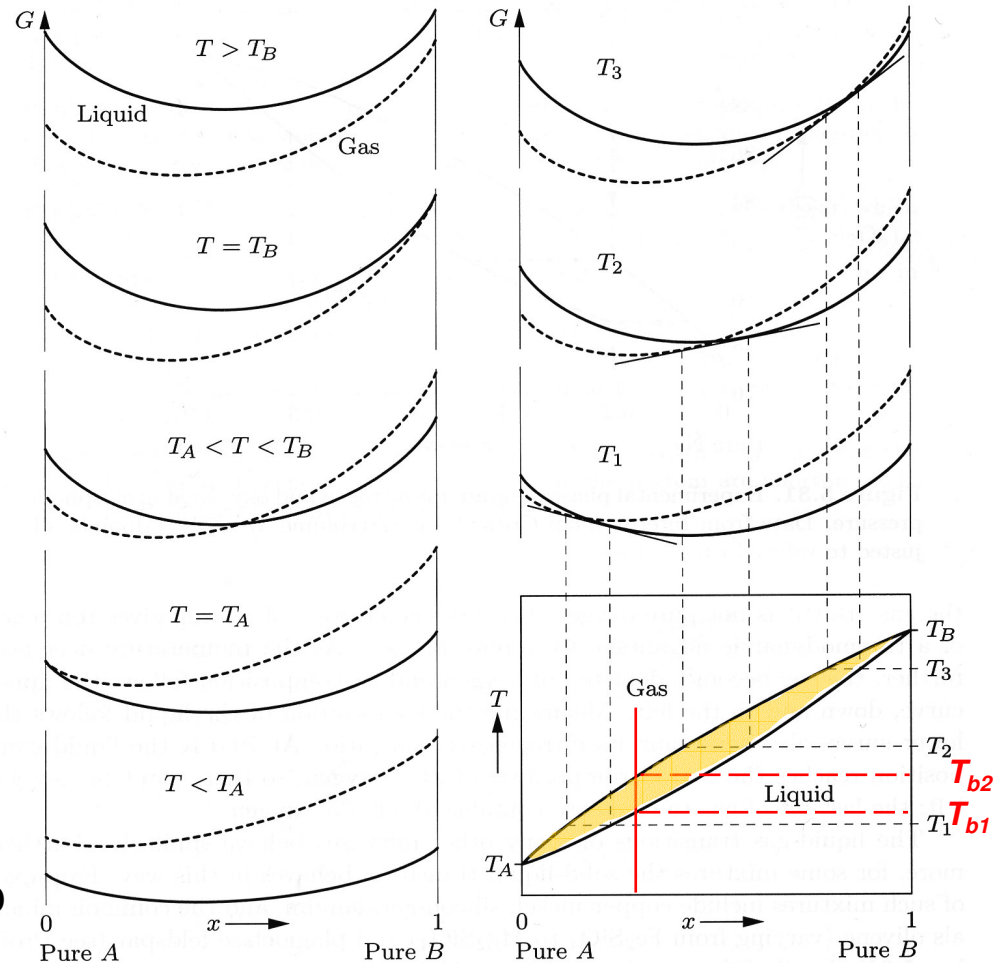
If we have a liquid at pint A that contains
a molar fraction x_1^A of component 1 and
start heating it:

- First the liquid heats to a temperature T'
at constant x_1^A and arrives to point B.

- Then phase separation takes place
(liquid starts to boil) and the system
consists of a mixture of liquid at point B
and gas at point C.

Boiling of a binary mixture

Bubble point curve

gas

T

Dew point curve

F

E

D

B

C

A

liquid

0

x_1^A

x_1

1
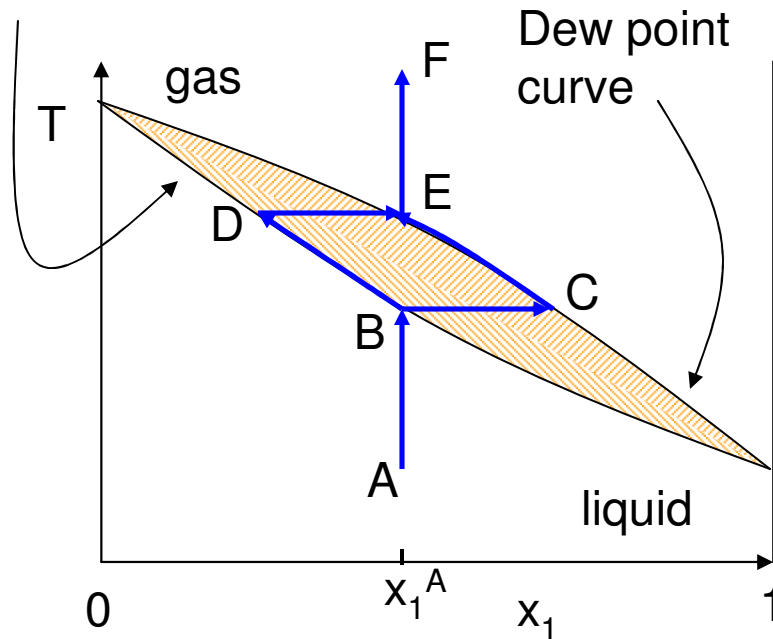
-As we continue increasing temperature, the fraction of gas phase increases while the fraction of liquid phase decreases. At the same time the mole fraction of component 1 in gas phase decreases and approaches the value x_1^A; the fraction of component 1 in the liquid phase moves away from the value x_1^A and also decreases. Finally, at point E we have gas with the original mole fraction x_1^A.

- Note that boiling of a binary mixture takes place over a finite temperature range! This is qualitatively different from boiling of a single-component liquid.
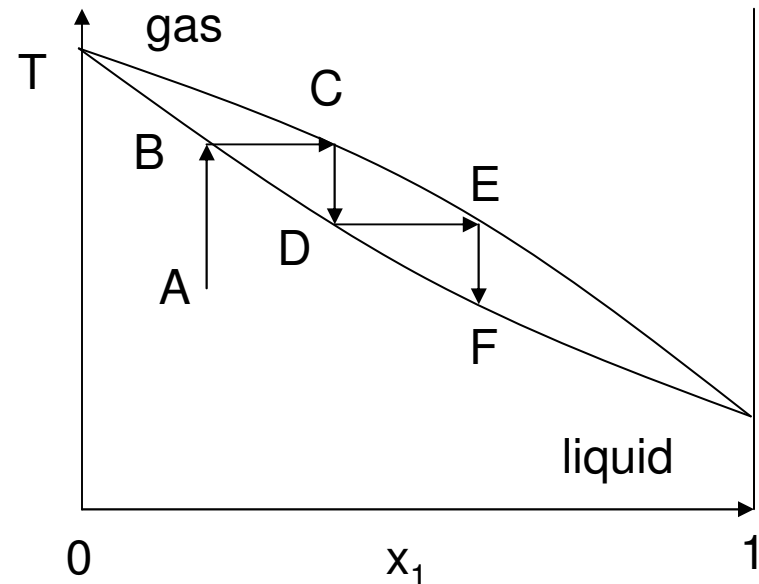
Distillation

The shape of the liquid-gas phase diagram of binary mixtures enables a method of separation of the two components called distillation.

Starting at point A (low concentration of component 1), we warm up the mixture until it reaches point B. At a slightly higher temperature a small fraction of liquid turns into gas with higher concentration of component 1 at point C.

Then we physically separate this gas from the liquid and cool it down to form liquid with high concentration of component 1 (point D).

The process can be repeated to get higher and higher concentrations of component 1 at the expense of reducing the mole number of the final product.
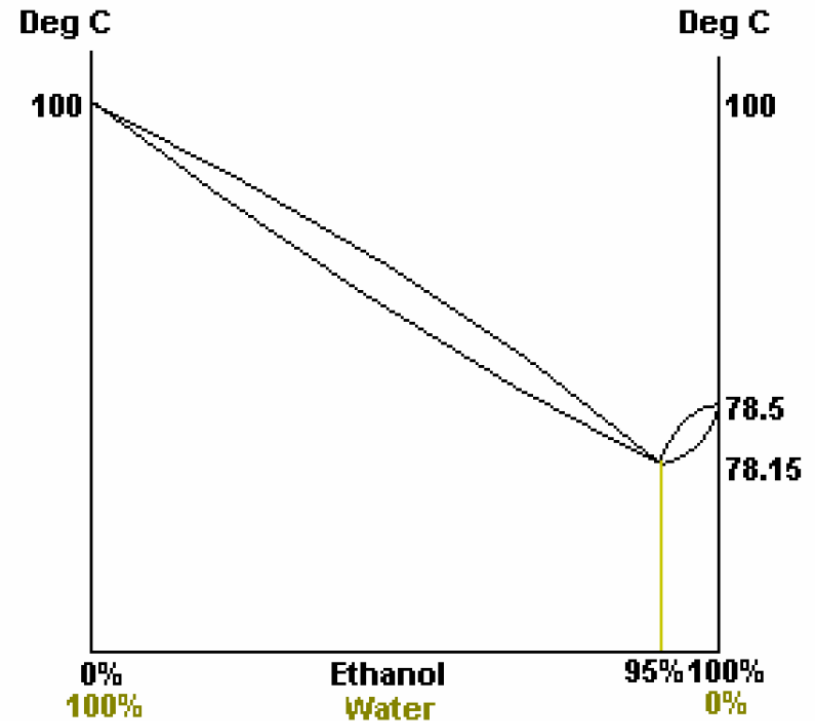
Distillation

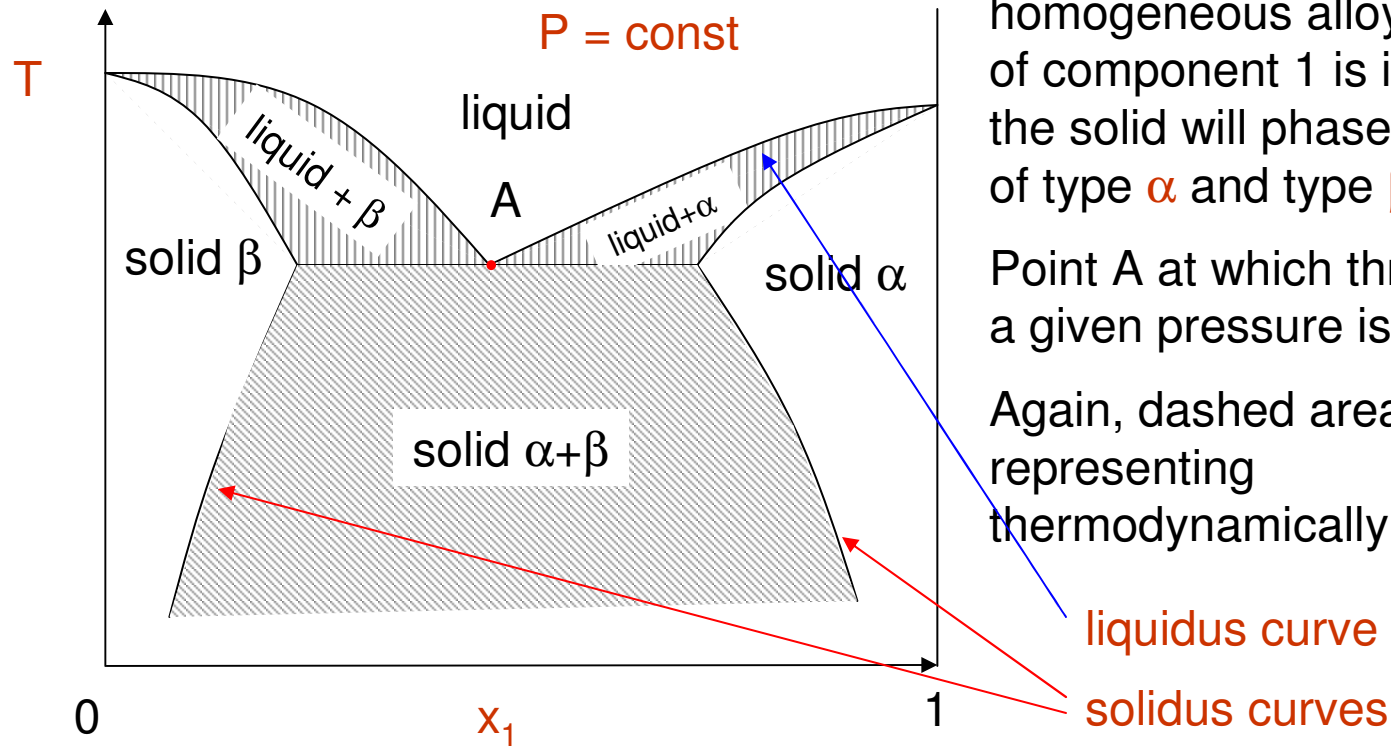More complicated two-component liquid-gas phase diagrams are possible (e. g. ethanol and water).

The details depend on the microscopic interactions between the molecules of the two components.

It is clear from the picture on the right that distillation can only produce 95%-pure ethanol from a water/ethanol mixture.

Binary solid – liquid phase diagram

Typical 2-component solid-liquid phase diagram.

solid β

liquid + β

P = const

liquid

A

liquid+α

solid α

solid α+β

liquidus curve

solidus curves

0   x₁   1

In general, not any concentrations of the components 1 and 2 and give a homogeneous alloy. If the mole fraction of component 1 is in the miscibility gap, the solid will phase-separate into alloys of type α and type β.

Point A at which three phases coexist at a given pressure is called the eutectic.

Again, dashed areas a holes representing thermodynamically unstable regions.

Liquid-Solid Phase Transitions in Binary Mixtures

To explain the solid-liquid phase diagram of a binary mixture with two possible types of solid crystals, we need to consider Gibbs energies of two solid phases and the liquid phase.

Intersections these Gibbs potential curves give rise to regions of phase separation between three possible phases.

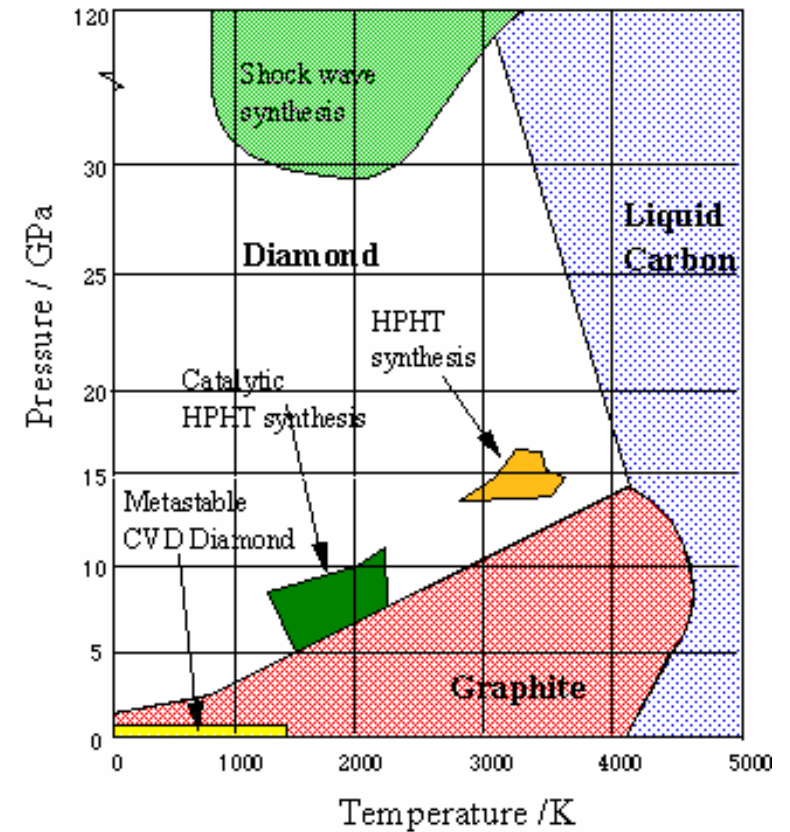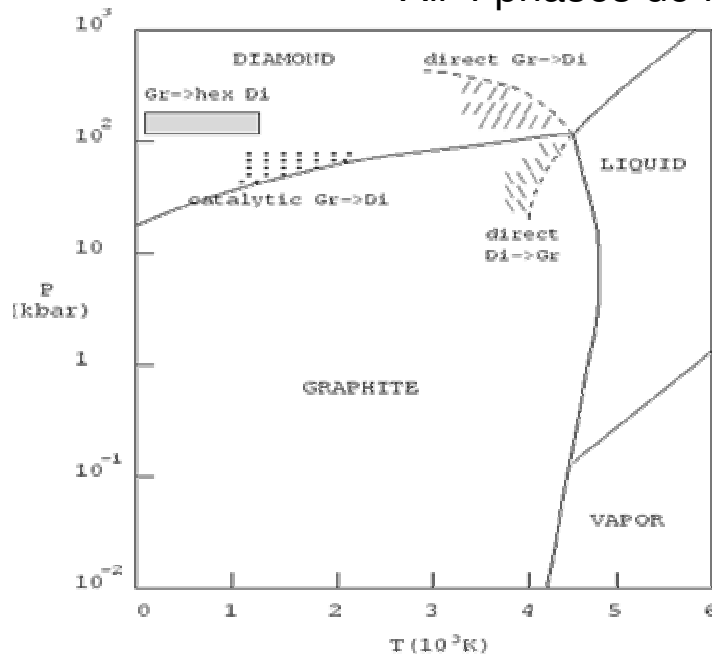More complex phase diagrams appear for more complex Gibbs potential curves.
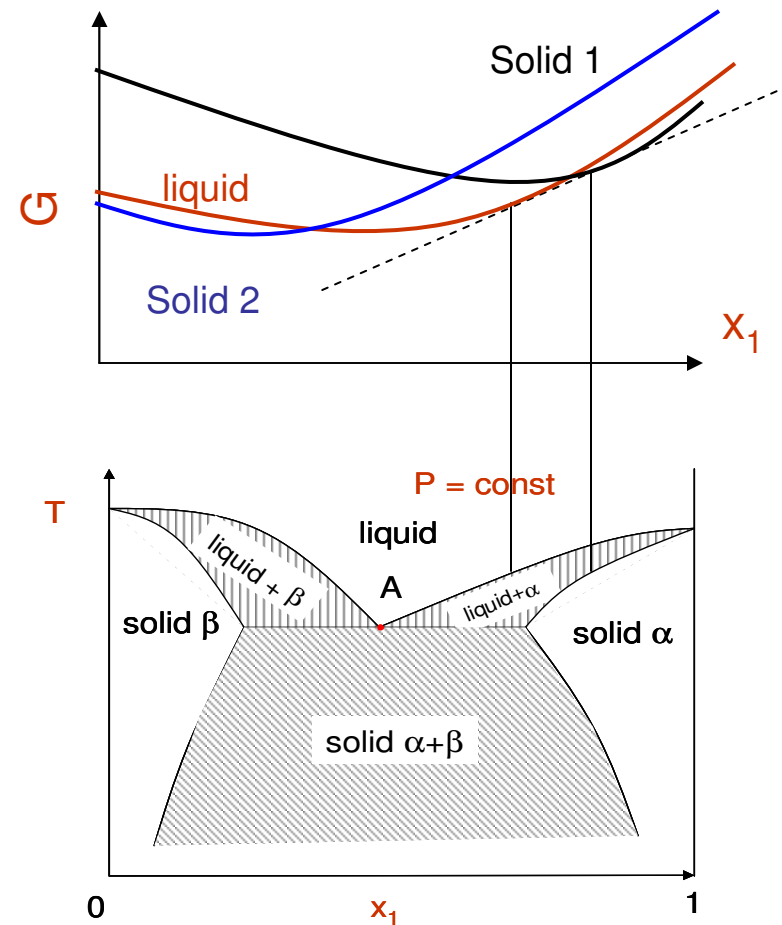
Examples of phase diagrams

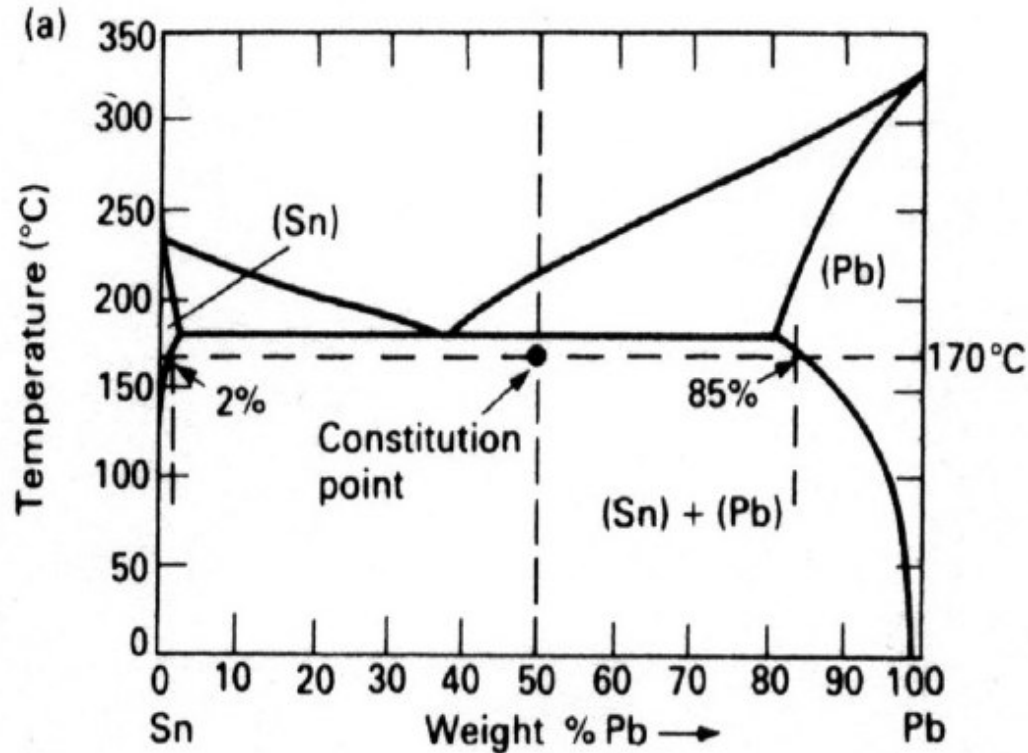Single – component

Carbon

2 triple points

All 4 phases do not coexist

Examples of phase diagrams

Pb - Sn

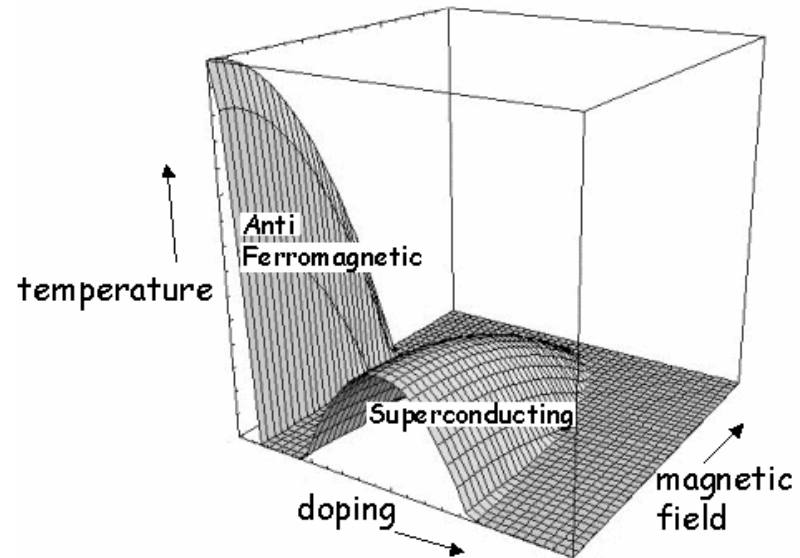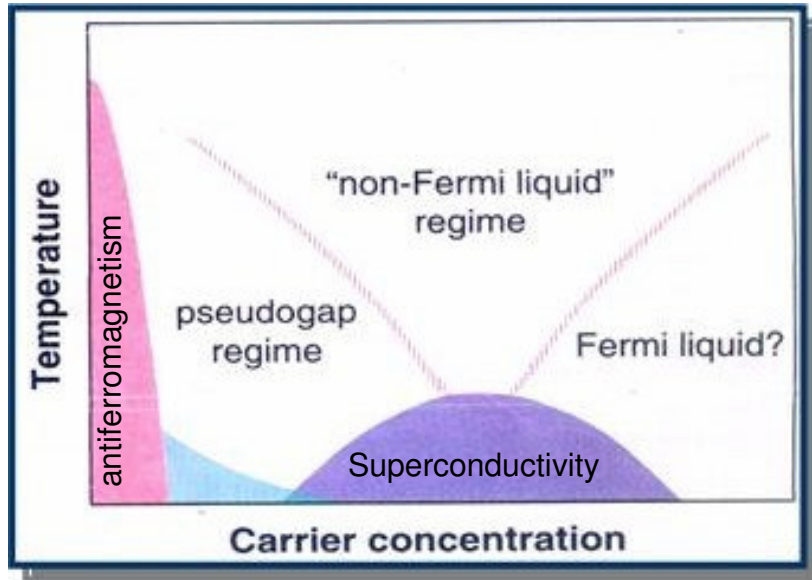2 – component, multiple phases

A 50-50 Pd-Sn alloy at 170 °C:

Two phases: (Sn) and (Pb)

Composition of (Sn): 2% Pb
Composition of (Pb): 85% Pb

Phase proportion: 42% (Sn) and 58% (Pb).

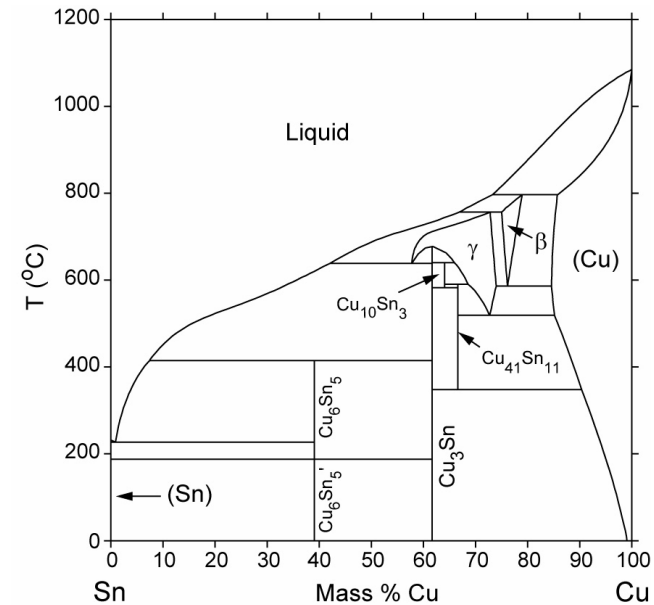# *Examples of phase diagrams – high temperature superconductors*

- The existence of states with qualitatively different electronic properties (different phases) is clear, however the microscopic interaction mechanisms between electrons remains a puzzle. - Challenge for theory – to reproduce the experimental phase diagram

Examples of phase diagrams
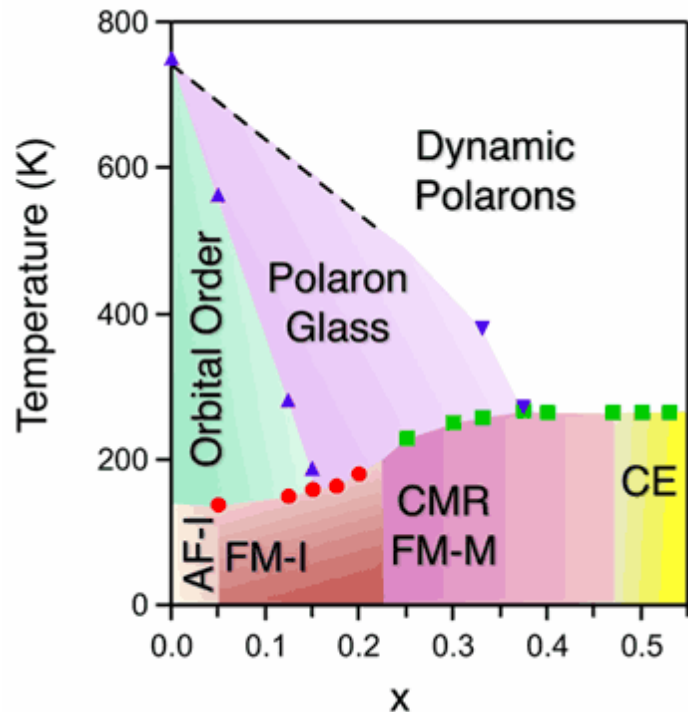
Phase diagram of a strongly correlated oxide material – $La_{1-x}Ca_xMnO_3$

Phase diagram of $Cu_{1-x}Sn_x$ binary alloy calculated from first principles (energy spectrum -> partition function -> free energy -> coexistence curves)

Examples of phase diagrams

Schematic density-temperature
phase diagram quarks and
gluons

Quark-gluon plasma at high
densities and temperatures

Condensation into baryons
(protons, neutrons) at lower
temperatures and densities
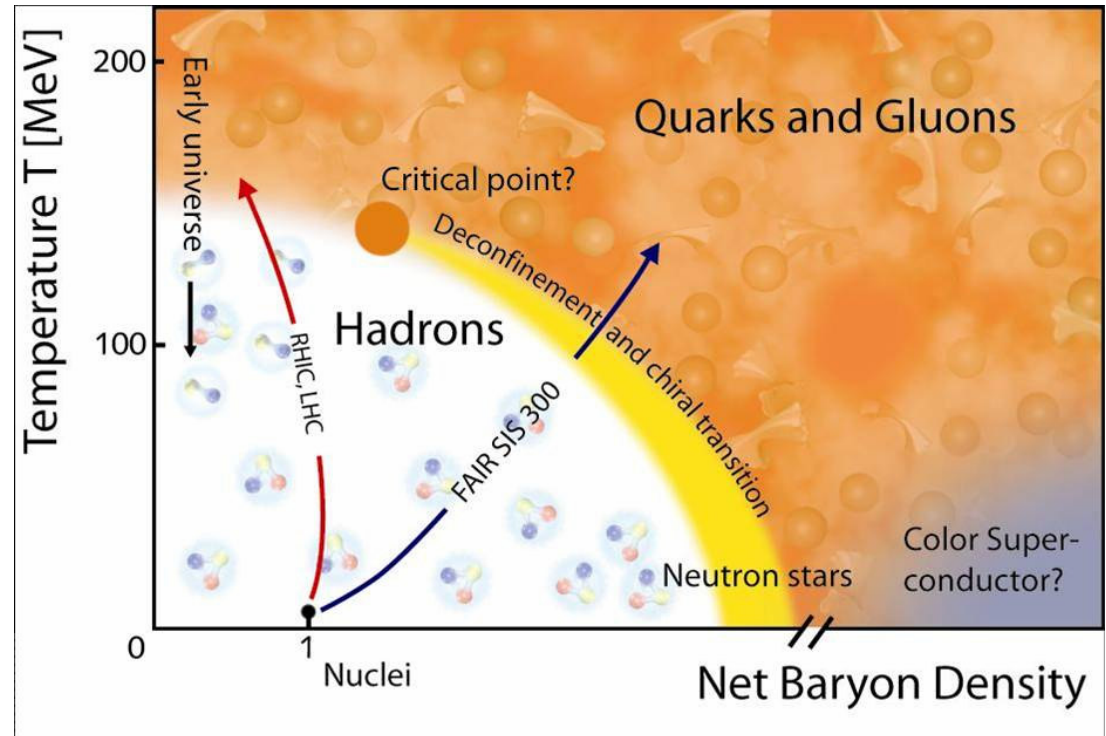
Classification of phase transitions

Outdated historical scheme:

First order: first derivative of the appropriate thermodynamic potential with respect to a thermodynamic variable is discontinuous at the phase transition.

Second order: first derivative is continuous but second derivative of the appropriate thermodynamic potential is discontinuous.

Third order ...

This classification scheme fails to classify phase transitions for which derivatives diverge at the transition point. (For example, we will see today that second derivatives diverge near the critical point).

Classification of phase transitions

Modern scheme:

First order: there is latent heat associated with transition from one phase to another.

Continuous: no latent heat associated with the phase transition. To make matter more confusing, sometimes continuous phase transitions are also called "second order".