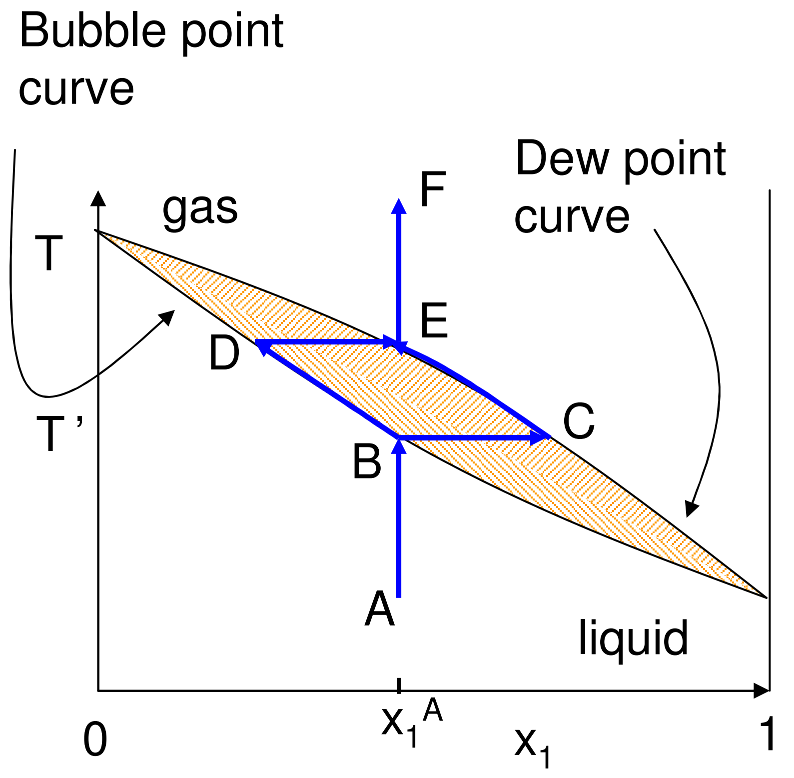
Boiling of a binary mixture



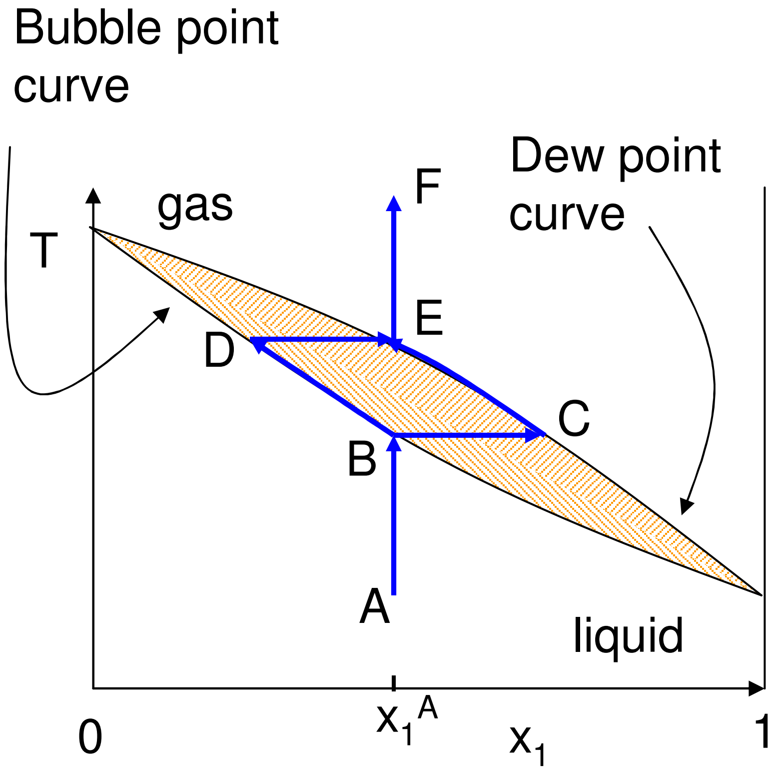
If we have a liquid at point A that contains a molar fraction x_1^A of component 1 and start heating it:

- 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.

Notes

Boiling of a binary mixture



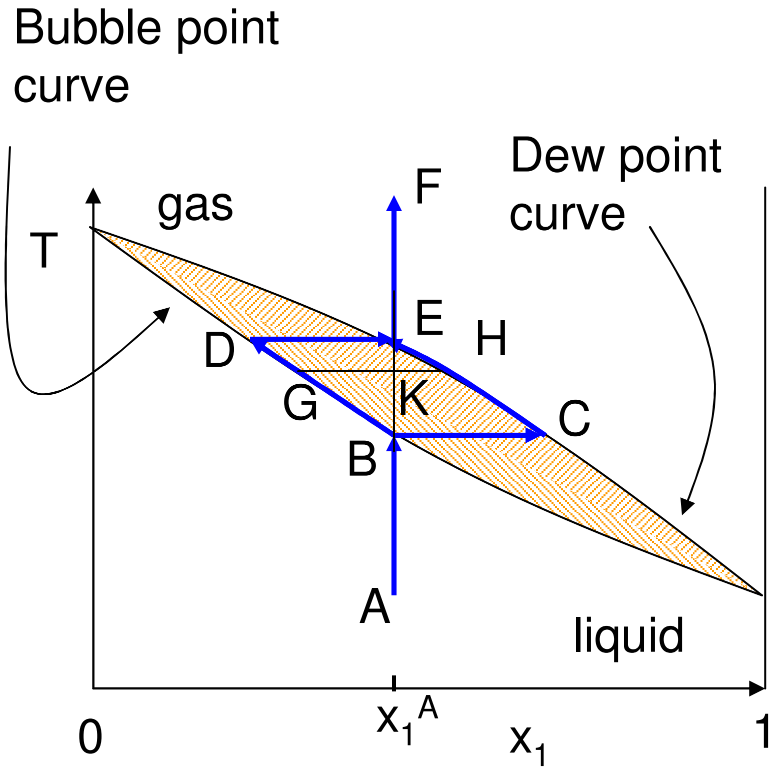
- As we continue increasing temperature, the fraction of gas phase increases while the fraction of liquid phase decreases.

- 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.

Notes

Boiling of a binary mixture



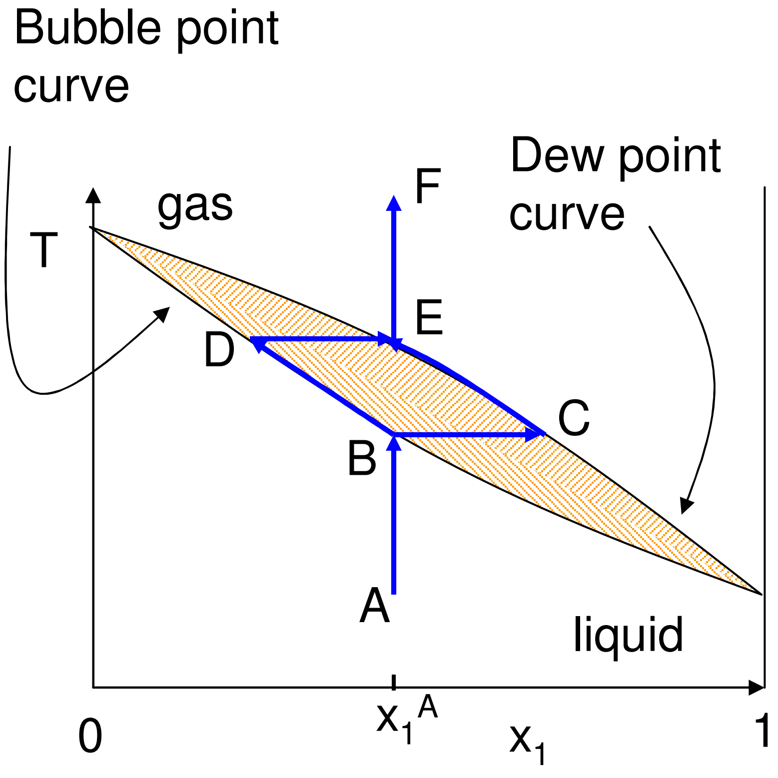
The mole fraction of liquid at point K can be determined from the lever rule:

$$x_L = \frac{N_L}{N_L + N_G} = \frac{KH}{GH}$$

- 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.

Notes

Boiling of a binary mixture



It may seem confusing that the mole fractions of material 1 decrease in both liquid and gas as the temperature is raised throughout the melting process. Is this possible?

This is possible if the molar fraction of x_1 in the material that is evaporating is greater than that in the liquid but smaller than that in the gas.

Such a process will decrease mole fractions of x_1 in both gas and liquid

Notes

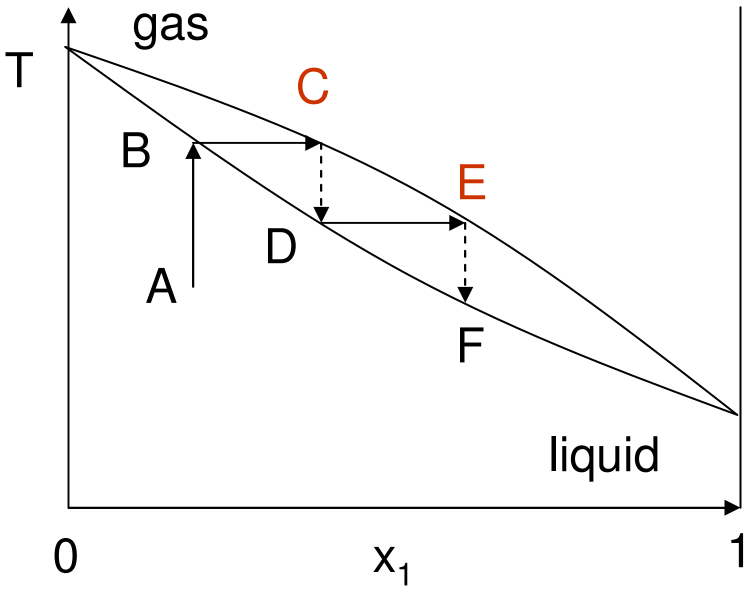
Distillation

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.



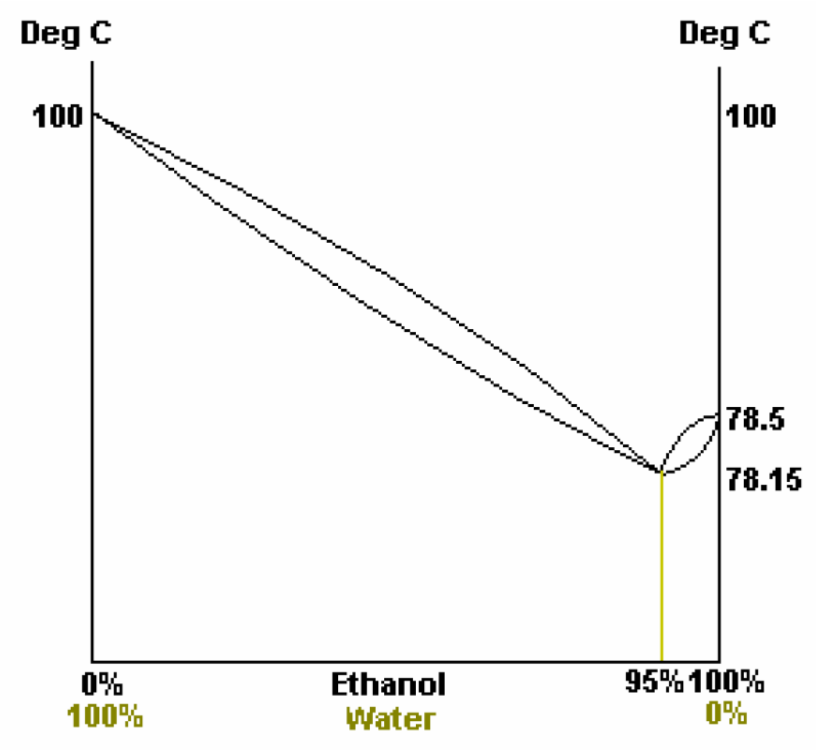
Notes

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.

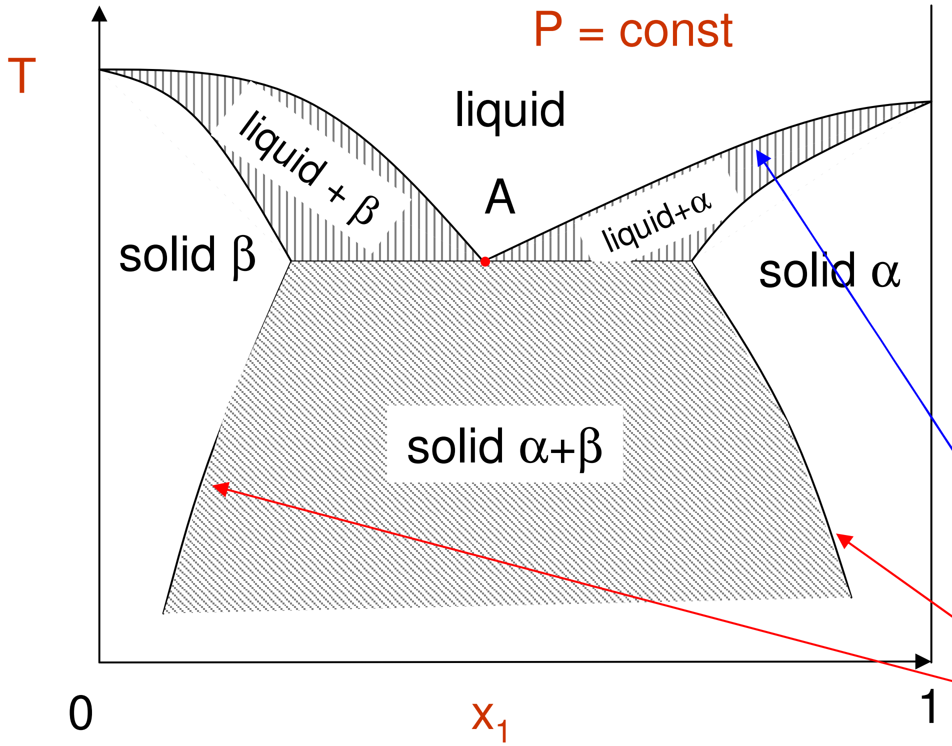
It is clear from the picture on the right that distillation can only produce 95%-pure ethanol from a water/ethanol mixture.



Notes

Binary solid – liquid phase diagram

Typical 2-component solid-liquid phase diagram.



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.

liquidus curve

solidus curves

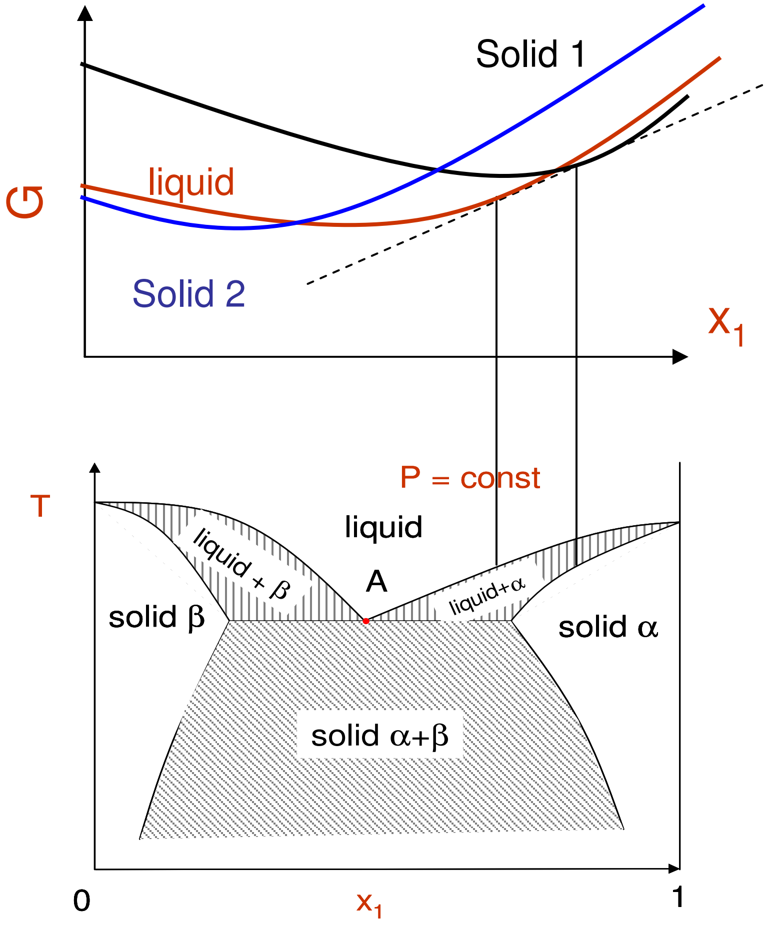
Notes

Liquid-Solid Phase Transitions in Binary Mixtures

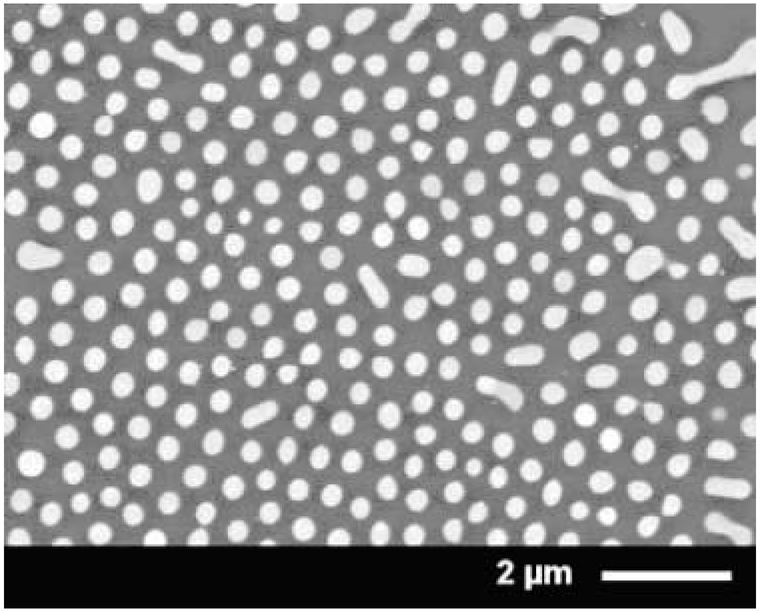
To explain the solid-liquid phase diagram of a binary mixture with two possible types of solid crystals, we need to consider Gibbs energies of two solid phases and the liquid phase.

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

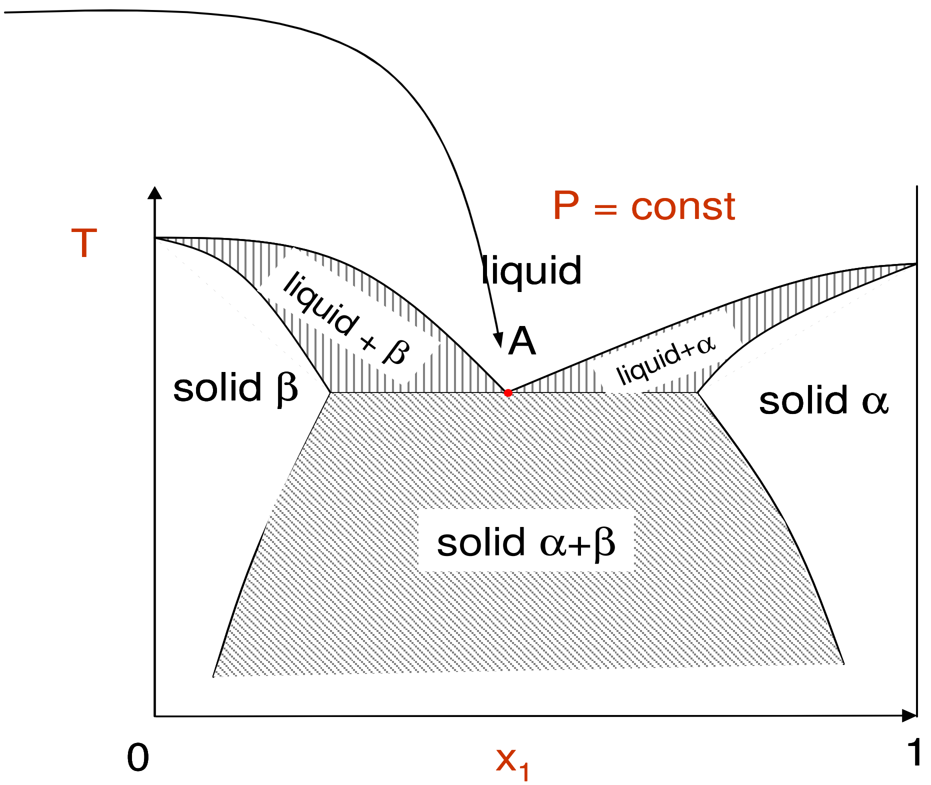
More complex phase diagrams appear for more complex Gibbs potential curves.



Binary solid – liquid phase diagram



Domains after cooling through the eutectic of SiNb alloy



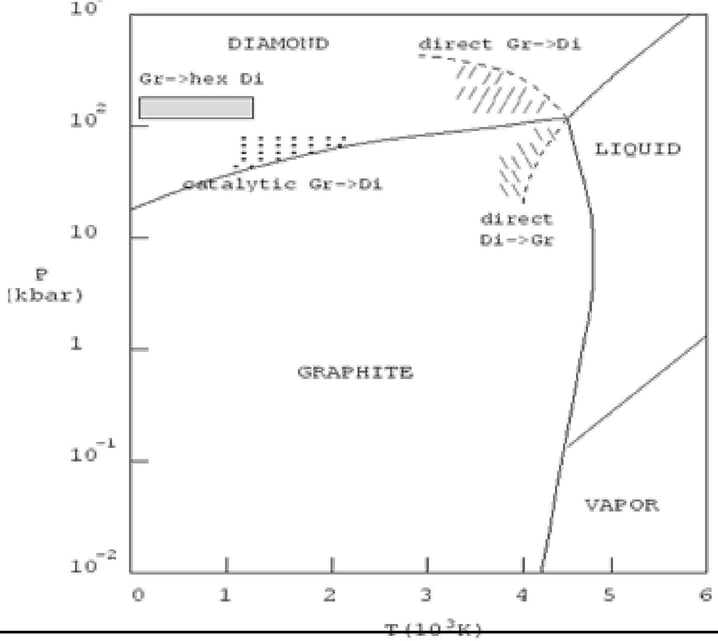
Examples of phase diagrams

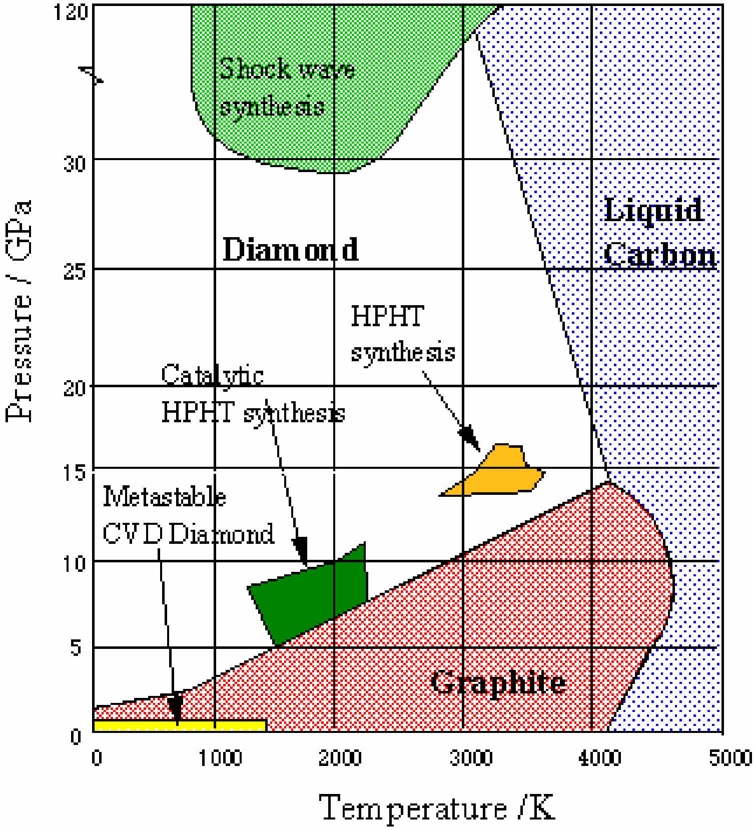
Carbon

Single – component

2 triple points

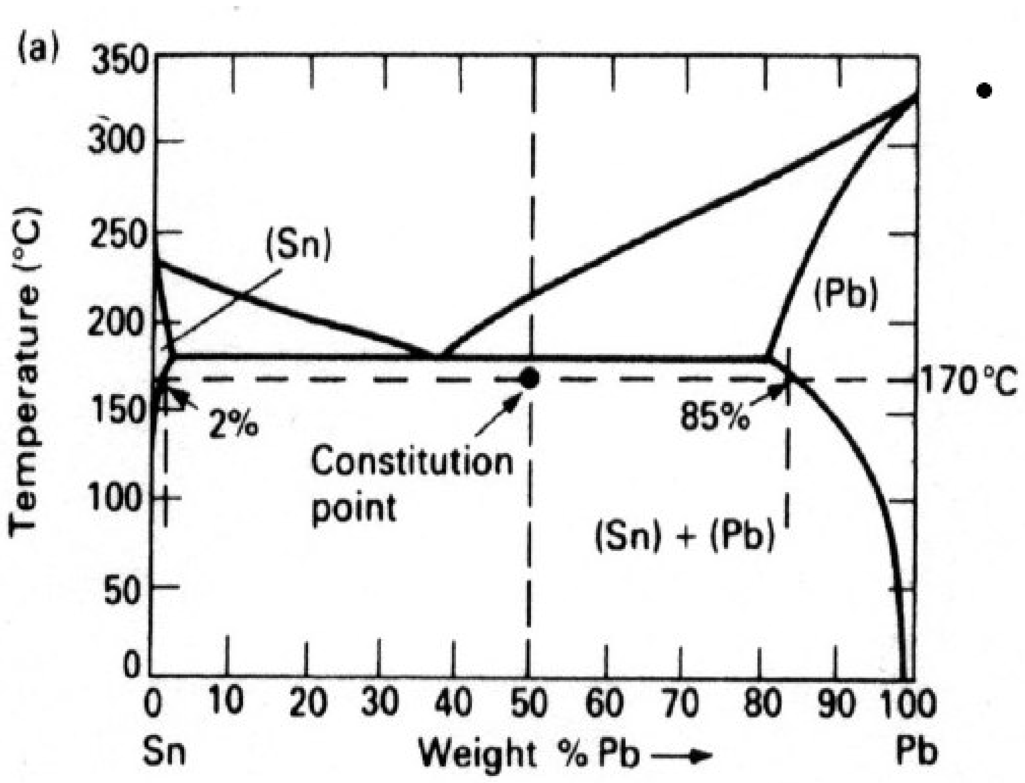
All 4 phases do not coexist





Notes

Examples of phase diagram



Pb - Sn

- 2 – component, multiple phases

A 50-50 Pb-Sn alloy at 170℃:

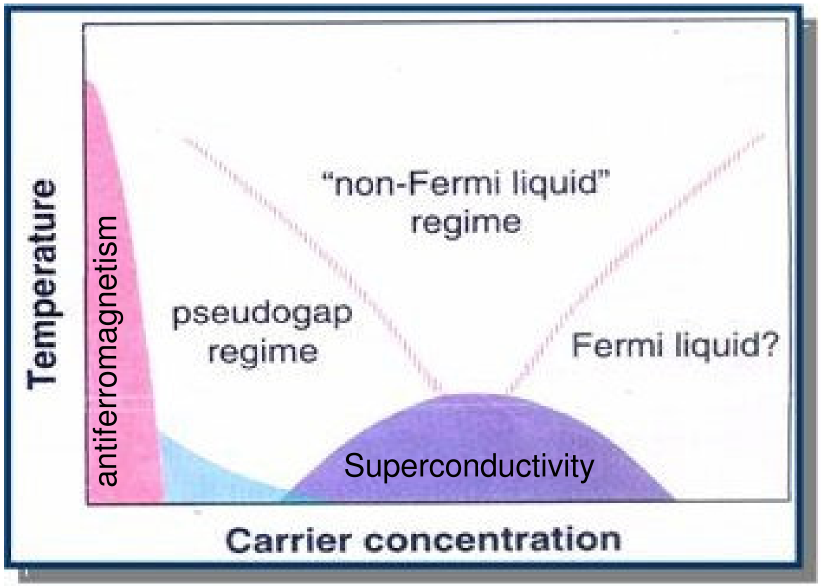
Two phases: (Sn) and (Pb)

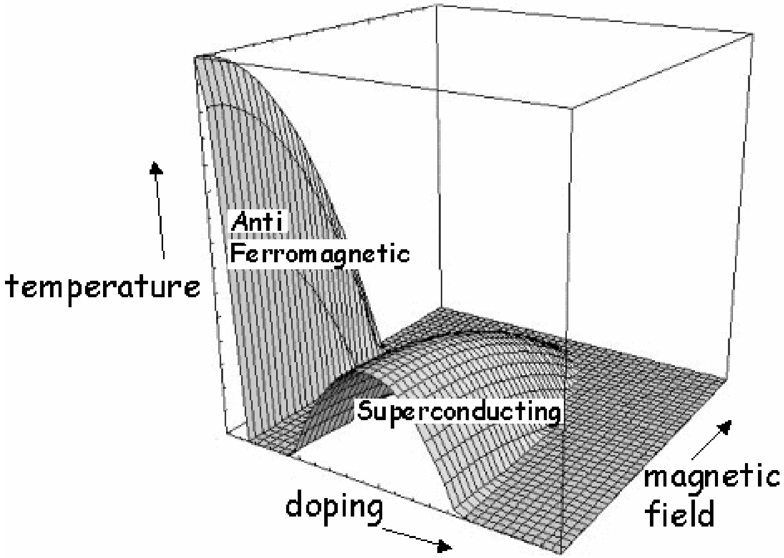
Composition of (Sn): 2% Pb
Composition of (Pb): 85% Pb

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

Notes

Examples of phase diagrams – high temperature superconductors

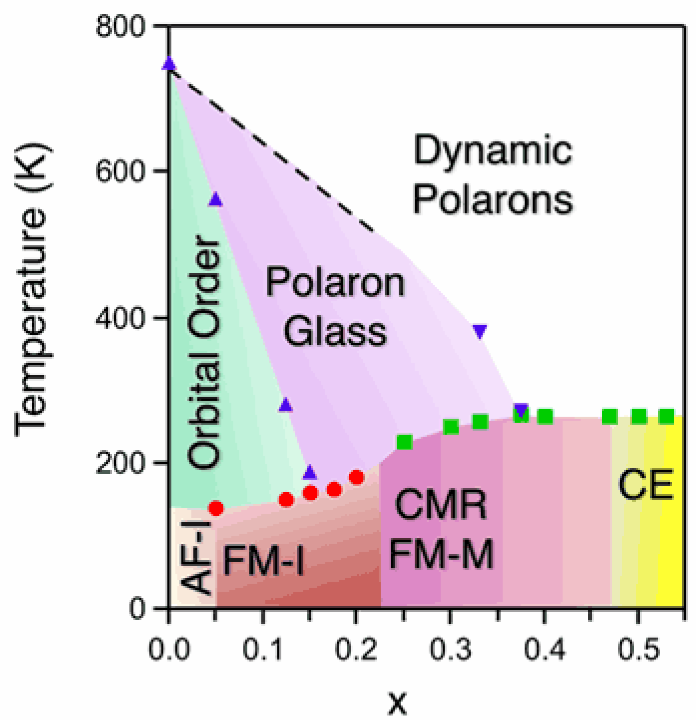




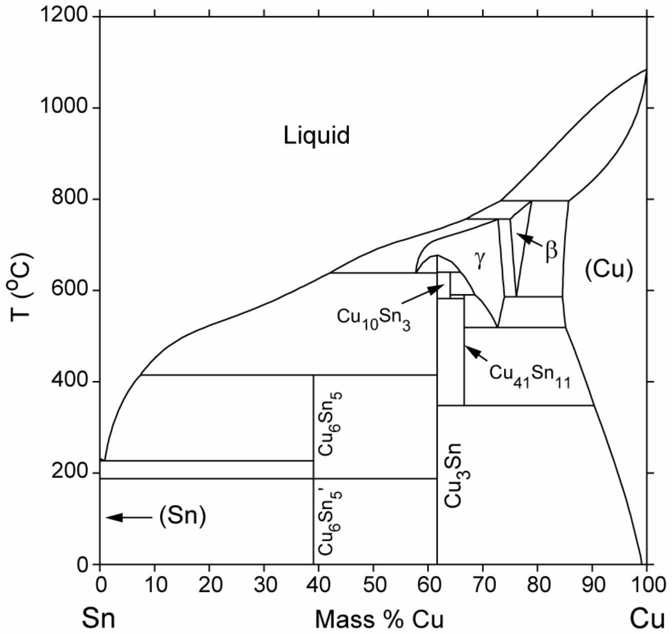
- The existence of states with qualitatively different electronic properties (different phases) is clear, however the microscopic interaction mechanisms between electrons remains a puzzle. - Challenge for theory – to reproduce the experimental phase diagram

Notes

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)

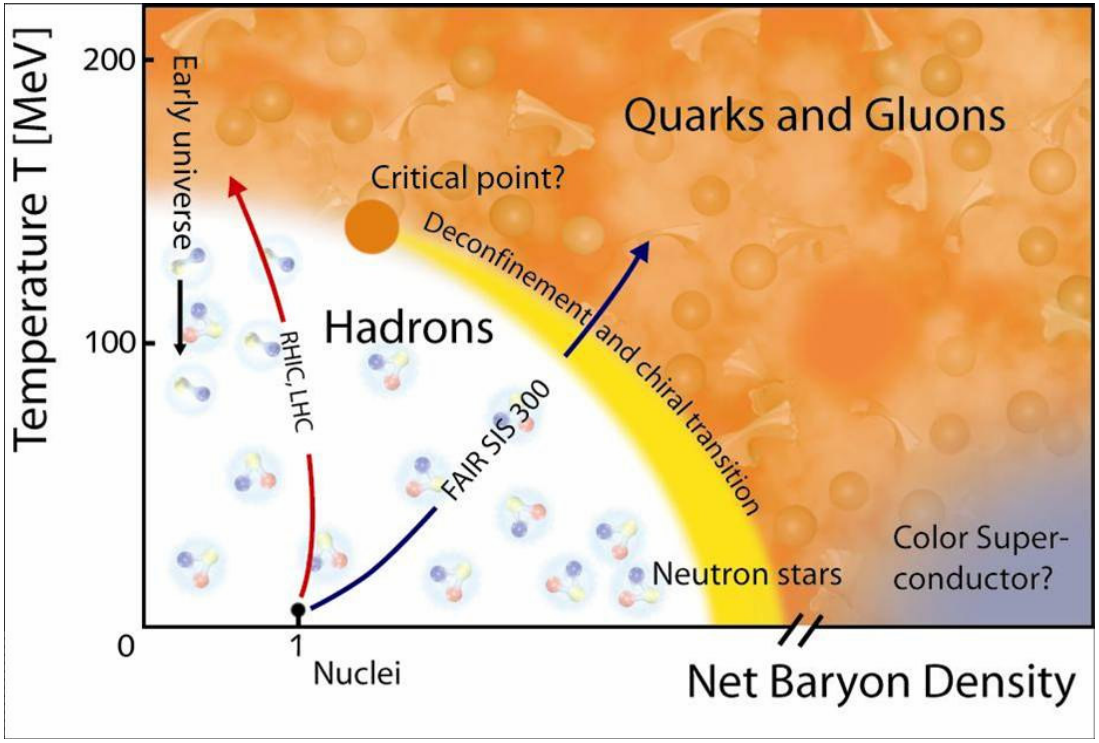
Notes

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



Notes

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 that second derivatives diverge near the critical point).

Notes

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 the matter more confusing, sometimes continuous phase transitions are called “second order”.

Notes