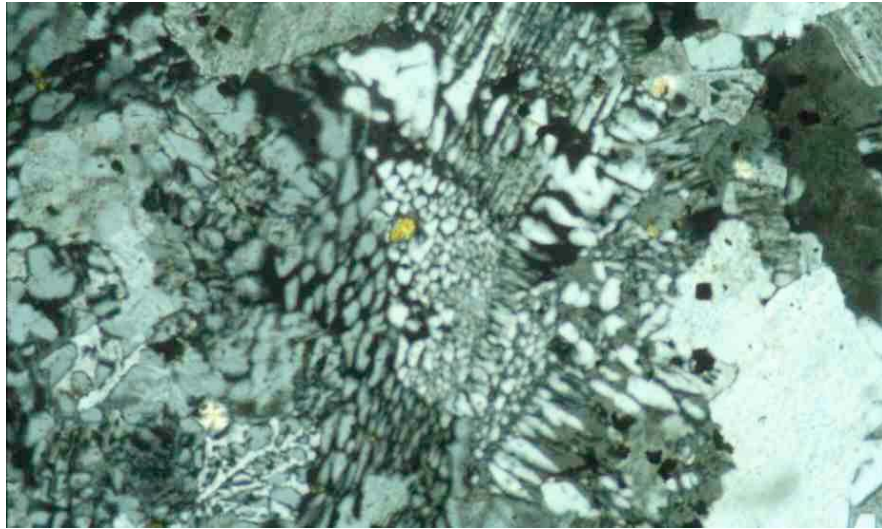


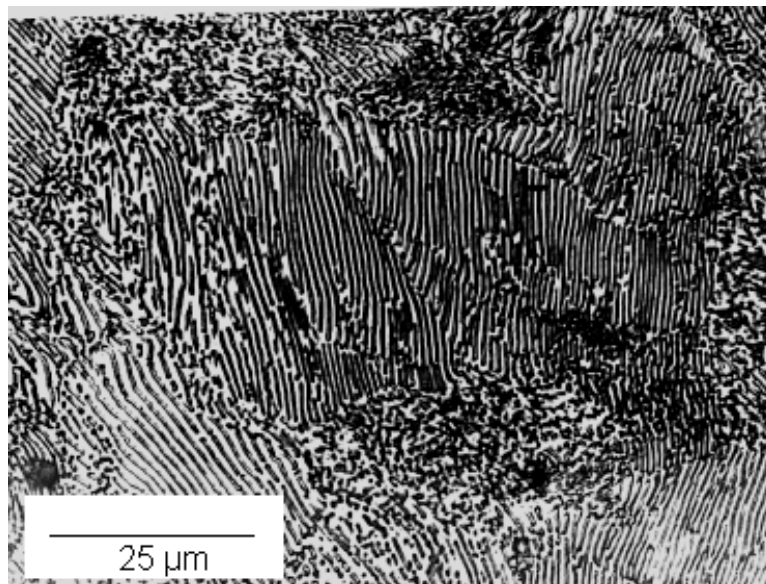
THE STRUCTURE OF MATERIALS: PHASE DIAGRAMS

The properties of any material are critically dependent upon its internal microstructure. This microstructure may consist of a 'simple' grain structure, or more complex multiphase components, with length scales which may range from a few atomic spacings to many microns. Microstructures form through thermodynamic and kinetic control, and the preparation of alloys and ceramics with variable composition leads to great flexibility in selecting and fine-tuning particular materials properties. Here I will discuss phase diagrams for two-component systems, which can tell us what phases we may expect to exist.



_____ 200 μm

Intergrowth of 2 different minerals in a rock, formed during solidification.



Pearlite: intergrowth of 2 different Fe-C phases in a steel, formed during cooling.

Websites and computer packages:

MATTER has two chapters (*Introduction to Phase Diagrams; Thermodynamics of Phase Diagrams*) that together provide a very good introduction to this topic. Also: <http://www.matter.org.uk/solidification/>

The DoITPoMS Micrograph Library has many images of microstructures, together with descriptions and explanations about them:

<http://www.msm.cam.ac.uk/doitpoms/miclib/index.php>

and there are Teaching and Learning Packages on *Optical Microscopy & Specimen Preparation, Diffraction and Imaging, Phase Diagrams & Solidification, Solidification of Alloys and Solid Solutions* at:

<http://www.msm.cam.ac.uk/doitpoms/tllib/index.php>

The Manchester University Internet Microscope has images illustrating many important metallographic phase diagrams, and textures:

<http://pwatlas.mt.umist.ac.uk/internetmicroscope/index.html>

Rocks under the Microscope:

<http://www.earth.ox.ac.uk/~oesis/micro/index.html>

Microscopy and Minerals Images:

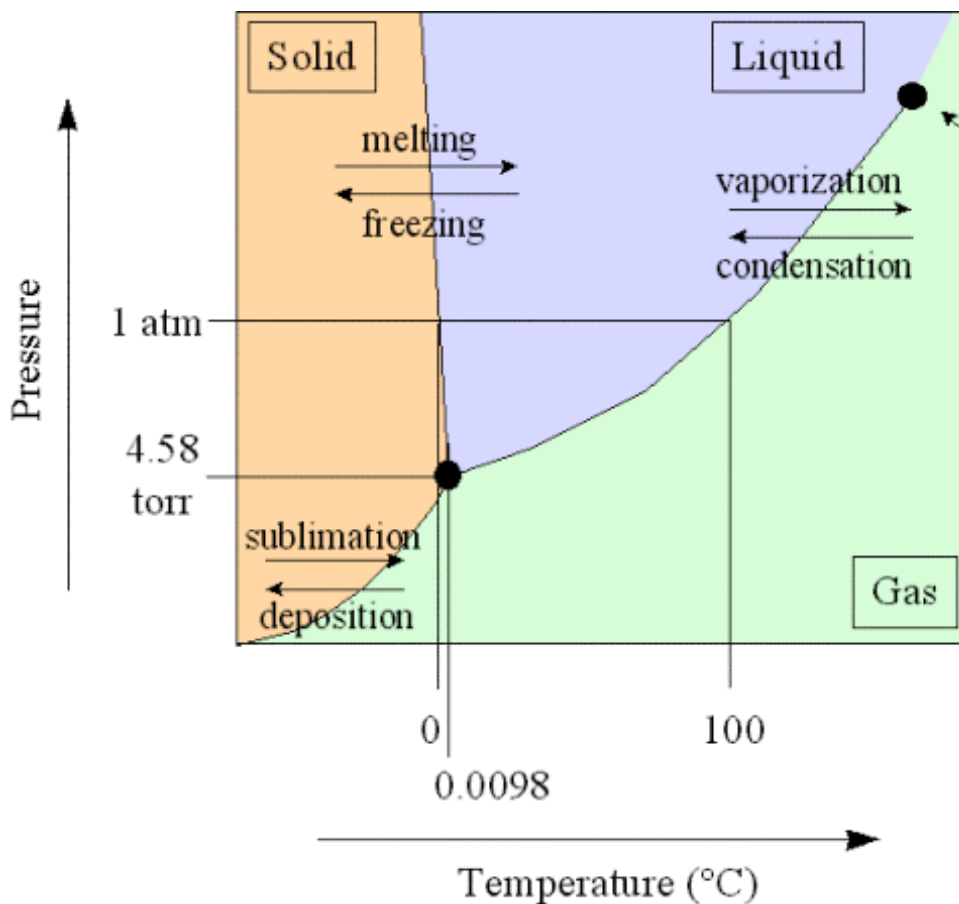
<http://jm-derochette.be/>

Thermodynamics and Phase Diagrams

A fundamental property of a material is that the state (*i.e.* solid, liquid, gas) in which it can exist is a function of temperature, pressure and composition. In turn, a solid may exist in different structural forms (*i.e.* with different internal arrangements of atoms or ions) under different conditions. **Thermodynamic** principles control the state and structure of different materials, and **equilibrium phase diagrams** are maps (*e.g.* in temperature–pressure or temperature–composition space) of the particular structures that exist at equilibrium under given conditions.

e.g. Water

Consider this familiar system: water can exist in one of three states (solid, liquid, vapour) depending on the pressure and temperature of the system.



(There are also many different structural forms of solid ice, which are not illustrated here!)

We can use **thermodynamics** to understand the pressure–temperature maps and temperature–composition maps that show which structures may exist under which conditions. However, we must also consider the **kinetics** of structural transformations between states in order to understand the rate at which transformations take place (some transformations, predicted by thermodynamics, may not happen at all!). Kinetic considerations also define how the structures of crystals and crystalline materials develop.

A **system** is a mixture of one or more different chemical **components**, each of which is an independent chemical variable. Under different conditions a system will comprise one or more physically distinct and chemically homogeneous **phases**. We are interested in the equilibrium state of a particular system under different physical conditions.

e.g. salt + H₂O

H₂O at 0°C

Internal Energy (U)

$$U = \text{potential energy} + \text{kinetic energy}$$

Enthalpy (H)

It is more convenient to consider constant pressure than constant volume, because this is the usual condition under which an experiment is performed. Enthalpy is the constant pressure version of the internal energy.

We define the enthalpy as

$$H = U + PV$$

Entropy (S)

Entropy is a measure of “disorder”, and has two main components:

- (a) configurational disorder (mixing different atoms over identical sites), and
- (b) thermal vibrations of the atoms about their mean positions.

Gibbs free energy (G)

The Gibbs free energy is a function designed to be useful for defining conditions of equilibrium. In particular G allows us to find the equilibrium state of a system, by considering only the properties of the system, and not also the properties of its surroundings. As its name suggests, Gibbs Free Energy can be thought of as the energy which is, or which can be, available to do useful work.

$$G = H - TS$$

Gibbs free energy, G , tends to a minimum at equilibrium

Thermodynamics of Solutions

Here we are concerned with temperature - composition diagrams (*i.e.* diagrams which show the equilibrium state of a system as a function of temperature and composition) for binary systems (systems with two components). In order to understand the origins of such equilibrium phase diagrams we need to know how the free energy of a phase varies with composition (at a given temperature).

Consider a mechanical mixture of two components, pure A and pure B. If this mechanical mixture is transformed, by annealing, into a single solution phase with A and B atoms distributed randomly over the atomic sites, there will be:

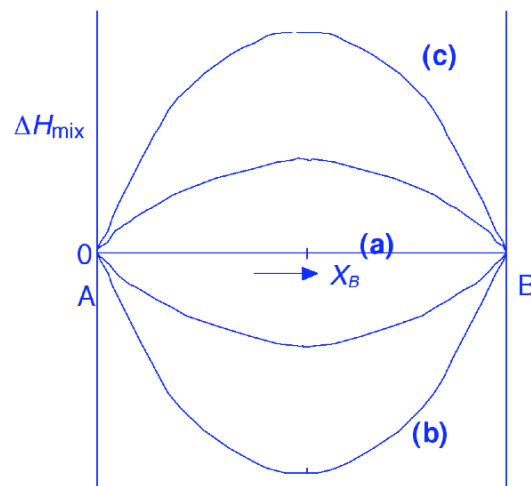
- (1) an enthalpy change associated with interactions between the A and B atoms, ΔH_{mix}
- (2) an entropy change, ΔS_{mix} , associated with the random mixing of the A and B atoms
- (3) a free energy of mixing, $\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}}$

(1) Enthalpy of mixing, ΔH_{mix}

It is assumed that only the potential energy part of U will undergo any significant change on mixing. Thus $\Delta H_{\text{mix}} \approx$ change in the potential energy, which is assumed to arise only from interactions between nearest-neighbour atoms.

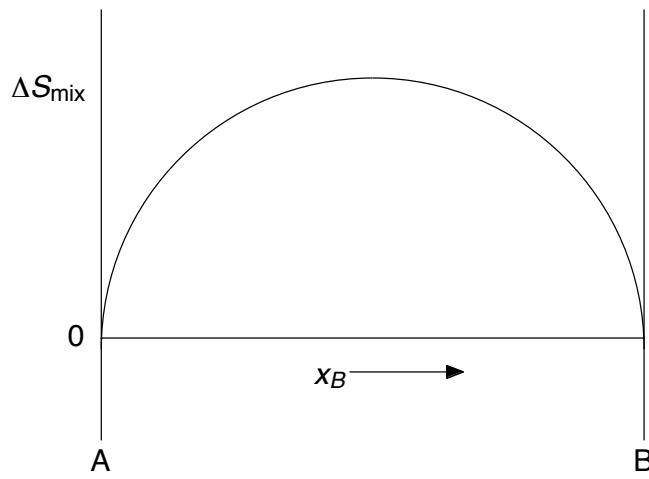
We can identify three cases:

- (a) If A–B interactions are energetically equivalent to A–A and B–B interactions, $\Delta H_{\text{mix}} = 0$, and we have an **ideal** solution.
- (b) If A–B interactions are energetically more favourable than A–A and B–B interactions, $\Delta H_{\text{mix}} < 0$, giving **negative** deviations from ideality and a tendency to form ordered structures or intermediate compounds (“mixing”).
- (c) If A–A and B–B interactions are energetically more favourable than A–B interactions, $\Delta H_{\text{mix}} > 0$, giving **positive** deviations from ideality and a tendency for the solution to segregate into A-rich and B-rich regions (“unmixing”).



(2) Configurational entropy of mixing, ΔS_{mix}

When mixing A and B atoms the only significant change is in *configurational* entropy



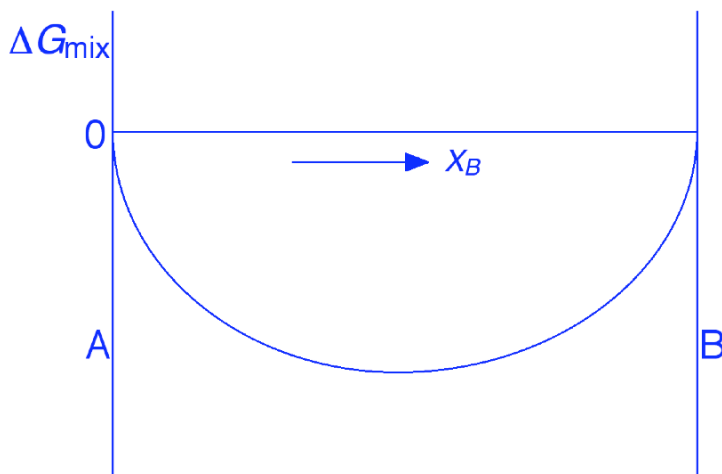
(ΔS_{mix} vs. composition has a different form from ΔH_{mix} : the curve has infinite gradient at the axes, which relates to the difficulty of obtaining pure substances.)

(3) Free energy of mixing, ΔG_{mix}

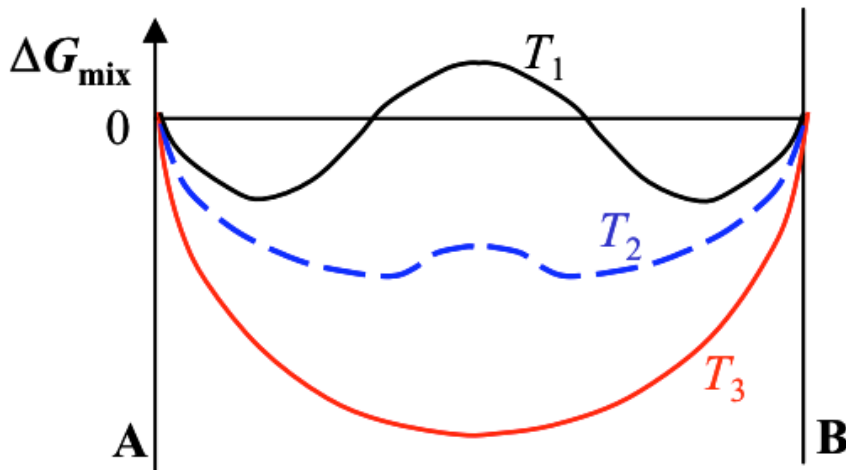
The results of the two previous sections can be combined to give the free energy of mixing:

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

(a) & (b) $\Delta H \leq 0$; ΔG_{mix} is negative for all temperatures:



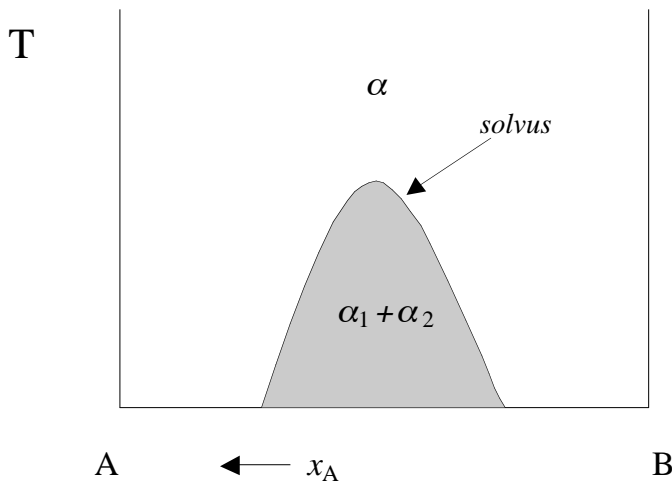
(c) $\Delta H \geq 0$; the shape of the ΔG_{mix} curve depends on T :



- at high T (e.g. T_3): the curve has a single minimum and there is complete solution.
- at low T (e.g. T_1): the ΔG_{mix} curve has a maximum and two minima. In the composition range between the two minima, a mixture of two phases is more stable than a single solution.

Therefore the predicted Equilibrium Phase Diagram shows **Phase Separation**:

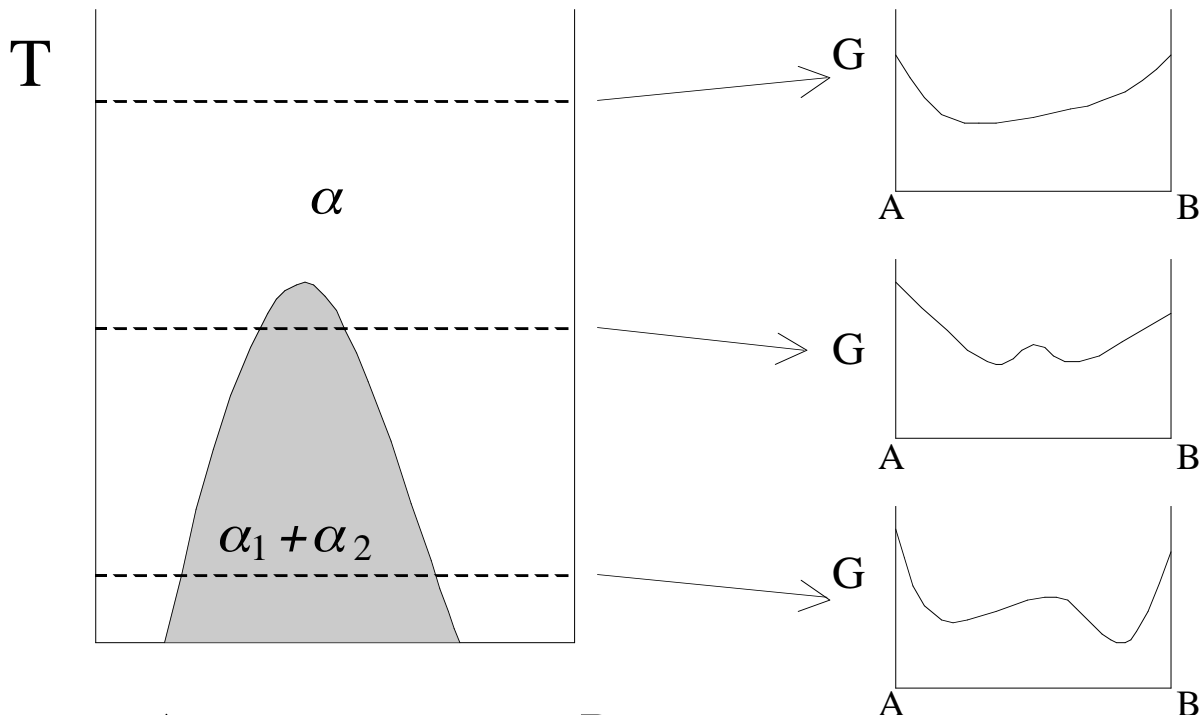
At high temperature there is complete solubility of the two components (due to entropic effects). This gives a continuous solution (which could be in a liquid or solid phase). At lower temperatures there is a field where two co-existing phases are more stable, i.e. the solution becomes unstable under the **solvus** curve:



Equilibrium Phase Diagrams and Free Energy–Composition Curves

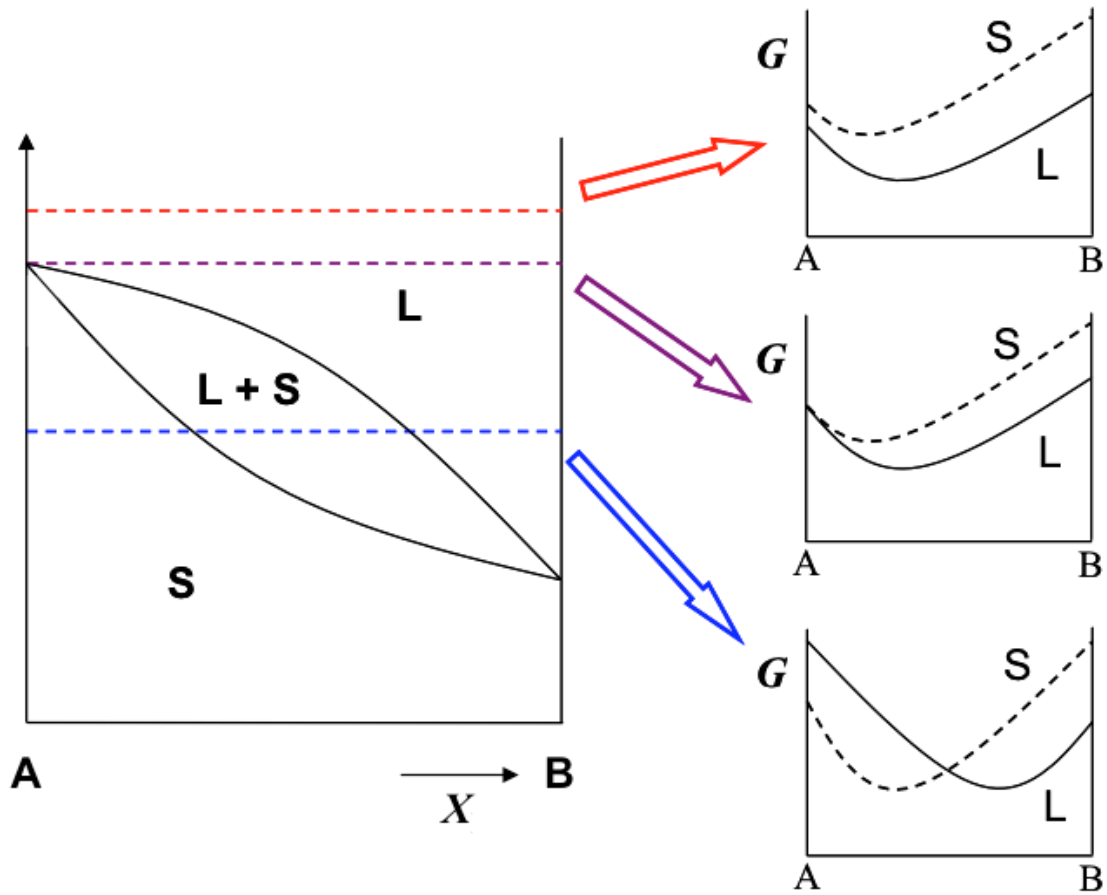
1. Phase separation

In the **single-phase region**, the free energy – composition curve shows that the lowest free energy is obtained when there is a single phase of the overall system composition: there is no way to lower the free energy by splitting into two phases of differing compositions.



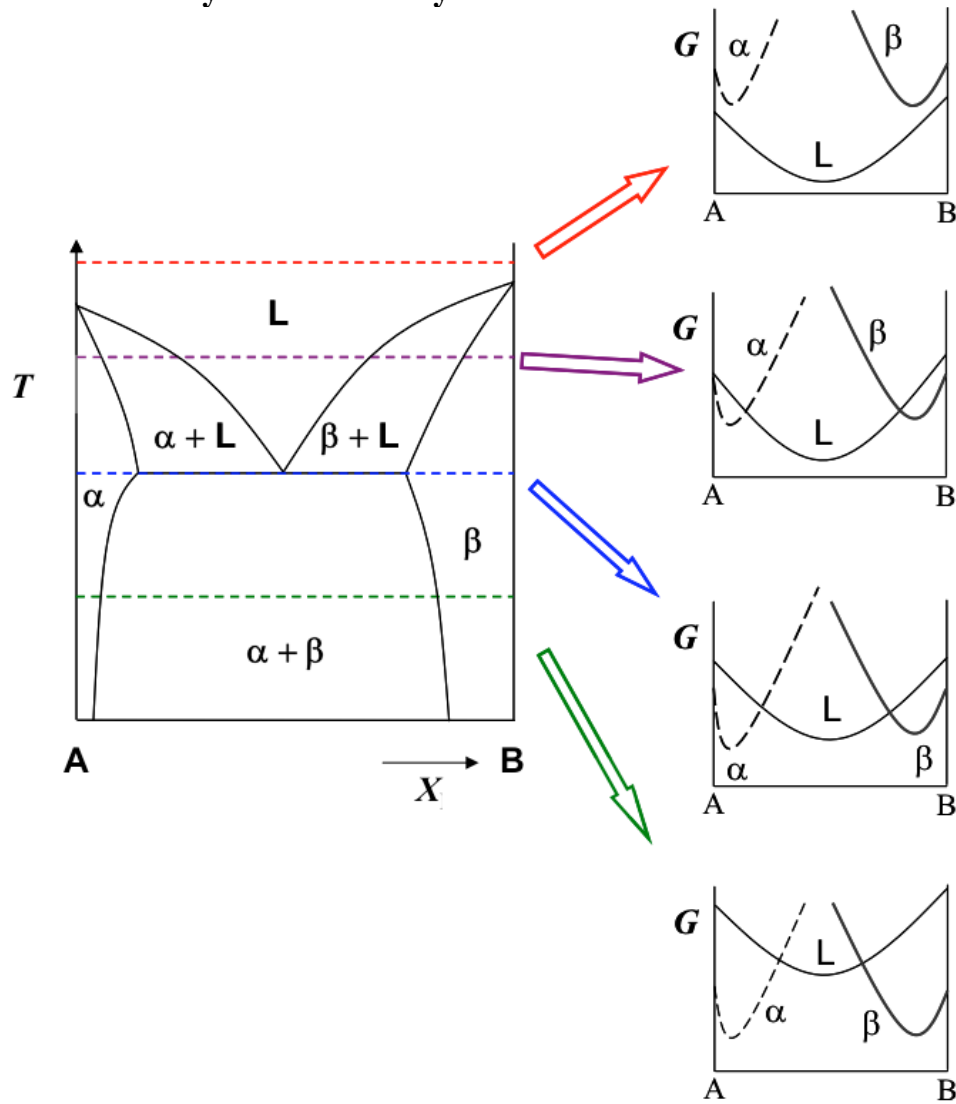
In the **two-phase region**, the free energy – composition curve shows that a uniform phase of the system composition would have a higher free energy than a mixture of two phases. The compositions of the two phases lie on the solvus at the ends of horizontal **tie-lines** at the system temperature.

2. Complete solubility in solid and liquid phases

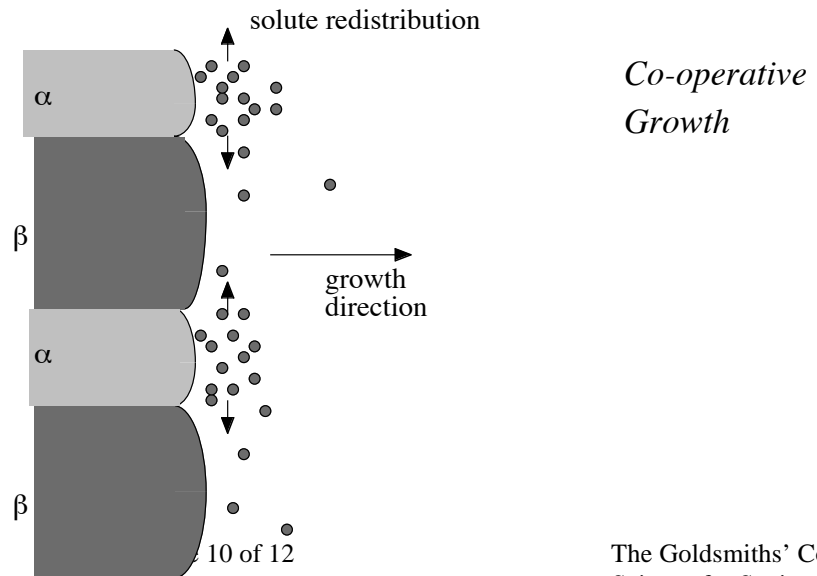


Except for the pure components, solidification / melting occurs over a temperature range. During solidification / melting the solid and liquid have different compositions.

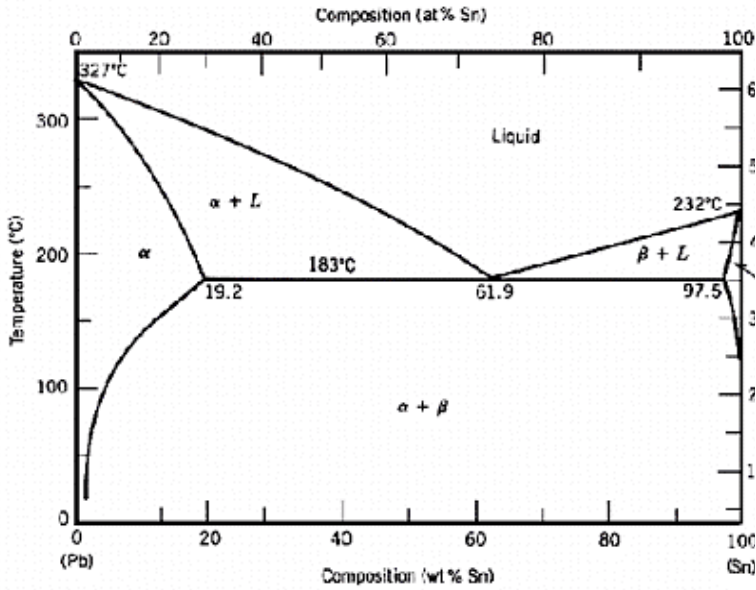
3. Incomplete solid solubility — a eutectic system



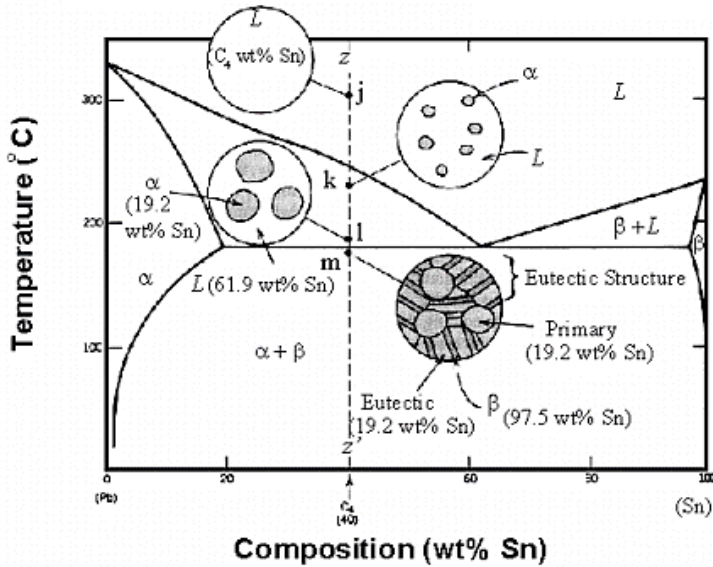
At the eutectic point (composition and temperature) the eutectic reaction is: $L \rightarrow \alpha + \beta$



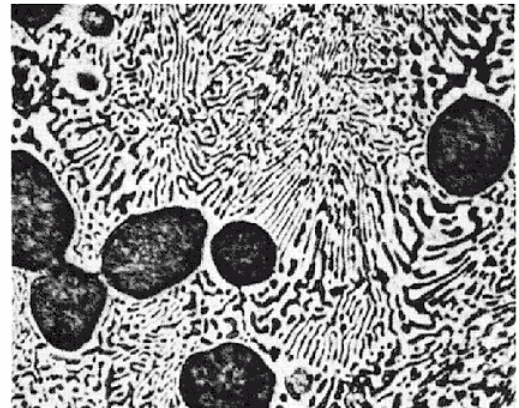
The Pb-Sn system



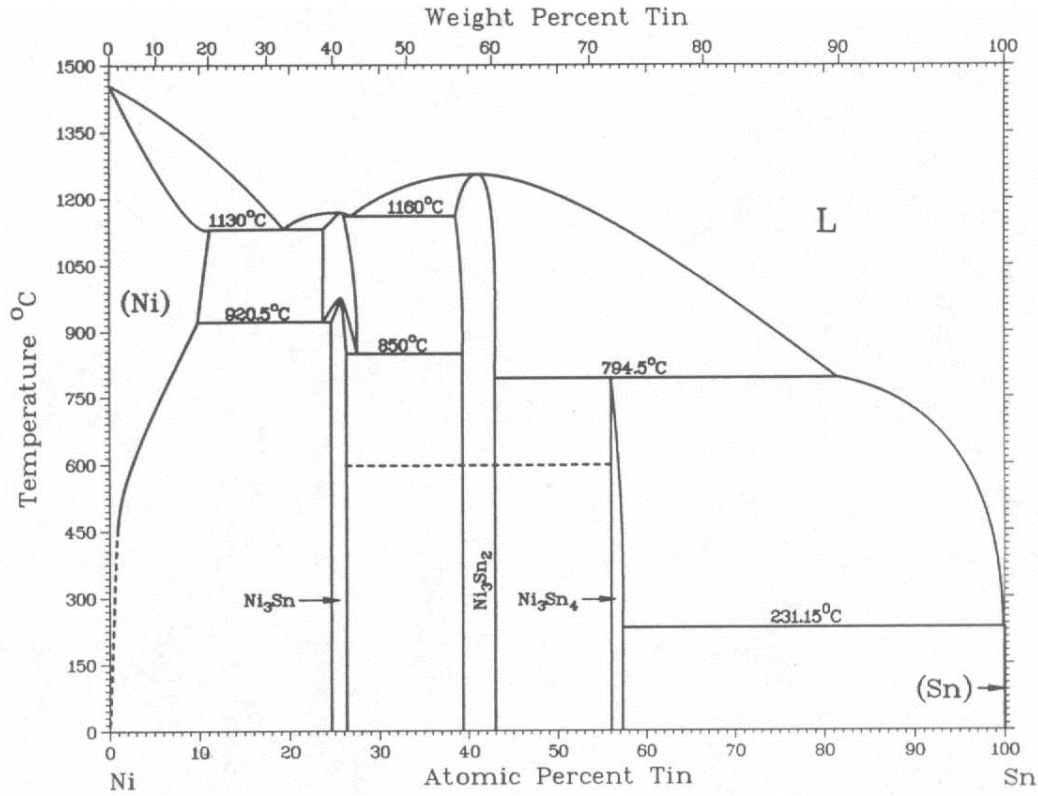
This provides a useful illustration of the relationship between the phase diagram and the resultant microstructure. There is a simple eutectic at 61.9 wt% Sn, where the melt (liquid) will solidify to form a mixture of two solid phases, α and β . The α -phase is close to pure Pb in composition; the β -phase is close to pure Sn in composition.



Solidification of Pb-rich liquid, which has a composition that lies away from the eutectic composition will lead to the development of a microstructure that contains a Pb-rich primary phase, set in a eutectic intergrowth.



A metallic system



A ceramic system

