

Lecture # 9

Binary Mixtures

A mixture is a system of two or more chemical species. Binary mixtures have only two constituents. If constituents are atoms (not molecules) a mixture is called an alloy.

Homogenous mixture – constituents are mixed at atomic scale

Heterogeneous mixture – contains two or more distinct phase.

The equilibrium properties of mixture are represented graphically by phase diagrams (P = 1 atm, but P is not so important)

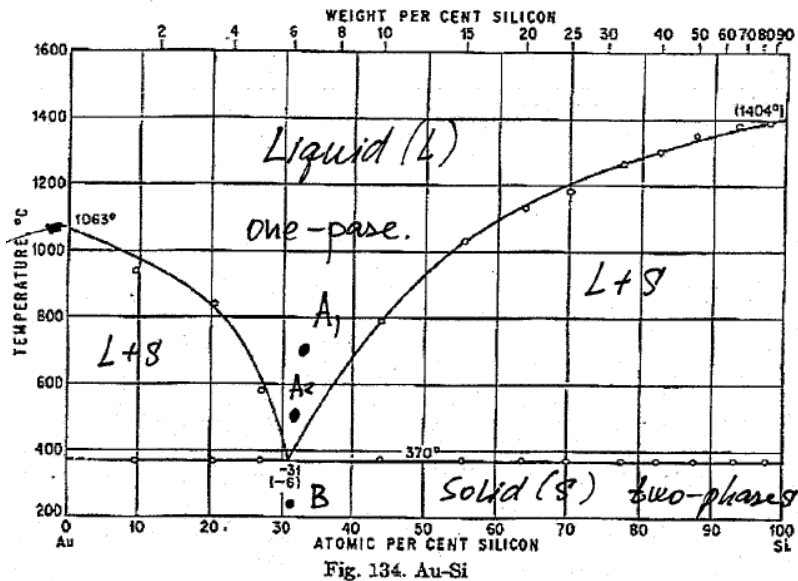


Fig. 134. Au-Si

Melting point of mixture of 69 at % of and 31 at % Si is 370°C – much lower the melting temperature of the alloy constituents: pure gold and pure silicon.

Microstructure of mixture in points A₁, A₂ – liquid phase is homogenous.

In liquid phase Au and Si atoms are randomly distributed on atomic scale.

Point B in phase diagram.

Liquid solidifies and simultaneously segregates into two separate phase - almost pure Au and almost pure Si.

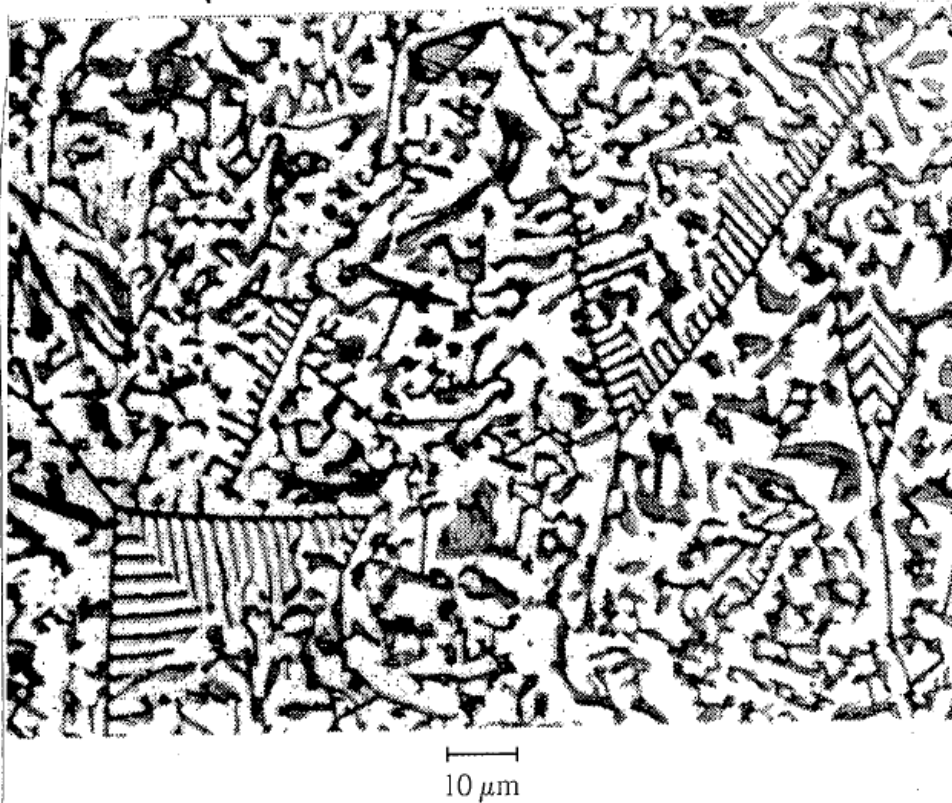


Figure 11.1 Heterogeneous gold-silicon alloy. When a mixture of 69 pct Au and 31 pct Si is melted and then solidified, the mixture segregates into a phase of almost pure Au (light phase) coexistent with a phase of almost pure Si (dark phase). Magnified about 800 times. The composition given is that of the lowest-melting Au-Si mixture, the so-called eutectic mixture, a concept explained later in the text. Photograph courtesy of Stephan Justi.

Au – Si phase diagram is one of the simplest diagrams. There are binary diagram that are incredibly complicated. They form a base for metallurgy.

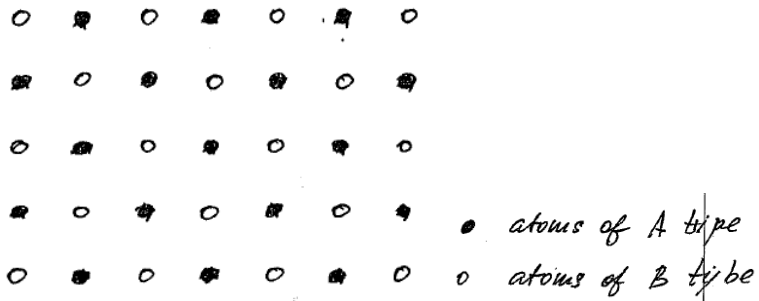
What determines whether two substances form a homogenous or heterogeneous mixture?
What is the composition of mixture?

Main Point: any system at a fixed temperature and pressure will evolve to the configuration with minimum Gibbs free energy.

- 1) $G_A + G_B > G_m$ – mixture is formed (homo)
- 2) $G_m > G_A + G_B$ – heterogenous mixture. (mixture is said to have solubility gap)
- 3) if at some A-B composition $G_m^{liquid} < G_m^{liquid} + G_B^{solid}$ the mixture will melt at lower temperature than the separate substances.

Some binary alloys form stable compounds

Compound AB has ordered positioned of A and B atoms in crystalline structure



(Of course real structures are very diverse)

Typically binary compounds have composition $A_m B_n$ where m and n are integer and usually small numbers

Example:

CoSi_2 (used as a constant to Si in Si technology)

Fe_3C – cementite important compound important in steel making)

Let us consider a simple binary mixture that does not form a compound in all composition range.

1) We will consider minimum of F rather than G and set $PV = 0$ (very good approximation for liquids and solids).

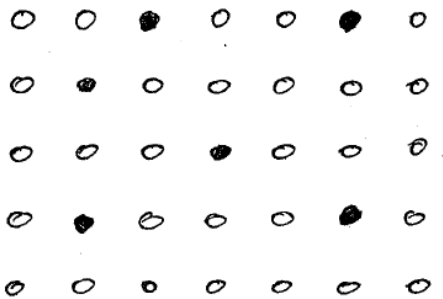


Figure shows an example of a solid crystalline random mixture

N_A – number of atoms of element A

N_B – number of atoms of element B

x – fraction of B atoms

$$x = \frac{N_B}{N_A + N_B} = \frac{N_B}{N}$$

$$1 - x = \frac{N_A}{N}$$

Suppose system forms homogeneous solution.

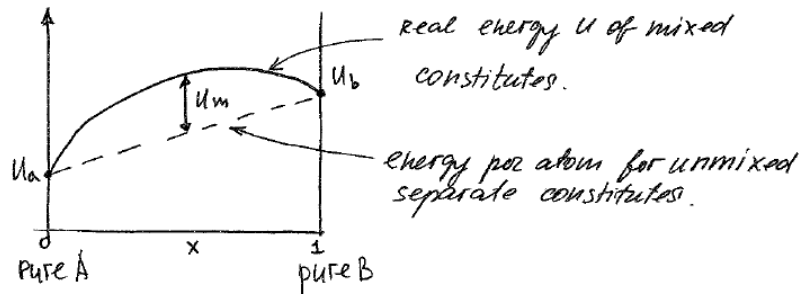
Then an average free energy per atom given by $f = F/N$

$$F = U - TS$$

So if we mix A and B elements both U and S change. Let u_A and u_B be the energy per atom of pure substance A and B (A and B are separated).

The average energy per atom of the separated constituents is

$$u = (u_A N_A + u_B N_B) / N = u_A + (u_B - u_A)x \text{ -- straight line}$$



In above example the energy of homogenous mixture (U) is larger than the energy of separated constituents. The energy excess is called energy of mixing (U_m).

U_m – can be both positive and negative. $U_m > 0$ – constituents do not want to mix energetically (as for example water and oil).

But by mixing AB we may get huge increase in entropy and because $F = U - TS$ has entropy term, TS may overcome U and make homogenous mixture more stable.

So let us compute entropy of mixing.

We have N “sites” and N_A , N_B atoms of A and B type that we can arrange in many different ways.

So we are going back to our favorite binomial distribution.

$$g = \frac{N!}{N_A! N_B!} \text{ -- multiplicity (number of possible different ways to arrange A and B atoms)}$$

$$S = k \ln g = k [\ln(N!) - \ln(N - N_B)! - \ln(N_B!)] \text{ we can farther simplify this equation}$$

by using the Stirling approximation

$$\frac{S}{k} = N \ln N - N - (N - N_B) \ln(N - N_B) + N - N_B - N_B \ln N_B + N_B =$$

$$= N \ln N - (N - N_B) \ln(N - N_B) - N_B \ln N_B$$

$$\text{with } x = \frac{N_B}{N}$$

$$S(x) = -N [(1-x) \ln(1-x) + x \ln x] k$$

Pont to notice: There always is a tendency for at least a very small portion of any element B to dissolve in any other element A, even a strong repulsion energy exists between B atom and the surrounding A atoms. Let $u > 0$ be the potential energy needed to “insert” a B-atom into a configurations where it is surrounded by A-atoms. Then at low concentration of B-atoms the total increase in energy after insertion xN number of B atoms is xNu .

The mixture entropy when $x \ll 1$ is

$$S = -kxN \ln x$$

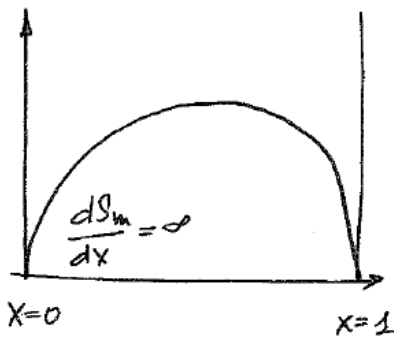
$$F = xNU + kxN \ln(x) \times T$$

which has minimum when

$$\frac{\partial F}{\partial x} = \frac{\partial}{\partial x} (N(xU + kTx \ln x)) = 0$$

$$x = \frac{\exp(-U/kT)}{\exp(+1)}$$

Real example: impurities of 3d metals (Co, Ni, Ti ...) in silicon. These elements have very low solubility in Si but can strongly affect the properties of a silicon device.



$$S_m = -kN \left[(1-x) \ln(1-x) + x \ln x \right]$$

The curve $S_m(x)$ has important property that the slope at the ends of the composition range is vertical.

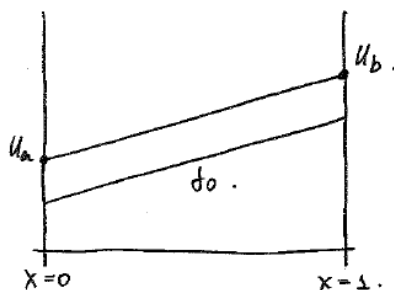
$$\frac{1}{kN} \frac{dS}{dx} = \ln(1-x) - \ln(x) = \ln\left(\frac{1-x}{x}\right)$$

which goes to $+\infty$ as $x \rightarrow 0$ and $-\infty$ as $x \rightarrow 1$

Let's consider now the quantity

$$f_0(x) = u(x) - (S - S_M)T / N - \text{Free energy per atom without mixing entropy contribution.}$$

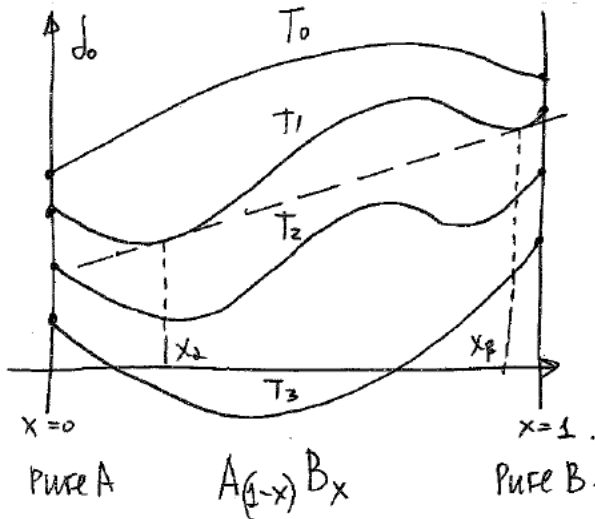
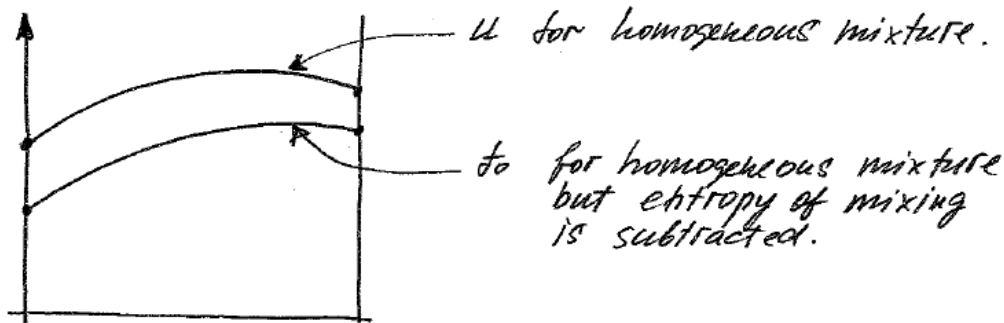
The non mixing part of entropy $(S - S_M)T$ is a linear function of composition x . If we assume that, then $f_0(x)$ has the same shape as $u(x)$ but shifted vertically.



*Dependence of free energy
on composition for
heterogeneous mixture.*



We now add mixing entropy to f_0 and plot f at different temperature.



$$f = U - TS' = f' - TS_m$$

$$T_3 > T_2 > T_1 > T_0$$

- At all finite temperature $f(x)$ turns up at both ends of the composition range, because of the infinite slope of mixing entropy.
- Below certain temperature T_M there is a composition range within which the negative second derivative of $f_0(x)$ curve is stronger than positive second derivatives of $-TS_M$ contribution. (points x_α, x_β on figure)

Between x_α, x_β the mixtures will spontaneously separate into A-element-rich phase of composition with composition $A_{(1-x_\alpha)}B_{x_\alpha}$ and B-element rich phase with composition $A_{(1-x_\beta)}B_{x_\beta}$

We say the system has a solubility gap or that two phases are immiscible.

- Above $T > T_M$ the curve has a positive second derivative at all compositions, so entropy wins and we have a homogeneous mixture at all x .

Model system with simple nearest-neighbor interaction between A and B atoms

Let us consider a model system $A_{1-x}B_x$ alloy in which attractive interaction between unlike atoms (A and B) is weaker than attraction interaction between like atoms (A and A or B and B). For simplicity we consider only nearest neighbor interaction and spent about interaction as different bonds;

A - A, B - B, A - B

The average energy of a single bond between A atom and its neighbor is

$$u_A = (1-x)u_{AA} + xu_{AB}$$

average energy per bond for B-Atom

$$u_B = (1-x)u_{AB} + xu_{BB}$$

The total energy is obtained by summing over all atoms types. If each atom has P nearest neighbor (for example for the cubic lattice $P=6$) the average energy per atom

$$u = \frac{1}{2}P[(1-x)u_a + xu_B] = \frac{1}{2}P[(1-x)^2 u_{aa} + 2x(1-x)u_{ab} + x^2 u_{BB}]$$

The factor $\frac{1}{2}$ appears because we want to count every bond only once

It is convenient to re-write the above result as

$$u = \frac{1}{2}P[(1-x)u_{aa} + xu_{BB}] + u_M = u_l + u_M$$

u_l – linear function of x

u_m – parabolic function,

$$u_m = Px(1-x)\left[u_{ab} - \frac{1}{2}(u_{aa} + u_{BB})\right] \text{ is the mixing energy.}$$

Figure

A solubility gap occurs wherever $\frac{d^2 f}{dx^2} < 0$, that is,

$$\frac{d^2 u}{dx^2} = \frac{d^2 u_M}{dx^2} < T \frac{d^2 s}{dx^2} \cong T \frac{d^2 s_M}{dx^2} \quad s_m - \text{entropy per atom.}$$

$$\frac{d^2 s_m}{dx^2} = -2P\left[u_{ab} - \frac{1}{2}(u_{aa} + u_{BB})\right] - \text{per atom.}$$

$$s_m = -kN[(1-x)\ln(1-x) + x\ln x]$$

$$s_m - \text{entropy per atom} = \frac{1}{N} S_m$$

$$\frac{d^2 s}{dx^2} = -\frac{k}{x(1-x)} \leq -\frac{k}{4}$$

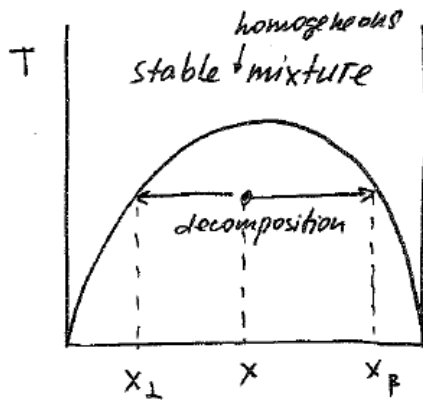
We want to find the lowest temperature T_m at which A-B system is completely mixed.

The second derivative of entropy contribution drops much faster with x (away from $x = \frac{1}{2}$) than energy contribution. So the lowest T_m occurs when $x = \frac{1}{2}$.

$$-\frac{kT_m}{4} = 2P\left[u_{ab} - \frac{1}{2}(u_{aa} + u_{BB})\right]$$

$$T_m = \frac{1}{k} \cdot \frac{1}{2}P\left(u_{ab} - \frac{1}{2}(u_{aa} + u_{BB})\right) - \text{lower limit of solubility gap}$$

System with solubility gap (phase diagram)



A homogeneous mixture of composition x will be unstable at temperature T if points (T, x) falls under the stability boundary curve the mixture than will be given by two separate Phases given by intersection of this curve with horizontal line for temperature T .

Examples: water-phenol phase diagram in the textbook (p.190) and lead-tin phase diagram (p. 198)

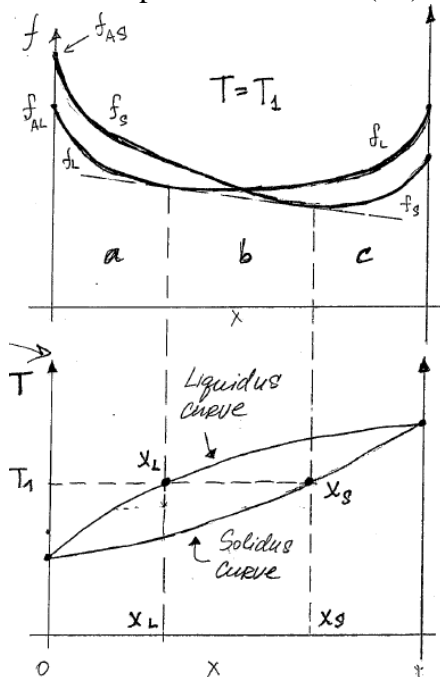
Phase equilibrium between liquid and solid mixtures,

When a small fraction of a homogeneous mixture freezes, the composition of the solid that forms is almost always different from that of the liquid.

Simple model

Assumption

- Solid and liquid do not have solubility gap
- Melting temperature of pure constitute A is smaller than the melting temperature of pure constitute B (T_B).



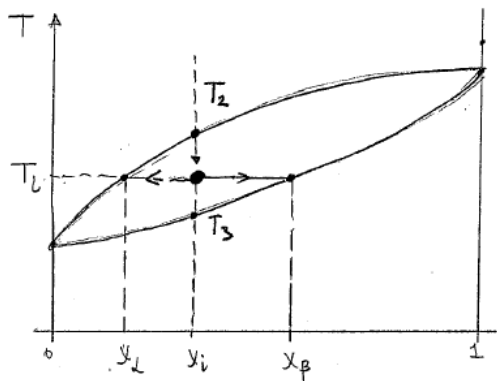
f_s - Free energy per atom for solid mixture

f_L - Free energy per atom for liquid mixture

The inclined dashed line in top figure is tangent to both f_L and f_s (notice at high T $f_L < f_s$ and at low T $f_s < f_L$)

Low figure above: At temperature T_1 we can define three-composition ranges with different phase states:

- a) $x < x_L$, The system in equilibrium is homogenous liquid.
- b) $x_L < x < x_s$. The system in equilibrium consists of two phases, a solid phase of composition x_L and liquid phase of composition x_s
- c) $x > x_s$ - Homogenous solid.



Decomposition of system at temperature T_i and composition x_i into liquid with composition x_α and solid with composition x_β

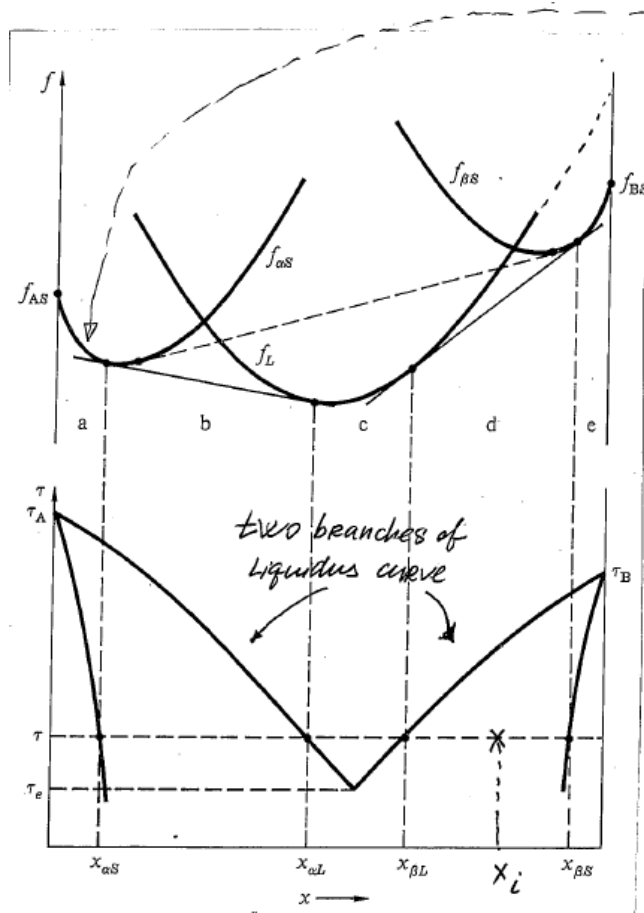
Solidification of the mixture starts at T_2 and ends T_3 . At $T_2 > T > T_3$ liquid and solid phases co-exist. At $T < T_3$ the thermodynamically stable state is a homogeneous solid. However for many solids atomic diffusion at $T \sim T_3$ is too slow. If cooling of the mixture proceeds relatively fast the inhomogeneity remains *frozen in* indefinitely.

Example: The phase diagram shown above realizes in Ge-Si binary mixture. Ge and Si have the same crystalline structure (diamond-type). But the melting temperature of Ge is 940°C and the melting temperature of Si is 1410°C .

Eutectics: Mixture with liquidus branches

There are many binary systems in which liquid phase remains liquid down to temperatures significantly below the lower melting temperature of constituents. Au-Si system is an example. The lower melting point for mixture occurs because the free energy of homogenous mixture is lower than the free energy of the two phases solid.

Such behavior is common among systems that exhibit solubility gap in solid but not in the liquid. It often appears in mixtures where pure constituents A and B have different crystal structures.



$f_s(x)$ - Is free energy for solid corresponding to different crystal structure α and β .

$f_{\alpha s}$ - Free energy for mixture with crystalline structure α

$f_{\beta s}$ - Free energy for mixture with crystalline β

f_L - Free energy of homogenous liquid

Composition ranges at temperature τ

(a) and (e) $x > x_{\beta s}, x < x_{\alpha s}$ the equilibrium state of system is homogenous solid.

(c) $x_{\alpha L} < x < x_{\beta L}$ the equilibrium state is homogenous liquid.

(b) and (d) for $x_{\alpha s} < x < x_{\beta s}$ and $x_{\beta L} < x < x_{\beta s}$, the equilibrium state is a liquid phase mixed with a solid phase.

For example at composition x_i we have coexistence of solid phase with composition $x_{\beta s}$ and liquid with composition $x_{\beta L}$

T_e – eutectic temperature

Another example $H_2O - NaCl$: mixture of salt and ice freezes at temperature $-21.2^\circ C$ at an eutectic point of 8.17 mol % of NaCl.