$$\Delta H_{mix} = \Omega X_A X_B \quad (2.24)$$

where: $\Omega = N_a z\varepsilon$.

Real solutions behaving in compliance with the equation (2.24) are defined as regular solutions. The change of ΔH_{mix} depending on composition is parabolic and it is depicted in Fig. 2.7, which clearly implies graphic determination of Ω.

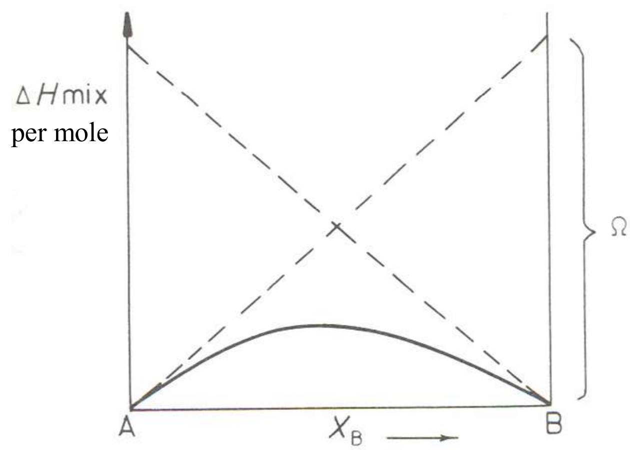


Fig. 2.7 Change of ΔH_{mix} with the composition of regular solutions

2.5 Activity

The equation (2.17) applied to chemical potential within an ideal solution is simple; it is therefore desirable to define a similar equation for any solution. That can be achieved by defining the activity of component in such manner that the Fig. 2.8 shows the distance *ac* equal to the value of $-RT\ln a_A$ and the distance *bd* matches the value of $-RT\ln a_B$. In this case:

$$\mu_A = G_A + RTln\, a_A \quad \text{a} \quad \mu_B = G_B + RTln\, a_B \quad (2.25)$$

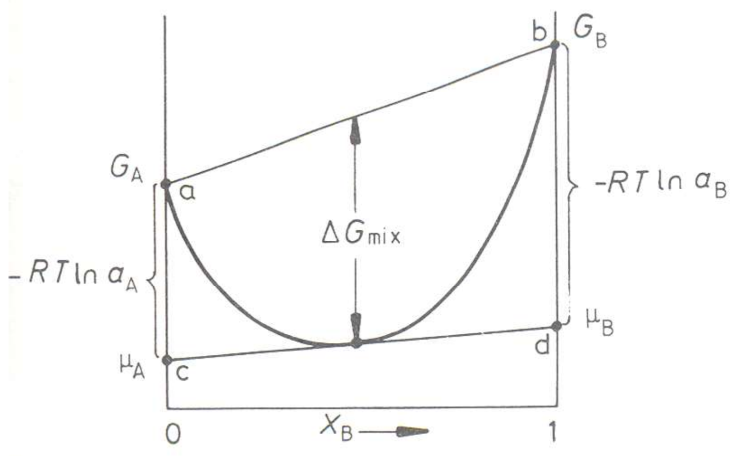


Fig. 2.8 Mutual relationship between the molar Gibbs free energy and activity

The values a_A and a_B will be generally different from values of X_A and X_B and the relation between these parameters will be changed with composition of the solution. Assuming that the crystal structures of pure components A and B are identical, the relationship between activity and molar fraction for any solid solution may be expressed graphically, as shown in the Fig. 2.9. Line 1 represents an ideal solid solution, where $a_A = X_A$ and $a_B = X_B$. If $\Delta H_{mix} < 0$, the activity of components of the solid solution will be lower compared to an ideal solid solution (curve 2) and vice versa; if $\Delta H_{mix} > 0$, the activity of components in a solid solution will be greater compared to an ideal solid solution (curve 3).

The ratio of activity and molar fraction is usually defined as the ***coefficient of activity*** of the particular component:

$$\gamma_A = \frac{a_A}{X_A} \qquad (2.26)$$

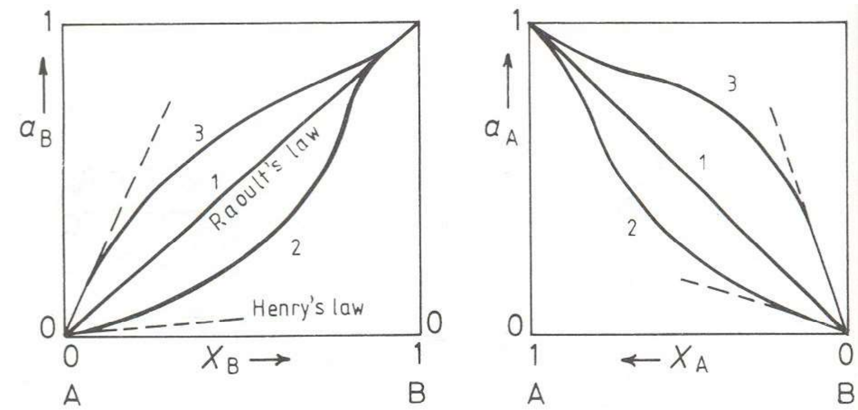
A diluted solution of component B in component A can be defined as:

$$\gamma_B = \frac{a_B}{X_B} \cong constant \quad (\textbf{\textit{Henry's law}}) \qquad (2.27)$$

And

$$\gamma_A = \frac{a_A}{X_A} \simeq 1 \quad (\textbf{\textit{Raoult's law}}) \qquad (2.28)$$

These equations can be applied to any solutions if diluted sufficiently. The component activity is just another way to describe the condition of a particular component of solid solution besides its chemical potential. Both the activity and chemical potential represent a measure of tendency of an atom towards leaving the solid solution. If the value of activity or of chemical potential is low, atoms will be reluctant to leave the solid solution, which means that e.g. component vapour pressure in equilibrium with the solid solution will be relatively low.



a) *b)*

Fig. 2.9 Change of activity depending on composition, a) a_B b) a_A. Line 1: ideal solid solution (Raoult's law), curve 2: $\Delta H_{mix} < 0$, curve 3: $\Delta H_{mix} > 0$.

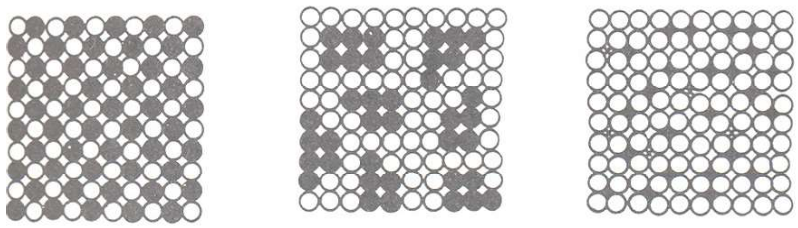
2.6 Real Solutions

The model mentioned above represents a useful description of the effect of configuration entropy and interatomic bond on the free energy in binary solutions but its use in practice is limited. This model is a way too great simplification of reality for many systems and it is unable to predict correct dependency of ΔG_{mix} on composition and temperature.

As far as alloys with mixing enthalpy different from zero (ε and $\Omega \neq 0$) are concerned, it may be assumed that the random configuration of atoms represents an equilibrium or the most stable configuration of atoms, which is not true and the calculated values of ΔG_{mix} will not correspond with the minimum of Gibbs free energy. The actual configuration of atoms will be a compromise that enables achievement of the lowest value of the internal energy with sufficient level of entropy to achieve the minimum value of Gibbs free energy. The internal energy in systems, where $\varepsilon < 0$, is reduced by increasing number of bonds type A – B, i.e. the configuration of atoms, as shown in the Fig. 2.10a. If $\varepsilon > 0$, the internal energy can be reduced by increasing the number of bonds type A – A and B – B, i.e. clustering of atoms in areas abundant with atoms of either A or B, Fig. 2.10b. The level of ordering or clustering of atoms will be reduced with rising temperature due to the increasing importance of entropy.

Systems with differences in atom size are associated with quasi-chemical models underestimating the change of internal energy during mixing of atoms, as these disregard the elastic distortion fields. If the difference in atom size is significant, this effect may prevail over the chemical term. If the difference in atom size is great, the interstitial solid solutions should be selected as more convenient from the energetic prospective, see Fig. 2.10c. Systems with strong chemical bond between atoms show tendencies towards development of intermetallic phases.

The rules associated with events of atom ordering (short- or long-range) in solids and basic characteristics of individual types of intermediary phases have been defined in the textbook of the course ***Structure and Properties of Solids***.



a) b) c)

Fig. 2.10 Diagram showing the real solid solutions, a) Substitutional solid solution with long-range ordering, b) Clustering of atoms of the same type, c) Interstitial solid solution.

2.7 Equilibrium in Heterogeneous Systems

It is fairly common that pure components A and B do not feature an identical crystal-structure at the temperature level considered. Such cases must be documented by two curves Gibbs free energy – one for each structure. Stable forms of pure components A and B at the particular temperature (and pressure) will be marked α and β. Let us assume that α features the FCC structure and the β will form the BCC structure. The molar free energy of pure component A with FCC structure shown in Fig. 2.11 is marked with the letter *a*, whereas the molar free energy of pure component B with BCC structure is marked with the letter *b*. The first step in drafting of the curve showing Gibbs free energy for the phase α with FCC structure lies in transforming the atoms of B from the stable BCC structure into an unstable configuration of FCC lattice. This step requires an increase of Gibbs free energy from point *b* to point *c*. This stage therefore allows drafting the curve showing Gibbs free energy for the phase α by mixing of atoms of pure components A and B with FCC structure – see Fig. 2.11a. The value of ΔG_{mix} for phase α with composition X is defined by the abscissa *de*. A similar procedure can be adopted for drafting the molar Gibbs free energy for phase β. The abscissa *af* in Fig. 2.11b reflects the transformation of atoms of pure component A from FCC into the BCC lattice. The Fig. 2.11b clearly shows that the lowest Gibbs free energy of binary alloys rich in component A will be identical to that of homogeneous α phase and the lowest Gibbs free energy of binary alloys rich in component B will be identical to that of homogeneous β phase. The situation is more complicated for alloys located near intersection formed by free energy curves. These cases can serve as evidence, that the total Gibbs energy can be minimised when allocating atoms into two phases.

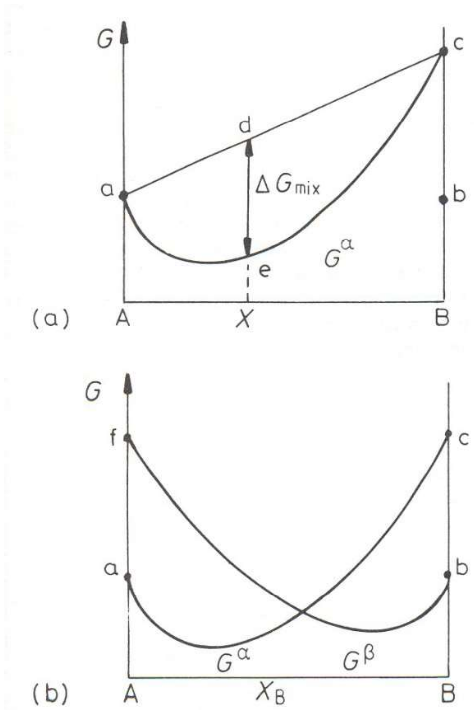


Fig. 2.11 a) Curve of molar Gibbs free energy for phase α, b) Curves of molar Gibbs free energy for phases α and β

The first aspect to be considered is the general characteristics of diagrams showing the molar Gibbs free energy in presence of phase mixtures. Let us assume we have an alloy comprising phases α and β with the molar Gibbs free energy of G^α and G^β respectively, Fig. 2.12. If the total composition of phase mixtures is equal to X_B^o , the relative number of moles of phases α and β is defined by the lever rule. The molar Gibbs free energy G in mixture of phases is defined by the point located on a straight line linking points *α* and *β*. That can be verified by means of geometric analysis, see Fig. 2.12. Vectors *ad* and *cf* represent the molar Gibbs free energy of phases present within an alloy. Point *g* lies in the intersection of vectors *be* and *dc*, so *bcg* and *acd* as well as *deg* and *dfc* represent similar triangles. The above implies that *bg/ad* = *bc/ac* and *ge/cf* = *ab/ac*. The lever rule states that 1 mole of alloy contains *bc/ac* moles of phase α and *ab/ac* moles of phase β. That implies both *bg* and *ge* represent separate contributions of phases α and β to the total Gibbs free energy of 1 mole of the alloy. The vector *be* represents the molar Gibbs free energy in mixture of phases α + β.

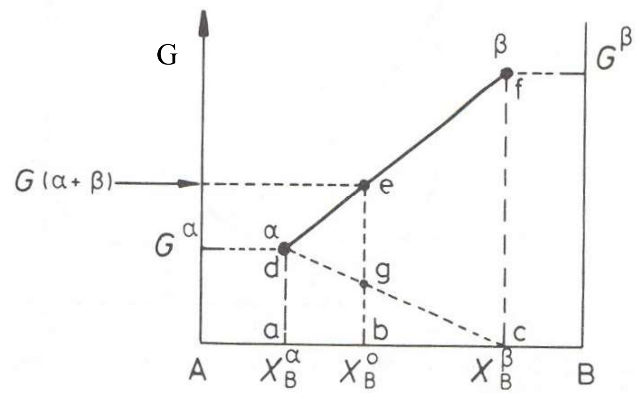


Fig. 2.12 Changes of molar Gibbs free energy in mixture comprising two phases

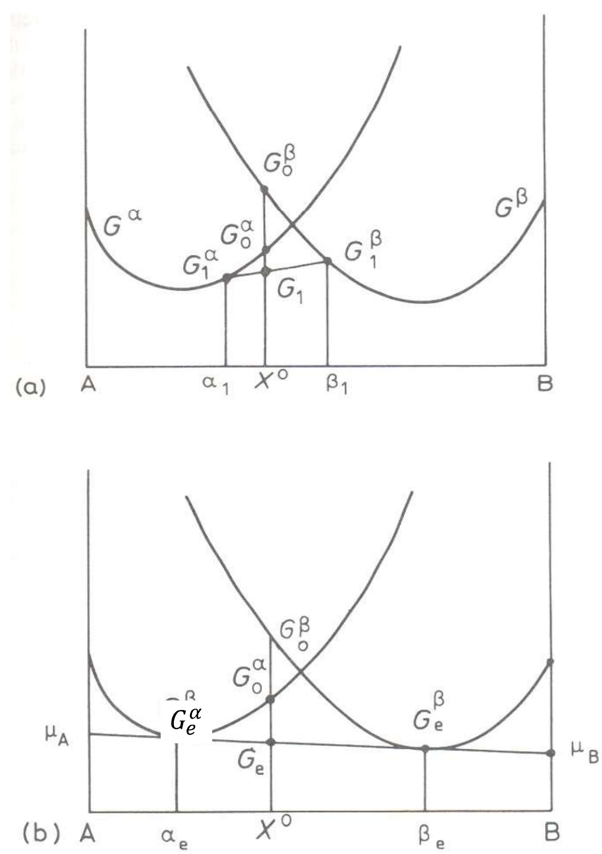
Let us assume an alloy with composition X^o, as shown in Fig. 2.13a. If the atom configuration corresponds with a homogeneous phase, then the free energy will be at its lowest in case of phase α , i.e. X_o^{α} per 1 mole. However, the facts above imply that the system is able to reduce its Gibbs free energy provided the atoms separate to form two phases of certain composition, e.g. α_1 and β_1. The Gibbs free energy within the system will be reduced to the value of G_1 in this case. Further reduction of free energy can be achieved in case, when the atoms of components A and B keep migrating between phases α and β until producing the compositions α_e and β_e. In this case, the free energy within the system will be at the minimum level and α_e and β_e represent equilibrium compositions of phases α and β.

This result is applicable in general and it can be applied to any alloy with its composition between α_e and β_e – the only changes happening here will concern the relative quantities of both phases in accordance with the lever rule. For alloy compositions found outside this interval the minimum Gibbs free energy lies on curves G^{α} and G^{β} and the equilibrium state of alloy corresponds with one homogeneous phase only.

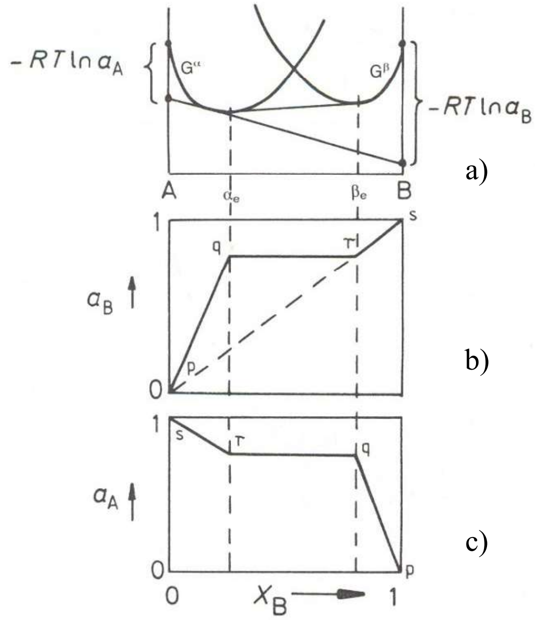
The Fig. 2.13 implies that tangents to curves of the Gibbs free energy found in equilibrium compositions of phases α and β are identical. In other words, one component needs to have identical chemical potential in both phases. That means the following applies to heterogeneous equilibrium:

$$\mu_A^{\alpha} = \mu_A^{\beta} \quad \text{and} \quad \mu_B^{\alpha} = \mu_B^{\beta} \tag{2.29}$$

The prerequisite for equilibrium within a heterogeneous system comprising two phases can be also expressed using the activity concept. A heterogeneous system comprising more than one phase can contain pure components of various crystalline structures. The most stable conditions with the lowest Gibbs free energy are usually defined as a state, where pure components adopt unit activity. As far as the discussed case is concerned, this is the situation, when the activity of component A in phase α composed by A (pure component) equals to 1, i.e. $X_A = 1$, $a_A^\alpha = 1$ and similarly $X_B = 1$, $a_B^\beta = 1$. This definition of activity is depicted in Fig. 2.14a. Figs. 2.14b and 2.14c show changes to activity of components A and B with composition of phases α and β. The areas with a single stable phase, i.e. A - α_e and β_e – B are associated with changing values of activity (or chemical potential) and ideal solutions should be considered to simplify the example, as these feature linear dependencies between the activity and composition.



Figs. 2.13 a) The Gibbs free energy in an alloy with composition X^o is equal to G_1 for a mixture of phases with composition including α_1 and β_1, b) with regards to the equilibrium, the minimum of Gibbs free energy of the alloy X^o is equal to G_e and this alloy comprises a mixture of phases including α_e and β_e



Figs. 2.14a – c Changes of activities a_A and a_B with composition for a system comprising ideal solutions α and β

The composition of equilibrium phase between α_e and β_e remains unchanged and activities remain unchanged. In other words, if there are two phases in equilibrium, activities of components within these phases must be identical:

$$a_A^\alpha = a_A^\beta \quad \text{and} \quad a_B^\alpha = a_B^\beta \tag{2.30}$$

2.8 Binary Phase Diagrams

The simplest type of a binary diagram identifies a system with full solubility of components A and B both in liquid and solid state (ideal solutions in both cases). The changes of Gibbs free energy will depend on temperature changes, as shown in the Fig. 2.15. Melting temperatures of pure components match the situation when $G^S = G^L$, i.e. at temperatures $T_m(A)$ and $T_m(B)$. The Gibbs free energy in both phases will be reduced as the temperature rises. These trends are important, as they define the relative positions of G_A^S, G_A^L, G_B^S and G_B^L in diagrams showing the molar Gibbs free energy at various temperature levels. When the temperature is high, where $T_1 > T_m(A) > T_m(B)$, the stable phase will be the liquid phase of pure components A and B. To simplify the example, let us assume that the liquid phase comes with a lower value of Gibbs free energy compared to the solid phase; this is applicable to any composition feasible within an A – B system. Reduction of temperature will produce two effects: the values of G_A^L and G_B^L will be rising faster than values of G_A^S and G_B^S and the G curves will flatten out due to lower contribution of the term $T\Delta S_{mix}$ towards the value of Gibbs free energy.

The rule at temperature level T_m(A) will be: $G_A^S = G_B^S$ and that represents a single point within the binary diagram. When the temperature T_2 is lower, curves of free energy will intersect and the common tangent means that the equilibrium state between points *A* and *b* is matched by a solid phase, while the interval between points *c* and *B* is associated with a liquid phase and the section between points *b* and *c* is matched by a mixture of two phases (S + L) with composition including *b* and *c,* Fig. 2.15c. These points are also marked in the phase diagram, Fig. 2.15f.

The interval between temperature levels T_2 and T_m(B) shows the value G^L rising faster than G^S, therefore the points *b* and *c* in Fig. 2.15c will shift to the right in the phase diagram, alongside the curves of solid and liquid. When the temperature reaches final level of T_m(B), points *b* and *c* will converge in a single spot, which is the point *d* in Fig. 2.15f. When below the temperature level T_m(B), the Gibbs free energy of solid phase will be always below the value of free energy of melt and solid phase will be the stable one for any composition.

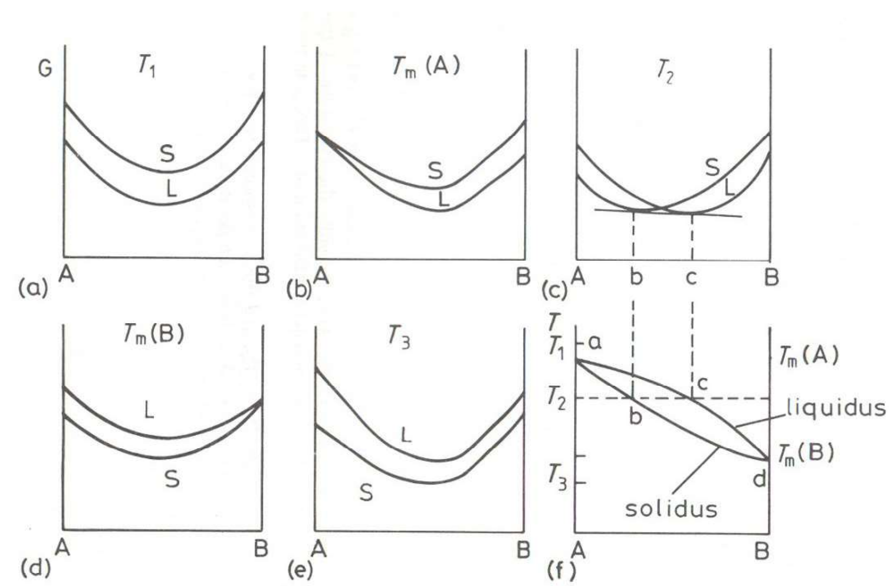


Fig. 2.15 Derivation of binary diagram for full solubility in both liquid and solid state using curves of the Gibbs free energy for the liquid (L) and solid (S) state respectively

2.9 The Interface Effect on Phase Equilibrium

The previous chapter shows curves of Gibbs free energy applicable to molar Gibbs free energy contained within an indefinite quantity of material in form of a perfect crystal. Surfaces (grain boundaries, interphase interfaces) have been ignored. However, these defects, while associated with other defects as dislocations or vacancies under real conditions, increase the Gibbs free energy of phases. The minimum Gibbs free energy of alloy, i.e. the equilibrium, is not achieved until all the dislocations and interfaces have been eliminated. Such condition is basically unachievable under practical circumstances.

Interphase interfaces may be extremely important at initial stages of phase transformations, where one phase, e.g. β, is present in form of very small particles in the matrix of α phase, Fig. 2.16a. If the phase α is exposed to the pressure of 1atm, the phase β is exposed to extra pressure Δp due to curvature of the α/β interface. If the energy contained within the interphase α/β interface is γ and the particles are spherical objects with the radius r, the value of Δp is then approximately defined by the following formula:

$$\Delta p = \frac{2\gamma}{r} \tag{2.31}$$

The expression for Gibbs free energy contains the term $p \cdot V$, therefore increasing the pressure must induce a rise of Gibbs free energy. For constant temperature:

$$\Delta G = \Delta p \cdot V \tag{2.32}$$

The contribution of curvature of particles within the phase β shown in the diagram of Gibbs free energy versus composition, see Fig. 2.16b, can be expressed as follows:

$$\Delta G_\gamma = \frac{2\gamma V_m}{r} \tag{2.33}$$

where V_m refers to the molar volume of phase β.

This increment of Gibbs free energy due to interfacial energy is defined as the ***capillary effect*** or ***Gibbs – Thomson effect.*** Composition of the phase α, which is in equilibrium with particles with the radius *r,* corresponds with the value of X_r.

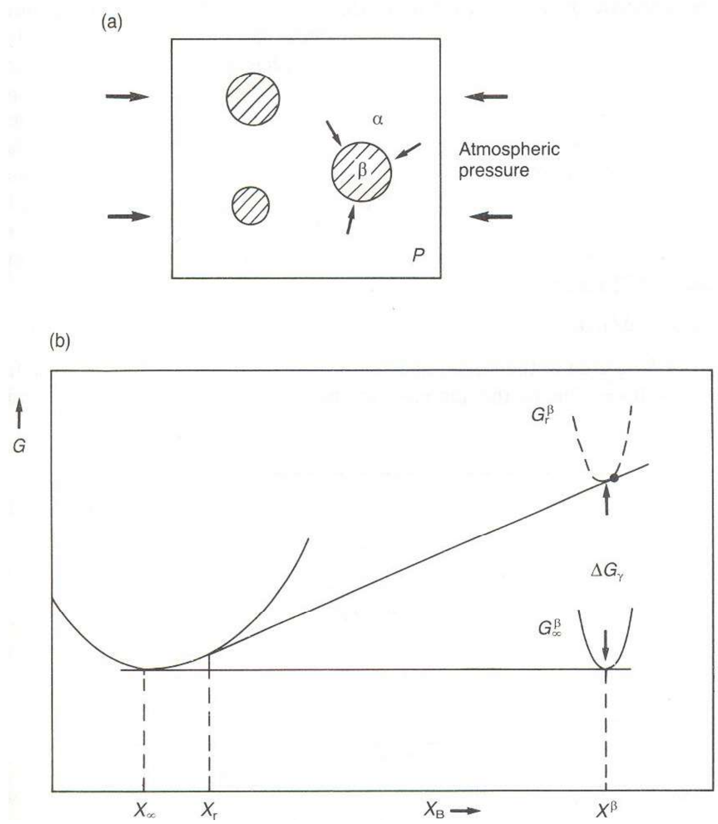


Fig. 2.16 Effect of interfacial energy on solubility of small particles

Summary of terms in this chapter

Ideal Solid Solution: mixing of atoms of A and B does not release or absorb any heat ($\Delta H_{mix} = 0$)

Chemical Potential: defines the change of Gibbs free energy of the system after a small change to chemical composition of the system

Regular Solid Solution: mixing of atoms of A and B releases or absorbs heat ($\Delta H_{mix} \neq 0$)

Coefficient of Activity: the ratio of activity and molar fraction of particular component ($\gamma_A = \frac{a_A}{X_A}$), it is $\gamma_A = 1$ for ideal solutions.

Gibbs – Thomson Effect: increment of free energy of the phase, induced by curvature of interface it is also defined as the **capillary effect.** It is very significant for initial stages of transformations.

Questions addressing the content covered

1. What is the difference between an ideal and a regular solution?

3. Classification of Phase Transformations

Study time: 2.5 hours

Objective: Completion of this chapter will enable you:

- differentiate between phase transformations based on the thermodynamic or kinetic approach,
- define basic types of phase transformations,
- differentiate between the first or second order transformations,
- define differences between continuous and discontinuous transformations.

EXPLANATION

3.1 Thermodynamic and Kinetic Classification

Most phase transformations belong to the ***first order transformations***, where at the equilibrium transformation temperature the first derivations of Gibbs free energy $\partial G/\partial T$ and $\partial G/\partial p$ are discontinuous. These transformations include for example melting of solid substance, Fig. 3.1a. As $\partial G/\partial T = -S$ and $\partial G/\partial p = V$, the first rate transformations are associated with discontinuous changes of volume and entropy. There is also a discontinuous change of heat content (enthalpy, H) relevant to the development of latent heat of transformation. The scope of specific heat coefficient is indefinite at the transformation temperature level, as adding a small amount of heat will convert more of the solid substance into melt without any temperature increase. These transformations enable achievement of the metastable state.

Fig. 3.1b characterises ***the second order transformations***. These transformations are associated with discontinuous second derivatives of the Gibbs free energy $\partial^2 G/\partial T^2$ and $\partial^2 G/\partial p^2$. Nevertheless, the first derivatives are continuous, which means the course of enthalpy H is also continuous. There is no development of latent heat at the transformation temperature, just a rapid increase of the coefficient of specific heat. These transformations cannot reach any metastable states. The second order transformations include, for example, the magnetic ordering in metal-based alloys.

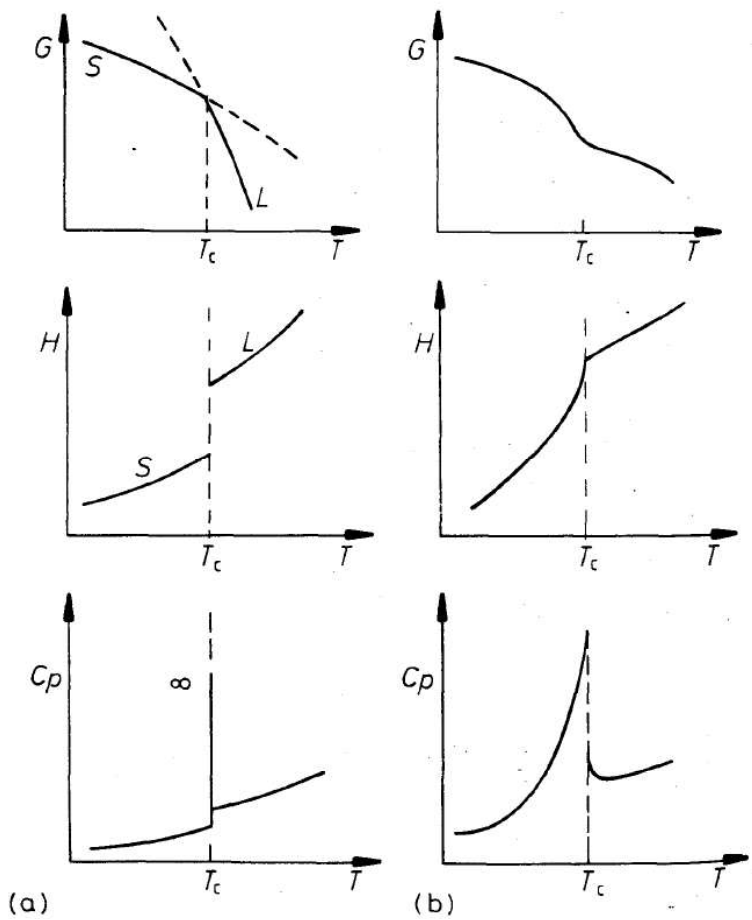


Fig. 3.1 Thermodynamic classification of phase transformations, a) first order transformation b) second order transformation, c_p is the isobaric coefficient of specific heat

Phase transformations can be characterised with respect to both nucleation and the growth process. As far as nucleation is concerned, phase transformations are divided to homogeneous and heterogeneous. The conditions for decomposition of an unstable phase in case of homogeneous transformations are identical at any point within the old phase. Homogeneous transformations can be typically represented by the spinodal decomposition. On the other hand, regarding heterogeneous transformations developed by formation of nuclei of the new phase, such nuclei start evolving at preferential spots within the old phase already. Heterogeneous transformations can be divided into three groups depending on the effect controlling the growth of the new phase, see Fig. 3.2. Referring to the thermally activated growth, phase transformations can be divided pursuant to the distance migrated by particular atoms: either short or long distance. The short distance migration is typical for single-component systems exhibiting allotropy. For basic classification of diffusion transformations associated with relocation of atoms over long distances see also the Fig. 3.2.

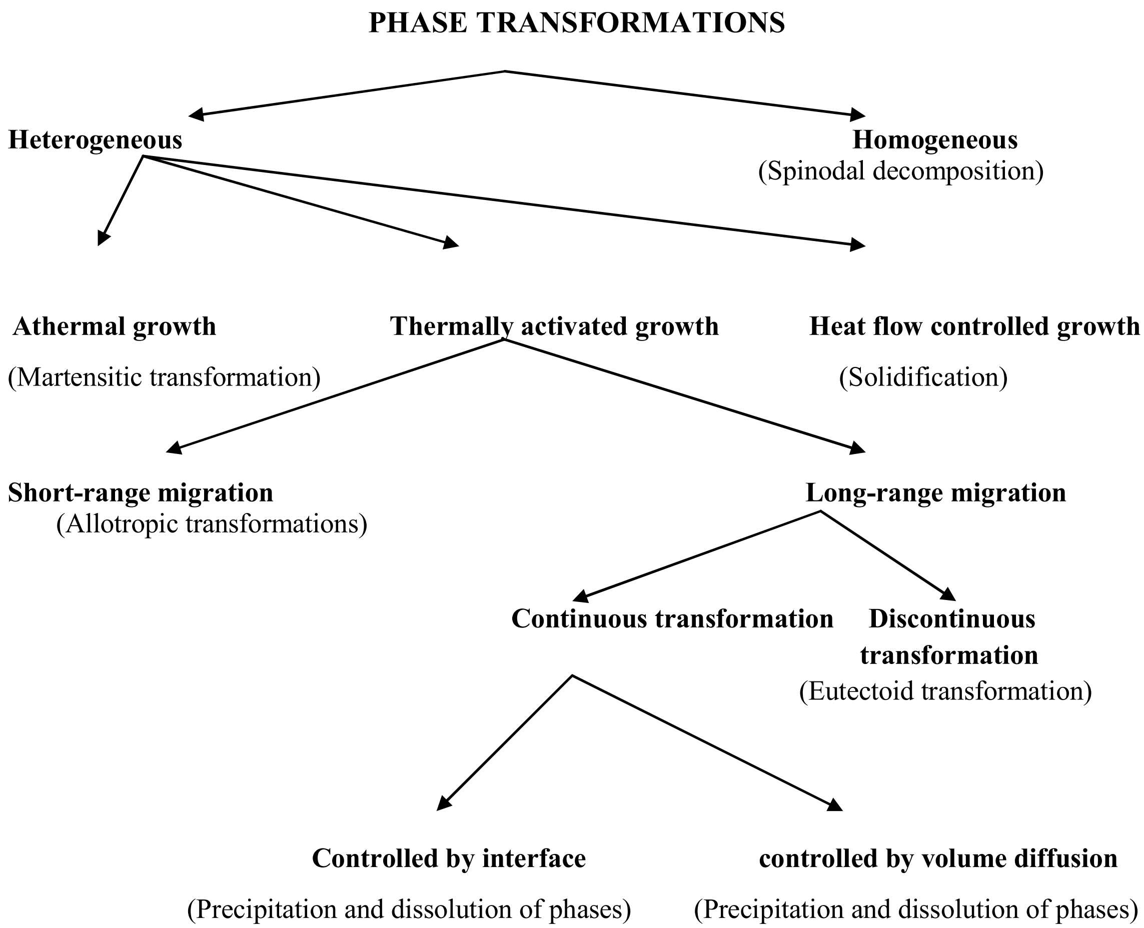


Fig. 3.2 Kinetic classification of phase transformations

Heterogeneous transformations: significant changes in atomic configurations within very small volumes, which are initially associated with the increase of Gibbs free energy in the system (at T = const., p = const.). Overcoming of the energetic barrier is followed by nucleation of a stable nucleus with subsequent growth of transformed areas.

Homogeneous transformations: fluctuations associated with minor changes to configuration of atoms within large volumes. Nucleation takes places throughout the entire system volume simultaneously and it is followed by a gradual decrease of Gibbs free energy.

Another option to divide transformations is represented by the ***growth mechanism*** (kinetic aspect):

Athermal growth: the rate of growth is not dependent on temperature; there is a certain similarity with plastic deformation.

Thermally activated growth: the interface movement is driven by means of repeated overcoming of energetic barriers; this growth mechanism is strongly dependent on temperature.

Growth controlled by heat flow: the interface movement speed depends on the intensity of supply or dissipation of heat in the area of interphase interface.

There are two different cases of thermally activated growth:

***Migration of atoms over a short distance*:** the phases on both sides of interface do not differ in terms of chemical composition.

***Migration of atoms over a long distance*:** the phases on both sides of interface differ in terms of chemical composition.

Migration of atoms over a long distance can be further divided into two different cases:

Continuous reaction: development of areas with a new phase results in changes of chemical composition within the whole remaining volume of the initial phase.

Discontinuous reaction: chemical composition of the initial phase is identical to the average composition of product resulting from a discontinuous reaction; however, the product of discontinuous reaction is composed of two phases of different compositions.

Questions addressing the content covered

1. What are the basic characteristics of the first order transformations?
2. What are the basic characteristics of the second order transformations?
3. What is the division of transformations with respect to the growth mechanism?
4. What is the difference between continuous and discontinuous phase transformations?
5. Why do certain phase transformations require a diffusion over a long distance?
6. What is the meaning of "athermal growth"?
7. What is a thermally activated process?

Exercises

Exercise 1