Fig. 2.3 shows ΔG_{mix} as a function of system composition and temperature. The actual Gibbs free energy in solution G will be also dependent on values of G_A and G_B. Combination of equations (2.2), (2.3) and (2.10) hence produces:

$$G = G_2 = X_A G_A + X_B G_B + RT(X_A \ln X_A + X_B \ln X_B) \tag{2.11}$$

This is shown in the diagram in Fig. 2.4. Rising temperature results in decrease of values G_A and G_B and the curve depicting Gibbs free energy will reflect a greater curvature. The drop of values G_A and G_B relates to heat entropy of both components, G is decreasing while the temperature rises at the rate given by –S.

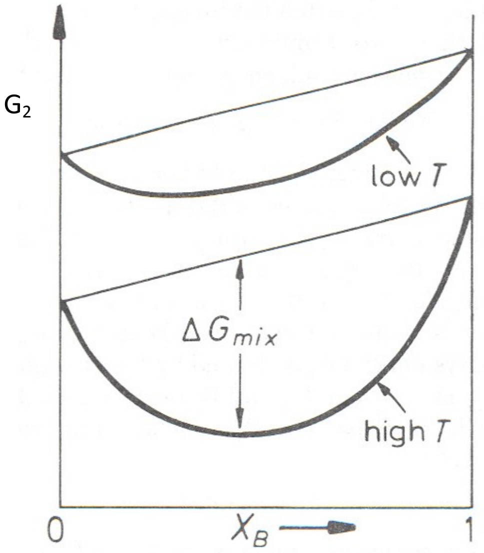


Fig. 2.4 Molar Gibbs free energy for an ideal solid solution

2.3 Chemical Potential

The point of interest pursued in solid solutions (alloys) is the change of free energy within particular phase in the case when the number of atoms in the system is increased or reduced. Adding a small quantity of atoms of A, i.e. dn_A moles, to a large volume of phase at a constant temperature and pressure, the size of system will increase by dn_A, therefore even the Gibbs free energy within the system will grow by a small value of dG′. In case dn_A is sufficiently low, dG′ will represent the proportional quantity of extra atoms of A:

$$dG' = \mu_A dn_A \; (T,\, p,\, n_B \; constant) \tag{2.12}$$

The constant of proportionality μ_A is called the ***partial molar free energy*** of component A or the ***chemical potential*** of component A within the particular phase. μ_A depends on composition of the phase; therefore dn_A must be low enough to prevent a substantial change to the composition of the solution. The chemical potential of component A is defined as follows:

$$\mu_A = \left(\frac{\partial G'}{\partial n_A}\right)_{T,p,n_B} \qquad (2.13)$$

The Gibbs free energy G′ is related towards the entire system. The regular symbol G is used to mark the molar Gibbs free energy, it is therefore independent on the system size. A similar equation can be written for the chemical potential of component B.

Separate contributions can be added up for a binary solution at constant temperature and pressure as follows:

$$dG' = \mu_A dn_A + \mu_B dn_B \qquad (2.14)$$

This equation could be further expanded for solutions containing more than two components. If changes of temperature and pressure are permitted, the general equation will be in this form:

$$dG' = -SdT + Vdp + \mu_A dn_A + \mu_B dn_B + \cdots \qquad (2.15)$$

If 1 mole of the initial phase contained X_A moles of component A and X_B moles of component B, the system size may increase without any change of the phase compositions provided the components A and B have been added at the correct ratio: $dn_A : dn_B = X_A : X_B$. Example: if the phase contains double the amount of A atoms compared to the quantity of B atoms (X_A = 2/3 and X_B = 1/3), the composition can be preserved even after addition of two atoms of A per one atom of B ($dn_A : dn_B = 2$). This method enables enlarging the system by 1 mole without any change of μ_A or μ_B. Adding X_A moles of the component A and X_B moles of the component B will increase the free energy within the system by the amount of molar Gibbs free energy G accordingly.

$$G = \mu_A X_A + \mu_B X_B \quad (\mathrm{Jmol^{-1}}) \qquad (2.16)$$

Knowledge of the dependency of molar Gibbs free energy on X_A and X_B helps determination of μ_A and μ_B by extrapolation of tangent to the curve G on the axis for pure components A and B, Fig. 2.5. It is evident that the values of μ_A and μ_B are going through systematic changes with respect to the phase composition.

Comparison of equations (2.11) and (2.16) will produce an expression of chemical potential of μ_A and μ_B for an ideal solution in the following form:

$$\mu_A = G_A + RT\ln X_A \tag{2.17}$$

$$\mu_B = G_B + RT\,ln\,X_B \tag{2.18}$$

For graphic depiction of these equations refer to the Fig. 2.6. The distance *ac* matches the expression – RTln X_A and the distance *bd* is equal to –RTln X_B.

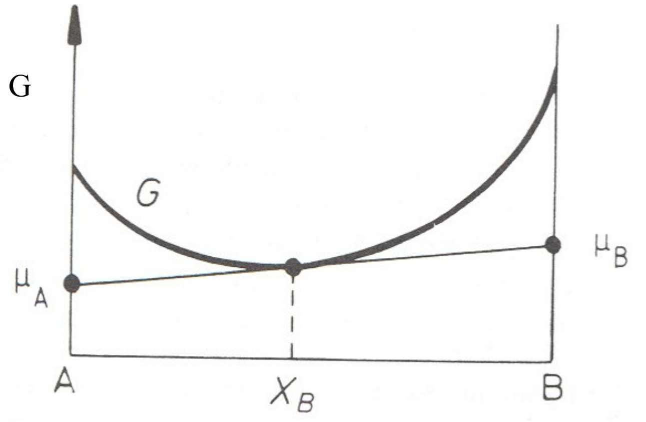


Fig. 2.5 Relation between the curve of Gibbs free energy for a solid solution and chemical potentials of components

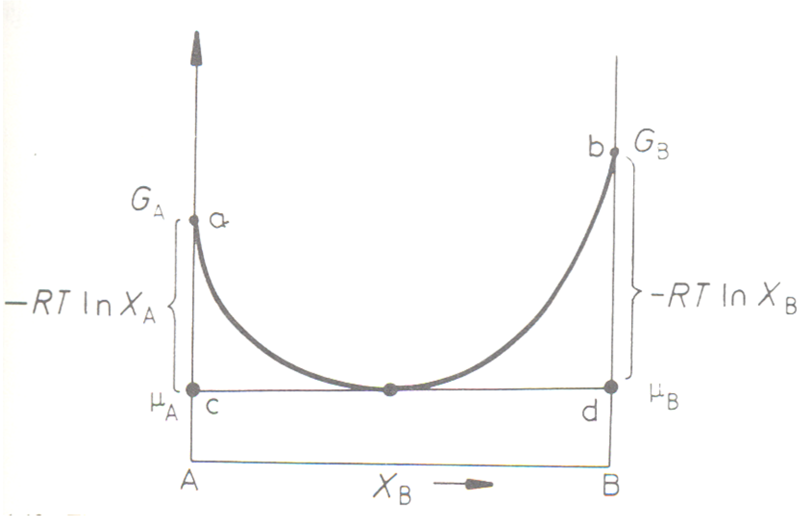


Fig. 2.6 Relations between the curve of Gibbs free energy and chemical potentials for an ideal solution

2.4 Regular Solutions

The development of a solid solution (mixing of atoms) is usually based on an endothermic or exothermic reaction in practice. The above mentioned model applicable to an ideal solution can therefore be extended with ΔH_{mix} using the so called "quasi-chemical approach". This model assumes that the heat for mixing (ΔH_{mix}) is associated with the bonding energy between adjacent atoms only. Volumes of pure components A and B must be necessarily identical and unchangeable during mixing, so the interatomic distances and bonding energies are independent on the composition.

The structure of a binary solid solution may contain three different types of interatomic bonds between atoms belonging to components A or B:

1. A – A bonds, the energy per bond is equal to ε_{AA},
2. B – B bonds, the energy per bond is equal to ε_{BB},
3. A – B bonds, the energy per bond is equal to ε_{AB}.

Assuming that zero energy matches the condition, when atoms are mutually distant almost to infinity, the values of ε_{AA}, ε_{BB} and ε_{AB} are negative, whereas the stronger their bonds, the greater their negativity will become. The internal energy of solid solution will depend on the number of bonds of the specific type P_{AA}, P_{BB} and P_{AB}:

$$E = P_{AA}\varepsilon_{AA} + P_{BB}\varepsilon_{BB} + P_{AB}\varepsilon_{AB} \tag{2.19}$$

Before mixing atoms of A and B, the system contains bonds A – A and B – B. Bearing in mind the relations between P_{AA}, P_{BB} and P_{AB} in the solid solution, the change of internal energy induced by mixing of atoms is given by:

$$\Delta H_{mix} = P_{AB}\varepsilon \tag{2.20}$$

Where:

$$\varepsilon = \varepsilon_{AB} - \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB}) \tag{2.21}$$

If $\varepsilon = 0$, $\Delta H_{mix} = 0$ and the solution is ideal. Atoms will be arranged in a random configuration in this case and the mixing entropy is defined by the following equation:

$$\Delta S_{mix} = -R(X_A \ln X_A + X_B \ln X_B) \tag{2.22}$$

Number of A-B bonds can be expressed:

$$P_{AB} = N_a z X_A X_B \quad \text{(number of bonds per 1 mole)} \tag{2.23}$$

where N_a is the Avogadro's number and z is the number of bonds per atom.

If ***ε < 0***, the atoms within solution will prefer being surrounded by atoms of the opposite type and this even will increase the value $P_{AB.}$

If ***ε > 0***, the number of bonds P_{AB} will tend to remain lower than in a solution with random configuration. Nevertheless, if the values of ε are not so far from zero, the equation (2.23) still represents a fair approximation:

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

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.

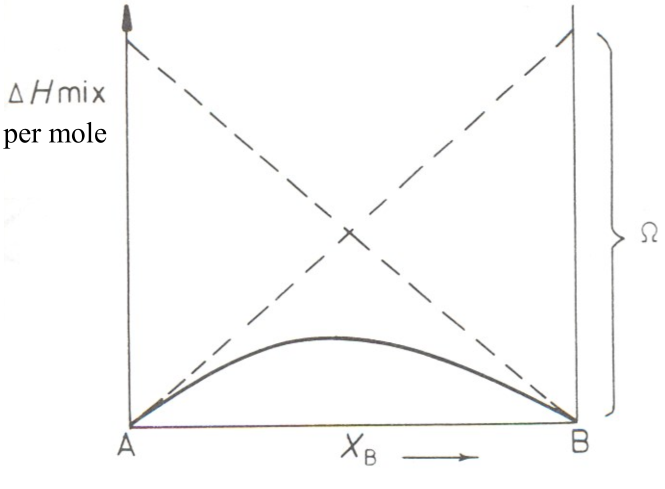


Fig. 2.7 Change of ΔH_{mix} with the composition of regular solutions

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 – RTln a_A and the distance *bd* matches the value of – RTln a_B. In this case:

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

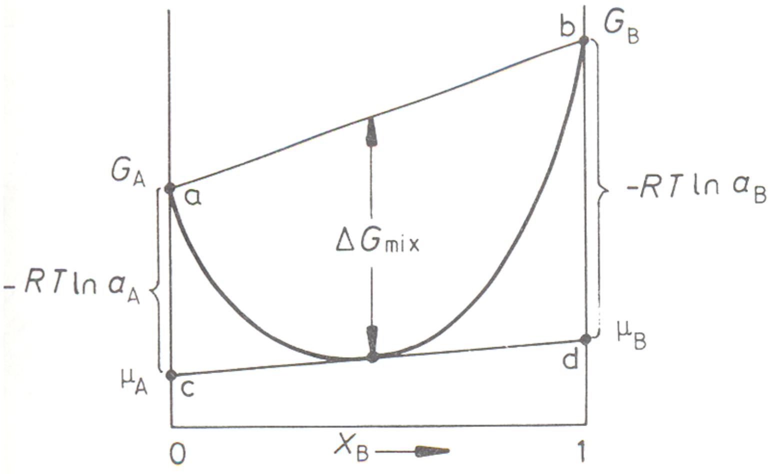


Fig. 2.8 Mutual relationship between the molar Gibbs free energy and activity

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:

$$\gamma_A = \frac{a_A}{X_A} \tag{2.26}$$

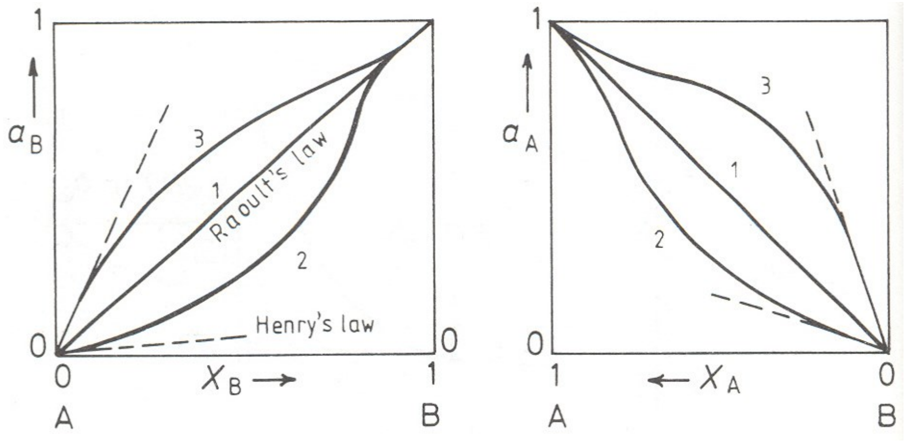
A diluted solution of component B in component A can be defined as:

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

And

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

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