

Introduction

Theoreticians have briefed the significance of the mixing properties of binary liquid alloys from both the scientific and the technological points of view. A precise understanding of the mixing properties and phase diagrams of the alloy system is elementary to establish a good arrangement between the experimental results, theoretical approaches, and empirical models for liquid alloys with a miscibility gap. All liquid binary alloys can be grouped into two distinct classes that either exhibit positive deviation (usually called segregating systems) or negative deviation (i.e. short-ranged ordered alloys) from Raoult's law or the additive rule of mixing. If the deviations are considerably large, they may conduct either phase separation or compound formation in the binary system.

There are liquid alloys, however, which do not belong exclusively to any of the above two classes. For instance, the excess Gibbs energy of mixing (G_M^{xs}) for Cd-Na, and Ag-Ge is negative at certain compositions, while positive at other compositions. In liquid alloys such as Au-Bi, Bi-Cd, and Bi-Sb, the enthalpy of mixing H_M is a positive quantity but G_M^{xs} is negative. Bi-Pb has positive H_M and G_M^{xs} in the solid phase as against the negative values of H_M and G_M^{xs} in the liquid phase. Systems such as Au-Ni and Cr-Mo exhibit immiscibility in the solid phase which is not visible in the interrelated liquid phase. Systems such as Ag-Te show intermetallic phases and large negative H_M values in the liquid phase concurrently with a liquid miscibility gap.

Systems such as Al-Bi, Al-In, Al-Pb, Bi-Ga, Bi-Zn, Cd-Ga, Ga-Pb, Ga-Hg, Pb-Zn, Pb-Si and Cu-Pb, etc, are represented by liquid miscibility gaps and exhibit enormous positive H_M . Their properties in the liquid phase tend to vary markedly as a role of composition (c), temperature (T), and pressure (p). The long-wavelength limit ($q \rightarrow 0$) of the composition-composition structure factors, $S_{cc}(0)$ diverges as the composition and temperature approach the critical values $c \rightarrow c_c$, and $T \rightarrow T_c$. $S_{cc}(0)$, which can instantly be obtained from thermodynamic functions (either acquired by taking the first composition derivative of the activity or through the second derivative of the Gibbs function), is very useful for establishing the immiscibility and the degree of segregation in binary liquid alloys. Additional thermodynamic, structural, and transport properties are also found to alter anomalously in the area of c_c and T_c .

A provided unary system is expressed by two pairs of independent variables, namely the mechanical degrees of freedom (pressure (p) or volume (Ω)) and the thermal degrees of freedom (temperature (T) or entropy (S)). The preference of independent variables is mostly a concern of free option; yet, there are four possibilities for creating such pairs have one mechanical and one thermal variable, say (S, Ω), (S, p), (T, Ω) and (T, p). These pairs guide to thermodynamic functions such as internal energy $E(S, \Omega)$, enthalpy $H(S, p)$, Helmholtz energy $F(T, \Omega)$, and Gibbs energy $G(T, p)$, respectively.

The enthalpy, H, merging the internal energy E to the mechanical degrees of freedom (p, Ω) is

$$H = E + p\Omega \quad (1)$$

or in differential form,

$$dH = \delta Q + \Omega dp \quad (2)$$

where

$$\delta Q = dE + pd\Omega$$

The Helmholtz energy, F, relates E to the thermal degrees of freedom (S, T), i.e.

$$F = E - TS \quad (3)$$

or,

$$dF = -SdT - pd\Omega \quad (4)$$

In the case of reversible isothermal and isochoric processes (T, Ω = constant), $dF = 0$, i.e. F remains invariant. Similarly, the Gibbs function establishes a relation between H and the thermal degrees of freedom, i.e.

$$G = H - TS \quad (5)$$

or

$$dG = -SdT + \Omega dp \quad (6)$$

In the case of a reversible isothermal reaction at constant pressure (T , p = constant), $dG = 0$, i.e. G remains invariant.

Also, H , F and G can readily be used to obtain the heat capacity C (C_p or C_Ω), entropy, isothermal (χ_T) and adiabatic (χ_S) compressibilities, the volume and the volume expansivity (α_p):

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_p = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_p \quad (7)$$

$$C_\Omega = \left(\frac{\partial E}{\partial T} \right)_\Omega = T \left(\frac{\partial S}{\partial T} \right)_\Omega = -T \left(\frac{\partial^2 F}{\partial T^2} \right)_\Omega \quad (8)$$

$$S = \left(\frac{\partial G}{\partial T} \right)_p = \left(\frac{\partial F}{\partial T} \right)_\Omega \quad (9)$$

$$\Omega = \left(\frac{\partial G}{\partial p} \right)_T \quad (10)$$

$$\chi_T \equiv -\frac{1}{\Omega} \left(\frac{\partial \Omega}{\partial p} \right)_T \quad (11)$$

$$\chi_S \equiv -\frac{1}{\Omega} \left(\frac{\partial \Omega}{\partial p} \right)_S \quad (12)$$

$$\alpha_p \equiv \frac{1}{\Omega} \left(\frac{\partial \Omega}{\partial T} \right)_p \quad (13)$$

At indicator, we furthermore have some important effects from isotherms of liquid-vapor phases which at the critical point must fulfill

$$\left(\frac{\partial p}{\partial \Omega} \right)_{T_c} = \left(\frac{\partial^2 p}{\partial \Omega^2} \right)_{T_c} = 0 \quad (14)$$

At $T = T_c$, the following physical properties become infinite, i.e.

$$C_p = T \left(\frac{\partial S}{\partial T} \right)_p = \infty \quad (15)$$

$$\alpha_p = \frac{1}{\Omega} \left(\frac{\partial \Omega}{\partial T} \right)_p = \infty \quad (16)$$

$$\chi_T = - \left(\frac{\partial \Omega}{\partial p} \right)_T = \infty \quad (17)$$

For a binary mixture, such as an A–B alloy consisting of c_A moles of component A and c_B moles of component B, rather than guiding to the fundamental values of their function, we define the function of mixing. For example, the Gibbs energy of mixing, G_M , is represented as

$$G_M = G(alloy) - c_A G_A^0 - c_B G_B^0 \quad (18)$$

where G_A^0 and G_B^0 are the Gibbs free energy of the two pure components. Equivalent definitions also exist for HM, SM and other functions. The integral quantities can also be divided into the partial quantities, i.e.

$$G_M = c_A \bar{G}_{M,A} + c_B \bar{G}_{M,B} \quad (19)$$

with

$$\bar{G}_{M,i} = RT \ln a_i \quad (i = A, B)$$

where $\bar{G}_{M,i}$ are the partial Gibbs energies and a_i are the thermodynamic activities of the component i. G_M defines the stability of the phases in a binary mixture. The curves describing G_M against c deviation can, in general, have a shape like either curve a or curve b as displayed in figure 1. For G_M as in curve a, the homogeneous solution is stable at all values of c at T_1 ; if not other phases (i.e. intermediate phases) in the system display more negative G_M values.

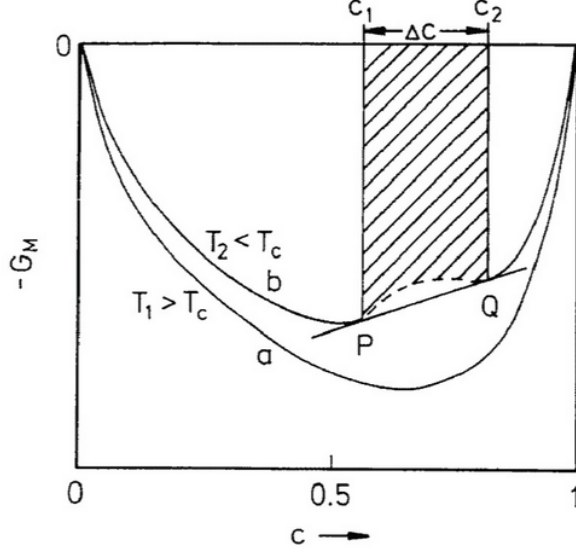


Figure 1: A schematic diagram symbolizing the Gibbs energy of mixing at constant T plotted against concentration. Curve a, complete mixing ($T_1 < T_c$). Curve b, incomplete mixing ($T_2 < T_c$), Δc represents the miscibility gap at T_2 .

For curve b, the homogeneous solution is varying in the composition range Δc , because G_M can be reduced if the mixture separates into two phases. The composition of these phases is provided by the points of contact P and Q of the common tangent line to the $G_M(c)$ curve. The reduced G_M values of these two phases are given by this line. Within the composition range Δc only the portions of the two phases change if the total composition of the alloy modifications. At P(c_1) and Q(c_2) the partial Gibbs energies of the components of both diverged phases are equivalent,

$$\overline{G}_{M,i}(c_1) = \overline{G}_{M,i}(c_2) \quad (i = A, B)$$

Hence P and Q indicate the limit of thermodynamic equilibrium. G_M diverts as a function of temperature from a concave to a convex surface for Δc at the spinodal. The points of inflection in the curves define the spinodal line. The critical composition and the critical temperature are determined from the conditions at $T = T_c$

$$\left(\frac{d^2 G_M}{dc^2}\right)_{c=c_c} = 0 \quad (20)$$

$$\left(\frac{d^3 G_M}{dc^3}\right)_{c=c_c} = 0 \quad (21)$$

At this step, it should be pointed out that the long-wavelength limit ($q \rightarrow 0$) of the structure factor $S_{cc}(q)$ which is well known as the concentration fluctuation, $S_{cc}(0)$, is also correlated to the thermodynamic function, i.e

$$S_{cc}(0) = RT \left(\frac{d^2 G_M}{dc^2}\right)_{T,P}^{-1} \quad (22)$$

As $c \rightarrow c_c$ and $T \rightarrow T_c$, one sees that

$$S_{cc}(0) \rightarrow \infty \quad (23)$$

Thus, a phase separation in a binary mixture is signaled by a strong enhancement of the concentration fluctuations. The ideal solution behavior (HM = 0) of a binary mixture is presented by

$$G_M^{id} = RT(c_A \ln c_A + c_B \ln c_B). \quad (24)$$

The distinctions in the thermodynamic behavior of a real binary solution and an ideal solution are represented by the excess quantities, i.e.

$$G_M^{xs} = G_M - G_M^{id} \quad (25)$$

or using equation (5)

$$G_M^{xs} = H_M - TS_M^{xs} \quad (26)$$

with

$$S_M^{xs} = S_M + R(c_A \ln c_A + c_B \ln c_B) \quad (27)$$

Observable indicators

Segregating liquid alloys

From the point of view of interatomic interactions, a binary alloy is either (i) an ordered alloy, where unlike atoms are chosen as nearest neighbors over like atoms, or (ii) a segregated alloy, where like atoms are chosen to pairs as nearest neighbors over unlike atoms. Unfortunately, there is no direct way to distinguish the constituent atoms and hence the identification of a nearest-neighbor pair of atoms is challenging. In this case either the structural data or the experimental thermodynamic functions (such as activity, the heat of mixing, excess Gibbs energy of mixing, excess heat capacity, etc) or other thermophysical data (such as viscosity, diffusivity, density, surface tension, electrical resistivity, etc) are supposed to extract information associated with interatomic interactions. Some of the empirical criteria as well as microscopic parameters which are used to identify segregated alloys are summarized below.

- (a) Alloys displaying positive deviations from Raoult's law.
- (b) The heat of formation and the excess Gibbs energy of mixing are positive.
- (c) The concentration fluctuation in the long-wavelength limit ($S_{cc}(0)$) is greater than the ideal value.

Table 1 provides a list of G_M^{xs} , H_M and S_M^{xs} at the equiatomic composition of segregating liquid alloys which are arranged according to the type of their phase equilibria. Of these Bi-Zn, Pb-Zn, Cu-Pb, Cd-Ga, Al-Bi, Al-In, Al-Pb, etc, exhibit liquid immiscibility. G_M^{xs} and H_M are comparatively large positive quantities. For these alloys only a few experimental heat capacity data are available. The data, in general, show a decrease in C_p with increasing temperature. The energetic and structural effects in the solution phase can be more directly seen by the excess heat capacity ΔC_p values:

$$\Delta C_p = C_p(c) - c_A C_{p,A} - c_B C_{p,B} \quad (28)$$

Table 1: Thermodynamic properties of liquid binary alloys at equiatomic composition displaying segregation.

Alloys	Ref.	T (K)	G_M^{xs}/RT	H_M/RT	S_M^{xs}/R
Al-Bi	(i)	900	0.814	0.823	0.09
Al-In		1150	0.54	0.49	-0.05
Al-Pb		1700	0.527	0.847	0.32
Bi-Ga	(ii)	550	0.493	0.433	-0.06
Bi-Zn		880	0.36	0.60	0.24

ΔC_p are positive and indicate maximum values near to T_c and c_c .