

Theoreticians have reported the importance of the mixing properties of binary liquid alloys from both the scientific and the technological points of view. An accurate knowledge of the mixing properties and phase diagrams of the alloy system are essential to establish a good understanding between the experimental results, theoretical approaches and empirical models for liquid alloys with 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 lead either to 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 example, 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 (HM) is a positive quantity but G_M^{xs} is negative. Bi–Pb has positive HM and G_M^{xs} in the solid phase as against the negative x_s values of H M and G M in the liquid phase. Systems such as Au–Ni and Cr–Mo exhibit immiscibility in the solid phase which is not visible in the corresponding liquid phase. Systems such as Ag–Te show intermetallic phases and large negative H M values in the liquid phase together 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 characterized by liquid miscibility gaps and exhibit large positive HM. Their properties in the liquid phase tend to change markedly as a function 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 directly be obtained from thermodynamic functions (either obtained by taking the first composition derivative of the activity or through the second derivative of the Gibbs function), is very useful for ascertaining the immiscibility and the degree of segregation in binary liquid alloys. Other thermodynamic, structural and transport properties are also found to change anomalously in the vicinity of c_c and T_c .