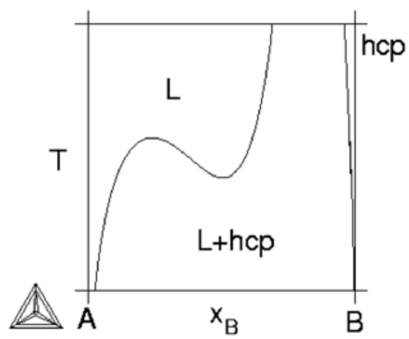
Exercises on Ch.15 Limit of stability and critical phenomena

15.3 Miscibility gaps

Exercise 15.3.1

The following part of a binary phase diagram was obtained when one used a thermodynamic database to calculate the hcp + liquid(L) equilibrium in a binary system. The result looks strange. Try to find the explanation.



Hint

The whole liquid boundary (the so-called liquidus) represents equilibrium with almost pure B. Use that fact in order to examine how μ_B varies at the points of maximum and minimum.

Solution

At the points of maximum and minimum we know $(d\mu_B/dx_B)_{T,P,N} = 0$. This looks like a stability condition. We can find μ_i in the first group of conjugate variables in Table 9.2. From its first row we can formulate the following stability condition: $(d\,\mu_B/dz_B)_{T,P,NA} = 0$. It is evident that the maximum and minimum would fall at the same compositions even if we had plotted the results with the z_B axis instead of the x_B axis. We may conclude that there is a liquid miscibility gap and its spinodal goes through the points of maximum and minimum.

15.5 Tri-critical points

Exercise 15.5.1

Examine the possibility of having a tri-critical point in the *T,P* phase diagram of a unary system by trying to model a change from first-order to second-order transition.

Hint

From Exercise 15.3 we know that we must use a symmetric G_m function in order to describe a second-order transition. It would thus be interesting to examine $G_m = g_o + (1/2)g_{\xi\xi}\xi^2 + (1/24)g_{\xi\xi\xi\xi}\xi^4 + (1/720)g_{\xi\xi\xi\xi\xi\xi}\xi^6$. In Section 15.2 it was used to describe a first-order transition. Examine if the parameters can be adjusted to make ξ_e for the ordered state approach zero which could change the transition to second-order.

Solution

The expression for ξ_e^2 in Eq. 15.13 can approach zero if $g_{\xi\xi\xi\xi} = 0$ but the expression for $dG_m/d\xi = 0$ in Eq. 15.41 shows that it will happen only if $g_{\xi\xi} = 0$ at the same time. Suppose $g_{\xi\xi}$ and $g_{\xi\xi\xi\xi}$ are both functions of *T* and *P*. It should then be possible that they both go through zero in a point in the *T,P* diagram. On the side where $g_{\xi\xi\xi\xi} < 0$ we have a first-order transition (see thick line in the diagram) as already described in Section 15.2. Where $g_{\xi\xi\xi\xi} > 0$ the result will be much like the first case where we did not use the ξ^6 term and were able to describe a second-order transition (dashed line).