Exercises on Ch.7 *Applications of molar Gibbs energy diagrams*

7.3 *Illustration of the Gibbs–Duhem relation*

Exercise 7.3.1

Prove analytically that $x_A\mu_A + x_B\mu_B + x_C\mu_C = y_A\mu_{AaCc} + y_B\mu_{BaCc}$ when $a + c = 1$ and the composition falls on the line between A_aC_c and B_aC_c.

Hint

$x_A = ay_A/(a + c) = ay_A$; $x_B = ay_B$; $y_A + y_B = 1$. The mole fraction of C is constant, $x_C = c$.

Solution

$y_A\mu_{AaCc} + y_B\mu_{BaCc} = y_A(a\mu_A + C\mu_C) + y_B(a\mu_B + C\mu_C) = y_Aa\mu_A + (y_A + y_B)c\mu_C + y_Ba\mu_B = x_A\mu_A + x_B\mu_B + x_C\mu_C$

Exercise 7.3.2

Consider a solution phase in a binary A–B system. Define A and AB as the two components. Where in the system will μ_{AB} have its highest value?

Hint

In a preceding section we treated this question graphically but now we should do it analytically. Start with the Gibbs–Duhem relation at constant *T* and *P* and replace the old set of components, A and B, with the new set, A and AB.

Solution

Let N_A and N_B be the contents according to the old set and N'_A and N'_{AB} according to the new set. Then $N_A = N'_A + N'_{AB}$; $N_B = N'_{AB}$; $\mu_{AB} = \mu_A + \mu_B$. The Gibbs–Duhem relation gives: $0 = N_A d\mu_A + N_B d\mu_B = (N'_A + N'_{AB})d\mu_A + N'_{AB}(d\mu_{AB} - d\mu_A) = N'_A d\mu_A + N'_{AB} d\mu_{AB}$; When $N'_A = 0$, i.e. when $N_A = N'_{AB} = N_B$, then we get $d\mu_{AB} / d\mu_B = 0$ and there is a maximum in μ_{AB} at the composition of AB.

7.4 *Two-phase equilibria in binary systems*

Exercise 7.4.1

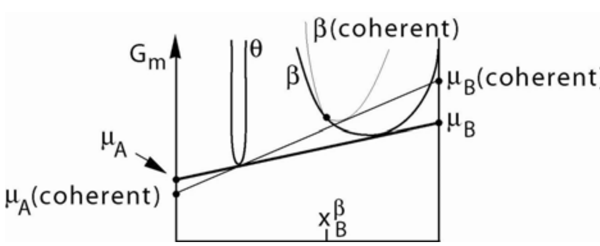
Suppose a solution phase β has a higher A content than required by equilibrium with an A-rich stoichiometric phase θ. When it comes into contact with θ it will precipitate θ and its surface layer will lose A and thus grow richer in B. Suppose that the lattice parameter varies strongly with the composition. The surface layer will then be under coherency stresses as long as it is coherent with the bulk of unchanged β. Examine if this phenomenon will increase or decrease the chemical potentials for the local two-phase equilibrium.

Hint

The stressed β material has an additional energy and should thus have a new G_m curve which is higher than the ordinary G_m curve but tangent to it at the initial β composition where there should be no stresses.

Solution

The common tangent construction shows that μ_B is higher but μ_A is lower. See diagram.



7.5 Allotropic phase boundaries

Exercise 7.5.1

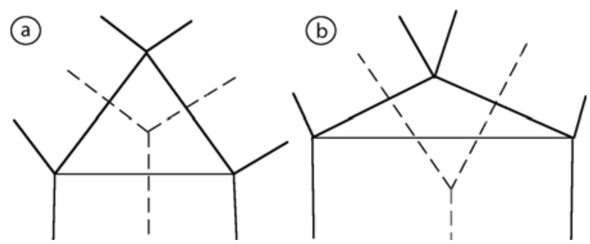
Consider an isobarothermal section of a ternary system with three phases taking part in a three-phase equilibrium. Each two-phase field has an allotropic phase boundary. Show reasonable positions of the three lines. Is it necessary or possible that they intersect inside or outside the three-phase triangle? Will there be one or three points of intersection?

Hint

In the ternary case, an allotropic phase boundary is the line of intersection between two G_m surfaces. The two phases must have the same G_m value along that line.

Solution

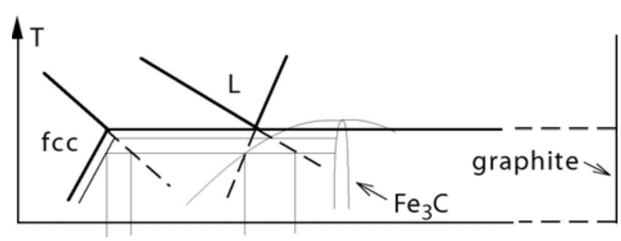
Consider the point where the $\alpha + \beta$ and $\alpha + \gamma$ lines intersect. There, α has the same G_m as β and γ. Consequently, β and γ also have the same G_m there and the $\beta + \gamma$ line must intersect in the same point. By simple constructions one may show that the intersection falls inside the three-phase triangle in a regular triangle but not in a very thin triangle (see diagram).



7.7 *Driving force for the formation of a new phase*

Exercise 7.7.1

On solidification an Fe-C melt normally first precipitates γ (fcc-Fe with dissolved C) and then either graphite (in grey cast iron), which gives a stable state, or cementite, Fe_3C, (in white cast iron), which gives a metastable state. Compare the driving forces for the nucleation of graphite and cementite from the melt at the temperature where the extrapolated lines for L/L + graphite and L/L + cementite intersect (see diagram).

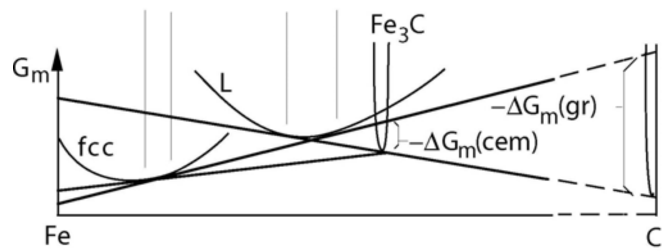


Hint

Make the comparison by means of a schematic molar Gibbs energy diagram and assume that the melt is in equilibrium with γ which has precipitated first. Start by drawing curves for L, cementite and graphite with a common tangent. Then draw a curve for γ showing that L is not stable. Finally, draw the common tangent to γ and L and evaluate by how much the curves for graphite and cementite fall below it. The eutectic liquid has <inline>.

Solution

$\Delta G_m^{gr} / \Delta G_m^{cem} = (1-0.17)/(0.25-0.17) = 10.4$ (see diagram). The larger composition difference is favoured during nucleation but not during growth, of course.



7.10 *Ternary systems*

Exercise 6.10.1

Use a geometrical interpretation of the equation for calculating a partial molar quantity in order to prove that the intercepts of a tangent plane in a ternary G_m diagram represent the partial Gibbs energies, as already indicated by Fig. 4.9.

Hint

Use a construction similar to the one described by Eq. 4.45 for volumes. Choose x_B and x_C as the independent composition variables.

Solution

$G_C = G_m + \partial G_m/\partial x_C - x_B \partial G_m/\partial x_B - x_C \partial G_m/\partial x_C$
$= G_m + (1 - x_C) \partial G_m/\partial x_C - x_B \partial G_m/\partial x_B$