Exercises on Ch.11 *Direction of phase boundaries*

11.4 *Direction of phase boundaries*

Exercise 11.4.1

The direction of an α/β phase field in a *T*,*P* diagram for a pure element is given by the Clapeyron equation, Eq. 8.17. Derive an expression for the direction of a corresponding phase boundary in an *H*,*S* diagram.

Hint

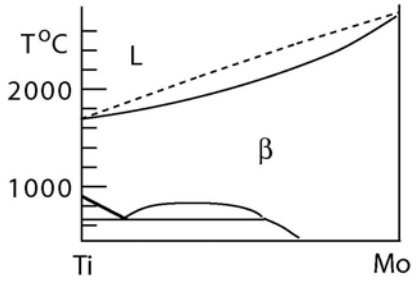
When the axes are not both potentials, the two phase boundaries α/β and β/α will be separated. One may consider either one. Let us take α. The final expression then contains properties of the α phase. Let us express them in terms of G^α and its derivatives G_T^α, G_P^α etc. It may then be convenient to start by considering H^α and S^α as functions of *T* and *P*. However, *T* and *P* are not independent because we want to follow the α + β two-phase equilibrium. Therefore, we know from the Clapeyron equation that $dT = dP \cdot (V_m^\alpha - V_m^\beta)/(S_m^\alpha - S_m^\beta)$. We may thus evaluate $(dH^\alpha/dP)^{\alpha+\beta}$ and $(dS^\alpha/dP)^{\alpha+\beta}$ and take their ratio and insert the expression for d*T*/d*P*.

Solution

$H^\alpha = G^\alpha + TS^\alpha = G^\alpha - TG_T^\alpha; (\partial H^\alpha/\partial T)_P = G_T^\alpha - G_T^\alpha - TG_{TT}^\alpha = -TG_{TT}^\alpha;$
$(\partial H^\alpha/\partial P)_T = G_P^\alpha - TG_{TP}^\alpha; dH^\alpha = (\partial H^\alpha/\partial P)_T dP - (\partial H^\alpha/\partial T)_P dT$
$= [G_P^\alpha - TG_{TP}^\alpha - TG_{TT}^\alpha dT/dP]dP$. We also get
$dS^\alpha = (\partial S^\alpha/\partial P)_T dP + (\partial S^\alpha/\partial T)_P dT = [-G_{TP}^\alpha - G_{TT}^\alpha dT/dP]dP$. Finally, by dividing the two expressions, we get $dH^\alpha/dS^\alpha = T + G_P^\alpha/[-G_{TP}^\alpha - G_{TT}^\alpha dT/dP]$. By inserting the value for d*T*/d*P* along the α + β equilibrium we find
$(dH^\alpha/dS^\alpha)^{\alpha+\beta} = T - G_P^\alpha/[G_{TP}^\alpha + G_{TT}^\alpha(V_m^\alpha - V_m^\beta)/(S_m^\alpha - S_m^\beta)]$.

Exercise 11.4.2

A published Ti–Mo phase diagram shows the liquidus as a dashed line, indicating insufficient experimental information. Try to predict its position from the solidus by evaluating the width of the two-phase field.



Hint

Consider the centre of the system. Lacking detailed information, we may assume that the heat of solution is equal to the average of the heat of solidification of the elements, − 15.45 and − 32.54 kJ/mol. Since the temperature is so high, it may be justified to neglect the contribution from the excess Gibbs energy in g_{22} which is thus approximated by RT/x_1x_2.

Solution

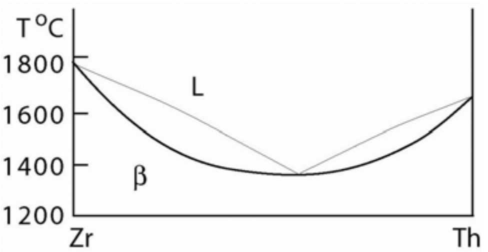
$$x_2^L - x_2^\beta = -\Delta H_m (dT/dx_2^\beta)_{coex}/(RT/x_1x_2)T = (-24000)\cdot 1200/8.3145\cdot 4\cdot (2150)^2 = -0.19$$

It seems that the authors have made the same calculation.

11.5 *Congruent melting points*

Exercise 11.5.1

The following diagram for the Zr–Th system has been proposed. The liquidus was not known experimentally and has been drawn tentatively with a thin line. Criticize it.



Hint

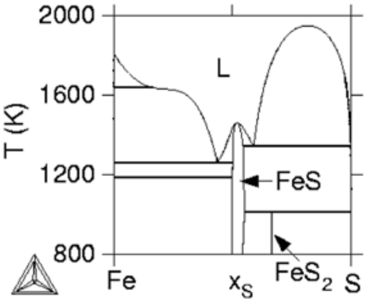
The line has not been carefully drawn at the melting minimum.

Solution

Both the solidus and the liquidus must be horizontal at the point of minimum according to Konovalov's rule. It is not very probable that g_{22} in a liquid would be very large, especially if g_{22} in the solid is not, and the present diagram does not indicate that it is.

Exercise 11.5.2

The liquidus in the Fe–S system becomes almost horizontal at 20 atom.% S. From the previous exercise one could perhaps expect to see a miscibility gap in the liquid phase just above the most horizontal point and, indeed, it was proposed long ago. However, it has not been observed experimentally. Try to find an explanation.



Hint

It is more common that a solution grows more ideal at higher temperatures. If there is a tendency to form a miscibility gap it is normally expected to grow stronger at lower temperatures.

Solution

g_{22}^{L} is close to zero on the liquidus and may go through zero below the liquidus. It seems most probable that a miscibility gap would be seen below the liquidus if solidification could be prevented in some way, i.e. there would be a metastable miscibility gap in the supercooled liquid phase.

Exercise 11.5.3

Use Richard's rule to estimate the slope of the liquidus from the melting point of A in a binary A–B system where the solubility of B in solid A is very low.

Hint

Richard's rule says that the heat of melting of a metal is approximately $RT_{\mathrm{m.p.}}$.

Solution

$K_B^{\alpha/L} = 0$ gives $(dT/dx_B^L)_{coex} = RT^2/\Delta H_m = RT_{m.p.}^2/(-RT_{m.p.}) = -T_{m.p.}$

Exercise 11.5.4

A pure element has a sharp melting temperature at a given pressure. The solid and liquid phases can be in equilibrium with each other at a different temperature if a second element is added and also if the pressure is changed. Consider how much should be added to the liquid phase if the temperature be changed by ΔT and the pressure by ΔP. Do this by deriving an expression for the value of $x_2^L - x_2^\alpha$.

Hint

Go back to the general equation for the direction of phase boundaries and apply it to a binary system.

Solution

This time we keep the dP term,
$(x_2^\alpha - x_2^L) g_{22}^L dx_2^L = -[x_1^\alpha (H_1^\alpha - H_1^L) + x_2^\alpha (H_2^\alpha - H_2^L)] dT/T + [x_1^\alpha (V_1^\alpha - V_1^L)$
$+ x_2^\alpha (V_2^\alpha - V_2^L)] dP$. For small x_2: $RT(x_2^\alpha - x_2^L) dx_2^L / x_2^L = ({}^oH_1^\alpha - {}^oH_1^L) dT/T$
$+ ({}^oV_1^\alpha - {}^oV_1^L) dP$. We can easily integrate if ΔT and ΔP are small and $(x_2^\alpha - x_2^L)/x_2^L$ is a constant. By integrating from 0 to x_2^α we get $x_2^\alpha - x_2^L = [-({}^oH_1^\alpha - {}^oH_1^L)\Delta T/T$
$+ ({}^oV_1^\alpha - {}^oV_1^L)\Delta P]/RT$. We may thus evaluate x_2^L if x_2^α is small or if $K_B^{\alpha/L}$ is known.

11.7 *Slope of phase boundaries in isothermal sections*

Exercise 11.7.1

The diagram shows the solubility of V_2O_3 in liquid Fe at 1873 K. It is evident that the solubility of O goes through a minimum. Apply the regular solution model and show the requirement for the minimum to occur. What parameter or combination of parameters can be evaluated from the position of the minimum?

Hint

Apply the regular solution model in order to express the derivatives of G_m. Insert the expressions in the final equation obtained without any approximations. Parameters will occur in two places. Neglect one combination of parameters at a time and examine if the result is realistic.

Solution

For a very dilute solution we expect the solubility curve for V_2O_3 to give a solubility product $(x_V)^2(x_0)^3$ = costant which yields 2log(mass%V) + 3log(mass%O) = constant.

That line can be fitted to the data points at low V contents but not at higher. There we must take into account the deviation from ideal behavior and shall try the regular solution model and identify the components as Fe = 1; V = 2; and O = 3. The regular solution model gives $G_m = \sum x_i(°G_i + RT\ln x_i) + x_1x_2L_{12} + x_2x_3L_{23} + x_3x_1L_{31}$. When evaluating g_{22} and g_{23} we must remember that x_1 is a dependent variable. $g_2 = °G_2 – °G_1 + RT(x_2/x_2 + \ln x_2 – x_1/x_1 – \ln x_1) + (x_1 – x_2)L_{12} + x_3L_{23} – x_3L_{31}$; $g_{22}=RT(1/x_2 + 1/x_1) –2L_{12}$; $g_{22}/RT – 1/x_1 – 1/x_2 = –2L_{12}/RT$; $g_{23}/RT(1/x_1) – L_{12} + L_{23} – L_{31}$; $g_{23}/RT – 1/x_1 = (L_{23} – L_{12} – L_{31})/RT$. With $\beta = V_2O_3$ we have $x_2^\beta = 0.4; x_3^\beta = 0.6; x_1^\beta = 0$. The diagram shows that the minimum is at log(mass%V) = 0.5 which gives mass%V = 3.2; $x_2^\alpha = 0.035$. We get 0.035 = 0.4/[0.4 – 0.035)($2L_{12}/RT$) + (0.6 – 0)($–L_{23} + L_{12} + L_{31}$) + 0] from the equation for the minimum. There are two simple alternatives.

Alt.1: $L_{23} – L_{12}– L_{31}$ can be neglected then $2L_{12}/RT = 31$. This would give a very large miscibility gap in the Fe–V system which has not been observed. Alt.2: If $2L_{12}/RT$ is much less than 31, then its term can be neglected and we get $(L_{23} - L_{12} - L_{31})RT = -19$ (or $\varepsilon_V^O = \varepsilon_O^V = -19$ if we use the last equation). This is regarded as a reasonable value because O and V have a strong affinity to each other.