# Exercises on Ch.10 Projected and mixed phase diagrams

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## **10.4** Coincidence of projected surfaces

## Exercise 10.4.1

Darken (1948) has published the following phase diagram for the Fe–Si–O system. We may regard it as an isobaric section at 1 bar and a projection along some chemical-potential axis. Let us concentrate on the invariant equilibrium 3. The lines radiating from that point are as follows: (e) magnetite + fayalite + melt; (h) wüstite + fayalite + melt; (g) magnetite + wüstite + fayalite; (i) magnetite + wüstite + melt.

It is known from experiments that the composition of the melt at point 3 falls at a lower Si content than fayalite  $(2FeO \cdot SiO_2)$ . Check if that is confirmed by the diagram. Knowing that the diagram concerns two more phases, metal and silica, it is possible to identify the other three invariant equilibria. Do that. Examine where the compositions of the melt at points 2, 4 and 5 fall relative to the other phases.



Hint

First decide which axis is projected. Then find out on which composition variable the diagram can give information. Remember that we can interpret the  $\log P_{02}$  axis as a way of expressing the oxygen potential without having a gas present.

#### Solution

We see no axis for Si or Fe. The diagram is thus projected in the direction of one of them and the other is the dependent variable. We can get information on the ratio  $N_{Si}/N_{Fe}$ . With the method illustrated in Fig. 10.11 we can mark the lines around point 3 in the following way: *e*-(w); *g*-(L); *h*-(mag); *i*-(fay). Their arrangements can be obtained from their relative compositions (see two alternatives in sketch 3a below). From the information given about the four lines we find that the first alternative applies here. We should thus correct Darken's diagram for point 3 as shown in sketch 3b.

We can go from point 3 to 4 by following line *h* which represents an equilibrium without magnetite. Point 4 is thus an equilibrium without magnetite which is understandable because we have gone to a lower value of  $P_{02}$ . Magnetite being the highest oxide has disappeared and the new phase is probably metal (see sketch 4).

As we follow line e from point 3 to 2 we lose wüstite and gain silica (see sketch 2). Finally, we may guess that point 5, falling between points 4 and 2, contains metal and silica in addition to melt and fayalite (see sketch 5).

Accepting Darken's constructions for the points 2, 4 and 5 we find the relative compositions as given in the sketches.

By comparing the position of L in the various diagrams, we find that it is thus necessary that L changes its composition relative to fayalite between 4 and 5 and moves back between 2 and 3. This is why the lines e and j are curved.



## Exercise 10.4.2

In Exercise 10.3 we discussed the reason why only three lines seem to intersect at point I in Fig. 10.5. How could one express the reason in terms of the present discussion on coincidence?

## Hint

There are three components in the system. The potential of one is used as an axis. We could apply the arguments to the remaining two components.

#### Solution

 $\text{Log}P_{\text{O2}}$  is plotted on one axis and it represents the chemical potential of O. The composition variable which is the same in the three phases, Fe, FeO and Fe<sub>3</sub>O<sub>4</sub>, is thus the ratio between the amounts of the other components, S and Fe, i.e.  $z_s \equiv N_s/N_{\text{Fe}}$ . It is in fact zero for these three phases because they all have  $N_s = 0$ .

## 10.6 The phase field rule and mixed diagrams

## Exercise 10.6.1

Test the equations for  $p_{max}$  and *d* by application to the following sections taken through a quaternary phase diagram at 1 bar.



#### Solution

 $p_{\text{max}} = r + 1 + n_{\text{pr}} + n_{\text{ms}} = c + 2 - n_s + n_{ms}$  and the smallest  $d = c + 2 - p_{\text{max}} - n_s + n_{\text{ma}} + n_{\text{ms}}$ . Diagram (a) has 0%D and thus c = 3. It has been sectioned twice (20% B and 1 bar),  $n_s = 2$ , but one of the sectionings was for a molar quantity (%B) and thus  $n_{\text{ms}} = 1$ . This gives  $p_{\text{max}} = 2 + 1 + 0 + 1 = 4$  and we can indeed see four phases at the horizontal line,  $L + \alpha + \beta + \gamma + \delta$ . The diagram has one molar axis (molar content of C) and thus  $n_{ma} = 1$ . We thus get  $d = c + 2 - p - n_s + n_{ma} + n_{ms} = 3 + 2 - 4 - 2 + 1 + 1 = 1$  and that is the horizontal line. Diagram (b) has one more component but also one more sectioned molar quantity. Thus,  $p_{\text{max}} = 2 + 1 + 0 + 2 = 5$  and indeed we see five phases at the horizontal line,  $L + \alpha + \beta + \gamma + \delta$ . We get the smallest d = 4 + 2 - 5 - 3 + 1 + 2 = 1 and this is for the horizontal line. Diagram (c) has 20%B and 80%D and c is thus 2 (only B and D). We get  $p_{\text{max}} = 1 + 1 + 0 + 1 = 3$  and we see three phases at a point,  $L + \beta + \delta$ . The smallest d = 2 + 2 - 2 - 2 + 2 - 3 - 2 + 0 + 1 = 0, in agreement with the fact that the three phases occur at a point.

## Exercise 10.6.2

Two sections of a system with a solid miscibility gap are here reproduced from Masing (1949). In the so-called vertical section a phase field  $S + \alpha + \beta$  appears twice. Check if the author has made an error or not.



## Hint

The three-phase field in an isothermal section is a triangle.

#### Solution

In the vertical section the three-phase triangle cannot appear twice at the same temperature. Consequently, the two  $S + \alpha + \beta$  regions must be separated in temperature. By sketching a series of triangles in the left-hand diagram, which is a temperature projection, we can see that the  $S + \alpha + \beta$  region, situated below the eutectic point e, must fall at lower temperatures than the other one.

## 10.8 Konovalov's rule

## Exercise 10.8.1

It is known that the three-phase equilibrium L/fcc + Mg<sub>2</sub>Si in the Al–Mg–Si phase diagram at 1 bar has a temperature maximum of 868 K at  $x_{Mg}^{L} = 0.110$  and  $x_{Si}^{L} = 0.045$ . Estimate the content of Mg in the Al-rich fcc phase at this equilibrium.

## Hint

The solubility of Si in the fcc phase is much lower than that of Mg.

## Solution

At the point of extremum the three phases must be on a straight line. Neglecting the Si content of fcc completely we find

$$\begin{vmatrix} 1 & x_{Mg}^{fcc} & x_{Si}^{fcc} \\ 1 & x_{Mg}^{L} & x_{Si}^{L} \\ 1 & x_{Mg}^{Mg_2Si} & x_{Si}^{Mg_2Si} \end{vmatrix} = \begin{vmatrix} 1 & x_{Mg}^{fcc} & 0 \\ 1 & x_{Mg}^{L} & x_{Si}^{L} \\ 1 & 2/3 & 1/3 \end{vmatrix} = x_{Mg}^{L} \cdot 1/3 - x_{Si}^{L} \cdot 2/3 - x_{Mg}^{fcc} \cdot 1/3 + x_{Mg}^{fcc} \cdot x_{Si}^{L} = 0 \\ x_{Mg}^{fcc} = (x_{Mg}^{L} - 2x_{Si}^{L})/(1 - 3x_{Si}^{L}) = (0.110 - 2 \cdot 0.045)/(1 - 3 \cdot 0.45) = 0.023 \text{ . In reality} \\ x_{Si}^{fcc} = 0.0037 \text{ , which is not quite negligible. The more exact result is 0.030.} \end{aligned}$$