Exercises on Ch.9 *Molar phase diagrams*

9.1 *Molar axes*

Exercise 9.1.1

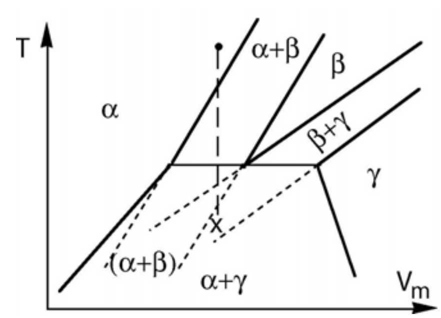
Experiments carried out with a pure element at constant *T* and *V* after rapid cooling from a higher *T* showed that an α phase was present initially. Then, a β phase nucleated and grew and consumed all α. Then, a γ phase nucleated and grew but some β remained. Finally the first phase, α, reappeared and consumed the remaining β and some of the γ. Sketch a simple *T,V* phase diagram with three phases and indicate a possible choice of *T* and *V* which could yield such a result.

Hint

Choose a simple three-phase equilibrium and draw the adjoining two-phases fields. Extrapolate the two-phase fields below the three-phase line.

Solution

The point representing the system must fall inside the α-phase field at the higher *T*.

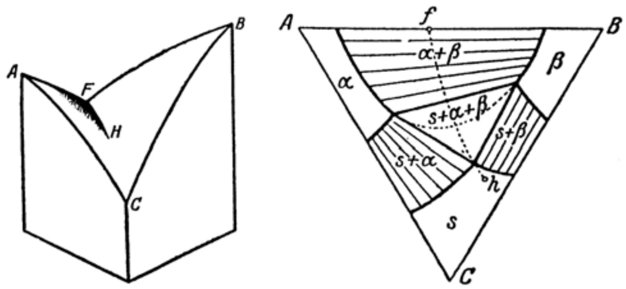


At the new *T* the point must fall on the β side of the α + β two-phase field but inside the β + γ two-phase field. Then it automatically falls inside the α + γ two-phase field if it is below the three-phase line (see diagram).

9.5 *Schreinemakers' rule*

Exercise 9.5.1

Find an error in the following isothermal section of a system with a solid miscibility gap (here denoted by $\alpha + \beta$). The letter 'S' signifies the liquid phase (German 'Schmelze'). (From Masing, 1949.)

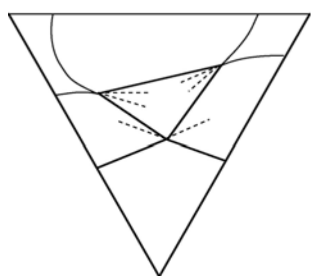


Hint

Remember Schreinemakers' rule.

Solution

The $(\alpha + \beta)/\beta$ boundary cuts into the three-phase triangle but the $(S + \beta)/\beta$ boundary cuts into a two-phase field. The diagram should look as the following sketch.



Exercise 9.5.2

It has been emphasized that Schreinemakers' rule cannot be proved for an H_m, V_m diagram. Show how the method used in this paragraph would fail for that type of diagram.

Hint

The method is based upon a Maxwell relation to be derived from the combined law. In the present case we need a form where H and V are the variables.

Solution

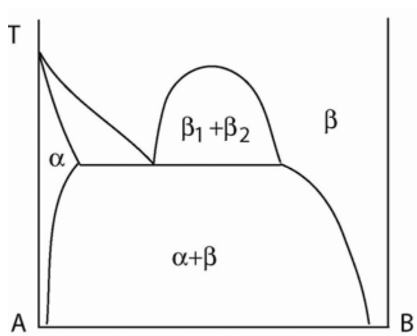
We could try to use the entropy scheme, $ds = (1/T)dU + (P/T)dV - (\mu_i/T)dN_i$ and we get. $(\partial[1/T]/\partial V)_{U,Ni} = (\partial[P/T]\partial U)_{V,Ni}$. *The* rule could thus be proved for a U_m, V_m diagram. However, if we introduce H through $U = H - PV$ we lose V as a variable, $dS = (1/T)dH - (V/T)dP - (\mu_i/T)dN_i$. We could try to change back to V by adding PV/T: $d(S + PV/T) = (1/T)dH + Pd(V/T) - (\mu_i/T)dN_i$.

Schreinemakers' rule could thus be proved for an H_m, V_m/T diagram but not for an H_m, V_m diagram. This fact is immediately evident from Tables 9.1–9.3 because H_m and V_m do not appear together in any set, i.e. in any one row.

9.6 *Topology of sectioned molar diagrams*

Exercise 9.6.1

Draw the zero-phase-fraction line for the β phase in the following *T,x* phase diagram for a binary system at 1 bar.

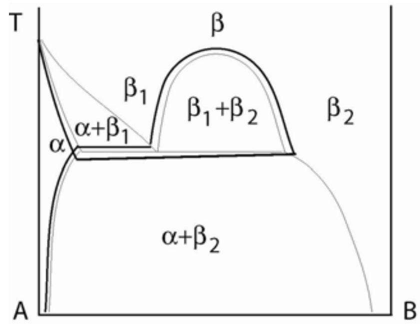


Hint

Due to the miscibility gap we can distinguish between β_1 and β_2. Draw the line for each one of them. Then join the two lines. Furthermore, imagine that the three-phase horizontal is a very thin triangle.

Solution

See thick line in diagram. It may be regarded as two lines meeting at the consolute point, one each for β_1 and β_2.


T
β
β_1
$\beta_1+\beta_2$
β_2
$\alpha+\beta_1$
α
$\alpha+\beta_2$
A
B