Exsercises on Ch.8 *Phase equilibria and potential phase diagrams*

8.1 Gibbs' phase rule. Exercise 1

8.2 Fundamental property diagram. Exercises 1 and 2

8.3 Topology of potential phase diagrams. Exercises 1, 2 and 3

8.4 Potential phase diagrams in binary and multinary systems. Exercise 1

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8.8 Direction of phase fields in potential phase diagrams. Exercises 1 and 2

8.1 Gibbs' phase rule

Exercise 8.1.1

Consider as a system the content of a vessel. In the vessel one has enclosed a certain amount of solid $CaCO_3$. On heating there is a dissociation into a new solid phase CaO and gaseous CO_2. Discuss whether this system behaves as a unary, binary or ternary system.

Hint

Examine how many independent components are required in order to form the compositions of all the phases.

Solution

It is most natural to select CaO and CO_2 as two independent components. $CaCO_3$ can form by combining them. Gibbs' phase rule thus yields for the three-phase equilibrium $v = c + 2 – p = 2 + 2 – 3 = 1$. We may conclude that at any given P all three phases may coexist only at a single T. Thus, on heating under atmospheric pressure $CaCO_3$ will suddenly dissociate completely into solid CaO and gaseous CO_2 when a certain T is reached. It behaves as a unary system.

8.2 *Fundamental property diagram*

Exercise 8.2.1

Show the derivation of an expression for the curvature $(\partial^2 T/\partial P^2)_{\mu A}$ and find its sign.

Hint

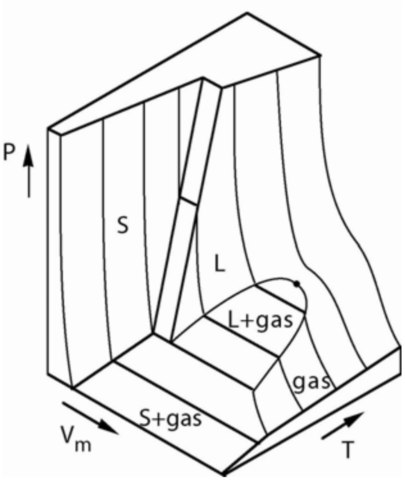
For a stable phase $(\partial P/\partial V) < 0$, whether T or S and N_A or μ_A are kept constant.

Solution

The Gibbs-Duhem relation yields $SdT - VdP + N_A d\mu_A = 0$; $(\partial T/\partial P)_{\mu A} = V/S$.
$(\partial^2 T/\partial P^2)_{\mu A} = [\partial(V/S)/\partial P]_{\mu A} = [\partial(V/S)/\partial P]_{\mu A,S} = (1/S)(\partial V/\partial P)_{\mu A,S} < 0$.

Exercise 8.2.2

The following diagram is a typical property diagram for a substance with three phases, solid(S), liquid(L) and gas. It has a critical point (indicated with a dot) where the difference between liquid and gas vanishes. The composite shape is not everywhere convex. Should it not be?



Solution

It is a property diagram but it is not a fundamental property diagram which should have only potential axes. V_m is an intensive quantity but not a potential.

8.3 *Topology of potential phase diagrams*

Exercise 8.3.1

Pure Fe at 1 bar transforms from γ to δ at 1667 K and from δ to L at 1811 K. It has been reported that in the *T,P* phase diagram the corresponding one-dimensional phase fields approach each other and intersect at $T = 1991$ K and $P = 5.2$ GPa.

The following table was presented, giving information on these two phase fields at the intersection. The intersection is, of course, a triple point and the third phase field is L + γ. Calculate its slope.

Reaction	ΔV(cm^3/mol)	dT/dP(K/GPa)
$\gamma \rightarrow \delta$	0.074	62
$\delta \rightarrow \mathrm{L}$	0.278	35

Hint

At a triple point $\Sigma\Delta V = 0$ and $\Sigma\Delta H = 0$. Insert ΔH from $\mathrm{d}P/\mathrm{d}T = \Delta H/T\Delta V$ in the second relation. Consider 1 mole.

Solution

$V^{\mathrm{L}} - V^{\gamma} = V^{\mathrm{L}} - V^{\delta} + V^{\delta} - V^{\gamma} = 0.278 + 0.074 = 0.352$; $H^{\mathrm{L}} - H^{\gamma} = H^{\mathrm{L}} - H^{\delta} + H^{\delta} - H^{\gamma}$ gives $T(V^{\mathrm{L}} - V^{\gamma})(\mathrm{d}P/\mathrm{d}T)^{\mathrm{L}+\gamma} = T(V^{\mathrm{L}} - V^{\delta})(\mathrm{d}P/\mathrm{d}T)^{\mathrm{L}+\delta} + T(V^{\delta} - V^{\gamma})(\mathrm{d}P/\mathrm{d}T)^{\delta+\gamma}$ and $(\mathrm{d}P/\mathrm{d}T)^{\mathrm{L}+\gamma} = 0.352/(0.278/35 + 0.074/62) = 38.5$.

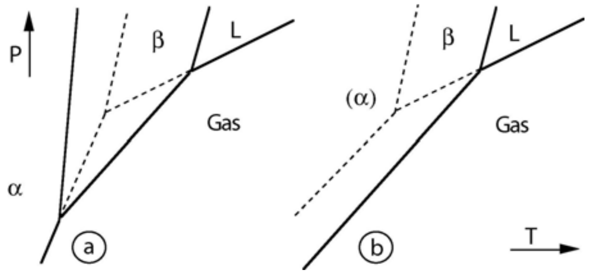
Exercise 8.3.2

When studying a pure liquid substance one finds that it solidifies to β on slow cooling but to α on rapid cooling. Sketch *T,P* phase diagrams for two cases: (a) where α is a stable low-temperature phase; and (b) where it is not stable at any temperature.

Hint

In order to compare the stabilities of α and β at low temperature it may be convenient to compare their vapour pressures. The gas phase should thus be included in the diagrams. The invariant melting points of β and α are found on the same L/gas phase boundary.

Solution



Exercise 8.3.3

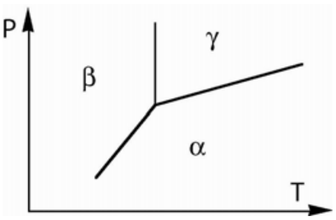
Consider a unary *T,P* phase diagram with a triple point α + β + λ. For the three lines meeting there, we have $(dP/dT)^{\alpha+\beta} = (H_m^\alpha - H_m^\beta)/[T(V_m^\alpha - V_m^\beta)]$, etc. Then $H_m^\alpha - H_m^\beta + H_m^\beta - H_m^\gamma + H_m^\gamma - H_m^\alpha = 0$ gives $(V_m^\alpha - V_m^\beta)(dP/dT)^{\alpha+\beta}$ $(V_m^\beta - V_m^\gamma)(dP/dT)^{\beta+\gamma} + (V_m^\gamma - V_m^\alpha)(dP/dT)^{\gamma+\alpha} = 0$. It is thus possible to calculate the slope of the third phase boundary from the other two if all the molar volumes are known. Suppose one only knows that $V_m^\beta - V_m^\gamma = 0$. From the above equation it would then seem that $(dP/dT)^{\alpha+\beta} = (dP/dT)^{\gamma+\beta}$ and α + β and λ + α should form a common line. Examine this conclusion by drawing a schematic phase diagram.

Hint

With the given condition we know the slope of the β + γ phase boundary.

Solution

To make α + β and γ + α coincide would be to make the angle of the α phase 180° in violation of the 180° rule. The mistake was to omit a term which has an indeterminate value 0·∞, since the β + γ line is vertical if $V_m^\beta - V_m^\gamma = 0$. The diagram shows a reasonable construction.



8.4 *Potential phase diagrams in binary and multinary systems*

Exercise 8.4.1

Suppose we want to calculate the equilibrium between three particular phases in a ternary system. For how many variables should we then specify values in order to get a unique answer.

Hint

With those variables we must specify a point in the *v*-dimensional space.

Solution

$v = c + 2 - p = 3 + 2 - 3 = 2$, e.g. *T* and *P*.

8.6 *Binary systems*

Exercise 8.6.1

Find an explanation why the line in Fig. 8.13(a) is less curved than the line in Fig. 8.13(b).

Hint

Consider the values at low temperatures of the quantities represented by the slopes.

Solution

The slopes of the two lines represent $\Delta_f^o S_{WC}$ and $\Delta_f^o H_{WC}$ respectively. The first one starts from zero at 0 K but the second one starts from a considerable value. Any change in slope will thus be much more visible in the first one.

8.7 *Ternary systems*

Exercise 8.7.1

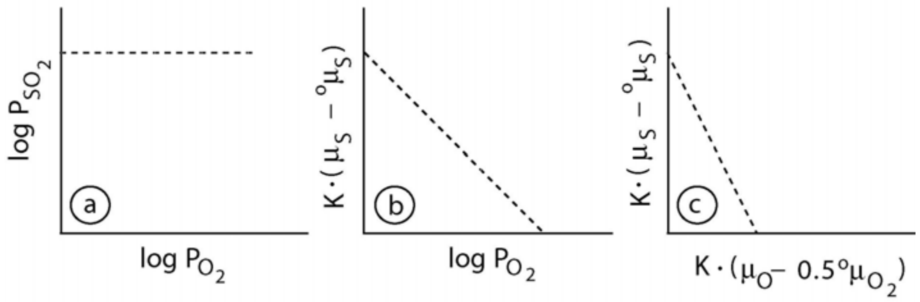
In principle, one could plot potential phase diagrams at constant *T* and *P* for various M–O–S systems with the axes for μ_O and μ_S. However, it is more practical to use axes for $\log P_{SO_2}$ and $\log P_{O_2}$ where the pressures refer to an imagined atmosphere, in equilibrium with the system. Start with such a diagram and let it have a line for a constant value of $\log P_{SO_2}$. Show how one can find the slope of the corresponding line in the μ_S, μ_O diagram.

Hint

It is usually assumed that the imagined atmosphere is ideal and thus $\mu_{O_2} = {}^o\mu_{O_2} + RT\ln P_{O_2}$ and $\mu_{SO_2} = {}^o\mu_{SO_2} + RT\ln P_{SO_2}$. Remember that $\mu_{SO_2} = \mu_S + 2\mu_O = \mu_S + \mu_{O_2}$.

Solution

$2\mu_O = \mu_{O_2} = {}^o\mu_{O_2} + RT\ln P_{O_2}$; $(2\mu_O - {}^o\mu_{O_2})/RT\ln 10 = \log P_{O_2}$;
$\mu_S = \mu_{SO_2} - \mu_{O_2} = {}^o\mu_{SO_2} - {}^o\mu_{O_2} + RT\ln P_{SO_2} - RT\ln P_{O_2}$;
$(\mu_S - {}^o\mu_S)/RT\ln 10 = \log P_{SO_2} - \log P_{O_2}$ where ${}^o\mu_S$ has been defined as ${}^o\mu_{SO_2} - {}^o\mu_{O_2}$.
Denote $1/RT\ln 10$ by *K* (see diagram).



8.8 *Direction of phase fields in potential phase diagrams*

Exercise 8.8.1

The direction of a one-dimensional phase field for a case with $p = c + 1$ has been derived. Try to apply the same method to the phase field for an invariant equilibrium.

Hint

According to Gibbs' phase rule we now have $p = c + 2$. We thus have one equation more and could now eliminate all μ_i and also another variable, say T.

Solution

Instead of multiplying the expression for the α phase with $\left| x_1^\beta x_2^\gamma ... x_{p-1}^\varepsilon \right|$, which is no longer a determinant because it has one row more than columns, we could now multiply with the determinant $\left| x_1^\beta x_2^\gamma ... x_{p-1}^\varepsilon H_m^\phi \right|$. Using similar determinants for the other phases and adding all the equations we obtain
$\left| H_m^\alpha x_1^\beta x_2^\gamma ... x_{p-1}^\varepsilon H_m^\phi \right| d(1/T) + \left| V_m^\alpha x_1^\beta x_2^\gamma ... x_{p-1}^\varepsilon H_m^\phi \right| dP/T - \left| x_i^\alpha x_1^\beta x_2^\gamma ... x_{p-1}^\varepsilon H_m^\phi \right| d(\mu_c/T) = 0$. In this case the determinants in front of $d(1/T)$ as well as $d(\mu_c/T)$ are zero and only the dP term remains. One thus obtains dP = 0 which is an example of the fact that no potential can vary in the phase field for an invariant equilibrium.

Exercise 8.8.2

The equation for dP/dT of a three-phase equilibrium in a binary system contains ordinary molar quantities and mole fractions. Show how the equation is modified if z fractions are introduced instead of x fractions.

Hint

Remember that $z_i = x_i/x_1$. We should thus divide all terms by $x_1^\alpha x_1^\beta x_1^\gamma$.

Solution

If we also remember that for any extensive quantity A one has $A_{\mathrm{m1}} = A_{\mathrm{m}}/x_1$, then we obtain

$$\frac{dP}{dT} = \frac{(z_2^{\gamma} - z_2^{\beta})H_{m1}^{\alpha} + (z_2^{\alpha} - z_2^{\gamma})H_{m1}^{\beta} + (z_2^{\beta} - z_2^{\alpha})H_{m1}^{\gamma}}{(z_2^{\gamma} - z_2^{\beta})V_{m1}^{\alpha} + (z_2^{\alpha} - z_2^{\gamma})V_{m1}^{\beta} + (z_2^{\beta} - z_2^{\alpha})V_{m1}^{\gamma}} \cdot \frac{1}{T}$$