Exercises on Ch.13 Transformations at constant composition

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13.1 The phase field rule at constant composition

Exercise 13.1.1

In Section 10.6 we derived Duhem's theorem which says that the state of a closed system is uniquely defined by choosing values for *T* and *P*. That seems to be in agreement with the present result for $p \le c$ which is d = 2, i.e. *T* and *P*. However, how can it be reconciled with the result for p > c yielding d = c + 2 - p < 2, i.e. only one of *T* and *P* or none of them?

Solution

For constant composition, where $n_s = n_m$, we have d = c + 2 - p and for a system with p = c + 1 we get d = c + 2 - c + 1 = 1. The phase field is thus one-dimensional and we can choose the value of *T* or *P* but not of both if one wants to stay within the phase field. However, Duhem's theorem does not concern a certain phase field. It only requires that one has chosen the composition. By varying *T* and *P* independently one may thus move from one phase field into another but for each combination of *T* and *P* Duhem's theorem says that there is always a particular state. Its number of phases, *p*, may be anything from 1 to c + 2. Higher values are forbidden by Gibbs'phase rule.

13.2 Reaction coefficients in sharp transformations for p = c + 1

Exercise 13.2.1

Prove that $\Sigma v^{j} = 0$ for the case p = c + 1, when the molar contents x_{i} are inserted as a_{i} in the expression for v^{j} .

Solution

$$\Sigma v^{j} = \left| x_{1}^{\beta} x_{2}^{\gamma} \dots x_{c}^{\varepsilon} \right| - \left| x_{1}^{\alpha} x_{2}^{\gamma} \dots x_{c}^{\varepsilon} \right| + \dots = \left| 1 x_{1}^{\beta} x_{2}^{\gamma} \dots x_{c}^{\varepsilon} \right| = 0 \text{ since } \sum_{i} x_{i}^{j} = 1. \text{ The result simply}$$

means that the number of moles of atoms does not change by the reaction.

13.7 Reaction coefficients at a constant chemical potential

Exercise 13.7.1

When an Fe–Mo alloy is carburized at 1273 K, it may transform by a eutectoid transformation $\alpha \rightarrow \gamma + M_6C$. The ideal composition of the initial Fe–Mo alloy for this transformation is defined by the α corner of the $\alpha + \gamma + M_6C$ triangle. Consider such an alloy but try to find a construction showing that it could transform to pure γ if the carbon activity is high enough. Use the enlarged detail of the phase diagram at 1273 K. Estimate that critical value of the carbon activity.



Hint

First try to find how one can evaluate the fractions of γ and M₆C if the transformation is caused by a very small driving force. Then investigate what happens to the fraction of M₆C if the driving force is higher.

Solution

The fraction of M₆C is proportional to $|u_{Fe}^{\alpha}u_{Mo}^{\gamma}| = |lu_{Mo}^{\gamma}| = u_{Mo}^{\gamma} - u_{Mo}^{\alpha}$. It will go to zero if u_{Mo}^{γ} approaches u_{Mo}^{α} . The construction in the diagram shows that this will happen at a value of approximately $a_C \approx 0.041 \cdot 0.0095 / 0.006 = 0.065$ if the carbon activity is proportional to the carbon content of γ and independent of the Mo content. The dashed line is an extrapolation of γ/α .



13.8 Compositional degeneracies for p = c

Exercise 13.8.1

In Exercise 13.11 we solved a computational problem caused by a degeneracy by adding an extra phase. Use Eq. 13.35 to discuss an alternative solution.

Solution

We get the same effect on the variance v in Gibbs' phase rule when decreasing c by n_{cd} as when increasing p by n_{cd} . In order to decrease c by $n_{cd} = 1$ we could choose SiO_2 and Al_2O_3 as the new set of components. Whether one should let $n_{cd} > 0$ affect the number of phases or components depends on the structure of the computer software to be used.

Exercise 13.8.2

Check if $Al_2O_3 + Si_3N_4 = SiO_2 + AIN$ can be a sharp transformation (neglecting the possible formation of intermediary phases). If so, evaluate the reaction coefficients.

Hint

Normally we can expect a sharp transformation when varying *T* under constant *P* and composition for a system with p = c+1. Here we have p = c and need a compositional degeneracy in order to obtain a sharp transformation. We should thus test the complete determinant.

Solution

	Al	0	Si	Ν	
Al_2O_3	2	3	0	0	
Si_3N_4	0	0	3	4	- 0
SiO_2	0	2	1	0	-0
AlN	1	0	0	1	

We thus have a degeneracy and can get a sharp transformation. In order to evaluate the reaction coefficients we should add an additional phase, e.g. pure Al. The composition matrix will then be

	Al	0	Si	Ν
Al_2O_3	2	3	0	0
Si_3N_4	0	0	3	4
SiO_2	0	2	1	0
AlN	1	0	0	1
c+1	1	0	0	0

and we obtain the reaction coefficients as

$$v^{Al_2O_3} = + \begin{vmatrix} 0 & 0 & 3 & 4 \\ 0 & 2 & 1 & 0 \\ 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \end{vmatrix} = - \begin{vmatrix} 0 & 3 & 4 \\ 2 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix} = + 6$$
$$v^{Si_3N_4} = - \begin{vmatrix} 2 & 3 & 0 & 0 \\ 0 & 2 & 1 & 0 \\ 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \end{vmatrix} = + \begin{vmatrix} 3 & 0 & 0 \\ 2 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix} = + 3$$
$$v^{SiO_2} = + \begin{vmatrix} 2 & 3 & 0 & 0 \\ 0 & 0 & 3 & 4 \\ 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \end{vmatrix} = - \begin{vmatrix} 3 & 0 & 0 \\ 0 & 3 & 4 \\ 0 & 0 & 1 \end{vmatrix} = -9$$
$$v^{AIN} = + \begin{vmatrix} 2 & 3 & 0 & 0 \\ 0 & 0 & 3 & 4 \\ 0 & 2 & 1 & 0 \\ 1 & 0 & 0 & 0 \end{vmatrix} = - \begin{vmatrix} 3 & 0 & 0 \\ 0 & 3 & 4 \\ 0 & 3 & 4 \\ 2 & 1 & 0 \end{vmatrix} = -12$$

We may give the arbitrary constant a value of 1/3 and obtain the coefficients + 2, + 1, - 3 and - 4 and the reaction formula will thus be $2Al_2O_3 + Si_3N_4 = 3SiO_2 + 4AIN$.

Exercise 13.8.3

Consider the reaction $NH_3(gas) + HCl(gas) \rightarrow NH_4Cl(solid)$. It is trivial to find the reaction coefficients but, nevertheless, show how they can be calculated with the method presented in this Section.

Hint

So far we have considered reactions between phases. Since we are now interested only in the amounts of each species taking part in the reaction, we may treat NH_3 and HCl as different phases although in reality there is only one gas phase. Then we have p = c = 3.

Solution

The reaction would correspond to a sharp transformation if there is one compositional degeneracy. This is confirmed because the composition determinant gives

$$\begin{array}{c|c}
N H Cl \\
NH_3 & | 1 & 3 & 0 \\
HCl & | 0 & 1 & 1 \\
NH_4Cl & | 1 & 4 & 1 \\
\end{array} = 0$$

In calculating the reaction coefficients let us omit the second column in order to simplify the calculations as much as possible. Then,

$$v^{NH_3} = \begin{vmatrix} 0 & 1 \\ 1 & 1 \end{vmatrix} = -1; \quad v^{HCl} = -\begin{vmatrix} 1 & 0 \\ 1 & 1 \end{vmatrix} = -1; \quad v^{NH_4Cl} = \begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix} = 1$$

Exercise 13.8.4

In Exercise 13.2 we considered the variance of the equilibrium $CaCO_3 \leftrightarrow CaO + CO_2$ in an N₂ atmosphere. Now, discuss the same transformation without N₂ present and consider the dimensionality of a phase field. That dimensionality has been given by Eqs. 8.23 and 10.5 and applied in Eq. 13.4. However, considering the effect of degeneracies, expressed by Eq. 13.35, we should now write $d = c + 2 - p - n_s + n_m - n_{cd}$ where n_{cd} is the number of degeneracies. For constant *P* and composition we get $d = c + 1 - p - n_{cd}$.

Hint

In the present case we have p = 3 and c = 3 and may normally expect $d = c + 2 - p - n_s + n_m$ where $n_s = c + 1$ and $n_m = c$ if we keep P and composition constant, i.e.,

d = c + 1 - p = 1 in the present case. However, we should check if there is a compositional degeneracy.

Solution

The composition determinant yields

	Ca	С	0	
$CaCO_3$	1	1	3	
CaO	1	0	1	=3-1-2=0
CO_2	0	1	2	

There is thus one compositional degeneracy and the dimensionality of h phase field will be $d = c + 1 - p - n_{cd} = 3 + 1 - 3 - 1 = 1$. We thus have a sharp phase transformation at any chosen value of *P*.

Exercise 13.8.5

Discuss the variance of the equilibrium between pure water, H_2O , and a gas composed of H_2O , H_2 and O_2 molecules in a system of constant composition.

Hint

We have p = 2 and c = 2 (H and O) and may thus have expected that d = c + 2 - p = 2 + 2 - 2 = 2. However, we should check if there is a compositional degeneracy.

Solution

The above expectation is justified if the composition is defined by starting with arbitrary amounts of H₂O, H₂ and O₂. On the other hand, if we start with pure water, H₂O, then the gas will have the same composition even if it dissociates into a mixture of H₂O, H₂ and O₂ molecules. In that case we have a composition determinant with two identical rows. There is thus a compositional degeneracy and we get $d = c + 2 - p - n_{cd} = 2 + 2 - 2 - 1 =$ 1. At constant *P* the equilibrium can be established at a single temperature, only, and by changing the temperature gradually through this value we will get a sharp phase transformation. (Here we have neglected the solubilities of H₂ and O₂ in water which are very low but, in principle, give the two phases slightly different compositions if we start from only water. Thus, d = 2.)

Exercise 13.8.6

Pure Zn is produced from ZnO by reduction with C under the formation of CO and CO_2 . Examine the variance of the equilibrium between these phases.

Hint

The temperature is high and Zn evaporates. There are three phases, gas, solid ZnO and solid C, and three components, Zn, O and C. We may thus expect that d = c + 2 - p = 3 + 2 - 3 = 2 but should check if there is a compositional degeneracy.

Solution

If we start from ZnO and C and no gas, then gas must form from ZnO and C and its composition must fall on the straight line between ZnO and C in the composition triangle. Thus, there is a compositional degeneracy. Mathematically, we may show this by considering x formula units of the reaction $2ZnO + C \rightarrow CO_2 + Zn$ and y formula units of $ZnO + C \rightarrow CO + Zn$. The gas will thus contain x + y moles of C, 2x + y moles of O and 2x + y moles of Zn. The composition determinant is obtained as

	С	Ο	Zn	
С	1	0	0	
ZnO	0	1	1	= 0
gas	x + y	2x + y	2x + y	

Thus, there is one compositional degeneracy and we get $d = c + 2 - p - n_{cd} = 3 + 2 - 3 - 1$ = 1. At constant *P* the three phases can be present at a single *T*, only. At any given *T*, the transformation will continue until a certain *P* value has been reached. On the other hand, if one starts to remove Zn from the gas by condensation, the degeneracy is relaxed and the variance will be d = 2.

Exercise 13.8.7

Suppose we have a computer program for the calculation of phase equilibria. When trying to calculate the equilibrium temperature at a pressure of 1 bar for four phases in a ternary system, we get the message, "cannot calculate because $d \neq 0$ ". What action could we take?

Hint

Evidently, the program is constructed to calculate sharp phase transformations. We have p = 4 and c = 3 and thus p = c + 1 and we thus expected a sharp transformation and ti be able to perform the calculation. However, the message indicates that there is some kind of compositional degeneracy. Let us accept this as a fact.

Solution

If there is one degeneracy, $n_{cd} = 1$, we have $d = c + 2 - p - n_{cd} = 3 + 2 - 4 - 1 = 0$ and at constant *P* we have d = -1. This may thus be a case of overlapping transformations. We should simply relax the condition P = 1 bar and can expect to calculate *T* as well as *P*. Then we could introduce a constant *P* equal to that value and calculate the reaction coefficients for any transformation involving three of the phases.

13.9 Effect of two compositional degeneracies for p = c - 1

Exercise 13.9.1

On heating solid NH₄Cl it will evaporate to gaseous NH₃ and HCl. Examine if this will happen at a particular T if P is kept at 1 bar or if it will happen over a range of T.

Hint

There can be only one gas phase and even though it has three components, N, H and Cl, it is evident that its composition cannot vary at all. It must have the same composition as the initial solid phase from which it is formed. We may thus conclude that the whole system behaves as if there is only one component, NH_4Cl . Justify this conclusion by using the method derived in this section.

Solution

We have the case p = 2 and c = 3 and thus p = c - 1 but both phases have the composition NH₄Cl and the composition matrix will thus be

 $\begin{array}{c|c} N H Cl\\ solid & 1 & 4 & 1\\ gas & 1 & 4 & 1 \end{array}$

By omitting one column at a time we find $\begin{vmatrix} 1 & 4 \\ 1 & 4 \end{vmatrix} = 0$ and $\begin{vmatrix} 1 & 1 \\ 1 & 1 \end{vmatrix} = 0$

and there are thus two compositional degeneracies. The transformation solid \rightarrow gas will thus be sharp at any chosen *P* value. It will then occur at a particular *T*.

Exercise 13.9.2

Discuss the variance of the equilibrium between the three solid phases NH_4Cl , K_2CO_3 , $(NH_4)_2CO_3$, and a liquid phase formed from them by melting.

Hint

We have p = 4 and c = 6 (N, H, Cl, K, C, and O) and may thus expect the value for p < c, i.e. d = 2. However, we should check on compositional degeneracies. In order to get the result d = 1 we need $1 = c + 2 - p - n_{cd} = 6 + 2 - 4 - n_{cd} = 4 - n_{cd}$; $n_{cd} = 3$, i.e. we need three compositional degeneracies. This is tested directly by studying the composition matrix. Notice that the liquid phase is not stoichiometric but due to the condition of electroneutrality we may represent its composition with $(NH_4)_x K_y Cl_z (CO_3)_{(x+y-z)/2}$.

Solution

The composition matrix is

Ν	Η	Cl	Κ	С	0
[1	4	1	0	0	0 -
0	0	0	2	1	3
2	8	0	0	1	3
$\lfloor x$	4 <i>x</i>	Z.	у	(x+y-z)/2	3(x+y-z)/2

It can be shown that all the determinants obtained by omitting any two columns are zero. Thus there are three compositional degeneracies and $d = c + 2 - p - n_{cd} = 6 + 2 - 4 - 3 = 1$. This is a sharp transformation at any chosen value of *P*.

Exercise 13.9.3

Consider the equilibrium between four phases in the A–B–C–D system. The molar contents of B, C and D are for each phase (0.20;0.20;0.40), (0.15;0.10;0.25), (0.14;0.08;0.22) and (0.13;0.06;0.19).

Hint

The phase field rule for constant composition yields d = c + 2 - p = 4 + 2 - 4 = 2. However, we should test for compositional degeneracies.

Solution

The composition matrix is

Α	В	С	D
0.20	0.20	0.20	0.40
0.50	0.15	0.10	0.25
0.56	0.14	0.08	0.22
0.62	0.13	0.06	0.19

The complete determinant is zero, but we do not need to take the trouble to show this if we suspect that there is another compositional degeneracy. Then the whole test can be done on minor determinants, obtained by omitting one row and then one column at a time. We get, for instance,

0.20	0.20	0.40		0.20	0.20	0.20	
0.15	0.10	0.25	= 0 and	0.50	0.15	0.10	= 0
0.14	0.08	0.22		0.62	0.13	0.06	

There are thus two compositional degeneracies and $d = c + 2 - p - n_{cd} = 4 + 2 - 4 - 2 = 0$ and at a constant *P* we have d = -1. We would thus have of overlapping sharp transformations if we vary *T*. Normally that could occur when p = c + 2. Here it can occur for p = c because there are two compositional degeneracies.

Exercise 13.9.4

Consider the equilibrium NaCl + ice + water + vapour.

Hint

There are four phases and four components and we could thus expect d = c + 2 - p = 4 + 2 - 4 = 2. However, we should check for compositional degeneracies. Water dissolves much NaCl, ice dissolves some but very little and there is practically no NaCl in the vapour. We may give the composition of the water as $x_{\text{Na}} = x_{\text{Cl}} = y$; $x_{\text{o}} = x_{\text{H}}/2 = (1 - 2y)/3$ and of ice in a similar way.

Solution

The composition determinant is zero because two columns are identical,

	Na	Cl	Н	О	
Na	1	1	0	0	
ice	z.	Z.	2(1-2z)/3	(1-2z)/3	- 0
water	y	у	2(1-2y)/3	(1-2y)/3	-0
vapour	0	0	2	1	

This proves that there is at least one compositional degeneracy. We can test if there is another one by omitting one row and one column. We get, for instance,

$$\begin{vmatrix} 1 & 0 & 0 \\ z & 2(1-2z)/3 & 2(1-2z)/3 \\ 0 & 2 & 1 \end{vmatrix} = \begin{vmatrix} 2(1-2z)/3 & (1-2z)/3 \\ 2 & 1 \end{vmatrix} = 0$$

Thus there are two compositional degeneracies and the phase field rule yields $d = c + 2 - p - n_{cd} = 4 + 2 - 4 - 2 = 0$ and for constant *P* we get d = -1. This is a case of overlapping transformations.