Exercises on Ch. 4 Practical handling of multicomponent systems

4.1 Partial quantities. Exercises 1 and 2

4.3 Alternative variables for composition. Exercises 1 and 2

4.6 Different sets of components. Exercise 1

4.7 Constitution and constituents. Exercise 1

4.8 Chemical potentials in a phase with sublattices. Exercises 1 and 2

4.1 Partial quantities

Exercise 4.1.1

Rearrange the derivatives in the Eq. 4.6 in such a way that it only contains terms of physical significance.

Hint

First multiply the first derivative by Σx_i which is equal to 1.

Solution

 $A_{\rm i} = A_{\rm m} + \sum x_{\rm i} [\partial A_{\rm m} / \partial x_{\rm i} - \partial A_{\rm m} / \partial x_{\rm i}]$

Exercise 4.1.2

Suppose one has the following expression for a ternary solution phase: $G_m = \sum x_i ({}^{\circ}G_i + RT \ln x_i) + x_A x_B x_C L_{ABC}$, where *L* is a ternary interaction parameter.

(a) Evaluate G_A directly from Eq. 4.5.

(b) Evaluate G_A after first eliminating x_A using $x_A = 1 - x_B - x_C$.

Solution

(a)
$$G_{A} = {}^{\circ}G_{A}(x_{A} + 1 - x_{A}) + {}^{\circ}G_{B}(x_{B} - x_{B}) + {}^{\circ}G_{C}(x_{C} - x_{C}) + RT\{x_{A}\ln x_{A} + \ln x_{A} + (x_{A}/x_{A}) - x_{A}[\ln x_{A} + (x_{A}/x_{A})] + x_{B}\ln x_{B} - x_{B}[\ln x_{B} + (x_{B}/x_{B})] + x_{C}\ln x_{C} - x_{C}[\ln x_{C} + (x_{C}/x_{C})]\} + L_{ABC}(x_{A}x_{B}x_{C} + x_{B}x_{C} - x_{A}x_{B}x_{C} - x_{B}x_{A}x_{C} - x_{C}x_{A}x_{B}) = {}^{\circ}G_{A} + RT\ln x_{A} + x_{B}x_{C}(1 - 2x_{A})Lx_{ABC};$$

(b) $G_{m} = (1 - x_{B} - x_{C}){}^{\circ}G_{A} + x_{B}{}^{\circ}G_{B} + x_{C}{}^{\circ}G_{C} + RT[(1 - x_{B} - x_{C})\ln(1 - x_{B} - x_{C}) + x_{B}\ln x_{B} + x_{C}\ln x_{C}] + (1 - x_{B} - x_{C})x_{B}x_{C}\cdot L_{ABC}$
Now we get $G_{A} = {}^{\circ}G_{A}(1 - x_{B} - x_{C} + x_{B} + x_{C}) + {}^{\circ}G_{B}(x_{B} - x_{B}) + {}^{\circ}G_{C}(x_{C} - x_{C}) + RT\{1 - x_{B} - x_{C})\ln(1 - x_{B} - x_{C}) - (1 - x_{B} - x_{C})/(1 - x_{B} - x_{C})] - x_{C}[-\ln(1 - x_{B} - x_{C}) - (1 - x_{B} - x_{C})/(1 - x_{B} - x_{C})] - x_{C}[-\ln(1 - x_{B} - x_{C}) - (1 - x_{B} - x_{C})/(1 - x_{B} - x_{C})] + x_{B}\ln x_{B} - x_{B}[\ln x_{B} + (x_{B}/x_{B})] + x_{C}\ln x_{C} - x_{C}[\ln x_{C} + x_{C}/x_{C}]] + L_{ABC}\{(1 - x_{B} - x_{C})x_{B}x_{C} - x_{B}[-x_{B}x_{C} + (1 - x_{B} - x_{C})x_{C}] - x_{C}[-x_{B}x_{C} + (1 - x_{B} - x_{C})x_{B}]\} = {}^{\circ}G_{A} + RT\ln(1 - x_{B} - x_{C}) + L_{ABC}[x_{B}^{2}x_{C} + x_{B}x_{C}^{2} - x_{B}x_{C}(1 - x_{B} - x_{C})] = {}^{\circ}G_{A} + RT\ln(1 - x_{B} - x_{C}) + L_{ABC}[x_{B}^{2}x_{C} + x_{B}x_{C}^{2} - x_{B}x_{C}(1 - x_{B} - x_{C})] = {}^{\circ}G_{A} + RT\ln(1 - x_{B} - x_{C}) + x_{B}x_{C}(1 - x_{B} - x_{C})]$

4.3 Alternative variables for composition

Exercise 4.3.1

Show the details of the derivation of the expression for μ_2 from G_m as a function of the *u* variables in a ternary system where component 3 has a special character.

Hint

Since components 1 and 2 have similar character, it may be convenient to define $u_i = N_i/(N_1 + N_2)$. Derive the partial derivatives of u_j with respect to N_2 . Derive μ_2 from $(\partial G/\partial N_2)_{N_1,N_3}$, where G is given by $G(N_1 + N_2)G_{m12}$.

Solution

$$\begin{split} u_{j} &= N_{j}/(N_{1} + N_{2}); \ \partial u_{1}/\partial N_{2} = -N_{1}/(N_{1} + N_{2})^{2} = -u_{1}/(N_{1} + N_{2}); \ \partial u_{2}/\partial N_{2} = (N_{1} + N_{2} - N_{2})/(N_{1} + N_{2})^{2} \\ &= (1 - u_{2})/(N_{1} + N_{2}); \ \partial u_{3}/\partial N_{2} = -N_{3}/(N_{1} + N_{2})^{2} = -u_{3}/(N_{1} + N_{2}). \text{ Now we can calculate the potentials from } G = (N_{1} + N_{2})G_{m12}(u_{1}, u_{2}, u_{3}): \\ \mu_{2} = G_{2} = (\partial G/\partial N_{2})_{N1,N3} = 1 \cdot G_{m12} + (N_{1} + N_{2})[\partial G_{m12}/\partial u_{1})(-u_{1})/(N_{1} + N_{2}) + (\partial G_{m12}/\partial u_{2})(1 - u_{2})/(N_{1} + N_{2}) + (\partial G_{m12}/\partial u_{3})(-u_{3})/(N_{1} + N_{2})] \\ &= G_{m12} + \partial G_{m12}/\partial u_{2} - \Sigma u_{i}\partial G_{m12}/\partial u_{i}. \end{split}$$

Exercise 4.3.2

One can easily derive $(\partial G_{\rm C}/\partial z_{\rm B})_{\rm zC} = (\partial G_{\rm B}/\partial z_{\rm C})_{\rm zB}$ from $\partial G_{\rm C}/\partial N_{\rm B} = \partial^2 G/\partial N_{\rm B} \partial N_{\rm C} = \partial G_{\rm B}/\partial N_{\rm C}$. Derive the same relation by using the Gibbs–Duhem relation.

Hint

Formulate the Gibbs–Duhem relation using the z variables by dividing with N_A . First consider a variation dz_B , then take the derivative with respect to z_C . Next, do it the other way around and compare the two results.

Solution

For any variation, $dG_A + z_B dG_B + z_C dG_C = 0$. If z_B is varied: $\partial G_A / \partial z_B + z_B \partial G_B / \partial z_B + z_C \partial G_C / \partial z_B = 0$; Take the derivative with respect to z_C : $\partial^2 G_A / \partial z_B \partial z_C + z_B \partial^2 G_B / \partial z_B \partial z_C + \partial G_C / \partial z_B + z_C \partial^2 G_C / \partial z_B \partial z_C = 0$ (a). If z_C is varied: $\partial G_A / \partial z_C + z_B \partial G_B / \partial z_C + z_C \partial G_C / \partial z_C = 0$; take the derivative with respect to z_B : $\partial^2 G_A / \partial z_C \partial z_B + \partial G_B / \partial z_C + z_B \partial^2 G_C / \partial z_C = 0$; take the derivative with respect to z_B : $\partial^2 G_A / \partial z_C \partial z_B + \partial G_B / \partial z_C + z_B \partial^2 G_C / \partial z_C \partial z_B = 0$ (b). Then, (a) – (b): $\partial G_C / \partial z_B - \partial G_B / \partial z_C = 0$.

4.6 Different sets of components

Exercise 4.6.1

It is difficult to measure the oxygen potential when it has low values. Suppose one has instead measured the chemical potentials of Ce_2O_3 and CeO_2 in a complicated multicomponent system. Show how one can calculate the oxygen potential.

Solution

 $2\mu_{CeO2} = 2\mu_{Ce} + 4\mu_{O}$ and $\mu_{Ce2O3} = 2\mu_{Ce} + 3\mu_{O}$ give $2\mu_{CeO2} - \mu_{Ce2O3} = \mu_{O}$

4.7 Constitution and constituents

Exercise 4.7.1

For a so-called 'reciprocal' system with two elements on each sublattice, $(A,B)_a(C,D)_c$, one often uses a solution model yielding the expression $G_m = y_A y_C \mu_{AaCc} + y_B y_C \mu_{BaCc} + y_A y_D \mu_{AaDc} + y_B y_D \mu_{BaDc}$. Examine if this expression is correct.

Hint

Use $\mu_{BaCc} = a\mu_B + c\mu_C$, etc., and $x_A = ay_A/(a + c)$, etc.

Solution

 $y_A y_C \mu_{AaCc} + y_B y_C \mu_{BaCc} + y_A y_D \mu_{AaDc} + y_B y_D \mu_{BaDc} = a \mu_A (y_A y_C + y_A y_D) + a \mu_B (y_B y_C + y_B y_D) + c \mu_C (y_A y_C + y_B y_C) + c \mu_D (y_A y_D + y_B y_D) = a \mu_A y_A + a \mu_B y_B + c \mu_C y_C + c \mu_D y_D = (a + c)(x_A \mu_A + x_A \mu_B + x_C \mu_C + x_D \mu_D) = G_m$ for one formula unit.

4.8 Chemical potentials in a phase with sublattices

Exercise 4.8.1

Consider a system with two sublattices and $a^t = a^u = 0.5$. The elements A and B can dissolve in both sublattices and one can thus evaluate the quantities $\mu_{A0.5B0.5}$ and $\mu_{B0.5A0.5}$. Under what conditions are they equal.

Hint

At internal equilibrium $\mu_A^t - \mu_B^t = \mu_A^u - \mu_B^u$.

Solution

 $2\mu_{A_{0,5}B_{0,5}} = \mu_A^t + \mu_B^u = \mu_A^u + \mu_B^t = 2\mu_{B_{0,5}A_{0,5}}$. They are equal at internal equilibrium and under such conditions one can evaluate the chemical potential of a compound between one atom of each of A and B in two ways, either as $2\mu_{A_{0,5}B_{0,5}}$ or as $2\mu_{B_{0,5}A_{0,5}}$.

Exercise 4.8.2

It is natural to start the expression for G_m of a solution phase with a term characteristic of a so-called 'mechanical mixture' $\sum x_i \circ G_i$ where $\circ G_i$ is the molar Gibbs energy of pure *i* and the mole fraction of *i* can be expressed with site fractions $x_i = \sum a^s y_i^s$ where $\sum a^s = 1$.

Consider a binary system with two sublattices and examine how the corresponding term in μ_A^t would look.

Hint

Apply $G_m = \sum x_i^o G_i$ to $\mu_i^t = G_m + (1/a^t) \cdot [(\partial G_m / \partial y_i^t) - \sum y_i^t (\partial G_m / \partial y_i^t)].$

Solution

 $\mu_A^t = (a^t y_A^t + a^u y_A^u)^o G_A + (a^t y_B^t + a^u y_B^u)^o G_B + (1/a^t) \cdot (a^t \cdot {}^o G_A - y_A^t a^t \cdot {}^o G_A - y_B^t a^t \cdot {}^o G_B)$ = ${}^o G_A + [a^u y_A^u - (1 - a^t) y_A^t]^o G_A + {}^o G_B + [a^u y_B^u - (1 - a^t) y_B^t]^o G_B$ = ${}^o G_A + a^u (y_A^u - y_A^t) ({}^o G_A - {}^o G_B)$. It may seem strange that the result is not simply ${}^o G_A$ which one would normally expect for the first term in an expression for μ_A , the molar Gibbs energy of pure A. However, the difference is not completely surprising because in a phase with a stoichiometric constraint it should not be possible to define the chemical potential of an element in a unique way and the formula given is just one alternative. However, it is necessary that such a difference has no effect in combinations satisfying the stoichiometric constraint, i.e. in $\mu_A - \mu_B$. That requirement is satisfied here.