Exercises on Ch.21 *Solution phases with sublattices*

21.3 *Reciprocal solution phases*

Exercise 21.3.1

Suppose ${}^E G_m$ for a reciprocal solution $(A,B)_r(C,D)_s$ contains a term ${}^1L^C_{AB} \cdot y_A y_B y_C (y_A - y_B)$. What is the corresponding term in ${}^E G_{A_r C_s}$?

Hint

Use either the expression derived for $\Delta_1 {}^E G_{M_b i_c}$ where M must be identified with C and *i* with A or start from the basic equation for ${}^E G_m$.

Solution

${}^E G_{A_r C_s} = \Delta_1 {}^E G_{M_b i_c} = {}^1L_{AB:C} \cdot y_B \{(y_A - y_B)[y_C \cdot 2 \cdot (1 - y_A) + y_A - y_C y_A] + y_C y_B\}$
$= y_B(2y_A y_C + y_A^2 - 3y_A^2 y_C - y_B y_C + 3y_A y_B y_C)$. The basic equation gives
${}^E G_{A_r C_s} = {}^1L_{AB:C} \cdot (y_A^2 y_B y_C - y_A y_B^2 y_C + 2y_A y_B y_C - y_B^2 y_C + y_A^2 y_B - y_A y_B^2$
$- 2y_A^2 y_B y_C - y_A^2 y_B y_C - y_A^2 y_B y_C + y_A y_B^2 y_C + 2y_A y_B^2 y_C + y_A y_B^2 y_C)$. This can be simplified to the same expression.

21.6 *Ionic solid solutions*

Exercise 21.6.1

In order for the solution phase $(Si^{+4},Al^{+3})_3(N^{-3},O^{-2})_4$ to extend to the AlN and Al_2O_3 corners of the $(Si_3N_4$–SiO_2–Al_2O_3–AlN diagram (which does not really happen) it would be necessary to introduce vacancies. Even though such vacancies are not very likely to form, show how many vacancies would be needed in the two cases.

Hint

Introduce vacancies into the formula to an amount required by electroneutrality if there are no O^{-2} in the first case and no N^{-3} in the second.

Solution

$(Al^{+3})_3(N^{-3}_{1-x},Va_x)_4$ gives 3·3 = 4·3(1 – *x*); *x* = 1/4.
$(Al^{+3}_{1-x},Va_x)_3(O^{-2})_4$ gives 3·3(1 – *x*) = 4·2; *x* = 1/9.