12.36 (a) For this portion of the problem we are to determine the type of vacancy defect that is produced on the Al_2O_3-rich side of the spinel phase field (Figure 12.25) and the percentage of these vacancies at the maximum nonstoichiometry (82 mol% Al_2O_3). On the alumina-rich side of this phase field, there is an excess of Al^{3+} ions, which means that some of the Al^{3+} ions substitute for Mg^{2+} ions. In order to maintain charge neutrality, Mg^{2+} vacancies are formed, and for every Mg^{2+} vacancy formed, two Al^{3+} ions substitute for three Mg^{2+} ions.

Now, we will calculate the percentage of Mg^{2+} vacancies that exist at 82 mol% Al_2O_3. Let us arbitrarily choose as our basis 50 MgO-Al_2O_3 units of the stoichiometric material, which consists of 50 Mg^{2+} ions and 100 Al^{3+} ions. Furthermore, let us designate the number of Mg^{2+} vacancies as *x*, which means that 2*x* Al^{3+} ions have been added and 3*x* Mg^{2+} ions have been removed (two of which are filled with Al^{3+} ions). Using our 50 MgO-Al_2O_3 unit basis, the number of moles of Al_2O_3 in the nonstoichiometric material is (100 + 2*x*)/2; similarly the number of moles of MgO is (50 – 3*x*). Thus, the expression for the mol% of Al_2O_3 is just

$$\text{mol\% } Al_2O_3 = \left[\frac{\dfrac{100 + 2x}{2}}{\dfrac{100 + 2x}{2} + (50 - 3x)}\right] \times 100$$

If we solve for *x* when the mol% of Al_2O_3 = 82, then *x* = 12.1. Thus, adding 2*x* or (2)(12.1) = 24.2 Al^{3+} ions to the original material consisting of 100 Al^{3+} and 50 Mg^{2+} ions will produce 12.1 Mg^{2+} vacancies. Therefore, the percentage of vacancies is just

$$\text{\% vacancies} = \frac{12.1}{100 + 50} \times 100 = 8.1\%$$

(b) Now, we are asked to make the same determinations for the MgO-rich side of the spinel phase field, for 39 mol% Al_2O_3. In this case, Mg^{2+} ions are substituting for Al^{3+} ions. Since the Mg^{2+} ion has a lower charge than the Al^{3+} ion, in order to maintain charge neutrality, negative charges must be eliminated, which may be accomplished by introducing O^{2-} vacancies. For every 2 Mg^{2+} ions that substitute for 2 Al^{3+} ions, one O^{2-} vacancy is formed.

Now, we will calculate the percentage of O^{2-} vacancies that exist at 39 mol% Al_2O_3. Let us arbitrarily choose as our basis 50 MgO-Al_2O_3 units of the stoichiometric material which consists of 50 Mg^{2+} ions 100 Al^{3+} ions. Furthermore, let us designate the number of O^{2-} vacancies as *y*, which means that 2*y* Mg^{2+} ions have been added and 2*y* Al^{3+} ions have been removed. Using our 50 MgO-Al_2O_3 unit basis, the number of moles of Al_2O_3 in the nonstoichiometric material is (100 – 2*y*)/2; similarly the number of moles of MgO is (50 + 2*y*). Thus, the expression for the mol% of Al_2O_3 is just