Conduction in Ionic Materials

18.D6 This problem asks, for the nonstoichiometric $Fe_{(1-x)}O$, given the electrical conductivity [1200 $(\Omega\text{-m})^{-1}$] and hole mobility (1.0 x 10^{-5} m^2/V-s) that we determine the value of x. It is first necessary to compute the number of holes per unit volume (p) using Equation 18.17. Thus

$$p = \frac{\sigma}{|e|\mu_h}$$

$$= \frac{1200\ (\Omega - \text{m})^{-1}}{(1.602 \times 10^{-19}\ \text{C})(1.0 \times 10^{-5}\ \text{m}^2/\text{V-s})} = 7.49 \times 10^{26}\ \text{holes/m}^3$$

Inasmuch as it is assumed that the acceptor states are saturated, the number of vacancies is also 7.49 x 10^{26} m^{-3}. Next, it is possible to compute the number of vacancies per unit cell by taking the product of the number of vacancies per cubic meter times the volume of a unit cell. This volume is just the unit cell edge length (0.437 nm) cubed:

$$\frac{\#\ \text{vacancies}}{\text{unit cell}} = (7.49 \times 10^{26}\ \text{m}^{-3})(0.437\ \text{x}\ 10^{-9}\,\text{m})^3 = 0.0625$$

A unit cell for the sodium chloride structure contains the equivalence of four cations and four anions. Thus, if we take as a basis for this problem 10 unit cells, there will be 0.625 vacancies, 40 O^{2-} ions, and 39.375 iron ions (since 0.625 of the iron sites is vacant). (It should also be noted that since two Fe^{3+} ions are created for each vacancy, that of the 39.375 iron ions, 38.125 of them are Fe^{2+} and 1.25 of them are Fe^{3+}). In order to find the value of $(1 - x)$ in the chemical formula, we just take the ratio of the number of total Fe ions (39.375) and the number of total Fe ion sites (40). Thus

$$(1 - x) = \frac{39.375}{40} = 0.984$$

Or the formula for this nonstoichiometric material is $Fe_{0.984}O$.