

Equilibrium Concentration of the Vacancy-Impurity Atom Complex

Advanced

- ▶ We consider a complex of one vacancy and one foreign atom (a Johnson complex) in thermodynamic equilibrium.
 - We start with a *number* n_F of foreign atoms that is given by external circumstances. Some, but not necessarily all of these atoms will form a complex with a vacancy. The number of these complexes we call n_C .
- ▶ We can calculate the equilibrium number of Johnson complexes exactly analogous to the equilibrium number of vacancies by simply defining a formation enthalpy G_C and doing the counting of arrangements and minimization of the free enthalpy procedure.
 - This obviously will give us

$$n_C = (N_C - n_C) \cdot \exp - \frac{G_C}{kT}$$

- With N_C = number of sites in the crystal where a vacancy could sit in order to form a Johnson complex.
- We take $N_C - n_C$ in full generality because the places already occupied ($= n_C$) are no longer available, and we do *not* assume at this point that $n_C \ll N_C$ applies as in the case of vacancies.
- ▶ N_C , of course, is *not* the number of atoms of the crystal as in the case of vacancies, but *roughly* the number of foreign atoms - after all, only where we have a foreign atom, can we form a complex.
 - If we don't look at the situation *roughly* but in detail, we need to consider that there are as many possibilities to form a foreign atom - vacancy pair as there are nearest neighbors. We thus find

$$N_C = n_F \cdot z - n_C \cdot z$$

- z is the coordination number of the lattice considered, i.e. the number of nearest neighbors. Again we do not neglect the places already taken, i.e. we subtract $n_C \cdot z$ from the total number of places.
- ▶ If we look at *concentrations*, we refer the numbers to the number of lattice atoms N which gives us for the concentration c_C of impurity atom - vacancy complexes

$$c_C = \frac{n_C}{N}$$

$$\frac{c_C}{c_F - c_C} = z \cdot \exp - \frac{G_C}{kT}$$

- ▶ We are essentially done. We have the concentration of Johnson complexes as a function of the concentration of the foreign atoms, the lattice type (defining z) and their formation enthalpy.
 - However, we would feel happier, if we could base the equation on material parameters which we already know - in particular on the equilibrium concentration of vacancies in the given material.
 - This needs a closer view on the formation enthalpy of the complex.
- ▶ As in the case of double vacancies, we may simply assume that there is a binding enthalpy between a vacancy and a foreign atom (otherwise there would be no driving force to form a complex in the first place).
 - We thus can write for G_C

$$G_C = G^V_F - (H_C - T \cdot \Delta S_C)$$

- G^V_F is the free enthalpy of vacancy formation, H_C is the **binding enthalpy** of a Johnson complex, and $T \cdot \Delta S_C$ is the "**association entropy**" of the complex, accounting for the entropy change of the crystal upon the formation of a complex.
- ▶ Inserting this in the equation above gives for the concentration of Johnson complexes in terms of vacancy parameters and binding energies:

$$\frac{c_C}{c_F - c_C} = z \cdot \exp - \frac{G^V_F}{kT} \cdot \exp \frac{H_C}{kT} \cdot \exp \frac{\Delta S_C}{k}$$

$$c_C = (c_F - c_C) \cdot c_V \cdot z \cdot \exp \frac{H_C}{kT} \cdot \exp \frac{\Delta S_C}{k}$$

$$= c'_F \cdot c_V \cdot z \cdot \exp \frac{H_C}{kT} \cdot \exp \frac{\Delta S_C}{k}$$

● We used the familiar equation $c_V = \exp - (G^V_F / kT)$ to get this result.

▶ We abbreviated the difference of the total concentration of foreign atoms and the concentration of Johnson complexes by c'_F ; i.e. $c'_F = (c_F - c_C)$ because this allows a simple interpretation of the equation.

● The point now is to recognize that c'_F is nothing but the concentration of foreign atoms which are still available for a reaction with a vacancy, and that the last equation therefore is nothing but the mass action law written out for the reaction



● With **F** = (available) foreign atom; **V** = vacancy, and **C** = Johnson complex.

▶ Looking closely (= thinking hard) you will notice that we now have a certain inconsistency in our book keeping:

● We always took into account that Johnson complexes already formed can *not* be neglected in counting possibilities, and we always corrected for that by using $c_F - c_C$ and so on - but we did *not* correct for the now more limited possibilities for positioning a single vacancy. We must ask ourselves if the presence of foreign atoms will change the equilibrium concentration of free vacancies.

● In other words, while we took the number of available positions for a vacancy in a complex to be $n_F \cdot z - n_C \cdot z$, we implicitly took the number of available positions for a free vacancy in the crystal to be simply N = number of lattice atoms.

● Being more precise, we have to subtract $n_F \cdot z$ from N because $n_F \cdot z$ positions are, after all, *not* available for *free* vacancies. We thus have to replace N by $N' = N - n_F \cdot z$ when we consider the number of free vacancies.

● The concentration of the free vacancies thus becomes $c_V = (1 - z \cdot c_F) \cdot \exp - (G^V_F / kT)$, or $\exp - (G^V_F / kT) = c_V / (1 - z \cdot c_F)$

● Using this in the [equation](#) for the concentration yields

$$c_C = \frac{(c_F - c_C) \cdot c_V \cdot z}{(1 - z \cdot c_F)} \cdot \exp \frac{H_C}{kT} \cdot \exp \frac{\Delta S_C}{k}$$

$$\approx \frac{c_F \cdot c_V \cdot z}{(1 - z \cdot c_F)} \cdot \exp \frac{H_C}{kT} \cdot \exp \frac{\Delta S_C}{k}$$

● The last approximation is, of course, attainable if $c_C \ll c_F$, and that is the equation given in the [backbone text](#).