

Solution to Exercise 2.2-1 "Properties for Johnson Complexes"

Illustration

- Discuss the equation for the concentration of vacancy - impurity atom complexes (Johnson complexes).
 - Consider an impurity atom concentration of **1 %** and **1 ppm**, a vacancy formation enthalpy of **1 eV** (neglect the formation entropy) and several binding energies (including extremes).
 - Discuss the concentration of Johnson complexes as a function of temperature and in relation to the concentration of the impurity atoms and the equilibrium concentration of vacancies.
- Use approximations, order-of- magnitude considerations and reasonable numbers whenever possible.
- The basic equation for the concentration of Johnson complexes is

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

- We first need to chose a coordination number, we take **z = 12** for **fcc** and **hcp** crystals. All other coordination numbers are smaller; we thus have the maximal effect of **z**.
- The given concentration of impurity atoms of **1 %** and **1 ppm** correspond to $c_F = 10^{-2}$ and $c_F = 10^{-6}$, respectively.
- First we note that the factor $1 - z \cdot c_F$ equals **0,88** or **0,999..**; i.e. we can forget it - at least for the low concentration.
- Next we calculate the ratios c_C / c_F and c_C / c_V in order to get a feeling how the Johnson complex concentration relates to the (fixed) concentration of impurity atoms and the (temperature dependent) equilibrium concentration of vacancies. We have

$$\frac{c_C}{c_F} = (12 \dots 13,6) \cdot c_V \cdot \exp \frac{\Delta S_C}{k} \cdot \exp \frac{H_C}{kT} = (12 \dots 13,6) \cdot \exp \frac{(H_F^V - G_B)}{kT}$$

$$\frac{c_C}{c_V} = (12 \dots 13,6) \cdot c_F \cdot \exp \frac{\Delta S_C}{k} \cdot \exp \frac{H_C}{kT} = (12 \dots 13,6) \cdot c_F \cdot \exp \frac{G_B}{kT}$$

- The numbers in the bracket span the range of the given c_F concentrations.
- Our first result thus is simple: The ratios asked for are directly proportional to the concentration of vacancies or foreign atoms, respectively. The proportionality factor is about **2** times the Boltzmann factor of the free enthalpy of complex formation. So let's look at the role of the binding energy.
- Let's look at binding energies (more precisely: binding free enthalpies G_B) of $-\infty$ eV (i.e. extreme repulsion between a vacancy and the foreign atom), **0 eV** (no interaction), $\frac{1}{2} H_F^V$ (strong interaction), and H_F^V (extreme interaction). This gives us

G_B	$-\infty$	0	$\frac{1}{2} H_F^V$	H_F^V
$\frac{c_C}{c_F}$	0	$\approx 12 c_V$	$\approx 12 \cdot (c_V)^{1/2}$	≈ 12
$\frac{c_C}{c_V}$	0	$\approx 12 c_F$	$\approx 12 \cdot c_F \cdot (c_V)^{-1/2}$	$\approx \frac{12 \cdot c_F}{c_V}$

What does it mean?

- First**, for extreme repulsion, we simply do *not* form Johnson complexes as we would expect.

- *Second*, for zero interaction, we form Johnson complexes just *at random* - a vacancy just does not care if it sits next to an impurity atom or not. The concentration thus is directly given by the product of the concentrations of the partners (the factor **12** just accounts for the **12** different ways to form a Johnson complex with one vacancy).
 - *Third*, for appreciable but not extreme binding energies the quotient c_C / c_F is always < 1 , because $(c_V)^{1/2} \ll 1$; it decreases rapidly with temperature. *This means that in equilibrium only a small part of the foreign atoms will form Johnson complexes.*
 - *Fourth*, for appreciable but not extreme binding energies the quotient c_C / c_V can be > 1 or < 1 , depending on $12c_F$ being larger or smaller than $(c_V)^{1/2}$. Below some temperature the vacancy concentration will always be so low that the ratio is > 1 , we then have *more* Johnson complexes than free vacancies. But that does not mean we have *many* - just more than the extremely few vacancies.
 - *Fifth*, for extreme binding energies we have a problem. The relations given just must be wrong - we cannot for example, have **12** times as many Johnson complexes as we have foreign atoms. What went wrong?
- Well, our starting formula is only valid under the assumption that $c_C \ll c_F$. This assumption is obviously violated for binding energies too large; we then must *not* use the simple formula.
- If we take the correct formula, we simply find that c_V times the exponential vanishes (i.e. c_C / c_V does not make sense anymore), and $c_C / c_F \approx z / (1 + z) \approx 1$ under all conditions, as we would expect.