Lecture 18
Defects in Ceramics 2
Ref: Barsoum, Fundamentals of Ceramics, Ch6, McGraw-Hill, 2000

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Topics to discuss....

Defects reactions
- Rules for defect reactions
- Stoichiometric defect reactions
- Defect reactions for compound crystals
- Non-stoichiometric defect reactions
- Extrinsic defect reactions
Defect Reactions

- Each defect can be treated as chemical entities and treat them in a manner referred to as defect chemistry.

- Formation of various defects and interactions of various defects may be conceptualised in terms of mass action equilibria by means of defect equations.

Rules for defect reactions

1. Mass Balance
   - Mass cannot be created or destroyed. Vacancies have zero mass.

2. Electroneutrality, or charge balance
   - Charge cannot be created or destroyed.

3. Preservation of regular site ratio
   - Ratio between the numbers of regular cation and anion sites must remain constant and equal to the ratio of the parent lattice.
   - Thus if a normal lattice site of one component is created or destroyed, the corresponding number of normal sites of the other constituent must be simultaneously created or destroyed so as to preserve the site ratio of the compound.
To generalise, for an $M_aX_b$ compound, the following relation has to be maintained at all times:

$$a(X_X + V_X) = b(M_M + V_M)$$

$$\frac{M_M + V_M}{X_X + V_X} = \frac{a}{b}$$

For example, in $\text{Al}_2\text{O}_3$:

$$\frac{M_{\text{Al}} + V_{\text{Al}}}{X_O + V_O} = \frac{2}{3}$$

Note that, this does not mean that the number of atoms or ions has to maintain that ratio, but only the number of sites.

Stoichiometric Defect Reactions

Crystal chemistry (cations/anions ratio) does not change.
No mass is transferred across the crystal boundary.

Important defects in this category include:

1. Schottky defects
2. Frenkel defects
Schottky defects

- In Schottky defects, electric-charge-equivalent numbers of vacancies are formed on each sub-lattice.

- For any compound MX (M^{z+}, X^{z-}), the Schottky defect reaction is:
  \[ \text{null} = V_M^{\ast\ast} + V_X^{\ast\ast} \]
  or, perfect crystal
  \[ \Delta g_S \]
  \( \Delta g_S \) is the free energy change for the formation of Schottky defect

- Schottky defect reaction for Al₂O₃:
  \[ \text{null} = 2V_{Al}^{\ast\ast} + 3V_{O}^{\ast\ast} \]

- In general, for an MₐOₐ oxide:
  \[ \text{null} = aV_M^{b\ast} + bV_O^{a\ast} \]

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Thermodynamics of Schottky defects

- Assume that the number of ways of distributing cation vacancies \( V_{\text{cat}} \) on \( (N_{\text{cat}} + V_{\text{cat}}) \) sites be \( \Omega_1 \), and number of ways of distributing anion vacancies \( V_{\text{an}} \) on \( (N_{\text{an}} + V_{\text{an}}) \) sites be \( \Omega_2 \).

- The configuration entropy
  \[ \Delta S = k \ln \Omega = k \ln \Omega_1 \Omega_2 \]
  where
  \[ \Omega = \frac{(N_{\text{cat}} + V_{\text{cat}})! (N_{\text{an}} + V_{\text{an}})!}{(N_{\text{cat}})! (V_{\text{cat}})! (N_{\text{an}})! (V_{\text{an}})!} \]
  and
  \[ \frac{N_{\text{cat}} + n_{\text{cat}}}{(N_{\text{an}} + n_{\text{an}})} = 1 \]
Finding minimum in free energy will yield

\[
\frac{V_{\text{an}}^{\text{eq}} V_{\text{cat}}^{\text{eq}}}{(N_{\text{an}} + V_{\text{an}}^{\text{eq}})(V_{\text{cat}}^{\text{eq}} + N_{\text{cat}})} \approx \frac{V_{\text{an}}^{\text{eq}} V_{\text{cat}}^{\text{eq}}}{N_{\text{an}} N_{\text{cat}}} = \exp\left(-\frac{\Delta h_S - T \Delta s_S}{kT}\right)
\]

Product of cation and anion vacancy concentrations
is a constant that depends only on temperature

When Schottky defects dominate, then

\[
[V_o] = [V_c] = \exp\left(\frac{\Delta s_S}{2k}\right) \exp\left(-\frac{\Delta h_S}{2kT}\right)
\]

where \( [V_c] = \frac{V_{\text{cat}}}{V_{\text{cat}} + N_{\text{cat}}} \) and \( [V_o] = \frac{V_{\text{an}}}{V_{\text{an}} + N_{\text{an}}} \)

Square brackets denote mole fractions of defects!
They are dimensionless!

**Frenkel Defects**

- A cation removed from its normal site to an interstitial site to form an interstitial – vacancy pair

- For any trivalent cation (M^{+3}), the Frenkel defect reaction is:

\[
M_{M}^x = V_{M}^{\text{m}} + M_{i}^{\text{m}}
\]

- For anti-Frenkel defect, an anion is removed form an interstitial – vacancy pair

- For oxygen ion (O^{2-}), the Anti-Frenkel defect reaction is:

\[
O_{O}^x = V_{O}^{\text{m}} + O_{i}^{\text{m}}
\]
Thermodynamics of Frenkel defects

- number of ways of distributing $n_i$ interstitials on $N^*$ interstitial sites be $\Omega_1$, and

\[ \Omega_1 = \frac{N^*!}{(N^* - n_i)! n_i!} \]

- number of ways of distributing cation vacancies $V_{\text{cat}}$ on $N_T$ total sites be $\Omega_2$.

\[ \Omega_2 = \frac{N_T!}{(N_T - V_{\text{cat}})! V_{\text{cat}}!} \]

The configurational entropy is the same

\[ \Delta S = k \ln \Omega_1 \Omega_2 \]

At equilibrium,

\[ \frac{V_{\text{cat}}^\text{eq} n_i^\text{eq}}{N_T N^*} \approx \exp \left( - \frac{\Delta g_F}{kT} \right) \approx \exp \left( \frac{T \Delta S_F}{kT} \right) - \exp \left( - \frac{\Delta h_F}{kT} \right) \]

$\Delta g_F$ = the free energy change for the formation of Frenkel defect

- Note that $N^*$ depends on crystal structure.

- For example, for 1 mol NaCl, if the ions migrate to tetrahedral sites, $N^* \approx 2N_{\text{AV}}$. 
Worked Example 6.1

Estimate the number of Frenkel defects in AgBr (rocksalt structure) at 500 ºC. The enthalpy of formation of the defect is 110 kJ/mol, and the entropy of formation is 6.6R. The density and molecular weight are 6.5 g/cm³ and 187.8 g/mol, respectively. State all necessary assumptions.

Let us assume that

1. the Frenkel disorder occurs on the cation sub-lattice
2. silver ions go into the tetrahedral sites. Then

\[ \frac{V_{cat} n_{eq}^{cat}}{N_T N_r} = \exp \left( \frac{T \Delta S_F}{kT} - \frac{\Delta h_F}{kT} \right) \]

\[ \frac{V_{cat} n_{eq}^{eq}}{2(6.02x10^{23})^2} = \exp \left( \frac{6.6R}{R} \exp \left( -\frac{110x1000}{8.314(500+273)} \right) \right) \]

\[ V_{cat} n_{eq}^{eq} = 1.957x10^{43} \text{ defects/mole}^2 \]

Worked Example 6.1

Estimate the number of Frenkel defects in AgBr (rocksalt structure) at 500 ºC. The enthalpy of formation of the defect is 110 kJ/mol, and the entropy of formation is 6.6R. The density and molecular weight are 6.5 g/cm³ and 187.8 g/mol, respectively. State all necessary assumptions.

In case of Frenkel disorder,

number of cation vacant site = number of interstitial sites

\[ V_{cat} n_{eq}^{cat} = 1.957x10^{43} \text{ defects/mole}^2 \]

\[ V_{cat} n_{eq}^{eq} = 4.43x10^{21} \text{ defects/mole} \]

And the corresponding number of defects/cm³ is

\[ V_{cat} n_{eq}^{eq} = 4.43x10^{21} \left( \frac{6.5}{187.8} \right) = 1.5x10^{20} \text{ defects/cm}^2 \]
Defects in Compound Crystals

**Possible defects:**
1. vacant sites on each sub-lattice
2. ions/atoms on interstitial sites
3. impurity ions/atoms on each sub-lattice
4. unassociated electrons and holes
5. combination of these defects

**Example:**

- Consider a crystal with a formula $M_aX_b$.
- If valence of $M$ is $z$, then the valence of $X$ will be $-(a/b)z$.
- Reaction with its surroundings when $M$ is added to its normal cation site:

$$M(g)\xrightarrow{M_aX_b} M_M^x + \left( \frac{b}{a} \right) V_X^{(a/b)z} + ze'$$
Example: Incorporating Si into SiO$_2$

\[ \text{Si}(g) \xrightarrow{\text{SiO}_2} \text{Si}^{x\text{Si}}_\text{Si} + 2V^{2\text{O}}_O + 4e' \]

Example: Incorporating Al into Al$_2$O$_3$

\[ \text{Al}(g) \xrightarrow{\text{Al}_2\text{O}_3} \text{Al}^{x\text{Al}}_\text{Al} + \frac{3}{2}V^{2\text{O}}_O + 3e' \]

or, \[ 2\text{Al}(g) \xrightarrow{\text{Al}_2\text{O}_3} 2\text{Al}^{x\text{Al}}_\text{Al} + 3V^{2\text{O}}_O + 6e' \]

Non-stoichiometric Defect Reactions

- Composition of crystal changes due to this defect because mass is transferred across the boundary of the crystal.

- For a general M$_a$O$_b$ oxide compound, two non-stoichiometric defects can occur:
  1. Metal excess, or oxygen deficient
  2. Oxygen excess, or metal deficient

- In both of these cases, a/b ratio is changed.
Metal excess, or oxygen deficient
(low oxygen partial pressure)

- has the general formula $M_{a+\delta}O_b$, or $M_aO_{b-\delta}$.
- places cation into interstitial site, or creating vacancy in oxygen site.
- using anion, typical defect reaction is:

$$O^x_O = \frac{1}{2}O_2(g) + V^{**}_O + 2e'$$

Redox reaction $V^x_O$

Electrons are usually weakly bonded; can be excited into the conduction band when species $O_2$ escape as natural, it leaves two electron behind

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**Figure 6.4** (a) The formation of an oxygen vacancy by the loss of an oxygen atom to the gas phase. This is a non-stoichiometric reaction because the crystal chemistry changes as a result. Note that as drawn, the electrons are localized at the vacancy site, rendering its effective charge zero. (b) A $V^*_O$ site is formed when one of these electrons is excited into the conduction band. (c) The escape of the second electron creates a $V^{**}_O$ site.

- $O^x_O \Rightarrow \frac{1}{2}O_2(g) + V^x_O$
- $V^x_O \Rightarrow V^*_O + e'$
- $V^*_O \Rightarrow V^{**}_O + e'$

$$O^x_O \Rightarrow \frac{1}{2}O_2(g) + V^{**}_O + 2e'$$
Example: \( \text{TiO}_{2-y} \)

\[
O_\circ^{x} \xrightarrow{T\text{iO}_{2}} \frac{1}{2}O_2(g) + V_0^{\circ} + 2e' \\
2T_i^{+4} + 2e' = 2T_i^{+3} \\
2T_i^{x} + O_\circ^{x} = 2T_i^{+} + \frac{1}{2}O_2(g) + V_0^{\circ}
\]

**Oxygen excess, or metal deficient**

(high oxygen partial pressure)

- has the general formula \( M_{a}O_{b+\delta} \), or \( M_{a-\delta}O_{b} \).
- places oxygen into interstitial site, or creating vacancy in cation site.

- using anion, typical defect reaction is:

\[
\frac{1}{2}O_2(g) = O_i^{\circ} + 2h^* \\
O_i^{x}
\]

This ionization creates holes in valence band
This hole moves through lattice and contribute to electrical conductivity
Example: $\text{Fe}_{1-x}\text{O}$

\[
\frac{1}{2}O_2(g) \xrightarrow{\text{FeO}} O^x_O + V^{''}_{\text{Fe}} + 2h^*
\]

\[
2Fe^{+2} + 2h^* = 2Fe^{+3}
\]

\[
2Fe^x_{\text{Fe}} + \frac{1}{2}O_2(g) = 2Fe^*_{\text{Fe}} + O^x_O + V^{''}_{\text{Fe}}
\]

Extrinsic Defect Reactions

- Defects created by impurities.
- Usually substitute host ions of the same or nearest electronegativity, even if the sizes of the ions differ. So cations substitute for cations and anions for anions. For example, in NaCl, Ca and O would be expected to occupy Na and Cl sites, respectively.

Example 1: Incorporating $\text{CaCl}_2$ into NaCl

\[
\text{CaCl}_2 \xrightarrow{2\text{NaCl}} \text{Ca}^*_\text{Na} + V^*_{\text{Na}} + 2\text{Cl}^x_{\text{Cl}}
\]

\[
\text{CaCl}_2 \xrightarrow{\text{NaCl}} \text{Ca}^*_\text{Na} + \text{Cl}^*_{\text{i}} + \text{Cl}^x_{\text{Cl}}
\]

Between these two reactions, which one is more probable?
Example 2: Doping MgO with Al₂O₃

\[ Al_2O_3 + 3MgO \rightarrow 2Al_{Mg}^\prime + V_{Mg}'' + 3O_{\overline{O}}^x \]

Example 3: Doping Al₂O₃ with MgO

\[ 2MgO + Al_2O_3 \rightarrow 2Mg_{Al} + 2O_{\overline{O}}^x + V_{O}''' \]

Next Class

Lecture 19

Electrical and Ionic Conduction in Ceramics