Thermodynamics

Thermodynamics of Defects

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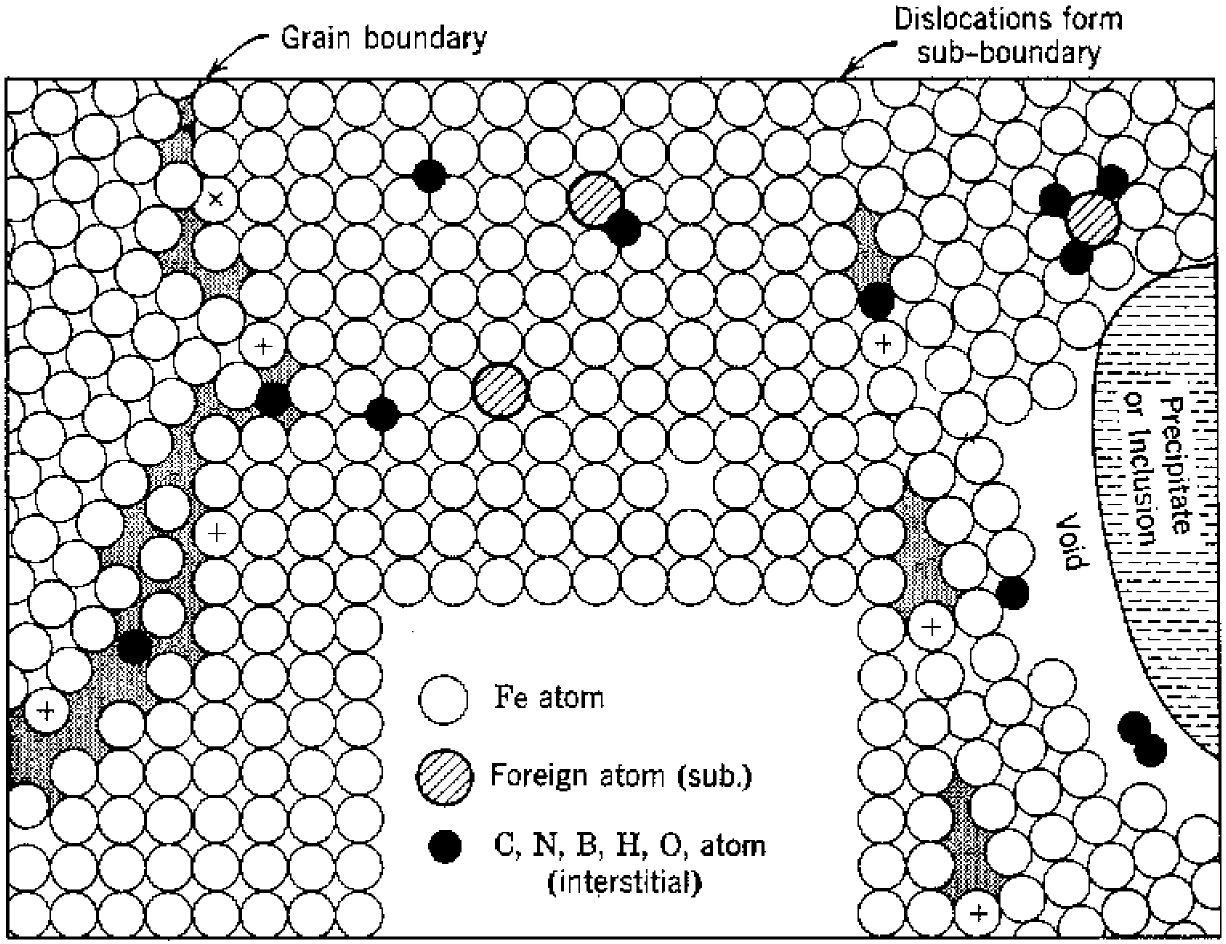
Defects and Defect Complexes in Metals – from L.S. Darken



Common imperfections

Scope

Role of Defects

1. Mechanical Properties
2. Kinetics of Phase Transformation
3. Electrical conductivity of Semi-conductors and ionic crystals
4. Luminescence Phenomena
5. Photoconductivity
6. Color

Purpose of Defect Chemistry

1. Control of the concentrations of various defects
2. Control of the crystal properties related to defects

Type of Defects

Point Defects

1. Atomic Defects
   - Vacancies
   - Interstitials
   - Impurities
   - Complexes

1. Electronic Defects

Line Defects

- Dislocations

Planar Defects

1. Surfaces
2. Interfaces

Point Defect – Concentration

Statistical Approach

1. An occupied state $E = 0$
2. An unoccupied state $E = E_v$

$$P_v = \frac{e^{-E_v/kT}}{Z} = \frac{n}{n+N} = \frac{e^{-E_v/kT}}{1+e^{-E_v/kT}}$$

$$\frac{n}{N} = e^{-E_v/kT}$$

Thermodynamic Approach

$$\Delta G = n\Delta H_v - T(\Delta S_v + \Delta S_c)$$

$$\Delta G = n(\Delta H_v - T\Delta S_v) - kT[(N+n)\ln(N+n) - N\ln N - n\ln n)]$$

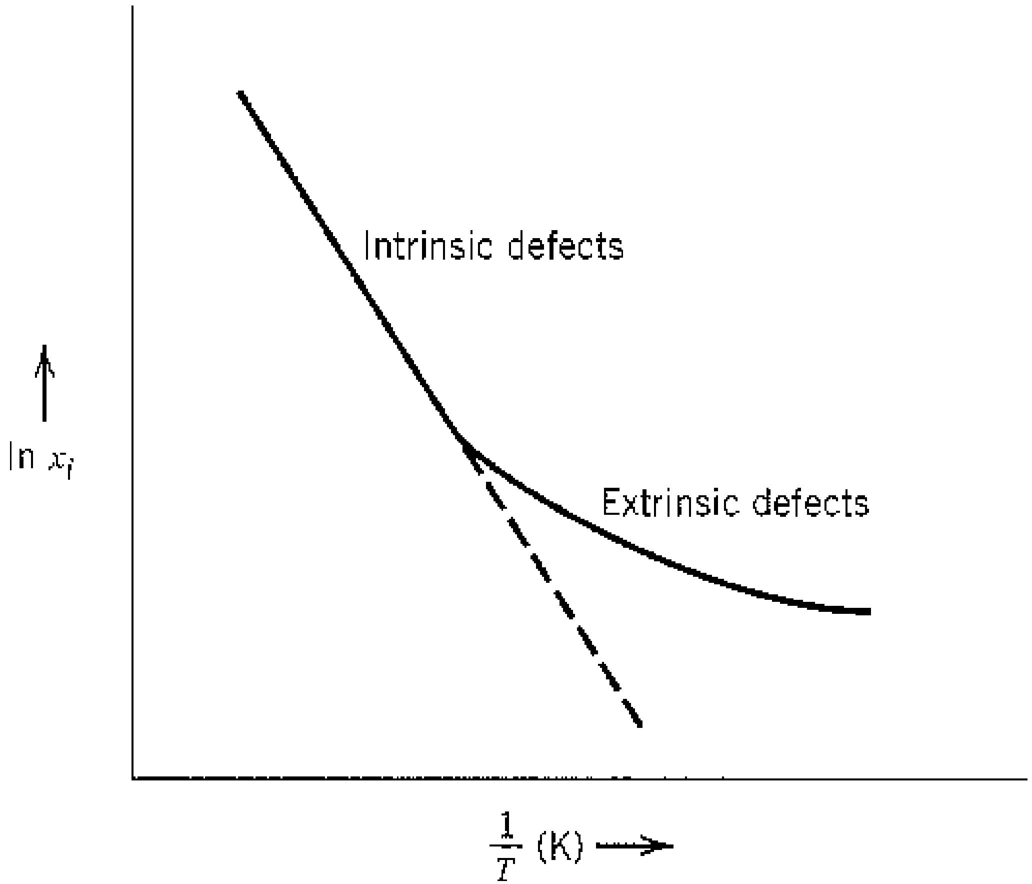
$$\frac{\partial \Delta G}{\partial n} = (\Delta H_v - T\Delta S_v) + kT\ln\frac{n}{N+n} = 0$$

$$x_v = \frac{n}{N+n} = \exp\left(\frac{\Delta S_v}{k}\right)\exp\left(\frac{-\Delta H_v}{kT}\right)$$

$$x_d = A\exp\left(\frac{-\Delta H_d}{kT}\right)$$

Point Defect – Intrinsic vs. Extrinsic

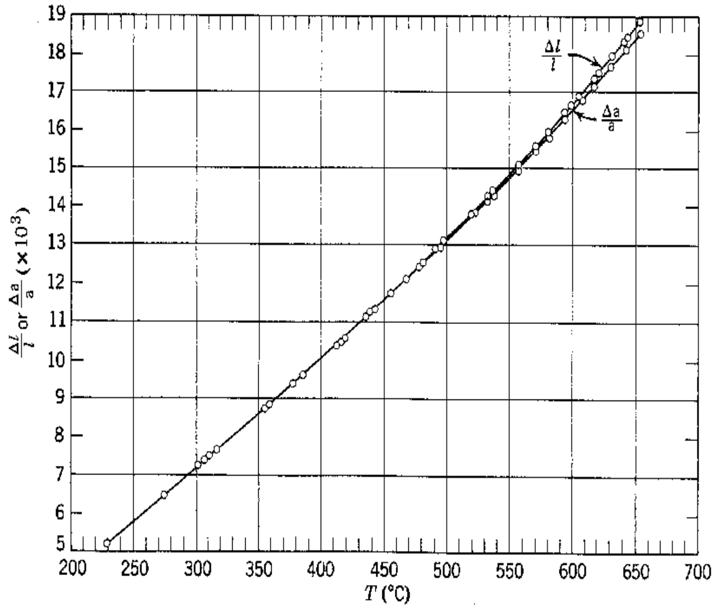
$$\ln x_d = \ln A - \left(\frac{\Delta H_d}{k}\right) \cdot \frac{1}{T}$$



Point Defect – Measurements of vacancy formation energy

Thermal expansion

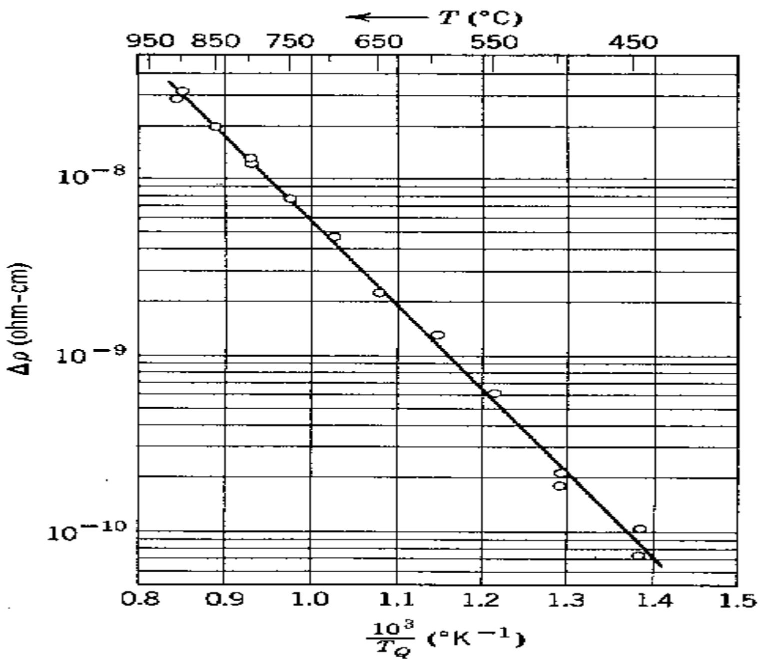
$$\frac{n_V}{N} = x_v = 3\left(\frac{\Delta l}{l} - \frac{\Delta a}{a}\right)$$



Relative length and lattice parameter changes of aluminum as a function of temperature. From R. O. Simmons and R. W. Baluffi, *Phys. Rev.*, 117, 52 (1960).

Temperature dependence of e-resistivity

$$\frac{\partial \ln(a x_v)}{\partial(1/T)} = -\frac{\Delta H_v}{k} = \frac{\partial \ln(\Delta\rho)}{\partial(1/T)}$$



J. E. Bauerle and J. S. Koehler, *Phys. Rev.*, 107, 1493 (1957)

Point Defect – vacancy-impurity interaction

$$n_v = n_v^{\text{int}} + n_{I-V}$$

Set $E_v^{\text{int}} = 0$

$E_{I-V} = E_{I-V}$

$$\frac{n_{I-V}}{n_v^{\text{int}}} = \frac{g_{I-V} \exp\left(\frac{-E_{I-V}}{kT}\right)}{Z}$$

$$\frac{n_{I-V}}{n_v^{\text{int}}} = \frac{g_{I-V} \exp\left(\frac{-E_{I-V}}{kT}\right)}{g^{\text{int}} + g_{I-V} \exp\left(\frac{-E_{I-V}}{kT}\right)} = \frac{Zn_I \exp\left(\frac{-E_{I-V}}{kT}\right)}{N - n_I - Zn_I + Zn_I \exp\left(\frac{-E_{I-V}}{kT}\right)}$$

$$N >> (Z+1)n_I$$

$$\frac{n_{I-V}}{n_v^{\text{int}}} = \frac{n_I}{N} Z \exp\left(\frac{-E_{I-V}}{kT}\right)$$

For $n_I/N=1\%$ and $E_{I-V}=-0.1\text{eV}$ $n_{I-V}/n_v^{int} = 0.63$ at 700K

Point Defect – impurity-defect interaction (nitrogen/dislocation in Fe)

$$n_N = n_N^{\text{int}} + n_{Nd}$$

Set $E_N^{\text{int}} = 0$

$E_{Nd} = E_{Nd}$

$$\frac{n_{Nd}}{n_N^{\text{int}}} = \frac{g_{Nd}\exp\left(\frac{-E_{Nd}}{kT}\right)}{g_N^{\text{int}} + g_{Nd}\exp\left(\frac{-E_{Nd}}{kT}\right)} = \frac{g_{Nd}\exp\left(\frac{-E_{Nd}}{kT}\right)}{g_N^{\text{int}}} \qquad for \qquad g_N^{\text{int}} >> g_{Nd}$$

$$n_N = n_N^{\text{int}}\left(1 + \frac{g_{Nd}}{g_N^{\text{int}}}\exp\left(\frac{-E_{Nd}}{kT}\right)\right)$$

For dislocation density = 5×10^{12} cm/cm^3

number of interstitial atoms = 4.3×10^7 /cm $(8.4 \times 10^{22})^{1/3}$

E_{Nd} = -0.3 eV, at 700K

$$n_{\text{N}} = 1.37\, n_{\text{N}}^{\text{int}}$$

Electronic Defect – electron/hole in conduction/balance band

$$N_c = \int_{E_g}^{\infty} g(E)\left[1+\exp\left(\frac{E-\mu}{kT}\right)\right]^{-1} dE$$

$$g(E) = 4\pi\left(\frac{2m_e^*}{h^2}\right)^{3/2}(E-E_g)^{1/2} = C_e(E-E_g)^{1/2} \qquad g(E) = 4\pi\left(\frac{2m_h^*}{h^2}\right)^{3/2}(-E)^{1/2} = C_h(-E)^{1/2}$$

$$1+\exp\left(\frac{E-E_F}{kT}\right) \approx \exp\left(\frac{E-E_F}{kT}\right) \qquad \textit{for} \qquad (E-E_F) >> kT$$

$$N_c = C_e\int_{E_g}^{\infty}(E-E_g)^{1/2}\exp\left(-\frac{E-E_F}{kT}\right)dE = C_e(kT)^{3/2}\exp\left(-\frac{E_g-E_F}{kT}\right)\int_0^{\infty}x^{1/2}e^{-x}dx$$

$$\int_0^{\infty}x^{1/2}e^{-x}dx = \frac{1}{2}\sqrt{\pi}$$

$$N_c = 2\left(2\pi\frac{m_e^*kT}{h^2}\right)^{3/2}\exp\left(-\frac{E_g-E_F}{kT}\right) \qquad N_h = 2\left(2\pi\frac{m_h^*kT}{h^2}\right)^{3/2}\exp\left(-\frac{E_F}{kT}\right)$$

Intrinsic Semiconductor, $N_c=N_h$

$$E_F = \frac{E_g}{2}+\frac{3}{4}kT\ln\frac{m_h^*}{m_e^*}$$

$$N_cN_h = 4\left(\frac{2\pi k}{h^2}\right)^3(m_e^*m_h^*)^{3/2}T^3\exp\left(-\frac{E_g}{kT}\right) = N_c^2$$

Defects in Stoichiometric Ionic Compounds – Kroger-Vink Notation

Symbol	Definition
M	Atom of electropositive element
X	Atom of electronegative element
M_M	M atom on M site (sometimes denoted as M_M^x)
N_M	N atom on M site
V_M	Vacancy on M site
M_i	M atom on interstitial site
$M_i^{\bullet}$	Positively charged M ion on interstitial site (singly ionized)
$M_i^{\bullet\bullet}$	Positively charged M ion on interstitial site (doubly ionized)
X_i'	Negatively charged X ion on interstitial site (singly ionized)
$V_X^{\bullet}$	Positively charged vacancy (relative to perfect lattice) on X site
V_M'	Negatively charged vacancy (relative to perfect lattice) on M site

1. **Electroneutrality**
2. **Mass conservation**
3. **Fixed Site ratio M:X**

Defects in Stoichiometric Ionic Compounds – Frenkel defect

$$M_M = M_i^* + V_M^{'}$$

$$K_1 = \frac{a_{M_i^*} a_{V_M^{'}}}{a_{M_M}} \cong [M_i^*][V_M^{'}]$$

$$\Delta G = n \ \Delta H_f - T\ (n \ \Delta S_f + \Delta S_c)$$

$$\Delta S_c = k \ln\left[\frac{(N+n_v)!}{N! n_v!}\frac{(N+n_i)!}{N! n_i!}\right]$$

$$\left(\frac{n_v}{N+n_v}\right)\cdot\left(\frac{n_i}{N+n_i}\right) = \exp\left(\frac{\Delta S_f}{k}\right)\exp\left(-\frac{\Delta H_f}{kT}\right)$$

$$[M_i^*][V_M^{'}] = \frac{N_A^2}{V^2}\exp\left(\frac{\Delta S_f}{k}\right)\exp\left(-\frac{\Delta H_f}{kT}\right)$$

$$null = V_X^* + V_M^{'}$$

$$K_2 = [V_X^*][V_M^{'}]$$

Coexistence of Frenkel and Schotty-Wagner defects

$$[V_M^{'}] = [M_i^*] + [V_X^*]$$

$$K_1 = [M_i^*][V_M^{'}]$$

$$K_2 = [V_X^*][V_M^{'}]$$

$$K_1 + K_2 = ([M_i^*] + [V_X^*])[V_M^{'}] = [V_M^{'}]^2$$

Between MX and M gas

$$M(g) = M_i^* + n' \qquad K_F = \frac{[M_i^*][n']}{P_M} \qquad \ln K_F = \ln[M_i^*] + \ln[n'] - \ln P_M$$

$$M_M = M_i^* + V_M' \qquad K_F' = [M_i^*][V_M'] \qquad \ln K_F' = \ln[M_i^*] + \ln[V_M']$$

$$null = n' + p^* \qquad k_i = [n'][p^*] \qquad \ln K_i = \ln[n'] + \ln[p^*]$$

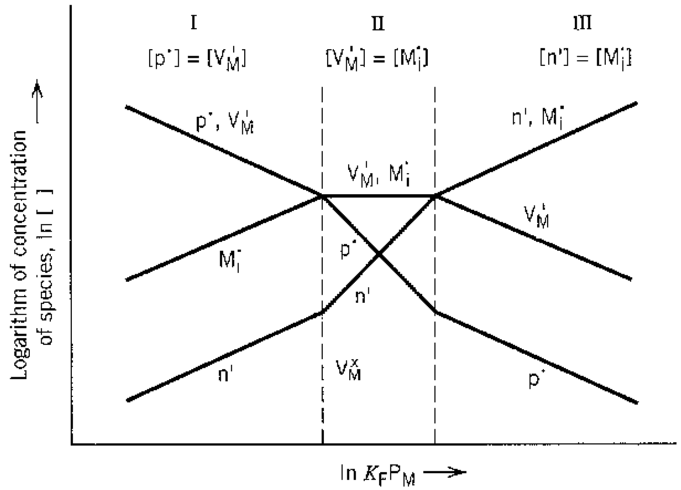
Electroneutrality $[n'] + [V_M'] = [p^*] + [M_i^*]$

Low P_M $[p^*] = [V_M']$

high P_M $[n'] = [M_i^*]$

in between $[M_i^*] = [V_M']$

$$2\ln[p^*] = -\ln K_F P_M + \ln K_F' K_i$$



Defects in Stoichiometric Compounds – Intrinsic/Extrinsic defects

Dilute solution of $CdCl_2$ in NaCl

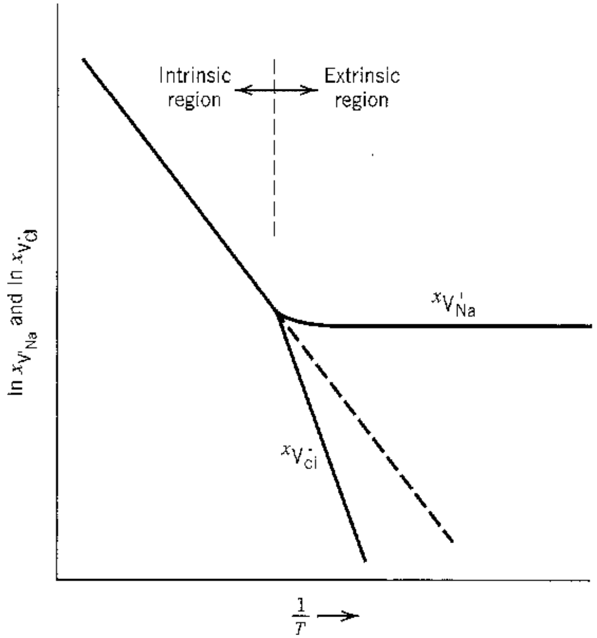
$$K_S = [V'_{Na}][V^*_{Cl}]$$

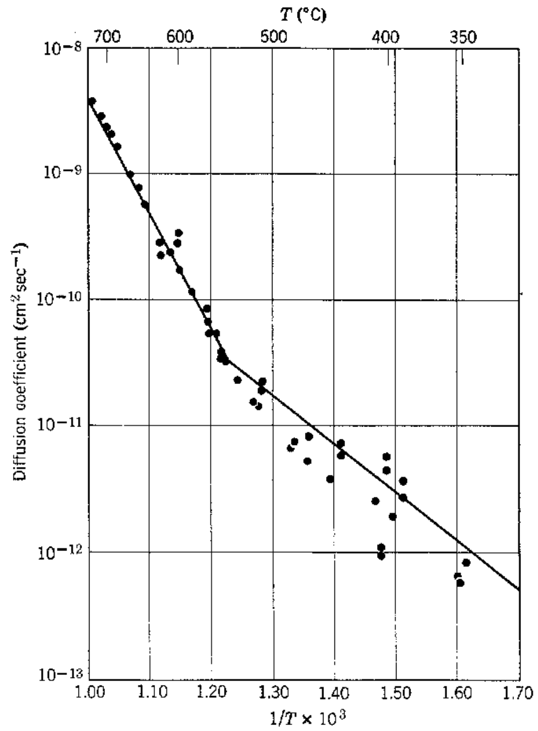
$$[V'_{Na}] = \frac{[Cd^*_{Na}] + ([Cd^*_{Na}]^2 + 4K_S)^{1/2}}{2}$$

$$[V'_{Na}] = [Cd^*_{Na}] + [V^*_{Cl}]$$

$$[V'_{Na}] = [Cd^*_{Na}] + \frac{K_S}{[V'_{Na}]}$$

$$[V'_{Na}]^2 - [Cd^*_{Na}][V'_{Na}] - K_S = 0$$





Defects in Stoichiometric Compounds – Determination of defect type

Density and Lattice parameter measurement: CaO doped ZrO_2

for 15mol% CaO : $Zr_{0.85}Ca_{0.15}O_{1.85}$

- Vacancy in Oxygen site
- Interstitial Cation

Measured lattice parameter: 5.131Å (CaF2 structure)

→ volume of unit cell: 135.08×10^{-24} cm^3

Mass of unit cell

1. $4 \times (0.15 \times 40.08 + 0.85 \times 91.22 + 1.85 \times 16)/N_A = 452.60 /N_A$

   → density = 5.57 g/cm^3

2. $4 \times (0.15 \times 40.08 \times (2/1.85) + 0.85 \times 91.22 \times (2/1.85) + 2 \times 16))/N_A$

   $= 489.29 /N_A$ → density = 6.01 g/cm^3

※ Experimentally measured density is close to 5.57

→ useful as oxide ion conductors in high temperature fuel cells and as oxygen pressure sensors in electrochemical cells

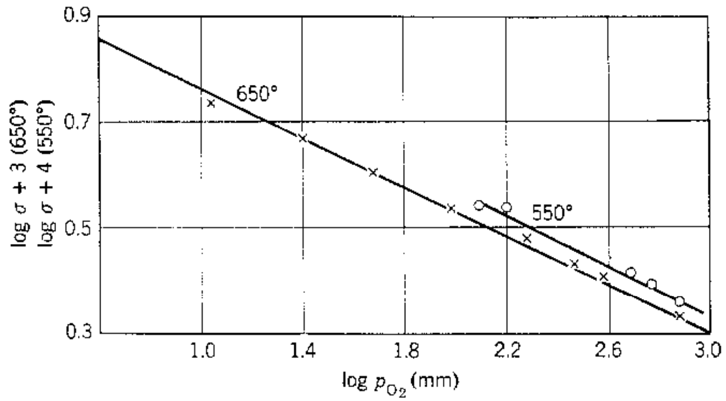
Defects in Stoichiometric Compounds – Determination of defect type

Electrical conductivity measurement:

ZnO becomes conductive if heated at low oxygen pressure

Experiments show: ZnO is an n-type semiconductor

and $\sigma \approx [n'] \approx P_{O2}^{-1/4}$



Two possibilities

(a) Formation of anion vacancies:

(b) Formation of cation interstitials

(a) $O_O = \frac{1}{2}O_2(g) + V_O^* + n'$ $\qquad K_a = p_{O_2}^{1/2} \cdot [V_O^*][n']$

(b) $Zn(g) = Zn_i^* + n'$ $\qquad K_b = \frac{[Zn_i^*][n']}{p_{Zn}}$

$Zn(g) + \frac{1}{2}O_2(g) = ZnO(s)$ $\qquad K = p_{Zn} \cdot p_{O_2}^{1/2}$ $\qquad K_b K = [Zn_i^*][n'] \cdot p_{O_2}^{1/2}$

$[Zn_i^*] = [n']$ $\qquad \sigma \cong [n'] \cong p_{O_2}^{-1/4}$

※Fast diffusion of Zn in ZnO support (b)

Example – Effect of impurity elements on the Oxidation rate of Zn