Zero-dimensional defects

Vacancies, Interstitials, substitutions

Why bother about point defects ?

Diffusion

Electronic conductivity

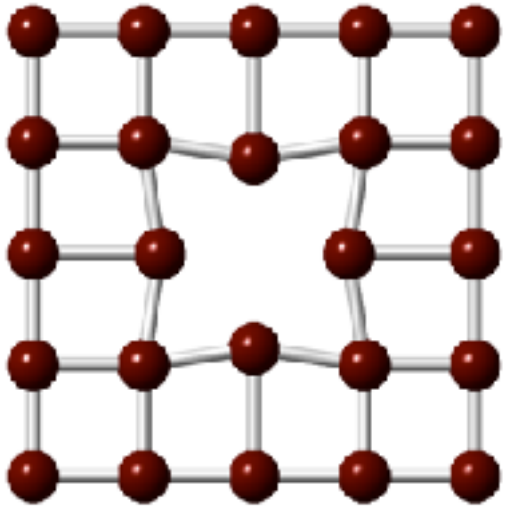
Dielectric constants

Metal oxidation

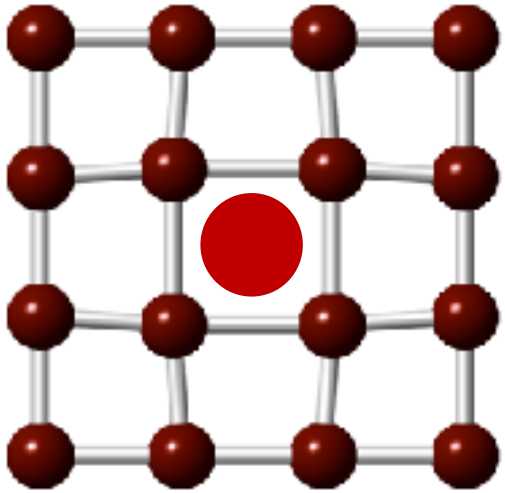
Solid electrolytes

Zero-dimensional defects

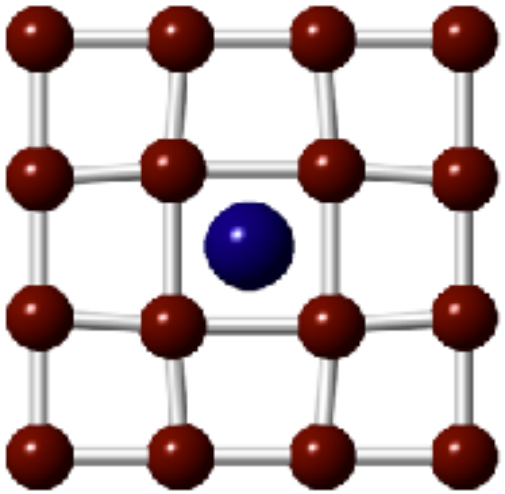
Vacancy



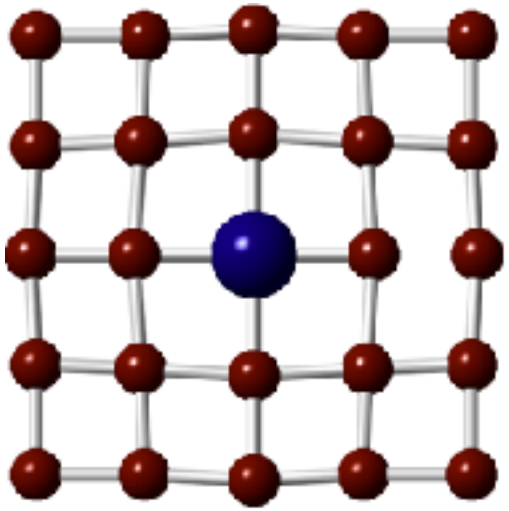
Self-Interstitial



Interstitial



Substitutional



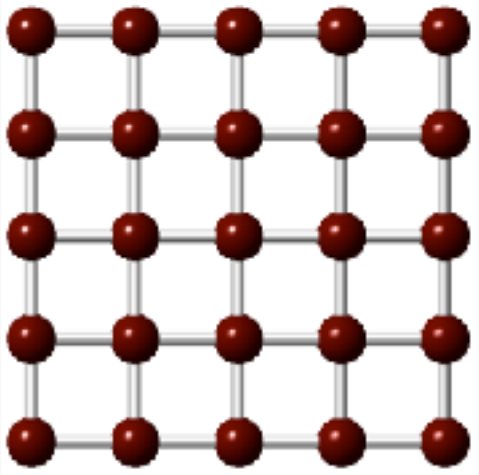
Missing atom or different position

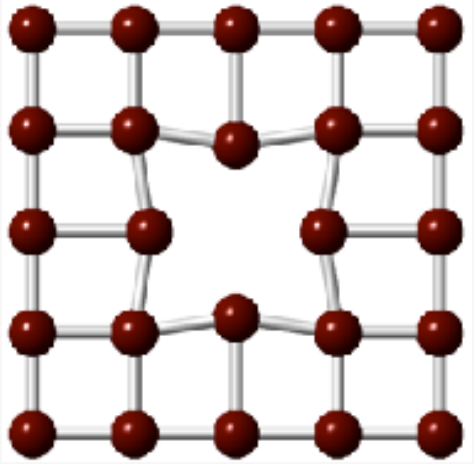
Foreign atom or impurity

Thermodynamics of point defects

- Simple case
  - Vacancies of atoms in a metal crystal

- Analysis of this simple case
  - Vacancies are a thermodynamic necessity!!

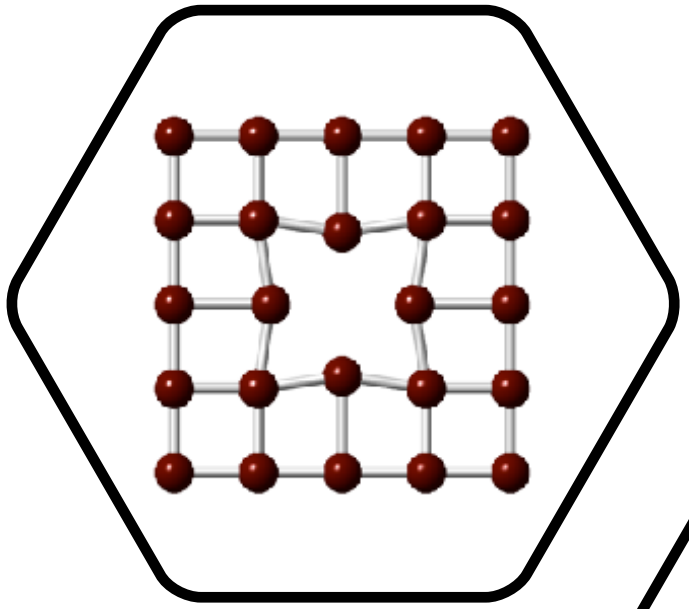




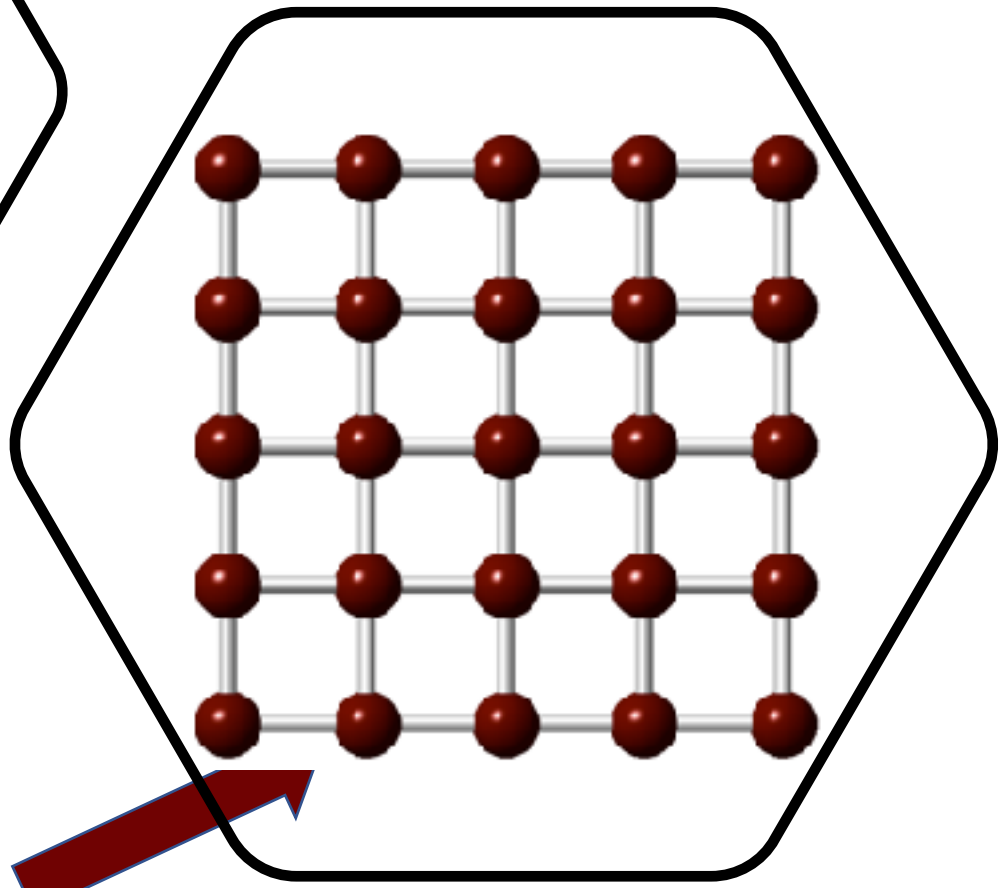
Which configuration has the lower Helmholtz free energy ?

What about free energy of the defective crystal ?

Free energy of perfect crystal



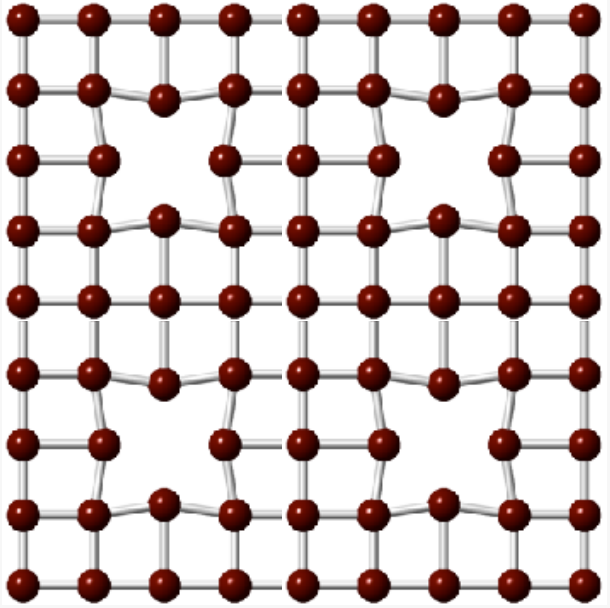
$$F_{\text{perf}} = U_{\text{perf}} - TS_{\text{perf}}$$



$$S_{\text{T,perf}} = 3Nk\left(\ln\left[\frac{kT}{h\nu}\right] + 1\right)$$

$$\therefore F_{\text{perf}} = U_{\text{perf}} - 3NkT\left(\ln\left[\frac{kT}{h\nu}\right] + 1\right)$$

Energy of defect formation



$$F_{\text{def}} = U_{\text{def}} - TS_{\text{def}}$$

But, what is U_{def}

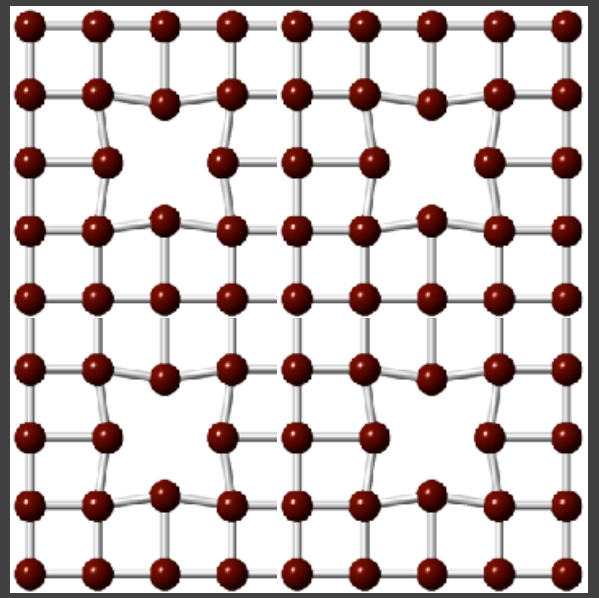
- It will cost some energy
- Assume only NN bonds are affected

$$U_{\text{def}} = \left(N - \zeta n_{\text{v}}\right) u_{\text{perf}} + \zeta n_{\text{v}} u_{\text{def}}$$

$$= N u_{\text{perf}} + n_{\text{v}}\, \zeta \left[u_{\text{def}} - u_{\text{perf}}\right]$$

$$\therefore U_{\text{def}} = U_{\text{perf}} + n_{\text{v}} u_{\text{d}}$$

Entropy of defect Formation – Vibrational component



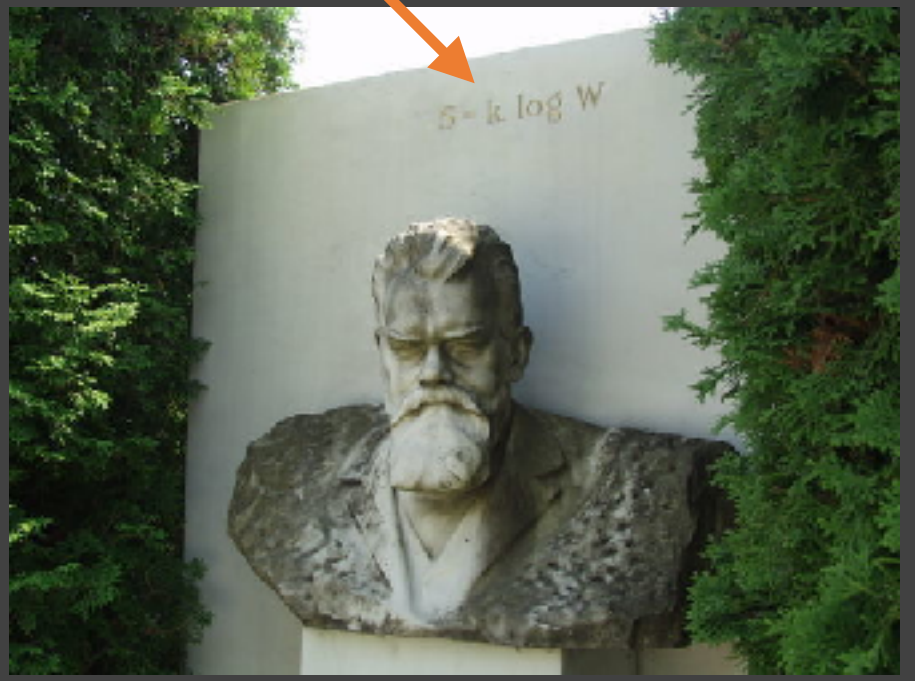
$$\frac{S_{\mathrm{T,def}}}{3k} = (N - \zeta n_{\mathrm{v}}) \left(\ln \left[\frac{kT}{h\nu} \right] + 1 \right) + \zeta n_{\mathrm{v}} \left(\ln \left[\frac{kT}{h\tilde{\nu}} \right] + 1 \right)$$

$$\Longrightarrow S_{\mathrm{T,def}} = 3kN \left(\ln \left[\frac{kT}{h\nu} \right] + 1 \right) + 3k\zeta n_{\mathrm{v}} \left(\ln \left[\frac{kT}{h\tilde{\nu}} \right] + 1 - \ln \left[\frac{kT}{h\nu} \right] - 1 \right)$$

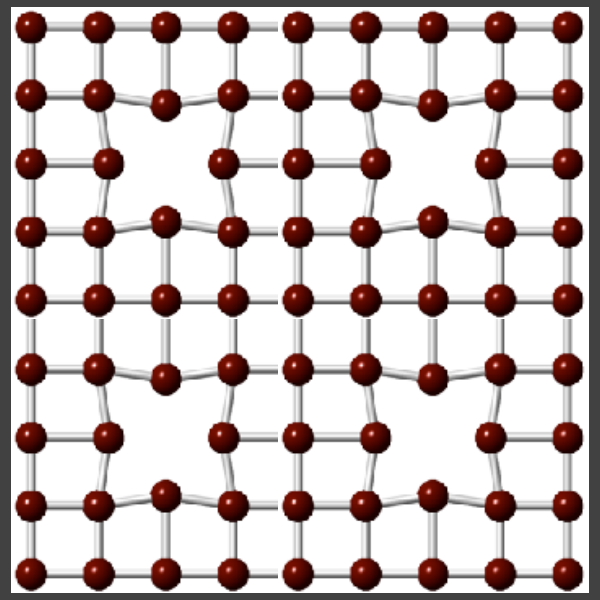
$$= S_{\mathrm{T,perf}} + 3k\zeta n_{\mathrm{v}} \ln \frac{\nu}{\tilde{\nu}} \longrightarrow \Delta s_{\mathrm{vib}}$$

Entropy of defect Formation – Configurational component

$$S_{def} = S_{T,def} + S_{config,def}$$



$$W = \frac{N!}{n_v!\ (N - n_v)!}$$



Stirling Approximation: $\ln p! = p \ln p - p$

$$S_{config,def} = k\left[N \ln\left(\frac{N}{N - n_v}\right) + n_v \ln\left(\frac{N - n_v}{n_v}\right)\right]$$

Entropy of defect Formation – Configurational component

$$S_{\text{config,def}} = k\left[N \ln\left(\frac{N}{N - n_{\text{v}}}\right) + n_{\text{v}} \ln\left(\frac{N - n_{\text{v}}}{n_{\text{v}}}\right)\right]$$

Rearranging terms and defining, $m = \frac{n_{\text{v}}}{N}$

We get,

$$S_{\text{config,def}} = -Nk\left[m \ln m + (1 - m)\ln(1 - m)\right]$$

Free energy of defect formation

$$\Delta F_{\mathrm{def}} = F_{\mathrm{def}} - F_{\mathrm{perf}}$$

$$= U_{\mathrm{perf}} + n_{\mathrm{v}} u_{\mathrm{d}} - TS_{\mathrm{T,perf}} - T\Delta s_{\mathrm{vib}} - TS_{\mathrm{config,def}} - \left(U_{\mathrm{perf}} - TS_{\mathrm{T,perf}} \right)$$

$$= n_{\mathrm{v}} u_{\mathrm{d}} + 3kT\zeta n_{\mathrm{v}} \ln \frac{\tilde{\nu}}{\nu} + NkT \left[m \ln m + (1-m) \ln (1-m) \right]$$

Internal energy of defect formation

Entropy of mixing

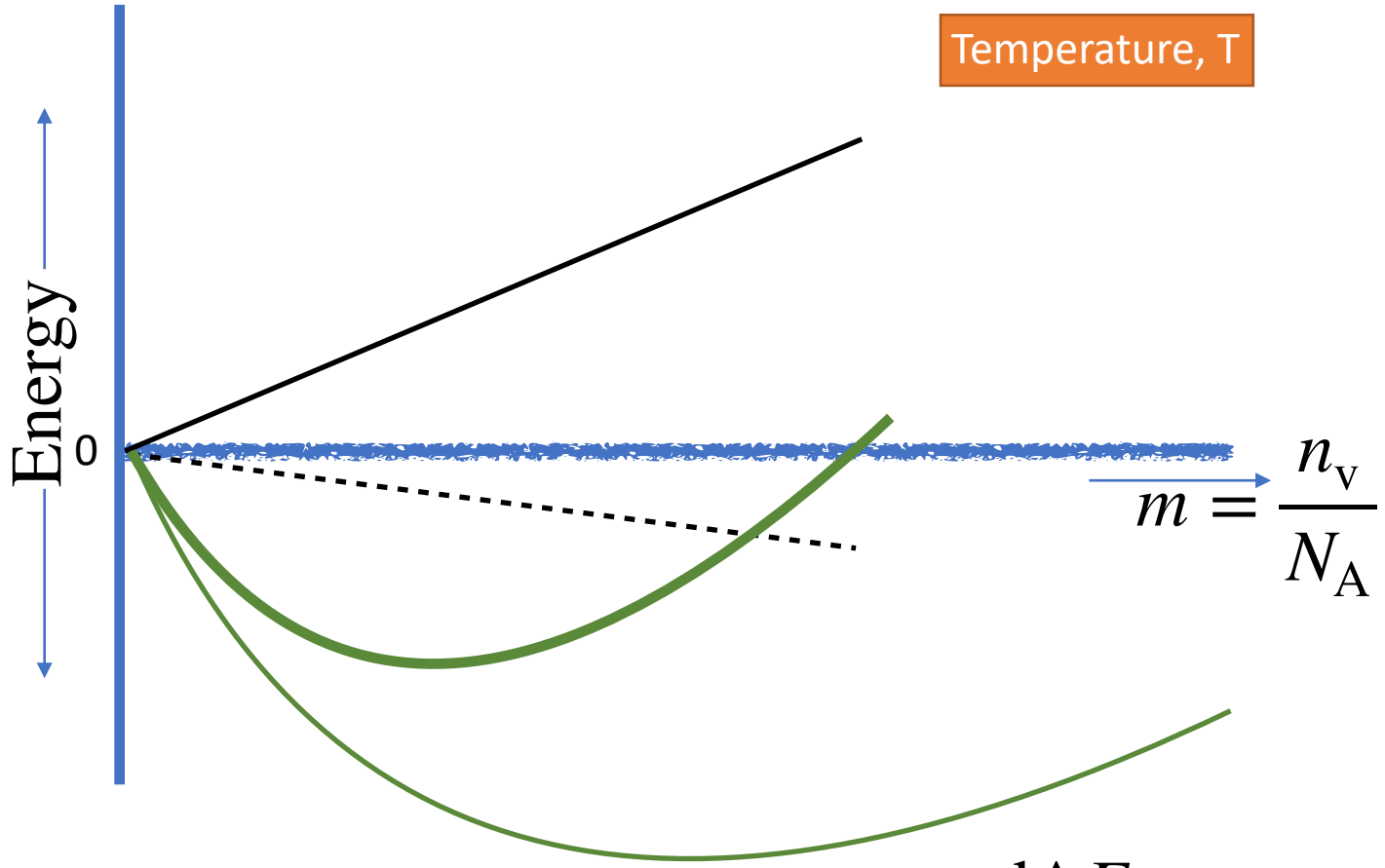
Excess vibrational entropy of defect formation

Multiply and divide 1st and 2nd terms by N, and take N = N_A

$$\Delta F_{\mathrm{def}} = m \left[U_{\mathrm{d}} + 3RT\zeta \ln \frac{\tilde{\nu}}{\nu} \right] + RT \left[m \ln m + (1-m) \ln (1-m) \right]$$

How does a plot of this function look like ?

Equilibrium Vacancy Concentration



The condition for a minimum is: $\frac{d\Delta F_{def}}{dm} = 0$

$$\Longrightarrow \quad m^{eq} = \frac{n_v^{eq}}{N_A} = \exp\left(-\frac{U_d - T\Delta S_{vib}}{RT}\right)$$

Free energy of defect formation $\longrightarrow \Delta F_f$

Problem

Material	Aluminum	Copper	Nickel
ΔF_f (kJ mol^{-1})	68	120	168
Melting point (°C)	660	1083	1453

Calculate equilibrium concentration of vacancies at:

- 0 K
- RT (300 K)
- melting point

Similarity to Mass Action Law

Trivial form of Mass action law for the reaction:

$$\text{Nil} \rightleftharpoons \text{Defect}$$

$$n_v^{eq} = N \times exp - \left(\frac{\Delta H_d}{RT}\right) \times exp\left(\frac{\Delta S_{vib}}{R}\right)$$