Day 25

→ Vacancies in a metal crystal

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Helmoltz Free Energy is lower for the defected crystal

→ Internal energy and Vibrational entropy

→ $n_v \longrightarrow$ no. of vacancies

→ $\omega \rightarrow$ no. of different configurations with same energy.

$$W = {}^{N}C_{n_v}$$

→ Stirling's approximation: $\ln p! = p(\ln p - 1)$ (for large p)

→ $m = \frac{n_v}{N}$

$$S_{config,\,def} = -NK[m \ln m + (1-m)\ln(1-m)]$$

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

$$F_{def} = U_{perf} + n_v U_d - TS_{t\,perf} - T\Delta S_{vis} - TS_{config,\,def}$$

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

So $\Delta F_{def} = n_v U_d + 3KT \sum n_v \ln \frac{\nu'}{\nu}$

$+NkT[m\ln m + (1-m)\ln(1-m)]$

$$= m\left[U_d + 3RT \sum \ln \frac{\tilde{\nu}}{\nu}\right] + RT[m\ln m + (1-m)\ln(1-m)]$$

$(Nk = R,\ N u_d = U_d)$

→ $\frac{d\,\Delta F_{def}}{dm} = 0$ gives equilibrium concentration

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

(For $\Delta F_f > 2.3\,RT$)

$$m^{eq} = \frac{1}{1 + \exp\left(\frac{\Delta F_f}{RT}\right)}$$

ΔF_f Range for metals: 50–150 kJ mol^{-1}

M.P for W (Tungsten) = 3500 K

→ Freeze in of vacancies