Day-24

→ Understanding device : Energy conversion and storage

→ zero-dimensional defects — clusters

- Atomic
- Electron or hole in a material (electronic structure)
- Ionic

→ metallic crystal

↓

Thermodynamics of point defect formation

→ Vacancies in a metallic crystal

↓

Thermodynamic necessity *

→ perfect crystal
vacancy in some region

} at a particular $T > 0$

* lower Helmoltz or Gibb's Free Energy

$T, P \rightarrow$ min. G $(H - TS)$

$T \rightarrow$ min. F (Helmoltz Free energy $= U - TS$)

$P \rightarrow$ min. Enthalpy (H)

$$\Delta F = \underbrace{F_{def.}}_{\text{defect}} - \underbrace{F_{perf}}_{\text{perfect}}$$

→ Vibrational entropy

$$S_{perf} = S_T = 3NK\left(\ln\left[\frac{KT}{h\nu}\right] + 1\right)$$

(mass spring system — coupled oscillators

only one vibrational frequency assumed

$N \rightarrow$ no. of atoms

$$F_{perf} = U_{perf} - 3NKT\left(\ln\left[\frac{KT}{h\nu}\right] + 1\right)$$

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

(Assume nearest neighbours affected)

$n_v \longrightarrow$ no. of vacancies

$\zeta \longrightarrow$ no. of nearest neighbours (zeta)

$$u_{per} = \frac{U_{perf}}{N} \qquad U = (N - \zeta n_v)\, u_{perf.} + \zeta n_v u_{def.}$$

$$= N u_{perf} + (u_{def.} - u_{perf})\zeta n_v$$

$$U_{def} = U_{perf} + n_v U_d$$

Vibrational freq. $\longrightarrow \nu$

Vibrational freq. $\longrightarrow \tilde{\nu}$

$N - \sum n_v \longrightarrow \nu$

$\sum n_v \longrightarrow \tilde{\nu}$

$$S_{T,def} = S_{perf} + \underbrace{3k \sum n_v \ln \frac{\nu}{\tilde{\nu}}}_{\Delta S_{vib}}$$

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

$S_{config.} \longrightarrow = k \ln \omega$

$\omega \longrightarrow$ no. of μ states for total same energy

${}^{N}C_{n_v}$: $N \longrightarrow$ no. of sites, $n_v \longrightarrow$ vacancies

$\longrightarrow$ Stirling's approximation

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

Basically, $\ln m! \approx m(\ln m - 1)$