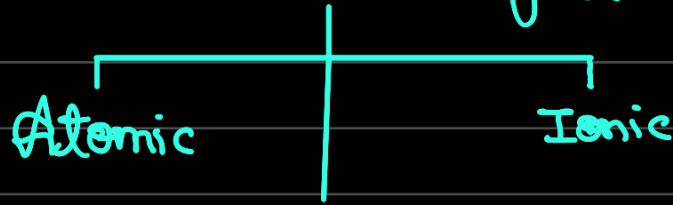


Day-24

→ Understanding device: Energy conversion and storage

→ zero-dimensional defects — clusters



Electron or hole in
a material
(electronic structure)

→ metallic crystal



Thermodynamics of point defect formation

→ Vacancies in a metallic crystal



Thermodynamic necessity *

→ perfect crystal } at a particular
vacancy in some region } $T > 0$

* lower Helmholtz
or Gibb's Free
Energy

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

$T \rightarrow \min. F \quad (\text{Helmholtz Free energy})$

$P \rightarrow \min. \text{Enthalpy } (H)$

$= U - TS$

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

→ Vibrational entropy

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

(mass spring system — coupled oscillators)

→ only one vibrational frequency assumed

$N \rightarrow$ no. of atoms

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

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

(Assume nearest neighbours affected)

$n_v \rightarrow$ no. of vacancies

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

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

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

$$U_{\text{def}} = U_{\text{perf}} + n_v u_d$$

vibrational freq. $\rightarrow \nu$

vibrational freq. $\rightarrow \tilde{\nu}$

$N - \zeta_{n_v} \rightarrow \nu$

$\zeta_{n_v} \rightarrow \tilde{\nu}$

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

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

$N \rightarrow$ no. of sites

$\zeta_{n_v} \rightarrow$ vacancies

$$= k \ln \omega$$

no. of ω states
for total same
energy

\rightarrow Stirling's approximation

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

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