Concentration of Point Defects
- need some thermodynamics ≡ science of observation
"energy" tends towards a minimum
"entropy" randomness tends towards a maximum
type of energy depends on variables controlled
e.g. can't control both P & V (one or the other)
usually control P
also, usually control T \[ \Rightarrow \] Gibbs free energy
\[ G = E + PV - TS \]  entropy
↑ absolute temp

• point defects: ↑ S and ↓ G ⇒ must occur un
some concentration until ↑ E too much.
Compare two possible configurations at same P & T
  e.g. with & without point defects
pick lower G configuration

\[ \Delta G = \Delta E + P\Delta V - T\Delta S \]

\[ \Delta H \quad \text{since } \Delta V \approx 0 \text{ for solids, } \Delta H \approx \Delta E \]

Point defects
  * wrong # of chemical bonds \( \Rightarrow \Delta E \uparrow \)
  * increase in randomness \( \Rightarrow \Delta S \uparrow \)

\[ S = k_b \ln \Omega \]
\( \Omega \) = # of equivalent but distinguishable ways the system can be arranged

\[ \] equivalent, but not distinguishable

\[ \] distinguishable, but not equivalent

\[ \] distinguishable & equivalent

Want to evaluate \( \Omega \) for an arbitrary number of vacancies.

Assumption:
  only source of entropy is configurational

Other possibilities: vibrational, electronic
1 vacancy amongst a total of \( N_0 \) sites:
\[ \Rightarrow \xi_1 = N_0 \]

2 vacancies amongst \( N_0 \) sites:
\[ \Rightarrow \xi_2 = \frac{N_0 (N_0 - 1)}{2} \]
only \( \frac{1}{2} \) are distinguishable.

3 vacancies:
\[ \Rightarrow \xi_3 = \frac{N_0 (N_0 - 1)(N_0 - 2)}{2 \cdot 3} \]

\( \eta_v \) vacancies:
\[ \Rightarrow \xi_v = \frac{(N_0 \eta_v - 1)...(N_0 - \eta_v)}{\eta_v^!} = \frac{N_0^!}{(N_0 \eta_v)! \eta_v^!} \]

\( n_a \) occupied sites

\[ G = G_0 + \Delta H_v \eta_v - k_b T \ln \left( \frac{N_0^!}{n_a^! n_v^!} \right) \]

with \( \eta_v \) without vacancy

system will spontaneously create vacancies so as to minimize \( G \)

evaluate \( \frac{\partial G}{\partial \eta_v} = 0 \) for large \( X \).

use Stirling's approximation: \( \ln X! \approx X \ln X - X \)

\[ \Rightarrow \frac{\eta_v}{(N_0 - \eta_v)^!} \propto \frac{\eta_v}{N_0^!} = \exp \left( \frac{-\Delta H_v}{k_b T} \right) \]

by concentration: \( \frac{\text{# vacancies}}{\text{# atom sites}} \)

typical metals

at RT: \( \sim 10^{-8} \)

near \( T_m \sim 10^{-3} \) \( (0.1\%) \)

also: \( \Delta H_c \gg \Delta H_v \)
\[ \frac{n_r}{N_0} = \exp \left( -\frac{\Delta H_r}{k_B T} \right) \]

\[ \ln \left( \frac{n_r}{N_0} \right) = -\frac{\Delta H_r}{k_B T} \]

\[ \ln \left( \frac{n_r}{N_0} \right) = \ln (X_v) \]

\[ (e^{-T}) \quad \frac{1}{T} \quad e^{\text{absolute temperature}} \]

Based on the assumption that all of the entropy is configurational \( \rightarrow \) randomly distributed, non-interacting defects.

Other sources of entropy, \( \Delta S_v \) per vacancy:
- vibrational
- electronic
\[ \Rightarrow \frac{n_r}{N_0} = \exp \left( \frac{\Delta S_v}{k_B} \right) \cdot \exp \left( -\frac{\Delta H_r}{k_B T} \right) \]

\[ \ln \left( \frac{n_r}{N_0} \right) = \frac{\Delta S_v}{k_B} + \frac{-\Delta H_r}{k_B T} \]

Now, intercept of above plot yields non-configurational entropy term.

Point defects influence many properties.

Mass diffusion coefficient is directly connected to point defects.

\[ \Delta G_v = \Delta H_r - T \Delta S_v - T \Delta S_{\text{config}} \]

* add to expression on middle of page 4.