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 } ⇒ Gibbs free energy

$$G = E + PV - TS$$

T — absolute temp; S — entropy

point defects: ↑S and ↓G ⇒ must occur in some concentration until ↑E too much.

Compare two possible configurations at same P & T

e.g. with & without point defects

pick lower G configuration

$$\Delta G = \underbrace{\Delta E + P\Delta V}_{\Delta H} - T\Delta S$$

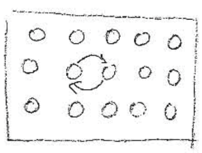
since $\Delta V \approx 0$ for solids, $\Delta H \approx \Delta E$

point defects

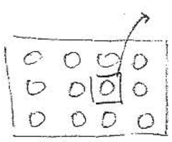
- wrong # of chemical bonds $\Rightarrow E \uparrow$
- increase in randomness $\Rightarrow S \uparrow$

$S = k_b \ln \Omega$ $\quad \Omega \equiv$ # of equivalent but distinguishable ways the system can be arranged

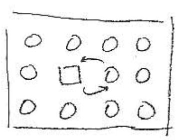
Boltzmann's const.



equivalent, but not distinguishable



distinguishable, but not equivalent



distinguishable & equivalent.

want to evaluate Ω 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:

$\Rightarrow \Omega = N_0$

2 vacancies amongst N_0 sites

$$\Rightarrow \Omega = \underbrace{N_0}_{1^{st}\ vac}\underbrace{(N_0 - 1)}_{2^{nd}\ vac} \div 2 \quad \Big\} \text{ only } 1/2 \text{ are distinguishable.}$$

3 vacancies

$$\Rightarrow \Omega = \frac{N_0(N_0-1)(N_0-2)}{2 \cdot 3}$$

n_v vacancies. $\Omega = \dfrac{(N_0)(N_0-1)\ldots(N_0-n_v+1)}{n_v!} = \dfrac{N_0!}{\underbrace{(N_0-n_v)!}_{n_a \equiv \#\text{ occupied sites}}\, n_v!}$

$$G = G_0 + \overset{\text{penalty}}{\Delta H_v \cdot n_v} - k_b \cdot T \ln\left(\frac{N_0!}{n_a!\, n_v!}\right)$$

G: with, G_0: without vacancy

system will spontaneously create vacancies so as to minimize G

evaluate $\dfrac{\partial G}{\partial n_v} = 0$

use Stirling's approximation: $\ln X! \approx X \ln X - X$ for large X.

$$\Rightarrow \frac{n_v}{(N_0-n_v)} \approx \underbrace{\frac{n_v}{N_0}}_{\text{concentration}} = \exp\left(\frac{-\Delta H_v}{k_b T}\right)$$

concentration: $\dfrac{\#\text{ vacancies}}{\#\text{ atom sites}}$.

typical metals

at RT. $\sim 10^{-8}$

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

also: $\Delta H_i >> \Delta H_v$