Entropy of mixing

Consider a solid made up of $N-t$ A atoms and t B atoms.

The number of possible configurations is

$$g(N,t) = \frac{N!}{(N-t)!\,t!} \qquad \text{KK Eq. 3.78}$$

$$\sigma(N,t) = \ln g(N,t) = \ln N! - \ln(N-t)! - \ln t!$$

using Stirling,

$$\sigma(N,t) \simeq N\ln N - N - \left[(N-t)\ln(N-t) - \cancel{N-t}\right] - \left[t\ln t - t\right]$$

$$= N\ln N - \cancel{N} - (N-t)\ln(N-t) + \cancel{N} \cancel{-t} - t\ln t \cancel{+t}$$

$$= N\ln N - (N-t)\ln(N-t) - t\ln t$$

$$= \cancel{N\ln\left(\frac{N}{N}\right)} - (N-t)\ln\left(\frac{N}{N} - \frac{t}{N}\right) - t\ln\left(\frac{t}{N}\right)$$

$$= -(N-t)\ln(1 - t/N) - t\ln(t/N)$$

with concentration $x \equiv t/N$, $\quad N = t/x \quad t = xN$

$$\sigma(x) = -N(1-x)\ln(1-x) - Nx\ln(x)$$

$$1 - x = 1 - \frac{t}{N} = \frac{N-t}{N}$$

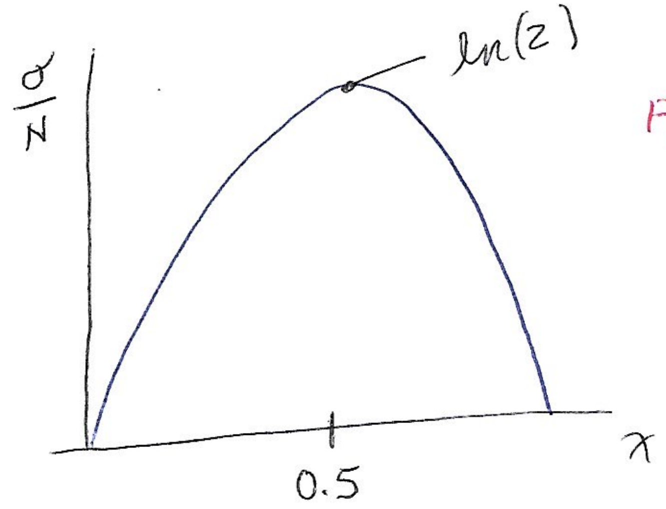
$$N(1-x)$$

$$\sigma(x) = -N\left[(1-x)\ln(1-x) + x\ln(x)\right] \qquad \text{KK Eq. 3.80}$$

Entropy of mixing for random solid solution

$$\frac{\sigma(x)}{N} = -\left[(1-x)\ln(1-x) + x\ln(x)\right]$$

x	$\sigma(x)/N$
0.00	0
0.25	0.562
0.50	0.693
0.75	0.562
1.00	0



KK Fig 3.10

Does the entropy of mixing help to mix the atoms?

$$F = U - \tau\sigma, \text{ so } \Delta F = F - F_0 = \Delta U - \tau\Delta\sigma$$

Assumme that the bonding energies are the same,

$U_{AA} = U_{BB} = U_{AB}$, then $\Delta U = 0$

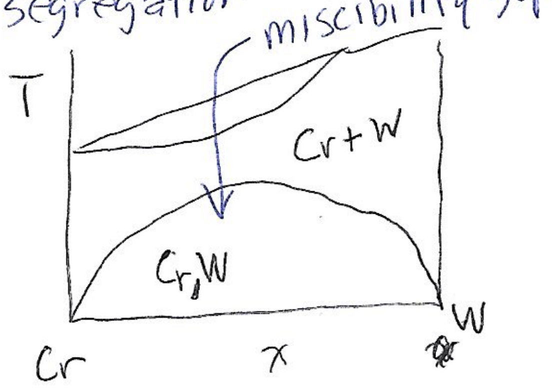
$$F = F_0 - \tau\Delta\sigma$$ KK Eq. 3.81

Since $\Delta\sigma > 0$, $F \leq F_0$, so entropy of mixing helps to stabilize the random solid solution

But nature is a fight between energy and entropy.

$(U_{AA}U_{BB})^{1/2} >> U_{AB}$

segregation

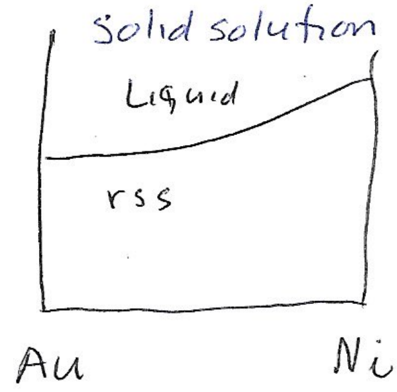


$(U_{AA}U_{BB})^{1/2} << U_{AB}$

ordering

$(U_{AA}U_{BB})^{1/2} \approx U_{AB}$

solid solution



Also notice that if $x << 1$, then

$$\frac{\sigma(x)}{N} \simeq -\left[\cancel{(1)\ln(1)} + x\ln(x) \right]$$

This has a minimum at composition $\frac{\partial \sigma(x)}{\partial x} = 0$

$$-\frac{\partial}{\partial x} x\ln(x) = +\left[x\frac{\partial}{\partial x}\ln(x) + \ln(x)\frac{\partial x}{\partial x} \right] = 0$$

$$= +\left[\frac{x}{x} + \ln(x) \right] = 0$$

$$\Rightarrow \ln(x) = -1 \Rightarrow x = e^{-1} \neq 0 \text{ !}$$

$$\frac{\partial F}{\partial x} = \frac{\partial}{\partial x}\left[N\left(Ux + x\ln(x)\tau\right] \right. = 0$$

KK Eq. 3.85

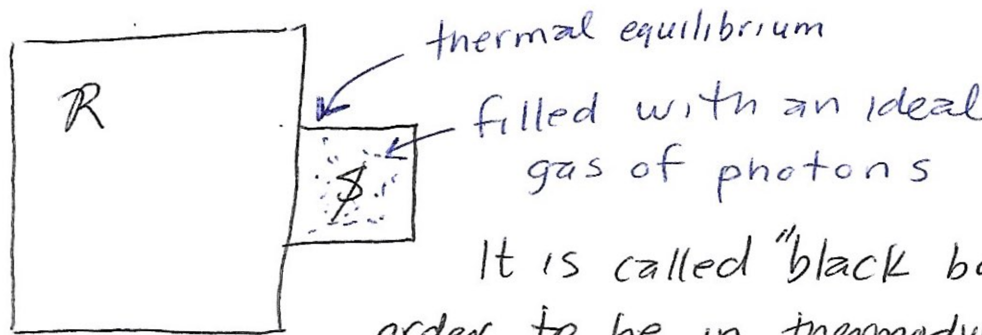
$$\frac{\partial F}{\partial x} = NU + N\tau(\ln(x)+1) = N(U + \tau\ln x + \tau) = 0$$

$$\cancel{x}\ln x = -\frac{(U+\tau)}{\tau} = -\frac{U}{\tau} - 1$$

$$x = e^{-1}e^{-U/\tau}$$ KK Eq. 3.86

You can't have a perfectly pure substance. Nature does not let you.

The Planck distribution describes the spectrum of the electromagnetic radiation in thermal equilibrium with a cavity, usually called ~~a~~ black body radiation.



It is called "black body" because, in order to be in thermodynamic equilibrium, the number of "particles" has to be conserved. Since no radiation escapes, the body is black.

The light spectrum of the Sun (and other stellar bodies) is very close to being the spectrum of a black box. That is because the photons inside the sun are in thermal equilibrium and only a tiny fraction escapes per unit time, so the number of particles is approximately conserved. The particles that do escape are representative of the particles in the box/sun.

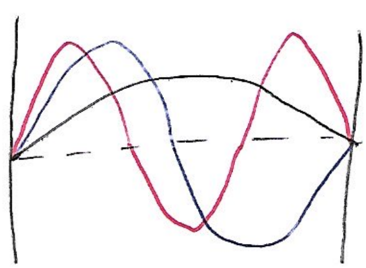
Photons are quantized, they energies are in integer multiples of $\hbar\omega = 2\pi f \hbar$. They interact with each other only very rarely, so in practice you can have many photons in the same energy state. if the number of photons is "s" in a given energy state, then the energy of that energy state is $\varepsilon_s = s\hbar\omega$.

KK Eq 4.1

This is the same as the energy for a harmonic oscillator (Pb. 3 from KK).

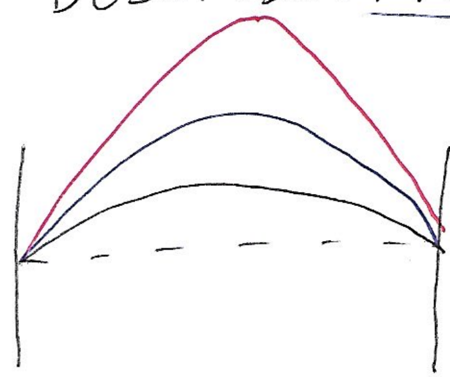
Mathematically, they are the same, but the physical processes are different!

DESCRIBES SOLIDS



Harmonic oscillator is localized, accomodates energy by increasing its frequency, "s" is the energy state or orbital. (quantum number)

DESCRIBES RADIATION



Electromagnetic waves (photons) are delocalized and can have "s" photons in energy state $\hbar\omega$. (mode)

Let's calculate the partition function Z of a photon gas in thermodynamic equilibrium.

$$Z(\tau) = \sum_s \exp(-\varepsilon_s/\tau) = \sum_{s=0}^{\infty} \exp(-s\hbar\omega/\tau)$$

KK Eq. 4.2

Let $\beta = \hbar\omega/\tau$, then $Z = \sum_{s=0}^{\infty} e^{-s\beta}$

$$Z = e^{0} + e^{-\beta} + e^{-2\beta} + \ldots$$

$$Z = 1 + e^{-\beta} + e^{-2\beta} + \ldots$$

$$Z - 1 = e^{-\beta} + e^{-2\beta} + e^{-3\beta} + \ldots$$

But also, $Z e^{-\beta} = e^{-\beta} + e^{-2\beta} + e^{-3\beta} + \ldots$

Hence, $Z e^{-\beta} = Z - 1 \Rightarrow Z e^{-\beta} - Z = -1 \Rightarrow Z(e^{-\beta} - 1) = -$

$$Z = -\frac{1}{e^{-\beta} - 1} = +\frac{1}{+(1 - e^{-\beta})} = \frac{1}{1 - \exp(-\hbar\omega/\tau)}$$

KK Eq. 4.3

The probability that the system is in the state "s" of energy $s\hbar\omega$ is given by the Boltzmann factor

$$P(s) = \frac{\exp(-s\hbar\omega/\tau)}{Z}$$ KK Eq. 4.4

So the thermal average of "s" is

$$\langle s \rangle = \sum_{s=0}^{\infty} s\,P(s) = Z^{-1} \sum_{s=0}^{\infty} s \exp(-s\hbar\omega/\tau)$$ KK Eq. 4.5

$$\langle s \rangle = (1 - e^{-\beta}) \sum_{s=0}^{\infty} s\, e^{-s\beta}$$

Let $u = -s\beta$

chain rule

$$\frac{d}{d\beta} e^{-s\beta} = \frac{de^{u}}{du}\cdot\frac{du}{d\beta} = e^{u}\frac{d}{d\beta}(-s\beta) = e^{u}(-s) = -se^{-s\beta}$$

so $-\frac{de^{-s\beta}}{d\beta} = se^{-s\beta}$ and $\langle s\rangle = (1-e^{-\beta})\sum_{s=0}^{\infty}\left(-\frac{de^{-s\beta}}{d\beta}\right)$

KK uses $y \equiv \hbar\omega/\tau$

$$\langle s\rangle = (1-e^{-\beta})\left[-\frac{d}{d\beta}\underbrace{\sum_{s=0}^{\infty} e^{-s\beta}}_{\text{same as partition function } (1-e^{-s\beta})^{-1}}\right]$$

$$\langle s\rangle = (1-e^{-\beta})\left[-\frac{d}{d\beta}(1-e^{-s\beta})^{-1}\right]$$

Let $u = 1-e^{-\beta}$

chain rule

$$\frac{d}{du}(u^{-1})\cdot\frac{du}{d\beta} = +u^{-2}\frac{d}{d\beta}(1+e^{-\beta}) = -(1-e^{-\beta})^{-2}e^{-\beta}$$

$$\langle s\rangle = (1-e^{-\beta})\left\{+\left[+(1-e^{-\beta})^{-2}e^{-\beta}\right]\right\} = \frac{\cancel{(1-e^{-\beta})}\,e^{-\beta}}{(1-e^{-\beta})^{\cancel{2}}}$$

$$\langle s\rangle = \frac{e^{-\beta}}{1-e^{-\beta}} \qquad \langle s\rangle = \frac{\frac{e^{-\beta}}{e^{-\beta}}}{\frac{1}{e^{-\beta}}-\frac{e^{-\beta}}{e^{-\beta}}} = \frac{1}{e^{\beta}-1}$$

$$\boxed{\langle s\rangle = \frac{1}{\exp(\hbar\omega/\tau)-1}}$$

Planck distribution function!

KK Eq. 4.6