Chemical equilibrium

Suppose $n_1 A_1 + n_2 A_2 \leftrightarrow n_3 A_3$

chemical reaction among species A_1, A_2, A_3

What determines equilib concentrations of A_1, A_2, A_3?

Consider total entropy as function of N_1, N_2, N_3

numbers of A_1, A_2, A_3

$S(N_1, N_2, N_3)$ $\quad$ N_i adjust to maximize S

$$dS = 0 = \sum_i \frac{\partial S}{\partial N_i} dN_i = \sum_i -\frac{\mu_i}{T} dN_i$$

(all species in equilib at common T)

Now if ~~changes by~~ N_3 decreases ~~by~~ $-dN$

Then N_1 and N_2 increase by $\frac{n_1}{n_3} dN$ and $\frac{n_2}{n_3} dN$

respectively.

or if

$$dN_3 = -n_3 dN$$
$$dN_1 = n_1 dN$$
$$dN_2 = n_2 dN$$

So

$$-\frac{\mu_1}{T} dN_1 - \frac{\mu_2}{T} dN_2 - \frac{\mu_3}{T} dN_3 = 0$$

$$\Rightarrow \mu_1 n_1 + \mu_2 n_2 - \mu_3 n_3 = 0$$

$$\boxed{\mu_1 n_1 + \mu_2 n_2 = \mu_3 n_3}$$

atom + photon $\leftrightarrow$ atom

$$\Rightarrow \mu_{atom} + \mu_{photon} = \mu_{atom} \Rightarrow \mu_{photon} = 0$$

Specific Heat of a Solid – Ionic Contribution   Debye Model

Classical Law of Dulong + Petit

$6N$ harmonic degrees of freedom – $\begin{cases} 3N \text{ momenta} \\ 3N \text{ normal coords} \end{cases}$

$$C_V = (6N)\left(\tfrac{1}{2}k_B\right) = 3Nk_B \quad \Rightarrow \quad \frac{C_V}{V} = 3k_B n \qquad n = \frac{N}{V}$$

In QM treatment, the $3N$ momenta + $3N$ normal coords can be thought of as $3N$ harmonic oscillators. These oscillations are the sound waves of vibration in the solid. We can approx their dispersion relation as

$$\omega = c_s |\vec{k}| \qquad \vec{k} \text{ is wave vector}$$

3 polarizations at each $\vec{k}$: $s = \begin{cases} L & \text{longitudinal mode, ion displacement} \parallel \vec{k} \\ T_1, T_2 & \text{transverse modes, ion displacement} \perp \vec{k} \end{cases}$

For a solid of volume V, the only sound modes are those that obey periodic boundary conditions

$$\mu = x, y, z \qquad k_\mu L = 2\pi n_\mu \qquad n_\mu = 0, 1, 2, \ldots \text{ integer}$$

ie $\frac{L}{\lambda} = n$ integer

$$\vec{k} = \frac{2\pi}{L}\vec{m}$$

The total number of sound modes = total number of oscillators $= 3N$. This sets an upper bound on $|\vec{k}|$

$$3N = \underbrace{3}_{\text{3 polarizations for each } \vec{k}} \sum_{|\vec{k}| < k_{max}} 1 = 3\frac{V}{(2\pi)^3}\int_{|\vec{k}|<k_{max}} d^3k = \frac{3V}{(2\pi)^3}\int_0^{k_{max}} dk\, 4\pi k^2$$

Assume all 3 polarizations have same sound speed c_s

$$3N = \sum_s \sum_{\vec{k}} = 3 \sum_{|\vec{k}| < k_{max}} = 3 \frac{V}{(2\pi)^3} \int_{|\vec{k}|<k_{max}} d^3 k$$

$$\frac{1}{(\Delta k)^3} = \frac{V}{(2\pi)^3}$$

$$\Rightarrow 3N = \frac{3V}{(2\pi)^3} \int_0^{k_{max}} dk\, 4\pi k^2 = \frac{3V}{(2\pi)^3} \frac{4\pi}{3} k_{max}^3$$

ion density $n = \frac{N}{V} = \frac{k_{max}^3}{6\pi^2}$

Call $\omega_{max} = c_s k_{max}$ $\qquad \omega_{max}$ = Debye freq

$k_B \Theta_D = \hbar \omega_{max}$ $\qquad \Theta_D$ = Debye temperature

$$\omega_{max}^3 = 6\pi^2 c_s^3 n \qquad \Theta_D = \frac{\hbar c_s}{k_B} (6\pi^2 n)^{1/3} \sim 200\text{-}300°K$$

Now $\langle E \rangle = \sum_s \sum_{\vec{k}} \hbar \omega_s(k) \left[\langle n_{sk} \rangle + \frac{1}{2} \right]$

boson occupation factor

$$C_V = \frac{\partial \langle E \rangle}{\partial T} = \sum_s \sum_k \frac{\partial}{\partial T} \left(\frac{\hbar \omega_s(k)}{e^{\beta \hbar \omega_s(k)} - 1} \right)$$

$$= \frac{\partial}{\partial T} \left(\frac{3 \hbar c_s}{(2\pi)^3} V \int_0^{k_{max}} dk\, 4\pi k^2 \frac{k}{e^{\beta \hbar c_s k} - 1} \right)$$

$$= \frac{\partial}{\partial T} \left(\frac{3 \hbar c V}{2\pi^2} \int_0^{k_{max}} dk \frac{k^3}{e^{\beta \hbar c_s k} - 1} \right)$$

$$\frac{C_V}{V} = \frac{3\hbar c_s}{2\pi^2}\int_0^{k_{max}} dk \; \frac{k^3 \left(\frac{\hbar c_s k}{k_B T^2}\right) e^{\beta\hbar c_s k}}{\left(e^{\beta\hbar c_s k}-1\right)^2}$$

$$= \frac{3\,(\beta\hbar c_s)^2 k_B}{2\pi^2}\int dk \, \frac{k^4 e^{\beta\hbar c_s k}}{\left(e^{\beta\hbar c_s k}-1\right)^2}$$

$$= \frac{3k_B}{2\pi^2}\left(\frac{1}{\hbar c_s \beta}\right)^3 \int_0^{x_{max}} dx \, \frac{x^4 e^x}{(e^x-1)^2} \qquad x_{max} = \frac{\hbar c_s k_{max}}{k_B T} = \frac{\theta_D}{T}$$

use $\theta_D = \frac{\hbar \omega_{max}}{k_B} \Rightarrow \theta_D^3 = \frac{\hbar^3 \omega_{max}^3}{k_B^3} = \frac{\hbar^3 6\pi^2 c_s^3 n}{k_B^3}$

$$\Rightarrow \frac{\hbar^3 c_s^3}{k_B^3} = \frac{\theta_D^3}{6\pi^2 n}$$

$$\frac{C_V}{V} = \frac{3}{2\pi^2} k_B \, 6\pi^2 n \left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} dx \, \frac{x^4 e^x}{(e^x-1)^2}$$

$$\frac{C_V}{V} = 9 n k_B \left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} dx \, \frac{x^4 e^x}{(e^x-1)^2}$$

limits: $T \to \infty$ so θ_D/T is small, integrand can be expanded for small x

$$\frac{x^4 e^x}{(e^x-1)^2} \approx \frac{x^4}{x^2} = x^2$$

$$\int_0^{\theta_D/T} dx \, x^2 \simeq \frac{1}{3}\left(\frac{\theta_D}{T}\right)^3 \Rightarrow \frac{C_V}{V} = 9 n k_B \left(\frac{T}{\theta_D}\right)^3 \cdot \frac{1}{3}\left(\frac{\theta_D}{T}\right)^3$$

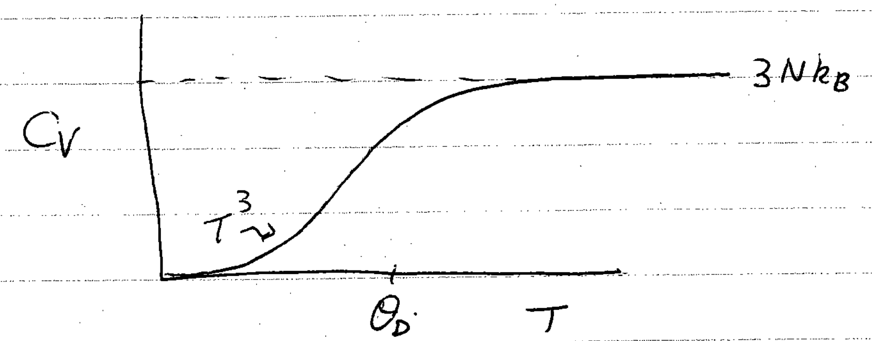
$= 3 n k_B$ classical result!

low T

$$\frac{C_V}{V} \simeq 9 n k_B \left(\frac{T}{\Theta_D}\right)^3 \underbrace{\int_0^\infty dx \; \frac{x^4 e^x}{(e^x-1)^2}}_{\text{do integral}}$$

$$= \frac{12\pi^4}{5} n k_B \left(\frac{T}{\Theta_D}\right)^3 \qquad \frac{4}{15}\pi^4$$

$\frac{C_V}{V} \propto T^3$ at low temperatures



Originally Einstein treated this problem quantum mechanically assuming constant frequencies of vibration

$\omega = \omega_0$ all modes.

Gave exponentially decreasing C_V at low T.
Debye mode is more physical.

Black Body Radiation

Cavity radiation — a volume V at fixed temp T absorbs + emits electromagnetic radiation. What are characteristics of this equilib radiation at fixed T?

EM waves with wave vector $\vec{k}$, freq $\omega = c|\vec{k}|$
two transverse polarizations for each $\vec{k}$.

Regard each mode as an oscillator. If excited to energy level n, the energy in the oscillator is

$$\epsilon = n\hbar\omega = n\hbar c k \Rightarrow n \text{ "photons" in this mode}$$

average energy in a given mode is therefore

$$\langle\epsilon\rangle = \hbar\omega\langle n\rangle = \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}$$

(ignore ground state energy $\frac{1}{2}\hbar\omega$ as it is T-indep constant)

For a volume $V=L^3$, periodic boundary conditions give the allowed wave vectors $\vec{k} = \frac{2\pi}{L}\vec{m}$ $\quad m_x, m_y, m_z$ integers

Density of states $g(\omega)$

two polarizations for each $\vec{k}$

$$\int g(\omega)\,d\omega = 2\sum_{\vec{k}} = \frac{2V}{(2\pi)^3}\int d^3k$$

$$\Rightarrow g(\omega)\,d\omega = \frac{2V}{(2\pi)^3}4\pi k^2 dk = \frac{V}{\pi^2}\frac{\omega^2 d\omega}{c^3}$$

$$g(\omega) = \frac{V\omega^2}{\pi^2 c^3}$$

average energy per volume at freq ω is

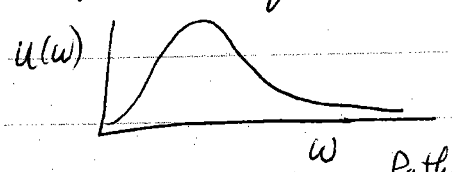
\# modes at freq ω

average energy in a given mode at freq ω

$$u(\omega) = \frac{g(\omega)}{V}\left(\frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\right)$$

$$u(\omega) = \frac{\hbar\,\omega^3}{\pi^2 c^3\,(e^{\beta\hbar\omega}-1)}$$ ← Black Body Spectrum

Plancks formula



Pathria fig 7.7

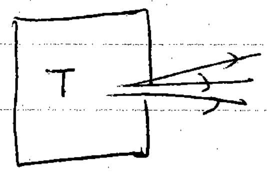
<u>Total energy density</u>

$$\frac{U}{V} = \int_0^\infty u(\omega)\,d\omega = \frac{\hbar}{\pi^2 c^3}\int_0^\infty d\omega\,\frac{\omega^3}{e^{\beta\hbar\omega}-1}$$

$$= \frac{\hbar}{\pi^2 c^3}\,\frac{1}{(\beta\hbar)^4}\underbrace{\int_0^\infty dx\,\frac{x^3}{e^x-1}}_{\frac{\pi^4}{15}} \qquad x = \beta\hbar\omega$$

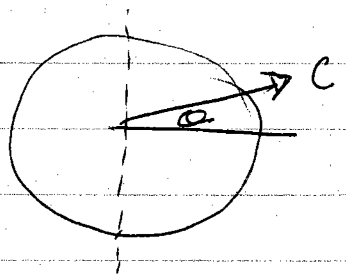
$$\frac{U}{V} = \left(\frac{\pi^2 k_B^4}{15\,\hbar^3 c^3}\right)T^4$$

- energy flux from a cavity, exiting from a hole



flux $\mathcal{F} = \left(\frac{U}{V}\right) c \; \langle \cos\theta \rangle$

$\left(\frac{U}{V}\right)$: energy density; c: speed; $\langle \cos\theta \rangle$: projection of velocity in outwards direction



$$\langle \cos\theta \rangle = \frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^{\pi/2} d\theta \, \sin\theta \cos\theta$$

← only in outward direction

$$= \frac{2\pi}{4\pi} \left(\frac{\sin^2\theta}{2} \right)_0^{\pi/2} = \frac{1}{4}$$

- $$\mathcal{F} = \left(\frac{U}{V}\right) \frac{c}{4} = \sigma T^4$$ ← Stefan Boltzman Law

where $\sigma = \dfrac{\pi^2 k_B^4}{60 \hbar^3 c^2} = 5.7 \times 10^{-8} \dfrac{W}{m^2 \cdot {}^\circ K^4}$

σ: Stefan's constant

We also have

$$\frac{pV}{k_B T} = \ln \mathcal{Z} = -\sum_k 2 \ln\left(1 - e^{-\beta \epsilon_k}\right)$$

2: polarizations

$$= -\frac{2V}{(2\pi)^3} \int dk \, 4\pi k^2 \ln\left(1 - e^{-\beta \hbar c k}\right)$$

$$= -\int_0^\infty d\omega \, g(\omega) \ln\left(1 - e^{-\beta \hbar \omega}\right)$$

$$= -\frac{V}{\pi^2 c^3} \int_0^\infty d\omega \, \omega^2 \ln\left(1 - e^{-\beta \hbar \omega}\right)$$