Excitation, ionisation and gas thermodynamical properties

thermodynamics

Recap of statistical physics

If N particles of total energy E on N_r levels of energy E_r

$$N = \sum_r N_r$$

$$E = \sum_r N_r E_r$$

The distribution of particles is such that

$$N_R = \frac{g_r}{e^{-\psi + \frac{E_r}{kT}} + \alpha}$$

g_r = statistical weight of level r (n° of internal freedom degrees)

ψ = degeneracy parameter

if $\alpha = 0$ $\longrightarrow$ Boltzmann
if $\alpha = -1$ $\longrightarrow$ Bose-Einstein statistics
if $\alpha = +1$ $\longrightarrow$ Fermi-Dirac

$\alpha = -1$: 0 spin or integer spin (photons, mesons, π, α-particles)

$\alpha = +1$: half-integer spin = e^-, e^+, protons, neutrons

ψ degeneracy parameter is such that $\psi = \frac{\mu}{kT}$, μ chemical potential

$$\mu_i \equiv \left(\frac{\partial U}{\partial N_i}\right)_{S,V}$$

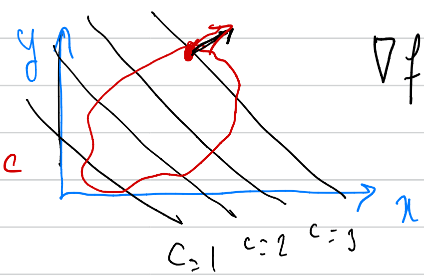
For $\psi \ll -1$ Bosons – Einstein
and Fermi – Dirac
converge to Boltzmann given $e^{-\psi + E_r/kT} \gg 1$

Remarque on the lagrange multiplier

When looking for a maximum of a function under certain conditions, one can introduce a lagrange multiplier which expresses this condition. The chemical potential is a lagrange multiplier. It impose a total number of particles on the distribution. Temperature is another one, which contrains the total energy.

$f(x,y)$

$g(x,y) = c$



$$\nabla f = \lambda \nabla g$$

Thermodynamic equilibrium

- Thermodynamic system with one given type of particles = governed by 2 of the variables T, P, V

- Thermodynamic system with a variety i of number of particles N_i

$U = U(S, V, N_i)$

$$\Rightarrow \quad dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \sum_i \underbrace{\left(\frac{\partial U}{\partial N_i}\right)_{S,V}}_{\equiv \mu_i} dN_i$$

- Thermal equilibrium : T reaches one equilibrium value

- Thermodynamical equilibrium : Thermal + chemical equilibrium

$$\sum_i \mu_i \, dN_i = 0$$

- No chemical reaction : dN_i indipendent $\Rightarrow \mu_i \, dN_i = 0 \;\; \forall i$

  and $\mu_i \neq 0 \Rightarrow dN_i = 0$, $\underbrace{\text{but for the photons}}$

  absorption
  émission

  $dN_i \neq 0 \Rightarrow \mu_i = 0$

Phase change reaction

Reaction $\sum_i \nu_i A_i = 0$

ν_i: stoichiometric coefficient

A_i: Symbol of element i

Example of ionization: $H^+ + e^- \rightleftharpoons H$

can be written $H^+ + e^- - H = 0$

$\nu_{H^+} = 1$ $\quad \nu_e = 1$ $\quad \nu_H = -1$

When ν_1 particles "1" disappear, ν_i appear
ν_1 appear, ν_i disappear

$$\Rightarrow \frac{dN_i}{\nu_i} = \frac{dN_1}{\nu_1} \Rightarrow dN_i = \frac{\nu_i}{\nu_1} dN_1$$

Given an arbitrary change dN_1; chemical equation $\sum_i \mu_i dN_i = 0$

$$\Rightarrow \sum_i \mu_i \frac{\nu_i}{\nu_1} dN_1 = \frac{dN_1}{\nu_1} \sum_i \mu_i \nu_i = 0$$

$$\Rightarrow \sum_i \mu_i \nu_i = 0$$

given $\psi_i = \frac{\mu_i}{kT}$ $\Rightarrow$ $\boxed{\sum_i \nu_i \psi_i = 0}$

Excited gas and atoms

We will infer the line intensity. For this, we need to know the population of the energy levels.

Let's consider N atoms in the energy states n, n' etc

Non degenerated particles

$$\psi \ll -1$$

$$e^{-\psi} \text{ very large} \qquad \equiv \alpha \to 0$$

$$N_n = g_n \, e^{\psi} \, e^{-E_n / kT}$$

$$\frac{N_{n'}}{N_n} = \frac{g_{n'}}{g_n} \, e^{-(E_{n'} - E_n)/kT}$$

$$N = \sum_n N_n \qquad E = \sum_n N_n E_n$$

Let's take level 1 as a reference.

$$\text{(a)} \qquad \frac{N_n}{N_1} = \frac{g_n}{g_1} \, e^{-(E_n - E_1)/kT} = \frac{g_n}{g_1} \, e^{-E_{n,1}/kT}$$

$$\text{(b)} \qquad N = \sum_n N_1 \frac{g_n}{g_1} \, e^{-E_{n,1}/kT} = \frac{N_1}{g_1} \underbrace{\sum_n g_n \, e^{-\frac{E_{n,1}}{kT}}}$$

Partition function : $u(T)$

If one wants to know the fraction of particles (atoms) in the energy level n

$$(a)+(b) \longrightarrow \frac{N_n}{N} = \frac{N_n}{N_1}\frac{N_1}{N} = \frac{g_n}{u(T)} e^{-(E_n-E_1)/kT}$$

$u(T)$ can be seen as the statiscal weight of the sample of atoms in the conditions that are considered.

- In principle one should have $u(T) \longrightarrow \infty$ given $n \longrightarrow \infty$
- $\max(E_{n,1})$ stays finite but the interactions between ions lower the continuum (ff opacity)

Let's take the example of hydrogen

$$E_n = -\frac{13.6}{n^2} \quad (eV)$$

$$\Rightarrow E_{n,1} = E_n - E_1 = 13.6 \frac{n^2-1}{n^2}$$

$$u(T) = \sum_n g_m e^{-\frac{E_{n,1}}{kT}}$$

$$= g_1 e^{-E_{1,1}/kT} + g_2 e^{-E_{2,1}/kT}$$

We can show $g_n = 2n^2$

$$\Rightarrow g_1 = 2 \quad g_2 = 8$$

$$u(T) = 2\times 1 + 8 \times \underbrace{2.7 . 10^{-9}}_{@ \cdot 6000K} \simeq 2$$

$(k = 8.617 \; 10^{-5} eV/K)$

Ionisation of gas (by collision) : Saha's law

Ionisation is achieved when a binded e^- on one energy level moves to an unbound level.

Thus kT must be at least equivalent to the excitation potential I_0

For example . $I_H = 13.6\ eV \equiv T \sim 10^5 K$.

The continuum starts above I_0

The Saha formula provides the relative concentrations of atoms in successive ionisation states. It is an extension of the Boltzmann law applied to the reaction

$$\text{neutral atom} \rightleftharpoons \text{ion} + e^-$$

let's consider n_{00}, n_{01}, and n_e → concentration of electrons

n_{00} → Concentration of neutral atoms

n_{01} → Concentration of ions

$n_{i,j}$

i → excitation level

j ← degree of ionisation

Statistical weight of neutral atom $= g_{00}$

... of e^- + ion $= g_{1e} = g_{01} \cdot g_e$

Energy of the system e^- + ion $\quad E = I_0 + \frac{p^2}{2m_e}$

We apply Boltzman at given p : $\frac{n_{01}(p)}{n_{00}} = \frac{g_{01} g_e}{g_{00}} e^{-\left(I_0 + \frac{p^2}{2m_e}\right)/kT}$

g_e ?

$$\frac{\text{available phase-space volume}}{\text{elementary phase-space cell}}$$

$$= (2s+1) \frac{d^3p\, d^3q}{h^3} \underset{s=\frac{1}{2}}{=} 2 \frac{dV\, 4\pi p^2 dp}{h^3}$$

$$dV = \frac{1}{n_e} \Longrightarrow \frac{n_{01} n_e}{n_{00}} = \frac{g_{01}}{g_{00}} \frac{8\pi p^2\, dp}{h^3} e^{-\left(I_0 + \frac{p^2}{2m_e}\right)/kT}$$

NB : The terms in e^{ψ} simplify given $\sum_i \nu_i \psi_i = 0$

$$\Longrightarrow \psi_{01} + \psi_e - \psi_{00} = 0$$

$$\left(N_r = g_r e^{\psi} e^{-E_r/kT} \right)$$

$r : 00 ; e^- ; 01$

If one wants the full population, one must sum on dp

$$\frac{n_{01}\, n_e}{n_{00}} = \frac{8\pi}{h^3} \frac{g_{01}}{g_{00}} e^{-I_0/kT} \int_0^\infty e^{-\frac{p^2}{2m_e kT}} p^2\, dp$$

we consider $$\int_0^\infty t^2 e^{-at^2} dt = \frac{1}{4a}\sqrt{\frac{\pi}{a}}$$

hence $$\int_0^\infty e^{-\frac{p^2}{2m_e kT}} p^2\, dp = \frac{\sqrt{\pi}}{4} (2 m_e kT)^{3/2}$$

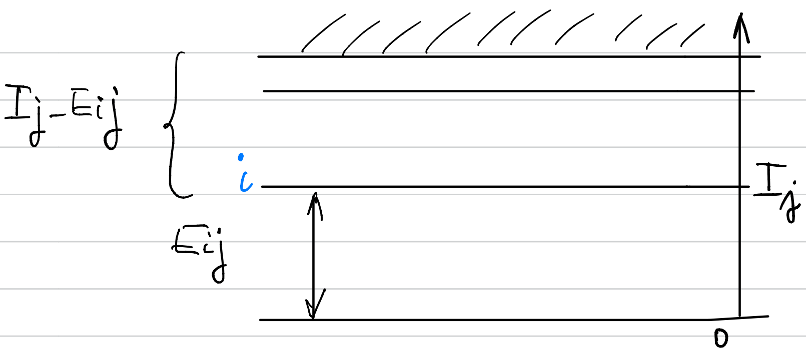
$$\boxed{\frac{n_{01}\, n_e}{n_{00}} = 2 \frac{g_{01}}{g_{00}} \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} e^{-\frac{I_0}{kT}}}$$

One can generalize to any ionisation degree $j \longrightarrow j+1$

$$\boxed{\frac{n_{0\,j+1}\, n_e}{n_{0\,j}} = 2 \frac{g_{0\,j+1}}{g_{0\,j}} \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} e^{-I_j/kT}}$$

and to any level of excitation

Saha Boltzmann $$\boxed{\frac{n_{0\,j+1}\, n_e}{n_{ij}} = 2 \frac{g_{0\,j+1}}{g_{ij}} \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} e^{-(I_j - E_{ij})/kT}}$$



E_{ij} = Excitation energy of the ion j on level i

$I_j - E_{ij}$ = ionisation potential from level $i, j \to i, j+1$

I_j ionisation potential from degree j to $j+1$

NB = ion and e^- are not bound, the free e^- can have a large range of different states.

let's express $\dfrac{n_{j+1}}{n_j}$ summed over all i

We have $\dfrac{n_i}{n} = \dfrac{g_i}{u(T)} e^{-E_i/kT}$ or $\dfrac{n_{ij}}{n_j} = \dfrac{g_{ij}}{u_j(T)} e^{-E_{ij}/kT}$

and $\dfrac{n_{0\,j+1}}{n_{j+1}} = \dfrac{g_{0\,j+1}}{u_{j+1}(T)} \underbrace{e^{-E_{0\,j+1}/kT}}_{1}$ $\longrightarrow n_{0\,j+1} = n_{j+1} \dfrac{g_{0\,j+1}}{u_{j+1}(T)}$

$$\frac{n_{0\,j+1}\, n_e}{n_{ij}} = n_{j+1} \frac{\cancel{g_{0\,j+1}}}{u_{j+1}(T)} \frac{n_e \; u_j(T)}{n_j \; \cancel{g_{ij}}} \cancel{e^{E_{ij}/kT}}$$

$$= 2 \frac{\cancel{g_{0\,j+1}}}{\cancel{g_{ij}}} \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} e^{-I_j} \cancel{e^{E_{ij}/kT}}$$

$$\boxed{\frac{n_{j+1}\, n_e}{n_j} = 2\, \frac{u_{j+1}}{u_j} \left(\frac{2\pi m_e kT}{h^2} \right)^{3/2} e^{-\frac{I_j}{kT}}}$$

Saha 1928.

We can express the formula as a function of the electronic pressure.

$$P_e = n_e kT$$

$$\frac{n_{j+1}}{n_j} = 2\, \frac{u_{j+1}}{u_j} \left(\frac{2\pi m_e}{h^2} \right)^{3/2} \frac{(kT)^{5/2}}{P_e}\, e^{-\frac{I_j}{kT}}$$

ionisation $\nearrow$ if $T \nearrow$ and if $P_e \searrow$

In logarithmic form, with χ the excitation potential in eV

$$\log\left(\frac{n_{j+1}}{n_j} P_e \right) = -\chi_j \frac{5040}{T} + \frac{5}{2} \log T - 0.48 + \log\left(2\, \frac{u_{j+1}}{u_j} \right)$$