Temperature and Atomic Spectra *

$$\frac{N_j}{N_0} = \frac{P_j}{P_0} \exp\left(-\frac{E_j - E_0}{kT}\right)$$

k = Boltzman Const

N_j = no. atoms in j^{th} state

N_0 = " " g.s.

g_i = stat. wt. of j^{th} st.

g_0 = " g.s.

E_j = Energy of j^{th} state

E_0 " " g.s.

$g = 2J + 1$

$J = L + S$ or $L - S$

L = tot. orbital A.M. quantm.

S = spin $\pm \frac{1}{2}$

Princ. QN — $N^{M}L_J$ — Multiplicity

Ex: 228.8 nm Cd line: $^1S_0 \leftarrow {^1S_1}$

in air acetylene flame $t \sim 2250$ C or 2523 K

$g_0 = 2(0) + 1 = 1$

$g_j = 2(1) + 1 = 3$

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^{10}\ \mathrm{cm\ s^{-1}}}{2.288 \times 10^{-5}\ \mathrm{cm}} = 1.310 \times 10^{15}\ \mathrm{s^{-1}}$$

$$E_j - E_0 = h\nu = (6.626 \times 10^{-27}\ \mathrm{erg\ s})(1.310 \times 10^{15}\ \mathrm{s^{-1}})$$
$$= 8.682 \times 10^{-12}\ \mathrm{erg}$$

$$N_j/N_0 = \left(\frac{3}{1}\right) \exp\left[\frac{-8.682 \times 10^{-12}\ \mathrm{erg}}{(1.38 \times 10^{-16}\ \mathrm{erg\ K^{-1}})(2523\ \mathrm{K})}\right]$$

$$= 3\, e^{-24.95} = 4.5 \times 10^{-11}$$

$\therefore$ not very many in j state.

Emission *

Intensity of emission $= I = \frac{\text{energy}}{s}$

$$I = \left(\begin{smallmatrix}\text{energy}\\ \text{per photon}\end{smallmatrix}\right)\left(\begin{smallmatrix}\text{no. atoms}\\ \text{in ex. state}\end{smallmatrix}\right)\left(\begin{smallmatrix}\text{Prob. that excited state}\\ \text{will emit in 1 sec}\end{smallmatrix}\right)$$

$$I = h\nu \left(\begin{smallmatrix}\text{no. atoms}\\ \text{per vol.}\end{smallmatrix}\right)\left(\frac{\text{Flame}}{\text{Vol}}\right)\left(\frac{N_j}{N_{TOT}}\right)(A_{nm})$$

Absorption

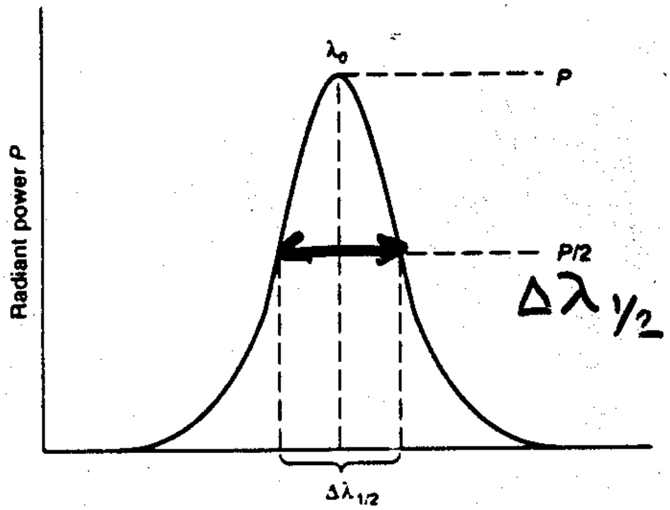
$$\frac{P}{P_0} = e^{-k \cdot (\text{no. of absorbers})} = e^{-k\left(\frac{\text{no.}}{\text{vol}}\right) \cdot \text{vol}}$$

Perturbing effects:

Doppler Broadening $\Delta\nu_0 = 7.16 \times 10^{-7}\, \nu_0 \sqrt{\frac{T}{M}}$

Pressure Broadening $\Delta\nu \propto n \underbrace{\sqrt{\frac{RT}{\mu}}}_{\text{Relative Velocity}} \underbrace{\left(\frac{\sigma + \sigma'}{2}\right)^2}_{\text{Prob. of Collision}}$

n = no vol^{-1}



8-6. FIGURE [redacted] Profile of an atomic line showing definition of the effective line width $\Delta\lambda_{1/2}$.

Ex: $Hg(g) + h\nu\,(253.7\,nm) \longrightarrow Hg^*(g) \longrightarrow Hg(g) + h\nu'$

lifetime $\approx 2 \times 10^{-8}\,s = \Delta t$

$\Delta\nu \cdot \Delta t \geq 1$ {or $h\Delta\nu \cdot \Delta t \geq h$ or $\Delta E \cdot \Delta t \geq h$}

$$\Delta\nu \sim \frac{1}{2 \times 10^{-8}\,s} = 5 \times 10^{+7}\,s^{-1}$$

Now $\nu = c\lambda^{-1}$ and $d\nu = -c\lambda^{-2}d\lambda$ so $d\lambda = \dfrac{\lambda^2 \Delta\nu}{c}$

Let $d\lambda = \Delta\lambda_{1/2}$ so

$$\Delta\lambda_{\frac{1}{2}} \simeq \frac{(253.7 \times 10^{-9}\,m)^2 \cdot (5 \times 10^{+7}\,s^{-1})}{3 \times 10^{8}\,m\,s^{-1}} = 1.1 \times 10^{-14}\,m = 1 \times 10^{-4}\,\text{Å}$$

This is the "natural line width" and is very small.

Doppler Broadening: $\Delta\nu_0 = 7.16 \times 10^{-7}\,\nu_0 \sqrt{\frac{T}{M}}$

Cf: $\frac{1}{2}mv^2 \cong kT$ or $v = \sqrt{\frac{2kT}{m}} = \text{Const}\sqrt{\frac{T}{m}}$

Pressure Broadening: $\Delta\nu \propto n' \sqrt{\frac{RT}{\mu}} \cdot \left(\frac{\sigma + \sigma'}{2}\right)^2$

no./unit vol

relative velocity

collision probability