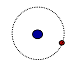
Electronic Energy Mode

- Let's begin examining internal energy of atoms/molecules by considering a monatomic gas



  - two kinds of energy/motion
    - translation and electronic which are separable, so $Q = Q_{tr}\, Q_{el}$
- Already examined translation, what about Q_{el}
- There is no general (simple) analytic model to describe the electronic energy levels and degeneracies of molecules/atoms
- Examine sum $$Q_{el} = \sum_i g_{el,i}\, e^{-\varepsilon_{el,i}/kT}$$
  - convenient to write in terms of **characteristic temperatures** for each level $\theta_{el,i} \equiv \varepsilon_{el,i}/k$ e.g., $J/(J/K) = K$

$$Q_{el} = g_0 + g_1 e^{-\theta_{el,1}/T} + g_2 e^{-\theta_{el,2}/T} + \ldots$$

Electronic Energies: Examples

- For convenience let lowest elec. energy level have "zero" elec. energy ($\theta_{el,0}$=0)

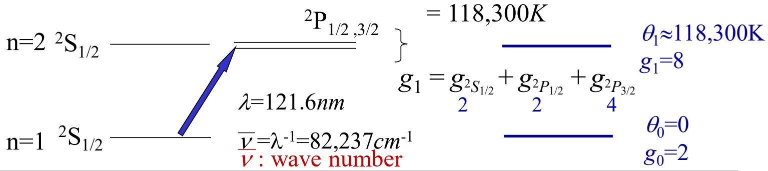
$$Q_{el} = g_0 + g_1 e^{-\theta_{el,1}/T} + g_2 e^{-\theta_{el,2}/T} + \ldots$$

N_i *essentially* 0

$$\begin{cases} T \ll \theta_{el,i} \Rightarrow g_i e^{-\theta_{el,i}/T} \approx 0 \\ T \gg \theta_{el,i} \Rightarrow g_i e^{-\theta_{el,i}/T} \approx g_i \end{cases}$$

i^{th} *level "saturated"*
(*exponential term at maximum*)

- For a great majority of atoms (and molecules) $\theta_{el,i}$ >few×10^4K for i > 1–3
- Example H atom $J = |\ell - s|, |\ell - s + 1|, \ldots \ell + s$
  - state ${}^{2s+1}\ell_J$; $g_J = 2J + 1$ $\quad \theta_1 = hc\bar{\nu}/k = 1.438 cmK\,\bar{\nu} = 118{,}300K$



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Electronic Energies: Examples

- Example H atom (con't)

$$Q_{el,H} \approx 2 + 8e^{-118{,}300K/T}$$

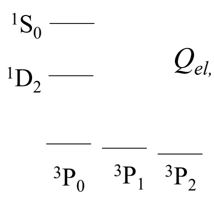
T (K)	$Q_{el,\mathrm{H}}$	$E_{el,\mathrm{H}}/Nk$ (K)
300	2.00	3×10^{-166}
5000	2.00	3×10^{-5}
20,000	2.02	1263

  – so $Q_{el,\mathrm{H}} \approx 2$ for most T of interest *Most H stay in ground elec. level*

  – and $E_{\mathrm{el}}/N = kT^2 \dfrac{1}{Q_{el}}\dfrac{\partial Q_{el}}{\partial T} \approx \dfrac{k}{2}\left(9.5\times10^5\,K\,e^{-118{,}300K/T}\right)$ *but small change in Q can be signif. on E*

- Example O atom

  – 4 outer shell electrons, more complex structure



$$\begin{array}{ccccc} {}^3P_2 & {}^3P_1 & {}^3P_0 & {}^1D_2 & {}^1S_0 \end{array}$$

$$Q_{el,O} = g_0 + g_1 e^{-\theta_1/T} + g_2 e^{-\theta_2/T} + g_3 e^{-\theta_3/T} + g_4 e^{-\theta_4/T} + \ldots$$

$$\approx\ 5 + 3e^{-227.6K/T} + e^{-326.4K/T} + 5e^{-22{,}818K/T} + e^{-48{,}594K/T}$$

Energies from physics.nist.gov/PhysRefData/Handbook/Tables/oxygentable5.htm

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Electronic Energies: Examples

- Example O atom (con't)

$$Q_{el,O} \approx 5 + 3e^{-227.6K/T} + e^{-326.4K/T} + 5e^{-22{,}818K/T} + e^{-48{,}594K/T}$$

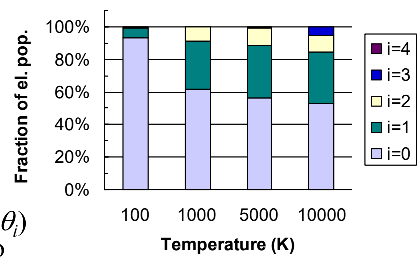
T(K)	$Q_{el,\mathrm{O}}$
100	5.35
1000	8.11
5000	8.86
10,000	9.41

$$f_i = \frac{g_i e^{-\theta_i/T}}{Q}$$

  – low T: ground level (i=0) contributes most to Q_{el}

  – medium T (~100-5000K): 1st three levels (i=0–2) have most of population (>99.5%)

  – med.-high T (~4000-7000K): i=0–2 nearly "saturated" ($T \gg \theta_i$) and i=4 nearly unpopulated, so could use



$$Q_{el,O} \approx 9 + 5e^{-22{,}818K/T}$$

approximating Q_{el} with quasi-two level electronic model

Electronic Energy: 2-Level Model

- Simple to examine a 2-level model analytically

$$Q_{el} = g_0 + g_1 e^{-\theta_1/T}$$

- For total electronic energy we have

$$E_{el} = NkT^2 \frac{1}{Q_{el}} \frac{\partial Q_{el}}{\partial T} = NkT^2 \frac{1}{\sum g_i e^{-\theta_i/T}} \frac{\partial\left(\sum g_i e^{-\theta_i/T}\right)}{\partial T}$$

  – but simpler approach, (no derivatives)

$$E = \sum N_i \varepsilon_i = N \sum \frac{g_i e^{-\theta_i/T}}{Q} k\theta_i$$

  – for 2 levels $E_{el} = Nk\theta_1 \dfrac{g_1 e^{-\theta_1/T}}{g_0 + g_1 e^{-\theta_1/T}}$

$$G \equiv (g_1/g_0) e^{-\theta_1/T}$$

$$e_{el} = R\theta_1 \frac{G}{1+G} \quad \Rightarrow c_{v_{el}} = R\left(\frac{\theta_1}{T}\right)^2 \frac{G}{(1+G)^2}$$

2-Level Elec.

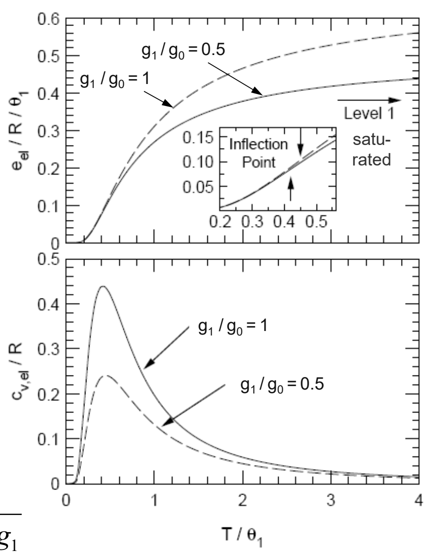
- Normalized values

$$\frac{e_{el}}{R\theta_1} = \frac{G}{1+G}$$

$$\frac{c_{v_{el}}}{R} = \left(\frac{\theta_1}{T}\right)^2 \frac{G}{(1+G)^2}$$

- Specific heat initially 0, rises, drops back to 0
  – why?
    - 2-level e_{el} "limited"

$$f_{1_{max}} = \frac{g_1}{g_0 + g_1}$$



Entropy of Electronic Energy Mode

- From entropy for internal mode (recall ln$N$ and 1 term associated with S_{tr}) $S_{el} = Nk\ln Q_{el} + \frac{E_{el}}{T}$
- For 2-level model

$$S_{el} = Nk\left[\ln\left(g_0 + g_1 e^{-\theta_1/T}\right) + \frac{\theta_1}{T}\frac{g_1 e^{-\theta_1/T}}{g_0 + g_1 e^{-\theta_1/T}}\right]$$

– for $Q \sim g_0$ ($T<\theta_1$)

$$S_{el} = Nk\left[\ln g_0 + \frac{\theta_1}{T}\frac{g_1}{g_0}e^{-\theta_1/T}\right]$$

change in S_{el} dominated by energy term