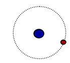
Electronic Energy Mode



- For example, consider monatomic gas
  - two kinds of energy/motion
    - translation and electronic

$$Q = Q_{tr} Q_{el}$$

- 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)

$$Q_{el} = g_0 e^{-\theta_{el,0}/T} + g_1 e^{-\theta_{el,1}/T} + g_2 e^{-\theta_{el,2}/T} + \ldots$$

Copyright © 2009 by Jerry M. Seitzman. All rights reserved.

Electronic Energies

- 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*

$$\begin{cases} T << \theta_{el,i} \Rightarrow g_i e^{-\theta_{el,i}/T} = 0 \\ T >> \theta_{el,i} \Rightarrow g_i e^{-\theta_{el,i}/T} = g_i \end{cases}$$

i^{th} *level "saturated" ("maxed out")*

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

$$\theta_1 = hc\bar{\nu}/k = 1.438 cmK\,\bar{\nu} = 118{,}300K$$

n=2 $^2S_{1/2}$ $^2P_{1/2,3/2}$

$$g_1 = g_{^2S_{1/2}} + g_{^2P_{1/2}} + g_{^2P_{3/2}}$$

θ_1≈118,300K
g_1=8

$\lambda = 121.6nm$

n=1 $^2S_{1/2}$

$$\bar{\nu} = \frac{1}{\lambda} = 82{,}237 cm^{-1}$$

θ_0=0
g_0=2

Copyright © 2009 by Jerry M. Seitzman. All rights reserved.

Electronic Energies

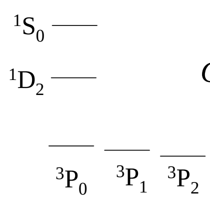
- Example H atom (con't)

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

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

  - so $Q_{el,H}\approx 2$ for most T of interest *Most H stay in ground elec. level*
  - $E_{el}/N = kT^2 \dfrac{1}{Q_{el}}\dfrac{\partial Q_{el}}{\partial T} \approx k\dfrac{1}{2}\left(9.5\times10^5 K\, e^{-118{,}300K/T}\right)$ *but small change in Q can be signif. on E*

- Example O atom
  - 4 outer shell electrons, more complex structure



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

$$Q_{el,O} = g_0 + g_1 e^{-\frac{\theta_1}{T}} + g_2 e^{-\frac{\theta_2}{T}} + g_3 e^{-\frac{\theta_3}{T}} + g4e^{-\frac{\theta_4}{T}} + \ldots$$

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

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

Copyright © 2009 by Jerry M. Seitzman. All rights reserved.

Electronic Energies

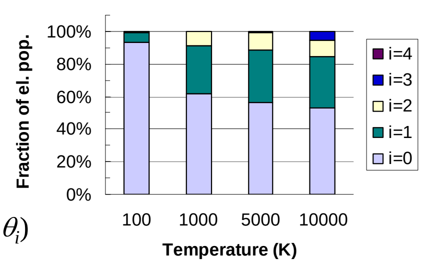
- Example O atom (con't)

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

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

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

  - low T: ground level (i=0) contributes most to Q_{el}
  - med T (~100-5000K): 1st three levels (i=0–2) have most of population
  - med. high T: i=0–2 nearly "saturated" (T>>θ_i) and i=4 nearly unpopulated



$$Q_{el,O} \approx 9 + 5e^{-\frac{22{,}818K}{T}}$$ **quasi-two level electronic model**

Copyright © 2009 by Jerry M. Seitzman. All rights reserved.

Georgia Tech College of Engineering School of Aerospace Engineering

Electronic Energy: 2-Level Model

- With only two energy levels, we can write

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

- For total elec. 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, (no derivs.)

$$E_{el} = \sum N_i \varepsilon_i = N\sum \frac{g_i e^{-\theta_i/T}}{Q} k\theta_1$$

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

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

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

Copyright © 2009 by Jerry M. Seitzman. All rights reserved.

Georgia Tech College of Engineering School of Aerospace Engineering

2-Level Elec.

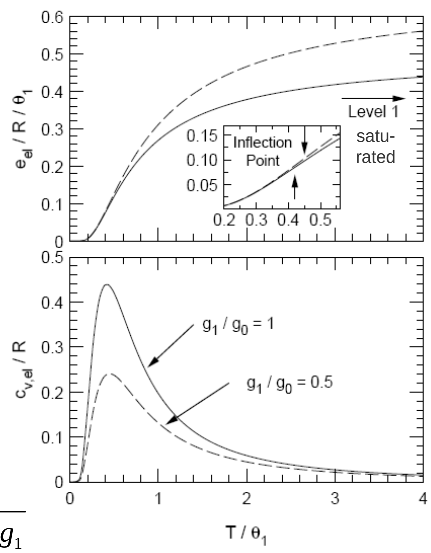
- Normalized values

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

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

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

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



Copyright © 2009 by Jerry M. Seitzman. All rights reserved.

Entropy of Elec. Mode

- From entropy for internal mode (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

Copyright © 2009 by Jerry M. Seitzman. All rights reserved.