5.60/BE.110: Thermodynamics and Kinetics (r08)
Recitation Handout for 10/19/2006

Quick summary of today's topics:

- Boltzmann's constant: $k=\frac{R}{N_A}=1.38\times10^{-23}\frac{J}{K}$
- Systems with degenerate energy levels:
  - Partition function: $q=\sum_i g_i e^{(\frac{-E_i}{kT})}$
  - The Boltzmann Distribution: $p_j=\frac{g_j e^{(\frac{-E_i}{kT})}}{\sum_i e^{(\frac{-E_i}{kT})}}=\frac{g_j e^{(\frac{-E_i}{kT})}}{q}$
  - At high temperatures (virtually no energy constraint) **every microstate** becomes equally likely to be populated.
  - At high temperatures, the probability of occupying each **energy level** is weighted by the degeneracy of that level.
- The many-particle partition function, Q:
  - Suppose q is the partition function of a single particle:
    - We assume that the particles are noninteracting and they are identical (same q).
    - Suppose there are N particles.
    - If they are *distinguishable*, then: $Q=q^N$
    - If they are *indistinguishable*, then: $Q=\frac{q^N}{N!}$
- The laundry list: (Calculating thermodynamic quantities from Q)
  - Internal energy: $U=\langle E\rangle=kT^2\frac{\partial lnQ}{\partial T}_{V,N}$
  - Entropy: $S=klnQ+\frac{U-E_0}{T}$, where E_0 is the energy of the reference state.
  - Helmholtz free energy: $A=-kTlnQ$
  - Chemical potential: $\mu=-kTln(\frac{q}{N})$
  - Pressure: $p=kTN\frac{\partial lnq}{\partial V}_{T,N}$
  - Gibbs free energy: $G=-kTNln(\frac{q}{N})$
  - Enthalpy: $H=kT^2\frac{\partial lnQ}{\partial T}_{V,N}+NkT$

Constructing an energy diagram and the partition function:
(Source: Spring 2006, Exam II)

In this problem you will consider an idealized diatomic molecule that can rotate and vibrate. But for simplicity, the molecule has only 4 energy levels. The 4 energy levels are labeled by the vibrational (v) and rotational (J) quantum numbers (v,J):

$$(v, J): \ (0, 0); \ (0, 1); \ (1, 0); \ (1, 1)$$

The energy of these states are given by the expression: $E_{v,J} = k(1000\text{v} + 10\text{J})$, where k is the Boltzmann constant.

The degeneracy of each energy level is given by: $g_{v,J} = 2\text{J} + 1$

1. Sketch the energy level diagram and express the partition function q as a function of T.

2. Estimate the value of q(T) at T = 0K, 100K, 10,000K

Using the laundry list:

Given a system of *distinguishable* molecules at T = 298K, $q = 1 \times 10^{20}$, and $\Delta U = U - E_0 = 3740 \frac{J}{mol}$, what is the *molar* entropy?

Remark: Unlike the energy quantities (*i.e.* U,H,A,G) the entropy has an *absolute scale* (Third law of thermodynamics) and the above expression gives the *absolute entropy* of the system. (Next lecture.)