University of Washington
Department of Chemistry
Chemistry 453
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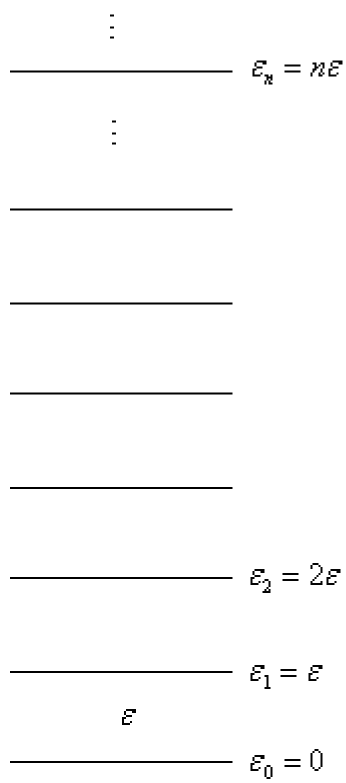
Lecture 5. 1/14/15

A. Internal Energy and Entropy of an Energy Ladder

- An infinite ladder of equally spaced energy levels is a model for the energetics of chemical bond vibrations. Later in the course we will use an energy ladder to calculate the energy of a bond vibrating in a diatomic or polyatomic gas molecule, and for an atom vibrating about its equilibrium position in a crystal.
- A schematic of the energy ladder is shown at the right in Figure 5.1. An infinite sequence of energy states are separated by a constant energy ε. Assigning the ground state ε_0 =0, the excited states have energy $\varepsilon_n = n\varepsilon$ where n=0, 1, 2, 3…
- The energy levels are not degenerate.
- The energy levels go on to inifinty.



- Figure 5.1: The energy ladder is a sequence of equally spaced energy levels. The ground state ε_0=0 and the spacing between the levels above the ground state is a constant ε. None of the energy levels is degenerate. In principle the energy levels continue to infinity.

- Given these assumptions the single particle partition function is

$$q = e^{-0\beta\varepsilon} + e^{-1\beta\varepsilon} + e^{-2\beta\varepsilon} + e^{-3\beta\varepsilon} + \ldots = \sum_{n=0}^{\infty} e^{-n\beta\varepsilon} \qquad (5.1)$$

where $\beta = \dfrac{1}{k_B T}$

- The series in equation 5.1 has the form $\sum_{n=0}^{\infty} x^n$, which converges to a finite sum if x<1, i.e. $\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$.
- Therefore the partition function for the energy ladder is, seeting $x = e^{-\varepsilon/k_B T} = e^{-\beta\varepsilon}$

$$q = \sum_{n=0}^{\infty} e^{-n\beta\varepsilon} = \frac{1}{1-e^{-\beta\varepsilon}} = \left(1-e^{-\beta\varepsilon}\right)^{-1} \tag{5.2}$$

  - Now the energy of a system of N particles can be evaluated:

$$U = Nk_B T^2 \left(\frac{\partial \ln q}{\partial T}\right)_V = \frac{Nk_B T^2}{q}\left(\frac{\partial q}{\partial T}\right)_V$$

$$= \frac{N}{\left(1-e^{-\varepsilon/k_B T}\right)^{-1}}\left(\frac{\partial}{\partial T}\left(1-e^{-\varepsilon/k_B T}\right)^{-1}\right)_V = \frac{N\varepsilon e^{-\varepsilon/k_B T}\left(1-e^{-\varepsilon/k_B T}\right)^{-2}}{\left(1-e^{-\varepsilon/k_B T}\right)^{-1}} = \frac{N\varepsilon e^{-\varepsilon/k_B T}}{\left(1-e^{-\varepsilon/k_B T}\right)} \tag{5.3}$$

- Suppose the energy ladder is used to treat the vibrational energetics of atoms in crystal lattices. Because such particles are confined to lattice positions and unlike a gas, do not switch between microstates quickly, for the purposes of counting such particles are distinguishable. Taking this into account $Q=q^N$ and so the entropy expression is:

$$S = \frac{U}{T} + k_B N \ln q = \frac{N}{T}\frac{\varepsilon e^{-\beta\varepsilon}}{\left(1-e^{-\beta\varepsilon}\right)} + Nk_B \ln\left(\frac{1}{1-e^{-\beta\varepsilon}}\right) = \frac{N}{T}\frac{\varepsilon e^{-\beta\varepsilon}}{\left(1-e^{-\beta\varepsilon}\right)} - Nk_B \ln\left(1-e^{-\beta\varepsilon}\right) \tag{5.4}$$

Note as T approaches zero S also approaches zero...which is the third law of thermodynamics.

- Heat Capacity of the Energy Ladder
  - The heat capacity is defined as

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{\partial}{\partial T}\frac{N\varepsilon e^{-\beta\varepsilon}}{1-e^{-\beta\varepsilon}} = N\varepsilon\frac{\partial}{\partial T}\frac{1}{e^{\beta\varepsilon}-1} = N\varepsilon\frac{\partial}{\partial T}\left(e^{\beta\varepsilon}-1\right)^{-1}$$

$$= -N\varepsilon\left(e^{\beta\varepsilon}-1\right)^{-2}\frac{\partial e^{\beta\varepsilon}}{\partial T} = -N\varepsilon\left(e^{\beta\varepsilon}-1\right)^{-2}\left(-\frac{\varepsilon e^{\beta\varepsilon}}{k_B T^2}\right) = Nk_B\left(\frac{\varepsilon}{k_B T}\right)^2\frac{e^{\beta\varepsilon}}{\left(e^{\beta\varepsilon}-1\right)^2}$$

  - Note that this equation means the heat capacity of a crystal changes a lot with temperature.
    - Suppose the temperature is very high so $\varepsilon \ll k_B T \quad or \quad \beta\varepsilon \ll 1$ and $e^{\beta\varepsilon} \approx 1+\beta\varepsilon$ Then for one mole $C_V = N_A k_B (\beta\varepsilon)^2 \frac{e^{\beta\varepsilon}}{\left(e^{\beta\varepsilon}-1\right)^2} \approx N_A k_B (\beta\varepsilon)^2 \frac{1+\beta\varepsilon}{(\beta\varepsilon)^2} \approx N_A k_B = R$

- Suppose the temperature is very lo so $\varepsilon \gg k_B T \quad or \quad \beta\varepsilon \gg 1$ Then

$$C_V = N_A k_B \left(\beta\varepsilon\right)^2 \frac{e^{\beta\varepsilon}}{\left(e^{\beta\varepsilon}-1\right)^2} \approx N_A k_B \left(\beta\varepsilon\right)^2 e^{-\beta\varepsilon} \approx 0$$

- So at low temperature a crystal has almost zero heat capacity and will not absorb heat while at high temperature the heat capacity approaches R. This behavior is observed experimentally and will be discussed later.

Example 5.1:

Suppose we have one mole of atoms in a lattice whose vibrational energetics are treated as an energy ladder. Calculate U, S, and C_V at T=1000K if $\varepsilon = 5.00\times10^{-21} J$.

$$\frac{\varepsilon}{k_B T} = \beta\varepsilon = \frac{5.00\times10^{-21} J}{\left(1.38\times10^{-23} JK^{-1}\right)\left(1000.K\right)} = 0.362$$

$$\therefore e^{-\varepsilon/k_B T} = e^{-0.362} = 0.696$$

$$U = \frac{N\varepsilon e^{-\varepsilon/k_B T}}{\left(1-e^{-\varepsilon/k_B T}\right)} = \frac{\left(6.02\times10^{23} mol^{-1}\right)\left(5.00\times10^{-21} J\right)\left(0.696\right)}{1-0.696} = \frac{2.10\times10^{3} Jmol^{-1}}{0.304} = 6.91\times10^{3} Jmol^{-1}$$

Assuming $Q=q^N$ the entropy is:

$$S = \frac{U}{T} - N_A k_B \ln\left(1-e^{-\beta\varepsilon}\right)$$

$$= \frac{6.91\times10^{3} Jmol^{-1}}{1000.K} - 8.31 JK^{-1}mol^{-1} \ln\left(1-0.696\right)$$

$$= 6.91 JK^{-1}mol^{-1} + 9.89 JK^{-1}mol^{-1} = 16.80 JK^{-1}mol^{-1}$$

The heat capacity of the energy ladder is:

$$C_V = N_A k_B \left(\frac{\varepsilon}{k_B T}\right)^2 \frac{e^{\beta\varepsilon}}{\left(e^{\beta\varepsilon}-1\right)^2} = \left(8.31 JK^{-1}mol^{-1}\right)\left(0.362\right)^2 \frac{e^{0.362}}{\left(e^{0.362}-1\right)^2}$$

$$= \left(1.10 JK^{-1}mol^{-1}\right)\frac{1.44}{0.44^2} = 8.2 JK^{-1}mol^{-1}$$