

University of Washington
Department of Chemistry
Chemistry 453
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Lecture 3. 1/09/15

A. Non-isolated Systems: Thermal Equilibration of Systems and Reservoirs

- Isolated systems are a convenient place to start discussion of large scale properties. In Chemistry 452 explanation of the laws of thermodynamics started with isolated systems. The energy of an isolated system is conserved (First Law). Also, the entropy of an isolated system is maximum when the system reaches equilibrium (Second Law).
- But in general most systems are not isolated. They are in contact with the surroundings. In such systems the energy is not fixed and the value of the energy is not for practical reasons measured directly nor can it be easily controlled. So for systems in contact with surroundings where energy can vary, using an ensemble of microstates each with fixed N , V , and E is not useful.
- An alternative is to fix N , V , and the temperature T , all three of which can be easily measured and controlled. Because the system now is not isolated its energy changes as it come to equilibrium. How do we use statistics to describe this system?

B. The Canonical Ensemble

- To deal with situations involving the equilibrium properties of non-isolated systems, a very different ensemble of systems is assembled.
- Assemble a large number of systems M each with fixed N, V, T . Surround the ensemble of systems with a rigid, adiabatic wall so no energy can be exchanged with the surroundings.
- The ensemble has overall energy E . The systems within the ensemble are separated by rigid diathermal walls and they need not have the same energy. However they do have the same particle number N , V , and T .
- This **canonical ensemble** would have the appearance shown Figure 3.1.
- The name canonical was given by Gibbs and implies “conventional use” because this ensemble is used most widely to deal with statistical problems in the physical sciences.

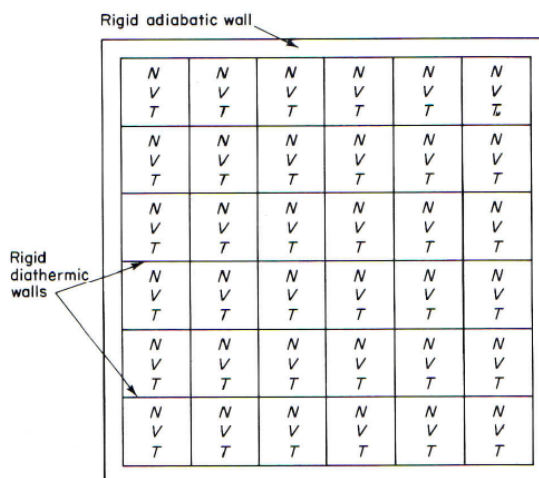


Figure 3.1: Visualization of a Canonical Ensemble, composed of a large number of microstates each with fixed N , V , T . The energies of these microstates can vary so the walls between them are rigid and diathermic. Diathermic means the walls are permeable to heat flow but impermeable to particle flow.

- Now although the overall energy is constant, the energies of the indi
- We can again express the overall energy of the ensemble as an average of the system energies. Let E_i be the i th value of system energy and if N_i systems have energy E_i the energy of the ensemble is

$$E = \sum_i N_i E_i \quad (3.1)$$

where

$$M = \sum_i N_i \quad (3.2)$$

- The set of numbers $\{N_i\}$ is called a distribution. Because each system has many possible energies available to it, there are many distributions that can satisfy equations 3.7 and 3.8. The number of ways of assigning systems in the ensemble to possible system energies is given by the number

$$W(\{N_i\}) = \frac{M!}{N_1! N_2! \dots} = \frac{M!}{\prod_i N_i!} \quad (3.3)$$

- It can be shown that for a large number of systems M , there exists a distribution $\{N_i^*\}$ for which $W(\{N_i^*\})$ is much, much larger than $W(\{N_i\})$ is for any other distribution. For all practical purposes the probability that a system has an energy E_i is dominated by this distribution and it has the form:

$$P_i = \frac{N_i^*}{M} = \frac{e^{-E_i/k_B T}}{\sum_i e^{-E_i/k_B T}} = \frac{e^{-E_i/k_B T}}{Q} \quad (3.4)$$

- If several microstates exist with the same energy, then equation 3.4 must be altered slightly. Suppose there are g_i microstates for an energy E_i . Equation 3.4 becomes:

$$P_i = \frac{g_i e^{-E_i/k_B T}}{\sum_i g_i e^{-E_i/k_B T}} = \frac{g_i e^{-E_i/k_B T}}{Q} \quad (3.5)$$

- Equation 3.5 is called the Boltzmann Distribution Law. It is frequently used to calculate two population ratios:

$$\frac{P_i}{P_j} = \frac{g_i e^{-E_i/k_B T}}{g_j e^{-E_j/k_B T}} = \frac{g_i}{g_j} e^{-(E_i - E_j)/k_B T} \quad (3.6)$$

- Using equation 3.4, the statistical forms for the internal energy and entropy for a system equilibrated with a surrounding heat reservoir are:

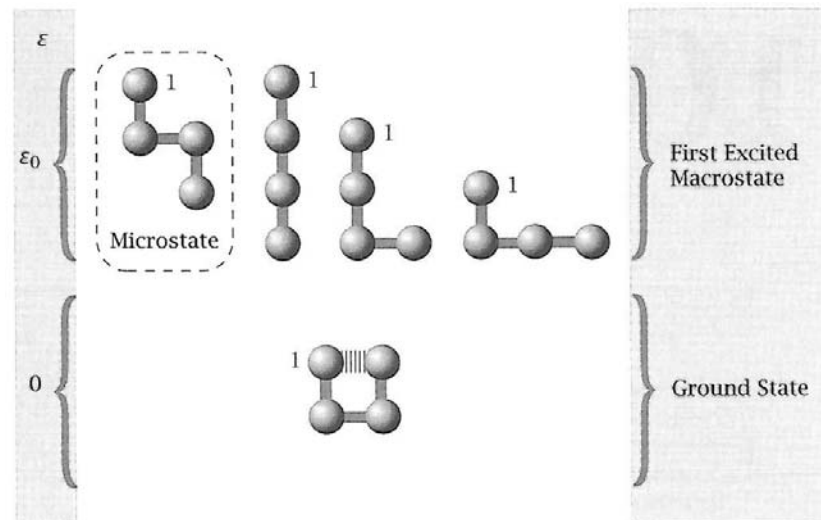
$$\frac{U}{N} = \langle E \rangle = \sum_i P_i E_i = \sum_i E_i \frac{g_i e^{-E_i/k_B T}}{Q}$$

$$\frac{S}{k_B N} = \sum_i P_i \ln P = \sum_i \left(\frac{g_i e^{-E_i/k_B T}}{Q} \right) \ln \left(\frac{g_i e^{-E_i/k_B T}}{Q} \right)$$
(3.7)

C. Example: Two Energy Level System

- Assume we have a protein which can at any temperature can be in one of two structural states. The protein may be structured (N) and will in this condition have an energy $E_0=0$. If a protein is unstructured (D) it has a higher energy $E_1=\epsilon$. . This physical picture is shown in Figure 3.2.
- Note in the unstructured or D state we designate 4 microstates to reflect the many shapes that a unstructured chain may assume. This means $g_1=4$.

Figure 3.2; A two energy level system where the structure protein is in the lower energy level and the unstructured protein is in a higher energy level. There are four energetically equivalent microstates and a single structured microstate.



- To obtain expressions for the energy and entropy of this system at any temperature and for any value of ϵ , we first calculate the probabilities for a protein to be in the N or S forms at a given T. These are:

$$P_0 = \frac{e^{-E_0/k_B T}}{e^{-E_0/k_B T} + 4e^{-E_1/k_B T}} = \frac{1}{1 + 4e^{-\epsilon/k_B T}}$$

$$P_1 = \frac{4e^{-E_1/k_B T}}{e^{-E_0/k_B T} + 4e^{-E_1/k_B T}} = \frac{4e^{-\epsilon/k_B T}}{1 + 4e^{-\epsilon/k_B T}}$$
(3.8)

- Plots of equations 3.7 with varying temperature are shown in Figure 3.3 for $\frac{\epsilon}{k_B} = 400K$. Note at low temperature the N form dominates but as the temperature increases the D forms become more numerous. The so-called melting

temperature is the temperature at which the N and D forms are equal in population. Figure 3.3 is called a denaturation profile.

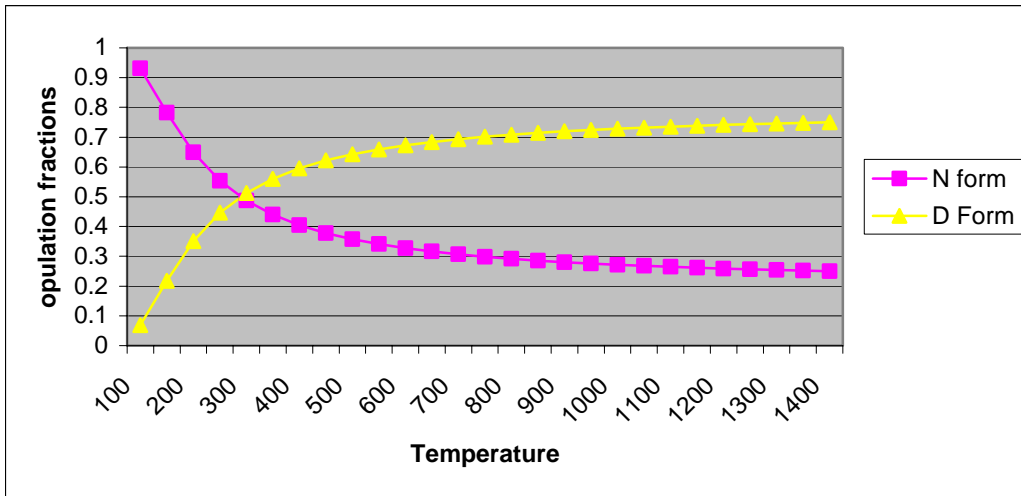


Figure 3.3: Structural populations of the protein system shown in Figure 3.3 as a function of temperature.

In this calculation it is assumed that $\frac{\epsilon}{k_B} = 400K$. With this assumptions $P_0=P_1$ at $T=300K$.

- How does the entropy for this system change as a function of temperature? This question is answered in Figure 3.4 where equation 3.6 is used to calculate the entropy. At low temperatures where only the N microstate is populated the entropy is minimum. The entropy peaks around 300K where the D and S populations are equal. At this temperature we have a maximum number of occupied microstates. As the temperature further increases the N microstate becomes less populated, the entropy decreases slightly but stays larger than its low temperature values because the four D microstates are now populated.

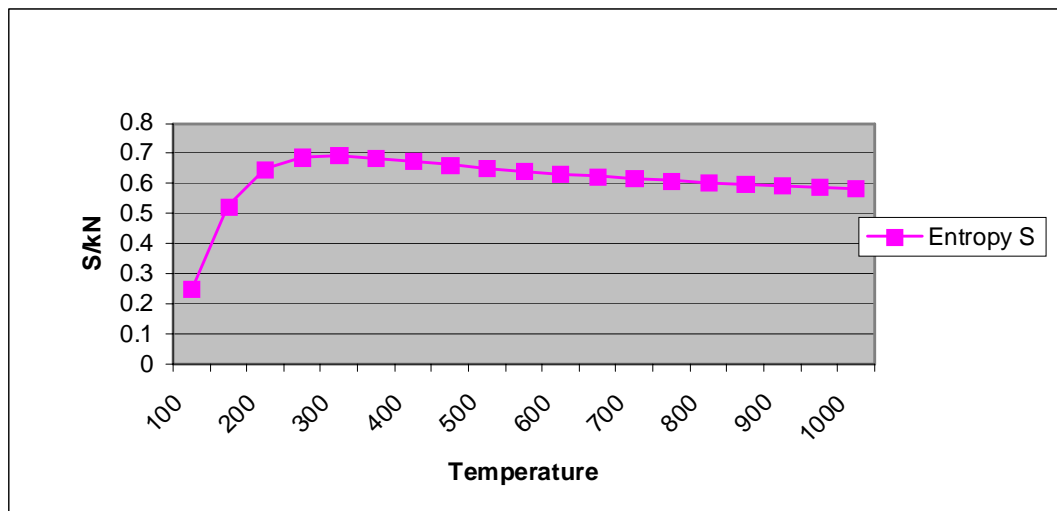


Figure 3.4: The entropy calculated with equation 3.6 using the two level system populations given in equation 3.7. The entropy is at a maximum value at $T=300K$ which corresponds in Figure 3.3 to the point where $P_0=P_1$.

D. Back to the Kinetic Theory of Gases

- In lecture 1 we derived with a simple elastic collision model the expression for the Maxwell-Boltzmann velocity distribution function:

$$f(v) = \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-mv^2/2k_B T} \quad (3.9)$$

- Recall that the normalization constant in equation 3.8 was obtained from:

$$4\pi \int_0^{\infty} u^2 e^{-mu^2/2k_B T} du = \left(\frac{2\pi k_B T}{m} \right)^{3/2} \quad (3.10)$$

- Equation 3.8 can be written;

$$f(v) = \frac{e^{-mv^2/2k_B T}}{4\pi \int_0^{\infty} u^2 e^{-mu^2/2k_B T} du} \quad (3.11)$$

- The Maxwell-Boltzmann velocity distribution function is a special case of equation 3.4, where $E=mv^2/2$ and the summation in the denominator of 3.4 has been replaced in 3.10 by an integration, reflecting the fact that velocities are continuously distributed.