University of Washington
Department of Chemistry
Chemistry 453
Winter Quarter 2015

Lecture 2. 1/07/15-1/09/15

> "We are not talking about truth. We are talking about something that seems like truth. The truth we want to exist"
> Stephen Colbert explaining the meaning of "truthiness", 2005.

A. Probability and Entropy

- The Kinetic Theory of Gases ala Boltzmann and Maxwell is a statistical theory of the properties of large scale gas phase systems. Can the statistical approach be generalized? The answer is yes.
- Everybody knows the meanings of probability and averages. How are these concepts so familiar to stock investors and gamblers applicable to large scale physical systems?
- Large scale physical systems have lots of parts. A liter of oxygen contains over 10^{22} molecules. These molecules are constantly rearranging themselves within this volume as shown in figure 2.. If the system is isolated, it has a fixed energy E and fixed number of molecules N. Assume the volume V of the system does not change. Each snapshot of the system as it changes in time is called a microstate.
- The number of microstates in an isolated physical system is a fundamental quantity that we will show determines the entropy.

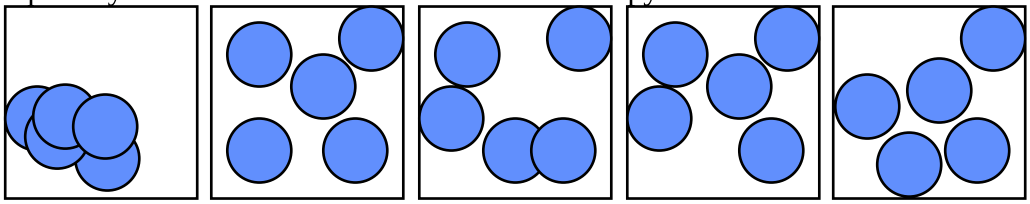

Figure 2.1 An isolated system of gas molecules with fixed E, N, and V, changes of positions of the molecules in time. Each "snapshot" is called a microstate.

- Macroscopic quantities like pressure and energy may be viewed as averages over these many microstates. But how do we take this average for isolated systems? An important principle that governs performing such averages is called the Postulate of Equal A Priori Probabilities. This postulate states that in isolated systems, all microstates are equally probable. If the number of microstates is $W(N,V,E)$, then the probability that each microstate occurs at any instant is

$$P = \frac{1}{W(N,V,E)} \tag{2.1}$$

- In theory then, we would have to calculate the time average using (2.1) as the probability of a microstate occurring at any instant. Such an average requires that the system be observed for a long enough time that all microstates are observed. For large numbers of particles the time average can be an impossible task.
- Josiah Willard Gibbs Jr. developed an alternative averaging method based on ensembles. In the ensemble method, all possible microstates are enumerated and assembled for averaging purposes.

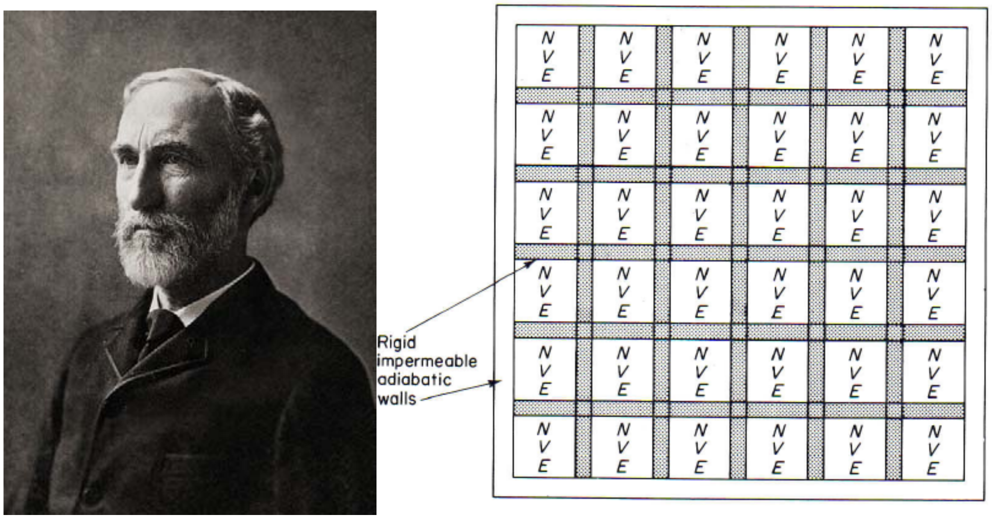

Figure 2.2: Left: J. Willard Gibbs Jr. Yale mathematical physics professor who founded independent of Maxwell and Boltzmann the field of statistical mechanics. Gibbs' version is based on ensemble averaging. Right: a microcanonical ensemble as conceived by Gibbs. To keep N and V constant in this mental construct, the wall between the microstates are rigid and impermeable. To keep the energy constant the walls are adiabatic and thus do not permit heat flow.

- An ensemble composed of isolated systems each with fixed E, V, and N and representing a unique microstate is called a microcanonical ensemble.
- A second important postulate of statistical mechanics is the Ergodic Postulate which states that the time average of a physical property is equivalent to the ensemble average, if the members of the ensemble replicate the physical state and surroundings of the system. For an isolated system that is ergodic the time average and the microcanonical ensemble average are equivalent.
- The Ergodic Postulate and the Postulate of Equal A Priori Probabilities are the two fundamental statements upon which statistical mechanics is built.
- Entropy of Isolated System: It is well-known from Chemistry 452 that

$$S_f - S_i = R\ln\frac{V_f}{V_i} = k_B \ln\left(\frac{V_f}{V_i}\right)^{N_A} \qquad (2.2)$$

$$or\ldots S = k_B \ln V^{N_A}$$

- For a single particle, the number of microstates is proportional to the volume V. For N ideal gas particles the number of microstates $W\left(N,V,E\right) \propto V^N$. Substituting this into equation (2.2) we obtain Boltzmann's entropy equation

$$S = k_B \ln W\left(N,V,E\right) \tag{2.3}$$

- The Boltzmann entropy equation is the fundamental relationship between the thermodynamic properties of large scale systems (i.e. S) and the statistical properties of large scale systems (i.e. W).
- The average of any physical property associated with an isolated ergodic system is the microcanonical ensemble average:

$$\left\langle X_i \right\rangle = \sum_i P_i X_i = \frac{1}{W\left(N,V,E\right)} \sum_i X_i \tag{2.4}$$

- Consequence of the Boltzmann Entropy Equation:
    - Example 1: Suppose we have an ideal gas confined to a spherical container and separated from a second equal container by a stop cock. We open the stopcock. Consider two possible outcomes where the gas remains in one volume and in the other outcome the gas distributes between the two volumes. Which outcome is more physically likely?

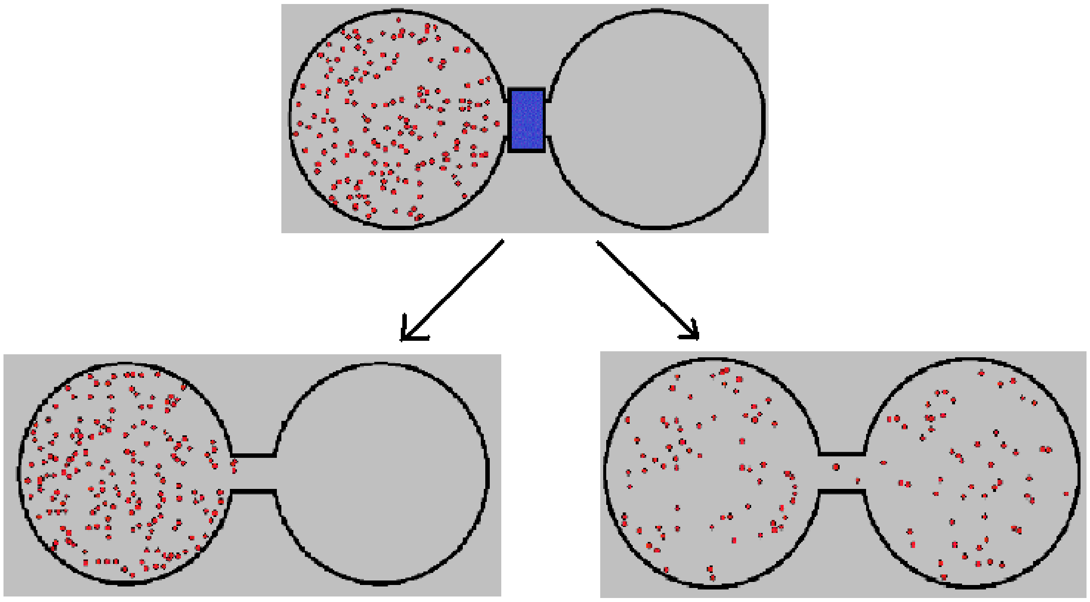

Figure 2.3: The partitioning of ideal gas molecules between two containers of equal size. Common experience shows the outcome will be an equal partitioning

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    - We know from common experience that the gas will equally partition between the two container. How does equation (2.3) predict this? Let us simply the problem to six molecules in two containers where each container has six sites that can be occupied. In Figure 2.4, we enumerate all the ways of arranging 6 molecules between 12 sites, with six sites in each container. There are 64 such microstates, as shown in Figure 2.4.

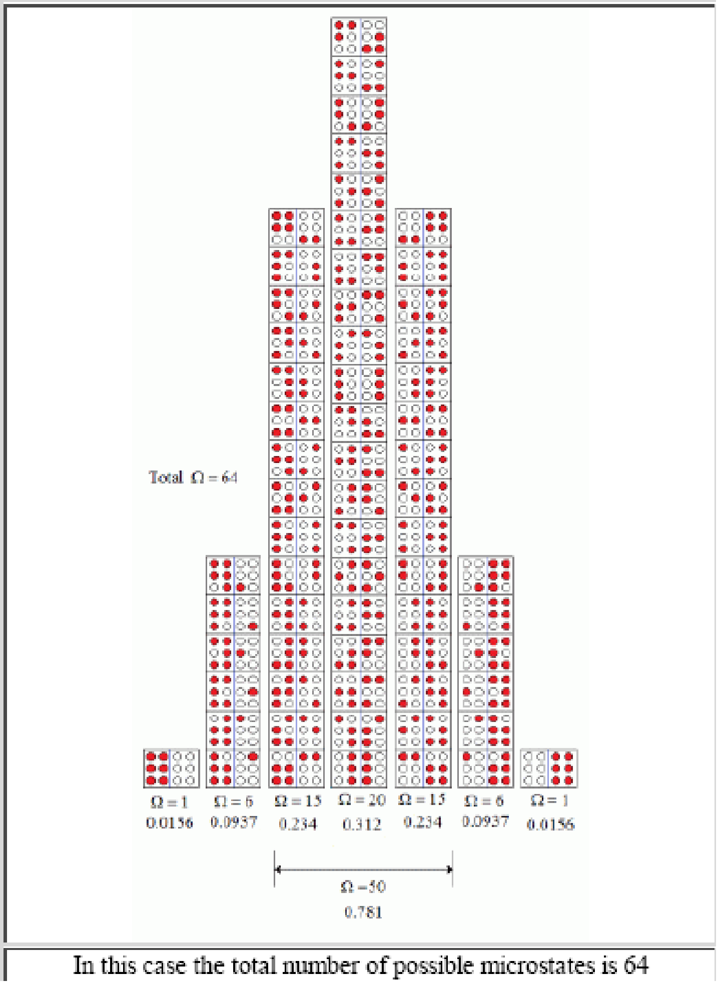

Figure 2.4: There are 64 ways (i.e. microstates) for arranging 6 particles between two equal-sized containers. The microstates where particles are equally partitioned between the bins are most numerous and will dominate any averaged property.

- The number of ways of arranging N particles between two bins such that N_1 particles are in bin 1 and N_2 particles are in bin 2 is given by the binomial coefficient expression:

$$W = \frac{N!}{N_1!N_2!} \tag{2.5}$$

- In figure (2.4) equation 2.5 is applied to the partitioning of 6 particles between two bins. There are 64 microstates for this system in total. There are exactly two microstates which correspond to all six particles in one bin or the other. Applying equation 2.5 to 6 particles in bin 1 and zero particles in bin 2:

$$W_{6,0} = W_{0,6} = \frac{6!}{6!0!} = 1 \tag{2.6}$$

- In contrast there are many more microstates for equal partitioning of particles between two bins:

$$W_{3,3} = \frac{6!}{3!3!} = 20 \tag{2.7}$$

- Equations 2.5-2.7show that molecules will equally partition between the two bins because there are many more microstates that correspond to that physical result than for other results. Therefore, as the system fluctuates through its many microstates, most of the time the system will be in microstates corresponding to equal partitioning of particles between the two bins. Any physical property produced by averaging over microstates will be dominated by the microstates that reflect equal partitioning.

B. Alternative Form for the Entropy: The Gibbs Entropy Equation

We can generalize equation 2.5 to any number of microstates and in doing so obtain an alternative form for the statistical entropy called the Gibbs Entropy Equation. Assume we have N ideal gas molecules where N_1 are in microstate 1, N_2 are in microstate 2, etc. Then W is the number of ways of arranging N particles among the microstates such that N_1 are in microstate 1, N_2 are in microstate 2, etc. W is given by:

$$W = \frac{N!}{N_1!N_2!\cdots N_M!} = \frac{N!}{\prod_{i=1,M} N_i!} \tag{2.8}$$

- Take the log of both side and then use Stirling's Approximation:

$$\begin{aligned}\ln W &= N\ln N - N - \sum_{i=1,M}\left(N_i \ln N_i - N_i\right)\\ &= \left(\sum_{i=1,M} N_i\right)\ln N - \sum_{i=1,M}\left(N_i \ln N_i\right) = -\sum_{i=1,M}\left(N_i \ln\frac{N_i}{N}\right)\end{aligned} \tag{2.9}$$

- We now substitute the Boltzmann entropy equation (2.3) into (2.6)

$$\begin{aligned}S &= -k_B\sum_{i=1,M}\left(N_i \ln\frac{N_i}{N}\right) = -k_B N\sum_{i=1,M}\left(\frac{N_i}{N}\ln\frac{N_i}{N}\right)\\ \therefore \frac{S}{k_B N} &= -\sum_{i=1,M}\left(\frac{N_i}{N}\ln\frac{N_i}{N}\right) = -\sum_{i=1,M}\left(P_i \ln P_i\right)\end{aligned} \tag{2.10}$$

The Gibbs entropy equation gives the entropy as a function of micro-state probabilities. However, this equation can be applied more broadly than shown here, as we will see.

- Example 2: Back to the Two Bin System.. Assume an isolated system composed of N identical particles that can be distributed between two bins such that:

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$$W(N,M)=\frac{N!}{M!(N-M)!} \qquad (2.11)$$

- The entropy is
  -

$$S/k_B = \ln N! - \ln M! - \ln(N-M)!$$

$$\therefore S/Nk_B = -\left[\frac{M}{N}\ln\frac{M}{N}+\left(1-\frac{M}{N}\right)\ln\left(1-\frac{M}{N}\right)\right] \qquad (2.12)$$

$$= -\left(f\ln f + (1-f)\ln(1-f)\right)$$

where we designate f as being the fraction of molecules in the left bin.

- Note the entropy is maximum at equilibrium when

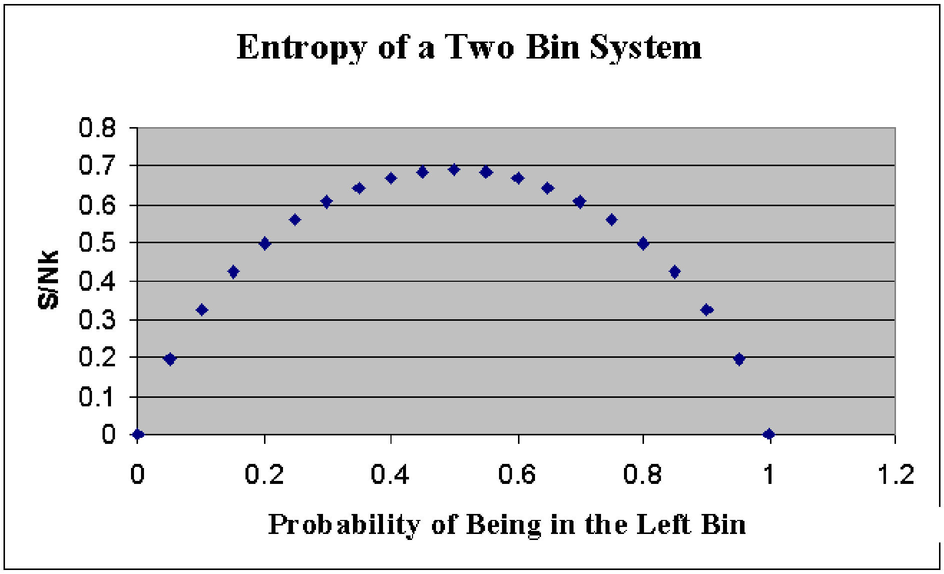
$$\frac{dS}{df}=0 \qquad (2.13)$$

- Solving 2.13 we find that $f^*=0.5$. At equilibrium the entropy is maximum, there is equal probablility of finding the bins populated, and W is also maximum. The macrostate with the largest number of microstates occurs at equilibrium.

- The variation of the equation 2.12 expression for entropy with f is shown in figure 2.5. The maximum entropy is

$$S/Nk_B = -\left(f^*\ln f^* + (1-f^*)\ln(1-f^*)\right) = -\ln\left(\frac{1}{2}\right) = \ln 2 = 0.693 \qquad (2.14)$$

Figure 2.5: Plot of equation 2.12 showing the entropy of a two bin l system as a function of the fraction of N particles that occupy the left bin.



C. Summary remarks:

- There are two postulates in statistical mechanics:
  i. Time averages are hard to calculate. The Ergodic Postulate says time averages are equivalent to ensemble averages.
  ii. The Postulate of Equal A Priori Probabilities says each microstate within the microcanonical ensemble occurs with equal probability

- An isolated system changes constantly in time between its many microscopic configurations called microstates.
- Macroscopic physical properties like thermodynamic state functions, pressure, etc. are times averages over these microstates
- A microcanonical ensemble is a mental construct used to describe statistically the thermodynamic properties of an isolated system.
- A microcanonical ensemble is composed the very large number of microstates, each with the same N, V, and E.
- Entropy has the statistical forms:

$$S = k_B \ln W \quad \text{...Boltzmann's Entropy Equation}$$

$$\frac{S}{k_B N} = -\sum_i P_i \ln P_i \quad \text{...Gibbs Entropy Equation}$$