Statistical Mechanics, Chapter 1: The Fundamental Equations of Statistical Mechanics

1.1. Introductory Remarks

§1. *Why do you need Statistical Mechanics?* In previous lectures, we used thermodynamics to study large systems, such as a gas or a liquid. To develop the theory we introduced work, heat, energy, entropy, and formulated the First and Second laws in terms of these quantities. Nowhere during this development did we need to know that the system is made of molecules. We invoked molecules occasionally, but their existence was never an essential part of the discussion. During the period in which the greatest developments in thermodynamics took place, some eminent physical chemists either denied the existence of molecules or dismissed the idea as an unnecessary hypothesis.

However, we know that molecules exist and it is natural to ask how the quantities introduced in thermodynamics depend on the properties of the molecules. For example, it would be nice to have equations that allow us to calculate the specific heat or the equation of state, from the interactions among the molecules and their vibrational and rotational energies.

What can we gain from such a theory? Perhaps, we can increase our understanding of thermodynamics in general, or of the thermodynamic properties of specific systems. For example, at high temperatures the specific heat at constant volume C_v is equal to $3R/2$ for all noble gases (R is the gas constant). Why this number? Why are the noble gases different from other gases? Why does the heat capacity of a gas increase with the number of atoms in its molecules? Why are the C_v values of certain diatomics such

as H_2 and HCl very similar and why do they differ from those of I_2 or Br_2? Thermodynamics cannot explain such similarities and differences. Statistical Mechanics — which is a theory that connects the thermodynamic properties of a body to the properties of the molecules in it — does.

Phenomenological thermodynamics introduces entropy in a very formal way and gives no physical interpretation to this central quantity. In some books, we are told that entropy is related to order: if a system is more ordered, its entropy is smaller. Where does this statement come from? What exactly is order? Why does entropy depend on it? Statistical Mechanics manages to answer these questions.

When you studied chemical kinetics, you learned that a large number of experiments established that most rate constants k satisfy the Arrhenius equation $k = A\exp[-E_a/RT]$. Here A is the so-called pre-exponential, E_a is the activation energy, and R is the gas constant. Phenomenological chemical kinetics cannot tell us why this functional form is so common, or the meaning of the activation energy E_a or of the pre-exponential A. Nor can it tell us how k is related to the motion of the atoms in a molecule or how the atoms in a molecule move during a chemical reaction. Statistical Mechanics answers these questions.

We have a natural desire to understand how the world around us works. But, one could argue that a practical person can use thermodynamic data without understanding why the values of certain quantities have some striking regularities, or why entropy and order are related. After all, thermodynamics was a useful science before the invention of Statistical Mechanics.

It turns out that Statistical Mechanics has practical applications. A

good example is provided by combustion reactions. These produce transient species, such as OH radicals, which are very reactive. We cannot isolate and purify them, to measure their thermodynamic properties, such as heat capacity, entropy, or energy of formation. Unless we know these properties, we cannot calculate how the temperature and the composition of a flame depend on the working conditions. This makes it harder to design boilers or engines that burn fuel efficiently and produce a minimum amount of pollutants. It so happens that it is rather easy to measure the emission spectrum of the OH radical in the flame and determine its vibrational and rotational energies. Using these quantities, Statistical Mechanics can calculate the thermodynamic properties of this transient species.

In the past decade, computers have become so powerful that we can use Statistical Mechanics to calculate the thermodynamic properties of gases, liquids, solids, polymers, proteins, and enzymes. In some of these calculations, we are not limited by shortcomings of Statistical Mechanics or by lack of computer power but by our incomplete knowledge of the energy of interaction between molecules. As our knowledge of these interactions improves, practical chemists, biochemists, and engineers will perform Statistical Mechanical calculations routinely to solve the problems that appear in their practice. As you read this, scientists at Merck, Pfizer, Schering-Plough, and other pharmaceutical companies are using computer programs based on Statistical Mechanics to help design better drugs.

§2. *Why is this theory statistical? A discussion based on Classical Mechanics.* The premise of Statistical Mechanics is simple: the motion

of the molecules in a material determines its macroscopic properties. Let us take this assertion seriously and think about its consequences. To make the argument simpler, I assume that the motion of the molecules inside any material is described by Classical Mechanics and that I know the forces of interaction between the atoms or the molecules present in the system. Given these assumptions, I can use Newton's equation to calculate how each atom in the system moves. If the premise of Statistical Mechanics is correct, this should allow me to understand the macroscopic properties of the material.

This is a fine idea, but as I pursue it I will find that I don't know how to implement it. To solve Newton's equation, I must know the positions and the velocities of all the atoms in the system at one time. If I know that, I can calculate the position and the velocity of each atom at all other times. Unfortunately, there is no experiment capable of telling me what the positions and velocities of each atom in the gas are at a given time. Nor do I have any reasonable hope that I can ever make such a measurement.

Even if I could determine the initial positions and velocities and solve Newton's equations, I do not know how to use this information to calculate the thermodynamic properties of the gas. I might assume that the energy of the system is the total mechanical energy of all the molecules in the system. But this cannot be quite right: I know that the energy depends on temperature, while the calculation I just mentioned has no temperature in it.

Greater difficulties appear when I start thinking about temperature, heat, entropy, heat capacity, etc. Mechanics does not tell me how to use the positions and the velocities of every molecule in the gas to calculate its entropy

or the temperature. To perform such calculations, *I must add new concepts to Mechanics,* and this is what Statistical Mechanics does.

Finally, here is the most powerful blow to my idea: a theory that describes the motion of each atom in the system has no connection with thermodynamic experiments. In thermodynamics I control the system very crudely, by fixing the temperature and the pressure. Let us call the state reached by fixing T and p, the *macroscopic state* of the system. The state specified by giving the momenta $\{\mathbf{p}_1, \ldots, \mathbf{p}_N\}$ and the positions $\{\mathbf{r}_1, \ldots, \mathbf{r}_N\}$ of the atoms will be called the *microscopic state* $C = \{\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N\}$ of the system. To use mechanics, I must know the microscopic state of the system. However, our experience with thermodynamics says that it is enough to know T and p. Thus, there is a tremendous reduction of the amount of information as I go from mechanics to thermodynamics. Statistical Mechanics must find a mathematical scheme for achieving this reduction; the theory has to show me how to intelligently throw away most of the information contained in the microscopic state.

To do this, I start with the observation that there are a very large number of microscopic states compatible with a given macroscopic state. This means that there are many sets of different momenta and positions that will give the same pressure and temperature. Let us call these microscopic states, the microscopic states compatible with fixed T and p. When I fix the temperature and pressure, the system could be in any one of these equivalent states. Statistical Mechanics recognizes that we have no way of determining in what microscopic state the system is. In the absence of this knowledge, the next thing is to know the probability $P(C(T, p))$ that the system has a

certain microscopic state $C(T, p) = \{\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N\}$. I use the notation $C(T, p)$ to indicate that this is a microscopic state for which the gas has the pressure p and temperature T. The probability $P(C(T, p))$ will depend on T and p.

Next I assume that the measured thermodynamic energy U is the average energy

$$U(T, p) = \sum_{C(T,p)} E(C(T, p)) \, P(C(T, p)) \tag{1}$$

The quantity $E(C(T, p))$ is the mechanical energy of the system in the microscopic state $C(T, p)$. This is the kinetic energy of all atoms in the system, plus the energy of the interaction between them. The sum in Eq. 1 is over all microscopic states compatible with T and p. The whole expression is the average energy at given values of temperature and pressure.

To define entropy, we need a new idea; mechanics alone is insufficient and Statistical Mechanics provides the necessary formula. Once we know the internal energy U and the entropy S, we can calculate all other thermodynamic quantities, by following the rules of thermodynamics.

Exercise 1 Go back and read your thermodynamics book and try to figure out how you can calculate all thermodynamic quantities if you know $U(T, p)$ and $S(T, p)$.

§3. *Why use a statistical method; a Quantum Mechanical discussion.* The argument just given is based on the assumption that I can describe the motion of the molecule by using Classical Mechanics. This is often a good approximation, but the world of the molecules is ruled by Quantum Mechanics and Statistical Mechanics must be based on it. Classical theories can only serve as an approximation.

To describe the microscopic states of a system, I must solve the time-independent Schrödinger equation. This gives me the energy eigenstates Ψ_i, and the corresponding energy eigenvalues E_i, that the system can have. If the system were alone in the world, its state would be the lowest energy eigenstate Ψ_0. However, in thermodynamics the system is in contact with a thermostat. I know from Quantum Mechanics that the interaction of a system with something (in our case the thermostat) causes transitions from the initial energy eigenstate Ψ_0 to other eigenstates Ψ_i. For a very large system the energy difference between various energy eigenstates is very small. Because of this, the contact with the thermostat will cause transitions to a very large number of eigenstates.

Exercise 2 Get your Quantum Mechanics book and find the formula for the energy eigenstates of a particle in a box. Calculate the first 10 energy eigenstates for an argon atom enclosed in a cubic box of volume 1 cm^3. Find out how much energy it takes to excite the system from the ground state to the tenth excited state. Then calculate the change of the internal energy per atom when you increase the temperature by 10 K (from 298 K to 308 K). use $c_p = 20.786$ J/mol K. Is this energy enough to excite the system from the ground state to the tenth excited state?

In a macroscopic experiment, I do not control the energy but instead the temperature and the pressure. There are many energy eigenstates that are compatible with a given pair T, p, and we do not know for sure what the microscopic state of the system is. Just as in the classical case, Statistical Mechanics provides the probability that for certain values for p and T, the system is in the microscopic state Ψ_i. With these probabilities, I can calculate the mean energy and the entropy of the system.

1.2. The Fundamental Equations of Statistical Mechanics

§4. *The fundamental equations are guesses.* I will give here the basic equations of Statistical Mechanics. They are not derived by logical arguments from laws of Nature that we take for granted; they were obtained by inspired, educated guesses. There are arguments that lead us to believe that these guesses are reasonable, but they don't prove them. We believe that the equations are correct because mathematical deductions based on them agree with a large number of results obtained by measurements. For example, the entropy and the specific heat of gaseous Xe calculated from these equations agree with the measured values.

Since this is your first encounter with Statistical Mechanics, I will write down the basic equations without presenting the rationalization used to justify them. Such justifications are better understood after you had some experience with the applications of the theory.

§5. *The fundamental equations: the probability that the system is in a specific state.* Consider a system containing N molecules in thermodynamic equilibrium. They are enclosed in a box of volume V and are in contact with a thermostat that keeps the temperature equal to T. From Quantum Mechanics I know that any system of N molecules in a box of volume V has an infinite number of energy eigenstates having the wave function Ψ_α and the energy $E_\alpha(N, V), \alpha = 0, 1, 2, \ldots$. In this notation it is understood that $E_0 \leq E_1 \leq E_2 \leq \ldots$.

The energy $E_\alpha = E_\alpha(N, V)$ is an energy of *the whole system.* Calculating it is a problem in Quantum Mechanics. In principle, to do this I write the

Hamiltonian H of the system, which is the sum of the kinetic energies of all atoms plus the interaction energy between them. Then, to obtain the energy eigenstates of the system, I solve the Schrödinger equation $H\Psi_\alpha = E_\alpha\Psi_\alpha$. This solution gives me a list of energy eigenstates Ψ_α and the corresponding energies E_α. Here α is an integer that labels the states.

Had the system been alone in the world, it would have slowly emitted radiation and gone into the lowest energy state. However, the interaction with the thermostat causes transitions from one energy eigenstate to another. Because of this, I no longer know what the state of the system is. However, Statistical Mechanics gives me the next best thing: the probability P_α that the system has the state Ψ_α, with energy E_α. This is given by

$$P_\alpha(N,T,V) = \frac{\exp[-E_\alpha(N,V)/kT]}{Q(N,T,V)} \tag{2}$$

with

$$Q(N,T,V) = \sum_{\alpha=1}^{\infty} \exp[-E_\alpha(N,V)/kT] \tag{3}$$

When applying these equations, it is necessary to distinguish between the states Ψ_α and the energies E_α. As you learned in Quantum Mechanics, it is possible that several states have *the same energy.* When this happens, we say that the sates having the same energy are *degenerate.* In most cases, there are physical reasons for such degeneracy. For example, the degenerate states of an electron in the hydrogen atom have the same energy but different angular momentum and spin. It is important to remember that the sum in Eq. 3 is over *all states.* If there are three states having the same energy ε, the term $\exp[-\varepsilon/kT]$ appears three times in the sum defining Q. You should also realize that the probability that a molecule has a specific energy

is different from the probability that the molecule is in a specific state having that energy. For example, if the states Ψ_7, Ψ_8, and Ψ_9 are degenerate and have the energy ε, then the probability that the system is in the state Ψ_7 is

$$\frac{\exp[-\varepsilon/kT]}{Q},$$

while the probability that the system has the energy ε is

$$\frac{3\exp[-\varepsilon/kT]}{Q}.$$

The eigenvalues E_α depend on the volume of the system and on the number N of particles. E_α depends on volume because the particles are confined to a box of volume V. As you have learned in the lectures on Quantum Mechanics, the energy of a particle in a box depends on the volume of the box. The dependence on the number of particles is easy to understand: very roughly speaking the total energy is the sum of the energy of all molecules so more molecules means higher energy. The energies E_α do not depend on temperature since this quantity does not appear in the Schrödinger equation.

The quantity k is the Boltzmann constant:

$$
\begin{aligned}
k &= 1.3806 \times 10^{-16} \text{ erg/K} = 0.695104 \text{ cm}^{-1}/\text{K} \\
&= 3.29977 \times 10^{-27} \text{ kcal/K} = 8.61771 \times 10^{-5} \text{ eV/K} \quad (4)
\end{aligned}
$$

§6. *The fundamental equations: connection to thermodynamics.* Eq. 2 is very useful, but it is not enough. To develop a molecular theory of thermodynamics, I must find a recipe for calculating thermodynamic properties. It can be shown that the Helmholtz free energy $A(N,T,V)$ is given by

$$A(N,T,V) = -kT \ln Q(N,T,V) \quad (5)$$

Equations 2, 3, and 5 are the starting point of Statistical Mechanics. The rest of these lecture notes will teach you how to use them to study a variety of chemical systems and phenomena.

§7. *Formulae for other thermodynamic quantities.* You have learned when you studied thermodynamics that you can calculate any thermodynamic quantity from the Helmholtz free energy. I summarize below the equations used to perform such calculations. These relationships are used throughout these lectures.

- The entropy S of the system is

$$S = -\left(\frac{\partial A}{\partial T}\right)_{N,V} \tag{6}$$

- The pressure p is

$$p = -\left(\frac{\partial A}{\partial V}\right)_{N,T} \tag{7}$$

- The internal energy of N molecules can be calculated from either

$$U = A + TS \tag{8}$$

  or

$$U = -T^2 \frac{\partial}{\partial T}\left(\frac{A}{T}\right)_{N,V} \tag{9}$$

- The enthalpy is

$$H = U + pV \tag{10}$$

- The specific heat at constant volume is obtained from

$$c_v = \left(\frac{\partial u}{\partial T}\right)_{N,V} \tag{11}$$

or

$$c_v = T \left(\frac{\partial s}{\partial T} \right)_{N,V} \tag{12}$$

where u and s are the energy and the entropy of a mole of substance.

- The specific heat at constant pressure is obtained from

$$c_p = \left(\frac{\partial h}{\partial T} \right)_{p,N} \tag{13}$$

or

$$c_p = T \left(\frac{\partial s}{\partial T} \right)_{p,N} \tag{14}$$

where h is the enthalpy per mole.

- The Gibbs free energy for N molecules is

$$G = A + pV = U - TS + pV = H - TS \tag{15}$$

The first equation is the definition; the second follows from the definition $A = U - TS$; the third is obtained by using the definition of enthalpy (which is H = U + pV).

- The chemical potential per molecule in a system with one component is

$$\mu = \left(\frac{\partial A}{\partial N} \right)_{T,V} \tag{16}$$

or

$$\mu = \frac{G}{N} \tag{17}$$

For a mixture, the chemical potential of component i is

$$\mu = \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_j} \tag{18}$$

where n_i is the number of moles of component i. The derivative is taken while keeping constant temperature, pressure, and the number of moles of components other than i. The subscript T, p, n_j reminds us of this.

The quantities U, S, A, H, C_v, and C_p are extensive: they are proportional to the number of molecules in the system. If I take $N = N_A = 60.222 \times 10^{23}$ (this is Avogadro's number, which is equal to the number of molecules in one mole), then I obtain the values of these functions per mole. If I divide by N, I obtain the values per molecule.

§8. *Summary of the recipe for calculating thermodynamic functions.* To start, I must calculate the quantum energies E_α of the system. Then I can obtain Q from Eq. 3 and all thermodynamic quantities from Eqs. 5–16. The only limitation in applying this theory is our inability to calculate the energies E_α for complicated systems. If such calculations could be performed reliably, the equations listed above would completely replace all thermodynamic measurements.

§9. *Classical Statistical Mechanics.* Many of the systems in which chemists are interested are described well by Classical Mechanics. In this case, Eqs. 2 and 3 take a different form (see Chapter @) and the partition function is easier to calculate. The computational methods are so powerful that if we know the interactions between the atoms in the system, we can calculate thermodynamic properties for liquids, solids, polymers, proteins, etc.