Introduction to Physical Chemistry – Lecture 7

I. LECTURE OVERVIEW

In this lecture, we will review the four laws of thermodynamics. We will then go on to define the concept of free energy, and derive a set of relationships between thermodynamic variables known as the *Maxwell relations*. We conclude by using the Maxwell relations to compute various thermodynamic relationships in various contexts.

II. THE LAWS OF THERMODYNAMICS

In the last lecture, you learned about the existence of another thermodynamic state function S, the entropy. We then went on to show that S may be defined by the differential expression, $dS = (\delta Q/T)_{rev}$, which is the second law of thermodynamics.

We are therefore ready to state all the laws of thermodynamics. They are:

1. **The Zeroth Law of Thermodynamics**: *If system A is in thermal equilibrium with system B, and system B is in thermal equilibrium with system C, then system A is in thermal equilibrium with system C.*

2. **The First Law of Thermodynamics**: $dU = \delta Q - \delta W$, *where $\delta W > 0$ signifies that work is done by the system on the surroundings.*

3. **The Second Law of Thermodynamics**: *There is a state function, called the entropy, that is defined by the relationship $dS = (\delta Q/T)_{rev}$.*

4. **The Third Law of Thermodynamics**: *The entropy of a perfect crystal at 0 K is 0.*

The Zeroth Law is called the Zeroth Law and not the First Law, because it was formulated after the other three laws. As discussed in the notes of Lecture 1, the Zeroth Law is necessary in order to construct a thermometer (I gave an explanation why in Lecture 2, but I will give a better and more complete explanation at the end of this lecture).

Basically, people were implicitly assuming the Zeroth Law without being aware of it, and only noticed this until after the first three laws were formulated. Because the zeroth law was regarded as more fundamental than the other three, it was decided to place it before the First Law, hence it was called the Zeroth Law. The Zeroth Law is proved in Appendix B of the last lecture, using the statistical-mechanical definition of entropy.

The First Law and Second Laws have been introduced already. I will simply point out that the Second Law is true by definition. Hopefully, this was clear from the previous lecture, where we explored the probabilistic basis for entropy. In any event, another way to state the Second Law is via $T = (\partial U/\partial S)_V$, but since this is simply the statistical mechanical definition of T, we see that the Second Law is true by definition.

Regarding the Third Law, this simply allows us to pick a reference point where an absolute value of entropy can be assigned. The law $dS = (\delta Q/T)_{rev}$ only allows us to compute changes in entropy. The Third Law says that at 0 K a perfect crystal has no entropy. This makes sense, since an object at 0 K cannot give off heat energy (otherwise it would get colder, which contradicts the definition of 0 K), and hence has no internal energy. In the language of quantum mechanics, we say that the system is in its *ground state*. In terms of degeneracies, by default there is only one way to distribute 0 internal energy among the various degrees of freedom of the system, so from statistical mechanics we get $S = k \ln \Omega = k \ln 1 = 0$.

III. THE HELMHOLTZ AND GIBBS FREE ENERGIES

Now that we have constructed the entropy, we can define two more very important state functions: The *Helmholtz Free Energy*, denoted A, and the *Gibbs Free Energy*, denoted G. The Helmholtz and Gibbs free energies are defined as,

$$A = U - TS$$
$$G = H - TS \tag{1}$$

We will see later on in the course that the Helmholtz and Gibbs free energies are very important state functions when attempting to compute the equilibrium states of systems. We will see why in a moment.

Starting with the First Law for reversible processes, we have

$$dU = TdS - PdV \tag{2}$$

Note that this equation is somewhat inconvenient to work with, because changes in U, i.e. dU, is dependent on changes in S, i.e. dS. Experimentally, it is much easier to directly measure changes in T, V, and P.

The enthalphy $H = U + PV$, hence if U changes to $U + dU$, P changes to $P + dP$, and V changes to $V + dV$, then,

$$
\begin{aligned}
H + dH &= U + dU + (P + dP)(V + dV) \\
&= U + dU + PV + VdP + PdV + dPdV \\
&= U + PV + dU + VdP + PdV \\
&= H + TdS - PdV + VdP + PdV \\
&= H + TdS + VdP \tag{3}
\end{aligned}
$$

where we ignored the term $dPdV$ because it is the product of two infinitesimals, and therefore infinitely smaller than the other terms. Since $dH = H + dH - H$, we have,

$$dH = TdS + VdP \qquad (4)$$

Note that, in this formulation, changes in H depend on changes in S, as is the case for U. However, changes in H also depend on changes in P, while for U the additional dependence is on V.

For the Helmholtz and Gibbs free energies, following a similar derivation to the one used for H, we get,

$$dA = -SdT - PdV$$
$$dG = -SdT + VdP \qquad (5)$$

Note that for A, the dependence is now directly on T and V, while for G the dependence is directly on T and P. Therefore, it is often much easier to work with these variables than U or H. In particular, a process that occurs reversibly at constant T and V must satisfy $dA = 0$, while a process that occurs reversibly at constant T and P must satisfy $dG = 0$. These conditions will allow us to develop criteria for phase and chemical equilibria later in the course.

IV.   THE MAXWELL RELATIONS

We will now derive a very powerful set of relationships among the thermodynamic variables known as the *Maxwell Relations*. We will then use the Maxwell relations to compute specific thermodynamic properties of materials.

To begin, consider a function $f(x, y)$. Under very general conditions, we can show that when taking the mixed partials of f, it does not matter in what order the derivatives are taken. That is, we have that,

$$
\begin{aligned}
(\frac{\partial}{\partial x})_y (\frac{\partial f}{\partial y})_x &= \frac{\partial^2 f}{\partial x \partial y} \\
&= \frac{\partial^2 f}{\partial y \partial x} \\
&= (\frac{\partial}{\partial y})_x (\frac{\partial f}{\partial x})_y \qquad (6)
\end{aligned}
$$

Now, applying this principle to the various thermodynamic variables defined in the previous section, we note the following:

$$
\begin{aligned}
(\frac{\partial}{\partial S})_V (\frac{\partial U}{\partial V})_S &= (\frac{\partial}{\partial V})_S (\frac{\partial U}{\partial S})_V \\
(\frac{\partial}{\partial S})_P (\frac{\partial H}{\partial P})_S &= (\frac{\partial}{\partial P})_S (\frac{\partial H}{\partial S})_P \\
(\frac{\partial}{\partial T})_V (\frac{\partial A}{\partial V})_T &= (\frac{\partial}{\partial V})_T (\frac{\partial A}{\partial T})_V \\
(\frac{\partial}{\partial T})_P (\frac{\partial G}{\partial P})_T &= (\frac{\partial}{\partial P})_T (\frac{\partial G}{\partial T})_P \qquad (7)
\end{aligned}
$$

Now, from the differential expressions for U, H, A and G derived in the previous section, we also have the following:

$$
\begin{aligned}
(\frac{\partial U}{\partial S})_V &= T \\
(\frac{\partial U}{\partial V})_S &= -P \\
(\frac{\partial H}{\partial S})_P &= T \\
(\frac{\partial H}{\partial P})_S &= V \\
(\frac{\partial A}{\partial T})_V &= -S \\
(\frac{\partial A}{\partial V})_T &= -P \\
(\frac{\partial G}{\partial T})_P &= -S \\
(\frac{\partial G}{\partial P})_T &= V \qquad (8)
\end{aligned}
$$

Putting everything together gives us the Maxwell relations,

$$
\begin{aligned}
(\frac{\partial T}{\partial V})_S &= -(\frac{\partial P}{\partial S})_V \\
(\frac{\partial T}{\partial P})_S &= (\frac{\partial V}{\partial S})_P \\
(\frac{\partial S}{\partial V})_T &= (\frac{\partial P}{\partial T})_V \\
(\frac{\partial S}{\partial P})_T &= -(\frac{\partial V}{\partial T})_P \qquad (9)
\end{aligned}
$$

V.   USING THE MAXWELL RELATIONS TO DERIVE THERMODYNAMIC RELATIONSHIPS

The Maxwell relations are an incredibly useful set of relationships between thermodynamic variables, because they connect seemingly unrelated changes between various thermodynamic properties of a system. We illustrate the power of the Maxwell relations by computing $(\partial U/\partial V)_T$ for a material.

A.   Computing $(\partial U/\partial V)_T$

The First Law of Thermodynamics for a reversible process states that $dU = TdS - PdV$, which implicitly takes the internal energy U to be a function of S and V. However, S is hard to measure, and so we would like to have an expression for U as a function of T and V. Writing $U = U(T, V)$, we then have the differential form,

$$dU = (\frac{\partial U}{\partial T})_V dT + (\frac{\partial U}{\partial V})_T dV \qquad (10)$$

The first term, $(\partial U/\partial T)_V$, we are familiar with. It is simply the heat capacity C_V ($= n\bar{C}_V$, where n is

the number of moles in the system). The second term, $(\partial U/\partial V)_T$, measures the dependence of a system's internal energy on volume, assuming the temperature is held constant. Intuitively, then, this quantity should provide a measure of the strength of the interparticle interactions in a material. The reason for this is that changing V essentially corresponds to changing the average distance between the particles of the system. Therefore, if U changes, this means that there must be interparticle forces whose average strength is affected by the change in interparticle distance. In short, if U changes due to a change in V, then this is due to the change in the *internal potential energy* of the system (remember, internal energy in general consists of both the kinetic energy of the random particle motions, as well as the potential energy due to interparticle interactions. This was discussed in Lecture 4. Up until now, though, we have been mainly dealing with ideal gases, for which there is no potential energy contribution to the internal energy).

To explicitly relate $(\partial U/\partial V)_T$ to easily measurable thermodynamic properties, let us consider S as a function of T and V, so $S = S(T, V)$. Then,

$$dS = (\frac{\partial S}{\partial T})_V dT + (\frac{\partial S}{\partial V})_T dV \tag{11}$$

From the First Law of Thermodynamics, we then have,

$$dU = T(\frac{\partial S}{\partial T})_V dT + (T(\frac{\partial S}{\partial V})_T - P)dV \tag{12}$$

so that,

$$C_V = T(\frac{\partial S}{\partial T})_V$$
$$(\frac{\partial U}{\partial V})_T = T\frac{\partial S}{\partial V}_T - P \tag{13}$$

This is where the Maxwell relations come in. We use the 7th Maxwell relation, namely,

$$(\frac{\partial S}{\partial V})_T = (\frac{\partial P}{\partial T})_V \tag{14}$$

Note that the right-hand side of this equation is in principle experimentally measurable, since it involves P, T, and V. We could choose to stop here, but we would like to massage this expression further.

Define the *coefficient of thermal expansivity*, denoted α, of a material by,

$$\alpha = \frac{1}{V}(\frac{\partial V}{\partial T})_P = \frac{1}{\bar{V}}(\frac{\partial \bar{V}}{\partial T})_P \tag{15}$$

Note that α measures the fractional change of molar volume with temperature. To determine α, one varies the temperature of a material at constant pressure, and plots $\bar{V}$ as a function of T. From this, $(\partial \bar{V}/\partial T)_P$ may be computed, and from this α may be computed.

Now, define the *coefficient of compressibility*, denoted κ, of a material by,

$$\kappa = -\frac{1}{V}(\frac{\partial V}{\partial P})_T = -\frac{1}{\bar{V}}(\frac{\partial \bar{V}}{\partial P})_T \tag{16}$$

The reason for the "-" sign is that we would like κ to be positive, so we need to correct for the fact that volume decreases as pressure increases.

To express $(\partial P/\partial T)_V$ in terms of α and κ, let us consider V as a function of T, P, so that,

$$dV = (\frac{\partial V}{\partial T})_P dT + (\frac{\partial V}{\partial P})_T dP = V\alpha dT - V\kappa dP \tag{17}$$

Now, consider an infinitesimal change in dT and dP that leaves V unchanged, so that $dV = 0$. Then this gives,

$$\frac{dP}{dT} = \frac{\alpha}{\kappa} \tag{18}$$

Since this expression was obtained under constant volume conditions, we obtain,

$$(\frac{\partial P}{\partial T})_V = \frac{\alpha}{\kappa} \tag{19}$$

giving finally, that,

$$(\frac{\partial U}{\partial V})_T = T\frac{\alpha}{\kappa} - P \tag{20}$$

Therefore, if we know α, κ, and P, we can compute $(\partial U/\partial V)_T$.

B. Proof that the internal energy of an ideal gas only depends on T

For an ideal gas, $P\bar{V} = RT \Rightarrow \bar{V} = RT/P$. Therefore,

$$\begin{aligned}
\alpha &= \frac{1}{\bar{V}}(\frac{\partial \bar{V}}{\partial T})_P \\
&= \frac{P}{RT}\frac{R}{P} \\
&= \frac{1}{T} \tag{21}
\end{aligned}$$

while,

$$\begin{aligned}
\kappa &= -\frac{1}{\bar{V}}(\frac{\partial \bar{V}}{\partial P})_T \\
&= -\frac{P}{RT} \times -\frac{RT}{P^2} \\
&= \frac{1}{P} \tag{22}
\end{aligned}$$

and so, for an ideal gas,

$$(\frac{\partial U}{\partial V})_T = T\frac{1/T}{1/P} - P = P - P = 0 \tag{23}$$

and so the internal energy of an ideal gas only depends on T.

C. $(\partial U/\partial V)_T$ for a van der Waals gas

We can illustrate how $(\partial U/\partial V)_T$ is connected to inter-molecular interactions by computing it for an equation of state that takes such interactions into account.

For a van der Waals gas, we have,

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} \qquad (24)$$

Here, it is easier to compute $(\partial U/\partial V)_T$ by computing $(\partial P/\partial T)_V$ directly, instead of going through α and κ first. We have,

$$\left(\frac{\partial P}{\partial T}\right)_{V,\bar{V}} = \frac{R}{\bar{V} - b} \qquad (25)$$

and so,

$$\begin{aligned}
\left(\frac{\partial U}{\partial V}\right)_T &= T\left(\frac{\partial P}{\partial T}\right)_V - P \\
&= \frac{RT}{\bar{V} - b} - \left(\frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}\right) \\
&= \frac{a}{\bar{V}^2} \qquad (26)
\end{aligned}$$

so,

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{\bar{V}^2} \qquad (27)$$

which is the internal pressure of the gas. Therefore, the dependence of the internal energy on volume is exactly connected to the strength of the interparticle interactions.

VI.   WHY DO WE NEED A ZEROTH LAW?

It may be somewhat confusing why a Zeroth Law of Thermodynamics is needed at all, given that it is directly obtainable from the definition of temperature. However, we need to remember that the definition of temperature that we saw in Lecture 6 only came with the development of statistical mechanics. When thermodynamics was starting out as a new branch of science, the connection between the various thermodynamic variables and the microscopic properties of a material wasn't yet known. So the connection between entropy and probability was not known either. Therefore, the physical basis for the existence of a concept such as temperature was not fully understood. This led to all kinds of paradoxes such as Maxwell's demon, and attempts to construct perpetual motion machines. These were largely unresolved until the advent of Statistical Mechanics in the 19th century and then Information Theory in the first half of the 20th century. I will bring up these issues later in the course, if time permits.

Of course, with the statistical mechanical approach, temperature is a concept that emerges naturally, and, as

can be seen from the proof in Appendix B of Lecture 6, the Zeroth Law is easy to prove, and therefore may be regarded as unnecessary to state.

However, let us go back in time, and imagine that we are living before we knew about the statistical basis for temperature. All we have is a vague notion of "hot" and "cold," and the observation that "heat" (whatever that is), always flows from a "hot" object to a "cold" one. To quantify this notion of "hot" or "cold," we would like to assign a number that measures the "hotness" or "coldness" of an object, and we choose to call this number the *temperature*. We would like to choose the numbers so that heat will always flow from a region of higher temperature to a region of lower temperature.

So, let's take some object in a well-defined state, and assign it a temperature. Let us label this object A, and its temperature T_A. Now, suppose we have another object, called object B, and we touch it to object A. We notice that there is no heat flow between the two objects, so we say that object B has the same temperature as object A. So, now we assign object B, in its particular state, to have temperature T_A. In principle, this is the temperature of object B independent of object A. So, now suppose we have another object, object C, which we touch to object A, and again, we notice no energy flow. Then again, object C is assigned a temperature T_A. But note that the temperatures assigned to objects B and C may not be well-defined, because they are connected to the object A. That is, we arbitrarily assigned a number to object A, given its current state, noticed no energy flow between A and B, and A and C, and therefore assigned the same number to B and C. But, for this number to be the measure of temperature that we're looking for, then it must be a property of B and C that does not depend on A, and we should be able to use this number to determine the direction of energy flow between B and C, again, independently of A.

Since B and C are both assigned a temperature T_A, when they are put in thermal contact, then there should be no energy flow between B and C. This is exactly the Zeroth Law: If system A is in thermal equilibrium with system B, and system A is in thermal equilibrium with system C, then system B is in thermal equilibrium with system C.

Let's reason this a bit further: Let us now consider the set of all objects in their appropriate energy states that are in thermal equilibrium with object A, in the state where it is assigned a temperature T_A. These objects are all assigned a temperature T_A as well, and are in thermal equilibrium with each other, according to the Zeroth Law. Therefore, the temperature T_A may be associated with all objects in the states where they are in thermal equilibrium with object A, in the state where it is assigned a temperature T_A. Although object A has been selected for measuring temperature, there is nothing special about it. Consider another object A'. If it has a temperature T_A, then it is in thermal equilibrium with object A in the state where it is assigned a temper-
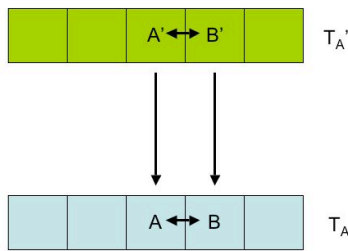
FIG. 1: A set of systems in thermal equilibrium with object A, assigned a temperature T_A, and a set of systems in thermal equilibrium with a copy of object A, denoted A', assigned a temperature $T_A' > T_A$. Heat will always from an object in thermal equilibrium with A' to an object in equilibrium with A.

ature T_A. But then, any other object that is in thermal equilibrium with A' at the temperature T_A will, by the Zeroth Law, also be in thermal equilibrium with A at the temperature T_A, and will therefore have a temperature T_A. This object will also be in thermal equilibrium with all objects in thermal equilibrium with A at temperature T_A.

Now, let's make sure that our measure of temperature deals with the direction of heat flow properly. Let's take object A, and change its state, which is assigned a temperature T_A'. Without loss of generality, we assume that $T_A' > T_A$. Now, consider any object, denoted object B', that is in thermal equilibrium with A when it is in a state that is given a temperature T_A'. Then object B' is

assigned a temperature T_A'.

Consider some other object, object B, that is in thermal equilibrium with A when it is in a state that is given a temperature T_A, so that object B has a temperature T_A. We claim that heat energy will flow from B' to B.

For suppose that heat energy were to flow from B to B'. If we make a copy of A, and put one in a state assigned a temperature of T_A, and place it in thermal contact with B, then we can reversibly transfer heat energy from this copy of A to B. If we put the other copy in a state assigned a temperature of T_A', rename it A', and place it in thermal contact with B', then we can reversibly transfer heat energy from B' to A'.

Therefore, we can reversibly transfer heat energy from A to B, irreversibly transfer this heat from B to B', and then reversibly transfer this heat from B' to A'. The net effect is that heat has been irreversibly transferred from A to A'. But this makes no sense. For how do we know that A' is hotter than A? Because the direction of heat flow is always from A' to A, and not the other way around. Since we cannot irreversibly transfer heat from A to A' (at least, not without doing any work on the system), it follows that we cannot irreversibly transfer heat from B to B', so heat has to flow from B' to B.

This means that our method of assigning temperatures allows us to unambiguously determine the direction of energy flow between any two objects.

Clearly, once we understand the statistical mechanical basis for all of this, the above line of reasoning becomes much shorter. You can think of the laws of thermodynamics as the postulates of geometry before people started computing with actual coordinate systems. Many of the early geometric proofs, although beautiful, became much easier to prove once you could just "crunch the numbers."