Fundamentals of Statistical Thermodynamics

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Lecture - 01

After having studied the concepts of chemical thermodynamics and applications of chemical thermodynamics obviously, it is very important for the students to understand whether the same thermodynamic quantities can be obtained by other means. Therefore, it is very important to understand the concepts of statistical thermodynamics. So what is these statistical thermodynamics and what is the need for having statistical thermodynamics? Statistical thermodynamics is a link between individual molecular properties and bulk thermodynamic properties. So what are these individual molecular properties and what are these bulk thermodynamic properties? Remember that when you studied classical thermodynamics, you were introduced to pressure, temperature, enthalpy, entropy, Gibbs free energy, equilibrium constant, and other related thermodynamic quantities. And you were also introduced to how to experimentally measure those properties. For example, in order to determine the enthalpy of a reaction experimentally, there are different approaches.

Direct approaches can be selected like calorimetry. There are different type of calorimeters available where you can measure the enthalpy change very precisely and directly. There are alternate methods also where several thermodynamic quantities can be measured. But in statistical thermodynamics, we will start talking about individual molecules, individual particles, and their properties and then make a connection with the deeper thermodynamic properties.

So let us begin from the very basics. We will initially start very slowly in developing various concepts so that everything is clear. I am sure that you have gone through basics of spectroscopy and what we learnt in spectroscopy is about how the energy levels of molecules can be calculated, can be determined, and related to their structures. Now having the knowledge of those energy levels, the next step is to learn how having such a knowledge can be used to account for the properties of matter in bulk. And therefore, statistical thermodynamics is introduced which as I just mentioned is link between individual molecular properties and bulk thermodynamic properties.

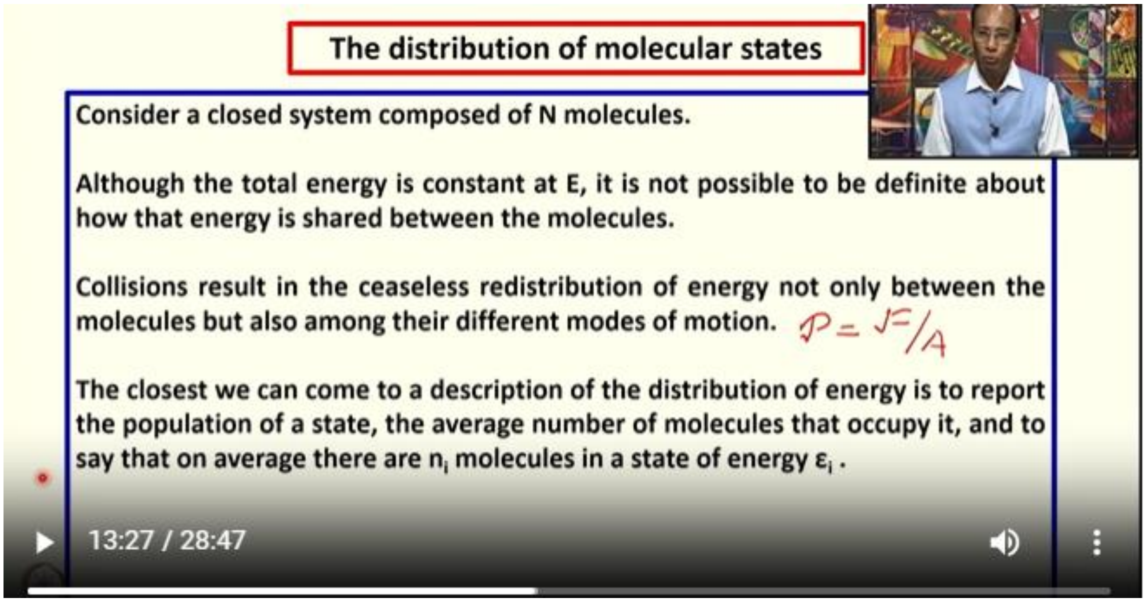
Now obviously, when we will start talking about the individual molecular properties and then we start connecting with the bulk thermodynamic properties, we will require some concepts, some results from quantum mechanics of individual molecules. And then when we switch over from the quantum mechanics of individual molecules to the thermodynamics of bulk samples. It will require recognizing that the latter deals with the average behavior of large number of molecules. So, when we talk about that the latter deals with the average behavior of large number of molecules, what I am talking about is that the bulk thermodynamic properties deal with the average behavior of large number of molecules. Let us go into a little bit more details of this.

So what we will do is we will introduce statistical thermodynamics in two stages. What are those stages? First the derivation of Boltzmann distribution for individual particles which may be of restricted applicability, but it certainly has the advantage of taking us directly to a result of central importance in a straightforward and elementary way. As I mentioned that we will develop the concepts in a very simple manner. And then what we will do is, we will extend the arguments to systems which are composed of interacting particles. Keeping these in mind and having a knowledge from spectroscopy that there are different energy states there are different energy levels.

So let us now start discussing about the distribution of molecular states. Let us consider a closed system which is composed of n molecules. We understand what is a closed system from the definition which was introduced in classical thermodynamics. There are n molecules and let us say the total energy of this system which is composed of n molecules is E. Total energy is E.

There are n molecules. It is not possible to define about how that energy is shared between molecules Because you know the molecules if we consider the gas molecules, those molecules are colliding, exchanging energy and we cannot pinpoint that which molecule has how much energy because these molecules are continuously colliding and they are exchanging energies. The energy is not only distributed or redistributed between the colliding molecules. But it is also shared between different modes of motion. What are those different modes of motion? To say a few translational, rotational, vibrational, there can be many others.

So therefore, that is why this statement is made that although the total energy is constant at E, it is not possible to be definite about how that energy is shared between the molecules. As I just discussed, collisions result in the ceaseless redistribution of energy not only between the molecules, but also among different modes of motion. So therefore, what can we do under such circumstances? If we cannot tell that a particular given molecule has this much energy, the closest what we can come is to a description of distribution of energy in terms of population of a state. And what is that population? Is the average number of molecules that occupy it and to say that on the average there are n i molecules in a state of energy E i. There are different energy states and depending upon the temperature, there will be different occupancy of these energy states. At the most what we can do is that let us say there are n 0 number of molecules in a state of energy E 0, n 1 number of molecules in a state of energy E 1, n 2 number of molecules in a state of energy E 2 and this way we can generalize that in terms of population of a state, we can specify that on the average there are n i molecules in a state of energy E i. Consider a gas which is enclosed in a container. This gas has several molecules. The pressure which is exerted by the gas on the walls of the container. how do we define that pressure? The pressure will be equal to let me write here



The distribution of molecular states

Consider a closed system composed of N molecules.

Although the total energy is constant at E, it is not possible to be definite about how that energy is shared between the molecules.

Collisions result in the ceaseless redistribution of energy not only between the molecules but also among their different modes of motion. $P = F/A$

The closest we can come to a description of the distribution of energy is to report the population of a state, the average number of molecules that occupy it, and to say that on average there are n_i molecules in a state of energy ε_i .

$$P = \frac{F}{A}$$

How much the force is exerted by the molecules per unit area that will form the pressure, but then you cannot specifically pinpoint that which particular molecule is constitutive to how much pressure and we talk about the average quantity over there. Therefore, pressure becomes an average quantity. So therefore, we talk in terms of here average number of molecules even when we talk about population of state. Now these population of states remain almost constant at a given temperature, but the precise identities of the molecules in each state may change at every collision. It is very important to understand this particular concept.

As I said that the molecules of the gas they are colliding with each other and how fast they collide will depend upon the temperature and that is why the statement that the population of the states remain almost constant at a given temperature, but since the molecules are colliding with each other they are exchanging their energies. Therefore, the precise identities of the molecules in each state may change. It is like saying that when a certain number of molecules are occupying a given energy state those molecules are not imprisoned. Those particular molecules are not imprisoned in that state. The residence may change, but the average number of molecules in each state that will remain constant that is the meaning of that. And what I just talked about in terms of for example, here pressure I was talking about force per unit area. There are so many molecules which are colliding the walls of the container and we cannot pinpoint which molecule is contributing how much force, how much pressure. We talk about the average quantities. In statistical thermodynamics, we will start connecting with individual particles, individual atoms if we are considering a system of atoms or individual molecules if we are considering a system consisting of molecules. So, what we will do? We will calculate the population of states for any type of molecule in any mode of motion whether it is translation, whether it is rotation or vibration, any temperature.

We will start developing equations, we will start developing concepts and understand how to calculate the population of the states. This is important to recognize that the restriction that we will apply in the beginning is that the molecules should be independent in the sense that the total energy of the system is some of their individual energy. This should be very clear. When I say that the molecules should be independent, let us say there are total n number of molecules in the system.Then n 0, n 1, n 2, n 3 etc. all these molecules are independent so that the total energy of the system is equal to the sum of the energy possessed by each individual independent particle or molecule. That means at this point, we are not permitting the molecules to interact with each other. Remember the difference between ideal gas and non-ideal gas. In an ideal gas, the molecules do not interact with each other. But in a non-ideal gas, the molecules interact with each other and if the molecules start interacting with each other, they will interact which will lead to either release of energy or absorption of energy.

Therefore, the total energy of the system will also consist of those contributions. Therefore, to begin with we will apply, we will put this restriction that the molecules should be independent and in the sense that the total energy of the system is a sum of their individual energies. Later on, when we build upon other concepts in statistical thermodynamics, we will permit the molecules to interact with each other and the corresponding changes will be or modifications will be discussed. So this is what I was talking to you that we are discounting at this stage the possibility that in a real system, a contribution to the total energy may arise from interaction between molecules. And obviously, the interaction between molecules will arise if there are functionalities in the molecules, there are groups in the molecules which can lead these molecules to either associate, undergo the interactions which bring them together or there could be repelling interactions.

It could be exothermic, it could be endothermic. So let us forget that the molecules can interact at this point and therefore, stick to the restriction that the molecules are independent. We also adopt the principle of equal a priori probabilities, the assumption that all possibilities for the distribution of energy are equally probable. See whenever we start building some concepts, some theories, we always list down some postulates that my developed theory, my developed equations will be valid if these postulates are followed. And that is why I have been discussing with you that what are the restrictions that we are imposing at this time so that the equations that we develop soon are under those restrictions.

Now let us start talking about configurations and weights. There are n number of molecules, we started with that, there are n number of molecules. There is energy, we talk about the system E is the energy. So therefore any individual molecule may exist in energy states E0, E1, etcetera, etcetera. As we just discussed that in spectroscopy you learned that there can be different energy states, there can be different energy levels. he occupancy of those states, those levels will depend upon the temperature amongst other factors. And when there are large number of molecules in a given system, depending upon the conditions an individual molecule may exist in any of the states E0, E1, etcetera, etcetera. Okay, let us keep in mind. And we shall always take E0, this one, as the lowest state. Now listen to me carefully what I am going to say. For the sake of convenience and for the sake of simplicity, let this lowest state be termed as zero of the energy, E0 is equal to zero. I repeat that any individual molecule may exist in states with energies E0, E1, etcetera, etcetera. What we will do is we will set this E0 equal to zero and then measure all other energies relative to that state. So when you have a set of energy levels, treat the lowest as zero. Is it always zero? It may not be always zero because you know that the oscillators, they have zero-point vibrational energy.

So that means if we set the lowest state as zero of energy, then in order to determine the internal energy of a system, we have to add a constant which is equal to the zero point energy. Now what is internal energy? It's important to redefine here what is internal energy. Internal energy of a system is equal to the sum of or the total energy added up in all the forms. That is the internal energy. Once again, the internal energy is the total energy of the system added up in all the forms.

Like if a molecule has translational degree of freedom, rotational degree of freedom, vibrational degree of freedom, electronic degree of freedom, any other degree of freedom, add up energy possessed by the molecule in all the form and that is equal to its internal energy. And if we set the lowest energy equal to zero as I mentioned over here, then zero is to be added to the total energy to calculate internal energy. Otherwise, whatever is the value at E0, that constant is to be added to obtain internal energy from the total energy. So that is why this comment that to obtain the actual internal energy U, we may have to add a constant to the calculated energy of the system. And the example that I took is that if we are considering the vibrational contribution to the internal energy, then we must add the total zero point energy of any oscillators in the sample.So, what we have done so far is introduced what is statistical thermodynamics and what is the need of studying statistical thermodynamics. We want to establish a link between the individual molecular properties with the bulk thermodynamic properties. And in order to develop various formulations, various equations and in order to move further, we will require some knowledge of spectroscopy, we will also require some knowledge of quantum mechanics and then we will take those concepts and connect with the bulk thermodynamic properties. We also discussed some sort of essential kind of postulates which will be followed before we derive certain equations. And I hope that the basic information that I shared with you in this lecture will be helpful in understanding developing further concepts which we will now discuss in the next lecture. Thank you very much. Thank you.