Advanced Chemical Thermodynamics and Kinetics
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Lecture - 22
Introduction to statistical thermodynamics 01

Hello everyone. So, today we will start a discussion on statistical thermodynamics or statistical mechanics.

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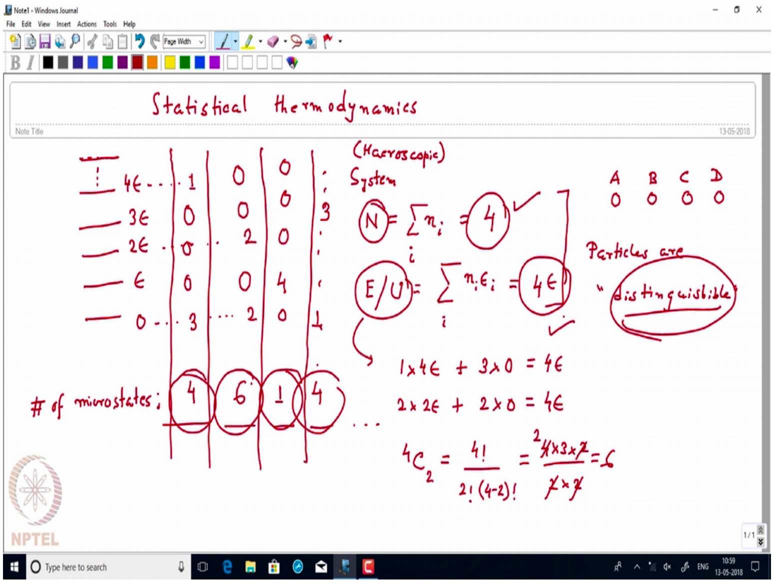

Statistical thermodynamics

(Macroscopic) System

$$N = \sum_i n_i = 4$$

$$E/U = \sum_i n_i \epsilon_i = 4\epsilon$$

$$1 \times 4\epsilon + 3 \times 0 = 4\epsilon$$

$$2 \times 2\epsilon + 2 \times 0 = 4\epsilon$$

$$^4C_2 = \frac{4!}{2!(4-2)!} = \frac{\cancel{4} \times 3 \times \cancel{2}}{\cancel{2} \times \cancel{2}} = 6$$

Particles are "distinguishable"

But since this is not a course on a statistical thermodynamics, we will just keep our discussion very brave. And we will only learn a few basic concepts in the statistical thermodynamics which will help you to understand the reaction dynamics in a better way because we will be using those formally or the relationship to understand them, the how reactions work.

So, the most important thing we are going to discuss here how to calculate partition functions. And we limit our discussion up to there. Now I will give you a general introduction, again not going into too much details, that how you should think about the statistics or how the Boltzmann statistics was developed.

So, now when and a around in 1880 or so, when Boltzmann actually showed this Maxwell's distribution of molecular speed or molecular energies, can be actually derived if you assume that the I mean any matter is composed of molecules and if you just talk about the statistics of those molecules you can derive the entire thing.

Now, the idea what Boltzmann was nurturing in mind is something like molecules have energy levels although he will show these energy levels are discrete energy levels like we use in quantum mechanics. But in original Boltzmann's derivation, those energy levels are considered to be continuous. Now again I am not going to derive the Boltzmann distribution here, you can actually refer to any standard textbook.

For example, you can have a looked at the physical chemistry textbook by Atkins. There he has Atkins and de Paula they have actually derived the Boltzmann distribution law. We just discussed the salient features on how what I what I prefer at the conceptual understanding of the Boltzmann distribution. Now what it tells is that the way we think about it, it is again it is not the original way that the Boltzmann distribution came, but it is the way we think about Boltzmann distribution today.

Suppose we have some energy levels, in the inner molecule. Take a very simple system let us say some molecules are there some particles inside a box. Now particle in a box energy levels are of course, not the way I have drawn it. It is not equally spaced, but suppose that molecules have some equally spaced energy level. For example, example vibrational energy levels like are like that. And suppose these energy levels have energies like this 0 epsilon 2 epsilon 3 epsilon something like that, 4 epsilon and so on. Suppose we have 4 particles in our system, so, then we have a system and system means it is a macroscopic system. In the sense that whatever we measure in thermodynamics as we emphasized many times, that classical thermodynamics is a macroscopic science without any detail of the microscopic understanding of the nature of the matter.

Now, and it is very much phenomenological science and people derive very nice relationship before 1850s or so around 1850s some Clausius, it is monumental work, but so, according to macroscopic thermodynamics you can actually define the total energy of the system. And suppose we are also saying that my system the macroscopic system is composed of some number of particles, but the number of particles is also fixed.

So, macroscopically I have 2 parameters; total number of particles and the total energy of the system. And suppose I have the total number of particles which I am writing as let us say capital N. Let me just write it as this and then also I am saying that my macroscopic system has another definition. And let me just write it in a slightly different regime for a reason I will just write some distribution here.

So, suppose I have N is the total number of particle and now what is this N? Suppose these energy levels I am writing as say I am saying that what is the energy of the ith energy level? So, i denotes for 0 1 2 3 something like that.

So, if the energy of an arbitrary level i is epsilon i, then and if the number of particles in that level is n i, then I can say that the capital N, the total number of particles is nothing but the number of particles in the ith energy level. And then you sum over all the energy level. And that we have taken let us take a number; let us say it is 4, I have 4 particles. And also say that the total energy sometimes I we will write it as E, sometimes we write it as U; it is the total internal energy and what that it would will be in terms of summation?

Suppose if I have n i particles in the level epsilon i, so, the energy contributed for by those particles will be n i times epsilon i. Because each particle has an energy epsilon i, in the ith level and there are n i particles in the ith level. So, the total energy will be n i into epsilon i for the ith level. So, for that total system I will have to take a summation over that and let us also take a number for that; let us say that is 2 epsilon. So, that is the description of my macroscopic system that I have 4 particles and the total energy is 2 epsilon.

Now, microscopically the system might have different configuration and that is what is interesting and what we are going to discuss right now. So, what do you mean by configuration. Let us give you an example. Suppose I have these 4 particles, and this 4 particles I have to arrange in such a way in these energy levels. So, that the total energy is 2 epsilon. Now how can I do it one easy way is that I can keep one particle let us say here in the energy level 4 epsilon, and all 3 particles I can give at a energy level 0.

So, you can see from this equation the total energy will be one particle in 4 epsilon level plus 3 particles in your 0 energy level. So, that is nothing but 4 epsilon; I think we took 2 epsilon let us just take the total energy to be 4 epsilon then we will have more number of distribution. Now the question is it an unique number in the sense that is it how many ways you can actually achieve this particular distribution.

Now, depends now whether these particles, these 4 particles are indistinguishable or distinguishable. Meaning suppose I have 4 particles like which I can level them like I have particle 1, which I can I am leveling as a I am particle to particle 3 and particle 4 and I can actually level them as A B C D or some let us say some color red green blue and black whatever. So, that I know actually which particle is which I mean it has a specific identity.

So, in this case I am also assuming that the particles are distinguishable and this is very, very important. Distinguishable and if the particles are distinguishable meaning we can distinguish, but separate or segregate one particle from any other particle. Then I can actually say this distribution the way I have write written it that 3 particles in energy 0 and one particle in energy 4 epsilon will have many distribution.

Why because this one particle can be the particle A, this can be the particle B this can be the particle C and this can be the particle D meaning when I am choosing the a particle in energy level 4 epsilon B C and D are in energy level 0 when I am choosing particle B in the energy level 4 epsilon then A C and D are in 0 something like that

So, the number of ways I can actually choose one particle in energy level 4 epsilon and 3 particles in energy level 0 is nothing but 4. So, what I am showing vertically, is basically that distribution and here I am basically writing the number of possible ways we can achieve this particular distribution. Now this possible ways means actually number of microstates.

So, what is a microstate? Now microstate means actually a specific distribution that the system has which is a microscopic distribution of the system; however, has to satisfy the macroscopic distribution, which is the total number of number of particles are 4 and total energies 4 epsilon.

Now, let us say can we actually have some other distribution of course, there are many distributions for example, I can actually put 2 in a particles in energy level let us say 2. And then the total energy will be 2 into 2 epsilon and to keep the total energy for epsilon i have to keep the other 2 particles in this other energy level. So, 0 energy level. So, then I will get the distribution as the same the macroscopic description as the same. So, what I am showing here, I can actually make a table like thing. So, this is another way of distribution.

So, in the first distribution I get 3 particles here 0 particle here 0 particle here 0 particle here and one particle there. The second distribution I have kept 2 particle here 0 particle in the energy level epsilon 2 particles in energy level 2 epsilon and for other cases I am keeping. So, how many ways I can achieve this distribution. Then again you have to think if the particles are distinguishable I am choosing 2 particles in energy level 2 epsilon. What are these 2 particles? It can be A B it can be A C it can be A B and then it can be also B C it can be B D and it can be C D. So, the total numbers are basically 6.

Now, how do I get this 6 mathematically, it is it is very interesting thing. So, it is a very easy thing if you have studied permutation and combination. So, I had 4 particles and I am choosing basically keeping them in 2 I mean picking up 2 at a time. So, that is nothing but the number of 4 C 2 which is a factorial 4 divided by factorial 2 into factorial of 4 minus 2 which is 2. So, 2 factorial is 2 factorial is 2 here.

And 4 factorial I can write it as 4 into 3 into 2 into 1 and divided by 2 into 2 and thus you can see that these 2 cancels and then gives me this number 6. That is how we get the 6 mathematical.

So, there will be 6 such states, now you see that moment I choose for that 2 particles for state 2 epsilon the other 2 particles in the 0 are automatically chosen. So, it is very straightforward. Now similarly you can actually have other distributions. For example, if I have 4 particles there will be one distribution that all the 4 particles will be in I mean in energy level epsilon, but that will have just number one.

Because it is just an unique distribution. And similarly I can also have many other ways you can think about it like I can put 3 particles in energy level 3 epsilon and I can have one particle in energy level here, then again there can be many different distribution you can think that that one particle in the 0 energy level can be chosen in 4 different ways it can be A or B or C or D. So, it will have number 4 something like that.

Now, what we see it is very interesting that number of micro state, since the particles are distinguishable that is changing from one distribution to the other distribution. So, if I ask you that what is the probability of having then what is the number of molecules or number of particles in an arbitrary energy level E I, which is basically n I, how to calculate it? So, then you say that ok so, I can actually it can vary but what on statistical ground if I have a huge number of particles and the sufficiently large amount of energy, so that I can have many possibilities, then you can argue that that distribution will be most probable which has the maximum number of microstates, provided all these microstates are equally probable in the sense that so, what we are saying suppose we have a macroscopic system, and the total number of microstates which correspond to that particular macro state which is defined as a fixed number of particles and fixed internal energy that I can achieve in many different ways. And then I am suppose just take a number suppose there are 100 microstates totally available to our system.

Now, out of this, 100 microstates I find that there are suppose a distribution, there are suppose 3 distribution, that I can have that I can actually have these microstates. And one distribution has suppose, 60 micro state and the other distribution suppose has 30 microstate and the third distribution has suppose 10 microstate just a way we have drawing that this is the vertically we have a distribution and that has 4 microstate these are 6 microstate, this is one microstate and this is 4 microstate something like that.

And if this number will continue of course, because we have not considered all the possibilities there are many other possibilities also. So, you can now say that that distribution will be most probable which has maximum number of microstates because all microstates are equally probable because all microstates satisfy these number, which is the total macroscopic for to satisfy the macroscopic description of the system on these 2 constraints that are my total number of particles and total energy is fixed.

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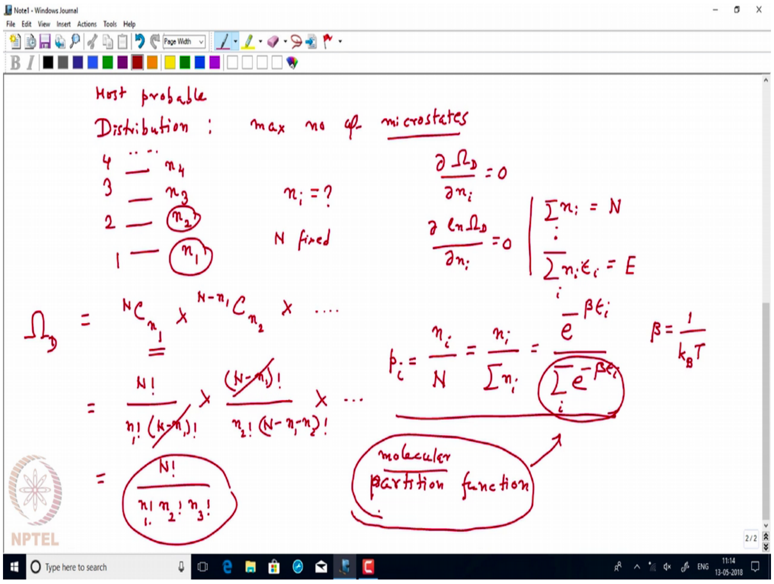

Most probable Distribution : max no of microstates

4 — n_4
3 — n_3
2 — $\boxed{n_2}$
1 — $\boxed{n_1}$

$n_i = ?$

N fixed

$$\frac{\partial \Omega_D}{\partial n_i} = 0$$

$$\frac{\partial \ln \Omega_D}{\partial n_i} = 0 \quad \Bigg| \quad \sum_i n_i = N, \quad \sum_i n_i \epsilon_i = E$$

$$\Omega_D = {}^{N}C_{n_1} \times {}^{N-n_1}C_{n_2} \times \ldots$$

$$= \frac{N!}{n_1!\,\cancel{(N-n_1)!}} \times \frac{\cancel{(N-n_1)!}}{n_2!\,(N-n_1-n_2)!} \times \ldots$$

$$= \boxed{\frac{N!}{n_1!\,n_2!\,n_3!}}$$

$$p_i = \frac{n_i}{N} = \frac{n_i}{\sum n_i} = \frac{e^{-\beta \epsilon_i}}{\boxed{\sum_i e^{-\beta \epsilon_i}}} \qquad \beta = \frac{1}{k_B T}$$

molecular partition function

Now, in this way what we do in statistical thermodynamics is the first thing you actually calculate the distribution or the most probable distribution, and the most probable distribution is by definition is that distribution which actually has a maximum number of a microstates. So, again a microstate is basically a microscopic description of the system. So, different microstates correspond to the same unique macroscopic description. So, one macroscopic system can have internally many microstates because many microstates correspond to the same physical macroscopic properties.

Now, how do you do it? So, basically you derive which you are not going to show you derive a general equation, how you can get the number of microstates for a specific distribution. And then you just take the derivative with respect to the change in particle and then you make it to be 0, because we are actually maximizing the number of microstates have to find which is the most probable distribution and then you do a very generalized to it in the sense that I will just give you a flavor.

suppose what I am saying here is that suppose the energy levels I am denoting as 1 2 3 something like that 4 and I am saying that I have chosen n 1 particles for energy level 1.

So, this n 1 n 2 or in general the n i has to be figured out and then I have I am choosing n 2 particles energy level 2, then n 3 particles for energy level 3 and 4 particles for energy level 4 something like that and so, then if the total number of particles is fixed then I can say that how many ways I can choose the per I can filling the first energy level and then you can easily say by combination that fine.

Ah I can choose it in n c n 1 different ways. Once you do that the second energy level are can be for that actually this into can be chosen in how many ways. So, once I have chosen n 1 particles on left with n minus n 1 particles and 2 out of those many particles I can actually choose n 2 particles to fill in the energy level 2 and so on.

So, the total number of distribution or total number of microstates for that particular distribution where I have n 1 particles in energy level one n 2 particles in energy level 2 or in general n i particles in energy level i will be something like that and you can actually easily do that. So, it will be n factorial by n 1 factorial into n minus n 1 factorial, the second thing will be n minus n 1 factorial divided by n 2 factorial into n minus n 1 minus n 2 factorial. That you will proceed and you will easily figure out that these factorials will get cancelled.

And so, ultimately at the end of the day what we will get is something like this. Which is n factorial divided by n 1 factorial into n 2 factorial into n 3 factorial something like that. And then you can actually so, that will be basically the total number of microstates in that distribution, if I just call it as a something like that sigma D suppose is a distribution at general distribution then the way you derive it is that you will maximize this number, but instead of taking the maximization like the differential of this sigma D with respect to n i making that to be 0.

We actually take if that is correct; we instead of taking the distribution function directly we take the logarithm of the distribution function and make that to be 0. Because there are you can easily see that if I use the logarithm of this thing then you can actually write the logarithm of n factorial and use something known as stalling approximation and in the denominator you see that it is a logarithm of many numbers n 1 factorial into n 2 factorials.

Then actually you can write it as a summation, because log of a into b into c is log of a plus log of b into plus log of c, that way. And then in use stalling approximation and many other things with that constraint what is the constraint that my total number of a particles is fixed. And also the total energy is fixed. And then you use something for a differ any differential equation with a constraint means actually if you have many variables in the differential equation.

Suppose I have a system of a variables, like I have x 1 x 2 x 3 something like that in this case also these variables are basically the number of particles that some varying a per energy level. So, the n i, I am varying. So, what is interesting here keeping the total n constant? So, what is interesting here is that, if I do that then I say that I cannot do it independently because all this system of equations are not linearly independent because of this constant. So, there is something called a Lagrange method of undetermined multiplier.

So, that you apply and then you basically solve the differential equation. And then ultimately at the end of the day you can actually calculate these n i for any general distribution, and you can show that these n i is basically proportional to or we can take a fraction that what is basically the probability of having some number of particles in energy level i that will be basically the number of particles divided by the total number of particles.

So, that is nothing but n i divided by sum over n i. And that n i from all this derivation you will see that that is given by a Boltzmann factor, which is nothing but scaled by the energy, exponential scaled by the energy and then you get expression like this. Where the beta this is given as 1 over the Boltzmann distribution times that absolute temperature.

Now, this derivation is given the way I have told you, after you use all these 2 constraints as well as the Lagrange method of undetermined multipliers. So, then you get this distribution function. Now, but the important quantity we see here is this quantity which is sum over e to the power minus beta epsilon i. And that we call as a partition function or you denote it as q. And this will be our starting point of discussion and because this is the key thing that we are going to use most heavily we are going to calculate this partition function for many systems for any energy levels.

So, we define this we call this as partition function. Or better the way I have shown it is better to call it as a molecular partition function. Because actually we started with a molecular energy levels and then derived this partition function there are also other ways of thinking about it you could actually think about the entire system and then enter macroscopic system and you could actually derive the statistics in a very different way from an ensemble approach, where do we actually say that fine I have many different microstates.

And then if I measure at a time say for example, at an instant, then I can find the system in one of this microstate. If I measure it in a different time then I can think that the system has different microstates, something like that. So, meaning if you just go back to our previous discussion.

Suppose I have this system which we just discussed composed of 4 particles which are A B C D which is distinguishable and the total number of particles are m, and the total energy is E or U, and then what we are going to see here is that if we have let us say a measure the microstate of the system at an instant. And suppose I do an measurement at right now, and I find that one m molecule or a particle is in energy level 4 and the 3 all other in energy levels 0.

And the next instant somebody else does a measurement and finds that C and D are in particle in energy level 2 epsilon and the other 2 adding 0. Then I come back and do the measurement again. Suppose I again find something like distribution 1, particle in C in energy level 4 epsilon and all others in 3 which means actually the system the macroscopic system at different time is going through different microstates.

So, at an instant it has a particular microstate, but this microstate it is changing. So, the system is time evolving. The question is what will be the average property of something let us say I talk about energy or total energy here is fixed or say something like say entropy of the system, which are average quantities. So, then I have to take the average over I have to take a time average over all these things. The question is if I want to do a time averaging then I have to solve a dynamical equation.

If the systems we have classically, then I have to do a classical equation, solve a classical equation motion. Because I need to know how these energy levels are being changed how the particles are moving from one energy level to another energy level or some other quantum mechanical kind given in Schrodinger equation or something like that.

But that is a very tedious exercise because in general this is not actually any macroscopic system is not just composed of 4 particles. It composed of millions and millions of molecules. So, our atoms and forever is finite energy will have so many impossibilities. So, you cannot just do it rather you say that fine, the time average of all these my of the system which is traversing through different microstates over time is as if taking an ensemble average.

Now, what is an ensemble? The ensemble is a thought process it is basically a hypothetical collection of the system corresponding to different microstates, but that course I mean which actually is a collection of different microstates of the system, but which is which correspond to the same macro state meaning as if you are you are thinking that ok. So, I have a collection of macroscopic system all macroscopic system for which the total energy and total number of particles is fixed.

And then I am saying that the macro state is evolving through different microstate is a conceptually equivalent to saying that I have different macros I have different systems with different microstate which correspond to the same macroscopic state, but then what I will do is that I will just do the statistics of all this system. Because those suppose the probability of having microstate where actually I have one particle in energy level 4 epsilon and 3 particles are in 0.

So, that will be weighted by this number. So, there is a statistical weightage for each such distribution. And then you do the statistics of those things and then you conceptually say in this case actually instance energy and the number of particles are conserved these macroscopic systems are not exchanging energy with respect to each other. And in a more general situation we actually say that fine these systems are not actually isolated system.

But that temperature is constant, but the energy is constantly fluctuating between them. Then we talked about it then you call that kind of ensemble as a canonical ensemble and the one which I gave the previous example is called a micro canonical ensemble. And in that we can actually do a ensemble approach on the statistical mechanics, which was put forward by Willard Gibbs, but we do not need to know all these I mean details.

Because what we will be doing is just restrict our discussion to this molecular partition function, and we will show how one can calculate this molecular partition function for different problems for different say energy levels, that is what we are going to do now.