Advanced Thermodynamics and Molecular Simulations
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Lecture - 04
Probability Distributions and Thermodynamic Equilibrium

Hello all of you. So in the last lecture we have been discussing the idea of probability. We first discussed the definitions of like probability, and then how can we combine them and then we did a playing card example and finally, we were discussing the idea of distributions in a coin toss examples. In this lecture, we will continue on that discussion and discuss the idea of a most probable distribution. That is what defines the thermodynamic equilibrium.

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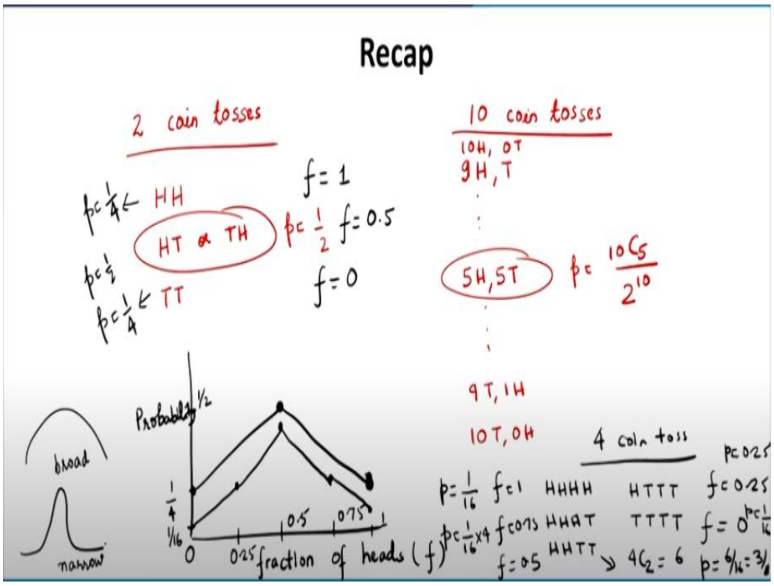
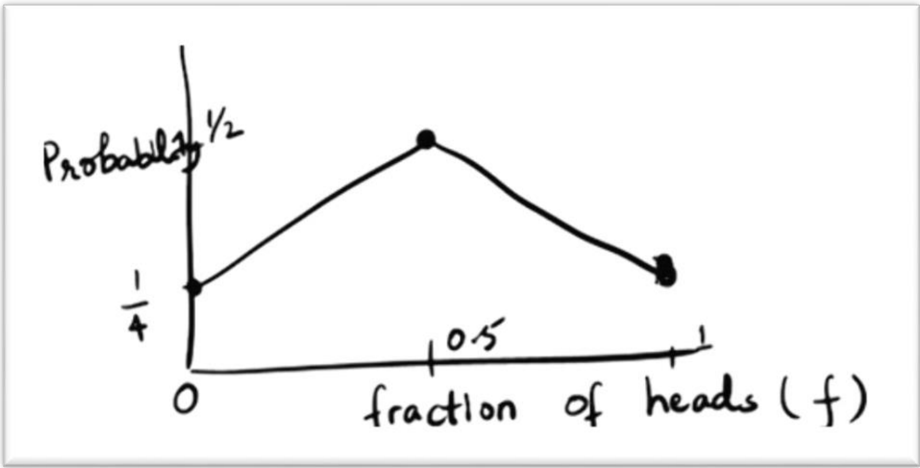


So just to quickly recap, what I was telling you is that, if I do an experiment on two coin tosses, and compare that to 10 coin tosses, then the probability that we will have equal number of heads and tails actually decreases as the number of tosses increases and we justified it by writing down all the possible distributions, which for the two coin tosses was 2 heads, 1 head and 1 tail, or tail and a head or 2 tails and then we said that the probability of that to happen is equal to 1 by 2. For 10 tosses, the number of possibility increases, so we can have 9 heads 1 tail, 10 head 0 tail, 5 head 5 tail and again the order is not important here, it can be any of the 5 out of the 10 and similarly,9 tail and 1 head or 10 tails and 0 head and we said the number of ways to this to happen is much lesser in comparison to total number of ways and the probability of this is-

$$p_c = \frac{C_5^{10}}{2^{10}}$$

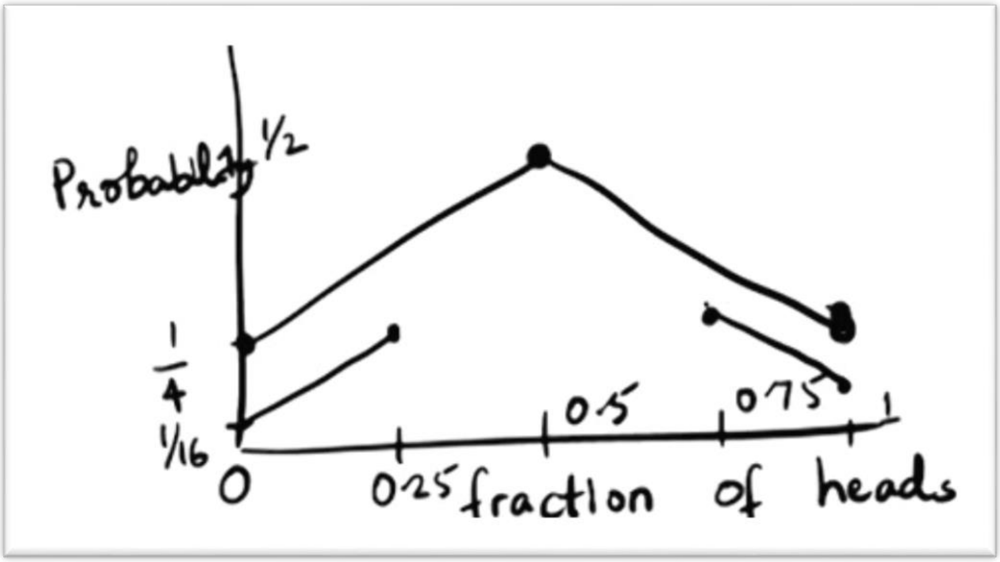
However, if I now rephrase the problem slightly, and I ask what how is the probability changing as a function of the fraction of heads that we are getting in the problem. So let us say for example, if I plot the probability versus the fraction of heads and clearly the fraction of head should be between 0 to 1, either you have no heads or you can have all heads or you can have any number of heads in between, which will correspond to a fraction between 0 to 1. So one thing is clear that in both these cases, the most probable case should be the one where the number of head and tails are equal, right that is always clear in this example as well for 10 tosses, you can do it yourself and convince yourself. But the number of ways of that to happen is changing in the two cases naturally as we discussed.

So one thing is clear that whatever this function looks like, it must have a peek at F = 0.5 where F is the fraction of head. However, how the distribution will look like is going to change. So in this particular case, when we have two coin tosses, naturally we have seen the probability of 2 heads was 1 by 4, probability of 2 tails was 1 by 4, probability of 1 head and 1 tail was 1 by 2 that will correspond to, the first case corresponds to f = 1 when the number of heads are 2 that is fraction equal to 1. Second case is f = 0.5 and the third case is f = 0 and for both f equal to 0 and 1, the probability is 1 by 4. However, for f = 0.5 the probability is 1 by 2. So the distribution looks like this-



Of course, we can do 10 tosses but let us go in like steps. Let us say for example we are doing four coin tosses. So when we are doing four coin tosses, then the number of possibilities increase. We can have for the 4 coin toss case, there are 4 possibilities. We can have all heads, we can have 3 heads and 1 tail, we can have 2 heads and 2 tails. We can have 1 head and 3 tails, or we can have all tails, right. So that corresponds to actually five possibilities that are possible. That is like the first case is f = 1. Second case is f equal to 3 by 4, that is 0.75. Third case is f = 0.5. Fourth case is f = 0.25 and the last case is f = 0, right. And we can find the probabilities there. So the first one will be p is 1 by 2 multiplied by 1 by 2. 1 by 2, 1 by 2 four times it becomes 1 by 16. The second case, the probability is, again 1 by 16. But we can do it in four different ways because either of the four can be a tail. There is only one tail, either of the four can be a tail. So this can be done in 1 by 16 into 4 that is 1 by 4 ways. The third case, similarly, I can do in 6 ways, because in total, we can have ${}^4C_2$ ways to pick 2 heads or ${}^4C_2$ ways to pick 2 tails and that is going to be 6. So probability should be something like 6 by 16, that is 3 by 8. And again for f = 0.25, the probability you can find will be same as f = 0.75 and that is 1 by 4.25. And the last one will be again 1 by 16.

And let us say I plot this for four tosses. So for f equal to 0 and 1, the numbers are much lesser they start from 1 by 16 then we have now a possibility of having f = 0.25 and f = 0.75 as well. And the probability of that to happen is 1 by 4. So it is somewhere here, somewhere here. And then finally, we have 3 by 8 probability of having equal number of head and tail. So that clearly the number is less than 1 by 2. It is somewhere here that is going to look like



Now I want you to start thinking how the distribution is going to evolve as I am increasing the number of tosses. So clearly, at f = 0.5, the probability is decreasing but at the same time, the distribution is also becoming narrower, right so this is what I refer as a broad distribution and this is what I refer as a narrow distribution. So while it is true, that the probability of having equal number of head and tail is decreasing, the probability of all heads and all tails are also decreasing by a much larger amount and more importantly, now we have more points on the plot as we are doing more and more cases.

So if I, instead of looking at the probability values, if I look at the distribution of probability, if I look at this plot, what we start to see for large N is the following.

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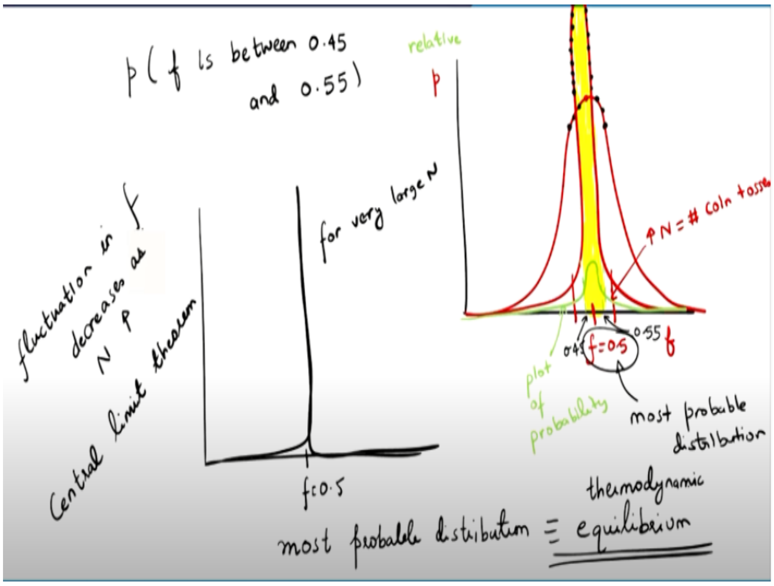
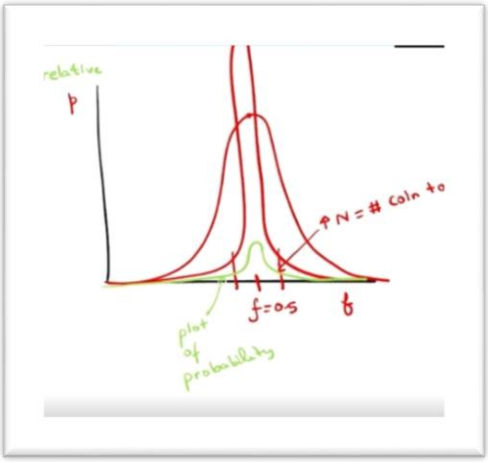
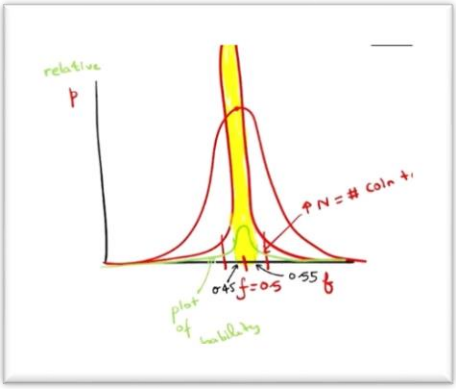


So if I look at the probability versus my f, my distribution will start to become more and more narrow, as I increase N, N being the number of coin tosses, okay. Now you may notice that I have moved the peak slightly up. So that is not quite true. The peak is actually going down. But I am focusing only on the shape of the curve, not really the position of the peak. Of course, we can divide the probability by a factor or whatever, we will come to that but the key point is that the peak is becoming narrower.

So if I do not look at the probability at a particular location f = 0.5, that probability is clearly decreasing. Actually, as I was telling you, the plot will not look like this. The plot will actually look like something like that, right. This is the plot of the probability. So peak should actually go down but if I do define something like some sort of a relative probability, which is defined in a manner that it scales the probability values, then we should see a narrowing of the peak, right. So we can always scale the numbers.



So what if I instead of looking at the probability values, if I look at the probability values, probability for the fraction to be in a certain range. If I rephrase the question and I ask, what is the probability that my f is between 0.45 and 0.55 and that probability is going to increase as I increase the number of tosses. The reason being that the distribution has narrowed, right more specifically, when I ask that the probability of f between 0.45 and 0.55 or any particular range, what we are looking at is actually area under the curve on this diagram that is, for example, an area like this, where this is my 0.45 and this is my 0.55 or in the normalized distribution, it is going to be this entire area under the curve.



The other way to say the same fact is that, as I increase the number of tosses, clearly the very point where the number of heads and number of tails become equal, the probability of that point on the plot actually decreases even though in the normalized plot, I have not plot in that particular way, the green line is the one where the peak has decreased but the red line is not that one, but nonetheless, the key point is that the particular value at the peak is not really very important.

If I look at that fraction to be in a certain range of values as opposed to being that precise exact value, right. So what I am trying to highlight here is that as I increase the number of tosses, the distribution gets narrower, that is one of the points. The peak goes down but also the number of points around the peak actually increases as we increase the number of tosses. So going from here to there, let us see if I have these possible outcomes in here, which are fewer in number than comparison to the possible outcomes in there and you can see that in the previous example as well. In the case of two tosses, we had only three possible outcomes. So we had we could either be f = 0 or be f = 1. When I am doing four tosses, then we have two additional outcomes. f = 0.25 and f equal= 0.75. If I do 10 tosses, then I will have even more outcomes closer to f = 0.5. So as I am increasing the number of tosses, we are having more and more points near the peak. So although the absolute probability for the peak reduces, the probability of f being in a range actually increases as I increase the number of tosses and therefore, what we can see, if I keep on increasing the number of tosses, we will have a scenario where the probability will start looking at like something like this very closely peaked at f = 0.5 for very large N.

It does not mean that f = 0.5 exactly have become highly probable all it means is that the probability of f being close to 0.5 has increased as we have increased the N. The other way to say the same thing and that is closer to the notion of thermodynamics is that this f = 0.5 we may say that it is my most probable distribution, but my f can take any value around it. So if I measure an f it may vary from 0.5 in different experiments. So what it says is that if I increase the number of tosses, my variation in f from 0.5, my variation in f from the most probable distribution actually decreases. In other words, what we can say is that the fluctuation in f, the fluctuation will be the deviation from the most probable distribution value that is 0.5. So fluctuation in f actually decreases N that is the number of tosses increases that is an extremely important property for the thermodynamics or statistical mechanics, which is the statement of what is known as a central limit theorem actually, the argument goes a bit further although I have drawn distributions looking like a Gaussian distribution it is actually true for any other distribution as well as the number of experiments increases, the fluctuations in the property decreases.

So going back to the idea I have discussed in the first class, we are talking about the molecular origin of properties. So whatever property we evaluate for a large system, let us say for example, temperature or pressure, ultimately they arise from molecular collisions and things of that sort that is what we discussed in the ideal gas case. Now what it tells you is that, when the number of the collisions for example are large, which is naturally the case for an ideal gas, the number of molecules are large in that case, the fluctuation in the property we are going to measure let us say temperature is going to be a smaller, right. So therefore, whatever evidence properties we define in thermodynamics, we can only have a small fluctuations around that average, because the number of molecules are very large so what we mean by the most probable distribution is not that we will have exactly the same value of the outcome as given by the most probable distribution, all it means that we will have many distributions close to the most probable distribution, and that is an idea that is central to that.

So I want to emphasize here that this need not be the case from the beginning of the molecular system going back to the ideal gas example, it need not be always true what actually happens is that this particular condition of a most probable distribution is only achieved when we are in a state of equilibrium and we are talking about thermodynamic equilibrium in this particular case, but we will do an example of chemical equilibrium next, where we demonstrate that this idea of equilibrium is very general and applies to any equilibrium that we see in the universe.

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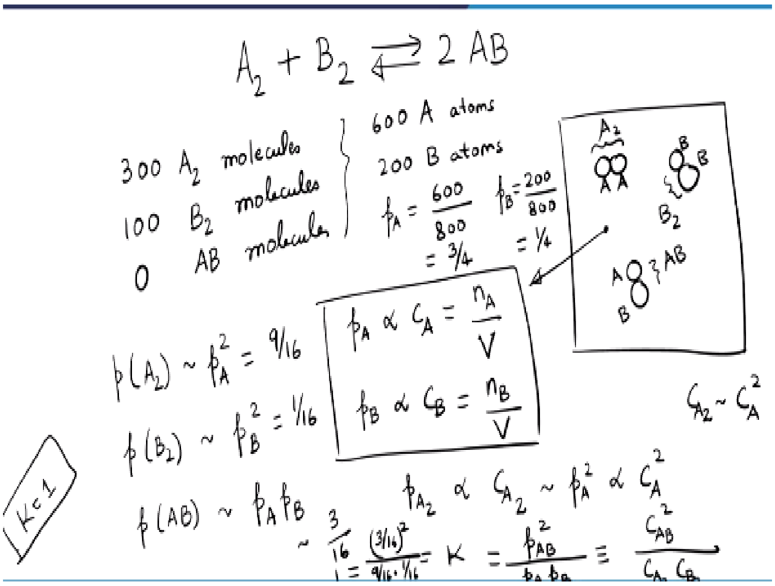

So let us say for example, if I look at a particular chemical reaction that is-

$$A_2 + B_2 \leftrightarrow 2AB$$

And let us assume that this reaction can happen in both forward and in the backward phase that means A_2 and B_2 can combine to form 2 AB or 2 AB can break down and form A_2 and B_2, right. And I am going to argue that the equilibrium of this chemical reaction or the chemical equilibrium can be derived purely on probability arguments using the idea of distributions I just mentioned.

So let us say for example, I start with some 300 A_2 molecules and some 100 B_2 molecules and let us say at the start, we had 0 AB molecules and we are looking at the progress of this particular chemical reaction. So now if I look at the system at a molecular level, what exactly are we going to have? We are going to have a species A and A forming A_2. We are going to have a species B and B forming B_2 and we are going to have a species A and B forming AB these are the three possibilities in this particular case.

Now let us break down this problem to atoms. How many atoms do we have in the system? So we have 300 A_2 molecules. They give rise to 600 A atoms. We have 100 B_2 molecules so they give rise to 200 B atoms and AB is also formed by A and B, but in any case we have 0 AB molecules. So now let me ask that if I simply put 600 A atoms and 200 B atoms in the box. Now they will combine in all possible ways and I am assuming that we do not have just A and B atoms lying in space, we have to be present as a molecule either A_2 or B_2 or AB. That is naturally the case that we assume in chemical reactions.

So now what is the probability that we form an A_2 molecule that is when two A have to come together? Now what is the probability of 2A coming together depend on? They will depend on how many A we have in the system and how when they combine with other A ultimately, if we have more A molecules, we will form more A_2 molecules, right? Similarly, what is the probability of forming an AB? They depend on the probability of finding an A and the probability of finding a B in the system, right? So if I now ask the question, a simple probabilistic question, what is the probability that at any particular point in this volume, where if two A come together, they form A_2 or A, B come together they form AB or whatever let us say I define a particular point in there. And I ask, what is the probability that we have two A atoms there forming an A_2.

Now what is the probability of having an A there that must depend on the number of A molecules in the system, right. So this probability of A_2 will depend on the probability of finding an A molecule in system that becomes the first molecule. Now the second A should also be found from the same volume, right so the molecule has two atoms so it should have find one A and another A. The probability of finding the first A is p A the probability of finding the second A is also p A. So it becomes-

$$p(A) \sim p_A^2$$

Similarly, my B_2 is going to be probability of finding a B molecule and a B molecule again. So it is B and B whenever we are doing an and operation, the probability gets multiplied. So we are going to have-

$$p(B) \sim p_B^2$$

Similarly, what is the probability of having an AB that is-

$$p(AB) \sim p_A p_B$$

So without doing like any chemical reaction stuff, simply using a probabilistic argument, what we have been able to get is the rate laws because what the probabilities are actually, what is the p_A? p_A is the probability of finding an A molecule at a particular point. What does it depend on? It depends on the concentration of A molecules, right. So-

$$p_A \propto C_A = \frac{n_A}{V}$$

So I am talking about atoms here. So probability is the probability of finding an A atom in there, right. So C_A is the concentration of A atoms that is equal to number of A atoms in the system divided by the volume of the box or whatever, where the experiment is being carried out.

Similarly,

$$p_B \propto C_B = \frac{n_B}{V}$$

this gives me-

$$p_{A_2} \propto C_{A_2} \sim p_{A^2} \propto C_{A^2}$$

And this precisely with the pre factor K gives me the rate law but I am not going there, I am talking about equilibrium but this is what gives rise to the idea of a rate law as well, right.

So if I now compute these values, what is the probability of A here. It is –

$$p_A = \frac{600}{800} = \frac{3}{4}$$

tells me the probability of finding an A out of the atoms in the box.

The probability of B is going to be-

$$p_B = \frac{200}{800} = \frac{1}{4}$$

$$p(A_2) \sim p_A^2 = \frac{9}{16}$$

$$p(B_2) \sim p_B^2 = \frac{1}{16}$$

$$p(AB) \sim p_A p_B \sim \frac{3}{16}$$

So if I now want to find the equilibrium constant of this particular system, what is it going to be- It is going to be the probability of forming AB divided by probability of forming A, probability of forming B and since there are two molecules of P of AB, this must be a squared. And why is that because these probabilities are proportional to concentration. So this would be equal to the-

$$k = \frac{p_{AB}^2}{p_{A_2} p_{B_2}} \equiv \frac{C_{AB}^2}{C_{A_2} C_{B_2}} = \frac{\left(\frac{3}{16}\right)^2}{\left(\frac{9}{16}\right) x \left(\frac{1}{16}\right)} = 1$$

So now you may very well ask what happens if I do some other combination of A and B atoms and the answer is that you will get the same value of the equilibrium constant.

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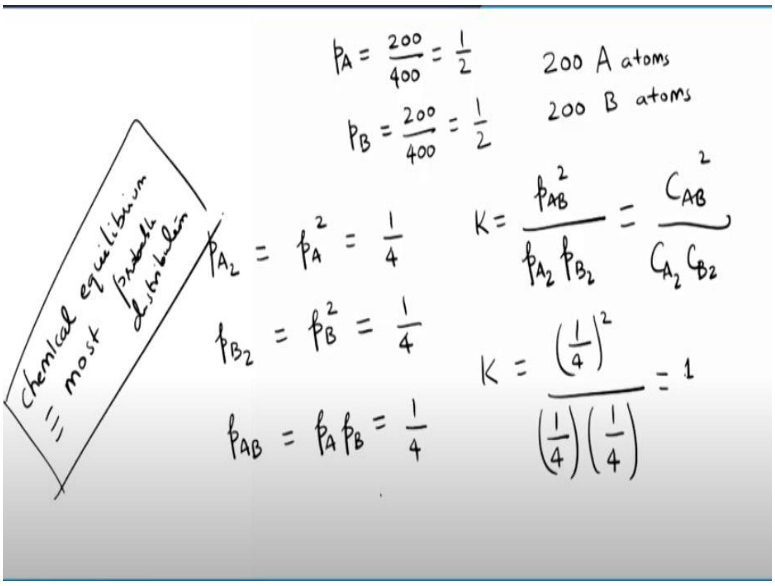

So let us say for example, if you had 200 A atoms and 200 B atoms. In that case-

$$p_A = \frac{200}{400} = \frac{1}{2}$$

$$p_B = \frac{200}{400} = \frac{1}{2}$$

$$p_{A_2} = p_A^2 = \frac{1}{4}$$

$$p_{B_2} = p_B^2 = \frac{1}{4}$$

$$p_{AB} = p_A p_B = \frac{1}{4}$$

So we have-

$$k = \frac{p_{AB}^2}{p_{A_2} p_{B_2}} = \frac{C_{AB}^2}{C_{A_2} C_{B_2}}$$

$$k = \frac{\left(\frac{1}{4}\right)^2}{\left(\frac{1}{4}\right)\left(\frac{1}{4}\right)} = 1$$

So irrespective of how many atoms of A and B I am starting with, I am getting the same equilibrium constant, right. So chemical equilibrium therefore simply refers to the most probable distribution of the molecules.

In the coming classes we will argue that even the thermodynamic equilibrium as we say, also refers to the most probable distribution. So at the core of it, the idea of the most probable distribution dictates the idea of equilibrium and actually, the force of nature actually is going towards the equilibrium and that means the nature wants to go towards the most probable distribution. It is purely driven by the rules of probability than anything subtle apart from that if I talk about equilibrium and one thing I want to mention here that should be clear to you, when I define probabilities for this particular example, I have been talking always of probability in relative terms that means that when I talk for example p_A I defined as 1 by 2, that is the probability of finding an A out of A and B. It is not the probability of finding A in the entire volume and the reason why that relative probability gave me the same meaning as an absolute probability is because I am looking at an equilibrium constant. So of course, the total number of ways will be larger in the absolute probabilities, but those basically cancels out in the equilibrium constant definition, right. So whenever we define probabilities here, they refer to the relative probability of finding an A out of A and B, not the absolute probability of finding an A in this particular volume.

So with this, I want to conclude here. In the next lecture, we will see how these ideas translate to the energy exchanges in molecular systems.

So with that, I conclude here. Thank you so much.