Chemical Principles II Professor Dr Arnab Mukherjee Department of Chemistry Indian Institutes of Science Education and Research, Pune Tutorial Problem - 09

Now we are going through some tutorial problems and then some of them we have already done before but some more we are going to do here. Simple ones, we will start with simple ones and then we will show some applications for systems of relevance, once you understand these problems I think you will be able to understand how one can use statistical thermodynamics for our desired thermodynamical properties also, but we will start with the probability problem, simple one.

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A box contains 3 marbles one red, one green and one blue, so I will denote it with the colors, one red, one green and one blue. Consider an experiment this is the black box, consider an experiment that consists of taking one marble from the box and then replacing it in the box and drawing the 2nd marble from the box, describe the Sample space. So in our sample space the 1st marble can be either read, green or blue and since we are replacing them back so again the box contains all the 3 marbles so that means for red it can be either red, green or blue. For green it can be either red, green or blue and for this one also it can be either red, green or blue.

So now if I can correspond to Sample space then this is one of the sample red-red, red-green, so if I write down all of them will today be red-red, red-green, red-blue, green-red, green-

green, green-blue, blue-red, blue-green and blue-blue, this will be the corresponding samples space because these are the all possibilities of outcome of the experiment that is described in this particular problem. Repeat when the 2nd marble is drawn without replacing the 1st marble, now we say that okay if I do that then I am not going to get the 1st model, now what will be the situation? Let us say if I take the red Marble 1st, in that case 2nd time either I am going to get green marble or I can get a blue Marble, these are the 2 possibilities in our samples space.

Let us say I had the green marble first, then I can either take the red Marble next time or I can take a blue Marble next time. Let us say I took the blue Marble 1st then 2nd time I could have taken either red or either green marble, so you can see in the 2nd space the number of points in the sample space is smaller because it is done without the placement whereas, the 1st one is done with replacement ok.

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Now let us go to the next problem, two green balls and one red ball are drawn from a barrel without replacement. So now I have two green balls and one red ball, there are 3 balls I drawn from the barrel without replacement, compute the probabilities PRG of drawing one red and one green ball in either order, which means I can either take a red one and then a green one or a green one and then a red one. So if I now do that, here we see this in either order means we can either take red one first and then green one or green one 1st and then red one, we will calculate the probabilities. So the PRG therefore will be PR multiplied by PG which is AND probability + PG multiplied by PR, so either order R followed by G and G followed by R.

Now what is the probability of drawing R? That is 1 by 3, once I draw the red I have full probability of getting the green which is 2 by 2. Now if I take the green 1^{st} which is 2 by 3 probability after that I have one green and one red left so the red will be 1 by 2. So now it is giving me 1 by 3 + 1 by 3, which is 2 by 3. Compute the probability of PGG, this is the problem second problem b, complete the probability PGG or drawing two green balls. So two green wall means first green has to be green and 2^{nd} also has to be green so PGG will use only AND probability because there is nothing OR taking place, so 1^{st} one will be 2 by 3 probability and 2^{nd} one I will be left with one green and one red only and that will be 1 by 2 so PGG will be probability 1 by 3.

So you will say that when I am talking about one and then one and then one, 1 and then so AND is there so there is multiplication. And if I have OR possibilities like for example here and that was a possibility where I had OR function. So this is the OR probability which is add up and this is AND probability which multiplies.

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Coming back to the 3rd problem, how many arrangements are there of 15 indistinguishable lattice gas particles distributed on 20 sites? So this problem I can draw like this, there are sides so these sides are kind of indistinguishable sides, I can name them as 1, 2, 3, 4, 5, 6, 7, 8, and there are 15 indistinguishable marble 15 indistinguishable lattice points lattice gas particles, so gas particles are indistinguishable. And the thing is that one lattice point will have only one particle so it is not that I can put multiple particles there so whenever I can do I cannot do that. So as I tell you that for indistinguishable particles indistinguishable cells, the distribution will follow the Star bar problem.

However, if you can put only one particle in 1 lattice site, it is basically how many ways you can choose those lattice sites in order to put the particle that becomes a question. So I have 15 such particles and I have in the 1st case 20 sites, so I have to choose now 15 out of 20 sites to put the particles that is it that is the only problem. So that means out of 20 sites I have to choose 15 of them to put the particles so the number of ways will be 20 C 15. In the 2nd case I have 16 sites left, so 16 C 15 and that is nothing but 16 factorial by 15 factorial and 1 factorial which is going to give us 16.

And in the case of C it is 15 C 15, it is going to give us 1, and in the case of 20 it will be 20 factorial by 15 factorial and 5 factorial which is going to give me 20 into 19 into 18 into 16, 17 into 16 divided by 5 into 4 3 into 2 into 1 whenever you do that with a calculator and that will tell us what the value is, 20 C 15 is 15,504 that is the number. So you see that is the number of lattice sites are increasing, the number of possibilities increases and therefore again entropy increases, this is an equivalent way of saying that there is a free space available for particles to expand ok, now going to the next problem.

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A scientist has constructed or secret peptide to carry a message. You know only the composition of the peptide which is 6 amino acid long. It contains one serine, one theonine, one cytosine, one arginine and two glutamates. What is the probability that the sequence SECRET will occur by chance? So now we have to see that how many possible words that one can make with that. So number of possible words that we can make is that we can take any of the 6 letters and put it in the 1st place of the word and then any of the 2nd letter, there will be 5 letters left then there will be 3 letters left, 2 letters left, 1 letter left, however, you

have to know that there are 2 Es so interchanging those 2 Es will actually give the same word so I have to divide by the factorial 2.

So total possibilities total possible words equal to 6 factorial by 2 factorial, which is 720 by 2 which is 360. Out of this there is only one word which is secret, so the probability is equal to 1 by 360. So note that the secret, exchanging these 2 Es has already been taken into account for the total probability total number of ways, so there exchange of these 2 does not gives rise to any new word that has been already taken into account.

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Now I go to the next problem, problem 5. Assume that for basis A, C, T and G occur with equal likelihood in a DNA sequence that means it can come anywhere. So out of these 4 anything can come like A, C, G, T whatever it can come and that is how the DNA is made right. So now what is the probability of finding the sequence a very particular sequence through a random choice? Now you see how many ways you can get, what is the probability of getting A in the 1st place? So there are 4 possible sequences and you are asking for just one particular one, so that will be 1 by 4. What will be the 2nd one? Again 1 by 4, what is the 3rd one, again 1 by 4, so like that when you go the answer is that 1 by 4 to the power n which is the length of the DNA.

In this particular case it is 1 by 4 to the power 9 so that is the probability of giving that particular sequence. Problem B also the same thing, although it is the same sequence AAA but each one is independent of the previous one therefore, for the b also since there are 9 letters are there and each letter has 1 by 4 the answer will be 1 by 4 to the power 9. Now in

case of C what is the probability of finding any sequence that has four A's, two T's, two G's and one C. Now 1st we will see how many that kind of sequences are possible, in order to see that we know that in the 9 letters sequence it can any of these 9 can come in the 1st place and then 8 will be remaining and then 8 will come in the 2nd place and things like that so there will be 9 factorial possibilities.

But we know that there are four A's which are common and two G's which are common and two T's are common and one C is common, so this is the number of sequences that we can create. We already know from the previous example that any such 9 letters sequence has a probability of 1 by 4 to the power 9, so this is the answer to this particular question is that it is 9 factorial by 4 factorial 2 factorial 2 factorial into 1 by 4 to the power 9, we will just calculate that and see what we are getting out of that.

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9 factorial divided by 4 factorial into 2 factorial into 2 factorial multiplied by 1 divided by 4, so we are getting as 0.014 as the probability of having sequences.



Let us come to problem number 7 which is called Monty Hall problem. So this problem is like this, long back there was a gameshow, the host was called Monty, hots's name was Monty Hall. So he would tell a set to choose a particular door, behind 2 doors there are 2 goats and behind one door there is a car. So let us say he will choose a particular door let us say he will choose door C then Monty will open another door behind which there is a goat, Monty knows where all the doors are so Monty will open a door behind which there is a goat.

And after you look at the goat Monty will ask you again, do you want to stick to your choice C or do you want to change it to B. Let us say Monty opens gate number A, you have chosen get number C, all the doors are closed before and Monty opens gate number A, so now the car is either behind C or behind B. Now Monty will ask again that we want to switch your choice to B or do you want to stick to see what should you do? Do you want to change? Why do you want to change? In A there is a goat for sure but behind B there can be a car or behind C also there could be a car, if you switch and if the car is behind C then you will not get it. So do think there is equal probability in both cases.

Okay so that is what the thing is that, people initially are very confused that what to do means maybe it is equivalent maybe it is random but eventually it turns out that it is actually not a random choice, there is definitely a higher probability for switching, you must switch. The reason is this, very simply 1st reason is that when all the doors are closed the probability that the car is behind C is 1 by 3, 1 by 3 and 1 by 3, so the probability that the car is behind C is 1 by 3, and 1 by 3, so the probability that the car is behind C is 1 by 3, and 1 by 3, so the probability that the car is behind C is 1 by 3, and 1 by 3, so the probability that the car is behind C is 1 by 3, and 1 by 3, so the probability that the car is behind C is 1 by 3, and 1 by 3, so the probability that the car is behind C is 1 by 3, and 1 by 3, so the probability that the car is behind C is 1 by 3, and 1 by 3, so the probability that the car is behind C is 1 by 3, and 1 by 3, so the probability that the car is behind C is 1 by 3, and 1 by 3, so the probability that the car is behind C is 1 by 3, and 1 by 3, so the probability that the car is behind C is 1 by 3, and 1 by 3, so the probability that the car is behind C is 1 by 3, and 1 by 3 we have a solution of the car is there is 2 by 3, and 1 by 3 we have a solution of the car is behind C is 1 by 3, and 1 by 3 we have a solution of the car is t

are 1 by 3 initially but then you have chosen that the car is behind C with the probability 1 by 3. That means the fact that the car is there in B and A is 2 by 3, now Monty opens the door A that means definitely car is not there which means this 2 by 3 now goes to only B, is it okay?

Okay so I will explain once, so let us say initially when you do not have when all the doors are closed then the probability that the car will be behind any door A, B, C is 1 by 3, which means that let us say you have chosen 3, this is B and this is A. That means the combine probability of B and A is 2 by 3 for the car to be there combine probability or it can be either in B or in C so it is 2 by 3 because it is the OR probability, right. Now Monty opens the door for A, and A for sure does not have a car, which means the probability that B has car is 2 by 3. Initially when the doors were not open but the fact that Monty knows which door has a goat and he opens only that door changes the probability. Now I will explain here, so let us say you are choosing we are calculating here all possibilities so it will make it clear.

So let us see we choose door number 1 and the car is also behind 1, so if the door number 1 let us see you choose that door A, some door where there is a car, let us say the car is here only, you choose C and the car is there. So then Monty will open any of the other 2 doors and then if you stay you will win, if you switch you will lose correct? Let us say you choose 1 and the car is behind door number 2 then Monty will open any of the 2 doors, Monty will open precisely one particular door which is 3, okay let us show all the possibilities once more. Actually I should not switch between A, B, C and 1, 2, 3, so let us do that 1, 2, 3 way.

So let us say you choose door number 1 and the car is behind door number 1, Monty will open any of the other 2 because the other 2 have goats now, and if you stay you will win and if you switch you will lose ok that means you should not switch in that case. Let us say you choose 1 and the car is behind 2, there are equal probabilities right that time if you switch you will win right. Let us say the car is behind 3 door number 3, if you switch you will win right. So you see if you choose 1 then two times you win if you switch and one-time you will lose. Similarly, the same thing is true for if you choose door number 2, there also 2 times you will win if you switch and one-time you will lose. Similarly if you choose 3, 2 times you will win and one-time you will lose if you switch so if you switch you will win more often than if you do not switch, probabilistically it is always advantages to switch.

So let us talk about 100 doors, so there are 100 doors and you choose one of the 100, what is the probability that the car will be there is one by 100 right and Monty opens all 98 doors, he know the goats where the courts are, now should you switch should you not switch? Because initially... We should switch so it becomes easier to think about when there are 100 doors, come only with 3 doors it becomes not so clear. So initially when you choose your probability was 1 by 100 and altogether 99 doors have probability that car is there 99 by 100. Now since Monty open all the doors, the car is there in 1 other door is 99 by 100 because that time also it was 99 by 100, now also it is 99 by 100 except that you now know all the other doors are goats.

So the fact that see initially A, initially choose the door C which has 1 by 3 probability, so B and C combine was 2 by 3 probability, is not it? Now you know that C does not have that, you choose door number A, and B and C have 2 by 3 probability of having the car and you know now that C does not have the car, so B will have 2 by 3 probability of car that means you should switch ok that is a famous Monty Hall problem.

Student: One more thing, if you know the (())(21:12)

Professor: No, the thing is that see initially why the probability was 1 by 3 because it was totally random choice right that is why it is 1 by 3, 1 by 3 and 1 by 3. Now whenever somebody opens the door, your sample space immediately reduces so you have that 2 by 3 probability in the 2 doors. Now, one is removing one possibility for you so it becomes much more it is not random anymore. See Monty knows that which door has the goat so it is not random, if Monty opens the door randomly then it would be a case but Monty knowing that he is going to open only the door with the goat is no longer random so all probability collapses to one particular door ok.

It is a very famous problem and in fact this table shows very very clearly that all the possibilities. If you just look at the table whatever you do, two cases if you switch you will win whatever you do and one case you will lose out of the 3. And in 99 case you will see 99 by 100 will be the other door.