Chemical Principles 2
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Estimating Entropy for Various Processes

Now we are going to show you some of the simple examples of how statistical calculation helps us understand how entropy plays an important role using very simple examples.

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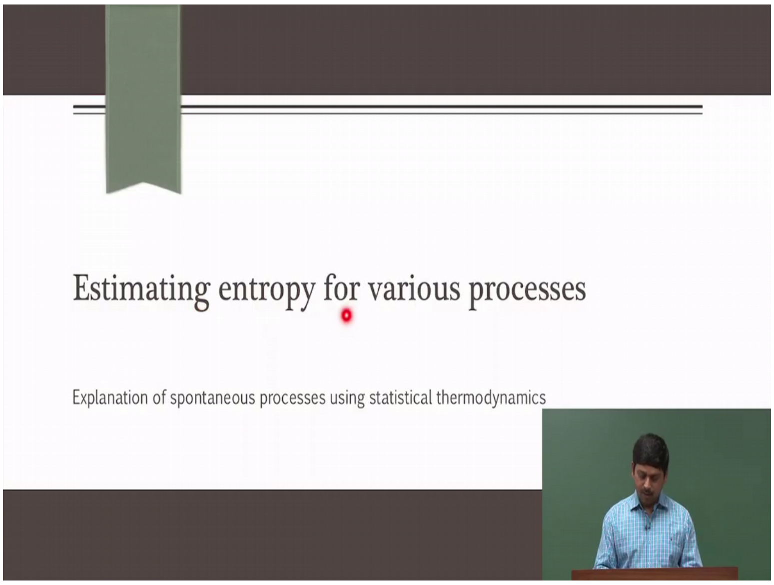

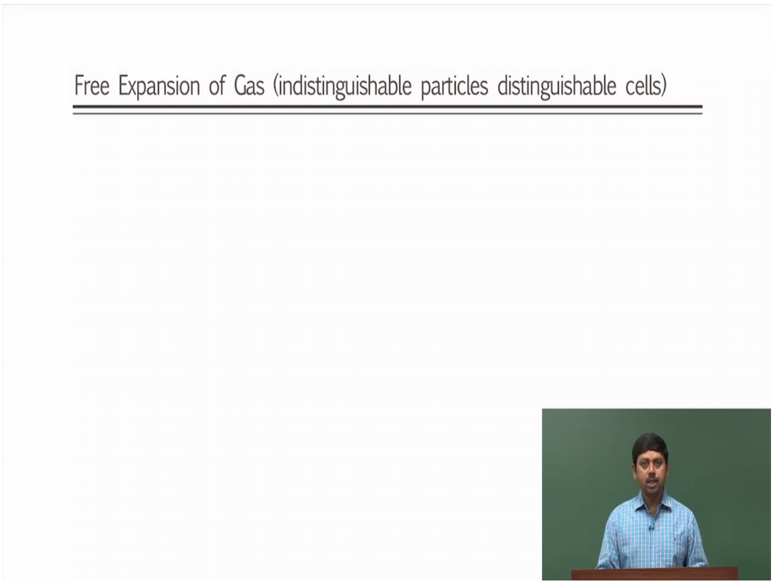

So estimating entropy for various processes and this part is taken mostly from Kendall's book of molecular dragging force, so first we will discuss about free expansion of gas. Remember in our description of classical thermodynamics we already mention that we already showed that how expansion of gasses into full volume will give rise to entropy.

Remember our discussion that the work done for free expansion is 0 and if it is an insulated system then heat change will be 0 and therefore internal energy change at least for ideal particle will be 0 and then we said that since it is an irreversible process we have to create a reversible path and if you do that then there will be a q reversible which is a nonzero which will give rise to an increase entropy.

Also intuitively you can understand that the particles which you have confined to only one part of the box now have more larger space to move around and therefore of course it should have higher entropy because it has more number of options. This example uses a very simple model, it is called lattice model which lattice models are models where particles occupy a particular space in a lattice points.

For example solid, you know that in a solid sodium chloride occupy particular lattice points and they do not move away from those lattice points the only vibrator around those lattice points unlike liquids and gases which translate solid particles cannot translate so rather they vibrate along its own equilibrium point. However they can have different configuration, they can attain different configurations based on allowed positions, it cannot occupy all possible position but it can occupy only lattice points for example in one-dimensional lattice it can occupy 0, 1, 2, 3 these are the positions whereas for non-lattice systems we call off lattice system their particles can occupy any positions, so idea is that using lattice points we make our life simpler for doing the calculation, so it is not exactly a model of free expansion, we have done that we have shown that using simulation and exact one almost.

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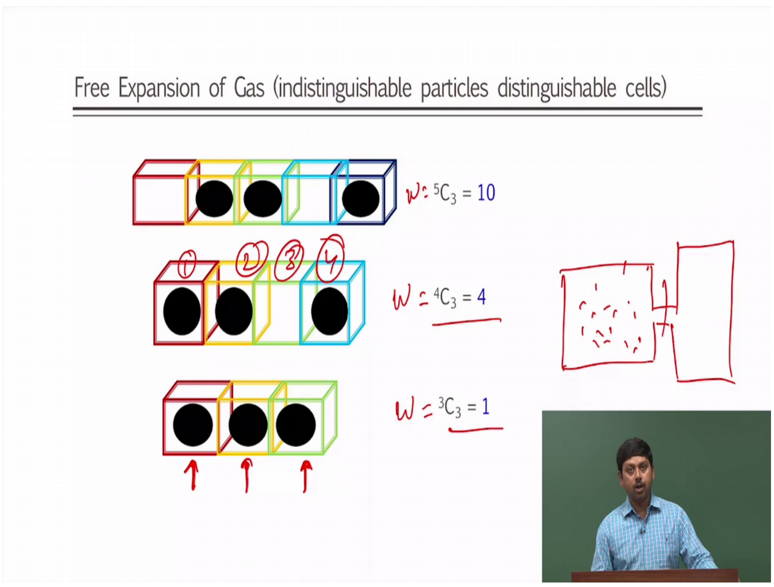

However here we are using for calculation purposes very simplistic model where the lattice are fixed like a box, so the particle can occupy either this point or this point or this point in a lattice and there let us say are 3 particles and each particle they are indistinguishable particle and each particle can occupy only one lattice point, not more than one particle can occupy lattice point.

So whenever you have the situation, so remember we discussed that whenever we have indistinguishable article but distinguishable cells then it should have star bar kind of problems right like it will follow the star bar statistics but only difference with this particular thing is that in that case one box could have contained multiple verticals, here the situation is slightly different, here only one particle can occupy one lattice point. It can be free or 1 not even 2, so here are essentially what we are choosing is that how many wastes I can choose the 3 particle for the 3 boxes, so basically we are choosing the box and since the indistinguishable it does not matter.

If the particles are distinguishable then I could have taken anyone of the particle, so that means 3 then for the 2nd lattice point I could have taken any 2 different ways that will be 2 and then for the 3rd particle there is only one possibility that would have given us 3 factorial ways but you know that 3 factual is nothing but permutation but you know that is when it is indistinguishable, when you grouping them together I have to divide 3 factorial as well, so it will become 3 factorial by 3 factorial which is nothing but 3C3, so how many groupings of 3 I can do out of the particle and that is 3C3 and we know that it is only one possible way.

Visually also you can see that there is no other way I can put 3 particles in 3 different boxes okay, so here essentially we are choosing the boxes and there is only one way of doing that, so there is very tight lattice there is no extra space available to it. Now let us say I am talking about free expansion, what is the expansion? There is no work done particles are free it is just has more possibility to go there is no energy advantage, no reason for it to go based on energy alone but there is just more availability and that is the situation given here.

I have 3 particles now but have 4 lattice points, so that means I can choose that which of the 3 boxes or lattice points would be filled by these 3 particles, which of the 3 out of how many? 4 Which of the 3 out of this poor will be filled and that is nothing but a combination problem of 4C3. 3 I have to fill up and have 4 situations I can put any 3 out of these 4 any 3, so if I number them and boxes are distinguishable I told you. If I number than as 1, 2, 3 and 4 I can choose 1, 2, 3; 2, 3, 4 I can choose 1, 3, 4 and I can choose 1, 2, 4, there are only 4 possible ways and that is 4C3. Now why we say free expansion?

It is free expansion because it does not have to do any work, whenever there is any external pressure is 0 it is called free expansion, if there is no pressure nothing as prohibiting the particle to go to the other lattice points and therefore it is free points and why and we see that that W has change from 1 to 4, it is just the possibility remember we discuss that entropy is nothing but possibility. Wherever there is more possibility there is more entropy, here exactly that example is given here more possibility is leading to more W leading to…more w means micro-states leading to more entropy.

Now increase it little bit further I have now 5 spaces and I have only 3 particles to fill up, more spaces more than it was before. Now I have to choose which of this 5 will be filled by this 3, so it should be 5C3 and there are 10 possibilities, so you see as the number of lattice point increasing compared to the number of particles it is w entropy both are increasing like w is increasing and that is why entropy is increasing, exactly that happens for free expansion case right whenever there is a particle here it has only this much space to occupy and then suddenly I have open a new chamber for the particle to move in just because it is more space to go, just because there is no restrictions for it to go, unless we restrict that is a different situation, I force the particle not to go that is a different situation. I am forcing the entropy do not increase and that is work against the entropy.

Entropy is possibility but if you reduce that of course you are reducing the possibilities by force but remember again one more thing that one cannot reduce, one cannot work being a part of the system for example we can clean up a room and reduce the entropy of the room but being a part of the environment, being a part of the universe we cannot really reduce the entropy of the universe because that we are just part of that by cleaning up the room we essentially have done some work created heat which is dissipated to the environment and eventually we have increase the entropy of the universe.

However we have decreased the entropy of the room, so that is a little bit of digration just to tell you that although you can do work reduce the entropy of a particular subsystem, the overall system which is isolated for a spontaneous process will always increase entropy okay, so now this we have seen that by very simple lattice model you can actually explain that free expansion is increased the entropy of the system.

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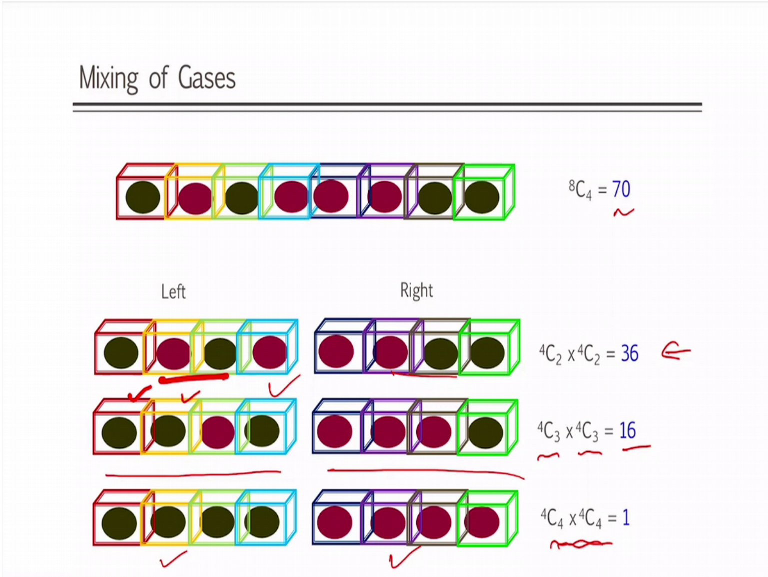

Now let us go to the next example mixing of gases, so we have seen that for mixing of gases entropy increases and we have seen that mixing of gases entropy increase is part due to the volume increase itself right because it was initially one part was occupied by let us say red particle, another part was occupied by blue particle and then we saw that when you join them together then blue particle went all over the 2 boxes, red particle went all over the 2 boxes.

Now we have a mix system the volume is now double which means that for blue particle also entropy has increases for red particle also entropy has increased but what if the situation is different what if we have the same box but only the particles are mixed, now we can do both the situations. Now let us take a left box well there are 4 boxes and 4 particles, we know looking at the figure itself that there is only 4C4 ways of doing it because there were 4 boxes I need to fill with 4 particles and only one particle in a box, so it is 4C4 and in this case the red particles again 4C4, so how many possible ways you can do that?

We can do that in 4C4 multiplied by 4C4 and why we are multiplying it? Remember n probability, n probability multiplies which means that I have to fill up left box with 4 particles and right box with 4 particles. I do not have an or choise, I may not choose not to fill, I have to fill it so I have an n probability or rather number of possibilities to calculate remember it is, when you calculate the probabilities numerator by denominator here we are talking about just the denominators or number of samples spaces and whenever there are 2 sample spaces they will multiply, for example remember how many possibilities are there for throwing a dice? 6 possibilities.

How many possibilities are there for throwing to dice? 36 possibilities. If you pair them 1, 6; 2, 6; 3, 6; 4, 6; 5, 6; 6, 6 then 2, 1; 3, 1; 4, 1; 5, 1; 6, 1 like that you will have 36 possibilities, so always the number of sample space for 2 different sample space will multiply and that is the reason also that it is multiplying. Now this is only unmixed and unmixed 2 systems, here we are not mixing it, we are taking a mixed situation in this case, so the left box now has a mixed situation where I have a mixture of particles, right box also have a mixture of particles and you know I have to fill up 3 boxes out of the 4 with black then automatically my red will be filled, so 4C3 ways of doing so and a right hand side also 4C3 of doing so.

Then total possibilities will be 4 into 4 are 16. Now instead of one red particle let us mix it even more, let us mix it equally still I know boxes are not mixed here okay only the particles are mixing only so that mean the volume is remaining constant but instead of one type particle I have 2 types of particles and there also you see now I have to fill up only 2 out of 4 boxes then automatically the other 2 will be decided, so it will be 4C2 multiplied by 4C2 and I get 36 possibilities.

So as you can see from unmixed situation to mixed situation the entropy increases and this increases just because of mixing of gases for a fixed volume but remember the other situations where I have one box of one particle another box of another particle and joined them together the volume becomes double, here the number of lattice points will become double, so instead of 4 it will become 8 and the number of particles will also become double instead of 4 it will be 8 and I have only 2 types of articles and that is the situation that is here. Now I have 8 lattice points and I have to choose 4 for red and 4 for black.

So how do I choose that, so I have to choose 4 out of 8 so 8C4 for the black and then automatically rest will be chosen I do not have to really choose for that. So let us do only 8C4 and what we observed that it is now 70, so here not only there is a mixing but also the volume has increased and because of these 2 effects that entropy is even more than a fully mixed system and that is where it shows that whenever there is a mixing will occur then entropy also will increase.

So let us see in other situations remember the balloon demo that we did where we put the balloon and stretched it and we left it, then it shrunk and the fingertip became cooler, so what happens in that case so when you leave the balloon on a table it is in its equilibrium state and it is not very long not very short but it is some intermediate situation. When you stretch it, lengthen it you are actually working against entropy, why? Because it is not the energy that holds the rubber it is a polymer that holds the polymer together.

I will show you in a moment that it is the entropy that makes it smaller, if you stretch it you are actually working against entropy then when you release it then it spontaneously releases and increases the entropy and that will actually take the heat out of your fingertip taking it cooler. Here again in (())(14:06) book we have shown very nice using lattice model that how one can explain that and this is the situation.

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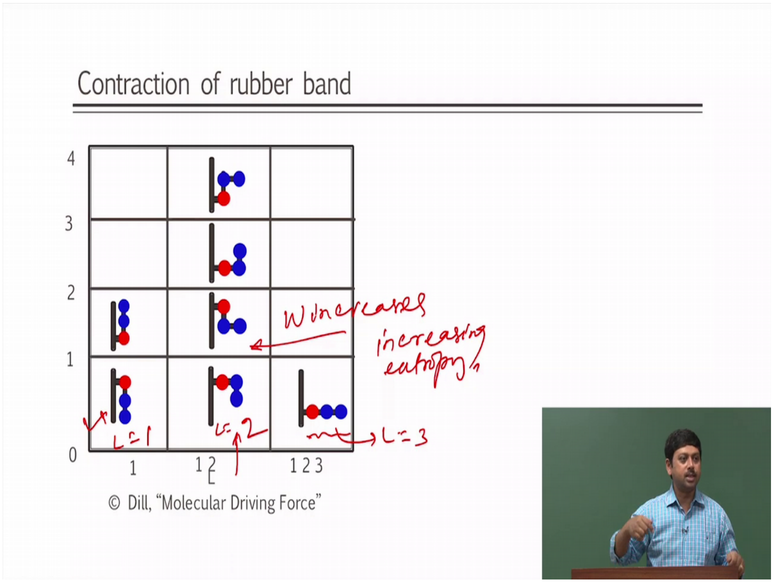

So this is a polymer of simple 3B polymer, 3B only and you see if it is totally elongated then the orientation has to be in one direction only and therefore there is only one way of doing so. If I put all the polymers in a straight manner, all the monomers in a straight manner in a polymer there is only one possibility, however in an intermediate situation see how many, so here the length is 3 right, here the L is 3 you can see that, here L is 2 you can see that and here L is 1 length is measured by how many monomers away it is from the wall.

Now here you see there are 4 possibilities, 4 possible ways to orient them when the length is intermediate. Now if you want to shrink it, it will again reduce the number of possibilities and that is the reason when you stretch it and when you release it your number of W increases, increasing your entropy okay and when it increases entropy you know that entropy is nothing but dq by t right, so when the balloon increases entropy your finger trip will release that heat and you will feel colder.

Student: (())(15:27)

Prof: When you stretch the balloon that time the balloon will…that time you working against entropy.

Student: (())(15:33).

Prof: Correct.

Student: (())(15:36).

Prof: The question is that if you stretch it then it should have more micro-state because it is actually kind of expanding situation, you are thinking of expansion right, so because the kind of volume or length is increasing, so the difference is that here when you are increasing a box size then you are free to move around and orient and make new possibilities but when you stretch them every monomer has to align in a particular direction, so if you calculate the angle between one monomer, the next monomer, the 3rd monomer they will be like 180 degree just like what is shown in in this particular example.

First monomer or to 2nd mono more to 3rd monomer they are linear because they are linear they have only one way of doing it, so it is…. we are not talking about monomer floating in a box, here the monomers are connected and we are talking about only how many configurations the monomer can attend. If you stretch it there is only one way of making it longer, take a rope for example if you take the row in a straight manner there is only one configuration that you can get but if you fold the rope then there is so many folds you know you always fold rubber in our hand, it will be smaller but it will have so many possibilities and that is the reason that it will have more microstate, so it is not exactly similar as when you expand in a lattice gas because in that case, the more lattice point will allow more configuration. Here we are not allowing that configurations because of again constrained that are present between the monomer itself, so for this polymer the heat will increase but the fingers will have to lose the heat.

Student: (())(17:29).

Prof: Yes, finger will have to lose the heat and that is the reason, so when you take a balloon and stretch it what is going to happen? Entropy will decrease, right? So if you touch that on your forehead you will feel hotter because it is using heat. Take a balloon stretch it and put in on your forehead you will feel it is hotter, why? Because the balloon is releasing heat to your head, why is it releasing heat? Because the entropy is decreased.