Chemical Principles II
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Most Probable Distribution is the Boltzmann Distribution

Now one thing we have done to simplify our whole calculations and that is we have taken equal spacing is, the energy levels are all equal and therefore we could actually manage to count using the partition thing because we use parting and 7 into 9 knowing very well that you know the sum up will give me 9 when I am partitioning 9 sum has to be 9 we knew that and then they since the integer goes you know in an integral manner like 1 plus 2 plus 3 say 1 plus 1 plus 1 like that 1, 2, 3 similarly energy levels were like 1, 2, 3 however if energy levels are all unequal then we cannot do the same thing, for example we have a very simple system.

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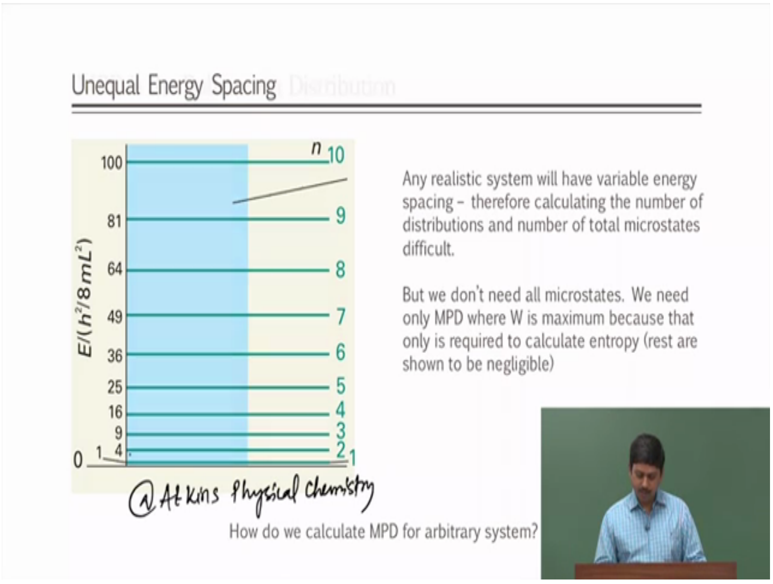

Like particle in a box and that does not give us unequal energy spacing is as you know that energy levels keep on increasing so this is taken from Atkins physical chemistry book this picture, so as you know that when the energy levels increased the difference keep on increasing so if you use this particle in a box concept it will be very difficult to do that the realistic system that we talked about for equal energy spacing is harmonic oscillator where the energy levels are equally spaced.

However it is not true when it is actually a realistic system, harmonic oscillator is solved by using a parabolic half kx square parabolic potential and that is how we get that however if it is a realistic system where let us say a bond is connected by to an atom is connected by two bonds simultaneously, so there will be an effect combined effect of motions of both the atoms it will be no longer a very simple harmonic oscillators anymore and therefore no longer equal spacing is.

So in realistic situations we may not get you know equal spacing is of energy levels and calculate the statistics the way we have done that till now, so therefore we need a more robust more you know rigorous approach to calculate these statistics. So as is mentioned here and in fact we have used in order to calculate for Maxwell-Boltzmann we have used all possible microstates right when you calculated the statistics of 5 units of energy in 4 particles or 7 units of energy in 9 particles we use all possible microstates and calculated that how many microstates will be there for the particle having ith energy level.

However we have mentioned before that we do not need that we only need one mick one distribution which is the most probable distribution we showed that when the number of particles goes very high for example is showed up to 10 to the power 8 or 9 that it is really narrow the it falls off within so we have shown a calculation right that for 10 to the power 23 particle with point 000000002 percent the distribution will decay to zero which means that most probable distribution is enough to give us the all possible microstates and therefore to give us an estimate of entropy.

So that means we have to know how to calculate most probable distributions irrespective of whatever the energy levels are we do not have to care about the energy levels irrespective of the energy levels energy spacing you should be able to get the distributions of particles in the most probable distribution will that follow an exponential distribution like this let us see that how do you calculate the MPD for an arbitrary system.

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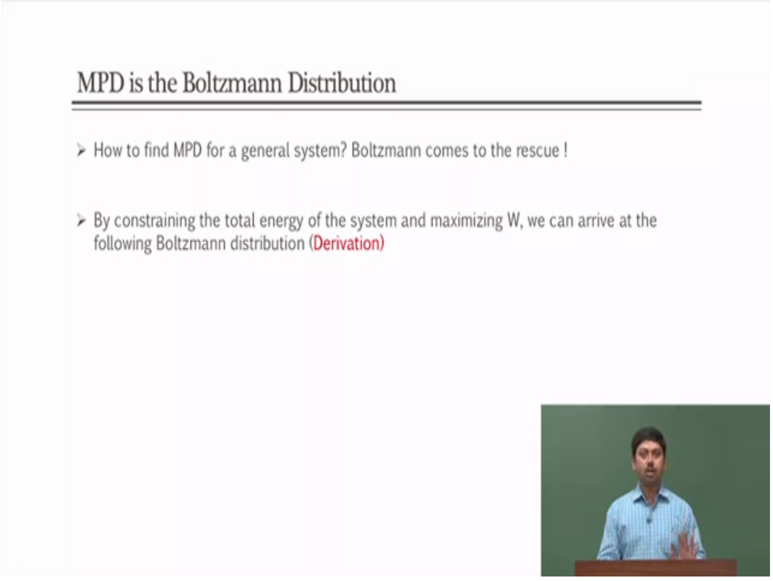

So we will see that MPD for a general system to calculate that the Boltzmann will actually come to a rescue Boltzmann distribution and we are going to maximize the W under the constraints of total energy and total number of particles and that will give us as you have seen the Maxwell Boltzmann distribution or an exponential distribution. So we are going to do the derivation however this derivation is not actually a part of this syllabus this you can take as an additional thing to for the completeness of this particular course, you can also find the derivation in the physical chemistry book of Hodgkin.

So this derivation is just for the completeness of the course rather than the part of the lecture.

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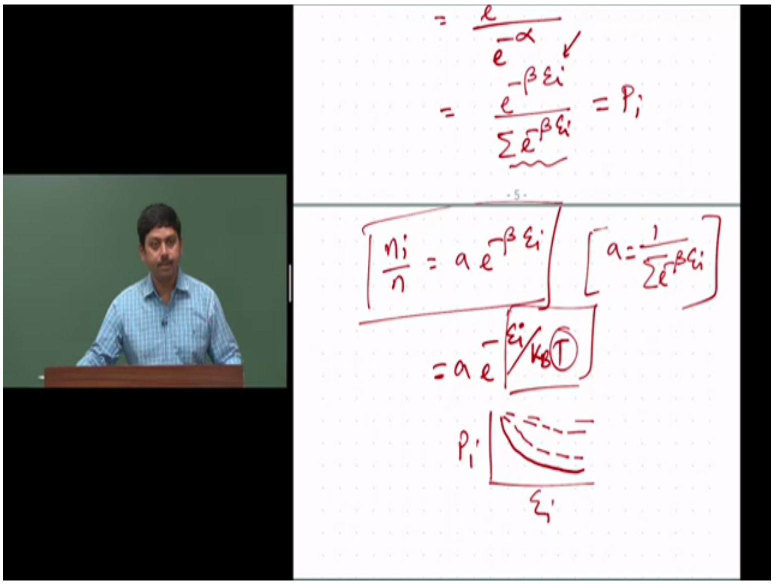

So for Maxwell Boltzmann distribution we know that W is in factorial by in 1 factorial in 2 factorial in 3 factorial etcetera which can be written as n factorial by product of n i factorial and that product runs over so many i is we do not know how many i is. So which you can see that in that case that W is a function of n i is because that will give us the that will give us a W if I know the in i.

So W now (func) becomes function of n i and we have 2 constraints one constraint is that the total number of particles sum over i is n which is a fixed quantity and total energy which is product of n i E i is some value E that is also fixed, so if we maximize this particular W under the constraints of this and this then we can see what kind of W we are going to get but whatever W we are going to get that will be the most probable distribution W for the most probable distribution and as we have as you have seen that that is enough for getting the statistics, so that most probable distribution will be enough.

Note here is that we have not specified how the energy spacing is need to be that is not required and so we do not have do not need an equal spacing is here anymore we only need that the total energy has to be conserved ok and that we know for systems we will be conserved for an isolated system the total energy will be conserved and also for other systems as well but we are not going to discuss that right now.

So now let us see how we can maximize the W, so in order to do that it is much easier to work with ln W than W and we know ln W will be ln of n factorial by product of i in n i factorial which is ln n factorial minus ln of product of n i factorial which is ln n factorial minus so product becomes sum in case of ln and it will be ln n i factorial, so which means now our W ln w is also a function of n i.

So now we can write then it is all variations of n is only will give us the maximum W for example we have seen that for two level systems if n i is 1 n 1 is 1 and n 2 is n minus 1 it gives us 1 distribution, if n 1 is 2 and n 2 is n minus 2 it gives another distribution and the most probable distribution is only when n i or n 1 becomes n by 2, so that means this W is basically a function of that time in 1 here there is there are multiple values of n 1, n 2 and n 3 is are there.

So we are trying to maximize the W with respect to some arbitrary i and i is arbitrary because i can be put as 1 or 2 or 3 whatever, so we can write the differential amount of W ln W as you have seen for any differential quantity when it is when it is a function of multiple variables can be written as del ln W by del n i dn i. Now since it is there is a sum over that we can put a sum i in order to satisfy the constraints there is a method called lagrajins lagrajin Lagrange method of undetermined multipliers which means that you have to multiply by some constants to those constraints and we can maximize the quantity.

So now if you write down the quantity that need to be maximized now is that d ln W is sum over i del ln W by del n i dn i plus alpha dn i, alpha is just one of the constraints un determinants constraints and minus beta is another constraints where we satisfy the condition of total energy and that needs to be equal to 0, as you know that for maximum minimum function the differentiation has to be done and that has to be equated to 0 because that gives us the value of maximum and minimum.

So now when you write them together del ln W by del n i plus alpha minus beta E i sum over dn i gives me 0 which means this quantity inside has to be 0 so del ln W by del n i plus alpha minus beta W i is equal to 0, what is ln W? ln W is as you know ln w is written here somewhere yeah no it will I have not yeah ln W is written here equation 1 ln n factorial minus sum over ln n i factorial.

So del ln W by del n i will be del ln n i n factorial by del n i minus sum over i del ln n i factorial by del n I, let us call it 1 and 2, so now let us do the 1 and 2 separately so 1 is del ln n factorial by del n i now we know that using Sterling is approximation that ln n factorial is n ln n minus n and the n itself is sum over n i, so let us write that del del n i of n ln n minus n let us write that as sum over n i ln n minus sum over n i.

Now once I do that I have this sum and then I do del del n i of n i ln n minus sum over del del n i of n i, now this is a product sum so the first term will be ln n and as you see the sum will go away because only one of the term will survive only one of the n i will survive, you can think of that you are differentiating with respect to n 1 and then you see that this is a sum of n 1 plus, n 2 plus, n 3 this one and therefore only one term will survive and you are going to get only one.

So ln n will survive plus now i have n i differentiation of ln n which means if I differentiate with respect to ln n let us do that in the next step left hand side I will still get 1 because only one term will survive, so ln n plus n i now when you differentiate this aspect to ln n what we are going to get is you are going to get 1 by n n i into 1 by n this sum is still there in this particular case and differentiation of sum of n i by n i minus 1, so then it is ln n.

Now this term is going to be 1 and sum of n i by n is going to be 1 minus 1 and you are going to get ln n, now let us do the second term what was the second term let us see second term was this particular term sum over i del ln n i factorial by del n n i is that the case let me see del n i factorial by del n i yes that is the case, so then sum over i del del n i ln n i n i n ln n i minus n i again in this case you have n i ln n i will be 1 by n i and the sum will go away because there is only one term that is going to survive and ln n i there is also sum the sum will go away because only one term is going to survive and in this case the second term will be just 1, so here this cancels giving me 1 plus ln n i minus 1 so they cancel and I get ln n i.

So 1 minus 2 is going to give me ln n minus Ln ln n i which is ln n by n i, now when I combine that with the other terms coming from this equation now going back to this equation let us call it equation 1 now plugging that into equation 1 we got this one as ln n by n i plus alpha minus beta E i, so then ln n by n i plus alpha minus beta E i is going to be 0 which means minus ln n i by n plus alpha minus beta E i is going to be 0 which means alpha minus beta E i is going to be ln n i by n which means n i by n is e to the power alpha minus beta E i which is by the product rule it will be e to the power alpha into the e power minus beta E i let us call the equation 2.

Now let us take sum of both the sides, so sum of n i by n over all i is sum of e to the power alpha e to the power minus beta E i, so sum of n i by n you know equal to 1 e to the power alpha is a constant will come out e to the power minus beta E i, now taking on the other side we get sum of e to the power minus beta E i is e to the power minus alpha let us call that equation 3.

Now let us put equation 3 in equation 2, so n i by n is equal to e to the power alpha e to the power minus beta E i and e to the power alpha or ok let us try it one more step e to the power minus alpha because alpha becomes minus alpha and we know that e to the power minus alpha is this one so put equation 3 in that and we get e to the power minus beta E i by sum over e to the power minus beta E i.

So you know n i by n is the probability, so the probability of being in the i state depends on the energy of that particular state whereas this one is nothing but constant so we get n i by n as a into e to the power minus beta E i remember this expression when we calculate the statistics from Maxwell Boltzmann here a is nothing but 1 by sum over e to the power minus beta E i which is nothing but a normalization constant, so this is the Maxwell Boltzmann distribution that we got from the statistics that we use by putting particle in the levels.

Now here for very general systems what you can see is that the most probable distribution with the total number of particles being fixed and total number total energy being fixed will give us this distribution no matter how the energy levels are which means that high energy levels will have less number of particles and low energy levels will have more particles and will follow an exponential distributions, if you increase that so now beta is can be shown to be inverse of temperature.

So as I said before that it is nothing but e to the power minus E i by k B T, K is called Boltzmann constant, so if T is larger then what is going to happen is that at higher and higher T then this quantity becomes smaller and the distributions getting can get more and more flatter for example let us say there is this particular distribution at some temperature if the temperature increases then what is going to happen is that 1 by k B T becomes if it is increasing it is it becomes even smaller, so the decay rate will be even smaller and then eventually it can be even smaller and for different energy levels your probable distribution can become more and more equal when the temperature becomes higher and higher.

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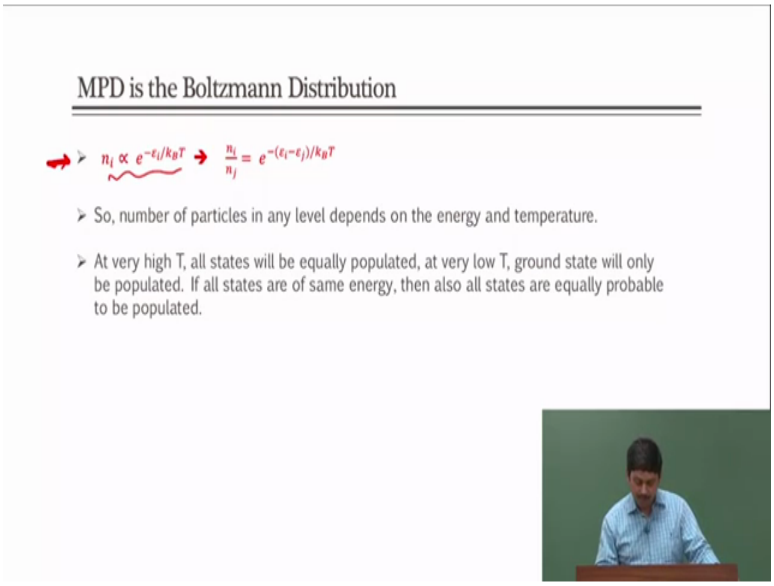

So now coming back to this so we have seen that n i by n i is proportional to the e power minus E i by k B T and there is a normalization constant so (tot) so number of particles in any level depends on energy and temperature and at very high temperature all states will be more or less equally populated at a very low temperature only ground state will be populated and that is very important conclusion from this particular Maxwell Boltzmann statistics.

If all states are of same energy then also all states will be equally populated that also we have seen even before we did that even Maxwell Boltzmann distribution also says that if all E i is are same then n i by n j will be equal for all of them only because they are different that is why it is so the proportional to the energy so if energy is same and the temperature is same then all of them will be equally populated.

So this one irrespective of how the energy spacing is whether they are (conn) you know equally spaced or the unequally spaced or whether they are degenerate all of that possibility can simply come from this particular equation that it shows that if they are equal of equal energy then there will be equally populated if they are separated then they will be differently populated and with the increasing energy there will be less and less number of particles at higher and higher level and with increasing temperature more and more particle will fill up the higher levels.