

**Chemical Principles II**  
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**Probability and Boltzmann Distribution**

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Boltzmann Distribution

$$e^{-\beta \epsilon_i}, a e^{-\epsilon_i/k_B T} \quad a = \frac{1}{\sum e^{-\epsilon_j/k_B T}}$$

$$p_i = \frac{n_i}{n} = \frac{e^{-\epsilon_i/k_B T}}{\sum_j e^{-\epsilon_j/k_B T}} = \frac{e^{-\beta \epsilon_i}}{Q}$$

Par HTR function

$$Q = e^{-0/k_B T} + e^{-\epsilon/k_B T} + e^{-2\epsilon/k_B T}$$

$$p_0 = \frac{1}{5} \quad p_1 = \frac{2}{5} \quad p_2 = \frac{1}{5}$$

Now let us talk about Boltzmann Distribution back again. We have already derived Boltzmann Distributions. Remember that when we calculated the particles in different levels for different distributions and then calculated how many particles are there in level 1, level 0, level 2 and things like that. And then we showed that it by fitting, by numerical fitting that it follows something like e to the power minus, e into to the power minus B epsilon.

So that B and B one can show that it is nothing but 1 by k B T that I also mentioned. So I will just remind you, so that is what we talked about and that is called probability. So probability of particle to occupy i th level is nothing but number of particle in the i th level divided by total number of particle, n i by n. And that is already I have shown the derivation in which we showed that it is nothing but e to the power minus e i by k B T. So energy of the i th level and divided by k B T. That is nothing but e to the power minus, remember we talked about beta E. It is nothing but the same thing, beta E i we said.

See this b is nothing but 1 by k B T, so it will be E i by k B T and that is what it is mentioned here. And there was a here and that a is nothing but a normalization constant and you can normalize, for normalization constant it must be this one so that when you sum over the whole quantity, then it becomes 1 because it is a probability. You know the probability. When you sum over the probability, it has to be 1. So when you sum over this particular quantity, it

has to be 1 and therefore this quantity in the denominator is just nothing but normalization constant.

And that is normally denoted as  $Q$  and this  $Q$  is called partition function. This partition function therefore is nothing but just a number. Why it is a number? Because it is a sum of exponentials of energy values basically. So if I have let you say three different energy values, let us say I have 0 energy value, 1 unit of energy value and 2 units of energy value. And let us say I have two particle in the zeroth level, two particle in the first level and one particle in the second level. How can I calculate my partition function? So I have to calculate my partition function by taking into account of this expression that it is  $e^{-\beta E_i}$ .

So in my partition function I will have  $e^{-\beta \cdot 0}$  plus  $e^{-\beta \epsilon}$ , plus  $e^{-2\beta \epsilon}$ . That will be my partition function. And what is my probability? My probability will be  $P_0$  will be  $2/5$ .  $P_1$  will be  $2/5$ . And  $P_2$  will be  $1/5$ . Okay, because there is only one particle in the two level. Is it clear?  $n_i$  we have used. And we have used the definition of partition functions to...

Student: Sir, we could do  $n_i/n$ . That is total number of...

$n_i/n$ .  $n_i$  is that number of particles in the  $i$ th level.

Student: And is it total number...

Total number of particle.

Student: Then how this exponential sum gives total number of particles?

No, exponential sum does not give it; it gives just the,  $n_i/n$  is denoted as here because  $n_i/n$  was fitted to this expression. So  $n_i/n$  was fitted to  $e^{-\beta E_i}$ . It was fitted to that. And this is a normalization constant. Why? Because such that the sum over  $n_i/n$  is nothing but 1. So that means sum over  $e^{-\beta \epsilon}$  is 1.  $a$  is just a constant, it will come out. So  $a e^{-\beta \epsilon} = 1$ . So  $1/a$  is nothing but sum over  $e^{-\beta \epsilon}$ . And that is what is shown here. So this can be written as  $e^{-\beta \epsilon} = 1/a$ . And  $1/a$  is nothing but this one, sum. It is just a normalization constant.


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### Boltzmann Distribution

$$p_i = \frac{n_i}{n} = \frac{e^{-\epsilon_i/k_B T}}{\sum_i e^{-\epsilon_i/k_B T}} = \frac{e^{-\epsilon_i/k_B T}}{Q}$$

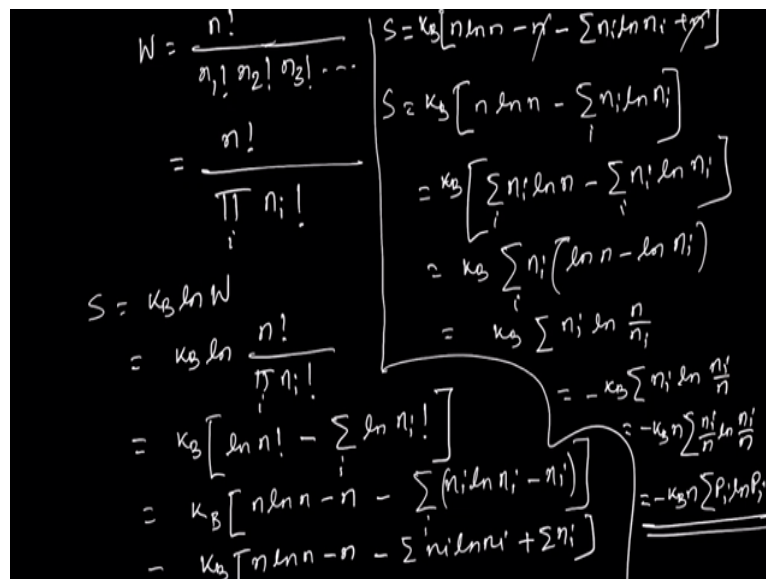
Q is called the partition function.  
With this probability, entropy is defined as,

$S = -k_B \sum_i p_i \ln p_i$  (see derivation)



So now this Q is called partition function. And with this probability the entropy will be defined by  $k_B \sum p_i \ln p_i$ . So I can just show you that in a very brief derivation.

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The handwritten derivation shows the following steps:

$$W = \frac{n!}{n_1! n_2! n_3! \dots}$$

$$= \frac{n!}{\prod_i n_i!}$$

$$S = k_B \ln W$$

$$= k_B \ln \frac{n!}{\prod_i n_i!}$$

$$= k_B [\ln n! - \sum_i \ln n_i!]$$

$$= k_B [n \ln n - n - \sum_i (n_i \ln n_i - n_i)]$$

$$= k_B [n \ln n - n - \sum_i n_i \ln n_i + \sum_i n_i]$$

$$= k_B [n \ln n - \sum_i n_i \ln n_i]$$

$$= k_B [\sum_i n_i \ln n - \sum_i n_i \ln n_i]$$

$$= k_B \sum_i n_i (\ln n - \ln n_i)$$

$$= k_B \sum_i n_i \ln \frac{n}{n_i}$$

$$= -k_B \sum_i n_i \ln \frac{n_i}{n}$$

$$= -k_B n \sum_i p_i \ln p_i$$

So we know that W is n factorial by n 1 factorial, n 2 factorial, n 3 factorial and things like that, which means that I can write that as n factorial by product of n i factorial. Correct? So now we know that entropy is  $k_B \ln W$  which means entropy is  $k_B \ln n$  factorial by product of n i factorial, which means I can write that as  $k_B \ln n$  factorial minus sum over  $\ln n_i$  factorial. The product becomes sum when we use  $\ln$ . In case of  $\ln$  the product becomes sum, that is why it is a sum.

Now once we have done that, we can write that as  $k_B n \ln n$  minus and, using Sterling's approximation minus we can write as,  $\sum_i n_i \ln n_i$  minus  $n_i$ . That I put as sum. So now I can write again  $k_B n \ln n$  minus  $n$ , minus  $\sum_i n_i \ln n_i$  plus  $\sum_i n_i$ . I will continue that derivation here. So  $S$  equal to  $k_B n \ln n$  minus  $n$  minus  $\sum_i n_i \ln n_i$  plus  $\sum_i n_i$ . So this  $n$  and this  $n$  cancels each other giving us  $k_B n \ln n$  minus  $\sum_i n_i \ln n_i$ . Now how can I do that? Now I can write the  $n$  as  $\sum_i n_i$ ,  $n_i \ln n$  minus  $\sum_i n_i \ln n_i$ .

Now I write  $k_B n_i$  take common,  $n_i \ln n$  minus  $\ln n_i$ . Now equal to  $k_B \sum_i n_i \ln n$  by  $n_i$ , equal to, now let us take a minus sign, minus  $k_B n_i \ln n_i$  by  $n$ . Let us take, let us multiply and divide by  $n$ , so minus  $k_B n_i$  by  $n$ ,  $\ln n_i$  by  $n$ , equal to minus  $k_B n P_i \ln P_i$ . And that is what is the proof.

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### Boltzmann Distribution

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$$p_i = \frac{n_i}{n} = \frac{e^{-\epsilon_i/k_B T}}{\sum_i e^{-\epsilon_i/k_B T}} = \frac{e^{-\epsilon_i/k_B T}}{Q}$$

Q is called the partition function.  
With this probability, entropy is defined as,

$$S = -k_B \sum_i p_i \ln p_i \quad (\text{see derivation}) \leftarrow$$

$$S = -k_B \sum_i p_i \ln p_i$$


So we see that, whenever we, for this case this is only for one particle. However for  $n$  particle we should write as minus  $n k_B P_i \ln P_i$ , if you have one particle, then this is the formula to use. And if there are  $n$  particles, then this is the formula to use. So now we are going to make use of this particular formula to understand something.

So remember, that note this  $P_i$  we are talking about, probabilities, normalized probability, that means for only one particle this formula is used. We can always use normalized probabilities and then it will be scaling as the number of particles increasing. For example, whatever the value we get for 1, you multiply it by the number of particles and you get for that many number. For example, we get entropy typically in per mole basis. Now if you have 10 moles system, it will be 10 into that, it is something like that. It is a per particle basis. And

you can, if you have got a number of particle multiplied by that 6.023 into power 23 and you will get the entropy per mole.

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### Boltzmann Distribution

$$p_i = \frac{n_i}{n} = \frac{e^{-\epsilon_i/k_B T}}{\sum_i e^{-\epsilon_i/k_B T}} = \frac{e^{-\epsilon_i/k_B T}}{Q}$$


Q is called the partition function.  
With this probability, entropy is defined as,

$$S = -k_B \sum_i p_i \ln p_i \quad (\text{see derivation})$$

For isolated system, all energies are equal. Therefore,

$$p_i = \frac{e^{-\epsilon/k_B T}}{Q} = \frac{1}{W}$$

$$S = -k_B \sum_i \left(\frac{1}{W}\right) \ln \left(\frac{1}{W}\right)$$

$$S = k_B \ln(W)$$


Now so I will just show you that how this particular formula  $p_i \ln p_i$ . So we have done the derivation starting from  $W$  and now we go back to the  $W$ . So for isolated system or systems where energies are all equal, or let us say for degenerate system where all the energies are same, in that case you know that probability is proportional to the energy. So if all energies are same, then I can write instead of  $e$ , I can write simply  $e$  for all probabilities. And it will be nothing but  $e$  to the power minus  $e$  by  $k_B T$  by  $Q$  or  $1$  by  $W$ . Why?

Because all probabilities are same. So if there are  $W$  number of microstate possible, then the probability of each microstate will be  $1$  by  $W$ , because they are all equal. And once I put now  $1$  by  $W$  in this particular formula, then I can write it this way, because  $p_i$  is  $1$  by  $W$ . So  $1$  by  $W \ln 1$  by  $W$ . Once I do that, I get back my  $k_B \ln W$ . So  $k_B \ln W$  is very general expression and  $p_i \ln p_i$  also is general where the probabilities are different but  $k_B \ln W$  is simply can be used for whatever.

So this is again the postulate which essentially, so how did it all start? So we started with  $k_B \ln W$ , then we said  $W$  is  $n$  factorial by  $n_i$  factorial into factorial, all that for distinguishable particles and from there we got back the Boltzmann statistics and from there again we got back  $W$  when all the microstates are all equal. So it only means that if the energies are all equal, we are going to get, we are going to simply count the number of  $W$  and that will give us the entropy. However if energies are not equal, then we cannot just simply count the  $W$ .

We have to use this particular formula, because then the number of microstates will be weighted by how probable they are. And that is where the distinction comes when systems are distributed in different levels differently.

So  $p_i$  is the probability, so  $p_i$  is more, then the probability of that microstate will be more to form. That means the weights of that particular microstates will be even more. So that we have to understand. So for example, if I buy 4 apples and 2 banana, and let us say 4 apples each of them cost 10 rupees and banana each of them cost 5 rupees, so 4 apples is 40, 2 banana is 10, so 50. And divided by 6, so it is definitely more weighted by the apples and then the bananas. So I can, whatever, so the probability of that is, probability of apple being there is 4 by 6 whereas banana being there is just 2 by 6. So when you take an average of an apple and banana, I can simply take 10 as the price of apple multiplied by 4 by 6, plus 5 multiplied by 2 by 6.

That will give rise to the value, same value that we can get by adding all of them together, 10 plus 10 plus 10 plus 10, plus plus plus 5, divided by 6. We will get the same result if we just multiply 10 into 4 by 6 plus 5 into 2 by 6. So that is an example of weighted averaging and weights are nothing but probabilities.

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The image shows handwritten mathematical derivations on a blackboard. On the left side, the entropy formula is simplified:

$$S = -k_B \sum p_i \ln p_i$$

$$= -k_B \sum \frac{1}{W} \ln \left( \frac{1}{W} \right)$$

$$= k_B \sum \frac{1}{W} \ln W$$

$$= \frac{1}{W} \ln W \cdot k_B \sum_{i=1}^W 1$$

$$= \frac{1}{W} \ln W \cdot W \cdot k_B$$

$$= k_B \ln W$$

On the right side, the probability  $p_i$  is defined and simplified under the assumption of equal energy levels:

$$p_i = \frac{e^{-\epsilon_i/k_B T}}{Q}$$

$$\epsilon_1 = \epsilon_2 = \epsilon_3 = \epsilon_4 = \epsilon$$

$$p_i = \frac{e^{-\epsilon/k_B T}}{Q}$$

$$= \frac{1}{Q e^{\epsilon/k_B T}}$$

$$= \frac{1}{W}$$

Let me just derive that how we are getting the  $k_B \ln W$ . So we know that  $S$  is minus  $k_B p_i \ln p_i$ . Now  $p_i$  we know as  $e$  to the power minus beta  $E_i$  or  $E_i$  by  $k_B T$ ,  $e$  to the power minus  $E_i$  by  $k_B T$  by  $Q$ , some value, some constant value which is a normalization constant, that is  $p_i$ . Now if all energies are equal, that means  $E_1$  equal to  $E_2$  equal to  $E_3$  equal to  $E_4$ ,

all states are equal, equal to  $E$ , then I can write  $P_i$  as  $e^{-E/k_B T}$  by  $Q$  which simply means that this is a constant term, this is a constant term and which means this is nothing but a constant term,  $1/W$ .

I can always put that, I can write one more step though so that it will become clear. I can always write that as  $1/Q$  into  $e^{-E/k_B T}$  or I can write  $1/W$ .  $1/W$  here is nothing but  $Q$  into  $e^{-E/k_B T}$ . So we know that  $P_i$  is  $1/W$ , so now let us put that here,  $-\ln(1/W)$ . Now when there is a minus and  $1/W$ , minus will become plus and it will give us  $\ln W$ . So we know that  $W$  is a constant, so let us take out  $W$  and  $\ln W$  and I will have a sum of 1 going from  $i$  to  $W$ , which will give me  $\ln W$  multiplied by  $W$ . And  $W$ ,  $W$  cancels giving me, oh,  $k_B$  is also there here, giving me  $k_B \ln W$ .

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### Boltzmann Distribution

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$$p_i = \frac{n_i}{n} = \frac{e^{-\epsilon_i/k_B T}}{\sum_i e^{-\epsilon_i/k_B T}} = \frac{e^{-\epsilon_i/k_B T}}{Q}$$

$Q$  is called the partition function.  
With this probability, entropy is defined as,


$$S = -k_B \sum_i p_i \ln p_i \quad (\text{see derivation})$$

For isolated system, all energies are equal. Therefore,

$$p_i = \frac{e^{-\epsilon_i/k_B T}}{Q} = \frac{1}{W}$$

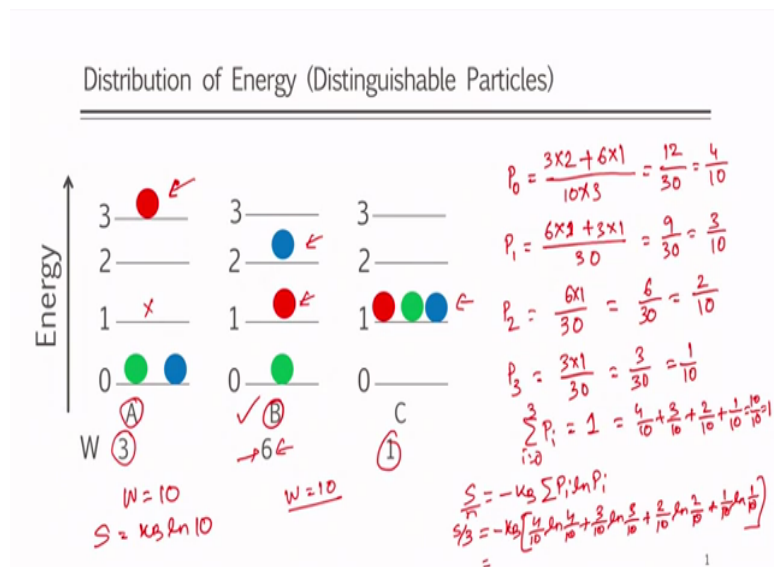
$$S = -k_B \sum_i \left(\frac{1}{W}\right) \ln \left(\frac{1}{W}\right)$$

$$S = k_B \ln(W)$$



So now we got  $k_B \ln W$ . Now let us see that how this  $p_i$  which is a probability of being in the  $i$ th state affects or helps us to understand that while the energy of a particular system remains constant or for example, image of the universe remaining constant, entropy keeps on increasing. And remember we even discussed in our intro slides that while the energy is conserved, the distribution of energy is not and that is an indication of increase of entropy.

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So let us understand through a simple problem. So remember we discussed about three particles distributed in four different energy levels and we saw that we were getting three possible distributions. One is distribution A where the  $W$  was, number of  $W$ , number of possible distributions were 3. And then the distribution B, where number of possible arrangements or number of microstates were 6. And the distribution C where the number of microstates was 1. The total  $W$  was 10 and the entropy obtained from that was  $k_B \ln 10$ .

Now let us see that with these new ways of calculating the number of particles in different levels, what kind of entropy values we get. So in order to calculate that, let us see that what is the probability of finding particle at zeroth energy level. You see that in the distribution A, there are two particles in the zeroth energy level. And since there are three possible ways of doing that, so we can write as 3 into 2. There is one particle at zeroth energy level but there are six possible  $W$ s. So therefore that will be 6 into 1.

And there is no particle in the zeroth level in the distribution C. And how many total number of particles are there? So as you can see there are 10 possible distributions each distribution has three particles, so there is total 30 particles. If I calculate that, it will be 6 plus 6, 12 by 30 giving us 4 by 10. Now let us calculate the same way the probability of finding particles in level 1. So as you can see there is no particle in distribution A but there is one particle in level 1 for distribution B and there are 6 possibilities, so 6 into 1.

And there are three particles in level 1 for distribution C and there is only one way of getting that. So therefore we get 3 into 1. So and divided by 30 again, so we get 9 by 30 or 3 by 10. Let us calculate now probability of finding particle in level 2 and you can see that in

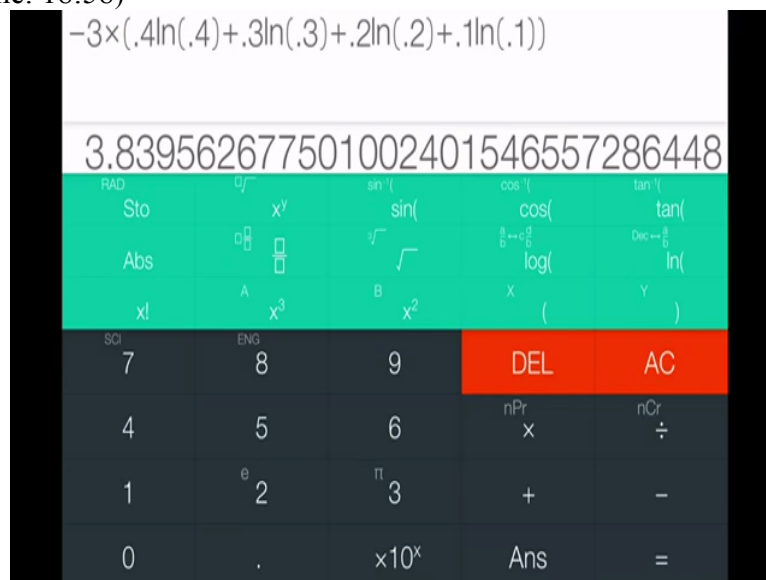


distribution B, there is a particle at level 2 and there are six possible ways of doing that, so we will get 6 by 30 or 6 into 1 by 30 you can say, so 6 by 30 and giving us 2 by 10.

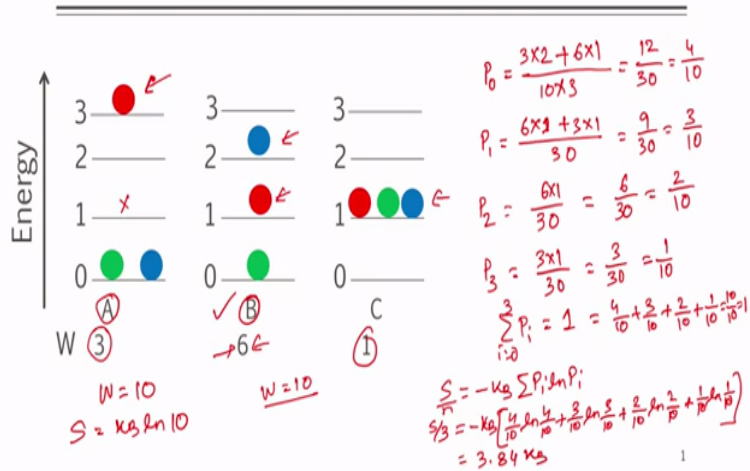
And finally let us calculate the probability of getting a particle in level 3. And you can see that there is one particle in level 3 for distribution A which has three possibilities, so it is 3 into 1 by 30, so 3 by 30 or 1 by 10. Now first thing to notice is that the sum over  $P_i$  is  $i$  going from 0 to 3 is equal to 1. As you can see 4 by 10 plus 3 by 10 plus 2 by 10 plus 1 by 10 is equal to 10 by 10 or 1.

Now to calculate the entropy we have to use the formula minus  $k_B$  sum over  $P_i \ln P_i$  which means it is minus  $k_B$  then 4 by 10  $\ln$  4 by 10 plus 3 by 10  $\ln$  3 by 10 plus 2 by 10  $\ln$  2 by 10 plus 1 by 10  $\ln$  1 by 10. And that is the entropy for one particle, so we should write as  $S$  by or  $S$  by 3,  $n$  equal to 3 we know. So now let us calculate and see what is the value that we get.

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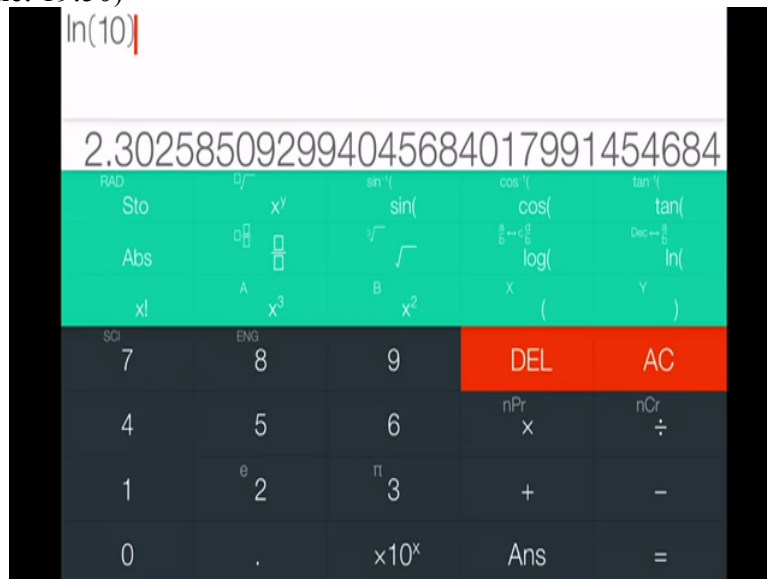


### Distribution of Energy (Distinguishable Particles)

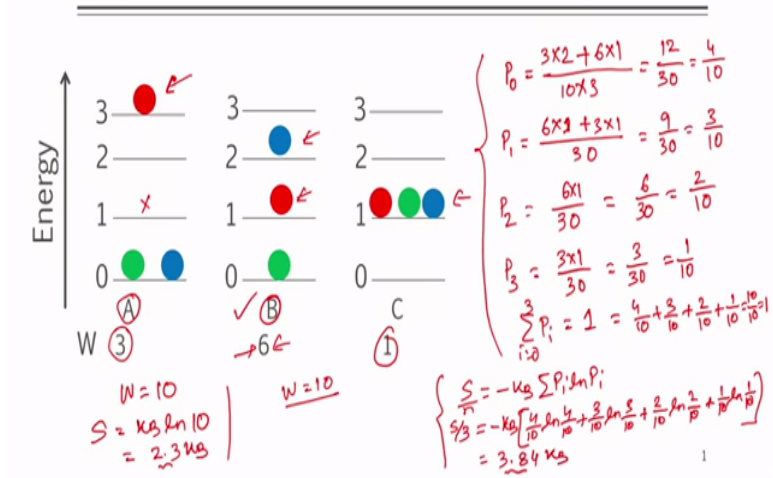


So  $4 \ln 0.4 + 3 \ln 0.3 + 2 \ln 0.2 + 1 \ln 0.1$ , we get minus 1.27 and we have to multiply that by 3 and there is a minus sign, so we have to put minus, so that much  $k_B$  we are going to get. 3 into, so 3.84 as you can see here, 3.84 is the value, 3.84  $k_B$  is the value.

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### Distribution of Energy (Distinguishable Particles)

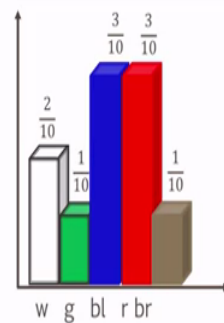


And  $k_B \ln 10$  is, so we can calculate that  $\ln 10$  is 2.3. So that is 2.3  $k_B$ . So as you can see, it is not exactly same, it is 2.3 to 3.84 but the reason is actually that our statistics is not enough to get exactly equal number but they are pretty close. If you have many more number of particles, then one can get much closer accuracy. Another closer similarity between these two number, another point you have to note that and this  $P_i$  is obtained only for the most probable distribution because when you get this formula  $P_i$  we had maximized  $W$  under some constraints and that gave us the most probable distribution, which is in this case is B.

However if you calculate  $P_i$ , it is from only this distribution, you are going to get equal probability for 0, 1 and 2 which may not be the right one. For example, we will get, for 0 you will get 1 by 3. 1 by 3 and 1 by 3 which will not give you the same number. So these discrepancies will be there only for the smaller number of particles, for higher statistics they are going to be the same thing. But now you know how to calculate the entropy both from the  $W$ , that means all possible distributions you can calculate all possibilities and get that  $W$ . Or you can calculate the probabilities of occupying a certain states and calculate the  $W$ .

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Distribution of Color of Socks



Entropy can be associated with anything  
 -- even color of socks

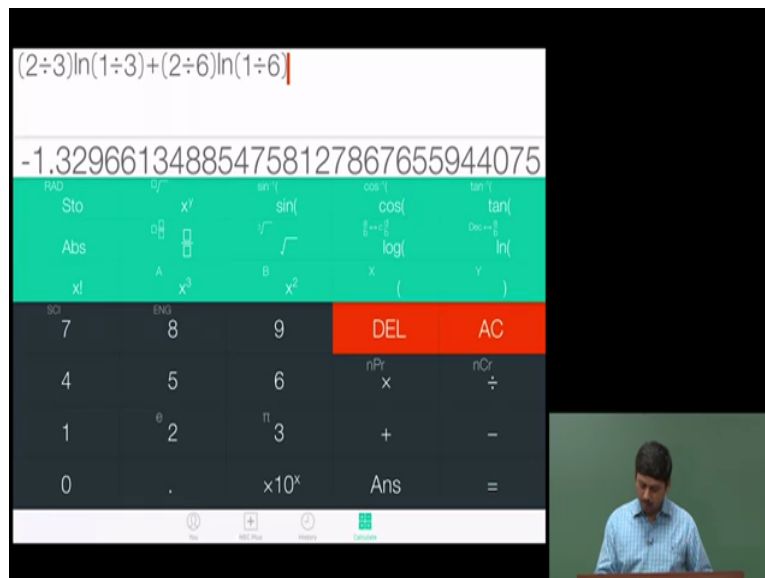
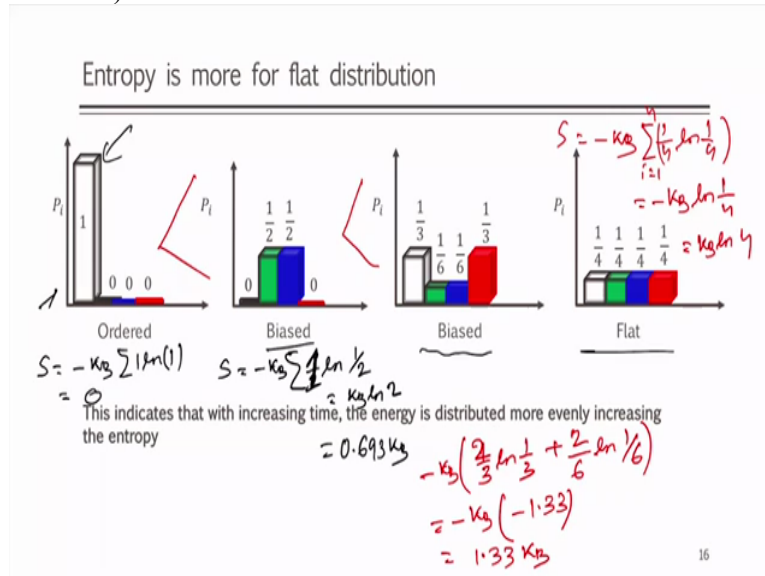
$$S = -100 \times k_B \left( \frac{2}{10} \ln \left( \frac{2}{10} \right) + \frac{1}{10} \ln \left( \frac{1}{10} \right) + \frac{3}{10} \ln \left( \frac{3}{10} \right) \times 2 + \frac{1}{10} \ln \left( \frac{1}{10} \right) \right)$$

For example, that entropy is just not, it not only can be applied to atoms and molecules with energy, it can be applied to anything. For example, we can talk about the probabilities or students wearing socks. So let us say, these are the probabilities that out of 100 as students, 20 students wear white socks on a day, on a given day, 10 students wear green socks, 30 students wear blue, 30 students wear red and 10 students wear brown socks. So probabilities of wearing socks for these students of different color is 2 by 10, 1 by 10, 3 by 10 and things like that.

So now we can use our entropy formula in order to calculate the entropy for this one also. Let us the number of students is 100, so  $100 \text{ k B } \sum p_i \ln p_i$  which is  $2 \text{ by } 10 \ln 2 \text{ by } 10$ . Let us forget the sum because we are summing up anyway,  $1 \text{ by } 10 \ln 1 \text{ by } 10$  plus  $3 \text{ by } 10 \ln 3 \text{ by } 10$  plus  $1 \text{ by } 10 \ln 1 \text{ by } 10$ . I am not going to do the sum but you can do that and see what value you get.

So the point is that one can in principle obtain entropy values for any probabilistic distributions, it need not be just energy. But then how meaningful that will be, that is a different question. But we can always say right that the entropy of the room is high or the entropy of the situation is more. So basically we are using in a sense that there are more possibilities that are happening around us. And that is the way loose way of talking about entropy. However you know that, you should not know that they are, there is subject called information entropy where this particular, exactly this particular formula except that  $k_B$  part is used where  $p_i \ln p_i$  is the entropy of the information. And that is cost an entropy. So that is very similar to this  $p_i \ln p_i$ .

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So now let us talk about that why entropy keeps on increasing in the universe and why that is the case. So let us say that the our energy distribution or energy of a particular system is always say 10 and or let us say energy is 1 not 10, 1. It is not 1 unit, you can say that is just some value 1. You can say 10 also, I think 10 will be better. So initially let us say all the 10 were in one particular place having unique probability, probability 1, that means all other probabilities of being there will be 0. And then it created a biased distribution as this kind and then it created more biased distribution of this kind and then it created a flat distribution of this kind.

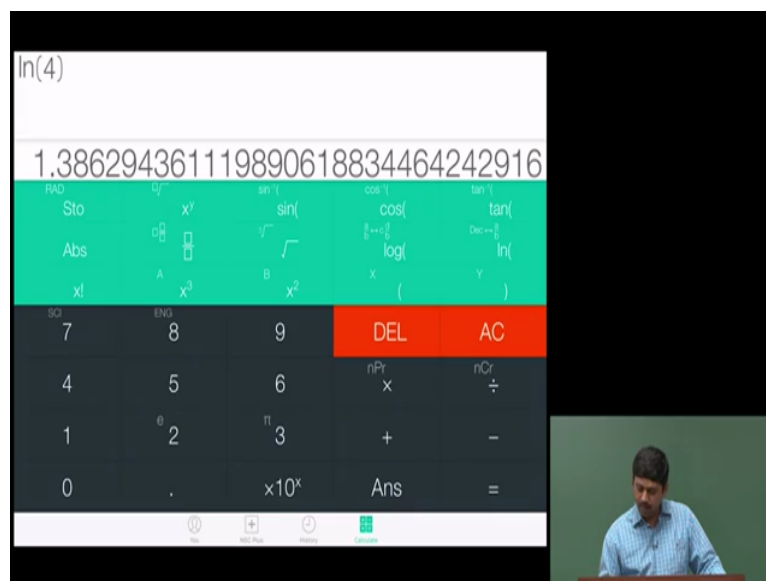
So now let us calculate that in all cases what will be the entropy values. For example, in this particular case I have  $k_B p_i \ln p_i$  which is  $1 \ln 1$  and you know  $\ln 1$  is 0, so it will give me 0. In this case I have  $-k_B p_i \ln p_i$ , so two  $p_i$  are 0, so I have only half  $\ln$  half twice.

Half ln half and half ln half, so 1 ln half, so 1 ln half is basically  $k_B \ln 2$ . And ln 2 is how much?  $k_B, 0.693 k_B$ , this particular thing. And now let us talk about this biased distribution. So there it will be 1 by 3 ln 1 by 3 twice, so it is 2 by 3 ln 1 by 3, plus ln 1 by 6, 1 by 6 ln 1 by 6, so 2 into 1 by 6 ln 1 by 6.

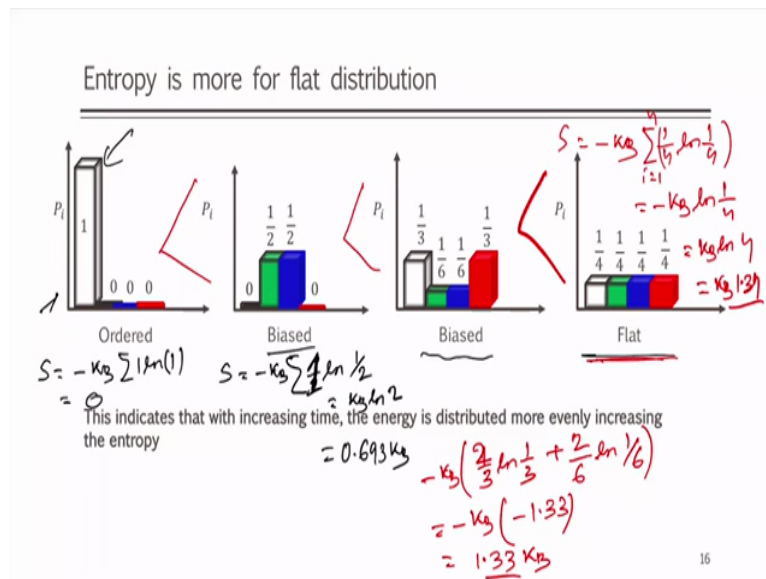
So this is the formula for the this one and let us see how much you get.  $k_B$  and ln 1 by 3 is, let us do the whole calculation, 2 by 3 ln 1 by 3 and 2 by 6 ln 1 by 6, let us do the whole calculation here. So 2 by 3 ln 1 by 3 plus 2 by 6 ln 1 by 6, so we got minus 1.32 or 1.33. Minus 1.33 giving us plus 1.33  $k_B$ , so you see this distribution, this biased distribution has more entropy than this biased distribution which has more entropy than this biased distribution. So I will just write this.

Now let us calculate the flat distribution where everything is the same value and what is the formula there? Again minus  $k_B$  sum over 1 by 4 ln 1 by 4, four terms,  $i$  equal to 1 to 4, so which is minus  $k_B \ln 1 by 4$  which is plus  $k_B \ln 4$ . So we have to just calculate ln 4 of this thing.

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Ln 4 is just the double of ln 2 because it is 2 square, so two times of ln 2, so 0.693 is doubled which is 1.39 approximately. So it is 1.39 k B basically. Now you see 1.39 is larger than 1.33, so this one the flat distribution has maximum entropy. So you see everywhere the total energy unit has not changed, it is just that how it has distributed from this completely distributing in place to becoming flatter. So that is what happening with our world. Initially you remember the Big Bang, the energy is a concentrated in one dot and as the time progresses that energy is getting distributed in everything.

And then more and more it gets distributed, more and more entropy increases because it is just that the probabilities are getting flatter and flatter. And that is why we said that although the energy is conserved, the distribution is not. And as long as the distribution is not going to be flat distribution, so when the entropy will be maximum? When everywhere there will be a equal population of energy units or energy distribution will be completely flat and that time the entropy will be maximum.

And that is the time where our universe will come to equilibrium and you know when that will happen. Where if that happens then every molecule will have to have the same amount of energy and that is, that will not allow the energy concentration in one particular place like what we see in organized system, like a human being or plants or animals or any organized growth will be going against that particular flat distributions. So that is why I say entropy is called the ultimate death, the because it shows us the future of the complete stillness rather.

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**Quantum and Classical Comparison**

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Thermodynamic observables such as energy, pressure, volume are averages weighted by the probability

Thermodynamics energy  $U = \langle E \rangle = \sum_i E_i P_i$

Observed pressure  $p = \langle p \rangle = \sum_i p_i P_i$

Observed volume  $V = \langle V \rangle = \sum_i V_i P_i$

Compare this with quantum mechanics where expectation value of an observable is also an weighted average. For a property p

$\langle a \rangle = \int \psi^* \hat{A} \psi d\tau$  where  $\psi^* \psi$  is the probability density.  $\rightarrow \int \psi^* a \psi d\tau \rightarrow \int \psi^* \psi a d\tau$

In statistical thermodynamics, we calculate similar averages weighted by the probability density:  $\langle E \rangle = \int P(E) E dE$ .

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So now where is the use of this? Because once we know the probability, then we can use that probability and calculate the average values of a particular property. For example, when you talk about microscopic property like energy, there are nothing but average energy weighted by the probability. When you talk about pressure, then it is nothing but average, then nothing but average pressure weighted by the probability. When you talk about volume, as I said that 1 liter volume, when you say that a normal temperature and pressure, 55.5 mole of water will have volume of 1 liter, it does not mean it will be exactly 1 liter.

It means that on an average it will be 1 liter. If you do a simulation with water, it will not be exactly 1 liter, it will be fluctuating and that when you take an average, it will be then exactly 1 liter. And that is what we measure experimentally. So all the microscopic thermodynamic quantity which is written on this side are nothing but average over the microstates with the probabilities of a certain state as a weight function. Just like in Quantum Mechanics, in Quantum Mechanics what we do? We calculate first the property using the operator. Once we get the observable using an operator, then it becomes, so this is the formula of expectation value.

Now let us say size the Eigen state or not even the Eigen state of A, what we get is that just I do one more step here, we get  $\psi^* A \psi dx$ , then  $d\tau$ , whichever, if it is very general, let us call it  $d\tau$ . And then what we get here is  $\psi^* \psi a d\tau$ .  $\psi^* \psi$  is the probability just like our  $p_i$  here. And  $a$  is the property just like our  $E$  here. So you see here also what we are essentially doing is that we are calculating the average values weighted by the probability density  $\psi^* \psi$ , which is nothing but this probability.



Meaning, what I am saying is that just like in Quantum Mechanics we get the expectation value from the probability distributions, we get similarly some expectation value based on the number of microstates and they are energy values. So that is where the connection between molecular thermodynamics and classical thermodynamics takes place. So in one line, the statistical thermodynamics, the average value obtained from atoms and molecules is what we observe in classical thermodynamics and that is what is, but we are not going to go into detail of that. You may look at other courses that are there.

For example, in NPTEL itself there is a course by Srabani Taraphder on introduction to molecular thermodynamics where you can get little bit more detailed descriptions of molecular thermodynamics and its applications into understanding realistic classical systems as well. So then you can get a better idea of how to club both of them together. Here we wanted to just give very brief outline of how to think about thermodynamics from atoms and molecules.