Chemical Principles II
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Tutorial Problem - 10

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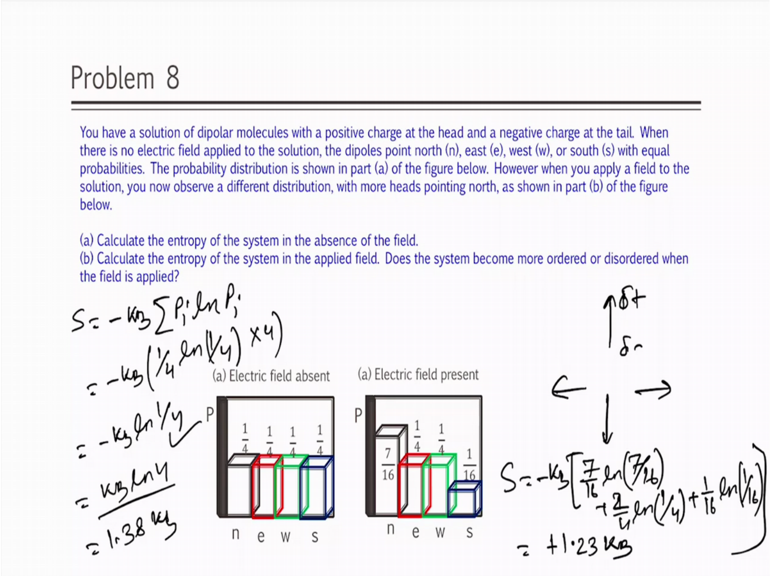

Problem 8

You have a solution of dipolar molecules with a positive charge at the head and a negative charge at the tail. When there is no electric field applied to the solution, the dipoles point north (n), east (e), west (w), or south (s) with equal probabilities. The probability distribution is shown in part (a) of the figure below. However when you apply a field to the solution, you now observe a different distribution, with more heads pointing north, as shown in part (b) of the figure below.

(a) Calculate the entropy of the system in the absence of the field.
(b) Calculate the entropy of the system in the applied field. Does the system become more ordered or disordered when the field is applied?

$$S = -k_B \sum P_i \ln P_i$$
$$= -k_B \left(\tfrac{1}{4} \ln(1/4) \times 4\right)$$
$$= -k_B \ln 1/4$$
$$= k_B \ln 4$$
$$= 1.38\, k_B$$

$$S = -k_B\left[\frac{7}{16}\ln(7/16) + \frac{2}{4}\ln(1/4) + \frac{1}{16}\ln(1/16)\right]$$
$$= +1.23\, k_B$$

(a) Electric field absent

(a) Electric field present

So now the problem number 8, you have solution of dipolar molecules with a positive charge at the head, it looks like this, Delta positive and a negative charge at the tail that is the convention right. When there is no electric field applied to the solution, so when there is no electric field the dipoles are you know randomly oriented. When there is no electric field applied to the solution, the dipoles point north, east, south and west with equal probabilities, this is because there is nothing to actually orient them right. The probability distribution is shown in part A so when the electric field is absent however, when you apply electric field to the solution you observe that a different distribution with more heads pointing north because probably you applied along the north direction electric field, north-south direction so you get a different probability as shown in the part figure B.

Calculate the entropy of the system in the absence of the field that means here and calculate the entropy of the system when the field is applied, thus the system becomes more ordered or disordered when the field is applied. So we can calculate entropy and say more ordered or disordered or we can physically 1st thing, if they are randomly oriented in all possible directions which means they are disordered in the 1st case, and if more is going towards the north that means they are ordered, but we can also calculate the entropy and see the same thing. So you know in that case whenever you have the formula for probability, then when you have the information for probability then the formula for entropy is P i L n P i.

For in the 1st case it is - K B 1 by 4 L n 1 by 4 four times multiplied by 4 which will give us - K B L n 1 by 4 which is K B L n 4 that is the formula that we get. In the other case it is - K B 7 by 16 L n 7 by 16 + 1 by 4 L n 1 by 4 two times which is 2 by 4 + 1 by 16 L n 1 by 16. We can calculate that using a calculator and see that but K B part we will keep the same so let us see what L n 1 by 4 gives us. L n 4 gives us 1.38 so it is 1.38 K B. And right-hand side let us see 7 by 16 and 1 by 16, so it is 7 divided by 16 L n 7 divided by 16 + 2 by 4 is 1 by 2, 1 divided by 2 L n 1 divided by 4, I have taken two terms already + 1 by 16 so 1 divided by 16 L n 1 divided by 16. Okay, so did I consider all of that so 7 + 1 by 4 is 4 by 16 so put for it is 15 + 1 is 16, yes correct, so I am getting - 1.23 so + 1.23 K B.

So 1.38 is of course more than 1.23 and therefore this is where the entropy is more. This is where the entropy is more and this is where the things are random that means it can point to any directions, normal, south, east, west. Here it is less random and entropy is also less so that is why people associate randomness with entropy because randomness gives us a flatter distribution with equal probability in every detection whereas, an ordered arrangement gives us peak distribution that means it is ordered, in one direction it is more and that will give us lesser entropy.

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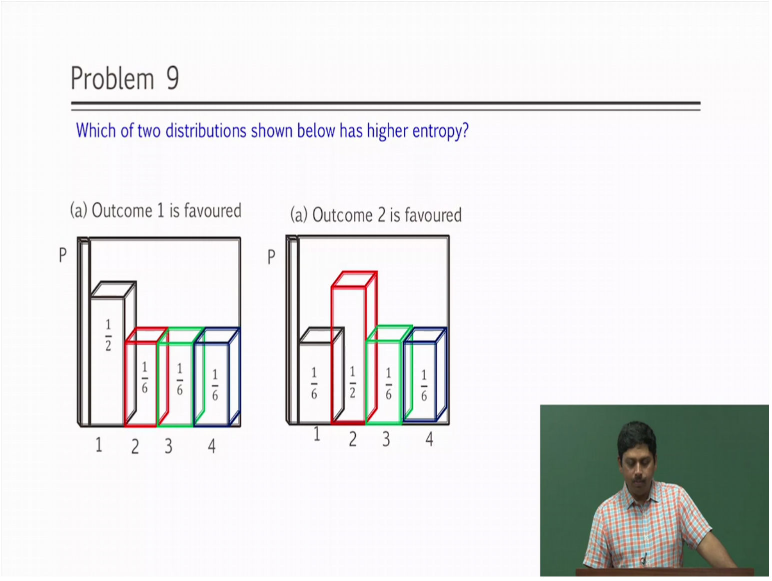

Problem 9

Which of two distributions shown below has higher entropy?

(a) Outcome 1 is favoured

(a) Outcome 2 is favoured

Same similar problem in the next one also, which of the 2 distributions shown below which of the 2 distributions have higher entropy. So you have to calculate that precisely and see that so half and 3 1 by 6 and here also half and 3 1 by 6, so this is a trick question you understand. You do not have to really do this problem because if you see whether this one is half or this one is half does not matter, at the end you will have the formula - K B sum over P i L n P i so whether the 1st term is different or 2nd term is different it does not matter because you are going to some over both, so both will have same entropy, I do not have to do the calculation, you can crosscheck of course by doing this.

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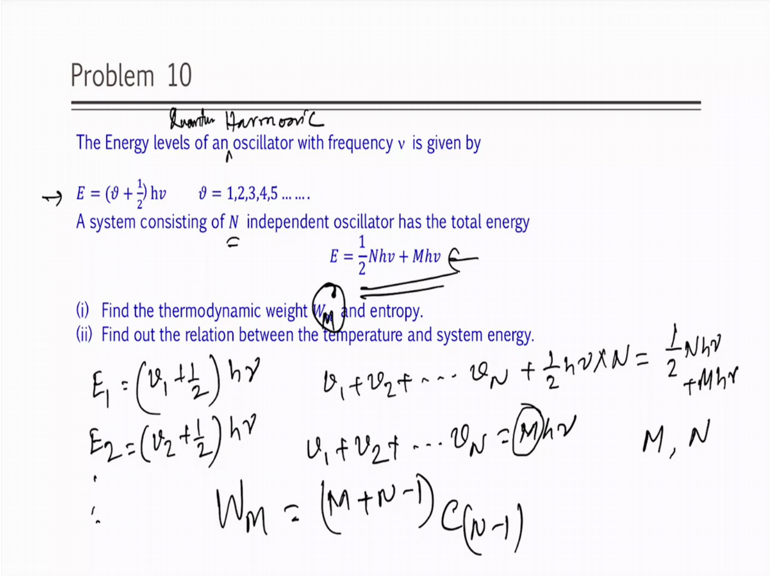

Problem 10

Quantum Harmonic

The Energy levels of an oscillator with frequency ν is given by

$E = (\vartheta + \frac{1}{2})h\nu \qquad \vartheta = 1,2,3,4,5 \ldots\ldots$

A system consisting of N independent oscillator has the total energy

$E = \frac{1}{2}Nh\nu + Mh\nu$

(i) Find the thermodynamic weight W_M and entropy.

(ii) Find out the relation between the temperature and system energy.

$E_1 = (v_1 + \frac{1}{2})h\nu$

$E_2 = (v_2 + \frac{1}{2})h\nu$

$v_1 + v_2 + \cdots v_N + \frac{1}{2}h\nu \times N = \frac{1}{2}Nh\nu + Mh\nu$

$v_1 + v_2 + \cdots v_N = Mh\nu$

M, N

$W_M = {}^{(M+N-1)}C_{(N-1)}$

Next problem, the energy levels of an oscillator with frequency Nu is written, harmonic oscillator of course a quantum harmonic oscillator, frequency Nu is written as this. A system consisting of an independent oscillator has a total energy this, find the thermodynamic weight W M, this M should be capital M and the entropy. So there are how many oscillators? N independent oscillators, right. So the 1st one let us call the 1st one as having E 1 energy, it is let us say V 1 + half h Nu, E 2 is V 2 + half h Nu and things like that, so when you add them you are going to get V 1 + V 2 + V n + half h Nu multiplied by N is equal to whatever is given here, half N h Nu + M h Nu, its means V 1 + V 2 + V n is M h Nu.

Now V 1 can be any value, V 2 can be any value, V 3 can be any value but some is constrained, which is like this that if I have M units of energy and I am distributing in N distinguishable particles, here the particles are oscillators because I know 1st oscillator because it is denoted by V 1, 2nd oscillator is denoted by V 2 so oscillators are distinguishable like boxes and you have there are N independent oscillators are there and you have total M units of energy so that are indistinguishable because you can give any amount of energy right.

So what is the formula in that case? You know basically you are having M units of energy distributed in N number of distinguishable particles that is the formula you have to use, it is a star bar formula so it is M + N – 1 so number of possible ways W M is M + N – 1 C N - 1 so that will be the answer to this particular question. Find the (())(8:21) find out the relation between temperature and system energy. Now once you get W M, you can get S as K B L n W, and you will learn later that we can write temperature as Del E by Del S at a constant volume. So here there is no question about the volume so and we the energy values also.

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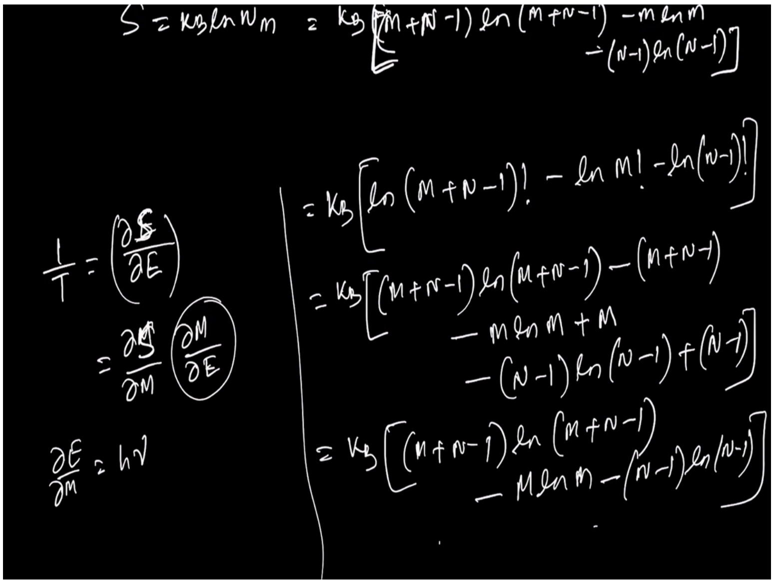

$$S = k_B \ln W_m = k_B\left[(M+N-1)\ln(M+N-1) - M\ln M - (N-1)\ln(N-1)\right]$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right) = \frac{\partial S}{\partial M}\boxed{\frac{\partial M}{\partial E}}$$

$$\frac{\partial E}{\partial M} = h\nu$$

$$= k_B\left[\ln(M+N-1)! - \ln M! - \ln(N-1)!\right]$$

$$= k_B\left[(M+N-1)\ln(M+N-1) - (M+N-1) - M\ln M + M - (N-1)\ln(N-1) + (N-1)\right]$$

$$= k_B\left[(M+N-1)\ln(M+N-1) - M\ln M - (N-1)\ln(N-1)\right]$$

Now 2nd problem is that find out the relation between temperature and system energy, I need some more space for that so what is the energy of the system? Energy of the system is M h Nu + half N h Nu, and what is our entropy which is K B L n W M and we know that K B L n W M we know which is M + N - 1 factorial divided by M factorial and N - 1 factorial. So L n of that we can use of course (())(9:34) approximation, so we can have K B L n M + N - 1 factorial – L n M factorial – L n N - 1 factorial. Okay, so you can have K B M + N – 1 L n M + N - 1 - M L n M ok so - M + N - 1 – M L n M + M - N - 1 L n N – 1 + N - 1, this will give us K B M + N – 1 L n M + N - 1 - M L n M – N – 1 L n N – 1.

So that is just S, and then we know the formula for temperature is 1 byT is Del S by Del E. So now what is our variable? Our variable is basically N, M and N both can vary right but if I have N number of independent oscillators then I can have M as the variable so it is del S by Del M, Del M by del E that is the formula, so we have to differentiate this quantity by M and we have to differentiate that quantity by E so we know that Del E by del M is h Nu therefore, Del M by Del E will be 1 by h Nu and Del S by del M we will have to do that by removing some more you know getting some more space out of this so let us do that, this is K B L n W M which is given as K B M + N - 1 L n M + N - 1 - M L n M - N – 1 L n N – 1, I will just remove now this space so now I will just get some more space.

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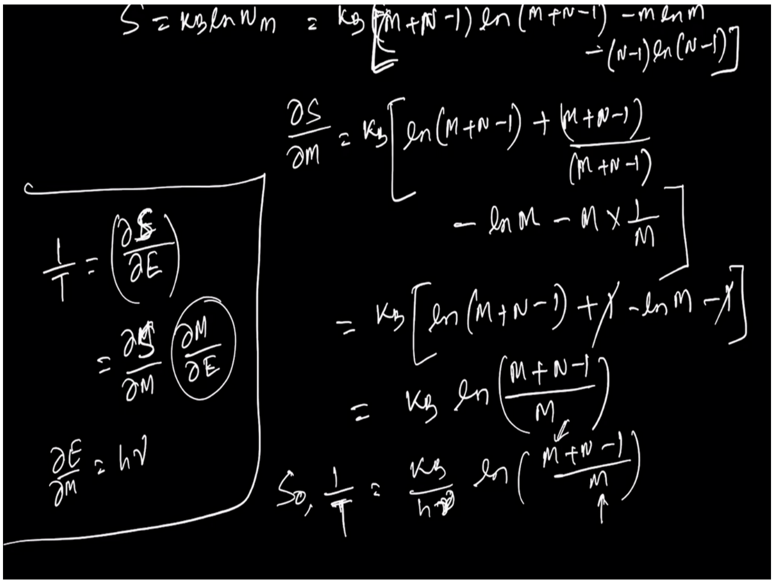

$$S = K_B \ln W_M = K_B \left[(M+N-1)\ln(M+N-1) - M\ln M - (N-1)\ln(N-1)\right]$$

$$\frac{\partial S}{\partial M} = K_B\left[\ln(M+N-1) + \frac{(M+N-1)}{(M+N-1)} - \ln M - M \times \frac{1}{M}\right]$$

$$= K_B\left[\ln(M+N-1) + \cancel{1} - \ln M - \cancel{1}\right]$$

$$= K_B \ln\left(\frac{M+N-1}{M}\right)$$

$$\text{So, } \frac{1}{T} = \frac{K_B}{h\nu}\ln\left(\frac{M+N-1}{M}\right)$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right) = \frac{\partial S}{\partial M}\left(\frac{\partial M}{\partial E}\right)$$

$$\frac{\partial E}{\partial M} = h\nu$$

Now Del S by Del M is equal to K B, first-term if I do it will become L n M + N - 1 derivative of M + N – 1 is just 1 + M + N - 1 multiplied by the derivative of L n quantity which is going to give us M + N – 1, and 2nd one is - L n M – N into 1 by M ok that is it, ok. And N is a constant term with respect to M so it will not come, which is K B L n M + N – 1 + 1 – L n M - 1 cancels each other giving me K B L n M + N – 1 by M, so therefore so 1 by T is nothing but K B by h Nu L n M + N – 1 by M. At a very high temperature 1 by T becomes 0 so and in right-hand side M becomes much bigger than N so therefore it will become M by N and 1 thousand right-hand side quantity will become 0 as well. So at high temperatures what is going to happen is that the particle is going to occupy much more higher levels and that is what is coming out from this particular one.

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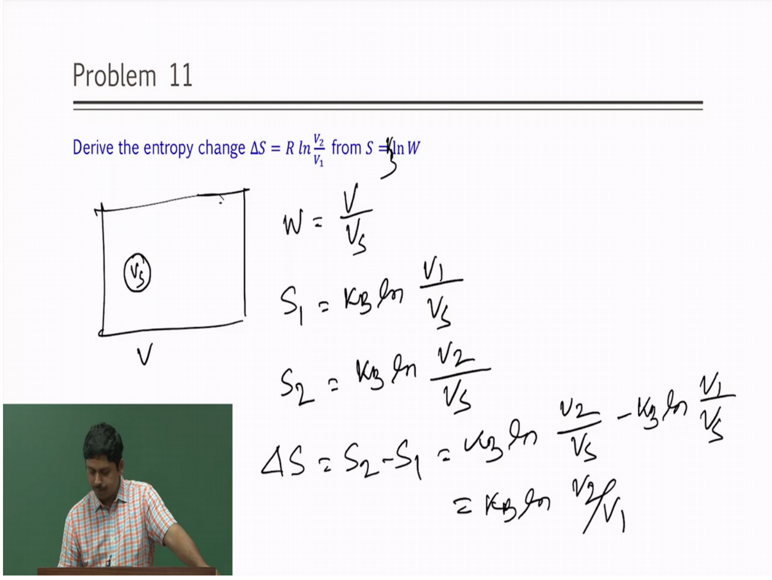

Problem 11

Derive the entropy change $\Delta S = R\ln\frac{V_2}{V_1}$ from $S = k_B \ln W$

$W = \frac{V}{V_S}$

$S_1 = k_B \ln \frac{V_1}{V_S}$

$S_2 = k_B \ln \frac{V_2}{V_S}$

$\Delta S = S_2 - S_1 = k_B \ln \frac{V_2}{V_S} - k_B \ln \frac{V_1}{V_S}$

$= k_B \ln V_2/V_1$

Ok so now go to problem number 11, so derive the entropy change Delta S as R L n V 2 by V 1 from S – L n W. Now in order to do that derivation let us imagine that in a volume V 1 or V, a particle is occupying only V S volume, so each particle occupies V S volume. So that means the number of possible W's that the particle can have if V by V S, so therefore when the particle was in V 1 the entropy will be K B L n V 1 by V S. And then when the particle will occupy V 2 then it will be K B L n V 2 by V s so therefore for Delta S it is S 2 - S 1 which is K B L n V 2 by V S - K B L n V 1 by V S equal to K B L n V 2 by V 1.

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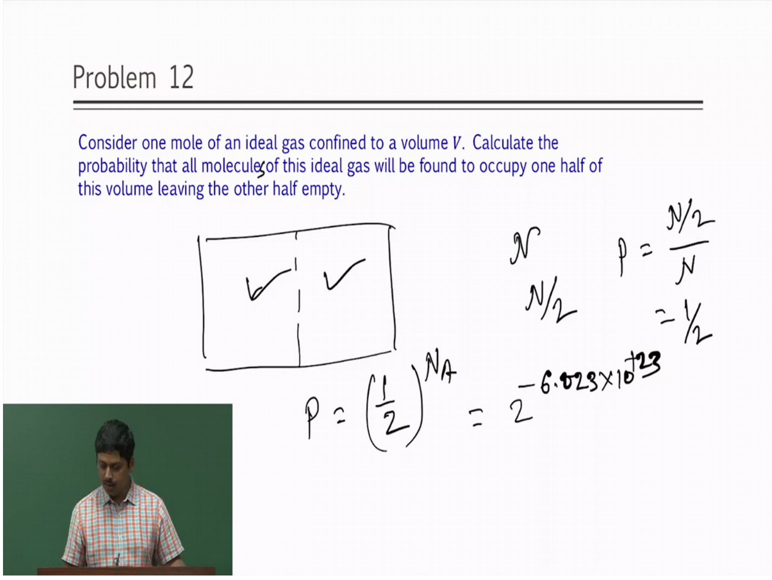

Problem 12

Consider one mole of an ideal gas confined to a volume V. Calculate the probability that all molecules of this ideal gas will be found to occupy one half of this volume leaving the other half empty.

N

$N/2$

$p = \frac{N/2}{N}$

$= 1/2$

$P = \left(\frac{1}{2}\right)^{N_A} = 2^{-6.023\times10^{23}}$

Now let us go to the next problem, problem number 12. Consider one mole of an ideal gas confined to a volume V, calculate the probability that all molecules of this ideal gas will be found to occupy one half of the volume leaving the other half empty. Now the thing is that the particle can be anywhere in the box right, and if I make the box into small small small small parts, then out of that house of the objects whatever I can break it up let us say I break this volume into N number of possible places then only half that means only in N by 2 the particle can be there, in other half it will not be there. So when you calculate the probability of that, it is nothing but N by 2 by N or half, so for every particle whether it will be on this half or that half is given by a probability half.

So now when you talk about that, when you talk about probability of 1 particle occupying one side it will be half and then the probability that all the particles of one mole gas all particles will occupy one half will be half to the power Avogadro number. And it will be an extremely small number because that will means that it will be 2 to the power - 6.023 into 10 to the power 23, it is extremely small number. So it is interoperable for one mole of gas to occupy just one half of the box + 23 correct ok so that is the thing.

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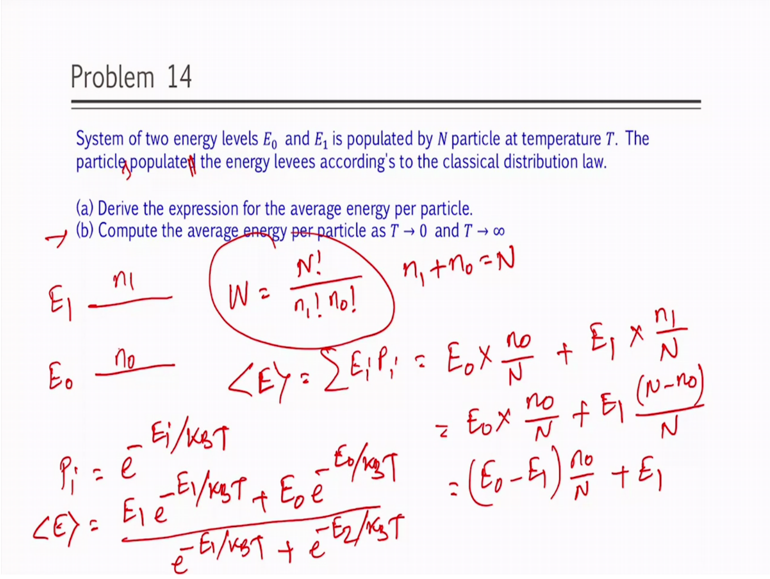

Problem 14

System of two energy levels E_0 and E_1 is populated by N particle at temperature T. The particle populated the energy levees according's to the classical distribution law.

(a) Derive the expression for the average energy per particle.
(b) Compute the average energy per particle as $T \to 0$ and $T \to \infty$

E_1 n_1

E_0 n_0

$$\boxed{W = \frac{N!}{n_1!\,n_0!}} \qquad n_1 + n_0 = N$$

$$\langle E \rangle = \sum E_i P_i = E_0 \times \frac{n_0}{N} + E_1 \times \frac{n_1}{N}$$

$$= E_0 \times \frac{n_0}{N} + E_1 \frac{(N-n_0)}{N}$$

$$= (E_0 - E_1)\frac{n_0}{N} + E_1$$

$$P_i = e^{-E_i/k_BT}$$

$$\langle E \rangle = \frac{E_1 e^{-E_1/k_BT} + E_0 e^{-E_0/k_BT}}{e^{-E_1/k_BT} + e^{-E_2/k_BT}}$$

So question number 14, a system of 2 energy level E0 and E1 is populated by N particles at temperature T, the particle populated the energy levels according to particle populate particles populate energy levels according to the classical distribution law, derive the expression for the average energy per particle ok and compute the average energy per particle as T tends to 0 and t tends to infinity. So now it is simple two level energy problem, so it is E 0 and E 1 and there are N particles altogether, I can have let us say n 1 particles here and n 1 particle or n 0 particle here and n 1 particle there that is better according to classical distribution law. So classical distribution law says that total N particle N factorial by N 1 factorial and N 0 factorial where our N 1 + N 0 is equal to N.

So derive the experience for the average energy of the particle so you know that average energy of the particle is E i P i which means I have 2 states only so I will not put a sum now, I have E 0 and P i which is the probability of being in the 0 is n 0 by N and E 1, the probability is n 1 by N ok. And I can yeah so that right now I can simplify it a little bit, E 0, n 0 by N + E 1 N – n 0 by N, so now I get E 0 – E 1 n 0 by N + E 1, this is the average energy that I get. Compute the average energy per particle as T tends to 0 and T tends to infinity. So now in order to compute the 2nd one I will have to assume that Boltzmann distribution is taking place even for such simple models, and we know that it follows Boltzmann distribution once it follows this statistic.

So therefore we can write P i as E to the power – E i by K B T, so if I use that P i value, the average energy again will be E 1 e to the power - E 1 by K B T + E 0 e to the power - E 0 by K B T divided by e to the power - E 1 by K B T + e to the power – E 2 by K B T, so you see I can write the average in both the ways they are basically the same thing.

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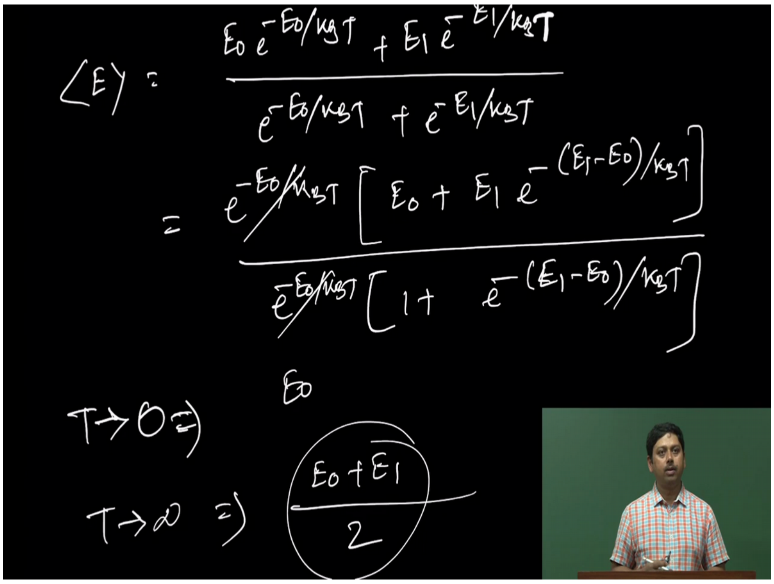

$$\langle E \rangle = \frac{E_0 e^{-E_0/k_BT} + E_1 e^{-E_1/k_BT}}{e^{-E_0/k_BT} + e^{-E_1/k_BT}}$$

$$= \frac{\cancel{e^{-E_0/k_BT}}\left[E_0 + E_1 e^{-(E_1-E_0)/k_BT}\right]}{\cancel{e^{-E_0/k_BT}}\left[1 + e^{-(E_1-E_0)/k_BT}\right]}$$

$$T \to 0 \Rightarrow \quad E_0$$

$$T \to \infty \Rightarrow \quad \boxed{\frac{E_0 + E_1}{2}}$$

Now so now let us simplify this process, average energy is E 0 e to the power - E0 by K B T + E 1 E e to the power - E 1 by K B T by e to the power - E 0 by K B T + e to the power - E 1 by K B T. Once I have that I can take and let us say e to the power – E 0 by K B T common and I get E 0 + E 1 into e to the power – E 1 – E 0 by K B T divided by 1 + e to the power – E 1 – E 0 by K B T, this cancels.

Now in the formula if I put a T equal to 0 what I am going to get? T = 0 means that this quantity will be infinity, this becomes 0 so I will get E 0 just E 0. And if T goes to infinity what I am going to get, then T infinity will become this will become 0 so I will get E 0 by E 1 in the numerator, and in the denominator I will get if T becomes infinity that becomes 0 1 + 1 = 2, so I will get the average energy. So at T equal to infinity I get average energy of the particle, whereas at T equal to 0 it will collapse into the ground level and I will get only the energy of the E 0 ok.

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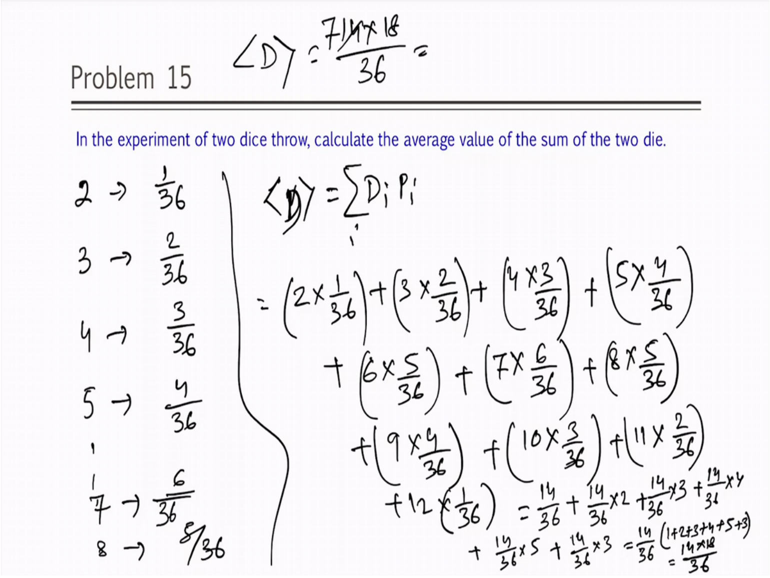

Problem 15 $\langle D \rangle = \frac{7\cancel{14}\times 18}{36} =$

In the experiment of two dice throw, calculate the average value of the sum of the two die.

$2 \rightarrow \frac{1}{36}$

$3 \rightarrow \frac{2}{36}$

$4 \rightarrow \frac{3}{36}$

$5 \rightarrow \frac{4}{36}$

$7 \rightarrow \frac{6}{36}$

$8 \rightarrow 8/36$

$$\langle D \rangle = \sum_i D_i P_i$$

$$= \left(2\times\frac{1}{36}\right)+\left(3\times\frac{2}{36}\right)+\left(4\times\frac{3}{36}\right)+\left(5\times\frac{4}{36}\right)+\left(6\times\frac{5}{36}\right)+\left(7\times\frac{6}{36}\right)+\left(8\times\frac{5}{36}\right)+\left(9\times\frac{4}{36}\right)+\left(10\times\frac{3}{36}\right)+\left(11\times\frac{2}{36}\right)+12\times\left(\frac{1}{36}\right)$$

$$= \frac{14}{36}+\frac{14}{36}\times 2+\frac{14}{36}\times 3+\frac{14}{36}\times 4+\frac{14}{36}\times 5+\frac{14}{36}\times 3 = \frac{14}{36}(1+2+3+4+5+3) = \frac{14\times 18}{36}$$

So now same way we calculate the average energy, you can calculate many other things for example, this particular problem tells us to calculate the average value of showing two dice. So now you know when you throw two dice, you can get either 2 or 3 or 4 or 5 or 6 or 7 or 8 or 9 or 10 or 11 or 12, but each of them come with different probabilities. So you know the probability of observing 2 in a sum of a dice is 1 by 36, probability of observing 3 is, 3 can be obtained from 2 + 1 or 1 + 2 so it is 2 by 36 and observing 4 will become again, I can get either 2 or 2, 1 or 3 or 3 or 1, so 3 by 36. Observing 5 will be 4 by 36 and things like that, observing 7 is 6 by 36 and it will decrease after that, 8 will be 5 by 36 again and things like that.

So what is the average value that we are going to observe, is that again the average value that we are going to observe, average value I will write as let us say dice throw so I will write average value as let us say D, it will be D i P i sum, which mean D i is the value so 2 come with 1 by 36 compatibility, 3 will come with 2 by 36 probability, 4 will come by 3 by 36 probability, 5 will come by 4 by 36 probability, 6 will come by 5 by 36 probability, 7 will come by 6 by 36 probability, 8 will come by 5 by 36, 9 will come by 4 by 36, 10 will come as 3 by 36, 11 will come as 2 by 36 and 12 will come as 1 by 36.

We can simplify that because by the symmetry of the problem is that I can get 2 and 12 by 1 by 36, so 14 by 36, I can get 3 and 11 as to why 36 so it is 14 by 36 into 2, I can get 10 and 4 against 14 by 36 with 3, I can get that means 14 by 36 with 4 which is 5 and 9 + I have 4 and 5 and 9, and then I have 6 and 8 again 14 by 36 but now 5 + I have just 7 into 6 by 36 that will be a separate thing to do, I do not have it twice because this is just one number so I can of course write as 14 by 36 into 3 which is 7 into 6, so I am writing 7 into 2 into 3 so 14 by 36 into 3. So now you see by the symmetry of the problem now I can take 14 by 36 common that leaves me with a sum of 1 + 2 + 3 + 4 + 5 so sum of 5 and + addition will be 3.

So how much that is you know, some of 5 is 5 into 6 by 2 so which is 15 and + 3 is 18 so it is nothing but 14 into 18 by 36 so this answer is average D is 14 into 18 by 36, let us simplify it a little bit so the answer is 7 basically as you can see so the expectation value of throwing 2 dice is 7.