Fundamentals of Statistical Thermodynamics

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Lecture – 24

Further discussion on entropy of a monatomic gas – II

In this lecture, we will continue our discussion on entropy of a monatomic gas by using Secur-Tetrode equation under different constraints. We discussed in the previous lecture that when the conditions are isothermal and then you allow the gas to expand, then we can use this formula delta S is equal to n r log V_F over V_i, constant temperature conditions. Substitute the values, you have n equal to 1 r and log 100 by 10 and what the result comes to result comes to 19.1 joules per Kelvin per mole, positive result. That means you increase the temperature, the entropy increases. Mathematically if you see V_F over V_i is more than 1, so logarithm of more than 1 is a positive quantity, so therefore delta S should be positive.

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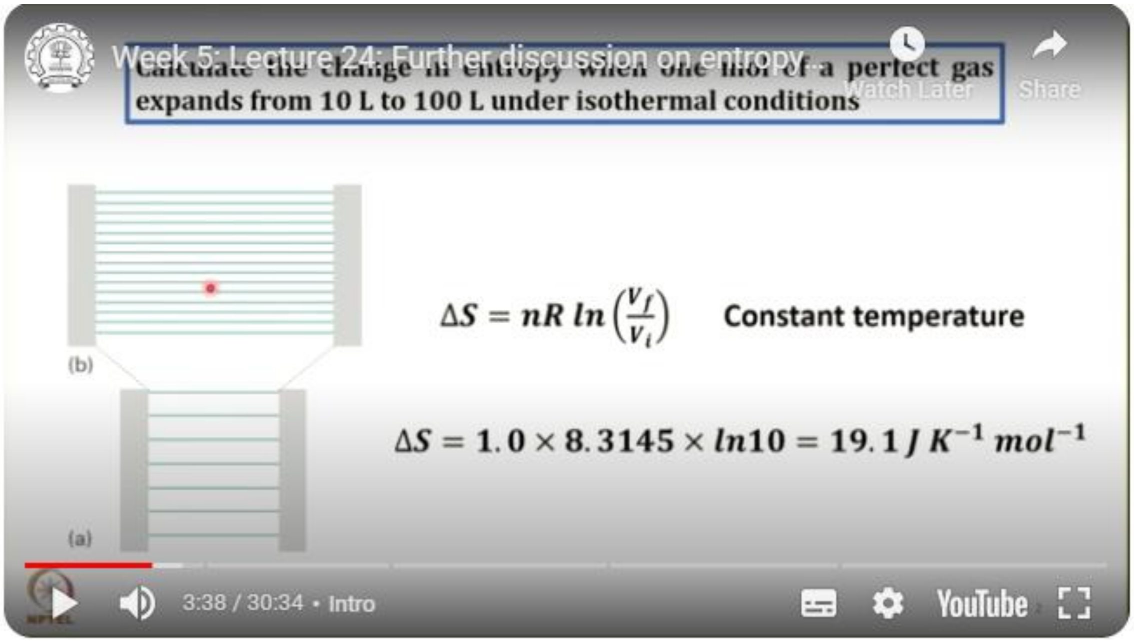

Calculate the change in entropy when one mol of a perfect gas expands from 10 L to 100 L under isothermal conditions

$$\Delta S = nR\ ln\left(\frac{V_f}{V_i}\right)$$ **Constant temperature**

$$\Delta S = 1.0 \times 8.3145 \times ln10 = 19.1\ J\ K^{-1}\ mol^{-1}$$

And we have interpreted it in terms of increase in population of thermally accessible states when the system undergoes expansion. Remember that we connected that to the length of the container because when you compare this Vi, this is state Vi, this is state V_f because L increases, therefore there is a decrease in the energy gaps. Here compared to this, these are having much lower energy gaps. So therefore, under isothermal conditions, the entropy of one mole of a perfect gas will increase by 19.1 joules per Kelvin per mole. Another thing which is worth noticing in this, although we say under isothermal conditions, but we have not mentioned, we have not given any temperature. That means if we carry out this expansion for the gas, let us say which is initially at 25 °C or 35 °C or at 45 °C and then we allow the gas to expand by 10 times, will the result be different? If you look into the formula, in this formula delta S equal to nR log V_F over Vi, whether you derive it by statistical means or you derive it by the concepts of chemical thermodynamics, Classical thermodynamics, you get the same result and in this result, nowhere temperature is there. So therefore, it does not matter at what temperature you begin with, this explanation will hold true that at a given temperature, if you increase the volume, there is going to be the change in the dimensions of the container, there is going to be an increase and since that comes in the denominator, the spacing between energy levels will increase and therefore, there will be more thermally accessible states. So even if it starts from 25 °C or if it starts from 35 °C or 45 °C , that relative change is going to be similar, therefore delta S is going to be same.

This is under constant temperature conditions. Now let us now discuss under constant pressure conditions. I was mentioning that you can use Sackur–Tetrode in different ways under constant temperature conditions and the constant pressure conditions, under constant volume conditions depending upon the requirement. So here the same question, similar question, calculate the change in entropy when 1 mole of a perfect gas expands from 10 liter to 100 liter under constant pressure conditions.

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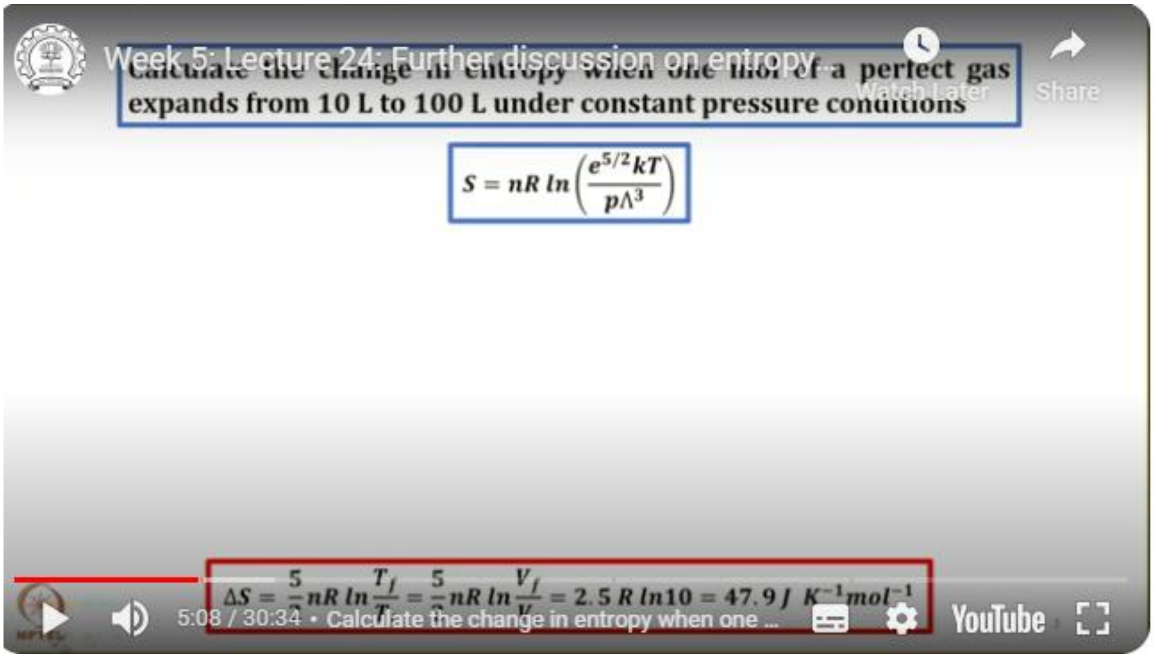

Calculate the change in entropy when one mol of a perfect gas expands from 10 L to 100 L under constant pressure conditions

$$S = nR\ln\left(\frac{e^{5/2}kT}{p\Lambda^3}\right)$$

$$\Delta S = \frac{5}{2}nR\ln\frac{T_f}{T_i} = \frac{5}{2}nR\ln\frac{V_f}{V_i} = 2.5\,R\ln 10 = 47.9\ J\ K^{-1}mol^{-1}$$

This is our Sackur–Tetrode which has pressure term in it. It says constant pressure condition. It does not specify temperature that means temperature can vary. How do we incorporate that variation of temperature? Let us see. We have in this thermal wavelength which is equal to betahsquare over 2 π m raised to the power 1 by 2 which is equal tohover 2 π m kT whole square. Therefore, when I substitute this h into entropy expression, what do I get? N R I get log exponential 5 by 2 kT upon B and now I need to put h cube. This is going to be h cube and here what I have is 2 π m kT raised to the power 3 by 2 and then I have this overall expression. Carefully examine what I have done. I have substituted for h. H is h over square root 2 π m kT. So e raised to the power 5 by 2 kT remains, pressure remains and instead of h cube I have written h cube divided by 2 π m kT raised to the power 3 by 2.

This is constant, exponential 5 by 2. Boltzmann is constant, mass is constant, pressure is constant, you know constant pressure conditions, Planck's constant is a constant. So therefore if I combine all these constants I can write this equal to N R log a.

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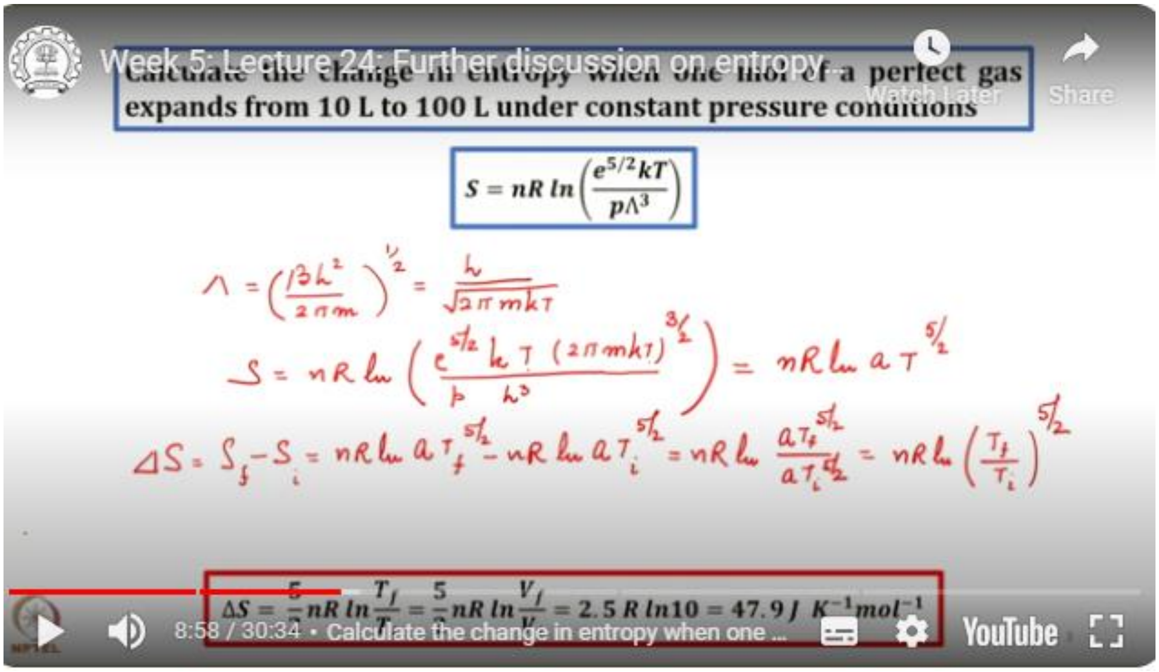

Calculate the change in entropy when one mol of a perfect gas expands from 10 L to 100 L under constant pressure conditions

$$S = nR\,ln\left(\frac{e^{5/2}kT}{p\Lambda^3}\right)$$

$$\Lambda = \left(\frac{\beta h^2}{2\pi m}\right)^{1/2} = \frac{h}{\sqrt{2\pi mkT}}$$

$$S = nR\ln\left(\frac{e^{5/2}kT\,(2\pi mkT)^{3/2}}{p\,h^3}\right) = nR\ln aT^{5/2}$$

$$\Delta S = S_f - S_i = nR\ln aT_f^{5/2} - nR\ln aT_i^{5/2} = nR\ln\frac{aT_f^{5/2}}{aT_i^{5/2}} = nR\ln\left(\frac{T_f}{T_i}\right)^{5/2}$$

$$\Delta S = \frac{5}{2}nR\,ln\frac{T_f}{T_i} = \frac{5}{2}nR\,ln\frac{V_f}{V_i} = 2.5\,R\,ln10 = 47.9\,J\ K^{-1}mol^{-1}$$

A it combines all the constant and temperature, one temperature term is this and other temperature term is this that means 1 plus 3 by 2 is equal to 5 by 2. Therefore, delta S which is equal to S final minus S initial is equal to nR log A T final 5 by 2 minus N R log A T initial raised to the power 5 by 2 and this is equal to nR log A T_f 5 by 2 over A T_i 5 by 2 which is equal to N R log T f by T i raised to the power 5 by 2 which is essentially this expression. Delta S is 5 by 2 nR log T final over T initial. So now since P_f V_f is N R T_f P_i V_i P_i V_i is nRT i and if pressure is constant then T f by T i is equal to V f by V i. So I replace T f by T i because pressure is constant by V_f by V_i. So 2.5 R log 10 which is 47.9 joules per kelvin per mole. Here you are not maintaining the temperature but you are maintaining the pressure. If you are maintaining the pressure here and if you are let us say you know your volume can change and your temperature can change and if you change the volume from 10 liter to 100 liter here you see the delta S is slightly more than what you got under constant volume conditions. Let us see do we get the same result by using classical thermodynamics. Again we go to the same expression d S is equal to d cube reversible by T which is equal to dhat constant pressure divided by temperature because we will derive expression for constant pressure conditions dhat constant pressure. So if the pressure is held constant then d Q is equal to dh and this is equal to C_p d T dh is C p d T and we have T and I can write this as n C_p m d T by T. Why I have converted into molar heat capacity. So we have d S is equal to n C p m d T by T. Now let us carry out integration on both sides when the temperature changes from T_i to T_f that means S at T i to S at T f from T i to T f. What I have is delta S is equal to n C p m log T f over T_i.

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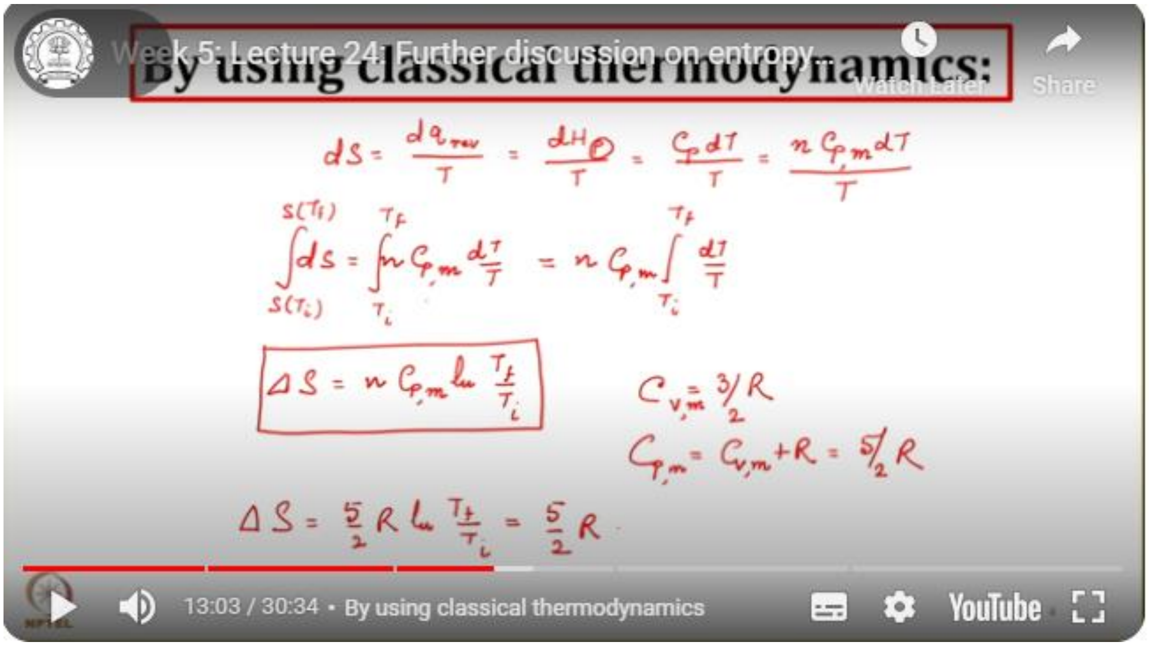

By using classical thermodynamics:

$$dS = \frac{dq_{rev}}{T} = \frac{dH_p}{T} = \frac{C_p\,dT}{T} = \frac{n C_{p,m}\,dT}{T}$$

$$\int_{S(T_i)}^{S(T_f)} dS = \int_{T_i}^{T_f} n C_{p,m} \frac{dT}{T} = n C_{p,m} \int_{T_i}^{T_f} \frac{dT}{T}$$

$$\boxed{\Delta S = n C_{p,m} \ln \frac{T_f}{T_i}}$$

$$C_{v,m} = 3/2\,R$$

$$C_{p,m} = C_{v,m} + R = 5/2\,R$$

$$\Delta S = \frac{5}{2} R \ln \frac{T_f}{T_i} = \frac{5}{2} R$$

This I can complete here n C p m T_i to T_f d T by T d T by T integration is log T. So now C_p m C_v is equal to 3 by 2 R molar 3 by 2 R. Obviously C_p m is going to be C_v m plus R C_p m minus C_v m is equal to R. So this is going to be 5 by 2 R. So delta S is equal to if we want molar change n is equal to 1 then 5 by 2 R log T_f over T_i which is equal to 5 by 2 R log V_f over V_i by the same arguments and we have 5 by 2 R V_f over V_i and the result that you have is the same that is 5 by 2 n R log T f over T i or 5 by 2 n R log V f over V i which is 47.9 joules per kelvin per mole. We get the same expression 5 by 2 R for n is equal to 1 of course, I can write here molar 5 by 2 R log V_f over V_i which is same as 5 by 2 R log V f over V i for n equal to 1. So 47.9 whether we use the classical thermodynamic results or we use the statistical thermodynamic results we see that we are able to get the same expression we are able to get the same result. Let us move forward to discuss further applications.

Let us discuss this question. The question is consider a system A consisting of subsystems A 1 and A 2 for which w 1 is 1 into 10 raise to the power 20, w 2 is 2 into 10 raise to the power 20. The question that is asked is what is the number of configurations available to the combined system also compute the entropies S S_1 and S_2 what is the significance of this results. So, what is given to us is a system A which consists of two subsystems A_1 and A_2 and there are there are corresponding weights we can write w for A, w_1 for A_1, w_2 for A_2. Similarly, S for A combined system A_1 and A_2 that is A and S_1 for A_1 and S_2 for A_2.

Since there are two subsystems A_1 and A_2, 1 and 2 if w_1 is the number of configurations in system 1 and w_2 in system 2 then the number of configurations of the combined system is w_1 into w_2 simple mathematics. So, w 1 is 10 raise to the power 20 that is given to us, w_2

is 2 into 10 raise to the power 20. So, the weight or the number of configurations of the combined system is 2 into 10 raising to the power 40 right. So, we are interested now we are you know we have been asked to compute the entropies S. The relationship between S and w is simple S is equal to K log w we discussed many times same definition will apply to S 1 and S 2 in with the subscripts 1 and 2. Since S is equal to K log w and w is 2 into 10 raise to the power 40 you substitute there K into log 2 into 10 raise to the power 40. Well this is simple mathematics you can do yourself. The value of this bracketed term is 92.8 and you put the expression or the value for Boltzmann constant the answer comes out to be 1.282 into 10 raise to the power minus 21 joules kelvin inverse. This is for the combined system. Now, let us do for S 1 same approach K log w_1 w_1 is 1 into 10 raise to the power 20. So, you put 10 raise to the power 20 and then you solve it by solving the answer comes out to 0.637 into 10 raise to the power minus 21. Do the same for system subsystem 2 for that use the weight which is given for the subsystem 2 into 10 raise to the power 20 and then you calculate this eventually the results comes to 0.645 into 10 raise to the power minus 21 joules per kelvin. What is interesting in this result? What is the significance of the result? For the combined system the entropy is 1.282 into 10 raise to the power minus 21 joules per kelvin. If you want to convert this into joules per kelvin per mole multiply by Avogadro constant. For system 1 subsystem 1 the value has come out to be 0.637 into 10 raise to the power minus 21. For subsystem 2 the value has come out to be 0.645 into 10 raise to the power minus 21 joules per kelvin. Obviously, summation of these two when you add these two you get this value. So, that is why this comment has been made that these results are significant in that they show that the statistical mechanical entropy is an additive property.

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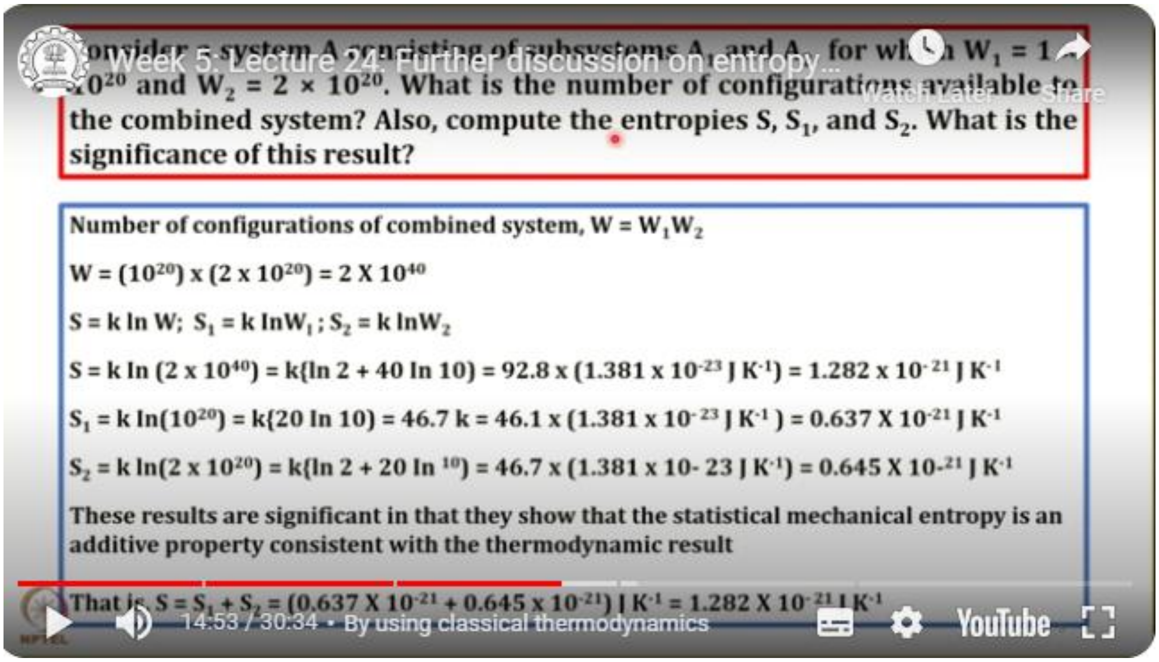

onsider a system A consisting of subsystems A_1 and A_2 for wh h $W_1 = 1$ 0^{20} and $W_2 = 2 \times 10^{20}$. What is the number of configurations available to the combined system? Also, compute the entropies S, S_1, and S_2. What is the significance of this result?

Number of configurations of combined system, $W = W_1W_2$

$W = (10^{20}) \times (2 \times 10^{20}) = 2 \times 10^{40}$

$S = k \ln W$; $S_1 = k \ln W_1$; $S_2 = k \ln W_2$

$S = k \ln (2 \times 10^{40}) = k\{\ln 2 + 40 \ln 10) = 92.8 \times (1.381 \times 10^{-23}\ J\ K^{-1}) = 1.282 \times 10^{-21}\ J\ K^{-1}$

$S_1 = k \ln(10^{20}) = k\{20 \ln 10) = 46.7\ k = 46.1 \times (1.381 \times 10^{-23}\ J\ K^{-1}) = 0.637 \times 10^{-21}\ J\ K^{-1}$

$S_2 = k \ln(2 \times 10^{20}) = k\{\ln 2 + 20 \ln {}^{10}) = 46.7 \times (1.381 \times 10- 23\ J\ K^{-1}) = 0.645 \times 10\text{-}^{21}\ J\ K^{-1}$

These results are significant in that they show that the statistical mechanical entropy is an additive property consistent with the thermodynamic result

That is, $S = S_1 + S_2 = (0.637 \times 10^{-21} + 0.645 \times 10^{-21})\ J\ K^{-1} = 1.282 \times 10^{-21}\ J\ K^{-1}$

When you say some property is additive that means the overall overall entropy let us say in this case if we talk in terms of entropy that should be equal to the entropy of subsystem 1 and entropy of subsystem 2 that is what is the meaning of additive property. So, I read the comment again that these results are significant in that they show that statistical mechanical entropy is an additive property that is overall entropy is the sum of the individual entropies of the subsystem. This number plus this number comes out to 1.282 into 10 raise to the power minus 21 joules per kelvin. So, therefore, the additive nature of the results applies over here.

Let us move forward and look at this question. The question is by what factor of the system does the number of available configurations increase when 100 joule of energy is added to a system containing 1 mole of particles at constant volume? If you read the statement again as I earlier mentioned that first you try to understand the given statement very carefully. The statement is by what factor does the number of available configurations increase? That means they are talking about how much the weight of a configuration will increase when 100 joule of energy is added 100 joule of energy is added. So, which energy we are talking about here? If you work on the system either by temperature by heat or you know by mechanical work basically you are changing the internal energy of a system.

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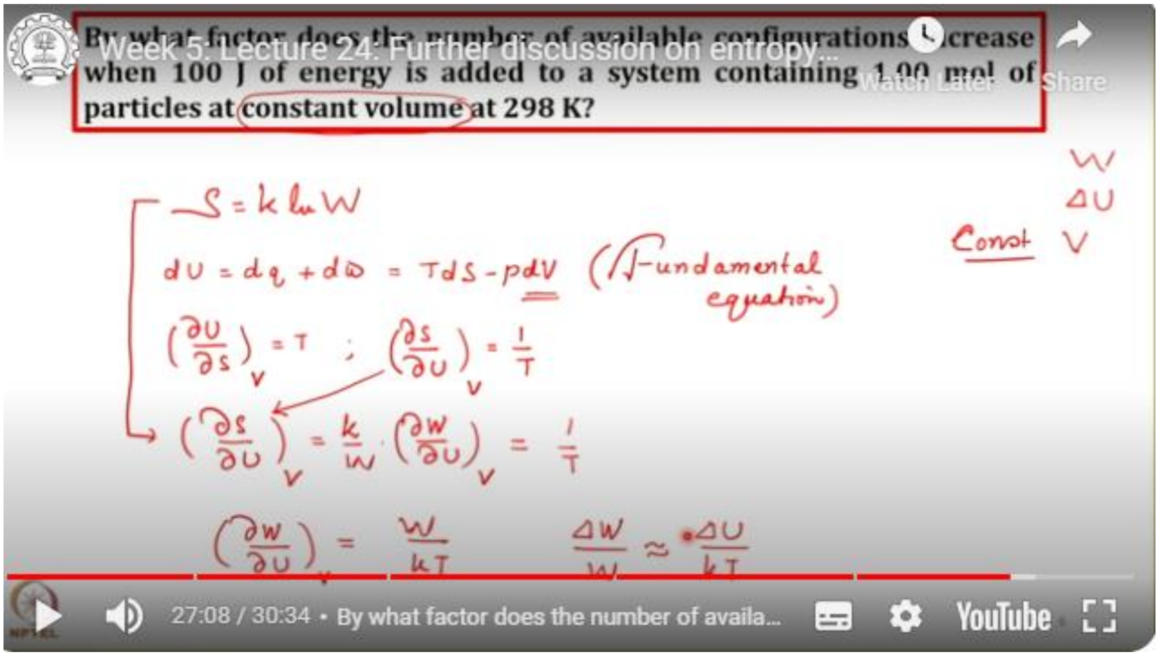

By what factor does the number of available configurations increase when 100 J of energy is added to a system containing 1.00 mol of particles at constant volume at 298 K?

$S = k \ln W$

$dU = dq + dw = TdS - pdV$ (Fundamental equation)

$\left(\frac{\partial U}{\partial S}\right)_V = T \; ; \; \left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}$

$\left(\frac{\partial S}{\partial U}\right)_V = \frac{k}{W} \cdot \left(\frac{\partial W}{\partial U}\right)_V = \frac{1}{T}$

$\left(\frac{\partial W}{\partial U}\right)_V = \frac{W}{kT} \qquad \frac{\Delta W}{W} \approx \frac{\Delta U}{kT}$

W

ΔU

Const V

Delta U is equal to q plus w. So, that means here they are talking about available configurations, they are talking about w and they are talking about delta u and we need to understand that we need to find out that by what factor this w changes when you pump in 100 joules of energy into the system at a given temperature under constant volume conditions. Remember constant volume condition this is another I can write here also constant volume may be this will help me in solving the question easily. So, now we need to develop an equation at constant volume which will allow a connection between w and delta u. So, start thinking which thermodynamic quantity can be easily connected with w and also can be easily connected with change in internal energy. The thermodynamic quantity that comes to mind obviously is the change is entropy because one equation that immediately comes to mind s is equal to k log w. It is allowing you to connect entropy with the configuration weight of a configuration. Now, I need to see if can I connect entropy with internal energy or changes in internal energy under constant volume conditions. Yes, write first law d u is equal to d q plus d w or I can write this as T d s minus p d v fundamental equation. This we remember in chemical thermodynamics or classical thermodynamics we call this as fundamental equation. Now, we can now invoke this constant volume condition then can I write del u del s at constant volume is equal to T or del s at constant volume is equal to T.So, this is del u at constant volume is 1 by T. Now, according to the given conditions I have a constant volume constraint I have brought in and I have brought in energy change and if I can now bring in entropy change then I have a way to develop an equation which will permit me to solve this question. So, I need to bring delta s somewhere d s. So, let us now work on this equation and let us write del s I am interested by del U. This is what I am interested in at constant volume is what it will be k by w and del w is equal by del u at constant volume. This is equal to I already know what this is this is 1 by T. Now, I have del w del u at constant volume is equal to T. Now, this is what I am interested in del w by k T. I rearrange this del w by del u del w del u at constant volume is w over k T. This equation allows me to write like this delta w by w. I can write approximately I can rewrite this as delta u by k T. This is what actually I am looking for. Your question says by what factor does the number of available configurations increase? This will allow me to get that factor. When 100 joules of energy is added to the system I know delta u is 100 containing 1 mole of particles at constant volume. This equation I have derived under constant volume condition at 298 k. So, I know 298 k. So, the equation developed is delta w by w is approximately same as delta u by k T and once you substitute the numbers you get delta u is given to you 100 joules. I converted into kilojoules k is Boltzmann constant temperature is 298 and you have 2.4 into 10 raise to the power 25. This is what I was looking for. So, the way to approach solving such equations, such questions is you look into the question and try to gather what information is given. They want to talk about available configurations that means I need to write down. I must develop an equation develop connect w with something which is given to me. Increase in energy that means I am talking about delta u. Constant volume conditions constant volume conditions these 3 information are given and finally, temperature is given. Now question is next look for w which is connected to s connected to s is equal to k log w that will help me. Delta U_i can connect with entropy how because d u is equal to T d s minus p d v and I can now use the constant volume conditions to convert into something else and eventually by applying all the given information we are able to come up with an expression which allows you to calculate the number of available configurations how they increase when a certain amount of energy is added to the system. So, therefore, whenever you start solving a question first try to understand the questions very very carefully note down what the information is given and then see that the given information can I connect with certain thermodynamic quantity which will allow me to solve these questions in an easy manner. I hope that you will be able to use the relationship between entropy and volume pressure or temperature which was described in second tetra equation in solving many more problems. Thank you very much. Thank you. .