Fundamentals of Statistical Thermodynamics

Prof. Nand Kishore

Department of Chemistry

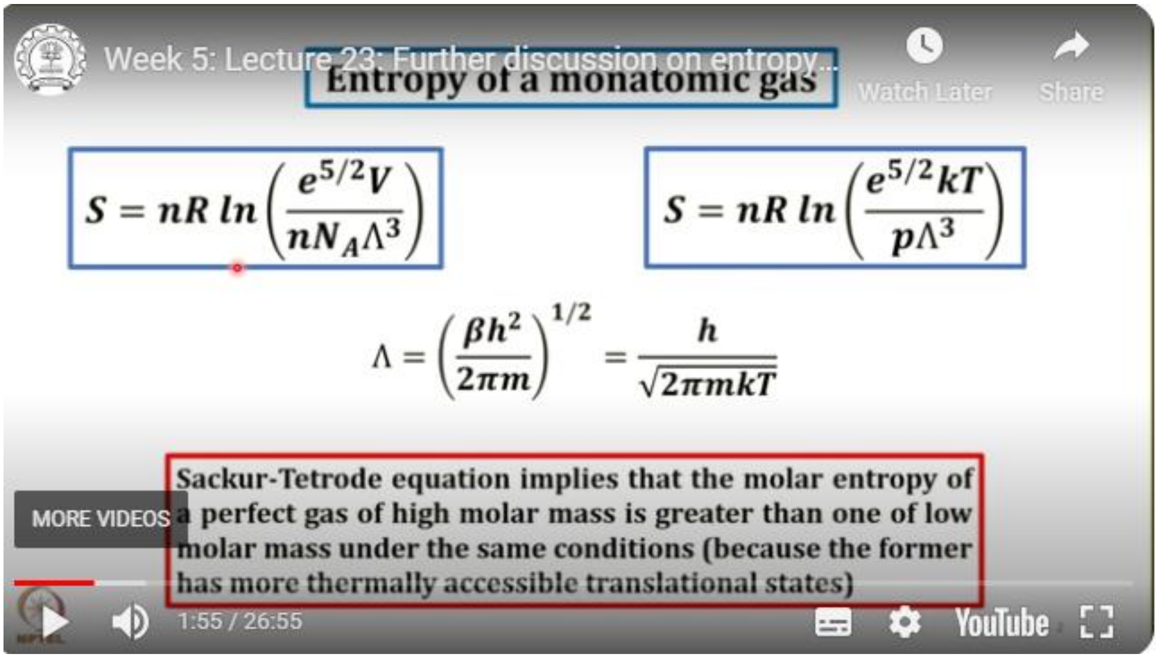
Indian Institute of Technology, Bombay

Lecture – 23

Further discussion on entropy of a monatomic gas - I

Welcome back. By now we have connected entropy with canonical partition function and also we have discussed how to recover molecular partition function from canonical partition function. That means, now we have means of connecting entropy with molecular partition function when we consider concept of ensembles. That means, after having described entropy in terms of canonical partition function, then we can further decide that depending upon whether the molecules are distinguishable or indistinguishable, how this equation can be further modified. So today, we will further discuss more on entropy, but let us take first an easy example that of a monatomic gas. So when we say about monatomic gas, it is understood that we are talking about perfect gases, we are talking about ideal situations. So therefore, in this discussion whenever required, we will use ideal gas equation. So in the previous lecture, we have talked about the Sackur–Tetrode equation which is basically an expression for entropy of a monatomic gas and this Sackur–Tetrode equation which connects entropy with volume and the thermal wavelength or entropy with pressure, thermal wavelength, temperature of course, temperature is hidden in thermal wavelength.

See Slide time: 1:55



Entropy of a monatomic gas

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

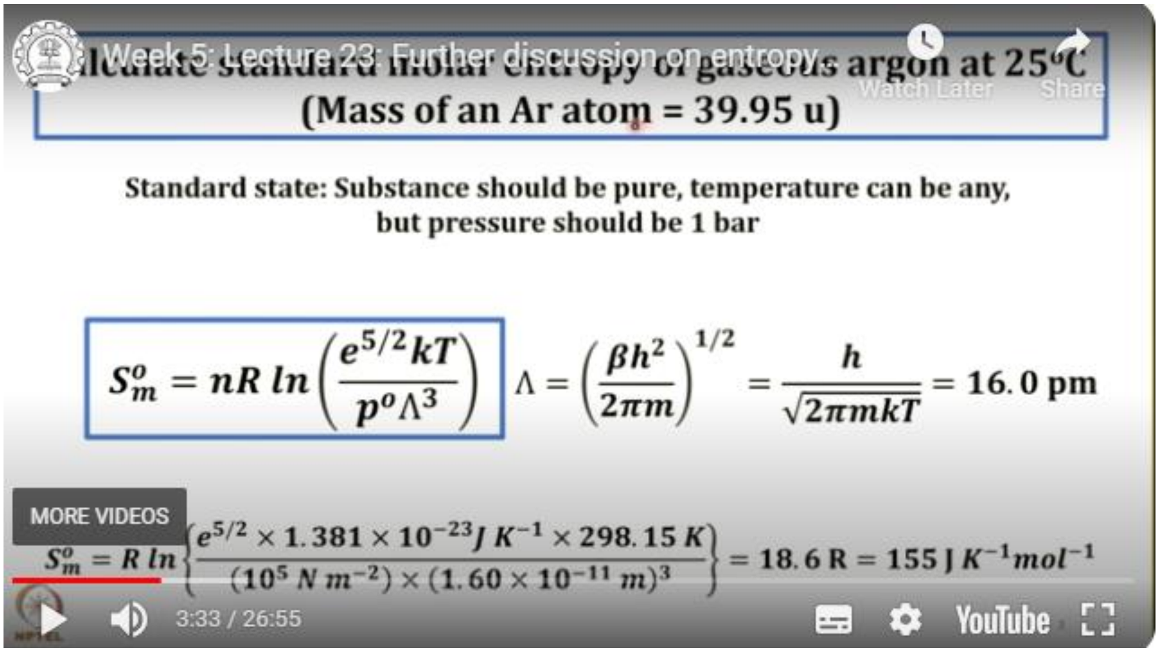
$$S = nR\,ln\left(\frac{e^{5/2}kT}{p\Lambda^3}\right)$$

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

Sackur-Tetrode equation implies that the molar entropy of a perfect gas of high molar mass is greater than one of low molar mass under the same conditions (because the former has more thermally accessible translational states)

These two forms of Sackur–Tetrode equation permit us to evaluate entropy under constant volume conditions, under constant pressure conditions or under constant temperature conditions. So depending upon the situation, we can use this equation and we also last time discussed that if the molar mass is higher, then thermal wavelength is lower. If thermal wavelength is lower, then entropy is higher and that is what is captured in this comment that Sackur–Tetrode equation implies that the molar entropy of a perfect gas of high molar mass is greater than one of the low molar mass. That means if low molar mass, λ will be high, if λ is high, then entropy will be less. Let us further now discuss about entropy. Let us start now discussing the applications of the formulae that we have so far derived. The first example that we will take is calculate standard molar entropy of a gaseous argon at 25 °C and the molar mass of argon is given over here, argon atom.

See Slide time: 3:33



lculate standard molar entropy of gaseous argon at 25°C
(Mass of an Ar atom = 39.95 u)

Standard state: Substance should be pure, temperature can be any,
but pressure should be 1 bar

$$\boxed{S_m^o = nR\,ln\left(\frac{e^{5/2}kT}{p^o\Lambda^3}\right)} \quad \Lambda = \left(\frac{\beta h^2}{2\pi m}\right)^{1/2} = \frac{h}{\sqrt{2\pi mkT}} = 16.0\ \text{pm}$$

$$S_m^o = R\,ln\left\{\frac{e^{5/2} \times 1.381 \times 10^{-23} J\,K^{-1} \times 298.15\,K}{(10^5\,N\,m^{-2}) \times (1.60 \times 10^{-11}\,m)^3}\right\} = 18.6\,\text{R} = 155\,\text{J}\,K^{-1}mol^{-1}$$

Now the things to notice in the given statement, you know, before we start attempting solving a problem, it is first of all wise to look at the problem statement very carefully and see what all information is given. What do they want? The question is calculate standard molar entropy. Standard that means they want us to calculate the entropy under standard state conditions. So standard state condition, what is a standard state condition? Standard state means substance should be pure, temperature can be any, but pressure should be one bar. Keep this definition of standard state in mind.

Pressure should be one bar, substance should be pure and temperature can be any. So therefore in the Secu-Tetrode equation, look at the symbols that are notations that I have used over here. S_m^0, m represents molar, this naught is used for standard state condition and the pressure also, we write P^0. What is the value of P^0? P^0 is one bar. That is what I was saying that when you try attempting solving a problem, first of all look at the problem statement.

Try to understand what all the information is given. Since they want us to calculate standard molar entropy, so automatically we will set the pressure equal to one bar. So in this formula of molar entropy, what we have? The temperature is given 25 °C. So on absolute scale, we will write it as 298 Kelvin or to be very precise 298.15 Kelvin. P_0 is given and λ which is β h square over 2 π m whole square root over h over 2 π m k T. Essentially you need the information on temperature and you need the information on molar mass. That is given 39.95 gram per mole. Substitute here and remember I have already discussed here we are talking about one atom when you put m over here.

So therefore, what you will be using the number 39.95 convert into kilogram that means multiplied by 10 raised to the power minus 3, and then divide by Avogadro constant. So as we have discussed earlier that here you have to put mass of one particle. After substituting all the constants or other values, you will get a thermal wavelength of 16 picometer, 16 into 10 raised to the power minus 12 meter. So now you have all the information to put into the formula.

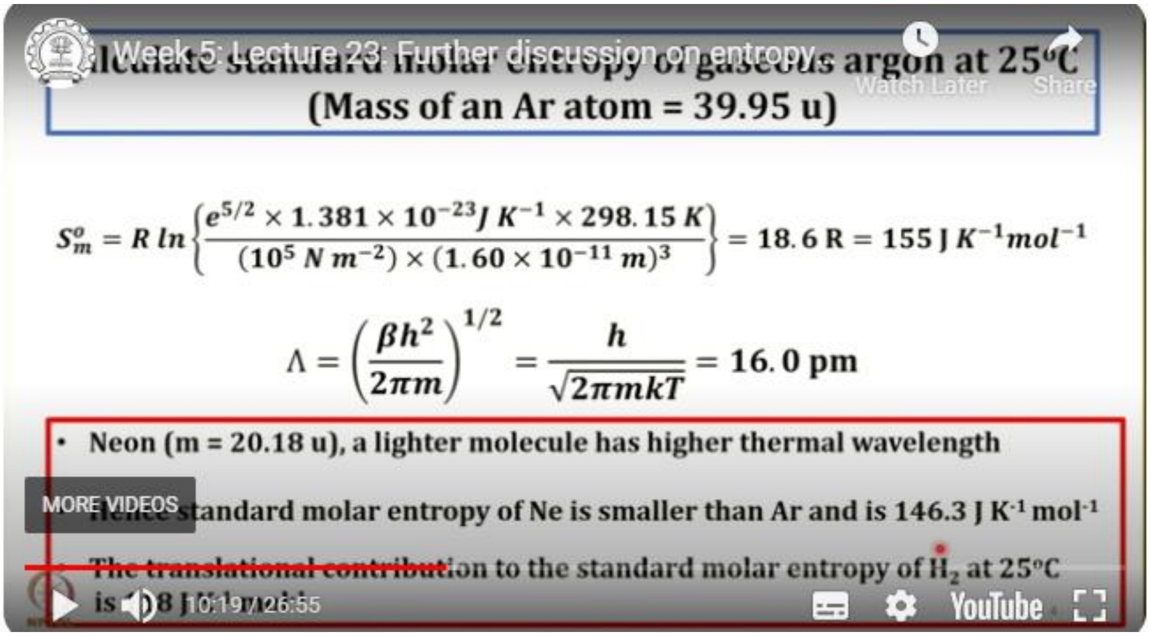
So S_m^0 is equal to R and since we are talking about molar N is equal to 1. The minimal 5 by 2 Boltzmann constant is 1.381 into 10 raised to the power minus 23 joules per Kelvin. Temperature is given 298.15 Kelvin and then pressure which is 1 bar and we have to use SI units here.

One bar is equal to 0.1 mega Pascal and then you convert that 0.1 mega Pascal into Newton per meter square, then one bar will turn out to be 10 raised to the power 5 Newton per meter square. And then we have here the thermal wavelength which is 16 πcometer which is 1 you convert into meter which is equal to 1.6 into 10 raised to the power minus 11 meter cube or 16.0 into 10 raised to the power minus 12 meter cube. After solving this we will get a molar entropy of 155 joules per Kelvin per mole. So therefore, the standard molar entropy of gaseous argon at 25 °C is 155 joules per Kelvin per mole. Thermal calculations we need to be careful about what value of P_0 should be put. We need to be careful about what value of molar mass to be put in what way that is you need to put for one particle.

All right. So we have obtained a molar entropy of 155 joules per Kelvin per mole from a thermal wavelength of 16 picometer. Let us take a look at some of the comments. Argon is 39.95 gram per mole. Neon molar mass is less 20.18. It is a lighter molecule. Lower molar mass if lower molar mass then thermal wavelength will be higher. If thermal wavelength is higher the entropy will be less. That is a reciprocal relation. So neon which has a molar mass of 20.18, it is a lighter molecule and has higher thermal wavelength. Therefore, standard molar entropy of neon will be smaller than argon and calculations suggest that it is 146.3. Argon was 155. Neon is 146.3. This is the effect of the molar mass. Let us take one more case that is standard molar entropy of hydrogen and the comment if you carefully look at the comment over here what is written in the comment. The translational contribution to the standard molar entropy translational contribution. Why I did not talk about only translational contribution in case of neon or argon because neon and argon which are atoms will have only translational degree of freedom will not have rotational and vibrational degrees of freedom. When it comes to hydrogen, it is a diatomic molecule.

The other contributions can also come in. So therefore, the translational contribution can be calculated by using Saku-Tetrode equation. All right. Here the molar mass is 2 and if it is molar mass is further less then thermal wavelength will be further higher and molar entropy will be further less and you can see now it is 118.118 joules per kelvin per mole. Argon with a molar mass of 39.95 has a molar entropy of 155.

See Slide time: 10:19



lculate standard molar entropy of gaseous argon at 25°C
(Mass of an Ar atom = 39.95 u)

$$S^o_m = R\ ln\left\{\frac{e^{5/2} \times 1.381 \times 10^{-23} J\ K^{-1} \times 298.15\ K}{(10^5\ N\ m^{-2}) \times (1.60 \times 10^{-11}\ m)^3}\right\} = 18.6\ R = 155\ J\ K^{-1} mol^{-1}$$

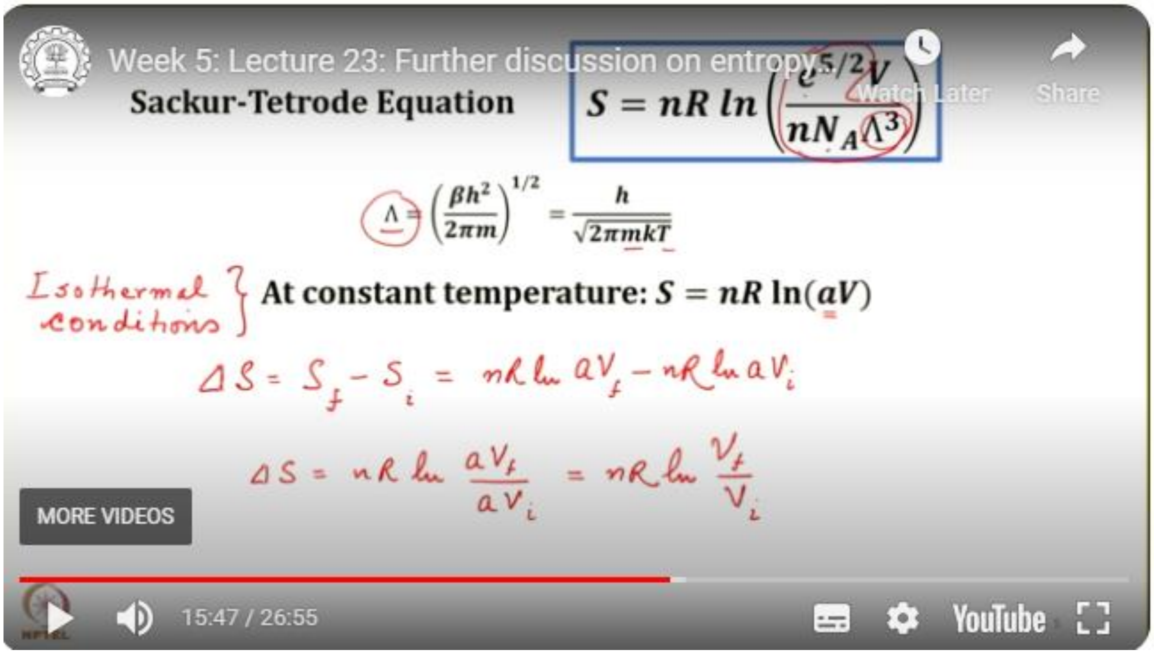
$$\Lambda = \left(\frac{\beta h^2}{2\pi m}\right)^{1/2} = \frac{h}{\sqrt{2\pi mkT}} = 16.0\ pm$$

- Neon (m = 20.18 u), a lighter molecule has higher thermal wavelength
- Hence standard molar entropy of Ne is smaller than Ar and is 146.3 J K^{-1} mol^{-1}
- The translational contribution to the standard molar entropy of H_2 at 25°C is [illegible]8 J [illegible]

Neon with a molar mass of 20.18 has molar entropy of 146.3. Hydrogen with a molar mass of 2 has a translational contribution to molar entropy as 118 joules per kelvin per mole. So you can clearly here look at that how the molar mass of the given species affects the molar entropy. Now let us further discuss about this Saku-Tetrode equation what other type of equations we can further develop from this. So Saku-Tetrode equation, this is one form, S is equal to n r log exponential 5 by 2 volume n times n a λ cube and we all know what is λ we do not need to elaborate now. Now let us maintain isothermal conditions.

Isothermal conditions mean constant temperature. If temperature is constant, now let us look at in the Saku-Tetrode equation what happens if temperature is constant.

See slide time: 15:47



Sackur-Tetrode Equation

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

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

Isothermal conditions } **At constant temperature:** $S = nR\ln(aV)$

$$\Delta S = S_f - S_i = nR\ln aV_f - nR\ln aV_i$$

$$\Delta S = nR\ln\frac{aV_f}{aV_i} = nR\ln\frac{V_f}{V_i}$$

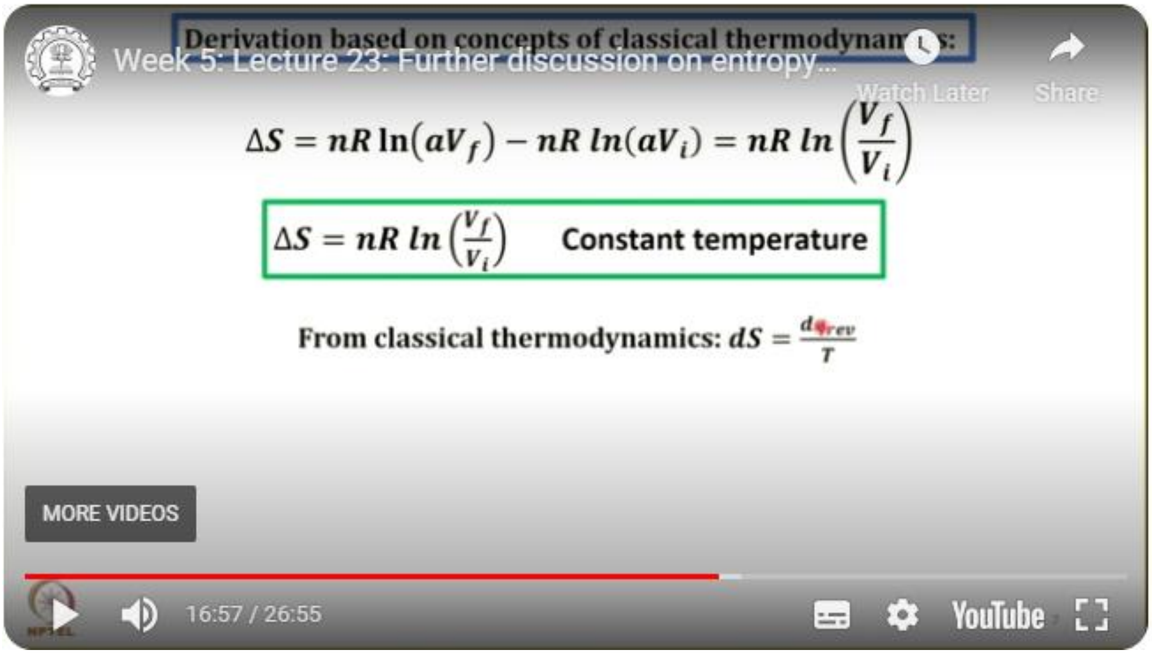
This exponential raised to the power 5 by 2 is a constant. Number of moles is a constant. Avogadro constant is a constant. And what about λ? λ you see here is h by 2 π m k T. If the temperature is constant and the molar mass is constant then λ is also constant. That means under isothermal conditions if you want to apply this expression for any changes happening in the system then essentially the λ thermal wavelength is constant. So therefore, everything other than volume that means all these parameters exponential 5 by 2 n n a λ cube this is all constant and I can combine all these constants into a right. So I write S is equal to n r log a times V.

Now you consider a gas and let that gas expand under isothermal conditions. Isothermal conditions. If we are considering isothermal conditions I can use this formula. Let us say expansion takes place from V_i to V_f then your delta S is S_f S_f minus S_i. What it will be? It will be n r log a V_f minus n r log a V_i

Which now I can write as delta S is equal to n r log a Vf over a Vi is equal to n r log V final over V initial. We have an expression now to calculate change in entropy when a gas expands under isothermal conditions and we have only used the statistical thermodynamics concepts over here. So this slide basically recaptures again what I have just discussed is that under constant temperature conditions S is equal to n r log a times V and then for any change where a gas expands from V final to V initial we have this expression delta S is equal to n r log V final over V initial. Remember that once again I am saying that we have used simply the statistical thermodynamics concepts over here. Does this result match with that obtained in classical thermodynamics discussion? Let us look at that.

Remember that the definition of dS is equal to dq reversible by d. The subscript reversible that is specifically to be noticed. All right if dS is equal to dq reversible by T.

See slide time: 16:57



Derivation based on concepts of classical thermodynam s:

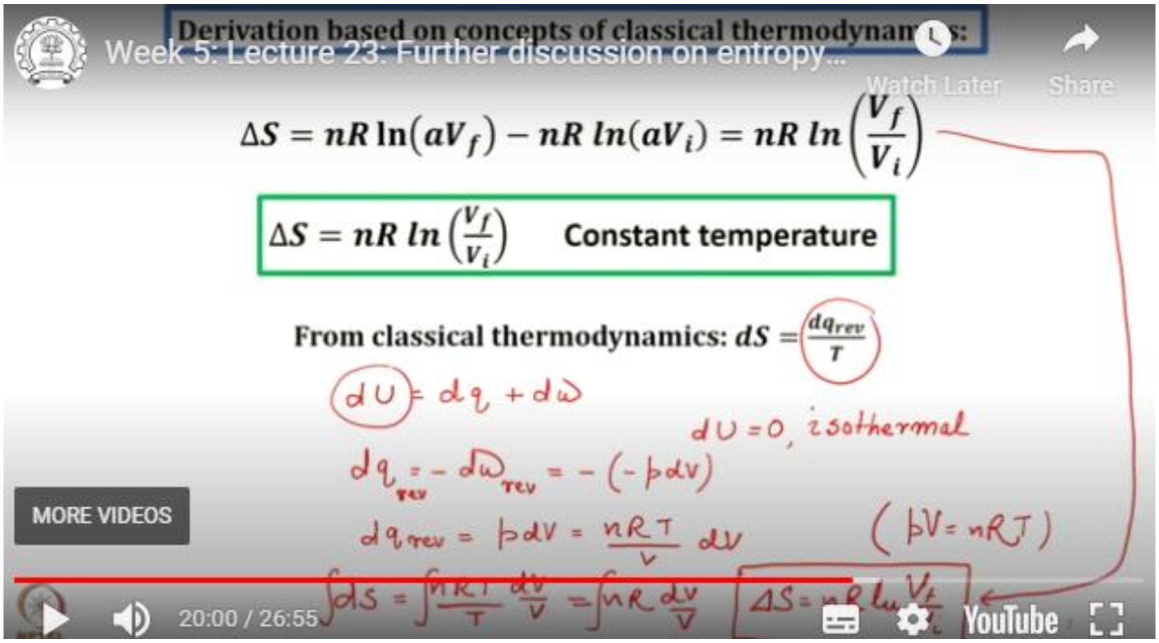
$$\Delta S = nR\ln(aV_f) - nR\,ln(aV_i) = nR\,ln\left(\frac{V_f}{V_i}\right)$$

$$\boxed{\Delta S = nR\,ln\left(\frac{V_f}{V_i}\right) \quad \text{Constant temperature}}$$

From classical thermodynamics: $dS = \frac{dq_{rev}}{T}$

then let us see what happens under constant temperature conditions. I will use the first law of thermodynamics du is equal to dq plus dw. If the temperature is constant then the change in internal energy is zero. We are so far talking about ideal situations, ideal gases. So constant temperature means this du is equal to zero right. Let me write du is equal to zero under isothermal conditions. So that means dq is equal to minus dw and if I invoke reversibility conditions then is not this equal to minus minus p dv. So what do I have now dq reversible is equal to plus p dv and since dq reversible is equal to pv is equal to nRT then I can write this as p is equal to nRT by v dv. I am interested in dq reversible by T. So dS then becomes dq reversible by T, dq reversible is nRT dv by v and divided by T which is nR dv by v and if I now integrate from Vi to Vf right. So then delta S will be equal to nR log v final over v initial. You apply the limits Vi and Vf over here then delta S will be equal to nR log Vf over Vi and you are essentially getting the same result. Let us take a look at the comment. So now we have shown that this expression delta S is equal to nR log Vf over Vi which by using the concepts of statistical thermodynamics we showed that at constant temperature this is nR log Vf over Vi and just now we also by using the classical thermodynamics concepts. Again we showed that under isothermal conditions or under constant volume conditions delta S is equal to nR log Vf over Vi. That is what is the comment over here that this is exactly the expression we obtained by using both classical thermodynamics and statistical thermodynamics.

See Slide time: 20:00



Derivation based on concepts of classical thermodynamics:

$$\Delta S = nR\ln(aV_f) - nR\,ln(aV_i) = nR\,ln\left(\frac{V_f}{V_i}\right)$$

$$\boxed{\Delta S = nR\,ln\left(\frac{V_f}{V_i}\right) \quad \text{Constant temperature}}$$

From classical thermodynamics: $dS = \frac{dq_{rev}}{T}$

$$dU = dq + dw$$

$dU = 0$, isothermal

$$dq_{rev} = -dw_{rev} = -(-p\,dV)$$

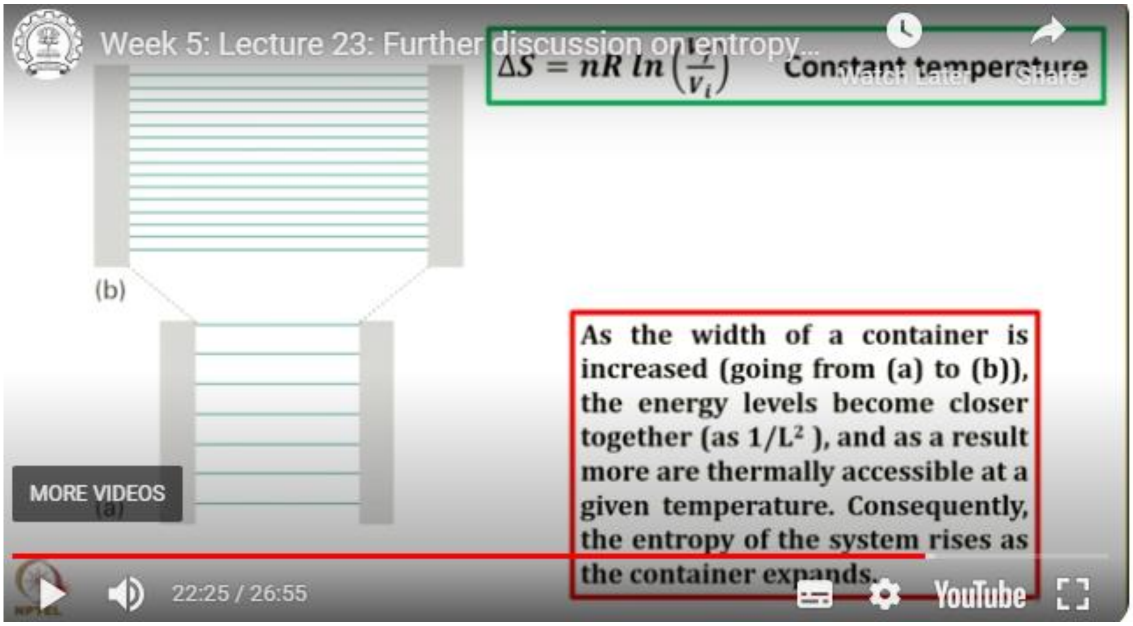
$$dq_{rev} = p\,dV = \frac{nRT}{V}\,dV \qquad (pV = nRT)$$

$$\int dS = \int \frac{nRT}{T}\frac{dV}{V} = \int nR\frac{dV}{V} \qquad \Delta S = nR\ln V_f$$

The classical expression is in fact a consequence of the increase in the number of accessible translational states when the volume of the container is increased. Look at this comment very carefully. The classical expression is in fact a consequence of the increase in the number of accessible translational states when the volume of the container is increased.

What it means is that you consider gas contained in a volume, certain volume in a container. Now you let the gas expand. The volume is expanding that means your dimensions a, b, c or length of the container that is all going up, right.

See slide time: 22:25



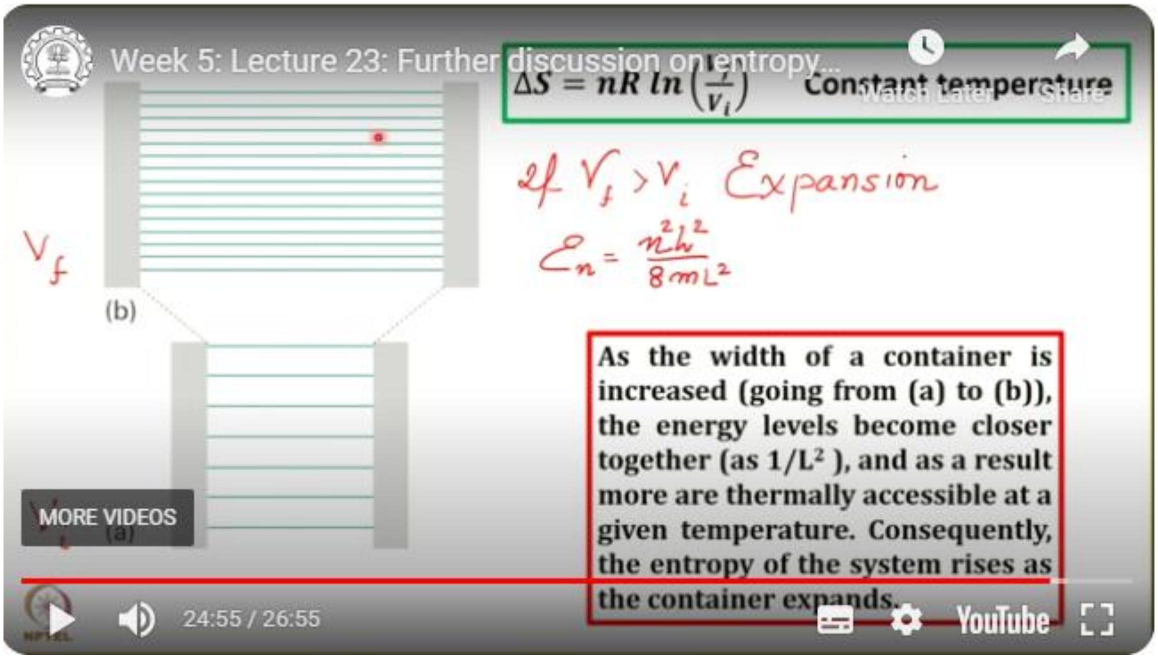
$\Delta S = nR\,ln\left(\frac{V_f}{V_i}\right)$ Constant temperature

As the width of a container is increased (going from (a) to (b)), the energy levels become closer together (as $1/L^2$), and as a result more are thermally accessible at a given temperature. Consequently, the entropy of the system rises as the container expands.

Even if you consider one dimension if you are expanding like this then the length of the container is increasing. What is the effect of the change in length of the container on the number of accessible thermal this translational states? That is what we need to consider. We will look at that. Now delta S is equal to nR log Vf over Vi. Obviously as we have been discussing that if Vf is greater than Vi, then the temperature of the container is greater than Vi. So, that means if Vf is greater than Vi that means we are talking about expansion and remember if we sort of you know for the sake of discussion if we restrict to one dimensional translational motion then remember En was equal to n square h square over 8 m L square, right. And if it is allowed in three dimension then you have En1, En2, En3 is equal to n1 square h square over 8 m L1 square plus n2 square h square over 8 m L2 square and so on and so on. I am not going into that details because that we have already covered.

But what is happening here is look at this scenario. A is corresponding to this is corresponding to Vi and B is corresponding to Vf expansion. So, you are allowing the system to undergo expansion. Expansion means you are increasing the value of L. So, if L square increases the energy En decreases and that is what you see over here that this you see that the spacing between the energy levels corresponding to different n that decreases. And that is the comment written over here that as the width of a container is increased going from A to B width is increased the energy levels become closer you can compare this versus this. This system has the energy levels much closer to each other than this system and as a result more thermally accessible states at a given temperature. So, given scenario this given scenario this at a given temperature this will have more thermally accessible states.

See Slide Time: 24:25



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

If $V_f > V_i$ Expansion

$\mathcal{E}_n = \frac{n^2h^2}{8mL^2}$

As the width of a container is increased (going from (a) to (b)), the energy levels become closer together (as $1/L^2$), and as a result more are thermally accessible at a given temperature. Consequently, the entropy of the system rises as the container expands.

Thermally accessible states and if there are more thermally accessible states if the then the molecules can distribute in different in larger number of thermally accessible states and therefore, there will be more disorder and therefore, there will be more entropy. So, this is the statistical definition or interpretation explanation of why the entropy of a gas increases when it undergoes expansion under isothermal condition from a initial volume to final volume.

Basically what we did was that we talked about what will be the population of different states isothermally when the gas is allowed to expand. We will discuss few more applications of Sécout-Tetrode equations. As I mentioned earlier that Sécout-Tetrode equation is very very important because it will allow you to calculate the entropy changes when the system undergoes change under constant volume conditions, under constant pressure conditions or uder constant temperature conditions. So, we will discuss morein the next lecture. Thank you very much. Thank you. Thank you.