Fundamentals of Statistical Thermodynamics

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Lecture – 22

Entropy of a monatomic gas

Welcome back. In the previous lecture, we have recovered molecular partition function from the more general canonical partition function. We discussed that how to connect these two partition functions for distinguishable molecules and for indistinguishable molecules. We also discussed conditions that when the molecules can become distinguishable and then we were trying to connect internal energy with molecular partition function. First, we talked about distinguishable molecules and it turned out that for distinguishable molecule, the expression for internal energy is the same that we had earlier derived when we were connecting internal energy with molecular partition function. Now let us discuss that if instead of distinguishable, if the molecules are indistinguishable, then what happens? Now let us talk for indistinguishable molecules.

If indistinguishable, then Q is equal to q raised to the power n over n factorial. That 1 over n factorial is required. Now let us see what happens. U minus U (0) from this expression is minus 1 by Q.

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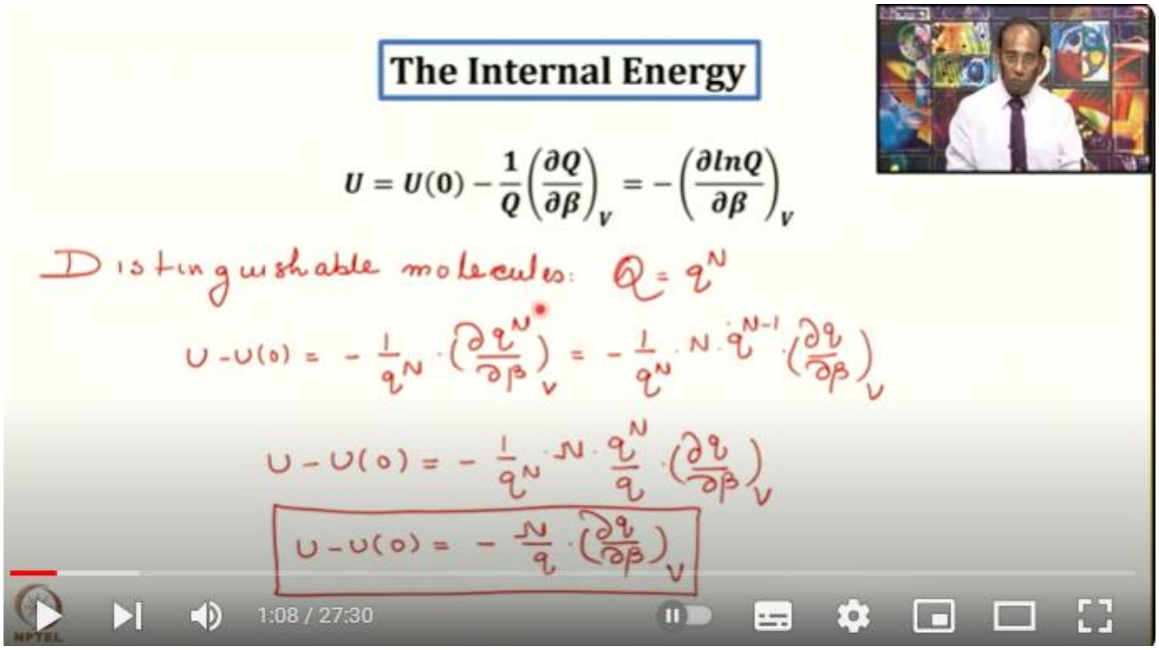


The Internal Energy

$$U = U(0) - \frac{1}{Q}\left(\frac{\partial Q}{\partial \beta}\right)_V = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_V$$

Distinguishable molecules: $Q = q^N$

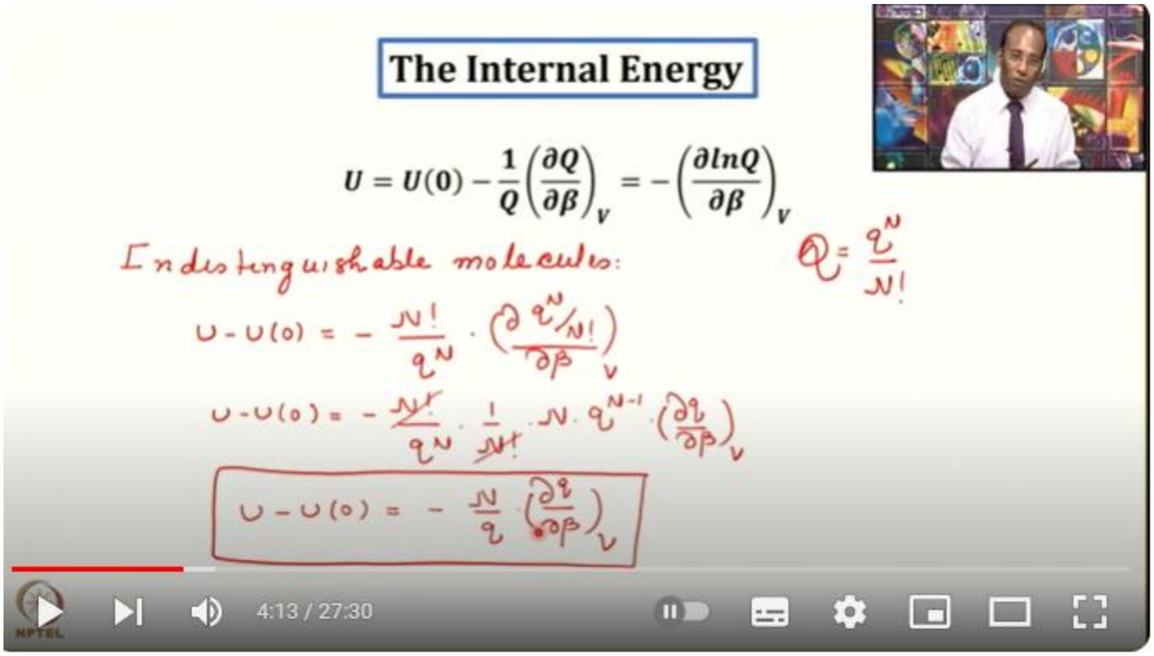
$$U - U(0) = -\frac{1}{q^N}\cdot\left(\frac{\partial q^N}{\partial \beta}\right)_V = -\frac{1}{q^N}\cdot N \cdot q^{N-1}\left(\frac{\partial q}{\partial \beta}\right)_V$$

$$U - U(0) = -\frac{1}{q^N}\cdot N \cdot \frac{q^N}{q}\cdot\left(\frac{\partial q}{\partial \beta}\right)_V$$

$$\boxed{U - U(0) = -\frac{N}{q}\cdot\left(\frac{\partial q}{\partial \beta}\right)_V}$$

That means minus n factorial over q raised to the power n that is minus n by Q minus 1 by q into derivative of q raised to the power n over n factorial with respect to β at constant volume. In other words, now what I have U minus U (0) is minus n factorial over Q raised to the power n. 1 by n factorial will come out from here and then I will have n into Q raised to the power n minus 1 into del q del β at constant volume. This is what I have. n factorial, n factorial cancel, and what I will have now U minus U (0) is equal to minus n by q into del q del β at constant volume because this q raised to the power n minus 1 is there which is q raised to the power n divided by q.

So q^n q^n will get cancelled and I will have minus n by q del q del β at constant volume. Interesting result to be now noted. Even for indistinguishable molecules, the internal energy is still in terms of molecular partition function the same as we got for distinguishable molecules. We have the same expression U is equal to U (0) minus n by q del q by del β at constant volume which in other words in terms of logarithmic terms also you can express which is minus n del log q by del β at constant volume. That means we have now shown that whether the molecule is distinguishable or indistinguishable you can use the same expression in terms of molecular partition function.



The Internal Energy

$$U = U(0) - \frac{1}{Q}\left(\frac{\partial Q}{\partial \beta}\right)_V = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_V$$

Indistinguishable molecules:

$$Q = \frac{q^N}{N!}$$

$$U - U(0) = -\frac{N!}{q^N}\cdot\left(\frac{\partial\, q^N/N!}{\partial \beta}\right)_V$$

$$U - U(0) = -\frac{\cancel{N!}}{q^N}\cdot\frac{1}{\cancel{N!}}\cdot N\cdot q^{N-1}\left(\frac{\partial q}{\partial \beta}\right)_V$$

$$\boxed{U - U(0) = -\frac{N}{q}\left(\frac{\partial q}{\partial \beta}\right)_V}$$

So same expression for distinguishable that is q equal to molecular partition function raised to the power n or indistinguishable Q is equal to q raised to the power n over n factorial. The expression turns out to be the same. So what are the points to be noted? That first we need to identify whether the molecules are distinguishable or indistinguishable. Use appropriate definition for the canonical partition function which at least for internal energy it shows that in both the cases the expression turns out to be same. Multiple energy and entropy are connected.

This we have discussed earlier also. So therefore obviously our next goal should be to discuss entropy, but now we will discuss entropy in terms of canonical partition function. Let us see what is the general expression that turns out to be in such cases. We have derived an expression or we have connected entropy with the canonical partition function that was S is equal to U minus U (0) by T plus K log Q. We will begin from this.

So when you say monatomic gas then we need to decide whether we should use q raised to the power n or we should use Q raised to the power n by n factorial. That means we need to decide whether the system given to us has distinguishable particles or indistinguishable particles or distinguishable atoms or indistinguishable atoms. When it is gas obviously it is not going to be distinguishable it is indistinguishable. Therefore, we need to use Q equal to q raised to the power n over n factorial. This is the expression that we need to use.

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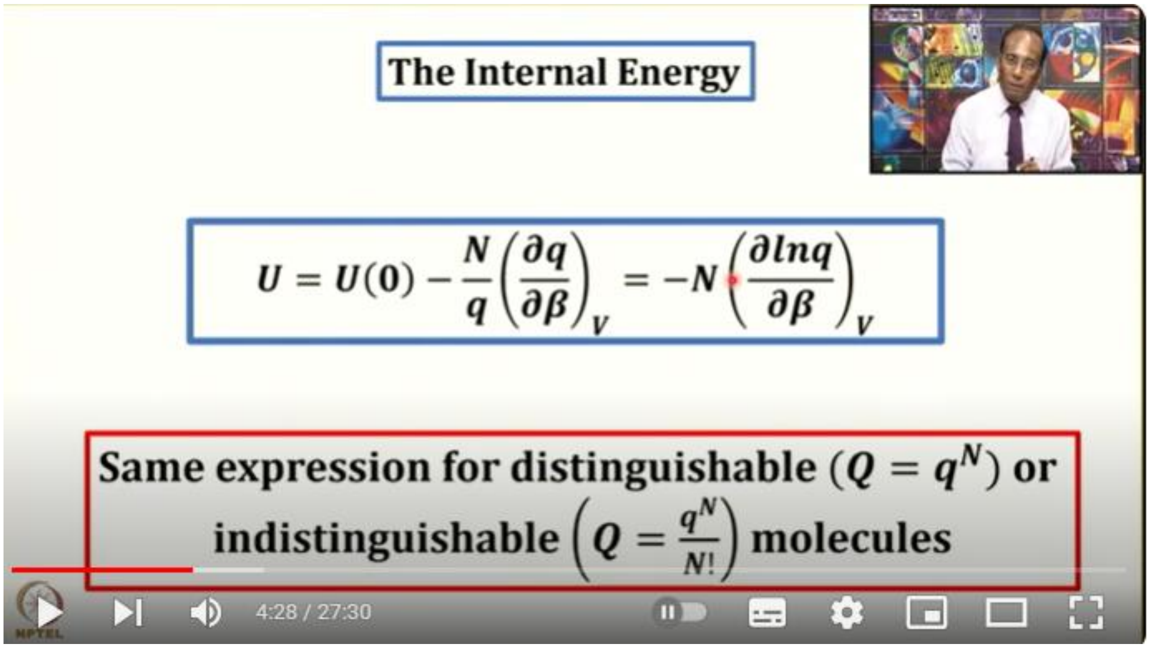

The Internal Energy

$$U = U(0) - \frac{N}{q}\left(\frac{\partial q}{\partial \beta}\right)_V = -N\left(\frac{\partial \ln q}{\partial \beta}\right)_V$$

Same expression for distinguishable ($Q = q^N$) or indistinguishable $\left(Q = \frac{q^N}{N!}\right)$ molecules

Let us use that. So I have S is equal to U minus U (0) by T plus K log q raised to the power n over n factorial. Now let us further expand this U minus U (0) by T plus K log Q raised to the power n minus K log n factorial. S is equal to U minus U (0) by T plus n K log Q minus K log n factorial. I can use Stirling approximation n log n minus n.

Let us take further U minus U(0) by T plus n K log Q minus n K log n plus n K. Remember n K is equal to caπ tal N can be small n times Avogadro constant K. That means n K is equal to now K times n A is equal to R. R is gas constant. So I have S is equal to U minus U (0) by T plus n R log Q minus n R log n plus n R.

We have the expressions in terms of molecular partition function, total number of molecules and of course we have the gas constant. Now obviously the next step is that we can we have to now work on U minus U (0) by T. You can use U minus U (0) in terms of canonical partition function then convert into molecular partition function then expand upon that. You can choose that route or what I can simply do is since it is monatomic perfect gas therefore I can use the result of equipartition theory. Natural energy of a monatomic gas which is free to move in three dimensions.

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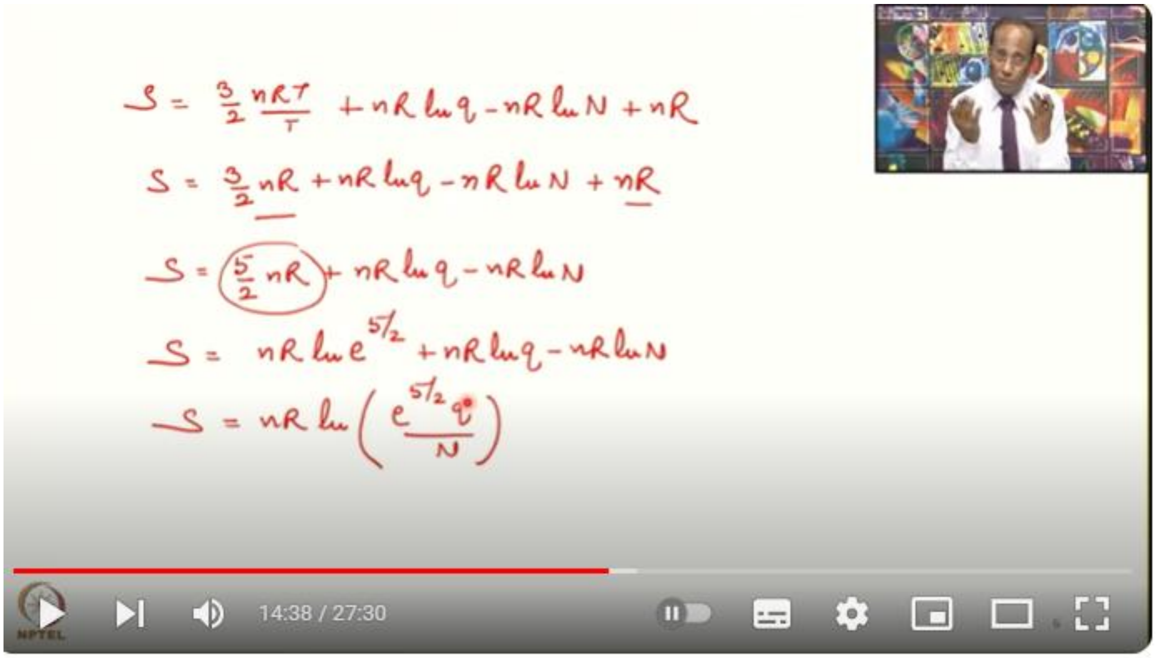

$$S = \frac{3}{2}\frac{nRT}{T} + nR\ln q - nR\ln N + nR$$

$$S = \underline{\frac{3}{2}}nR + nR\ln q - nR\ln N + \underline{nR}$$

$$S = \boxed{\frac{5}{2}nR} + nR\ln q - nR\ln N$$

$$S = nR\ln e^{5/2} + nR\ln q - nR\ln N$$

$$S = nR\ln\left(\frac{e^{5/2}q}{N}\right)$$

Remember that result was 3 by 2 n R T. I once again say we need to find out what we should write in terms of U minus U (0) by T. U minus U (0) if you go back to previous slide we have this expression right and it is the same expression whether Q is Q raise to the power n or Q is q raise to the power n by n factorial and then we can express in terms of molecular partition function and then write the expression for Q and come up with the result you are still going to get 3 by 2 n R T. You can do it or let us for the time being use the result from equipartition theorem. So, what do we have now? S is equal to U minus U (0) is 3 by 2 n R T divided by T because that is what is the first expression U minus U (0) by T plus n R log q minus n R log n minus n R log n and plus n R plus n R this is what we have now.

Let us continue this is 3 by 2 n R plus n R log q minus n minus n R log n and I have another n R term here. I can combine this 3 by 2 n R with this n R. So, what I have 3 by 2 plus 1 is 5 by 2 n R plus n R log q minus n R log n. Let us see can we now convert this 5 by 2 n R into some logarithmic term we can do that. So, it is going to be n R log exponential 5 by 2 plus n R log q minus n R log n right.

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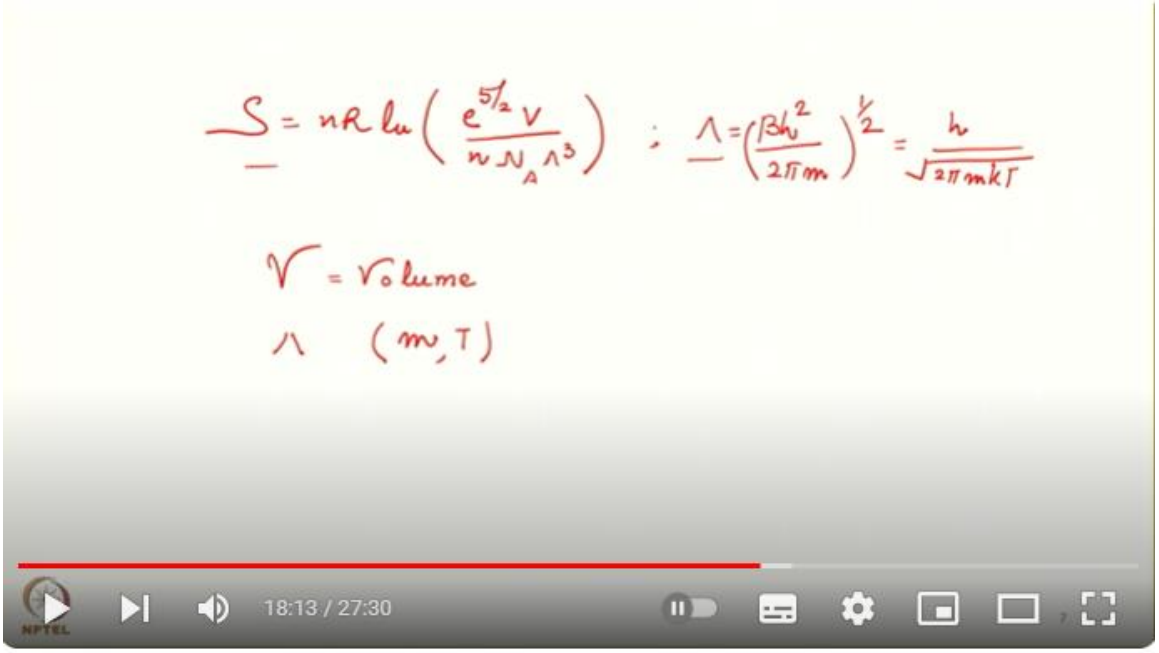

$$S = nR\ln\left(\frac{e^{5/2}V}{nN_A\Lambda^3}\right) \; ; \; \Lambda = \left(\frac{\beta h^2}{2\pi m}\right)^{1/2} = \frac{h}{\sqrt{2\pi mkT}}$$

V = Volume

$\Lambda \quad (m, T)$

So, this 5 x n R log exponential 5 by 2 is 5 by 2 n R ok. So, S now becomes n R log what I have is exponential 5 by 2 q by n that is what I have now. Now, we need to decide what we should write for q. This is a partition function and partition function will depend upon your degrees of freedom. The given system is monatomic gas perfect gas.

Monatomic will have translational degree of freedom it does not have rotational it does not have vibrational. Electronic we will discuss later it is not required here. So, that means we need to consider only translational degree of freedom and translational partition function. You remember was V upon λq where λ was equal to β h square over 2 π m.

Let us substitute. So, n is a S is a n R log exponential 5 by 2 V upon λ q V upon λ Q and instead of n let me write n times n A. The expression that I have now is S is equal to n R log exponential 5 by 2 instead of q I have written V by λ q instead of n I have written n times Avogadro constant. What I have now is S is equal to n R log exponential 5 by 2 V n Avogadro constant λ Q where your λ is equal to β h square over 2 π m raise to the power 1 by 2 or you can write this as H over square root 2 π m kT you have expressed β in terms of temperature. I can now calculate the statistical entropy. To calculate this what I need is volume what I need is a value of λ and if you see here λ h is constant 2 π is constant m depends mass of the particle and it will depend upon the temperature.

So, you need the mass of the particle and temperature that will decide the value of λ. So, therefore, from the knowledge of translational partition function now here we are able to get the entropy of the system provided we know its volume provided we know its temperature and also the mass these are the parameters properties that we require. So, we have now been able to obtain an expression from S is equal to U minus U (0) by T plus k log Q S is equal to n R log exponential 5 by 2 V over number of moles into Avogadro constant into λq where λ thermal wavelength we already know is given by β h square by 2 π m. This expression is called Sacher-Tetrode equation. So, remember this equation

Sacher-Tetrode equation which allows you to connect entropy with the volume with number of moles and with the thermal wavelength fine we have this expression.Now this expression is in terms of volume Sacher-Tetrode equation and since we are talking about monatomic gas monatomic gas we assume these are ideal gases assuming ideality let us use the gas law ideal gas law and see what shape it takes if I use p V is equal to n R T then V upon n is equal to R T upon p this V upon n I can substitute here V upon n. So, what do we get this exponential term will become let me write here only n R log exponential 5 by 2 V upon n is R T upon p then I have n A and then I have λ Q. Then R is equal to K times Avogadro constant this is another equation that means R upon n A is equal to K R upon n A is equal to K. So, therefore, the new expression that we get is exponential 5 by 2 R upon n A is K T upon p λ Q. We have Sackur–Tetrode in terms of volume we have Sackur–Tetrode equation in terms of pressure.

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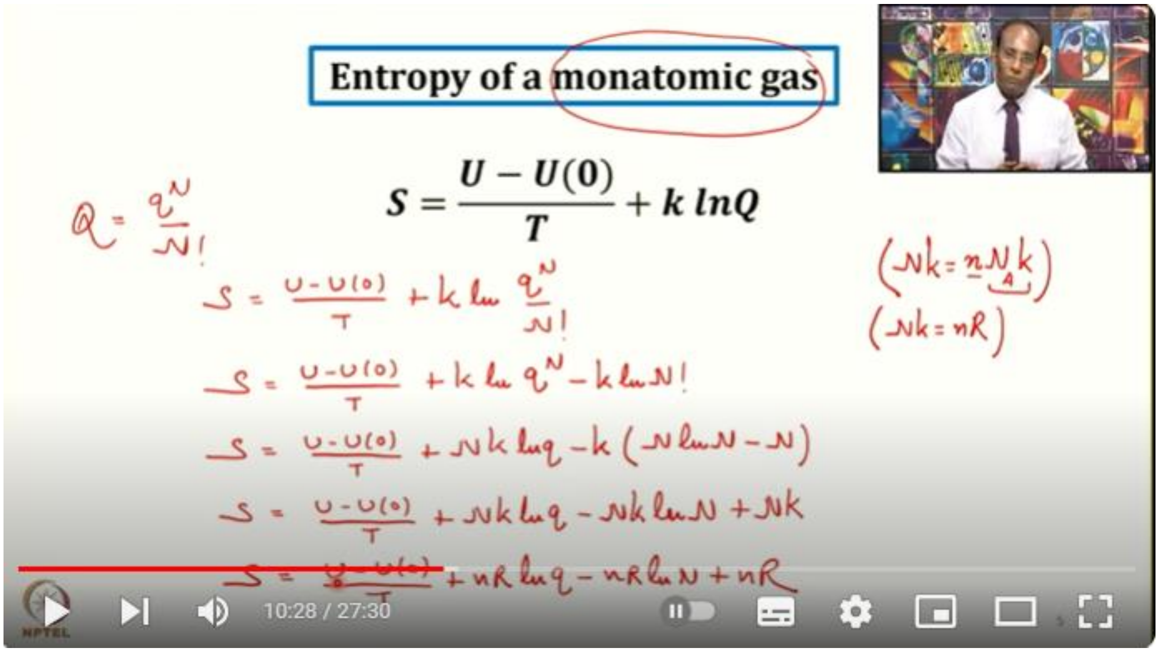

Entropy of a monatomic gas

$$S = \frac{U - U(0)}{T} + k\,lnQ$$

$Q = \frac{q^N}{N!}$

$S = \frac{U-U(0)}{T} + k \ln \frac{q^N}{N!}$

$S = \frac{U-U(0)}{T} + k \ln q^N - k \ln N!$

$S = \frac{U-U(0)}{T} + Nk \ln q - k(N \ln N - N)$

$S = \frac{U-U(0)}{T} + Nk \ln q - Nk \ln N + Nk$

$S = \frac{U-U(0)}{T} + nR \ln q - nR \ln N + nR$

$(Nk = n\underbrace{N_A k})$

$(Nk = nR)$

In both the cases you see λ is there λ is there temperature term is there. In fact, λ also depends upon temperature Sacher-Tetrode equation allows you to calculate entropy based upon partition function. And remember partition function whether we talk about molecular partition function or we talk about canonical partition function you can calculate the partition function from the knowledge of energy levels. That means the information that you require is from spectroscopy. Once you have the information about partition function you are able to then translate that in terms of derivable thermodynamic quantities. Now here we have done what we have done is we have simply used Q is equal to V upon λ Q and then come up with these equations which are basically different forms of the Sacher-

Tetrode equation one connects entropy with volume the other connects entropy with pressure.

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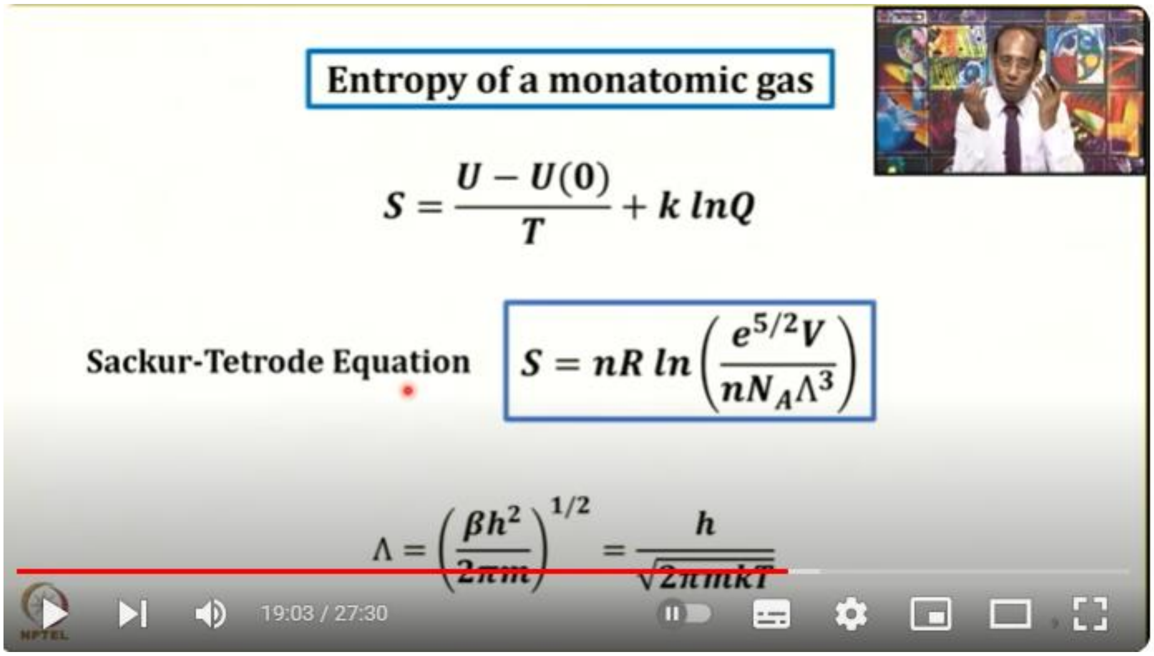

Entropy of a monatomic gas

$$S = \frac{U - U(0)}{T} + k\,lnQ$$

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

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

Let us now consider this comment Sacher-Tetrode equation implies that the molar entropy of a perfect gas of a high molar mass is greater than one of the low molar mass. That means the molar entropy of a perfect gas of high molar mass is greater than one of low molar mass under the same conditions. Why? The molar entropy of a perfect gas of high molar mass why? The molar mass that comes into the denominator high molar mass means lesser thermal wavelength. If lesser thermal wavelength then the molar entropy is high and that is what is the comment 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.

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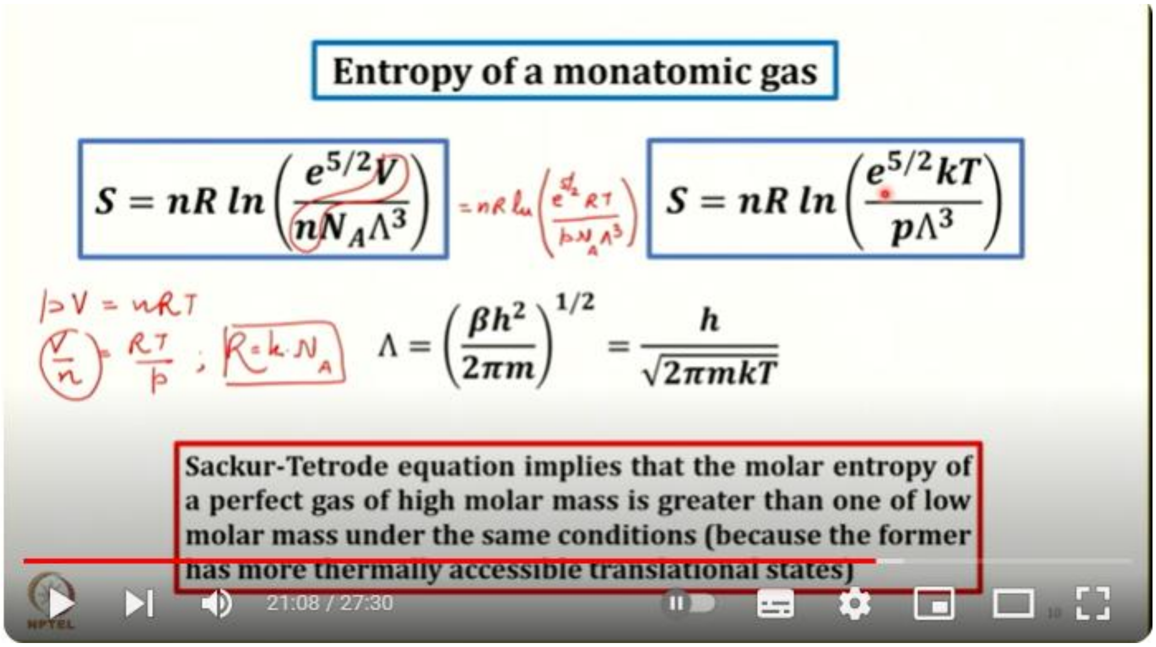

Entropy of a monatomic gas

$$\boxed{S = nR\ln\left(\frac{e^{5/2}V}{nN_A\Lambda^3}\right)} = nR\ln\left(\frac{e^{5/2}RT}{pN_A\Lambda^3}\right) \quad \boxed{S = nR\ln\left(\frac{e^{5/2}kT}{p\Lambda^3}\right)}$$

$pV = nRT$

$\frac{V}{n} = \frac{RT}{p}$; $\boxed{R = k \cdot N_A}$

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

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)

More thermally accessible translational states because you have for high molar mass you have lesser value of thermal wavelength and then in order to connect with the thermally accessible states we need to think about Q translational is equal to V upon λ Q. If λ is small then Q t is more and if Q t is more then directly it tells that there are more thermally accessible translational states. Now, if you carefully examine these two expressions whether entropy expressed in terms of volume or entropy expressed in terms of temperature λ is the term you examine here is depending upon molar mass and is depending upon temperature. So, that means if you fixed if you fix the temperature constant temperature constant temperature means isothermal conditions then for a given system of a fixed molar mass then this also becomes constant. Carefully understand that if you consider an isothermal process where the temperature is constant for a given system this whole term becomes constant at a given temperature.

In that case the entropy will simply depend upon volume in other words it will also depend upon the pressure. So, therefore when you allow the system to change from one state to another state under constant temperature conditions then you should be able to derive expressions for delta S in terms of changes in volume or in terms of changes in pressure under constant temperature conditions. We will derive such expressions and see how to use that and also compare the results with the results that we got in classical thermodynamics, but that we will do in the next lecture. Thank you very much.