Fundamentals of Statistical Thermodynamics

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Lecture – 12

Obtaining expression for beta

Let us now talk about those constants, you know, α and β which we used in Lagrange's method of undetermined multipliers. Earlier we have talked about α in terms of exponential α in one of the lectures and today we are going to express β in terms of temperature. We have been discussing that β is equal to 1 over k T, but today we will show, we will prove that β is equal to 1 over k T. We will need to bring in a discussion on internal energy to derive that. Let us consider only the particle or molecule is able to move or free to move only in three dimensions, that is translational partition function. We are not allowing rotation vibration that means we are talking the case of atoms.

Atoms will only have translational degrees of freedom, electronic will be there, but let us not consider electronic at this moment. Recall the discussion when you were learning the equipartition theorem. A perfect gas, a perfect monatomic gas, is considered only translational. The equipartition expression for the internal energy of a perfect gas, you remember that this was equal to 3 by 2 nRT, 1/2 nRT in one dimension, and 3 by 2 nRT in three dimensions.

So we are going to use the result of the equi-partition theorem and by using the concepts of statistical thermodynamics, I will derive that U minus U(0) is equal to 3 n by 2 β.

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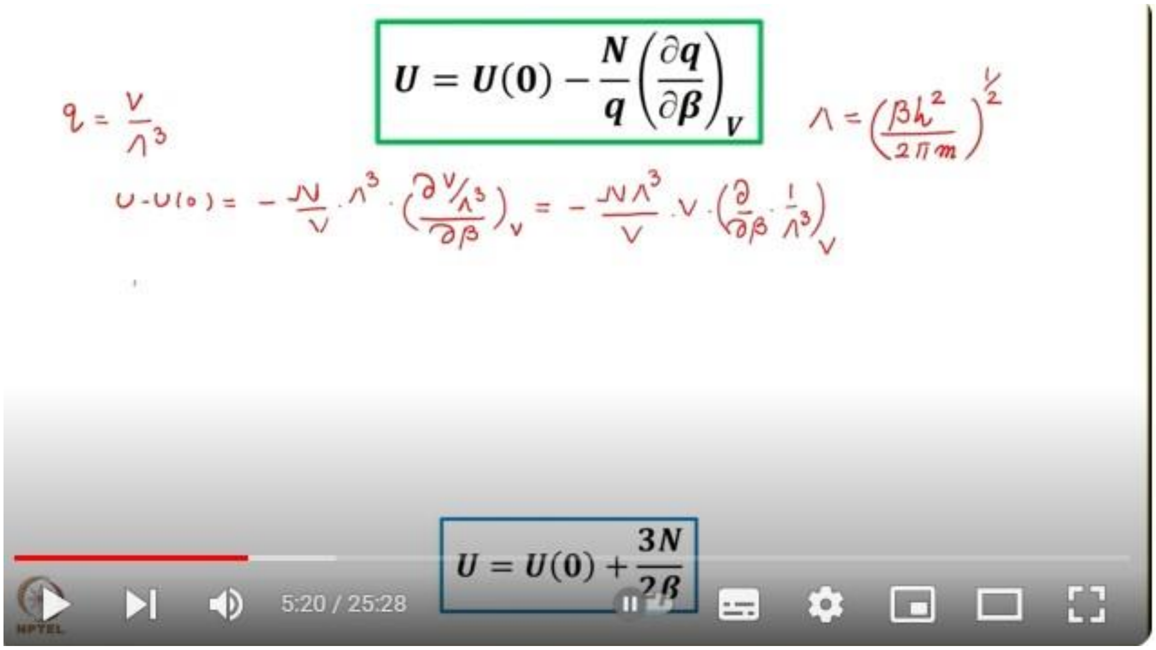

$$U = U(0) - \frac{N}{q}\left(\frac{\partial q}{\partial \beta}\right)_V$$

$$q = \frac{V}{\Lambda^3} \qquad \Lambda = \left(\frac{\beta h^2}{2\pi m}\right)^{\frac{1}{2}}$$

$$U - U(0) = -\frac{N}{V}\cdot\Lambda^3\cdot\left(\frac{\partial V/\Lambda^3}{\partial \beta}\right)_V = -\frac{N\Lambda^3}{V}\cdot V\cdot\left(\frac{\partial}{\partial\beta}\cdot\frac{1}{\Lambda^3}\right)_V$$

$$U = U(0) + \frac{3N}{2\beta}$$

I am going to derive that where n is the number of molecules and β is what we are looking for. We want to find out an expression for β. So once I have derived this, what I will then do is I will compare these two and then equate 3 n by 2β equal to 3 by 2 nRT, and then I will obtain an expression for β.

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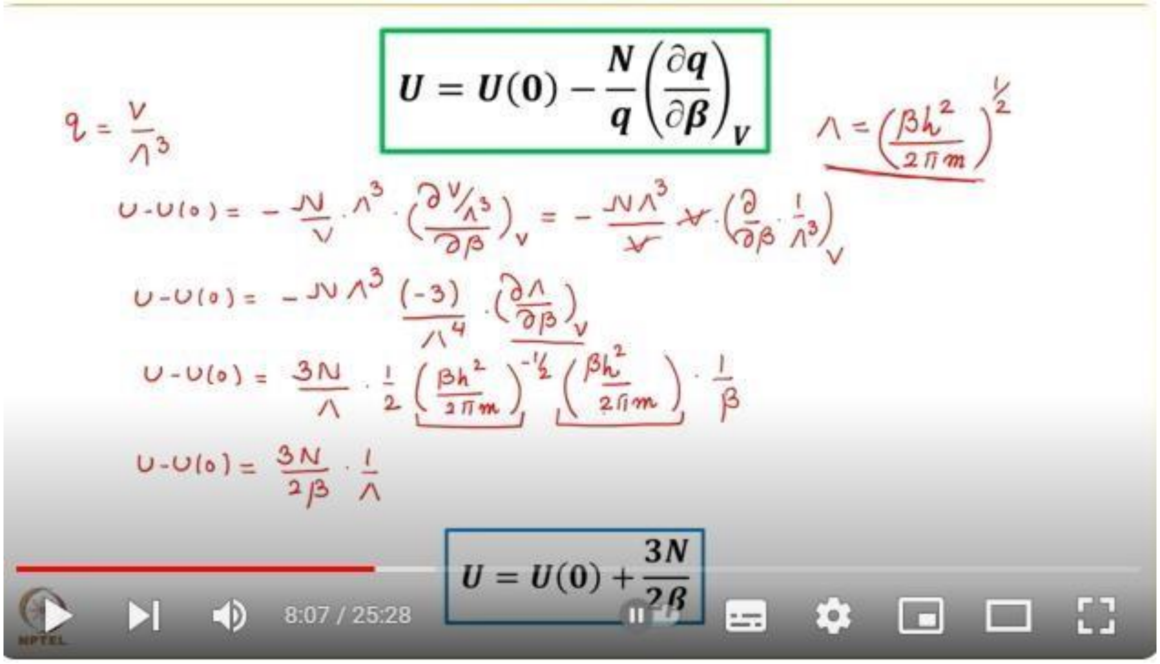

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$$U - U(0) = -N\Lambda^3\,\frac{(-3)}{\Lambda^4}\cdot\underline{\left(\frac{\partial\Lambda}{\partial\beta}\right)_V}$$

$$U - U(0) = \frac{3N}{\Lambda}\cdot\frac{1}{2}\underbrace{\left(\frac{\beta h^2}{2\pi m}\right)}^{-\frac{1}{2}}\underbrace{\left(\frac{\beta h^2}{2\pi m}\right)}\cdot\frac{1}{\beta}$$

$$U - U(0) = \frac{3N}{2\beta}\cdot\frac{1}{\Lambda}$$

$$U = U(0) + \frac{3N}{2\beta}$$

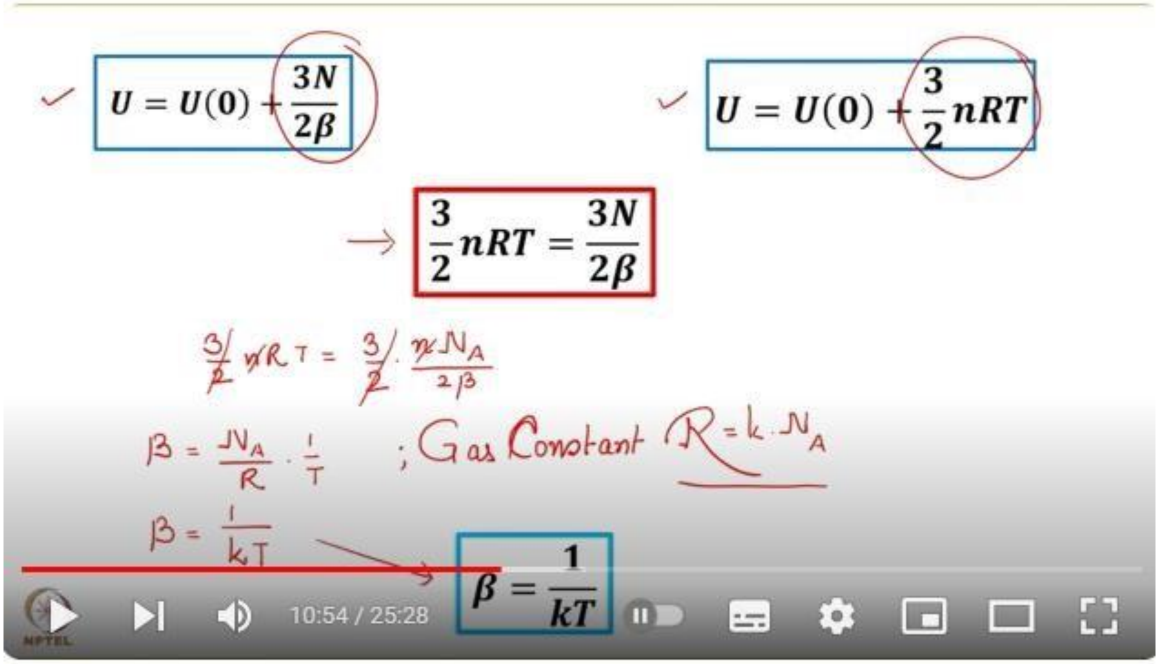
We have already talked about internal energy.U is equal to U(0) minus n by q ∂ q by ∂ β constant volume. We are talking about translational contribution. So, therefore, the translational partition function that we know is equal to v upon λ q. We are going to use that and we are also going to use an expression for λ which is equal to β h square over 2π m square. We are going to use both these expressions.

So U minus U (0) is equal to minus n by q minus n by q. By q is v into λ q. This is q into ∂ q by ∂ β at constant volume. That means ∂ v upon λ q ∂ β at constant volume. So what I am going to get from here now? This is equal to minus n λ q divided by v and constant volume means v can come out into volume into ∂ ∂ β of 1 by λ q at constant volume. This is the expression now we are looking at. Let us work on this now. So that means U minus U (0) is equal to volume and volume can cancel out. So we have minus n λ q. This is λ raise to the power minus 3.

So derivative is minus 3 over λ 4 into ∂ λ ∂ β at constant volume. So what are we getting now? u minus U (0) is equal to 3 n divided by λ, λ q by λ 4 into ∂ λ by ∂ β at constant volume. Let us now act on this. This is going to be 1 by 2 into β h square over 2πm minus 1 by 2 and another term that will come is h square over 2 π m.

Fine. So I used this definition of λ and I took the derivative of λ with respect to

β. See slide time: 10:54



✓ $$\boxed{U = U(0) + \frac{3N}{2\beta}}$$

✓ $$\boxed{U = U(0) + \frac{3}{2}nRT}$$

$$\rightarrow \boxed{\frac{3}{2}nRT = \frac{3N}{2\beta}}$$

$$\cancel{\frac{3}{2}}\cancel{n}RT = \cancel{\frac{3}{2}}\cdot\frac{\cancel{n}N_A}{2\beta}$$

$$\beta = \frac{N_A}{R}\cdot\frac{1}{T}$$; Gas Constant $\underline{R = k\cdot N_A}$

$$\beta = \frac{1}{kT} \rightarrow \boxed{\beta = \frac{1}{kT}}$$

So I have this expression U minus U (0) is equal to 3 n by λ half β h square 2πm minus raise to the power minus 1 by 2 and into I have h square over 2 π m. Now I need to further simplify this expression. An easy way to simplify is you multiply by β and divide by β. No harm done. Now you recognize that these two are the same terms. So what I have now? My U minus U (0) is equal to 3 n by 2 β. I am combining this β over here into 1 by λ and this product is nothing but λ. It is β h square over 2 π m square root into λ. So therefore, I get this expression.

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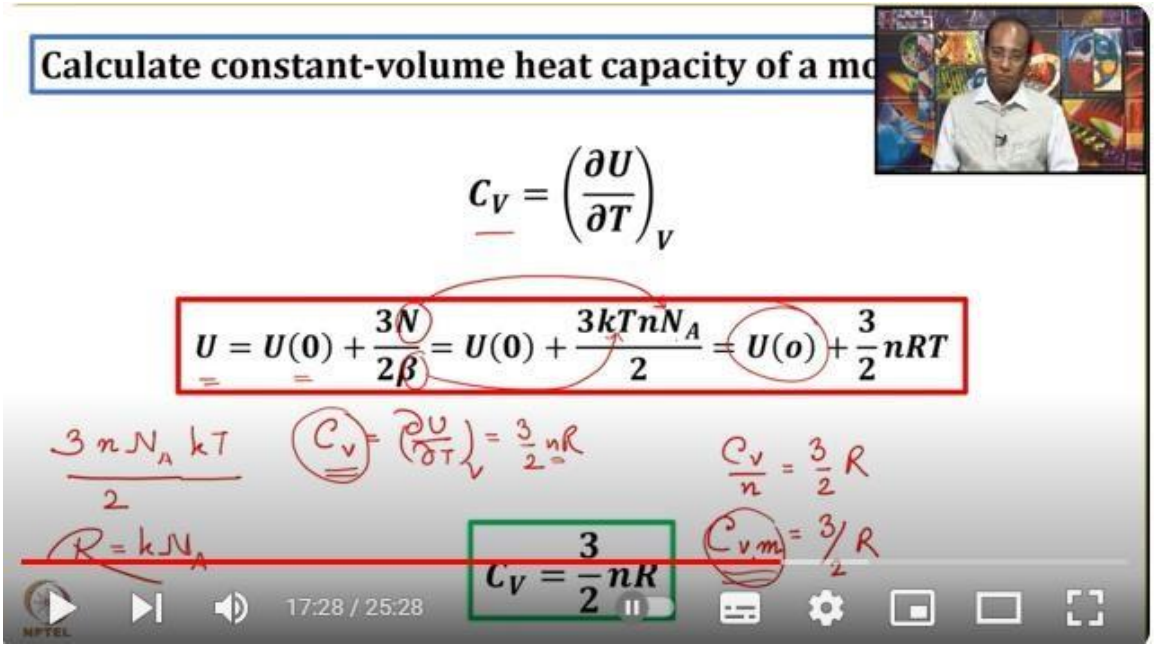

Calculate constant-volume heat capacity of a mo

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$U = U(0) + \frac{3N}{2\beta} = U(0) + \frac{3kTnN_A}{2} = U(o) + \frac{3}{2}nRT$$

$$\frac{3nN_A kT}{2}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}nR$$

$$\frac{C_V}{n} = \frac{3}{2}R$$

$$R = kN_A$$

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

$$\boxed{C_V = \frac{3}{2}nR}$$

U is equal to U (0) plus 3 n by 2 β. What we have done is we have used the equipartition theorem and internal energy is 3 by 2 n r t and then exclusively we use the translational contribution and we arrived at an expression that U Minus U (0) or U is equal to U (0) plus 3 n by 2 β. Let us proceed further. So we derived 3 n R t U is equal to U (0) plus 3 n by 2 β and we know that u is equal to U (0) plus 3 by 2n r t. This is from the equipartition theorem.

Now if you compare these two, this and this are equal and that is what is equated over here. 3 by 2 n r t is equal to 3 n by 2 β. So, let us further work on this. You have 3 by 2 n r t. This is equal to 3

by 2. Instead of n, I can write a number of moles into the Avogadro constant that is equal to N, the number of molecules divided by 2 β. So, this is the equation. Your 3 by 2, 3 by 2, n, n they cancel and β is equal to N_A Avogadro constant divided by R into 1 by T.

Remember that gas constant R is equal to k times N_A where N_A is Avogadro constant, k is Boltzmann constant. Therefore, N_A upon R is equal to 1 upon k.

So, β is equal to then 1 over k T. We are using this R is equal to k times N_A. So, we have the expression. So, β is equal to 1 by 2 n r t. So, β equal to 1 over k T. This is an expression that we have been using earlier, but now we have shown by using the translational partition function and equipartition theorem result that β is equal to 1. So, this completes our discussion on the undetermined multipliers. You remember that we wanted to put one of the terms equal to 0. The term which was actually not independent, but we made independent in d log w that term. So, that you know we can set that equal to 0 for a certain value of α and for a certain value of β which were actually undetermined multipliers.

Exponential α or α we have discussed earlier and β we prove here that β is equal to 1 over k T. And as I have repeatedly said that sometimes you know people work in terms of β, sometimes people work in terms of just temperature. So, therefore, do not get confused. All right, let us move forward. Once we have the knowledge of internal energy, we can calculate constant volume heat capacity.

Heat capacity is a very important thermodynamic quantity because it allows the determination of temperature-dependent thermodynamic quantities. For example, if I know the enthalpy change for a reaction at one temperature, I can calculate the change in enthalpy at another temperature if I have the knowledge of heat capacity. We can use the Kirchhoff law Any thermodynamic quantity if you determine at one temperature and if you want to connect with the same or if you want to calculate the same thermodynamic quantity at another temperature, the connector is heat capacity. Therefore, heat capacity is a very important thermodynamic quantity.

Usually, you talk about heat capacities under two constraints. One is constant volume and other is constant pressure. When you keep constant volume, we use the symbol C_v and that definition, the mathematical definition of C_v is ∂ u by ∂ t at constant volume. U, we have just derived an expression that U is equal to U (0) plus 3N by 2 β. Now, let us see what is this 3N by 2 β.
3n, n is N times Avogadro constant and divided by 2 and β is equal to 3n by 2 β. Now, let us write, let us see what is this 3n by 2 β. 3n, n is N times Avogadro constant and divided by 2 and β is 1 over K T. Now, let us see what is this 3n by 2 β. So, that is what is being done over here that instead of n, I am writing n times N_A and for β, you are writing K T.

And then, the second that I am using R, gas constant is equal to K times N_A. So, K times N_A becomes R. So, it basically becomes R times N_A. So, it becomes 3 by 2nRT. That is what was the result from equipartition theorem that U is equal to U (0) plus 3 by 2 nRT. Now, you can take the derivative. C_v is equal to ∂U by ∂t at constant volume. This is a constant volume. This is a constant volume. So, its derivative is equal to 0, and at constant volume, derivative with respect to temperature is simply going to be 3 by 2 n R. Remember that this is the actual heat capacity at constant volume for a given size of the system.

You can always express these thermodynamic quantities in terms of molar properties. That is, let us say I write here C_v, I take n on the other side is equal to 3 by 2 R, and per mole, C_{vm}, molar heat capacity is equal to 3 by 2 R. We should always look at whether we are talking about C v or we are talking about $C_{v\,m}$. C_v, heat capacity at constant volume, it depends upon the size of the system, how many grams, how many moles because it involves n. When you talk about the molar property, that does not depend upon the size because you are calculating or determining heat capacity at constant volume for 1 mole of a substance.

Therefore, do not get confused when you come across the terms C_v and C_{vm}. Since we are talking about heat capacity over here and in future also we are going to talk more about heat capacity, it makes a sense here to discuss how to experimentally measure heat capacity. If you look into this definition, C_v is equal to ∂U by ∂T at constant volume. In fact, I can introduce right here, although we will solve the numerical problems later on that, C_p, heat capacity at constant pressure is ∂H by ∂T at constant pressure. So, we talk about constant pressure constraint, we talk about constant volume constraint and we discussed that experimental measurements of C_v requires the measurements of change in internal energy that means a bomb calorimeter will be useful.

And if experimentally I were to measure C_p, then I require a calorimeter which can work under constant pressure conditions. A literal meaning of C_v and C_p, let us try to examine. C_v or C_p, both ∂H, ∂U, remember that q at constant volume is equal to ∂U and q at constant pressure is equal to ∂H, this is from your previous knowledge. So, both ∂U or ∂H if we are talking about infinitesimally small quantities, then I will write dq at constant volume is equal to dU and dq at constant pressure is equal to dH. So, whether we are talking about dU or ∂U or we are talking about dH or ∂H, we are essentially talking about the heats.

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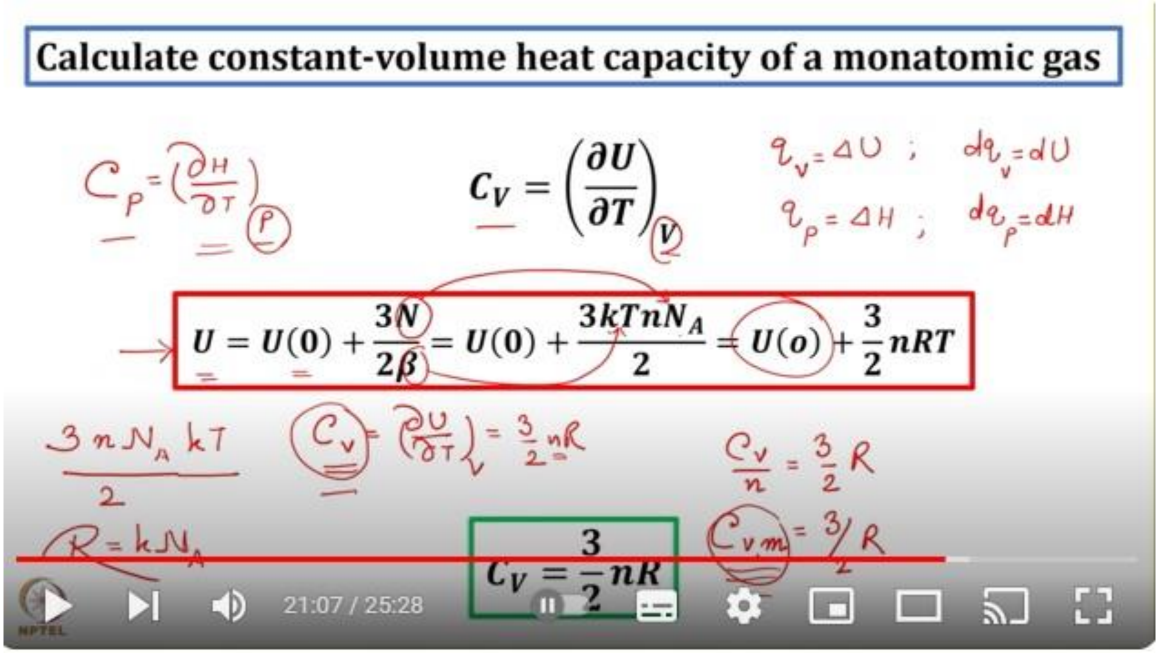

Calculate constant-volume heat capacity of a monatomic gas

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P \qquad C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$q_v = \Delta U$; $dq_v = dU$

$q_p = \Delta H$; $dq_p = dH$

$$\boxed{U = U(0) + \frac{3N}{2\beta} = U(0) + \frac{3kTnN_A}{2} = U(o) + \frac{3}{2}nRT}$$

$$\frac{3nN_A kT}{2} \qquad C_v = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}nR \qquad \frac{C_v}{n} = \frac{3}{2}R$$

$$R = kN_A \qquad \boxed{C_V = \frac{3}{2}nR} \qquad C_{vm} = \frac{3}{2}R$$

In one case it is constant volume and in the other case it is constant pressure. So, experimental measurements of heat capacities require the amount of heat required to change the temperature by 1 Kelvin either under constant volume conditions, if we are talking about C v or under constant pressure conditions, if we are talking about constant pressure. By applying the concepts of statistical thermodynamics, we connected internal energy with partition function. So, we connected internal energy and from that we came up with this kind of expression that is U is equal to U 0 plus 3n by 2 β and that partition function was expressed in terms of degeneracies and energy levels. So, that means you can also get the information on C_p and C_v from the respective spectroscopic data because when you are talking about an atom, a monatomic gas for example, there here if you look into the question statement, it talked about monatomic gas.

That means you are only talking about translational degree of freedom. A monatomic system, an atom cannot have vibrational or rotational degree of freedom. You also know from your previous knowledge that the value of C_p and C_v will be temperature dependent because the different contributions set in at different temperatures. Here we are only talking about monatomic gas. So, we are only including the translational contribution.

So, C_v is equal to 3 by 2 nR and C_{vm} is equal to 3 by 2 R and as I just mentioned, C_p and C_v are very important thermodynamic quantities because they are connectors. So, they are the components of thermodynamic property at one temperature to thermodynamic property at another temperature and also if we are going through the literal meaning, the amount of heat required to raise the temperature by 1 Kelvin. The amount of heat required to raise the temperature by 1 Kelvin is going to also depend upon how strong the system is. What is the type of bonding which keeps different molecules together in the material? Right now, we are not talking about beyond independent molecules. We will talk about solids and liquids later on, but I am just trying to give you a literal meaning of C_p and C_v.

Since it is the amount of heat required to raise the temperature by 1 Kelvin, it also depends upon how strong the system is. Here we have discussed C_v and when we derive an expression between partition function and enthalpy, then we will talk about C_p also. Remember that C_p and C_v are also connected with each other. C_p minus C_v is equal nR that is for the ideal gases whereas, for the nonideal gases, you remember from the concepts of chemical thermodynamics, if the systems are interacting, there may be other terms in it. The take home lesson from this lecture is that by using the result of equipartition theorem and considering the translational partition function that is for a system which is free to move only in three dimensions having translational degree of freedom, we could establish that β is equal to 1 over k T.

With this knowledge, now in the next lectures, we will start connecting partition function with other thermodynamic quantities and provide an interpretation to those thermodynamic quantities. Thank you very much. Thank you.