Fundamentals of Statistical Thermodynamics

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Lecture – 25

The Thermodynamic Functions (Pressure)

Welcome back to the next lecture of Statistical Thermodynamics. By now we have connected some thermodynamic quantities with molecular partition function and have also discussed how to recover molecular partition function from the more general canonical partition function. Continuing now connecting partition function with other thermodynamic quantities, today we will talk for pressure. Amongst various thermodynamic functions, pressure is an important quantity. In classical thermodynamics, you remember that we define pressure as average force exerted by the gas molecules on the walls of the container per unit area. In terms of statistical thermodynamics, today we will connect pressure with molecular partition function and also with canonical partition function.

Let us proceed. We have earlier discussed and derived expressions connecting internal energy with canonical partition function. This is the expression which connects internal energy and canonical partition function. We have also so far derived an expression for entropy of a monatomic gas.

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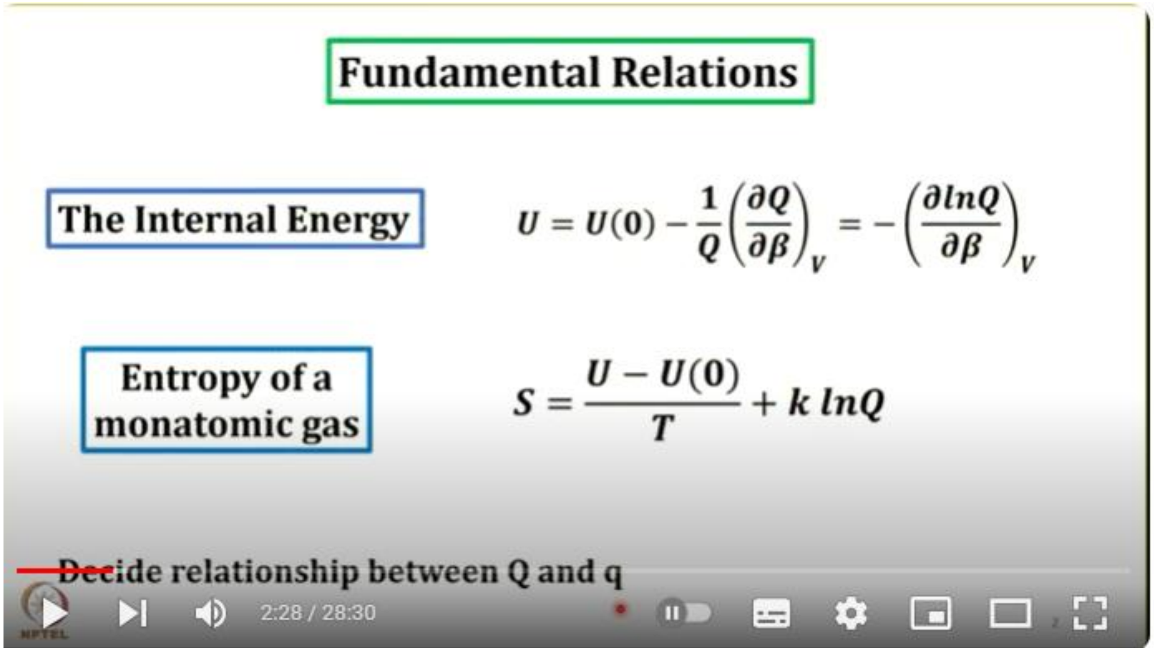

S is equal to U minus U (0) by t plus k log q. Capital Q we have been referring to canonical partition function. Now, when we proceed further in connecting these thermodynamic quantities to other thermodynamic quantities, we need to decide the relationships between canonical partition function and molecular partition function. And these relationships will be depending upon whether the particles are distinguishable or the particles are indistinguishable. And we very well know by now that we will be using either Q is equal to Q raise to the power n or we will be using Q is equal to Q raise to the power n by n factorial. So, we need to decide whether we will be using this equation or we will be using this equation. If it is distinguishable, we will use Q is equal to Q raise to the power n. And if the molecules are indistinguishable, we will use Q is equal to Q raise to the power n by n factorial. By keeping this in mind, now let us move forward in deriving the relationships between canonical partition function or molecular partition function with pressure. The equation that eventually we will derive is A minus A(0) is equal to minus k T log Q.
Now, how to get this? A which is called Helmholtz energy or Helmholtz function. You also sometimes call Helmholtz free energy. What is the definition of Helmholtz energy? The definition is A is equal to U minus TS. This is the definition. U T S are system properties.

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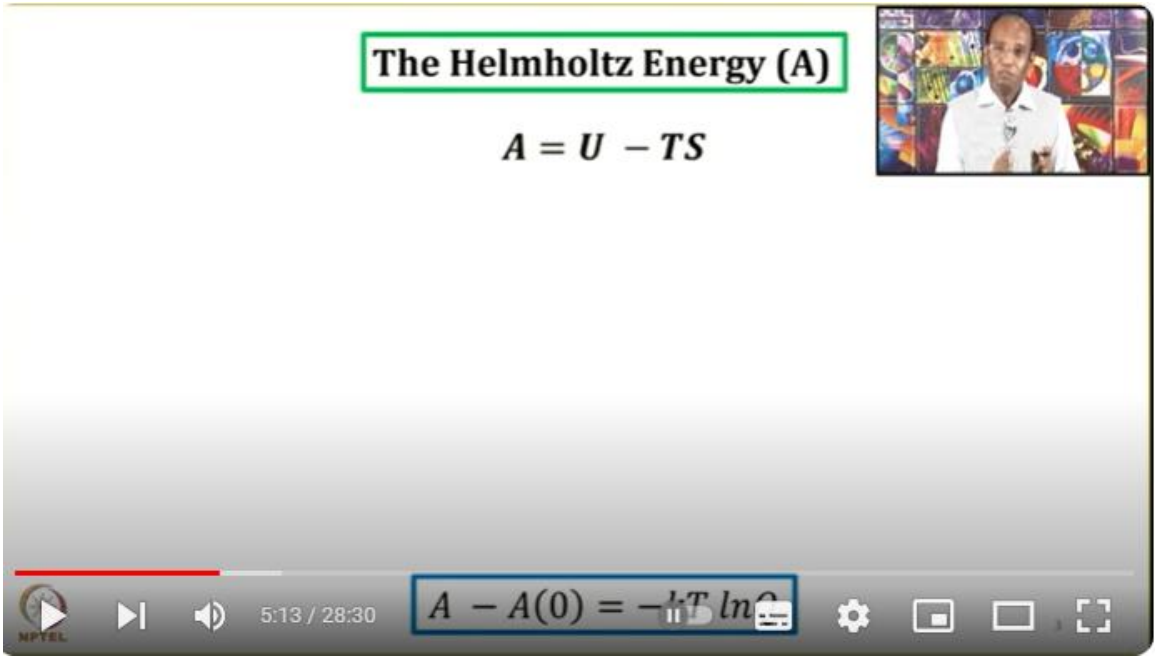

Therefore, A the Helmholtz energy itself becomes system property. Before we derive expression for pressure, we will first derive the expression between Helmholtz energy and canonical partition function because pressure can be connected with Helmholtz energy or changes in Helmholtz energy. We will discuss that soon. But first of all, let us derive a relationship for Helmholtz energy connecting with canonical partition function. We know the definition of A.A is equal to U minus T S. In the beginning, only we have discussed that we cannot ignore the zero point energies. Therefore, all the thermodynamic quantities that I will describe over here will be with reference to zero point values. Zero point values means when the temperature is absolute zero. So, let us see when temperature is absolute zero, can I write A at absolute zero is equal to U at absolute zero because when T is equal to zero, A is equal to U.

Therefore, A at absolute zero is equal to U at absolute zero. Now, I can rewrite this equation as A minus A zero is equal to U minus U(0) minus T S because A zero is equal to U(0). Why I am doing this? Because I want to write the expressions including their values at zero point. Now, we already know the expressions for U minus U(0) and we already know the expression for entropy. What is that expression? Take a look at this previous slide.

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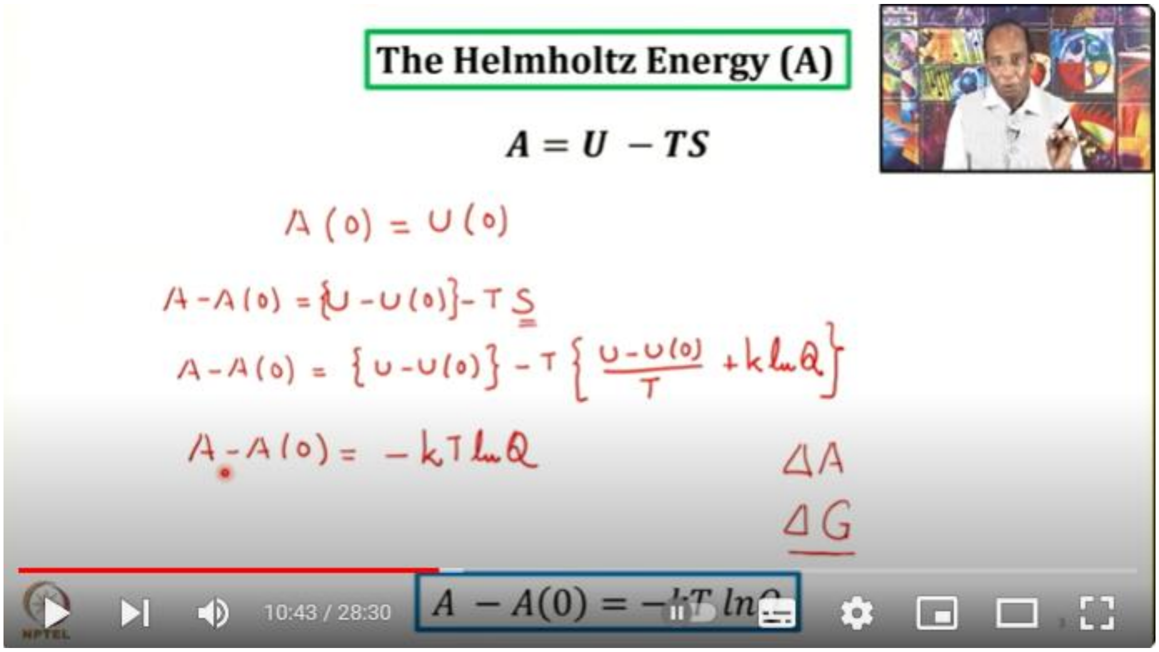

Entropy is given by U minus U (0) by T plus K log Q. I will make use of this expression and proceed further. So, let us now move forward. A minus A zero is equal to I will retain U minus U (0). I will just tell you why I am retaining this so that my derivation further becomes bit easier.

Minus T and entropy is U minus U(0) by T plus K log Q. This is the expression for entropy. Just take a look at back. S is equal to U minus U (0) by T plus K log Q and that is what I substitute over here. S is equal to U minus U (0) by T plus K log Q. Now, if you carefully examine this U minus U(0) and T and T cancel, U minus U(0) will cancel. This will cancel with this. That is why I did not write U minus U (0) in terms of canonical partition function because they are getting cancelled over here. If they cancel here, then let us proceed what we have. A minus A zero is equal to minus K T log Q.

I have an expression for the Helmholtz energy. Now, remaining you know how to then further use it for applications depending upon system to system, you will decide whether you need to put Q is equal to molecular partition function Q raise to the power n or molecular partition function Q raise to the power n divided by n factor. Very simple derivation. The first step was we need to set up the values at absolute zero and then A minus A zero is equal to U minus U (0) minus T n. We simply substituted the expression for entropy and we came up with an expression for A minus A zero is equal to minus K T log Q.

So, this expression suggests that if we can measure experimentally the canonical partition function which we can express in terms of molecular partition function. That means by spectroscopic means we can now get the value for Helmholtz energy by using this expression. Remember that Helmholtz energy is a very important thermodynamic quantity. If you go back to the concepts of chemical thermodynamics, usually the two thermodynamic quantities changes of which were very widely discussed were either delta

A or delta G. Delta A is a measure of maximum work that a system can do. Maximum work that a system can do inclusive of pressure volume work and non-pressure volume work. Whereas, delta G is a measure of maximum non-pressure volume work that you can extract from the system just like an electrical work. Any changes in the value of A can give you information about the maximum work that a system can do. That is the significance of Helmholtz energy or the changes in Helmholtz energy. So continuing the discussion further, delta A is a maximum work that can be drawn from the system inclusive of pressure volume and non-pressure volume.

Delta G is maximum non-pressure volume work. I am not talking about criteria of spontaneity over here. I am only talking about changes in the thermodynamic quantities which reflect on the maximum work which you can draw from a system. Obviously, the questions will be how to get these. Experimentally, how to get these? How do we get delta A? How do we get delta G? If we just look at this expression, A is equal to U minus T S, then delta A will be equal to delta U minus T delta S at constant temperature.

That means, experimentally in order to obtain delta A, you need to get delta U, you need to get delta S.

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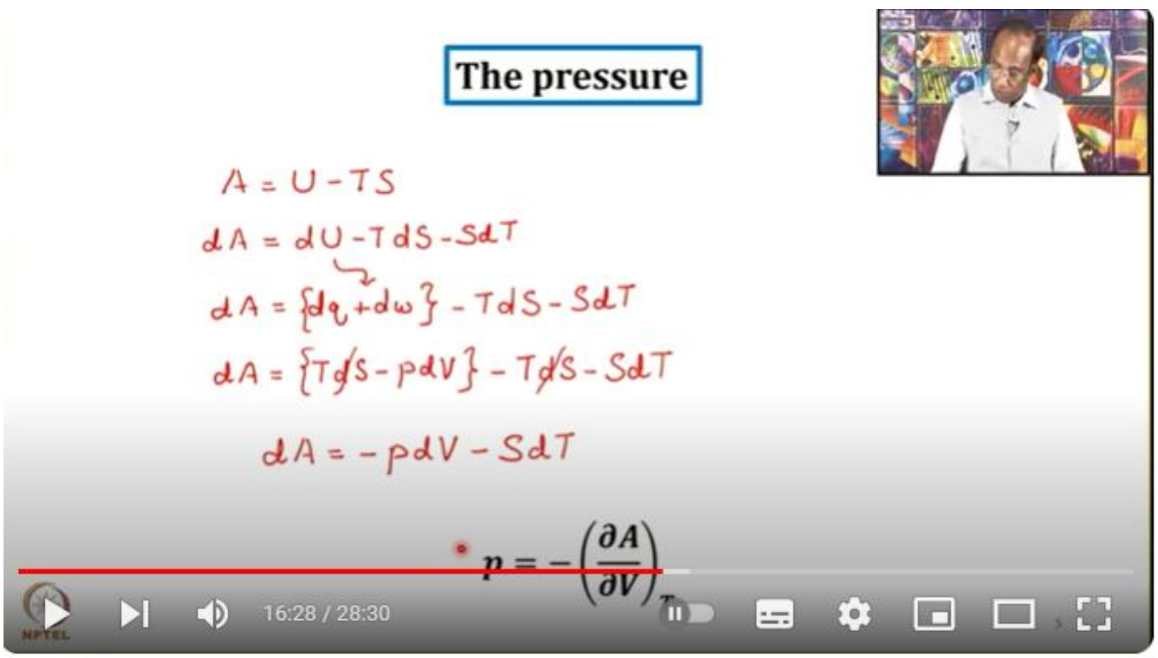

Therefore, you require calorimetry. But here, look at the definition of A, A minus A 0 is equal to minus k T log Q by spectroscopic means also you can get the value of delta A depending upon the conditions. So, therefore, discussion on the Helmholtz energy is very very important.

Let us move further. Our original aim was to connect pressure with the molecular partition function. As shown here, pressure is related to the Helmholtz function by this partial derivative delta A by delta V at constant temperature. First of all, let us try to derive this equation. Very simple. We need to remember the definition of Helmholtz energy or Helmholtz function.

A is equal to U minus T S. Let there be some advancement in the reaction. So, change in Helmholtz energy will be equal to dU minus T delta S at constant temperature. Delta S T dS minus S dT. I am not keeping temperature constant as of now. Proceed further, dA is equal to dU. dU I can write the first law of thermodynamics, dU is equal to dQ plus dW. This is dU minus T dS at constant temperature. So, this is equal to dU minus T dS at constant temperature minus S dT. Let us assume reversibility. dQ is equal to T dS, dW is minus P dV.

Whether you assume reversibility or irreversibility, you remember that we have earlier discussed that dU is equal to T dS minus P dV because U is a state function. Therefore, dU is equal to T dS minus P dV gives rise to this fundamental equation that dU is equal to T dS minus P dV and let us write the remaining minus T dS minus S dT. Remember that we are keeping the composition constant so far. Now, your T dS and T dS cancel. So, I have dA is equal to minus P dV minus S dT.

Now, I have dQ is equal to minus P dV minus S dT. Again, I emphasize that this equation dA is equal to minus P dV minus S dT is very important. Why? Because it allows you to connect changes in Helmholtz function with pressure and with entropy. That means by using this expression, you can obtain pure thermodynamic definitions of pressure and also of entropy. At present, we are interested in pressure.

So, let us you know we keep temperature constant. If you keep temperature constant, then dT is equal to 0 and del A by del V at constant temperature is equal to minus P or in other words, P is equal to minus del A by del V at constant temperature. This is a pure thermodynamic definition of pressure. No assumptions involved over here and we have already connected Helmholtz function with canonical partition function. If you just look back the previous slide, this one A minus A 0 is equal to minus kT log Q.

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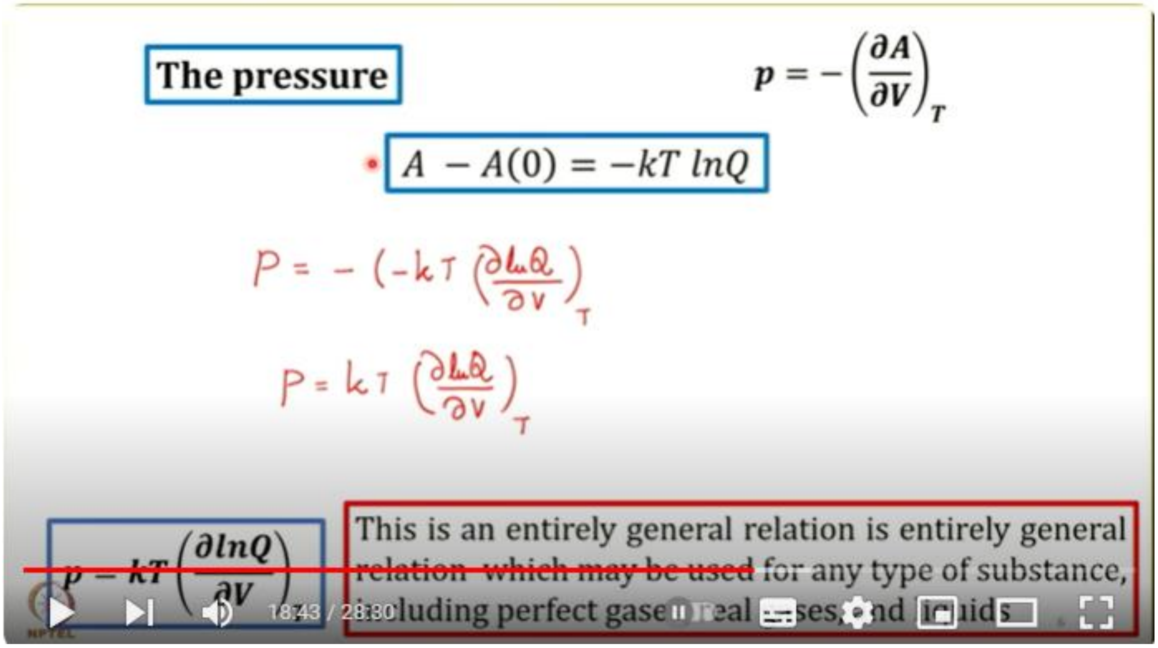

Once we have this information, now we can put in the pressure expression and get the desired result. So, pressure expression we have derived P is equal to minus del A by del V at constant T. Therefore, now substituting this P is equal to minus I will take derivative of this expression. Temperature is constant. So, I will say minus kT del log Q del V at constant temperature.I am taking the derivation of derivative of this. So, this gives me pressure is equal to plus kT del log Q del V at constant temperature. We have an expression for pressure in terms of canonical partition function. P is equal to kT del log Q by del V at constant temperature. As I earlier mentioned, no assumptions involved.
herefore, this is an entirely general relation and it may be used for any substance including perfect gases, real gases and liquids. Only what we need to decide is that Q, what to use for Q, whether Q when can be used for connected with molecular partition function, it is Q raise to the power n or it is Q raise to the power n by n factorial. So, we have now two equations which we can further apply to obtain other useful thermodynamic information. One is the expression for the Helmholtz function and the second is expression for the pressure. If you slightly go back and if I just point out on this expression, if we can derive an expression for pressure in terms of changes in Helmholtz function by keeping temperature constant, then it should also be possible for me to derive an expression for entropy in terms of A by keeping volume constant.

That is the beauty of these thermodynamic transformations that without doing additional experiments, you can obtain one thermodynamic quantity from another by keeping some constants. Now, let us apply the derived expression in showing that for an ideal gas, P v is equal to n R T. When we talk about an ideal gas, let us take the example of monatomic perfect gases. Second thing is that when you want to derive an expression, it is also possible always better to start with a very simple system. You can start with a complicated system also that will allow you to eventually arrive at the same result, but why not start with a simple system.

Let us use that and we start with a monatomic perfect gas. Argon, helium, neon, these are some of the examples. Now, we need to decide what should be used for Q canonical partition function in terms of molecular partition function. Monatomic perfect gas, you cannot distinguish one molecule of the gas from another molecule of the gas. Therefore, the system contains indistinguishable molecules.

Expression to be used will be Q raise to the power n by n factor. And Q molecular partition function, which contribution to be used? Since we are talking about monatomic perfect gas, there will be translational degree of freedom and there will be electronic degree of freedom. But, as we discussed earlier, this electronic energy levels are far apart. Therefore, when we talk about usually at normal temperatures, the electronic contribution to the partition function is usually equal to degeneracy of the ground state and derivative of that number will be 0. So, for the time being, we will ignore that and we will only consider the translational contributions.

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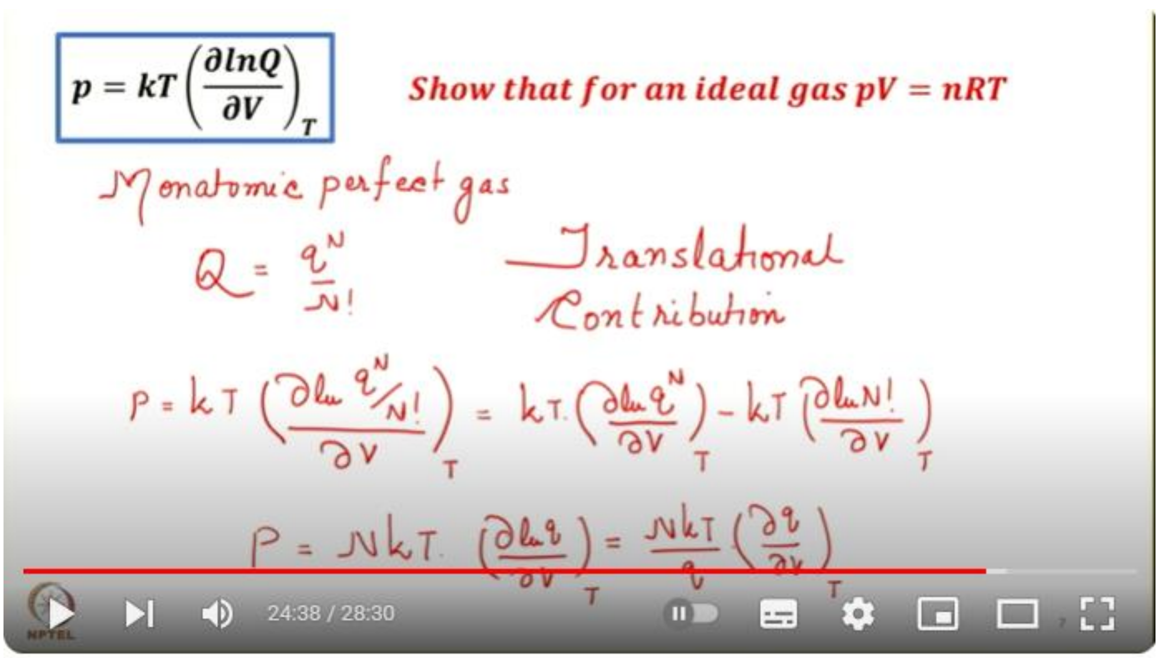

Remember, translational contribution. So, P is equal to k T del log Q raise to the power n by n factor. So, this is the translation by n factorial del V at constant temperature, which is equal to k T, I have del log Q raise to the power n del V at constant temperature and then the next part also I can take, my minus k T del log n factorial del V at constant temperature. Now, concentrate on this one, is a derivative of some number. So, therefore, at constant temperature, this derivative of a constant number is 0. So, we should only then focus on this. Let us focus on this and see what we get. We have P is equal to n k T del log Q del V at constant temperature. That is all we have now. So, now, or I can write this as n k T Q del Q del V at constant temperature, right.

Log Q is 1 by Q d Q by d beta. So, this is equal to 1 by Q del Q by del V at constant T. Let us proceed. What we have now is P is equal to n k T by Q, P is equal to n k T by Q del Q by del V at constant T, del Q at constant temperature. del V at constant T. Q translational is V upon lambda Q. So, therefore, what I have P is equal to n k T Q is equal to V upon lambda Q. Derivative of the partition function with respect to volume at constant temperature, the point to be noted over here, we need to take derivative of this with respect to volume at constant temperature. Lambda, which is equal to lambda is equal to H over 2 pi m k T. Or beta h square by 2 pi m. If temperature is constant, then whole this lambda becomes constant.

So, making use of that fact, this 1 by lambda Q temperature is constant. So, therefore, this lambda becomes constant. So, let us take the derivative of this then. Then derivative with respect to volume at constant temperature is 1 upon lambda Q into del V del V at constant temperature.

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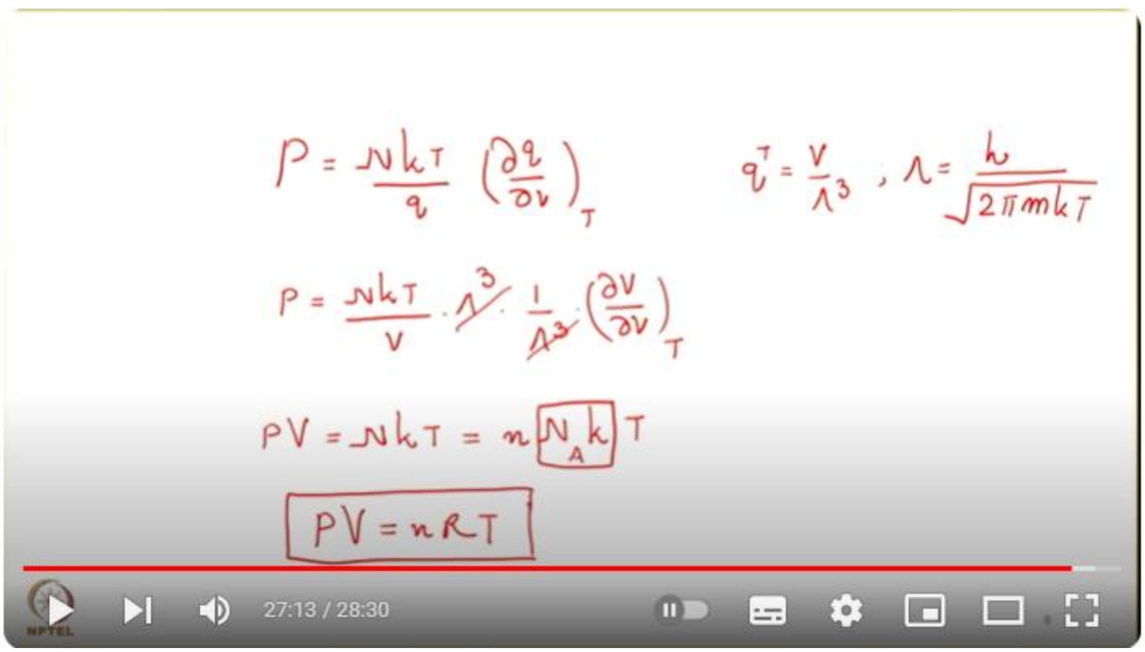

So, your this and this cancel. So, P V is equal to n k T n is equal to small n number of moles into Avogadro constant into Boltzmann constant into temperature Boltzmann constant into Avogadro constant is universal gas constant. So, therefore, P V is equal to n r T. This was our target. This was our goal. So, therefore, from the definition of pressure in terms of canonical partition function by using an ideal gas, monatomic ideal gas, we have now recovered P V is equal to n r T, which is the ideal gas equation from our discussion.

Same way as we will see in the next lecture, we will be able to recover or we will be able to derive same thermodynamic expressions that we have derived in chemical thermodynamics. Now, we will do it based upon the principles of statistical thermodynamics. Thank you very much. .