Fundamentals of Statistical Thermodynamics

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Lecture: 26

The Thermodynamic Functions (Enthalpy)

Welcome back to our continuing efforts on connecting the canonical partition function or molecular partition function with various thermodynamic quantities. After having connected canonical partition function with pressure and Helmholtz function, now in this lecture let us connect the canonical partition function with another very important thermodynamic quantity which is enthalpy. Enthalpy which is denoted by the letter H and the change in enthalpy delta H forms a very important thermodynamic signature because exothermicity of the reaction or endothermicity of the reaction is expressed in terms of the sign of delta H. Not only qualitatively speaking the exothermicity of the reaction or endothermicity of the reaction, the magnitude along with the sign decides the extent of interactions. We have earlier discussed that enthalpy of a reaction can be experimentally determined by use of calorimetry. And now when we derive an expression between the enthalpy and molecular partition function or enthalpy and canonical partition function, we will see that the similar information can also be obtained by spectroscopic methods.

Let us proceed. We will need the earlier derived expressions. For example, U is equal to U (0) minus 1 by q del q by del at constant volume and which is equal to U(0) minus del log q by del β at constant volume. We have also derived expression for pressure del log q by del v at constant temperature.

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Fundamental Relations

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

Pressure
$$p = kT\left(\frac{\partial \ln Q}{\partial V}\right)_T$$

The Enthalpy
$$H = U + pV$$

$$H = U + nRT$$
$$at\ T = 0\ ;\quad H(0) = U(0)$$
$$H - H(0) = \{U - U(0)\} + pV$$

Now it is the term for enthalpy. By the same arguments, we will not forget this thermodynamic quantity or thermodynamic properties at 0, absolute 0. So by using the similar arguments, H is equal to u v u plus pV is equal to n r t. I can use the ideal gas system here because I just want to get an expression for H 0. There is no harm in using the ideal gas equation over here.

So that means at t equal to 0, I can write H (0) is equal to U(0). In that case, I can write this equation as H minus H (0) is equal to u minus U (0) plus pV. What is the advantage of expressing like this? U minus U (0), I already have an expression. For pressure, I already have an expression. So therefore, now it is so easy to get an expression between enthalpy and pressure.

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The Internal Energy

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

Pressure

$$p = kT\left(\frac{\partial \ln Q}{\partial V}\right)_T$$

The Enthalpy

$$H = U + pV$$

$$H - H(0) = U - U(0) + pV$$

$$H - H(0) = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_V + kTV\left(\frac{\partial \ln Q}{\partial V}\right)_T$$

$$H - H(0) = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_V + kTV\left(\frac{\partial \ln Q}{\partial V}\right)_T$$

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Let us see. So we just wrote that H minus H (0) is equal to U minus U (0) plus pV. How do we define enthalpy? Sometimes when such a question is raised, usual answer is enthalpy is equal to heat content, something like that. You know these kind of answers we come across. Pure thermodynamic definition of enthalpy is H is equal to u plus pV where U, p and V are system properties. I am reiterating that this expression H is equal to u plus pV is not just applicable for ideal gas. This is applicable to all the systems in whatever state the system is. Please remember that this internal energy, pressure and volume are system properties. With this knowledge, let us move forward. So H minus H (0)is equal to U minus U(0). U minus U(0) we already have. U minus U (0) is equal to, so U minus U(0) we already know what it is equal to minus del log q del β at constant volume. This is U minus U (0) plus pV, pV we already know. So it becomes k T and v comes here, del log q del v at constant temperature. So very easily we are able to obtain an expression for H minus H (0)which is minus del log q by del β at constant volume plus k T v into partial derivative of log q with respect to volume at constant temperature.

This is a general relation, fundamental relation which connects enthalpy with canonical partition function. And obviously the next part is application of this equation. And when you apply this equation, you need to again decide q canonical partition function, how to be expressed in terms of molecular partition function. Let us apply this concept in calculating the enthalpy of a perfect monatomic gas at a general temperature T. There are two ways of calculating the enthalpy of a perfect monatomic gas at general temperature T. One is a very quick way. We remember the equipartition theorem. By equipartition theorem, the internal energy of a monatomic perfect gas which is or the atoms which are free to move in three dimensions is 3 by 2 nRT. This you remember from the equipartition theorem. Now H minus H (0) is equal to U minus U(0) plus pV.

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Calculate the enthalpy of a perfect monatomic gas at temperature T

By equipartition theorem: $U - U(0) = \frac{3}{2}nRT$

$$H - H(0) = U - U(0) + pV$$

$$H - H(0) = \frac{3}{2}nRT + nRT$$

$$\boxed{H - H(0) = \frac{5}{2}nRT}$$

So H minus H (0) is equal to U minus U (0) is 3 by 2 nRT plus pV is equal to nRT ideal gas. So what we get is H minus H (0) is equal to 5 by 2 nRT. We did not have to do much. We just used equipartition theorem and we just used the ideal gas law, pV is equal to nRT and very quickly we are able to obtain an expression for H minus H (0)or the enthalpy is equal to 5 by 2 nRT. And if we are asked to calculate the enthalpy of a perfect monatomic gas at a general temperature T exclusively by using this equation, then the process is little lengthier and in order to derive the same expression, you will see that we get the same result.

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Calculate the enthalpy of a perfect monatomic gas at t[...]

$$H - H(0) = -\left(\frac{\partial lnQ}{\partial \beta}\right)_V + kTV\left(\frac{\partial lnQ}{\partial V}\right)_T$$

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

$$H - H(0) = -\left(\frac{\partial \ln q^N/N!}{\partial \beta}\right)_V + kTV\left(\frac{\partial \ln q^N/N!}{\partial V}\right)_T$$

$$H - H(0) = \left\{-N\left(\frac{\partial \ln q}{\partial \beta}\right)_V + \left(\frac{\partial \ln N!}{\partial \beta}\right)_V\right\} + kTV\left\{N\left(\frac{\partial \ln q}{\partial V}\right)_T - \left(\frac{\partial \ln N!}{\partial V}\right)_T\right\}$$

We will have to decide again an expression for Q to be used and for that we look into the problem statement, the question statement which says apply this to perfect monatomic gas. So by the same arguments monatomic gas, single atoms, translational and electronic, electronic we are not going to consider here. Only translational we are going to consider. Therefore, the partition function that we will use is that for the translational contribution. But the first thing to recognize here that Q is to be used in terms of molecular partition function which is q raised to the power n by n factorial. Let us start proceeding. So H minus H (0) is equal to minus del log Q raised to the power n by n factorial del β at constant volume plus K T v del log Q raised to the power n by n factorial with respect to del v at constant temperature. What are the constraints? That is important. Further expand this H minus H (0) is equal to minus n del log q del β at constant volume plus del log n factorial del β at constant volume. This is the first one.

The second term is plus K T v and inside we have n del log q del v at constant temperature minus del log n factorial with respect to volume at constant temperature. I have just expanded in both cases. This n is coming over here and negative sign is already there del log q by with respect to del β at constant volume and since n is in the denominator minus minus becomes positive therefore, partial derivative of log n factorial with respect to β at constant volume. Similarly, in the second one K T v and del log q by del v at constant T minus partial derivative of n factorial at constant temperature with respect to volume at constant temperature. It is easy to recognize that these are constant numbers and this log n factorial, log n factorial their derivatives will become 0.

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Calculate the enthalpy of a perfect monatomic gas at t

$$H - H(0) = -\left(\frac{\partial lnQ}{\partial \beta}\right)_V + kTV\left(\frac{\partial lnQ}{\partial V}\right)_T$$

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

$$H - H(0) = -\left(\frac{\partial ln \, q^N/N!}{\partial \beta}\right)_V + kTV\left(\frac{\partial ln \, q^N/N!}{\partial V}\right)_T$$

$$H - H(0) = \left\{-N\left(\frac{\partial ln \, q}{\partial \beta}\right)_V + \left(\frac{\partial ln \, N!}{\partial \beta}\right)_V\right\} + kTV\left\{N\left(\frac{\partial ln \, q}{\partial V}\right)_T - \left(\frac{\partial ln \, N!}{\partial V}\right)_T\right\}$$

So, we can simply ignore this. We need to consider only this part and this part because the other parts are 0. Let us carry this forward. So, what I will write is now H minus H (0) is equal to let us bring back from the previous one. Minus n del log Q by del β at constant volume minus n del log Q del β at constant volume.

This is 1 and the second one was plus K n K T v plus n K T v and we have derivative of log Q with respect to volume at constant temperature. Derivative of log Q at constant volume with respect to temperature. Let us double check that. First is minus n del log Q del β at constant volume minus n del log Q del β at constant volume. Very fine. Second one is n K T v del log Q del v at constant temperature. n K T v del log Q del v at constant temperature. Let us proceed further. H minus H (0)is equal to minus n by Q del Q del β at constant volume. Fine. Plus n K T v by Q del Q del v at constant temperature and since we are now discussing for monatomic perfect gas, we will consider only translational contribution to molecular partition function. That means Q is equal to Q T is equal to v upon lambda Q. The particle or the gas atoms which are free to move in three dimensions. Now let us do that. H minus H (0) is equal to minus n by Q. Q is v upon lambda Q into derivative of Q with respect to β. That means v upon lambda Q with respect to β at constant volume plus n K T v Q is equal to v upon lambda Q and we have del v upon lambda Q with respect to volume at constant temperature. Fine. Let us continue. H minus H (0)is equal to minus n upon v into lambda Q.

Volume is constant. So I can take volume out and then inside I have del del β of 1 by lambda Q at constant volume plus v and v cancel, n K T of course I have lambda Q and since temperature is constant this lambda Q comes out and del v del v also cancel. Here also this lambda Q and lambda Q will cancel out. Let us take it forward and write H minus H 0. So I have H minus H (0)is equal to minus this v and v I can cancel now minus n lambda Q minus n lambda Q into derivative of 1 by lambda Q with respect to β del del

β of 1 by lambda Q del del β of 1 by lambda Q at constant volume plus what I had was n K T n K T.

$$H - H(0) = -N\left(\frac{\partial \ln q}{\partial \beta}\right)_V + NkTV\left(\frac{\partial \ln q}{\partial V}\right)_T$$

$$H - H(0) = -\frac{N}{q}\left(\frac{\partial q}{\partial \beta}\right)_V + \frac{NkTV}{q}\left(\frac{\partial q}{\partial V}\right)_T$$

$$q = q^T = \frac{V}{\Lambda^3}$$

$$H - H(0) = -\frac{N}{V}\cdot\Lambda^3\cdot\left(\frac{\partial V/\Lambda^3}{\partial \beta}\right)_V + \frac{NkTV}{V}\cdot\Lambda^3\cdot\left(\frac{\partial V/\Lambda^3}{\partial V}\right)_T$$

$$H - H(0) = -\frac{N}{V}\cdot\Lambda^3\cdot V\left\{\frac{\partial}{\partial \beta}\cdot\frac{1}{\Lambda^3}\right\} + \frac{NkT\Lambda^3}{\Lambda^3}$$

We proceed from here. So what we get? H minus H (0) is equal to minus n lambda Q derivative of lambda Q with respect to β lambda depends upon β. Therefore we need to perform this differentiation which will be minus 3 by lambda 4 into derivative of del del β of lambda at constant volume plus n K T. What do we have now? H minus H (0) is equal to 3 n by lambda into what is lambda? β is equal to β H square by 2 pi m square root. Let us take derivative of this with respect to β. It will be 1 by 2 β H square 2 pi m minus 1 by 2 into H square by 2 pi m and then derivative of β with respect to β plus n K T.

We are now closer to the result. I have H minus H (0) is equal to 3 n by 2 lambda into β H square over 2 pi m raise to the power minus 1 by 2 into. Now I will do some very small trick. I will multiply by β H square over 2 pi m and I will divide by β. Why I am doing this is very simple now that these two together is lambda. So H minus H (0)is equal to then 3 n by 2 β because lambda lambda cancel plus n K T β is equal to 1 over K T that means 3 by 2 n K T plus n K T which is equal to 5 by 2 n K T.
Very simple just mathematical manipulations. We have obtained H minus H (0) is equal to 5 by 2 n K T. Let us carry it forward. So we have H minus H (0) is equal to 5 by 2 n K T.

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$$H - H(0) = -N\Lambda^3 \left\{ \frac{\partial}{\partial \beta} \cdot \frac{1}{\Lambda^3} \right\}_V + NkT$$

$$H - H(0) = -N\Lambda^3 \frac{(-3)}{\Lambda^4} \cdot \left(\frac{\partial \Lambda}{\partial \beta} \right)_V + NkT$$

$$H - H(0) = \frac{3N}{\Lambda} \cdot \frac{1}{2} \cdot \left(\frac{\beta h^2}{2\pi m} \right)^{-\frac{1}{2}} \cdot \frac{h^2}{2\pi m} + NkT \qquad \Lambda = \left(\frac{\beta h^2}{2\pi m} \right)^{\frac{1}{2}}$$

$$H - H(0) = \frac{3N}{2\Lambda} \left[\left(\frac{\beta h^2}{2\pi m} \right)^{-\frac{1}{2}} \cdot \frac{\beta h^2}{2\pi m} \right] \frac{1}{\beta} + NkT$$

$$H - H(0) = \frac{3N}{2\beta} + NkT = \frac{3}{2}NkT + NkT = \frac{5}{2}NkT$$

H minus H (0) is equal to 5 by 2. This I will write n times Avogadro constant into Boltzmann constant into temperature and then I will again highlight that the Boltzmann constant into Avogadro constant is equal to gas constant. So what we have H minus H (0) is equal to 5 by 2 n RT. This is the same result that we obtained by using equipartition theorem. Remember the previous discussion. When we use the equipartition theorem H is equal to U plus PV we converted that to H minus H 0 is equal to U minus U(0) plus n RT and easily got an expression that H minus H 0 is equal to 5 by 2 n RT.

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$$H - H(0) = \frac{5}{2} NkT$$

$$H - H(0) = \frac{5}{2} \cdot n \boxed{N_A k} T$$

$$\boxed{H - H(0) = \frac{5}{2} nRT}$$

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But then we decided that let us proceed exclusively by using canonical partition function. We connected canonical partition function with the molecular partition function and then started working by taking the molecular partition function equal to translational contribution because an atom can only give translational contribution. Electronic contribution we did not consider again reiterating that electronic contribution at normal temperature is usually equal to degeneracy of the ground state and when you take a derivative of that it becomes 0. So therefore, that does not contribute. Therefore, we need to take only translational contribution unless the temperature is very very high.

So both by using equipartition theorem and by using explicit canonical partition function we obtained the same expression that is H minus H (0)is equal to 5 by 2 n RT. Now we have this expression H minus H (0) is equal to 5 by 2 n RT. We can further apply this. One simple quick application is to derive an expression for heat capacity. C_p heat capacity at constant pressure is del H del T at constant pressure.

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The handwritten content on the slide reads:

$$H - H(0) = \frac{5}{2} N k T$$

$$H - H(0) = \frac{5}{2} \cdot n \boxed{N_A k} T$$

$$\boxed{H - H(0) = \frac{5}{2} n R T}$$

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P = \frac{5}{2} n R$$

$$C_{p,m} = \frac{5}{2} R$$

Monatomic Perfect gas

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

$$C_p - C_v = n R$$

$$C_p = \frac{3}{2} n R + n R$$

$$C_p = \frac{5}{2} n R$$

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 Apply this. So take the derivative of this. This is simply 5 by 2 n R. This is an expected result because we were discussing for a monatomic perfect gas. This is the system we have been discussing. Monatomic perfect gas. For monatomic perfect gas you know that Cv is equal to 3 by 2 n R and C_p minus C_v is equal to n R. Therefore, C_p is equal to 3 by 2 n R plus n R. Therefore, C_p is equal to 5 by 2 n R. Same result. Always remember to interpret, how to interpret different notations. For example, if I consume n here then I will write C_{pm} is equal to 5 by 2 R. I have divided both sides by n so that now I express this thermodynamic quantity heat capacity in terms of molar quantity because you don't need to worry about the size of the system if you express in terms of molar quantities.

So do not confuse when you come across C_p or you come across C_{pm}. C_p is the heat capacity for a given size of a system. C_{pm} is the heat capacity for one mole of the system. Therefore, always you should be able to interpret whether we are given C_p or we are given C_{pm} and accordingly you apply these expressions further. So in this particular lecture what we have done is that by using UK partition theorem or by using exclusively molecular partition function on or canonical partition function we have got the expression for enthalpy and then we showed that the same result is obtained whether you use equipartition theorem or you use exclusive these equations connecting enthalpy and canonical partition function H minus H(0) is equal to 5 by 2 nRT.

 Remember that whatever we have been discussing so far is for monatomic perfect gas. When the system is not perfect, when the system is not monatomic perfect gas, when the system is diatomic perfect gas even if you include the perfect behavior for diatomic systems then the other contributions will come in. For example, for a diatomic molecule in addition to translational contribution you will also have rotational contribution and vibrational

contribution. So therefore, be careful that what contribution to include when applying certain expressions to certain systems. We will discuss numerical problems where we will cover all these aspects. Thank you very much. Thank you.