Fundamentals of Statistical Thermodynamics

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Lecture: 27

The Thermodynamic Functions (The Gibbs Energy)

Welcome back. We have been discussing thermodynamic functions in terms of canonical partition function and hence molecular partition function. The various thermodynamic functions that we have discussed so far include Helmholtz function, enthalpy, pressure, entropy. Today we are going to discuss another very important thermodynamic function that is the Gibbs function or Gibbs energy. In chemistry, whenever we talk about spontaneity of a process, the first question, the first answer rather that spontaneously comes is that a process will take place spontaneously if the value of delta G at constant temperature and pressure is negative. Please note, if we just say that the value of delta G should be negative, then the process is spontaneous, then that answer is incomplete.

The constraints must be specified that is for a spontaneous process, delta G at constant temperature and pressure should be negative. Similarly, whenever we talk about the spontaneity in terms of properties of system alone, we need to provide the constraints. For example, if we talk in terms of Helmholtz function, delta A at constant temperature and volume should be negative for spontaneous process. So therefore, it is important to specify the constraints.

Today we talk about Gibbs energy or Gibbs function. How do we define Gibbs energy? The answer to that comes here that Gibbs energy is defined or Gibbs function is defined in terms of enthalpy and entropy. If someone asks you a question, what is Gibbs energy or what is Gibbs function, the straight answer is that Gibbs function or Gibbs energy is G is equal to H minus dS. As usual, this G H or S, these are system properties. Now, sometimes we transform an equation into another form, which is more useful in the sense that the properties that we want to discuss or the equations that we want to establish become easier. For example, here when I say G is equal to H minus dS, I can write H equal to U plus PV. This is for H minus dS is already there. So, now the new form of this is U minus dS plus PV. I am just rearranging it, so that we can recognize that the value of H is equal to H minus dS plus PV. So, I can now define G also as G equal to A plus PV.

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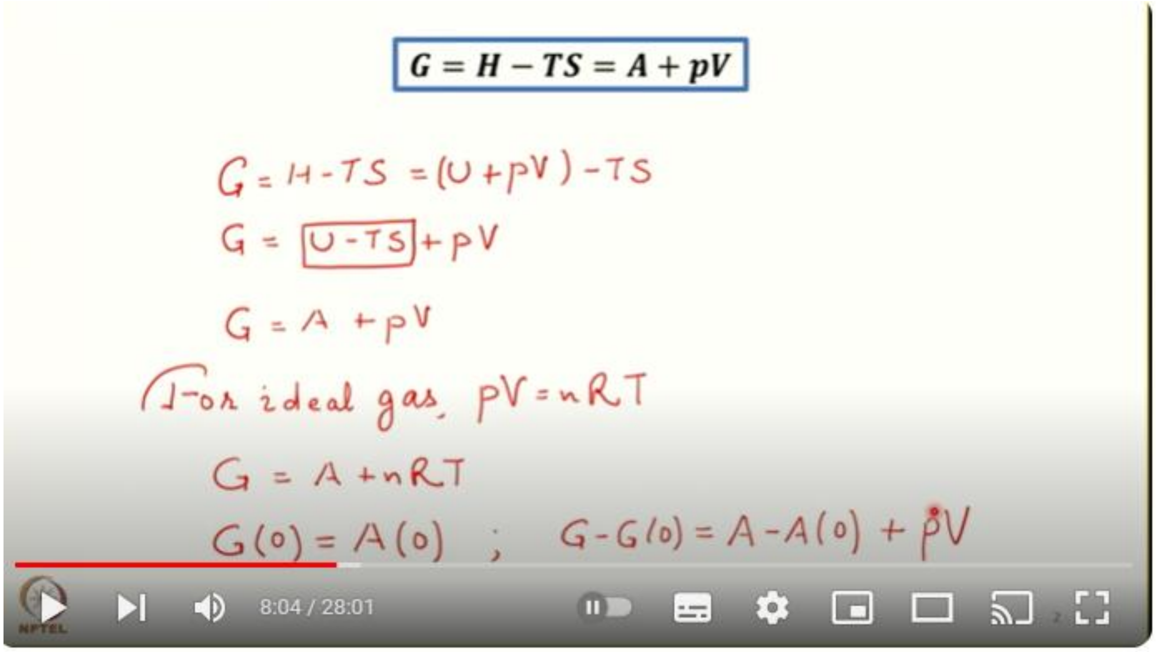

$$\boxed{G = H - TS = A + pV}$$

$$G = H - TS = (U + pV) - TS$$

$$G = \boxed{U - TS} + pV$$

$$G = A + pV$$

For ideal gas, $pV = nRT$

$$G = A + nRT$$

$$G(0) = A(0) \quad ; \quad G - G(0) = A - A(0) + pV$$

We have now Gibbs function in terms of Helmholtz function and pressure and volume. Keep in mind that the changes in Gibbs function and the changes in Helmholtz function provide very important information. Revisiting that the change in Helmholtz function is a measure of maximum work that you can draw from a system and the change in Gibbs function is a measure of maximum non-pressure volume work that you can draw from a system. Here, you have an expression which can connect both delta G and delta A and the connectors are these changes in pressure and volume. Now, on the same lines when we want to connect with the canonical partition function, we usually will refer to the zero-point value. For ideal system, for ideal gas, PV is equal to nRT. So, therefore, I can write G is equal to A plus PV. Plus nRT or G at absolute zero is equal to A at absolute zero. Why did I do this? Because as I have always been saying that when you want to derive certain equations, you may take a route which gives you that equation easily and in this case, if I use the properties of ideal gas, I am able to establish this that G zero is equal to A zero. That means, now I can write another equation that is G minus G zero is equal to A at absolute zero A minus A zero plus PV.

I am just connecting this with this G and look at when I write with reference to their zero point values. Now, what I need is if I want to write this and I want to now connect this G with canonical partition function, then I need an expression for pressure and I need an expression for volume. Remember that we already have derived an expression which connects A with canonical partition function and which connects P with canonical partition function and what are those equations? Let us take a look at it. A minus A zero, we have already derived is equal to minus k T log Q. K is Boltzmann constant, T is temperature in Kelvin and Q is canonical partition function.

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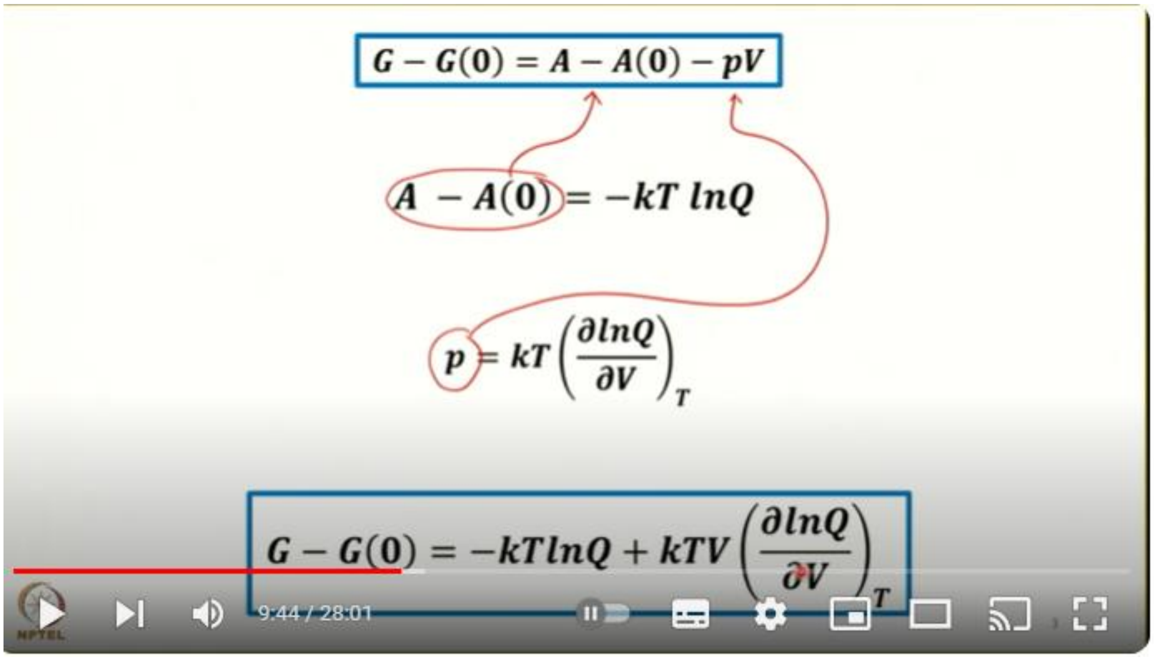

$$\boxed{G - G(0) = A - A(0) - pV}$$

$$A - A(0) = -kT\ lnQ$$

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

$$\boxed{G - G(0) = -kTlnQ + kTV\left(\frac{\partial lnQ}{\partial V}\right)_T}$$

Now, what I need is for we have also derived an expression which connects pressure with canonical partition function. Here pressure is equal to k T into partial derivative of log Q with respect to volume at constant temperature. So, now if you substitute A minus A zero value over here, then you will get an expression and pressure expression over here. What you get? You get is this expression. G minus G zero is equal to minus k T log Q plus k T V.

This V volume comes from here into partial derivative of log q with respect to volume at constant temperature. So, here we have expression which connects G with capital Q which is canonical partition function and hence, for a given system we need to establish the pressure and pressure of the system. Whether the system consists of distinguishable molecules or indistinguishable molecules and then we have to use this expression accordingly. Now, as I said that A and G, they are very useful thermodynamic quantities because not only delta A and delta G give infinite pressure information about maximum work or non-pressure volume maximum work available from the system, but the changes in A and the changes in G can give you lot of information. For example, let us have a short discussion.

If I start with A, A is a Helmholtz-Pascal function or Helmholtz energy, A is equal to U minus T s. So, I have d A is equal to d U minus T d s minus S d T or d A is equal to d U is equal to T d s minus S d T or d U minus P d V minus T d s minus S d T. This T d s minus P d V comes from d U. T d s, T d s cancel. So, I have d A is equal to minus P d V minus S d T.

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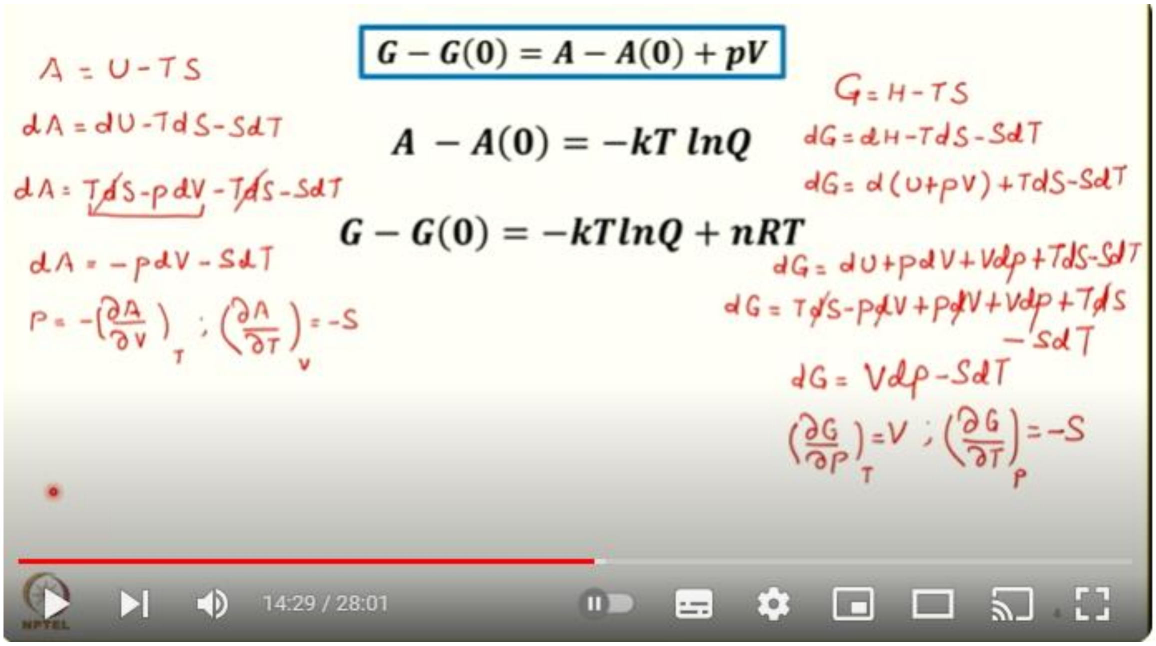

$$\boxed{G - G(0) = A - A(0) + pV}$$

$$A = U - TS$$

$$dA = dU - TdS - SdT$$

$$dA = \underbrace{T\cancel{d}S - pdV} - T\cancel{d}S - SdT$$

$$dA = -pdV - SdT$$

$$P = -\left(\frac{\partial A}{\partial V}\right)_T ; \left(\frac{\partial A}{\partial T}\right)_V = -S$$

$$A - A(0) = -kT\,lnQ$$

$$G - G(0) = -kT\,lnQ + nRT$$

$$G = H - TS$$

$$dG = dH - TdS - SdT$$

$$dG = d(U + pV) + TdS - SdT$$

$$dG = dU + pdV + Vdp + TdS - SdT$$

$$dG = T\cancel{d}S - p\cancel{d}V + p\cancel{d}V + Vdp + T\cancel{d}S - SdT$$

$$dG = Vdp - SdT$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V ; \left(\frac{\partial G}{\partial T}\right)_P = -S$$

As discussed in the previous lecture probably that from this equation, now we derive two further equations. One is that pressure is equal to minus partial derivative of A with respect to volume at constant temperature. This is one definition and the second derivation is partial derivative of A with respect to temperature at constant volume is minus S. Then, if I start with G, G is equal to H minus T S. For some advancement, d G is equal to d H minus T d s minus S d T and we keep on further expanding d H H is equal to U plus P V plus T d s minus S d T.

So, this is one definition. Extend it further. I have d G is equal to d U plus P d V plus V d P plus T d s minus S d T. No problem. So, d G is equal to now in place of d U, I will have I will use fundamental equation T d s minus P d V plus P d V plus V d P plus T d s minus S d T.

You have T d s cancelling with T d s, P d V cancelling with P d V. So, I have dG is equal to V d P minus S d T. Therefore, pressure derivative of Gibbs function at constant temperature is volume and temperature derivative of Gibbs function at constant pressure is minus S.

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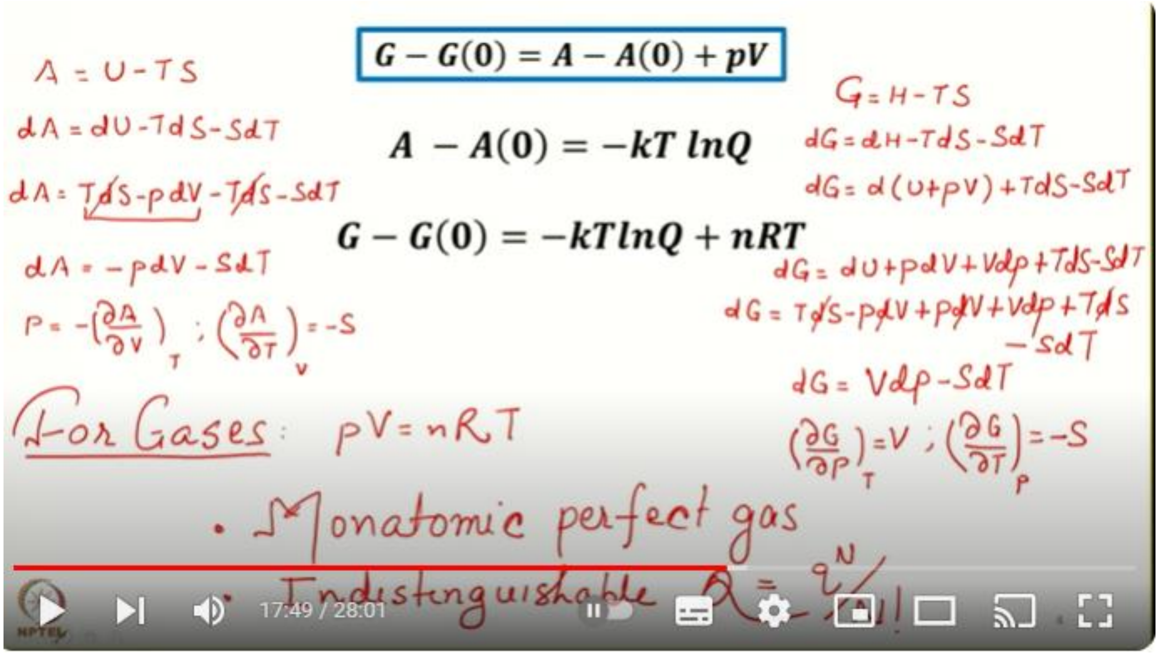

$$\boxed{G - G(0) = A - A(0) + pV}$$

$$A - A(0) = -kT\ln Q$$

$$G - G(0) = -kT\ln Q + nRT$$

$A = U - TS$

$dA = dU - TdS - SdT$

$dA = \underbrace{\cancel{TdS} - pdV}_{} - \cancel{TdS} - SdT$

$dA = -pdV - SdT$

$p = -\left(\frac{\partial A}{\partial V}\right)_T ; \left(\frac{\partial A}{\partial T}\right)_V = -S$

$G = H - TS$

$dG = dH - TdS - SdT$

$dG = d(U + pV) + TdS - SdT$

$dG = dU + pdV + Vdp + TdS - SdT$

$dG = \cancel{TdS} - \cancel{pdV} + \cancel{pdV} + Vdp + \cancel{TdS} - SdT$

$dG = Vdp - SdT$

$\left(\frac{\partial G}{\partial p}\right)_T = V ; \left(\frac{\partial G}{\partial T}\right)_p = -S$

For Gases: $pV = nRT$

- Monatomic perfect gas
- Indistinguishable $Q = q^N/N!$

As you will notice that such equations allow you to obtain pure thermodynamic definitions of some quantities, thermodynamic quantities in terms of different derivatives. For example, look at here.

The entropy can be defined as temperature derivative of Helmholtz function at constant volume and at the same time entropy can also be defined as temperature derivative of Gibbs function at constant pressure. So, therefore, when we have expressions connecting Helmholtz function and expressions connecting Gibbs function with canonical partition function, then what we have is then we can also obtain entropy, volume and some other thermodynamic quantities in terms of canonical partition function through such correlations. Now, if we selectively consider only gas, let us say we selectively choose only gases. For gases, P V is equal to N R T. When I write P V is equal to N R T, that means I am assuming that the gas under consideration is an ideal gas.

So, therefore, if I choose to work with ideal gas and consider this equation, A minus A(0) is minus k T log q and I substitute minus k T log q and then I have plus N R T in place of P V I am using N R T and further if I choose to work with monatomic perfect gas, then as we have been discussing recently that we need not consider rotational and vibrational contributions and for the sake of discussion, we can also exclude electronic contributions under normal conditions of temperature. And secondly, indistinguishable molecules, indistinguishable molecules or atoms. And then, we have to consider rotational and vibrational contributions. And for the sake of discussion, we can also exclude electronic contributions under normal conditions of temperature. And secondly, indistinguishable molecules, indistinguishable molecules or atoms.

And then, we have to consider rotational and vibrational contributions. That means, I will write q is equal to q raised to the power n over n factorial. These we need to now consider. So, therefore, for discussion ahead, I will choose this equation and then use q is equal to q raised to the power n by n factorial and then proceed further. Let us carry it forward. That is, G minus G(0) is equal to minus K T log q plus n R T minus K T log q plus n R T. And we will use this equation. So, we have to consider rotational contributions. So, q is equal to q raised to the power n over n factorial indistinguishable molecules.

Let us proceed. G minus G(0) is equal to minus K T log q raised to the power n over n factorial plus n R T. Let us continue G minus G_0 is equal to minus K T log q raise to the power n plus K T log n factorial because n factorial is in the denominator plus n R T. G minus G(0) is equal to minus n R T. Now, K T log q plus K T I will use Stirling approximation log n factorial is n log n minus n plus n R T. Proceeding further G minus G (0) n K is equal to n R we have discussed many times n R T log q plus n R T log n minus n R T plus n R T.

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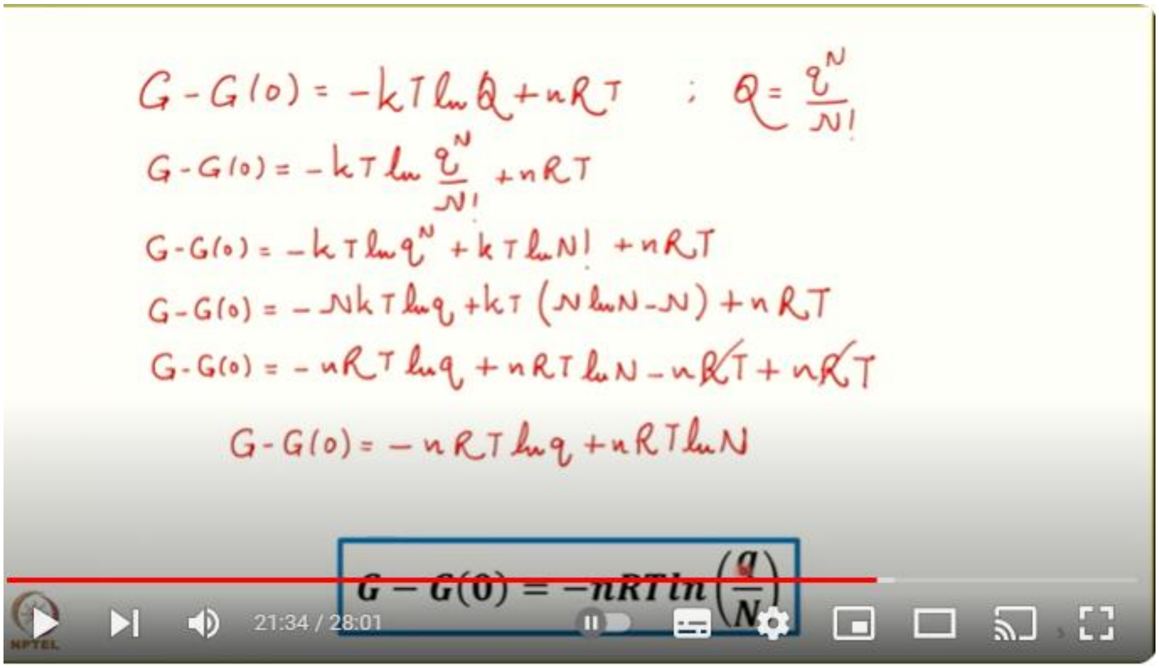

$$G - G(0) = -kT\ln Q + nRT \quad ; \quad Q = \frac{q^N}{N!}$$

$$G - G(0) = -kT\ln\frac{q^N}{N!} + nRT$$

$$G - G(0) = -kT\ln q^N + kT\ln N! + nRT$$

$$G - G(0) = -NkT\ln q + kT(N\ln N - N) + nRT$$

$$G - G(0) = -nRT\ln q + nRT\ln N - n\cancel{R}T + n\cancel{R}T$$

$$G - G(0) = -nRT\ln q + nRT\ln N$$

$$\boxed{G - G(0) = -nRT\ln\left(\frac{q}{N}\right)}$$

This n R T n R T go. So, therefore, I have G minus G (0) is equal to minus n R T log q raise to the power n plus n R T. So, G minus G (0) is equal to minus n R T log q plus n R T log n. I will take minus n R T as common and once you take that as common you have this expression G minus G (0) is equal to minus n R T log q by n. It is worth noticing here that we started with Gibbs function in terms of canonical partition function and when we end up it connecting with the molecular partition function what we have in the expressions is number of moles gas constant temperature molecular partition function and the total number of molecules atoms or particles. Now, remember that this is the molecular partition function.

Since, we have decided to initially apply it to monatomic perfect gas therefore, this molecular partition function is equal to the translational contribution to the partition function. This obtained equation into another how is that? So, I have G let me write G by n minus G by n G (0) by n is equal to minus R T log q over n into n A. What I have done is I have divided both the sides by the number of moles and I have converted the total number of particles or total number of molecules as number of moles into Avogadro constant. So, G by n is the molar Gibbs function minus molar Gibbs function at absolute 0 minus is equal to minus molar Gibbs function at absolute minus R T log q_m by Avogadro constant. It is much easier if we deal with the molar properties because then we do not need to worry about the size of the system.

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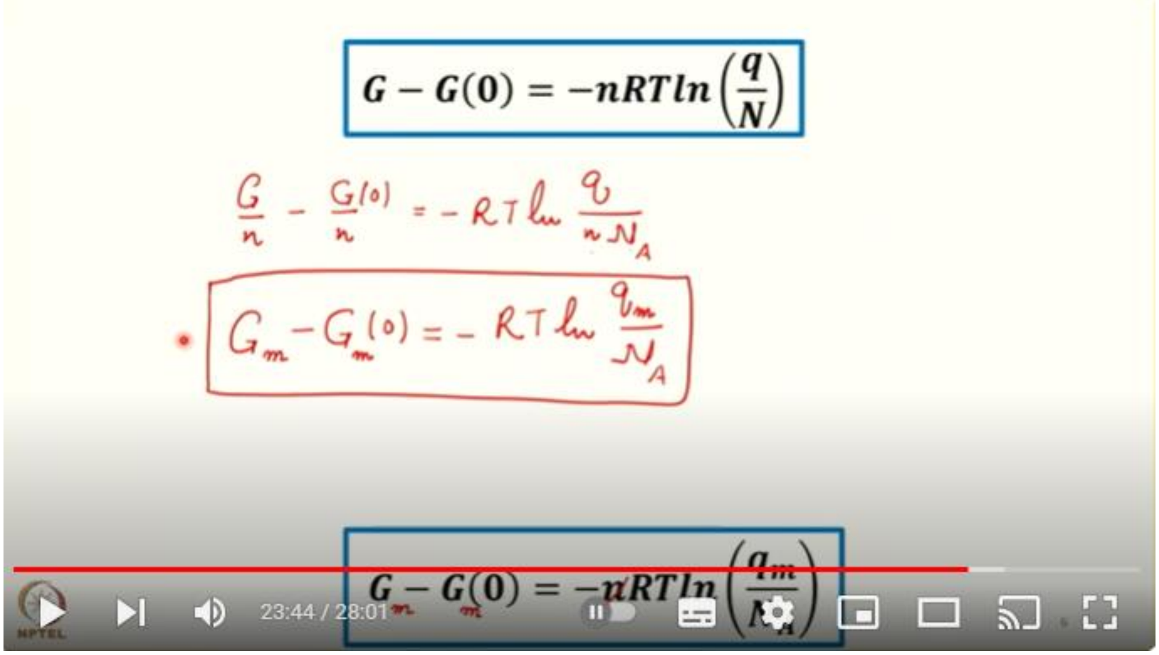

$$\boxed{G - G(0) = -nRT\ln\left(\frac{q}{N}\right)}$$

$$\frac{G}{n} - \frac{G(0)}{n} = -RT\ln\frac{q}{nN_A}$$

$$\boxed{G_m - G_m(0) = -RT\ln\frac{q_m}{N_A}}$$

$$\boxed{G_m - G_m(0) = -nRT\ln\left(\frac{q_m}{N_A}\right)}$$

Therefore, the equation which connects the molar Gibbs function with molar partition function is G_m minus G_m^0 or G_m^0 is equal to minus R T log q_m by n A. If you want you can leave in terms of the actual size of the Gibbs function and as I said sometimes it becomes very helpful when you compare the molar properties and then you divide by n you can discuss in terms of the molar Gibbs function. So, what we have is now G_m molar Gibbs function is molar Gibbs function G_m minus G_m^0 is equal to minus R T log q_M by n A and standard states we have discussed many times. What is a standard state? Substance should be pure, temperature can be any, pressure has to be 1 bar. In standard state Gibbs function in standard state molar Gibbs function will be written like this.

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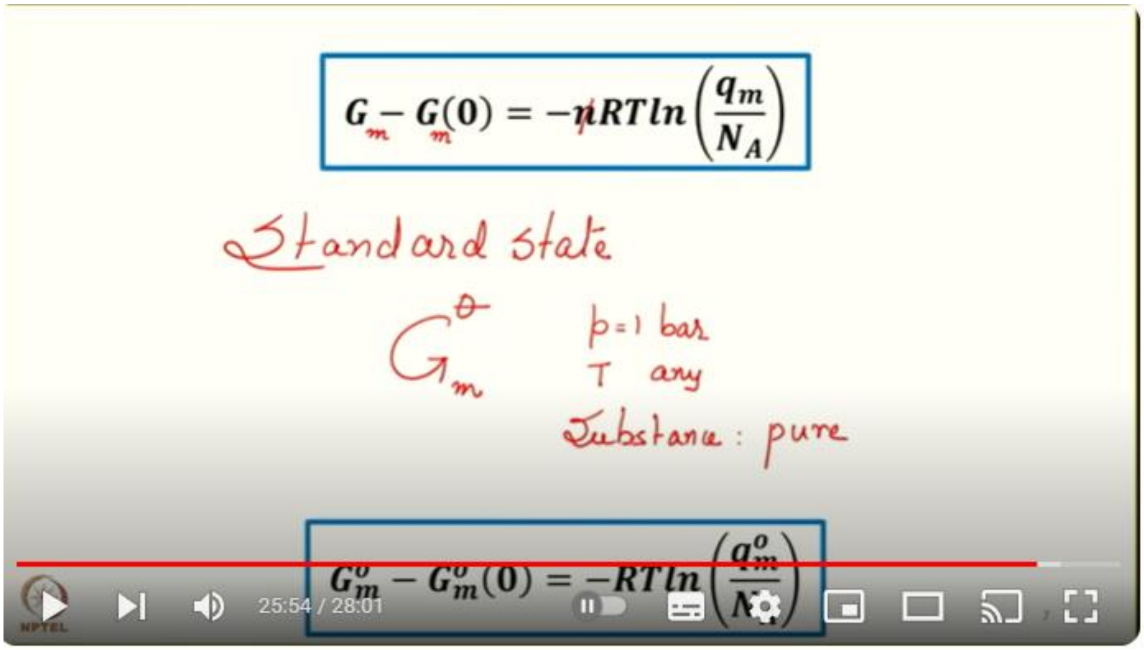

$$\boxed{G_m - G_m(0) = -\cancel{n}RT\ln\left(\frac{q_m}{N_A}\right)}$$

Standard state

G_m^θ

p = 1 bar

T any

Substance : pure

$$\boxed{G_m^o - G_m^o(0) = -RT\ln\left(\frac{q_m^o}{N_A}\right)}$$

Pressure is equal to 1 bar, temperature any, substance in pure form and if I apply this condition the new equation that I develop now in terms of standard state is G_m^0minus G_m^0 at 0 is equal to minus R T log q_M^0 by n A. Just note down these differences I have which I have put naught naught naught that means pressure is 1 bar. What is the significance of putting this condition of standard state over here is that when I utilize this equation when I use this equations in future to connect with other thermodynamic properties then it becomes easy. For example, it becomes very important to understand the meaning of delta G^0 and the meaning of delta G always distinguish between delta G and delta G^0. Delta G^0 is connected to equilibrium constant by minus R T log K.

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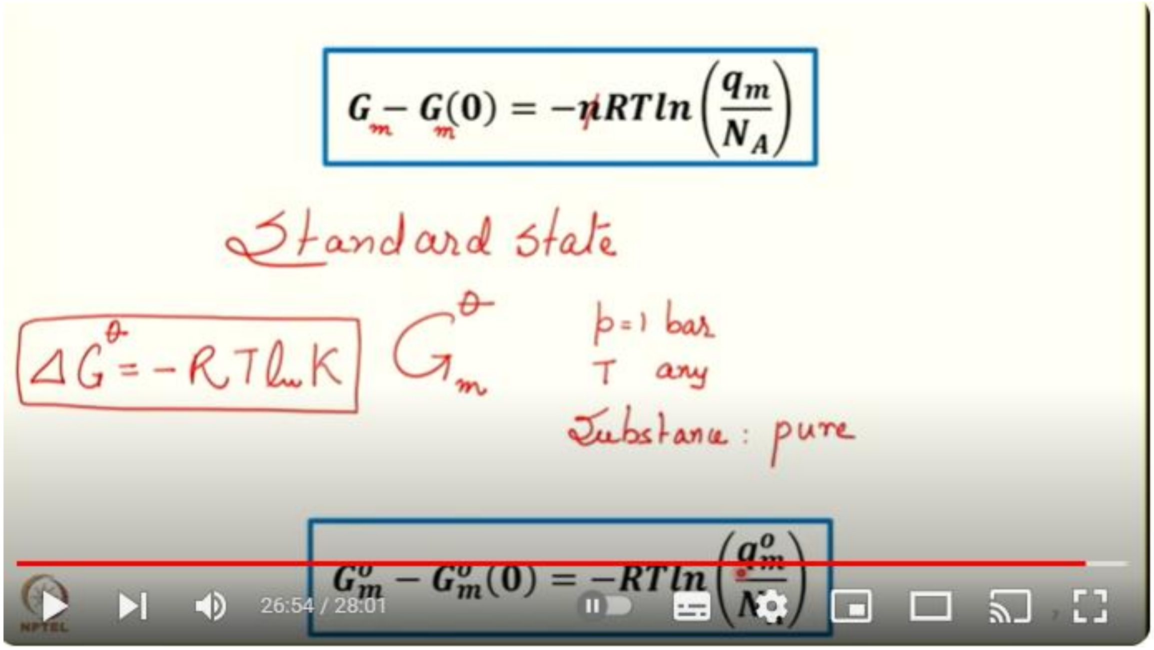

$$\boxed{G_m - G_m(0) = -\cancel{n}RT\ln\left(\frac{q_m}{N_A}\right)}$$

Standard state

$$\boxed{\Delta G^{\ominus} = -RT\ln K}$$

$G_m^{\ominus}$

$p = 1$ bar

T any

Substance : pure

$$\boxed{G_m^o - G_m^o(0) = -RT\ln\left(\frac{q_m^o}{N_A}\right)}$$

Now you will be able to appreciate that if at a later stage I need to connect G M naught or free energy Gibbs function under standard state conditions with equilibrium constant then I need an expression in terms of G M naught. That is the reason we have now expressed this in terms of standard state so that any differences in the value of molar Gibbs function under standard state conditions can be connected with equilibrium constant. So I hope that the discussion on Gibbs function and its relevance has been useful and here we demonstrate that we can get Gibbs function or molar Gibbs function from the value of molecular partition function that is from spectroscopic observations.

Thank you very much. Thank you.