Fundamentals of Statistical Thermodynamics

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Lecture: 45

Relation between equilibrium constant K and partition function q

Welcome back. Today, we are going to discuss a very important thermodynamic quantity that is equilibrium constant. In classical thermodynamics, we have already discussed equilibrium constant at length and connected with the change in standard molar Gibbs energy. In statistical thermodynamics considerations, we are going to connect this equilibrium constant with molecular partition function. The experimental measurement of equilibrium constant can be done in a variety of methods. There can be spectroscopic methods, there can be calorimetric methods, there can be direct methods where a suitable fitting of the model to the experimental data points can give the value of equilibrium constant.

Alternatively, we can get the value of equilibrium constant from the value of $\Delta G°$ and $\Delta G°$ is equal to $\Delta H°$ minus $T\Delta S°$. So, therefore, there are variety of methods calorimetric spectroscopic and there may be some other methods which you can use for experiments. So, experimental determination of equilibrium constant. Even when we talk about the spectroscopic determination of equilibrium constant and then those who have consulted the book by Lakowicz and are dealing with the interaction between ligands and biological macromolecules like proteins, then Stern-Volmer kind of analysis can give you the value of quenching constant which under certain circumstances can become equal to equilibrium constant.

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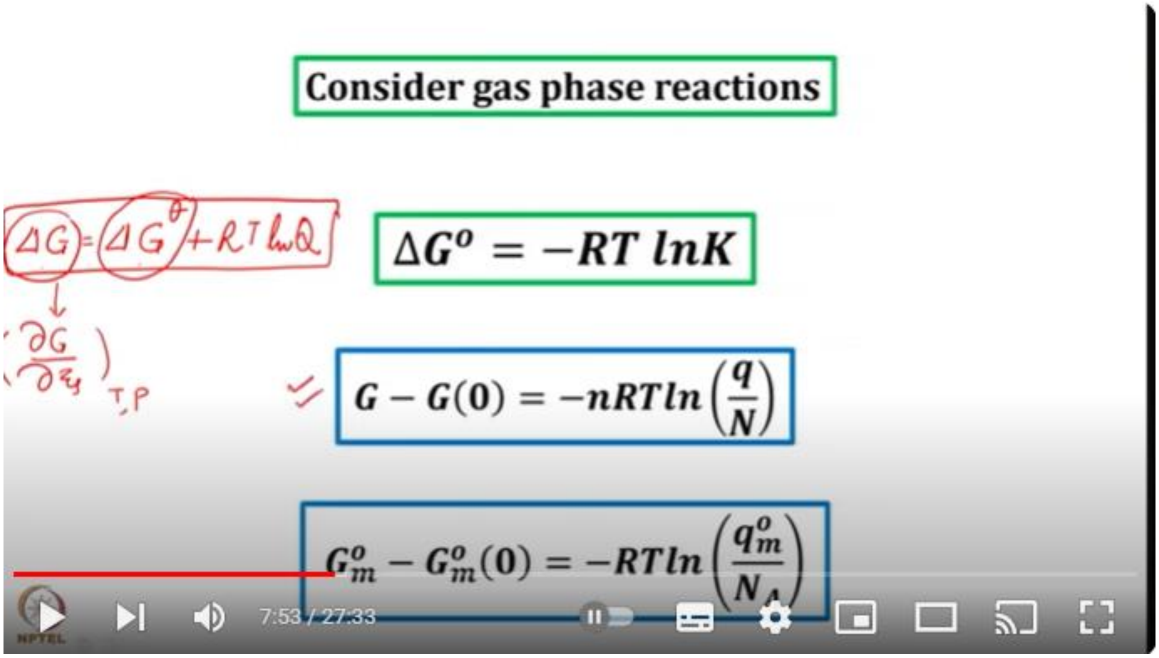

Consider gas phase reactions

$$\Delta G = \Delta G^{0} + RT\ln Q$$

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P}$$

$$\Delta G^{o} = -RT\ lnK$$

$$G - G(0) = -nRTln\left(\frac{q}{N}\right)$$

$$G^{o}_{m} - G^{o}_{m}(0) = -RTln\left(\frac{q^{o}_{m}}{N_A}\right)$$

In this course, we have been talking about the molecular partition function and by now we have discussed all contributions to the molecular partition function. For example, translational contribution, rotational contribution, vibrational contribution, electronic contribution, these are the four major contributions that constitute that form the overall molecular partition function and which can be related to various thermodynamic quantities. In today's lecture as I just said we are going to connect the equilibrium constant with the partition function q. What is the significance of equilibrium constant? Just as a recap to earlier knowledge equilibrium constant is a very important thermodynamic quantity because it tells you how much product is formed. Equilibrium constant is the ratio of the concentrations of the product to that of the concentrations of the reactants weighted by the power of their respective stoichiometric numbers.

In industry equilibrium constant is very important because as I just said equilibrium constant is directly related to the amount of product formed and therefore, in industry they are always in finding out appropriate conditions which can be tuned to achieve a desired value of equilibrium constant. And the molecular partition function since we have discussed that it is connected to the energy levels of the molecule and therefore, that means, here also the determination of equilibrium constant by statistical means is in fact, spectroscopic method of evaluating the value of equilibrium constant. Let us begin our discussion. There are two things I want to highlight to begin with one is that we will discuss ideal systems first ideal gases. So, therefore, initially I will restrict to gas phase reaction and also the gas phase reactions mean I will talk about ideal gases non ideality we will bring later. Equilibrium constant K is related to ΔG° by this equation ΔG° is equal to minus RT log K.

In classical thermodynamics we derive this equation ΔG° is equal to minus RT log K based upon a certain derivation which was ΔG is equal to ΔG° plus RT log K. In this equation ΔG is the change in Gibbs free energy ΔG° is the change in Gibbs free energy under standard state conditions remember difference between ΔG and ΔG° it is a common mistake sometimes we do not differentiate between the two, but these two convey entirely different meaning this ΔG is actually the slope ΔG ΔX_i at constant temperature and pressure. That means, the positive or negative value of this ΔG is going to decide in which direction the reaction is spontaneous at equilibrium ΔG is always 0 this slope is 0 and Q is equal to K. So, therefore, when you rearrange that you get ΔG° is equal to minus RT log K. The purpose of this discussion was to again highlight the difference between ΔG and ΔG° these two are not the same quantities these two are different quantities.

Now, since today's task is to correlate K with q. That means, we have to connect this K somehow with the Gibbs free energy or the changes in Gibbs free energy under standard state conditions from our previous discussion we have derived this equation G is equal to G_0 this is absolute 0 T is equal to 0 is equal to minus nRT log q by n this we have discussed earlier and we had also discussed that n number of molecules is number of moles times Avogadro constant. So, therefore, when you convert this upper equation this equation and write n is equal to small n times N_A then q divided by n becomes q_m molar partition function and throughout you divide by n if this equation is divided throughout by n it results into this equation where n is consumed into per molar quantity. That means, what I am writing here is G by n is equal to G_m molar quantity and we have invoked standard state conditions you see throughout this° has been put why I am putting this standard state conditions because the relationship that I am interested in connecting is ΔG° is equal to minus RT log K. So, therefore, I need to have expressions for Gibbs free energy under standard state conditions ok.

From here onwards we will talk for the Gibbs free energy under standard state conditions. So, what is a standard state? First of all, we should be clear on what is a standard state we have also discussed or your teachers might have already discussed with you what is a standard state. Usually, the answer comes temperature 25 °C no temperature can be any substance should be in its pure form and pressure should be 1 bar that is the latest recommendations of IUPAC what is a standard state the substance should be pure in its pure form pressure should be 1 bar this is very important pressure should be 1 bar temperature can be any there is no fixation of temperature you can have standard state conditions at any temperature. For example, you have nitrogen N_2 the standard state of nitrogen N_2 is gas at 25 °C if you reduce the temperature towards 0 K the standard state will be different. So, therefore, temperature can be any substance should be in its pure form and pressure should be 1 bar. In other words, P° this ° here signifies the standard state conditions that is 1 bar and since here we are dealing with ideal cases ideal gases, I will write pv is equal to nRT that is a perfect gas equation or ideal gas equation. So, that means, here V I can write this as V by n is equal to RT by p and then after that if I invoke standard state condition then V by n becomes V_m^0 and p instead of p I write p° what it suggests is that when you are dealing with the gaseous systems and treating the gases at ideal gases then you can always calculate the volume by using RT by p° volume need not be given to you you should be able to calculate from the knowledge of gas constant and from the knowledge of temperature p° is anyway 1 bar. So, therefore, under standard state conditions it is easier to get V_m^0 no data needs to be given it is very important to understand the concept of standard states. I hope this description of standard state is clear to you. Now, let us express the molar Gibbs function under standard state conditions for any species j any species j.

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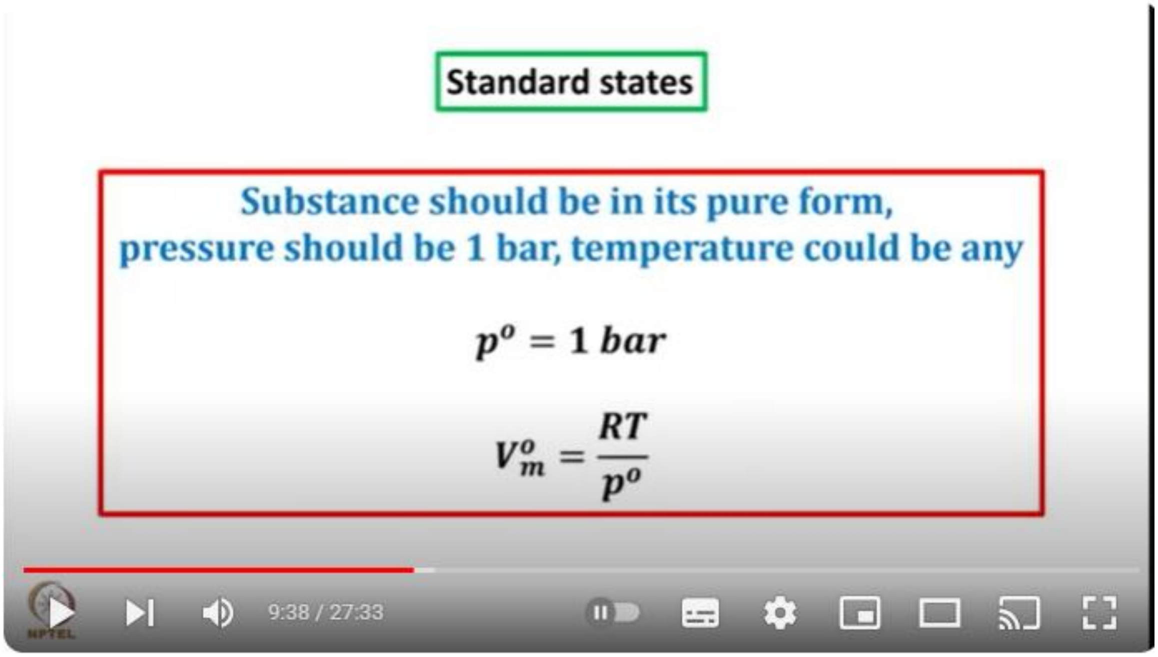

Standard states

Substance should be in its pure form, pressure should be 1 bar, temperature could be any

$$p^o = 1\ bar$$

$$V_m^o = \frac{RT}{p^o}$$

So, G°_m minus G°_m at 0 is equal to minus RT log $q^0_{j,m}$ by N_A. So, this is the expression m stands for molar j stands for species j° stands for standard state conditions N_A is the Avogadro constant and as mentioned over here $q^0_{j,m}$ is the standard state molar partition function of species j. Now, consider any reaction any gas phase reaction one such example is a moles of a reacting with b moles of b to form c moles of c and d moles of d. This is the expression that we are going to use this one this expression allows me to express molar Gibbs function of j under standard state conditions in terms of molar Gibbs function molar Gibbs function of j at absolute 0 and the molecular partition function. What I am interested in is knowing ΔG° and some books will write a subscript r you can write r means reaction.

So, reaction Gibbs free energy change under standard state conditions can be obtained from summation j ν_j $G^0_{m,j}$ under standard state condition. What it means if I expand this for this reaction let me put a partition over here that means for this reaction the way I will expand this expression is in this let me explain various notations r stands for reaction this symbol stands for standard state condition ν_j is the stoichiometric number which is positive for products and negative for reactants. I repeat ν_j is the stoichiometric number which is positive for products and negative for reactants use this positive for products that means what I will write is equal to I open this summation this will be c times $G^0_{m,c}$ plus d times

$G^0_{m,d}$ minus c times $G^0_{m,d}$ minus a times minus b times $G^0_{m,b}$. When I said positive for products and negative for reactants that stoichiometric number it is becoming clearly here, I am writing c and d both has positive numbers they are products a and b they are negative numbers here written over here these are the reactants. What I will do is now let us go step by step I am interested in finding this expression summation j ν_j $q^0_{m,\mathrm{d}}$ minus c times $G^0_{m,j}\nu_j$ I will retain ν_j over here and in bracket I will use this expression over here this is equal to $G^0_{m,j}$ at absolute zero minus RT at absolute zero minus R T log $q^0_{j,m}$ by N A we have simply substituted for G^0_m this means I can now write ΔG^0_r is equal to summation j ν_j over here.

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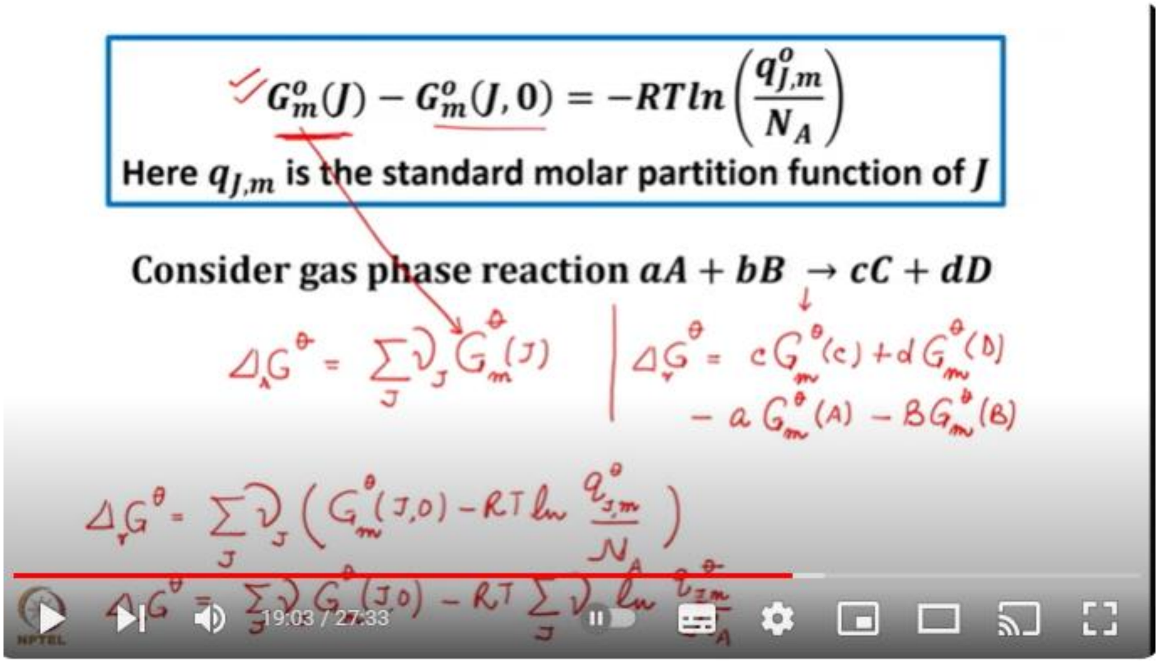

$$G^o_m(J) - G^o_m(J,0) = -RT\ln\left(\frac{q^o_{J,m}}{N_A}\right)$$

Here $q_{J,m}$ is the standard molar partition function of J

Consider gas phase reaction $aA + bB \rightarrow cC + dD$

$$\Delta_r G^\theta = \sum_J \nu_J G^\theta_m(J)$$

$$\Delta_r G^\theta = cG^\theta_m(C) + dG^\theta_m(D) - aG^\theta_m(A) - BG^\theta_m(B)$$

$$\Delta_r G^\theta = \sum_J \nu_J \left(G^\theta_m(J,0) - RT\ln\frac{q^\theta_{J,m}}{N_A}\right)$$

$$\Delta_r G^\theta = \sum_J \nu_J G^\theta_m(J,0) - RT\sum_J \nu_J \ln\frac{q^\theta_{J,m}}{N_A}$$

ν_j g m° j at absolute zero minus R T is common constant it comes out so this one j ν_j log $q^0_{j,m}$ by N_A try to understand it. What is simply done is we use this equation which says that reaction Gibbs free energy under standard state conditions can be obtained from the standard state Gibbs function of the products and reactants weighted by their stoichiometric number and what I did was then I retained ν_j of this and for $G_{m,j}$ I substituted this and we arrive at the next equation which is equal to $\Delta_r G°$ is equal to this summation at absolute zero minus R T into this expression ν_j log $q^0_{j,m}$ by N A we will get this expression. We will continue from here so what we have is $\Delta_r G°$ is equal to summation j ν_j $G_{m,j}$ zero this is my first expression from the previous equation and this is my this one minus R T log minus R T summation j ν_j log $q_{j,m}^0$by N_A purely general equation this is what we had minus R T ν_j log $q_{j,m}^0$by N_A. Now if you very carefully look at this, this is also very important because this is a very important condition. So, this is also ΔG° at absolute zero so that means I have under general conditions ΔG° is equal to this is ΔG° for j at absolute zero minus R T and then allow me to write next expression. So, this is the $\Delta_r G°$ is equal to ΔU I will say J at zero minus R T summation.

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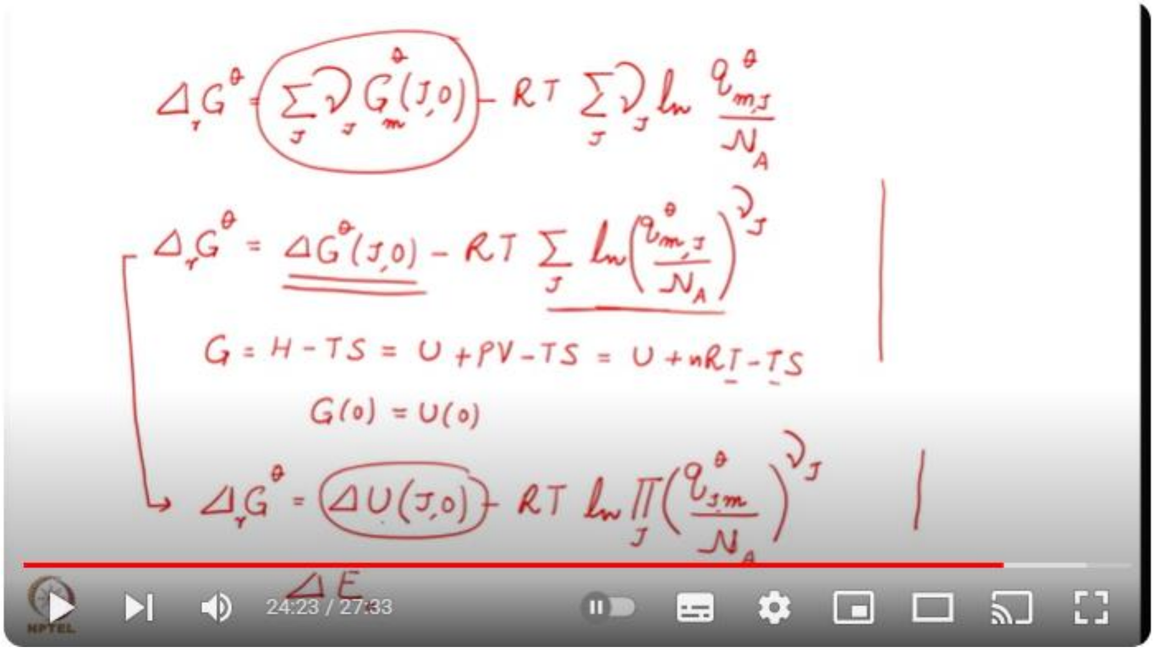

$$\Delta_r G^\theta = \boxed{\sum_J \nu_J G_m^\theta(J,0)} - RT \sum_J \nu_J \ln \frac{q^\theta_{mJ}}{N_A}$$

$$\Delta_r G^\theta = \underline{\underline{\Delta G^\theta(J,0)}} - RT \underline{\sum_J \ln\left(\frac{q^\theta_{m,J}}{N_A}\right)^{\nu_J}}$$

$$G = H - TS = U + PV - TS = U + nRT - TS$$

$$G(0) = U(0)$$

$$\Delta_r G^\theta = \boxed{\Delta U(J,0)} - RT \ln \prod_J \left(\frac{q^\theta_{Jm}}{N_A}\right)^{\nu_J}$$

$$\Delta E$$

When you open the summation, this is log a plus log b plus log b plus log c right and when you say log a plus log b plus log c etcetera that will be equal to log a into b. So, I have used that mathematical transformation I hope by now it is clear how we got this expression. What we will do is that instead of ΔU we will write this as ΔE_0 just a symbol to describe that this is the difference in the 0-point energies instead of ΔU, U shows internal energy we will just write rewrite in the term ΔE° ok. So, the new expression that we get now is $\Delta_r G°$ is equal to $\Delta_r G°$ E° minus R T log j $q_{j,m}^0$by N_A raise to the power stoichiometric number.

So, by now we have an expression for ΔG° and we have some expression for Δ from right hand side which is expressed in terms of change in 0-point energies and the molecular partition functions. That means, the right-hand side of this equation can now spectroscopically be determined. So, what we have other equations that we have with us are ΔG° is equal to minus R T log k R T log R T by N a raise to the power 0. This expression this equation we have derived when you were learning in classical thermodynamics r is a matter of convenience usually r is written for reaction. Now, you see this ΔG° and this ΔG° can be equated and once you have these two equations we can come up with an expression for equilibrium constant.

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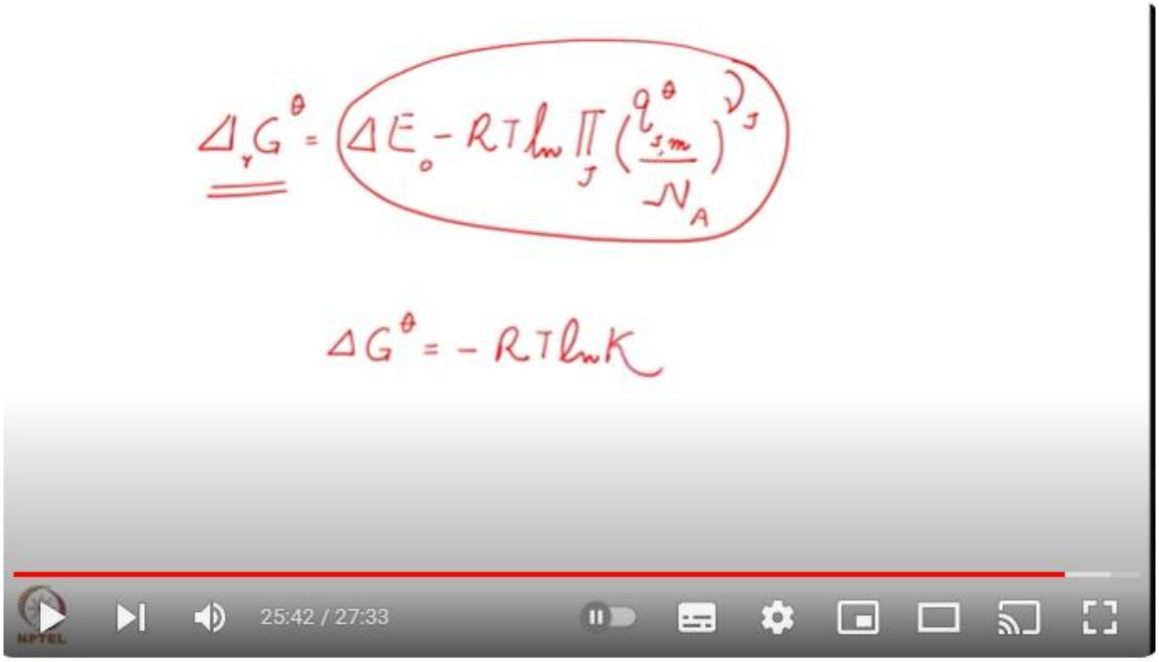

$$\underline{\underline{\Delta_r G^\ominus}} = \boxed{\Delta E_0 - RT\ln \prod_J \left(\frac{q^\ominus_{J,m}}{N_A}\right)^{\nu_J}}$$

$$\Delta G^\ominus = -RT\ln K$$

So, you might have noted the strategy since we wanted to develop a connection between equilibrium constant and molecular partition function and we realize that the equilibrium constant can easily be expressed in terms of changes in standard molar Gibbs energy. So, we decided to express Gibbs energy in terms of molecular partition function. Then through a series of steps we have come up to this expression where the right-hand side can be spectroscopically determined. The next step will be to equate these two and then come up with an expression for equilibrium constant, but that we will discuss in the next lecture.

Thank you very much. Thank you.