Fundamentals of Statistical Thermodynamics

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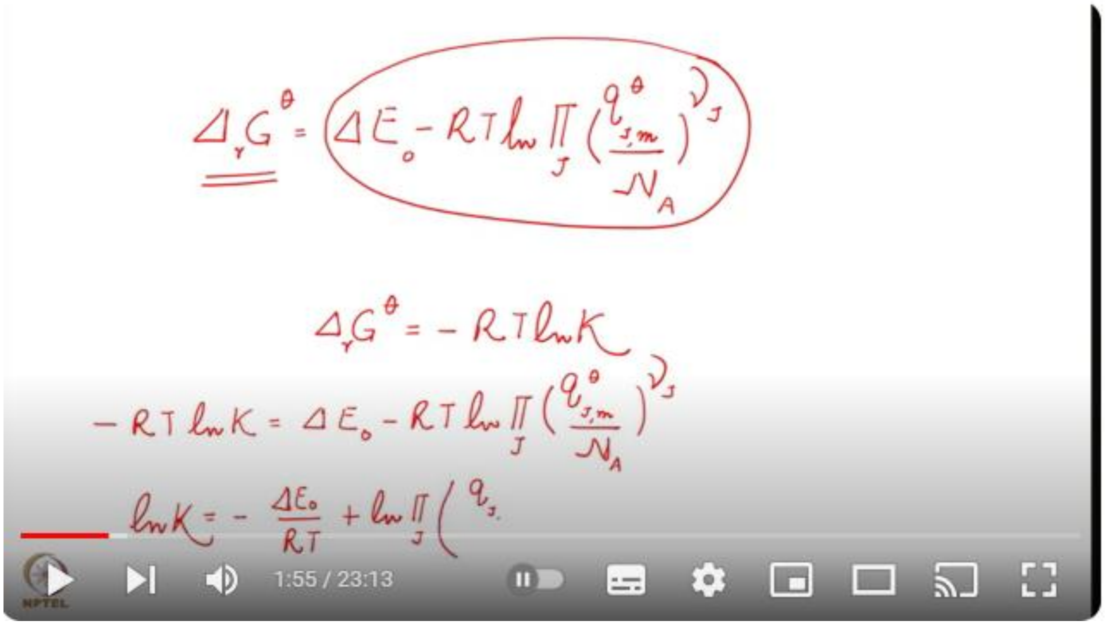
Lecture: 46

Relation between equilibrium constant K and partition function q (continued)

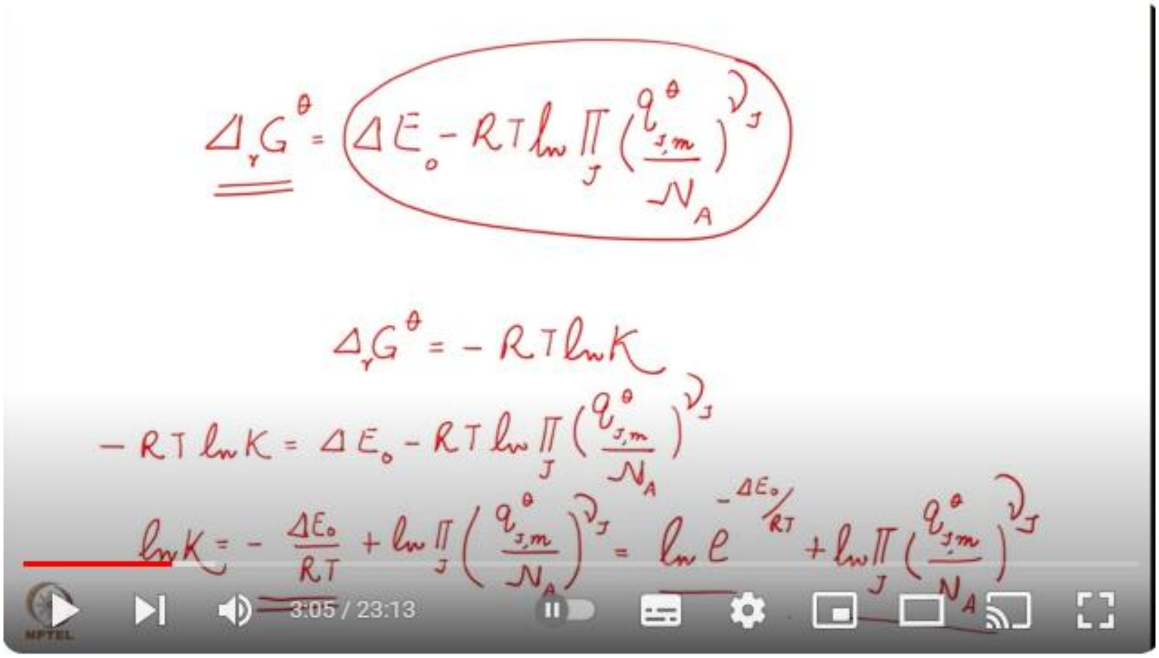
Welcome back to the lecture which is devoted to connecting equilibrium constant with molecular partition function. In the previous lecture, we started with an expression for the Gibbs function or Gibbs free energy and we expressed Δ G° in terms of Δ E° and the molecular partition function as presented here in this expression. And then we were discussing that since Δ G° is equal to minus RT log K, we can equate the two. Once we equate the two, the new equation that I have is minus RT log K is equal to Δ E° minus RT log π j $q_{j,m}^{0}$ by N_A Avogadro constant and raised to the power stoichiometric number. This equation can be rewritten as log K is equal to minus Δ E° by RT plus log π_j $q_{j,m}$ by N_A raise to the power stoichiometric number. If I can further extend this, I can write log exponential minus Δ E° by RT plus log this product $q_{j,m}^{0}$ by N_A raise to the power stoichiometric number.

See Slide time: 1:55



If you carefully examine what I have done, I have expressed minus Δ E° by RT as log exponential minus Δ E° by RT. Why I did that was that I have a logarithmic function on the left-hand side, and this is log A plus log B which is equal to log A into B, and then I can get rid of the log on both sides. Keep this equation in mind, and from this equation, I can write K is equal to the product of $q_{j,m}$ standard state divided by N_A stoichiometric number into exponential minus Δ E° by RT. This I am getting from the previous one log K is equal to log exponential this into this log A into B and then you can get rid of the logs and you come up with this expression that equilibrium constant is equal to the product of molar partition function under standard conditions for species j divided by Avogadro constant raised to the power stoichiometric number into exponential minus ΔE° by RT.

See Slide time: 3:05



Once again reemphasizing that this stoichiometric number is positive for products and negative for reactants. Going back to your discussion in classical thermodynamics, equilibrium constant is a dimensionless quantity, and here if you now examine each and every term, you will see that the dimensions, the units, they cancel out, and equilibrium constant turns out to be a dimensionless quantity. In classical thermodynamics, you used to express equilibrium constant as the ratio of activities of the products and reactants, and here if you see this N_A, which is included within the bracketed term, whatever is the stoichiometric number, this makes the entire thing a dimensionless quantity. Therefore, in order to evaluate the value of equilibrium constant by using statistical thermodynamic principles, what you need to know, you need to know the molar partition function, you need to know the stoichiometry of the reaction, you need to know zero-point energy difference, and gas constant temperature of a hydro constant are anyway the quantities that are required. What we will do now is that this equation which we have developed is the same equation now written in a typed form that K is equal to $\pi_j\ q^0_{j,m} \pi\ N_A$ raise to the power stoichiometric number into exponential minus Δ RE° by R 3.

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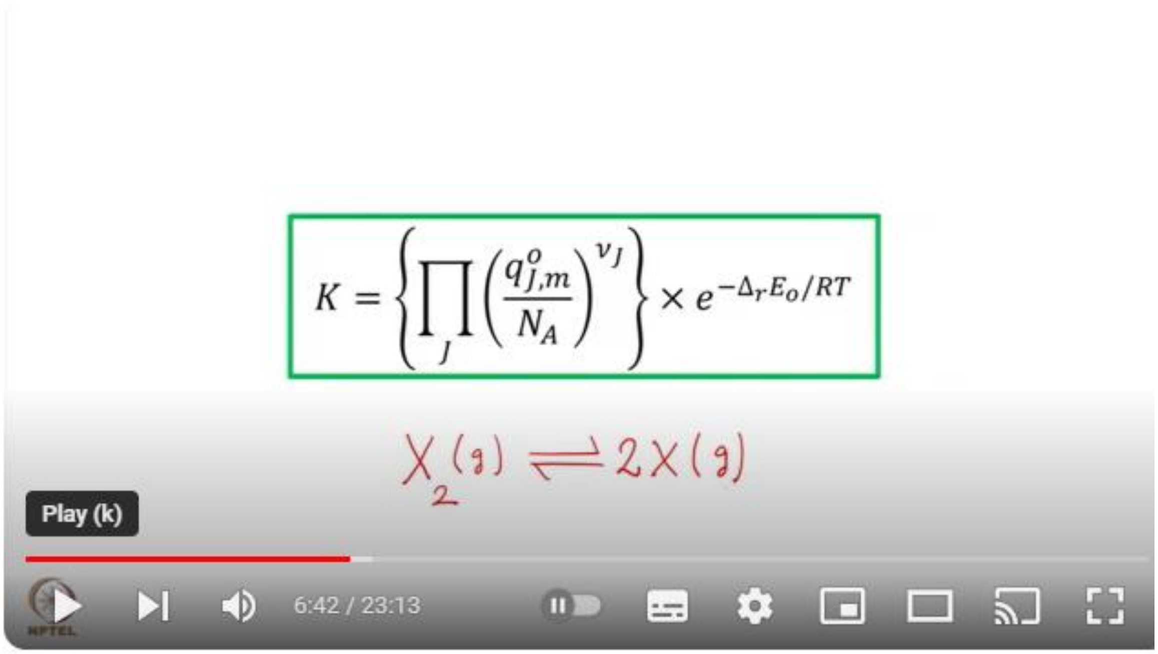

Now we can think of applying this developed equation to the variety of reactions. The first reaction that I will like to discuss with you is the dissociation reaction X_2 gas forming 2X items. Let us see, we apply to this, and in the future, I will avoid writing g because we are anyway discussing the situation in the gaseous state, alright. Now our system is X_2 going to 2X. So, we have to use this X_2 gas forming 2X items. So, K will be equal to this ν j is positive for products and negative for reactant for product it is plus 2.

So, what I will write q of X m° by N_A this number stoichiometric number is 2 and then I will have in the denominator for the reactant X_2 that is q of X_2 m° by N_A this is going to be for the reactant into exponential minus Δ E° by N_A. Now, if you do the mathematical rearrangement of this, you get $q^{\circ}_{x,m}$ square divided by q°_{x} for 2 into 1 over N_A because 1 over N_A will come from excess N_A in the numerator part and exponential minus Δ R E° by R T we have come up to this expression that is easy so far. Now, when you talk about the dissociation reactions like this, then Δ R E° is twice the internal energy of X in the numerator and X at absolute 0 minus internal energy of X_2 at absolute 0, and what is actually this, this is X_2 going to 2X this is dissociation. So, instead of writing Δ E° I can as well write the dissociation energy at absolute 0 of X x bond so that means, I need to have information on the dissociation energy of X x bond alright. So, going back to my expression it was $q^{\circ}_{X2,m}$ square divided by $q^{\circ}_{X2,m}$ into 1 over N_A was excess into exponential minus Δ R E° by N_A.

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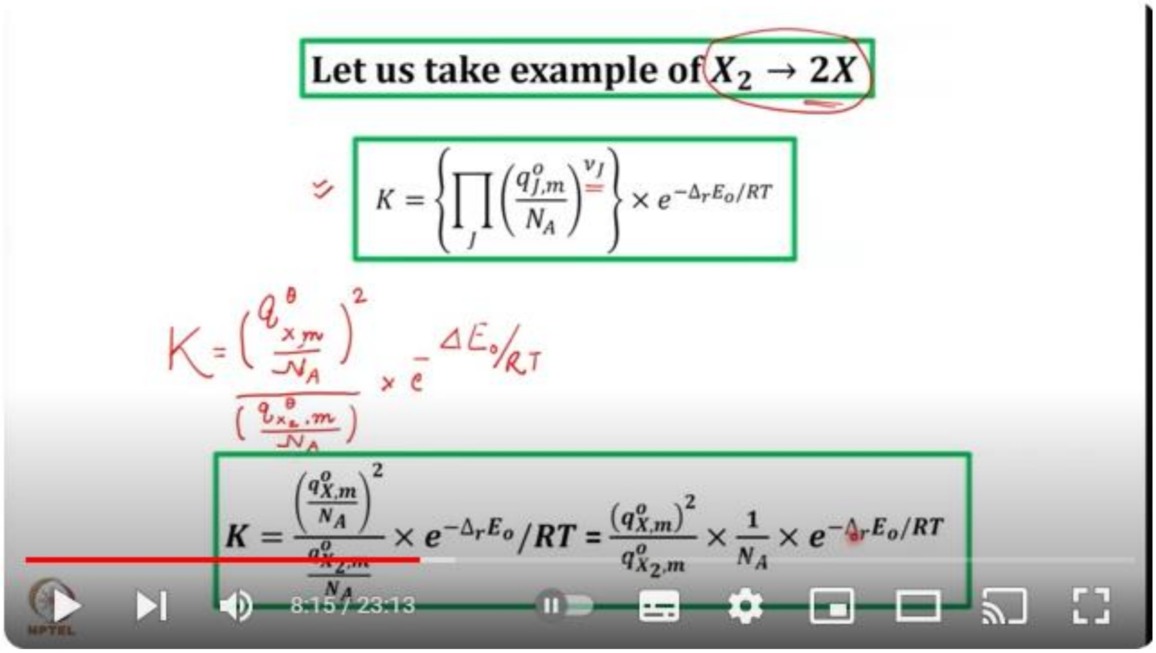
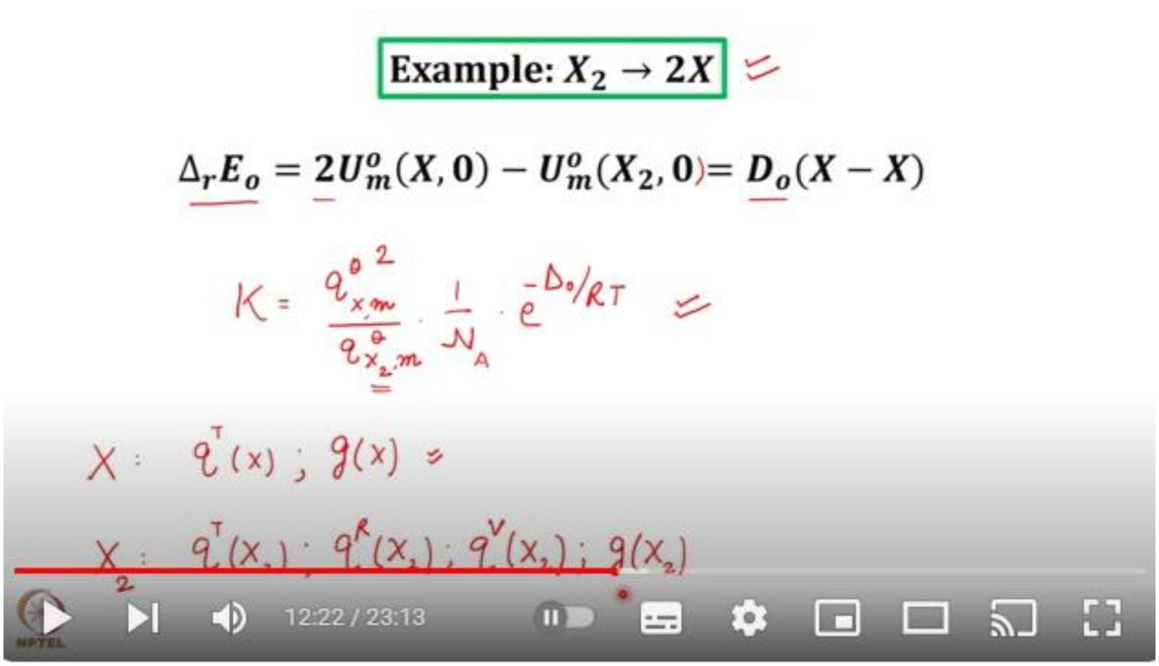


Now, if you look at this expression, this is equal to 1 over N_A into exponential minus D_0 by R T where from I get this expression from this one $q_{x,m}$ square over $q^{\circ}_{X2,m}$ 1 over N_A exponential minus Δ R E° this Δ R E° we have said that this is equal to d° and we have this expression now. Now, you carefully examine the numerator is for X X is an atom, the denominator is for X_2 X_2 is a molecule an atom can have translational degree of freedom and electronic degree of freedom there is no rotation and vibration in the atom for a molecule there is translational degree of freedom, there is rotational degree of freedom, there is vibrational degree of freedom, there is electronic degree of freedom that means, for X I will have q translational X I will have q translational of X and I will have g X which is the degeneracy of the ground state electronic states I require this information for molecule X_2 I will require q translational for X_2 I will require q rotational for X_2 because being a diatomic molecule it can undergo rotation I will require q vibrational and I will also require the degeneracy of the ground state I repeat in the expression for K you notice that the numerator is q X square where X is an atom an atom can have translational degree of freedom and you also require knowledge of the degeneracy of the ground state why degeneracy of the ground state because electronic states are assumed to be or are far separated. So, therefore, their contribution is usually coming from the ground state term X_2 being a molecule diatomic you will have translational degree of freedom you will have rotational degree of freedom you will have vibrational degree of freedom you will have the electronic term that is the ground state electronic term degeneracy of the ground state. Now with this information what I have I go back to this K is equal to $q^{\circ}_{X,m}$ ok I am just not I am not writing because we assume it is standard state this square over $q_{X2,m}$ into 1 by N_A into exponential minus D_0 by R t this is where we are now $q_{x,m}$ is equal to V_m by λ X cube find out the value of λ X cube. And it will also have a contribution from degeneracy of the ground state overall partition function is multiplication of the partition functions $q_{X2,m}$ is V_m here I will put standard state left hand side you assume as standard state everything is actually in the standard state over λ X_2 cube into I need q R into vibrational into the degeneracy of X_2.

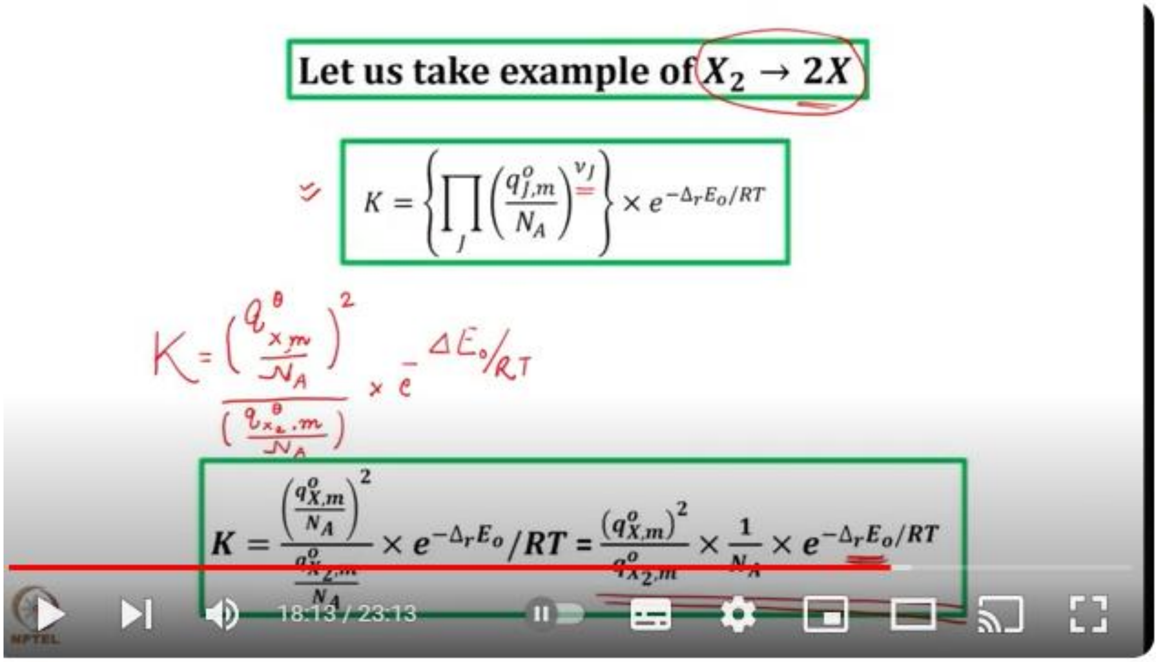
See Slide time:12:22



What I have done is I have included translational contribution rotational contribution vibrational contribution electronic contribution what we will do is we will substitute these both q's into this expression and let us see what it turns out to be. What I have done is I have included translational contribution rotational contribution vibrational contribution electronic contribution what we will do is we will substitute these both q's into this expression and let us see what it turns out to be. So, what we will do is let us put K is equal to $q_{x,m}$ square that means V_m is equal to $q_{x,m}$ square. So, V_m° square by λ_x it is a square so raise to the power 6 into g X square now divided by V_m° λ_{X2} into q_R into q_R^2 square. So, this is the expression X_2 into q^v (X_2) into g_{X2} and there is exponential minus D_0 by RT molar volumes are the same PV_m is equal to you need to use P V is equal to NRT P V is equal to NRT.

Or I will say P° standard state into V_m V by N is equal to V_m is equal to RT that means according to this V_m° is equal to RT by P P° rather this and this will cancel. So, what we have remembered that there is one more N_A term and we should include that N_A somewhere here into N_A I will just put here. So, what I have now K is equal to V instead of V_m° I will put RT by P° into I will put g_X square into λ_{X_2} of course, this has to be q divided by λ X divided by λ X to the power 6 q_R (X_2) q_v (X_2) g_{X2} into N_A N_2 exponential minus Δ E° by RT. Next is use R is equal to k times Δ V times Avogadro constant. So, that means this R by N_A I can just use k R by N_A use k that is the k this temperature is there and g_X square use this $g_{X,m}^2$ into λ_x cube divided by P° P° is there then you have g_{X2} is their q_R (X_2) q^v $(X_{2)}$ λ (X_6) and into exponential minus E_0 by RT.

See Slide time: 18:13



Now, try to understand that how to arrive at this expression from this expression the shape of this expression or the form of this expression is similar to that you used in chemical thermodynamics because there also what was its equilibrium constant was equal to the ratio of the activities of the products and reactants weighted by their stoichiometric number. Here also this actually is a ratio and how it is a ratio is since your reaction is X_2 going to 2X. So, it is q_x square divided by q_{X_2} and since each q is divided by N_A you have 1 by N_A in the denominator then exponential minus E_0 by RT. Now, after that you have to decide that the numerator and denominator or for a given species what type of contributions can enter. So, if you are dealing with only atoms then you will have translational degree of freedom electronic degree of freedom. If you are dealing with the molecules then the molecules since we are dealing with the gases you have a translational degree of freedom you have rotational degree of freedom you have vibrational degree of freedom and you have electronic degree of freedom. So, this showed that for X_2 going to 2X $\Delta E°$ is simply the dissociation energy and this dissociation energy you can obtain from the zero-point vibrational energy we will take up an example later on to show that how dissociation energy at 0 K can be calculated from the vibrational wave number data.

But for the time being remember that depending upon whether your reactant or products are atoms or molecules you need to take their partition functions accordingly. Remember that the number of terms appearing here or in any of the expression is going to depend upon your type of reaction. Here we have taken a very simple dissociation reaction there can be reactions in which you have atoms also you have diatomic molecules also you have triatomic molecules also and you have multi atomic molecules also. And there can be more than 1 is to 1 type means there can be reactions of a moles of a plus b moles of b is equal to c moles of c plus d moles of d that means you will have to account for the partition function of each one a b c and d each one of them that is a b c or d can either be simply an atom or it can be a diatomic molecule it can be a triatomic molecule it can be a multi atomic molecule. The examples include for a monatomic you have just ideal gases helium neon argon etcetera. Diatomic you will have carbon monoxide nitrogen Cl_2 I_2 etcetera. Triatomic you can have water and similar other molecules carbon dioxide is another carbon diatomic molecule. Then you can have multi atomic molecules. So, the situations can become more and more complex as the number of atoms involved in a molecule increase. Therefore, you will have to very carefully decide how many terms and which terms are to be included in the denominator or are to be included in the denominator. We will discuss this in more details when we take specific numerical problems and then I will explain to you that when you are using a particular formula when you are using a particular expression whether it is allowed under those conditions of temperature or not, but all those we will discuss in the next lecture. Thank you very much. Thank you.