# Fundamentals of Statistical Thermodynamics

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## Lecture – 56

## Problem Solving

In this lecture, we will focus on some problem solving. We have developed many equations which connect thermodynamic quantities with the partition function. And some very important thermodynamic quantities are Gibbs function, enthalpy, entropy, and equilibrium constant. Today, we will focus on these thermodynamic quantities and see how to evaluate the numbers for certain systems. First, the enthalpy and Gibbs function going back to to chemical thermodynamics enthalpy p H was defined as U plus p V and Gibbs function Gibbs free energy was defined as G is equal H minus TS. I reemphasize on the word free, you should know why G or A are called Gibbs free energy or Helmholtz free energy, what is free in this free energy.

Let us address some questions, the question is what are the rotational contributions to $C_p^{\circ}$, H° and G° for oxygen gas at 298 K. The given information to you is the moment of inertia and they are asking you only to focus on rotational contribution. The thermodynamic quantities to be addressed are heat capacity enthalpy and Gibbs free energy. Heat capacity and enthalpy are connected with each other, once you have an expression for enthalpy you can take its temperature derivative it becomes heat capacity.

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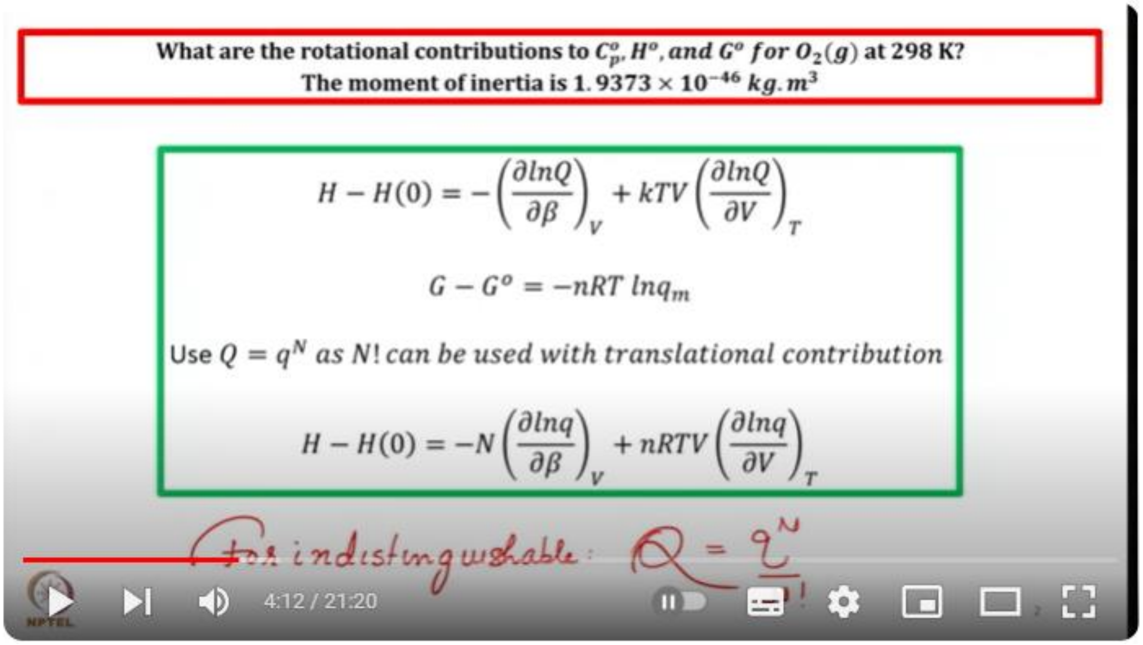

**What are the rotational contributions to $C_p^o, H^o$, and $G^o$ for $O_2(g)$ at 298 K?**
**The moment of inertia is $1.9373 \times 10^{-46}\ kg.m^3$**

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

$$G - G^o = -nRT\ lnq_m$$

Use $Q = q^N$ as $N!$ can be used with translational contribution

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

For indistinguishable: $Q = \frac{q^N}{N!}$

Now going back to our earlier discussion, enthalpy is defined relative to H (0) with momentum with minus δ log Q by δβ at constant V plus k T V δ log Q by δ V at constant temperature, this is an expression that we derived. Q is canonical partition function and we also derived G minus G (0) is equal to minus nRT log $Q_m$ that also we have derived. What we have done here is, we have to decide even you know the original definition will be in terms of canonical partition function, but I have then converted into molecular partition function. The given system is oxygen gas, oxygen gas is a system which consists of molecules which are indistinguishable. Therefore, for indistinguishable molecules, the canonical partition function is equal to q raise to the power N and also there is N factorial. Now the question is whether we should be using this N factorial term here also with G also with A also no, you need to see n factorial is appearing only once and it makes a sense to use this n factorial term with the translational contribution and that gives you sackur-tetrode equation. So, if you include n factorial term, you have to include only once include with translational contribution that gives you the sackur-tetrode equation and you can easily get the translational contribution to entropy. Similarly, here, you can include with the translational partition function, you do not need to include this 1 by n factorial with each term. So, when you substitute here without n factorial Q is equal to q raise to the power n, your enthalpy will turn out to be H minus H (0) is equal to minus n δ log q by δβ at constant V plus here when you put Q is equal to q raise to the power N, n K will become n R. So, n

R T V δ log q δ V at constant temperature. So, it should be easier for you now to see the connection between these two equations that is important to understand that n factorial is not required with each contribution. So, what we have now is G minus G (0) is equal to minus n R T log q and here we are talking about the rotational contribution because they want us to find out the rotational contribution. Now the other equation is H minus H (0) is equal to minus n δ log q by δβ at constant volume plus n R T V δ log q δ V at constant temperature. These are the equations that we need to. Now we want to find out the rotational contribution.

The given molecule is oxygen. Oxygen means it is a linear molecule. Once it is a linear molecule that means I will use $q^R$ is equal to 1 upon σ h cβ b and the logarithm of this log $q^R$ is equal to this is going to be log of 1 over σ h cβ b that means this is minus log σ h cβ b. This is what we are having. Once we have an expression for log q in terms of σ h cβ b where you know that β is equal to 1 over k T we are given the temperature which is 298 K and once you substitute this you can get the value of H minus H (0) you can also get the value of G minus G (0).

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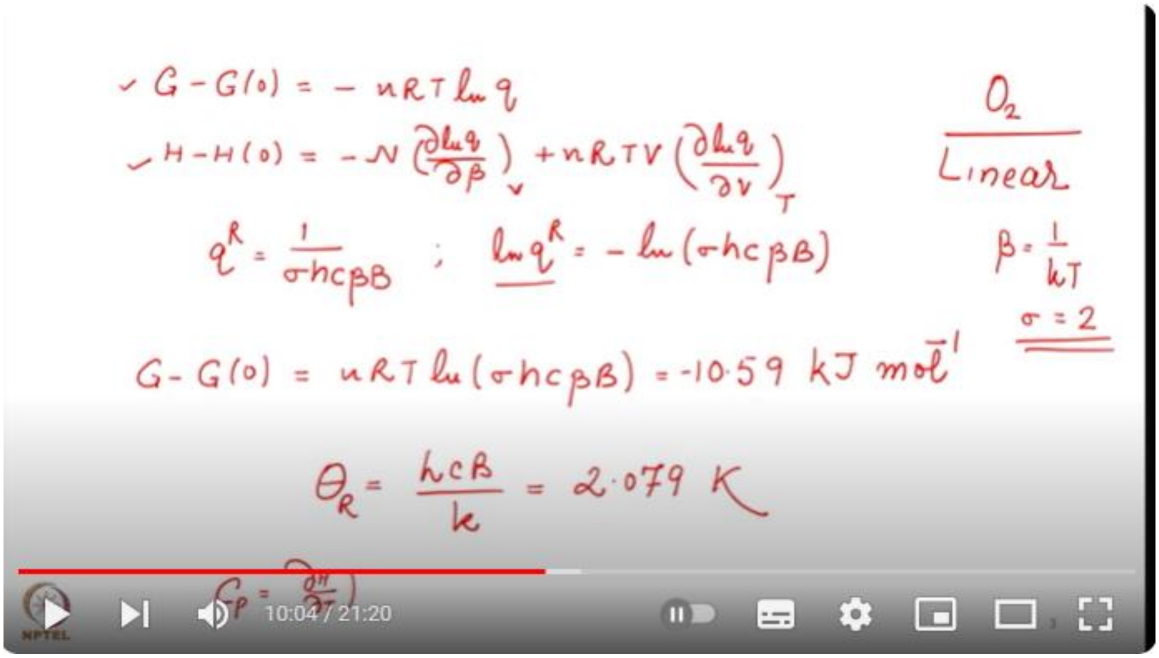

$$G - G(0) = -nRT \ln q$$

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

$$q^R = \frac{1}{\sigma hc\beta B} \; ; \; \ln q^R = -\ln(\sigma hc\beta B)$$

$$G - G(0) = nRT \ln(\sigma hc\beta B) = -10.59 \text{ kJ mol}^{-1}$$

$$\theta_R = \frac{hcB}{k} = 2.079 \text{ K}$$

$$C_p = \left(\frac{\partial H}{\partial T}\right)$$

$O_2$

Linear

$$\beta = \frac{1}{kT}$$

$$\sigma = 2$$

For example, when you substitute here in G minus G (0) G minus G (0) according to my calculations which is you know n R T log Q n R T log Q log Q here is log σ h cβ b substitute all the numbers you will get this equal to minus 10.59 kilo joules per mole. We have this contribution of G minus G (0) since oxygen is linear that means for oxygen σ is equal to 2 because 180° rotation leaves the molecule in an indistinguishable state substitute all the values and get the number. Now remember that in order to use this equation whether you have to use in H minus H (0) or you have to use in G minus G (0) you have to first of all calculate $\theta_r$ which is equal to h c b by k and you substitute the numbers this is coming to 2.079 k. The given temperature 298 K is much higher than this and therefore, I have shown you the method that once you have q you can substitute here you can get enthalpy also you can get the free energy also and this you do yourself c p is equal to δ H δ T at constant pressure. So, you need to take derivative of this with respect to temperature at constant pressure. So, by this method you can have the contributions to $C_p$ H and G I am not solving everything I have just shown you the method. So, you please try yourself. Now, let us go to another kind of problem a similar problem we have discussed earlier calculate k p for the following reaction $H_2O$ plus DCl forming HDO plus HCl it is an exchange reaction we have to find $K_p$ whether you write $K_p$ or you write K it means the same thing the given information to you is in terms of moment of inertia $I_x$ times $I_v$ time y times $I_z$ is 5.84 into

10 raised to the power minus 141 kilo gram cube meter 6 for $H_2O$ you are also given this number for HDO remember that $H_2O$ and HDO they are non-linear molecule. So, therefore, they have three all three moments of inertia a b c rotational constants instead of a b c what is given here is I x I y I z this product for the other two molecules which is DCl plus HCl which are linear rotors for that only one moment of inertia is required and for DCl this number is given for HCl is also this number is given. The remaining information is assume the electronic and vibrational contributions to be negligible at this temperature that means they are asking you only to consider translational contribution and rotational contribution they are telling you that assume that electronic and vibrational contributions are negligible at this temperature ok let us see how to now address this. This is the usual definition for equilibrium constant I said whether you write K or $K_p$ it does not matter it is the same thing. So, you have $\overset{\circ}{q}_j$ by $N_A$ raised to the power stoichiometric number this is the product ν j is positive for products negative for reactants you need ΔE°.

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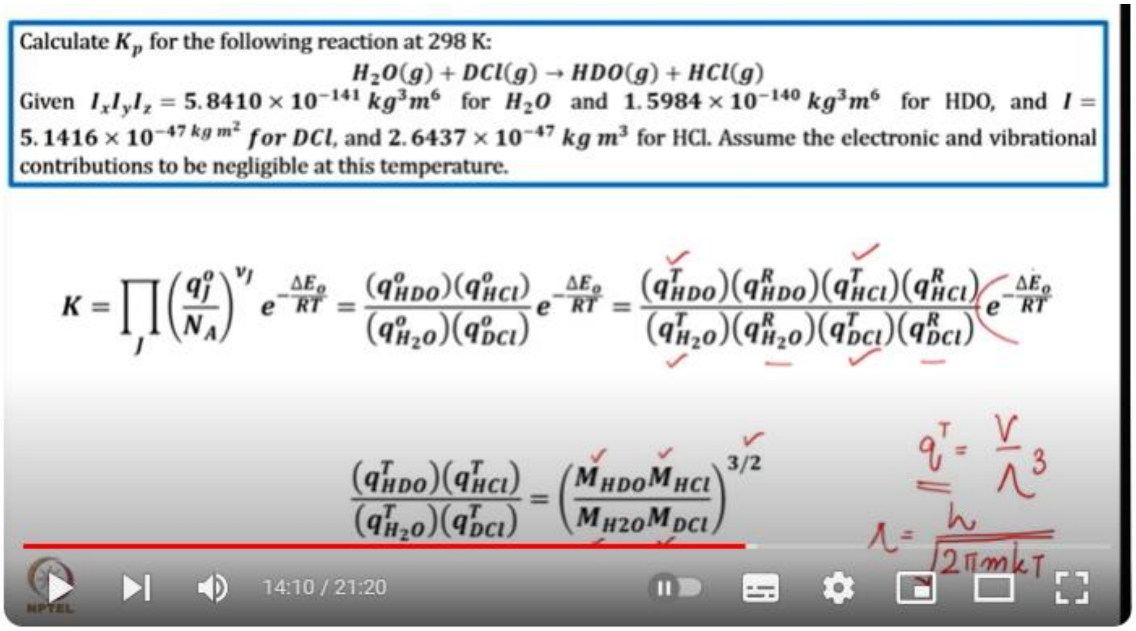

Calculate $K_p$ for the following reaction at 298 K:

$$H_2O(g) + DCl(g) \rightarrow HDO(g) + HCl(g)$$

Given $I_xI_yI_z = 5.8410 \times 10^{-141}\ kg^3m^6$ for $H_2O$ and $1.5984 \times 10^{-140}\ kg^3m^6$ for HDO, and $I = 5.1416 \times 10^{-47\ kg\ m^2}$ $for\ DCl$, and $2.6437 \times 10^{-47}\ kg\ m^3$ for HCl. Assume the electronic and vibrational contributions to be negligible at this temperature.

$$K = \prod_j \left(\frac{q_j^o}{N_A}\right)^{\nu_j} e^{-\frac{\Delta E_o}{RT}} = \frac{(q^o_{HDO})(q^o_{HCl})}{(q^o_{H_2O})(q^o_{DCl})} e^{-\frac{\Delta E_o}{RT}} = \frac{(q^T_{HDO})(q^R_{HDO})(q^T_{HCl})(q^R_{HCl})}{(q^T_{H_2O})(q^R_{H_2O})(q^T_{DCl})(q^R_{DCl})} e^{-\frac{\Delta E_o}{RT}}$$

$$\frac{(q^T_{HDO})(q^T_{HCl})}{(q^T_{H_2O})(q^T_{DCl})} = \left(\frac{M_{HDO}M_{HCl}}{M_{H2O}M_{DCl}}\right)^{3/2}$$

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

$$\Lambda = \frac{h}{\sqrt{2\pi mkT}}$$

So, when you write it for this reaction it will be q° for HDO q° for HCl divided by q° for water into q° for DCl each $N_A$ $N_A$ $N_A$ term gets cancelled into exponential minus ΔE° by R T. Now HDO will have translational contribution as well as rotational contribution H c l will have translational contribution and rotational contribution similarly water will have translational and rotational contribution and DCl will also have translational and rotational contribution. So, other electronic and vibrational you are getting now we also know that translational partition function v upon lambda q where lambda is equal to H upon 2 π m k T that means q $^T$ is directly proportional to 3 by 2 power of m. So, q T when you take the ratio all other quantities will cancel out what will remain is molar masses and their raised to the power 3 by 2 a similar problem we have discussed earlier also right. So, we have taken care of translational translational translational translational remaining now this rotational that ratio is remaining and also the exponential term.

Now see how this rotational thing is made easy for triatomic molecules the rotational partition function in terms of moments of inertia will take up this form while deriving we have used a b c where b is h cross by 4 π cI in any case when you convert that in terms of moment of inertia then this is the expression in this expression 8 π square is constant 8 π cube is constant h cube is constant k and T is fixed that means if you represent all these constant quantities as c then you have $I_x$ $I_y$ $I_z$ square root divided by σ. So, therefore, when you take the ratio of the non-linear molecule for non-linear molecule you are given $I_x$ $I_y$ $I_z$ these are given to you and this symmetry number this comes in the denominator therefore, when you take the ratio symmetry number for water for which q is in the denominator the symmetry number will be in in the numerator. So, from this ratio of the moments of energies and symmetry numbers we can have this ratio for the non-linear molecule similarly for linear molecules since there is only one moment of inertia and we need to use their symmetry number these are the only two things which are left over after cancellation by various constant numbers. So, very easy way of handling these type of questions k which was the ratio of all these molecular partition functions which for translational contribution we have expressed as the ratio of the molar masses then we have also expressed for non-linear molecules in terms of the ratio of $I_x$ $I_y$ $I_z$ for linear molecules also we have discussed moments of inertia ratio and more importantly their symmetry numbers these make a difference for water it is two for dcl one HDO one σ HCl one because by 180° rotation will give same configuration of water twice in one complete rotation and in DCl and HDO by 180° rotation only gives the different confirmation. Once you substitute all these numbers into this complicated equation you are getting finally, a value of 4.873 although we have discussed the similar question earlier when we are dealing with this kind of questions remember that each one for example, $H_2O$ is a non-linear molecule. So, therefore, the overall partition function can be a product of translational rotational vibrational electron here you are given some respite that is you ignore electronic and vibrational contribution if this information were not given you would have had to evaluate the electronic and vibrational contributions also and since you are ignoring those two the ratios of translational contribution are only depending upon the molar masses and the ratios of the rotational contribution are mostly or only dependent upon the moments of inertia and symmetry number once this information is available you can easily come to a final answer for the equilibrium constant. So, I hope you will appreciate over here that here the equilibrium constant which you are getting is not from calorimetric measurements, but this you are getting from the spectroscopic measurements you have to know how to get the translational energy levels how to get the rotational energy levels and if vibrational contribution and electronic contribution is there then you need to worry about those also. The question just by looking at the problem statement appeared very difficult, but when you actually start doing it then this ratio is mostly cancelling out some common factors and the overall solution becomes relatively easier. I have shown you for the equilibrium constant similarly you can work it out for various other thermodynamic properties where in some cases the ratio will cancel out many constant factors, but in other cases you will have to deal with how to make this question solvable easily.

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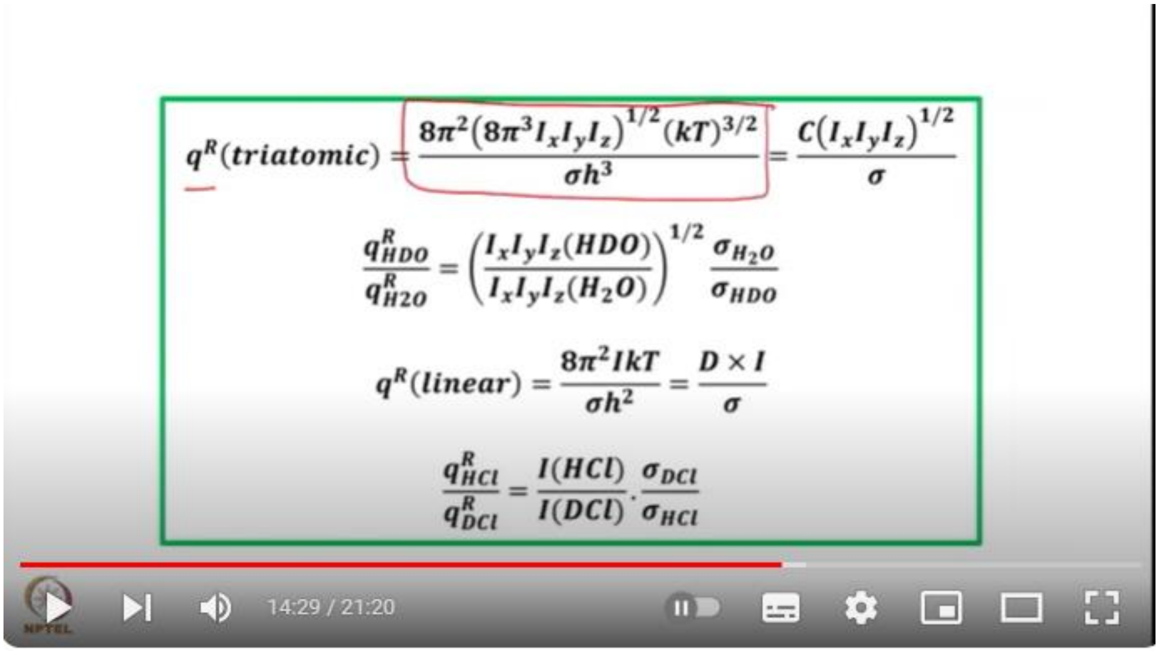

$$\underline{q}^R(triatomic) = \boxed{\frac{8\pi^2(8\pi^3 I_x I_y I_z)^{1/2}(kT)^{3/2}}{\sigma h^3}} = \frac{C(I_x I_y I_z)^{1/2}}{\sigma}$$

$$\frac{q^R_{HDO}}{q^R_{H2O}} = \left(\frac{I_x I_y I_z(HDO)}{I_x I_y I_z(H_2O)}\right)^{1/2} \frac{\sigma_{H_2O}}{\sigma_{HDO}}$$

$$q^R(linear) = \frac{8\pi^2 IkT}{\sigma h^2} = \frac{D \times I}{\sigma}$$

$$\frac{q^R_{HCl}}{q^R_{DCl}} = \frac{I(HCl)}{I(DCl)} . \frac{\sigma_{DCl}}{\sigma_{HCl}}$$

Remember that once you have temperature dependent equilibrium constant suppose if you were given this data as a function of temperature and if you can calculate the equilibrium constant as a function of temperature then even without doing any further experiments you can use the Van't Hoff equation which is δ log k by δ T at constant pressure is equal to Van't Hoff H by RT square this is Van't Hoff equation.

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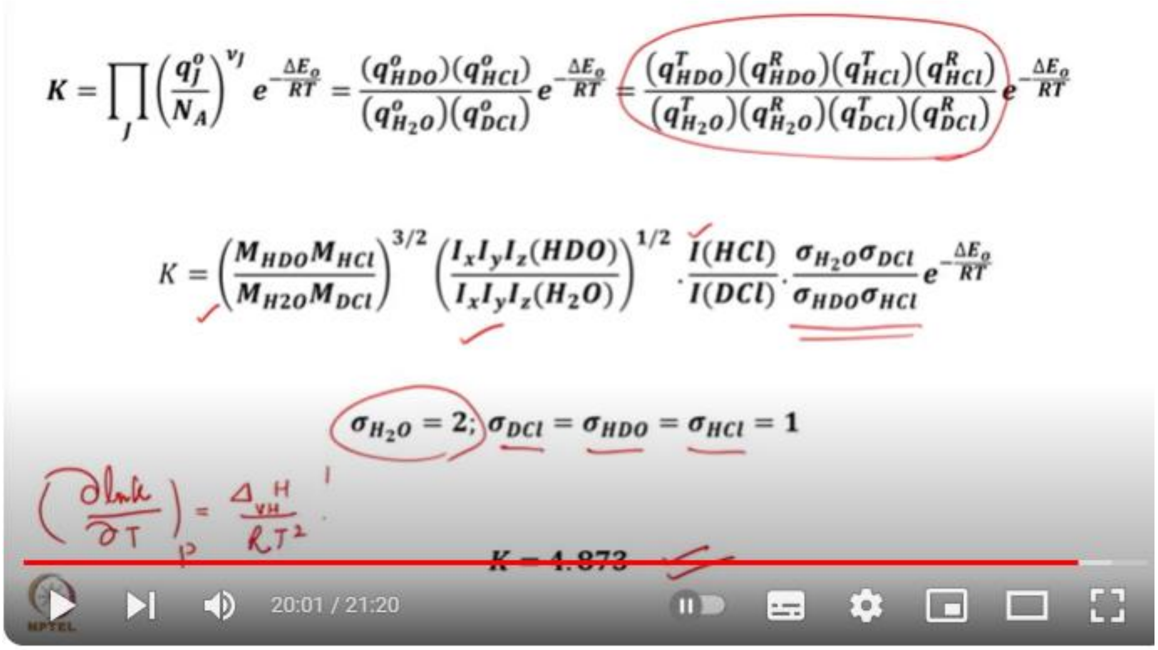

$$K = \prod_J \left(\frac{q_J^o}{N_A}\right)^{\nu_J} e^{-\frac{\Delta E_o}{RT}} = \frac{(q_{HDO}^o)(q_{HCl}^o)}{(q_{H_2O}^o)(q_{DCl}^o)} e^{-\frac{\Delta E_o}{RT}} = \frac{(q_{HDO}^T)(q_{HDO}^R)(q_{HCl}^T)(q_{HCl}^R)}{(q_{H_2O}^T)(q_{H_2O}^R)(q_{DCl}^T)(q_{DCl}^R)} e^{-\frac{\Delta E_o}{RT}}$$

$$K = \left(\frac{M_{HDO}M_{HCl}}{M_{H2O}M_{DCl}}\right)^{3/2} \left(\frac{I_xI_yI_z(HDO)}{I_xI_yI_z(H_2O)}\right)^{1/2} \cdot \frac{I(HCl)}{I(DCl)} \cdot \frac{\sigma_{H_2O}\sigma_{DCl}}{\sigma_{HDO}\sigma_{HCl}} e^{-\frac{\Delta E_o}{RT}}$$

$$\sigma_{H_2O} = 2; \sigma_{DCl} = \sigma_{HDO} = \sigma_{HCl} = 1$$

$$\left(\frac{\partial \ln k}{\partial T}\right)_P = \frac{\Delta_{vH} H}{RT^2}$$

$$K = 4.873$$

So, whenever you are dealing with problems on equilibrium constant do not forget Van't Hoff equation because temperature dependence of equilibrium constant at constant pressure can give you the value of enthalpy of reaction. If time permits, we will solve some more numerical problems, but we also have to do Fermi direct statistics that we will be doing in the next lecture. Thank you very much. Thank you.