

# Fundamentals of Statistical Thermodynamics

Prof. Nand Kishore

Department of Chemistry

Indian Institute of Technology, Bombay

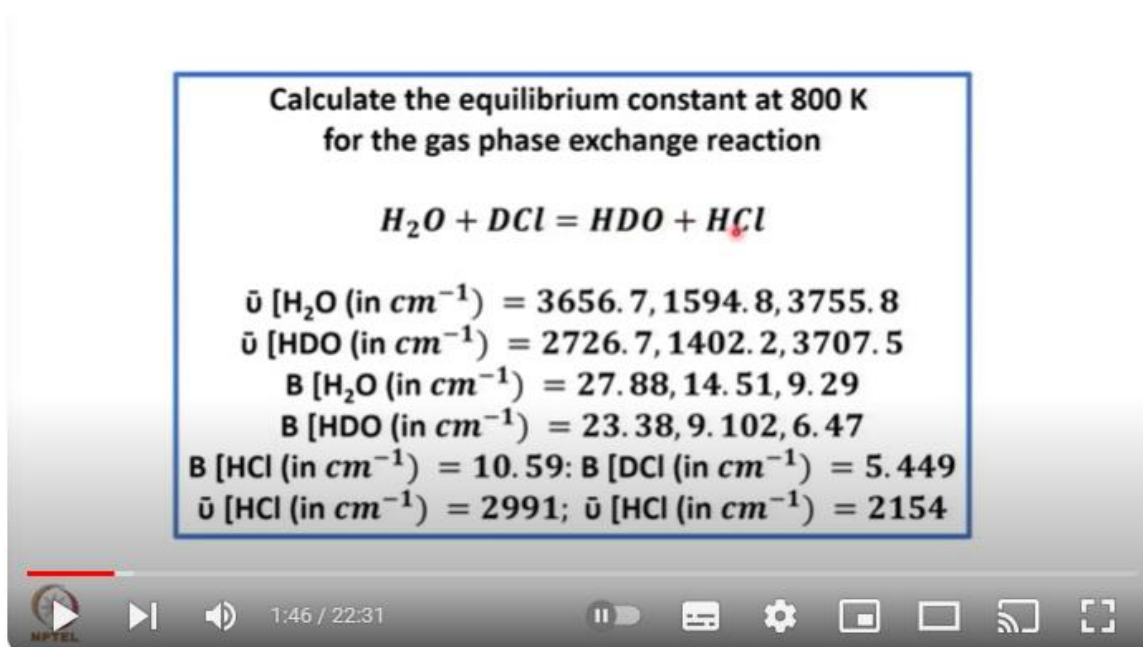
Lecture: 48

## Relation between equilibrium constant K and partition function q (Applications-2)

Welcome back. We have been discussing some applications of the connection of equilibrium constant with the molecular partition function. In the previous lecture, we took the example of the dissociation of the disodium molecule to sodium atoms. That example was simple because on the reactant side you had just one molecule and on the product side you had just one type of atoms. But sometimes the situation can be complex. Your reaction can involve multi-atomic molecules.

In that case, each molecule may have a different kind of modes of motion. For example, let us take the case of this gas-phase exchange reaction. What we have here is water plus DCl forming HDO plus HCl. This is a simple gas phase exchange reaction.

See Slide time: 1:46



Calculate the equilibrium constant at 800 K  
for the gas phase exchange reaction

$$H_2O + DCl = HDO + HCl$$

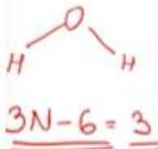
$\bar{u}$  [ $H_2O$  (in  $cm^{-1}$ )] = 3656.7, 1594.8, 3755.8  
 $\bar{u}$  [ $HDO$  (in  $cm^{-1}$ )] = 2726.7, 1402.2, 3707.5  
B [ $H_2O$  (in  $cm^{-1}$ )] = 27.88, 14.51, 9.29  
B [ $HDO$  (in  $cm^{-1}$ )] = 23.38, 9.102, 6.47  
B [ $HCl$  (in  $cm^{-1}$ )] = 10.59; B [ $DCl$  (in  $cm^{-1}$ )] = 5.449  
 $\bar{u}$  [ $HCl$  (in  $cm^{-1}$ )] = 2991;  $\bar{u}$  [ $HCl$  (in  $cm^{-1}$ )] = 2154

MPTEL 1:46 / 22:31

But this is not as simple as dealing with disodium going to sodium atoms because number one here the number of molecules in the reactants and products is more, and you also have a triatomic molecule H<sub>2</sub>O. So, the more the number of molecules in the reactants and products, the more will be the calculations because the overall partition function is going to be the product of the partition function for each mode of motion for each molecule. I repeat, for the product of each mode of motion for each molecule. For example, the water molecule here; water can have translational degree of freedom, it can also have rotational degree of freedom, it can also have vibrational degree of freedom, and if there is an electronic degree. Similarly, DCl is a linear molecule.

Here you will have all translational rotational vibrational electronic is possible. HDO translational rotational vibrational electronic. Similarly, for HCl. So, in order to solve this question, you require a lot of data. The wave numbers vibrational wave numbers for H<sub>2</sub>O are 3656.7, 1594.8, 3755.8. Water is a non-linear molecule OHH non-linear molecule. The normal modes of vibration are 3 and minus 6, and in this case, in the case of water, 3 times 3 is 9 minus 6 is equal to 3 and those wave numbers are given here 3656.7, 1594.8, 3755.8. HDO is also a non-linear molecule. Okay, HDO being a non-linear molecule, you have again 3 modes of vibration, normal modes of vibration.

See Slide time: 5:51



$3N - 6 = 3$

**Calculate the equilibrium constant at 800 K  
for the gas phase exchange reaction**

$$\text{H}_2\text{O} + \text{DCl} = \text{HDO} + \text{HCl}$$

$\bar{u} [\text{H}_2\text{O} (\text{in } \text{cm}^{-1}) = 3656.7, 1594.8, 3755.8$   
 $\bar{u} [\text{HDO} (\text{in } \text{cm}^{-1}) = 2726.7, 1402.2, 3707.5$   
 $\checkmark B [\text{H}_2\text{O} (\text{in } \text{cm}^{-1}) = 27.88, 14.51, 9.29$   
 $\checkmark B [\text{HDO} (\text{in } \text{cm}^{-1}) = 23.38, 9.102, 6.47$   
 $\textcircled{B} [\text{HCl} (\text{in } \text{cm}^{-1}) = 10.59; \textcircled{B} [\text{DCl} (\text{in } \text{cm}^{-1}) = 5.449$   
 $\checkmark \bar{u} [\text{HCl} (\text{in } \text{cm}^{-1}) = 2991; \checkmark \bar{u} [\text{HCl} (\text{in } \text{cm}^{-1}) = 2154$

$K = \frac{\left\{ \frac{q_{\text{HDO}}}{N_A} \right\} \left\{ \frac{q_{\text{HCl}}}{N_A} \right\}}{\left\{ \frac{q_{\text{H}_2\text{O}}}{N_A} \right\} \left\{ \frac{q_{\text{DCl}}}{N_A} \right\}} e^{-\Delta E_0/RT}$

Rotational constant for water 27.88, 14.51, 9.29 non-linear rotor. Both H<sub>2</sub>O and HDO are non-linear rotor; therefore, you will require the values for A, B, C, 3 rotational constants.

HCl being linear and DCl being linear is a linear rotor. So therefore, you will require only one rotational constant for each, and for a diatomic linear molecule, there is only one normal mode of vibration. So therefore, there is only one value given for HCl, and there is only one value given for DCl. With this data, now we have to proceed and evaluate the value of the equilibrium constant. Equilibrium constant, now let us write down the expression.

I will write  $q_{HDO}$  by  $N_A$  into  $q_{HCl}$ , let me write in the bracket, divided by  $N_A$  then I have  $q_{H_2O}$  divided by  $N_A$  into  $q_{DCl}$  divided by  $N_A$  into exponential minus  $\Delta E_0$  by  $RT$ . When you write like this all these Avogadro constants will cancel out. The resulting expression is  $q_{HDO}$ ,  $q_{DCl}$ ,  $q_{H_2O}$ , and  $q_{DCl}$ . I have written here the standard state conditions into  $\Delta$  minus  $\Delta E_0$  by  $RT$ . HDO and H<sub>2</sub>O let me write for  $q_{HDO}$  I am not writing  $N_A$  just to make it more simpler but assume that this is standard state. This is going to be  $q$  translational HDO, it can undergo rotation also HDO, it can undergo vibration also HDO and I will rule out electronic because if at all there is a contribution that is going to be nearly 1.

See Slide time: 7:56

$$q_{(HDO)} = \frac{q^T_{(HDO)} \cdot q^R_{(HDO)} \cdot q^V_{(HDO)}}{N_A}$$

$$q_{(HCl)} = \frac{q^T_{(HCl)} \cdot q^R_{(HCl)} \cdot q^V_{(HCl)}}{N_A}$$

$$\vdots$$

$$q_{(H_2O)}$$

$$q_{(DCl)}$$

$$K = \frac{q^o(HDO) \times q^o(HCl)}{q^o(H_2O) \times q^o(DCl)} \times e^{-\Delta E_0 / RT}$$

So, I am not incorporating I am not including the electronic contribution. And similarly, you will also have  $q$  for HCl; this also you will have  $q^T$  (HCl)  $q$  it can undergo rotation also HCl into  $q$  vibrational HCl and similarly, I can write for  $q_{H_2O}$  and  $q_{DCl}$ . Now if you examine carefully, you will require  $q^T$ ,  $q^R$ ,  $q^V$  for each molecule alright. So, you have this  $q$  translational,  $q$  rotational,  $q$  vibrational for each molecule that you need to calculate that means it can be very cumbersome and it can be very lengthy process. Now if you look at the problem statement, calculate the equilibrium constant at 800 K for the gas phase exchange reaction with the given numbers there is no additional information given.

And what we discussed is that I need translational, rotational, vibrational contribution for each contribution.  $q$  translational is equal to  $V_m^\circ$  by  $\lambda^3$  where  $\lambda$  is equal to  $h$  over square root  $2\pi m k T$  see how this given problem can be simplified.  $h$  is constant, Planck's constant  $2\pi k T$  is fixed you are given the temperature that means this  $\lambda$  is inversely proportional to square root of  $m$  at a given temperature  $\lambda$  is inversely proportional to square root of  $m$  that means  $q$  is going to be directly proportional to the 3 by 2 1 by 1.5 fifth power of  $m$ ,  $m$  is here mass and you can always express in terms of molecular weight. So that means when you consider this ratio and since this is only the mass of let us see here it is mass of one particle and Avogadro constant everything gets cancelled.

See Slide time: 10:41

Handwritten equations:

$$q^T = \frac{V_m^\circ}{\lambda^3}$$

$$\lambda = \frac{h}{\sqrt{2\pi m k T}}$$

$$\lambda \propto \frac{1}{\sqrt{m}}$$

$$q^T \propto M^{3/2}$$

Video player interface showing the calculation:

$$\frac{q^T(HDO) \times q^T(HCl)}{q^T(H_2O) \times q^T(DCl)} = \frac{\{M(HDO) \times M(HCl)\}^{3/2}}{\{M(H_2O) \times M(DCl)\}^{3/2}} = \frac{(19.02 \times 36.46)^{3/2}}{(18.02 \times 37.46)^{3/2}} = 1.041$$

So that means this ratio is directly you can calculate from the ratio of their molar masses you do not need to calculate anything else right this is where we said that  $q_T$  is directly proportional to  $m$  raised to the power 3 by 2. So molar mass of HDO, molar mass of HCl, molar mass of  $H_2O$ , and molar mass of HCl when you substitute all this you get a value of this ratio approximately 1. This ratio is approximately 1 this gives another information that the translational states occupied by these molecules are almost the same similar ok. So, we have found out a very easy way of dealing with the ratio of translational contributions. Now let us look at rotational contributions for a linear rotor like your DCl like HCl the rotational contribution to the partition function is given by  $kT$  by  $\sigma hcB$  where we know the  $\sigma$  is symmetry number and  $B$  is rotational constant and for a non-linear rotor you have  $1$  by  $\sigma kT$  over  $hc \pi$  over  $ABC$  all right.

Now the systems that we have we have  $H_2O$  by  $H_2O$  we have HDO we have HCl and we have DCl  $\sigma$  for  $H_2O$  HDO HCl DCl  $\sigma$  for this is 1 this is also 1 because you can distinguish when you rotate by  $180^\circ$  this is also  $180^\circ$  this is also 1 only this is 2 because in a complete  $360^\circ$  rotation the  $H_2O$  molecule will appear twice in the same state. So, when you take the ratios of the rotational contributions to the partition function what will remain see  $k$  will cancel  $T$  will cancel  $h$  will cancel  $c$  will cancel only the rotational constants and the symmetry number will remain and by using these 2 equations and these 2 ratios when you substitute you will see what remains is the symmetry number of water which is 2 others are all 1 1 1 1 we don't need to worry about that and what else will remain  $ABC$  for  $H_2O$  and  $ABC$  for HDO  $B$  for HCl and  $B$  for DCl and when appropriately substituted in that expression you have all the numbers and then you get 1.702. So, you see you do not need to evaluate the full value of the rotational partition function for either linear rotor or non-linear rotor when you are writing when you are expressing in terms of the ratio many things get cancelled and things get simplified. So, this ratio is coming out to be 1.702.

See Slide time: 13:26

✓ For linear rotor:  $q^R = \frac{kT}{\sigma hcB}$

✓ <sup>non-</sup> For linear rotor:  $q^R = \frac{1}{\sigma} \left(\frac{kT}{hc}\right)^{3/2} \left(\frac{\pi}{ABC}\right)^{1/2}$

H<sub>2</sub>O, HDO, HCl, DCl  
 2, 1, 1, 1

$$\frac{q^R(\text{HDO}) \times q^R(\text{HCl})}{q^R(\text{H}_2\text{O}) \times q^R(\text{DCl})} = \frac{2 \times (27.88 \times 14.51 \times 9.29)^{1/2} \times 5.449}{(23.38 \times 9.102 \times 6.417)^{1/2} \times 10.59} = 1.702$$

Now next comes a vibrational contribution vibrational contribution  $q^v$  is  $1$  upon  $1$  minus exponential minus  $\beta hc \bar{\nu}$  you are given the value of vibrational wave number you are given temperature you can easily calculate the value of vibrational partition function. Remember that  $q^v$  vibrational is a function of the wave number of the vibrational is a product of vibrational partition function for each normal mode alright. So, therefore, you will require if you look at here let's look at the problem statement you have the vibrational wave number 3 vibrational wave number for water 3 for HDO. So therefore, in the numerator, you will have 3 for this and 1 for this 4 in the numerator and denominator 3 for this and 1 for this 4 in the denominator and let's see that is what you have here you have 4 in the numerator and 4 in the denominator these vibrational wave numbers are chosen from that table. So, corresponding to these vibrational wave numbers you can evaluate the vibrational partition function and substitute over here this evaluation can be done by this calculate for each normal mode of vibration and substitute over there we have discussed many times that the vibrational contribution to partition function is usually not very large.

Therefore, you expect this ratio also to be close to 1 in any case calculate remember again I will write  $q^v$  of  $k$   $k$ th mode this is individual right. So overall partition function vibrational partition function vibrational partition function for mode 1 into vibrational partition wave function vibrational partition function for mode 2 mode of vibration into vibrational

partition function for normal mode 3 and continue continue that is the partition function is multiplicative. Now what we had the expression was let us note down the equation then it will be easier for us the equation is  $\text{H}_2\text{O} + \text{DCL} \rightleftharpoons \text{HDO} + \text{HCL}$  this is the reaction and  $K$  what we wrote was  $q^\circ$  of HDO into  $q^\circ$  for HCL over  $q^\circ$  for  $\text{H}_2\text{O}$  into  $q^\circ$  for DCL into exponential minus  $\Delta E^\circ$  by  $RT$ . Our now purpose is to find out the differences in zero-point energies remember what is the value of zero-point energy you have zero-point vibrational energy oscillator has a zero-point vibrational energy which is equal to half  $h c \bar{\nu}$  half  $h c \bar{\nu}$ . That means, the  $\Delta E^\circ$  by  $h c$  will be equal to half  $\bar{\nu}$  differences in the  $\bar{\nu}$ s alright the zero-point vibrational energy is half  $h c \bar{\nu}$  and when you use half  $h c \bar{\nu}$  add up that for the product and from that subtract for the reactants you will get the value of  $\Delta E^\circ$  by  $h c$  right.

See Slide time: 16:01

Handwritten notes on a video player screen:

$$q^v = \frac{1}{1 - e^{-\beta h c \bar{\nu}}}$$

Below this, the partition function for a molecule with  $k$  vibrational modes is given as:

$$q^v(k) = q^v(1) \cdot q^v(2) \cdot q^v(3) \dots$$

The video player interface shows a calculation for the equilibrium constant  $K$  at 298 K:

$$K = \frac{q^v(\text{HDO}) \times q^v(\text{HCl})}{q^v(\text{H}_2\text{O}) \times q^v(\text{DCl})} = \frac{q(2726.7) \times q(1402.2) \times q(3707.5) \times q(2991)}{q(3656.7) \times q(1594.8) \times q(3755.8) \times q(2154)}$$

The video player controls show the time 16:01 / 22:31.

So, here I will say summation  $j v_j \bar{\nu}_j$ . So, I can take a number you can take and when you substitute all these numbers you know for the products you look back for the products for HDO plus DCL this is for HDO 2726 1403 3707 and HCL wave number is 2991. So, these three numbers are the same 3 plus 1 4 take the addition of that and then for the reactants you subtract the corresponding number when you do that this difference comes out to minus 162  $\text{cm}^{-1}$  this is  $\Delta E^\circ$  by  $h c$  ok.

See Slide time: 18:21



$$K = \frac{q^\ominus(\text{HDO}) \cdot q^\ominus(\text{HCl})}{q^\ominus(\text{H}_2\text{O}) \cdot q^\ominus(\text{DCl})} \times e^{-\frac{\Delta E_0}{RT}}$$

$$\frac{\Delta E_0}{hc} = \frac{1}{2} \sum_J \bar{\nu}_J$$

$$\frac{\Delta E_0}{hc} = \frac{1}{2} \times [(2726.7 + 1402.2 + 3707.5 + 2991) - (3656.7 + 1594.8 + 3755.8 + 2145)] = -162 \text{ cm}^{-1}$$

And when you multiply by  $h c$  you can get the value of  $\Delta E^\ominus$  difference in the zero-point energies alright. Now, we know the value of  $\Delta E^\ominus$  this all we have expressed as the ratio of translational rotational vibrational partition functions we calculated for 1.041 we calculated for 1.041 we calculated for 1.0707.

See Slide time: 20:36



$$K = \frac{q^{\circ}(\text{HDO}) \times q^{\circ}(\text{HCl})}{q^{\circ}(\text{H}_2\text{O}) \times q^{\circ}(\text{DCl})} \times e^{-\Delta E_0/RT}$$

$$K = 1.041 \times 1.707 \times 1 \times e^{1.4386 \times 162/800} = 2.41$$

I left for you to calculate for vibrational deliberately I left for you to calculate vibrational by, but I will tell you since vibrational energy levels are separated far separated you expect this ratio also to be close to 1. And then exponential minus  $\Delta E^{\circ}$  by R T or  $\Delta E^{\circ}$  by k T if you are expressing per mole or not. So, substituting all those numbers what you have is a final answer of 2.41 the question was complex, but we discussed how to simplify a complex problem because the ratio of these partition functions they take a shape where many factors cancel out and you have a simplified version either in terms of molecular masses molar masses or in terms of their rotational constants and vibrational wave numbers.

We also discussed how to get this zero-point difference in zero-point energies from the vibrational wave number data. So, I hope that by now you have understood how to calculate the equilibrium constant for a reaction from the knowledge of molecular partition functions. When I say from the knowledge of molecular partition function, I mean that from the knowledge of corresponding spectroscopic data which gives information about rotational constants or vibrational wave numbers. Electronic contribution we deliberately did not include because we always find that the electronic contribution to molecular partition function is usually close to 1 or close to degeneracy of the ground state. In any case, we will further solve similar questions and try to clarify if there are any problems in

dealing with such questions, but that we will be doing in the coming up lectures. Thank you very much.