

## Fundamentals of Statistical Thermodynamics

Prof. Nand Kishore

Department of Chemistry

Indian Institute of Technology, Bombay

### Lecture – 53

#### Problem solving (continued)

Welcome back, let us continue with the problem solving. In the previous lecture, we took some examples where the developed equations could be applied in solving some numerical problems. Let us now extend our discussion to another type of problem. The question is, calculate the standard molar entropy of  $\text{N}_2$  gas at 298 K from its rotational constant is given,  $B$  is equal to  $1.9987 \text{ cm}^{-1}$  and its vibrational wave number is given. The problem that we discussed in the previous lecture was based upon moment of inertia.

See Slide Time: 5:15

Calculate the standard molar entropy of  $\text{N}_2(\text{g})$  at 298 K from its rotational constant  $B = 1.9987 \text{ cm}^{-1}$  and its vibrational wavenumber  $2358 \text{ cm}^{-1}$

Standard state  $\theta, p^\theta = 1 \text{ bar}; S_m^\theta$

$$S = \frac{U - U(0)}{T} + k \ln Q$$

Indistinguishable  $Q = \frac{q^N}{N!}$

$$S = \frac{U - U(0)}{T} + k \ln \frac{q^N}{N!} = \frac{U - U(0)}{T} + k \ln q^N - k \ln N!$$
$$S = \frac{U - U(0)}{T} + Nk \ln q - k \{ N \ln N - N \} \quad \left| \begin{array}{l} kN = \frac{k}{n} N_A \\ = nR \end{array} \right.$$
$$S = \frac{U - U(0)}{T} + nR \ln q - nR \ln N + nR$$

Remember,  $B$  is equal to  $h$  cross by  $4 \pi c_i$ . So, if I know moment of inertia, I can get the rotational constant and towards the vibration side there we talked about frequency and here

we are talking about the wave number. So,  $h\nu$  is equal to  $hc\bar{\nu}$ . So, these should be easily interconvertible.

The question that we need to address here is the standard molar entropy of nitrogen gas. When I say standard molar, we are talking about the standard state. Standard states that we represent by the symbol this and we put pressure here is equal to 1 bar and molar, molar means I will talk about  $S_m^\circ$ . This is what basically I mean. For the sake of simplification, I will not write  $m^\circ$ .

I will simply write  $S$ , but you take it as standard molar entropy. The question says that you evaluate, you calculate the standard molar entropy from the given values of rotational constants and vibrational wave number. So, therefore, we need to find out such a connection. Basically, we need to connect entropy with the molecular partition function. So, we know that entropy is equal to  $U$  minus  $U(0)$  by  $T$  plus  $K \log q$  that we know.

Now, since we are dealing with nitrogen gas, when you are dealing with nitrogen gas, the gas molecules are indistinguishable. When the molecules are indistinguishable, then canonical partition function is equal to  $q$  raised to the power  $n$  by  $n$  factorial. So, what I have now is  $S$  is equal to now  $U$  minus  $U(0)$  by  $T$  plus  $K \log q$  raised to the power  $n$  over  $n$  factorial, which is now I can write  $U$  minus  $U(0)$  by  $T$  plus  $K \log q$  raised to the power  $n$  minus  $K \log n$  factorial. Let me rewrite it  $S$  is equal to  $U$  minus  $U(0)$  by  $T$  plus  $n K \log q$  minus  $K \log n$  factorial is  $n \log n$  minus  $n$ .  $S$  is equal to  $U$  minus  $U(0)$  by  $T$   $n K$  is equal to  $n R$  we have discussed many times  $\log q$  minus  $n R \log n$  plus  $n R$ .

We are doing this  $K$  times  $n$  is equal to  $K n$  is equal to  $n$  times  $n A$  and  $K$  into  $n A$  is  $R$  which is equal to  $n R$  this is what we have done. Let me write down this on the next slide. What I have is  $S$  is equal to  $U$  minus  $U(0)$  by  $T$  this is 1, then we had  $n R \log q$  plus  $n R \log q$  minus  $n R \log n$  minus  $n R \log n$  plus  $n R$ . Now we need to also connect this  $U$  minus  $U(0)$  by  $T$  with the molecular partition function and that also we know  $U$  minus  $U(0)$  is equal to minus  $n$  by  $q \delta q$  by  $\delta \beta$  at constant volume which I can write as minus  $n \delta \log q \delta \beta$  at constant volume  $d q$  by  $q$  can be written as  $d \log Q$ . Now sometimes it becomes easier if you differentiate with respect to temperature than when you differentiate with respect to  $\beta$   $\beta$  is equal to  $1$  by  $K T$ .

See Slide Time: 11:05

$$\begin{aligned}
 S &= \frac{U - U(0)}{T} + nR \ln q - nR \ln N + nR \\
 U - U(0) &= -\frac{N}{q} \left( \frac{\partial q}{\partial \beta} \right)_V = -N \left( \frac{\partial \ln q}{\partial \beta} \right)_V \\
 \frac{d}{dT} &= \frac{d\beta}{dT} \cdot \frac{d}{d\beta} = -\frac{1}{kT^2} \cdot \frac{d}{d\beta} \\
 \frac{d}{d\beta} &= -kT^2 \frac{d}{dT} \\
 \beta &= \frac{1}{kT} \\
 U - U(0) &= NkT^2 \left( \frac{\partial \ln q}{\partial T} \right)_V \\
 S &= \boxed{NkT \left( \frac{\partial \ln q}{\partial T} \right)_V} + nR \ln q - nR \ln N + nR = \boxed{Nk \left( \frac{\partial T \ln q}{\partial T} \right)_V} + nR - nR \ln N
 \end{aligned}$$

So, therefore, temperature derivative can also be done with respect to temperature or it can be with respect to  $\beta$ . Now you consider  $d$  by  $d T$  let us I write  $d$  by  $d T$  I can write as  $d$  by  $d T$  into  $d$  by  $d \beta$  mathematically that is allowed and remember  $\beta$  is equal to  $1$  over  $k T$  therefore,  $d d \beta$  therefore, when you take its derivative, it will come minus  $1$  over  $K T$  square this is  $d \beta$  by  $d T$  into  $d d \beta$ . So, that means,  $d d \beta$  I can write as minus  $K T$  square  $d$  by  $d T$  this is mathematically allowed, I will now use this information over here that means, now I have  $U$  minus  $U(0)$  is equal to minus sign and minus sign will go away. So, I will have it is square minus minus plus  $n K T$  square into  $\delta \log q$  by  $\delta T$  at constant volume. What I have done is simply change the differentiation from  $d d \beta$  to  $d d T$ .

Now let us substitute this information into this expression what I have now  $S$  is equal to  $U$  minus  $U(0)$  by  $T$ . So, therefore, one  $T$  with  $T$  square one  $T$  will get cancelled. So, I will have  $n K T \delta \log q \delta V \delta T$  at constant volume plus  $n R \log q$  minus  $n R \log n$  plus  $n R$  we have reached up to this, this  $T$  square becomes  $T$  because  $U$  minus  $U(0)$  by  $T$  is used. Now what I will do next is to make the things little easier I will combine these two terms. Let us say if I combine these two terms, I can write  $n$  times  $k \delta T \log q \delta T$  at constant volume plus  $n R$  minus  $n R \log n$ .

This  $n K$  also I can write  $n R$ . So, therefore, now I will write  $S$  is equal to  $n R \delta T \log q \delta T$  at constant volume plus  $n R$  minus  $n R \log n$ . Let me write this I hope this is clear to you that these two can be combined to write this derivative if you open up this derivative you

will get this expression. For example, when you act upon  $\delta T \log q$  by  $\delta T$  then it is derivative of A into B. So, T into  $\delta \log q$  by  $\delta T$  at constant volume this first term then plus  $\log q$  plus  $\log q$  this term  $n R$  is anyway common.

See Slide Time: 18:05

Handwritten notes on a video player showing the derivation of the translational partition function and entropy for  $N_2(g)$ .

Top left (boxed):  $S = nR \left( \frac{\partial T \ln q}{\partial T} \right) + nR - nR \ln N$

Top right:  $Q = \frac{q^N}{N!}$

Middle left:  $N_2(g): T, V, R$

Middle: Translational  $q^T = \frac{V}{\lambda^3} = \frac{V}{h^3} (2\pi m k T)^{3/2}$

Below middle left:  $T = 298 \text{ K, std. st. cond.}$   
 $p V_m^\theta = RT$   
 $V_m^\theta = RT/p = 24.78 \text{ L} = 24.78 \times 10^{-3} \text{ m}^3$

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

Bottom (crossed out):  $S = nR \ln \left\{ \frac{e^2 (2\pi m k T)^{3/2} V_m^\theta}{N_A h^3} \right\} = 150.4 \text{ J K}^{-1} \text{ mol}^{-1}$

Let us write this expression on the next page for further solving. So, I have S is equal to  $n R \delta T \log q \delta T$  at constant volume plus  $n R$  minus  $n R \log n$ . The given question is on nitrogen gas. Nitrogen gas is going to have translational degree of freedom, is going to have vibrational degree of freedom, is going to have rotational all translational vibrational degrees of freedom are there. So, therefore, I need to calculate the entropy due to translational contribution, rotational contribution, vibrational contribution.

First of all let us talk about translational. When I talk about translational, I talk about translational, then  $q$  translational is equal to  $V$  upon  $\lambda^3$ ,  $\lambda$  is equal to  $h$  upon root  $2 \pi m k T$ . So, that means, this is equal to  $V$  upon  $\lambda$  so that means, this is equal to  $V$  upon  $\lambda^3$  upon  $h^3 (2 \pi m k T)^{3/2}$ . This is what I am going to get  $V$  upon  $\lambda^3$ . We are asked to solve this at  $T$  equal to  $298 \text{ K}$   $25^\circ \text{C}$  and we are given standard state conditions right.

I said I am not writing not, but assume that this is not that means, I can get  $V^\theta$   $V P$   $v_m^0$  is

equal to  $R T$  where  $P$  is also  $P^\circ$  which is 1 bar by using this you can get  $V_m^\circ$  equal to  $R T$  by  $P^\circ$  temperature is given pressure is given which is 1 bar you can convert into atmosphere and use the you know appropriate units. This comes out to 24.7 K. 24.78 liter which is equal to 24.78 into 10 raise to the power minus 3-meter cube. When you actually substitute this  $q T$  into here listen to me carefully. When you put this  $q T$  into here and write an expression for translational contribution go back to secur-tetrode equation. We have included  $n$  factorial factor and come up with this expression including  $n R$  minus  $n R \log n$ . Therefore, this expression when you put this expression for  $n$  factorial factor.

When you apply for translational contribution will eventually take the form of secur-tetrode equation and what is secur-tetrode equation  $n R \log I$  will write  $e$  raise to the power 5 by 2  $2 \pi m k T$  raise to the power 3 by 2 into  $V^\circ$  by  $R T$  by  $P^\circ$ . I will put  $V_m^\circ$  right I am I am not writing standard state on that side, but consider this as a standard state this is equal to or I will have  $n$  a into  $h$  cube. I am not deriving this because we have derived it earlier. In fact, when you put  $q T$  is equal to  $V$  by  $h$  cube  $2 \pi m k T$  raise to the power 3 by 2 here in this expression you are going to get this secur-tetrode equation. We know the value of  $P$   $v_m^0$  we know for nitrogen 28 divided by Avogadro constant into 10 raise to the power minus 3.

We know Boltzmann constant we know Planck's constant we know Avogadro constant and when you substitute the values this is coming to be equal to 150.4 joules per K per mole. We have got now the translational contribution. We still have to get the rotational contribution and vibrational contribution let us now work towards obtaining rotational contribution. If we go back or we can just take a look at this expression.

Full translational contribution we have already included the  $n$  factorial expansion. Remember we used  $q$  is equal to  $q$  raise to the power  $n$  by  $n$  factorial. This molecular partition function is the product of translational rotational vibrational etcetera, but  $n$  factorial is not coming with each  $q$   $n$  factorial is coming only one that we are including here along with the translational contribution. You can include with rotational also vibrational whatever because this factor is going to come only once. We have included here in secur-tetrode equation therefore, we need not use it when we discuss rotational contribution or we discuss vibrational contribution.

Let us now switch over to rotational contribution. So, rotational for rotational contribution

what I will do is I will use same thing  $n R \delta T \log q$  by  $\delta T$  constant volume and I am not going to use the rest of the term because those have already been used with the translational contribution. Now  $q$  rotational is equal to  $1$  upon  $\sigma h c \beta B$  that we know. I can write this as  $T$  over  $\sigma h c \beta B$  is equal to  $1$  over  $k T$  all right. So, what I will do now is I will substitute here  $S^R$  is equal to  $n R$  into  $S^R$  by  $\delta T$  constant volume.

See Slide Time: 22:10

$$S^R = nR \left( \frac{\partial \ln q}{\partial T} \right)_v$$

$$q^R = \frac{1}{\sigma h c \beta B} = \frac{kT}{\sigma h c B} \quad \checkmark$$

$$S^R = nR \cdot \left\{ \frac{T}{q} \cdot \frac{\partial q}{\partial T} + \ln q \right\}_v = nR \cdot \left\{ \frac{T \cdot \sigma h c B}{kT} \cdot \frac{k}{\sigma h c B} + \ln q \right\}$$

$$S^R = nR \cdot \{ 1 + \ln q \} = nR \cdot \left\{ \ln \left( \frac{kT}{\sigma h c B} \right) + 1 \right\} = 41.14 \text{ J K}^{-1} \text{ mol}^{-1}$$

Side notes:  
 $k \theta_R = h c B$   
 $\theta_R = 2.87 \text{ K}$   
Given  $T = 298 \text{ K}$

Let us see what do I get if I keep  $T$  by  $q \delta q \delta T$  this one will come plus  $\log q$  will come into  $\delta T$  by  $\delta T$  1 this all is going to be at constant volume. Let us see what we get  $T$  by  $q$   $T$  by  $q$   $Q$  is  $k T$  by  $\delta T$  by  $\delta T$  constant volume. So, this is  $k T$  into  $\sigma h c \beta$  into  $\delta q$  by  $\delta T$  when I take derivative of the partition function with respect to  $T$  this is going to be  $k$  over  $\sigma h c \beta$  that is it  $n$  plus  $\log q$  this is the bracketed term and you already have here  $n R$ . So, what I have now  $S^R$  is equal to  $n R$  into  $k T \sigma h c \beta$  and  $k T \sigma h c \beta$  cancels. So, I have  $1$  plus  $\log q$  where  $q$  here is  $q^R$  only or what I have  $n R$  into  $S^R$  by  $\delta q$  into  $\log q$  is what  $q$  is  $k T$  over  $\sigma h c \beta$  this is  $\log q$  plus  $1$  this is what I have, but remember that we are using the high temperature result because we are using  $q^R$  is equal to  $k T$  by  $\sigma h c \beta$  which is only possible if the temperature rotational temperature is higher than the actual temperature.

So, for that what you will do is you will use  $k \theta_R$  is equal to  $h c \beta$  use this you put in

the value you will get  $\theta_r$  is equal to 2.87 K right and your given temperature is equal to 298 K which is much higher than 2.87 K. So, therefore, it is justified to use  $q_r$  is equal to  $kT$  over  $\sigma h c b$ . Now, you substitute the values and what you will get is 41.14 joules per K per mole  $k$  is Boltzmann constant  $T$  is the temperature which is given to you  $\sigma$  is equal to in this case it is nitrogen. So, therefore,  $\sigma$  is equal to 2 and  $h$  is Planck's constant  $c$  is speed of light and  $b$  is the rotational constant. We have done for rotational contribution also and now let us talk about the vibrational contribution. So,  $S_v$  is equal to  $N_r \delta T \log q_v$ ,  $q_v$  here is  $q_v$  over  $\delta \beta \delta T$  at constant volume. So, what I have now is let us do it  $q_v$  vibrational is  $1$  over  $1$  minus exponential minus  $h c \bar{\nu}$  by  $k T$ .

See Slide Time: 26:35

$$S^v = nR \left\{ \frac{\partial \ln q^v}{\partial T} \right\}_v$$

$$q^v = \frac{1}{1 - e^{-hc\bar{\nu}/kT}} \quad ; \quad \ln q = -\ln(1 - e^{-hc\bar{\nu}/kT})$$

$$S^v = nR \left\{ T \cdot \frac{(-1)}{(1 - e^{-hc\bar{\nu}/kT})} \cdot (-e^{-hc\bar{\nu}/kT}) \cdot \left( \frac{hc\bar{\nu}}{kT^2} \right) + \ln q^v \right\}$$

$$S^v = nR \cdot \left\{ \left( \frac{hc\bar{\nu}}{kT} \right) \cdot \frac{e^{-hc\bar{\nu}/kT}}{1 - e^{-hc\bar{\nu}/kT}} - \ln(1 - e^{-hc\bar{\nu}/kT}) \right\}$$

$$\frac{hc\bar{\nu}}{kT} = 11.38$$

$$S^v = \text{Nearly zero} \sim 0$$

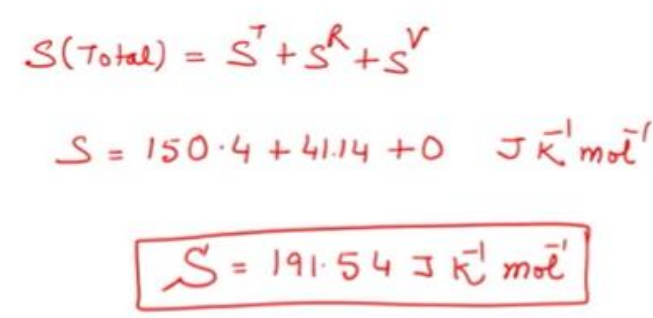
I am writing in terms of temperature therefore, my  $S^v$  becomes  $nR$  it will be easier if I talk in terms of  $\log q$ . I am not writing  $v$  here for simplicity. So, this is minus  $\log 1$  minus exponential minus  $h c \bar{\nu}$  by  $k T$  this is what I have. Now, let us take the step forward and expand this differentiation what I have now  $T$  into derivative of  $\log q$  derivative of this which is going to be minus  $1$  divided by  $1$  minus exponential minus  $h c \bar{\nu}$  by  $k T$  into minus exponential minus  $h c \bar{\nu}$  by  $k T$ . Next derivative is equal to  $h c \bar{\nu}$  by  $k T$  square with a plus sign this is what will come then plus  $\log q$  by  $k T$  into  $h c \bar{\nu}$  by  $k T$ .

So, this is what I have now. So, this is what I have now  $q_v$  let us combine now  $S$  is equal



to what it will come  $N_r$  into  $h c \bar{\nu}$  by  $k T$  that is coming from this term and this term and then I have  $q_v$  into  $h c \bar{\nu}$  into exponential minus  $h c \bar{\nu}$  by  $k T$  divided by  $1$  minus exponential minus  $h c \bar{\nu}$  by  $k T$  and  $\log q_v$  already we have it is minus  $\log 1$  minus exponential minus  $h c \bar{\nu}$  by  $k T$  right quite complicated term substitute the value  $h c \bar{\nu}$  by  $k T$ , all numbers are given to you  $\bar{\nu}$  is given to you when you calculate this comes to 11.38 and when you use this into this expression what you will find that  $S_v$  vibrational contribution is nearly 0 approximately 0 numbers are going to be very small.

See Slide Time: 27:50



$$S(\text{Total}) = S^T + S^R + S^V$$

$$S = 150.4 + 41.14 + 0 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\boxed{S = 191.54 \text{ J K}^{-1} \text{ mol}^{-1}}$$

So, now we have  $S$  total let us say this will be  $S$  translational plus  $S$  rotational plus  $S$  vibrational we have  $S$  total is equal to  $S$  translational was 150.5 into 10 to the power of 0.4  $S$  rotational was 41.14 and this was 0. So, many joules per K per mole. So, therefore, your entropy comes out to 191.54 joules per K per mole. Quite a lengthy numerical problem, but at least it discusses how the different contributions must enter in when you evaluate the overall thermodynamic quantity. Here we have shown for the case of entropy, but suppose if the question is for Gibbs function or for Helmholtz function or enthalpy then you must include the translational contribution rotational contribution or vibrational contribution whichever contribution whichever mode of motion is fully active.



In this particular case you noticed that there is a sizable number coming up from translational contribution and rotational contribution and vibrational contribution was nearly 0. So, I hope that this particular example has brought in clarity on how to calculate a thermodynamic quantity from the molecular partition function which has different contributions such as translational, rotational, vibrational and if the temperature is so high then the electron. We will discuss a few more problems, but in the next lecture. Thank you very much. Thank you.