

**Statistical Thermodynamics for Engineers**  
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**Lecture 52**

**Thermodynamic properties of ideal monoatomic and diatomic gas**

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free energy

$$p = NkT \left( \frac{2 \ln z}{2V} \right) T$$

$$pV = NkT$$

equation of state  
for an ideal gas.

Pressure arises solely  
from translational mode

So, welcome to lecture number 41 of the Statistical Thermodynamics course. So, as we saw that we have been able to establish that what are the translational modes and for Monatomic gas.

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For entropy

$$\left( \frac{S}{R} \right)_{tr} = \frac{3}{2} \ln \left[ \frac{2\pi m k T}{h^2} \right] + \ln \left( \frac{V}{N} \right) + \frac{5}{2}$$

Substitute  $p = NkT$

$$\left( \frac{S}{R} \right)_{tr} = \ln \left[ \frac{(2\pi m)^{3/2} (kT)^{3/2}}{h^3 p} \right] + \frac{5}{2}$$

So, we already wrote the definition pressure, now, we are going to look at look at the entropy for entropy, we are the translational component of entropy translation it is 3 by 2 just use the

transfer function, not the partition function definition entropy plus  $\ln V$  upon  $n$  plus 5 upon 2. So, if you substitute now, substitute  $PV$  equal to  $NKT$  we get  $S$  by  $R$  is a small  $s$  remember  $s$  translational equal to  $\ln \frac{2\pi m}{h^2} \frac{3}{2} KT$  plus 5 by 2  $\ln P$  plus 5 by 2.

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$$\left(\frac{S}{R}\right)_{tr} = \ln \left[ \frac{(2\pi m)^{3/2} kT}{h^3 P} \right] + \frac{5}{2}$$

$$\left(\frac{S}{R}\right)_{tr} = \frac{5}{2} \ln T + \frac{3}{2} \ln M - \ln P - 1.1516$$

$T$  is  $K$   
 $M$  is the molecular weight (kg/kmol)  
 $P$  is the pressure (bar)

only holds in the dilute limit

This particular equation can be converted to the form right next if we do the evaluation properly so,  $T$  is in  $K$  in Kelvin  $M$  is the molecular weight given in  $Kg$  per Kilomol.  $P$  is the pressure in bar so, it only holds this equation only holds in the dilute limit and it is not appropriate when the temperature approaches absolute 0. So, this is the this is the form that we see.

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Determine the contribution to Helmholtz free energy (kJ/mole) from translational mode at 500K and 2 bars for He

$$\left(\frac{A}{RT}\right)_{tr} = - \left[ \ln \left( \frac{z_{tr}}{N} \right) + 1 \right]$$

$$\frac{z_{tr}}{N} = \left( \frac{2\pi m kT}{h^2} \right)^{3/2} \frac{kT}{P}$$

Now, let us do a very simple problem here. So, say the question is determine, determine the contribution to Helmholtz free energy of  $k_B T$  per mole from the translational mode at 500 kelvin and 2 bars for  $(\text{O}_2)$  which is monatomic in nature this is a question. So, Helmholtz free energy again if you recall the definition or it can be written in terms of the transfer function. So,  $Z_{tr}$  by  $N$  equal to given as  $\frac{2\pi m K T}{h^2}$  by  $h^2$  square 3 by 2  $K T$  by  $P$ .

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$$\frac{Z_{tr}}{N} = \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} \left( \frac{k_B T}{P} \right)$$

$$\frac{Z_{tr}}{N} = \frac{(2\pi m)^{3/2} (k_B T)^{5/2}}{h^3 P}$$

$$= \frac{[2\pi (4.0026) (1.6605 \times 10^{-27})]^{3/2} [(1.3807 \times 10^{-23}) (500)]^{5/2}}{(6.6261 \times 10^{-34})^3 (2 \times 10^5)}$$

$$\frac{Z_{tr}}{N} = 5.808 \times 10^5$$

Now,  $Z_{tr}$  by  $n$  is equal to  $\frac{2\pi m^3}{h^3} \frac{(k_B T)^{5/2}}{P}$  divided by  $h^3$  to  $p$  if you now substitute the numbers see  $2\pi \cdot 4.0026 \cdot 1.6605 \times 10^{-27}$  3 by 2  $1.3807 \times 10^{-23} \cdot 500$  is entire thing is raise to the power 5 by 2 divided by  $6.6261 \times 10^{-34}$  cube 2 into 105. So, from here we calculate this actually leads to  $Z_{tr}$  by  $N$  is equal to  $5.808 \times 10^5$ .

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$$\left(\frac{a}{RT}\right)_{tr} = -\left[\ln\left(\frac{Z_{tr}}{N}\right) + 1\right]$$
$$= -(13.272 + 1.000)$$
$$= -14.272$$
$$a_{tr} = -14.272 (8.3145 \text{ J/K.mol})$$
$$= -58.333 \text{ kJ/mol}$$

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Then, then of course, so, if you now substitute this substitute in the expression translation is equal to minus again we are writing  $\ln Z_{tr}$  by  $N$  plus 1. It is equal to minus 13.272 plus 1.000 is equals to minus 14.272. So, we obtain  $a_{tr}$  is equal to minus 14.272  $8.3145$  joule per kilomole per kelvin per mole into 500 kelvin which would give you the ultimate answer which is minus 58.333 kilojoules per mole. So, this is one sample problem that when we have shown that this is indeed possible to do this.

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Electronic mode

Direct summation on relevant term symbols and energy levels ( $cm^{-1}$ )

Appendix J

First few electronic levels only matter as higher ones are impossible because of too high  $T$  reverse

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Now, let us look at the final mode which is the electronic mode other electronic now the electronic mode requires a direct summation on the relevant term symbols and energy levels right. So, it requires on the relevant term symbols if requires direct summation relevant term

symbols and energy levels which is basically centimeter inverse. So, this is tabulated in Appendix J of the book, appendix free to go there and check.

In most cases the first few electronic levels need to be considered because higher excited levels of typical temperature is almost improbable the first few electronic levels of the matter levels only matter as higher ones are improbable because of the high temperature requirement high temperature required.

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The screenshot shows a digital notebook with the following handwritten content:

Term Symbol	$T_e$ ( $\text{cm}^{-1}$ )
$2P_{1/2}$	0
$2P_{3/2}$	112.1
$2S_{1/2}$	25347.8

Below the table, the partition function is calculated:

$$Z_{el} = g_0 + g_1 e^{-E_1/KT}$$

at 1000K:  $= 2 + 4 \exp\left[\frac{-1.4387(112.1)}{1000}\right] = 5.4042$

So, nevertheless you can establish cutoff on a case by case basis high temperatures. For example, if you consider we consider only 3 electronic levels for atomic aluminum for this case, we would normally require only the first 2 levels for calculating the partition function because the huge gap between the second and the third levels, so if we look at atomic aluminum. So, let us look at the term symbol here. And this is  $T_e$  which is centimeter inverse  $2p$  half you recall the symbols 0  $2P$  3 by 2 112.1 and  $2s$  half is about 25347.8.

So, as you can see that there is a huge gap there is a huge gap, it only required the first 2 levels because you see the second and the third level there is a huge gap when we calculate the partition function for gaseous ( $\text{Al}$ )(10:47), so, that this partition function therefore, electronic evaluated at 1000 Kelvin 1000 kelvin will be  $G$  naught plus  $G_1 e$  to the power of  $e_1$  by  $KT$  which is equal to 2 plus 4 exponential minus 1.4387 into 112.1 divided by 1000 Kelvin this gives you a number which is 5.4042.

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$$Z_{el} = g_0 + g_1 e^{-\epsilon_1/kT}$$

$$\text{at } 1000K = 2 + 4 \exp\left[\frac{-(1.4388)(121)}{1000}\right]$$

$$= 5.4042$$

$$T \left( \frac{\partial \ln Z}{\partial T} \right)_V = \left[ \frac{\partial}{\partial T} T^2 \left( \frac{\partial \ln Z}{\partial T} \right) \right]_V$$

So, contribution for any of any energy mode to properties like internal energy and heat capacity is basically you know comes through  $T \ln Z$  by  $dt$  at constant  $V$  and  $dt$  partial the partial respect to  $t$ . So, you always need these quantities to calculate the salient features but the electronic case contributions of those these 2 expressions can be derived on the term by term differentiation of the partition function at the electronic levels.

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$$T \left( \frac{\partial \ln Z_{el}}{\partial T} \right)_V = \frac{Z'_{el}}{Z_{el}}$$

$$\left[ \frac{\partial}{\partial T} T^2 \left( \frac{\partial \ln Z_{el}}{\partial T} \right) \right]_V = \frac{Z''_{el}}{Z_{el}} - \left( \frac{Z'_{el}}{Z_{el}} \right)^2$$

$$Z_{el} = \sum_j g_j e^{-\epsilon_j/kT}$$

$$Z'_{el} = \sum_j g_j \left( \frac{\epsilon_j}{kT} \right) e^{-\epsilon_j/kT}$$

So, the algebra is like this there for write it could yell you can stick to  $T^2$  by  $Z_{el}$ ,  $Z_{el}$  this is the primary differentiation in first differentiate, where with write  $Z_{el}$  is basically sorry it is not the differentiations just write the expressions it is differentiation but not in the form.

We will just write it in a second. So,  $Z_{el}$  prime is equal to  $G_j$  so, this is the differentiation first one and then of course, we differentiated again.

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$$Z_{el} = \sum_j g_j e^{-\epsilon_j/kT}$$

$$Z'_{el} = \sum_j g_j (\epsilon_j/kT) e^{-\epsilon_j/kT}$$

$$Z''_{el} = \sum_j g_j (\epsilon_j/kT)^2 e^{-\epsilon_j/kT}$$

$$\left(\frac{u}{RT}\right)_{el} = \left(\frac{h}{RT}\right)_{el} = \frac{Z'_{el}}{Z_{el}}$$

$$\left(\frac{c_v}{R}\right)_{el} = \left(\frac{c_p}{R}\right)_{el} = \frac{Z''_{el}}{Z_{el}} - \left(\frac{Z'_{el}}{Z_{el}}\right)^2$$

So, this provides you this is a very long tedious differentiation process of we can see here, so, this is the you differentiate it once and then you  $(\frac{d}{dT})$ (14:31) and then you differentiate it another time. So, second derivative. So, immediately preceding expressions for provides now the required tools for evaluating the contribution. So, the different to the different thermodynamic properties or an ideal monoatomic gas. So,  $u$  by  $RT$   $el$  is equal to  $h$  by  $RT$  first differentiate the first derivative and then  $C_V$  by  $R$   $el$  is equal to  $C_p$  by  $R$   $el$  is equal to the second derivative square.

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$$Z_{el} = \sum g_j e^{-\epsilon_j/kT}$$

$$\left(\frac{U}{RT}\right)_{el} = \left(\frac{h}{RT}\right)_{el} = \frac{Z'_{el}}{Z_{el}}$$

$$\left(\frac{C_v}{R}\right)_{el} = \left(\frac{C_p}{R}\right)_{el} = \frac{Z''_{el}}{Z_{el}} - \left(\frac{Z'_{el}}{Z_{el}}\right)^2$$

$$\left(\frac{S}{R}\right)_{el} = \frac{Z'_{el}}{Z_{el}} + \ln Z_{el}$$

Similarly, we can obtain for S by R el plus ln Zel. So, now if you have to calculate the specific heat so, so, these are the expressions.

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calculate specific heat at constant volume (J/k.mol) for N at 3000 K

$$\left(\frac{C_v}{R}\right)_{tr} = 3/2$$

$$\left(\frac{C_v}{R}\right)_{el} = \frac{Z''_{el}}{Z_{el}} - \left(\frac{Z'_{el}}{Z_{el}}\right)^2$$

Now if we if the problem is that calculate specific heat at constant volume which is J by K mole for nitrogen at 3000 kelvins. So, the contribution or the specific heat for a constant volume  $C_v$  by R tr translational mode is only 3 by 2 you can already, now the electronic mode which is  $C_v$  by R electronic which is given as  $Z_{el}$  double prime  $Z_{el}$  minus  $Z_{el}$  divided  $Z_{el}$ . So, this can be done electronic contribution can be easily determine by setting up the table or we can set up a table and then we can compute all the quantities from there.



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$$\left(\frac{C_v}{R}\right) T_s = \frac{3}{2}$$

$$\left(\frac{C_v}{R}\right) eE = \frac{Z'_{cl}''}{Z_{cl}} - \frac{(Z'_{cl})^2}{(Z_{cl})^2}$$

$E_j$	$g_j$	$E_j/kT$	$g_j e^{-E_j/kT}$	$g_j (E_j/kT) e^{-E_j/kT}$
0	4	0	4	0
19.229	10	9.2216	$9.880 \times 10^{-3}$	$9.1183 \times 10^{-3}$

So, like we did in the last time this is  $E_j g_j E_j$  by  $kT$ . This is a tabulated form this  $g_j$  into exponential  $E_j$  by  $kT$  then it is the  $g_j E_j$  by  $kT$  into exponential minus  $E_j$  by  $kT$  and so on and so forth. So, you understand how each other so these quantities are given, so, I am just going to combine the few which is 0  $g_j$  is equal to 4  $E_j$  by  $kT$  is equal to 0. So, this becomes 4 this becomes 0 and the next one is also 0. So, the next energy level 229 is therefore given as this is 10 this is 9.2216 This is  $9.880 \times 10^{-3}$  to the power minus 4 this is  $9.1183 \times 10^{-3}$  into 10 to the power minus 3 and so on and so forth.

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0	4	0	4	0
19.229	10	9.2216	$9.880 \times 10^{-3}$	$9.1183 \times 10^{-3}$
28.839	6	13.830	$9.9137 \times 10^{-6}$	$8.1787 \times 10^{-5}$

$$\left(\frac{C_v}{R}\right) eE = \frac{Z'_{cl}''}{Z_{cl}} - \frac{(Z'_{cl})^2}{(Z_{cl})^2}$$

$$= \frac{8.527 \times 10^{-2}}{4.0010} - \frac{(9.2001 \times 10^{-3})^2}{(4.0010)^2}$$

$$= 0.02129$$

So, similarly you can tabulate is 3. So, if we consider the first 3 electronic energy levels of nitrogen is also given in Appendix J 0.1, the energy corresponding to the fourth is very high.

So, for nitrogen, so, for a given thermodynamic temperature of about 3000 Kelvin, it does not really matter, maybe for your convenience, it is  $6 \times 10^{13.830}$  is  $5.9137 \times 10^{-6}$  this is  $8.1787 \times 10^{-5}$ .

So, the final row of the table you sum up all these quantities you sum up and then you find out so, you sum up across these levels, because that is what is required. So, your  $C_v$  by  $R$  for electronic will be equal to once again let us write it electronic the definitions now, each one of these terms, so, it is  $8.5217 \times 10^{-2}$  divided by  $4.0010 \times 10^{-9.2001}$  into  $10^{-3}$   $4.0010^2$ . So, this is actually 0.02129.

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$$\frac{C_v}{R} = \left(\frac{C_v}{R}\right)_{tr} + \left(\frac{C_v}{R}\right)_{el}$$

$$= 1.5000 + 0.0213 = 1.5213$$

$$C_v = 12.649 \text{ J/K.mol}$$


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Diatomic gases

$$Z_{tot} = \left(\frac{2\pi m kT}{h^2}\right)^{3/2} V$$

CM based coordinate system

So, the summing up the traditional things if do the complete summation which is basically  $C_v$  by  $R$   $C_v$  by  $R$  translational plus  $C_v$  by  $R$  electronic. So, this gives you 1.5000 plus 0.0213 which is 1.5213 therefore  $C_v$  becomes 12.649 joule per kilomole. So, this is the this is the standard arguments now, so, we have done a couple of problems to show for diatomic gases the evaluation of the thermodynamic properties for diatomic gases requires that you take consideration of now the rotational and the vibrational modes as well as all the translational electronic modes.

For diatomic case complete mode separation again if you recall, it requires a simplex model and the combined rigid rotter and the harmonic oscillator type model. So, using this model the property calculations can be written and the straightforward we will get into some of the relevant contributions in particular the separate contributions from the rotational and the vibrational modes and merely added to the translation on the electronic modes.

So, that is what we are going to do in this diatomic gases. So, for diatomic gases we have a slightly as we said already. So, this is what we are going to do we are simply going to add therefore, the 2. So, the translational mode of a diatomic gas, I mean that the translational partition function is based on the conversion to center of mass coordinates that we already know.

So,  $Z_{tr}$  here is  $2 \pi m k T$  by  $h$  squared  $3$  by  $2$  into  $V$  and  $m$  is equal to  $m_1$  plus  $m_2$ . So, this is the center of mass based coordinate system which you already did coordinate system and now, that total mass represents both the nuclei after chosen diatomic molecule as well.

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$Z_{tr} = \left( \frac{2\pi m k T}{h^2} \right)^{3/2} V$   
 $m = m_1 + m_2$   
 CM based coordinate system

Upper electronic levels of diatomics tend to be lot higher than the ground electronic level

$Z_{el} = \sum_j g_j e^{-E_j/kT} \approx g_0$

So, the electronic mode we observe upper energy levels of diatomic states to be substantially higher in the ground and electronic level. So, upper electronic levels of diatomic tend to be a lot higher in to to be substantially higher than the ground electronic level. So, therefore, yours partition function for the electronic level is  $\sum g_j e^{-E_j/kT}$  will almost reduce to  $g_0$  which is the ground because there are however, there are exceptions like oxygen and nitric oxide for example, which are actually this is not quite correct.

They need substantial electronic contribution demands adherence to the consistent 0 of energy which we already discussed, which we will discuss now. So, in the in the following section, but, so, the 0 of energy for a diatomic molecule can be set either at the minimum the most potential defining the ground electronic state or at the ground vibrational state with this particular most potential.

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electronic level

$$Z_{el} = \sum_j g_j e^{-\epsilon_j/kT} \approx g_0$$

min of Morse potential ground elec. state

So, if you look at this if this is your most potential, you can set this or you can set this so, this is that this is the 0 this is the 0 minimum of the this is the minimum of the most potential of most potential for the ground electronic state whereas, this is the vibrational 0 for the ground electronic state. So, another possibilities to set the 0 the ground electronic state correspond to those atoms produced by dissociation. This of course, requires that we define and dissociation energy as well as a binding energy. So, so, there are there are varieties of things that we then need to need to do for doing this.

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Zero of energy

dissociation energy is  $D_0$

binding energy is  $D_e$

potential ground elec. state

$T_0$ ,  $T_e$ ,  $D_0$ ,  $D_e$

So, let us if we draw this diagram properly, let us see the possibilities. So, this is one this is the other one. So, you are this is your first this is ground vibration. This is T naught then this

is your  $T_e$ . You can also define something like a dissociation. So, that means if you do this things back a little bit so, this is this particular thing is your  $D_0$  and this is your  $D_e$ . Understand what  $D_e$  and dissociations are.

So, dissociation energy is  $D_0$ . Binding energy is  $D_e$ . So, as we showed in this particular figure. So, there are various possibilities therefore, for establishing or we call the 0 of energy various possibilities to establish the 0 of energies and we can compile all of them in a table and define the internal energy for it in diatomic molecule. So, this is required because why this is required, because we have to discuss that how the rotational on the vibrational bands comes into the picture.

So, the 0 of energy is the data is actually very important. So, in our next lecture we are going to finish this off we are going to see that how this can be done, for how to establish the 0 of energy and what are the different possibilities. So, we are going to look at a table we are going to basically combine the table and therefore then we can start to define the rotation and the vibrations (0)(27:00).