

**Statistical Thermodynamics for Engineers**  
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**Lecture 55**

**The Ro-vibrational partition function and Introduction to intersection of Radiation and Matter**

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rigid rotor and HO model

$$Z_{R-V} = \frac{1}{8} \sum_{j=0}^{\infty} \sum_{l=0}^j (2j+1) e^{-\frac{l(l+1)\hbar^2}{8Ik_B T}}$$

Using Euler-Maclaurin expansion  
with  $\frac{\theta_{R-V}}{T}$

$$Z_{R-V} = Z_{R-V}^0 Z_{corr}$$

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$$Z_{R-V} = Z_{R-V}^0 Z_{corr}$$

$$Z_{R-V}^0 = \frac{1}{8} \frac{y}{1 - e^{-y}}$$

$$Z_{corr} = 1 + \frac{y}{3} + \frac{y^2}{15} + \frac{2y}{y} + \frac{5}{e^y - 1} + \frac{2y \cdot y}{(e^y - 1)^2}$$

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$$+ \frac{3}{e^t - 1} + \frac{15}{(e^t - 1)^2} + \frac{2\gamma t}{(e^t - 1)^2}$$

→ first order correction to simplex soln.

→ auxiliary second order correction factor

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So, welcome to lecture number 44, the Statistical Thermodynamics course. So, we wrote what is called the partition function or the combined Ro-vibrational model. So, again using Euler Maclaurin expansion with, theta R-V by T we can this will lead to Z R-V is equal to Z R-V there is a zero then there is a Z correction. So, here of course, Z R-V zero is given as  $1 + \frac{3}{e^t - 1} + \frac{15}{(e^t - 1)^2} + \frac{2\gamma t}{(e^t - 1)^2}$ . So, it is a long expression just bear with me, plus delta by t minus 1 plus 2x star into t y et minus 1 square.

So, if we look at these set of these three equations out of this, this represents what we call a first order correction, order correction to the simplex solution. And this however, tells you it is an auxiliary second order correction.

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$$+ \frac{3}{e^{\epsilon} - 1} + \frac{2x^* \epsilon}{(e^{\epsilon} - 1)^2}$$

→ first order correction to simplex soln.

→ auxiliary second order correction factor

$$Z = Z_{tr} Z_{el} Z_{R-V} Z_{corr}$$

$$Z_{el} = \sum_j g_{el,j} e^{-\frac{\epsilon_{el,j}}{kT}}$$

So, given in essence the total partition function then becomes this is the total partition function which is  $Z_{tr} Z_{el} Z_{R-V}$  and then there is a  $Z_{corr}$  correction, where your  $Z_{el}$  electronic is given  $\sum_j g_{el,j} e^{-\frac{\epsilon_{el,j}}{kT}}$ . So, all terms except you can see this particular term over here can be calculated in the same fashion as for the rigid rotor harmonic oscillator model except that you use  $T$  and  $Y$  instead of  $\theta_v$  by  $t$  and  $\theta_r$  by  $t$ .

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$$Z = Z_{tr} Z_{el} Z_{R-V} Z_{corr}$$

$$Z_{el} = \sum_j g_{el,j} e^{-\frac{\epsilon_{el,j}}{kT}}$$

$$T \left( \frac{\partial \ln Z_{R-V}}{\partial T} \right)_{\#} = 1 + \frac{t}{e^{\epsilon} - 1} \left[ \frac{\partial \ln Z_{tr}}{\partial T} \right]_{\#}$$

$$\left[ \frac{\partial}{\partial T} T \left( \frac{\partial \ln Z_{R-V}}{\partial T} \right) \right]_{\#}$$

$$= 1 + \frac{t^2 e^{\epsilon}}{(e^{\epsilon} - 1)^2} \left[ \frac{\partial}{\partial T} T \left( \frac{\partial \ln Z_{tr}}{\partial T} \right) \right]_{\#}$$

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$$Z_{R-V} = Z_{R-V}^0 Z_{corr}$$

$$Z_{R-V}^0 = \frac{1}{\sigma} \frac{1}{y(1-e^{-\epsilon})}$$

$$Z_{corr} = 1 + \frac{t}{3} + \frac{t^2}{15} + \frac{2t}{y} + \frac{5}{e^{\epsilon}-1} + \frac{2t\epsilon}{(e^{\epsilon}-1)^2}$$

→ first order correction to simplex sol.  
 → auxiliary second order correction factor

So, using the same principle therefore, now we can calculate the differentials, the usual derivatives. So, this is  $d \ln Z_{R-V}$  divided by  $dt$  at constant volume this is given as  $1 + t$  by  $e^t$  minus  $1/T$   $d \ln Z_{corr}$  divided by  $dt$  at constant volume. And then of course, you have  $T^2 d \ln Z_{R-V}$  by  $dT$  (4:01) is equal to  $1 + t$  square  $e^t$  by  $e^t$  minus  $1$  square plus  $d$  by  $dT$   $T^2 d \ln Z_{corr}$  divided by  $dT$  (4:24).

The first if you look at these two terms of both the equations the first two terms of this equation let us say, that obviously arises from this obviously arise from this. Hence all Rotational contributions to the thermodynamic properties are obtained by simply adding a second order correction term to the primary terms which are closely associated with a rigid rotor at that harmonic oscillator models.

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Handwritten notes in a digital notebook showing the derivation of the first derivative of the partition function  $Z$  with respect to temperature  $T$  at constant volume  $V$ . The notes include the following equations:

$$\left[ \frac{\partial}{\partial T} T^2 \left( \frac{\partial \ln Z_{corr}}{\partial T} \right) \right]_{\neq}$$

$$= 1 + \frac{t^2 e^t}{(e^t - 1)^2} \left[ \frac{\partial}{\partial T} T^2 \frac{\partial \ln Z_{corr}}{\partial T} \right]_{\neq}$$

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

$$Z'_{corr} = -\frac{y}{3} - \frac{y^2}{15} + \frac{2\gamma}{15} + t \frac{(\delta e^t - 2x^*)}{(e^t - 1)^2} + \frac{4x^* t^2 e^t}{(e^t - 1)^3}$$

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Handwritten notes in a digital notebook showing the same derivation as above, followed by a table for polyatomic and linear non-linear molecules:

polyatomic		linear	Non-linear
n: # of atoms		3	3
Trans		2	3
Rotation		3n-5	3n-6
Vibration			

So, furthermore, we can write  $T d \ln Z$  correction divided by  $dT$  at constant volume is equal to the first derivative divided by this correction. And in this way you could write all the other expansion terms also in this particular fashion and just let me write down the correction top that is  $y$  by 3 minus  $y$  square by 15 plus  $2 \gamma$  by 15 plus  $t \delta e^t$  minus  $2x^*$  star divided by  $e^t$  minus 1 square plus  $4x^* t^2 e^t$  divided by  $18$  minus 1 cube.

So, in essence, this is the example of how to use the semi rigorous model to find out the required terms for you know,  $u$ ,  $(\dots)$ (6:14) and  $C$ . So, this brings to a partial closure that you know, we have found out ways in which you can calculate. So, you have a simplex model, we have a more complex model. So, we have done how to do diatomic gases more or less. Of course, there is a polyatomic gas as well which is outside the scope.

But you can say a few things that when a gas, when you evaluate the thermodynamic properties for gaseous  $(\text{O}_2)$  composed of polyatomic molecules, it depends on whether the associated molecular structure is linear or non-linear. For example, linear molecules are carbon-di-oxide as one example. So, there can be here the atoms are basically arranged around a simple single condition, whereas for water, it is very different. So, that means that geometric arrangement actually dictates whether how many rotational degrees of freedom there could be, for example, linear polyatomics has got two degrees of rotation whereas, non-linear can exhibit three such degrees of rotation.

So, polyatomic just as a very brief thing, if it is linear and then there is non-linear. So, translation is basically the same, rotation you have 2 versus 2 then of course, vibration is  $3n - 5$  versus  $3n - 6$  respectively if it is composed of where  $n$  is the number of atoms. As you can see that each vibrational mode designates a Inter nuclear distance or angle because oscillation reflects a local electronic potential. So, we are not covering this but this is something that you can read once again you can do a similar type of separation, complete mode separation and then you can like in a diatomic molecule you can evolve a set of rules to how to take care of this. So, we are going to stop here and we are going to shift a little bit towards spectroscopy and see how spectroscopic measurements for concentrations temperatures etc. can be performed.

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The image shows a digital notebook interface with the following content:

- Title:** Interaction of radiation with matter
- Text:** Einstein A and B coefficients
- Text:** Consider a collection of  $N$  two level systems in a vol  $1\text{m}^3$
- Diagram:** A two-level energy diagram with two horizontal lines representing energy levels. The upper level is labeled  $E_1$  on the left and  $N_1$  on the right. The lower level is labeled  $E_0$  on the left and  $N_0$  on the right.

On the left side of the notebook, there is a vertical label: "Statistical Thermodynamics for Engineers Lec44". On the right side, there is a small video feed showing a person.

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$E_0$  —————  $N_0$   
 $E_1$  —————  $N_1$

If the # of systems with energy  $E_1$  is  $N_1$   
 # of systems with energy  $E_2$  is  $N_2$ .

→ constant temperature  $T$  and bathed by radiation density  $A_0(T)$   
 → Assume the system is in thermal eq.

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→ constant temperature  $T$  and bathed by radiation density  $A_0(T)$   
 → Assume the system is in thermal eq.

$N_1 + N_0 = N$   
 $\frac{N_1}{N_0} = e^{-h\nu_{10}/kT}$   
 $\nu_{10} = E_1 - E_0$

So, let us try to look at now the problem of interaction of radiation with matters. The interaction of radiation with matter. So, here we bring first the concept of Einstein A and B coefficients, we will see what these means in a second. So, the first consideration is consider a collection of  $N$  two level systems. Say in a volume 1-meter cube, where the upper energy level is  $E_1$  and the lower energy level is  $E_0$ . The upper energy level is  $E_1$  and the lower energy level is  $E_0$ .

So, these are the two energy levels. This is  $E_1$  and this is  $E_0$ , there is  $N_1$  and  $N_0$  are the number of particles in each of this energy levels. So, the number of systems so, if we write it like this, if number of systems with energy  $E_1$  is  $N_1$  and number of systems with energy  $E_0$  is  $N_0$ . So, and this is, this system is at a constant temperature  $T$  and bathed by

radiation density  $\rho$ . So, this is the state of the system and we can also say that this system let us assume that this system is in thermal equilibrium.

And the populations  $N_1$  and  $N_1 + N_0$  is equal to  $N$ , so, that is the population and they are related  $N_1$  by  $N_0 e^{-\frac{h\nu_{10}}{kT}}$  where  $\nu_{10}$  is nothing but  $\frac{E_1 - E_0}{h}$ . So, this is the state. So, the idea is therefore, so,  $\nu_{10}$  is basically the difference in energy between the two levels.

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$N_0$

$\nu_{10} = \frac{E_1 - E_0}{h}$

$E_1 - E_0 = h\nu_{10}$

$E_1$   $N_1$

$E_0$   $N_0$

$B_{1 \leftarrow 0}$   $B_{1 \rightarrow 0}$   $A_{1 \rightarrow 0}$

Diagram showing two energy levels,  $E_0$  and  $E_1$ , with populations  $N_0$  and  $N_1$  respectively. A red arrow labeled  $B_{1 \leftarrow 0}$  points from  $E_0$  to  $E_1$ . Two red arrows labeled  $B_{1 \rightarrow 0}$  and  $A_{1 \rightarrow 0}$  point from  $E_1$  to  $E_0$ . The energy difference is labeled  $E_1 - E_0 = h\nu_{10}$ . The frequency  $\nu_{10}$  is defined as  $\nu_{10} = \frac{E_1 - E_0}{h}$ . A blue arrow labeled  $N_0$  points to the  $E_0$  level.

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$E_1$   $N_1$

$E_0$   $N_0$

$B_{1 \leftarrow 0}$   $B_{1 \rightarrow 0}$   $A_{1 \rightarrow 0}$

Three possible processes can change the state of the system from  $E_0 \rightarrow E_1$  or  $E_1 \rightarrow 0$

- $\rightarrow$  absorption
- $\rightarrow$  spontaneous emission
- $\rightarrow$  stimulated emission

Diagram showing two energy levels,  $E_0$  and  $E_1$ , with populations  $N_0$  and  $N_1$  respectively. A red arrow labeled  $B_{1 \leftarrow 0}$  points from  $E_0$  to  $E_1$ . Two red arrows labeled  $B_{1 \rightarrow 0}$  and  $A_{1 \rightarrow 0}$  point from  $E_1$  to  $E_0$ . The text below explains that these three processes can change the state of the system from  $E_0 \rightarrow E_1$  or  $E_1 \rightarrow 0$ .

So, let us redraw it in a little bit again the same thing so, this is  $E_1 N_1$ , this is  $E_0 N_0$  and let us draw few lines and then we will see what those things are, this is  $B_{1 \leftarrow 0}$   $B_{1 \rightarrow 0}$  just hold on and we will explain what these lines actually means. So, we are writing a few

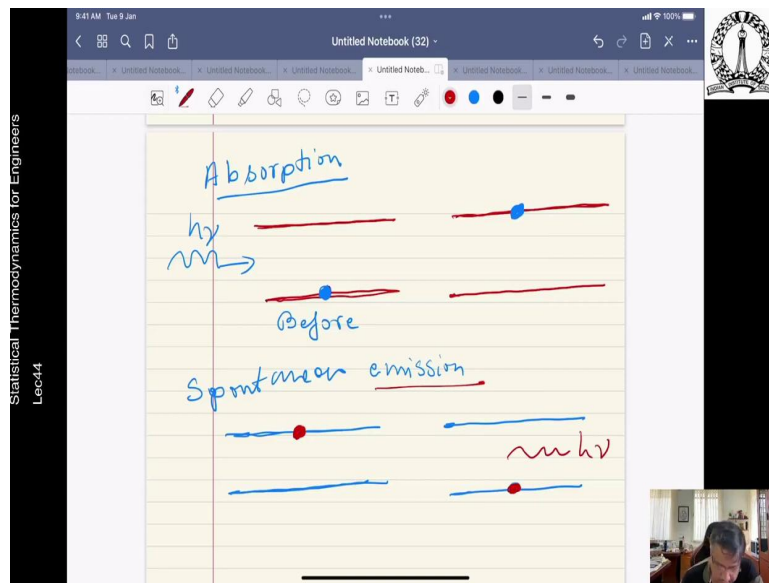


things and  $E_1 - E_0$  is equal to  $h\nu$ . So, this is the expression that we have.

So, there are three possible ways so, because see the system is in thermal equilibrium. So, there are three possible processes that can change the state of the system from  $E_1$  to  $E_0$  or from  $E_0$  to  $E_1$ . So, there are three possible processes can change the state of the system from  $E_0$  to  $E_1$  or  $E_1$  to  $E_0$ . So, these processes are we write it there can be absorption, there can be something called spontaneous emission and then there can be something called stimulated emission.

So, when there is when this particular system is now bathed with radiation. So, what happens when absorption results from the presence of a radiation density of a precise frequency that is needed to drive a transition from the ground state to the excited stage.

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Before

Spontaneous emission

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Before

Absorption

Spontaneous emission

stimulated emission

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stimulated emission

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$$\frac{dn_1}{dt} = B_{1 \leftarrow 0} \rho(\nu_{10}) n_0$$

rate constant  
(Einstein absorption coeff. or B coefficient)

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$\gamma_{10} = E_1 - E_0$   
 $E_1 - E_0 = h\nu_{10}$   
 $E_1$   $N_1$   
 $E_0$   $N_0$   
 $B_{1 \rightarrow 0}$   $A_{1 \rightarrow 0}$   
 $\rho_{1 \rightarrow 0}$   
 Three possible processes can change the state of the system from  $E_0 \rightarrow E_1$  or  $E_1 \rightarrow 0$   
 $\rightarrow$  absorption

So, let us draw the different types of transitions so, that you are able to get it properly that what is absorption what is spontaneous emission and what is stimulated emission. Absorption, let us do this one first. So, this is what the system looks like. So, this is a system this is before and this is after, so after what happens, after the absorption is over this particular particle is now at a excited stage. So, this process is called absorption.

Then of course, there is something called spontaneous emission. So, in case of this spontaneous emission what will happen? There is something at the excited stage. So, now, this is coming back to the ground state or the and there is an immediate variation.

Now we come to the something called simulated emission. This is much similar to the emission looks like so, there was this the excited stage I have  $h\nu$  that is hitting this. So, now, what happens is that in the next you have now, particles now residing the ground state when there is  $2h\nu$  amount of energy that is released. So, this is called stimulated emission. This is spontaneous emission and this is absorption. So, it is clear that how the energy diagram should work.

So, this is for a two level system. So, absorption results from the presence of radiation density which is row b of a precise frequency which is needed to drive the transition from the ground state to the excited stage. So, let us write it  $dN_1$  by  $dt$  that is there is a change in population at the upper energy level and this is driven by  $B_{0 \rightarrow 1}$  there is a radiation of precise frequency into  $N$  naught. So, this is basically nothing but a rate constant also known as Einstein absorption coefficient or B coefficient. So, this is called a rate constant, this rate constant is actually what is called the Einstein B coefficient or absorption coefficient.

So, the system, so can understand So, there is a change in the population at the upper energy level when it is being hit by a radiation of a particular frequency of a precise frequency which drives the transition some articles of some systems are promoted to the  $N_1$  to the  $E_1$  level basically and this is the rate constant that you see which is precisely what we have drawn here this is the rate constant, so, this is the B coefficient.

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If the system is already in an excited state, then a photon of energy  $h\nu_{10}$  can induce the system to make a transition to ground state

$$\frac{dN_1}{dt} = -B_{1 \rightarrow 0} \rho_0(\nu_{10}) N_1$$

↓  
stimulated emission coefficient.

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↓  
stimulated emission coefficient.

If the system in excited state can spontaneously emit a photon at a rate

$$\frac{dN_1}{dt} = -A_{1 \rightarrow 0} N_1$$

↓  
A coefficient

So, that is good, now similarly if the system is already in an excited state, then a photon of energy  $h\nu_{10}$  can induce the system to make a transition to the ground state. So, that means  $dN_1$  by  $dt$  will be given us minus this time. So, this is  $1 \rightarrow 0$  row  $\nu_{10}$  into  $N_1$ , remember this is  $N_1$  not  $N_0$ . So, this is called stimulated emission coefficient.

So, finally, if a system is already in excited state, so, this is a system which was there in the excited state you are just hitting it with a photon with a small with a particle of light and it induces a cascade or a transition to the ground state and two photons are emitted in the process. Now, finally, if the system is also in an excited stage, it can spontaneously emit a photon also.

If the system without any interaction in fact with radiation in excited state can spontaneously you know emit a photon at a rate  $dN_1$  by  $dt$  equals to minus  $A_{1 \rightarrow 0}$  into  $N_1$  where this is basically the  $A$  coefficient, that is why the name Einstein  $A$   $B$  coefficient. So, since the system is at equilibrium the rate of population of the excited state by absorption must balance the rate of depopulation by stimulated and spontaneous emission.

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If the system is in thermal equilibrium, rate of population of excited state by absorption must balance the rate of depopulation by stimulated and spontaneous emission.

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of excited state by absorption must balance the rate of depopulation by stimulated and spontaneous emission.

$$N_0 B_{1 \leftarrow 0} \rho_0 = A_{1 \rightarrow 0} N_1 + B_{1 \rightarrow 0} \rho_0 N_1$$

$$\frac{N_1}{N_0} = e^{-\frac{h\nu_{10}}{kT}} = \frac{B_{1 \leftarrow 0} \rho_0}{A_{1 \rightarrow 0} + B_{1 \rightarrow 0} \rho_0}$$

$$\rho_0(\nu_{10}) = \frac{A_{1 \rightarrow 0}}{B_{1 \leftarrow 0} e^{h\nu_{10}/kT} - B_{1 \rightarrow 0}}$$

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$$N_0 B_{1 \leftarrow 0} = A_{1 \rightarrow 0} + B_{1 \rightarrow 0} \rho_\nu N_1$$

$$\frac{N_1}{N_0} = e^{-\frac{h\nu_{10}}{KT}} = \frac{B_{1 \leftarrow 0} \rho_\nu}{A_{1 \rightarrow 0} + B_{1 \rightarrow 0} \rho_\nu}$$

$$\rho_\nu(\nu_{10}) = \frac{A_{1 \rightarrow 0}}{B_{1 \leftarrow 0} e^{h\nu_{10}/KT} + B_{1 \rightarrow 0}}$$

$$\rho_\nu(\nu_{10}) = \frac{8\pi h^3 \nu_{10}^3}{c^3} \frac{R}{e^{h\nu_{10}/KT} - 1}$$
 ↓  
 Planck's function

So, if the system is in thermal equilibrium rate of population of excited state by absorption must balance must balance the rate of depopulation which by stimulated and you know spontaneous emission is not that correct? So, in other words,  $N_0 B_{1 \leftarrow 0}$  is equal to  $A_{1 \rightarrow 0} + B_{1 \rightarrow 0} \rho_\nu N_1$ . So, this is the equation that we can write. And then on the top of that we have a ratio of  $N_1$  by  $N_0$ , we already have a ratio of  $N_1$  by  $N_0$ .

So,  $N_1$  by  $N_0$  is given as  $e^{-h\nu_{10}/KT}$  which is equal to therefore is equal to  $B_{1 \leftarrow 0} \rho_\nu$  divided by  $A_{1 \rightarrow 0} + B_{1 \rightarrow 0} \rho_\nu$ . This is what it is. So, if we now solve for  $\rho_\nu$  the equation if you solve for this then  $\rho_\nu$  is equal to  $A_{1 \rightarrow 0}$  divided by  $B_{1 \leftarrow 0} e^{-h\nu_{10}/KT} + B_{1 \rightarrow 0}$ .

This is what you are going to get where your  $\rho_\nu$  also  $\rho_\nu$  is given by the Planck's function, so, it is  $\frac{8\pi h^3 \nu_{10}^3}{c^3} \frac{R}{e^{h\nu_{10}/KT} - 1}$ . So, if these two expressions have to be valid. So, if come to the next class that what are the necessary conditions for these two equations to be valid in the first place.

So, these are both equivalent expressions right one is given by the Planck's function and one we just now divide, by this simple two level systems. So, therefore, now we will see what is the end product of this kind of arrangement, so, that we will see in the next class and we will continue this particular lecture and see how this can be used for you know concentration measurements and stuff like that.