Trace and ultra trace analysis of metals Using atomic absorption spectrometry

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Lecture – 13

Theoretical basis of AAS IV

In the last class, I had said that atomic absorption is the measurement of the n layer absorbance from the free atoms in the environment by electromagnetic radiations. So, the detailed aspects of absorption we will be discussing here.

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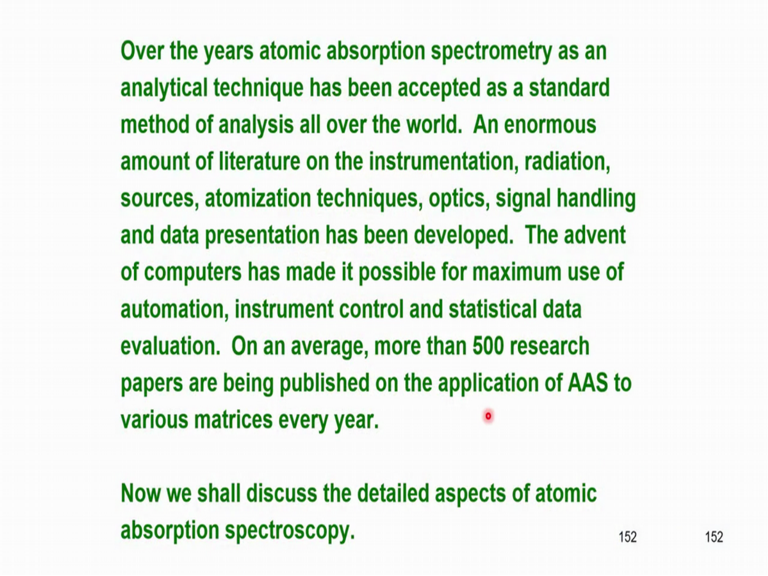

Over the years atomic absorption spectrometry as an analytical technique has been accepted as a standard method of analysis all over the world. An enormous amount of literature on the instrumentation, radiation, sources, atomization techniques, optics, signal handling and data presentation has been developed. The advent of computers has made it possible for maximum use of automation, instrument control and statistical data evaluation. On an average, more than 500 research papers are being published on the application of AAS to various matrices every year.

Now we shall discuss the detailed aspects of atomic absorption spectroscopy.

There is certain amount of repetition here, but I think it will be good for you.

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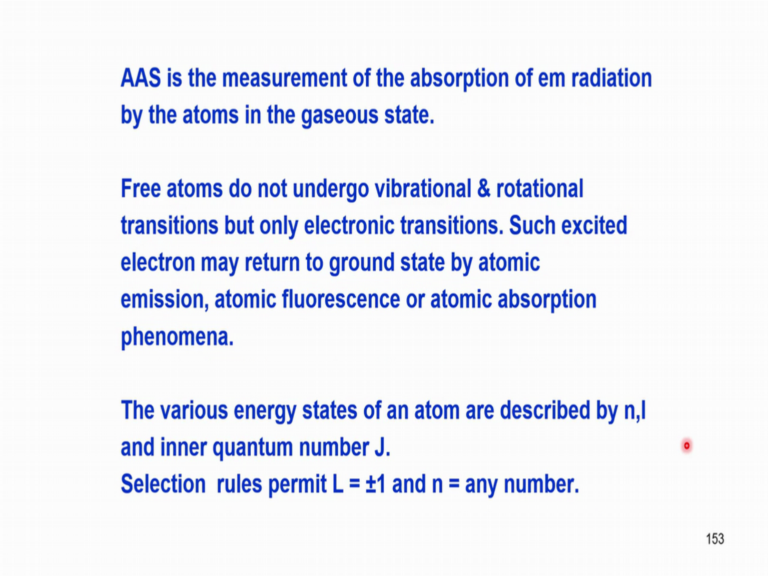

AAS is the measurement of the absorption of em radiation by the atoms in the gaseous state.

Free atoms do not undergo vibrational & rotational transitions but only electronic transitions. Such excited electron may return to ground state by atomic emission, atomic fluorescence or atomic absorption phenomena.

The various energy states of an atom are described by n,l and inner quantum number J.
Selection rules permit L = ±1 and n = any number.

So, basically what we are talking about is that the atomic absorption spectrometry is the measurement of the absorption of electromagnetic radiation by the atoms in the gaseous state. Why gaseous state? Because, in the gaseous state most of the free atoms and most of the atoms are and molecules are free. So, they can move about, they can absorb radiation; they can emit radiation and do all kinds of things. So, free atoms do not have vibrational and rotational transitions this we should understand.

Earlier, I had that told you that molecules will have vibrational and rotational and electronic energy levels, but free atoms in the gaseous state do not have vibrational and rotational transitions. That means they have only electronic transitions, such a excited electron. So, whenever we supply electromagnetic energy they go for the electrons are excited from ground state to the higher state and then they may return to the ground state by atomic emission or atomic fluorescence or at atomic absorption phenomena.

So, what do we mean that? Basically whenever the electrons go to the next higher energy level we call the whole atom as being present in the excited state. From the excited state in the vapour phase only the excited atom can revert to the ground state by thermal means; that means, no radiation is given out. Or it may give out a radiation corresponding to the different wavelength; longer wavelength and lesser energy that is known as atomic fluorescence. Atomic fluorescence is also an analytical technique nowadays and it is being used widely, several atomic fluorescence instruments are available in the market. And they are being used for multi element determination of elements in several matrices, such as coal and alloys materials etcetera.

Or the third party it may return by atomic absorptions phenomena; that mean, the intensity of the incident radiation is reduced when atomic absorption takes place. So, when they return to the ground state the energy is lost by the heat which is not detected spectrally. So, the various states energy states of an atom are described by quantum numbers; you are all familiar and then n l and j and SPDF you are familiar, but l and other thing these all are for the atoms; n l and j inner quantum number.

So, selection rules say that the orbital angular momentum should be plus or minus 1 and n can be any number. That means, the excitation can take place by plus or minus 1 unit and it may go to a principal quantum number can be anything.

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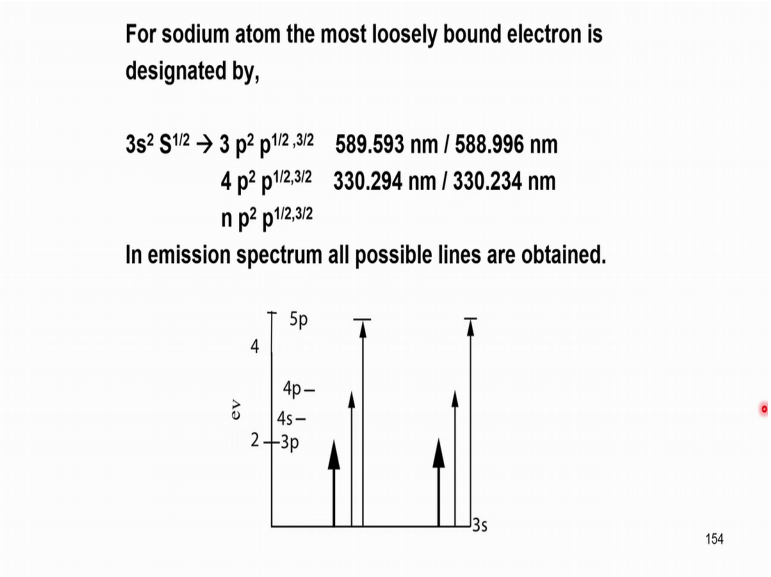

For sodium atom the most loosely bound electron is designated by,

$3s^2\ S^{1/2} \rightarrow 3\ p^2\ p^{1/2,3/2}$ 589.593 nm / 588.996 nm
$4\ p^2\ p^{1/2,3/2}$ 330.294 nm / 330.234 nm
$n\ p^2\ p^{1/2,3/2}$

In emission spectrum all possible lines are obtained.

So, for sodium atom: the most loosely bound electron, there is only one electron in the outermost orbital and that is defined by 3s 2 and S half that is the electronic state of sodium. So, they look at this slide now and I want you to remember the electronic structure of filling the atoms and here the in the outermost orbital they are 2 electrons in 3s 2 and 1 electron in the s orbital. So, this can give rise to 3 p 2 and p half and p 3 by 2.

So, the total angular momentum and the energy states are defined by these numbers. So, from 3 it can go to 3s 2 3 S half 3, it can go to 3 p 2 p half or p 3 by 2 and then it can go to 3 p 2 4 p 2 these s 2 electrons will go to p 2 and this can be one half plus or 3 by 2 total.

Or it can go to n p 2 p half p 3 by 2. So, what do we exactly mean in this case is in emission spectrum all these lines are obtained; what are those lines? 589.593 that is one and another is 588.996. Two different states 3 p 2 p half and 3 p 2 p 3 by 2; 3 p 2 p half corresponds to 589.593 nanometers and 3 p 2 p 3 by 2 would correspond to 588.996. That is if suppose if the electron goes to next higher energy state then that state is defined by 4 p 2 p half p 3 by 2 and this will correspond to 330.294 nanometers and 130.234 nanometers.

Now, you can imagine that means, the excitation energy for the from 3 p 2 3 to 4 energy level is higher from two s 2 to 3 p 2 is lower than getting it excited to 4 p 2. That means, the higher you go higher you want to excite the electron more is the energy required. So, the resonance line should be always lower that is what we mean. So, for sodium it is 589.593 nanometers and the corresponding spin if it gets added up it goes to 3588.996 nanometres.

So, in emission spectrum 3s 2 to 3 p 2, 4 p 2, n p 2 all these things are possible. So, in emission spectrum every line excitation line you will get except the forbidden lines. But in general you will see that there are several emission lines. Now I have drawn this here in the figure here it is electron volts this is the ground state 3 s, so it can go to 3 p low energy this is 3 p half 3 p 1 by 2 this is 3 p 3 by 2. And then it can go to 4 p 4 p it would not go, so 3 p 4 p 5 p like that the amount of energy required also is higher because if it goes to 3 p state the electron volts required is only 2 electron volts, whereas if it is a for 5 p it is almost 4 electron volts.

That means, almost all electrons in an atom can be excited to higher energy states, and these higher energy states require more and more energy as you try to excite the electrons. But what we are interested is in the lowest energy state that is two s 2 3s 2 to 3 p 2.

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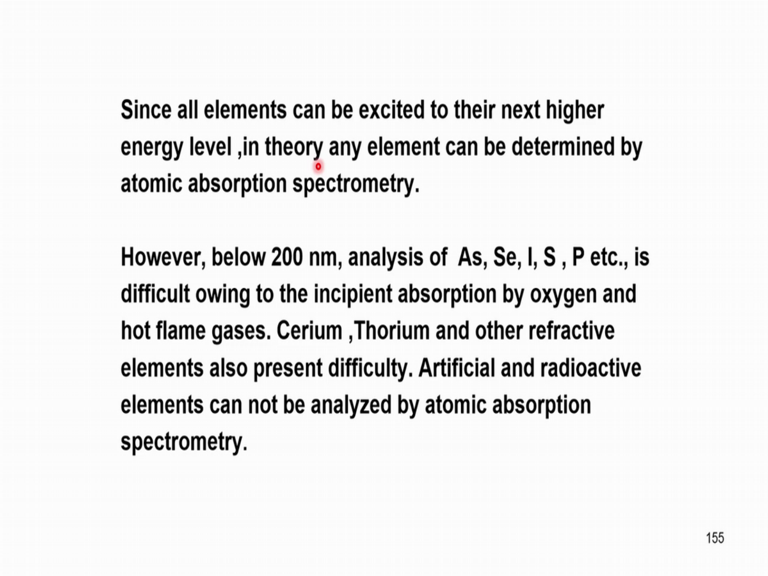

Since all elements can be excited to their next higher energy level ,in theory any element can be determined by atomic absorption spectrometry.

However, below 200 nm, analysis of As, Se, I, S , P etc., is difficult owing to the incipient absorption by oxygen and hot flame gases. Cerium ,Thorium and other refractive elements also present difficulty. Artificial and radioactive elements can not be analyzed by atomic absorption spectrometry.

Since, all elements can be excited to the next higher energy level in theory any element can be determined by atomic absorption spectrometry in theory not always, but there are difficulties. For example, below 200 nanometers analysis of arsenic, selenium, iodine, sulphur, phosphorus, etcetera it is difficult owing to the incipient absorption by oxygen. That means, in the vapour phase what we would come across is not only the free atoms in the vapour state, but also water molecules, oxygen molecules, nitrogen and several other species will be there.

So, all these things have absorption in the absorption range UV range below 200 nanometers, most of the molecules especially air molecules like oxygen, nitrogen, etcetera, carbon monoxide, carbon dioxide, many of them; they have absorption spectrum occurring in the UV that is they are all molecular species. But whenever you want to determine any element you have to get it in the vapour state anyway. So, in the vapour state if the absorbance line is to less than 200 the oxygen also will absorb, so it will contribute.

So, the actual intensity of the radiation would be the sum of the atomic absorption as well as molecular absorption by species like oxygen, nitrogen, etcetera, nitric oxide, several species are there. So, this is what we mean that below 200 nanometers it is difficult to analyze, because even though arsenic, selenium, iodine, sulphur, phosphorus, etcetera they have resonance lines below 200, but absorption by oxygen and hot flame gases prevent us to get very clear picture

Similarly, there are certain elements like cerium, thorium, and then chromium, tungsten and several other elements which are refractive in nature; that means, they have very high melting point and boiling point. Even if you heat them to 3000 degree or 4000 degree Kelvin you would not get the vapour phase at all. That means, the concentration of atoms in the vapour phase in equilibrium with the solid is very less. So, refractive elements do not lend themselves easily for atomic absorption spectrometry. And what are these refractory elements? They are cerium, thorium, tungsten, vanadium, etcetera, and these are called as refractive elements.

And then of course, you cannot do the atomic absorption spectrometry for radioactive elements, because the first of all the radioactive elements are normally short lived that is number one; and they are all produced under special conditions of bombardment of the neutrons and electrons etcetera on the nuclear targets. So, they are not only short lived, but they are produced only in nuclear reactors and the lifetime of the some of the radioactive elements are so short that it does not make any sense trying to determine them by atomic absorption spectrometry.

So, what we are saying basically you cannot do determination of elements below 200 nanometers that is one of the requirements, it should have a resonance line about 200 nanometers and then it should not be refractive index even though this refractive index refractive elements problem can be overcome to some extent. That we will see later as we discussed further. So, another problem is artificial and radioactive elements they cannot be determined by atomic absorption, because of the inherent conditions of the production and short life times.

So, now we will discuss about the thermal excitation. So, how do I get an element in the vapour phase? So, there are several methods. So, we have to appreciate that the atoms any at element you want to determine must be brought into vapour state to produce free atoms. So, it is for atomic absorption to occur you have to produce a population atoms in this free state. How do you do that? Supply the energy melted and then heat it further boil it convert it into vapour state that is a very standard process to convert anything into vapour.

So, we produce a population of atoms in the ground state by exposing a sample of the analyte to high temperatures. So, how do you expose a sample to high temperature? You can put it in the flame or you can simply heat it. How do you heat it? You take a Bunsen burner or LPG gas or something like that you can heat it or you can put it in the flame directly. Take a container and heat it using Bunsen burner or LPG gas until the substance melts that is not really ideal for atomic absorption spectrometry, but we can also provide by high electric current and all that electric heating it can be done. And at high temperatures prevailing in the flames what happens, suppose I introduce it into this flame not a melted take it in a pot and then melt it. So, I directly introduce it into the flame. So, the flame temperature will be very high as we all you know.

So, the compounds my sample analyte sample is usually in the form of a salt; 99 percent of the time it is in the form of a salt solution. So, solids also we can analyze by atomic absorption spectrometry, but that requires special precautions; 99 percent of the time we assume that we have an oversample, oversample is dissolved in an acid or alkali or whatever it is any sample for that matter to be analyzed must be brought into a solution from the there should be a definite relation between the sample weight and the solution form to which it is diluted. So, that solution we introduce into the flame.

So, in the flame what we have free electrons; any flame will have a lot of free electrons abundantly available. If there are free, electrons if I can produce free atoms in the flame the electrons can free ions in the flame electrons can attach themselves to the metals metal ions and then convert into free atoms and that free atom can get excited to next higher energy level; that is the mechanism. So, at high temperatures most of the substances that is the samples which we normally try to analyze in the laboratory; it may be a jewellery solution, it may be a pharmaceutical solution, it may be a food solution, it may be an over brought in to a solution like that most of these samples are dissolved and in the liquid form.

So, the ions in the flame the salts vaporized sodium chloride will dissociate into n a plus and chloride; chloride minus ions; water will dissociate into h 2 2 h plus and o 2 minus ion. Like that any other salt present along with the sample will dissociate into ions which in turn pick up the electrons available in this flame.

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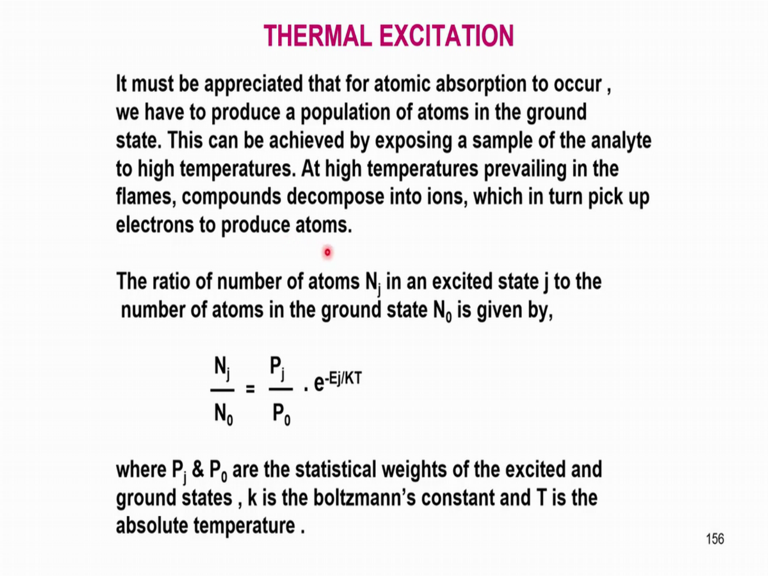

THERMAL EXCITATION

It must be appreciated that for atomic absorption to occur, we have to produce a population of atoms in the ground state. This can be achieved by exposing a sample of the analyte to high temperatures. At high temperatures prevailing in the flames, compounds decompose into ions, which in turn pick up electrons to produce atoms.

The ratio of number of atoms N_j in an excited state j to the number of atoms in the ground state N_0 is given by,

$$\frac{N_j}{N_0} = \frac{P_j}{P_0} \cdot e^{-Ej/KT}$$

where P_j & P_0 are the statistical weights of the excited and ground states , k is the boltzmann's constant and T is the absolute temperature .

So, then they produce atoms this is the only way we know how to produce free atoms in the laboratory. So, the ratio of number of atoms N j; total number of atoms in the excited state j to the number of atoms in the ground state is given by N j that is total number of atoms in the excited state divided by N 0 that is total number of atoms in the ground state. Remember both the atoms excited as well as unexcited are in the vapour state. So, that number ratio is given by another ratio that is P j by P 0 into e to the power of minus E j by KT. So, here we say P j and P 0 are the statistical weights of the excited and ground state. That means, it is an statistical average of the excited and ground state at that temperature. What is the temperature? T, capital T that is the absolute temperature and K is known as the Boltzmann constant and E j is the difference in energy for excitation.

So, this expression is very important in atomic absorption spectrometry and this is the starting equation whenever we want to try to convert it into a theoretical calculations. So, P j by P 0 is the statistical weight ratio. This can be determined this data is available in databases and E j is the energy difference that is available by in the experiments and in databases available, K is the Boltzmann constant and T is the absolute temperature.

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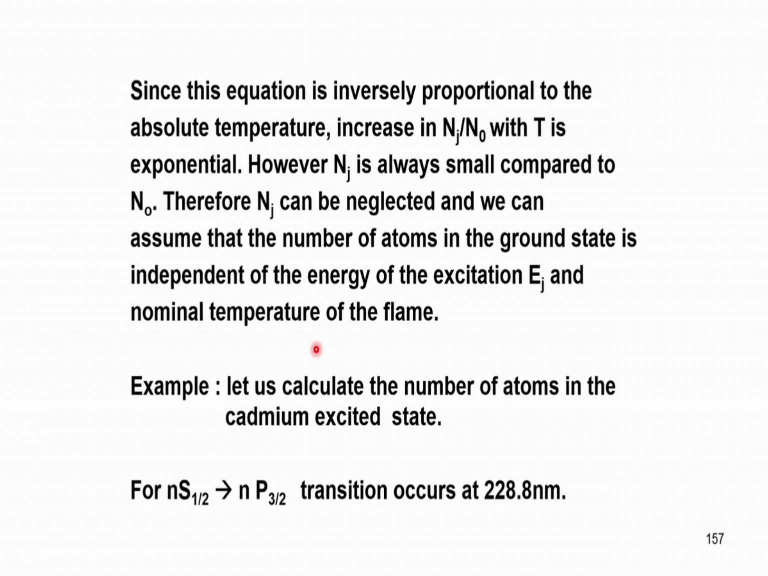

Since this equation is inversely proportional to the absolute temperature, increase in N_j/N_0 with T is exponential. However N_j is always small compared to N_o. Therefore N_j can be neglected and we can assume that the number of atoms in the ground state is independent of the energy of the excitation E_j and nominal temperature of the flame.

Example : let us calculate the number of atoms in the cadmium excited state.

For $nS_{1/2} \rightarrow n\,P_{3/2}$ transition occurs at 228.8nm.

Since this equation is inversely proportional to the temperature. Remember where is T here? T is e to the power of minus E j by divided by KT; that means T is in the denominator. So, the higher the temperature more is the concentration. It is inversely proportional to the absolute temperature, increase in the N j by N 0 which temperature is exponential, because there is an exponential term also involved in this. And the higher temperature I produce the increase is not arithmetical, but it will be exponential. So, if I do it at 2000 degrees particular concentration of the free atoms at 3000 it may not be double it may be 3 times 4 times like that the it is exponential increase that is what we call it is.

However, N j is always small; now that is number of excited atoms in the free state even in the flame is very very small; even in the flame compared to the number of atoms in the ground state that is N 0. So, in this expression N 0 is always higher compared to N j so; that means, maximum number of atoms are in the ground state and very few number of atoms free atoms are in the higher state even though the ratio is very less and relationship is exponential.

So, N j we can neglect in that equation and you can assume that the number of atoms in the ground state is independent of the energy of excitation and nominal temperature of the flame. What we mean here is in this expression neglect N j what happens. So, this it is very less, so N 0 is very high. So, E j also we assume it to be independent of the excitation energy. That means, if the flame an exact amount of energy is supplied, because the temperature of the flame is always a combination of the gas and oxidizer mixture: gas is the LPG gas oxidizer is air it in your homes here we will use something else that we will discuss. So, what we are saying is the number of atoms in the ground state are always higher whatever is your excitation temperature whether it is flame or not.

Now let us calculate the number of atoms for cadmium in the excited state. So, I am giving you this data that is the transition is from there n S half to n P 3 by 2; transition occurs this transition occurs at 228.38 nanometers. How do I get this data? It is available in the database; for in the database what it says is cadmium electron can be excited to next higher energy state in the cadmium and the transition is 1 s 1 by 2 to n p 3 by 2 and this transition requires occurs at 228.8 nanometer corresponding electronic electron volt you can always calculate; that is no problem at all.

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$P_j / P_o = 3$

$$\nu = c / \lambda = \frac{2.998 \times 10^{10} \text{ cm/sec}}{2.288 \times 10^{-5} \text{ cm}} = 1.310 \times 10^{15} \text{ sec}^{-1}$$

$$E_j - E_o = h\nu = 6.626 \times 10^{-27} \text{ erg.sec} \times 1.310 \times 10^{15} \text{ sec}$$

$$= 8.682 \times 10^{-12} \text{ erg}$$

$$N_j / N_o = 3 \exp\left(\frac{-8.682 \times 10^{-12} \text{ erg}}{1.3805 \times 10^{-16} \text{ erg k}^{-1} \quad (2730) \text{ k}} \right)$$

$$= 4.5 \times 10^{-11}$$

Now the statistical weight age of the excited to the ground state that is P j by P 0 is 3. That means, statistically excited atoms are 3 times compared to P 0. So, what do we do now? We know the wavelength, we know the Boltzmann constant, we know the velocity of light, and we can calculate the frequency. So, the frequency is nothing but c by lambda that is 2.998 into 10 raised to 10 centimeter per second; that is the velocity of light divided by 2.288 into 10 raised to minus 5 centimeter this is the cadmium excitation energy which I had give shown here, but converted into centimeters here it is nanometers.

So, this quantity is 1.310 into 10 raise to 15 seconds inverse. Now I can calculate E j minus E 0 the energy difference between the excited to ground state is h mu. So, h is Planck’s constant that is 6.626 into 10 raise to minus 27 ergs seconds and then multiplied by 1.310 into 10 raise to 15. What do I get? I get a number that is 8.682 into 10 raise to minus 12.

Now, this energy E j we put it in the equation when the Boltzmann equation; that is in this equation N j by N 0 we know, P j by P 0 we know, E j we have calculated T is the temperature and k is Boltzmann constant it is also determined. So, putting all these numbers in this equation N j by N 0 what I get is 4.5 into 10 raised to minus 11. So, this is a simple like calculation of the ratio of excited to ground state atoms.

So, what does it physically mean? If I supply energy corresponding to 228.8 nanometers to cadmium vapour what I get is there are 4.5 into 10 raise to 11 atoms in the ground state and 1 atom in the excited state. So, what temperature we have taken? We have taken a temperature of 2730 Kelvin. So, you can convert it into degree centigrade, so minus 273 etcetera and then it is almost 2500 degrees. At 2500 degrees there is only 1 atom of cadmium in the excited state compared to 4.5 into 10 raised to plus 11 in the ground state that is N 0 is 4.5 into 10 raised to 11 and N j is only 1.

So, for every 4.5 into 10 raised to minus 11 atoms there is only one atom in the excited state do the 4.5 into 10 raised to 11 atoms are in the ground state.

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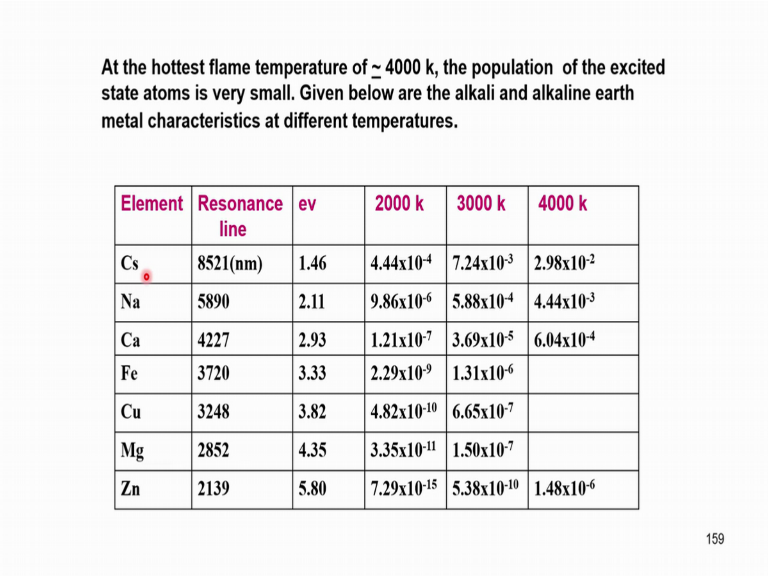

At the hottest flame temperature of ~ 4000 k, the population of the excited state atoms is very small. Given below are the alkali and alkaline earth metal characteristics at different temperatures.

Element	Resonance line	ev	2000 k	3000 k	4000 k
Cs	8521(nm)	1.46	$4.44x10^{-4}$	$7.24x10^{-3}$	$2.98x10^{-2}$
Na	5890	2.11	$9.86x10^{-6}$	$5.88x10^{-4}$	$4.44x10^{-3}$
Ca	4227	2.93	$1.21x10^{-7}$	$3.69x10^{-5}$	$6.04x10^{-4}$
Fe	3720	3.33	$2.29x10^{-9}$	$1.31x10^{-6}$	
Cu	3248	3.82	$4.82x10^{-10}$	$6.65x10^{-7}$	
Mg	2852	4.35	$3.35x10^{-11}$	$1.50x10^{-7}$	
Zn	2139	5.80	$7.29x10^{-15}$	$5.38x10^{-10}$	$1.48x10^{-6}$

Similarly, I can calculate at the hottest temperature of a flame is around 4000 Kelvin not more than that the gas temperature which you get at home in your LPG is around 600 to 800 degrees; 600 mostly and if you use oxy acetylene flame etcetera which people use for welding it may be around 2 and half to 3000; now, the hottest temperatures that can be obtained as a flame is around 4000 Kelvin.

So, the population of the atoms in this expression even if I make it 4000 that is even if I make it 4000 instead of 2730 I do not get enough atoms in the excited state at all. So, now, I give you the sum of the atoms some table of the excited to ground state atoms which we have done earlier for different elements. Now for CCM what is the resonance line 8521 nanometers that is 852.1 and electron volt is 1.46. And at 2000 it is one excited atom out of 4.4 into 10 raise to 4 atoms that is 44000 atoms are there in the ground state and 1 atom of CCM is there in the excited state at 2000 Kelvin.

What happens to 3000? At 3000 for every 1000 7200 ground state atoms there is one in the excited state, so 1000 times less. So, at 4000 Kelvin I have for every 298 atoms there is 1 in the excited state. So, the ratio as I increase the ratio of the excited atoms becomes more. Similarly, for sodium it is 589.0 and at 2000 it is 1 in 9.86 into 10 raised to plus 6 and at 3000 it is 5 atoms, 1 atom for every 5.8 into 10 raised to 4 that is 58000 atoms and at 4000 it will be 1 in 4400 atoms.

Similarly, but look at calcium it is 1 in 10 raised to minus 7 and at 3000 it is 1 in 10 raised to minus 5 and at 4000 it is one in 10 raised to 4. Now compare these three data to the remaining four data that is iron copper magnesium and zinc. For iron what happens there is one at 2000 degrees only one excited atom out of 10 raised to 7 ground state atoms and of course it becomes slightly more at 3000 degrees 1 out of 3.6 into 10 raise to 5 and 4000 it is. But look at iron what happens, there is 1one in 10 raise to 2.2 into 10 raise to plus 9 atoms; that is 1 million, 10 million, 100 million, 1000 million. In 1000 million atoms of the ground state there is only one in the excited state. Similarly at 3000 it is less, lower for other elements copper it is one in 10 raised to 10, 1 is 10 raised to 7 at 3000 degrees. So, like that for magnesium it is 10 raised to minus 11. So, this is how we take a look at this table.

So, what does this table teaches? This table teaches us that at any temperature the ground state atoms are more in thousands and millions than the excited state which are in 1 or 2 atoms maybe 4 or 5 atoms. So, this table is very important, we will continue our discussion after a small break.

Thank you.