Modern Instrumental Methods of Analysis

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Lecture No. # 18

Atomic Absorption Spectrometry-2 Theoretical Aspects

Next session, of our discussion on Atomic Absorption, in the last class we were discussing how we can produce the atoms, in the ground state. So, by introducing the sample into the flame, the solution will evaporate and then, the compounds will form compounds will subsequently melt decompose into ions; and the ions will pick up the electrons from the flame to produce the atoms.

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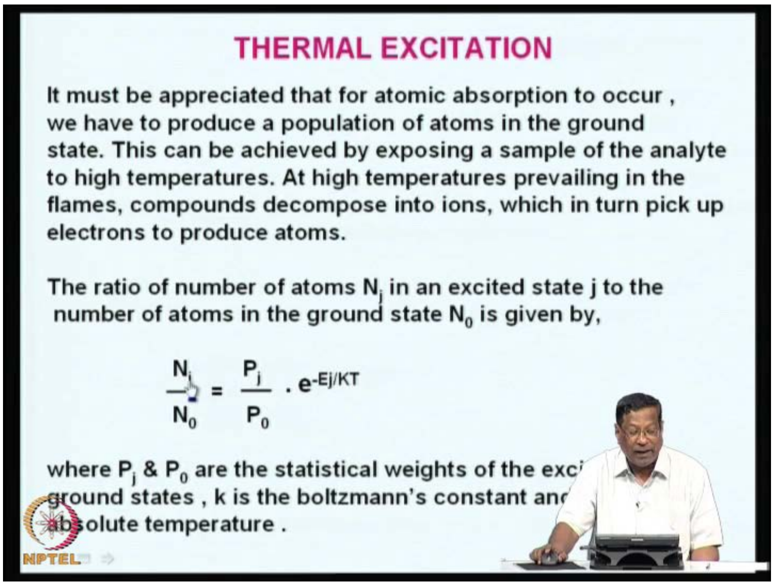

THERMAL EXCITATION

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,

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

where P_j & P_0 are the statistical weights of the exc ground states , k is the boltzmann's constant an absolute temperature .

Now, let us try to quantify some of these ideas, 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 this expression N j by N 0 is equal to P j by P 0 and then, multiplied by e to the power of minus E j into divided e j divided by k T. Where P j and P 0 as the statistical weights of the excited and ground states and k is the boltzmann constant, t is the absolute temperature, N j is the number of atoms in the excited state and N 0 is the number of atoms in the ground state.

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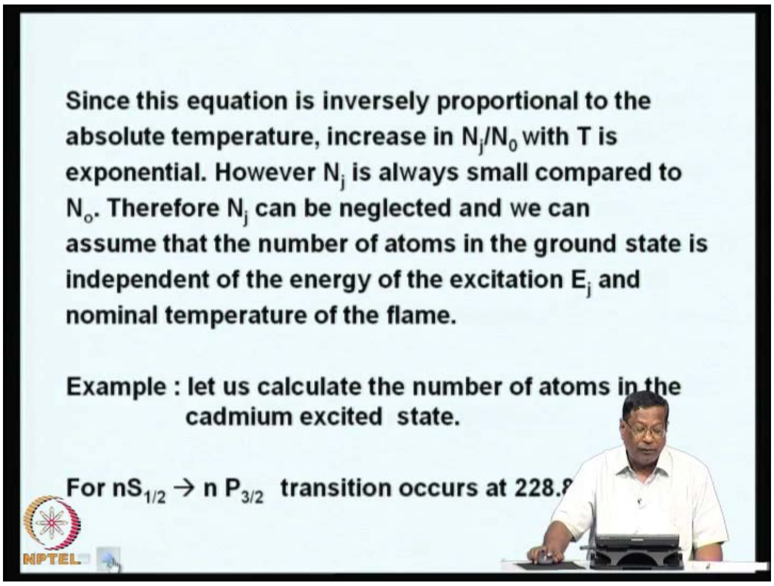

Since this equation is inversely proportional to the absolute temperature, increase in N_j/N_0 with T is exponential. However N_j is always small compared to N_o. Therefore N_j can be neglected and we can assume that the number of atoms in the ground state is independent of the energy of the excitation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

Since, this equation is inversely proportional to the absolute temperature increase in N j by N 0 with T is also exponential, this you can reduce from the nature of the equation itself. However, N j is always small compared to N 0 that means, the number of electrons atoms, number of atoms in the excited state is always small compared to the number of atoms in the ground state.

Therefore, we can neglect N j in that equation (Refer Slide Time: 02:22), in this equation N j, now we can assure that the number of atoms in the ground state is almost independent of the energy of the excitation, that is E j. And nominal temperature of the flame, whatever it is may be around 1100 to 1200 or 2000 whatever it is. So, we using this expression, we can determine the number of atoms in the excited state.

Let us, calculate the number of atoms in the cadmium excited state, so for this the expression is n S half it goes to electron in the n s by 2 goes to n P 3 by 2 that is the transition and this transition occurs at 228.8 nanometers, so this information is available from the experiments.

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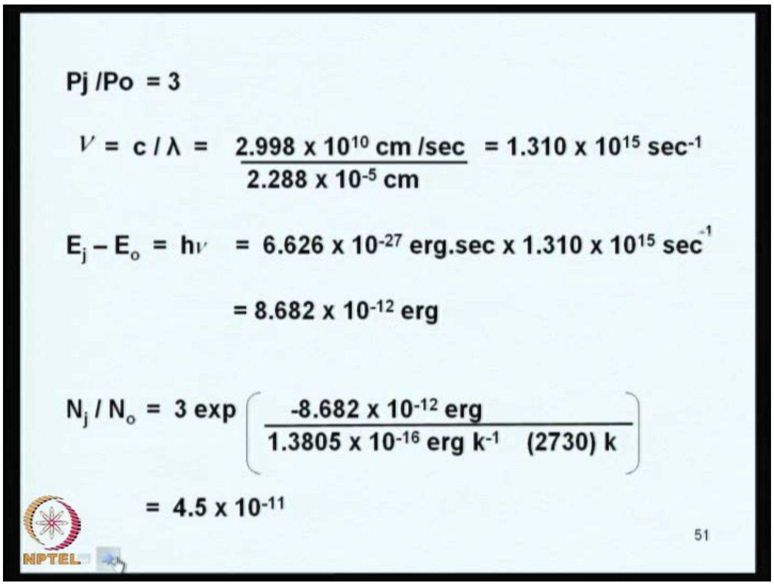

$P_j / P_o = 3$

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

$$E_j - E_o = h\nu = 6.626 \times 10^{-27} \text{ erg.sec} \times 1.310 \times 10^{15} \text{ sec}^{-1}$$

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

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

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

Now, for most of the elements P j by P 0 that is the statistical probability is 3. So, we introduce these numbers into that expression, that is, in this expression P j by P 0 E j and k T, etcetera. We introduce into these equations and then we know the wavelength, so we can convert this frequency into frequency that is, frequency is C by lambda that is 2.998 into 10 raise to 10 centimeter per second divided by 2.288 into 10 raise to minus 5 centimeter that is the wavelength.

So, you get around approximately 1.310 into 10 rise to 15 seconds inverts. Now, E j by E 0 we can calculate the energy difference, that corresponds to h nu and we know the frequency here, from the previous expression. We know planks constant multiply these two you will get 6.626 into 10 raise to minus 27 erg seconds multiplied by 1.310 into 10 rises to 15 seconds that is frequency.

Now, this gives you approximately 8.682 into 10 raise to minus 12 ergs and then N j by N 0, we can calculate using these expressions and what you see 4.5 into 10 rise to minus 11. The number of atoms in the ground state and the number of atoms in the excited state if you take the ratio, we will get 4.5 into 10 rise to minus 11 atoms. In other words, you can say for every 10 rise to 11 atoms in the ground state, you will find 4.5 atoms in the excited state at this temperature of 2730 kelvin, there is a temperature what you have used that is, this tells you that the number of atoms in the excited state is really very small out of 10 rise to 11 only 4.5 atoms you are getting and in the excited state.

So, what is the hottest flame temperature? It could be around 4000 degree Kelvin, the population of the excited atoms even if you raise it to 4000 kelvin, the population would be very, very small almost negligible. Now, we can calculate similarly, for other elements like sodium, potassium, cesium, etcetera and I will show you a table, where the temperatures of 2000, 3000 and 4000 kelvin are used, to calculate the number of atoms in the excited state using the same expression, what you have used in the previous light.

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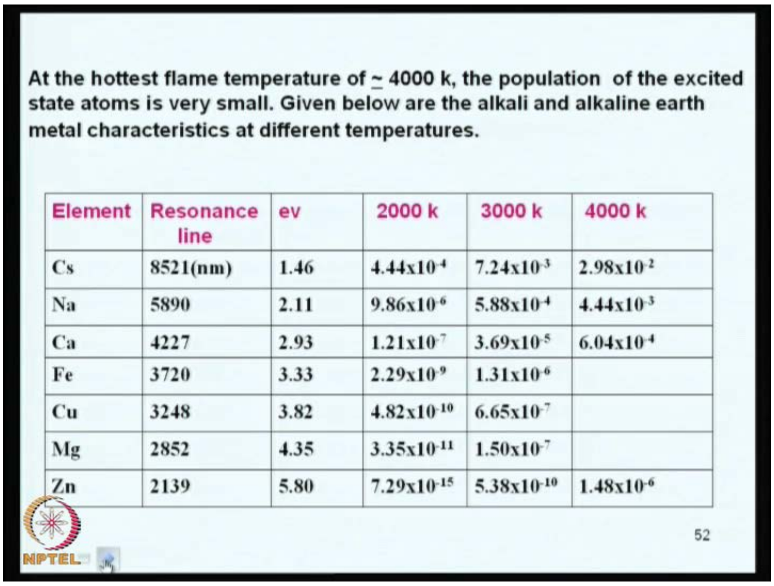

At the hottest flame temperature of $\simeq$ 4000 k, the population of the excited state atoms is very small. Given below are the alkali and alkaline earth metal characteristics at different temperatures.

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

Now, if you take a look at this table, the element cesium it is a resonance line that is lambda is 8521 nanometers and the energy difference is 1.46 e v at 2000 kelvin if you use, this expression you will get 4.4 into 10 rise to minus 4 that is, out of every 10000 atoms only 4.44 atoms are in the excited state. Suppose you increase it to 3000, then the order improves by about 1 unit that is 7.24 into 10 rise to minus 3, that means out of every thousand atoms, you will find 7 atoms in the excited state.

Suppose, you increase it to 4000 kelvin, then you will find the order still improves and out of every hundred atoms, you will find 3 atoms in the excited state but, suppose you do the same calculation for sodium, then what happens you take the resonance line and take the e v energy difference. And then calculate at 2000, 3000, 4000 you will find at 9.86 and 5.88 into 10 rise to minus 4 and 4.44 atoms the in the excited state around 4000 kelvin and here it is 10 rise to minus 6 that is at 2000 kelvin.

Sodium and cesium, they are alkaline metals, suppose you go to alkaline earth metals, then the situation changes drastically, now here the for alkaline metal alkaline earth metal calcium 4227 is the resonance line. And you will find that at 2000 degree kelvin Nj by N 0 is of the order of about 1.21 into 10 rise to minus 7; that means out of 10 rise to 7 atoms you will find only 1 atom in the excited state. Improve it to 3000 degrees 3.69 into 10 rise to minus 5 that is out of 10,000 4 atoms.

Now, 4000 slightly better, suppose you go to iron, iron the resonance line is at 372 and the number of atoms in the at 2000 degrees kelvin in the excited state is only 2. 2 9 out of 10 rise to 9 atoms, that is out of 1,000,000,000, you will find only 2 2 or 3 atoms in the excited state at 3000 it is slightly better, which shows 1.31. Similarly, you can calculate for number of atoms and for copper, for example, at 2000 kelvin out of 10 rise to 10 atoms you will find only 5 atoms in the excited state, for magnesium it is out of 10 rise to 11 3 atoms and zinc, cadmium, etcetera if you go you will find that out of 10 rise to 15 atoms only 7 atoms are in the excited state.

So, the sum total of this table, what we can derive is basically the number of calculations, which shows that the number of atoms in the excited state, whatever be the element it is quite small in the excited state. In the ground state they are always more a number, so in emission what happens, we 1 measures the difference between the 0 signal and the sample signal.

So, if you want to measure the atomic emission, first you have to get the atoms in the excited state and we always know that using flame, the number of atoms in the excited state or of the order few numbers maybe about maximum 10 out of 10 rise to 15, 10 rise to 10, 11, 10 rise to 5 like that. So, the in emission one measures the difference between the 0 signal, that is when there is no excitation and the sample signal, whenever we are able to excite, so the limit of detection is governed only by the electrical noise.

Now, in atomic absorption, we have to measure between the noise level of the blank and finite signal corresponding to the element, so the sensitivity is always governed by the noise level of the signals. Therefore, we need to find out ways how to increase the number of atoms in the excited state, then only we will be able to get the atomic emission and we have to find out ways. And means how to provide the maximum number of atoms in the ground state it is not the sample in solution, it is not the ions, it is not the electrons but, your sample must be converted into atoms only that is the catch.

So, what we do is we understand that free atoms do not undergo vibrational and rotational transition they undergo electronic transitions, this we have covered earlier. So, the excited electrons may return to the ground state by atomic emission or by atomic fluorescence or atomic absorption this also we have covered. So in atomic absorption spectrometry, it involves the measurement of the absorption of electromagnetic radiation by the number of atoms in the gaseous state.

If the excitation is by optical radiation, the atoms absorb the radiation of definite frequency, this absorbed energy is lost subsequently in the form of heat. So, the absorption spectrum of an element consists of number of lines which appear closer and closer together and decrease in regularity of the intensity, until the all the individual spectral lines merged together to give you one continuous spectrum.

And in the absorption of sodium for example, so far 57 absorption lines have been absorbed and identified their corresponding frequency or the wavelength, in contrast to absorption, the emission lines are always more numerous and they do not exhibit the same regularity of the absorption spectrum; so this point, we will have to understand.

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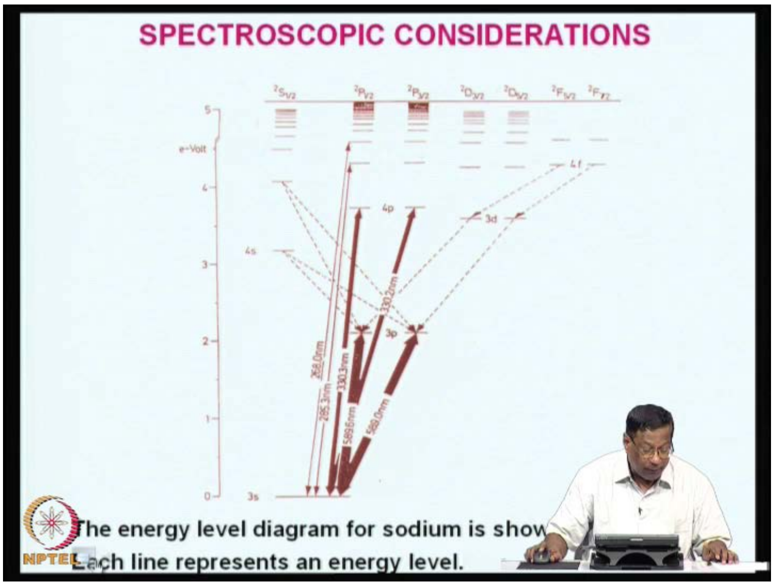

SPECTROSCOPIC CONSIDERATIONS

The energy level diagram for sodium is show
Each line represents an energy level.

And when I show you this sodium spectrum in the next slide you will see that the energy difference is put in as electron volts and these all the radiation excitations start from 3 S ground state. And you will see here number of lines, until they are merging together nearby in this range and then similarly, this corresponds to 2 S half and another energy level corresponds to 3 P by 2 and 2 3, 3 by 2, 2 D 3 by 2, 2 d S by 2, 2 F s by 2 and 2 F d by 2.

So, you can see that numbers of possibilities are there for excitation from the ground state for example; here you can see it goes straight away up to 4.5 volts and then 1 around 4 here. there is one, here there is one, here there is one here (Refer Slide time: 15:35). So, a number of excitations are possible for the sodium, so how to identify each of these lines and how we, how we try to look at identifying these lines and try to understand their spectrum.

So, if the sodium vapour is excited thermally using a hot flame or electrically, terms with arbitrary n principle number and l can be obtained that is n can be 1, 2, 3, 4 up to infinity, l can be 1, 2, 3, 4, etcetera. And the emission spectrum contain all the emission lines starting from 3 S 2 to S 1 half similarly, complex emission spectrum can be obtained for all other elements, what do you mean by similarly, complex emission means, almost all the elements show the same figure like this sodium almost for almost all elements, you can get a figure like this, only thing is there energy differences will be different the spectral lines and the corresponding energies will be different.

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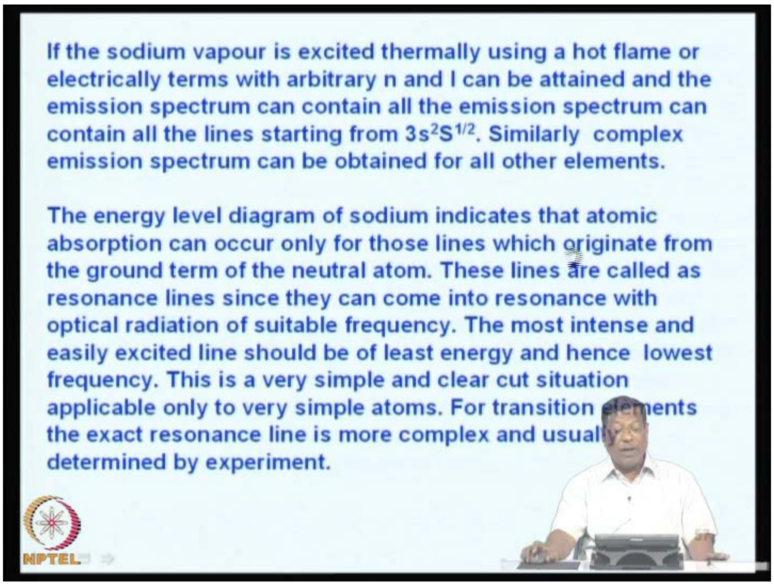

If the sodium vapour is excited thermally using a hot flame or electrically terms with arbitrary n and l can be attained and the emission spectrum can contain all the emission spectrum can contain all the lines starting from $3s^2S^{1/2}$. Similarly complex emission spectrum can be obtained for all other elements.

The energy level diagram of sodium indicates that atomic absorption can occur only for those lines which originate from the ground term of the neutral atom. These lines are called as resonance lines since they can come into resonance with optical radiation of suitable frequency. The most intense and easily excited line should be of least energy and hence lowest frequency. This is a very simple and clear cut situation applicable only to very simple atoms. For transition elements the exact resonance line is more complex and usually determined by experiment.

So, the energy level diagram of sodium indicates the atomic absorption lines, occur only for those lines which originate from the ground state of the neutral atom, because excited element concentration of the atoms in the excited state is always very small, that we have seen in the previous slides, when we calculated the number of atoms in the excited state.

So, the line corresponding to minimum energy is called a resonance line, since they can come the atoms, can come into resonance with optical radiation of suitable frequency that means, you the minimum energy level and the optical energy, optical radiation, electromagnetic radiation if it coincides if the frequency or the energy coincides with the minimum energy of sodium excitation, then it is called as resonance energy.

So, the most intense and easily excited line should be of least energy and hence it should be having lowest frequency, this is a very simple and clear cut situation applicable only to simple elements, that is like sodium, potassium, etcetera. But, for transition elements the exact resonance line and resonance spectrum emission spectrum are much more complex and usually they are determined by the experiments, rather than theoretical calculations.

So, in order to analyze the spectrum it is necessary for us to know, which spectral term corresponds to the spectral lines, this information is provided by the selection rules of l s coupling and delta j values and they have to change by minimum 1 unit and n is the principle quantum number, which can alter an any movement, by any number, by any amount. Now, we have discussed many of these terms earlier in our discussion, especially when we are discussing fluorescence, etcetera; now again let us recapitulate our knowledge about the energy states of an electron in an atom, we will go very quickly because, we have already discussed all these things.

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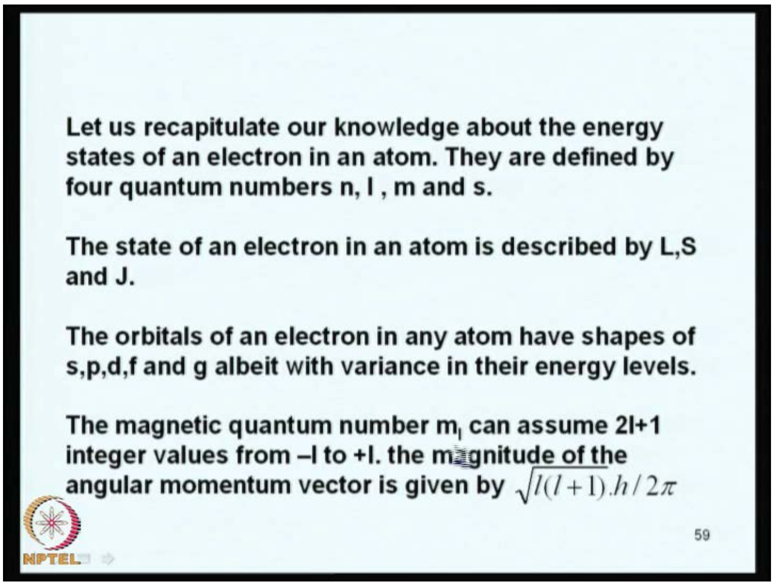

Let us recapitulate our knowledge about the energy states of an electron in an atom. They are defined by four quantum numbers n, l , m and s.

The state of an electron in an atom is described by L,S and J.

The orbitals of an electron in any atom have shapes of s,p,d,f and g albeit with variance in their energy levels.

The magnetic quantum number m_l can assume 2l+1 integer values from –l to +l. the magnitude of the angular momentum vector is given by $\sqrt{l(l+1)}.h/2\pi$

And we know that most of the electrons have defined by four quantum numbers n, l, m and s, the state of an electron in an atom is described by l, s, n and j, that means the energy levels are described by these terms they are capital L, S, J, l s and j denoted. Now the orbitals or an electron in any atom have shapes of s p d f and g orbital’s albeit with variance in their energy level, it is all same for all elements.

So, the magnetic number, quantum number m l can assume 2 l plus 1 configurations from minus l to plus l, this also we have discussed earlier; the magnitude of the angular momentum vector is given by square root of l into l plus 1 into h by 2 pi. So, we can discuss all these numbers right now, because to understand how complex is situation can be for an emission spectrum. So, the orbital angular momentum can be square root of l into l plus 1 multiplied by h by 2 pi, that is a very strong standard number.

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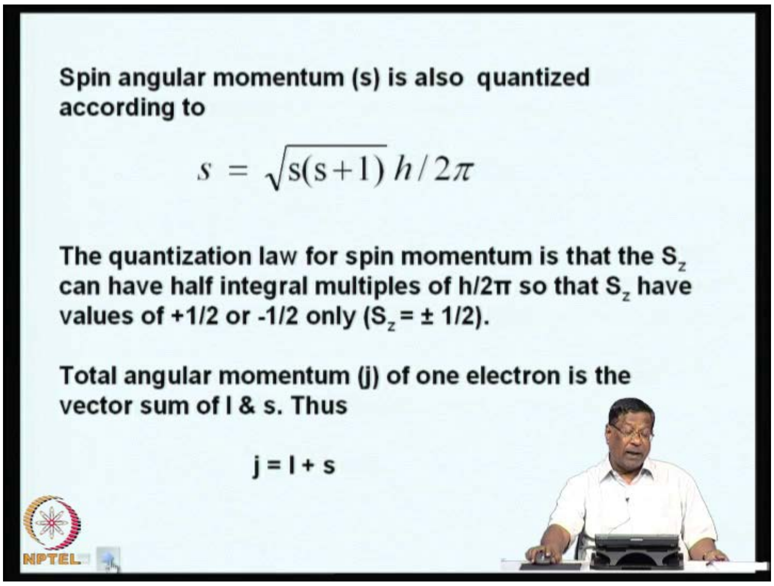

Spin angular momentum (s) is also quantized according to

$$s = \sqrt{s(s+1)}\, h/2\pi$$

The quantization law for spin momentum is that the S_z can have half integral multiples of $h/2\pi$ so that S_z have values of +1/2 or -1/2 only ($S_z = \pm 1/2$).

Total angular momentum (j) of one electron is the vector sum of l & s. Thus

$$j = l + s$$

Similarly the spin angular momentum S is also quantified according to S into s plus 1 multiplied by h by 2 pi, this quantization law for spin momentum is that S z there this I remember all these things are having they are all vectors the orbital shapes other things.

So, the quantization law for spin momentum is that S z can have half integrals; half h by 2 pi because, each electron can spin only in one direction and the other one can be in opposite direction. In order to satisfy the poly exclusion principle that is each electron should be indentified by four different quantum state that is no to electron can have the same quantum number.

So, they have values of plus half or minus half, that is the recession precision through which the electron undergoes; so the total angular momentum j of one electron is the vector sum of l S l and S that is we can have the.

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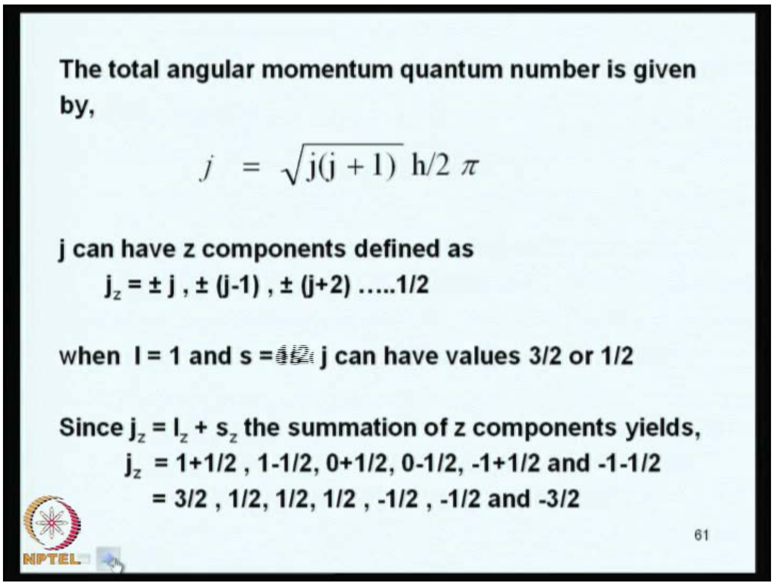

The total angular momentum quantum number is given by,

$$j = \sqrt{j(j+1)}\ h/2\pi$$

j can have z components defined as

$j_z = \pm j, \pm (j-1), \pm (j+2) \ldots\ldots 1/2$

when l = 1 and s = 1/2 j can have values 3/2 or 1/2

Since $j_z = l_z + s_z$ the summation of z components yields,

j_z = 1+1/2 , 1-1/2, 0+1/2, 0-1/2, -1+1/2 and -1-1/2

= 3/2 , 1/2, 1/2, 1/2 , -1/2 , -1/2 and -3/2

We can add them as if they are two vectors. So the total angular momentum is given by j into j plus 1 for each electron, we can have a coupling and then, the for j we can have the combined quantum number also similarly, because these two are for number of elements, number of electrons, we write single electron we write j and total number of electrons, we write capital J.

So, J can have z components defined as plus or minus j plus or minus j minus 1 j plus 2 like that up to j half, so when l is equal to 1 and s is equal to half j can have values 2, 1 plus 1 by 2 that is 3 by 2 or 1 minus 1 by 2 that is 1 by 2. Since j z that is z component is also derived from the orbital angular momentum and spin quantum numbers, the summation of z components gives, so many states 1 plus 1 by 2, 1 minus 1 by 2, 0 plus half, 0 minus half like that.

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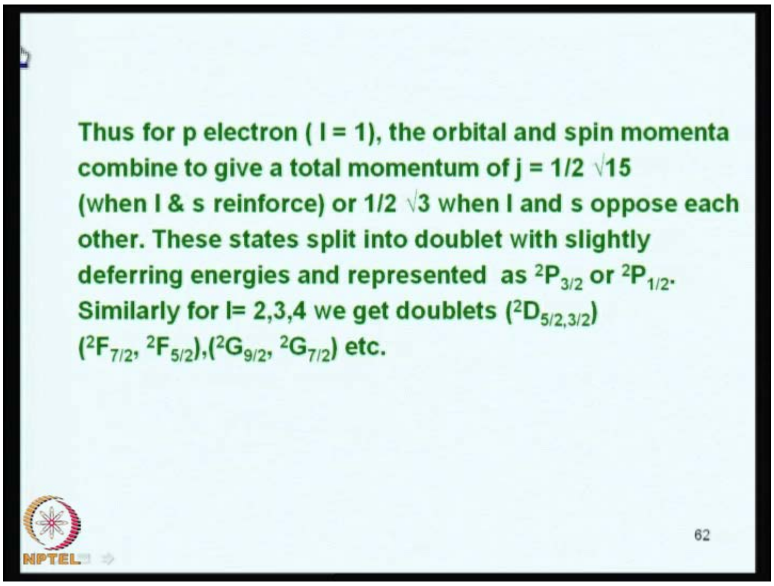

Thus for p electron ($l = 1$), the orbital and spin momenta combine to give a total momentum of $j = 1/2\ \sqrt{15}$ (when l & s reinforce) or $1/2\ \sqrt{3}$ when l and s oppose each other. These states split into doublet with slightly deferring energies and represented as $^2P_{3/2}$ or $^2P_{1/2}$. Similarly for l= 2,3,4 we get doublets ($^2D_{5/2,3/2}$) ($^2F_{7/2}$, $^2F_{5/2}$),($^2G_{9/2}$, $^2G_{7/2}$) etc.

So, many number of states for each element for each electron in the atom, so far P electron the orbital and spin quantum number can give combined to give a total values of j 1 by 2 into 15, where l and s reinforce or 1 by 2 into root 3, when l and s oppose each other. These state split into doublet with slightly differing energies that means the combined vector will they will have two different states but, they are not different by too much energy due they are very close to each other but, still they are doublet.

And these doublet frequencies will be differing by very small amount and represented as 2 P 3 by 2 or 2 P 1 butt; similarly, for l is equal to 2, 3, 4, etcetera we get only doublets that is 2 D 5 by 2, 2 D 3 by 2 and then, if we go for still higher energy level that is f levels, we get 2 F 7 by 2, 2 F 5 by 2 like that, we will be able to get a number of atom number of energy levels.

So, the total number of orbital angular momentum of an atom is basically, the sum of all quantized angular momenta of the individual electrons, these states is also quantized. So, the orbital angular momentum can interact with the magnetic movement due to spin, this is termed as Russell Saunders coupling or simply L S coupling.

So, the L S interaction gives multiple splitting of each of each term, so the coupling scheme for heavy atoms is called as j j coupling, so there is only a slight different but, the terms what we get, are entirely different for simple elements, for heavy elements and number of it depends upon the number of electrons in the auto most orbital’s, etcetera; so in my next slide shows you L S coupling for S and P electrons.

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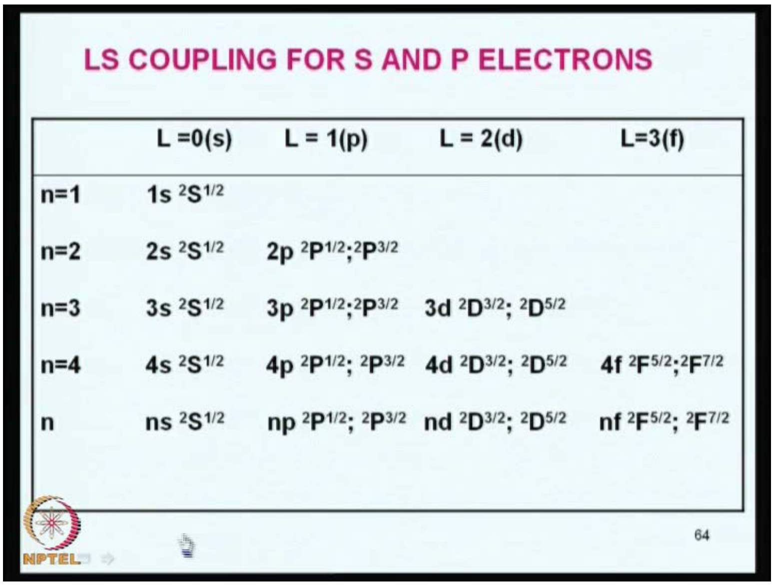

LS COUPLING FOR S AND P ELECTRONS

	L =0(s)	L = 1(p)	L = 2(d)	L=3(f)
n=1	1s $^2S^{1/2}$			
n=2	2s $^2S^{1/2}$	2p $^2P^{1/2}$;$^2P^{3/2}$		
n=3	3s $^2S^{1/2}$	3p $^2P^{1/2}$;$^2P^{3/2}$	3d $^2D^{3/2}$; $^2D^{5/2}$	
n=4	4s $^2S^{1/2}$	4p $^2P^{1/2}$; $^2P^{3/2}$	4d $^2D^{3/2}$; $^2D^{5/2}$	4f $^2F^{5/2}$;$^2F^{7/2}$
n	ns $^2S^{1/2}$	np $^2P^{1/2}$; $^2P^{3/2}$	nd $^2D^{3/2}$; $^2D^{5/2}$	nf $^2F^{5/2}$; $^2F^{7/2}$

So, the next slide shows n is equal to 1, n is equal to 2, n is equal to 3, n is equal to 4 and n can be anything; and for L a is equal to 0, L is equal to 1, I have one more column L is equal to 2 d and 3 f, L is equal to 1, L is equal to 0 is s electron, L is p and 2 is d, 3 is f. So, for each of this, we get 1 S 2 S by 2 and then 2 P 2 by 2, 2 P 1 by 2 and then 3 D 3 by 2, 3 D 5 by 2 in addition to all other previous numbers.

So, the numbers of lines keep on increasing due to L S coupling, for S and P electrons depending upon the number of principle quantum number, where we decide to look for combinations of L S L S coupling.

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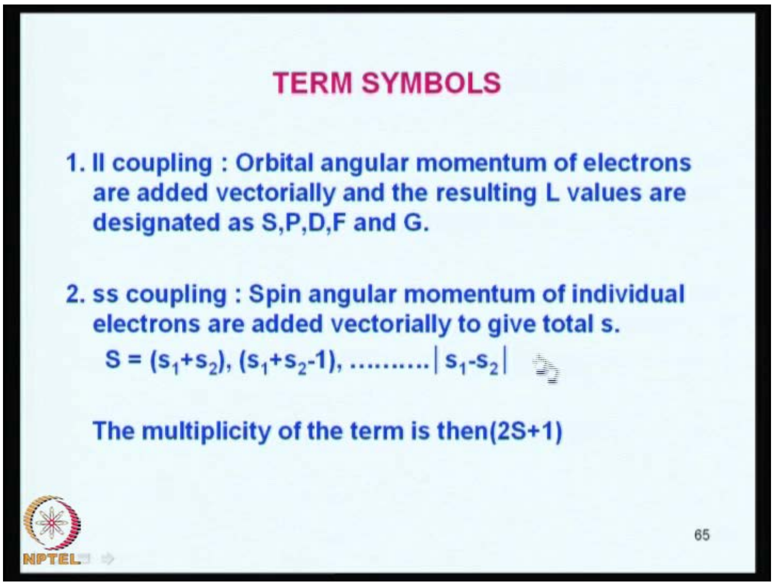

TERM SYMBOLS

1. ll coupling : Orbital angular momentum of electrons are added vectorially and the resulting L values are designated as S,P,D,F and G.

2. ss coupling : Spin angular momentum of individual electrons are added vectorially to give total s.

   $S = (s_1+s_2), (s_1+s_2-1), \ldots\ldots\ldots |s_1-s_2|$

   The multiplicity of the term is then(2S+1)

So, we can have different term symbols for different kinds of mixing, the vector summation that is we can have l l coupling and then s s coupling, orbital angular momentum of electrons are added vectorially and the resulting l values are designed as capital S, capital P, capital D, capital F, etcetera. Similarly, s s coupling involves only the spin angular momentum of the individual electrons and they are added vectorially to give s plus s 1 plus s 2, s 1 plus s 2 minus 1, etcetera until you get s 1 minus s 2. So, the multiplicity of the term is 2 s plus that is, so many numbers of spectral lines are with differing energy are possible so.

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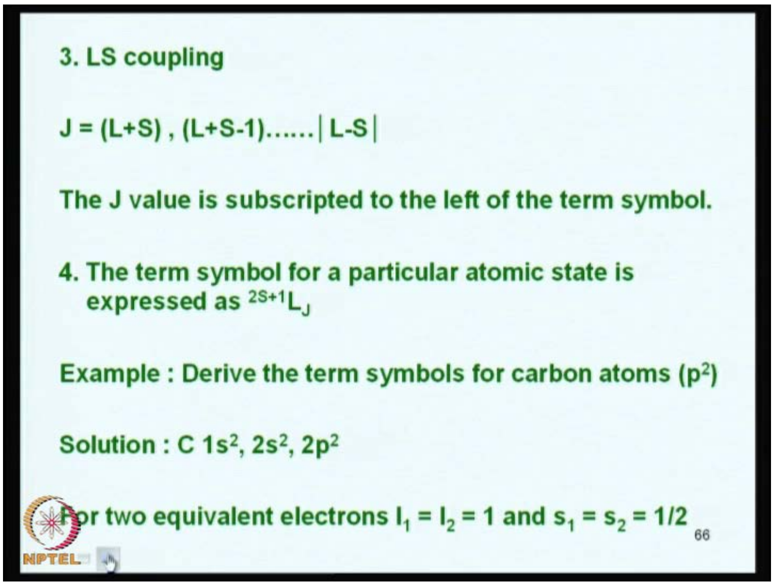

3. LS coupling

$J = (L+S) , (L+S-1)\ldots\ldots |L-S|$

The J value is subscripted to the left of the term symbol.

4. The term symbol for a particular atomic state is expressed as $^{2S+1}L_J$

Example : Derive the term symbols for carbon atoms (p^2)

Solution : C $1s^2$, $2s^2$, $2p^2$

For two equivalent electrons $l_1 = l_2 = 1$ and $s_1 = s_2 = 1/2$

Now, let us take a look at L S coupling third one that is J should be having values varying from L plus S, L plus S minus 1 to L minus S; so this J value when you write in the spectrum, we write it to the left of the term symbol, that is 2 S plus 1, etcetera. So the term symbol for a particular atomic state is expressed as 2 s plus 1 and write capital L and then J value here, now take a let us take a small example, that is we will derive the term symbols for carbon atoms, that is it is having 2 P electrons.

So, the structure of carbon atoms is given by 1 s 2, 2 s 2 and 2 p 2 for two equivalent electrons l 1 is equal to l 2 is equal to 1 and for s electrons it is s 1 is equal to s 2 is equal to 1 by 2, that is we are forgetting we are not taking into account 1 s 2 but, only the 2 s 2 and 2 p 2 orbitals; so far that the values are l 1, l 2 is equal to 1, s 1 and s 2 are 1 by 2.

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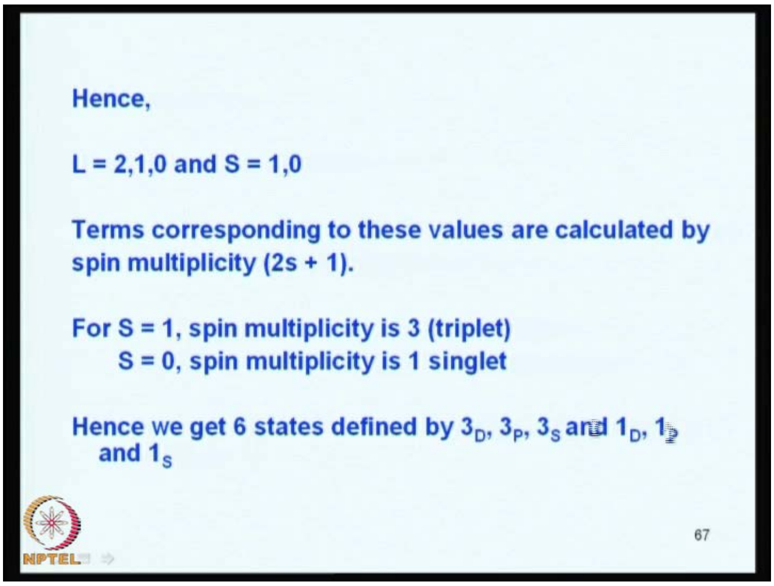

Hence,

L = 2,1,0 and S = 1,0

Terms corresponding to these values are calculated by spin multiplicity (2s + 1).

For S = 1, spin multiplicity is 3 (triplet)
S = 0, spin multiplicity is 1 singlet

Hence we get 6 states defined by 3_D, 3_P, 3_S and 1_D, 1_P and 1_S

Now, we try to combine this and when we combine this, we can have capital L values like 2, 1, 0 and capital S should be some of the capital S should be 1 and 0, that means when the spins are combined, we get 1 spins are opposing we get 0 and then L can have values 2 L plus L that is z 3 that is 2 1 and 0.

So, the terms corresponding to these values are calculated by spin multiplicity that is 2 S plus 1, so for S plus L S is equal to 1, the multiplicity is triplet that is 3, 3 is called as triplet and for S is equal to 0 spin multiplicity is singlet, that is only 1. So, we get t 6 states just by combining these energy levels that is 3 D, 3 P, 3 S, 1 D, 1 P and 1 S.

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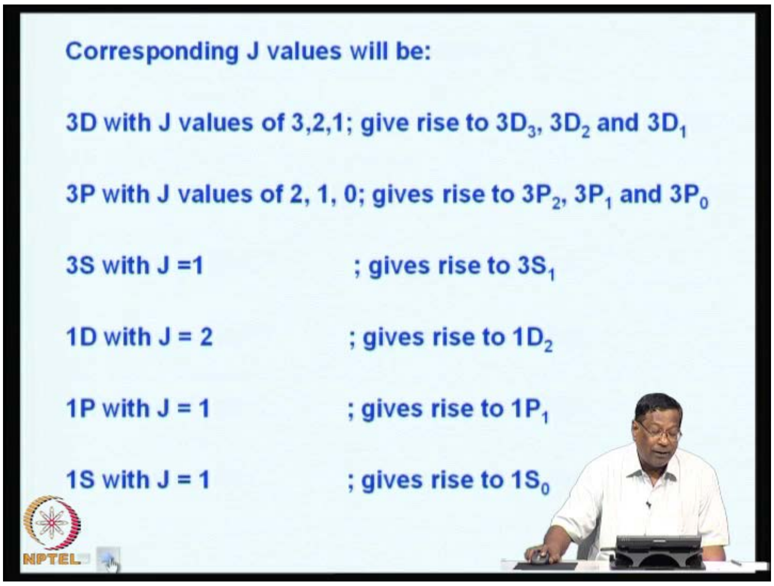

Corresponding J values will be:

3D with J values of 3,2,1; give rise to $3D_3$, $3D_2$ and $3D_1$

3P with J values of 2, 1, 0; gives rise to $3P_2$, $3P_1$ and $3P_0$

3S with J =1 ; gives rise to $3S_1$

1D with J = 2 ; gives rise to $1D_2$

1P with J = 1 ; gives rise to $1P_1$

1S with J = 1 ; gives rise to $1S_0$

So, corresponding J values, we can calculate the they will be having for 3 D, J values will have 3 2 and 1, so this gives rise to 3 D 3, 3 D 2 and 3 D 1 states; similarly, 3 P with J values of 2 1 and 0 gives you 3 P 2, 3 P 1 and 3 P 0. So, 3 S electron which J is equal to 1 gives rise to 3 S 1 similarly, 1 D will give you 1 D 2, 1 P will give you 1 P 1 and 1 S will give you 1 S 0 that means, so many energy levels for each for carbon are possible.

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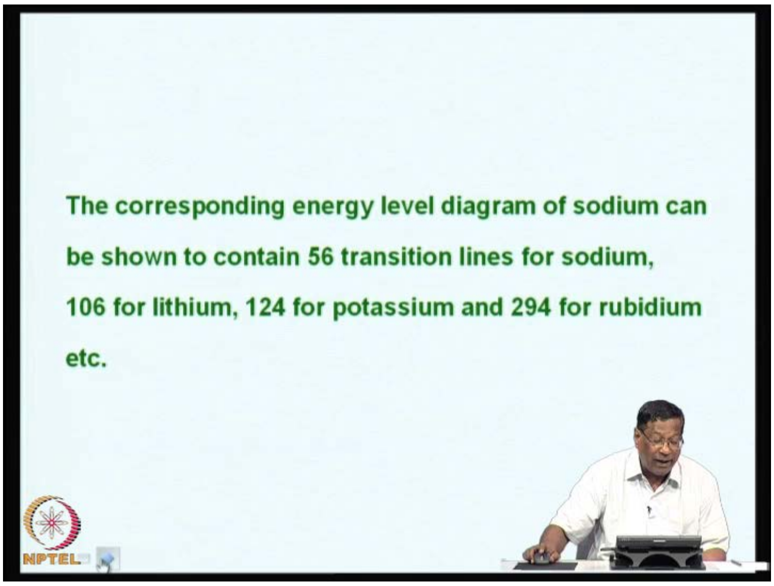

The corresponding energy level diagram of sodium can be shown to contain 56 transition lines for sodium, 106 for lithium, 124 for potassium and 294 for rubidium etc.

So, the corresponding energy level, similar energy level diagram for sodium can be shown to contain 56 transition lines for sodium and 106 for lithium, 124 for potassium and 294 lines for rubidium, etcetera all these things have been identified and put in the database and all the transitions the all the transitions are possible.

And they can be estimated measured and put into the database but, for our purpose what we understand is for atomic absorption to occur, we must have the number of atoms in the ground state and the higher energy state, the the with the minimum energy transitions is known as resonance line and that resonance line is defined by L S coupling or J J coupling and S S coupling and for the calculation of the resonance line.

Now, the number of lines are possible with respect to each element, that also we should remember, so after all this what we can do is we have to find ways how to produce the atoms in the ground state for atomic absorption to occur. Basically, what we are looking at is how to generate the atoms in the ground state, because the purpose of our discussion is analytical science not the spectroscopic science.

But, it is important for us to appreciate that number of atomic lines are possible, which can confused one but, we should always select the resonance line with the lowest energy state, which can take the electrons from the ground state, when the electromagnetic radiation is passed and it must excite the electrons to the next higher energy level. So, that number, we have already discussed how many we can generate at different temperatures but, still the temperatures.

What we are talking about, even though the number of atoms in the excited states are very small the the measurement of atomic absorption is always possible because these, because we measure the absorption from the ground state and the energy difference between the excited state; so the signal corresponding to the excitation is what we are measuring in atomic absorption.

Now, let us take a look at the instrumentation, how an atomic absorption spectrometer can be constructed, in my introduction talk on atomic absorption, I had discussed that single beam A C, single beam D C can be measured, single beam double beam A C instrument can be measured can be constructed, etcetera.

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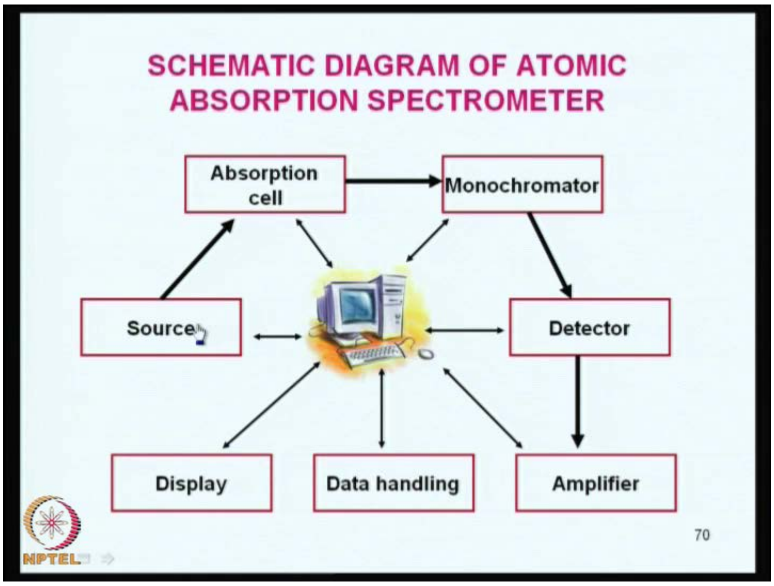

SCHEMATIC DIAGRAM OF ATOMIC ABSORPTION SPECTROMETER

Now, let us take a look at the architecture of atomic absorption spectrometer, now my next slide shows you the basic component of the atomic absorption and like all other instruments, here you need a source that is here. And then you need an absorption cell, where you can produce the atoms in the ground state and then what happens from the source radiation is passed through the absorption cell and then you need a monochromator to separate unwanted radiations.

But, you are supposed to measure only the source line, the intensity of the source line after passing through the atomic absorption and that radiation after you separate all other radiations using a monochromator, we take it to the detector here. And this detector is connected with an amplifier to amplify the signal and from the amplifier the signal is handled and correlated with the concentration and then, we can do some data handling statistically analysis, etcetera and then we can have a display.

So, this is how the atomic absorption spectrometer should function, now you will be surprised to see why I have put a computer in the center, that is because nowadays, the instrumentation has become, so well organized that several functions of the atomic absorption or for that matter any instrument can be handled by the computer microprocessor.

So, you can use a microprocessor to give voltage to the source and then, light off the lamp measure the absorbance use a monochromator for adjusting the wavelength, etcetera using a servomotor and then detectors and then take it to the detector optics and optics can be organized and then, adjusted using a microcomputer and microprocessor and then, we have a detector amplifier and data handling all these tasks can be done by the computer.

And this is where the atomic absorption spectrometry scores over many other equipment, because most of the functions are taken over by the microprocessor and computer and it leaves minimum for the practitioner to do to adjust the positions and other things, positions of the source, absorption, cell, height, weight and height, length, etcetera but, still the chemistry the computer cannot do anything.

So, we have to understand the different kinds of the components that go into atomic absorption spectrophotometer, so let us proceed to our discussion on the sources, so the radiation sources, we have are hollow cathode lamps that is one type of radiation source this we have already discussed, during our theoretical discussion, that we need radiation of the only the resonance line.

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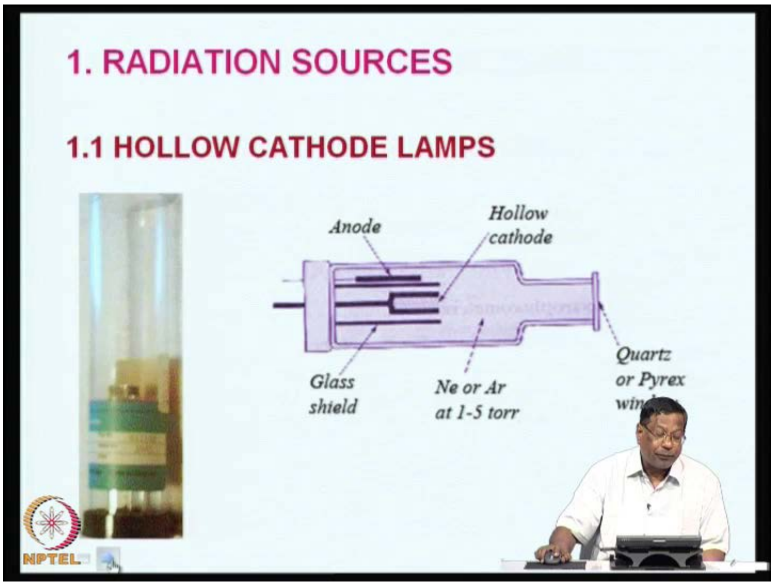

1. RADIATION SOURCES

1.1 HOLLOW CATHODE LAMPS

And the only way we can produce this radiation with enough intensity is to use a hollow cathode lamp, that is a lamp made of the made of the same element as the analyte, here I am showing you the hollow cathode lamp, the figure on the left shows you an actual hollow cathode lamp in the used in the instrument. And the figure on the right shows you the schematic diagram of a hollow cathode lamp, here you can see that at the backside here, what where my handle is pointing out it is only the electrical connection and this is made of glass up to the outer portion except this portion, this is made of quartz because, the radiation coming out of a hollow cathode lamp should pass con usually contains ultraviolet lights.

So, if we use glass we the radiation will be absorbed by the glass, so most of the hollow cathode lamps are constructed using a quartz window and then, here you can see that the there is one anode and cathode. This cathode is in the form of a ring the middle one and on the top there is anode, which is a sort of a filament and then, there is a glass shield completely shield and then putting there is neon or argon gas filled at about 1 to 5 torrs; so this is the basically the construction of a hollow cathode lamp.

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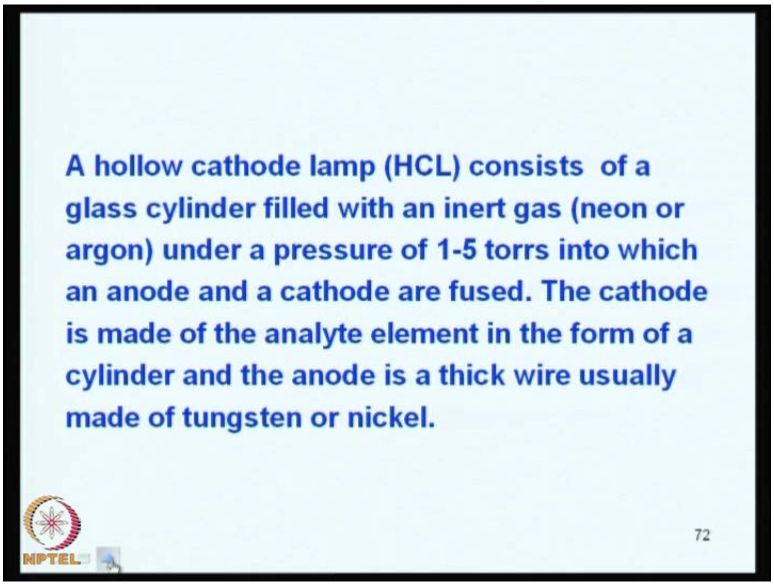

A hollow cathode lamp (HCL) consists of a glass cylinder filled with an inert gas (neon or argon) under a pressure of 1-5 torrs into which an anode and a cathode are fused. The cathode is made of the analyte element in the form of a cylinder and the anode is a thick wire usually made of tungsten or nickel.

So, it actually consists of we can define it like this, a hollow cathode lamp consists of a glass cylinder filled with an inert gas using neon or argon, under a pressure of 1 to 5 torrs into which an anode and cathode are fused. The cathode is made of the same in analyte element in the form of a cylinder and the anode is a thick wire, usually made of tungston or a nickel anode can be common. So, a voltage of several hundred volts is required to light the lamp, your normal voltage in our day to day life is 230 volts, we need almost 300, 400 volts sometimes even less but, several hundred volts is the requirement to light the hollow cathode lamp.

So, the applied voltage usually generate approximately 5 to 15 milli amperes of current and that sets up a glow discharge of the carrier gas that is neon or argon; so when we pass the volt (Refer Slide Time: 42:09), when we apply the voltage inside this the gas is there and this gas starts discharging, that means it will give you some sort of light and the gas will ionized to give the ions. And ions will migrate towards the cathode and anode depending upon, whether they are positive or negative ions, so this is the basic process that happens in the hollow cathode lamp.

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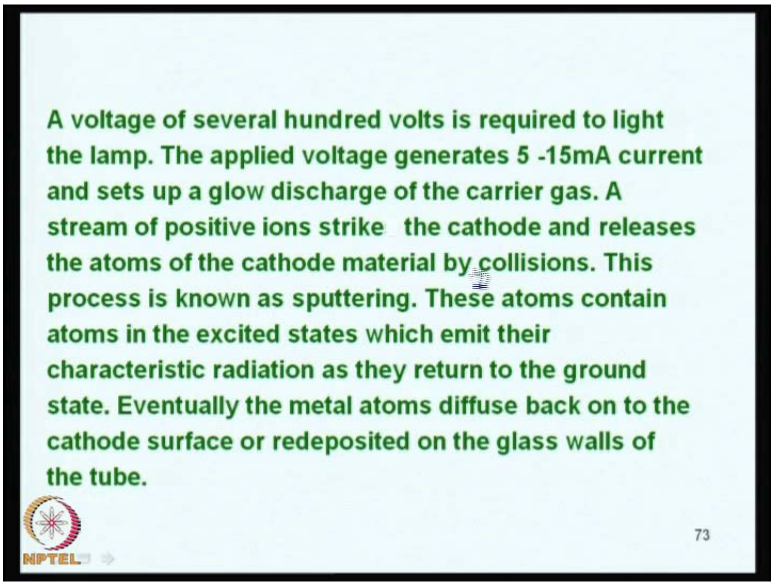

A voltage of several hundred volts is required to light the lamp. The applied voltage generates 5 -15mA current and sets up a glow discharge of the carrier gas. A stream of positive ions strike the cathode and releases the atoms of the cathode material by collisions. This process is known as sputtering. These atoms contain atoms in the excited states which emit their characteristic radiation as they return to the ground state. Eventually the metal atoms diffuse back on to the cathode surface or redeposited on the glass walls of the tube.

Whenever we start operating, the hollow cathode lamp, so you take a hollow cathode lamp fill it will neon or argon set up a glow discharge and positive ions will strike the cathode and releases the atoms of the cathode material by collision.

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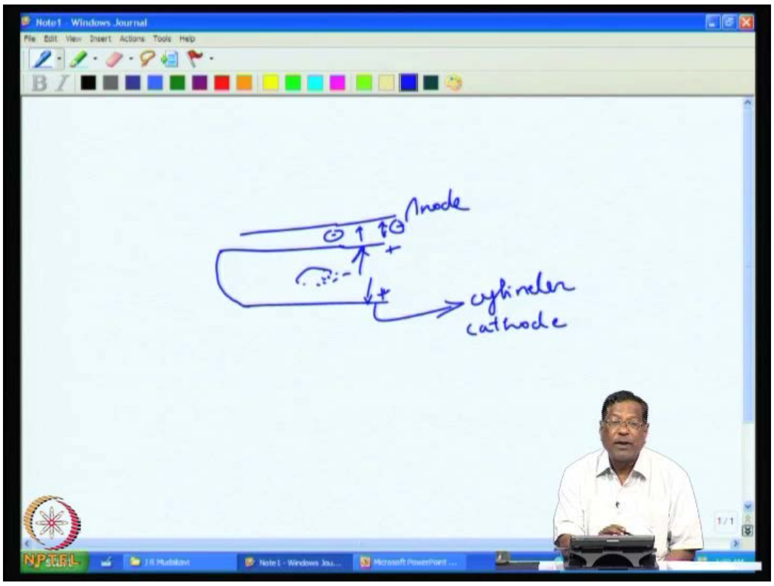

what do you mean is the ions, this is your hollow cathode lamp and then there is argon gas filled here in all the spaces and the positive ions will strike the cathode and the negative ions will strike the anode. This is anode negative ions and positive ions will go and hit the cylinder, this is in the form of a cylinder and that is cathode. This is the basic process in which the ions will come and bombard the cathode.

now what happens when they come when they become energetic they will strike the cathode and the elements atoms in the cathode will also get energized and they will start sputtering, that means they come out of the system. And then they will the positive atom ions will be inside the hollow cathode cylinder and these ions will before they strike the anode they will get excited, they will pick up the free electrons from the from the gas ionized gas. And they will become atoms they get excited to take the higher energy level before they reach the electrode due to their kinetic process, they emit the radiation and then get settled into either onto the glass or onto the cathode material that is the basic process.

So, the process is the gas, first the gas will start ionizing it will sputter the atoms in the cathode and from the cathode the atoms will get excited and reach the cathode in the gaseous form. And during that process they emit the radiation, that is characteristic radiation corresponding to the same element, that is the resonance line, this is what we have discussed earlier because, the atomic resonance line has to be of the order of 0.002 nanometers accuracy.

So, getting back to this our discussion (Refer Slide Time: 46:01), the atoms contain the atoms in the excited state emit their characteristic radiation as they return to the ground state, eventually the metal atoms will have to diffuse back onto the cathode surface or get redeposited on the glass walls of the tube. So, many times when you start operation of an atomic absorption (Refer Slide Time: 46:22) you will see that the we will see a mirror like substance in this region.

So, these are all the atoms you will see something like silver mirror in some parts of the glass, that is the place where the atoms are redepositing after the function, so either they are deposited on the glass (( )) or onto the cathode itself. So, the cylindrical configuration of the cathode the function, why you should have cylindrical composition of the cathode and only wire as an anode, it is a simple thing it concentrates the emitted radiation; and it also enhances the possibility of redeposition onto the confined space, where we have a ringed structure.

So, the electron atoms can go back on the cathode material, there is another possibility that these these radiation coming out of it will become focused, it is easy to handle from the output from a cylindrical cathode, then then a filament cathode. So, the efficiency of the hollow cathode lamp depends upon the geometry as well as applied voltage, that is why we make it cylindrical and we keep on playing with the applied voltage, so that higher, the voltage higher is the current and greater is the intensity of the emitted radiation.

This advantage is somewhat offset by the increasing Doppler broadening, that means if you increase the voltage indiscriminately, there will be more atoms, there will be more disorder thermal motion of the atoms and the radiation will become weak corresponding to that frequency.

So, the intensity also will be much less, so there is always a compromise when you operate the hollow cathode lamp it should you should operate it at as low voltage as possible. So, after sometime what happens now, the concentration the lamp will get fatigued and the fatigued lamp will require more voltage to give you the same intensity but, it is always at the cost of the sensitivity of the determination.

So, there is a great linkage between the operating voltage and the intensity, higher the voltage there is another problem, that is increase number of unexcited atoms you know we have discussed earlier that; whatever is the temperature the number of atoms in the ground state is always more compare to number of atoms in the excited state that is of the order of few atoms out of 10 rise to 15 or something like that.

Now, what happens in the gas cloud if there are number of atoms they are capable of absorbing the same element same radiation emitted by the excited atoms, now what we need is the excitation from the source, that is the radiation line, now if there are more unexcited atoms in the same gas cloud they will absorb the radiation.

So, this is known as self reversal, if you observe in your town, where there are sodium lamps on the streets you would have seen that quite often the lamps they switch on and switch off switch on and switch off on it is own even though the current is there. So, this if you have not seen that I request you to go and observe some of these lamps, sodium vapour lamp on the or the street lamps they will keep on observing the same radiation lamp goes off lamp extinguishes and then again it comes on, when the number of atoms becomes less.

So, the electrons atoms will go back to the ground state and then radiation again some atoms will get excited, again the lamp will switch on, this phenomenon is known as self reversal; that means unexcited atoms, we will always absorb part of the radiation. And this is also used this principle is very useful for us in the background correction also that we will discuss later but, for the time being, we have to understand that the increase number of unexcited atoms in the gas cloud are capable of absorbing the radiation.

So, this process lowers the intensity therefore, we have to ensure that the radiation, we always operate it at the minimum voltage and optimum intensity, so in if you buy a hollow cathode lamp for atomic absorption, they will always indicate what is the optimum voltage you should operate, sometimes as the lamp ages the you may not get the same intensity; in that case you should increase it by 10 volts or 15 volts or slightly increased voltage to get the same intensity.

Therefore, every hollow cathode lamp has certain amount of life, that is known as self life, the self life is also indicated by the manufacturer on the life. So, that at the end of 2 years you may have to replace lamp or something like that and people have to follow the instructions fairly fairly seriously to get optimum output.

Now, you can construct a variety of hollow cathode lamps, because for each analyte for cadmium, you need a cadmium lamp, manganese you need a manganese lamp, iron you need iron lamp, chromium chromium like that, you have to have a library of hollow cathode lamps if you want to work with atomic absorption. This is a cost, this adds to the cost of atomic absorption process, where you want to determine you have to buy each hollow cathode lamp costs about 25 to 30,000 rupees and very few hollow cathode lamp manufacturers are there.

So, the instrument manufacturers usually outsource the hollow cathode lamp and then they try to modify the connectors, so that they can use the modified lamps for that purpose, so that the applicability of a given hollow cathode lamp is suitable only for that manufacturer.

So, we you can construct hollow cathode lamps for most of the elements and by use suppose you use an alloy, then what happens an alloy is basically a mixture of number of elements. So, why not make a hollow cathode lamp of an alloy, what are the advantages? The advantages are all the elements present in a hollow cathode lamp can be excited and you can do the multi element analysis, using the same source; so that is one advantage another advantage is it may reduce the cost of the of making so many elements.

So, one single hollow cathode lamp will also be able to you can choose, whatever element you want if the element is there is the alloy, so that is possible and multi element determination is possible. So, we can use different alloys to make hollow cathode lamps and then at least 2 to 3 elements 5 elements, you can determine using the same lamp.

Now it is not the using a multi element hollow cathode lamp, can also lead to slight difficulties that is because, the most volatile element initially when you operate the all the elements will come into the gas cloud and then, they will settle down; but, then when settling down the most volatile element is the one which gets excited, in the next operation compare to not so most not so volatile element that means 1 or 2 elements will be preferentially dominating compare to the all the alloying elements.

So, one has to be slightly careful regarding the multi element analysis, if you want to use an alloy but, still commercial such systems are available. Now let us discuss, about a hollow catho vapour discharge and other source one is hollow cathode lamp, are there any other sources which can give this kind of radiations, which we can use in atomic absorption.

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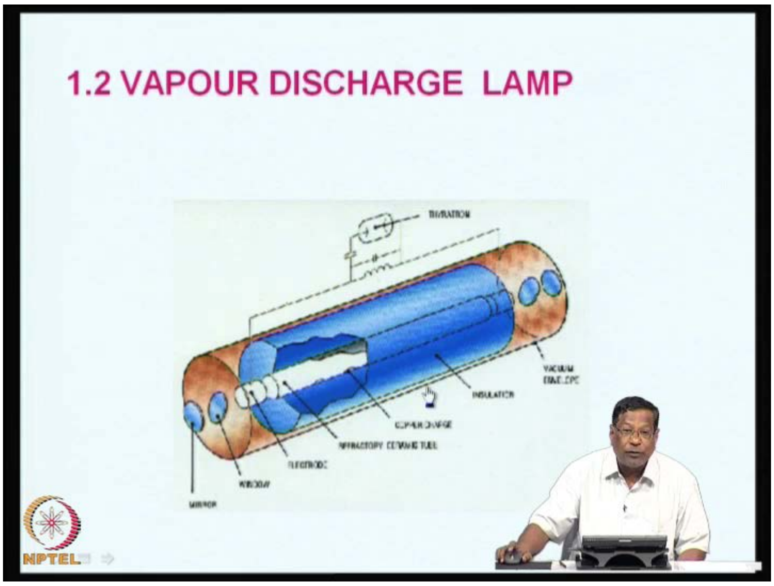

1.2 VAPOUR DISCHARGE LAMP

Now here, I am showing you a vapour discharge lamp, this is just like a mercury vapour lamp and only thing is the vapour here are the connections and then we have a lamp vapour deposited here, some of the element that is deposited here; and then we have the we have the electrical connections and then these are the electrodes and when you operate this is also operated under vacuum. And there is some amount of insulation is necessary and again the windows in this range have to be of the made of cards; so, all other this outer shield should be glass, etcetera they remain the same.

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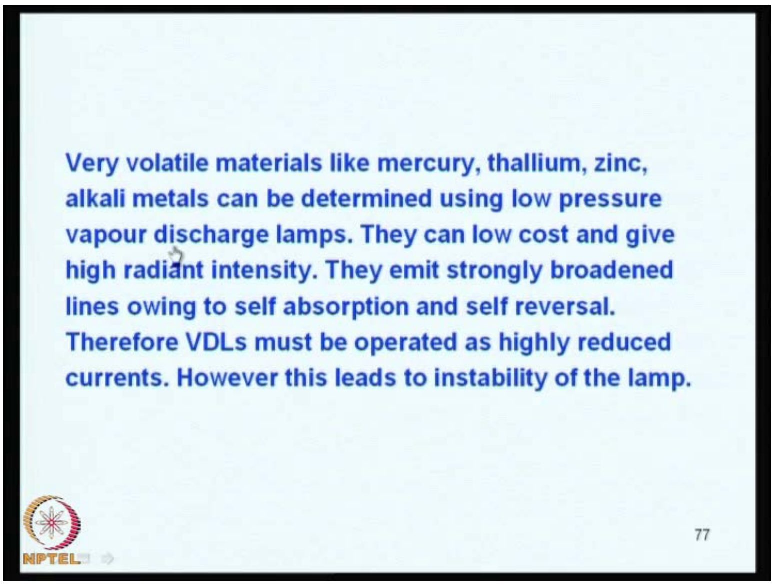

Very volatile materials like mercury, thallium, zinc, alkali metals can be determined using low pressure vapour discharge lamps. They can low cost and give high radiant intensity. They emit strongly broadened lines owing to self absorption and self reversal. Therefore VDLs must be operated as highly reduced currents. However this leads to instability of the lamp.

So, very volatile materials like mercury, thallium, zinc, alkaline metals, etcetera can be determined using low pressure vapour discharge lamps, these are such lamps, we would have seen in your day to day life, mercury lamps, etcetera in the markets, etcetera they are available, they are of low cost give high high radiant intensity. They emit strongly broadened lines, going to self absorption also and self reversal also therefore, (( )) must be operated at highly reduced currents. However this leads to instability of the lamp, we will continue our discussion in the next class regarding electro the less discharge lamps, thank you.