Course on Stereochemistry
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Module No 01
Lecture 03: Project Ion Formulae Rules for Drawing

Okay welcome back to this course on stereochemistry. In the last lectures, what we have introduced to use the concept of chirality and stereo isomerism. We have seen that there are molecules which have the same constitution, same molecular formula but they can be different. And these, the range between these molecules stereo isomerism. Now stereo isomerism, we have seen that they are of 2 types, one on one side there is this Enantiomerism and other side is the Diastereomerism.

Or you can say that the stereo isomers are classified into Enantiomers and Diastereomers. What are Enantiomers? Enantiomers or the non-super opposable mirror images of each other. Okay? Molecules which are non-super opposable mirror images, are called Enantiomers. And they have the ability to rotate the plane of plane polarised light, either in a clockwise fashion or in an anticlockwise fashion.

Now regarding the other class that is the Diastereomers, Diastereomers or not was images of each other but they have the same molecular formula, they have the same constitution. Only the stearic disposition of the groups in space are different. Okay? So what about the rotation of Diastereomers? Now Diastereomers also can have rotations, they can also, they can also have rotations.

So they can also be chiral, okay? Only thing is that Diastereomers are not connected by mirror image relationship. If a molecule, we know also that the condition for chirality is that it is the absence of certain elements of symmetry which makes a molecule chiral. We just revisit quickly what are those elements of symmetry. A molecule is chiral when there is no I, that is the centre of symmetry or the inversion point present.

There is no sigma that is the plane of symmetry which is not present and the alternating axis of symmetry which is denoted as SN, that should also not be present. Okay? So a molecule devoid of I, Sigma and SN will be chiral. And this, there is another term which was earlier used was that the molecules which like these 3 elements of symmetry are called disymmetric molecules and we went a step ahead a little bit because we know that I is equated to S2, that means whenever a molecule has I, a centre of symmetry, the molecule is bound to have a twofold alternating axis of symmetry.

And whenever there is a plane of symmetry present in a molecule, the molecule must have an S1axis, so one fold alternating axis of symmetry. So it will be sufficient to say that the minimum condition for chirality is the absence of SN axis okay where N could be 1, N could be 2 or N could be any other number. But for for you students at this stage, I think I will say that you better mention all these together that 1st you tell that the molecule should be dissymmetric.

So it should be devoid of I, Sigma and SN. And since I is equated to S2 and Sigma is equated to S1, so it is sufficient to say that the molecule becomes chiral when it is devoid of an alternating axis of symmetry. Okay? Now let us come to this molecule which show chirality. Okay? Chiral molecules are those which as as as we have said that are those which are which can have a mirror image which is not superimposable on it.

That means, it shows a non-superimposable image. Those molecules become chiral and the condition of catalytic, we have checked, explained in terms of symmetry, okay? Now these chiral molecules have the ability to rotate the plane of plane polarised light. Okay? And that is the characteristic of a chiral molecule.

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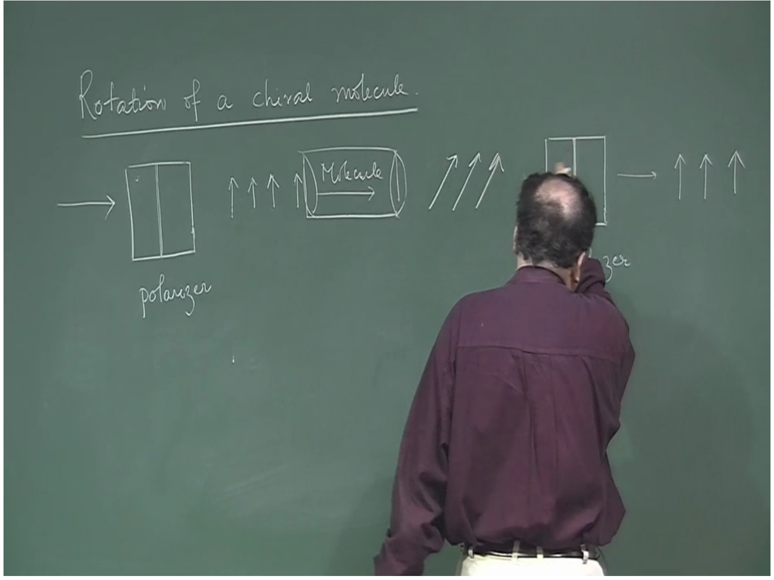

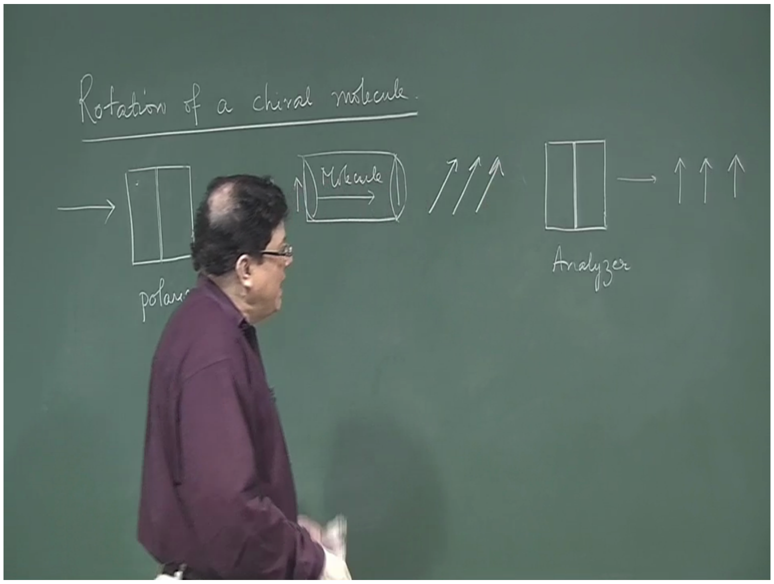

So if you have a plane polarised light which is generated by what is called a polariser, a polariser is would be made up of crystals and not all crystals were certain particular type of crystals. So when light passes through the through the crystal, it comes out as plane polarised light. Okay? And the plane of polarisation will depend on the what is called the principle section of the of the polariser.

Now the polariser can be noticed polarisers are also available in as as sheets, as thin sheets, transparent sheets are also available as polarisers. So what I am saying that it has got a principle section and this principle section, this plane of plane polarised light is actually is actually co-axial with the principle section. But without getting into the very intricate details, you can understand it simply by thinking that there is a, there is a slit in the plate and when light is passing through it, so only the vibrations which take place along this the axis, they will pass through.

So the vibrations are all now are aligned to this to the slit, the slit. And so that is the plane polarised light. Now this plane polarised light, if it passes through a molecule in a solution, molecule, if the molecule is liquid then it is okay. If it passes through a molecule which is a liquid or in a solution kept in a what is called a cell, kept in a cell, then this plane polarised light will interact the molecule and ultimately if the molecule is not chiral so the plane of plane polarisation, the plane of polarisation of the plane polarised light, that remained co-axial, that means the plane does not change.

The plane does not rotate. That remain co-axial with the slit which is actually also called the principle section of the of the of the polariser okay? Now how do you know that the plane has not rotated? So you actually place another another sheet which also which also have the ability to produce polarised light but this is used as, because this is used to analyse whether there is any rotation in the plane of polarisation, this is called an analyser now.

And if the principle section, that means if we have simplified it as just like having a slit in the middle, so if light comes and if this slit which is the principle section again I repeat that is co-axial with this and if there is no rotation in the plane of plane polarised light after passing through this molecule, then what happens? Light will pass through with the same intensity. So there will be no decrease of intensity. So it will pass through.

But if there is, if there is a rotation of the plane of plane polarised light then what will happen? This will not remain like this. The plane of polarisation will not change. The plane will change and if the plane changes, so what happens? Some of the light, so the light will cannot pass through, all the lights cannot pass through some, so the light will become diminished if you make it coaxial, these 2 axis are remaining in the same direction. So to have the, so some of the light will be partly cut out.

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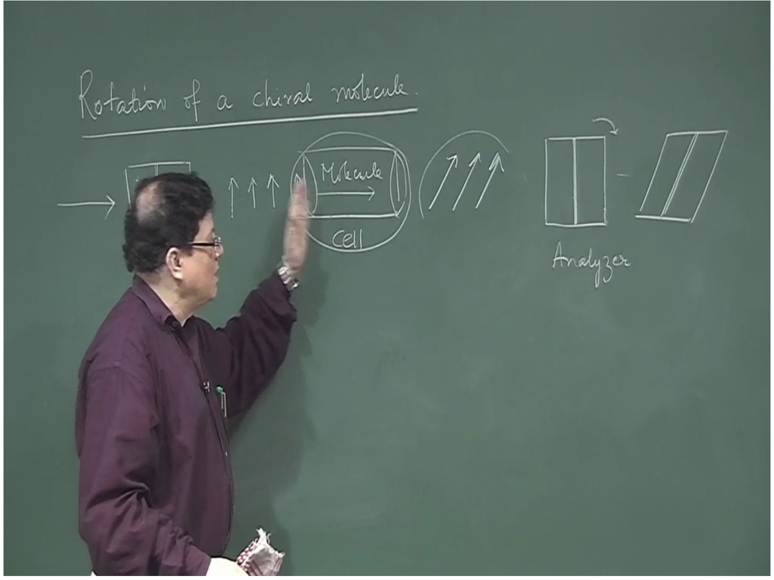

To to get the maximum intensity, what we have to do? We have to rotate it and we have to rotate it in this direction like this so that this slit or the principle section, that becomes now coaxial with the rotated light which has which has been rotated by the the molecule that was in the cell okay? So this amount of the much you are rotating, that gives you the the amount of rotation that these molecules have have done to the plane of plane polarised light okay? Another thing, so this is one way to to know whether the molecule is chiral 1st of all and then how much is the is the rotation that it is introducing into the plane of plane polarised light okay?

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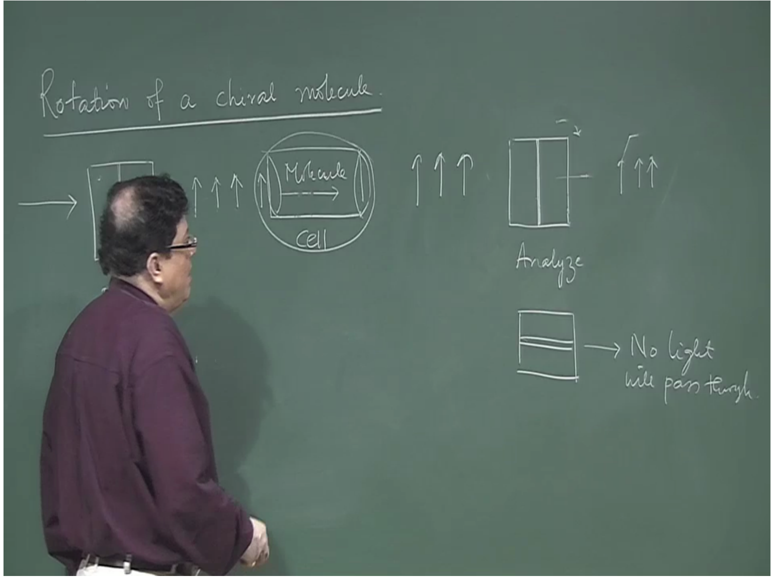

If you, suppose this is not rotated, suppose this remain the same, this molecule is not chiral so it will not rotate the plane of plane polarised light. So now the full intensity of light will come out from this side. If you now rotate it by 90 degrees and make it orthogonal, the axis, this slit is now orthogonal to this slit. So what will happen? All the light because it is perfectly perpendicular so all the light will be cut out and it will be no no light will pass through, no light will pass through.

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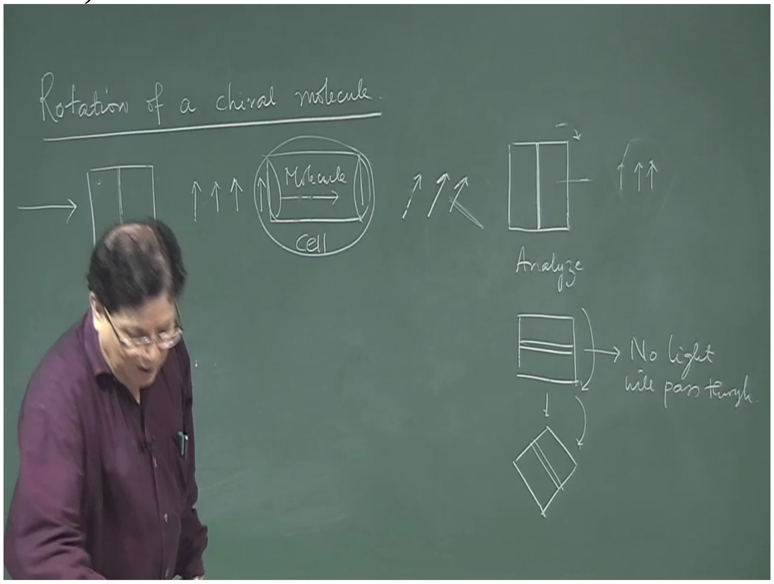

If suppose this gets rotated, so if the molecule is chiral, so this gets sorted it. So now this is no longer orthogonal to the plane of plane polarised light because it got rotated also in order to cut the entire, cut off the entire light, so what we have to do, we have to rotate this and rotate this in this direction so that the slit now becomes orthogonal, so THE slit now becomes orthogonal to the plane of polarization.

So there are 2 ways to, so now the amount of rotation that you need to cut ofF the light is again the amount of rotation that is that is induced into the plane polarised light by these molecules okay? So there are 2 ways, either you get the bright, the brightest brightest light here and then see how much rotation you have to, you have to do to bring the light to the brightest position.

Or you make it orthogonal so that no light will pass through. Now if there is a rotation, then you have to rotate this further so that it becomes orthogonal to this plane of polarisation and this amount of rotation is it will be the same as this. So either you get the brightest brightest field where all the light is passing through or the other way round, you cut off the entire life.

So amount of rotation to cut off the entire light or the amount of rotation to come back to the full brightness is the rotation that has been induced by these molecules to the plane polarised light, okay? Now next is that on what factors this rotation depends. This rotation is obviously that will depend on the nature of the molecule that is the 1st thing. If you different molecules have different compatibility to the rotation. Either to the right or to the either to the clockwise direction or to the anticlockwise direction now for a particular molecule, so the 1st thing is that it depends it varies from molecule to molecule.

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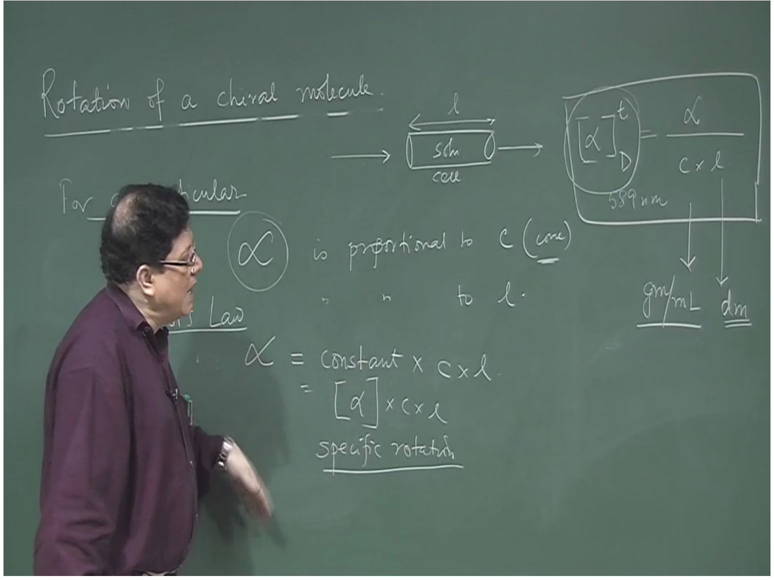

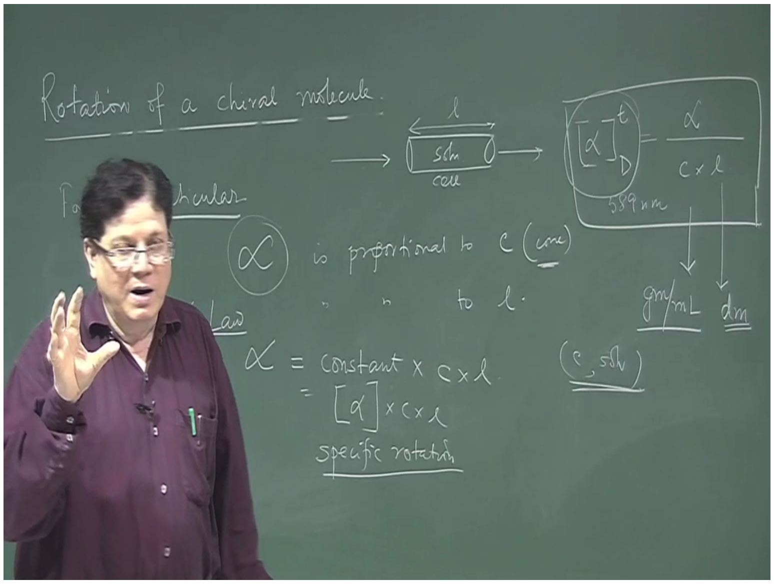

The 2nd is that if for a particular molecule for a particular molecule, the rotation which is denoted as alpha, that is proportional concentration to C, C section of the compound in solution, the chiral compound in solution. And it is also proportional to the path length. That means this is your polariser going through a solution of a compound. So this is called the cell. The solution is here and this is what is the the length through with the light interacts the solution. So this is called the path length and then it comes out. So it depends if you lengthen it, then also the amount of rotation will increase. If you make it concentrated, the amount of rotation will also increase.

So it is directly proportional to C and it is directly proportional to L. So if you combine these, so alpha becomes a constant into C into L. And this constant is denoted by again alpha but within a 3rd bracket. And then alpha into C into L, which is what is called Biot's law. Okay? So what is this this constant? That Alpha which is written in 3rd bracket, that is called the specific rotation okay?

Now the specific rotation is the intensive property and not this, the rotation because the rotation will vary with concentration. If you take more concentrated solution, alpha will increase. If you take longer path length, alpha will increase but the specific rotation is constant provided of course there are other other issues here, provided the wavelength of the light is fixed at at a particular value and also provides you carry the experiment at a particular temperature.

So this specific rotation is dependent on the wavelength of light that is used and it is also dependent on the temperature that is also used for the measurement okay? Usually, we write the specific rotation as this denotes the wavelength, now D denotes the wavelength of light that comes out from the sodium lamp and that is 589 nanometre and this is T that is denoted in degrees centigrade.

Usual, normally we measure it at 25 degrees centigrade but if you measure it at other temperature, one should mention that what is the temperature okay? I write here, D is fixed because D is 589 nanometre. You do not have to write 589, you just write D, that is the wavelength of the sodium lamp. And this is the temperature. So that will be is equal to the rotation that you observed by C into L.

So this is how you calculate the specific rotation. However, like specific resistance, you know specific resistance is also very similar. That resistance is proportional to the diameter of the wire through which the current is passing and the length of the wire. So ultimately, you get a very similar sort of thing that specific rotation is the specific resistance is the resistance divided by length and the diameter.

Here it is divided by the concentration and length. However, you have to fix the unit of concentration and the length because in order to compare the values of alpha D, the specific rotation from compound to compound or for same compounds, if you want to compare the similarity of compounds, then you need to sign a unit for concentration and also unit for length. Now what is the standard procedure?

The concentration is expressed in gram per millilitre and the length is expressed in decimetre, that is interesting, decimetre. Not millimetre, not centimetres but it is decimetre okay? So again I repeat, on what are the factors on which alpha D depends? Of course, it depends on the type of compound. Number 2, it depends on the wavelength of light that is used. It depends on the temperature.

It also very slightly but it depends on the solvent that is used to for the measurement. Solvent also plays an important role in rotation. And the bear's law is true only for little bit (())(18:38). As you make it really concentrated, if the concentration is too high, then bear's law also does not hold good. So when you mention the alpha D, if you look at the books or if you look at the literature, you will see that the scientists are writing not only the specific rotation value but they also write within bracket, the concentration and the solvent.

So these have to be mentioned that which solvent it has been measured and what is the concentration so whether it is 1 gram per millilitre or 5 gram per millilitre, so the concentration should also be mentioned. This is required if you want to compare one substance with another substance, okay? So that is what is the specific rotation and now let us work out a problem, how to calculate the specific rotation?

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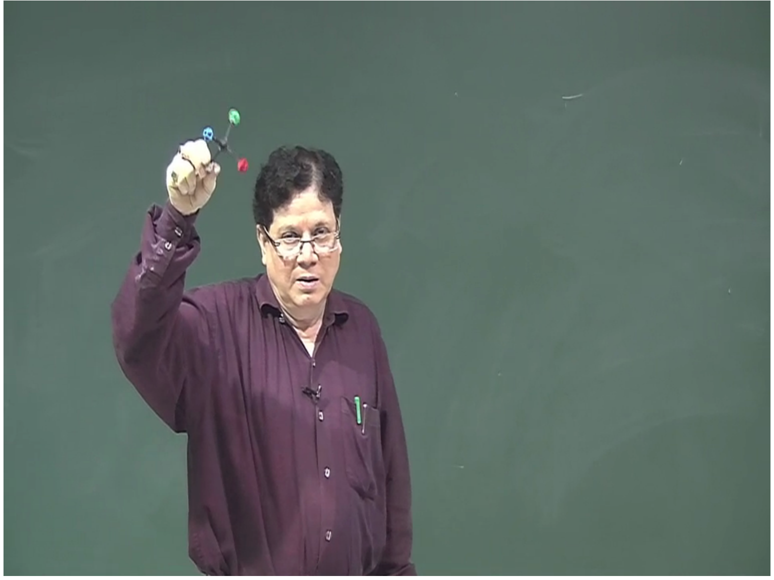

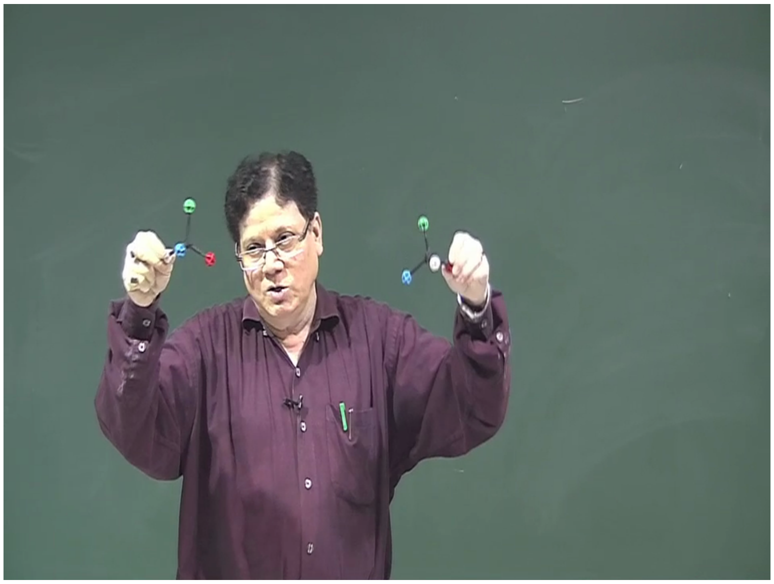

The specific rotation of a pure chiral molecule is the of the pure chiral molecule will be the highest value that you can obtain. Suppose these are the the pair of Enantiomers and suppose the left-hand gives the rotation in the - since that means lever rotatory or the anticlockwise and this gives the rotation in the clockwise fashion, so this is the dextro rotatory compound or the + compound okay?

Now suppose this has a specific rotation of say + 100 degree your compound. Now if I start mixing this left-hand molecule into this system, then what will happen? The rotation will start decreasing because you are mixing some of the - molecules with the + molecules okay? So there are certain in a mixture of these 2 molecules, there may be different types of mixtures I can obtain from these 2 systems.

1st of all, I can have pure molecules, that is optically pure compounds we say. When we have a mixture, the question is what will be there, what is the ratio of these 2? If the ratio is 1 is to 1, that is 50-50, then there will be no rotation because the amount of rotation it imparts into the plane polarised light is exactly equal in magnitude and opposite to what this left-hand molecule is trying to do okay?

So the ultimately the resultant becomes 0. So that is what is called a racemic mixture. But there are certain, there may be mixtures where this is present in 80 percent, this is present in 20 percent ? And how do we know? How do we really measure the percentage of one Enantiomer over the other in a mixture? Again I repeat, if it is pure molecule, you that will match with the alpha D that is reported in the literature.

If it is not the pure molecule, is that is, if it is 50-50 mixture, then there will be no rotation. So these 2 cases are simple. But when there is some rotation but which is not the actual alpha D value, then you have to calculate what is called the optical purity of the molecule or what is called the Enantiomeric axis of the molecule. So you need to know the ratio of the 2 + and - compounds. So a problem will solve this.

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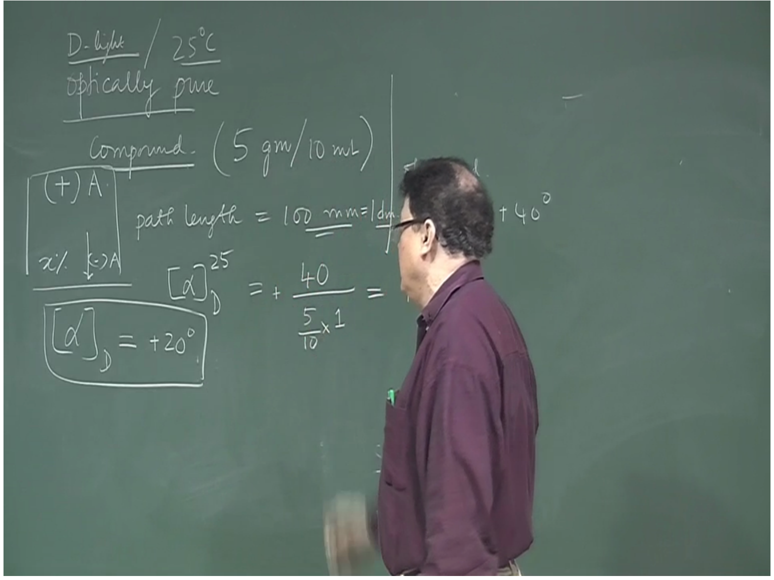

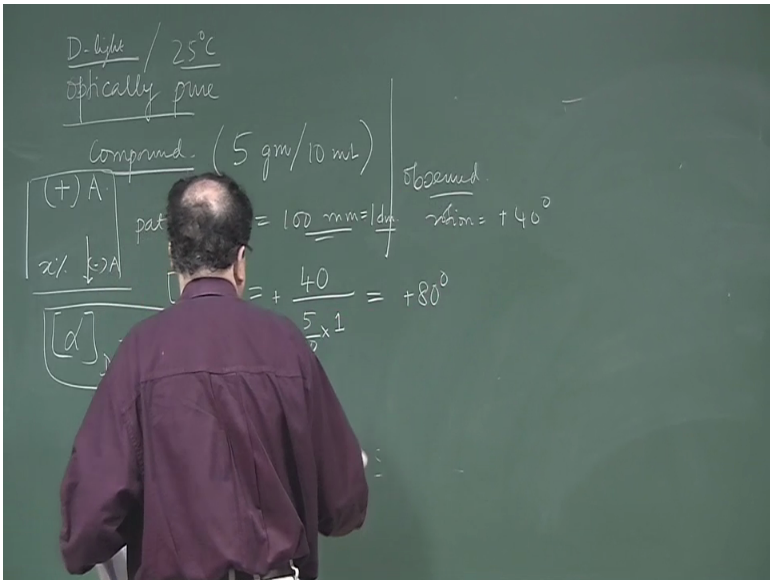

Suppose we have taken a an optically pure compound, an optically pure compound and the amount taken was suppose 5 gram in 5 gram let us just check this problem, 5 gram in 10 millilitre. So 10 millilitres of solution was taken in which 5 gram of the optically pure chiral compound was dissolved. And suppose the cell, the path length is 100 millimetre. So that means the cell through which it is passing, the cell has a length of 100 millimetre.

So what is the alpha D? The alpha and the light which was suppose that D light of sodium, sodium D light, okay? So alpha D and the measurement was taken at 25 degrees centigrade. So you just write, alpha D 25 will be equals to what was the the observed rotation? I did not say. Suppose the observed rotation when light pass through the observed rotation is supposed + 40 degree.

So then what will be alpha D? So it will be alpha that is 40, put the sign +. It is a dextro rotatory compound and then divided by 5 by 10 into 100 millimetre is equal to 1 decimetre. So since the unit is expressed, I said the unit of path length is decimetre. So this is 1 decimetre. So if you do that, it will become as + 80 degree.

So the alpha D for this compound is + 80 degree. Now suppose, now to this optically pure compound, suppose I denote it as + A and I I mix X percent of - A to it okay? X percent of - A to this mixture and then I measure the alpha D value. And what I find? That suppose the alpha D now of this mixture is + 20 degree.

So now from these values, we need to calculate what is the percentage of + A in the mixture and what is the percentage of - A in the make sure. Okay? So we erase this because that is already done. Remember, the actual alpha D is + 80 degree then it is optically pure. So no - A was mixed.

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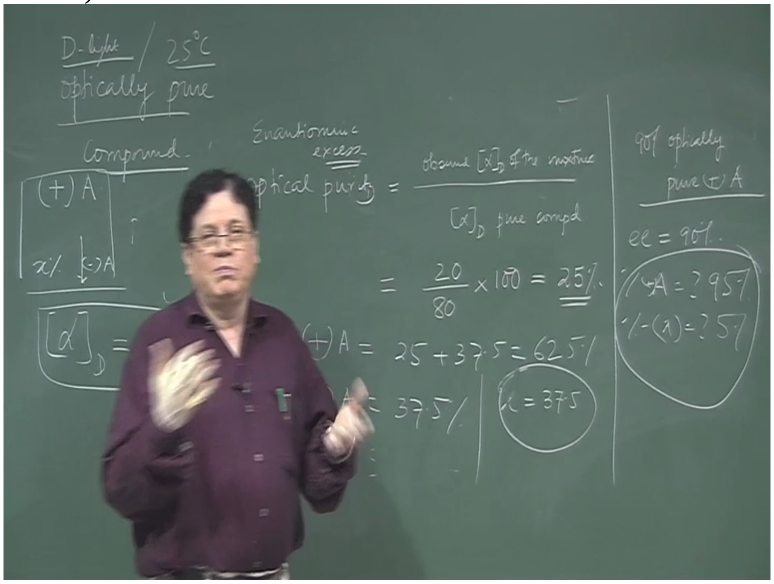

So optical purity, this is a new term, optical purity actually gives from the optical purity, you can calculate how much + A is there, how much - A is there. What is optical purity? Optical purity is the observed alpha D of the mixture. That means + M mixed with some - A and the the alpha D of pure, pure compound okay? So we know that both the values are this is given, + 20 so that will be 20 by 80 but it is usually expressed in percentage.

So since the 100, so that makes it 25 percent. Optical purity, by definition it is observed, alpha D of the mixture divided by alpha D of pure compound. But what is the concept behind it? Alpha D has, this optical purity has a value, 25 percent. It means that the rest percent of the mixture is a racemic mixture. Rest 75 out of the rest 75, 37 dollar 5 is the + A and $ 37 dollar 5 percent is - A okay?

So optical purity is the excess that you have over the racemic pair, over the percentage of racemic pair, that is what is called percentage optical purity, okay? That is also called, the Enantiomeric excess, that is also called the Enantiomeric excess. Enantiomeric excess means, again I repeat, that means the amount, the excess amount that you will have over the racemic amount okay?

So in this case optical purity or Enantiomeric axis is 25 percent. Now how to calculate how much + A is there? Total + A is 25, + half of the remaining 75, that is 37 dollar 5. So that makes it 62 dollar 5 percent. And what is the extent of - A? That is only 37 dollar 5 percent. So your X, the value of X here is 37 dollar 5. So you have mixed 37 dollar 5 37 dollar 5 percent of - A to this mixture.

So that gives you 25 percent optically pure material or the Enantiomeric excess of the mixture is 25 percent okay. Just to, the other way around suppose I say that in a mixture, a mixture has 90 percent optically pure A, 90 percent optically 90 percent optical pure class A, that means the optical purity of the mixture is 90 percent or the Enantiomeric excess which is written as EE is 90 percent.

Then calculate the percentage of A + A how much and calculate the percentage of - A, that is how much. So you can easily calculate because EE is 90 90 percent, that means the 10 percent off it is the racemic mixture because Enantiomeric as I said is the excess over the racemic amount. So the racemic amount is 10 percent and out of this racemic 10 percent, 5 percent is + A and 5 percent is - A.

So this becomes 5 percent and this becomes 95 percent okay? So that that is the backward calculation for optical purity or EE is given, then you can calculate the percentage of + A or - A or if you want to know the optical purity of a sample, you have to measure the alpha D and then if the alpha D of the pure compound is known, then you can calculate the Enantiomeric excess or the optical purity of the sample, okay? Thank you.