Introductory Organic Chemistry
Dr. Neeraja Dashaputre
Department of Chemistry
Indian Institute of Science Education and Research, Pune

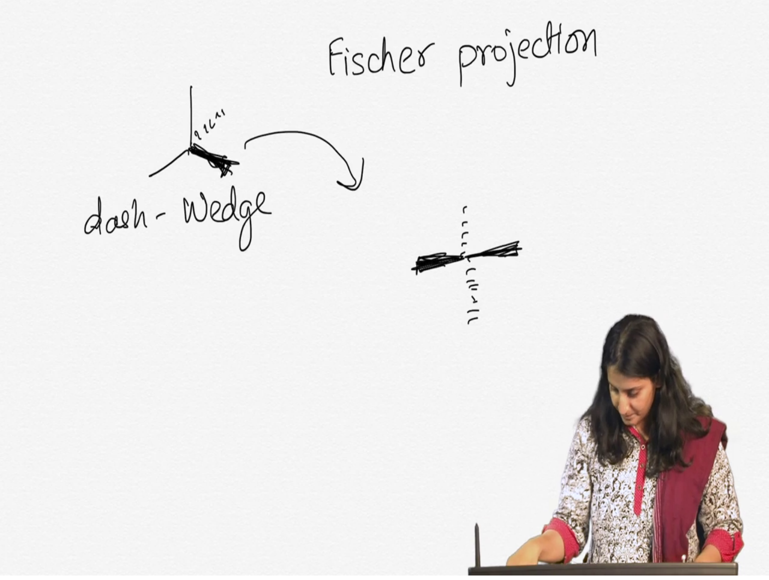
Lecture - 15
Chirality and Stereochemistry
Part - 2

So, far we have looked at representations of molecules using the dash and wedge representation.

(Refer Slide Time: 00:23)

Meaning, if you have a chiral center and if you want to represent the groups on the, on this particular carbon for example, you have these two groups in the plane of the paper, then the red group is coming towards you and the green group is going away from you.

(Refer Slide Time: 00:41)



And in other words you could have represented them using these dashes and wedges like these.

So, if you have a wedge meaning the group is coming towards you; if you have a dash that means, that group is going away from you. But when you have multiple stereo centers in the molecule what happens is, drawing these dash and wedge structures become a little tedious. So, in order to draw a molecules that have more than one stereo center what we use is a representation called as the Fischer projection. So, we are going to look at what Fischer projection is.

Okay, so, this is dash and wedge and we are going to convert this to a Fischer projection. So, for example, if a dash and wedge structure looks like this to you, wherein you are looking at it from this point, a Fischer projection for the same molecule can be drawn when you look at the molecule like this. Okay, so I am changing your view point from here; now I am going to change it such that you start visualizing the molecule like this, okay.

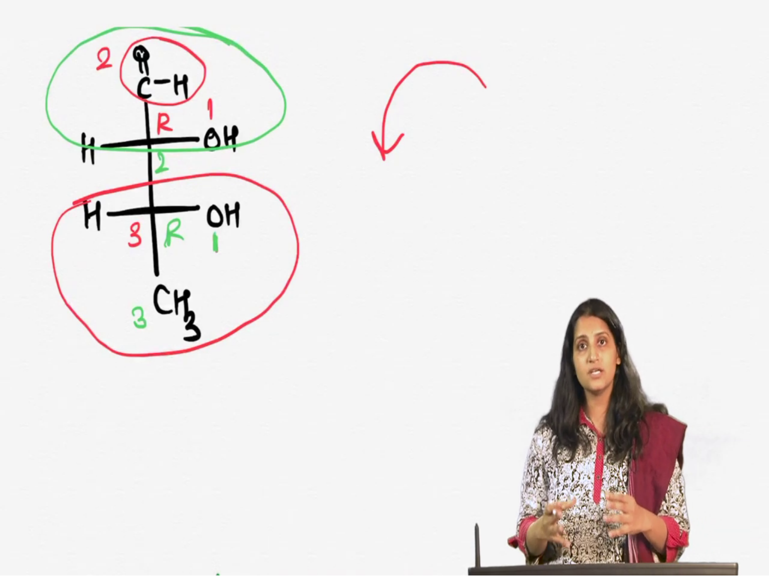
So, the same representation now becomes such that horizontally 2 groups are coming towards you and vertically 2 groups are going away, okay. So, what you have here is horizontally for example, horizontally the red and the green one are coming towards you and vertically the white and the blue one are coming towards me that is really going away from you.

(Refer Slide Time: 02:29)

So, if I want to draw these Fischer projections properly what we have is somewhat like this, but really when we project it, you just draw a cross like this. A cross where in the horizontal groups are coming towards you, the vertical groups are going away. You can always remember that Fischer projection kind of looks like a bow tie that is the person is wearing a bow tie. So, that’s how I remember that the horizontal groups are always coming towards me, okay. So, this is how that person is wearing a bow tie.

So, now let’s place a particular molecule and draw a particular molecule in which we are representing it using a Fischer projections. So, I am going to draw this one here.

(Refer Slide Time: 03:13)



Okay. So, now let us look at how to assign the R and S to the Fischer's centers. So, remember all the rules are the same except for one rule; when you draw a Fischer projection you want to; it is typically drawn such that the carbon backbone is vertical. So, in this case all the 4 carbons in the molecule are represented vertically that is the only one new rule that you have to remember when you are assigning Fischer projection. Other than that all the other rules are exactly the same. So, we go ahead and rank all the substituents on the carbon such that the higher atomic number gets the higher priority and so on.

So, in this case you do have first priority going to this oxygen, the second priority now between this C=O H group and this one really big group here, you can imagine that the top carbon is attached to 2 oxygens or rather it is really double bonded to an oxygen. So that gets the second priority and this bottom carbon here gets the third priority.

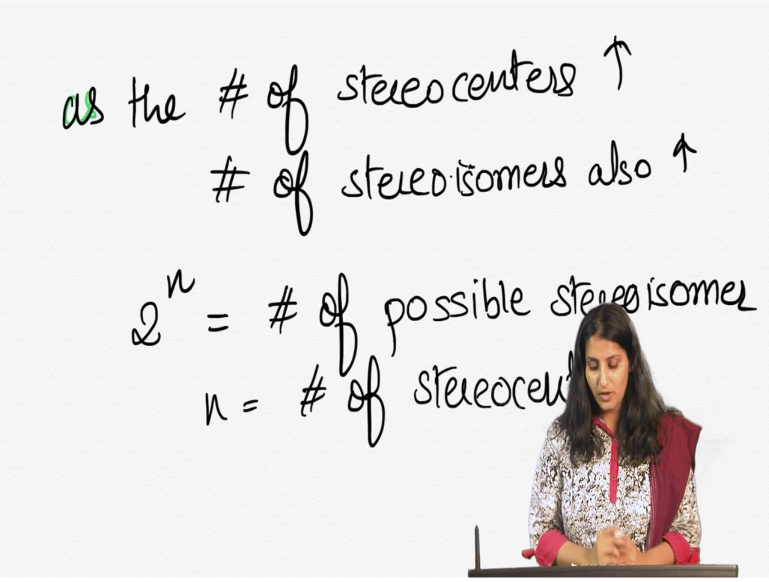
So, now if I really look at it what I see is that it is moving such that it looks like S ok, but remember in Fischer projection the horizontal lines are coming towards you. So, even though it looks like S this one is really R so, the first one is R. What about the bottom one? I will apply the same rules; now this is one.

Now, if you think about the top group that is this one and the bottom methyl; the top carbon is attached to an oxygen whereas, the bottom methyl is attached to all 3 hydrogens. So do, you have a second priority to the top carbon and methyl gets the third priority. Now this also looks like S, but remember the least priority group that is hydrogen is coming towards you. So, again it looks like S, but it is actually R, ok. So, that is how we assign the Fischer projections stereo centers as R and S.

So, these type of projections are very useful to write molecules with multiple stereo centers, especially molecules like carbohydrates or other biomolecules, you will see that Fischer projections provide a great and a quick way to represent the molecule on the paper. Remember that in biomolecules for example, you have really numerous stereo centers. So, we are going to see some of the examples now and you will realize why Fischer projections becomes so popular.

So, before we go ahead and look at molecules with multiple stereo centers I want you to recognize that as we go on increasing the number of stereo centers in the molecule, the number of possible stereo isomers also increase. So, I want to write that down.

(Refer Slide Time: 06:15)



as the # of stereocenters ↑

# of stereo isomers also ↑

2^n = # of possible stereoisomer

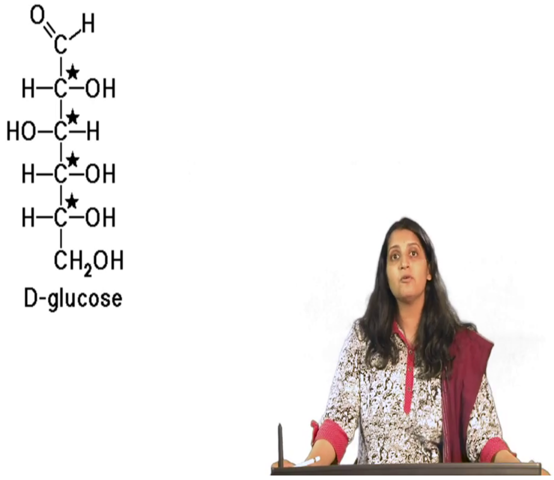
n = # of stereocen

That as the number of stereo centers increase, the number of stereoisomers also increase, right? And this is not really difficult to imagine, but I want you to ponder over by how much? Just want to revise what stereoisomers are; so, stereoisomers are the molecules which are equivalent to each other in their molecular formula, in their structural formula, but it just differs in the way the substituents are represented in the 3 D space. So, they, it differs in the arrangement of the molecule in the 3 D space, right?

So, now let us look at one of the molecules. So, we just looked at a molecule in which there were 2 stereo centers and remember that molecule can have the 2 stereo centers as RR RS SR or SS, right? So, there are 4 possibilities for a molecule with 2 stereo centers. Let's now go on increasing the number of stereo centers; the typical rule to give out the number of stereoisomers is that if it is, that the number of possible stereoisomers for any molecule is 2 raised to n (2^n) , where n is a number of stereo centers.

So, now let us look at a possible stereoisomer for example, let's take glucose.

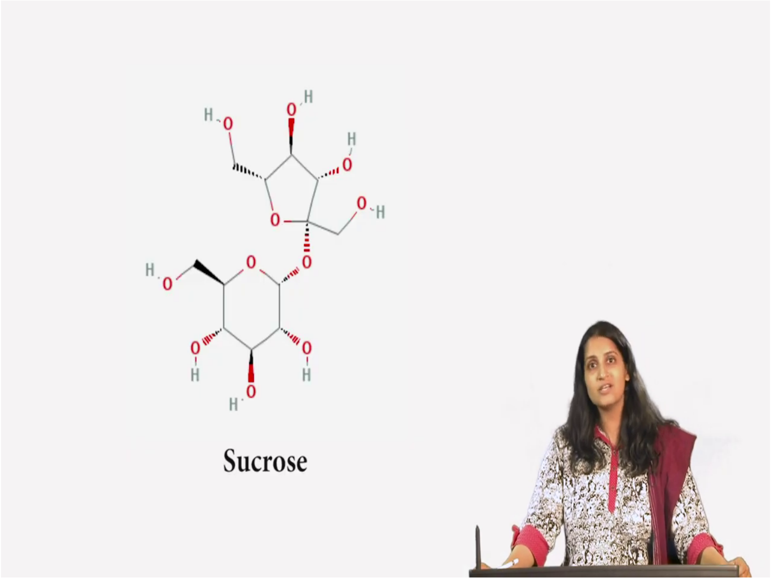
(Refer Slide Time: 08:11)



So, the open chain form of glucose has around 4 stereo centers right and these 4 stereo centers meaning the possible stereoisomers of glucose in an open form is 2 raised to 4 (2^4) that is 16.

Let’s just move on to sucrose.

(Refer Slide Time: 08:31)

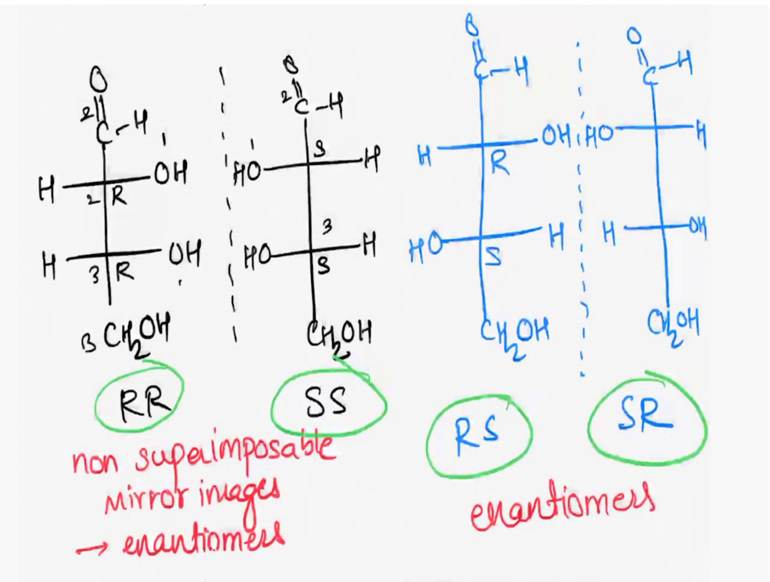


Now, sucrose here has 9 stereo centers, being a bigger sugar, this sucrose is the same sugar that you have in your kitchen; sucrose for example, has 9 stereo centers. So, you can imagine that the number of stereoisomers for sucrose goes 2 raised to 9 that is 512 different types of sucrose if you want to make, different stereoisomers of sucrose if you want to make you can really make them, okay.

As you can imagine having more and more number of stereo centers in the molecule really increases the complexity of the molecule because now you can create those many stereoisomers of the same molecule. So, now, let us look at one of the examples, but I want to point out that we are talking about a number of maximum possible stereoisomers. So, 2 raised to 9 is the number of maximum possible stereoisomers of sucrose and we will look at some examples where the number falls a little short than the maximum possible number and we will look at why these formula calls for maximum possible number.

So, now let us look at one of the molecules that has 2 stereo centers. So, I am going to draw a molecule here.

(Refer Slide Time: 09:41)



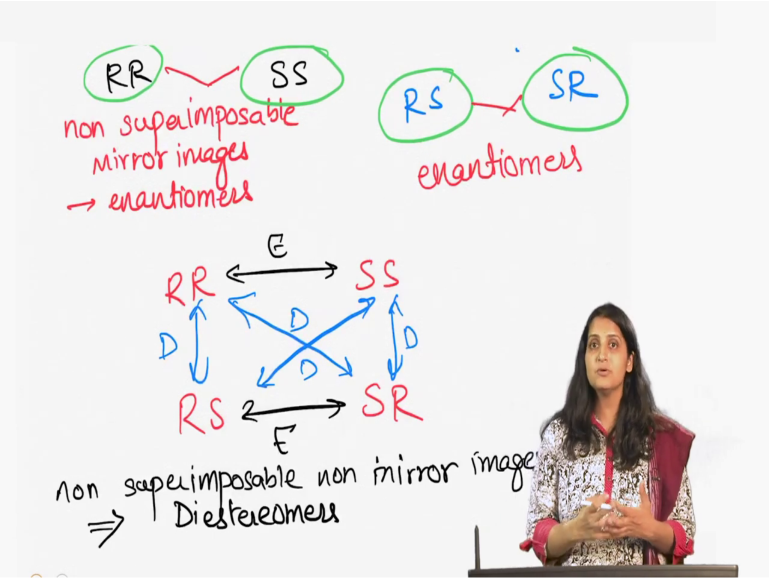
Now, let us assign the R and S to the stereo centers here. I have oxygen as the first priority; this is the second; this as the third. So, this moves like S, but remember the least priority group is coming towards you. So, this is R not S. The same way for the bottom carbon, I have 1, 2, 3 moves like S, but the hydrogen is coming towards you so, this is R indeed. So, I have one stereo isomer where in the 2 stereo centers are R and R.

Now, let us draw its mirror image, right. So, if I draw its mirror image what do you have, you have 1, 2, 3; moves like R, but the hydrogen is coming towards you so, it is S. The bottom one is also S. So, I have one molecule RR and I have a one molecule that is S and S. Now if you really look at these 2 molecules they are non super imposable mirror images so in fact, they are enantiomers, right?

So, they are non super imposable mirror images, they are enantiomers of each other, but now let us keep one of the stereo centers the same and change the other. So, I am going to keep the top stereo center the same; going to write it in a different ink, going to keep the top stereo center the same as the first one and I am going to change this other one, right. Remember the top is the same so, this one is still R, if you look at the bottom one, the bottom one is now very similar to this one here so, this is S, right?

If I take its mirror image what do I find? Right. So, if we take that mirror image what do we find is that, we have a another set of stereoisomers now this is not the same molecule as before because now we have changed one of the stereo centers right. So, if I look at the first one this is RS and its mirror image is going to be SR. So, what we see here is that we have 4 stereoisomers we have RR SS RS and SR these are the 4 stereoisomers we have. If I ask you what is the relationship between RS and SR they are also enantiomers of each other, because they are non super impossible mirror images of each other. But now if the question is asked what is the relationship between RR and RS, okay. So, now we are talking about RR and RS; so, these 2 are enantiomers, these 2 are enantiomers.

(Refer Slide Time: 13:09)



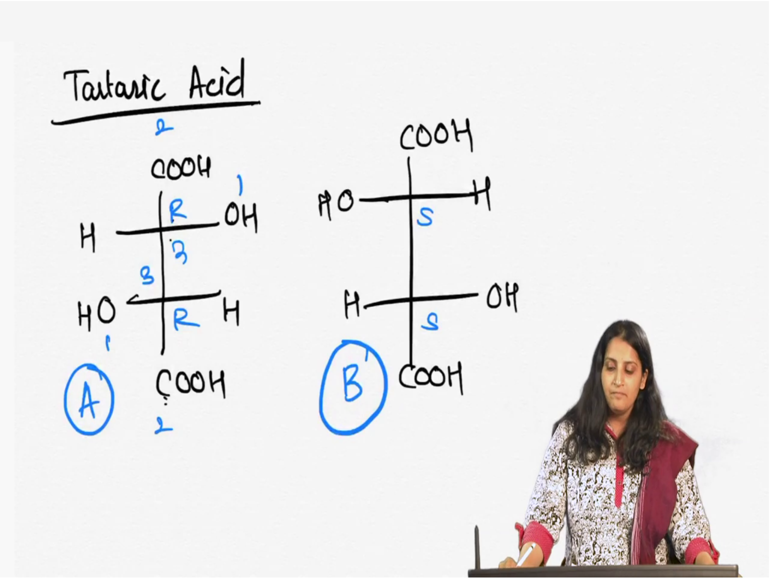
Let me just redraw it here. So, we have RR, we have SS, we have RS and we have SR and we have said that these 2 are enantiomers of each other; these 2 are enantiomers of each other. Okay, so now, let’s continue.

So, now if I ask you what is the relationship between RR and RS or RR and SR remember one of the stereo center is the same, but the other one is changed right. So, it’s no longer a mirror image; also they are not super imposable. So, really the relationship between RR and RS is they are non super impossible non mirror images, right. So, they are non super imposable non mirror images and thus they are diastereomers of each other. So, this is a new term; we have learnt a new term which was enantiomers in the last one, now this one is diastereomers which is non super impossible non mirror images.

So, in this case for example, you have RR and SR as diastereomers, you have SS and RS as diastereomers, RR and RS as a diastereomer and SS and SR are a pair of diastereomers. So, if you really see for a molecule that has 2 stereo centers you have 2 pairs of enantiomers and you have 4 pairs of diastereomers present.

Now we are going to look at one more example. So, this is the example of tartaric acid okay.

(Refer Slide Time: 15:03)

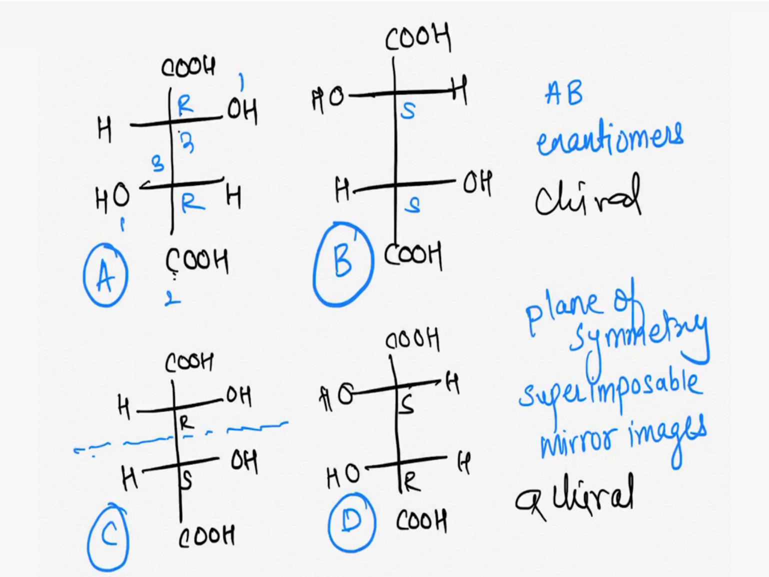


So, I am going to draw a molecule of tartaric acid now; tartaric acid you must have heard this name before. It was really isolated from grapes, but it’s one of the main ingredients of the tartar sauce. So, what we are going to do is, we are going to draw the molecule that is present as tartaric acid, okay. So, this is the molecule.

Okay so, now let us assign the stereo centers of tartaric acid you have 1 2 3, this moves like S, but the hydrogen is coming towards you so, this is R and then you have 1 2 3 this moves like S, but the hydrogen is coming towards you so, this is R. So, this is an RR molecule of the tartaric acid I am going to call it the molecule A, okay. I am going to draw a mirror image of the same.

Now, if I want to write down the stereo centers these are going to be S and S, let's call it the molecule B, okay. So, we have 2 pairs of enantiomers of tartaric acid, right A and B are enantiomers of each other right.

(Refer Slide Time: 16:27)



Now I am going to do the same thing, I am going to keep one of the stereo centers the same, but I am going to change the other, okay. So, I am going to keep the top one the same so, this is still R; you want to change the bottom such that this becomes like this. So, this is now S and if I draw its mirror image, this is gonna be like this. Let us call these molecules as C and D.

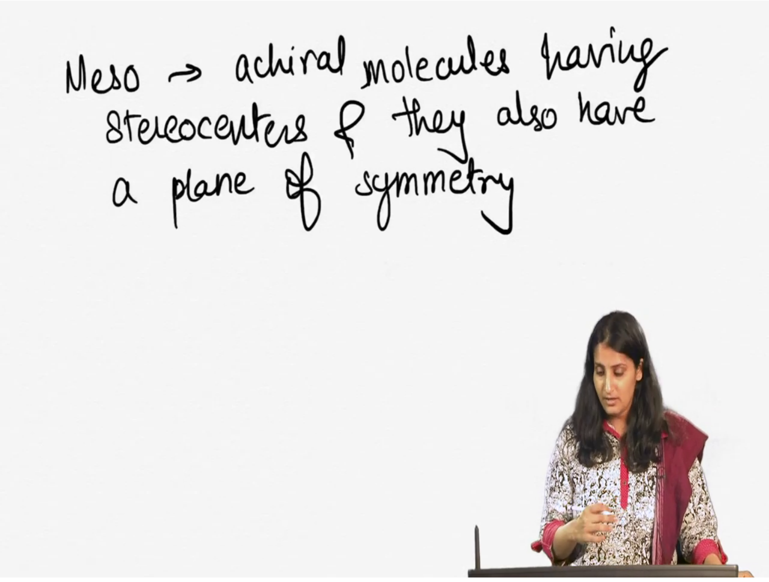
Now I want you to look at the molecule C and D very carefully, if you really see there is a plane that goes through the molecule such that you can really flip this molecule on the top of itself right such that all the groups will match. So, for example, if I have a plane that goes through here and if I try to kind of fold the molecule on that edge then the OH and OH will match with each other, the hydrogen and hydrogen will match with each other and the COOH and COOH will match with each other.

So, what you really have in this molecule is its plane of symmetry. So, there exists a plane of symmetry in this molecule; same goes for D. So, C and D really are mirror images of each other, but they are super imposable mirror image of each other because they have plane of symmetry. So in fact, you can imagine that I can take D completely and kind of flip it over C and all the groups will coincide with each other. So, what you have here is that C and D are super imposable mirror images, okay.

So, as a result of which what you can see is that in fact, they are the same molecule they are not 2 different molecules, but they are really just one particular molecule. So in fact, for tartaric acid you have possibility of 2 raised to 2 that is total of 4 stereoisomers, but that is the maximum possible. In reality tartaric acid only gives you 3 one of them is RR, the other one is SS and the other, the next one is the mesocompound. Okay, so this is a new terminology.

So, what is a mesocompound ? Okay so, in this case for example, the stereoisomers C and D are called as a mesocompound, a mesocompound contains two or more chiral centers, but really is achiral in nature, okay.

(Refer Slide Time: 19:21)



Meso → achiral molecules having stereocenters & they also have a plane of symmetry

So, mesocompound are achiral in nature. Remember because they have a plane of symmetry, so we had said that having an asymmetry was really essential for chirality to exist right. So, since there is a plane of symmetry mesocompounds are achiral. So, if I subject a mesocompound to a polarimeter for example, what is going to happen is that you will not see the rotation of plane polarized light in either direction, because you have few molecules moving the light towards one direction, the other ones will move it back. So, in the sense overall the total rotation of plane polarized light will be 0.

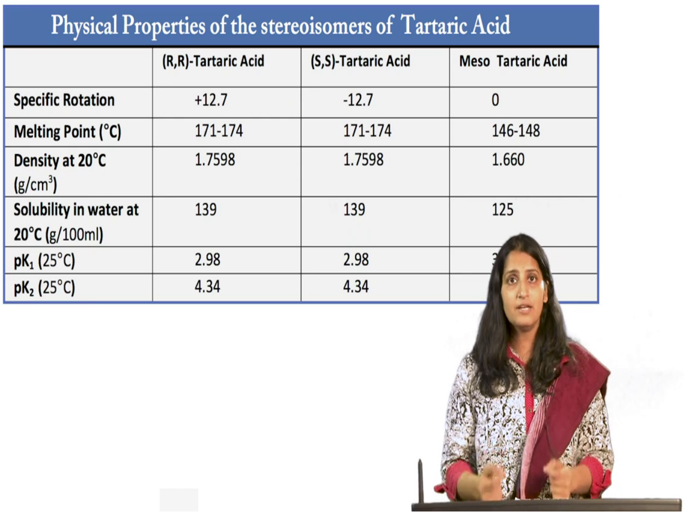
So, what are mesocompounds? They are achiral; they do have some chiral centers though, so they do exist, they do have stereo centers. So, they are achiral molecules having stereo centers and they also have a plane of symmetry right. So, as we just saw the mesocompound of tartaric acid has a plane of symmetry in it, okay. So, when we have to figure out if a molecule has a mesocompound or not we first need to figure out if it has a plane of symmetry and in fact, we are going to look at some of the examples in the tutorials wherein there could be a case where the molecule has stereo centers, but it is achiral because there is lack of asymmetry. Okay.

Now, I just want to go back and revise that tartaric acid for example here, does have two enantiomers. So, if I just take pure A it's going to rotate the plane of plane polarized light; pure B will do the same thing, but if I have C or D which is really just the same molecule, C and D are not going to rotate the plane polarized light. Okay.

Now, if I take an equal mixture of A and B which is a 50 - 50 mixture which is called, also called, as a racemic mixture. Now racemic mixture, is an, is a mixture of two enantiomers in equal ratio. What's going to happen is that, a racemic mixture is also not going to show you any rotation of plane polarized light that is because you have two molecules present which are trying to rotate the light in two different, two opposite directions and as a result the null movement is 0, okay. A and B for example here, are chiral; but C and D are achiral; so that's something to also ponder over here.

So, we have looked at the properties of enantiomers and we have said that enantiomers have identical physical and chemical properties in achiral environments. So, meaning that if I just dissolve a pair of enantiomers into various solvents water, methanol, ethanol, DMSO, DMF any of these solvents; what's going to happen is that they are gonna probably behave the same way, right? Meaning all the physical and chemical properties are gonna be exactly identical.

(Refer Slide Time: 22:47)



Physical Properties of the stereoisomers of Tartaric Acid

	(R,R)-Tartaric Acid	(S,S)-Tartaric Acid	Meso Tartaric Acid
Specific Rotation	+12.7	-12.7	0
Melting Point (°C)	171-174	171-174	146-148
Density at 20°C (g/cm^3)	1.7598	1.7598	1.660
Solubility in water at 20°C (g/100ml)	139	139	125
pK$_1$ (25°C)	2.98	2.98	3
pK$_2$ (25°C)	4.34	4.34	[illegible]

Just to show you that what I have done is I have gotten the properties of RR tartaric acid and SS tartaric acid here. If you really see, the melting point is exactly the same 171 to 174; the density is the same, the solubility is the same; density is same up to the 4 decimal point, right? Solubility is the same; the pKa which really talks about the chemical property, it's a chemical property. So, pKa is also the same except the rotation of plane polarized light. So, if I look at this specific rotation the specific rotation is (-) 12.7 for the SS stereoisomer and it is (+)12.7 for the RR stereo isomer, right. So, you have two enantiomers giving you two separate specific rotations here.

Now, if I really want to compare the properties of a diastereomer as compared to the enantiomers. So, I have also gotten the meso-tartaric acid here and now let us look at that. Now if you really compare the properties are not vastly different, but they are definitely different from that of the enantiomers. So, for example, meso-tartaric acid has the melting point of about 146 to 148. So, there is about a 20 degrees difference between the melting points of these compounds, you also have it, having lesser density that is at 1.66; the solubility is different, the pKa is different, the other pKa, the second pKa is also different.

So, what it shows is that diastereomers have different properties than enantiomers. So, if you really see here the RR tartaric acid or the SS tartaric acid is a diastereomer to the meso tartaric acid. So, what really, what we are observing is that, enantiomers have the same chemical and physical properties, but when I look at a pair of diastereomers they differ in their chemical as well as physical properties, okay. So, now, what we are going to do is, we are going to see the use of this property being used in order to resolve enantiomers, okay?

Thank you.