Chemical Applications of Symmetry and Group Theory

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Lecture – 11

Hello everyone very good morning. So, let us start the day 1 of week 3 of the (Refer Time: 00:20). So, in last couple of weeks we learnt about the symmetry elements and symmetry operations of any given molecular structure and we learnt how to find out a symmetry element, and how to generate the symmetry operations from that particular symmetry element. So, in that way we could find out all the you know possible symmetry operations of that particular, for that particular molecular structure, and we also learnt about the group mathematical group as well as we learnt about the molecular point group or symmetry point group or simply the point group where the elements consist of the symmetry operations of a given molecular structure.

And we learnt a few more things like you know how to utilize this point group symmetry to find out whether a molecular (Refer Time: 01:22) or whether a molecular be you know polar in nature, that polar in nature or not. So, what we are going to do this week is as follows. So, we will learn at particular technique to combines different symmetry operations and that is called group multiplication.

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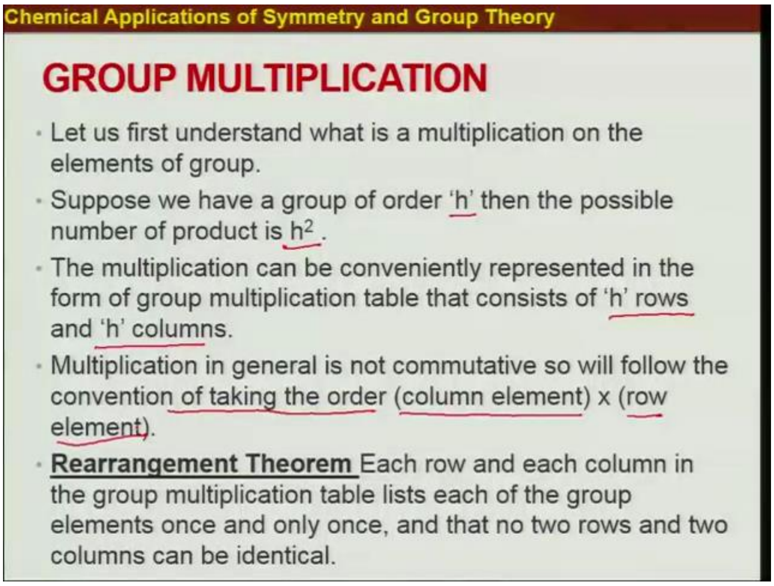

So, we will learn about group multiplication table as well and we will also learn a way to find out suppose you are giving a point group, any point group for examples, D 4 D and then I ask you (Refer Time: 02:06) tell me what are the symmetry operations that this particular point group contains, that is what are the elements of this particular point group. So, how to do that that there is way which is a done by using stereo graphic projection. So, we learn about the stereo graphic projection and, then we will try to learn how to form a representation of particular symmetry operations. So, like you know we are calling C 3 C 4 or sigma h S 4 all these symmetry operations, how to represent them. So, are there any mathematical frame works to do that?

So, there is a mathematical frame work which utilizes the matrix representations. So, we will learn a little bit about the basic matrix algebra, and then we will know will learn how we can utilize this matrix algebra, to form representation of the symmetry operations, and also we will learn how to take those representations and form the representation of the group as a whole.

So, let us get started with a group multiplication. So, we have learnt how to combine rather we should say that, we have seen some of the combinations of symmetry operations in a particular point group. So, what we did there we operated the see we are talking about a binary combination of 2 symmetry operations. So, what we did is we operated 2 symmetry operations successively, on the molecular structure and found out that what could be the other operation that could lead to this change which one is getting by operating 2 symmetry operations successively. So, that is how we figured out.

Now, if we want to know the exhaustible list of such binary combinations that are possible in a particular point group, in one particular order and possible reverse order meaning like, if I want to find out the binary combination A B I should be able to know also the result of B A like, we have shown you like sigma b prime in case of C 2 fee. So, we did not look at what would happen if you operated in reverse way right that is sigma B double prime and sigma b prime sigma ok. So, group multiplication table provides you that particular way to get the exhaustible list of the binary combination for these symmetry operations. So, when we say here multiplication that means, nothing, but the successful operations.

So, on your screen if you look at if we take a group, which has an order h. So, if you have a point group which has an order h. Order is the total number of elements in a group that means, in case of point group total number of symmetry operations that are there in the point group is the order of the group, which is represented by h here. So, then how many such binary product that we can expect for a group, so obvious answer will be it will be h square which is given here because h number of symmetry operations will combine with another h number of operations including itself, and then it will give h square number of total products and here on your screen if you look at you can find out how to do this multiplication. So, this multiplication it can be represented conveniently in the form of a table right that we are already said.

And in that table it will be a like square table where you have h number of rows and h number of columns. So, what you do essentially is something like this.

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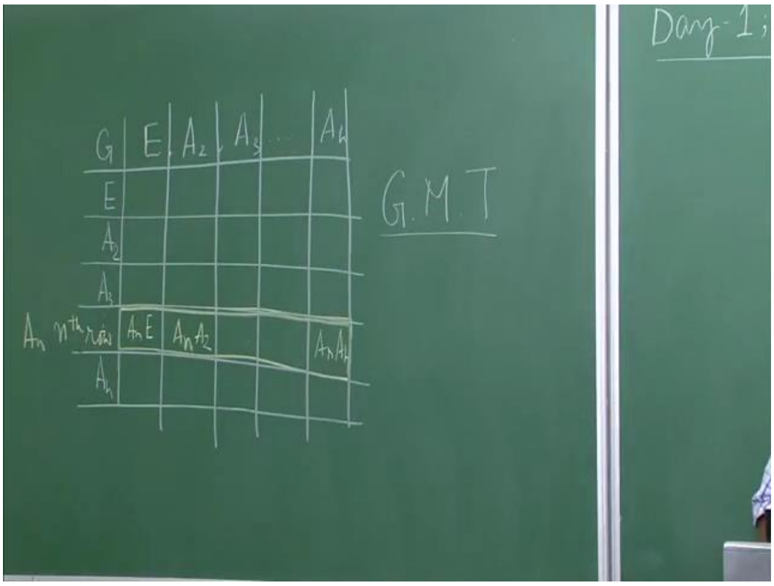

So, for given point group say I have a point group say G. So, if I have h number of elements. So, I have (Refer Time: 07:08) e then suppose I have A 2 A 3 up to A h then what we do in order to get a group multiplication table is following. So, we write also the same symmetry operations in general in case of group we write all the elements that are there in this group in the column also in the same orders. So, we will write E, A 2, A 3, up to A h. So, by now you probably have figured out what are we going to do next. So, we will get each number of rows and each number of columns right, each of this units in each of this cells. So, by cell I mean this area each of these cells will contain one product and how will be the product. So, this multiplied by this. So, you will get you know the results here and this as a whole is the group multiplication table.

So, we will follow a particular convention here which is also written on your screen. So, the convention is we take the order as first we will take the column element, and will multiply it with a row element. So, in the sense what I showed you here is first we will take this and then multiply with this similarly will take this and then multiply with any one of the row elements. Now at this point there is one theorem called re-arrangement theorem, which is important in the context of this group multiplication table. So, what does this theorem say? It says that each row and each column in the group multiplication table lists each of the group elements only once and that no 2 rows and no 2 columns can be identical. So, the proof of this theorem is pretty simple that if I look at this particular table is here. So, I will take any particular say row of this group multiplication table say I will take some nth row. So, this is my nth row now, how will be the multiplications it will be like you know here I will have A n as the elements. So, it will have A n E.

So, I will have A n E, I will have then A n A 2 and so on. So, if you look at all those up to say I have A n A h, now this A E 2 AA h all these are unique elements of this group. So, none of this elements are same, that already we have learnt. Now, their combinations when I have say like A n E or A n A 2 all these combinations also going to give me different products since all the A's are different. So, all these products also are going to give me different results. So, in this nth row I have each new below elements is form, by this binary product which all will be different, similarly I can choose any of these rows. So, all of them will be you know having each different elements that are formed.

Now, since I am not going to repeat the same binary operation going from one row to another row that means, they also will be different in the sense that all these rows will be completely different, what does it mean that means, what exactly is written here on this re-arrangement theorem that is each row lists each of the group elements only once, and that no 2 rows are identical fine. So, that is easily visible from this and same thing can be said about the columns I could do these things in terms of a column also. So, this re-arrangement theorem also pretty good. Now, let us look at some of this group multiplications table. So, let us first take the group multiplication table with order 2 we will term it as G 2.

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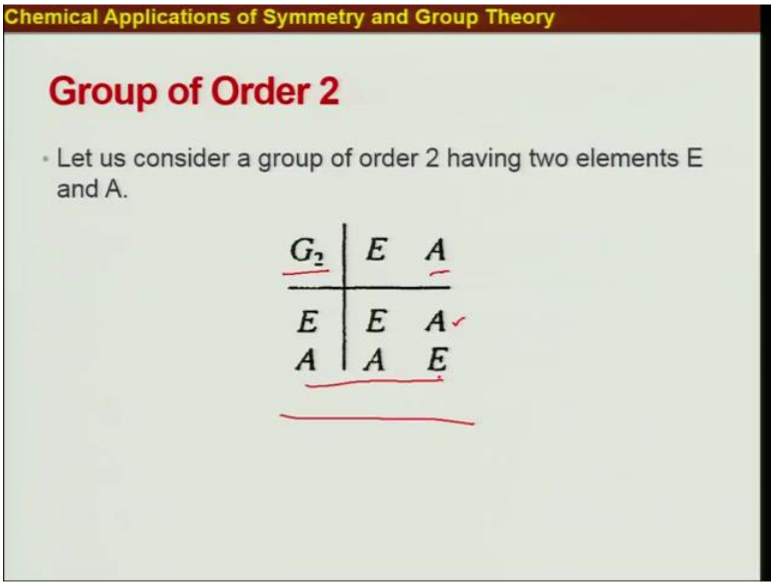

So, any order of the group we will call it like G n for the group multiplication table. So, in case of G 2 we can see we are using the same approach as I just showed you on the black board. So, in case of second order to group what of the elements that we have one is the real one that is identity, and any other element that can be present here. So, we are taking that as this element A. So, there is only one combination that is possible because I know that identity combines with any element to give the same element back.

So, you know E product E obviously, it is E and then E product A will give me back A. So, this one also very easily you can figure it out therefore, it is very easy to find the group multiplication table for G 2.

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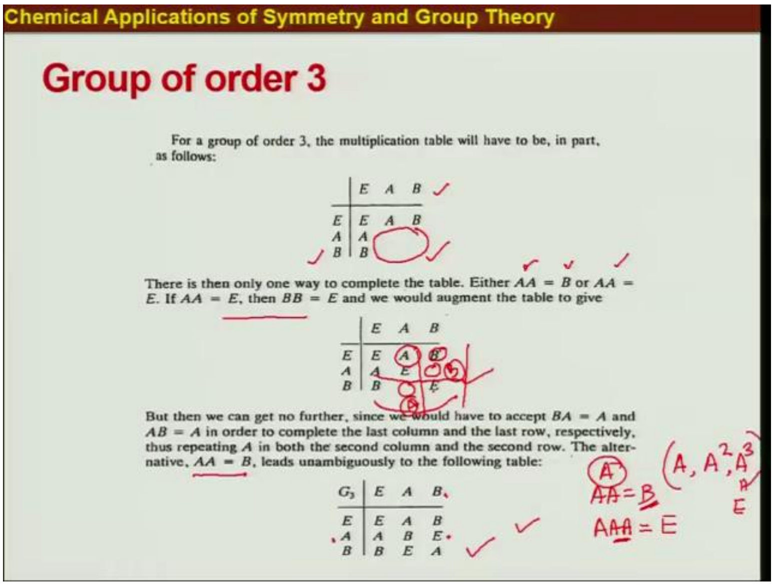

Now, let us look at a little higher group that is group of order 3. So, how do we form the group multiplication table for order group of order 3. So, let us have a look at here on your screen. So, first you write down the all the elements along the row and the column, then you start multiplying by following the combination row that we just stated. So, E combines with all the elements and gives you back the same element. So, the first row and the first column that is very easily figured out, so that is very trivial and one can write it out fine. So, then we are left out with this region which will contain 4 different products.

So, how to go about them, so we can do that only in one way, now if we suppose choose that E followed by A is equals to B or A followed by A equals to E which means A is its own inverse now out of this 2 choices if we take AA that is a followed by A is identity then B followed by B also has to be identity. So, that is implied and if we take that argument, and try to follow this one then we can get up to this where I have you know AA equals to E and then BB combines to give E when I have to fill up this part. So, these 2 elements we are left with choice and like B A and A B these 2 products. So, you have to have A here and B here in order to satisfy this row condition now that will lead you to a problem because this satisfies a row condition that is no 2 elements of this row are same, but when you look at the column side what do you have, you have the repetition of the product you know same elements. So, you have in the second one you have A twice while here you have B twice that is completely disallowed so that means, that we cannot have a condition which is AA equals to E or BB equals to E.

Then, what are we left with we left with a condition that is AA equals to B. So, instead of having A equals to E if we choose AA equals to B then we can end up getting this particular table, and you can do it yourself step by step suppose you choose this conditions E E equals to B write it up, and then keep doing the rest fill the blanks that are there and in this particular multiplication table, now here if you look at in this particular multiplication table, you will see no 2 rows or no 2 columns are identical that is for sure, and you know in a single column or single row no 2 elements are getting repeated. So, this exactly follows the notion of group multiplication table. So, this is a unique a kind of way to find out the group multiplication table of order 3 in the same way you can, keep going in a higher order like group of order 4 group of order 5 and 6 and so on.

Now, this in this particular case of G 3 we have a pretty interesting thing here comes are you see we have chosen AA equals to B. Now we have a first A then AA equals to B and then I have AA A equals to E you can see that easily because here a is b so that means, I can replace this part by B. So, it is essentially A B and let see what is A B means. So, A multiplied by B is E that is what we have written. So, in this particular case I really do not need to actually look at anything else like b, because this I will take this element A and then keep operating it then I will get like AA square A cube and so on. And that will generate all the elements of this particular group. So, sincerely what we have is like AA square and A cube where A cube is nothing, but the identity.

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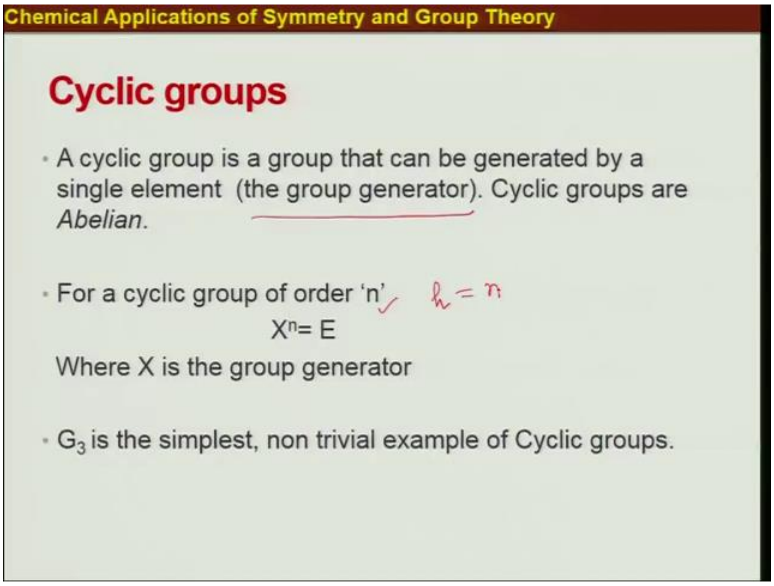

So, this type of group which can be generated, so G 3 can be generated by a single element which is A here, so AA square and A cube equals to E. So, this type of particular group which can be generated by one single element, which is known as the group generator is known as cyclic groups because you can easily figure this out like you have A and A square and then A cube in this particular of case G 3 A cube means E. So, A 4 means again A again A square again A cube. So, it is like cycle is going around. So, it is only AA square and identity these are the 3 elements, but this is a group itself and this is specially called cyclic group.

Now, some specific things about cyclic group is for a cyclic group of order n we just looked at order n equals to 3. So, for any general group which is cyclic in nature and has an order n essentially this means h equals to n then X to the power n equals to E where X is the group generator. We just had an example, in terms of this G 3 where the generator was A and this G 3 is the simplest example, of a cyclic groups and this is a non trivial example, of you know cyclic groups otherwise one can think of G 2 or G 1 you can say in terms of only element identity, they will satisfy the condition of a cyclic group, but they are trivial. So, this is the first non trivial example, of you know cyclic group G 3.

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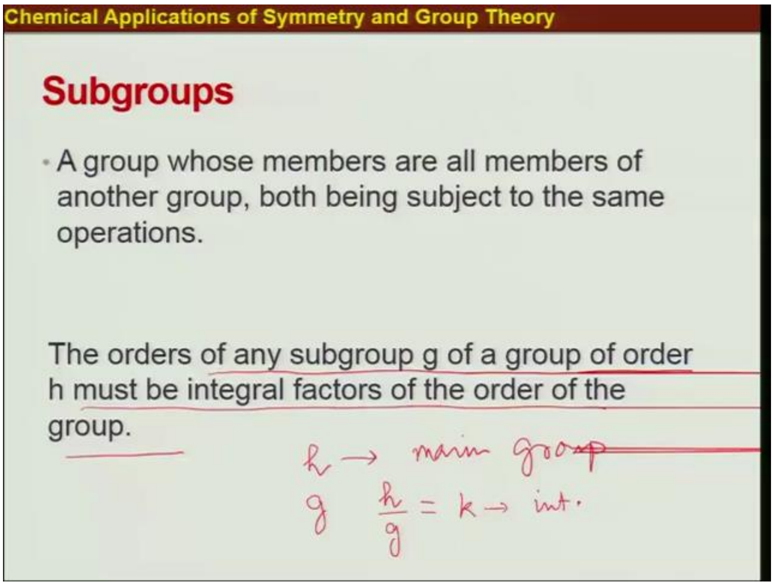

So, now let us look at some of the more concepts here which is known as subgroup. So, what is the sub group? If you look at the screen a group whose members are all members of another group both being subjected to the same operations, so what it means is as follows if I have a group of certain order say I have a group of order 6. Now out of this 6 elements in that group if 3 of them forms a group that is possible we will see how in that case, in this small subject of those elements which satisfies the criteria of forming a group will be a sub group of the main large group that is the group of order 3 which I was talking about will be a sub group of the main group having an order 6. And there is a specialty like the subgroup cannot have any order there is certain definite condition for a sub group to satisfy in order to call one you have to be called as sub group and that is the order of that sub group has to be an integral factor of the order of the main group that is what is written here, there is the order of any subgroup G of a group of order h must be integral factors of the order of the group.

So, in other word what it does it mean? So, suppose I have the main group having an order h. So, this is the say if I write main group then if there is a sub group order should be such that if the order is G then it should be such that h by g equals to k, where k is an integer that is the condition of formation of subgroup g. So, what does that mean that if I have a group of order 6 then the, sub groups that can actually be form will have or can have the order 1 2 and 3 out of that one is the trivial example, and you know 2 will be another 1 and third will other sub group that is possible is having order 3.

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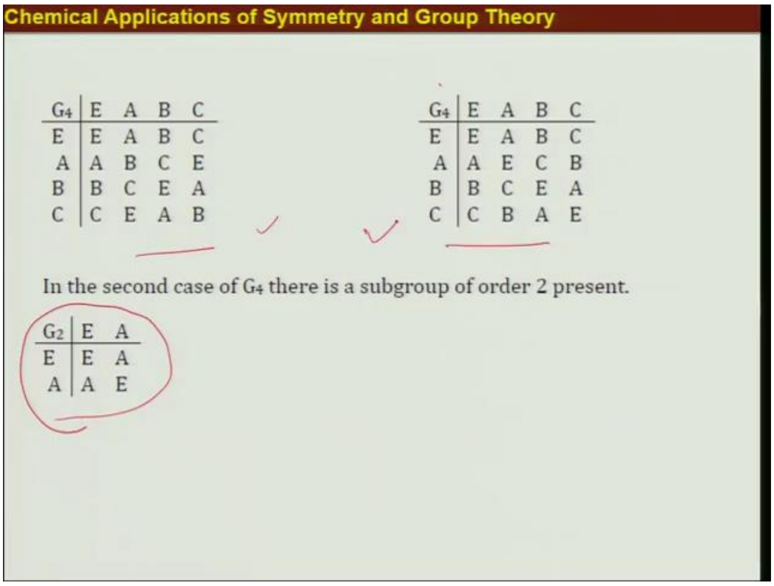

So, here we will look at some of more some other group multiplication tables that is G 4. So, on your screen you have 2 different sets of group multiplications table for a group having order 4 it is 1 and here is 2.

Now, you can see that this 2 are different group multiplication table. So, you can actually form more than one type of group multiplication tables for certain orders. So, G 4 is an example, we will not be you know deriving this group multiplication table we showed one example with G 3 the simplest one, and you should able to form this 2 different G 4s with that principle, that you have already learned. So, one thing you can look at here, that from this G 4 you can take out a sub group which has an order 2 group will have an unique 2 multiplication table that we have already seen, that will be a G 2 and you can easily find out group multiplication table for G 2 from this any 2 G 4s.

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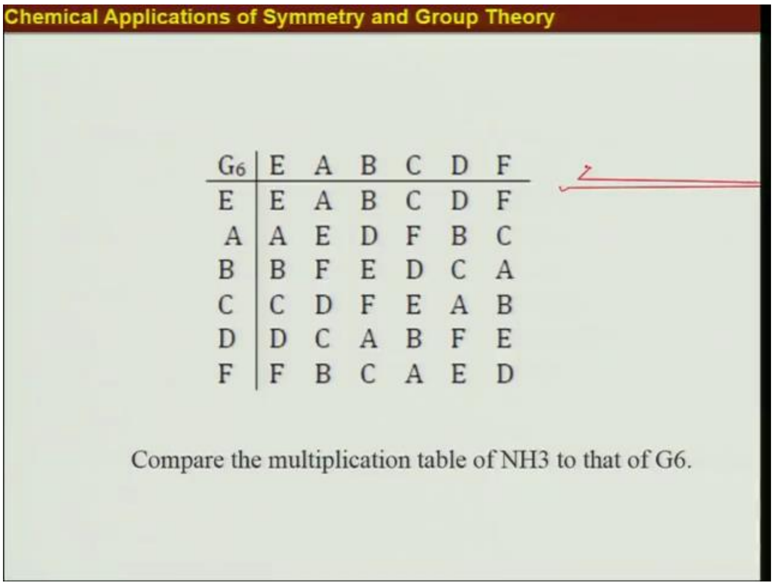

G6	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	E	D	F	B	C
B	B	F	E	D	C	A
C	C	D	F	E	A	B
D	D	C	A	B	F	E
F	F	B	C	A	E	D

So, now similarly you can find out for what is G 5 and you can also find out about G 6. So, on your screen right is a group multiplication table for a group, which has order 6 we call it g 6, but this is not the unique multiplication table, that is possible for a group having order 6 you can form more than this, another type of group multiplication table and you should try forming that group multiplication table yourself. Now if suppose I give you this particular group multiplication table can we compare it with multiplication table for a particular point group which also has an order 6. So, what is group that you can imagine which is an order 6, the easiest option will be C 3 v you take ammonia has an example, and if you go through all symmetry operations you can have for ammonia you will find that error on the 6 symmetry operations that are possible identity C 3 C 3 square sigma v sigma v prime sigma v double prime. There are 6 elements in that particular point group.

Now, can we compare the multiplication table which is on your screen right now and that with multiplication table of C 3 v particularly that is for ammonia.

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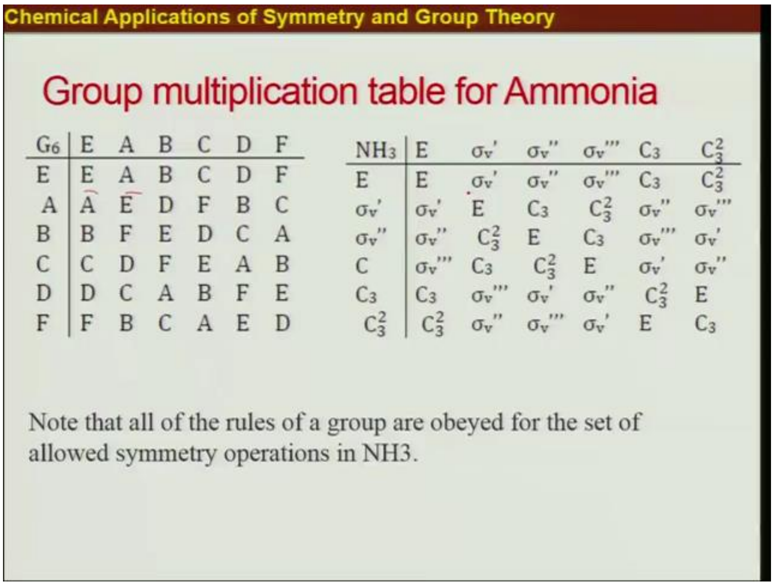
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Group multiplication table for Ammonia

G_6	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	E	D	F	B	C
B	B	F	E	D	C	A
C	C	D	F	E	A	B
D	D	C	A	B	F	E
F	F	B	C	A	E	D

NH_3	E	σ_v'	σ_v''	σ_v'''	C_3	C_3^2
E	E	σ_v'	σ_v''	σ_v'''	C_3	C_3^2
σ_v'	σ_v'	E	C_3	C_3^2	σ_v''	σ_v'''
σ_v''	σ_v''	C_3^2	E	C_3	σ_v'''	σ_v'
C	σ_v'''	C_3	C_3^2	E	σ_v'	σ_v''
C_3	C_3	σ_v'''	σ_v'	σ_v''	C_3^2	E
C_3^2	C_3^2	σ_v''	σ_v'''	σ_v'	E	C_3

Note that all of the rules of a group are obeyed for the set of allowed symmetry operations in NH3.

So, let us have a look at that now G 6 is again there on the screen and you have also the group multiplication table for the symmetry operations of ammonia. So, what do you see? So, here all the multiplications are provided now what you should do is to find out what is the similarity become these 2, and once you have a close look at both the tables one for g 6 which is an abstract group, and this point symmetry point group for C 3 v that is I mean ammonia here you see that, all the rules of a group are obeyed by this group multiplication table for ammonia. So, all the symmetry operations here they follow this principles which is already something we that we already know.

Now, the most interesting fact here you will find out if you look at the correspondence between the elements, that are formed what are product actually which formed by this group multiplication and compared each of the table. So, you compared you know the elements at row one column one or say row n column n, and you try to find out what is the similarity there.

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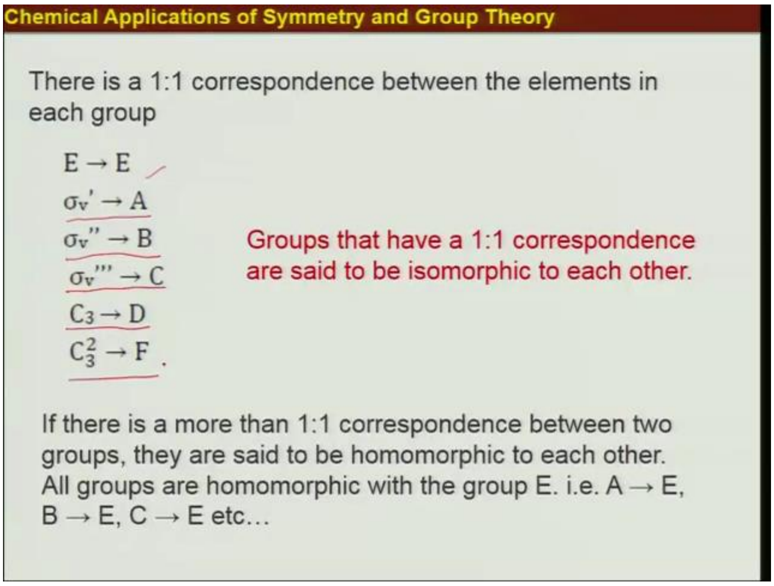

And what you will see there is that there is an 1:1 correspondence between the elements in each of the groups for example, you will see that identity is same for both of them which is not something which you are surprised with, and then essentially the sigma v prime is nothing, but a in G 6 the sigma v double prime is B in G 6 sigma v triple prime is C in G 6 while C 3 and C 3 square are D and F respectively in case of G 6 and this is an wonderful thing that if you can form a generalized the group multiplication table. Then for any given molecule you should be able to identify the product of any 2 symmetry operations. Once you have figured out what is the corresponding elements in that point group multiplication table, for that molecular once you have figured out what is your abstract group for group multiplication table for that same order group.

So, we will stop here today and we will resume from the same point in the following class.

Thank you very much.