M. Sc. Semester-II, Paper : CC-06 (Inorganic Chem.)

Unit-3 Group theory in Chemistry [Dr. Birendra Kumar, Dept of Chem. Maharaja College, Ara]

⇒ **Representation of Group by Matrices:** Before discussion on the topic, first we discuss about Matrix and multiplication of Matrices.

* **Matrix?**

A matrix is a triangular array of numbers or symbols, called elements that has the following general form: $\begin{bmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{bmatrix}$

In the matrix, vertical sets of elements are called columns and the horizontal ones rows. The symbol A_{ij} means the matrix element in the i^{th} row and j^{th} column. e.g. A_{12} means element in 1st row & 2nd column, similarly A_{23} means element in 2nd row & 3rd column etc. When the numbers of rows equals the number of columns, the matrix is called square matrix. The elements A_{ij} of a square matrix for which $i = j$ (i.e. A_{11}, A_{22}, A_{33}) are called the diagonal elements and the other elements are called off diagonal.

When each of the diagonal elements of a square matrix equals 1 and all off diagonal elements are zero, the matrix is called as Unit matrix. e.g. a 3x3 unit matrix is shown as: $\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$

* **Multiplication of Matrices:** Multiplication of two matrices, A_{ij} & B_{jk} is given as: $A_{ij} \cdot B_{jk} = C_{ik}$. During multiplication, following points should be kept in mind:
(i) Number of columns in matrix A (i.e. j) must be equal to the number of rows in matrix B (i.e. j) (ii) Multiplication of a (i×j) matrix with a (j×k) matrix gives a (i×k) matrix.
(iii) To get the elements of matrix C, the rows of matrix A is multiplied by columns of matrix B.

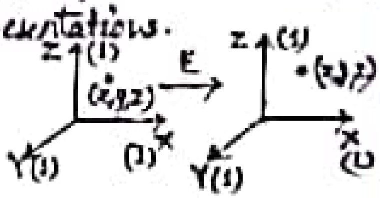
For example:
$$\underset{(3\times2\ \text{matrix})\ A}{\begin{bmatrix} 1 & 2 \\ 3 & 4 \\ 5 & 6 \end{bmatrix}} \cdot \underset{(2\times3\ \text{matrix})\ B}{\begin{bmatrix} 2 & 4 & 6 \\ 3 & 5 & 7 \end{bmatrix}} = \begin{bmatrix} 1\times2+2\times3 & 1\times4+2\times5 & 1\times6+2\times7 \\ 3\times2+4\times3 & 3\times4+4\times5 & 3\times6+4\times7 \\ 5\times2+6\times3 & 5\times4+6\times5 & 3\times6+6\times7 \end{bmatrix} = \underset{(3\times3\ \text{matrix})\ C}{\begin{bmatrix} 8 & 14 & 20 \\ 18 & 32 & 46 \\ 28 & 50 & 72 \end{bmatrix}}$$

Here matrix elements of C are obtained by multiplication of rows of matrix A with columns of matrix B.

Representation?

Representation can be defined as a set of matrices which represents the symmetry operations of a point group. The set of vectors of the coordinate axes (x, y & z) with respect to which the matrices are represented is called basis of the representations. The set of vectors may be translational, rotational, bond vectors and atomic wave functions.

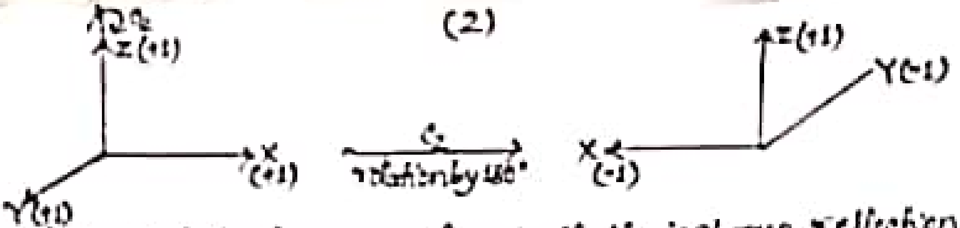
Representation of a point group by matrices: Let us consider C_{2v} point group (e.g. H_2O). The representations for symmetry operations of C_{2v} w.r.t coordinate axes (x, y & z) are shown below. The character of symmetry operation is the dimensions of representations.



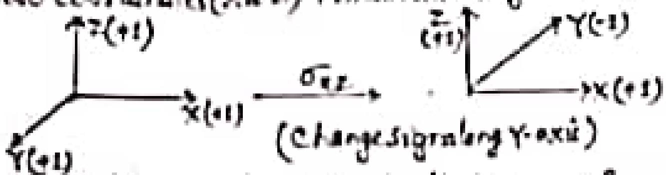
Identity (E): When a point with coordinate (x, y, z) is subjected to the identity operation, its new coordinates are the same as the initial ones (x, y, z). This may be expressed in a matrix equation as follows: $E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$ (Three dimensional representation) Character = 3.

C_2 operation: $\phi = +180°$ $C_2 = \begin{bmatrix} \cos180 & \sin180 & 0 \\ -\sin180 & \cos180 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$ (One dimensional representation) Character = 1

Above C_2 operation can also be visualized w.r.t coordinate axes:



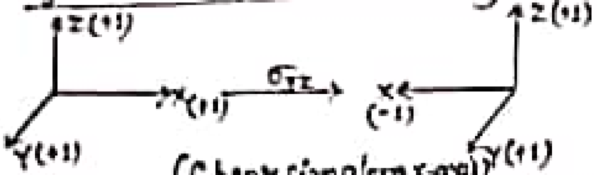
σ_{xz} (plane of reflection): If xz plane of reflection is chosen, reflection of a point has the effect of changing the sign of the coordinate (Y) measured perpendicular to the plane (xz) while two coordinates (X & Z) remain unchanged. This shown as follows.



(Change sign along Y-axis)

$$\sigma_{xz} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$ (One dimensional representation) Character = 1.

σ_{yz} (Plane of reflection): Similarly, if yz plane of reflection is chosen.



(Change sign along x-axis)

$$\sigma_{yz} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$ (One dimensional representation) Character = 1

Representation for coordinates (X, Y & Z) can be expressed as:

Coordinate	E	C_2	σ_{xz}	σ_{yz}
X	1	-1	1	-1
Y	1	-1	-1	1
Z	1	1	1	1

(ii) C_{2h} point group (e.g. trans $C_2H_2Cl_2$): Trans $C_2H_2Cl_2$ or

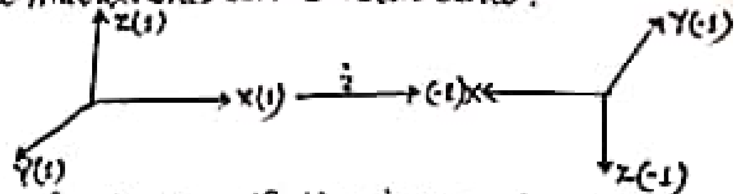
has C_{2h} point group. C_{2h} is composed of four symmetry operations: E, i, C_2 and σ_h. Matrices for E & C_2 symmetry operations are obtained as in example (i) given below:

Matrix for identity (E): $\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$; Matrix for C_2: $\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$

For inversion (i) and σ_h operations, matrices constructed as follows.

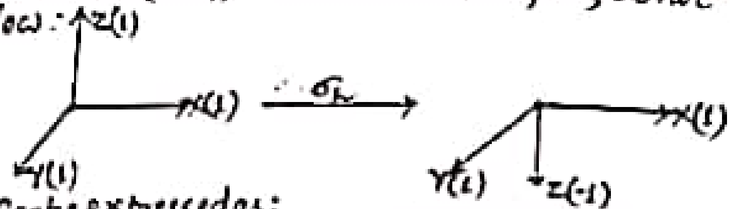
Inversion (i): To simply change the signs of all the coordinates without permuting any, we clearly need a negative unit matrix. This can be shown below:

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \cdot \begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} -X \\ -Y \\ -Z \end{bmatrix} \text{ i.e. } i = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$



Horizontal plane of Symmetry (σ_h) or, Reflection operation: On performing the reflection in xy planes, only coordinates perpendicular to reflection planes (Z) changes sign while the other two coordinates (X & Y) remains the same, i.e. do not change sign. This can be shown below:

$$\sigma_{xy} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} X \\ Y \\ -Z \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$



Representation for coordinates (X, Y & Z) can be expressed as:

Coordinate	E	i	C_2	σ_h
X	1	-1	-1	1
Y	1	-1	-1	1
Z	1	-1	1	-1

The combination of two symmetry operations can be obtained by multiplying the corresponding matrices in the same order. If we carry out rotation (C_2) and reflection (σ_h) in succession we will get inversion (i)

$$C_2 \cdot \sigma_h = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = i$$

⇒ **Reducible & Irreducible Representations:**

We have - for n-atomic molecule, a representation generated/reduced consist of $3n \times 3n$ matrices. Inorder to minimise the size of the matrices for easier calculations, it is required to reduce them to more manageable size. This means reducing them eventually to those of irreducible representation, which are representations of the smallest possible dimensions. Hence, representations may be reducible & irreducible.

Reducible representations : A representation of higher dimensions which can be reduced to representation of lower dimensions is called reducible representations.

A reducible representation and its reduction can be understood by carrying out similarity transformation.

Suppose A, B, C, D is a representation of a group in which $[B] \cdot [C] = D$.

If only the diagonal elements of matrices (A, B, C, D) of the representation are shown and similarity transformation is carried out with matrix (X), the following matrices are obtained:

$$[X^{-1}][A][X] = [X^{-1}]\begin{bmatrix} A_1 & & \\ & A_2 & \\ & & A_3 \end{bmatrix}[X] = \begin{bmatrix} \boxed{A_1'} & & \\ & \boxed{A_2'} & \\ & & \boxed{A_3'} \end{bmatrix}; \quad [X^{-1}][B][X] = [X^{-1}]\begin{bmatrix} B_1 & & \\ & B_2 & \\ & & B_3 \end{bmatrix}[X] = \begin{bmatrix} \boxed{B_1'} & & \\ & \boxed{B_2'} & \\ & & \boxed{B_3'} \end{bmatrix}$$

$$[X^{-1}][C][X] = [X^{-1}]\begin{bmatrix} C_1 & & \\ & C_2 & \\ & & C_3 \end{bmatrix}[X] = \begin{bmatrix} \boxed{C_1'} & & \\ & \boxed{C_2'} & \\ & & \boxed{C_3'} \end{bmatrix}; \quad [X^{-1}][D][X] = [X^{-1}]\begin{bmatrix} D_1 & & \\ & D_2 & \\ & & D_3 \end{bmatrix}[X] = \begin{bmatrix} \boxed{D_1'} & & \\ & \boxed{D_2'} & \\ & & \boxed{D_3'} \end{bmatrix}$$

Here X is the matrix having same order as matrices of representation.

If in the original representation $[B] \cdot [C] = [D]$, the resultant matrices have been block-factorised as such $[B_1'][C_1'] = [D_1']$; $[B_2'][C_2'] = [D_2']$; $[B_3'][C_3'] = [D_3']$.

Then, various set of matrices given below: $\left| \begin{matrix} A_1', B_1', C_1', D_1' \\ A_2', B_2', C_2', D_2' \\ \cdots \end{matrix} \right|$ are in themselves representation of the group.

The set of matrices A, B, C, D are called reducible representations.

Irreducible representation: These representations which cannot be further reduced to representations of lower dimensions are called irreducible representations.

In other words, if it is not possible to find a similarity transformation which will reduce all the matrices of a given representation in above manner the representation is said irreducible representations. Hence, in above example, $\left| \begin{matrix} A_1', B_1', C_1', D_1' \\ A_2', B_2', C_2', D_2' \\ \cdots \end{matrix} \right|$ are called irreducible representations.

The reducible representation (Γ^{red}) and the corresponding irreducible representations ($\Gamma_1, \Gamma_2, \Gamma_3$) can be expressed as: $\Gamma^{red} = \Gamma_1 + \Gamma_2 + \Gamma_3$.

The characters of the matrices of the reducible representation are the sum of the characters of the resulting irreducible representations.

⇒ The great orthogonality theorem:

All the properties of group representations and their characters which deal problems in valence theory and molecular dynamics can be derived from one basic theorem, known as the great orthogonality theorem. It can be expressed mathematically as: $\sum_R [\Gamma_i(R)_{mn}][\Gamma_j(R)_{m'n'}]^* = \frac{h}{\sqrt{l_i l_j}} \delta_{ij} \delta_{mm'} \delta_{nn'}$

[where h = order of the group, l_i & l_j = dimensions of i & j, irreducible representations, R = Symmetry operations of the group, $[\Gamma_i(R)_{mn}]$ = element in the m^{th} row and the n^{th} column of the matrix corresponding to an operation R in the irreducible representation, $[\Gamma_j(R)_{m'n'}]^*$ = complex conjugate which can be replaced by the term itself if it does not contain imaginary/complex number].

The theorem states following: (i) The number of irreducible representations in a group is equal to the number of classes of group.

(ii) The sum of the squares of the dimensions of the irreducible representations is equal to the order of the group, i.e., $\sum l_i^2 = l_1^2 + l_2^2 + l_3^2 \cdots = h$

(iii) The sum of the squares of the characters of an irreducible representation is equal to the order of the group, i.e., $\sum [\Gamma_i(R)]^2 = h$

(iv) The sum of products of corresponding characters of the irreducible representations is equal to zero, i.e; $\sum [\Gamma_i(R)_{mn} \cdot \Gamma_j(R)_{mn}] = 0$ (when $i \neq j$)

(v) In a given representation (reducible or irreducible), the characters of all matrices belonging to the same class are identical.

* Explanation of the theorem: Let us consider C_{2v} point group. The C_{2v} point group includes four symmetry operations: E, C_2, σ_{xz} & σ_{yz}. Each symmetry operation belongs to a separate class. By this theorem, the number of irreducible representations of a group is equal to the number of classes in the group. So, C_{2v} point group will have four irreducible representations: $\Gamma_1, \Gamma_2, \Gamma_3$ & Γ_4.

Again, the sum of squares of the dimensions of the irreducible representations is equal to order of the group, i.e. $l_1^2 + l_2^2 + l_3^2 + l_4^2 = h = 4$ $\therefore l_1 = l_2 = l_3 = l_4 = 1$.

Thus, each of the four irreducible representations of C_{2v} point group is one dimensional.

Since the dimensions of the representation are equal to the character of the identity operations of the irreducible representation, E should be equal to 1 in all of them, i.e., for Γ_1, Γ_2, Γ_3, Γ_4, $E = 1$.

Since, the sum of the squares of the characters of an irreducible representation is equal to the order of the group (i.e., 4). Let one of the irreducible representation and all the characters must be equal to 1. So Γ_1 : E 1, C_2 1, σ_{xz} 1, σ_{yz} 1.

Since the characters of the irreducible representations of the same group are orthogonal to each other, hence characters of each of the remaining th...

irreducible representations has two (+1) and two (-1). Hence, we have :

C_{2v}	E	C_2	σ_{xz}	σ_{yz}
$\Gamma_1 \to A_1$	1	1	1	1
$\Gamma_2 \to A_2$	1	1	-1	-1
$\Gamma_3 \to B_1$	1	-1	1	-1
$\Gamma_4 \to B_2$	1	-1	-1	1

In irreducible representation (i) Γ_1 is labelled as A_1 as it is one dimensional and shows symmetry to the principal rotation axis & $\sigma_v(xz)$ (ii) Γ_2 is labelled as A_2 as it is also one dimensional and symmetry to principal axis but unsymmetrical to vertical plane, $\sigma_v(xz)$ (iii) Γ_3 is given the symbol B_1 as it is one dimensional and unsymmetrical w.r.to C_2 but symmetrical w.r.to $\sigma_v(xz)$ (iv) Γ_4 is given the symbol B_2 as it is also one dimensional, unsymmetrical to principal axis C_2 & vertical plane $\sigma_v(xz)$.

=> <u>Character table</u>: A character table lists the characters of all the symmetry classes for the irreducible representations of a point group. It is sufficient to know only the characters of each symmetry class of a point group to which a molecule belongs.

* <u>Features of Character table</u>: A character table consists of different areas denoted by Roman numerals. It is very necessary to explain the meaning and indicate the source of the information given in these areas. Consider the C_{3v} <u>point group</u> for reference in the discussion.

C_{3v}	E, $2C_3$, $3\sigma_v$				
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	$(x,y)(R_x,R_y)$	$(x^2-y^2, xy)(xz, yz)$
II	I			III	IV (Area)

In top row, upper left corner is the Schoenflies symbol for the point group, and then symmetry operations of the point group/elements of the group listed.

<u>Area-I</u>: The characters of the irreducible representations of the group are present in this.

<u>Area-II</u>: In this area, the irr. representation or its set of characters by the Mulliken symbol.

<u>Area-III</u>: In this, there are six symbols: x, y, z, R_x, R_y & R_z. The first three represent the Cartesian coordinates (x,y,z) while R_x, R_y & R_z represent rotations about x, y & z axes. This area lists the transformation properties of vectors along the x, y & z axes.

<u>Area-IV</u>: This area indicates transformation properties of squares & binary products of the coordinates. Although there are six possible square & binary products (x^2, y^2, z^2, xy, yz & zx), only five are ever indicated. Since $x^2+y^2+z^2 = r^2$, one of the linear combination is redundant (i.e, r^2 is the square of radius of the $x^2+y^2+z^2$ sphere). The direct product of two vectors is obtained by multiplying the species for each, e.g., $xy = B_1 \times B_2 = A_2$.

* <u>Construction of character table</u>: A character table can be constructed by two ways. The various steps involved in first method are as follows:

(i) Write down all the symmetry operations/elements of the point group and then group them into classes. Otherwise at least total number of classes which equals the order of the group must be known.

(ii) Total number of irreducible representation equals the total number of classes.

(iii) Determine the dimensions of irreducible representations using first statement of the great orthogonality theorem.
(iv) Statements (3-5) of the great orthogonality theorem are used in fixing the characters.
(v) Generate representations using certain basis vectors. Typical are the x, y & z; R_x, R_y & R_z and their squares as basis and check.

⇒ For example, character table for C_{2v} point group (e.g. H_2O) constructed using above method.

C_{2v} point group consists of four operations: $E, C_2, 2\sigma_v$.

(i) Number of classes = 4 ($E, C_2, \sigma_{xz}, \sigma_{yz}$). Therefore no. of irreducible representations = 4 (by statement-1 of the theorem)

(ii) By statement-2 of the theorem, $\sum l_i^2 = h$

Let irreducible representation are l_1, l_2, l_3 & l_4

$\therefore l_1^2 + l_2^2 + l_3^2 + l_4^2 = h = 4 \quad \therefore l_1 = l_2 = l_3 = l_4 = 1$

(iii) (a) The transformation properties of vector along the x, y & z axes (Area-III) can be found as follows: let us consider a vector along z-axis. The E (identity) does not change the direction of the head of the vector, nor does $C_2, \sigma_{xz}, \sigma_{yz}$. Hence, its characters are 1, 1, 1, 1. Thus, the vector z transforms under the symmetry operations of C_{2v} point group according to the species A_1 (Mulliken Symbol). Similarly operation on x & y show that they belong to irreducible representations B_1 & B_2 respectively. If there is change in the direction of the head of the arrow, the character is -1 (Table-1).

Table-1

Vector	E	C_2	σ_{zx}	σ_{yz}	Symbol
z	1	1	1	1	A_1
y	1	-1	-1	1	B_2
x	1	-1	1	-1	B_1

Table-2

Rotation vector	E	C_2	σ_{zx}	σ_{yz}	Symbol
R_z	1	1	-1	-1	A_2
R_y	1	-1	1	-1	B_1
R_x	1	-1	-1	1	B_2

(b) Similar assignments (Area-II) could be made to rotation axes R_x, R_y & R_z representing rotations about x, y & z axes, shown by curved arrows. If the direction of the head of the arrow does not change due to operation, the character is +1. If it changes to opposite, the character is -1. The R_x, R_y & R_z transform as the species B_2, B_1 & A_2 respectively (Table-2).

(iv) For Area-III to assign the squares and binary products of the vectors, the characters are squared or direct products are obtained. e.g., the characters of x^2 are (Table-3):

Table-3

	E	C_2	σ_{zx}	σ_{yz}	Symbol
x^2	$1\times1 = 1$	$-1\times-1 = 1$	$1\times1 = 1$	$-1\times-1 = 1$	A_1

Table-4

	E	C_2	σ_{zx}	σ_{yz}	Symbol
xy	$1\times1 = 1$	$-1\times-1 = 1$	$1\times-1 = -1$	$-1\times1 = -1$	A_2
xz	$1\times1 = 1$	$-1\times1 = -1$	$1\times1 = 1$	$-1\times1 = -1$	B_1
yz	$1\times1 = 1$	$-1\times1 = -1$	$-1\times1 = -1$	$1\times1 = 1$	B_2

Similarly y^2 & z^2 also belong to A_1 irreducible representation.
Direct product is obtained by multiplying the characters of two vectors (Table-4).
Thus, the four columns of the character table can be shown below (Table-5):

C_{2v}	E	C_2	σ_{xz}	σ_{yz}	
A_1	1	1	1	1	z, x^2, y^2, z^2
A_2	1	1	-1	-1	R_z, xy
B_1	1	-1	1	-1	x, R_y, xz
B_2	1	-1	-1	1	y, R_x, yz