4.12 Character Table

A more compact and self-explanatory representation table of a point group is said as 'character table'. The character tables of molecular point groups are important from the point of view of their application to chemical problems. The character of reducible and irreducible representation of symmetry operation of a point group are arranged in the character table and are used for understanding the various problems like atomic orbitals, hybrid orbitals, molecular orbitals in polyatomic molecules, crystal field theory of complex compounds, electronic and vibrational spectra of molecules.

Symbol for irreducible representation :

The symbol for the irreducible representation was given by Mulliken and hence called as Mulliken symbol. The rules are as follows :

(i) All unidimentional representations are represented either by A or B, two dimensional representations are represented by E and three dimensional representations are represented by T.

(ii) One dimensional representations which are symmetrical with respect to the principal axis (i.e., character of C_n operation is +1) are designated as *A* while those antisymmetric in this respect (i.e., character of C_n operation–1) are designated as *B*.

(iii) Those irreducible representations which are symmetrical with respect to the subsidiary axis, or in its absence to σ_v plane, subscript 1, (i.e., A_1, B_1, E_1, T_1) is used and for antisymmetric subscript 2 (i.e., B_1, A_2, E_2, T_2) is used.

(iv) Primes and double primes are attached to all *A*, *B*, *E* or *T* to indicate the symmetric and antisymmetric with respect to σ_h. *A'* or *E'* appears forth σ_h having +1 and *A''* or *E''* appear for the σ_h having –1.

(v) Subscript *g* and *u* are used to indicate the symmetric and antisymmetric to the inversion. If the point group has no centre of symmetric, *g* or *u* are not used. Term *g* stands for gerade (centro symmetric) and *u* stands for ungerage (non-centro symmetric)

Construction of character table for C_{2v} point group :

There are total of four symmetric operations C_{2v} point group i.e., E, $C_{2(2)}$, σ_{xz}, σ_{yz}

(i) There operations belong to four different classes hence there are four irreducible representations. Let be $\Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4$.

(iii) It is also requires that the sum of the square of the dimensions of these representations equal h (order of the group) i.e., 4. Hence each representation must be unidimensional so that

$$1^2 + 1^2 + 1^2 + 1^2 = 4$$

Because the character of identity operation is equal to the dimension of the representation and hence *E* must be equal to one (1) in all of them.

	E	$C_{2(2)}$	σ_{xz}	σ_{yz}
Γ_1	1			
Γ_2	1			
Γ_3	1			
Γ_4	1			

(iii) The sum of the square of the character of an irreducible representation must be equal to 4 as

$$\sum_{R}[\chi_i(R)]^2 = 4$$

i.e. $1^2 + 1^2 + 1^2 + 1^2 = 4$

	E	$C_{2(2)}$	σ_{xz}	σ_{yz}
Γ_1	1	1	1	1
Γ_2	1			
Γ_3	1			
Γ_4	1			

(iv) The sum of the square of the character of other irreducible representation must be equal to four and the character must also be orthogonal. Hence character must include two +1 & two −1.

Therefore, we will have

	E	$C_{2(2)}$	σ_{xz}	σ_{yz}
Γ_1	1	1	1	1
Γ_2	1	−1	−1	1
Γ_3	1	−1	1	−1
Γ_4	1	1	−1	−1

All there representation are also orthogonal to one another taking $\Gamma_2.\Gamma_3$, we have

$$(1)(1) + (-1)(-1) + (-1)(1) + (1)(-1) = 0$$

The complete character table for the point group C_{2v} is as follows :

C_{2v}	E	$C_{2(2)}$	σ_{x2}	σ_{y2}		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_2	xy
B_1	1	−1	1	−1	x, R_y	x_z
B_2	1	−1	−1	1	y, R_x	y_z
I	II				III	IV

In the upper left corner is the schonflies notation for the group and the upper row of the table are listed the symmetry operations grouped into classes.

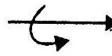
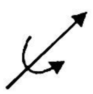
Area I : Area I represents the symbol for the irreducible represnetation according to the Mulliken. All these irreducible representation are of unidimensional and hence A or B symbol be used. Because upper two irreducible representations are symmetrical with respect to the principal axis and hence A's are written and lower two representation are anti symmetrical with respect to the principal axis and hence B'sare written. Subscript 1 or 2 are written for the symmetrical and antisymmetrical respectively with respect to σ_{xz}.

Area II : Area II of the character table are the characters of the irreducible representation of the point group C_{2v}.

Area III : Area III represents the Cartesian coordinates or rotational axis corresponding to irreducible representation. In order to assign the Cartesian coordinate or rotational axis, we must perform the operations on them and enquire the character.

Consider a vector along z–axis. The operations E, $C_{2(2)}$, σ_{xz}, σ_{yz} do not change the direction of the head of the vector. Hence its character are 1, 1, 1, 1. Thus the vector z transforms under the symmetry operations into A_1. Similarly X and Y vector transform into B_1 and B_2 representation.

Rotational axis R_x, R_y and R_z represent rotation about x, y and z–axis. To understand the transformation by rotational axis, we should mark a curved arrow and symmetry operation is performed. If the direction of the head of the arrow does not change due to operation, the character is +1 and –1 for the change of head of arrow :

			E	C_2	σ_{xz}	σ_{yz}	Transformation into
R_2	z 	R_2	1	1	–1	–1	A_2
R_y	 Y	R_y	1	–1	1	–1	B_1
R_y	Y 	R_x	1	1	–1	1	B_z

Area IV : Area IV represnets squares binary products to the irreducible representation. For assignment of the square and binary products of the vectors, the characters are squared or direct products are obtained. x^2, y^2 and z^2 belongs to A_1 irreducible representation. The product of character of X & Y belongs to A_2, product of X & Z belongs to B_1 and product of Y & Z belongs to B_2 representations.

Construction of character table for C_{3v} point group :

(i) There are total of six symmetry operations present in C_{3v} point group i.e., $E, C_3^1, C_3^2, \sigma_a, \sigma_b, \sigma_c$. These operations are divided into the three classes are hence there are $E, 2C_3, 3\sigma_v$ three irreducible representations. Let it be Γ_1, Γ_2 and Γ_3.

(ii) The sum of the square of the dimensions (character of the identity operation) should be equal to 6

$$\sum l_i^2 = l_1^2 + l_2^2 + l_3^2 = 6$$

The only value of the l_i that with satisfy this requirement and 1, 1, and 2.

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1		
Γ_2	1		
Γ_3	2.		

(iii) Every point group possesses one representation which is totally symmetric. In this representation, all the operations have the character value one(1). Thus we have

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1

It can be seen that the summation of the square, of the character of the operations is equal to 6.

$$1^2 + 2 \times 1^2 + 3 \times 1^2 = 6$$

(iv) Γ_2 (second irreducible representation) must be orthogonal to Γ_1. since $\chi_2(E)$ must always be positive and hence Γ_2 must consist of three +1 and three −1. This is only possible if Γ_2 has 1, 1 and −1.

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	1	−1

(v) One third representation will be of two dimensions and hence $\chi_3(E)$ is 2. In order to find out the values of $\chi_3(C_1)$ and $\chi_3(\sigma_v)$ we make the use of the orthogonality relationship. Γ_1 & Γ_3 are orthogonal to each other and Γ_2 & Γ_3 are also.

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	1	-1
Γ_3	2	$\chi_3(C_3)$	$\chi_3(\sigma_v)$

$$\sum_R \chi_1(R).\chi_3(R) = (1).(2) + 2(1).\chi_3(C_2) + 3.(1)\chi_3(\sigma_v) = 0 \quad \text{... (i)}$$

and $$\sum_R \chi_2(R).\chi_3(R) = (1).(2) + 2(1).\chi_3(C_3) + 3.(-1)\chi_3(\sigma_v) = 0 \quad \text{... (ii)}$$

Solving eqn. (i) & (ii),

$$2\chi_3(C_3) + 3\chi_3(\sigma_v) = -2 \quad \text{... (iii)}$$

$$2\chi_3(C_3) - 3\chi_3(\sigma_v) = -2 \quad \text{... (iv)}$$

Both equations are added

$$4\chi_3(C_3) = -4$$

$$\therefore \quad \chi_3(C_3) = -1$$

This value is substituted in equation (iii)

$$2(-1) + 3\chi_3(\sigma_v) = -2$$

$$3\chi_3(\sigma_v) = 0$$

$$\therefore \quad \chi_3(\sigma_v) = 0$$

Thus the complete set of character of irreducible representation of C_{3v} point group is :

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	1	-1
Γ_3	2	-1	0

The complete character table for the point group C_{3v} is as follows :

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_2	
E	2	−1	0	(x, y) (R_x, R_y)	$(x_2 - y_2, xy)$ (xz, yz)
I		II		III	IV

In the upper left corner in the schonflies notation for the group and the upper row of the table are listed the symmetry operations grouped into the classes.

Area I represents the symbol for the irreducible representations according to the Mulliken. This is why these symbols ar called as Mulliken symbol.

Because first two irreducible representations are uni dimensional and hence *A* or *B* are used. The character of principal axis of rotation for both the representations are symmetrical and hence *A* is used. Subscript 1 is written for the symmetrical character (+1) of operation σ_v which subscript 2 is written for the unsymmetrical character (−1) of operation σ_v. The symbol *E* show the two dimensional representation.

Area II—In area II of the table are the characters of the irreducible representation of the point group.

Area III—Area III gives the transformation properties of cartesian coordinates *x*, *y*, *z* and rotations about *x*, *y* and *z* axes. i.e., R_x, R_y and R_z.

The vector along *z*-axis remains unchanged with respect to *E*, C_3 and σ_v operations. The matrices and character for the transformation of coordinate *z* by these operations are :

	E	C_3	σ_v
Matrices	[1]	[1]	[1]
Character	1	1	1

This set of characters corresponds to the A_1 representation and hence *z* transforms or the A_1 represntation. This is why *z* is written in the A_1 representation.

The matrices and character for the transformation of coordinates x and y by the operators E, C_3 and σ_v are :

	E	C_3	σ_v
Matrices	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$
Character	[2]	[−1]	[0]

This set belongs to the E representation. It is important that x and y are inseparable in this respect.

Transformation properties of R_x, R_y and R_z – The rotation axis R_z can be shown as an arrow around z–axis. On performing E or C_2, the direction of the head of the arrow remains same (character = +1). However, on performing σ_v, the direction of the head of the arrow changes (character = −1). Thus its character is 1, 1, −1 and belongs to representation A_2. This is why R_2 is written for A_2 representation. R_x and R_y form a two dimensional representation and belongs to E.

Area IV – In this area of the table, squares and binary products of coordinate according to their transformation properties are described. The squares of the vectors $(x^2 - y^2)$ and z^2 belong to A1. $x^2 - y^2$ and xy takes together and xz, yz taken together belong to E.