5.04, Principles of Inorganic Chemistry II
MIT Department of Chemistry
Lecture 3: Similarity Transforms, Classes and Representations

A <u>similarity transformation</u> is defined as

$$v^{-1} \bullet A \bullet v = B$$

where B is designated the similarity transform of A by X and A and B are <u>conjugates</u> of each other. A complete set of operators that are conjugate to one another is called a <u>class</u> of the group.

Let's determine the classes of the group defined by E, C_3, C_3^2, σ_v, σ_v', σ_v'' … the analysis is facilitated by the construction of a multiplication table:

right operator (columns); Left operator (rows)

	E	C_3	C_3^2	σ_v	σ_v'	σ_v''
E	E	C_3	C_3^2	σ_v	σ_v'	σ_v''
C_3	C_3	C_3^2	E	σ_v'	σ_v''	σ_v
C_3^2	C_3^2	E	C_3	σ_v''	σ_v	σ_v'
σ_v	σ_v	σ_v''	σ_v'	E	C_3^2	C_3
σ_v'	σ_v'	σ_v	σ_v''	C_3	E	C_3^2
σ_v''	σ_v''	σ_v'	σ_v	C_3^2	C_3	E

constructed from using a stereographic projection

$E^{-1} \bullet C_3 \bullet E = E \bullet C_3 \bullet E = C_3$

$C_3^{-1} \bullet C_3 \bullet C_3 = C_3^2 \bullet C_3 \bullet C_3 = C_3^2 \bullet C_3^2 = C_3$

$(C_3^2)^{-1} \bullet C_3 \bullet C_3^2 = C_3 \bullet C_3 \bullet C_3^2 = C_3 \bullet E = C_3$

$\sigma_\sigma^{-1} \bullet c_3 \bullet \sigma_v = \sigma_v \bullet C_3 \bullet \sigma_v = \sigma_v \bullet \sigma_v' = C_3^2$

$(\sigma_v')^{-1} \bullet C_3 \bullet \sigma_v' = \sigma_v' \bullet C_3 \bullet \sigma_v' = \sigma_v' \bullet \sigma_v'' = C_3^2$

$(\sigma_v'')^{-1} \bullet C_3 \bullet \sigma_v'' = \sigma_v'' \bullet C_3 \bullet \sigma_v'' \bullet \sigma_v = C_3^2$

$\therefore C_3$ and C_3^2 form a class

Performing a similar analysis on σ_v will reveal that σ_v, σ_v', and σ_v'' form a class, and E is in a class by itself. Thus there are three classes: E, (C_3, C_3^2), (σ_v, σ_v', σ_v''.

Additional properties of transforms and classes are:
1) no operator occurs in more than one class
2) order of all classes must be integral factors of the order of the group
3) in an Abelian group, each operator is in a class by itself

Similarity transformations give rise to irreducible representations, which lead to a useful tool in group theory – the character table. The general strategy for determining irreducible representations is as follows: $\underline{A}$, $\underline{B}$ and $\underline{C}$ are matrix representations of symmetry operations of an arbritrary basis set (i.e., elements on which symmetry operations are performed). There is some similarity transform operator v such.

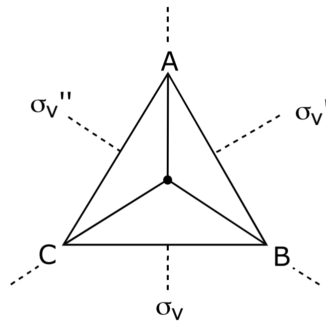
$$\underline{A}' = v^{-1} \bullet \underline{A} \bullet v$$
$$\underline{B}' = v^{-1} \bullet \underline{B} \bullet v$$
$$\underline{C}' = v^{-1} \bullet \underline{C} \bullet v$$

where ν uniquely produces block-diagonalized matrices-matrices possessing square arrays along the diagonal and zeros outside the blocks

$$A' = \begin{bmatrix} A_1 & & \\ & A_2 & \\ & & A_3 \end{bmatrix} \qquad B' = \begin{bmatrix} B_1 & & \\ & B_2 & \\ & & B_3 \end{bmatrix} \qquad C' = \begin{bmatrix} C_1 & & \\ & C_2 & \\ & & C_3 \end{bmatrix}$$

Matrices $\underline{A}$, $\underline{B}$, and $\underline{C}$ are reducible. Sub-matrices A_i, B_i and C_i obey the same multiplication properties as $\underline{A}$, $\underline{B}$ and $\underline{C}$. If application of the similarity transform does not further block-diagonalize A′, B′ and C′, then the blocks are irreducible representations. The character is the sum of the diagonal elements of their irr. rep.

Continuing with our exemplary group: E, C_3, C_3^2, σ_v, σ_v', σ_v''… let's define the arbitrary basis … a triangle



The basis set is described by the triangles vertices, points A, B and C. The transformation properties of these points under the symmetry operations of the group are:

$$E\begin{bmatrix}A\\B\\C\end{bmatrix}=\begin{bmatrix}A\\B\\C\end{bmatrix}=\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}\begin{bmatrix}A\\B\\C\end{bmatrix} \qquad \sigma_v\begin{bmatrix}A\\B\\C\end{bmatrix}=\begin{bmatrix}A\\C\\C\end{bmatrix}=\begin{bmatrix}1&0&0\\0&0&1\\0&1&0\end{bmatrix}\begin{bmatrix}A\\B\\C\end{bmatrix}$$

$$C_3\begin{bmatrix}A\\B\\C\end{bmatrix}=\begin{bmatrix}B\\C\\A\end{bmatrix}=\begin{bmatrix}0&1&0\\0&0&1\\1&0&0\end{bmatrix}\begin{bmatrix}A\\B\\C\end{bmatrix} \qquad \sigma_v'\begin{bmatrix}A\\B\\C\end{bmatrix}=\begin{bmatrix}B\\A\\C\end{bmatrix}=\begin{bmatrix}0&1&0\\1&0&0\\0&0&1\end{bmatrix}\begin{bmatrix}A\\B\\C\end{bmatrix}$$

$$C_3^2\begin{bmatrix}A\\B\\C\end{bmatrix}=\begin{bmatrix}C\\A\\B\end{bmatrix}=\begin{bmatrix}0&0&1\\1&0&0\\0&1&0\end{bmatrix}\begin{bmatrix}A\\B\\C\end{bmatrix} \qquad \sigma_v''\begin{bmatrix}A\\B\\C\end{bmatrix}=\begin{bmatrix}C\\B\\A\end{bmatrix}=\begin{bmatrix}0&0&1\\0&1&0\\1&0&0\end{bmatrix}\begin{bmatrix}A\\B\\C\end{bmatrix}$$

These matrices are not block-diagonalized … however a suitable similarity transformation will accomplish the task,

$$v=\begin{bmatrix}\frac{1}{\sqrt{3}}&\frac{2}{\sqrt{6}}&0\\\frac{1}{\sqrt{3}}&-\frac{1}{\sqrt{6}}&\frac{1}{\sqrt{2}}\\\frac{1}{\sqrt{3}}&-\frac{1}{\sqrt{6}}&-\frac{1}{\sqrt{2}}\end{bmatrix} \quad ; \quad v^{-1}=\begin{bmatrix}\frac{1}{\sqrt{3}}&\frac{1}{\sqrt{3}}&\frac{1}{\sqrt{3}}\\\frac{2}{\sqrt{6}}&-\frac{1}{\sqrt{6}}&-\frac{1}{\sqrt{6}}\\0&\frac{1}{\sqrt{2}}&-\frac{1}{\sqrt{2}}\end{bmatrix}$$

Applying the similarity transformation with C_3 as the example,

$$v^{-1} \bullet C_3 \bullet v = \begin{bmatrix} \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} \\ \frac{2}{\sqrt{6}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{6}} \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{bmatrix} \bullet \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix} \bullet \begin{bmatrix} \frac{1}{\sqrt{3}} & \frac{2}{\sqrt{6}} & 0 \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{2}} \end{bmatrix}$$

$$= \begin{bmatrix} \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} \\ \frac{2}{\sqrt{6}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{6}} \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{bmatrix} \bullet \begin{bmatrix} \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{3}} & \frac{2}{\sqrt{6}} & 0 \end{bmatrix}$$

$$= \left[\begin{array}{c|cc} 1 & 0 & 0 \\ \hline 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{array}\right] = C_3^{\ *}$$

if $v^{-1} \bullet C_3 \bullet v$ is applied again… no further block diagonalization and same trace will be obtained… an irreducible representation

The similarity transformation applied to other reducible representations yields:

$$v^{-1} \bullet E \bullet v = E^* = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$v^{-1} \bullet C_3^{\ 2} \bullet v = C_3^{\ 2*} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$$

$$v^{-1} \bullet \sigma_v \bullet v = \sigma_v^* = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$v^{-1} \bullet \sigma_v'' \bullet v = \sigma_v''^* = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix}$$

$$v^{-1} \bullet \sigma_v' \bullet v = \sigma_v'^* = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix}$$

As above, the block-diagonalized matrices do not further reduce under re-application of the similarity transform… all are irreducible representations

Thus a 3×3 reducible representation, Γ_{red}, has been decomposed under a similarity transformation into a 1 (1×1) and 1 (2×2) block-diagonalized irreducible representation, Γ_{irr}. The traces (i.e. sum of diagonal matrix elements) of the Γ_{irr}'s under each operation yields the <u>characters</u> of the representation. Taking the traces:

	E	C_3	C_3^2	σ_v	σ_v'	σ_v''
Γ_1	1	1	1	1	1	1
Γ_2	2	-1	-1	0	0	0

Note: characters of operators in the same class are identical

$\Rightarrow$

	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	2	-1	0

This collection of characters for a given irreducible representation, under the operations of a group is called a <u>character table</u>. Thus from a completely arbitrary basis, a character table is born.