5.04 Principles of Inorganic Chemistry II
Fall 2008

Lecture 2: Operator Properties and Mathematical Groups

The **inverse** of A (defined as $(A)^{-1}$) is B if $A \cdot B = E$

For each of the five symmetry operations:

$(E)^{-1} = E \Rightarrow (E)^{-1} \cdot E = E \cdot E = E$

$(\sigma)^{-1} = \sigma \Rightarrow (\sigma)^{-1} \cdot \sigma = \sigma \cdot \sigma = E$

$(i)^{-1} = i \Rightarrow (i)^{-1} \cdot i = i \cdot i = E$

$(C_n^m)^{-1} = C_n^{n-m} \Rightarrow (C_n^m)^{-1} \cdot C_n^m = C_n^{n-m} \cdot C_n^m = C_n^n = E$

e.g. $(C_5^2)^{-1} = C_5^3$ since $C_5^2 \cdot C_5^3 = E$

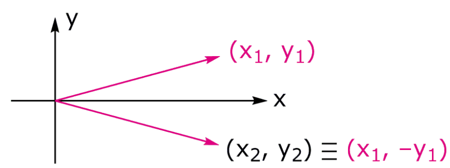
$(S_n^m)^{-1} = S_n^{n-m}$ (n even) $\Rightarrow (S_n^m)^{-1} \cdot S_n^m = S_n^{n-m} \cdot S_n^m = S_n^n = C_n^n \cdot \sigma_h^n = E$

$(S_n^m)^{-1} = S_n^{2n-m}$ (n odd) $\Rightarrow (S_n^m)^{-1} \cdot S_n^m = S_n^{2n-m} \cdot S_n^m = S_n^{2n} = C_n^{2n} \cdot \sigma_h^{2n} = E$

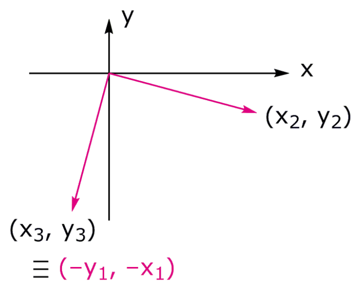
Two operators **commute** when $A \cdot B = B \cdot A$

Example: Do $C_4(z)$ and $\sigma(xz)$ commute?

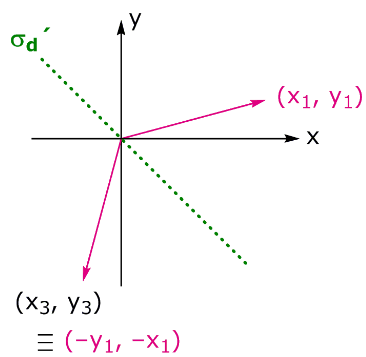
$C_4(z)\ \sigma(xz)(x_1, y_1, z_1)$



$C_4(z)(x_1, -y_1, z_1)$



σ_d'



z_1 does not change with σ_d'

$\therefore\ C_4(z)\sigma(xz) = \sigma_d'$

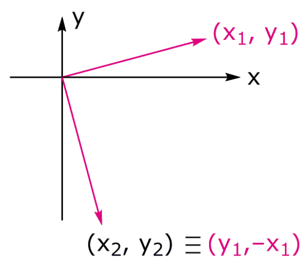
… or analyzing with matrix representations,

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

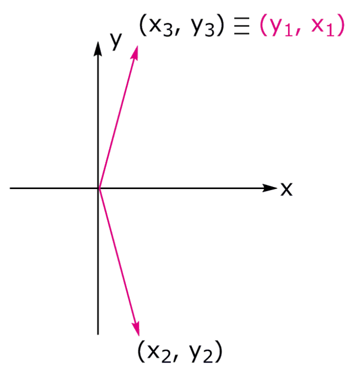
$$C_4(z) \cdot \sigma_{xz} = \sigma_d{'}$$

Now applying the operations in the inverse order,

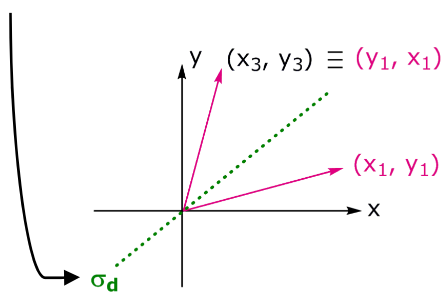
$\sigma(xz)\ C_4(z)(x_1, y_1, z_1)$



$\sigma(xz)(y_1, x_1, z_1)$



σ_d



$\therefore \quad \sigma(xz)C_4(z) = \sigma_d$

… or analyzing with matrix representations,

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

$$\sigma_{xz} \cdot C_4(z) = \sigma_d$$

$\therefore \quad C_4(z)\sigma(xz) = \sigma_d{'} \neq \sigma(xz)C_4(z) = \sigma_d$ ➡ so $C_4(z)$ does not commute with $\sigma(xz)$

A collection of operations are a mathematical group when the following conditions are met:

closure: all binary products must be members of the group

identity: a group must contain the identity operator

inverse: every operator must have an inverse

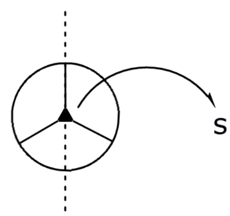
associativity: associative law of multiplication must hold

$(A \cdot B) \cdot C = A \cdot (B \cdot C)$

(note: commutation not required… groups in which all operators do commute are called **Abelian**)

Consider the operators C_3 and σ_v. These do not constitute a group because identity criterion is not satisfied. Do E, C_3, σ_v form a group? To address this question, a stereographic projection (featuring critical operators) will be used:

σ_v plane normal to paper

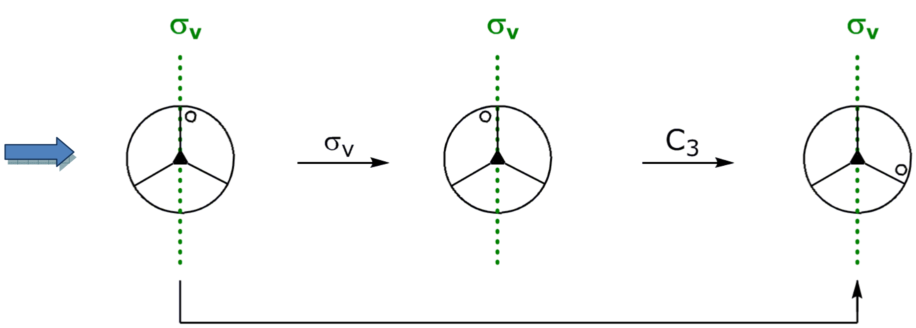


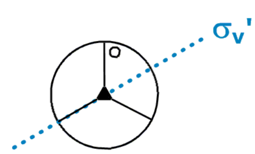
signifies C_3 (normal to paper)

So how about closure?

$C_3 \cdot C_3 = C_3^2$ (so C_3^2 needs to be included as part of the group)

$C_3 \cdot \sigma_v = ?$





$\therefore \quad C_3 \cdot \sigma_v = \sigma_v'$

Thus E, C_3 and σ_v are not closed and consequently these operators do not form a group. Is the addition of C_3^2 and σ_v' sufficient to define a group? In other terms, are there any other operators that are generated by C_3 and σ_v?
… the proper rotation axis, C_3:

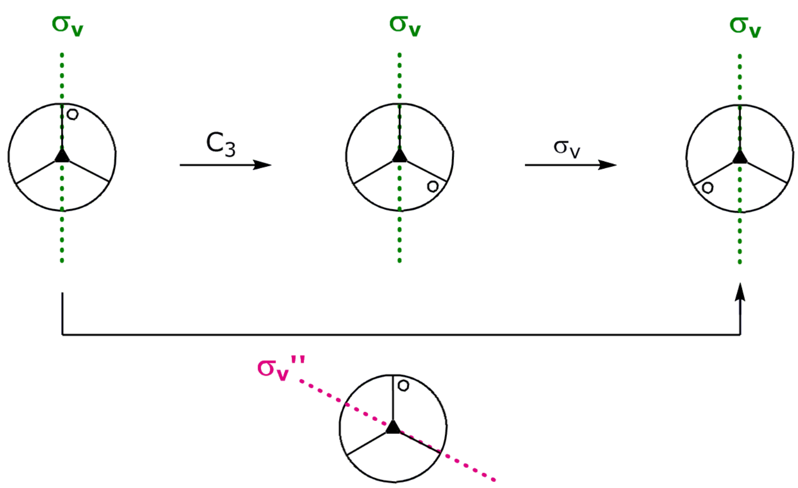
C_3
$C_3 \cdot C_3 = C_3^2$
$C_3 \cdot C_3 \cdot C_3 = C_3^2 \cdot C_3 = C_3 \cdot C_3^2 = E$
$C_3 \cdot C_3 \cdot C_3 \cdot C_3 = E \cdot C_3 = C_3$
etc.

$\therefore$ C_3 is the **generator** of E, C_3 and C_3^2 ➡ note: these three operators form a group

… for the plane of reflection, σ_v

σ_v
$\sigma_v \cdot \sigma_v = E$
$\sigma_v \cdot \sigma_v \cdot \sigma_v = E \cdot \sigma_v = \sigma_v$
etc.

So we obtain no new information here. But there is more information to be gained upon considering C_3 and σ_v. Have already seen that $C_3 \cdot \sigma_v = \sigma_v'$ … how about $\sigma_v \cdot C_3$?



$\therefore \quad C_3 \cdot \sigma_v = \sigma_v''$

Will discover that no new operators may be generated. Moreover one finds

	E^{-1}	C_3^{-1}	$(C_3^2)^{-1}$	σ_v^{-1}	$(\sigma_v')^{-1}$	$(\sigma_v'')^{-1}$
inverses	↓	↓	↓	↓	↓	↓
	E	C_3^2	C_3	σ_v	σ_v'	σ_v''

The above group is closed, i.e. it contains the identity operator and meets inverse and associativity conditions. Thus the above set of operators constitutes a mathematical group (note that the group is not Abelian).
Some definitions:

Operators C_3 and σ_v are called **generators** for the group since every element of the group can be expressed as a product of these operators (and their inverses).

The **order** of the group, designated h, is the number of elements. In the above example, h = 6.

Groups defined by a single generator are called **cyclic** groups.

Example: $C_3 \rightarrow E, C_3, C_3^2$

As mentioned above, E, C_3, and C_3^2 meet the conditions of a group; they form a cyclic group. Moreover these three operators are a **subgroup** of E, C_3, C_3^2, σ_v, σ_v',σ_v''. The order of a subgroup must be a divisor of the order of its parent group. (Example $h_{subgroup} = 3$, $h_{group} = 6$ … a divisor of 2.)

A **similarity transformation** is defined as: $v^{-1} \cdot A \cdot v = B$ where B is designated the similarity transform of A by x and A and B are **conjugates** of each other. A complete set of operators that are conjugates to one another is called a **class** 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

	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

may construct easily using stereographic projections

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

$C_3^{-1} \cdot C_3 \cdot C_3 = C_3^2 \cdot C_3 \cdot C_3 = E \cdot C_3 = C_3$

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

$\sigma_v^{-1} \cdot C_3 \cdot \sigma_v = \sigma_v \cdot C_3 \cdot \sigma_v = \sigma_v \cdot \sigma_v' = C_3^2$

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

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

$\therefore$ C_3 and C_3^2 from 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:

$$E, (C_3, C_3^2), (\sigma_v, \sigma_v', \sigma_v'')$$

Additional properties of transforms and classes are:

- no operator occurs in more than one class
- order of all classes must be integral factors of the group's order
- in an Abelian group, each operator is in a class by itself.