C734b: Symmetry and Chemical Applications

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Part I: Fundamentals of Group Theory

The Rules of the Game

Group: a collection of objects called elements which obey certain rules which interrelate them:

Rule 1: The product of any 2 elements in the group and the square of each element must be an element in the group.

Let the set of elements = $\{g_k\}$

When we say multiplication → $g_ig_j \equiv$ "carry out operation implied by g_j and then that implied by g_i". This is a right-to-left convention

∴ Rule 1 implies "closure"

for all g_i, g_j ε $\{g_k\}$, $g_ig_j = g_\ell$ where g_ℓ is a member of $\{g_k\}$

In group theory multiplication is not necessarily commutative; that is, $g_ig_j \neq g_jg_i$

However, if they do, the groups are called **Abelian** groups

Rule 2: One element in the group must commute with all others and leave them unchanged.
≡ identity element (designated by E)

$$\Rightarrow Eg_i = g_i E = g_i \quad \forall\ g_i \in \{g_k\}$$

Rule 3: The associative law of multiplication holds:

$$\Rightarrow g_i(g_j g_k) = (g_i g_j)g_k$$

This property holds for any continued product

For example:

$$\begin{aligned}&(g_A g_B)(g_C g_D)(g_E g_F)(g_G g_H)\\ &= g_A(g_B g_C)(g_D g_E)(g_F g_G)g_H\\ &= (g_A g_B)g_C(g_D g_E)g_F(g_G g_H)\\ &\text{etc.}\end{aligned}$$

Rule 4: Every element g_i must have an inverse or reciprocal, g_i^{-1} which is also an element of the group

$$g_i g_i^{-1} = g_i^{-1} g_i = E;\ \ g_i^{-1} \in \{g_k\} \forall\ g_i \in \{g_k\}$$

Group Multiplication Tables

The number of elements g in a group, G, is called the order of the group, say “h”.

$$\therefore G \equiv G(h)$$

This means there are h x h = h^2 possible products to completely and uniquely define a group, G (abstractly)

These can be presented in a **group multiplication table**.

Consists of h rows and h columns. Each row and column is labelled by a group element.

Each entry in table under a given column and along a row = product of elements heading the column and row.

$$\because\ g_i g_j \neq g_j g_i \text{ necessarily}$$

Take as convention: product = (column element) x (row element)

Rearrangement Theorem

Each row and column in a group multiplication table lists each group element once and only once

$\Longrightarrow$ No two rows or columns may be identical

$\Longrightarrow$ Each row and column is a rearranged list of group elements

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For example:

$$\begin{array}{c|cc} G(2) & E & A \\ \hline E & EE & AE \\ A & EA & AA \end{array} \qquad \equiv \begin{array}{c|cc} G(2) & E & A \\ \hline E & E & A \\ A & A & E \end{array}$$

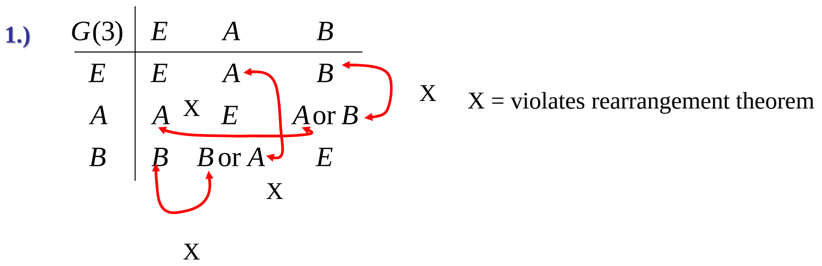
Note: A = A^{-1} since AA = E (Rule 4)

Another example:

$$\begin{array}{c|ccc} G(3) & E & A & B \\ \hline E & E & A & B \\ A & A & AA & BA \\ B & B & AB & BB \end{array} \begin{array}{l} \\ \leftarrow \text{rule 2} \\ \\ \\ \end{array}$$

↑
rule 2

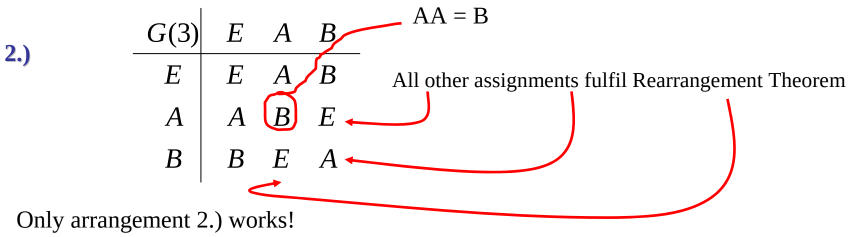
There are limited choices here:
Either 1.) AA = E or 2.) AA = B



1.)

$G(3)$	E	A	B
E	E	A	B
A	A	E	A or B
B	B	B or A	E

X = violates rearrangement theorem



2.)

$G(3)$	E	A	B
E	E	A	B
A	A	B	E
B	B	E	A

AA = B

All other assignments fulfil Rearrangement Theorem

Only arrangement 2.) works!

Cyclic Groups

G(3) is the simplest nontrivial example of a cyclic group.

If a sequence $g_1, g_1^2, g_1^3 \ldots$ repeats itself at $g_1^{h+1} = g_1$ because $g_1^h = E$, then the set $\{g_1, g_1^2, \ldots, g_1^h = E\}$ which is the period of the group is the cyclic group C of order h; that is, C(h).

Note: for G(3) the period is:

{A, AA, AAA} ≡ {A, B, BA} = {A, B, E}

∴ G(3) ≡ cyclic group C(3)

Properties of Cyclic Groups

1.) Such groups are Abelian since group elements of the form $g_1^M g_1^N = g_1^N g_1^M$ for all M, N.

2.) For a finite cyclic group the existence of the inverse of every group element is guaranteed.

$$\because\ g_1^h = E \Rightarrow g_1^1 g_1^{h-1} = E$$

$$\Rightarrow g_1^{h-1} = g_1^{-1}$$

True for all elements $\{g_k\}$ since g_1 was not specified

Example: $\omega = e^{-\frac{2\pi i}{n}}$ generates a cyclic group of order n.

Why? $\omega^n = e^{-2\pi i} = \cos(2\pi) - i\sin(2\pi)$ = 1- 0 =1 =E

$\therefore \left\{\omega, \omega^2, \omega^3, \cdots, \omega^n\right\}$ is a cyclic group of period n.

If every element of a group can be expressed as a finite product of powers of elements in a particular sub-set, the elements in this sub-set are called the **group generators**.

For example: if the group generators are $\{g_1, g_2\}$ then

$G_i = (g_1)^p(g_2)^q$

For a cyclic group, the group generator is one element, g_1.

Example: Permutation Group S(3)

A permutation operator P rearranges a set of objects.

If for example P{a, b, c, …} = {b, a, c,…}

This means that P ≡ operator which interchanges a and b.

Important:
P_{ij} means “interchange objects **CURRENTLY** at the locations **ORGINALLY** occupied by objects i and j.

Means can consider the original configuration as objects allocated to certain boxes (like electrons in orbitals).

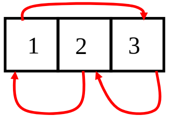
∴ P_{ij} means “interchange the contents of the ith and jth box, whatever they currently happen to be”.

Consider 3 objects.
The number of permutations is 3! = 3x2x1 = 6.

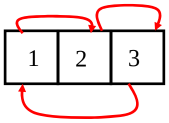
$P_0 \equiv E$ ∴ if [1 | 2 | 3]

P_0 [1 | 2 | 3] ≡ [1 | 2 | 3] = original configuration

Let P_1 and P_2 correspond to the two cyclic permutations:

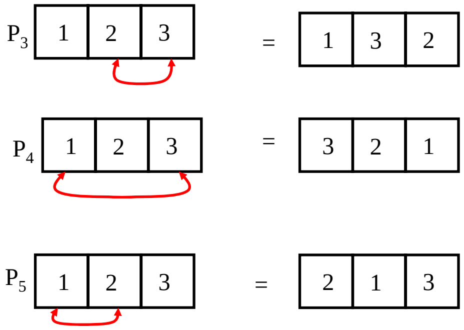


P_1 [1 | 2 | 3] = [2 | 3 | 1]



P_2 [1 | 2 | 3] = [3 | 1 | 2]

Let P_3, P_4 and P_5 correspond to the 3 binary interchanges:

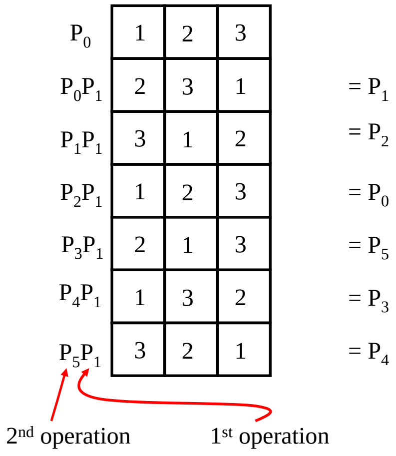


P_3	1	2	3	=	1	3	2
P_4	1	2	3	=	3	2	1
P_5	1	2	3	=	2	1	3

$\{P_0, P_1, P_2, P_3, P_4, P_5\}$ constitute a group: S(3)

If so all binary products will be elements of S(3)

Example: Binary products with P_1:



P_0	1	2	3	
P_0P_1	2	3	1	$= P_1$
P_1P_1	3	1	2	$= P_2$
P_2P_1	1	2	3	$= P_0$
P_3P_1	2	1	3	$= P_5$
P_4P_1	1	3	2	$= P_3$
P_5P_1	3	2	1	$= P_4$

2nd operation

1st operation

= one row or one column as required by Rearrangement Theorem.

In this way one can construct the entire multiplication table.

Multiplication Table for the S(3) permutation group

$S(3)$	P_0	P_1	P_2	P_3	P_4	P_5
P_0	P_0	P_1	P_2	P_3	P_4	P_5
P_1	P_1	P_2	P_0	P_5	P_3	P_4
P_2	P_2	P_0	P_1	P_4	P_5	P_3
P_3	P_3	P_4	P_5	P_0	P_1	P_2
P_4	P_4	P_5	P_3	P_2	P_0	P_1
P_5	P_5	P_3	P_4	P_1	P_2	P_0

Conjugate Elements and Classes

Elements can be separated into smaller sets called **classes** using a **similarity transformation**

If $g_i, g_j, g_k \in G$ and $g_i^{-1} g_i g_j = g_k$

then g_k is the **transform** of g_j and g_j and g_k are conjugate elements

The complete set of elements conjugate to g_i form a **class**.
The number of elements in a class is called the **order** of the class (≡ integral factor of h)

i) Every element is conjugate with itself.
True if there is at least one element X such that:

$$g_i = X^{-1} g_i X \quad \text{for any } g_i \in \{g_k\}$$

Works if X = E

ii) If an element A is conjugate with B, then B is conjugate with A

If $$A = X^{-1}BX$$

$$\Rightarrow \exists Y \ni B = Y^{-1}AY$$

$$A = X^{-1}BX \quad \therefore XAX^{-1} = XX^{-1}BXX^{-1} = B$$

If $$Y = X^{-1} \quad \Rightarrow XAX^{-1} = Y^{-1}AY = B$$

This is possible since any element, say X, must have an inverse, say Y.

iii) If A is conjugate to B and C then B and C are conjugate of each other.

If $$A = X^{-1}BX \quad \text{and} \quad A = Y^{-1}CY$$

where {Y, X} are elements of G.

$$\Rightarrow X^{-1}BX = Y^{-1}CY$$

$$\therefore C = \left(YX^{-1}\right)B\left(XY^{-1}\right) \quad \text{or} \quad B = \left(XY^{-1}\right)C\left(YX^{-1}\right)$$

but $$\left\{X^{-1}, Y^{-1}, YX^{-1}, XY^{-1}\right\} \in G$$

Let $$YX^{-1} = Z^{-1} \quad \text{and} \quad XY^{-1} = Z$$

$$\therefore C = Z^{-1}BZ$$

Therefore C is conjugate to B and vice-versa

Example: Use multiplication table for S(3) to find elements which are conjugate with P_1

row

$P_0^{-1}P_1P_0 \quad = P_0^{-1}P_1 \quad = P_0P_1 \quad = P_1$

col. read off table

Similarly:

$P_1^{-1}P_1P_1 = P_1^{-1}P_2 = P_2P_2 = P_1$

$P_2^{-1}P_1P_2 = P_2^{-1}P_0 = P_1P_0 = P_1$

$P_3^{-1}P_1P_3 = P_3^{-1}P_5 = P_3P_5 = P_2$

$P_4^{-1}P_1P_4 = P_4^{-1}P_3 = P_4P_3 = P_2$

$P_5^{-1}P_1P_5 = P_5^{-1}P_4 = P_5P_4 = P_2$

$\Rightarrow \quad \{P_1, P_2\}$ form a class

Physical meaning of classes

The operation $B = X^{-1}AX$ is the net operation obtained by first rotating object to some equivalent position X, next carrying out the operation A, then undoing the initial rotation by X^{-1}.

Thus, B is the same physical operation as A (such as a rotation through some angle) but performed about some different but physically an equivalent axis which is related to the axis of A by group operation X^{-1}

Subgroups

A subset H of G contained within G that is itself a group with the same laws of binary composition is a **subgroup** of G

Note: in S(3), $\{P_0, P_1, P_2\}$ satisfies closure and is therefore a subgroup.

E is always a trivial subgroup of order 1.

Some groups have no subgroups other than E; some have more than one.

Restriction:
The order of any subgroup h, of a group of order g must be a divisor (factor) of g

that is, g/h = k where k is an integer.

Proof:

Let sub group = $\{A_1, A_2, A_3, \ldots, A_h\}$ (order = h).

Take an element B which is a member of G but not in $\{A_1, A_2, A_3, \ldots, A_h\}$

Form h products of B with the subgroup elements.

$= \{BA_1, BA_2, BA_3, \ldots, Ba_h\}$

These products are **not** in the subgroup

For example: if $BA_2 = A_4$ and $A_5 = A_4^{-1}$

$\Rightarrow \quad BA_2A_5 = A_4A_5 = BE = B$

This is impossible since B is not a member of the subgroup.

Therefore, $\{A_1, A_2, \ldots, A_h\}$ and $\{BA_1, BA_2, \ldots, BA_h\}$ form a larger group of at least 2h members.

If $g > 2h$ choose a different element C which is a member of G but not $\{A_1, A_2, \ldots, A_h\}$ or $\{BA_1, BA_2, \ldots, BA_h\}$

$\Rightarrow$ g must be ≥ 3h

Repeat this k times until there are no more elements which are different from $\{A_i\}$, $\{BA_i\}$, $\{CA_i\}$ etc.

Then $g = kh$ where k is an integer

$\therefore \quad g/h = k$

However, it does not follow that for a given group that there are subgroups of all orders which are divisors of g.
Furthermore there can more than one subgroup of a given order.

Question: Can groups as a whole be multiplied?

Answer is yes.

Direct Products

Suppose $A = \{a_i\}$ and $B = \{b_j\}$ are two groups of order a and b, respectively.

If $a_i b_j = b_j a_i \quad \forall a_i \in A, \forall b_j \in B$

the direct product $G = A \otimes B$

is a also a group of order ab with elements $a_i b_j = b_j a_i$, $i = 1, \ldots, a$; $j = 1, \ldots, b$

Example:

$A = \{a_1, a_2\}$ $\qquad B = \{b_1, b_2, b_3\}$

$G = A \otimes B = \{a_1B, a_2B\}$ or $\{Ba_1, Ba_2\}$

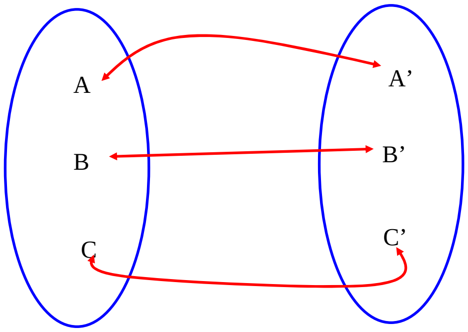
$= \{a_1b_1, a_1b_2, a_1b_3, a_2b_1, a_2b_2, a_2b_3\}$ Order = 2x3 =6

More on direct products later. They're important!

Two important terms in group theory are isomorphic and homomorphic

Two groups are isomorphic if there is a one-to-one correspondence between the elements of the two groups

Isomorphic mapping:



Isomorphic implies if AB = C then A’B’ = C’
Both groups have the same multiplication table except perhaps for a change in symbols or in the meaning of the operations

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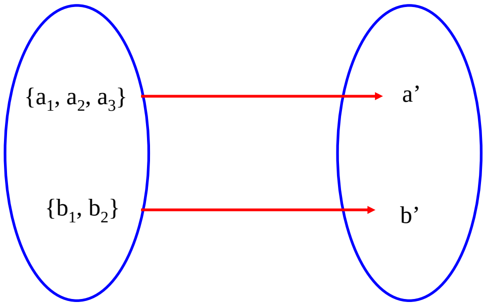
Two groups are homomorphic if there is a many-to-one relationship between some of the elements of the group



The structure of the two homomorphic groups are no longer identical but multiplication rules are preserved

This will be seen when discussing **Character Tables**.