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# Pólya's Isomer Enumeration Method: A Unique Exercise in Group Theory and Combinatorial Analysis for Undergraduates

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George Pólya (1887–1985) was a celebrated mathematician who made major contributions to many fields of mathematics (*1*). He authored one of the best problem-solving texts for undergraduates, *How to Solve It: A New Aspect of Mathematical Method*, which has been translated into 17 languages and has sold more than a million copies (*2*). To chemists, he is best known for his enumeration theorem that combines elements of group theory with combinatorial analysis (*3*). When applied to chemistry, this theorem can be used to elucidate the number of isomers for a multitude of substitutions on a molecular framework (e.g., determine the number of possible fluorinated benzene derivatives, $C_6H_{6-x}F_x$). Research scientists have used this enumeration method not only to determine the number of possible isomers for a molecule (*4*) but also to solve problems in NMR spectroscopy (*5*–*7*) and crystallography (*8*). Several reviews demonstrating the isomer enumeration method (IEM) have appeared in the chemical literature (*4*, *9*–*12*). Several articles on isomer enumeration—mainly counting the total isomers of substituted coordination complexes (*13*, *14*) and porphines (*15*, *16*)—have appeared in this *Journal* over the years, though none explicitly cited the works of Pólya.

Pólya's method relies heavily on the tracking of atomic position changes upon application of symmetry operations (*17*). For example, if the six hydrogens in benzene were labeled *a* through *f* clockwise around the benzene ring, then application of a $C_6$ clockwise rotation would permute hydrogen atom *a* onto the old position of hydrogen atom *b*, permute hydrogen atom *b* onto hydrogen atom *c*, and so on. The derivation of permutation groupings is one underlying concept in the foundation of group theory. In Pólya's IEM, permutation groupings for every symmetry element in the point group of the molecule are found. The mathematics of combinatorial analysis is then used to extract a polynomial expression from the permutation groupings to yield the total number of isomers per substitution. This article demonstrates the use of IEM as an additional group theory exercise in an undergraduate chemistry course.

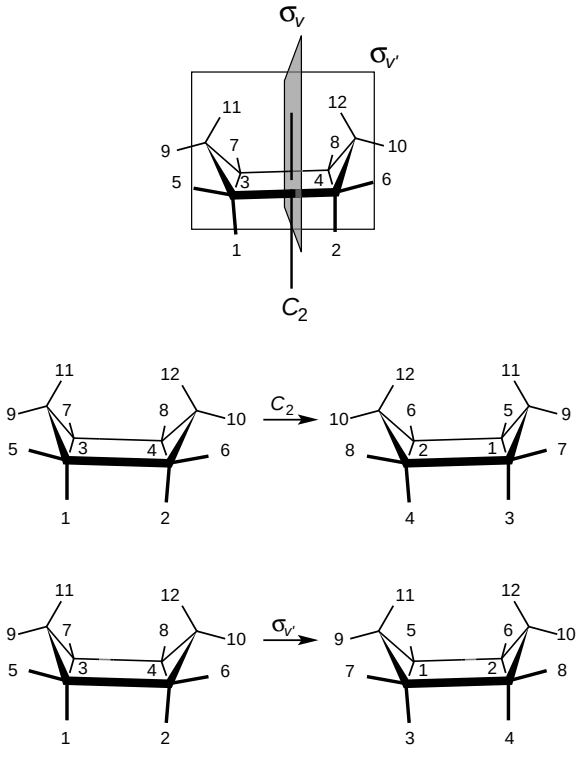


Figure 1. Above: The symmetry elements in the boat form of cyclohexane ($C_{2v}$). Below: Interchange of hydrogen atoms upon application of $C_2$ and $\sigma_v'$ symmetry operations.

## Statement of the Problem

How many total deuterated isomers of boat and chair cyclohexane, $C_6H_{12-x}D_x$, exist? The stated problem can be solved with Pólya's IEM. The detailed solution for boat cyclohexane is given below, and the results for chair cyclohexane are given at the end of the article with the full solution intended as a supplemental exercise.

## Solution for Boat Cyclohexane

The first step in the IEM is assigning the point group for boat cyclohexane. The boat conformation belongs to $C_{2v}$ point group that contains four symmetry elements $E$, $C_2$, $\sigma_v$, and $\sigma_v'$.

The next step involves determination of the cycle index for each symmetry operation within the assigned point group (*4*). Upon application of each symmetry element in $C_{2v}$, the hydrogen atoms in boat cyclohexane interchange. By mapping the change of atomic positions (called a vertex interchange), permutation groupings can be formed. For example, the vertex interchanges for $C_2$ and $\sigma_v'$ operations are depicted in Figure 1. The cycle index is a symbolic expression written in terms of $f_n^m$ where $m$ is the number of the cycles in the permutation grouping and $n$ is the length of the cycle. For the $C_2$ axis, the cycle index is $f_2^6$ because there are six cycles of length two. Table 1 summarizes the vertex interchanges, permutation groupings, and cycle indices for all $C_{2v}$ symmetry elements in boat cyclohexane. The molecule's cycle index, $Z$, is equal to the sum of cycle indices of symmetry operations divided by the order of the point group. Therefore, the cycle index of boat cyclohexane is equal to the sum of the cycle indices for all sym-

metry operations in $C_{2v}$ divided by 4. This is shown in eq 1.

$$Z(\text{boat–}C_6H_{12}) = \tfrac{1}{4}(f_1^{12} + 2f_2^6 + f_1^4 f_2^4) \quad (1)$$

The above expression, however, tells us nothing of isomers. The next step in IEM is to substitute each cycle index in eq 1 with the polynomial expression $f_n^m = (1 + x^n)^m$. The equation that results from this substitution is eq 2.

$$Z(\text{boat-}C_6H_{12}) = \tfrac{1}{4}[(1 + x)^{12} + 2(1 + x^2)^6 + (1 + x^4)(1 + x^2)^4] \quad (2)$$

The last step in IEM is the expansion of the polynomial in eq 2. The polynomial can be expanded by hand (without the aid of a computer) and it is a good exercise for students—requiring time and patience. Otherwise, expansion of polynomials is easily carried out in software programs such as *Mathematica* or *Maple*. For boat cyclohexane the expanded polynomial is given in eq 3.

$$Z(\text{boat–}C_6H_{12}) = 1 + 4x^1 + 22x^2 + 60x^3 + 139x^4 + 208x^5 + 252x^6 + 208x^7 + 139x^8 + 60x^9 + 22x^{10} + 4x^{11} + x^{12} \quad (3)$$

This polynomial yields much information! The power of $x$ indicates the number of substituted deuteriums and the coefficient of $x$ gives the number of isomers for that number of substitutions. Therefore there is only 1 isomer in which no deuteriums are present, yet there are 4 isomers with one sub-

**Table 1. Demonstration of IEM for Boat Cyclohexane**

| Symmetry Element | Vertex Interchange | Permutation Grouping | Cycle Index | Polynomial |
|---|---|---|---|---|
| $E$ | $\begin{pmatrix}1&2&3&4&5&6&7&8&9&10&11&12\\1&2&3&4&5&6&7&8&9&10&11&12\end{pmatrix}$ | $\begin{pmatrix}1\\1\end{pmatrix}\begin{pmatrix}2\\2\end{pmatrix}\begin{pmatrix}3\\3\end{pmatrix}\begin{pmatrix}4\\4\end{pmatrix}\begin{pmatrix}5\\5\end{pmatrix}\begin{pmatrix}6\\6\end{pmatrix}\begin{pmatrix}7\\7\end{pmatrix}\begin{pmatrix}8\\8\end{pmatrix}\begin{pmatrix}9\\9\end{pmatrix}\begin{pmatrix}10\\10\end{pmatrix}\begin{pmatrix}11\\11\end{pmatrix}\begin{pmatrix}12\\12\end{pmatrix}$ | $f_1^{12}$ | $(1 + x)^{12}$ |
| $C_2$ | $\begin{pmatrix}1&2&3&4&5&6&7&8&9&10&11&12\\4&3&2&1&8&7&6&5&10&9&12&11\end{pmatrix}$ | $\begin{pmatrix}1&4\\4&1\end{pmatrix}\begin{pmatrix}2&3\\3&2\end{pmatrix}\begin{pmatrix}5&8\\8&5\end{pmatrix}\begin{pmatrix}6&7\\7&6\end{pmatrix}\begin{pmatrix}9&10\\10&9\end{pmatrix}\begin{pmatrix}11&12\\12&11\end{pmatrix}$ | $f_2^6$ | $(1 + x^2)^6$ |
| $\sigma_v$ | $\begin{pmatrix}1&2&3&4&5&6&7&8&9&10&11&12\\2&1&4&3&6&5&8&7&10&9&12&11\end{pmatrix}$ | $\begin{pmatrix}1&2\\2&1\end{pmatrix}\begin{pmatrix}3&4\\4&3\end{pmatrix}\begin{pmatrix}5&6\\6&5\end{pmatrix}\begin{pmatrix}7&8\\8&7\end{pmatrix}\begin{pmatrix}9&10\\10&9\end{pmatrix}\begin{pmatrix}11&12\\12&11\end{pmatrix}$ | $f_2^6$ | $(1 + x^2)^6$ |
| $\sigma_v'$ | $\begin{pmatrix}1&2&3&4&5&6&7&8&9&10&11&12\\3&4&1&2&7&8&5&6&9&10&11&12\end{pmatrix}$ | $\begin{pmatrix}1&3\\3&1\end{pmatrix}\begin{pmatrix}2&4\\4&2\end{pmatrix}\begin{pmatrix}5&7\\7&5\end{pmatrix}\begin{pmatrix}6&8\\8&6\end{pmatrix}\begin{pmatrix}9\\9\end{pmatrix}\begin{pmatrix}10\\10\end{pmatrix}\begin{pmatrix}11\\11\end{pmatrix}\begin{pmatrix}12\\12\end{pmatrix}$ | $f_1^4 f_2^4$ | $(1 + x)^4(1 + x^2)^4$ |

NOTE: Table layout modeled after Rouvay (*4*).

**Table 2. Demonstration of IEM for Chair Cyclohexane**

| Symmetry Element[a] | Vertex Interchange | Permutation Grouping | Cycle Index | Polynomial |
|---|---|---|---|---|
| $E$ | $\begin{pmatrix}1&2&3&4&5&6&7&8&9&10&11&12\\1&2&3&4&5&6&7&8&9&10&11&12\end{pmatrix}$ | $\begin{pmatrix}1\\1\end{pmatrix}\begin{pmatrix}2\\2\end{pmatrix}\begin{pmatrix}3\\3\end{pmatrix}\begin{pmatrix}4\\4\end{pmatrix}\begin{pmatrix}5\\5\end{pmatrix}\begin{pmatrix}6\\6\end{pmatrix}\begin{pmatrix}7\\7\end{pmatrix}\begin{pmatrix}8\\8\end{pmatrix}\begin{pmatrix}9\\9\end{pmatrix}\begin{pmatrix}10\\10\end{pmatrix}\begin{pmatrix}11\\11\end{pmatrix}\begin{pmatrix}12\\12\end{pmatrix}$ | $f_1^{12}$ | $(1 + x)^{12}$ |
| (2)$C_3$ | $\begin{pmatrix}1&2&3&4&5&6&7&8&9&10&11&12\\3&1&2&6&4&5&10&7&12&8&9&11\end{pmatrix}$ | $\begin{pmatrix}1&2&3\\3&1&2\end{pmatrix}\begin{pmatrix}4&5&6\\6&4&5\end{pmatrix}\begin{pmatrix}7&8&9\\10&7&8\end{pmatrix}\begin{pmatrix}10&11&12\\12&9&11\end{pmatrix}$ | $f_3^4$ | (2)*$(1 + x^3)^4$ |
| (3)$C_2'$ | $\begin{pmatrix}1&2&3&4&5&6&7&8&9&10&11&12\\4&6&5&1&3&2&11&9&8&12&7&10\end{pmatrix}$ | $\begin{pmatrix}1&4\\4&1\end{pmatrix}\begin{pmatrix}2&6\\6&2\end{pmatrix}\begin{pmatrix}3&5\\5&3\end{pmatrix}\begin{pmatrix}7&11\\11&7\end{pmatrix}\begin{pmatrix}8&9\\9&8\end{pmatrix}\begin{pmatrix}10&12\\12&10\end{pmatrix}$ | $f_2^6$ | (3)*$(1 + x^2)^6$ |
| (3)$\sigma_d$ | $\begin{pmatrix}1&2&3&4&5&6&7&8&9&10&11&12\\3&2&1&5&4&6&10&8&9&7&12&11\end{pmatrix}$ | $\begin{pmatrix}1&3\\3&1\end{pmatrix}\begin{pmatrix}4&5\\5&4\end{pmatrix}\begin{pmatrix}7&10\\10&7\end{pmatrix}\begin{pmatrix}11&12\\12&11\end{pmatrix}\begin{pmatrix}2\\2\end{pmatrix}\begin{pmatrix}6\\6\end{pmatrix}\begin{pmatrix}8\\8\end{pmatrix}\begin{pmatrix}9\\9\end{pmatrix}$ | $f_1^4 f_2^4$ | (3)*$(1 + x)^4(1 + x^2)^4$ |
| $i$ | $\begin{pmatrix}1&2&3&4&5&6&7&8&9&10&11&12\\5&6&4&3&1&2&12&9&8&11&10&7\end{pmatrix}$ | $\begin{pmatrix}1&5\\5&1\end{pmatrix}\begin{pmatrix}2&6\\6&2\end{pmatrix}\begin{pmatrix}3&4\\4&3\end{pmatrix}\begin{pmatrix}7&12\\12&7\end{pmatrix}\begin{pmatrix}8&9\\9&8\end{pmatrix}\begin{pmatrix}10&11\\11&10\end{pmatrix}$ | $f_2^6$ | $(1 + x^2)^6$ |
| (2)$S_6$ | $\begin{pmatrix}1&2&3&4&5&6&7&8&9&10&11&12\\4&5&6&2&3&1&11&12&7&9&8&10\end{pmatrix}$ | $\begin{pmatrix}1&2&3&4&5&6\\4&5&6&2&3&1\end{pmatrix}\begin{pmatrix}8&9&10&11&12\\12&7&9&8&10\end{pmatrix}$ | $f_6^2$ | (2)*$(1 + x^6)^2$ |

NOTE: Table layout modeled after Rouvay (*4*).
[a]Number in parentheses before the symmetry element represents the number of that element type.

stituted deuterium, 22 with two substituted deuteriums, 60 with three substituted deuteriums, etc., for a total of 1119 possible deuterated isomers of boat cyclohexane!

Using the same methodology for chair cyclohexane ($D_{3d}$) one could arrive at the eqs 4, 5, and 6 (Table 2).

$$Z(\text{chair–}C_6H_{12}) = {}^1\!/_{12}(f_1^{12} + 2f_3^4 + 4f_2^6 + 2f_6^2 + 3f_1^4f_2^4) \quad (4)$$

$$Z(\text{chair–}C_6H_{12}) = {}^1\!/_{12}[(1+x)^{12} + 2(1+x^3)^4 + 4(1+x^2)^6 + 2(1+x^6)^2 + 3(1+x)^4(1+x^2)^4] \quad (5)$$

$$Z(\text{chair–}C_6H_{12}) = 1 + 2x^1 + 10x^2 + 24x^3 + 54x^4 + 76x^5 + 96x^6 + 76x^7 + 54x^8 + 24x^9 + 10x^{10} + 2x^{11} + x^{12} \quad (6)$$

As can be seen by inspection of eq 6, there are only 429 possible isomers for the more symmetric chair form.

## Summary

Pólya's isomer enumeration method is an elegant and powerful example of mathematics in chemistry. This method can be used as an additional source of class material beyond what is covered in traditional chemistry group theory texts. We would like to note that a common student error is determining an incorrect permutation grouping for a symmetry operation. This mistake is easily spotted since it results in an expanded polynomial with fractional coefficients. Students must be advised to carefully reexamine the permutation groupings (or interchange of atoms) for each symmetry operation.

## Literature Cited


1. Schiffer, M. M. *Math. Mag.* **1987,** *60*, 268–270. This entire issue is dedicated to Pólya and his work.
2. Pólya, G. *How to Solve It: A New Aspect of Mathematical Method*, 2nd ed.; Princeton University Press: Princeton, NJ, 1973.
3. Pólya, G. *Z. Kristallogr.* **1936,** *93*, 415–443.
4. Several examples can be found in Rouvray, D. H. *Chem. Soc. Rev*. **1974,** *3*, 355–372, and references therein. In this paper, we use the terminology of Rouvay.
5. Crundwell, G. A.; Cowans, B. A.; Hopkins, J. A.; Grutzner, J. B.; Kahr, B. *J. Solid State Chem.* **1999,** *145*, 327–335.
6. Balasubramanian, K. *Chem. Rev*. **1985,** *85*, 599–618.
7. Balasubramanian, K. *J. Chem. Phys*. **1980,** *73*, 3321–3337.
8. Moore, P. M.; Araki, T. *Am. Min.* **1976,** *61*, 74–87.
9. Cyvin, B.; Cyvin, S. *Chem. Intel*. **1999,** *5*, 50–54.
10. McDaniel, D. H. *Inorg. Chem*. **1972,** *11*, 2678–2682.
11. Kennedy, B. A; McQuarrie, D. A.; Brubaker, C. H. Jr. *Inorg. Chem*. **1964,** *3*, 265–268.
12. Hill, T. L. *J. Chem. Phys.* **1943,** *11*, 294–297.
13. Trimble, R. F. Jr. *J. Chem. Educ*. **1954,** *31*, 176–179.
14. Bailar, J. C. Jr. *J. Chem. Educ*. **1957,** *34*, 334–338.
15. Blackman, D. *J. Chem. Educ*. **1973,** *50*, 258–259.
16. Pilgrim, R. L. C. *J. Chem. Educ*. **1974,** *51*, 316–318.
17. The application of IEM to boat cyclohexane requires a basic understanding of Group Theory. There are many excellent introductory Group Theory textbooks for undergraduates. At Central Connecticut State University, we currently use the text by Carter, R. L. *Molecular Symmetry and Group Theory*; Wiley: New York, 1998.