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The Enumeration of Reaction Pathways Using Burnside's Lemma

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Formulas are given for the number and statistical weights of reaction pathways from one molecular conformation to another via a given transition state. Arbitrary mechanistic assumptions can be incorporated into this enumeration. These formulas arise as straightforward generalizations of an expression for the number of double cosets in any group, which can be proven in one line using Burnside's lemma.

Key words: Combinatorics – Reaction pathways – Burnside's lemma – Double cosets.

The systematic enumeration of rearrangement pathways has traditionally been carried out using one of two general classes of counting procedures: those arising from Burnside's lemma and Pólya's theorem [1–7] and those arising from the double coset formalism [8, 9]. The purpose of this note is to show that these two methods are intimately related in that Burnside's lemma can be used to provide simple proofs of several formulas for the numbers of double cosets, and that this relationship can be exploited to generalize rearrangement counting formulas to count reactions through a given transition state employing a given mechanism. A particularly appealing feature of this use of Burnside's lemma is that all the enumeration formulas so produced have a striking formal similarity.

Of course, the particular concentration here on enumeration of reaction pathways is not meant to obscure the considerable body of literature on other combinatorial problems in chemistry, of which references [10–16] provide a small sampling.

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Let Γ be a finite group permuting the elements of a finite set S. Define an equivalence relation, $\sim$, on S by letting $s_1 \sim s_2$ if and only if for some $\gamma \in \Gamma$, $\gamma s_1 = s_2$. Let Ω be the set of equivalence classes, called Γ-orbits. Then Burnside's lemma says that the number of equivalence classes is given by the formula $|\Omega| = \sum_{\gamma \in \Gamma} |\{s \in S: \gamma s = s\}|$, where for any set X, $|X|$ denotes the number of elements of X. This can also be written as $|\Omega| = \sum_{\gamma \in \Gamma} \sum_{s \in S} \chi(\gamma s = s)$, where χ (statement) = 1 if the statement is true, and 0 otherwise. Burnside's lemma is extremely important in combinatorics generally; Pólya's theorem and its many generalizations are special cases of this result. Proofs of Burnside's lemma (which are extremely simple) can be found in references [17–20], and references [21, 22] present reviews of the use of this and related theorems in the enumeration both of isomers and of crystal structures.

Now let G be any finite group, and let A and B be subgroups of G. If $g \in G$, the set $AgB = \{agb: a \in A \text{ and } b \in B\}$ is called a double coset. It is easy to prove that if $g, h \in G$ then either $AgB = AhB$ or $AhB \cap AgB = \emptyset$. Unlike ordinary cosets, however, disjoint double cosets need not have the same number of elements. Ruch et al. [8] have shown that the number, z, of double cosets is given by

$$z = \frac{|G|}{|A||B|} \sum_{C_r} \frac{|A \cap C_r||B \cap C_r|}{|C_r|} \tag{1}$$

where the sum runs over all conjugacy classes C_r in G. In this formula, A and C_r are both subsets of G, and $|A \cap C_r|$ is the number of elements of G contained in both A and C_r. They also showed that if A and B are the permutation groups induced by the point groups of the n atoms in a molecule in the initial and final states of some reaction, and if G is the symmetric group $\mathscr{S}_n$ of all $n!$ permutations of these atoms, then z counts the polytopal rearrangements between these 2 states.

We wish first to show that Eq. (1) can be obtained from Burnside's lemma in a one-line argument. To do this, regard the direct product $A \times B$ as a permutation group on the set G with the action $(a, b)g = agb^{-1}$. Under this action, $(A \times B)g = \{agb: a \in A, b \in B\} = AgB$, so the $A \times B$-orbits are exactly the double cosets. By Burnside's lemma, these are counted by

$$\begin{aligned} z &= |A \times B|^{-1} \sum_{a,b,g} \chi(agb^{-1} = g) = |A|^{-1}|B|^{-1} \sum_{a,b,g} \chi(g^{-1}ag = b) \\ &= |A|^{-1}|B|^{-1} \sum_{a,b,C_r} \chi(a \in C_r)\chi(b \in C_r) \frac{|G|}{|C_r|} \\ &= \frac{|G|}{|A||B|} \sum_{C_r} \frac{|A \cap C_r||B \cap C_r|}{|C_r|} \end{aligned}$$

where C_r runs over the conjugacy classes of G. The third equality in this argument arises because $g^{-1}ag$ can equal b only if a and b lie in the same conjugacy class, and because if a and b both lie in C_r, then the number of $g \in G$ such that $g^{-1}ag = b$ is $|G|/|C_r|$. The alternative proof of Eq. (1) given in [8] is significantly more complex.

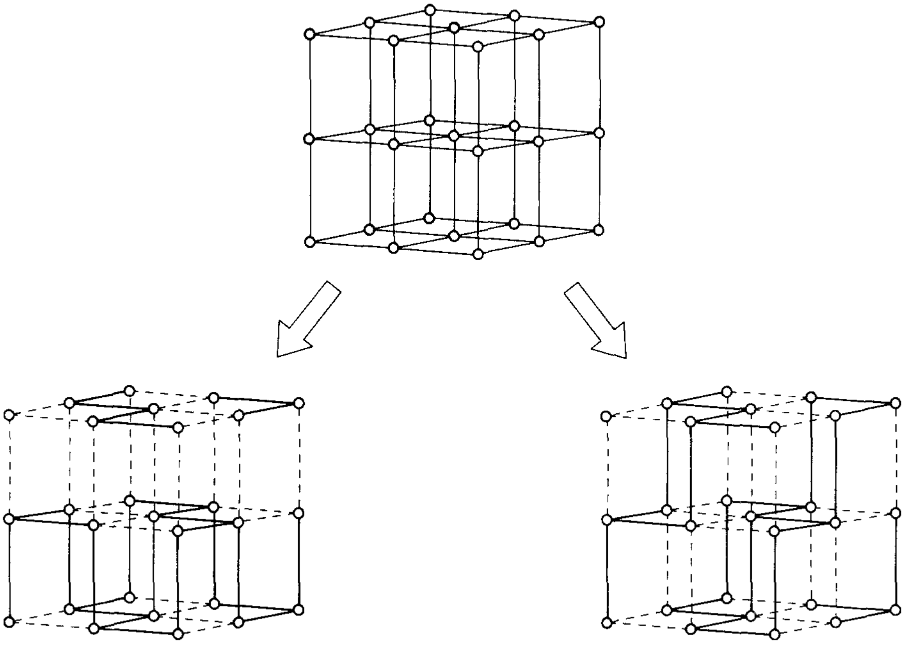

Fig. 1. The derivation of the structures of black P (lower left) and As (lower right) from the simple cubic structure (top). Heavy lines in the structures of black P and As represent bonded contacts which are shortened with respect to the dashed lines (nonbonded contacts)

Arguments like this one can easily be used to prove other formulas arising from the double coset formalism. For example, formula (4a) of [9], stated there without proof, follows from a one line argument even simpler than that above.

We now consider a chemical problem involving the enumeration of reaction pathways in solid state reactions, which can be resolved using a generalization of Eq. (1). Molecular examples will be addressed subsequently.

As shown in Fig. 1, the structures of black P and As can both be derived from the simple cubic structure by a bond-breaking process [23, 24]. Phosphorus itself is known to occur in all these structures, transforming with increasing pressure in the order black P$\rightarrow$$A7(As)\rightarrow$simple cubic [25]. It is therefore reasonable to postulate as in reference [26] that the simple cubic structure might be a transition structure between black P and As in the lower pressure transformation. One then asks how many reaction pathways there are from black P to As via the simple cubic intermediate. Such a reaction consists conceptually of a (bond-forming) movement of the atoms to produce 6 equivalent octahedral bonds at each site, followed by another (bond-breaking) motion yielding the As type. In reality, however, one expects that bonds which are formally formed and then rebroken in this process will not actually be altered in the course of the reaction. Thus the three reactions shown in Fig. 2, which involve breaking 2, 6 and 10 bonds, respectively, might be expected to have very different barriers. That is,

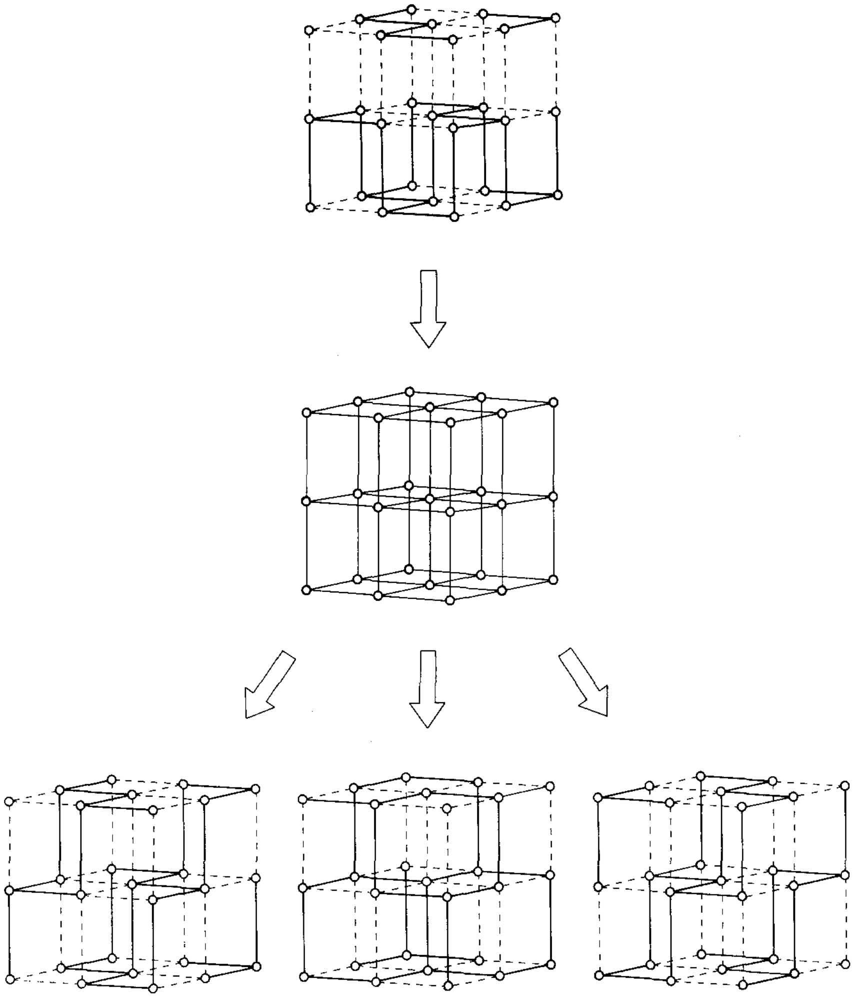

Fig. 2. The three possible reactions from the black P to the As structure via a simple cubic transition state. The structure at the top is black P, and all three drawings at the bottom show the As structure (in the middle drawing it is rotated 90° with respect to the other two). The left path involves breaking and reforming 2 bonds per 8 atom unit cell, the central path, 6 bonds, and the right path, 10 bonds

the actual transition states of these reactions would probably not be simple cubic, but might be sufficiently close to simple cubic to be identified with it for conceptual purposes. Another way of phrasing all of this is to say that the transition state is regarded as a symmetric state with memory.

To give a more mathematical description of this process, observe that both the black P and As structures can be regarded as colorings of the edges of the 8 atom superstructure of the simple cubic structure in two colors, "bond" and "no bond" [23, 24]. All the colorings of these edges can be permuted in the natural way by the space group $Pm3m$ of the simple cubic parent structure, and the colorings representing one of these structures form a single $Pm3m$-orbit. A reaction from black P to As can then be represented by a pair of colorings (c_1, c_2) where c_1 lies in $\omega_1 = Pm3m(c_1)$, the orbit of all colorings representing black P, and $c_2 \in \omega_2$ represents As. If γ is an element of $Pm3m$, then $(\gamma c_1, \gamma c_2)$ and (c_1, c_2) represent equivalent reactions, so to enumerate reaction pathways we must count equivalence classes.

In general, then, let Γ be a finite group permuting a finite set S, which we will normally regard as a set of colorings of some symmetrical transition state. Let ω_1 and ω_2 be two Γ-orbits in S, and let Γ act on $\omega_1 \times \omega_2$ via $\gamma(f_1, f_2) = (\gamma f_1, \gamma f_2)$ for any $f_1 \in \omega_1, f_2 \in \omega_2$. Let $c_1 \in \omega_1$ and $c_2 \in \omega_2$, and let Γ_1 and Γ_2 be the automorphism groups of c_1 and c_2, respectively, in Γ (i.e. $\Gamma_i = \{\gamma \in \Gamma \colon \gamma c_i = c_i\}$). By Burnside's lemma, the number $|\Omega|$ of Γ-orbits in $\omega_1 \times \omega_2$ is given by

$$|\Omega| = |\Gamma|^{-1} \sum_{\gamma\in\Gamma} \sum_{f_1\in\omega_1} \sum_{f_2\in\omega_2} \chi(\gamma(f_1,f_2) = (f_1,f_2))$$

$$= |\Gamma|^{-1} \sum_{\gamma\in\Gamma} \left\{ \sum_{f_1\in\omega_1} \chi(\gamma f_1 = f_1) \right\} \left\{ \sum_{f_2\in\omega_2} \chi(\gamma f_2 = f_2) \right\}.$$

Now any $f_1 \in \omega_1$ can be written $f_1 = \gamma_0 c_1$ for exactly $|\Gamma_1|$ choices of $\gamma_0 \in \Gamma$. Further, $\gamma\gamma_0 c_1 = \gamma_0 c_1 \Leftrightarrow \gamma_0^{-1}\gamma\gamma_0 c_1 = c_1 \Leftrightarrow \gamma_0^{-1}\gamma\gamma_0 \in \Gamma_1$. Thus

$$\sum_{f_1} \chi(\gamma f_1 = f_1) = |\Gamma_1|^{-1} \sum_{\gamma_0\in\Gamma} \chi(\gamma_0^{-1}\gamma\gamma_0 \in \Gamma_1) = |\Gamma_1|^{-1} \frac{|\Gamma|}{|C_\gamma|} |C_\gamma \cap \Gamma_1|,$$

where C_γ is the conjugacy class of γ in Γ. Substituting this and the corresponding expression for the sum over ω_2 into the expression for $|\Omega|$ yields

$$|\Omega| = \frac{|\Gamma|}{|\Gamma_1||\Gamma_2|} \sum_{C_\gamma} \frac{|C_\gamma \cap \Gamma_1||C_\gamma \cap \Gamma_2|}{|C_\gamma|}, \tag{2}$$

the sum running over all the conjugacy classes in Γ. Observe that while this formula is formally identical to Eq. (1) or to that of Ref. [9], the interpretation given it is new. It is regarded as counting reaction pathways from a crystal or molecule of symmetry Γ_1 to one of symmetry Γ_2 via a transition state of symmetry $\Gamma \supseteq \Gamma_1 \cup \Gamma_2$ and having the property that the initial and final states have unique representations as orbits of colorings of the transition state.

The statistical weight of a reaction (c_1, c_2) in $\omega_1 \times \omega_2$ can also be calculated simply. To count the reactions equivalent to (c_1, c_2), i.e. those in $\Gamma(c_1, c_2)$, we note that $\gamma(c_1, c_2) = (c_1, c_2)$ if and only if $\gamma \in \Gamma_1 \cap \Gamma_2$, so that $|\Gamma(c_1, c_2)| = |\Gamma|/|\Gamma_1 \cap \Gamma_2|$. Further, $\gamma c_1 = c_1$ if and only if $\gamma \in \Gamma_1$, so $|\omega_1| = |\Gamma c_1| = |\Gamma|/|\Gamma_1|$, and $|\omega_1 \times \omega_2| = |\Gamma|^2/|\Gamma_1||\Gamma_2|$. Thus, the fraction of reactions in $\omega_1 \times \omega_2$ equivalent to (c_1, c_2), i.e. the statistical weight of (c_1, c_2), is given by $|\Gamma(c_1, c_2)|/|\omega_1 \times \omega_2| = |\Gamma_1||\Gamma_2|/|\Gamma_1 \cap \Gamma_2||\Gamma|$. In this formula, Γ_1 and Γ_2 are the symmetry groups of c_1 and c_2, respectively, so different choices of (c_1, c_2) in $\omega_1 \times \omega_2$ result in different values for $|\Gamma_1 \cap \Gamma_2|$, and hence, different statistical weights.

The arithmetic involved in applying Eq. (2) to the problem of reactions from black P to As is contained in the Appendix. We give here a simpler molecular

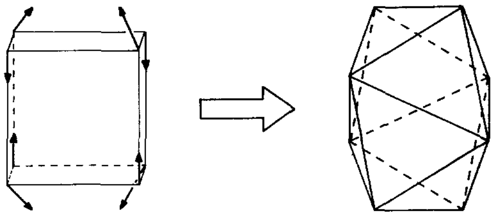

Fig. 3. The distortion of a cube to form a dodecahedron. In this distortion, one of the cube's constituent tetrahedra is elongated and the other is flattened. The dodecahedron thus has point group D_{2d}

example of this formula's use, the enumeration of pathways from one dodecahedral cage to another via a cubal intermediate.

As shown in Fig. 3, a dodecahedron can be regarded as a distorted cube. The distortion can be described as a coloring of the vertices of the cube in which the colors are vectors connecting corresponding vertices in the cube and in the dodecahedron. Of course, most such assignments of vectors to the vertices of a cube will not produce dodecahdra. Indeed, all dodecahedra derivable from the cube by these small displacements lie in a single orbit of colorings under the cube's point group O_h. A dodecahedral rearrangement via a cubal transition state consists of moving the atoms back along these vectors to their cubal positions, then out along a symmetry-equivalent set of vectors to form a new dodecahedron. In an actual reaction the transition state might not be exactly cubic, so inequivalent pathways may have different barriers.

The inequivalent pathways may be counted using Eq. (2) with $\Gamma = O_h$, the point group of the cube, and $\Gamma_1 = \Gamma_2 = D_{2d}$, the point group of the dodecahedron. The arithmetic is shown in Table 1, and the four reactions are shown in Fig. 4. These

Table 1

C_γ	$\lvert C_\gamma \cap D_{2d}\rvert$	$\dfrac{\lvert C_\gamma \cap D_{2d}\rvert^2}{\lvert C_\gamma\rvert}$
E	1	1
$8C_3$	0	0
$6C_2$	0	0
$6C_4$	0	0
$3C_4^2$	3	3
i	0	0
$6S_4$	2	$\frac{2}{3}$
$8S_6$	0	0
$3\sigma_h$	0	0
$6\sigma_d$	2	$\frac{2}{3}$
Sum		$\frac{16}{3}$

The use of formula (2) to count dodecahedral rearrangement processes with a cubal transition state. The number of these reactions is

$$\frac{|O_h|}{|D_{2d}|^2}\sum\frac{|C_\gamma \cap D_{2d}|^2}{|C_\gamma|}=\frac{48}{64}\left(\frac{16}{3}\right)=4$$

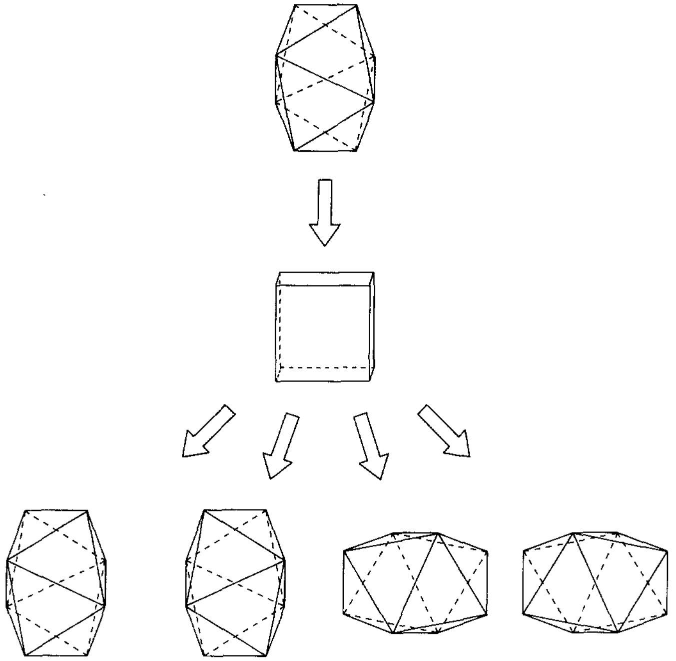

Fig. 4. The four dodecahedral rearrangement processes with cubal transition states. The leftmost of these represents the identity rearrangement

four reactions represent only a tiny fraction of the 698 polytopal rearrangements which would be obtained if, as in Ref. [9], the group O_h in Eq. (2) were replaced by the symmetric group $\mathcal{S}_8$ of all 8! permutations of the vertices. (This can be regarded as corresponding physically to a transition state in which all 8 atoms are collapsed to a single point, a configuration having symmetry $\mathcal{S}_8$.)

While formula (2) can thus provide a much more refined enumeration than that of all polytopal rearrangements, it is still limited by the assumptions that Γ_1 and Γ_2 be subgroups of Γ and that the initial and final states have unique representations as orbits of colorings of the transition state. Many reaction processes fail to satisfy these conditions. For example, in the Berry process (Fig. 5) for

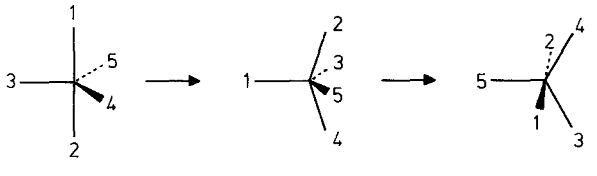

Fig. 5. The Berry pseudorotational rearrangement of a trigonal bipyramid via a square pyramidal transition state. Here and in Fig. 6 the numbers are not atom labels but fixed labels of the sites in the framework. Thus, this particular setting of the Berry process can be written (λ, ρ) where $\lambda = \binom{1\ 2\ 3\ 4\ 5}{2\ 4\ 1\ 5\ 3}_T^I$ and $\rho = \binom{1\ 2\ 3\ 4\ 5}{5\ 4\ 2\ 3\ 1}_F^T$. This notation means that, for example, the atom at site 1 of the left trigonal bipyramid is taken by λ to site 2 in the square pyramid and then taken by ρ to site 4 in the right trigonal bipyramid

rearranging a trigonal bipyramidal molecule via a square pyramid, the initial and final states have symmetry D_{3h} and the transition state has symmetry $C_{4v} \not\geq D_{3h}$. Further, from the initial state there are three paths to the transition state, so that the former cannot be uniquely described as a coloring of the latter. Even without these assumptions, however, Burnside's lemma can be used to obtain the number of reaction pathways in a form very similar to Eq. (2).

Suppose that geometries I, T and F of the initial, transition, and final states of a molecule in some reaction are specified, and that R_I, R_T and R_F are the rotation groups of these states. (The reason for considering the rotation groups rather than the full point groups will be discussed below). Suppose further that we are given a set Λ of mappings from I to T which contains the chemically allowed transformations from the initial to the transition state, and a set P of allowed transformations from the transition to the final state. If the n atomic sites in I, T and F are numbered in some arbitrary fashion, then the mappings in Λ and P as well as the operations in R_I, R_T and R_F can be regarded as permutations of $1, 2, \ldots, n$. An element of R_I in which atom j is rotated to $r(j)$ will be denoted $\begin{pmatrix} 1 & 2 & \cdots & n \\ r(1) & r(2) & \cdots & r(n) \end{pmatrix}_I^I$. In the same fashion, an element λ of Λ will be written $\begin{pmatrix} 1 & 2 & \cdots & n \\ \lambda(1) & \lambda(2) & \cdots & \lambda(n) \end{pmatrix}_T^I$ and so on. We shall also follow the convention that multiplication operates from left to right, so that

$$\begin{pmatrix} 1 & \ldots & n \\ r(1) & \ldots & r(n) \end{pmatrix}_I^I \begin{pmatrix} 1 & \ldots & n \\ \lambda(1) & \ldots & \lambda(n) \end{pmatrix}_T^I = \begin{pmatrix} 1 & \ldots & n \\ \lambda(r(1)) & \ldots & \lambda(r(n)) \end{pmatrix}_T^I$$

defines the action of $r\lambda$.[1] Thus, in the Berry process with the labeling in Fig. 5, the elements of Λ are

$$\begin{pmatrix} 1 & 2 & 3 & 4 & 5 \\ 2 & 4 & 1 & 5 & 3 \end{pmatrix}_T^I, \quad \begin{pmatrix} 1 & 2 & 3 & 4 & 5 \\ 4 & 2 & 1 & 3 & 5 \end{pmatrix}_T^I,$$

$$\begin{pmatrix} 1 & 2 & 3 & 4 & 5 \\ 3 & 5 & 1 & 2 & 4 \end{pmatrix}_T^I, \quad \begin{pmatrix} 1 & 2 & 3 & 4 & 5 \\ 5 & 3 & 1 & 4 & 2 \end{pmatrix}_T^I,$$

and the 8 similar maps in which $4 \to 1$ or $5 \to 1$.

A reaction in this setting is an ordered pair (λ, ρ) in $\Lambda \times P$. In order to count distinct reaction pathways it is necessary to define which of these ordered pairs are to be equivalent. The most natural equivalence relation is one defined by three conditions: $(\lambda, \rho) \sim (r_I \lambda, \rho)$ for any $r_I \in R_I$; $(\lambda, \rho) \sim (\lambda, \rho r_F)$ for any $r_F \in R_F$; and $(\lambda, \rho) \sim (\lambda r_T^{-1}, r_T \rho)$ for any $r_T \in R_T$. Fig. 6, which shows a representative reaction of the Berry process and several equivalent reactions, may help to motivate this definition. The three conditions in the definition can also be combined into the single condition that for any $r_I \in R_I$, $r_T \in R_T$ and $r_F \in R_F$,

$$(\lambda, \rho) \sim (r_I \lambda r_T^{-1}, r_T \rho r_F^{-1}). \tag{3}$$

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[1] Actually, to be consistent we should write, for example, not $\lambda(r(a))$ but $1r\lambda$. Since it will not prove necessary to use such notation below, we have for clarity committed the abuse of defining left to right multiplication of permutations in terms of right to left composition of functions.

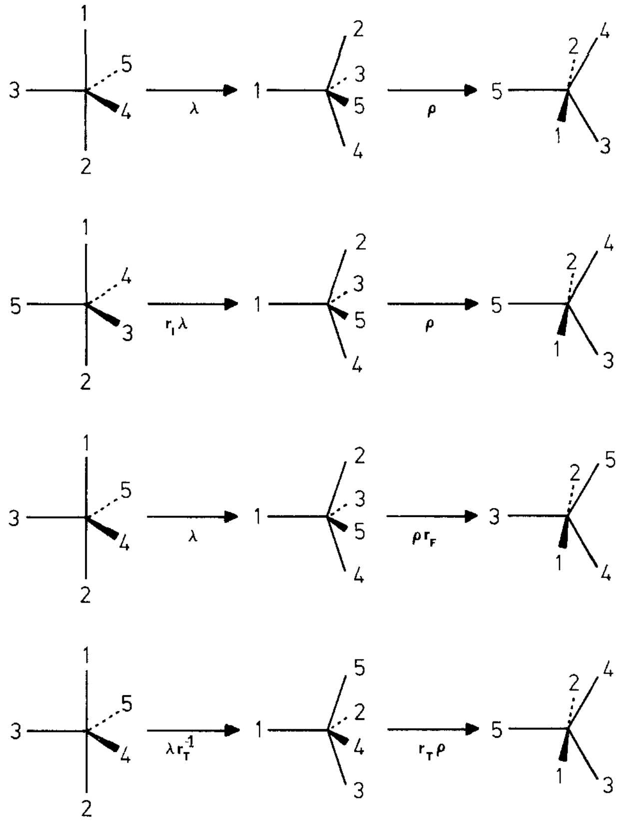

Fig. 6. Four equivalent reactions representing the Berry process. The first is the reaction (λ, ρ) of Fig. 5. The second is $(r_I\lambda, \rho)$, where r_I is the threefold rotation $\left(\begin{smallmatrix}1&2&3&4&5\\1&2&4&5&3\end{smallmatrix}\right)_I^I$; and the third is $(\lambda, \rho r_F)$ where r_F is the same rotation of the final state, $\left(\begin{smallmatrix}1&2&3&4&5\\1&2&4&5&3\end{smallmatrix}\right)_F^F$. The last is $(\lambda r_T^{-1}, r_T\rho)$, where r_T is the fourfold rotation $\left(\begin{smallmatrix}1&2&3&4&5\\1&3&4&5&2\end{smallmatrix}\right)_T^T$ of the transition state

The equivalence classes in this relation can thus be described as $R_I \times R_T \times R_F$-orbits in $\Lambda \times P$, where the permutation of $\Lambda \times P$ corresponding to (r_I, r_T, r_F) is defined by $(r_I, r_T, r_F)(\lambda, \rho) = (r_I\lambda r_T^{-1}, r_T\rho r_F^{-1})$. Counting the distinct reaction pathways is then equivalent to counting these orbits, which can be done using Burnside's lemma:

$$|\Omega| = |R_I \times R_T \times R_F|^{-1} \sum_{r_T} \sum_{r_I} \sum_{r_F} \sum_{\lambda} \sum_{\rho} \chi((r_I\lambda r_T^{-1}, r_T\rho r_F^{-1}) = (\lambda, \rho))$$

$$= |R_I \times R_T \times R_F|^{-1} \sum_{r_T} \left\{ \sum_{\lambda, r_I} \chi(r_I\lambda r_T^{-1} = \lambda) \right\} \left\{ \sum_{\rho, r_F} \chi(r_T\rho r_F^{-1} = \rho) \right\}.$$

To simplify this expression, note that $r_I\lambda r_T^{-1} = \lambda \Leftrightarrow \lambda r_T\lambda^{-1} = r_I$, so $\sum_{\lambda, r_I} \chi(r_I\lambda r_T^{-1} = \lambda) = \sum_{\lambda} \chi(\lambda r_T\lambda^{-1} \in R_I)$, and

$$|\Omega| = |R_I \times R_T \times R_F|^{-1} \sum_{r_T} \sum_{\lambda} \chi(\lambda r_T\lambda^{-1} \in R_I) \sum_{\rho} \chi(\rho^{-1} r_T\rho \in R_F). \tag{4}$$

Further simplification requires some information about the sets Λ and P. Clearly the group action of $R_I \times R_T \times R_F$ defined on $\Lambda \times P$ makes sense only if $\Lambda = R_I \Lambda R_T$. Thus, Λ can be written as a disjoint union of "double cosets", $\Lambda = R_I\lambda_0 R_T \,\dot{\cup}\, R_I\lambda_1 R_T \,\dot{\cup} \cdots \dot{\cup}\, R_I\lambda_m R_T$. In most practical situations (for example, in the case of the Berry process) it is in fact the case that

$$\Lambda = R_I\lambda_0 R_T \quad \text{and} \quad P = R_T\rho_0 R_F. \tag{5}$$

Let us therefore assume Eq. (5) hold and rewrite Eq. (4). First, it is necessary to determine the number of ways in which a given $\lambda \in \Lambda$ can be written as $r_I\lambda_0 r_T^{-1}$. Since $r_I\lambda_0 r_T^{-1} = \lambda_0 \Leftrightarrow \lambda_0 r_T \lambda_0^{-1} = r_I$, λ_0 itself has $|\lambda_0 R_T \lambda_0^{-1} \cap R_I|$ such representations. It is easy to see that the same is true of any other $\lambda \in \Lambda$, since $r_I\lambda_0 r_T^{-1} = \bar{r}_I\lambda_0\bar{r}_T^{-1} \Leftrightarrow \bar{r}_I^{-1} r_I \lambda_0 r_T^{-1}\bar{r}_T = \lambda_0$. Thus,

$$\begin{aligned}
\sum_{\lambda} \chi(\lambda r_T \lambda^{-1} \in R_I) &= |\lambda_0 R_T \lambda_0^{-1} \cap R_I|^{-1} \sum_{\bar{r}_T}\sum_{\bar{r}_I} \chi((\bar{r}_I\lambda_0\bar{r}_T^{-1}) r_T (\bar{r}_T\lambda_0^{-1}\bar{r}_I^{-1}) \in R_I) \\
&= |\lambda_0 R_T \lambda_0^{-1} \cap R_I|^{-1} |R_I| \sum_{\bar{r}_T} \chi(\lambda_0 \bar{r}_T^{-1} r_T \bar{r}_T \lambda_0^{-1} \in R_I) \\
&= \frac{|R_I|}{|\lambda_0 R_T \lambda_0^{-1} \cap R_I|} \frac{|R_T|}{|C_{r_T}|} |\lambda_0 C_{r_T} \lambda_0^{-1} \cap R_I|,
\end{aligned}$$

where C_{r_T} is the conjugacy class of r_T in R_T. Inserting this and the corresponding expression for the sum over P into Eq. (4) yields

$$|\Omega| = \frac{|R_T|}{|\lambda_0 R_T \lambda_0^{-1} \cap R_I||\rho_0^{-1} R_T \rho_0 \cap R_F|} \sum_{C_{r_T}} \frac{|\lambda_0 C_{r_T} \lambda_0^{-1} \cap R_I||\rho_0^{-1} C_{r_T} \rho_0 \cap R_F|}{|C_{r_T}|}. \tag{6}$$

Formula (6) closely resembles Eqs. (1) and (2), especially if one recalls that in those cases λ_0 and ρ_0 could both be taken to be the identity permutation. Indeed, Eq. (6) reduces to Eqs. (1) and (2) under the appropriate hypotheses. The validity of Eq. (6) depends on that of assumption (5), but even in the event (5) is not satisfied, the above argument allows us to write

$$|\Omega| = \sum_{i,j} \frac{|R_T|}{|\lambda_i R_T \lambda_i^{-1} \cap R_I||\rho_j^{-1} R_T \rho_j \cap R_F|} \sum_{C_{r_T}} \frac{|\lambda_i C_{r_T} \lambda_i^{-1} \cap R_I||\rho_j^{-1} C_{r_T} \rho_j \cap R_F|}{|C_{r_T}|},$$

where (λ_i, ρ_j) runs over all pairs of "double coset" representatives in Λ and P.

For the sake of completeness, we apply Eq. (6) to the Berry process, even though the result that there is up to symmetry only one nonidentity rearrangement is perhaps obvious. The groups R_I and R_F are D_3, while $R_T = C_4$. We can take λ_0 to be the map $\binom{1\ 2\ 3\ 4\ 5}{2\ 4\ 1\ 5\ 3}_T^I$ shown in Fig. 5, and ρ_0 to be its "inverse" $\binom{1\ 2\ 3\ 4\ 5}{3\ 1\ 5\ 2\ 4}_F^T$. The only elements r_T or R_T such that $\lambda_0 r_T \lambda_0^{-1} \in R_I$ (or, equivalently, $\rho_0^{-1} r_T \rho_0 \in R_F$) are 1 and C_4^2. Thus, formula (6) produces

$$|\Omega| = \frac{4}{2\cdot 2}\left\{\frac{1\cdot 1}{1} + \frac{1\cdot 1}{1}\right\} = 2,$$

as expected.

Finally, we consider some other notions of equivalence which might be imposed on $\Lambda \times P$. The relation defined by Eq. (3) based on rotation groups rather than full point groups was chosen in order to exclude as equivalents of (λ, ρ) such reactions as $(g_I\lambda, \rho)$, $(\lambda g_T^{-1}, g_T\rho)$ and $(\lambda, \rho g_F)$, where g_j is an improper operation in the point group of state j. These reactions, which involve a coupling of the reaction (λ, ρ) with a reversal of chirality, may not only not be equivalent to (λ, ρ), but not be chemically allowed at all. For example, if I, T and F all represent a tetrahedral molecule, λ and ρ are the identity, and $g_I = \sigma_d$, one would clearly not expect (λ, ρ) to be equivalent to $(g_I\lambda, \rho)$. In at least one case, however, some revision of (3) is appropriate. If all three of the point groups G_I, G_T and G_F of I, T and F are achiral and if $g_j \in G_j \backslash R_j$ for $j = I, T, F$, then $(g_I\lambda g_T^{-1}, g_T\rho g_F^{-1})$ represents a reaction which is a mirror image of (λ, ρ). Such a reaction should have the same barrier as (λ, ρ) and be counted as its equivalent, though in the enumeration provided by Eq. (6) they are counted as distinct.

To effect this new enumeration, replace Eq. (3) by the condition that $(\lambda, \rho) \sim (s_I\lambda s_T^{-1}, s_T\rho s_F^{-1})$ whenever $(s_I, s_T, s_F) \in R_I \times R_T \times R_F \cup (G_I \backslash R_I) \times (G_T \backslash R_T) \times (G_F \backslash R_F)$. The same argument used to produce Eq. (6) then results in an expression for $|\Omega|$ as an average of two terms, one equal to Eq. (6) and one equal to the expression produced from Eq. (6) by replacing R_I by $G_I \backslash R_I$, R_T by $G_T \backslash R_T$, R_F by $G_F \backslash R_F$, and the sum over conjugacy classes in R_T by a sum over conjugacy classes in $G_T \backslash R_T$.

Of course, any number of new equivalence relations reflecting the ability or inability of particular experimental techniques used to study reactions to determine the chirality of I, T or F or to determine other molecular features can be written down in this way; and the inequivalent reactions under these new definitions can then be determined using Burnside's lemma just as above.

This note should then demonstrate the utility of Burnside's lemma both as a conceptual aid in phrasing enumeration problems and as a tool in the proof of such results. It further illustrates that equations formally similar or identical to that for the number of double cosets in $\mathscr{S}_n$ can be used to obtain not only polytopal rearrangements but much more finely detailed counts of reaction paths with a given transition state. That such a wide class of problems can be resolved in a single general formalism is an indication of the power of this counting technique.

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Appendix

Enumeration of Reactions black P → simple cubic → As.

Table 2

g	$\lvert C_g\rvert$	$\lvert C_g\cap\Gamma_1\rvert$	$\lvert C_g\cap\Gamma_2\rvert$	$\frac{\lvert C_g\cap\Gamma_1\rvert\lvert C_g\cap\Gamma_2\rvert}{\lvert C_g\rvert}$
1	1	1	1	1
$m(xxz)$	12	2	6	1
$2(xx\frac{1}{4})$	12	2	6	1
$i(\frac{1}{4}\frac{1}{4}\frac{1}{4})$	1	1	1	1
$\tau(\frac{1}{2}\frac{1}{2}0)$	3	1	3	1
$i\tau\sim i(00\frac{1}{4})$	3	1	3	1
Sum				6

The classes which must be considered in using Eq. (2) to count the reaction pathways from black P to As. The coordinates of each operation correspond to the original (NaCl) cubic unit cell. Thus m is the mirror at xxz in this cell, τ is a translation taking 000 to $\frac{1}{2}\frac{1}{2}0$, and so on. The total number of reaction pathways is

$$\frac{|\Gamma|}{|\Gamma_1||\Gamma_2|}\cdot 6=\frac{384}{16\cdot 48}\cdot 6=3$$

In order that all groups and sets dealt with be finite, we take the quotient groups of the space groups of these three idealized structure types with the group P1(2, 2, 2) of translations generated by the 3 orthogonal edges of the 8 atom (NaCl) cell shown in Fig. 1. The resulting finite groups have orders $|\Gamma|=|Pm3m/\mathrm{P}1(2,2,2)|=384$, $|\Gamma_1|=|Pmna/\mathrm{P}1(2,2,2)|=16$, and $|\Gamma_2|=|\mathrm{R}\bar{3}m/\mathrm{P}1(2,2,2)|=48$. The elements of Γ_2 are the images of symmetries whose linear parts are powers of $\bar{3}$, mirrors m normal to (110) (with respect to the NaCl cell), and 2-fold rotors 2 normal to these mirrors. The only such operations which are potentially conjugate to elements of Γ_1 have linear part m, 2, or $\bar{3}^3=i$. Consideration of these symmetries lets one quickly list all classes C_r in Γ such that $|C_r\cap\Gamma_1||C_r\cap\Gamma_2|\neq 0$. This is done in Table 2, which summarizes as well the rest of the calculation of the number of reaction pathways. The reason for including $i\tau$ in this Table but not $m\tau$ and 2τ is that m and $m\tau$ are conjugate in Γ, as are 2 and 2τ. The resulting 3 reaction pathways have already been shown in Fig. 2.

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