Review

Double Cosets in Chemistry and Physics

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1. Introduction

A variety of seemingly rather different ideas that are pursued while classifying objects of physics and of chemistry can be analyzed on the basis of a uniform algebraic scheme, and connected problems like the one of counting and others can easily be solved when use is made of a concept that refers to the decomposition of groups into subsets, known as double cosets. Beyond this, studies on the classification of molecules and of chemical reactions indicate that an even broader mathematical classification idea covers exactly the natural scope of requirements, playing the rôle of an algebraic counterpart of nature. This concept concerns the classification of bijections under the aspect of symmetry equivalence, symmetry being understood as a property that is related to both the range and the domain and is built from the respective symmetries with varying degrees of mutual correlation. With reference to the type of classes defined correspondingly, double cosets appear as classes for situations where no correlation is observed. Since, besides a formalistic profit, also the conceptual profit in having available the more general scheme is considerable, a review on the application of double cosets should be pursued under the encompassing aspect of bijection classes.

Aiming primarily at an understanding of the classification philosophy encountered in the various problems and, in order to provide the prerequisites for further investigations in the field of applications, we shall give an extensive presentation of this new concept. The present paper also contains a historical introduction exhibiting the increasing significance of double cosets for applications and it accounts for essentially all the applications known in chemistry. As

to physics, some intuitive examples will demonstrate the basic rôle of double cosets for a diversity of problems akin in nature. However, we shall omit the relevant consequences concerning representation theory as used in physics for the evaluation of quantum mechanical matrix elements, since a concerned discussion would entail a dramatic increase in size of the present article and would contain primarily technical information on how to handle very complicated formalisms occurring with problems that are of interest largely to a group of specialists.

Double cosets were introduced as a generalization of cosets, and a number of their properties (along with formulas for their enumeration and orders) were established in a paper by G. F. Frobenius [1] in 1887. J. S. Frame [2], [3], [4], in the fourties, started and extensively developed the theory of DC algebras and DC matrices[1]. He also utilized double cosets for the construction of irreducible representations and for the discussion of various related problems in later publications [5], [6], [7]. I. Schur [8] in 1933 and, later on, H. Wielandt [9], [10], [11] studied DC- and related algebras in view of permutation groups. For connections with representation theory compare C. W. Curtis and T. V. Fossum [12]. In a systematic treatment of induced representations by G. W. Mackey [13] double cosets play a decisive rôle. His rather programmatic theory was implemented later by A. J. Coleman [14] in a paper on the symmetric group, by S. L. Altmann [15] in view of point groups, and by A. Kerber [16] who treated wreath products. Indeed, some ideas in Mackey's theory can be traced back to a method introduced ad hoc by E. Wigner [17] in 1939 when constructing the irreducible representations of the Lorentz group. In summation, double cosets like conjugacy classes represent a mathematically significant structure of groups. The step to a less specific but still relevant classification concept which encompasses, as particular cases, the classification into double cosets as well as into conjugacy classes was made very recently by W. Hässelbarth, T. H. Seligman and the authors [18], [19]. Without reference to particular properties, subsets of groups according to this concept were termed *bilateral classes*. With regard to the classification of bijections they reflect an interpretation of symmetry equivalence of most satisfying generality. In particular, because of this interpretation bilateral classes promise significant applications outside the field of pure mathematics.

Like Wigner's fundamental paper, mentioned above, there are a number of publications in physics and in chemistry where double cosets appear in particular form and context, but are not recognized as such. R. McWeeny and F. Yonezawa [20] in their study of pairs of interacting atoms found different types of interaction phenomena uniquely related to certain sets of cosets in the symmetric group. Actually, their classes are double cosets; recognition of this fact allows the formulation of a corresponding classification for multiple sets of interacting atoms. The way of generating the symmetric group S_6 as demonstrated by T. Yamanouchi [21] exemplified a rationale for generating groups by what are,

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[1]   We abbreviate "double coset" to DC in composite expressions like DC algebra.

in fact, double cosets. Within the context of nuclear structure calculations A. Hassit [22] found that H. A. Jahn's [23] (single-) coset analysis of fractional parentage coefficients did not account for all the simplifications possible. Thereafter H. A. Jahn [24] extended Hassit's observation and developed what may be regarded as theorems on special double cosets and DC coefficients of the symmetric group. Double cosets of the symmetric group occur explicitly in the papers of H. Horie [25], F. Sasaki [26], and A. J. Coleman [27], but are presented as a rather special tool for decomposing the antisymmetrizer (or Boson symmetrizer). The success of an explicit use of double cosets is beautifully illustrated in C. Herring's contribution [28], [29] on the Heisenberg spin Hamiltonian where exchange processes are characterized correspondingly, though this aspect of this theory was not appreciated for some time.

A new period of research concerning the rôle of double cosets in physics and chemistry began in 1969 when two main aspects emerged, the one referring to a refined use of symmetry as a simplifying means in calculations, the other to double cosets as a mathematical tool suitable for a conceptual analysis of classifying structures, in particular structures of interest to the chemist, and for their formal manipulation. The first topic, the evaluation of quantum mechanical matrix elements (with some of the developments in papers by P. Kramer and T. H. Seligman [30], [31], [32], by C. A. Carlisle, F. A. Matsen, and one of the authors (D.J.K.) [33], by J. J. Sullivan [34], by E. R. Davidson [35], by W. F. Siems and R. D. Poshusta [36], and by R. W. J. Roël [37] shall not be treated here. Rather, the classification of isomers, configurations, and isomerization processes as first pointed out by W. Hässelbarth, B. Richter, and one of the authors (E.R.) [38], [39] is to be the focus of our review.

2. Double Cosets

a) Elementary Properties

Double cosets partition groups in a way characterized by a pair of subgroups. With A and B denoting subgroups of G the partitioning may be indicated as an $A\backslash/B$-double coset decomposition, where each particular subset of this type may be identified by one of its elements, say g, according to the definition

$$AgB \equiv \{agb \,|\, a \in A, b \in B\}, \, g \in G. \tag{2.1}$$

These subsets establish equivalence classes since membership of two group elements in the same $A\backslash/B$-double coset is expressed through an equivalence relation

$$g' \sim g'' \Leftrightarrow \exists a \in A, b \in B: g' = ag''b. \tag{2.2}$$

With reference to a given choice of representative elements g_i, $i = 1, 2, \ldots$ and with $\bigcup$ denoting the disjoint union, the decomposition of G into double cosets reads as

$$G = \bigcup_i Ag_iB. \tag{2.3}$$

In contrast to cosets, double cosets associated with a given pair of subgroups A, B, as a rule, do not have the same order or cardinality. Left and right cosets result from specialization of $A\backslash/B$-double cosets if either A or B are chosen to be the unit subgroup of G. An $A\backslash/B$-double coset is at the same time a union of right cosets of A and a union of left cosets of B; in fact, it is the smallest set containing a given element g, and decomposing into A-right as well as into B-left cosets.

Since A-right and B-left cosets partition $A\backslash/B$-double cosets, the corresponding coset intersections $Ag'\cap g''B$ do so as well. Provided the elements g' and g'' belong to the same double coset AgB we may write $g' = a'gb'$, $g'' = a''gb''$ and find

$$Ag'\cap g''B = a''(Ag \cap gB)b'$$
$$= a''(A \cap gBg^{-1})gb' = a''g(g^{-1}Ag \cap B)b'. \tag{2.4}$$

Therefore, $A\backslash/B$-double cosets decompose into subsets that arise from left and right multiplication of $Ag \cap gB$ with the representative elements of the $(A \cap gBg^{-1})$-left coset decomposition of A and the $(g^{-1}Ag \cap B)$-right coset decomposition of B, respectively,

$$AgB = \overset{\cdot}{\underset{st}{\bigcup}} a_s(Ag \cap gB)b_t, \tag{2.5}$$

where

$$A = \overset{\cdot}{\underset{s}{\bigcup}} a_s(A \cap gBg^{-1})$$

$$B = \overset{\cdot}{\underset{t}{\bigcup}}(g^{-1}Ag \cap B)b_t.$$

The constituent subsets of AgB as in Eq (2.5) have equal cardinality, and the intersection groups involved are isomorphic

$$d(g) = |Ag \cap gB| = |a_s(Ag \cap gB)b_t| = |A \cap gBg^{-1}| = |g^{-1}Ag \cap B|$$
$$A \cap gBg^{-1} \cong g^{-1}Ag \cap B. \tag{2.6}$$

The intersection sets $a_s(Ag \cap gB)b_t$ consist of all those elements of the right coset Agb_t that can also be written as an element of the left coset a_sgB. Therefore, $d(g)$ represents the number of times each element of AgB is produced if any $a \in A$, $b \in B$ is used to form a product agb. Hence, $d(g)$ will be called the repetition frequency and a formula for the cardinality of double cosets follows immediately:

$$|AgB| = \frac{|A||B|}{|Ag \cap gB|}. \tag{2.7}$$

In case of finite groups, a formula for the number of $A\backslash/B$-double cosets is derived from Eq (2.7) by summing the reciprocal double coset orders assigned

to each element of G, and by rewriting this sum in terms of Kronecker δ-functions

$$z(A \backslash / B) = \sum_{g \in G} \frac{|A \cap gBg^{-1}|}{|A||B|} = \frac{1}{|A||B|} \sum_{a \in A} \sum_{b \in B} \sum_{g \in G} \delta_{a, gbg^{-1}}.$$

As the order of a conjugacy class C_r equals the centralizer index of the elements contained in this class we annotate

$$\sum_{g \in G} \delta_{a, gbg^{-1}} = \begin{cases} |G|/|C_r|, & \text{if } a, b \text{ are of the same class, say } C_r, \\ 0, & \text{otherwise.} \end{cases}$$

From this one derives expression (2.8). Both this one and Eq. (2.9) were already given by G. F. Frobenius [1], [40] in 1887 and in 1898.

$$z(A \backslash / B) = \frac{|G|}{|A||B|} \sum_r \frac{|A \cap C_r||B \cap C_r|}{|C_r|} \tag{2.8}$$

$$z(A \backslash / B) = \sum_\gamma |\gamma \downarrow i(A)||\gamma \downarrow i(B)|. \tag{2.9}$$

Formula (2.9), cited here without proof, is related to representation theory, the numbers $|\gamma \downarrow i(A)|$ and $|\gamma \downarrow i(B)|$, respectively, indicating how often the identity representations of A and B occur in the irreducible representation Γ^γ of G. Formula (2.8) is convenient primarily for the counting of double cosets of the symmetric group S_n.

The repetition frequency (2.7) is of particular use to sum decompositions of the type

$$\sum_{g \in G} \theta(g) = \sum_i \sum_{a \in A} \sum_{b \in B} \frac{1}{d(g_i)} \theta(ag_ib) \tag{2.10}$$

where $\theta(g)$ could be numbers, wave functions, or operators, functionally dependent on the elements of G. For continuous groups, corresponding decompositions of integrals over the space of parameters are based on the concept of measure if the repetition frequency is not finite (cf. Refs. [41], [42]).

3. The Orthogonal Group and The Symmetric Top

Familiar and mutually related topics profitably revisited, if emphasis is laid on the rôle double cosets play, touch upon the Euler angle decomposition of rotations, its use in the classical and quantum-mechanical treatments of the symmetric top, and upon the representation theory of the orthogonal group $O^+(3)$. Though only reinterpretation of facts known, the subsequent presentation also may be taken as a valuable preparation for an understanding of problems encountered in many fields of physics concerning the evaluation of quantum mechanical matrix elements. As mentioned in the introduction this latter field of application is not treated here, explicitly.

A most convenient way to describe the orientation of a body in space relative
to a space-fixed cartesian coordinate system x, y, z is in terms of a sequence of
three rotations acting on a body-fixed coordinate system x', y', z' which initially
coincides with the x, y, z-frame. These rotations by angles γ, β and α with
$0 \leq \gamma \leq 2\pi$, $0 \leq \beta < \pi$ and $0 \leq \alpha < 2\pi$ are first taken around the z-axis, then the
y- and finally around the z-axis again. With $|\alpha, \beta, \gamma\rangle$ and $|0, 0, 0\rangle$, respectively,
representing the body in its final and initial position we have

$$|\alpha, \beta, \gamma\rangle = R_z(\alpha)R_y(\beta)R_z(\gamma)|0, 0, 0\rangle. \tag{3.1}$$

Besides these *active* transformations it is of advantage to use so-called passive
ones describing the same relative change of positions from the viewpoint of the
body, i.e. to refer the position of the x, y, z-frame to x', y', z'. In terms of passive
transformations, relation (3.1) reads

$$|\alpha, \beta, \gamma\rangle = R_{z'}(-\gamma)R_{y'}(-\beta)R_{z'}(-\alpha)|0, 0, 0\rangle. \tag{3.2}$$

Active transformations commute with passive ones, and that is one of the
advantages when using both. The substitution of an active by a passive transfor-
mation or vice versa depends on the position of the body in space when the
operator acts. With this in mind, the replacement is carried out as $R_{q'}(\omega) \leftrightarrow R_p(\omega)$
where q' and p denote coinciding axes of body- and space-fixed frames, respec-
tively.

Following the product decomposition of a rotation $R(\alpha, \beta, \gamma)$ as used in (3.1)
one verifies that the first action on the initial situation, that is the rotation $R_z(\gamma)$,
may be replaced by $R_{z'}(\gamma)$ and then commuted with the preceding active transfor-
mation factors. This means that the rotation $R_{z'}(-\gamma)$ around the body-fixed
axis z' may be carried out independently of the other transformations; the
rotation $R_z(\alpha)$ to be performed after $R_y(\beta)$, however, moves the body-fixed axis
z' around z on the surface of a cone. Thus, the set of operations of $O^+(3)$ is
obviously classified by the parameter β in that all the rotations $R(\alpha, \beta, \gamma)$ with
a given value of β in common lead the body from the initial position $|0, 0, 0\rangle$
to any position with the body-fixed axis z' lying on the associated cone around
z. Recasting of the operations in terms of active rotations exclusively, necessitates
the sequence of factors as given in Eq. (3.1). It follows that the classification of
body positions with the z'-axis on concentric cones around z is given by the
$O^+(2)\backslash/O^+(2)$ double coset decomposition of $O^+(3)$ as

$$O^+(2)R_y(\beta)O^+(2) = \{R_z(\alpha)R_y(\beta)R_z(\gamma)|0 \leq \alpha < 2\pi, 0 \leq \gamma < 2\pi\}. \tag{3.3}$$

Note that the classification, as we have seen, can be analyzed either in terms of
subgroups of $O^+(3)$, where attention has to be paid to the sequence of factors,
or alternatively in terms of subgroups of two isomorphic groups as represented
by active and passive transformations using the advantage of not being bound
to the sequence of operations.

Note further that the denotation of rotations by Euler angles is unique with the
exception of $\beta = 0$ where $R(\alpha, 0, \gamma) = R(\alpha', 0, \gamma')$ if $\alpha + \gamma = \alpha' + \gamma'$. This fact is
also recognized from the repetition frequency formula (2.6) since we have
$d(R_y(\beta)) = 1$ if and only if $\beta \neq 0$.

The obvious phenomenon in physics where the $O^+(2)\backslash/O^+(2)$ decomposition of $O^+(3)$ is the natural classification aspect is the symmetric top. Classically, the system of a symmetric top with a given rotational energy in a field-free space has the spatial symmetry of a sphere, expressible by rotations relative to the laboratory frame and independently therefrom, it has the axial symmetry of the top. With initial conditions given this symmetry is reduced but two subsymmetries responsible for positions during the motion survive, that is the axial symmetry of the total angular momentum fixed in space and the axial symmetry of the top. Since two groups $O^+(2)$ that represent these axial symmetries are subgroups of $O^+(3)$ groups with mutually commuting elements the above argumentation concerning the substitution of active by passive transformations and vice versa holds. Thus, referring to one single $O^+(3)$ group, classes of equivalent top positions, i.e. positions compatible with the initial conditions, correspond to the $O^+(2)\backslash/O^+(2)$ decomposition of $O^+(3)$.

As far as the abstract group $O^+(3)$ is concerned, clearly, like this group itself its irreducible representations $D^F(R(\alpha, \beta, \gamma))$ should be viewed in the light of the $O^+(2)\backslash/O^+(2)$ decomposition which, again, in accordance with the Euler angle factorization, reads as

$$D^F_{mn}(R(\alpha, \beta, \gamma)) = \sum_{p,q} D^J_{mp}(R_z(\alpha)) D^J_{pq}(R_y(\beta)) D^J_{qn}(R_z(\gamma))$$

$$= e^{im\alpha} D^J_{mn}(R_y(\beta)) e^{in\gamma}. \tag{3.4}$$

With this choice of row and column labels right- and left-hand factors have become simpler allowing to identify irreducible representations of $O^+(2)$

$$D^J_{mn}(R_z(\omega)) = e^{i\omega m} \delta_{mn}. \tag{3.5}$$

The evaluation of the matrix elements is straightforward except for the double coset generators $R_y(\beta)$, where Jacobi polynomials can be used to advantage (cf. Ref. [43]).

Let us think of irreducible representations in general as sets of bijections of the representation space onto itself; then a basis is preferably chosen to by symmetry-adapted, i.e. such that restriction to a subgroup representing this symmetry leads to block diagonalization and restriction to double cosets with this subgroup as left- and right-hand factor leads to triple products of matrices with a class-specific generating matrix in the middle. The particular type of double cosets in our examples distinguished by right- and left-hand factors appears to be characteristic of the usual type of representations and is associated with the fact that the bijections refer to the particular case where range and domain are identical.

The symmetric top treated quantum mechanically exhibits again the utility of the $O^+(2)\backslash/O^+(2)$ decomposition in a slightly different form which we want to sketch very briefly as it is related to the representations of $O^+(3)$ given above. The Hamiltonian reads

$$H = \frac{1}{2\theta} L^2 + \frac{1}{2\theta'} L^2_{z'}. \tag{3.6}$$

Here, θ and θ' denote scalars, $L^2 = \sum L_q^2 = \sum L_{q'}^2$ is the total angular momentum operator, L_z and $L_{z'}$ its components along the space-fixed and body-fixed axes z and z', respectively. $H, L^2, L_{z'}$ and L_z establish a set of commuting operators to be diagonalized simultaneously. Therefore, eigenstates $|FMN\rangle$ exist that, in the Schrödinger representation, are functions on the space-fixed sphere, in Dirac notation $\langle \alpha, \beta, \gamma | FMN \rangle$, satisfying the relations

$$L^2 \langle \alpha, \beta, \gamma | JMN \rangle = J(J+1)\langle \alpha, \beta, \gamma | JMN \rangle$$

$$L_z \langle \alpha, \beta, \gamma | JMN \rangle = M \langle \alpha, \beta, \gamma | JMN \rangle \qquad (3.7)$$

$$L_{z'}\langle \alpha, \beta, \gamma | JMN \rangle = N \langle \alpha, \beta, \gamma | JMN \rangle$$

and thus we have

$$H\langle \alpha, \beta, \gamma | JMN \rangle = \left\{ \frac{J(J+1)}{2\theta} + \frac{N^2}{2\theta'} \right\} \langle \alpha, \beta, \gamma | JMN \rangle. \qquad (3.8)$$

These functions are derived with the aid of the $O^+(2)\backslash/O^+(2)$ double coset decomposition of $O^+(3)$ and its connection to active and passive transformations along with the rules for their mutual substitution

$$\begin{aligned}
\langle \alpha, \beta, \gamma | JMN \rangle &= \langle 0, 0, 0 | R_z^\dagger(\gamma) R_y^\dagger(\beta) R_z^\dagger(\alpha) | JMN \rangle \\
&= e^{-i\alpha M} \langle 0, 0, 0 | R_{z'}(\gamma) R_y^\dagger(\beta) | JMN \rangle \\
&= e^{-i\alpha M} \langle 0, 0, 0 | R_y^\dagger(\beta) R_{z'}(\gamma) | JMN \rangle \\
&= e^{-i\alpha M} \langle 0, 0, 0 | R_y^\dagger(\beta) | JMN \rangle \, e^{i\gamma N} \\
&= e^{-i\alpha M} D_{MN}^J(R_y^\dagger(\beta)) \, e^{i\gamma N}. \qquad (3.9)
\end{aligned}$$

From the conventional normalization it follows that the numerical factor associated with the last step in Eq. (3.9) is equal to one. Since the resulting functions establish a complete set, the conclusions presented in Eq. (3.9) prove that it is the set of eigenfunctions of the symmetric top. The elegance of this derivation is due to the particular means employed and it may be appreciated when comparing with the effort that arises in checking that $\langle \alpha, \beta, \gamma | JMN \rangle$ satisfies the Schrödinger equation (cf. Ref. [43]).

4. Bilateral Classes

It will become apparent, particularly in Chapters 5 and 6, that many physical and chemical classification problems related to double cosets allow interpretation in terms of a classification of bijections. A casual examination of the various class concepts available in group theory, on the other hand, indicates that most of them permit interpretation related in some way to bijections; a unifying aspect, however, has not been stated until 1976 when the concept of bilateral classes was introduced and investigated [18], [19]. The present Chapter is devoted to this idea since we anticipate interesting applications in the future, as well as a better understanding of the particular rôle double cosets play in applications.

Concepts commonly used for a classification of elements of a group G refer to one or two subgroups $A, B \subseteq G$ as shown in the following list:

a) right coset $\qquad Ag \equiv \{ag | a \in A\}$

b) left coset $\qquad gB \equiv \{gb | b \in B\}$

c) double coset $\qquad AgB \equiv \{agb^{-1} | a \in A, b \in B\}$

d) conjugacy class $\qquad {}^{\backslash A /}\langle g \rangle \equiv \{aga^{-1} | a \in A\}.$

In case (d) the choice $A = G$ is common. The covering concept of "bilaterial class" is defined by the rather natural extension

$$ {}^{Q}\langle g \rangle \equiv \{sgt^{-1} | (s, t) \in Q\} \tag{4.1} $$

where Q is a subgroup of $G \times G$.

One easily specializes to double cosets and conjugacy classes, respectively, by subjecting the subgroup Q alternatively to the particular choices of (4.2), the notation used here fitting into a systematic scheme discussed later,

$$ C^{A \backslash / B} \equiv \{(a, b) | a \in A, b \in B\} $$
$$ Q^{\backslash A /} \equiv \{(a, a) | a \in A\}. \tag{4.2} $$

The classes quoted and others not listed above are found to be particular types of bilaterial classes. Beyond that, bilaterial classes either non-specialized or specialized by non-conventional requirements apparently fill a gap in the realm of classification concepts, desirable for applications in physics and in chemistry.

As to classification schemes in a given group the concept of double coset, as we have seen, is the more special one compared with the idea of bilaterial classes Z. The opposite statement, however, applies it bilaterial classes in a group G are compared to particular double cosets in the direct product $G \times G$. This statement can be verified by the aid of a map χ from $G \times G$ onto G, defined as

$$ \chi : \begin{cases} G \times G \twoheadrightarrow G \\ (g', g'') \mapsto g'g''^{-1}. \end{cases} \tag{4.3} $$

The elements of $G \times G$ mapped onto the same image element in G establish the left cosets of the so-called diagonal subgroup $Q^{\backslash G /}$ of $G \times G$ as given in (4.2). Note, however, that $Q^{\backslash G /}$, as a rule, is not an invariant subgroup in $G \times G$ and, consequently, χ is not a group homomorphism. Using any given subgroup $Q \subseteq G \times G$ with elements $(a, b) \in Q$ one concludes from the relation

$$ \chi : (ag'g, bg''g) \mapsto ag'g''^{-1}b^{-1} \tag{4.4} $$

that, associated with the map χ, there is a bijection $\hat{\chi}$ from the set of $Q \backslash / Q^{\backslash G /}$ double cosets of $G \times G$ onto the set of bilaterial classes ${}^{Q}\langle g \rangle$ of G

$$ \hat{\chi} : \begin{cases} \{Q(g', g'')Q^{\backslash G /} | (g', g'') \in G \times G\} \twoheadrightarrow \{{}^{Q}\langle g \rangle | g \in G\} \\ Q(g', g'')Q^{\backslash G /} \mapsto {}^{Q}\langle g'g''^{-1} \rangle. \end{cases} \tag{4.5} $$

The one-to-one correspondence as expressed in Eq. (4.5) provides technical means for the transfer of formulas, as for enumeration, from double cosets to bilateral classes. Beyond this, it concerns the basic classification philosophy relevant to a diversity of phenomena in physics and in chemistry. To cover the major scope of requirements as far as applications are concerned it will be rewarding to start with a classification of purely mathematical objects; i.e. to talk about bijections and their classification in view of symmetry.

Let G be the unrestricted symmetric group, defined as the group of bijections on a set R. Let M and N be two further sets equicardinal with R, and let ξ, η be a pair of bijections from R onto M and N, respectively, both commuting with the elements of G,

$$\left.\begin{array}{ll} \xi : R \twoheadrightarrow M & g \circ \xi = \xi \circ g \\ \eta : R \twoheadrightarrow N & g \circ \eta = \eta \circ g \end{array}\right\} \forall g \in G. \tag{4.6}$$

Commutativity as stipulated here can possibly define the action of the group G on M and N when it is known in respect of R, or it may be taken alternatively as the defining property of the particular choice of ξ and η in case the action has already been defined on R, M, and N. Regardless of the viewpoint, each pair of simultaneous bijections from R onto M and N can be presented with reference to ξ and η as an operator ω, element of an operator set $\Omega' \times \Omega''$,

$$\omega = (g' \circ \xi, g'' \circ \eta) \in \Omega' \times \Omega'', (g', g'') \in G \times G$$

$$\omega : R \mapsto U_\omega \subseteq M \times N \tag{4.7}$$

where Ω' and Ω'' are the sets of bijections from R onto M and from R onto N, respectively. Each operator ω maps R onto a particular subset U_ω of $M \times N$, which represents a one-to-one correspondence between and M and N. Hence the image U_ω also determines a bijection from, say, N onto M. Such a subset or the bijection associated does not change if prior to ω a bijection of R onto itself is performed. Therefore, equivalence classes in $\Omega' \times \Omega''$ are specified through the image the operators produce upon application to R. To put this result into a simple form it helps to use again the map χ slightly extended beyong the range of definition in Eq. (4.3) and to refer to a reference bijection ε from N onto M as follows:

$$\chi : \begin{cases} \Omega' \times \Omega'' \twoheadrightarrow \Omega \\ (g' \circ \xi, g'' \circ \eta) \mapsto g' g''^{-1} \circ \varepsilon, \varepsilon \equiv \xi \circ \eta^{-1}. \end{cases} \tag{4.8}$$

Accordingly we obtain an interpretation of (4.5) in terms of bijection classes

$$\hat{\chi} : \begin{cases} \{Q(g', g'')Q^{\backslash G/} \circ (\xi, \eta) | (g', g'') \in G \times G\} \twoheadrightarrow \{^Q\langle g \rangle \circ \varepsilon | g \in G\} \\ Q(g', g'')Q^{\backslash G/} \circ (\xi, \eta) \mapsto {}^Q\langle g' g''^{-1} \rangle \circ \varepsilon. \end{cases} \tag{4.9}$$

The one-to-one correspondence (4.9) touches upon facts related to geometry and physics. First, a left coset of $Q^{\backslash G/}$ in application to (ξ, η) collects all the operators of $\Omega' \times \Omega''$ that represent the same bijection from N onto M; second, right cosets of Q, applied thereafter, may be taken as collecting symmetry

equivalent bijections from N onto M. Acting from the left on both the range and the domain the group Q appears as the symmetry group of bijections defined with satisfying generality since range and domain are equally taken into consideration. Statement (4.9) shows that the symmetry equivalence of bijections, in this most general interpretation, is equally well taken into account when bilateral classes of G are applied to a reference bijection ε. As to an appreciation of the present result, it helps primarily those concerned with applications to have a most intuitive understanding of the symmetry concept mentioned. That is why an intimate knowledge of the structure of subgroups of a direct square $G \times G$ is desired. This structural information has already been made available by E. Goursat [44] in 1889.

According to Goursat's theorem, given in reference to finite groups, any subgroup of a direct square is characterized by a pair of subgroups A, H and B, K in each of the factors of $G \times G$ and an isomorphism μ. It is required that A and B be invariant subgroups of H and K, respectively, such that the factor groups are isomorphic $H/A \cong K/B$; μ denotes any chosen isomorphism map between these factor groups. The determinative quantities of a subgroup Q of $G \times G$ subsequently specified by the label $A \backslash H \mu K / B$ are properly defined through

$$H \equiv \{g' \in G | (g', g'') \in Q\} \qquad K \equiv \{g'' \in G | (g', g'') \in Q\}$$
$$A \equiv \{g' \in G | (g', e) \in Q\} \qquad B \equiv \{g'' \in G | (e, g'') \in Q\}$$

(4.10)

as one proves corroborating the properties postulated. For convenience we refer to a system of elements of H and K representative for A- and B-cosets, respectively, and to a map concerning their indices which are fixed provided μ is given,

$$\mu : \begin{cases} H/A \twoheadrightarrow K/B \\ Ah_i \mapsto Bk_{\mu(i)}. \end{cases}$$

Any subgroup Q of $G \times G$ and an associated bilateral class $^Q\langle g \rangle$, according to the characteristic label $A \backslash H \mu K / B$, permit a formal account as follows:

$$Q^{A \backslash H \mu K / B} \equiv \{(ah_l, bk_{\mu(l)}) | ah_l \in Ah_l \in A/H, bk_m \in Bk_m \in B/K\}$$
$$\equiv \bigcup A(h_l, k_{\mu(l)})B \equiv \bigcup Ah_l \times Bk_{\mu(l)}$$
$$^{A \backslash H \mu K / B}\langle g \rangle \equiv \{ah_l g k_{\mu(l)}^{-1} b^{-1} | ah_l \in Ah_l \in A/H, bk_m \in Bk_m \in B/K\}$$
$$\equiv \bigcup Ah_l g k_{\mu(l)}^{-1} B.$$

(4.11)

Note that any bilateral class may always be conceived as a particular union of double cosets.

Goursat's theorem becomes a statement in relation to intuition as we need it, if one adds an interpretation in terms of *correlation* with emphasis on the rôle played by the subgroups $A \times B$ and $H \times K$. Both of these groups are members

of a chain

$$A \times B \subset Q \subset H \times K. \tag{4.12}$$

$A \times B$ and $H \times K$ are particular direct products in respect of $G \times G$ in that the direct factors of these subgroups are subgroups of the respective direct factors of $G \times G$. This fact entails that the elements of $A \times B$ or of $H \times K$ represent all the combinations of elements admissible from the left and from the right factors in $A \times B$, denoted by A and B or by H and K, respectively; in other words, when passing from $G \times G$ to $A \times B$ or to $H \times K$ it is not the combination but the selection of elements of each factor that is reduced. This phenomenon shall be stated by saying that both $A \times B$ and $H \times K$ are uncorrelated subgroups of $G \times G$.

Reexamination of the definition presented in (4.10) shows that $A \times B$ is the greatest uncorrelated subgroup contained in Q, and $H \times K$ is the smallest uncorrelated subgroup containing Q^2. With this in mind one verifies the following summary:

With reference to $G \times G$ it is correct to call the direct product $H \times K/A \times B$ with elements (Ah_i, Bk_j) an uncorrelated factor group. Restriction to elements of the form $(Ah_i, Bk_{\mu(i)})$ leads from $H \times K/A \times B$ to its subgroup $Q/A \times B$. Thus it is demonstrated that the isomorphism μ introduces correlation inherent to Q in the uncorrelated factor group $H \times K/A \times B$ leading to the group $Q/A \times B$ which presents this correlation in pure form as the only uncorrelated element is the unit element. Because of this result we call $Q/A \times B$ the correlation group of Q.

From the foregoing discussion it follows that correlation is the property that permits a natural classification of subgroups of $G \times G$ in view of structural particularities. Two limiting cases are distinguished by $Q/A \times B = Q$ and $Q/A \times B = E$, characterized as, we shall say, by the *absence of correlation* and by *total correlation*, respectively. If neither of these conditions is fulfilled we speak of *partial correlation*.

The following list gives some more detailed specification of the type of subgroups and of the associated type of bilateral classes. It is recommended to think in terms of bijections where our terminology refers to symmetry. Then we have symmetries in reference to range and domain, uncorrelated, totally correlated, and partially correlated. The groups A and B play the part of symmetry groups of range and domain, respectively. H and K encompass all the operations involved in symmetry operations. The associated classes thus denote bijection classes in view of symmetry equivalence. The following list contains a particular selection of cases that are of prime interest. The notation proposed has already been used, to some extent, in the present Chapter. E denotes the identity

---

[2]   In this context 'greatest' and 'smallest' are statements expressing that all other subgroups of this type either are contained in the group in question or contain it, respectively.

subgroup, ι specifies the identity isomorphism; if there is no choice in the isomorphic map μ is replaced by a dash.

1) $A\backslash/B$ no correlation, (short form of $A\backslash A - B/B$)

$$Q^{A\backslash/B} \equiv A \times B$$

$$^{A\backslash/B}\langle g \rangle = AgB.$$

2) $\backslash H\mu K/$ total correlation, (short form of $E\backslash H\mu K/E$)

$$Q^{\backslash H\mu K/} \equiv \{(h, \mu(h)) | h \in H\}$$

$$^{\backslash H\mu K/}\langle g \rangle \equiv \{hgk^{-1} | h \in H, k = \mu(h)\}$$

$$\mu : \begin{cases} H \twoheadrightarrow K \\ h \mapsto \mu(h). \end{cases}$$

3) $A\backslash H/A$ (partial) diagonal correlation, (short form of $A\backslash H\iota H/A$)

$$Q^{A\backslash H/A} \equiv \bigcup_l Ah_l \times Ah_l$$

$$^{A\backslash H/A}\langle g \rangle \equiv \bigcup_l Ah_l g h_l^{-1} A.$$

4) $\backslash H/$ (total) diagonal correlation, (short form of $E\backslash H\iota H/E$)

$$Q^{\backslash H/} \equiv \{(h, h) | h \in H\} \equiv (H \times H)_D$$

$$^{\backslash H/}\langle g \rangle \equiv \{hgh^{-1} | h \in H\}.$$

The number of bilateral classes contained in a given decomposition of a group G, the orders of the single classes, and their repetition frequencies are easily deduced if one recalls the connection with double cosets in the direct product group $G \times G$ (cf. Eq. (4.4)). Thus, from Eqs. (2.6), (2.4), and (2.9), formulas (4.13), (4.14), and (4.15) are obtained with the convenient abbreviation Q for $Q^{A\backslash H\mu K/B}$ and $i = |H/A| = |K/B|$; $d(^O\langle g \rangle)$ and $|^O\langle g \rangle|$, respectively, denote the repetition frequency and the order of a bilateral class $^O\langle g \rangle$. The number of these classes in G is denoted by $z(^O\langle \rangle)$.

$$d(^O\langle g \rangle) = \sum_l |Ah_l g \cap gBk_{\mu(l)}| = \sum_l |Ah_l \cap gBk_{\mu(l)}g^{-1}| \tag{4.13}$$

$$|^O\langle g \rangle| = \frac{i|A||B|}{\sum_l |Ah_l \cap gBk_{\mu(l)}g^{-1}|} \tag{4.14}$$

$$z(^O\langle \rangle) = \frac{1}{i|A||B|} \sum_{g \in G} \sum_l |Ah_l \cap gBk_{\mu(l)}g^{-1}|$$

$$= \frac{|G|}{i|A||B|} \sum_r \sum_l \frac{|C_r \cap Ah_l||C_r \cap Bk_{\mu(l)}|}{|C_r|} \tag{4.15}$$

5. Arrangements

Classification of Molecules with the Same Gross Formula

An understanding of many phenomena in chemistry takes advantage of, or is entirely based upon, an appropriate classification of compounds and their molecules. Molecules made up of the same kind and number of atoms but differing in their spatial structure are called "isomers", a concept which is equally used to distinguish the compounds thereof. A classification like this is necessitated and referred to by the name of "permutational isomers" if the isomers are derivatives of a so-called parent compound with which they have a representative "molecular skeleton" in common, differing only in the distribution of a given assortment of ligands on given skeletal sites. One specializes to the concept of "stereoisomers" if the molecules show only limited mobilities such that differentiation is disclosed by structural characteristics compatible with the assumption of a rigid skeleton. If the skeleton is not particularly simple, has spatial symmetry, and some of the ligands are of the same, some of different kind, then a survey of distinguishable stereoisomers requires systematic means. A concept like molecule or even isomer is not always obvious. Molecules distinguishable at a low temperature may not be distinguishable if the temperature is high, or a time-averaged structure may be entirely different for experiments where the characteristic observation time is not the same. Thus, for these and other reasons a more adaptable notion of configuration, subsequently called Q-configuration, is required in order to obtain a classification of steroisomers according to broader equivalence ideas. To be in a position to translate a vague conception of such chemical objects into a mathematically clear-cut formalism and to have a mathematical tool available to handle systematically all sorts of concerned questions touches upon some basic needs in stereochemistry.

The number of stereoisomers can be found with combinatorial methods given by G. Pólya [45] in 1937. His procedure was not designed to help with a formulation of the classification idea or to be of use to an analysis of individual characteristics of single classes. Bilateral classes, however, and double cosets in particular, applied to bijections, in short, "bijection classes" are the mathematical objects which, acting the part of an algebraic analogue, reflect the type of classification ideas under discussion. This fact also involves a simple method of enumeration both of isomers and of more complex configurations according to a diversity of classification ideas, and, in addition, allows an immediate translation of a variety of related problems from an intuitive level to an algebraic formalism, thus providing a more rigorous analysis. The fortunate equivalence between chemical reality and mathematical objects was first pointed out in particular reference to double cosets [38] in 1970. Yet, the generalization achieved with the concept of bilateral classes met a demand in the field of stereochemistry.

a) Permutational Stereoisomers (Subsequently Abbreviated to Stereoisomers)

Without loss of essentials for the present classification problem, the reader may imagine a set of simplified models named *standard models*, introduced by one

of the authors (E.R) [46] in 1977, and taken as a substitute of the chemical reality of stereoisomers. A simple rigid geometrical figure with a given number of distinguished points and the same number of spheres each centered at one of these points constitutes a model of said type. Different kinds of ligands in a derivative are indicated by different diameters of spheres distributed correspondingly. Visually distinguishable models obviously represent distinguishable stereoisomers. In many cases, these models though being extremely simplified correctly represent the overall symmetry of the real chemical object. Individual deformations of skeleton and ligands as observed in real molecules mostly do not reduce the overall symmetry as indicated by the associated standard model. The relation between standard models and chemical reality is thoroughly discussed in the above-mentioned paper [46]. When looking at standard models in lieu of molecules we resort to a simplified picture avoiding cumbersome analyses of whether symmetry statements correct in respect to the model, apply to nature strictly or in an approximative sense only.

Classification according to stereoisomers is trivial as every arrangement of spheres constitutes its own species as long as skeletons without spatial symmetry are concerned and no pair of identical ligands appears. The situation changes when symmetries are observed. First, due to skeletal symmetry certain rearrangements of ligands may lead to the same result as a proper rotation of the whole molecule does, and, therefore, are not recorded by most of the usual experiments. Second, the particular ligand system, as for differentiation according to ligands of the same and of different type, is characterized in that exchanges of equally sized spheres are not noticeable; as a consequence reduction of distinguishable stereoisomers follows. In short, two permutation groups A and B representing spatial symmetry of the molecular skeleton and permutational symmetry of the ligand system, respectively, contribute to the viewpoint responsible for symmetry equivalence. Both of these groups may be interpreted as a representation of symmetry in terms of ligand permutations. As to stereoisomers, A is a homomorphic image of the pure rotational symmetry of the skeleton and B characterizes the particular ligand system, composed of t kinds of ligands, by the direct product $B \equiv S_{\alpha_1} \times S_{\alpha_2} \times \cdots \times S_{\alpha_t}$ with the symmetric groups S_{α_i} of degree α_i, satisfying $\sum_1^t \alpha_i = N$.

The intuitive conception of bilateral classes as invoked in Chapter 4 takes effect in view of the present classification objective. The set of ligands and the set of skeletal sites act the part of range and domain of bijections representing stereoisomers, provided there be no symmetry. For the more general cases including symmetry, classes of symmetry equivalent bijections are sought where the requisite symmetry is $A \times B$, which is a subgroup of $S_N \times S_N$ and is uncorrelated in its dependence on range and domain. Such classes, therefore, are determined by double cosets as

$$^{A \times B}\langle g_r \rangle \circ \varepsilon \equiv A g_r B \circ \varepsilon. \tag{5.1}$$

The far-reaching analogy between steroisomers and their algebraic counterpart is to be utilized for a variety of questions. One of prime interest refers to the

symmetry of individual stereoisomers. The total skeletal symmetry is specified, in terms of permutations, by a group that shall be denoted by H disregarding whether it is identical with A or not. In case of chiral skeletons we have $H = A$; this identity may also happen to come about in exceptional cases of achiral skeletons i(e.g., of planar skeletons). However, the standard situation for achiral skeletons is that the elements of A, representing proper rotations per definitionem, do not represent improper rotations at the same time; so A is a proper subgroup of H. The symmetry of a given stereoisomer is represented by the permutation group S_r according to Eq. (5.2)

$$S_r = H \cap g_r B g_r^{-1}. \tag{5.2}$$

Since S_r is invariant under the substitution $g_r \to g_r' \in Hg_r B$ up to conjugation with elements of H, it refers to the associated isomer; it represents the molecular symmetry since it contains those elements of H which, at the same time, are elements of the group $g_r B g_r^{-1}$, effecting permutations among correspondingly distributed spheres of equal sizes.

Note, finally, the enumeration of stereoisomers is performed through the use of formulas (2.8) and (2.9). Preference is given to (2.8).

The classification given in (5.1) differentiates between mirror-image stereoisomers that possibly occur in case of molecules with an achiral skeleton and exclusively achiral ligands. Such so-called *enantiomers*, as a rule, occur if the achiral skeleton is not a planar one. To disregard enantiomerism means that we preclude enantiomers from being members of different classes. All one has to do is to use H instead of A since then improper rotations do not lead to distinguishable objects. Such classes, mostly called stereoisomers, as well, according to a nomenclature convention in chemistry are defined by

$$^{H \times B}\langle g_r \rangle \circ \varepsilon = Hg_r B \circ \varepsilon. \tag{5.3}$$

One usually speaks of a *configuration* if in contrast to the above emphasis is laid upon differentiation between enantiomers.

Q-Configurations and Partially Correlated Symmetries

Enantiomerism among stereoisomers may occur even when chiral ligands belong to the ligand system. Necessary prerequisites are an achiral skeleton, a racemic ligand system, i.e. the ligands must be either achiral or, if chiral, pairwise enantiomeric, and an appropriate fixation at the ligand sites. When chiral ligands are involved a classification omitting the distinction of enantiomers just because a sufficiently simple anschauung is not available appears to be confusing even for very simple skeletons. The classification objective, however, is significant since a diversity of chemical and of physical properties of chemical compounds do not depend on enantiomerism, and experiments designed correspondingly do not even record respective differences.

Transition from a stereoisomer to its mirror image, i.e. reflection of the whole object, results when a permutation of ligands equivalent to a rotation of the skeleton is combined with a simultaneous substitution of each chiral ligand by

its mirror image; appropriate fixation being presumed. This latter requirement can be dropped because it is superflous when colored standard models are discussed instead. For these models we stipulate colored spheres, white ones for achiral ligands, green and red ones of equal size for chiral ligands that are mirror images. In application to the models, reflections only in conjunction with an overall exchange of the colors red and green are an equivalent of the transition from one isomer to its enantiomer.

Recalling the definition of the groups A and H, and in view of the present conditions, one confirms the coset decomposition $H \equiv A \,\dot\cup\, \sigma A$ where the permutation σ represents a reflection but not at the same time a rotation of the skeleton. Let B denote the symmetry group of the ligand system established by all the permutations among spheres of equal size *and* color, and τ be a permutation that effects exchange of each red sphere by an equally sized green one. So there is a group $K = B \,\dot\cup\, \tau B$ distinguished in that B is a symmetry group of the ligand system and the coset τB contains all the permutations among spheres of equal size that effect the total exchange of the colors green and red. Thus, as before, $A \times B$ is the symmetry group answerable for symmetry equivalence in case enantiomers be distinguished while, in addition, the set $\sigma A \times \tau B$ has to be added in order to establish the symmetry in cases this distinction be not made. In short, partially correlated symmetry under discussion is given by the group

$$Q^{A \backslash H - K/B} \equiv (A \times B) \,\dot\cup\, (\sigma A \times \tau B). \tag{5.4}$$

With the results of Chapter 4 in mind the desired classes are found to be (comp. [47])

$$^{A \backslash H - K/B}\langle g_r \rangle \circ \varepsilon \equiv (A g_r B \cup A \sigma g_r \tau B) \circ \varepsilon. \tag{5.5}$$

Note that for the particular cases where σ, or τ, or both, do not exist, enantiomerism does not occur. Correspondingly the symmetries become uncorrelated and the associated classes simplify to double cosets as follows:

$$
\begin{aligned}
&\nearrow A \times K: {}^{A \times K}\langle g_r \rangle \circ \varepsilon \\
Q^{A \backslash H - K/B} &\rightarrow H \times B: {}^{H \times B}\langle g_r \rangle \circ \varepsilon \\
&\searrow A \times B: {}^{A \times B}\langle g_r \rangle \circ \varepsilon.
\end{aligned}
\tag{5.6}
$$

The distinction of enantiomers and its respective omission touch to a great extent upon the prevalent classification interest in the field of stereochemistry. The numbers of classes associated can be used to count chiral and achiral objects separately, in the cases discussed up to here. The numbers of achiral and of chiral stereoisomers denoted by z_α and z_χ, respectively, are obtained from the following system of equations that is easily verified,

$$
\begin{aligned}
z\left({}^{A \backslash H - K/B}\langle\,\rangle \right) &= z_\alpha + \tfrac{1}{2} z_\chi \\
z\left({}^{A \backslash B}\langle\,\rangle \right) &= z_\alpha + z_\chi.
\end{aligned}
\tag{5.7}
$$

According to a requirement mainly arising from the conditions encountered in nature, as mentioned in the beginning of the present Chapter, a concept is

recalled that covers classification objectives where various differentiations, obviously present in case of rigid molecules, are not made. The skeleton may undergo internal twists, rotations or oscillations such that the observations under discussion concern a time-averaged molecular structure which can be characterized by experimentally non-distinguishable situations, so-called conformations. Correspondingly, the skeletal symmetry groups A or H or both must be adapted to the particular requirements. On the other hand, the ideal of ligand assortment symmetry, too, may be subjected to various interpretations in order to match the disregard of particular differences of ligands, e.g. of isotopic atoms, or to take into account restrictions in the spatial relationship among ligands, e.g. among those partially bridged together.

A particular situation arises in connection with so-called bidentate ligands, i.e. pairs of ligands bridged together. As the two partners of a bridge are considered non-separable, the group B has to be chosen accordingly. Permutations of ligand members which do not effect simultaneous permutations of equivalent bridges must not be contained in the group B, and the mutual exchanges of the members of bridges belong to B if the bridges have a symmetry which is to be represented in this way. Spatial constraints imposed by limited lengths of bridges need to be handled with special care. One finds explicit discussion of bidentate ligands, as well as of other "constrained" situations in the literature [48].

Whatever the particular classification objective may be, either to satisfy theoretical requirements or to match experimental facts, it is concerned with the distribution of ligands at the sites of a skeleton. Therefore it always leads to the problem of classifying bijections which was solved in Chapter 4. For obvious reasons we shall call such classes Q-configurations where Q is a subgroup of $S_N \times S_N$ chosen appropriately.

Examples and Supplementary Remarks

The following examples are to facilitate the technical evaluation of the theory presented; they are selected to achieve this with a minimum effort and without being trivial, to allow an intuitive testing of single steps. The chemist may take the objects presented in Figs 1 to 3 as the models of the allene skeleton and its derivatives. The numbering of skeletal sites in Fig. 1 is standard also to the other figures; thereto related, the action of the group H and its subgroup A can be verified as symmetry operations associated with the achiral skeletal symmetry D_{2d} and its chiral subsymmetry D_2, respectively. Subsequently, however, these permutations are to be interpreted as acting on spheres which are placed at respective sites.
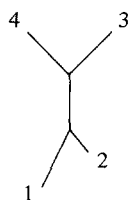
$$D_2: = A \equiv \{(1),\ (12)(34),\ (13)(24),\ (14)(23)\}$$

$$(12)A \equiv \{(12),\ (34),\ (1324),\ (1423)\}$$

$$D_{2d}: = H \equiv A \cup (12)A$$

Fig. 2 shows, illustrated by standard models, stereoisomers with exclusively achiral ligands and their respective classification with and without distinction of enantiomers, i.e. $Q^{A\backslash/B}$- and $Q^{H\backslash/B}$-configurations, on the assumption that one kind of ligands occur twice in the ligand assortment. The elements of the group B (like those of A) are related to site numbers and represent the composition of the ligand assortment in reference to the stereoisomer associated with $A(1)B$. Moreover, the symmetry groups of the stereoisomers are explicitly worked out according to Eq. (4.2).

$$B \equiv \{(1), (34)\}$$

$$H \cap B \equiv \{(1), (34)\}$$

$$H \cap (23)B(23) \equiv \{(1)\}$$

$$H \cap (24)B(24) \equiv \{(1)\}$$
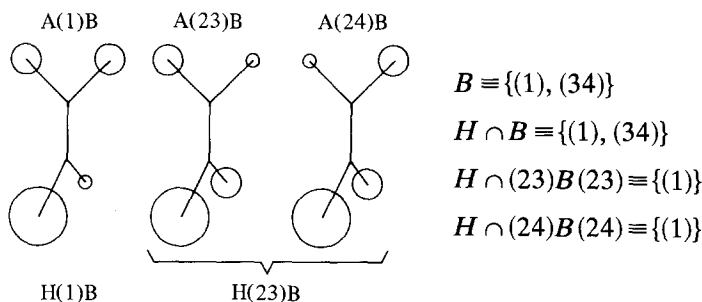
Table 1 and a formula for the order of conjugacy classes C_r of the symmetric group S_N provide all the information needed for ready application of formula (2.8). In the expression for $|C_r|$ the letter l denotes the length of a cycle, and $a_l(r)$ the number of times a cycle of length l occurs in a permutation of the class C_r.

Table 1

C_r	$|C_r|$	$|C_r \cap A|$	$|C_r \cap B|$	$|C_r \cap H|$
$(\cdot)$	1	1	1	1
$(\cdot\,\cdot)$	6	0	1	2
$(\cdot\,\cdot)(\cdot\,\cdot)$	3	3	0	3
$(\cdot\,\cdot\,\cdot)$	8	0	0	0
$(\cdot\,\cdot\,\cdot\,\cdot)$	6	0	0	2

$$|C_r| = \frac{N!}{\prod_l l^{a_l(r)} a_l(r)!}$$

$$z\left(^{A\backslash/B}\langle\rangle\right) = \frac{24}{2\cdot 4} \cdot 1 = 3$$

$$z\left(^{H\backslash/B}\langle\rangle\right) = \frac{24}{2\cdot 8}\left(1 + \frac{2}{6}\right) = 2$$

The more complicated case of four different ligands, two of them achiral and two of them chiral but mirror images of each other, is illustrated in Fig. 3. The enantiomeric ligands, following a suggestion by V. Prelog [49], are represented by equal spheres with mirror-image letters F and ꟻ as the substitutes of the colors red and green used earlier. Since B is the unit subgroup in the present example, $A\backslash/B$-double cosets degenerate to right cosets of A. Configurations without a differentiation of enantiomers are represented by bilateral classes associated with the group $Q^{A\backslash H - K/B}$ as indicated in the figure. Counting can be performed by virtue of formula (4.11). The numbers of chiral and achiral stereoisomers are determined according to Eq. (5.7).
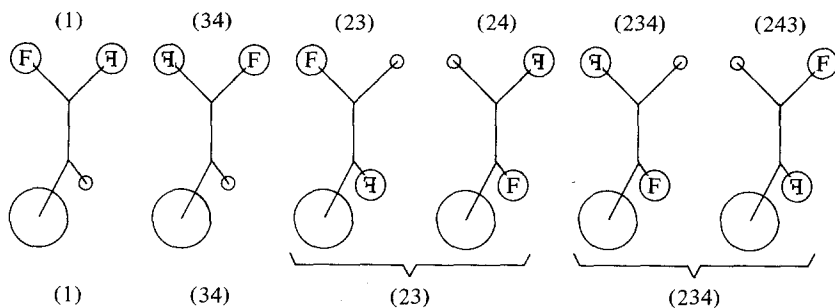
$$H \equiv A \cup (12)A$$

$$K \equiv B \cup (34)B, B = \{(1)\}$$

$$Q^{A\backslash H - K/B} \equiv A \times B \cup (12)A \times (34)B$$

$$^{A\backslash H - K/B}\langle(1)\rangle \equiv \{(1), (12)(34), (12)(24), (14)(23)\}$$

$$^{A\backslash H - K/B}\langle(34)\rangle \equiv \{(34), (12), (1324), (1423)\}$$

$$^{A\backslash H - K/B}\langle(23)\rangle \equiv \{(23), (1243), (1342), (14), (1234), (24), (13), (1432)\}$$

$$^{A\backslash H - K/B}\langle(234)\rangle \equiv \{(243), (123), (134), (142), (124), (234), (132), (143)\}$$

$$z\left(^{A\backslash/B}\langle\rangle\right) = 6 = z_\alpha + z_\chi$$
$$z\left(^{A\backslash H - K/B}\langle\rangle\right) = 4 = z_\alpha + \tfrac{1}{2}z_\chi \qquad z_\alpha = 2, z_\chi = 4.$$

Fig. 4 illustrates what has been called Q-configuration; the model skeleton shown can be identified with the one of ethane and its derivatives. At a low temperature these molecules have a more or less rigid skeleton of symmetry D_{3d}, but as the temperature increases, they allow internal rotation around the axis of the figure such that the symmetry group associated, written in terms of the Schönflies notation, is $(C_3 \times C_3)C_{2v}$. The chiral subsymmetries are D_3 and $(C_3 \times C_3)C_2$, respectively. For specification of a racemic ligand system which contains achiral ligands exclusively or in part the groups B or both B and K are used as discussed. The groups A and H as listed in the figure apply when rotation occurs:
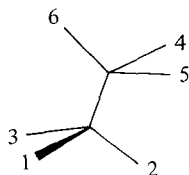
$$(C_3 \times C_3)C_2: A \equiv [\{(1), (123), (132)\} \times \{(1), (456), (465)\}] \cdot \{(1), (14)(26)(35)\}$$

$$(C_3 \times C_3)C_{2v}: H \equiv A \cup (14)(25)(36)A.$$

Summing up, several main goals may be stated in connection with the classification of stereoisomers feasible whenever possible with the mathematical instruments presented: firstly, to give a precise meaning to configuration concepts conceived rather vaguely; secondly, to transform the classification idea into a

clear-cut form such that the classification is easily worked out; thirdly, to count the number of classes; fourth, to generate the appropriate class labels; and fifth, to find an at least partial characterization of individual classes which is more informative than mere labeling. The first three points have been brought forward here in detail while canonical labeling is the topic of papers by H. Brown, L. Hjelmeland, and L. Masinter [50], H. Brown and L. Masinter [51], and H. Brown [52]. The individual characterization of single configurations according to particularities of any kind is a challenge which cannot be satisfied in any case since possibly nothing of this kind does exist. Mere labeling, though a colorless substitute, then has to be used in place of the above or as a supplementary means to make the notation complete where natural characteristica do no suffice. An obvious individual criterion is configurational symmetry, as pointed out earlier. There are other possibilities such as the subclassification of a configuration in terms of constituent "conformations" or the like. A classical issue strongly associated with the subclassification is the identification of steroisomers as members of a single so-called "structural isomer". Some special mathematics useful to an analysis of such questions is found elsewhere [48].

6 Rearrangements

Classification of Chemical Reactions

Permutations are used to label and classify not only chemical species but also reaction processes which cause permutational isomerization or, in other words, reorganization of compounds from one permutational isomer to another. Basically, such changes are explained as the result of intermediate deformations of the molecular skeleton by twisting motions, inversions, vibrations, etc. Summing up, it is observed that the mechanisms of such reactions primarily depend on the properties of the skeleton, and secondarily on the substituent ligands.

This experience, as a first approximation, offers to classify isomerization processes on the basis of a complete neglect of all the effects that are due to the particular type of ligands. Limitations inherent to such an idealization have to be kept in mind, nevertheless, respective comprehension will have its merits if based upon such a scheme generally applicable even though, and just because, deviations from rules involved have to be expected for which, in turn, one may hope to find an interpretation with physically, or chemically, realistic rationales. This situation explains proposals made since 1970 to discuss the reaction mechanism involved on the basis on an appropriate classification and to describe concerned classification schemes in this context in a more or less semi-empirical and ad hoc manner [53], [54], [55]; in particular it explains the attempt to give a precise definition of the classification idea and to develop mathematical means that allow for strict analysis and for formal application [39], [56], [57].

The appropriate means to discuss the classification of rearrangements evidently are the same as those which have proved to be valuable in case of arrangements. This, one infers from the exposition of Chaps. 4 and 5. Within the context of

arrangements, bijections from a system of ligands onto the equicardinal set of skeletal sites were under discussion; now bijections from the set of skeletal sites onto itself have to be classified. The arguements needed for the present problem differ slightly from those of Chap. 4, and, yet, contribute further structural viewpoints and an even stronger appreciation of the part played by bijection classes. The subsequent argumentation may be followed with this goal in mind.

Isomerization reactions involve that the skeleton, after intermediate deformations, finally coincides with its initial geometry. Therefore, one may be certain that rearrangements of ligands are equivalent if they can be identified by conjugation with some elements of the group H which represents the total skeletal symmetry, i.e. equivalence of g and g' follows from $g' = hgh^{-1}$, $h \in H$. Preceding and succeeding rearrangements that only act as rotations of the educt and of the product, respectively, also, do not change the result of a given rearrangement; in other words, the equivalence of permutations g and g' also follows from $g' = a'ga''$; $a', a'' \in A$. Summarizing, two classification principles have to be taken into account leading to the classes $\{hgh^{-1}|(h, h) \in Q^{\backslash H/}\}$ and $\{a'ga''^{-1}|(a', a'') \in Q^{A\backslash/A}\}$, each of these representing a sufficient condition and both, together, a necessary alternative for equivalence in the sense requested. These two conditions have consequences in common as expressed through the intersection group $Q^{\backslash H/} \cap Q^{A\backslash/A} = Q^{\backslash A/}$, but the very group fully accounting for symmetry equivalence, as we need it, has to be defined as the smallest group containing both of these subgroups, $Q^{\backslash H/}$ and $Q^{A\backslash/A}$. Thus one obtains the symmetry group required and the appertaining classes as follows:

$$Q^{A\backslash/A} v Q^{\backslash H/} = A \times A \cup \sigma A \times \sigma A = Q^{A\backslash H - H/A}$$
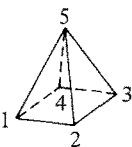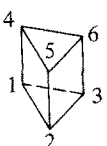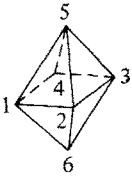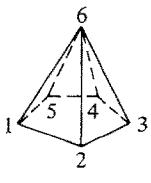$$^{A\backslash H - H/A}\langle g \rangle \circ \varepsilon = (AgA \cup A\sigma g\sigma^{-1}A) \circ \varepsilon.$$

(6.1)
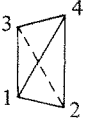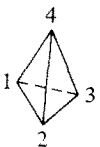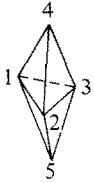
In the case of a chiral skeleton, σ does not exist and thus the rearrangement classes are double cosets $AgA \circ \varepsilon$. The same simplification, in principle, comes about when the skeleton is achiral and no distinction is made between products with ligands in mirror-image positions; then the classes derived simplify to so-called racemic rearrangement classes

$$^{H\backslash/H}\langle g \rangle \circ \varepsilon = HgH \circ \varepsilon.$$

(6.2)

From a concise historical review on the present subject one obtains some nice illustration of how mutual profit accrues from the confrontation of chemical and of purely mathematical questions. In contrast to the classification of arrangements, where the chemically significant problems are solved by double coset decomposition, the classification concerning isomerization processes necessitates classes that are unions of double cosets even in case of the standard situation. This fact had been stated and rationalized at first [39] when the concept of bilateral classes was not yet available. The arguments used in that paper are essentially those ones presented above, and a representative list of examples contained therein is, in part, reproduced in table 2 where each of the permutations quoted stands for its own class. J. Musher [55], at almost the same time, arrived by intuitive means at the correct permutation classes for the particular cases of

Table 2

Skeleton	Symmetry	Number of Modes	Representatives of Modes
	C_{2v}	6	(1), (12), (13), (123), (13)(24), (1324)
	C_{3v}	4	(1), (12), (14), (124)
	D_{3h}	6	(1), (12), (14), (124), (14)(25), (1425)
	C_{4v}	7	(1), (12), (13), (15), (125), (135), (12)(35)
	D_{3h}	20	(1), (12), (14), (34), (123), (124), (142), (234), (12)(34), (12)(45), (13)(45), (14)(23), (14)(25), (15)(34), (1234), (1243), (1254), (1432), (1543)
	O_h	5	(1), (12), (13), (125), (12)(35)
	C_{5v}	24	(1), (12), (13), (16), (123), (126), (135), (136), (12)(35), (12)(36), (13)(26), (13)(56), (15)(36), (1236), (1263), (1325), (1356), (1352), (1365), (1523), (1563), (12)(356), (13256), (16523)

^a excerpt from Ref. [39].

octahedral and of trigonal bypyramidal skeletons and named them modes. The utility of double cosets for the construction of rearrangement classes became rather obvious from the moment when their relevance for the concept of configuration was analyzed [38]. It was, however, the occurrence of unions of double cosets which indicated in a convincing way that classes more general than double cosets might establish the algebraic classification concept needed as a satisfactory counterpart or reality in nature. It turned out that this very concept, in respect of arbitrary groups, is the one covering, as special cases, all the conventional types of classes long used in group theory, and that, moreover, further types of particular interest are easily derived upon specialization. As for application in chemistry, confusion among the various interpretations of the idea of modes ought to be ruled out. Therefore, we propose to call bijection classes in application to isomerization processes *Musher modes*.

With the concept of bijection classes and its structural modalities available limitation to isomerization processes on skeletons of identical geometry for both the educt and the product is no longer needed. We extend our understanding of the concept of a skeleton, therefore, to the notion of a set of sites distributed on some carrier of possibly disconnected parts, as for geometry and number, possibly different for the educt and for the product. The only assumption introduced for the sake of simplified presentation because further simplification arises when dropped, is that both the educt and the product have achiral symmetries represented by groups $H = A \cup \sigma A$ and $K = B \cup \tau B$, respectively. Following the arguments already used, two symmetry aspects have to be taken into account, the uncorrelated symmetry, distinguished by proper rotations and represented by elements of the group $A \times B$, and the correlation group $Q/A \times B$ isomorphic with the subgroup $\{(e, e), (\sigma, \tau)\}$ of $H \times K$. These associated classes are

$$^{A \backslash H - K/B}\langle g \rangle = AgB \cup A\sigma g\tau B. \tag{6.3}$$

In case the educt, or the product, or both of them, have chiral skeletons, partial correlation in the symmetry disappears as $Q^{A \backslash H - K/B}$ simplifies to $Q^{H \backslash K}$, where either H, or K, or both H and K, become identical with the subgroups A or B, or both A and B, respectively. This means that corresponding classes are represented by $A \backslash /K$, or $H \backslash /B$, or $A \backslash /B$-double cosets. Material in this context is extensively discussed in W. G. Klemperer's papers [56] though he tends to avoid unions of double cosets.

Recalling the notion of partially correlated symmetry in its general form, analyzed in Chap. 4, one can hardly imagine a situation that accounts for all sorts of mobilities allowed in the skeleton of both the educt and the product, where the classification of reaction processes could not be described by bijection classes. There is, however, an exceptional situation that needs further consideration. This situation appears when reference is made to the kinetic rates of rearrangement processes and the hypothesis of microscopic reversibility is accepted. Then, one obtains equal rates for forward and backward reactions between species of the same free energy. In mathematical terms, this stipulation means that both a permutation and its inverse are regarded as members of the same class [39],

[57]. Thus, in forming so-called kinetic modes one has to construct unions of the type

$$^{Q}\langle g\rangle \cup {}^{Q}\langle g^{-1}\rangle. \tag{6.4}$$

Since the unification of bilateral classes leads sometimes, but not always, to bilateral classes, as one confirms by inspection, it follows that arguments leading to kinetic modes are not rationalized through the idea of symmetry equivalence of bijections. This statement, surprising or not, is not at all trivial and touches upon a fact that is by no means obvious from pure anschauung.

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