of the redox sites in the film are accessible as oxidation sites, presumably only those sites on the surface. Considering the pH encapsulation effect described earlier, this conclusion is not unreasonable. It is also known from kinetic and mechanistic studies that there are rather severe microscopic constraints on the oxidation of 2-propanol by (trpy)(bpy)RuO^{2+}.[23] For example, when the rate constants for the oxidation of $(CH_3)_2CHOH$ are compared with those of $(CD_3)_2CDOH$, the kinetic isotope effect is ~18. The microscopic sensitivity of the oxidation mechanism, a lack of permeability of the substrate into the film, and the difference in medium properties between aqueous solution and the interior of the film may all play a role in explaining the observed site selectivity. A small but noticeable (~10%) increase in catalytic current was observed at pH 2 (H_2SO_4) perhaps consistent with an "opening" of the electrode film. However, under these conditions the thicker films are slowly leached from the surface.

As shown in Figure 8, the magnitude of the catalytic currents for the oxidation of 2-propanol increases with increasing 2-propanol concentration. The homogeneous oxidation of 2-propanol by (trpy)(bpy)RuO^{2+} has been found to be first order in both Ru(IV) and alcohol.[23] The beginning of a saturation effect can be observed in Figure 8 at high alcohol concentrations. The saturation effect suggests that if the mechanism remains the same on the film, the composition of the environment around the redox sites may be rich in alcohol compared to the case for bulk solution or perhaps that at high 2-propanol concentrations the rate-limiting step is changing from oxidation of substrate to reoxidation of the redox sites at the surface of the films.

The observed catalytic currents increase with increasing surface area of the electrode. An increase to ~100 μA under conditions identical with those above was observed when films were adsorbed on a medium porosity reticulated vitreous carbon electrode with a 2-cm^3 working volume. At pH >6 the electrode films are apparently stable to dissolution from the electrode surface. A typical half-life of the catalytic current is greater than 30 turnovers on the basis of the total number of ruthenium sites in the film.

The experiments described here are, in the end, limited by the reaction described in the previous section in which the redox sites in the films are converted into an unknown couple having $E_{1/2}$ ≈ 0.63 V. The ability of the film to catalyze the net electrochemical oxidation of 2-propanol is, however, impressive in some ways. Catalytic experiments with the homogeneous analogue, $(bpy)_2(py)RuO^{2+}$, show that on a per site catalytic turnover basis, the homogeneous system is less stable by a factor of at least 6. In the homogeneous case the decomposition pathway appears to be loss of a pyridyl group and oxo-bridge formation.[11] Although the problem of oxo-bridge formation appears to have been solved in the polymer film, the new pathway described above intervenes to limit the useful catalytic lifetimes of the film.

p-Toluic acid and a mixture of the xylenes, with added surfactant (0.02 M sodium dodecylsulfate), were also investigated as substrates. From the homogeneous electrocatalytic experiments it is known[4c] that with (trpy)(bpy)RuO^{2+} as the oxidant the substrate oxidation reactions are

$$CH_3C_6H_4CO_2^- \xrightarrow[+2H_2O]{-6e^-,\,-7H^+} C_6H_4(CO_2)_2^{2-}$$

$$C_6H_4(CH_3)_2 \xrightarrow[+4H_2O]{-12e^-,\,-14H^+} C_6H_4(CO_2)_2^{2-}$$

The aromatic substrates gave catalytic currents of approximately one-fourth of those observed for 2-propanol at equivalent concentrations, but the reactions were not studied in detail.

Binding the catalyst in the film offers the advantages inherent in the chemically modified surfaces approach: (1) use of relatively small amounts of the catalytic reagent and (2) the conversion of a homogeneous system into a heterogeneous one with the possibilities for flow-through design. In the long run there may be additional advantages associated with substrate concentration effects in the films and with an inhibition of deleterious side reactions which lead to unwanted products or to the decomposition of the catalytic sites themselves. The observation of such a pathway here is discouraging since it limits the effective catalytic lifetimes of the films. However, given our ability to make designed chemical modifications at the redox sites in the film, we regard our initial observations as encouraging toward an ultimate goal of developing a series of chemically modified electrodes which have a high functional group specificity toward oxidation and/or reduction.

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(23) Thompson, M. S.; Meyer, T. J., manuscript in preparation.

Isomers and Isomerization: Elements of Redfield's Combinatorial Theory

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Abstract: Basic principles of Redfield's 1927 enumeration theory are reviewed. The theory is shown to incorporate, supersede, and simplify many of the last decade's developments in molecular combinatorics.

The past decade has witnessed a growing awareness of the applicability of discrete combinatorial structures to the precise formulation and understanding of broad classes of molecular phenomena. The chemically and mathematically classical problem of enumerating distinct isomers of specified composition of a molecular frame and the allied, more contemporary one of enumerating distinct reorganizational processes for those isomers have attracted many theoretical and experimental investigators.[1-8] It appears to have escaped notice that both problems can in large

(1) (a) Ugi, I.; Marquarding, D.; Klusacek, H.; Gokel, G.; Gillespie, P. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 703-730. (b) Dugundji, J.; Gillespie, P.; Marquarding, D.; Ugi, I.; Ramirez, F. In "Chemical Applications of Graph Theory"; Balaban, A. T., Ed.; Academic Press: New York, 1976; pp 107-174.

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measure be subsumed under mathematical constructs set forth over 50 years ago by J. H. Redfield.[9]

We exhibit fundamentals of Redfield's masterpiece, "The Theory of Group-Reduced Distributions", and demonstrate how disparate aspects of modern chemical combinatorics are united by his methodology.[10-13]

Consider m sets $X_1, X_2, ..., X_m$, each consisting of n elements. The elements of each set are arrayed in horizontal n-tuples, so as to form $m \times n$ matrices. Matrices which are column equivalent, i.e., differ only by reordering of intact columns, present the same *correspondence* (relative relation, superposition) of set elements. There are a total of $(n!)^m$ matrices under consideration, and $(n!)^m/n! = (n!)^{m-1}$ correspondences C.

When there is a nontrivial group action $\Gamma:C$ on the classes of matrices, we must elicit the number of nonequivalent types or patterns of correspondence. An element $\gamma \epsilon \Gamma$ acting bodily on a matrix is defined by its component permutations $\gamma_i:X_i$ acting on the individual matrix rows. Group elements are composed by component multiplication.

$$\gamma^M = (\gamma_1, \gamma_2, ..., \gamma_m)\begin{pmatrix} X_{11} & X_{12} & \cdots X_{1n} \\ X_{21} & X_{22} & \cdots X_{2n} \\ \vdots & \vdots & \vdots \\ X_{m1} & X_{m2} & \cdots X_{mn} \end{pmatrix} =$$

$$\begin{pmatrix} \gamma_1 \cdot X_{11} & \gamma_1 \cdot X_{12} & \cdots & \gamma_1 \cdot X_{1n} \\ \gamma_2 \cdot X_{22} & \gamma_2 \cdot X_{22} & \cdots & \gamma_2 \cdot X_{2n} \\ \vdots & \vdots & & \vdots \\ \gamma_m \cdot X_{m1} & \gamma_m \cdot X_{m2} & \cdots & \gamma_m \cdot X_{mn} \end{pmatrix} = M'$$

Burnside's fundamental lemma[13b] for the number of patterns N (see eq 1) requires that we characterize the number $I(\gamma)$ of

$$N(C,\Gamma) = \frac{1}{|\Gamma|}\sum_{\gamma \epsilon \Gamma} I(\gamma) \tag{1}$$

correspondences which are invariant for each $\gamma \epsilon \Gamma$. In other terms, we must determine the properties of those matrices which γ transforms to another in the same correspondence class.

Two typical components of γ, γ_u and γ_v, are written in disjoint cycle notation and arranged in matrix-like manner (a), with cycles of the same length in the same position. It is crucial to observe

(a) γ_u: (10)(4)(2) (8,5) (7,12,1,11) (13,9,3,6)
γ_v: (7)(11)(4) (9,13) (5,10,6,1) (8,3,12,2)
$(\rho) = (1^3 2^4)$

(b) X_u 10 4 2 8 5 7 12 1 11 13 9 3 6
X_v 7 11 4 9 13 5 10 6 1 8 3 12 2

that simple neglect of the separating symbols in (a) yields a portion (b) of the full correspondence invariant to (γ_u, γ_v). The number of subcorrespondences fixed by (γ_u, γ_v) thus comes to the number of forms γ_v can manifest relative to a given expression of γ_u. These different manifestations consist of (1) intracycle, circular rearrangement of the constituent elements and (2) intercycle reordering of cycles of common length. (Invariance of the correspondence clearly demands that γ_u and γ_v possess the same number j_k of cycles of k elements, as signified by the partition (ρ) of n: $(1^{j_1} 2^{j_2} ... k^{j_k} ... n^{j_n})$.) A k cycle in γ_v can be initiated with any of its k elements, providing (k^{j_k}) representations of the cycles in given order. Reordering of k cycles is accomplished in $j_k!$ ways, to yield $(k^{j_k} j_k!)$ representations. All occurring cycle lengths therefore furnish $\prod_{k=1}^{n}(k^{j_k} j_k!)$ representations of γ_v,[14] which are interpreted above as (γ_u, γ_v) invariant subcorrespondences. All the X_i and all m components of γ are brought into effect multiplicatively, to give the total number of patterns of correspondence.

$$N(C,\Gamma) = \frac{1}{|\Gamma|}\sum_{\gamma \epsilon \Gamma}[\prod_{k=1}^{n} k^{j_k(\gamma)} j_k(\gamma)!]^{m-1} \tag{2}$$

It is to be emphasized that only γ's whose component permutations all map to a common cycle partition (ρ) are nonzero contributors. To effect the above evaluation, Redfield introduced cycle indicator monomials in an arbitrary indeterminate variable s, $z(\gamma_i;s) = s_1^{j_1(\gamma_i)} s_2^{j_2(\gamma_i)} ... s_n^{j_n(\gamma_i)}$, and an operator "cap" $(\cap)$ for transforming them to the required number.[15]

$$z(\gamma_1;s)\cap z(\gamma_2;s)\cap ...\cap z(\gamma_m;s) \equiv$$
$$[\prod_k k^{j_k(\gamma)} j_k(\gamma)!]^{m-1} \text{ when } j_k(\gamma_u) = j_k(\gamma_v) \equiv j_k(\gamma), \forall\ u,v$$
$$0 \text{ otherwise}$$

By indexing each of the γ's as $\gamma^l = (\gamma_1^l, \gamma_2^l, ..., \gamma_m^l)$, the pattern result takes the form

$$N(\Gamma,C) = \frac{1}{|\Gamma|}\sum_{l=1}^{|\Gamma|} z(\gamma_1^l)\cap z(\gamma_2^l)\cap ...\cap z(\gamma_m^l) \tag{3}$$

In many instances the group Γ separates as a direct product of subgroups $\Gamma_i = \{\gamma_i^1, \gamma_i^2, ...\}$ acting in uncorrelated fashion on the X_i.[3d,e,16] The number of patterns is then the cap product of group cycle indices, $Z(\Gamma_i;s) = |\Gamma_i|^{-1} \sum_{\gamma_i \epsilon \Gamma_i} z(\gamma_i;s)$.

$$N(\Gamma,C) = Z(\Gamma_1;s)\cap Z(\Gamma_2;s)\cap ...\cap Z(\Gamma_m;s) \tag{4}$$

It is useful to note that the index of the symmetric group, $Z(S_n)$, is the identity element of cap multiplication.

We now review some applications of this aspect of Redfield's theory. If $\Gamma_i = \Gamma(G_i)$, the automorphism group of n-vertex graph G_i, the cap product appearing above is the number of distinct superpositions (matchings, stackings) of the graphs.[17] We will

(2) (a) Gielen, M.; Venlautem, N. *Bull. Soc. Chim. Belg.* **1970**, *79*, 679–688. (b) Jesson, J. P.; Meakin, P. *Acc. Chem. Res.* **1973**, *6*, 269–275; *J. Am. Chem. Soc.* **1974**, *96*, 5760–5772. (c) Musher, J. I. *J. Chem. Educ.* **1974**, *51*, 94–97. (d) Willem, R.; Brocas, J.; Fastenakel, D. *Theor. Chim. Acta* **1975**, *40*, 25–31. (e) Bouman, T. D.; Trindle, C. *Ibid.* **1975**, *37*, 217–231. (f) Mislow, K. *Acc. Chem. Res.* **1976**, *9*, 26–33. (g) Gust, D.; Patton, A. *J. Am. Chem. Soc.* **1978**, *100*, 8175–8181. (h) Balaban, A. T. *Rev. Roum. Chim.* **1978**, *23*, 733–746.

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(4) (a) Klemperer, W. G. *J. Chem. Phys.* **1972**, *56*, 5478–5489. (b) Klemperer, W. G. *Inorg. Chem.* **1972**, *11*, 2668–2678. (c) Klemperer, W. G. *J. Am. Chem. Soc.* **1973**, *95*, 380–396; *Ibid.* **1973**, *95*, 2105–2120. (d) Hutchings, M. G.; Johnson, J. B.; Klemperer, W. G.; Knight, R. R. *Ibid.* **1977**, *99*, 7126–7132.

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(6) (a) Klein, D. J.; Cowley, A. H. *J. Am. Chem. Soc.* **1975**, *97*, 1633–1640. (b) *Ibid.* **1978**, *100*, 2593–2599.

(7) Davidson, R. A. Ph.D. Thesis, The Pennsylvania State University, 1977.

(8) (a) Nourse, J. G. *J. Am. Chem. Soc.* **1977**, *99*, 2063–2069. (b) Nourse, J. G. *Ibid.* **1979**, *101*, 1210–1216.

(9) Redfield, J. H. *Am. J. Math.* **1927**, *49*, 433–455.

(10) Well before the flowering of chemical interest, Redfield's theory was essentially rediscovered by R. C. Read.[17a] The special case of mappings between sets subject to double group action was then treated by N. G. de Bruijn,[18a,b] thereby generalizing Pólya's 1937 theorem.[11] Only relatively recently have mathematicians themselves sorted through the convoluted sequence of development.[12,13,17b] Vis-a-vis Redfield, chemists presently find themselves in a somewhat embarrassing position, comparable to that of these other workers some fifteen years ago.

(11) Pólya, G. *Acta Math.* **1937**, *68*, 145–254.

(12) Foulkes, H. O. *Can. J. Math.* **1966**, *18*, 1060–1071.

(13) (a) Harary, F.; Palmer, E. *Am. J. Math.* **1967**, *89*, 373–384. (b) "Graphical Enumeration"; Academic Press: New York, 1973.

(14) In other terms,[4] this is the order of the automorphism group of γ_v: $|\times_k S_{jk}[C_k]|$.

(15) It may be argued that polynomials are extraneous complications to the problem at hand, being mere information-carrying devices devoid of fundamental significance. In response, notational and symbolic systems to facilitate and succinctly manage complex operations are historically pivotal to mathematical development. Polynomials are more than justified in the present context by the felicitous consequences of their use.

(16) This situation is often addressed (e.g., in enumerative graph theory) to the exclusion of more general, concerted group actions pertinent to a significant number of chemical problems (ref 7 and unpublished studies). The formal description, that of different representations $\chi_i(\Gamma)$ of a single group on different subsets, is central in de Bruijn's fashioning of enumeration theory[18] (cf. ref 3d,e).

(17) (a) Read, R. C. *J. London Math. Soc.* **1959**, *34*, 417–436; *Ibid.* **1960**, *35*, 344–351. (b) *Can. J. Math.* **1968**, *20*, 808–841.

generalize the interpretation to any set of (necessarily distinguishable) objects: isomers are superpositions of ligands and molecular skeleta, while isomer superpositions are isomerization modes (or the basis for them). In different and often obscure terminology, Redfield counted both kinds of correspondence in 1927.

The case $m = 2$ is obviously most significant, for then the correspondences are bona fide bijective mappings. These were counted as specializations of injective mappings by de Bruijn[18] and as (Γ_1,Γ_2) double cosets by Ruch,[3a] Klemperer,[4a] and Brown[5a] and co-workers. Klemperer's argumentation and formulation most closely resemble those of Redfield. Some formidable group theoretic tools led Ruch to his popular formula,[3a] which when rearranged and stripped of redundant quantities is equivalent to the cap interaction of Γ_1,Γ_2 cycle indices.

$$N(\Gamma_1,\Gamma_2) = \frac{|S_n|}{|\Gamma_1||\Gamma_2|}\sum_{(\rho)}\frac{|\Gamma_1\cap C_{(\rho)}|\,|\Gamma_2\cap C_{(\rho)}|}{|C_{(\rho)}|} \tag{5}$$

$$N(\Gamma_1,\Gamma_2) = Z(\Gamma_1;s)\cap Z(\Gamma_2;s) \tag{6}$$

To count isomers of a frame Γ_1 by an achiral ligand set of partition $(\rho) = (1^{j_1}2^{j_2}\ldots n^{j_n})$ (i.e., j_k subsets, each consisting of k indistinguishable ligands), the appropriate group is the direct product $\Gamma_2 = S_1^{j_1} \times S_2^{j_2} \times \ldots \times S_n^{j_n}$, conveniently symbolized by $\prod S(\rho)$. In practice it is frequently desirable to refine the enumeration by reserving subsets of skeletal sites for selected subsets of ligands. The compound bijection is pieced together from the subbijections $X_{1j} \leftrightarrow X_{2j}$. Distinct, noninteracting variables for each skeleton and associated ligand subset may be shown to effect the required discrimination.[7,19]

$$N = Z(\Gamma_1;s,t,u)\cap[Z(\textstyle\prod S(\rho_1);s)\cdot Z(\prod S(\rho_2);t)\cdot Z(\prod S(\rho_3);u)] \tag{7}$$

$(\rho) = (\rho_1;\rho_2;\rho_3)$ is the compound ligand partition. Comparable techniques of mapping restriction are applicable to the dynamic problem below.

When mixtures of achiral and chiral ligands are distributed over an achiral frame,[3d,c] the frame and ligand actions are correlated: permutations induced by reflections simultaneously transform chiral ligands to their enantiomeric conjugates. Only racemic ligand partitions, which exhibit overall stability to transformation, are entertained. We either may directly employ the first Redfield formula or take pains to make explicit the proper permutation combinations.

(1) The full frame group is dissected into the rotational subgroup Γ_1^0 and its coset of reflective permutations: $\Gamma_1' = \Gamma_1^0 \cup \sigma\Gamma_1^0$.

(2) Correspondingly, the chiral ligand group Γ_{2c} is dissected into pure permutation and permutation-enantiomer exchange components: $\Gamma_{2c}' = \Gamma_{2c}^0 \cup \epsilon\Gamma_{2c}^0$.

A collection of chiral ligands such as $A_3B_3C_2\bar{A}_3\bar{B}_3\bar{C}_2$ is characterized by a compound partition, $(\rho_c;\bar{\rho}_c) = (3^2 2;3^2 2)$, and a wreath product symmetry group, $\Gamma_{2c}' = S_2[\prod S(\rho_c)] = S_2[S_3^2 \times S_2]$. The base of this group, $E_2[\prod S(\rho_c)] \simeq [\prod S(\rho_c)]^2$, is the index two subgroup of pure permutations, and its coset consists of conjugate ligand exchanges. The total ligand group is the direct product of its achiral and chiral constituents, $\Gamma_2' = \Gamma_{2a} \times \Gamma_{2c}'$, where $\Gamma_{2a} = \prod S(\rho_a)$. Appropriate coupling of group and coset indices yields expression 8.[20] Neglecting the coefficient, the first term counts total stereoconfigurations and the second term enumerates those which are achiral.

$$N' = \tfrac{1}{2}[Z(\Gamma_1^0)\cap Z(\Gamma_{2a} \times \Gamma_{2c}^0) + Z(\sigma\Gamma_1^0)\cap Z(\Gamma_{2a} \times \epsilon\Gamma_{2c}^0)] \tag{8}$$

The so-called dynamic problem of enumerating differentiable patterns of isomerization is handled expeditiously by Redfield's methods. Viewed as superpositions of isomers or labeled graphs, the nature of the problem would be widely comprehended by both chemists and combinatorialists. The transformations of all (ρ) isomers[8a] are given by eq 9, where Γ_1 and Γ_3 are frame groups

$$N = Z(\Gamma_1;s)\cap Z(\Gamma_2;s)\cap Z(\Gamma_3;s) \tag{9}$$

and Γ_2 is the ligand group, $\prod S(\rho)$. The first cap pair enumerates initial isomers, the second pair gives product isomers, and the composite yields patterns of correspondence between them. When $\Gamma_3 = \Gamma_1$, the transformations are pure permutational isomerizations on a fixed skeleton. When all ligands are identical, $\Gamma_2 = S_n$, the patterns degenerate to pure skeleton superpositions.[21] To circumscribe the calculation to particular initial and final (ρ) isomers with respective symmetry groups Γ_a and Γ_b, distinctive index variables isolate subsets of sites occupied by identical ligands, which map together.[22]

$$N = Z(\Gamma_a;s,t,u)\cap Z(\Gamma_b;s,t,u) \tag{10}$$

Attractive attributes of the Redfield formalism are the versatility and clarity of formulation. The basic simplicity of the questions considered stands unobscured by procedural and notational details, which necessarily enter equivalent, lower dimensional descriptions. We believe the approach will go far in enhancing utilization of combinatorial structures in chemistry. Comprehensive examination of Redfield theory, properties of the more general cup $(\cup)$ operator, higher matrix symmetries, and detailed chemical applications are undertaken in other contributions.

(18) (a) de Bruijn, N. G. *Ned. Akad. Wetensch.* **1959**, *A62*, 59–69. (b) "Applied Combinatorial Mathematics"; Beckenbach, E. F., Ed.; Wiley: New York, 1964, pp 144–184. (c) *Nieuw Arch. Wiskunde* **1971**, *19*, 87–112. (d) *J. Combinatorial Th.* **1972**, *12*, 14–20.

(19) It is assumed that the X_{1j} are unions of frame group orbits. If this condition does not pertain, we must effectively redefine the frame by descending to a subgroup of Γ_1 appropriate to the problem. Also, equivalences between the ligand subsets are forbidden.

(20) The form of expression 8 is typical for partially correlated group action, e.g., Hässelbarth–Ruch modes[3b] are counted by $^1/_2[Z(\Gamma_1^0)\cap Z(\Gamma_1^0) + Z(\sigma\Gamma_1^0)\cap Z(\sigma\Gamma_1^0)]$.

(21) The appropriate frame group, group element correlation, and combination of basic isomerizations into higher classes (modes) are decided by distinguishability in the overall experimental situation (ref 3b,6a,2d,4). Possibly, the present analysis could be extended to compute the number of modes when an isomerization and its inverse are regarded as equivalent.

(22) Thus, the 38 rotationally distinct types of isomerization of the three $(\rho) = (32)$ trigonal-bipyramid isomers[8a] may be decomposed into 2, 4, and 12 intraisomer, degenerate isomerizations and 2·2, 2·2, and 2·6 interisomer, nondegenerate isomerizations.