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POLYA'S METHOD FOR THE ENUMERATION OF ISOMERS.

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The aim of this lecture is to illustrate the practical uses of G. Polya's method for the enumeration of isomers as described generally by Prof. Kerber in the previous lecture. The enumeration of the number of isomer alkylderivatives $C_nH_{2n+1}X$ presented by Polya, Acta Mathematica 68, 145-254 (1937), is chosen as a demonstrative example.

1. Introduction

Polya's enumeration method is characterized by the systematic derivation of enumeration series such as

$$s(x) = \sum_{n=0}^{\infty} S_n x^n \tag{1}$$

In applying this series to a particular class of compounds, the natural number n characterizes all the isomers corresponding to the same molecular weight and the coefficient S_n represents the number of these isomers: in the above example n is the number of carbon atoms in the alkyl group. In more complicated cases n may represent the samllest set of natural numbers defining the brutto formula of the compounds considered. S_n is then replaced by a function of the members of that set. The variables in enumeration series like (1) correspond to figures of a given set; e.g. x may represent carbon atoms, y those carbon atoms which are substituted asymmetrically, etc.

The cycle index (Zyklenzeiger) of the corresponding group plays an important role in the derivation of the enumeration series. The meaning of the cycle index is illustrated in the following example:

How many different distributions of differently coloured spheres over the 6 points of an octahedron exist if the octahedron is

(A) rotating freely or

(B) fixed in space?

(A) will be calculated first. The rotations of the octahedron form the group

$$\underset{\sim}{O} = \{E,\ 6C_4,\ 3C_2',\ 6C_2',\ 8C_3\} \tag{2}$$

The axes of these rotations and the labels of the points of the octahedron are shown in Fig. 1. Each rotation of the octahedron

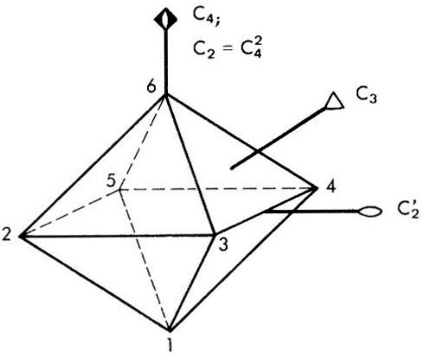

Fig. 1 Labelling of the points of an octahedron and axes of rotation.

maps its points {1, 2, 3, 4, 5, 6} onto itself; therefore, each rotation corresponds to a particular permutation of these 6 points. The rotations about the axis shown in Fig. 1 correspond to the following permutations

$$
\begin{aligned}
E &\sim \begin{pmatrix}1, & 2, & 3, & 4, & 5, & 6\\ 1, & 2, & 3, & 4, & 5, & 6\end{pmatrix} = \begin{pmatrix}1\\1\end{pmatrix}\begin{pmatrix}2\\2\end{pmatrix}\begin{pmatrix}3\\3\end{pmatrix}\begin{pmatrix}4\\4\end{pmatrix}\begin{pmatrix}5\\5\end{pmatrix}\begin{pmatrix}6\\6\end{pmatrix}\\
C_4 &\sim \begin{pmatrix}1, & 2, & 3, & 4, & 5, & 6\\ 1, & 3, & 4, & 5, & 2, & 6\end{pmatrix} = \begin{pmatrix}1\\1\end{pmatrix}\begin{pmatrix}2, & 3, & 4, & 5\\ 3, & 4, & 5, & 2\end{pmatrix}\begin{pmatrix}6\\6\end{pmatrix}\\
C_2 &\sim \begin{pmatrix}1, & 2, & 3, & 4, & 5, & 6\\ 1, & 4, & 5, & 2, & 3, & 6\end{pmatrix} = \begin{pmatrix}1\\1\end{pmatrix}\begin{pmatrix}2, & 4\\ 4, & 2\end{pmatrix}\begin{pmatrix}3, & 5\\ 5, & 3\end{pmatrix}\begin{pmatrix}6\\6\end{pmatrix}\\
C_2' &\sim \begin{pmatrix}1, & 2, & 3, & 4, & 5, & 6\\ 6, & 5, & 4, & 3, & 2, & 1\end{pmatrix} = \begin{pmatrix}1, & 6\\ 6, & 1\end{pmatrix}\begin{pmatrix}2, & 5\\ 5, & 2\end{pmatrix}\begin{pmatrix}3, & 4\\ 4, & 3\end{pmatrix}\\
C_3 &\sim \begin{pmatrix}1, & 2, & 3, & 4, & 5, & 6\\ 2, & 3, & 4, & 6, & 1, & 3\end{pmatrix} = \begin{pmatrix}1, & 2, & 5\\ 2, & 5, & 1\end{pmatrix}\begin{pmatrix}3, & 4, & 6\\ 4, & 6, & 3\end{pmatrix}
\end{aligned}
\tag{3}
$$

Similar rotations also follow for rotations about the axes not shown in Fig. 1.

Each permutation may be partitioned into several cycles of order ν, where ν gives the number of the points interchanged by the cycle considered. The permutation corresponding to E is partitioned into 6 cycles of order 1; the permutation corresponding to C_2 into 2 cycles of order 1 and 2 cycles of order 2; and so on. Obviously, all the permutations corresponding to rotations of the same kind are partitioned in the same way.

For each cycle of the order ν a function

$$f_\nu = \sum_j x_j^\nu = \langle x^\nu \rangle \tag{4}$$

may be correlated wherein the x_j's represent the particular figures of the given set. So the symmetry elements (3) of the group $\underset{\sim}{Q}$ correspond to the following functions:

$$E \sim f_1^6; \quad C_4 \sim f_1^2 \cdot f_4; \quad C_2 \sim f_1^2 \cdot f_2^2; \quad C_2' \sim f_2^3; \quad C_3 \sim f_3^2 \tag{5}$$

The cycle index $Z(\underset{\sim}{G})$ of a group $\underset{\sim}{G}$ combines these functions (5), corresponding to $\underset{\sim}{G}$ symmetry elements (2), with the orders of the group and the classes of the group. Following this procedure the cycle index $Z(\underset{\sim}{O})$ of the group $\underset{\sim}{O}$ results

$$Z(\underset{\sim}{O}) = \frac{1}{24}\left[f_1^6 + 6\ f_1^2 \cdot f_4 + 3\ f_1^2 \cdot f_2^2 + 6\ f_2^3 + 8\ f_3^2\right] \tag{6}$$

If spheres in 3 different colours are available, the set of the figures may be denoted by $\{x, y, z\}$. The answer to (A) is obtained by introducing the functions (4)

$$f_\nu = \langle x^\nu \rangle = x^\nu + y^\nu + z^\nu$$

into the cycle index (6). Simple straightforward calculation results in the enumeration series $R(x, y, z)$

$$\begin{aligned} R(x,y,z) = {} & \langle x^6 \rangle + \langle x^5 y \rangle + 2\langle x^4 y^2 \rangle + 2\langle x^4 yz \rangle + \\ & + 2\langle x^3 y^3 \rangle + 3\langle x^3 y^2 z \rangle + 6\langle x^2 y^2 z^2 \rangle \end{aligned} \tag{7}$$

The coefficient of $\langle x^a y^b z^c \rangle$ in (7) is the number of different distributions of <u>a</u> spheres of the first colour over the 6 points of the freely rotating octahedron.

If the octahedron is fixed in space each point can only be mapped onto itself. The corresponding group contains only one element, the identity. Therefore, the cycle index is given by f_1^6. In answering question (B) an analogous procedure leads to the enumeration series $Q(x,y,z)$

$$\begin{aligned} Q(x,y,z) &= (x + y + z)^6 = \\ &= \langle x^6 \rangle + 6\langle x^5 y \rangle + 15\langle x^4 y^2 \rangle + 30\langle x^4 yz \rangle + \\ &\quad + 20\langle x^3 y^3 \rangle + 60\langle x^3 y^2 z \rangle + 90\langle x^2 y^2 z^2 \rangle \end{aligned} \tag{8}$$

for the different distributions of spheres in 3 different colours over the 6 points of an octahedron fixed in space.

2. Free Trees and Rooted Trees

Since the alkanes are acyclic compounds their CH-graphs and their C-graphs correspond to free trees. In the CH-graphs of alkanes each carbon atom is represented by a vertice of degree 4 and each hydrogen atom by a vertice of degree 1. Therefore, the CH-graphs of alkanes contain only two sorts of vertices: those of degree 1 corresponding to H and those of degree 4 corresponding to C. In the C-graphs only the carbon atoms are represented by vertices which may have degree 1, 2, 3, or 4, respectively. The CH-graph and the C-graph of iso-pentane are illustrated in Fig. 2

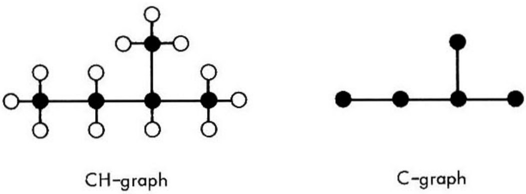

Fig. 2 CH-graph (a) and C-graph (b) of isopentane, C_5H_{12}, (free trees).

The alkylderivatives result from the alkanes when one hydrogen atom is substituted by the atom or the group X. In the CH-graphs and the C-graphs this hydrogen atom is marked by the root point (Wurzelpunkt) W indicated by a full triangle (▼).

Fig. 3. shows the CH-graph and the C-graph of the optically active iso-amyl group. It should be noted that the root point is not a vertex of the graph. Also, that edge connecting the root point to a vertex of the graph, does not belong to the graph; this edge is usually called trunk (Stamm) and the vertex at which it ends, the main vertex (Hauptknotenpunkt). A tree connected to a root point is called a rooted tree (Setzbaum).

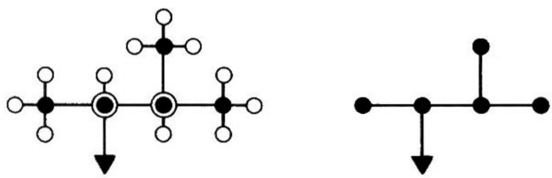

Fig. 3

The rooted graphs of the optically active isoamyl group: (a) CH-graph; (b) C-graph.

At any of its vertices each tree or rooted tree may be partitioned into as many rooted trees (branches (Äste)) as the degree of vertex indicates. If the partitioning occurs at the main vertex of a rooted tree the resulting branches are called main branches (Hauptäste). If, in a particular vertex, all the branches or main branches are different, the vertex is an asymmetric vertex. Fig. 4 illustrates the partitioning of the rooted tree at the main vertex (C-graph; Fig. 3) and a partitioning of the free tree (CH-graph; Fig. 2).

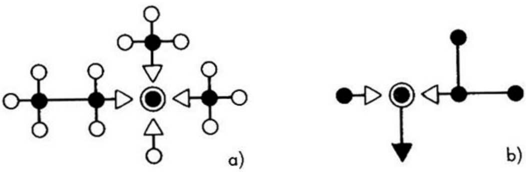

Fig. 4 Partition of a (a) free tree (b) rooted tree.

3. Edge Wreaths and Their Groups. Congruency.

The edge wreath (Kantenkranz) consists of a vertex and all the edges incident to that vertex. The vertex of the edge wreath is the center (Zentrum). Since an edge wreath contains edges which are incident to only a single vertex, it is neither a graph nor a subgraph.

Fig. 5 shows an edge wreath around the center P containing k edges which are labelled by the numbers

$$j = 1, 2, 3, \ldots, k-1, k$$

Fig. 5 also shows an image of that edge wreath which is around the center P'. When the edge wreath P is mapped onto its image P' a permutation of the edges is induced

$$\begin{bmatrix} 1, & 2, & 3, & \ldots\ldots, & k-1, & 1 \\ i_1, & i_2, & i_3, & \ldots\ldots, & i_{k-1}, & i_k \end{bmatrix} \quad (9)$$

wherein the i_j's are the images of the edges j. All the permutations corresponding to such mappings form the group of the edge wreath.

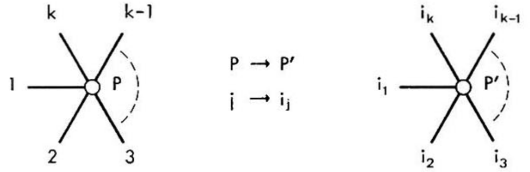

Fig. 5 Mapping of an edge wreath.

Congruency: Polya defines two graphs, G and G' congruent if and only if a bijective mapping from G onto G' and from G' onto G exists which has the following properties:

(1) each vertex is mapped onto a vertex of the same kind;

(2) each edge is mapped onto an edge;

(3) the edge relation is preserved; and

(4) the permutation of the edge labels in each edge wreath which is induced by the mapping belongs to the concerned group.

It can be seen that congruency is a stronger concept than isomorphism.

The group of the edge wreath to which condition (4) refers is determined by the particular interpretation of the graph. There are three types of interpretations:

(1) The graph reflects the pure topology of the edge relation. This means that all edges of an edge wreath are equivalent to each other. Therefore, each edge may be mapped onto each

edge of the corresponding edge wreath. Consequently, all the k! permutations of the k edges of an edge wreath correspond to a possible mapping and, therefore, the group of the edge wreath is the symmetric group S_k.

(2) The graph reflects the relationships between the elements (vertices or atoms) of a three dimensional object (molecule). Only those mappings which preserve the relative geometry of the object are possible. In this case a subset of the permutations forms the group of the edge wreath which consequently must be a subgroup of S_k. The case where 4 edges (k = 4) point from the center to the corners of a tetrahedron is of special interest. Two different types of labelling, distinguished as right-handed and left-handed tetrahedron are possible (Fig. 6). It is obvious that a single transposition (interchange of the labels of two points) leads from the right- to the left-handed tetrahedron and vice versa. Consequently, only an even number of transpositions preserves the relative geometry of the right- or left-handed

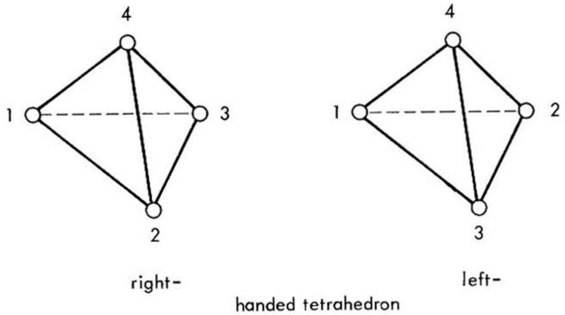

Fig. 6

tetrahedron. Furthermore, only these even permutations form the desired subgroup of S_4, the alternating group A_4.

It is important to note that if two or more of the figures interchanged by the permutations of an alternating group A_k are equal, the positions of these equivalent figures may or may not be interchanged without altering the configuration. This means that if at least two of the figures permuted are equivalent, the permutations leading from one to the other configurations in A_k may always be made even.

If all the figures of the configurations are different, two transitivity systems result in A_k: those of the odd and the even permutations. However, if all the figures are not different, only a single transition system occurs in A_k. The combinations consisting of different figures are counted once in the cycle index of S_k and twice in the cycle index of A_k. Therefore, the enumeration for these combinations is given by the cycle index of $(A_k - S_k)$. On the other hand, the enumeration for combinations of figures not entirely different, counted once in both S_k and A_k, is given by the cycle index $S_k - (A_k-S_k) = (2\ S_k-A_k)$.

(3) The graph reflects the relationships in a planar object. Taking the congruency conditions into account only a mapping which induces a cyclic permutation in the k edges of the edge wreath is possible. The group formed by these permutations is the cyclic group Z_k.

In mapping a rooted tree the root point has to be mapped onto a root point and the trunk onto a trunk. Consequently, in mapping the edge wreath of the main vertex of a rooted tree from all the above permutations only those permutations which preserve the label of the trunk are allowed. Exactly $(k-1)!$ permutations from the $k!$ permutations of S_k obey that restriction and form the symmetric group S_{k-1}. Of the 12 permutations of A_4 3 permutations forming $A_3 = Z_3$ preserve the label of the trunk. From the k permutations of Z_k, however, only the identical permutation obeys the restriction forming the identic group E_{k-1}. For $k=4$ the following is obtained:

Interpretation of the graph:	Topological	Three Dimensional	Planar
Ordinary vertex	S_4	A_4	Z_4
Main vertex	S_3	$A_3 = Z_3$	E_3

Since the configuration of carbon atoms in alkylderivatives is non-planar, only the topological (S_4) and the three dimensional (A_4) interpretations of their graphs are meaningful. The cycles indices of these groups are

$$Z(S_3) = \frac{1}{6}\left[f_1^3 + 3f_1f_2 + 2f_3\right]$$
$$Z(A_3) = \frac{1}{3}\left[f_1^3 + 2f_2\right] \qquad (10)$$

The cycle indices for combinations with and without repetitions are:

$$2.Z(S_3) - Z(A_3) = f_1f_2$$
$$Z(A_3) - Z(S_3) = \frac{1}{6}\left[f_1^3 - 3f_1f_2 + 2f_3\right] \qquad (11)$$

4. Enumeration Series

Three enumeration series are considered

$$s(x) = \sum_n S_x x^n$$
$$s(x) = \sum_n R_n x^n \qquad (12)$$
$$q(x) = \sum_n Q_n x^n$$

All of the three series count the numbers of different rooted trees with n vertices of degree 4 of which α are asymmetric. s(x), the first series, counts the different rooted trees if the graph is interpreted three-dimensionally; the group of the edge wreath of the main vertex is A_3. r(x), the second series, counts the same rooted trees as s(x), but the graph is interpreted topologically; the group of the edge wreath is S_3. q(x), the third series, counts only those different rooted trees which have no asymmetric vertices if the graph is interpreted topologically; no group can be defined for the edge wreath.

Since the chemical graphs of alkylderivatives are rooted trees, the coefficients in the series (12) count the number of different $C_nH_{2n+1}X$:

S_n . . . all sterically different $C_nH_{2n+1}X$'s (group A_3): each member of a pair of antipodes is counted once for itself;

R_n . . . all topologically different $C_nH_{2n+1}X$'s (group S_3): stereoisomer alkylderivatives are counted only as pairs of antipodes;

Q_n . . . all those $C_nH_{2n+1}X$'s which do not occur in pairs of antipodes (no particular group).

q(x) enumerates a subset of that set which is enumerated by r(x): therefore, $Q_n \leq R_n$. Since the concerned group of the edge wreath used in establishing $s(x)$ is a subgroup of that group used in establishing $r(x)$, it is less transitive and therefore, $R_n \leq S_n$. It follows that

$$Q_n \leq R_n \leq S_n \tag{13}$$

In order to evaluate the enuneration series (12), a rooted CH-tree with n vertices of degree 4 is considered. The main vertex is K. As shown in Fig. 7, two cases are distinguished:

(1) <u>The main vertex K has degree 1 (Fig. 7a)</u>:

This is only possible if $n=0$. No main branches exist. Only the single rooted tree shown in Fig. 7a meets these requirements. Since this rooted tree is counted in each of the series (12),

$$Q_0 = R_0 = S_0 = 1 \tag{14}$$

(2) <u>The main vertex K has degree 4 (Fig. 7b)</u>:

There are three main branches which together contain (n-1) vertices of degree 4. The group of the edge wreath of K is either S_3 or A_3.

Fig. 7 Edge wreaths, the main vertex has (a) degree 1; (b) degree 4 .

Two rooted trees with n vertices of degree 4 partitioned at the main vertex are congruent to each other only if the configurations of their 3 main branches are equivalent in respect to the group concerned. The following theorem (Polya, loc. cit.): is formulated:

The number of the incongruent rooted trees with n vertices of degree 4 is equal to the number of the inequivalent configurations of three rooted trees (respecting the group concerned) which together contain (n-1) vertices of degree 4.

The number of the inequivalent configurations is given by the cycle index (10) of the group concerned in which the functions f_a^b have to be replaced by $s(x^a)^b$ or $r(x^a)^b$. Both of these cycle indices correspond only to the (n-1) vertices of the 3 main branches. In order to establish a correspondence between these cycle indices and the whole rooted tree which contains an additional vertex (the main vertex K), the cycle indices must be multiplied by x. Use of eq. (14) leads to:

$$s(x) = 1 + \frac{x}{3}\,[s(x)^3 + 2s(x^3)] = \sum_0^\infty n\; S_n x^n$$

$$r(x) = 1 + \frac{x}{6}\,[r(x)^3 + 3r(x)r(x^2) + 2r(x^3)] \qquad (15)$$

$$= \sum_0 n\; R_n x^n$$

As shown in the appendix, eq. (15) leads to recursion formulas such as

$$S_{t+1} = \frac{2}{3}S_{t/3} + 2 \sum_{\substack{0 \le u \le v \le w \\ t=u+v+w}}\sum\sum \left\{\frac{S_u \cdot S_v \cdot S_w}{(1+\delta_{uv}+\delta_{uw})!\,(1+\delta_{vw}-\delta_{uw})!}\right\} \qquad (16)$$

It should be noted that the summation indices, u, v, w=t-u-v, reflect the different possibilities for the distribution of the $t=(n-1)$ vertices over the 3 main branches of the rooted tree.

In this way the series $s(x)$ and $r(x)$ can be explicitely written as

$$\begin{aligned} s(x) &= 1 + x + x^2 + 2x^3 + 5x^4 + 11x^5 + \ldots \\ r(x) &= 1 + x + x^2 + 2x^3 + 4x^4 + 8x^5 + \ldots \end{aligned} \tag{17}$$

For $n=4$ there is 1 pair of antipodes; for $n=5$ there are 3 pairs of antipodes. Since the members of a pair of antipodes are sterically different but topologically identical, each member of the pair is counted once in $s(x)$; but only the pair is counted in $r(x)$. Therefore, the number of pairs of antipodes is given by

$$(S_n - R_n) \tag{18}$$

5. The Enumeration Series q(x)

The derivation of the enumeration series $q(x)$ is somewhat more complicated. The coefficients Q_n count exactly those isomers $C_nH_{2n+1}X$ which do not contain an asymmetric vertex of degree 4. It is necessary to distinguish between symmetric and asymmetric vertices. The variable x represents all vertices of degree 4. A further variable y is necessary for those vertices of degree 4 which are asymmetric.

If $R_{n\alpha}$ denotes the number of rooted CH-trees with n vertices of degree 4 of which α are asymmetric, the R_n represents the sum

$$R_n = R_{n0} + R_{n1} + R_{n2} + \ldots = \sum_{\alpha=0}^{n} R_{n\alpha} \tag{19}$$

Series (19) contains Q_n since by definition

$$Q_n = R_{n0} \tag{20}$$

If y represents the asymmetric vertice of degree 4, the enumeration series $R_n(y)$ counts the number of the rooted CH-trees containing n vertices of degree 4 of which α are asymmetric:

$$R_n(y) = R_{n0} + R_{n1}y + R_{n2}y^2 + \ldots = \sum_{\alpha=0}^{n} R_{n\alpha}y^{\alpha} \tag{21}$$

For $y=1$ the series (21) changes into R_n but for $y=0$ series (21) gives Q_n:

$$\begin{aligned} R_n(1) &= R_n \\ R_n(0) &= Q_n \end{aligned} \tag{22}$$

The introduction of the variable y necessitates an expansion of the original figure set $\{x\}$ to $\{x,y\}$. Consequently, the one variable series $r(x)$ changes into the two variable series

$$\Phi(x,y) = \sum_{n=0}^{\alpha} \sum_{\alpha=0}^{n} \left[R_{n\alpha}y^{\alpha}\right] x^n = \sum_{n=0}^{\alpha} \sum_{\alpha=0}^{n} R_{n\alpha}x^n y^{\alpha} \tag{23}$$

The two possible cases, $n=0$ and $n<0$, are considered separately. For $n=0$ the following relationship corresponding to (14) is obtained

$$R_0 = R_{00} = Q_0 = 1 \tag{24}$$

However, for $n>0$, a somewhat more detailed discussion is necessary. For the R_n rooted trees considered here two different situations may occur: the main vertex K may be symmetric or asymmetric.

If the main vertex K is symmetric at least 2 of the 3 main branches are congruent. As discussed at the end of section 3, for combinations with repetitions the cycle index is given by

$$Z(2S_3 - A_3) = f_1 f_2 \tag{25}$$

Taking into account that the 3 main branches contain $n-1$ vertices of degree 4 of which α are asymmetric, the contributions of these rooted trees are

$$x\Phi(x,y)\Phi(x^2,y^2) \tag{26}$$

Multiplication by $x = x.y^0$ is necessary because the main vertex K is not counted in (25) and is a symmetric vertex.

If the main vertex K is asymmetric the 3 main branches are congruent to each other. In this case combinations without repetitions are considered. The cycle index is given by

$$Z(A_3 - S_3) = \frac{1}{6}\left[f_1^3 - 3f_1f_2 + 2f_3\right] \tag{27}$$

Since the 3 main branches contain $n-1$ vertices of degree 4 of which $\alpha-1$ are asymmetric, the contributions of these rooted trees are obtained by the multiplication of (27) by xy

$$\frac{xy}{6}\left[\Phi(x,y)^3 - 3\Phi(x,y)\Phi(x^2,y^2) + 2\Phi(x^3,y^3)\right] \tag{28}$$

Summing up the different contributions to $\Phi(x,y)$, namely the equations (24), (26) and (28),

$$\begin{aligned} \Phi(x,y) &= 1 + x\Phi(x,y)\Phi(x^2,y^2) + \\ &\quad + \frac{xy}{6}(x,y)^3 - 3\phi(x,y)\phi(x^2y^2) + 2\phi(x^3,y^3) \end{aligned} \tag{29}$$

By inserting $y=1$, eq. (29) becomes $r(x)$; but by inserting $y=0$, eq. (19) changes into the series

$$\begin{aligned} q(x) &= 1 + xq(x)q(x^2) = \\ &= 1 + x + x^2 + 2x^3 + 3x^4 + 5x^5 + \ldots \end{aligned} \tag{30}$$

Since a particular combination of the 3 main branches containing asymmetric vertices is counted twice in S_n, once in R_n, and not at all in Q_n, the following relationship is obtained

$$Q_n = R_n - (S_n - R_n) = 2R_n - S_n \quad (31)$$

With the enumeration series s(x) and r(x), eq. (15), and the series q(x), eq. (30), all the enumeration series for alkylderivatives are explicitely given.

6. Enumeration of Alkane Isomers

Analogous enumeration series are derived for the isomer alkanes. The CH-graphs of alkanes are free trees which do not contain a main vertex. The partition into branches, therefore, takes place at the so-called centers of the free trees.

The centers are non-ordinary vertices of the free tree. The ordinary vertices are defined as those vertices at which one branch containing more than half of the vertices of the graph grows. Fig. 8 illustrates that:

(1) a free tree consisting of n vertices has either 1 or 2 centers;

(2) if the free tree has only one center no branch with n/2 or more vertices grows from it;

(3) if the free tree has two centers then

 (3.1) these centers are neighbors

 (3.2) the number of vertices n is even and

 (3.3) from each center exactly one branch with n/2 vertices develops.

Fig. 8a shows the CH-graph of 2,3-Dimethyl-pentane, C_7H_{16}, as a free tree with one center. Fig. 8b shows the CH-graph of 2-Methyl-pentane, C_6H_{14}, as a free tree with two centers.

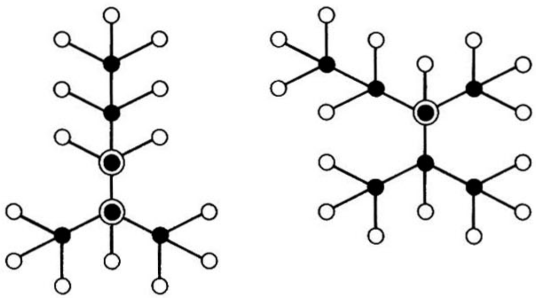

Fig. 8 The centers of free trees.

APPENDIX

Derivation of Enumeration Series s(x)

As discussed in the text for the enumeration series $s(x)$ expression (15) is obtained

$$s(x) = 1 + \frac{x}{3}\left[s(x)^3 + 2s(x^3)\right] = \sum_{0}^{\infty} S_n x^n \quad (15)$$

It follows from definition (4) that $s(x^3)$ is expressed by

$$s(x^3) = \sum_{0}^{\infty} S_n x^{3n} \quad (32)$$

On the other hand $s(x)^3$ is calculated as follows

$$s(x)^3 = \left[s(x)\right]^3 = \\ = \left[\sum_u S_u x^u\right]\left[\sum_v S_v x^v\right]\left[\sum_w S_w x^w\right] = \\ = \sum_u \sum_v \sum_w S_u S_v S_w x^{u+v+w} \tag{33}$$

The indices u, v, w are independent of each other; they run from 0 to ∞ . By ordering the terms into increasing powers x^t, t=u+v+w, the following results

$$s(x)^3 = \ldots =$$

$$= S_0S_0S_0 +$$

$$+ (S_1S_0S_0 + S_0S_1S_0 + S_0S_0S_1)\ x +$$

$$+ \left[(S_2S_0S_0 + S_0S_2S_0 + S_0S_0S_2) + (S_1S_1S_0 + S_1S_0S_1 + S_0S_1S_1)\right]\ x^2 +$$

$$+ \left[(S_3S_0S_0 + S_0S_3S_0 + S_0S_0S_3) +\right.$$

$$+ (S_2S_1S_0 + S_2S_0S_1 + S_1S_2S_0 + S_1S_0S_2 + S_0S_2S_1 + S_0S_1S_2) +$$

$$\left. + S_1S_1S_1\right]\ x^3 +$$

$$+ \left[(S_4S_0S_0 + S_0S_4S_0 + S_0S_0S_4) +\right.$$

$$+ (S_3S_1S_0 + S_3S_0S_1 + S_1S_3S_0 + S_0S_3S_1 + S_0S_1S_3 + S_1S_0S_3) +$$

$$+ (S_2S_2S_0 + S_2S_0S_2 + S_0S_2S_2) +$$

$$\left. + (S_2S_1S_1 + S_1S_2S_1 + S_1S_1S_2)\right]\ x^4 \ \ldots =$$

$$= S_0^3 + 3S_0^2S_1 \cdot x + (3S_0^2S_2 + 3S_0S_1^2)\cdot x^2 +$$

$$+ (3S_0^2S_3 + 6S_0S_1S_2 + S_1^3)\cdot x^3 +$$

$$+ (3S_0^2S_4 + 6S_0S_1S_3 + 3S_0S_2^2 + 3S_1^2S_2)\cdot x^4 + \ldots = \ldots$$

There are only three types of coefficients, S_a^3, $S_b^2S_c$, $S_dS_eS_f$ which appear 1, 3, or 6 times, respectively, in the coefficients of x^t, if t=3a ot t=2b+c or t=d+e+f. The numbers are precisely those numbers which correspond to different distributions of 3 objects over 3 distinct places: if the 3 objects are equivalent, 1 different distribution is possible; if 2 of the objects are equivalent, 3 different distributions are possible; and if all the objects are different, 6 different distributions exist.

$$\begin{aligned} &S_a \;.\;.\;.\;.\;.\;.\; 1 = (3!)/(3!) \\ &S_b S_c \;.\;.\;.\;.\; 3 = (3!)/(2!1!) \\ &S_d S_e S_f \;.\;.\;.\; 6 = (3!)/(1!1!1!) \end{aligned} \tag{34}$$

For $u \leq v \leq w$ (34) can be generalized to

$$(3!) \cdot [\,(1+\delta_{uv} + \delta_{uw})!\,(1+\delta_{vw} - \delta_{uw})!\,]^{-1} \tag{35}$$

Inserting (35) into (33)

$$s(x)^3 = \sum_{0}^{\infty} t \left[x^t \left\{ \sum_{\substack{0 \leq u \leq v \leq w \\ t=u+v+w}} \sum \sum \frac{(3!)S_u S_v S_w}{(1+\delta_{uv}+\delta_{uw})!\,(1+\delta_{vw}-\delta_{uw})!} \right\} \right] \tag{36}$$

Introducing (32) and (36) into (15) the following expression is obtained

$$s(x) = 1 + \sum^{\infty} t \; x^{t+1} \left\{ \frac{2}{3} S_{t/3} + \sum_{\substack{0 \leq u \leq v \leq w \\ t=u+v+w}} \sum \sum \frac{2S_u S_v S_w}{(1+\delta_{uv}+\delta_{uw})!\,(\delta_{vw}-\delta_{uw})!} \right\}$$

The comparison of the coefficients leads to eq. (16). Starting with $S_O = 1$ the S_n's are expanded consecutively.

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