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Hurwitz's counting isomers of alkanes

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Since 2011 Holger Helmstetter is studying mathematics and latin at the University of Würzburg with the aim of becoming a teacher. In his thesis he already took a closer look at Hurwitz's journal entry about the enumeration of the isomeres of alkanes.

During her Ph.D. studies in number theory at the University of Würzburg from 2011 to 2014, Nicola Oswald enlarged her research field with history of mathematics. At the moment she has a post-doc position in history and pedagogy of mathematics in the working group of Klaus Volkert at the University of Wuppertal.

1 Introduction: Cayley on trees

A tree is by definition a connected graph without circuit. This notion has been introduced in 1847 by Gustav Robert Kirchhoff in context of his studies on electric networks and (independently) Karl Georg Christian von Staudt (cf. Biggs et al. [3, p. 38]). Ten years later, Arthur Cayley started his studies on trees motivated by a similarity between these objects and differential operators. Meanwhile trees have been studied within graph theory for various reasons and even with respect to applications outside mathematics. Interest-

Das Betätigungsfeld des Mathematikers Adolf Hurwitz (1859–1919) kann als erstaunlich facettenreich beschrieben werden. Insbesondere in den mathematischen Notizbüchern des langjährigen ETH Professors, die heute in der Bibliothek der ETH Zürich verwahrt werden, lassen sich unerwartete Arbeiten sowie Beweisskizzen zu Themenfeldern aus nahezu allen Disziplinen der Mathematik finden. So auch ein Eintrag aus dem Jahr 1918, in dem Hurwitz Ansätze von Arthur Cayley (1821–1895) aufgreift, um die Anzahl von speziellen Bäumen im graphentheoretischen Sinne zu bestimmen, so genannte Isomere von Alkanen. Diese Aufgabenstellung aus der Chemie beruht auf der Darstellung chemischer Verbindungen durch Strukturformeln, welche sich seit den 1860er Jahren etabliert hatten. Hurwitz' Arbeiten hierzu blieben unveröffentlicht und sind weitgehend unbekannt. Interessanterweise ging sein junger Kollege George Pólya (1887–1985) Jahre nach Hurwitz das gleiche Problem mit neuen Methoden an und erzielte dadurch grosse Fortschritte.

ingly, Cayley considered rooted trees in order to distinguish isomorphic objects.[1] Using the method of generating functions, Cayley succeeded in establishing a recursive formula for the number A_n of rooted trees with n edges. Moreover, building on the identity

$$(1-x)^{-1}(1-x^2)^{-A_1}(1-x^3)^{-A_2}(1-x^4)^{-A_3}\cdots = 1 + A_1x + A_2x^2 + A_3x^3 + \cdots\,,$$

he computed the quantities A_n for increasing n as

$$1, 2, 4, 9, 20, 48, 115, 286, 719, 1842, 4766, 12486, \ldots$$

(that is sequence A000081 in Sloane's On-Line Encyclopedia of Integer Sequences, oeis.org).

Around the same time structural formulae have been introduced for chemical compounds by several chemists independently, for example, by August Friedrich Kekulé in 1854 and Archibald Couper a little later (cf. [3, p. 56]). Already in 1874 Cayley published a paper [5] on the mathematical theory of isomers in which he applied his theory of trees to alkanes C_nH_{2n+2} (also *paraffine* as it appears in Hurwitz's notes). Whereas alkanes are uniquely determined by the structural formula C_nH_{2n+2} for $n = 1, 2, 3$ (namely, methane, ethane, and propane) already in the case $n = 4$ (butane) there exists an isomer:

butane: $\mathrm{C - C - C - C}$

isobutane: $\begin{array}{ccc} & & \mathrm{C} \\ & & | \\ \mathrm{C} & - & \mathrm{C} \\ & & | \\ & & \mathrm{C} \end{array}$

For the sake of simplicity we have stripped off all hydrogens in the above kenograms (molecular graphs). In order to see that by this procedure no information about the molecule is lost recall that carbon has valence 4 and hydrogen has valence 1. This gives exactly ten hydrogen atoms for both kenograms, each of which bound to one carbon atom.[2] With increasing n the number of isomers grows. One year later, Cayley [6] computed the number of isomers of C_nH_{2n+2} up to $n = 13$, his first eleven values being correct:

$$1, 1, 1, 2, 3, 5, 9, 18, 35, 75, 159\,;$$

see Rains & Sloane [24] (and A000602 in Sloane's On-Line Encyclopedia)[3] for more values and further information. Cayley's method relies on a recurrence; a slightly different approach by Adolf Hurwitz aims at computing the number of isomers explicitly.

The ETH professor was an integral part of the European mathematical community of his time. He had obtained his doctorate supervised by Felix Klein at the Universities of Munich and Leipzig, was supported by Karl Weierstrass and Hermann A. Schwarz in Berlin

[1] A tree with a distinguished vertex (the root) is called a rooted tree. For further notions from graph theory we refer to Diestel [8]. Nevertheless, aiming at a language close to Hurwitz's original, we try to avoid the use of graph theory as much as possible.

[2] Actually, by this reasoning we only omit the proof that the structure formula for alkanes is indeed correct and this follows from a simple application of the handshaking lemma.

[3] Actually, A00602 counts the number of unrooted quartic trees and unlabeled nodes; the unrooted trees represent the carbon 'skeletons' with all hydrogen atoms erased (as in the kenograms for $n = 4$ above).

and Göttingen and had received his first professorship at the University of Königsberg on promotion of Ferdinand von Lindemann in 1884. When he and his family moved to Zurich in 1892, Adolf Hurwitz became an active member of the scientific Swiss community. He was an engaged ETH teacher and researcher until his death in 1919. Throughout his academic life, Hurwitz not only published a huge number of mathematical articles, he furthermore wrote 30 mathematical notebooks[4] [15] which are nowadays stored in the ETH archive (ETH-Bibliothek) providing a "rich treasure trove for interesting and further examination appropriate thoughts and problems" as his friend and colleague David Hilbert stated in [12, p. 199].

2 Hurwitz's diary entry

Adolf Hurwitz's last diary contains an entry of ten pages length related to the counting problem of isomers of alcanes, bearing the date 20 May 1918. The short introduction to the problem shows that Hurwitz knew about Cayley's work,[5] for counting the isomers of hydrocarbons $\mathsf{C}_n\mathsf{H}_{2n+2}$, however, Hurwitz followed another strategy which we shall explain now in detail.

In view of carbons having valency 4 we may call a carbon of *primary* (resp. *secondary, tertiary, quartenary*) *type* if it is bound to exactly one (resp. two, three, four) further carbon atom. Accordingly, the number of carbons and hydrogens in $\mathsf{C}_n\mathsf{H}_{2n+2}$ can be rewritten as

$$\begin{cases} \kappa_1 + \kappa_2 + \kappa_3 + \kappa_4 = n, \\ \quad 3\kappa_1 + 2\kappa_2 + \kappa_3 = 2n + 2, \end{cases} \tag{1}$$

respectively, where κ_1 counts the number of primary carbons, κ_2 the number of secondary carbons, and so forth. Now let us consider each carbon skeleton as a graph. Since each edge (a chemical bond) connects two vertices (carbons), the number of edges can be computed from (1) as

$$\tfrac{1}{2}(\kappa_1 + 2\kappa_2 + 3\kappa_3 + 4\kappa_4) = \tfrac{1}{2}\{(4(\kappa_1 + \kappa_2 + \kappa_3 + \kappa_4) - (3\kappa_1 + 2\kappa_2 + \kappa_3)\} = n - 1.$$

Consequently, any such graph is indeed a tree. Moreover, we deduce the inequality $\kappa_1 \leq 2$ which immediately implies that the number $\mathfrak{m}_2(n)$ of isomers of $\mathsf{C}_n\mathsf{H}_{2n+2}$ with two carbons of primary type is equal to $\mathfrak{m}_2(n) = 1$. Moroever, one can easily deduce $\kappa_1 \leq \frac{2(n+1)}{3}$, and although Hurwitz did not write this down in his diary entry, it seems that he first followed the idea of counting isomers according to increasing values for κ_1, but for some reason changed his mind later (see Figure 1). A few pages later Hurwitz computed his first non-trivial number of isomers of a certain type, namely: *the number* $\mathfrak{m}_3(n)$ *of isomers of* $\mathsf{C}_n\mathsf{H}_{2n+2}$ *with exactly three primary carbons is given by*

$$\mathfrak{m}_3(n) = \left\lfloor \frac{n(n-2)+4}{12} \right\rfloor, \tag{2}$$

where $\lfloor x \rfloor$ denotes the largest integer less than or equal to x. For this purpose, following Hurwitz, we distinguish isomers with exactly three primary carbons with respect to their

[4] See more about Adolf Hurwitz's life and work in [18] as well as about the variety of his mathematical diaries in [20].

[5] Since Hurwitz copied Cayley's erroneous data for the number of rooted trees with n edges, we may assume that he did not study Cayley's papers in detail.

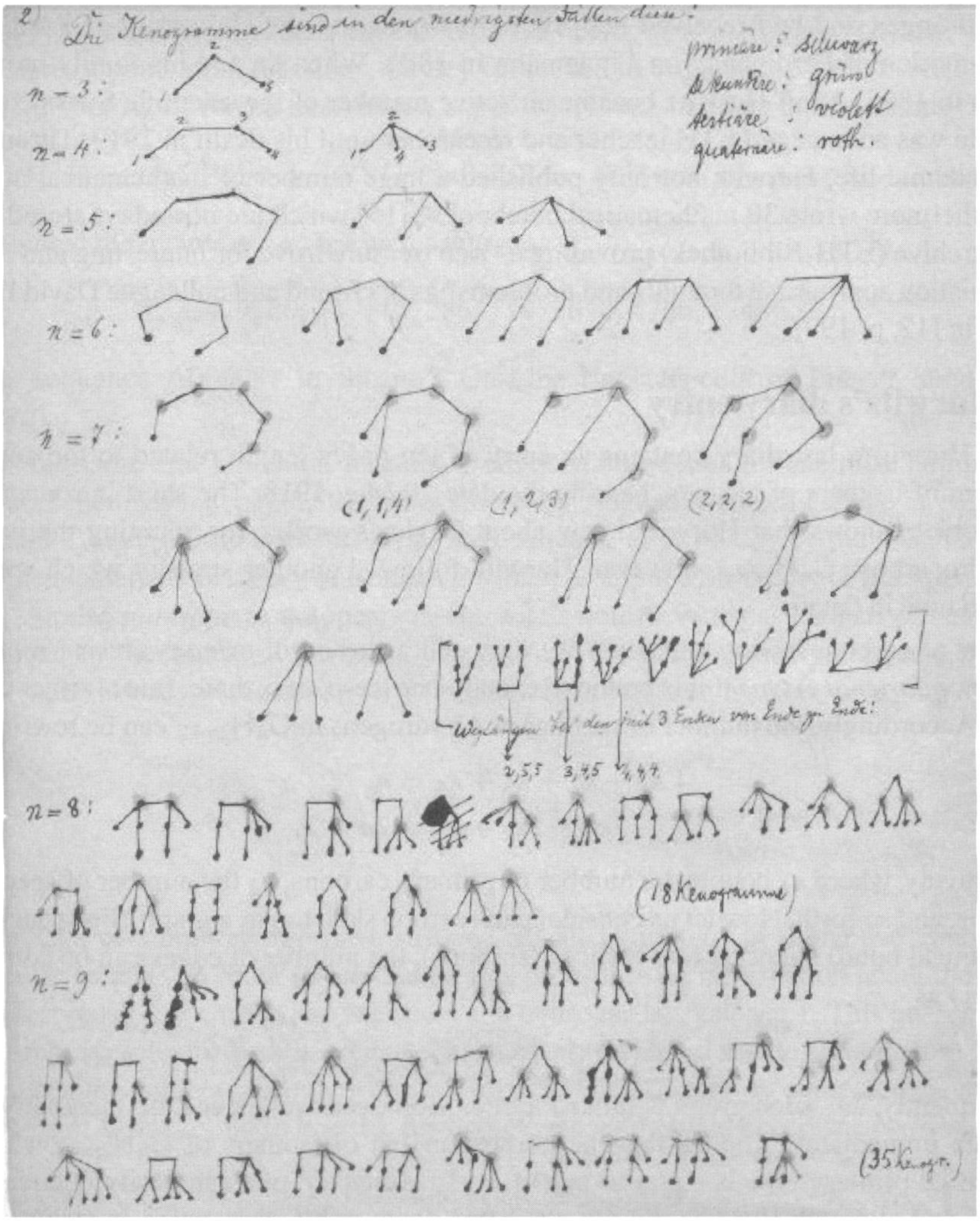
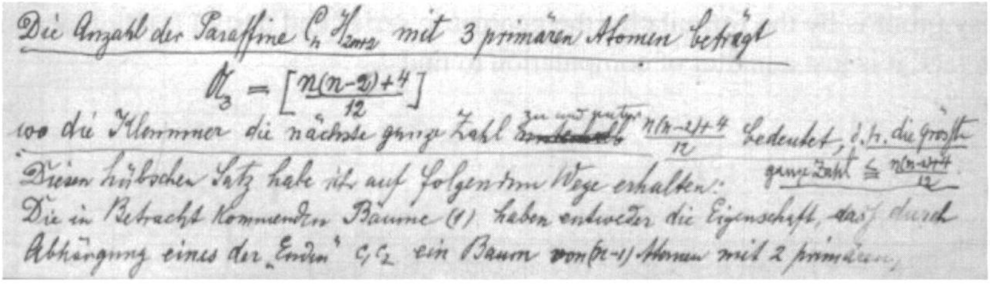


Figure 1 Hurwitz's diary entry includes a complete list of all kenograms of C_nH_{2n+2} isomers for $n = 3, \ldots, 9$, [15, p. 2].

longest chain. First we consider those isomers having a longest chain of $n-1$ carbons. In this case there are $n-3$ vertices where an additional carbon can be added (for an isomer with three primary carbons), however, some of the possible molecules are identical (e.g., the pair where the carbon is either added at second position or position $n-2$). Taking into account the parity of n, the number of isomers having a longest chain consisting of exactly $n-1$ edges equals

$$\frac{1}{2}\left(n-2+\frac{(-1)^n-1}{2}\right).$$

The above reasoning is based on the simple observation, used by Hurwitz several times,



Die Anzahl der Paraffine $C_n H_{2n+2}$ mit 3 primären Atomen beträgt

$$\mathfrak{A}_3 = \left[\frac{n(n-2)+4}{12}\right]$$

wo die Klammer die nächste ganze Zahl $\frac{n(n-2)+4}{12}$ bedeutet, d.h. die größte ganze Zahl $\leq \frac{n(n-2)+4}{12}$.
Diesen hübschen Satz habe ich auf folgendem Wege erhalten:
Die in Betracht kommenden Bäume (1) haben entweder die Eigenschaft, daß durch Abhängung eines der „Enden" $C_1 C_2$ ein Baum ~~von (n-1) Atomen~~ mit 2 primären,

Figure 2 Quotation with Formula (2) from Hurwitz's diary [15, p. 3].

that removing a leaf[6] from a tree with n vertices leads to a tree with $n-1$ vertices while adding a leaf to a tree with $n-1$ vertices gives a tree with n vertices. The number of isomers having a longest chain of less than $n-1$ carbons, however, equals $\mathfrak{m}_3(n-3)$. In fact, there is a bijection between the set of those isomers and the set of 'reduced isomers' where all carbons of primary type are stripped off and the number of primary carbons is still equal to 3; for example the isomer (2, 2, 2) in Figure 1 is mapped to isobutane. Hence, we arrive at the recursion

$$\mathfrak{m}_3(n) = \mathfrak{m}_3(n-3) + \frac{1}{2}\left(n - 2 + \frac{(-1)^n - 1}{2}\right),$$

valid for $n \geq 3$, with the initial values $\mathfrak{m}_3(0) = \mathfrak{m}_3(1) = \mathfrak{m}_3(2) = 0$. Next, the generating function can be computed as

$$\begin{aligned}\sum_{n\geq 0} \mathfrak{m}_3(n)x^n &= x^3 \sum_{n\geq 0} \mathfrak{m}_3(n)x^n + \frac{1}{2}x^3\left(\sum_{n\geq 0}(n+1)x^n - \frac{(-1)^n+1}{2}x^n\right)\\ &= x^3 \sum_{n\geq 0} \mathfrak{m}_3(n)x^n + \frac{1}{2}x^3\left(\frac{1}{(1-x)^2} - \frac{1}{1-x^2}\right)\\ &= \frac{x^4}{(1-x)(1-x^2)(1-x^3)},\end{aligned}$$

where we have used formulae for the geometric series and its derivatives. In order to find an explicit formula for the coefficients, Hurwitz made use of an interesting formula from his '*exercise book*' which has posthumously been published as *Exercises on Number Theory* [14],[7] namely

$$\frac{1}{(1-x)(1-x^2)(1-x^3)} = \sum_{x_1,x_2,x_3\geq 0} x^{x_1+2x_2+3x_3} = \sum_{n\geq 0}\varphi(n)x^n \tag{3}$$

where

$$\varphi(n) = \left\lfloor \frac{n(n+6)}{12} \right\rfloor + 1. \tag{4}$$

[6]that is a vertex of a tree with degree 1.

[7]The formula in question can there be found as Exercise 65 on page 63.

The easy proof is by the formula for the geometric series and partial fraction decomposition. In fact, it is just a matter of computation to find

$$\begin{aligned}
&\frac{1}{(1-x)(1-x^2)(1-x^3)} \\
&\quad = \frac{17}{72(1-x)} + \frac{1}{4(1-x)^2} + \frac{1}{6(1-x)^3} + \frac{1}{8(1+x)} + \frac{1}{9}\left(\frac{z}{z-x} + \frac{z^2}{z^2-x}\right)
\end{aligned}$$

with z being a primitive third root of unity $z = -\frac{1}{2} + i\frac{\sqrt{3}}{2}$. Next, applying the formula for the geometric series and derivatives, one gets

$$\begin{aligned}
&\frac{17}{72}\sum_{n\geq 0} x^n + \frac{1}{4}\sum_{n\geq 0}(n+1)x^n + \frac{1}{6}\sum_{n\geq 0}\frac{1}{2}(n+2)(n+1)x^n + \\
&\qquad + \frac{1}{8}\sum_{n\geq 0}(-1)^n x^n + \frac{1}{9}\left(\sum_{n\geq 0} z^n x^n + \sum_{n\geq 0} z^{2n} x^{2n}\right) = \sum_{n\geq 0}\varphi(n)x^n,
\end{aligned}$$

where

$$\begin{aligned}
\varphi(n) &= \frac{17}{72} + \frac{1}{4}(n+1) + \frac{1}{12}(n+1)(n+2) + \frac{1}{8}(-1)^n + \frac{1}{9}(z^n + z^{2n}) \\
&= \frac{n(n+6)}{12} + \frac{47 + 9(-1)^n + 8(z^n + z^{2n})}{72}.
\end{aligned}$$

It is not difficult to see that the second term on the right-hand side is so small such that the integer $\varphi(n)$ equals the integral part of the first term on the right. This proves Hurwitz's exercise (4) as well as Formula (2).

Moreover, Hurwitz found another aspect from his counting isomers by noticing that $\mathfrak{m}_3(n)$ also equals the number of solutions of the linear diophantine equation

$$n - 4 = 1x_1 + 2x_2 + 3x_3 \tag{5}$$

in non-negative integers. This follows immediately from (3). Consequently, there exists a bijection between the solutions of the latter equation and the isomers in question. Of course, Hurwitz used a different language, his reasoning, however, provides an interesting characterization: those isomers having a longest chain equal to $n-1$ are associated with solutions of the form $(x_1, x_2, 0)$. All other isomers have a longest chain of length at most $n-2$ and thus contain a subtree associated with a solution (x_1, x_2, x_3'); hence the larger isomer is related to the solution $(x_1, x_2, x_3'+1)$. Indeed, given a molecule consisting of three primary and one tertiary carbon (isobutane) we may add a chain of x_3 many carbons to each of the three ends, then further x_2 carbons at two of the three ends, and, finally, x_1 carbons to one of the two ends from the x_2 carbon chains were attached (see Figure 3). Hurwitz gave even another characterization, however, the one above is more relevant for his and our next aim, namely, the case of four carbons of primary type.

Here Hurwitz provided a similar result: *The number* $\mathfrak{m}_4(n)$ *of isomers* C_nH_{2n+2} *having exactly four carbons of primary type equals the coefficient of* x^{n-5} *in the power series*

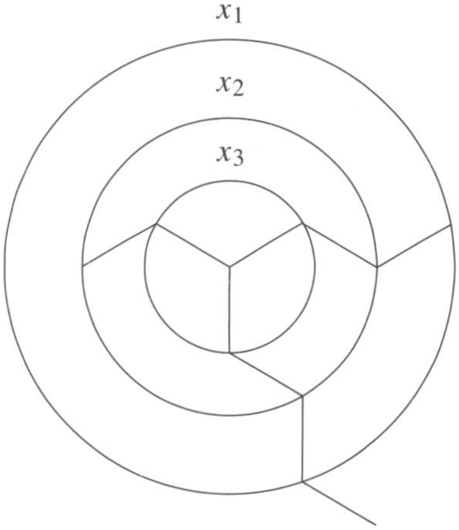
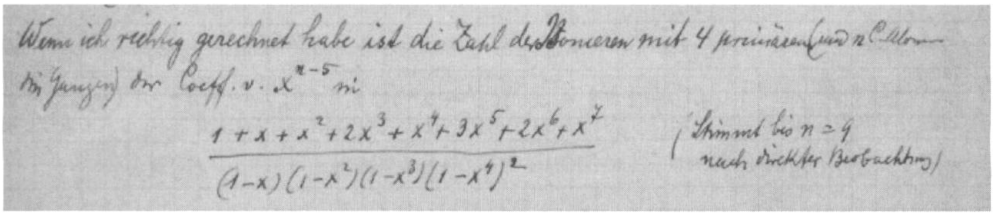


Figure 3 An example for Hurwitz's characterization.



Wenn ich richtig gerechnet habe ist die Zahl der Isomeren mit 4 primären (und n C-Atomen im Ganzen) der Coeff. v. x^{n-5} in

$$\frac{1+x+x^2+2x^3+x^4+3x^5+2x^6+x^7}{(1-x)(1-x^2)(1-x^3)(1-x^4)^2}$$

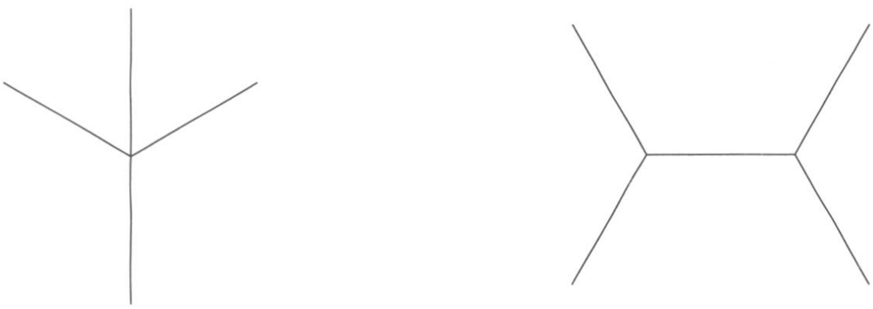
(Stimmt bis $n=9$ nach direkter Beobachtung)

Figure 4 Actually, Hurwitz was reluctant whether his derivation of Formula (6) is without any miscalculation. Our study confirms that he was indeed correct.

expansion of

$$\frac{1+x+x^2+2x^3+x^4+3x^5+2x^6+x^7}{(1-x)(1-x^2)(1-x^3)(1-x^4)^2}. \tag{6}$$

For the proof we first observe that (1) implies that either $\kappa_4 = 1$ and $\kappa_3 = 0$ or $\kappa_4 = 0$ and $\kappa_3 = 2$ (see Figure 5).



$K_4 = 1$ and $K_3 = 0$ $\qquad$ $K_4 = 0$ and $K_3 = 2$

Figure 5 The two categories of isomers having exactly four primary carbons.

With a rather analogous reasoning as above we may identify any such isomer having $\kappa_4 = 1$ and $\kappa_3 = 0$ with a solution of

$$n - 5 = x_1 + 2x_2 + 3x_3 + 4x_4 \tag{7}$$

in non-negative integers x_i. For $n \geq 5$ the number of such solutions is equal to the coefficient of x^{n-5} in the series expansion of

$$\frac{1}{(1-x)(1-x^2)(1-x^3)(1-x^4)}.$$

The isomers with $\kappa_4 = 0$ and $\kappa_3 = 2$, however, are related to the integer solutions of

$$n - 6 = x_1 + x_2 + 2x_3 + x_4 + 2x_5 \tag{8}$$

under the additional restriction $x_2 + 2x_3 \leq x_4 + 2x_5$. The inequality here avoids counting of isomorphic trees twice. It follows that the latter number of solutions is given by the coefficient of x^{n-6} in the series expansion of

$$\frac{1}{2}\left(\frac{1}{(1-x)^3(1-x^2)^2} + \frac{1+x^4}{(1-x)(1-x^2)(1-x^4)^2}\right) = \frac{1+x^2+x^3+x^4}{(1-x)^2(1-x^2)(1-x^4)^2}.$$

This leads to Formula (6).

The diary entry shows no attempt to prove an explicit formula for $\mathfrak{m}_4(n)$ which is probably related to the amount of computation needed. Using a computer algebra package, one easily finds the expansion

$$\begin{aligned}
&\frac{1+x+x^2+2x^3+x^4+3x^5+2x^6+x^7}{(1-x)(1-x^2)(1-x^3)(1-x^4)^2} \\
&\quad = 1 + 2x + 4x^2 + 8x^3 + 14x^4 + 24x^5 + 37x^6 + 56x^7 + 80x^8 + 115x^9 + \\
&\qquad + 155x^{10} + 209x^{11} + 272x^{12} + 355x^{13} + 447x^{14} + 564x^{15} + 694x^{16} + \\
&\qquad + 857x^{17} + 1034x^{18} + 1249x^{19} + 1483x^{20} + \cdots
\end{aligned}$$

Hence, for $n = 5$ there is exactly one isomer with four primary carbons, for $n = 6$ there exist two, for $n = 7$ already four and so forth.

Next, Hurwitz considered the question of counting isomers having a fixed number of primary carbons depending on the number of secondary carbons, however, he did not succeed. Counting the number of isomers by ordering them with respect to the number of primary carbons and applying formulae as (2) and (6) would not lead much further. Actually, with growing κ_1 the number of different categories resulting from (1) grows linearly: *the number of solutions of* $\kappa_1 = \kappa_3 + 2\kappa_4 + 2$ *in non-negative integers is equal to* $\lfloor \frac{\kappa_1}{2} \rfloor$. This follows by a similar reasoning as above. The generating function for the number of categories $F(\kappa_1)$ with κ_1 primary carbons is

$$\sum_{\kappa_1 \geq 2} F(\kappa_1) x^{\kappa_1} = \frac{x^2}{(1-x)(1-x^2)},$$

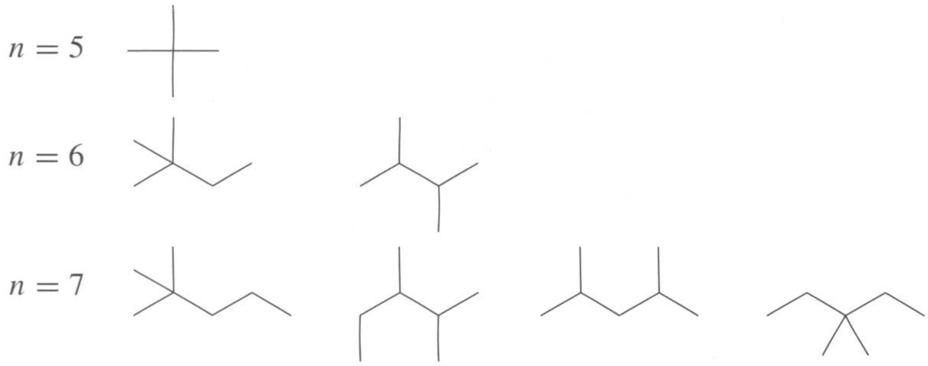


Figure 6 Isomers of C_nH_{2n+2} with four primary carbons for $n = 5, 6, 7$.

and partial fraction decomposition shows

$$F(\kappa_1) = \frac{\kappa_1 + 1}{2} - \frac{3}{4} + \frac{1}{4} \cdot (-1)^{\kappa_1} = \left\lfloor \frac{\kappa_1}{2} \right\rfloor.$$

Although the number of categories grows moderately slowly, Hurwitz's approach cannot be successful since the number of isomers of C_nH_{2n+2} grows exponentially, however, this was not known when Hurwitz was writing his diary entry (although he might have guessed it by comparison with Cayley's theorem on the number of rooted trees).

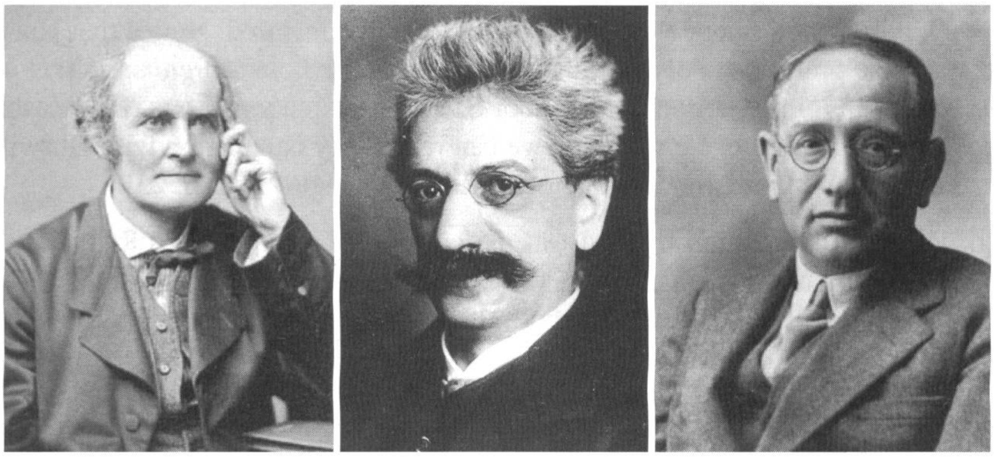


Figure 7 From left to right: Arthur Cayley (1821–1895), Adolf Hurwitz (1859–1919) and George Pólya (1887–1985).

3 George Pólya's aftermath

The next character in our story is George (György) Pólya who was working at ETH Zurich from 1914 (on the inititaive of Hurwitz) until 1940. After Hurwitz's death in 1919 Pólya was taking care about Hurwitz's mathematical estate, investigating the diaries, and finally editing Hurwitz's collected works. However, there seems to be no direct impact of Hurwitz's diary entry on alkanes to Pólya's landmark paper [19], written in German, later, in the year of Pólya's death, translated to English and published with additional comments by

R.C. Read as [23]. His *combinatorial enumeration of groups, graphs, and chemical compounds* (that is the title) has been considered as one of the most important methods in combinatorics. Pólya started his investigations on graph theoretical aspects related to chemical compounds already in 1935;[8] he might have been inspired by reading math courses to students of chemistry.[9] In 1937, he proved among many other and more general results that the number of C_nH_{2n+2} isomers is asymptotically equal to

$$\text{constant} \times \rho^{-n} n^{-5/2} \qquad \text{with} \quad \rho = 0,35\ldots$$

For small n the number of alkane isomers is well known; e.g., $C_{32}H_{66}$ has 27 711 253 769 isomers which is pretty close to the asymptotical value above (without the undetermined constant). Pólya's enumeration method relies on Cayley's use of generating functions (which, of course, is also a tool in Hurwitz's approach) and deeper results from group theory. In particular, Burnside's lemma[10] and the so-called cycle index play a central role. For the latter ingredient Pólya thanks Issai Schur explicitly in [19, § 20], for mentioning a parallel reasoning in the works of Georg Ferdinand Frobenius. In fact, the theory of characters of the symmetric group, developed by Frobenius and his pupil Schur around 1900, prepares the ground for Pólya's powerful method; Pólya refers to Schur's lecture notes [26] and Frobenius' article [10].[11] Moreover, Pólya mentions several chemists, namely, H.R. Henze & C.M. Blair for extending Cayley's computations as well as the pair of the chemist Arthur Constant Lunn and the mathematician James K. Senior [16] for discovering a relation between isomers and the symmetric group.

Very likely, Pólya knew about Hurwitz's note but was not inspired. Notice that Hurwitz is mentioned in the preface of Pólya's rather famous exercise book *Aufgaben und Lehrsätze der Analysis* [22], jointly written with Gábor Szegő. As a matter of fact, Pólya estimated Hurwitz very highly; in his *picture book* we can read: "My connection with Hurwitz was deeper and my debt to him greater than to any other colleague" [21, p. 25].

Much of Pólya's enumeration method was anticipated by John Howard Redfield already in 1927. In his only mathematical article [25], published in his lifetime, Redfield followed a similar road as Pólya a decade later but, although it appeared in a good journal, was not noticed by the community for a long time.[12] Only in the 1950s, after Redfields death, Frank Harary rediscovered Redfields paper and made its content public.[13]

[8] see [23] for references to his first articles on this topic in 1935.

[9] see the obituray [2, p. 566]; for details about his life we refer to [1].

[10] which was already known by August-Louis Cauchy; Burnside gave in his *Theory of Groups* from 1897 credit to Frobenius. See Neumann [17] for details.

[11] There has been a letter exchange between Pólya and Schur in the period from November 1935 until Februar 1936 on the use of methods from representation theory; these letters are listed in the new edition [27] of Schur's notes [26] by Stammbach. The authors are grateful to the referee for this remark.

[12] It should be noticed that Redfield's exposition is with 23 pages rather short compared with 110 pages of Pólya; nevertheless, Pólya's paper [19] was originally published in German which was a lingua franca in the 1930s, however, that changed drastically after World War II.

[13] For more information on this topic we refer to [23, p. 118–122].

4 A final word about Hurwitz

Hurwitz's reasoning is close to Cayley; the only new idea is the recursion formula for isomers having exactly one tertiary carbon. About his motivation we can only speculate.[14] In fact, Hurwitz had always been interested in combinatorical questions. For instance, in articles from 1891 and 1902 he counted certain Riemann surfaces with respect to the number of branching points. It is apparent from [13] that Hurwitz was aware of Frobenius' theory of the group determinant and character theory for symmetric groups, e.g., [9], a forerunner of Frobenius' later paper [10] which is mentioned by Pólya [19].[15] Hurwitz's diary entry contains certain terms which also appear in Frobenius' character theory. Notice that a permutation is said to be of type $[x_1, x_2, \ldots, x_m]$ if it contains x_1 cycles of order 1, x_2 cycles of order 2, and so on. Consequently,

$$1x_1 + 2x_2 + \cdots + mx_m = m$$

is the total number of objects that have been permutated. This is more or less a sentence from Pólya's landmark paper [19, p. 157], and it reminds us of expressions appearing in Hurwitz's notes, namely in the relations (5), (7) and (8). Thus, Hurwitz's characterization of the isomers associated with a special type is intimately related with permutations of the symmetric group. However, Hurwitz did not make use of permutation groups and character theory for his counting problem of isomers; this observation has been first made by Redfield [25] in 1927, followed by Lunn & Senior [16], and finally elaborated in great detail by Pólya [19] around 1935/37.

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[14] In a very different context certain chemical compounds, including hydrocarbons, were very much in discussion at the time of Hurwitz's diary entry, May 1918: sulfur mustard stands for a group of cytotoxic and vesicant chemical warfare agents; they were first used as chemical warfare in World War I by the German army causing large blisters on the exposed skin and in the lungs. Some of them are created by use of ethene C_2H_4.

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