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Asymptotic isomer enumeration in chemistry. II

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This is a sequel to a recent paper by John Knopfmacher (1998) on the problem of asymptotic enumeration of different kinds of isomers of *ensembles* or *mixtures* of molecules, involving together with other atoms a large number n of carbon atoms, *in total*. The new kinds of mixtures to be chosen for application below require and are treated with the aid of both the previous mathematical tools, and new theorems based on *different* techniques.

1. Introduction

In a recent paper [4] (called part I below) the present first named author investigated some problems concerning the asymptotic enumeration of all isomers (of various kinds) of *ensembles* or *mixtures* of molecules, involving together with other atoms a large *total* number n of atoms of some *special* interest (e.g., carbon atoms, usually).

Previously, major contributions towards the enumeration of isomers of important kinds of *molecules alone* were published by G. Pólya in 1937 in a famous paper, translated in book form [6] in 1987. Some of Pólya's results were used in part I as starting points towards solving the extended problem of enumerating corresponding more general chemical ensembles or mixtures. This was done with the aid of some mathematical tools explained at length in part I. At the same time, it was noted that the extension of certain of Pólya's results would require the development of a *modified* mathematical treatment, based on different types of asymptotic formulae and additional techniques.

The *main aim* of the present article is to carry out those indicated extensions. Again these will be highlighted by the listing of a *selection* of asymptotic formulae for some particular types of chemical mixtures. However, once more, it seems worth emphasizing that the *general methods* to be developed might possibly be *as worthy* of attention as the explicit applications to be listed below, if not more so.

Notes. Since this paper is intended to be a *sequel* to part I, starting with the same *initial* concepts and steps (which were developed in detail in part I), frequent references

will be made to part I in lieu of detailed repetitions. It seems, however, worth repeating here that, while the indicated isomers of mixtures are *theoretically* feasible in terms of enumeration, for steric reasons the mathematically allowed isomers would not always be chemically viable in a laboratory sense (cf., say, Klein and Seitz [2]).

2. Some enumeration results of Pólya for molecules

Consider the following particular sets of molecular formulae:

(i)

$$\Lambda_k = \{\mathrm{C}_n\mathrm{H}_{2n+2-2k}\colon\ n = 1, 2, 3, \ldots\},$$

for general unsaturated hydrocarbons containing k double bonds, where $k \geqslant 0$ is some fixed non-negative integer. Then Λ_0 is the set Γ_1 discussed in part I. Pólya (cf. [1,6]) showed that the number $\sigma_n^*(\Lambda_k)$ of all structural isomers of molecules of type $\mathrm{C}_n\mathrm{H}_{2n+2-2k}$ satisfies

$$\sigma_n^*(\Lambda_k) \sim c_k q_1^n n^{(3k-5)/2} \quad \text{as } n \to \infty, \tag{2.1}$$

where $c_k > 0$ and $q_1 > 1$ are constants. In particular, $c_1 = 1/4$.
For the $k = 0$ asymptotic formula, the number of alkanes is $\sim N^{-5/2} q^N$, then for $k = 1$ there are no more than N (or even $N - 1$) places to add a double bond, so that the number of $k = 1$ alkanes is (no more than) $\sim N^{-3/2} q^N$. According to Pólya, the asymptotic count for all ($k = 1$) hydrocarbons with formula $\mathrm{C}_N\mathrm{H}_{2N}$ (acyclic or not) is $\sim N^{-1} q^N$.

(ii)

$$\Lambda'_k = \{\mathrm{C}_n\mathrm{H}_{2n+2-k}X_1X_2\ldots X_k\colon\ n = 1, 2, 3, \ldots\},$$

for k-fold substituted paraffins with distinct non-alkyl ligands $X_1, \ldots, X_k$, where $k \geqslant 0$ is some fixed non-negative integer. Then $\Lambda'_0 = \Lambda_0 = \Gamma_1$ again, while Λ'_1 is the set Γ_2 discussed in part I. Pólya (cf. [1,6]) showed that the number $\sigma_n^*(\Lambda'_k)$ of all structural isomers of molecules of type $\mathrm{C}_n\mathrm{H}_{2n+2-k}X_1X_2\ldots X_k$ satisfies

$$\sigma_n^*(\Lambda'_k) \sim c'_k q_1^n n^{(2k-5)/2} \quad \text{as } n \to \infty, \tag{2.2}$$

where $c'_k > 0$ is a constant, and q_1 is as before.

(iii) Let $\Lambda'_0 = \Lambda_0 = \Gamma_1$, and $\Lambda'_1 = \Gamma_2$ as above. Let $\kappa_n^*(\Lambda'_0)$ denote the number of structural isomers of paraffin molecules of type $\mathrm{C}_n\mathrm{H}_{2n+2}$ *without* asymmetric carbon atoms (achiral paraffins). Also let $Q_n^*(\Lambda'_1)$ denote the number of structural isomers of alcohol molecules of type $\mathrm{C}_n\mathrm{X}_{2n+1}\mathrm{OH}$ *without* asymmetric carbon atoms (achiral planted alcohols). Pólya (cf. [1,6]) showed that

$$\kappa_n^*\big(\Lambda'_0\big) \sim c q_0^n, \quad Q_n^*\big(\Lambda'_1\big) \sim 2c q_0^n \quad \text{as } n \to \infty, \tag{2.3}$$

where $c > 0$ and $q_0 > 1$ are constants.

3. An extended abstract prime number theorem

In part I, it was shown by the present first named author that the problem of estimating the number of isomers (of some chosen kind) of chemical Γ-mixtures containing n carbon atoms in total, where Γ is a given set of molecular formulae, can be reformulated mathematically in terms of an associated *additive arithmetical semigroup* (additive a.s.) G_Γ.

The number $\sigma_n(\Gamma)$, or $\sum_n(\Gamma)$, of constitutional (structural) isomers, or (respectively) stereoisomers, of general Γ-mixtures with n carbon atoms in total then corresponds to the number $G_\Gamma^{\#}(n)$ of elements of degree n in G_Γ, while the related number $\sigma_n^*(\Gamma)$, or $\sum_n^*(\Gamma)$, for the Γ-*molecules* corresponds to the number $P_\Gamma^{\#}(n)$ of *prime* elements of degree n in G_Γ.

The asymptotic enumeration results of Pólya for molecules quoted in section 2 may now be reformulated to provide concrete examples for which the following hypothesis is valid:

Axiom $\Phi(\alpha)$. G is an additive a.s. with the property that there exist real constants $C > 0,\ q > 1$, and α (depending on G) such that

$$P^{\#}(n) \sim Cq^n n^{-\alpha} \quad \text{as } n \to \infty.$$

The special case of this axiom for which $\alpha > 1$ was discussed in part I, under the heading "Axiom Φ". The new cases $\alpha = 1$, and $\alpha < 1$, are illustrated by the examples of section 2, and require different mathematical techniques from the previous case. Apart from the chemical examples, all three cases of axiom $\Phi(\alpha)$ are also satisfied by a variety of *further* mathematical examples, stemming from geometry and graph theory and without obvious connections with chemistry. Such mathematical examples and their associated additive arithmetical semigroups have been investigated by J. Knopfmacher and Warlimont [5], who prove the following extension of the (inverse) abstract prime number theorem subject to axiom Φ (cf. A. Knopfmacher and J. Knopfmacher [3], and part I):

Theorem 3.1. Let G denote any additive a.s. satisfying axiom $\Phi(\alpha)$ above:

I. If $\alpha > 1$ then

$$G^{\#}(n) \sim CZ_G\big(q^{-1}\big)q^n n^{-\alpha} \quad \text{as } n \to \infty,$$

where

$$Z_G(y) = \sum_{r=0}^{\infty} G^{\#}(r)y^r.$$

II. If $\alpha = 1$ then $G^{\#}(n) = q^n n^{C-1+o(1)}$, i.e.,

$$\log q^{-n} G^{\#}(n) \sim (C-1)\log n \quad \text{as } n \to \infty.$$

III. If $\alpha < 1$ then $G^{\#}(n) = q^n \exp\{(B_\alpha + \mathrm{o}(1))n^{(1-\alpha)/(2-\alpha)}\}$, i.e.,

$$\log q^{-n} G^{\#}(n) \sim B_\alpha n^{(1-\alpha)/(2-\alpha)} \quad \text{as } n \to \infty,$$

where

$$B_\alpha = B_\alpha(C) = \frac{2-\alpha}{1-\alpha}\big(C\Gamma(2-\alpha)\big)^{1/(2-\alpha)},$$

in terms of Euler's gamma function.

The mathematical proofs for the new cases $\alpha = 1$, and $\alpha < 1$, of this theorem are given by J. Knopfmacher and Warlimont [5], and are quite lengthy. Unfortunately, mathematical examples can be provided (cf. [5]) to show that one cannot in general hope for better than logarithmic estimates in the new cases $\alpha = 1$ and $\alpha < 1$.

The next section lists the specific applications of theorem 3.1 to asymptotic enumeration of the particular kinds of chemical mixtures which arise from the examples discussed in section 2.

4. Some specific enumeration for mixtures

Considering the specific examples of molecular enumeration due to Pólya which were listed in section 2, let the respective counting functions for the associated chemical *ensembles* or *mixtures* be denoted by *now dropping* the asterisks in the relevant notations used for counting only molecules. Then theorem 3.1 leads to the following new asymptotic enumeration formulae for mixtures:

Example 1. (See (2.1)). Here $\sigma_n^*(\Lambda_k) \sim c_k q_1^n n^{-\alpha}$ as $n \to \infty$, where $\alpha = (5-3k)/2$. When $k = 1$, case II of theorem 3.1 implies that

$$\sigma_n(\Lambda_1) = q_1^n n^{-3/4+\mathrm{o}(1)} \quad \text{as } n \to \infty. \tag{4.1}$$

When $k \geqslant 2$, case III of theorem 3.1 implies that

$$\sigma_n(\Lambda_k) = q_1^n \exp\big\{\big(b_k + \mathrm{o}(1)\big)n^{(3k-3)/(3k-1)}\big\} \tag{4.2}$$

for an explicit constant b_k, as $n \to \infty$.

Example 2. (See (2.2)). Here $\sigma_n^*(\Lambda_k') \sim c_k' q_1^n n^{-\alpha}$ as $n \to \infty$, where $\alpha = (5-2k)/2$. When $k \geqslant 2$, case III of theorem 3.1 implies that

$$\sigma_n\big(\Lambda_k'\big) = q_1^n \exp\big\{\big(b_k' + \mathrm{o}(1)\big)n^{(2k-3)/(2k-1)}\big\} \tag{4.3}$$

for another constant b_k', as $n \to \infty$.

Example 3. (See (2.3)). Here $\kappa_n^*(\Lambda_0') \sim cq_0^n \sim \frac{1}{2}Q_n^*(\Lambda_1')$ as $n \to \infty$. Thus case III of theorem 3.1 implies that

$$\begin{aligned} \kappa_n\big(\Lambda_0'\big) &= q_0^n \exp\big\{\big(2\sqrt{c} + \mathrm{o}(1)\big)\sqrt{n}\,\big\}, \quad \text{and} \\ Q_n\big(\Lambda_1'\big) &= q_0^n \exp\big\{\big(2\sqrt{2c} + \mathrm{o}(1)\big)\sqrt{n}\,\big\}, \quad \text{as } n \to \infty. \end{aligned} \tag{4.4}$$

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