Contributions to the Theory of Mass Action Kinetics
I. Enumeration of Second Order Mass Action Kinetics

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Z. Naturforsch. **33 a**, 827–833 (1978); received April 19, 1978

By investigating the reaction diagram in its own right, it is possible to solve the problem of enumerating all the different types of mass action kinetics up to second order. The amount of non isomorphic complex sets for a given number of species and of non isomorphic reaction networks and reversible reaction networks which can be derived from a given number of complexes is given.

1. Introduction

To speak of chemical kinetics usually means either to speak of the dynamic behavior of a given reaction scheme or of the determination of rate constants and reaction mechanisms. For these purposes the reaction diagram is considered as a more or less useful shorthand to derive a system of differential equations to be dealt with or simply to assign a rate constant to an elementary reaction.

Making the reaction diagram in its own right the subject of investigation, however, yields rather surprising results concerning the dynamic behavior of reaction networks. It is the zero deficiency theorem, derived by Horn [1], Feinberg [2], and Feinberg and Horn [3], which connects the algebraic structure of a reaction network with its dynamic behavior. It allows to identify all those reaction schemes which decay to a single equilibrium point. For mass action kinetics with elementary reactions up to second order Horn [4] developed a graph theoretical method which even simplifies the application of the zero deficiency theorem.

However, as this note does not deal with the dynamic behavior of reaction networks, the reader interested in this topic is referred to the work by Horn and Jackson [5], Horn [1, 4], and Feinberg [2, 6].

The aim of this note is to determine the number of different mass action kinetics with elementary reactions of at most second order. The solution to this problem is facilitated by the graph theoretical description of mass action kinetics given by Horn [4]. An appropriate tool for enumerating these graphs is a method developed by Pólya [7] commonly used in graphical enumeration problems (see Harary [8, 9], Oberschelp [10], Harary and Palmer [11]). Thus, the graph theoretical description of mass action kinetics by Horn and the enumeration theory by Pólya enables us to answer the following questions:

1. How many non isomorphic complex sets are there for a given number of species?
2. How many non isomorphic reaction networks are there for a given number of complexes?
3. How many of them describe reversible mass action kinetics?

But first it is necessary to define terms like complex set, reaction network, etc.

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2. Notation

Before giving the necessary formal definitions it might be useful to discuss an example. In the chemical literature a reaction network is represented by a diagram, for example

$$
\begin{array}{l}
\rightarrow S_1 \rightleftarrows S_2 \rightarrow \\
\quad S_2 + S_3 \rightleftarrows 2\,S_3 \\
\quad S_1 + S_3 \rightarrow S_4 \\
\qquad \uparrow \\
\qquad S_5
\end{array}
\qquad \text{(E)}
$$

which is interpreted by saying: S_1 is supplied to the reactor; S_2 is removed from the reactor; S_1 reacts to S_2 and vice versa; S_2 and S_3 react to $2\,S_3$ and vice versa; S_1 reacts with S_3 to S_4, S_4 reacts to S_5, S_5 reacts to S_1 and S_3, where the S_i, $i = 1, 2, \ldots, 5$, represent chemical species.

It is obvious that the "reaction arrow" defines a relation on the set of the entities that appear on either side of the arrow, which will be called complexes.

But it is not so obvious that the "plus sign" can be extended to a symmetric relation on the set of species. This will be done by introducing a new species S_0 which we call zero species. This species will be introduced into the reaction network if there are complexes which consist of only one normal (i. e. reacting) species or of no normal species.

To demonstrate this construction, the example given above is to be rewritten in the following way:

$$\begin{array}{c} S_0 + S_0 \\ \downarrow \quad \nwarrow \\ S_1 + S_0 \rightleftarrows S_2 + S_0 \\ S_2 + S_3 \rightleftarrows S_3 + S_3 \\ S_1 + S_3 \rightarrow S_4 + S_0 \\ \nwarrow \quad \swarrow \\ S_5 + S_0 \end{array} \qquad (E')$$

It can be shown that the introduction of the zero species does not change the dynamic behavior of any mass action kinetics. It is even possible to get more information about mass action kinetics by introducing this zero species [12].

The example given above suggests the following definition for a reaction network.

Definition 1

A *reaction network* is defined to consist of the following three objects:

(i) a non empty, finite set $\mathbf{S} = \{S_0, S_1, \ldots, S_m\}$ called *species set*. It will be convenient to denote the $m+1$ elements of $\mathbf{S}$, called *species*, by their subscript, i. e. $S_i := i$.

(ii) a symmetric relation $\mathbf{C} \subset \mathbf{S} \times \mathbf{S}$. The elements of $\mathbf{C}$ are called *complexes* C_i. It is assumed that for each $i \in \mathbf{S}$ there exists a $j \in \mathbf{S}$ such that $(i, j) \in \mathbf{C}$.

(iii) an irreflexive relation $\mathbf{R} \subset \mathbf{C} \times \mathbf{C}$ whose elements are called *reactions*. It is assumed that for each $C_i \in \mathbf{C}$ there exists a $C_j \in \mathbf{C}$, $C_i \neq C_j$, such that $(C_i, C_j) \in \mathbf{R}$ or $(C_j, C_i) \in \mathbf{R}$.

To demonstrate the application of this definition we go back to the example (E'). Here the species set $\mathbf{S}$ is given by $\mathbf{S} = \{S_0, S_1, S_2, S_3, S_4, S_5\} := \{0, 1, 2, 3, 4, 5\}$. The complexes are $C_1 = (0, 0)$, $C_2 = (0, 1)$, $C_3 = (0, 2)$, $C_4 = (2, 3)$, $C_5 = (3, 3)$, $C_6 = (1, 3)$, $C_7 = (0, 4)$, and $C_8 = (0, 5)$, which form the complex set $\mathbf{C} = \{C_1, C_2, \ldots, C_8\}$. Elements of $\mathbf{R}$ are (C_2, C_1), (C_3, C_2), (C_2, C_3), (C_1, C_3), (C_5, C_4), (C_4, C_5), (C_7, C_6), (C_8, C_7), and (C_6, C_8).

To each of the relations $\mathbf{C}$ and $\mathbf{R}$ we can construct a graph. It is this graph theoretical aspect which enormously facilitates the enumeration of non isomorphic mass action kinetics.

Definition 2

Given a complex set $\mathbf{C}$ derived from a species set $\mathbf{S}$. A graph constructed according to the following rules will be called *Horn graph H:*

(i) a one-to-one correspondence between the elements of $\mathbf{S}$ and the nodes of the graph, called species nodes;

(ii) two species nodes i and j are connected by an arc if $(i, j) \in \mathbf{C}$;

(iii) the node corresponding to the zero species will be called root.

For a given complex set the corresponding Horn graph is composed of the following elements:

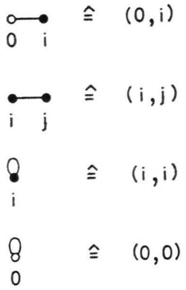


Fig. 1. Graph representation of bimolar complexes.

For the complex set $\mathbf{C}$ of the example (E') the corresponding Horn graph is given by

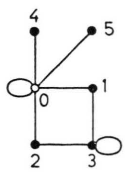


Fig. 2. Horn graph for the reaction diagram E'.

According to Def. 1 (ii) a Horn graph has no isolated node.

Definition 3

Given a set of reactions $\mathbf{R}$ for a given complex set. A graph constructed according to the following rules will be called *reaction graph:*

(i) The nodes of the graph correspond uniquely to the complexes.
(ii) Two nodes C_i, C_j are connected by a directed arc if $(C_j, C_i) \in \mathbf{R}$, i. e. $C_i \to C_j$.

Again, isolated nodes are excluded by Definition 1 (iii).

Definition 4

If $\mathbf{R}$ is symmetric then the reaction graph and the reaction network will be called *reversible.*

Definition 5

Two complex sets $\mathbf{C}$ and $\mathbf{C}'$ with $|\mathbf{C}| = |\mathbf{C}'|$ and $|\mathbf{S}| = m$ are called *isomorphic,* $\mathbf{C} \sim \mathbf{C}'$, if there exists a permutation $\mathbf{P}$ such that

(i) $C_i \in \mathbf{C} \Leftrightarrow \mathbf{P}\, C_i \in \mathbf{C}'$ and
(ii) $(0, 0) = \mathbf{P}(0, 0)$.

Definition 5′

Two Horn graphs H_1 and H_2, derived from $\mathbf{C}$ and $\mathbf{C}'$ are called isomorphic

(i) if there is a bijective mapping between the nodes of H_1 and H_2 which preserves the adjacency relation, and
(ii) if the root of H_1 is mapped into the root of H_2.

As can immediately be seen, the isomorphism of complex sets is an equivalence relation, for

(i) $\mathbf{C} \sim \mathbf{C}$ (reflexivity),
(ii) $\mathbf{C} \sim \mathbf{C}'$ implies $\mathbf{C}' \sim \mathbf{C}$ (symmetry),
(iii) $\mathbf{C} \sim \mathbf{C}'$ and $\mathbf{C}' \sim \mathbf{C}''$ implies $\mathbf{C} \sim \mathbf{C}''$ (transitivity).

That means that two isomorphic complex sets have the same properties. Therefore, we want to enumerate the non isomorphic complex sets constructed from a given species set $\mathbf{S}$. Isomorphic complex sets only differ in the numbering of their species.

Definition 6

Two complex sets are *structural isomorphic* if Def. 5 (i) is fulfilled but not necessarily Def. 5 (ii). A representative of an equivalence class of structural isomorphic complex sets will be called *structure.* The definition for graphs is according to Def. 5′. The difference between isomorphic and structural isomorphic complex sets is due to the fact that in the latter case the zero species is considered as a normal species.

By the definition of the Horn graph the following theorem [4] is obvious.

Theorem

Two complex sets are (structural) isomorphic if and only if the corresponding graphs are (structural) isomorphic.

Thus, we can describe a complex set by the corresponding Horn graph, which facilitates the decision whether two given complex sets are isomorphic or not.

3. Enumeration Method

The appropriate method to enumerate the non isomorphic graphs as defined above is provided by Pólya's theory. Without going into any details this theory may be briefly summarized (for more detail, see e. g. Harary and Palmer [11] or Oberschelp [10]). The presentation given below follows the work by Oberschelp [10, p. 57 ff], who gives a very elegant formulation for the enumeration formulas.

The basis of Pólya's enumeration method is a permutation theory which connects the structure preserving point permutations with the permutations of unordered (i. e. Horn graphs) or ordered (i. e. reaction graphs) pairs, which are induced by the point permutations. The problem is to find the cycle indices of the pair groups induced by the symmetric group S_n (n is the number of points). The cycle index $Z(S_n)$ of the symmetric group S_n is given by a polynomial in n variables

$$Z(S_n) = \frac{1}{n!} \sum_{(p)} c(p)\, z_1^{p_1} z_2^{p_2} \ldots z_n^{p_n} \qquad (1)$$

where the summation is over all partitions of n [i. e. p is an n-tuple $p = (p_1, p_2, \ldots, p_n)$ with $\sum_{i=1}^{n} i\, p_i = n$]. $c(p)$ is given by

$$c(p) = \frac{n!}{1^{p_1} p_1!\, 2^{p_2} p_2! \ldots n^{p_n} p_n!}\,. \qquad (2)$$

The cycle index we have to use is given by

$$Z(S_n^{(2)}) = \frac{1}{n!} \sum_{(p)} c(p) z_1^{l_1} z_2^{l_2} \ldots z_{\binom{n}{2}}^{l_{\binom{n}{2}}} . \qquad (3)$$

Here, the $l(p) := (l_1, l_2, \ldots, l_{\binom{n}{2}})$ are partitions of $\binom{n}{2}$. The summation is again over all partitions p of n. The determination of the $l_i(p)$ is possible by

$$l_i(p) = \frac{1}{i}\left(\sum_{[f;g]=i} \frac{1}{2} f g p_f (q_q - \delta_{fq}) + \left(\binom{i}{2} - \frac{i}{2} \delta_i(2)\right) p_i + i p_{2i} \right) \qquad (4)$$

for symmetric relations (i.e. reversible reaction graphs) and for Horn graphs by adding p_i to each $l_i(p)$ of (4). In Eq. (4) the summation is over the least common multiples $[f;g]$ of i, δ_{fg} is the Kronecker symbol and

$$\delta_i(2) = \begin{cases} 1 & \text{if } i \text{ is divisible by 2} \\ 0 & \text{in all other cases} \end{cases} .$$

If the cycle index is known, the second step of Pólya's method consists of inserting $(1+z^i)$ for z_i into the polynomial $Z(S_n^{(2)})$. This can be represented by a double series

$$F(z, y) = \sum_{i=1}^{\infty} \sum_{k=1} \lambda_{ik}\, z\, k\, y\, i = Z(S_n^{(2)})\,[z_k/1 + z^k], \qquad (5)$$

where λ_{ik} gives the number of non isomorphic graphs with i nodes and k arcs.

4. Enumeration Results

In stating the results we proceed in the following order: first, the number of non isomorphic structures σ_m (m is the number of species or number of nodes of the Horn graphs) is determined. Then, the non isomorphic Horn graphs (with root) h_m are enumerated. The sum of σ_m and h_m is the number of all non isomorphic complex sets which can be constructed from a species set with m species.

After enumerating the complex sets, the number of non isomorphic reversible reaction networks (graphs) ϱ_n and non isomorphic reaction networks r_n, constructed from a complex set with n complexes, will be computed.

It should be noted that a direct application of equations (3) and (4) leads to incorrect results because those formulas always contain the number of graphs with isolated nodes. These can be eliminated by simple subtraction.

4.1. Number of non isomorphic structures σ_m

Applying Equation (4) to determine the $l_i(p)$ for Horn graphs without root yields for $i = 1, 2, \ldots, 5$

$$l_1(p) = \binom{p_1+1}{2} + p_2 ,$$
$$l_2(p) = p_1 p_2 + p_2^2 + p_4 ,$$
$$l_3(p) = p_1 p_3 + p_3^2 + \binom{p_3+1}{2} + p_6 ,$$
$$l_4(p) = p_1 p_4 + 2 p_2 p_4 + 2 p_4^2 + p_8 ,$$
$$l_5(p) = p_1 p_5 + 2 p_5^2 + \binom{p_5+1}{2} + p_{10} .$$

Substituting the values of the $l_i(p)$ into (3) gives the enumeration polynomial

$$Z(S_1^{(2)}) = z_1 ,$$
$$Z(S_2^{(2)}) = \frac{1}{2} (z_1^3 + z_1 z_2) ,$$
$$Z(S_3^{(2)}) = \frac{1}{3!} (z_1^6 + 3 z_1^2 z_2^2 + 2 z_3^2) ,$$

and so on.

Replacing $1 + z^i$ for z_i results in

$$s_1 = 1 + z ,$$
$$s_2 = 1 + 2z + 2z^2 + z^3 ,$$
$$s_3 = 1 + 2z + 4z^2 + 6z^3 + 4z^4 + 2z^5 + z^6 .$$

Here the coefficients give the number of structures with k arcs (k is the exponent of z). The corresponding structures are depicted in Figure 3.

By inspecting Fig. 3 it can be seen that the structures for $m = 1$ contradict Def. 1, and thus do not represent any complex set which gives rise to a reaction network. For $m = 2$ there are three structures which contradict Def. 1. Those are the structures corresponding to 1 and $2z$ in s_2, which have to be cancelled. Comparing the structures for $m = 2$ and $m = 3$ shows the general cancellation procedure. It can be seen that the structures s_2 are those which have an isolated node if $m = 3$. Thus, the number of non isomorphic structures may be computed by

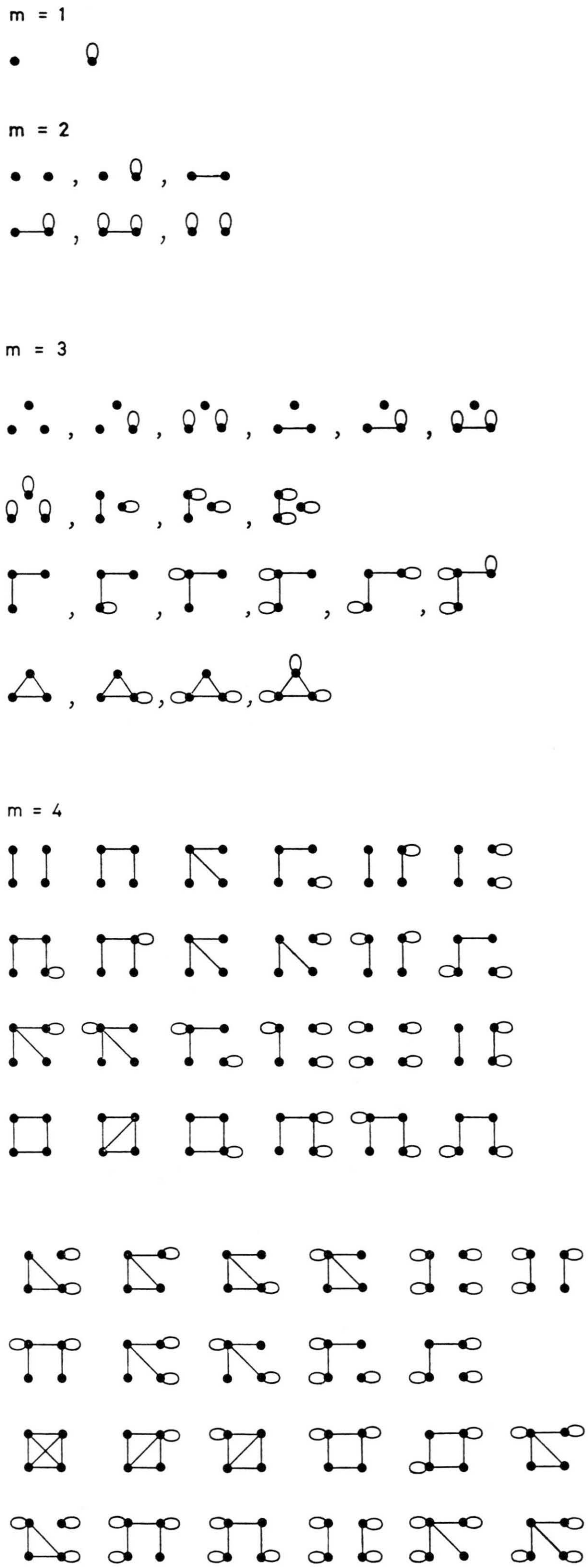
$$\sigma_m = s_m - s_{m-1} \qquad m = 3, 4, \ldots \qquad (6)$$

where $m = 1, 2$ are special cases.

In observing Eq. (6), the results will be represented in a double series,

$$\sigma(y, z) = \sum_{i=1}^{\infty} \sum_{k=0}^{\binom{i+1}{2}} \sigma_{ik}\, z^k y^i \qquad (7)$$

where the exponents of y and z denote the number of nodes (species) and arcs (complexes), respec-



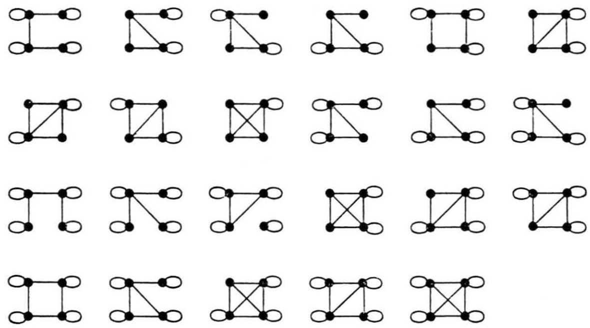


Fig. 3. Non isomorph Horn graphs with $m=1, 2, 3, 4$ species.

tively, and σ_{ik} denotes the number of non isomorphic structures with i nodes and k arcs. The numbers for $i=1, 2, \ldots, 6$ are

$$\begin{aligned}\sigma(y,z) = {} & y^2(2z^2+z^3) \\ & + y^3(2z^2+5z^3+4z^4+2z^5+z^6) \\ & + y^4(z^2+5z^3+13z^4+16z^5 \\ & + 16z^6+11z^7+5z^8+2z^9+z^{10}) \\ & + y^5(2z^3+12z^4+34z^5 \\ & + 59z^6+83z^7+89z^8+74z^9+51z^{10} \\ & + 29z^{11}+13z^{12}+5z^{13}+2z^{14}+z^{15}) \\ & + y^6(z^3+6z^4+31z^5 \\ & + 97z^6+214z^7+393z^8+590z^9+722z^{10} \\ & + 754z^{11}+653z^{12}+482z^{13}+306z^{14} \\ & + 172z^{15}+83z^{16}+35z^{17} \\ & + 14z^{18}+5z^{19}+2z^{20}+z^{21}) \\ & + \ldots .\end{aligned} \qquad (8)$$

4.2. *Number of non isomorphic Horn graphs with root h_m*

For Horn graphs with root the cycle index has to be changed (see Harary [8]). This modification may be characterized by the following rule: given a partition p of n by $p=(p_1, p_2, \ldots, p_n)$. Add one to p_1 and then compute the $l_i(\tilde{p})$ with $\tilde{p}=(p_1+1, p_2, \ldots, p_n)$. The rest of the formula is as before.

As before, graphs with isolated nodes must be cancelled. If g_m is the number of non isomorphic graphs with m species nodes and the root, then the number of non isomorphic Horn graphs h_m is given by

$$h_m = g_m - g_{m-1} - \sigma_m, \quad m \geqq 3. \qquad (9)$$

For $m<3$ the graphs with only one complex must be considered separately by inspection. Applying

Equation (9) the result is represented, as before, in a double series

$$h(y,z) = \sum_{i=1}^{\infty} \sum_{k=0}^{\binom{i+2}{2}} h_{ik} z^k y^i \tag{10}$$
$$\begin{aligned} &= y(3z^2 + z^3) \\ &\quad + y^2(4z^2 + 10z^3 + 9z^4 + 4z^5 + z^6) \\ &\quad + y^3(z^2 + 12z^3 + 34z^4 \\ &\quad + 48z^5 + 45z^6 + 29z^7 + 12z^8 + 42z^9 + z^{10}) \\ &\quad + y^4(5z^3 + 37z^4 + 117z^5 + 227z^6 \\ &\quad + 325z^7 + 348z^8 + 284z^9 + 185z^{10} \\ &\quad + 972z^{11} + 39z^{12} + 13z^{13} + 4z^{14} + z_{15}) \\ &\quad + y^5(z^3 + 17z^4 + 112z^5 + 399z^6 + 988z^7 \\ &\quad + 1903z^8 + 2917z^9 + 3692z^{10} + 3741z^{11} \\ &\quad + 3229z^{12} + 2339z^{13} + 1430z^{14} \\ &\quad + 746z^{15} + 333z^{16} + 126z^{17} + 42z^{18} \\ &\quad + 13z^{19} + 4z^{20} + z^{21}) \\ &\quad + \ldots . \end{aligned}$$

Setting $z = 1$ in (8) and (10) and evaluating the brackets yields σ_m and h_m, respectively. These numbers are given in Table 1.

4.3. Number of reversible reaction networks ϱ_n

The number of reversible reaction graphs is identical to the number of ordinary graphs without loops and isolated nodes. Thus we have to apply Eqs. (3) and (4). To avoid isolated nodes ϱ_n is computed by

$$\varrho_n = q_n - q_{n-1} \tag{11}$$

where q_n is the number of ordinary graphs with n nodes. Now the nodes of the graph correspond to the complexes. Thus, ϱ_{nk} gives the number of reaction networks which consist of n complexes and k reversible reaction arrows (i. e. $2k$ reaction arrows).

The numbers are given by a double series

$$\varrho(z,y) = \sum_{i=1}^{\infty} \sum_{k=0}^{\binom{i}{2}} \varrho_{nk} z^k y^n \tag{12}$$
$$\begin{aligned} &= z y^2 + y^3(z^2 + z^3) \\ &\quad + y^4(z^2 + 2z^3 + 2z^4 + z^5 + z^6) \\ &\quad + y^5(z^3 + 4z^4 + 5z^5 \\ &\quad + 5z^6 + 4z^7 + 2z^8 + 7z^9 + z^{10}) \\ &\quad + y^6(z^3 + 3z^4 + 9z^5 + 15z^6 \\ &\quad + 20z^7 + 22z^8 + 20z^9 + 14z^{10} \\ &\quad + 9z^{11} + 5z^{12} + 2z^{13} + z^{14} + z^{15}) \\ &\quad + y^7(z^4 + 6z^5 + 20z^6 + 41z^7 + 73z^8 \\ &\quad + 110z^9 + 133z^{10} + 139z^{11} + 126z^{12} \\ &\quad + 95z^{13} + 64z^{14} + 40z^{15} + 21z^{16} \\ &\quad + 10z^{17} + 5z^{18} + 2z^{19} + z^{20} + z^{21}) \\ &\quad + \ldots . \end{aligned}$$

4.4. Number of non isomorphic reaction networks r_n

To enumerate these numbers, Eq. (3) and (4) have to be modified. The new equations are:

$$Z(S_n^0) = \frac{1}{n!} \sum_{(p)} c(p) z_1^{t_1} z_2^{t_2} \ldots z_{n^2}^{t_{n^2}} \tag{13}$$

and

$$t_i(p) = \Big(\sum_{[f;g]=i} (f;g) p_f p_g \Big) - p_i \tag{14}$$

where $(f;g)$ denotes the greatest common divisor of f and g (note that $[f;g](f;g) = fg$).

Applying the same procedure as in 4.1.–4.2., and cancelling isolated nodes, the double series now is given by

$$r(z,y) = \sum_{i=1}^{\infty} \sum_{k=0}^{i(i-1)} r_{nk} z^k y^n \tag{15}$$
$$\begin{aligned} &= y^2(z + z^2) \\ &\quad + y^3(3z^2 + 4z^3 + 4z^4 + z^5 + z^6) \\ &\quad + y^4(z^2 + 9z^3 + 23z^4 + 37z^5 + 47z^6 \\ &\quad + 38z^7 + 27z^8 + 13z^9 + 5z^{10} + z^{11} + z^{12}) \\ &\quad + y^5(3z^3 + 34z^4 + 118z^5 + 331z^6 \\ &\quad + 669z^7 + 1128z^8 + 1477z^9 + 1665z^{10} \\ &\quad + 1489z^{11} + 1154z^{12} + 707z^{13} \\ &\quad + 379z^{14} + 154z^{15} + 61z^{16} + 16z^{17} \\ &\quad + 5z^{18} + z^{19} + z^{20}) \\ &\quad + \ldots . \end{aligned}$$

To compare ϱ_n with r_n it should be noted that z^i in $\varrho(z,y)$ corresponds to z^{2i} in $r(z,y)$.

Table 1. Number of non isomorphic structures σ_m and Horn graphs h_m constructed from m species.

m	1	2	3	4	5	6	7	8
σ_m	0	3	16	70	454	4, 552	74, 168	2, 129, 348
h_m	4	29	184	1, 682	21, 970	347, 757, 798		

Table 2. Number of non isomorphic reaction networks r_n and reversible reaction networks ϱ_n constructed from n complexes.

n	2	3	4	5	6	7	8
ϱ_n	1	2	7	23	122	888	11, 302
r_n	2	13	202	9, 390	1, 531, 336	880, 492, 496	1, 792, 447, 159, 408

The sums of the brackets of (12) and (15) are given in Table 2 for ϱ_n and r_n.

The number q_n of non isomorphic reaction networks with n complexes with at least one irreversible elementary reaction is simply the difference

$$q_n = r_n - \varrho_n . \tag{15}$$

By combining the results of 4.1. and 4.2. with the number of non isomorphic reaction networks, it is possible to compute the number of non isomorphic mass action kinetics.

Let $\bar{\sigma}_n$ and $\bar{h}_n$ denote the number of non isomorphic structures and Horn graphs with root, respectively, with n complexes

$$\bar{\sigma}_n = \sum_{i=1}^{n/2} \sigma_{in} , \qquad \bar{h}_n = \sum_{i=1}^{\frac{n-1}{2}} h_{in} \qquad (16), (17)$$

and $\mu_n = \bar{\sigma}_n + \bar{h}_n$, (18)

the number of non isomorphic complexes sets with n complexes. Then the number of non isomorphic mass action kinetics Γ_n with n complexes is

$$\Gamma_n = \mu_n r_n . \tag{19}$$

The number of reversible mass action kinetics $\tilde{\Gamma}_n$ is

$$\tilde{\Gamma}_n = \mu_n \varrho_n . \tag{20}$$

For $n = 2$ and $n = 3$ we can get this number from Eq. (8) and (10). Thus, we get

$$\Gamma_2 = 28 , \qquad \tilde{\Gamma}_2 = 14 ,$$
$$\Gamma_3 = 416 , \qquad \tilde{\Gamma}_3 = 64 ,$$
$$\Gamma_4 = 28{,}280 , \qquad \tilde{\Gamma}_4 = 980 .$$

The number of mass action kinetics with only three species which form $n = 5$ complexes is easily calculated to be $(\varrho_{35} + h_{35})(r_5 + \varrho_5) = 46{,}950$.

5. Discussion

By investigating the reaction diagram in its own right, it is possible to solve the problem of enumerating all the different types of mass action kinetics up to second order. The answers to the questions asked in the introduction are given in the Tables 1 and 2. Table 1 gives the amount of non isomorphic complex sets for a given number of species (σ_m and h_m). Table 2 gives the amount of non isomorphic reaction networks r_n and reversible reaction networks ϱ_n which can be derived from n complexes.

A few examples given at the end of the last chapter demonstrate the enormous number of different mass action kinetics. If one were to write down explicitly, let us say, the 49,950 mass action kinetics consisting of three species which form five complexes, every chemist would say that a lot of them are not reasonable from a chemical point of view. But what is meant by "chemically reasonable" would differ from chemist to chemist. Thus, the main consequence of the big numbers obtained is that they point to a serious problem, namely: What are "chemically reasonable" kinetics, without referring to something so subjective as chemical intuition? Trying to find an answer to this question seems to be a worthwhile task.

Acknowledgement

A grant by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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