

Decomposition of reaction networks: the initial phase of the permanganate/oxalic acid reaction

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Abstract The determination of all chemical reaction networks composed of elementary reactions for a given net chemical reaction is one of the fundamental problems in chemistry, since the decomposition elucidates the reaction mechanism. It is essential in a wide range of applications: from the derivation of rate laws in physical chemistry to the design of large-scale reactors in process engineering where presence of unexpected side products can disturb operation. As an example we consider the well-known permanganate/oxalic acid reaction. We characterize all intermediate substances that can in principle act (auto-)catalytic, list all possible additional intermediate substances that would suffice to start the reaction without assuming presence of any autocatalyst. In particular, we propose for the first time a minimal network in which the well-known autocatalyst Mn^{2+} is produced. To derive our results we present an automatic method to determine whether a net chemical reaction can be explained by some reaction network with a given list of intermediate substances, how to generate all such networks, and how to suggest more intermediate substances if no network with the initially given substances exists.

Keywords Reaction networks · Elementary reactions · Reaction mechanisms · Network decomposition

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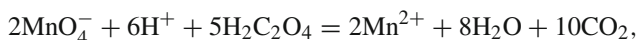
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Traditionally performed by hand, the principles of mechanically generating chemical reaction mechanisms appear to be well established [1]. Automatic tools, however, are rare, and even the promising recent approach by Kovacs et al. suffers from ad-hoc assumptions in its final steps [2].

The problem we study can be stated as

Problem 1 (*Reaction Decomposition*) Given a chemical reaction, say the permanganate/oxalic acid overall reaction



find all chemical reaction networks consisting of elementary reactions only. A reaction is considered to be *elementary* if at most two species (molecules, ions, atoms, radicals, electrons) meet to react.

The permanganate/oxalic acid reaction has been studied extensively since 1866 [3–6]. Still, the suggested reaction mechanisms leave open questions, for example: Do the 19 substances considered in the literature (Suppl. Table 1) suffice to explain the overall reaction? If not, which intermediate substances are missing? Which (auto-) catalysts may start the reaction?

We will first show that the permanganate/oxalic acid reaction indeed cannot be explained without assuming presence of a catalyst or an additional intermediate substance.

Let us call $2\text{MnO}_4^- + 6\text{H}^+ + 5\text{H}_2\text{C}_2\text{O}_4$ the *initial state* and $2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 10\text{CO}_2$ the *final state*. A reaction network is a network of nodes and arcs connecting these two states using elementary reactions and possibly many intermediate states. From a mathematical point of view, each node in a reaction network can be labeled by a 19-dimensional state vector of nonnegative integers, where the i th component encodes the number of times that species i occurs in a given state (see Sect. 1). For example, the initial state is a 19-dimensional vector with zeroes everywhere, except in the positions encoding the species MnO_4^- , H^+ , and $\text{H}_2\text{C}_2\text{O}_4$, where we have numbers 2, 6, and 5. Each arc in the reaction network corresponds to an elementary reaction so that the states that it connects satisfy the material balance of this elementary reaction. Now we may enumerate all *theoretically possible* states that can be reached from the initial state via a sequence of elementary reactions, for example in a breadth-first search manner. For the permanganate/oxalic acid overall reaction, surprisingly, despite considering all 1,022 elementary reactions, only 55 other states can be reached from the initial state and the desired final state is *not* among them. Thus, there is no possible reaction network explaining the overall reaction.

We should note that this as well as the following results is independent of reaction kinetics: If any knowledge about reaction kinetics were to be used the number of states reachable could only decrease, as the specified kinetic would be limiting the freedom of combinations considered. Results can hence only be strengthened by extra assumptions or experimental results.

Kovacs et al. [2] assume that Mn^{2+} , being a catalyst for the reaction, is available during the “spontaneous” starting of the reaction. We show that 8 of the 19

species they considered can in fact take that position: Mn^{2+} , MnC_2O_4 , MnO_2 , Mn^{3+} , $[\text{MnO}_2 \cdot \text{H}_2\text{C}_2\text{O}_4]$, $[\text{Mn}(\text{C}_2\text{O}_4)]^+$, $[\text{Mn}(\text{C}_2\text{O}_4)_2]^-$, and $[\text{H}^+ \cdot \text{MnO}_2 \cdot \text{H}_2\text{C}_2\text{O}_4]^+$: If we assume that one of the 19 substances may act catalytically, the computation is identical to what we did above, except that the potentially catalytic substance is added in equal amounts to both the initial and the final states. We obtain the eight catalysts listed, and it is even sufficient to choose a stoichiometric coefficient of one.

Alternatively, by analysing the intermediate results of the algorithm, we can specify 83 new putative intermediate substances that allow the construction of a reaction network without a catalyst (Suppl. Table 2). To find a suitable 20th species, we observe that the 55 reachable states are formed by 6 species only. Thus, there are $\binom{6}{2} + \binom{6}{1} + \binom{6}{1} = 27$ elementary reactions among these 6 species. Moreover, in order to continue from the currently possible states, the result of at least one of these elementary reactions must contain a missing 20th species. This bounds the number of Mn, C, H, O atoms in the missing species to 2, 4, 8, and 8, respectively. Assuming an electrical charge between $4-$ and $4+$, we tested all possible candidates as 20th species.

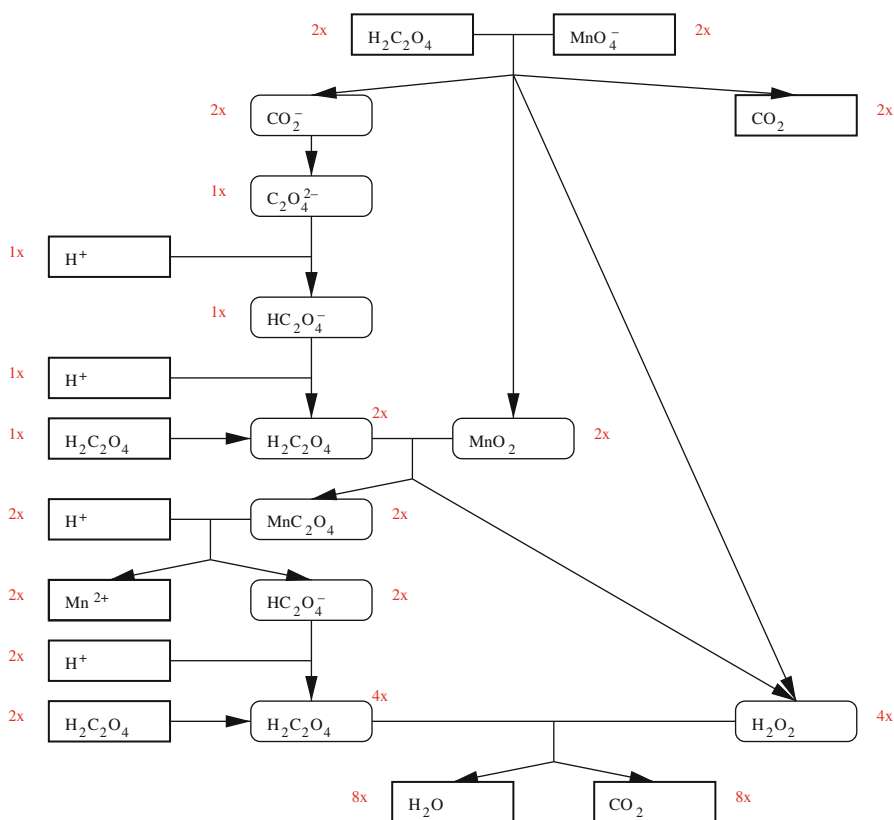


Fig. 1 A minimal reaction network for the permanganate-oxalic acid reaction: H_2O_2 could be produced in two different regions of the network

Using the approach described above, we found that there are 83 species each of which would suffice as 20th species to allow the construction of a chemical reaction network explaining the overall reaction (Suppl. Table 2). Being mechanically generated without taking into account structural consistency these include many unreasonable, but also some interesting candidates like MnO_3 and H_2O_2 . As noted above, removing candidate species from the list can only strengthen results of our method, hence we left even species like C^+ in the table.

In order to reduce the number of candidates, we dropped the following 4 of the 19 species assumed (Suppl. Table 1): $[\text{H}^+ \cdot \text{MnO}_2 \cdot \text{H}_2\text{C}_2\text{O}_4]$, $[\text{MnC}_2\text{O}_4 \cdot \text{MnO}_4^- \cdot \text{H}^+]$, $[\text{MnC}_2\text{O}_4^{2+} \cdot \text{MnO}_3^-]^{2+}$, and $[\text{MnC}_2\text{O}_4^{2+} \cdot \text{MnO}_3^- \cdot \text{H}^+]^{2+}$. These species were only postulated to bridge the gap between Mn(VII) and Mn(IV). Repeating our computations, we found that only 11 out of the 83 candidates can still help to explain the overall reaction. These are $\text{C}_2\text{H}_2\text{O}_6^-$, C_2O_5^- , CH_2O_4^- , CH_2O_4 , CO_3^- , CO_3 , H_2O_2^- , H_2O_2 , HO , O^- , and O . In our illustration below we concentrate on H_2O_2 . We note that presence of trace amounts of H_2O_2 appears to be not out of question, although it has mainly been discussed as a product of the oxidation of oxalic acid when performing the reaction in the presence of oxygen [7]. It is well-known that H_2O_2 is

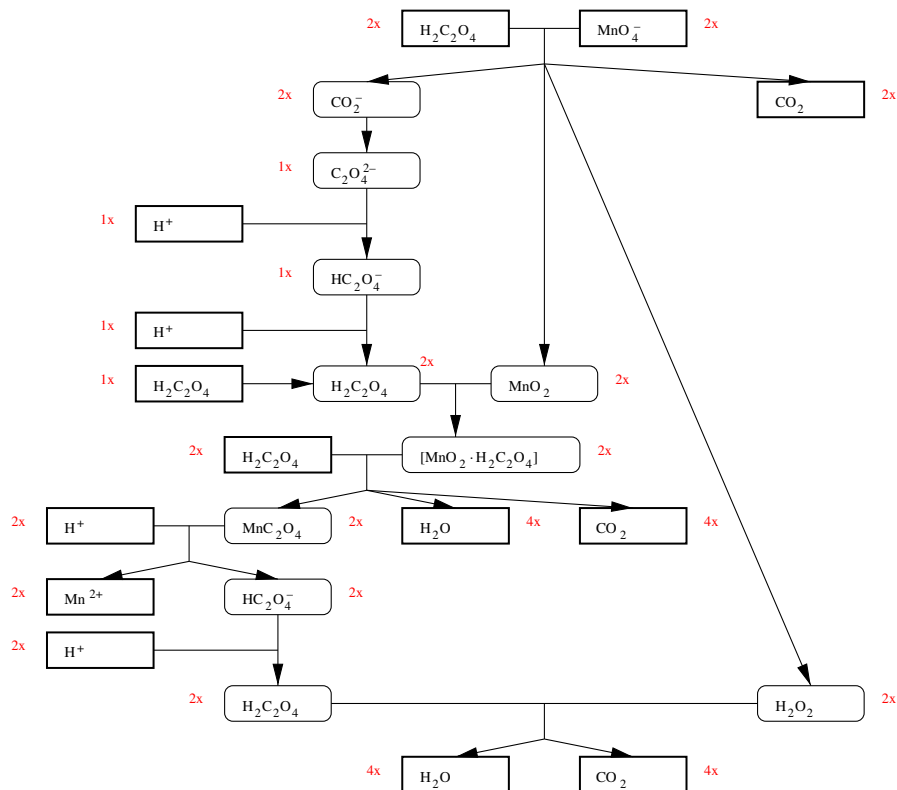
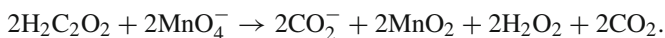


Fig. 2 A minimal reaction network for the permanganate-oxalic acid reaction. H_2O_2 is only produced in one region of the network

also highly reactive with permanganate, so it is to be expected that it cannot accumulate during the reaction, and therefore was not previously considered as an intermediate [4].

Figures 1 and 2 show two possible networks involving the creation of H₂O₂ at the beginning and potentially at a later stage of the overall reaction. Once Mn(II) has been created, it acts as an autocatalyst. See Fig. 3 for a minimal reaction network explaining this autocatalysis, and Fig. 4 for an alternative. The figures are to be read as follows: species are the nodes of the graph, directed edges symbolize elementary reactions. Nodes with rounded corners are intermediates, rectangular nodes are substances appearing in initial or final state. Stoichiometric coefficients are written besides the nodes, e.g. in Fig. 1 the reaction starting at the top is



Theoretically these networks explain the whole reaction. However, it is well-known that the reaction proceeds in three distinct phases, including the autocatalytic and rapid reaction involving Mn(II) [7]. The trace amounts of H₂O₂ produced in this network are in accordance with the very slow start of the first phase of the reaction progress,

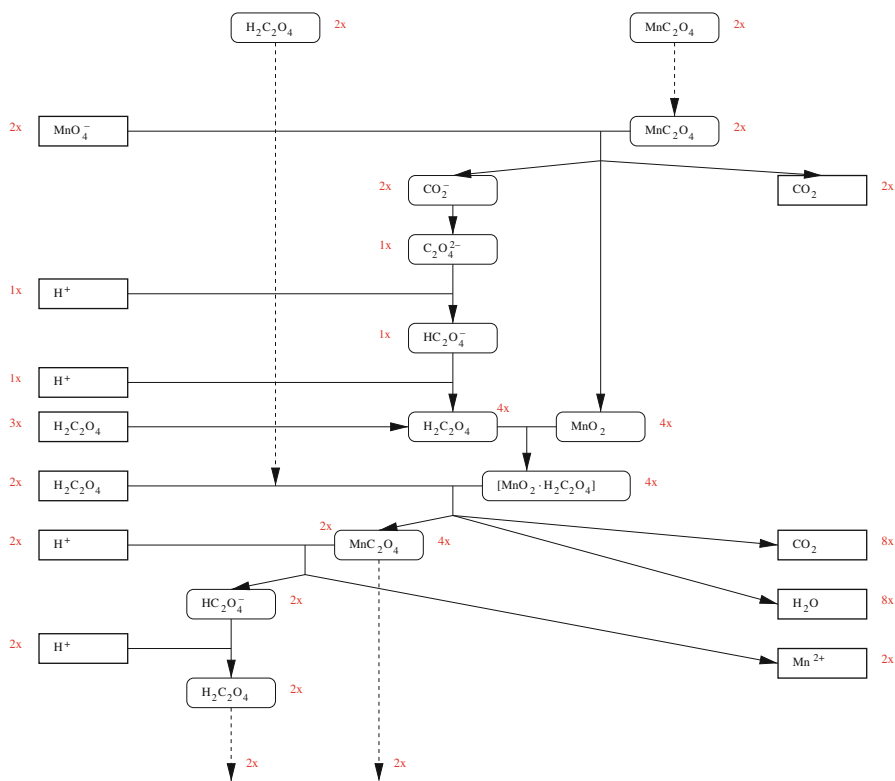


Fig. 3 A minimal autocatalytic reaction network for the permanganate-oxalic acid reaction using Mn(II)

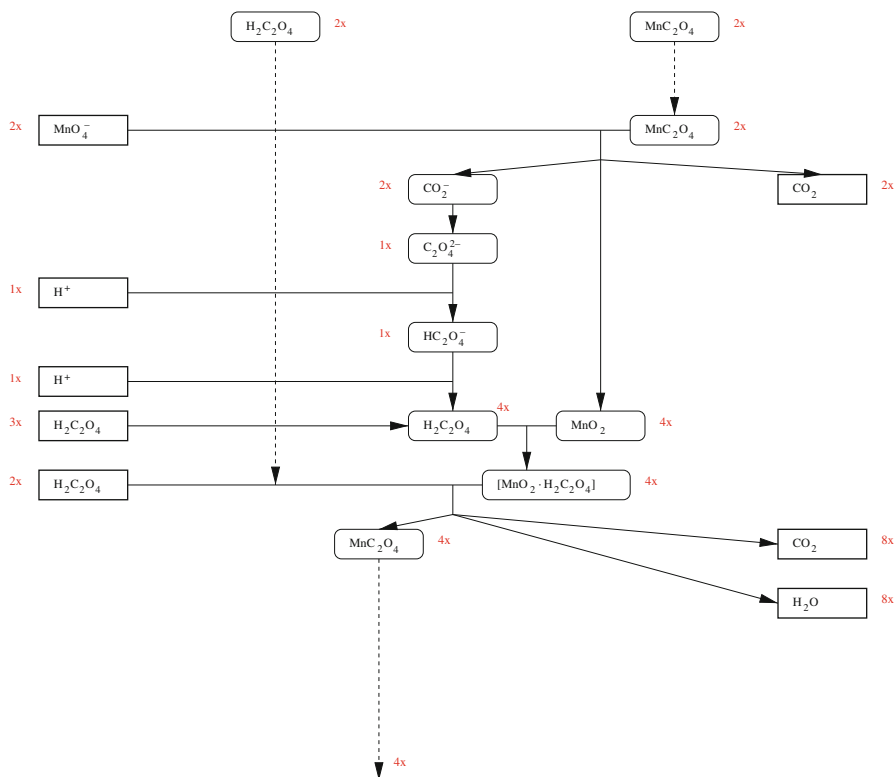


Fig. 4 A minimal autocatalytic feedback cycle for the permanganate-oxalic acid reaction via Mn(IV) and Mn(II)

given that permanganate is also highly reactive with it [4]. Once the reaction has progressed with this initial-phase network, however, Mn(II) is available, and can serve in the autocatalytic phase, see Fig. 3. Our networks include only the bare essential components necessary to explain the overall reaction. They can be refined by adding additional species, and hence elementary reactions, for example to model presence of Mn(III) [8]. Clearly, the presented approach is also applicable to the determination of underlying network structures for arbitrary other reactions.

1 Methods

The solution to the network decomposition problem involves several steps.

First, a chemical expert needs to specify a set of potential intermediate species that may appear in the reaction network. This choice should be supported by experiments. For the permanganate/oxalic acid reaction we use the 19 widely accepted species [2] (Suppl. Table 1).

Second, all elementary reactions need to be enumerated [2]. For this, write down a matrix D with a column for each species and a row for all elements appearing in them.

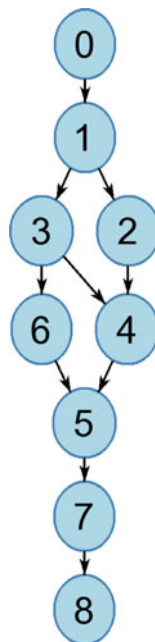
The entry in row i and column j is given by how many times element i occurs in species j . Denote column j of D by D_j . For each single species j and each pair of species k_1, k_2 solve the linear diophantine equation with nonnegative integer variables x given by $Dx = D_j$ and $Dx = D_{k_1} + D_{k_2}$. In this way *all* theoretically possible elementary reactions among the given species can be computed. For the permanganate/oxalic acid reaction, one has to solve 209 such linear systems and obtains 1,022 *mathematically* possible elementary reactions. Rather simple chemical reasons may reduce this number already down to 673 *chemically* more meaningful reactions, although this number can probably be reduced further [2].

Third, the overall chemical reaction needs to be decomposed and *all* valid reaction networks explaining the overall reaction have to be enumerated. For this we build a directed graph with nodes given by state vectors and elementary reactions as edges. A state vector is an integral vector x whose components are the stoichiometric coefficients of the species present in the given state. For example, the initial state of the permanganate/oxalic acid reaction is given by the 19-dimensional vector which is zero except for the three components MnO_4^- , H^+ , and $\text{H}_2\text{C}_2\text{O}_4$ where the entries are 2, 6, and 5, respectively. An elementary reaction r is given by a 19-dimensional vector with at most 2 negative entries (the species consumed by the reaction). A reaction r is *applicable* in state s_i if $s_i + r \geq 0$. For each applicable reaction r we connect state s_i to state $s_i + r = s_j$. In this graph we can perform breadth-first-search to determine all reachable states, and thereby check whether the final state is among them. Note that a path in this graph contains more information than a flux vector obtained in stoichiometric network analysis: There, only the overall count of how many times an elementary reaction occurs can be determined [9]. In contrast, the path decomposition determines exactly in which sequence elementary reactions are occurring.

Typically, as soon as there is one network explaining the reaction, there will be many alternatives. Most commonly, they follow the same basic structure, but use a different order of the elementary reactions in sections of the network, where many states can be converted into each other via reversible reactions. This is not of interest, as it blocks the view onto structurally different networks. To alleviate this problem we can group into clusters those sets of states that can be mutually converted into each other by a sequence of elementary reactions. Mathematically, a cluster is defined as a strongly connected component of the digraph given by the states and elementary reactions. We can then form a coarser network, composed of the clusters as nodes, and put an arc from cluster a to cluster b if there exist some state s_a in cluster a and some state s_b in cluster b such that s_a can be transformed into s_b via some elementary reaction.

For the permanganate/oxalic acid reaction using 16 species we find 9 such clusters, see Fig. 5. In the cluster graph we find only 3 paths from cluster 0 to cluster 8. The arcs between clusters correspond to critical elementary reaction. For example, there is only one such reaction connecting states from cluster 0 to states from cluster 1: $\text{H}_2\text{C}_2\text{O}_4 + \text{MnO}_4^- \rightarrow \text{MnO}_2 + \text{CO}_2 + \text{CO}_2^- + \text{H}_2\text{O}_2$. The possible pathways through a cluster can be expanded independently. Note that two paths in the cluster network can still lead to the same reaction network, since elementary reactions may be applied in different order or in parallel.

Fig. 5 Cluster graph corresponding to Figs. 1 and 2. Cluster 0 contains the initial state, cluster 8 contains the final state. There are three paths from cluster 0 to cluster 8. The arcs between clusters correspond to critical elementary reaction. For example, there is only one such reaction connecting states from cluster 1: $\text{H}_2\text{C}_2\text{O}_4 + \text{MnO}_4^- \rightarrow \text{MnO}_2 + \text{CO}_2 + \text{CO}_2^- + \text{H}_2\text{O}_2$



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