Search for reaction pathways with P-graphs: Methanation of Carbon Dioxide with Hydrogen

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Abstract

The effects of carbon dioxide in the atmosphere can be reduced by closing anthropogenic cycles. The methanation of carbon dioxide with hydrogen provide an option in this direction. Nevertheless, the reaction mechanism of this system is under discussion.

The search of reaction pathways is a key matter when studying a reaction system, specially to find an expression for kinetics. The proposal of new pathways and the discussion of their feasibility can be structured with the application of P-graphs, in order to perform a combinatorially complete search of pathways in the first step of a kinetic study. By imposing constraints, the searching algorithm allows to compose feasible pathways. These constraints include mass balances and the existence of known intermediates.

The search domain to find feasible pathways in the methanation of carbon dioxide can be reduced with the use of reaction blocks. No feasible

pathway is lost in this process. The set of possible mechanisms have been reduced from 31 billion to 71 possible pathways, presented as an option to explain the reaction mechanism in this system. A procedure is presented to integrate experimental data, so as to discriminate the reaction mechanism among these 71 options.

Keywords: Methanation, P-Graph, Reaction pathways, Hydrogen, Carbon dioxide

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1. Introduction

The climate effects of atmospheric CO_2 has been the subject of study in the last 3 decades [1, 2] and many efforts has been directed to its capture from industrial gas streams, mainly by absorption in amines [3] and adsorption on solids [4].

After separation, different downstream processes could be implemented for mitigating global climate change, as reuse, geological storage or ocean storage [5]. Despite the huge potential of the last two options, the net cost of reuse is far more attractive [6].

Since the main industrial source of carbon dioxide is the combustion of fossil fuels, it seems attractive to recycle the CO_2 and reduce it to a fuel such as CH_4 [7]. In this strategy, the generated methane could be an energy vector since we need energy to generate H_2.

The methanation of CO_2 through hydrogenation (Eq.1, [8]) has been performed on different catalysts [9], but the reaction mechanism is subject of debate [10].

$$CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O \quad \Delta H^0 = -165\, kJ/mol \tag{1}$$

Even though the decomposition of CO_2 to adsorbed CO is widely accepted as an intermediate step [10] and the participation of formate-like species has been reported [11, 12, 13], the mechanism on the catalyst surface is still not clear.

In other contexts, the P-graph theoretic method [14, 15, 16] has been adopted to explore the mechanisms of catalytic [17] and biochemical reactions [18]. In a large scale, P-graphs have also been used to synthesize process networks [19], to optimize industrial complexes [20], to optimize

regional energy [21] and biomass supply chains [22], to optimize renewable energy systems [23], to select technologies for reducing carbon emissions [24], to design sustainable supply chains [25], and to economically allocate resources [26], among other applications.

Within the context of reaction pathway identification, P-graphs show a wide set of attractive properties when compared with other methods as linear algebraic methods [27, 28], convex methods [29, 30], combinatorial analysis [31], and reaction route graphs [32]. These properties include [33]: the unique representation of each pathway, a complete set of direct pathways, a complete set of combinatorially feasible pathways, a complete set of acycle feasible pathways, a graph representation, and combinatorial acceleration.

The classical proposal of mechanisms can be substituted by a combinatorially complete exploration of pathways between reactants and products, avoiding bias in the selection of the mechanism. Furthermore, the construction of new mechanisms can integrate feasibility criteria (e.g. mass balance) for a complete definition of feasible routes instead of an exhaustive search. In such a strategy, a mechanism proposal should be divided into three stages:

1. Create a list of all stoichiometrically feasible mechanisms. They are combinatorially feasible mechanisms with stoichiometric balance. It is an exploration of pathways *in silico*.

2. Filter the results comparing with reported intermediate species or causality relations reported in reaction systems (e.g. an intermediate molecule always reacts forming another defined molecule).

3. Compare with real data. Further experiments can be conducted for discriminating the mechanism.

This work exploits the combinatorial structure of CO_2 methanation on a catalyst for reducing the set of possible mechanisms from billions to dozens of options. We consider the reported intermediates on a catalyst surface, showing all the feasible mechanisms in this system for further discussion.

The aforementioned exploration has been performed with P-graph algorithms [14, 15, 16] and a reduction with reaction blocks [34].

The aim is to cover the first two steps of the previous list in the case of CO_2 methanation. Pointing to the third step, the stoichiometrically feasible mechanisms reported herein are a guide for further experiments and future demonstration of the reaction mechanism.

2. Methodology

The methodology of the present work is based on previous efforts in P-Graph theory [14, 15, 16]. P-graphs has two types of nodes (e.g. points and bars) for species and reactions, respectivelly. They have been created for uniquely represent processes and reaction systems, avoiding the ambiguity of digraphs or signal-flow graphs when a synthesis problem is presented [14]. The P-graph structure is very close to Species-Reaction graph structure (SR graph) [35], but without labels on edges.

Briefly describing this technique (Fig.1), a global reaction (E) is needed to define global reactants and products. These species should be included in all generated P-graphs. This is the first constraint for accepting a combinatorial pathway as feasible. After the definition of a set with global

reactants (R) and global products (P), a set of feasible reactions has to be defined. This set is called O (from operations). This set could be constructed from experimental experience, including all the reactions considered feasible by the scientific community (Fig.1a). The set of reactions (O) imposes new species: the intermediates. Strictly, the set O is a list of reactions. The species involved in all the aforementioned sets (reactants, products and intermediates) are listed separately [14].

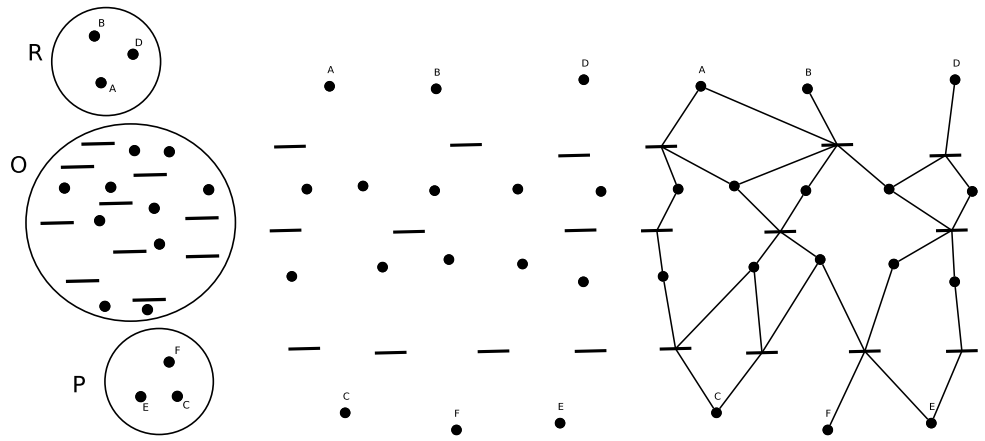
The next step is the Maximal Structure Generation (MSG) [15, 16] (different from a superstructure [36]). This structure is the largest one that must be taken into account in the construction of mechanisms, and it is also the simplest one that contains all combinatorial pathways [15]. The Maximal Structure is the universal set of all possible P-graphs in the problem. Then, all relations in the set O should be included in the Maximal Structure (Figs. 1b and 1c). No direction is imposed in the arcs of any P-graph, because both direct and reverse reactions are considered for each element in O.

A well formed mechanism has to satisfy the mass balance within the network. The direction of the reactions does matter in this case. Anyway, the mass balance can either be evaluated in forward or backward overall direction.

Focusing on combinatorial possibilities, each reaction can be included (or not) in a mechanism. If a reaction is included, it can participate in a direct ($\rightarrow$) or reverse way ($\leftarrow$) into the mass balance, defining 3 options of participation: no participation, direct way inclusion, and reverse way inclusion. If a mechanism has no reactions then is not a combinatorially feasible mechanism, therefore this alternative is usually removed from the

Name herein	**Reaction**	**Reported by**
1	$H_2 + 2s \rightleftarrows 2Hs$	[37]
2	$CO_2 + s \rightleftarrows CO_2s$	[12]
3	$CO_2s + s \rightleftarrows COs + Os$	[12]
4	$COs + s \rightleftarrows Cs + Os$	[37]
5	$COs \rightleftarrows CO + s$	[37]
6	$Cs + Hs \rightleftarrows CHs + s$	[37]
7a	$CHs + Hs \rightleftarrows CH_2s + s$	[37]
7b	$CH_2s + Hs \rightleftarrows CH_3s + s$	[37]
7c	$CH_3s + Hs \rightleftarrows CH_4s + s$	[37]
7d	$CH_4s \rightleftarrows CH_4 + s$	[37]
8	$Os + Hs \rightleftarrows OHs + s$	[37]
9	$OHs + Hs \rightleftarrows H_2Os + s$	[37]
10	$H_2Os \rightleftarrows H_2O + s$	[37]
11	$COs + Hs \rightleftarrows HCOs + s$	[10]
12	$HCOs + s \rightleftarrows CHs + Os$	[10]
13	$COs + OHs \rightleftarrows HCO_2s + s$	[11]
14	$HCO_2s + OHs \rightleftarrows CO_2s + H_2Os$	[11]
15	$HCO_2s + s \rightleftarrows CO_2s + Hs$	[11]
16	$COs + Hs \rightleftarrows Cs + OHs$	[12]
17	$HCO_2s + s \rightleftarrows HCOs + Os$	[12]
18	$CO_2s + OHs \rightleftarrows HCO_3s$	[13]
19	$HCO_3s + Hs \rightleftarrows HCO_2s + OHs$	[13]

Table 1: Reactions considered in the system.



(a) Sets (b) All elements (c) Maximal Structure

Figure 1: Maximal structure generation (MSG).

combinatorial enumeration of pathways. The number of combinatorial candidates for being a mechanism is then $3^n - 1$, with n the number of reactions in set O.

Table 1 shows all species and reactions included in the CO_2 methanation system, with a reference to other works for sustaining its inclusion. All these reactions have been signed as elementary and will be understood as feasible reactions in the methanation system. Taking all of them, the number of combinatorially feasible mechanisms is $3^{22} - 1 \approx 31$ billion. A theoretical reduction of the reaction system allows to aggregate reactions with common (and exclusive) intermediates during the search of feasible pathways. This technique and its theoretical background have been presented in other article [34].

In this case, the reactions 7a to 7d will be considered a reaction block (R7), because these reactions are connected in series (common intermediates) and all their intermediates are not included in any reaction

outside the block (exclusive intermediates). This reduction maintains the number of feasible mechanisms from the disaggregated reaction set [34]. This theoretical reduction of the system infers 19 reactions, and therefore ≈ 1 billion of combinatorially feasible mechanisms.

An algorithm has to connect global reactants and products through the reactions network for generating candidate mechanisms. This algorithm must consider all the pathways with a satisfied mass balance. A general algorithm written in Algol was published by Friedler et al. [16] for this purpose.

The routines for MSG and the search for candidate mechanisms with P-graph theory were adapted from previous developments [15, 16] and implemented in GNU Octave [38].

3. Results

The aforementioned methodology was applied over the reaction system shown in Table 1. This search considers a reaction block (Reaction 7) composed by reactions 7a, 7b, 7c, and 7d. Within the $3^{19} - 1 \approx 1$ billion combinatorial options, 91 feasible mechanisms were found. Further filtration was performed looking for reported intermediates on catalyst surface: COs and HCOs, reported by Eckle et al [10]. This filter imposes the participation of these species and infers 71 feasible mechanisms for the CO_2 methanation system. These feasible mechanisms are listed in Table 2 with a reference to the reactions included in each mechanism. These mechanisms are also represented as P-graphs in Appendix A.

Number	Reaction set										
1	1	10	2	8	9	3	11	12	7		
2	1	10	2	9	-4	16	3	11	12	7	
3	1	10	2	8	9	3	12	13	17	7	
4	1	10	2	9	16	3	6	-11	-12	7	
5	1	10	2	8	9	11	12	-13	-15	7	
6	1	10	2	9	-4	16	12	-15	17	7	
7	1	10	2	8	9	11	12	-13	-14	7	
8	1	10	2	9	-4	16	12	17	-14	7	
9	1	10	2	9	-3	11	12	-13	-15	7	
10	1	10	2	9	3	11	12	-13	-17	7	
11	1	10	2	8	3	11	12	13	14	7	
12	1	10	2	8	3	11	12	-15	14	7	
13	1	10	2	8	3	11	12	-17	14	7	
14	1	10	2	9	-3	12	-13	-15	17	7	
15	1	10	2	9	-3	11	12	-13	-14	7	
16	1	10	2	8	3	12	13	17	14	7	
17	1	10	2	9	11	12	-13	-15	-17	7	
18	1	10	2	9	-3	12	-13	17	-14	7	
19	1	10	2	8	11	12	-13	-15	14	7	
20	1	10	2	-4	16	12	-15	17	14	7	
21	1	10	2	9	11	12	-13	-17	-14	7	
22	1	10	2	-3	11	12	-13	-15	14	7	
23	1	10	2	3	11	12	-13	-17	14	7	
24	1	10	2	-3	12	-13	-15	17	14	7	
25	1	10	2	11	12	-13	-15	-17	14	7	
26	1	10	2	8	9	4	6	-11	-15	17	7
27	1	10	2	8	9	16	6	-11	-15	17	7
28	1	10	2	8	9	4	6	-11	17	-14	7
29	1	10	2	8	9	16	6	-11	17	-14	7

30	1	10	2	9	-4	16	3	12	13	17	7
31	1	10	2	9	-4	16	6	-11	-15	17	7
32	1	10	2	9	4	3	6	11	-13	-17	7
33	1	10	2	9	4	3	6	-12	-13	-17	7
34	1	10	2	9	-4	16	11	12	-13	-15	7
35	1	10	2	9	16	3	6	11	-13	-17	7
36	1	10	2	8	4	3	6	11	-17	14	7
37	1	10	2	9	16	3	6	-12	-13	-17	7
38	1	10	2	9	-4	16	6	-11	17	-14	7
39	1	10	2	8	4	3	6	-12	-17	14	7
40	1	10	2	9	16	3	6	-12	15	-17	7
41	1	10	2	8	16	3	6	11	-17	14	7
42	1	10	2	-8	16	3	6	-12	-17	14	7
43	1	10	2	9	-4	16	11	12	-13	-14	7
44	1	10	2	9	4	6	11	-13	-15	-17	7
45	1	10	2	9	16	6	-11	-12	-15	17	7
46	1	10	2	9	4	6	-12	-13	-15	-17	7
47	1	10	2	9	16	3	6	-12	-17	14	7
48	1	10	2	8	4	6	-11	-15	17	14	7
49	1	10	2	8	16	6	-11	-15	17	14	7
50	1	10	2	9	4	6	11	-13	-17	-14	7
51	1	10	2	-4	16	3	6	11	-17	14	7
52	1	10	2	9	16	6	-11	-12	17	-14	7
53	1	10	2	9	4	6	-12	-13	-17	-14	7
54	1	10	2	4	16	3	6	-12	-17	14	7
55	1	10	2	-4	16	3	11	12	13	14	7
56	1	10	2	-4	16	3	11	12	-15	14	7
57	1	10	2	-4	16	3	11	12	-17	14	7
58	1	10	2	-4	16	3	12	13	17	14	7
59	1	10	2	-4	16	6	-11	-15	17	14	7
60	1	10	2	16	3	6	-11	-12	13	14	7
61	1	10	2	16	3	6	-11	-12	-15	14	7
62	1	10	2	4	3	6	11	-13	-17	14	7
63	1	10	2	16	3	6	11	-12	-17	14	7
64	1	10	2	4	3	6	-12	-13	-17	14	7
65	1	10	2	-4	16	11	12	-13	-15	14	7
66	1	10	2	16	3	6	11	-13	-17	14	7
67	1	10	2	16	3	6	-12	13	-17	14	7
68	1	10	2	16	3	6	-12	-15	-17	14	7
69	1	10	2	4	6	11	-13	-15	-17	14	7
70	1	10	2	16	6	-11	-12	-15	17	14	7
71	1	10	2	4	6	-12	-13	-15	-17	14	7

Table 2: Feasible mechanisms for CO_2 methanation expressed as reaction sets. The participation of COs and HCOs is imposed, because they have been signed as well known intermediates [10].

Fig. 2 shows a histogram for the participation of each reaction from Table 1 in the filtered pathways informed in Table 2. In this histogram both direct ($\rightarrow$) and reverse ($\leftarrow$) ways have been classified in a single reaction.

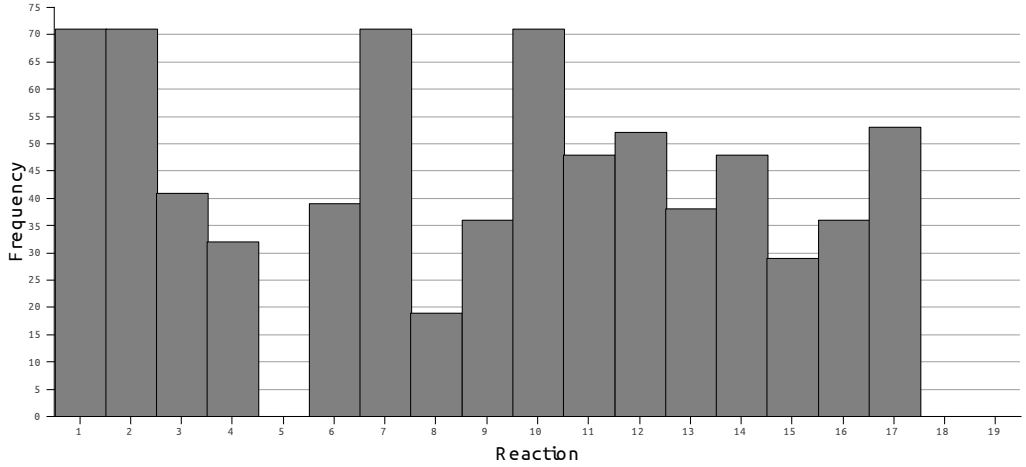


Figure 2: Histogram for the appearance of each reaction within the 71 filtered pathways represented in Table 2 and Appendix A.

Reactions 1, 2, 7, and 10 are present in the complete set of filtered pathways. Since Reaction 7 is a reaction block [34], all filtered pathways should include reactions 7a to 7d from Table 1.

Fig. 3 shows a Maximal Structure after the aforementioned pathway filtration. This structure is the union of all the pathways in Table 2. The direction of reactions has not been included in this graph, because most reactions can participate in a direct or reverse way in the set of feasible pathways after filtration. This Maximal Structure after filtration has been marked taking into account the information from Fig. 2: species and reactions highlighted with gray are present in the complete population of filtered pathways.

In order to propose a final mechanism, further information is necessary. In this context, experimental information is crucial. The experimental efforts would demonstrate or discard the presence of the following adsorbed

species: Cs, Os, OHs, HCO_2s. The evolution of these adsorbed species on surface is also significant for the proposal of a final mechanism. With all this information, the role of reactions 3, 4, 6, 8, 9, 11, 12, 13, 14, 15, 16, and 17 can be clarified.

4. Discussion

As mentioned before, experimental information is necessary to elucidate the mechanism of CO_2 methanation. The information provided in Fig.3 and Table 2 can structure a search tree. The following example illustrates this point. We assumed the hypothetical availability of experimental information about molecular characterization of intermediates on catalyst surface. The branches and scenarios have been supposed to show how the provided information could be used to suggest the scientific questions in order to find the mechanism of CO_2 methanation. Accordingly, we first propose the search algorithm and then we illustrate its application with an example.

We define a *confirmed* reaction or species as those forced to be included in the reaction mechanism, otherwise the mechanism is not a *feasible pathway* as defined in [34]. The confirmed reactions and species have been marked with gray in Fig.3. The inclusion of all other reactions and species have to be proved through logic and experimental data. These reactions and species will be called *free*. Reactions and species could also be *discarded* during the search of the reaction mechanism.

We propose the following algorithm to find the reaction mechanism:

1. Within the P-graph, find a reaction with n species: $(n-1)$ of them have to be confirmed, and one of them free.

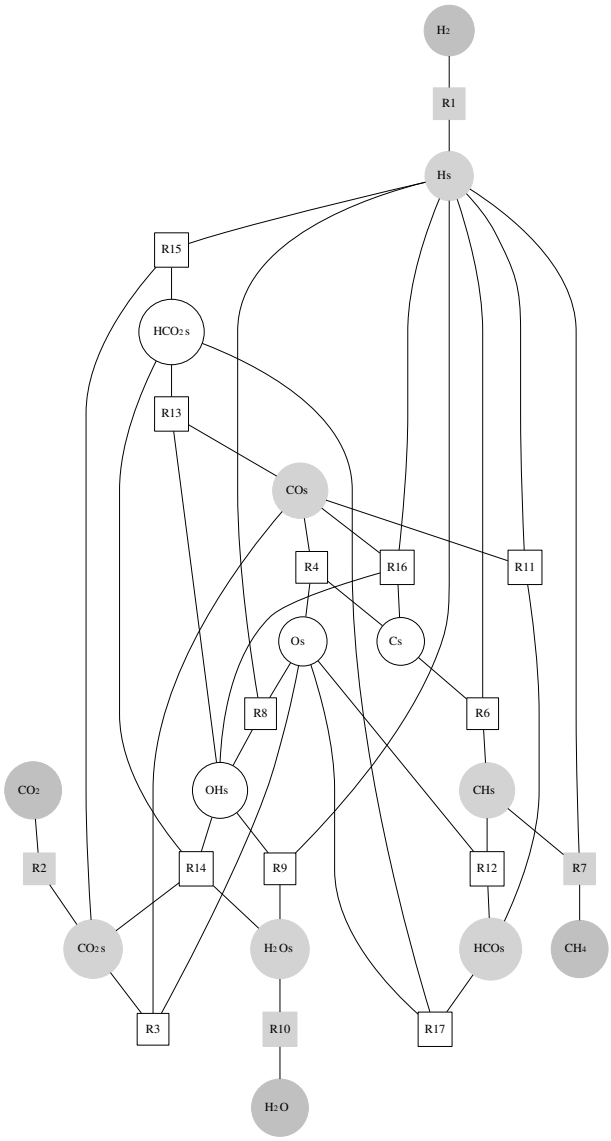


Figure 3: Maximal structure after pathway filtration. The participation of COs and HCOs is imposed, because they have been signed as well known intermediates [10]. Species and reactions marked with gray are present in all filtered pathways (Table 2). The active site on surface (s) has been omitted in this representation to ease the reading.

2. Structure the question about the existence of the free species from the last step.

3. Structure the answers to the last question: No (0) or Yes (1). Within the Fig.3 and Table 2, state the logic consequences of each scenario. The scenarios (0) and (1) are excluding.

4. Include experimental information about the existence of the analysed species and conclude the veracity of each scenario: (0) or (1) will be true. Impose the respective logic consequences on Fig.3 and Table 2.

5. If all species are confirmed, stop. Else, return to step 1 with the new information.

With this algorith, researchers can minimize the list of feasible pathways with the molecular characterization of species. After this sequence of steps, all confirmed and discarded species will be defined with no free species.

The algorithm could finish either with a clear mechanism (all reactions will be either confirmed or discarded) or with remaining free reactions. If there are free reactions at the end of the algorithm, the mechanism is still not clear. Thus, other experiments are needed in order to distinguish which free reactions have to be confirmed or discarded in the pathway to compose a reaction mechanism. This experiments are different from the molecular characterization of intermediates. To confirm or discard the remaining free reactions is necessary a causality relation among species: the demonstration of a transition.

Taking into account the Fig.3, the search algorithm can be applied over the CO_2 methanation system as follows:

Iteration 1:

1. Reaction 6.
2. Does Cs exist on catalyst surface?
3. Possibilities are:
   (0) No. Accordingly, reactions 4, 6, and 16 are discarded. Reaction 12 is confirmed, thus Os is confirmed with no further experiments. Is not possible to confirm nor discard reaction 3.
   (1) Yes. Cs is confirmed. Is not possible to confirm nor discard reaction 6.
4. Let scenario (0) be true[1].
5. Go back to step 1.

After this iteration, there are 20 feasible pathways. Using the nomenclature from Table2, the feasible pathways are: 1, 3, 5, 7, 9 to 19, and 21 to 25.

Iteration 2:

1. (0) Reaction 8.
2. (0) Does OHs exist on catalyst surface?
3. (0) Possibilities are:

[1]Hypothetical experiments performed to evaluate the veracity of scenarios (0) and (1).

(0) No. Accordingly, reactions 8, 9, 13, and 14 are discarded. Nonetheless, this scenario is infeasible because reactions 9 and 14 are excluding. One of them has to exist, otherwise H_2Os cannot be connected with global reactants, violating a necessary condition to have feasible pathways [34]. Then, this scenario is infeasible.

(1) Yes. OHs is confirmed. Is not possible to confirm nor discard reactions 8 and 9.

4. (0) No additional information is needed. Scenario (1) is verified by logic.

5. (0) Go back to step 1.

After this iteration, the set of feasible pathways remains unaltered.

Iteration 3:

1. (01) Reaction 14.

2. (01) Does HCO_2s exist on catalyst surface?

3. (01) Possibilities are:

   (0) No. Accordingly, reactions 13, 14, 15, and 17 are discarded. Reactions 3 and 9 are confirmed, otherwise CO_2s and H_2Os are disconnected from global products and reactants, respectivelly. Reaction 11 is confirmed, otherwise $HCOs$ is either accumulated or extinguished in the reaction pathway. Two reactions are needed surrounding each intermediate, one to produce this

component; another to consume it. Reaction 8 is confirmed, otherwise OHs cannot be connected with global reactants.

(1) Yes. HCO_2s is confirmed. Is not possible to confirm nor discard reactions 3, 8, 9, 11, 13, 14, 15, and 17.

4. (01) Let scenario (0) be true[2].

5. (01) All species have been confirmed or discarded. Stop.

Taking the aforementioned assumptions into consideration, the scenario 3.(010) is confirmed. After this iteration, the only feasible pathway is the first one. Thus, the concluded reaction mechanism is shown in Appendix A, Fig.4.

It is important to highlight the end of this algorithm: let the scenario (1) be true in step 3.(01). Within the scenario 3.(011), we still have 20 feasible pathways. As mentioned before, further experiments should be necessary to elucidate the reaction mechanism in this case. These experiences have to discriminate among reactions, because molecular characterization of intermediates is not enough to settle the reaction mechanism.

5. Conclusions

The search of reaction pathways with P-graphs and the application of reaction blocks to reduce the combinatorial space aim at systhematizing the definition of a reaction mechanism. Mass balance criteria can be included during a combinatorially complete search, in order to find a

[2]Hypothetical experiments performed to evaluate the veracity of scenarios (0) and (1).

maximal structure where all phisically feasible pathways can be found. After obtaining this general structure, the search methodology can be formalized through a series of steps presented herein. These steps integrate experimental data in a logic evaluation tree.

When applied over the CO_2 methanation system, this technique allows to state the participation of reactions 1, 2, 7a, 7b, 7c, 7d, and 10 in all feasible pathways. Other reactions have to be confirmed through new experimental data about species on surface. The use of this information to confirm or discard feasible pathways have been illustrated with a hypothetical case.

This technique exploits the combinatorial structure of a reaction system. In the case of CO_2 methanation on a catalyst, the set of possible mechanisms have been reduced from billions to dozens of options. This computational search allows to focus the scientific analysis on a reduced set of species and partial reactions, defining further experiments in order to elucidate the reaction pathway of any chemical system.

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Appendix A: P-graph representation of the 71 feasible mechanisms for CO_2 methanation reaction including COs and HCOs as intermediates

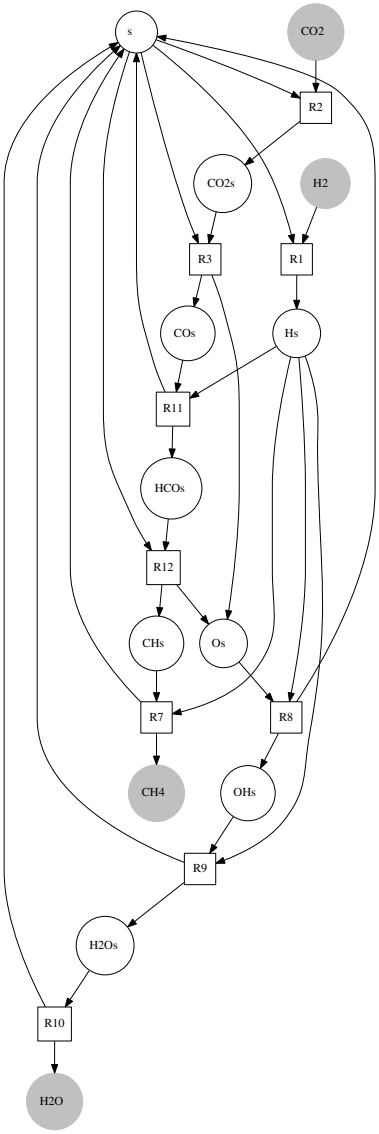
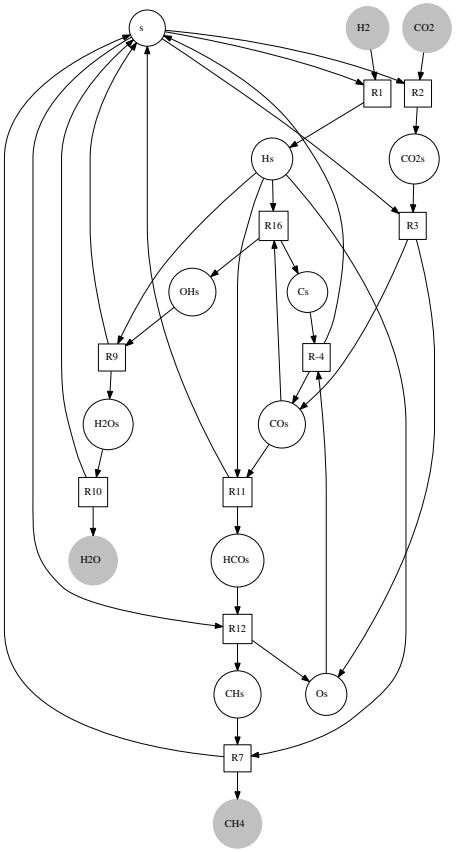


Figure 4: P-graph N.1.



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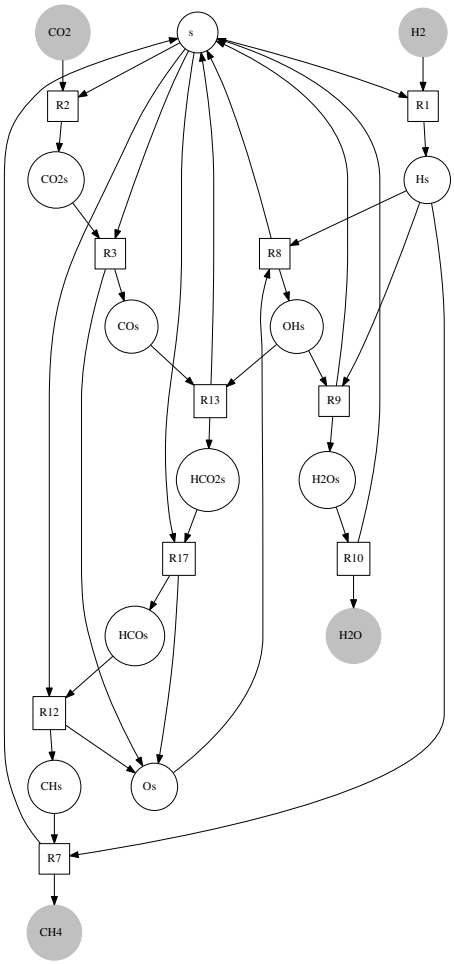


Figure 6: P-graph N.3.

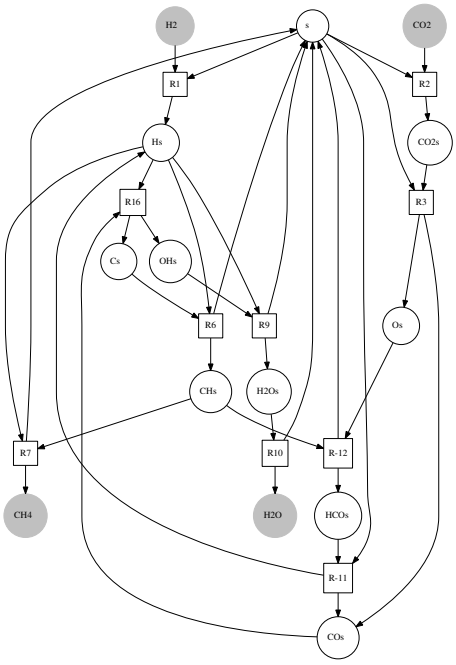


Figure 7: P-graph N.4.

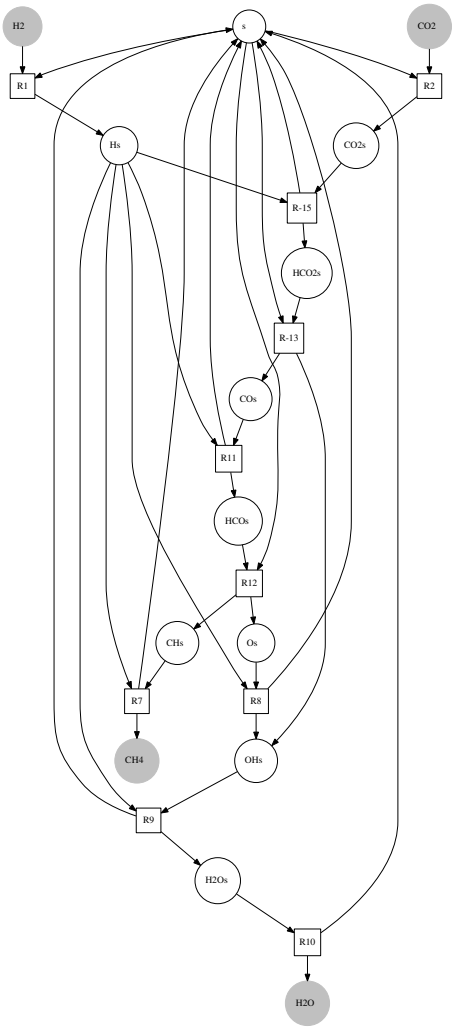


Figure 8: P-graph N.5.

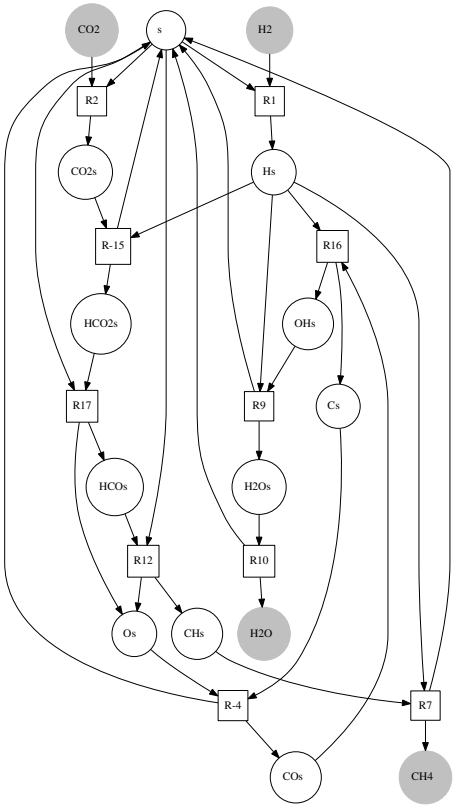


Figure 9: P-graph N.6.

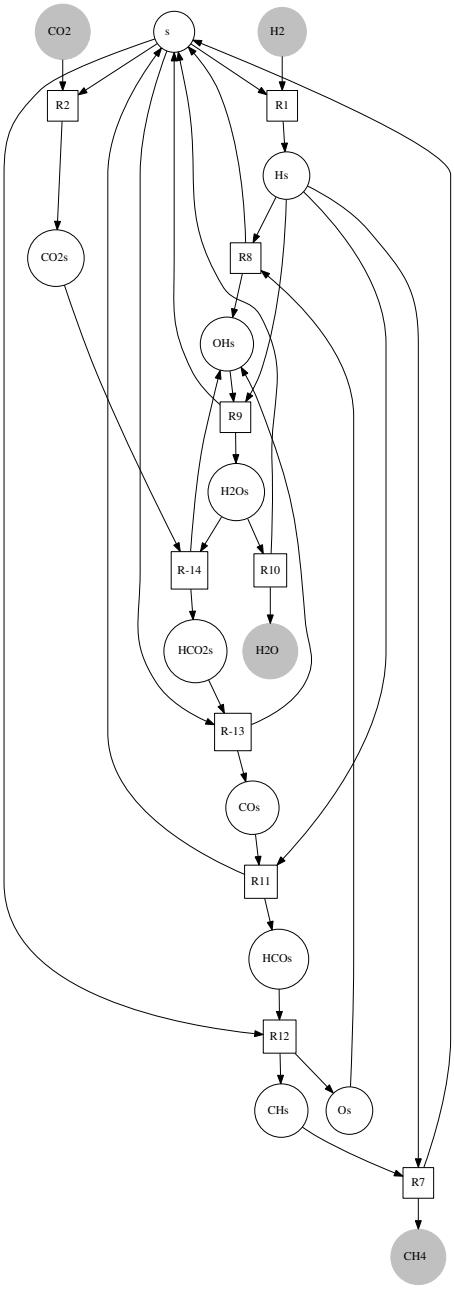


Figure 10: P-graph N.7.

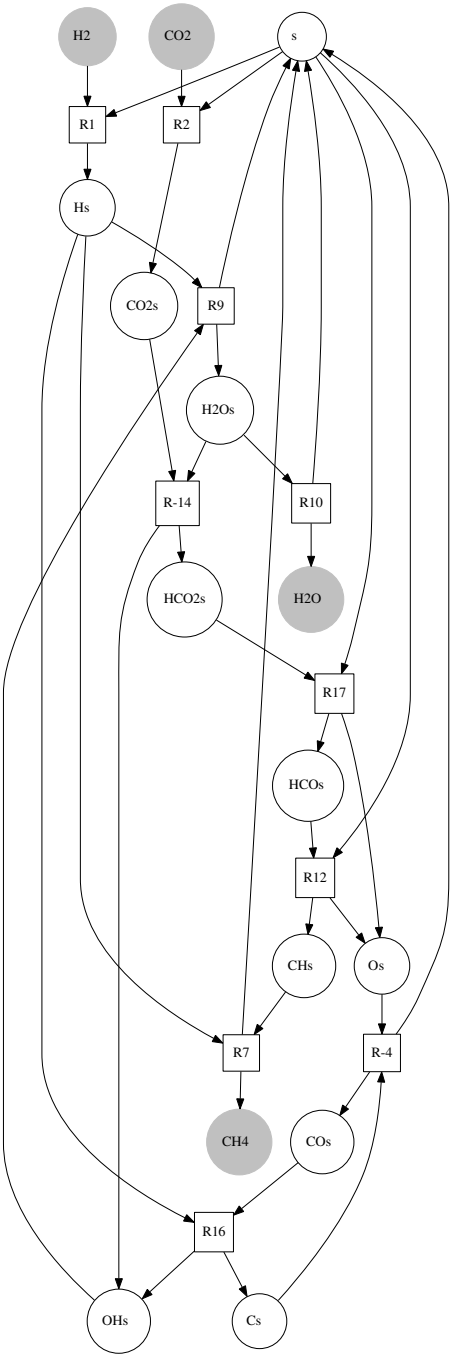


Figure 11: P-graph N.8.

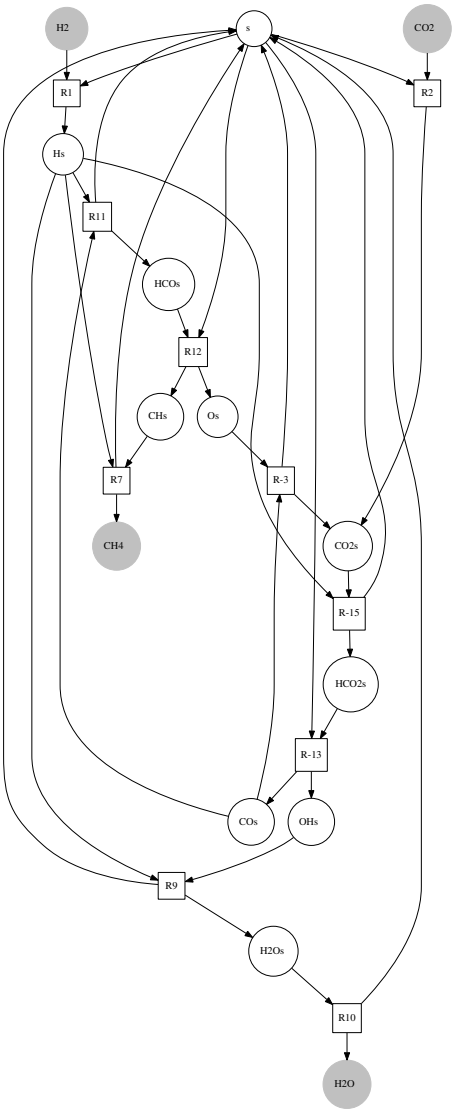
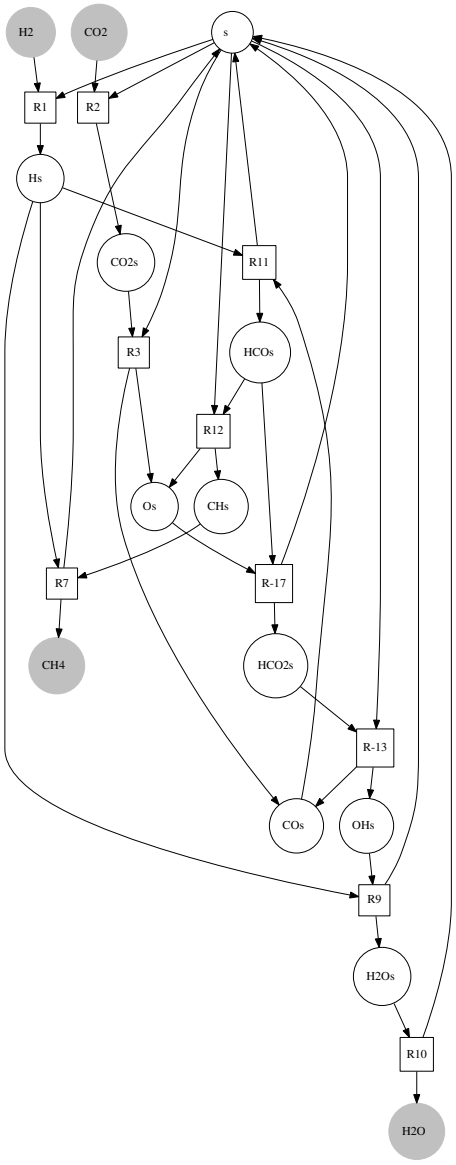


Figure 12: P-graph N.9.



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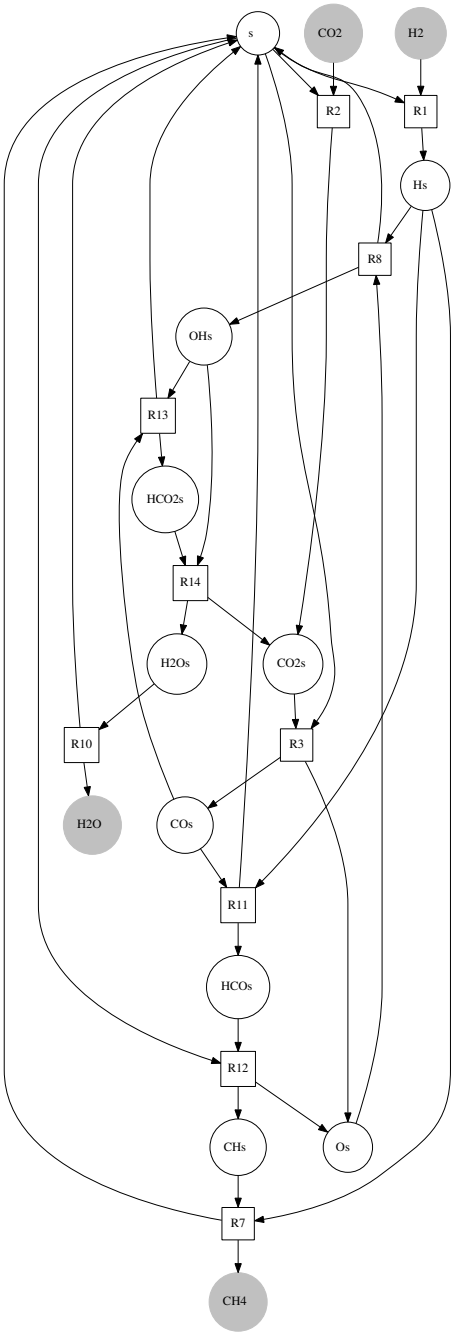

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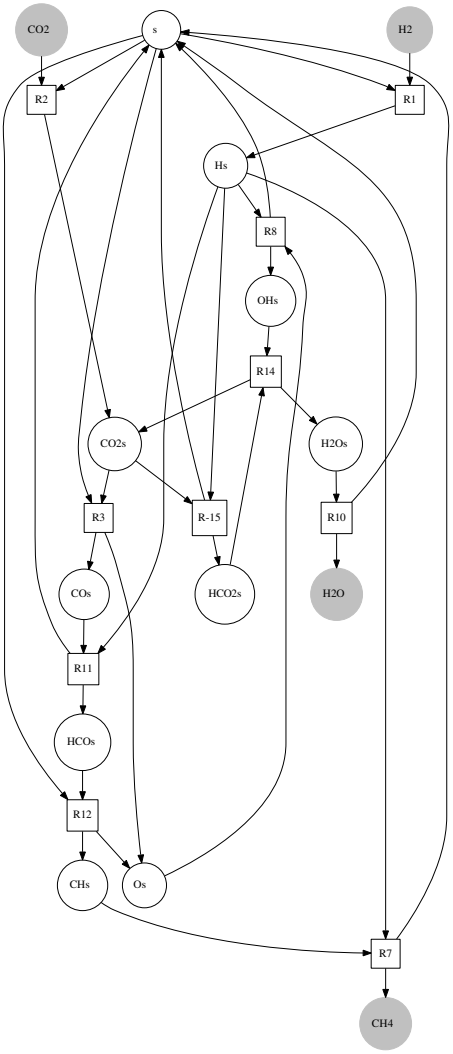

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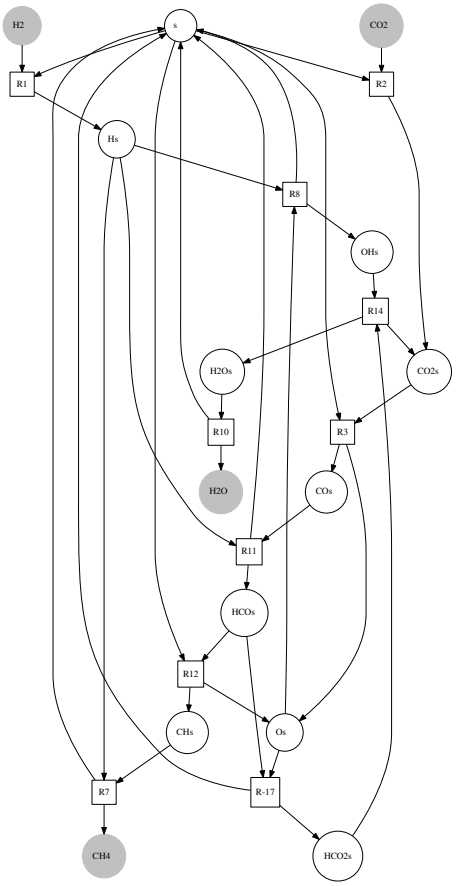
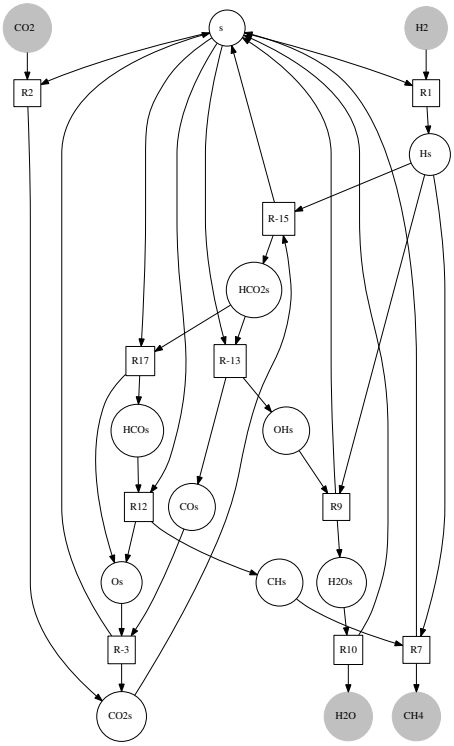


Figure 16: P-graph N.13.



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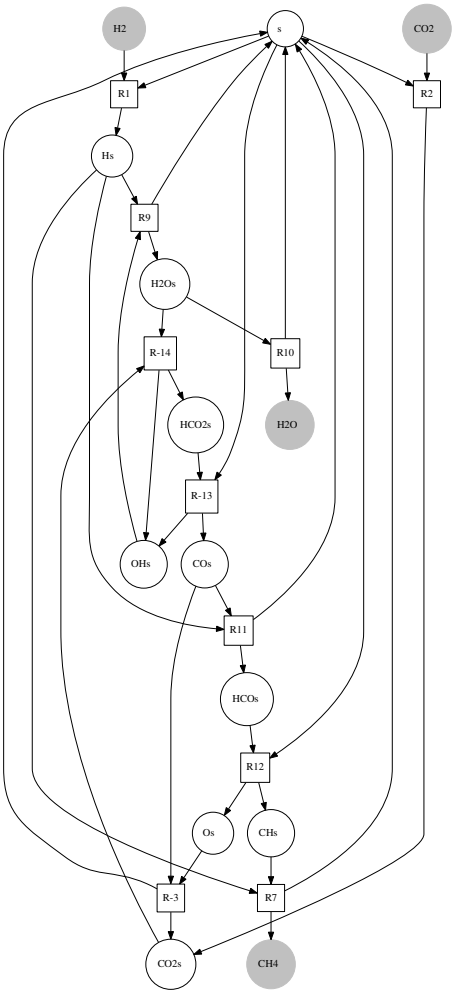

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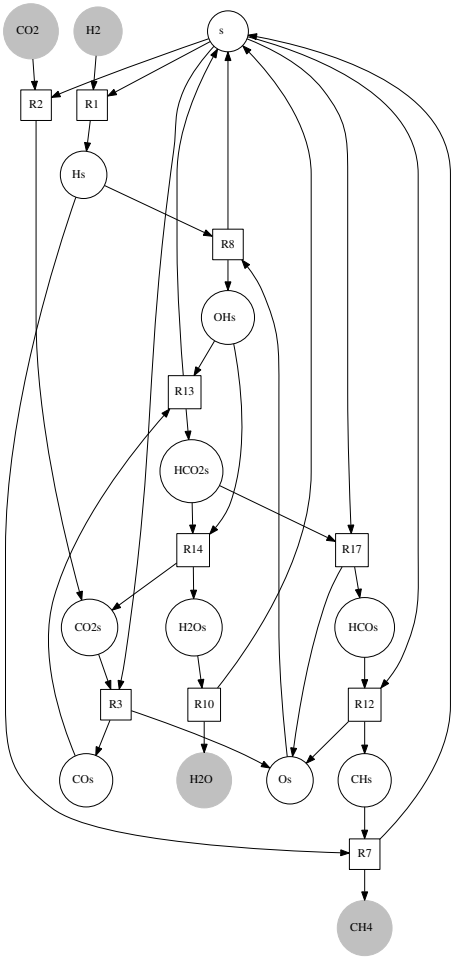
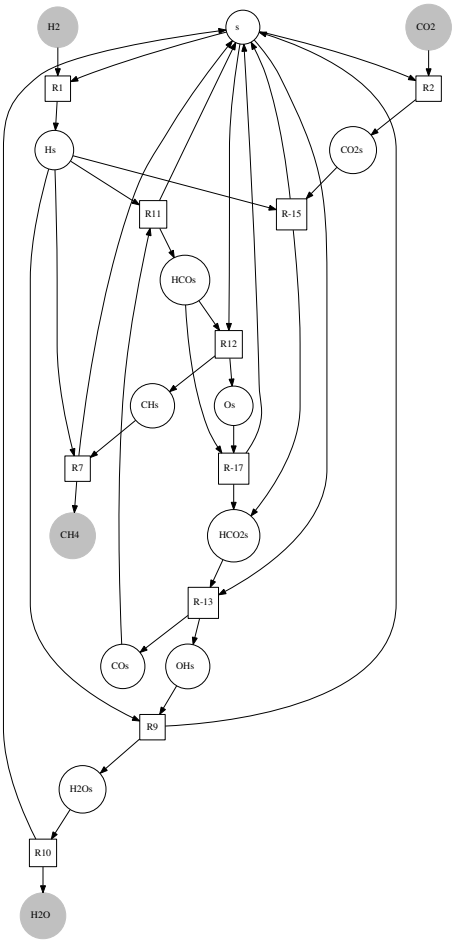


Figure 19: P-graph N.16.



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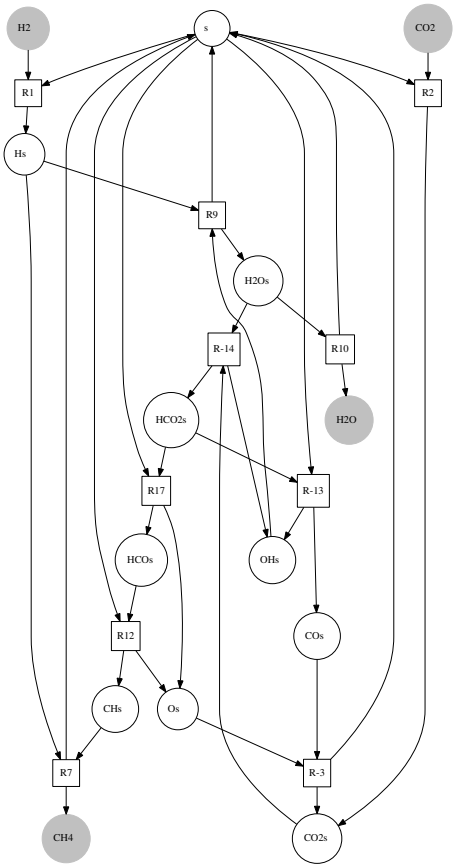

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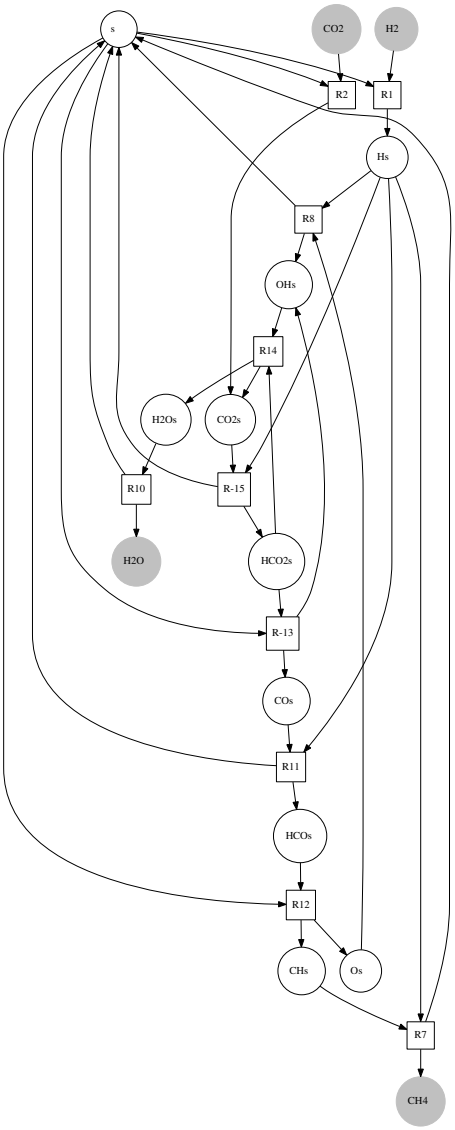

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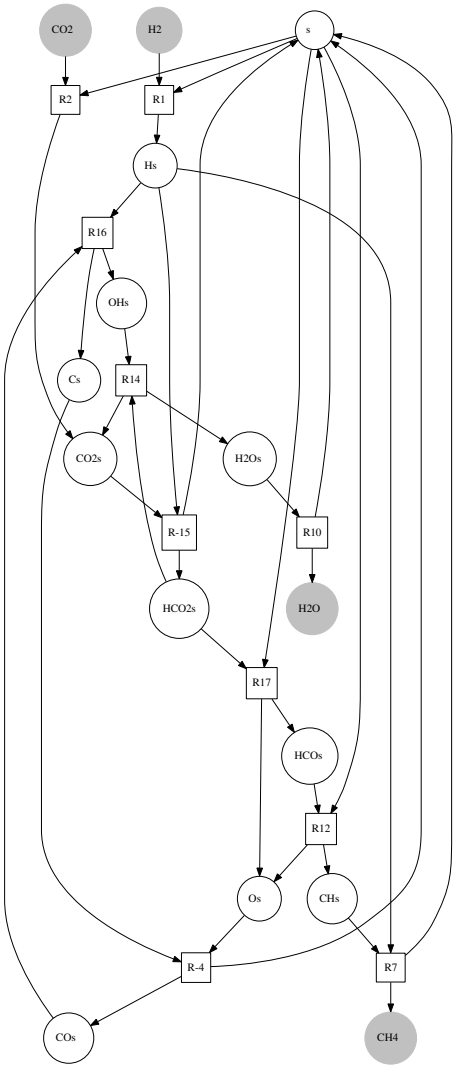

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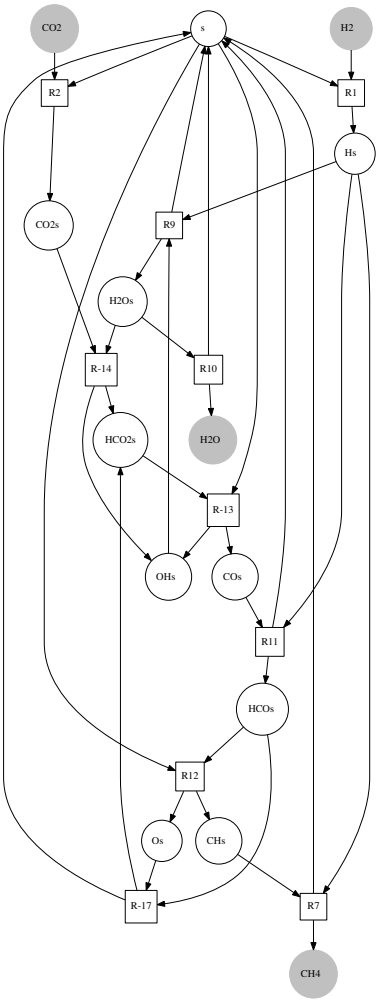

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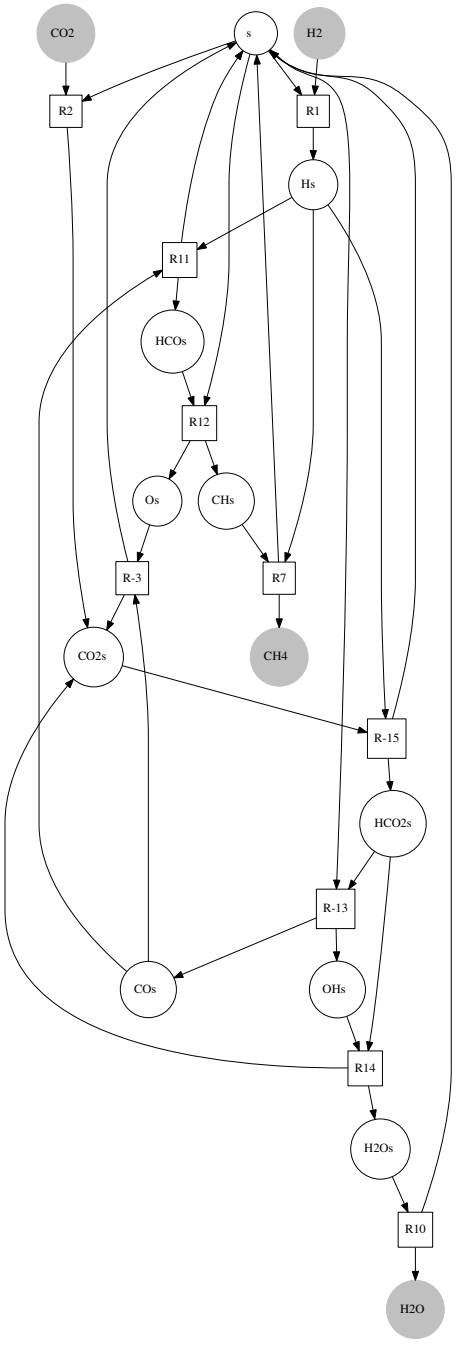
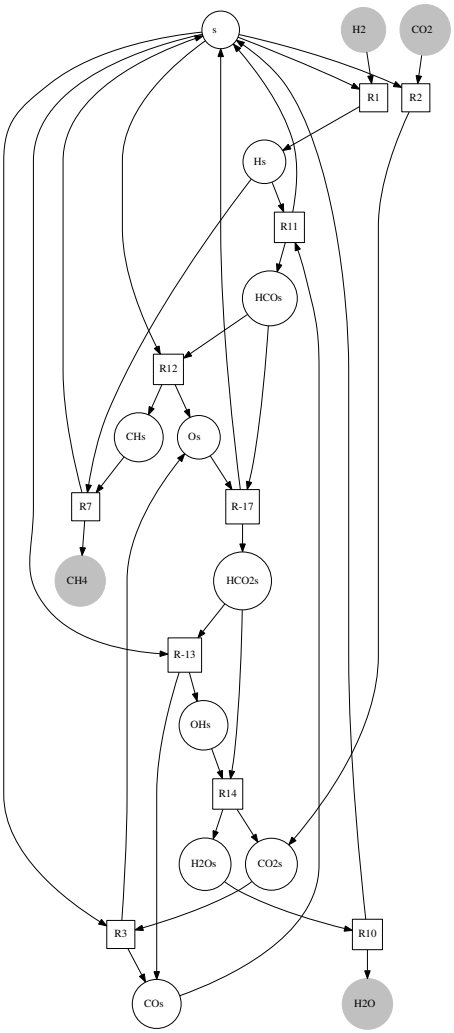


Figure 25: P-graph N.22.



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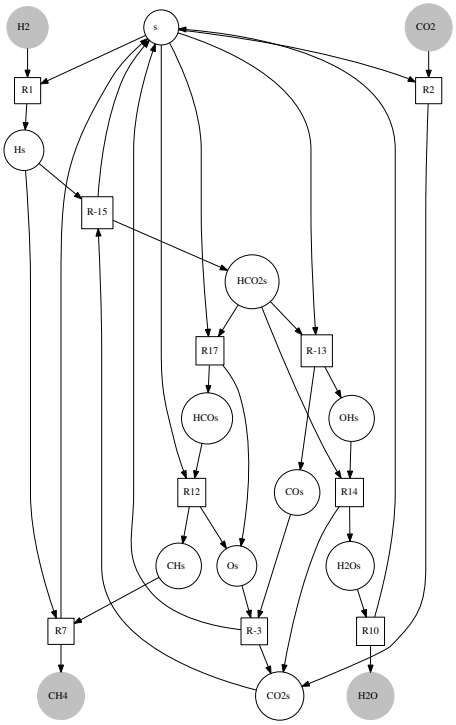

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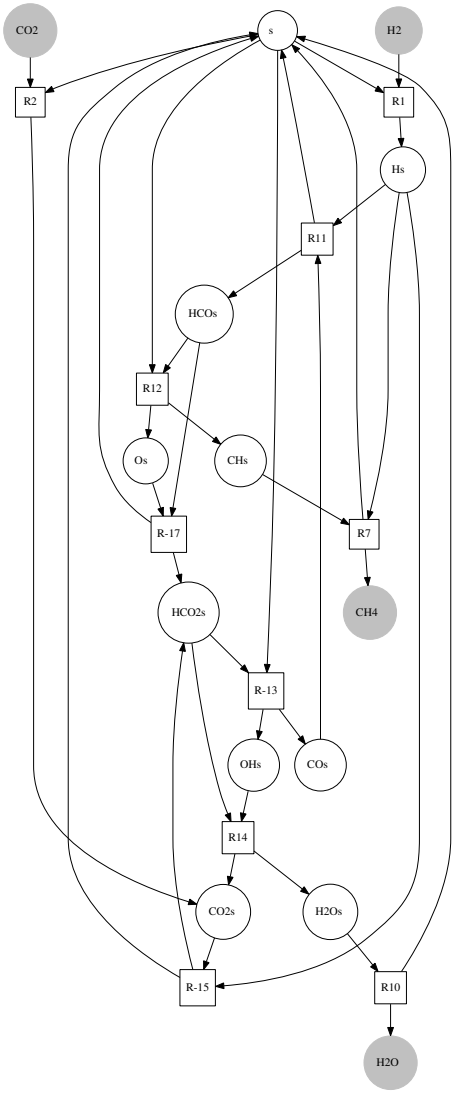

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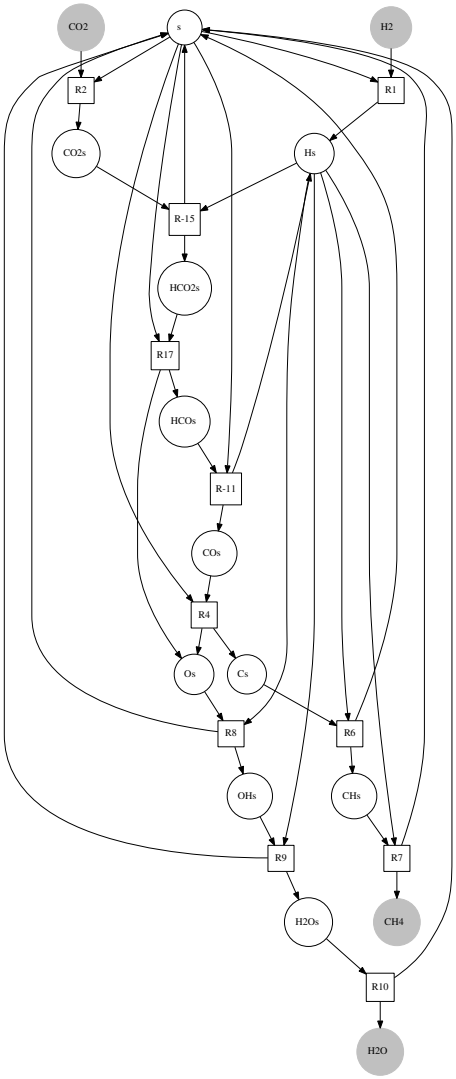

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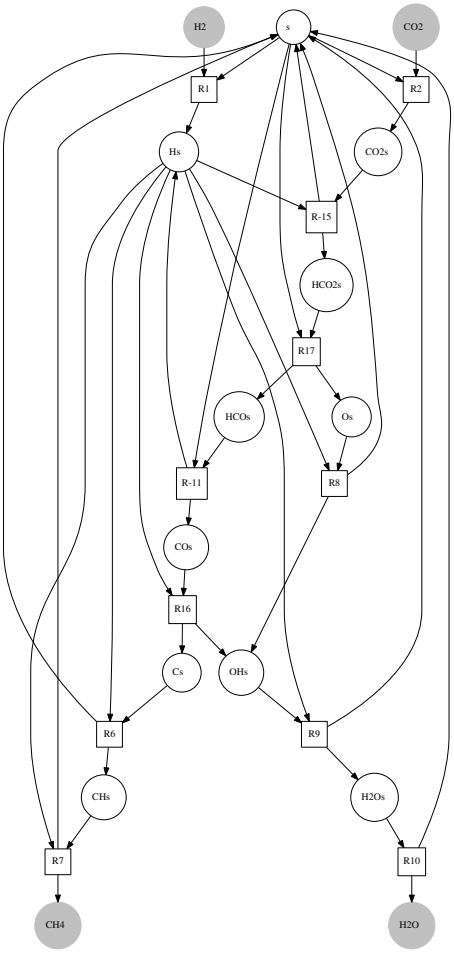

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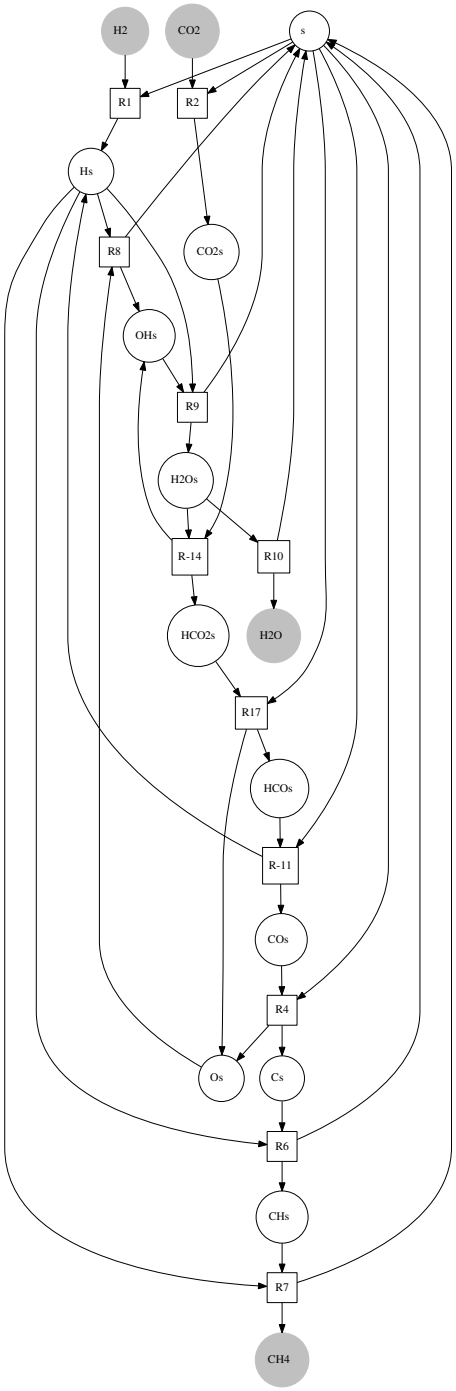

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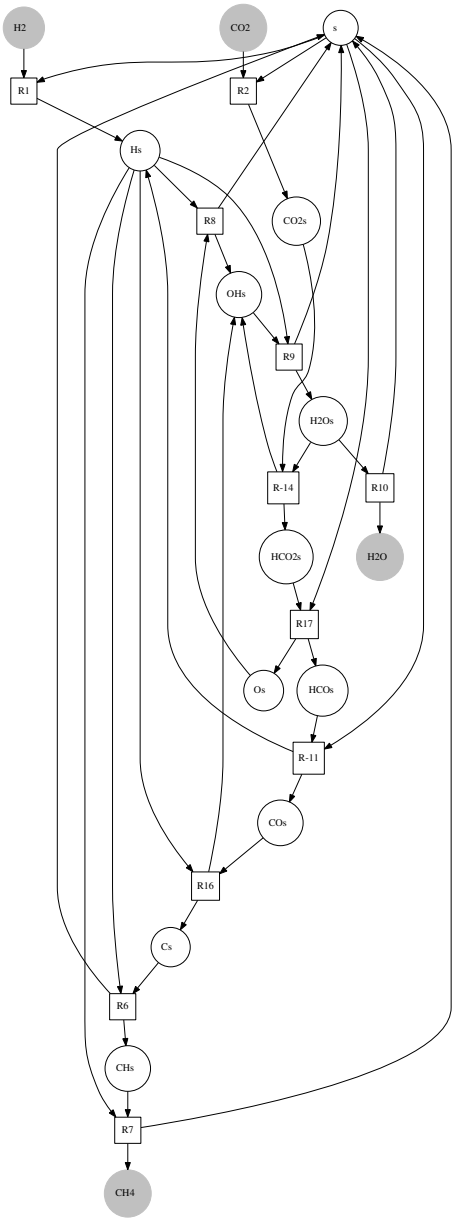

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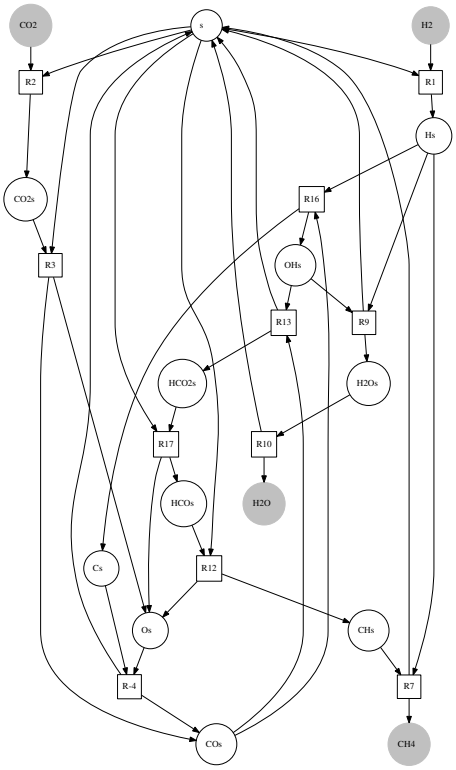

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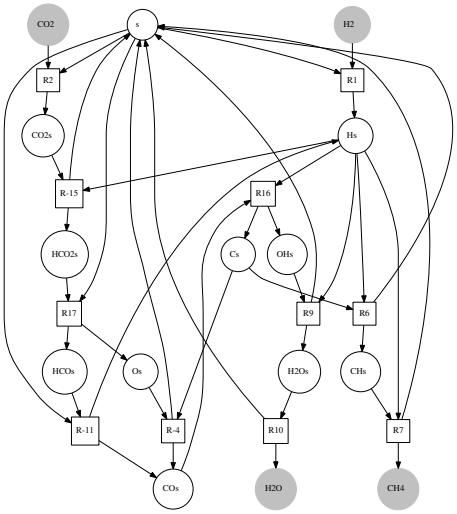

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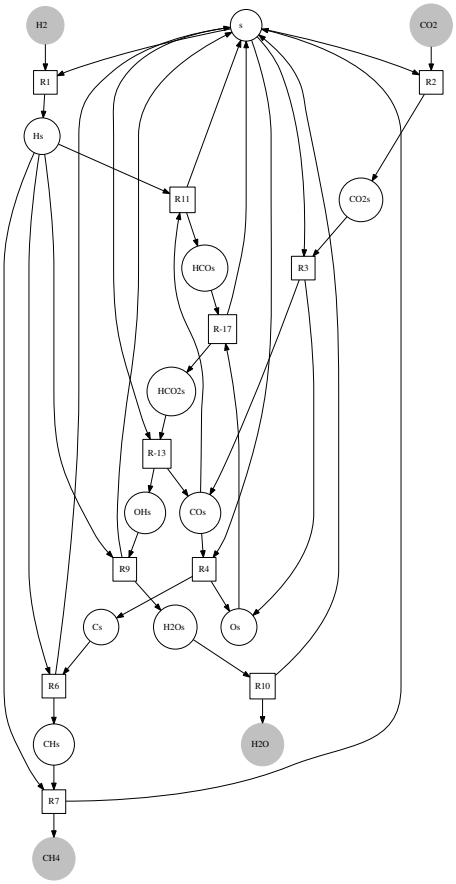

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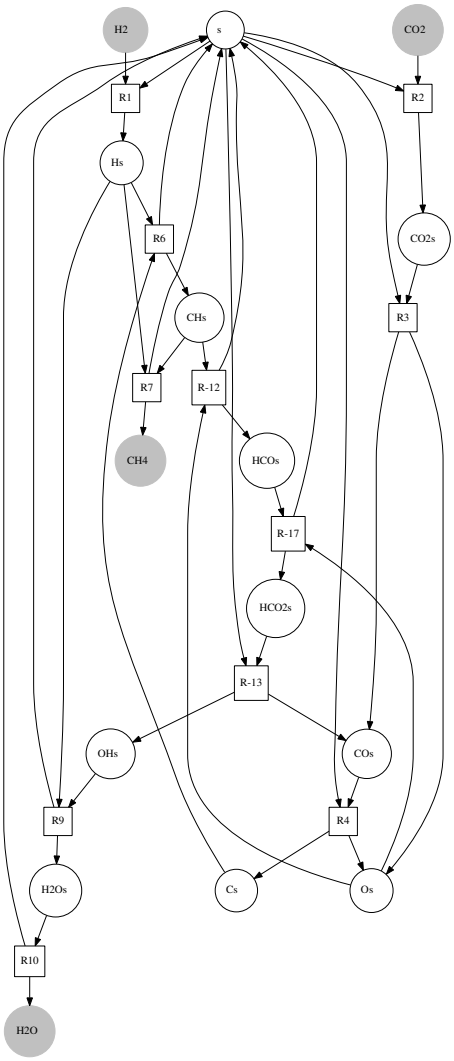

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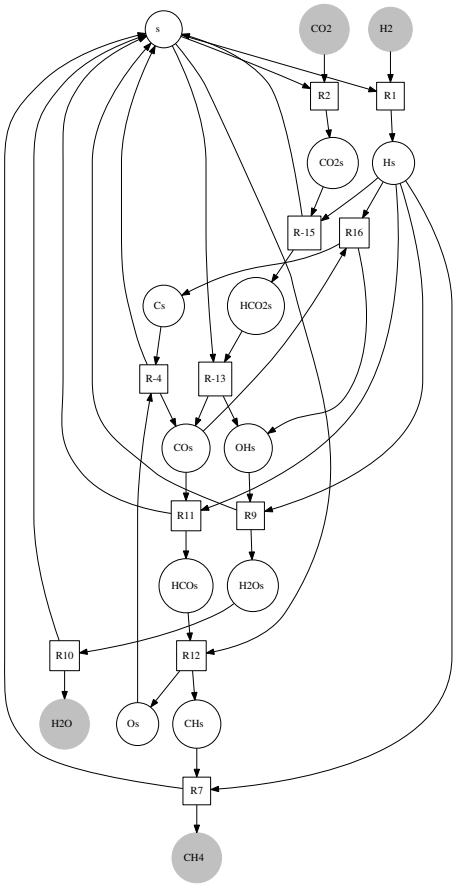

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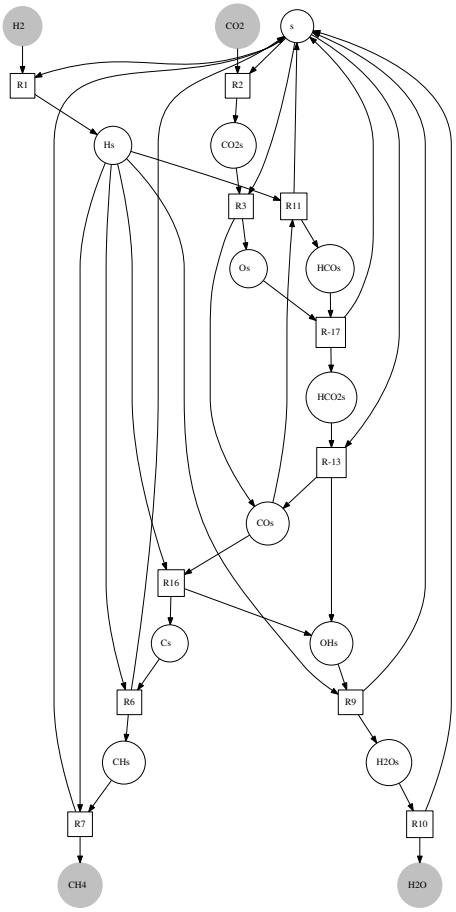

Figure 38: P-graph N.35.

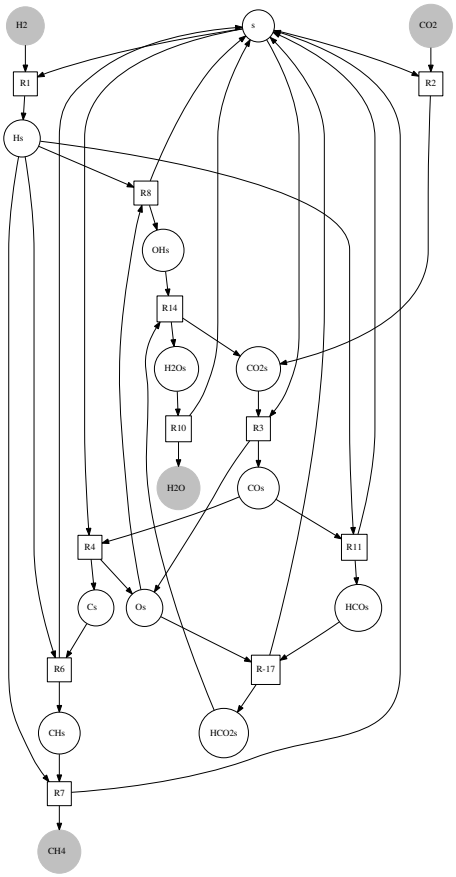

Figure 39: P-graph N.36.

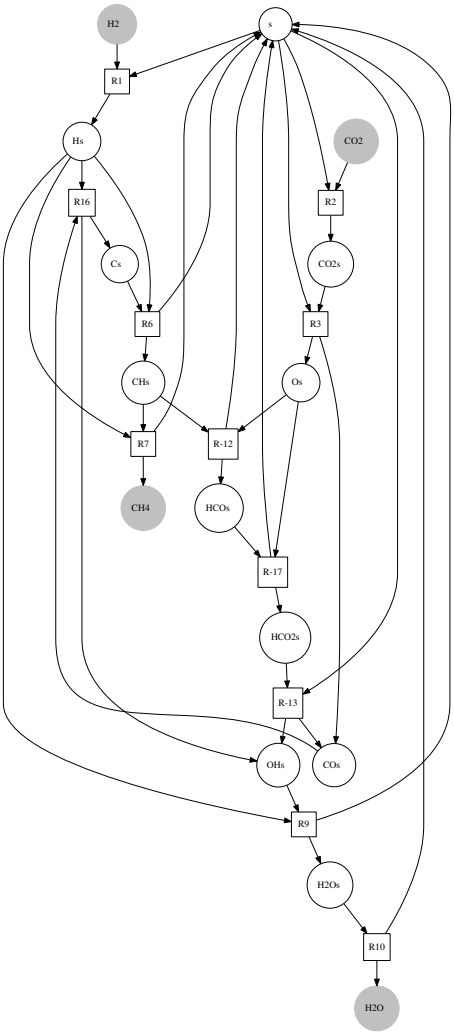

Figure 40: P-graph N.37

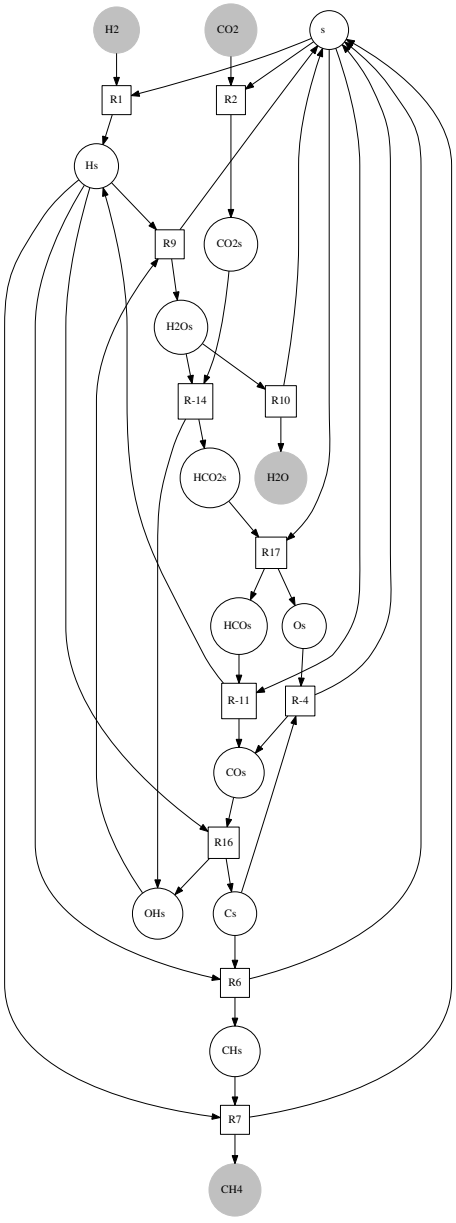

Figure 41: P-graph N.38.

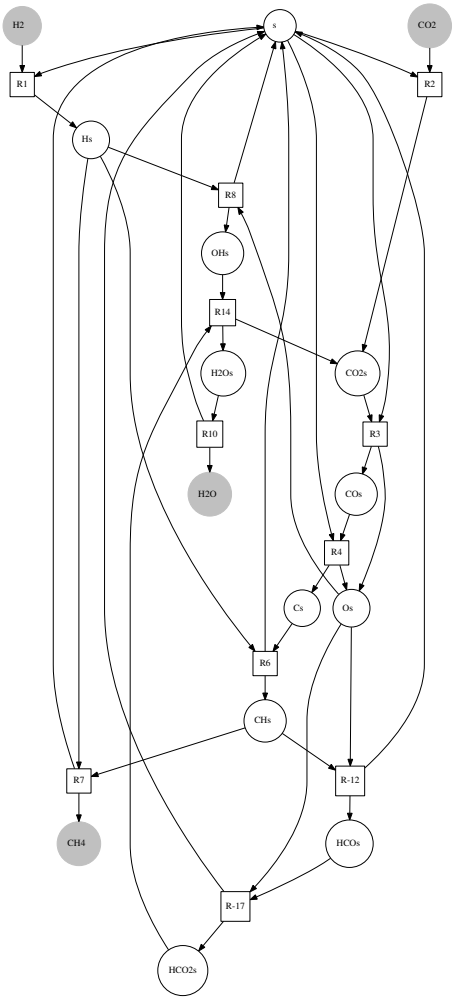

Figure 42: P-graph N.39.

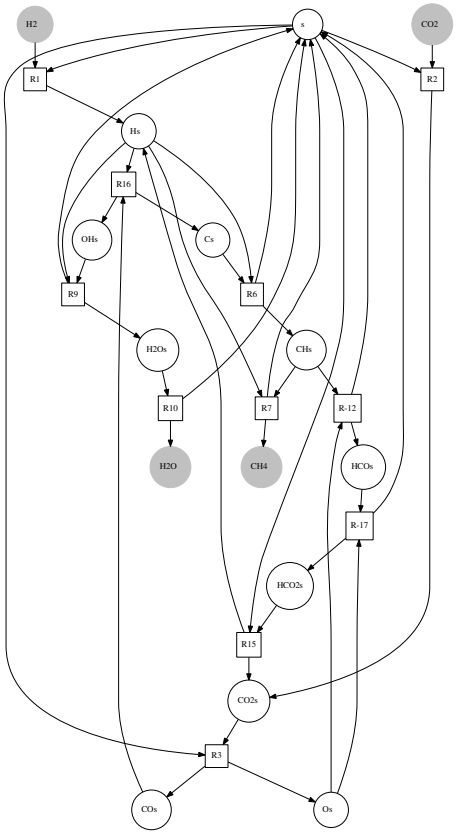

Figure 43: P-graph N.40.

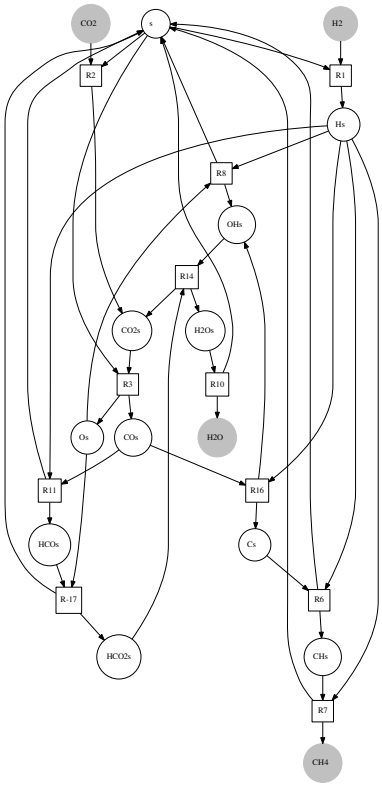

Figure 44: P-graph N.41.

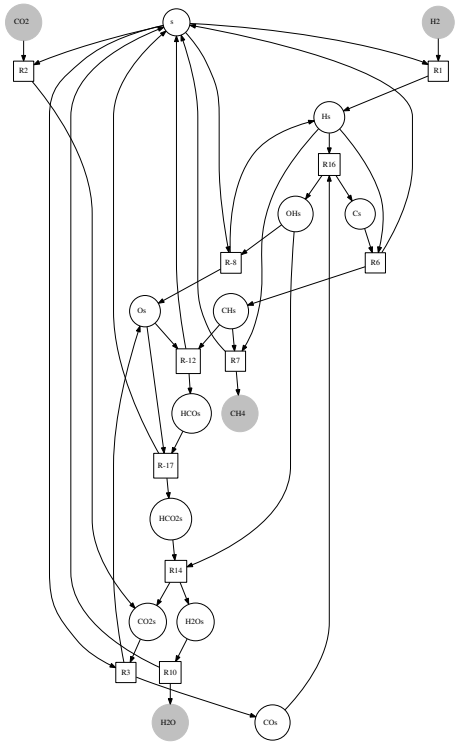

Figure 45: P-graph N.42.

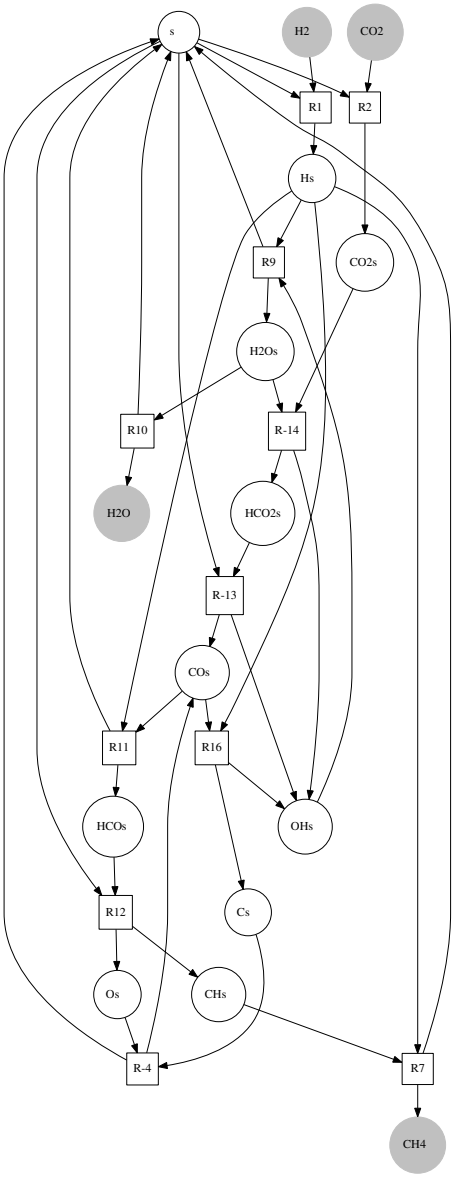

Figure 46: P-graph N.43.

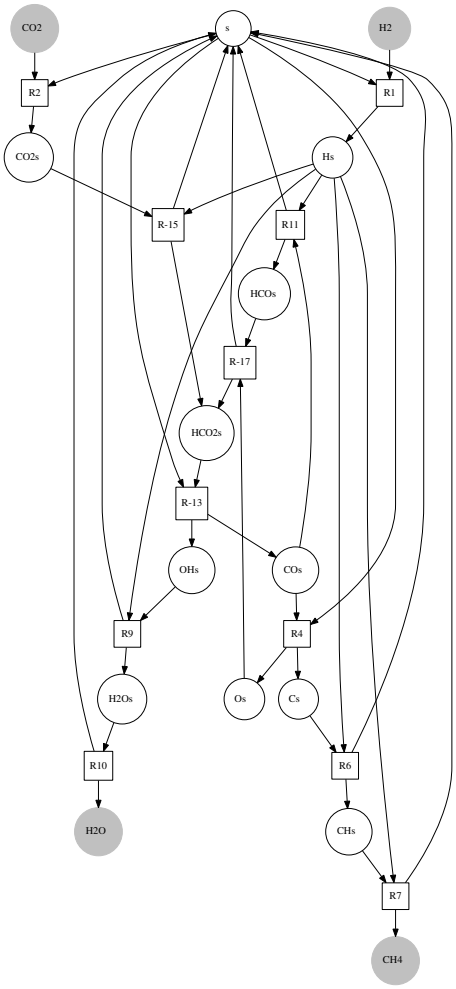

Figure 47: P-graph N.44.

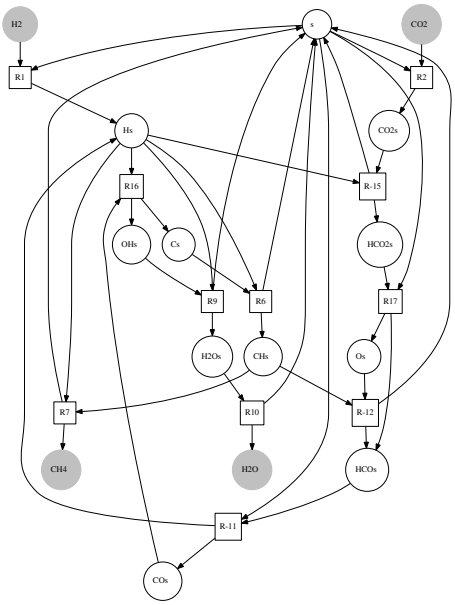

Figure 48: P-graph N.45.

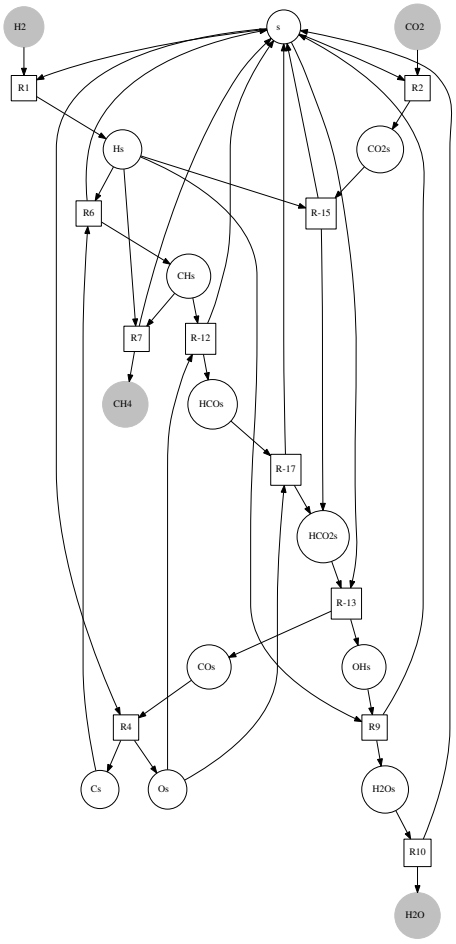

Figure 49: P-graph N.46.

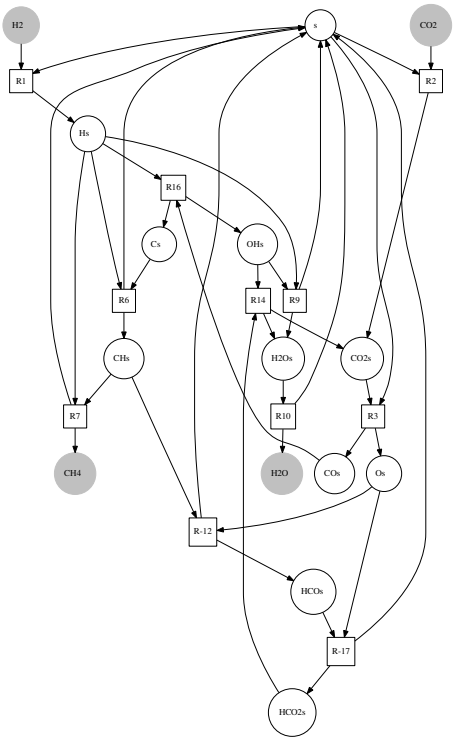

Figure 50: P-graph N.47.

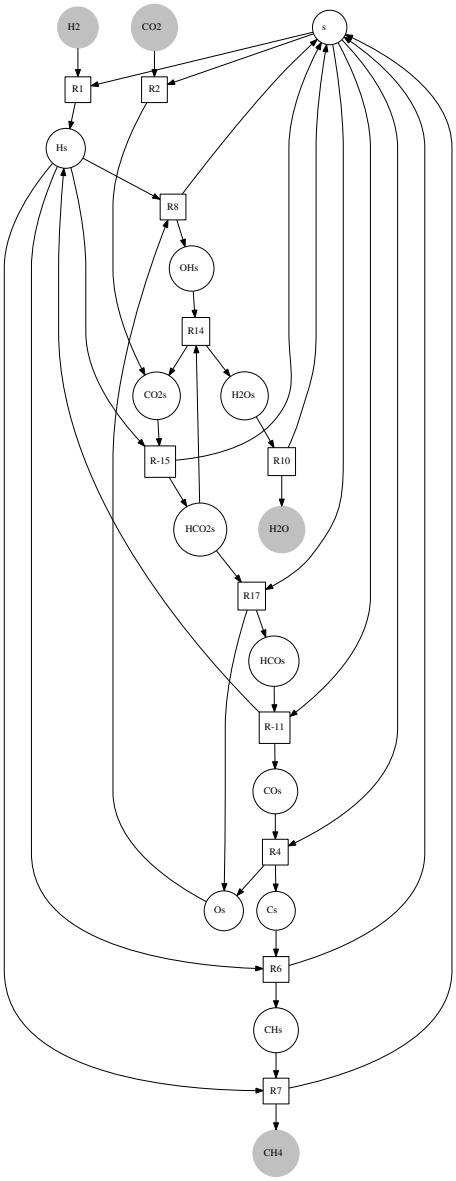

Figure 51: P-graph N.48.

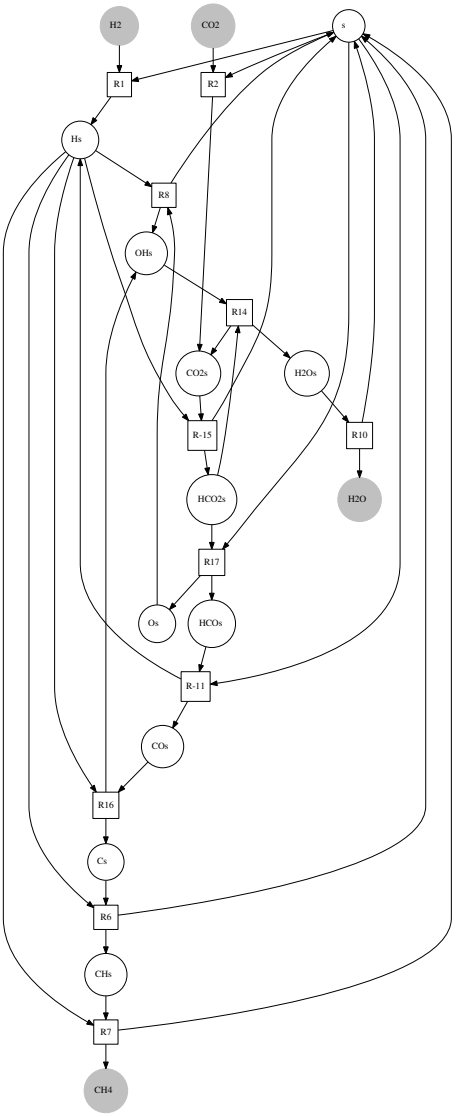

Figure 52: P-graph N.49.

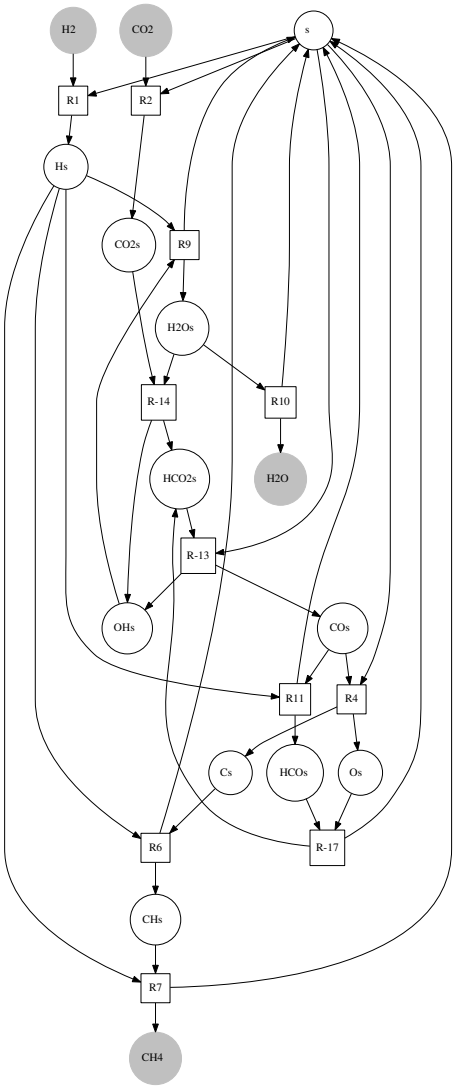

Figure 53: P-graph N.50.

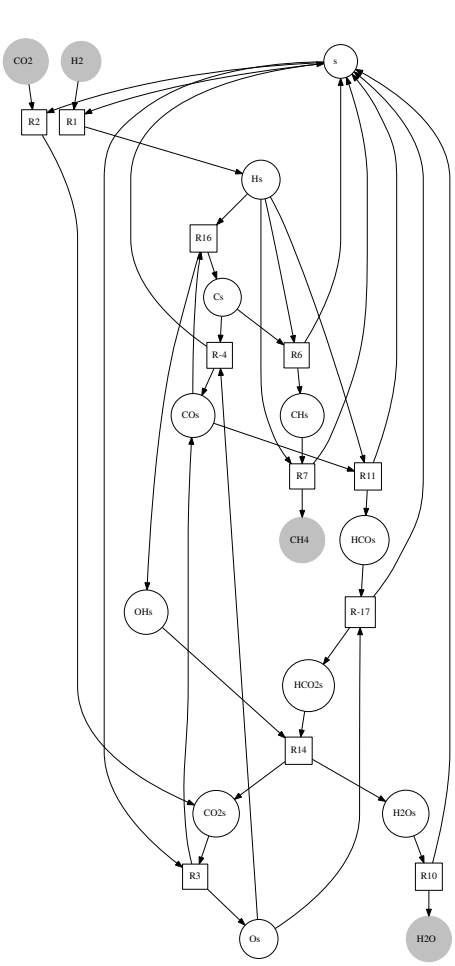

Figure 54: P-graph N.51.

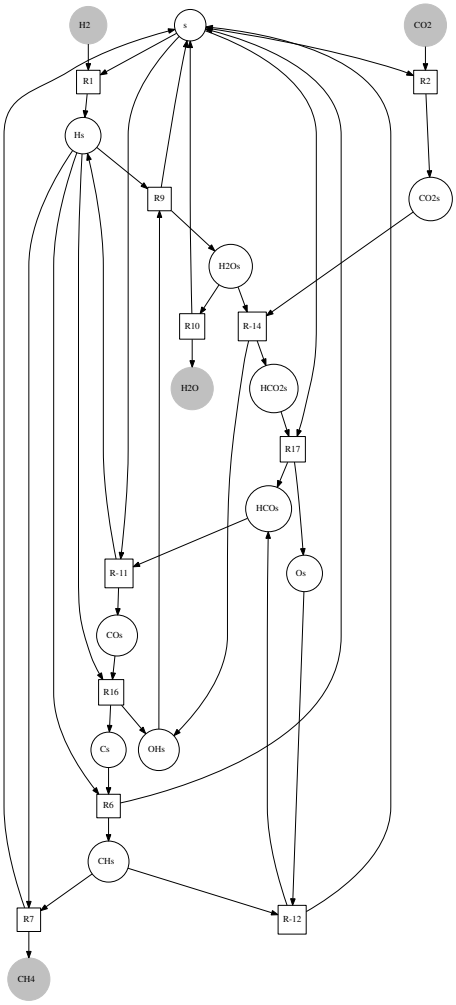

Figure 55: P-graph N.52.

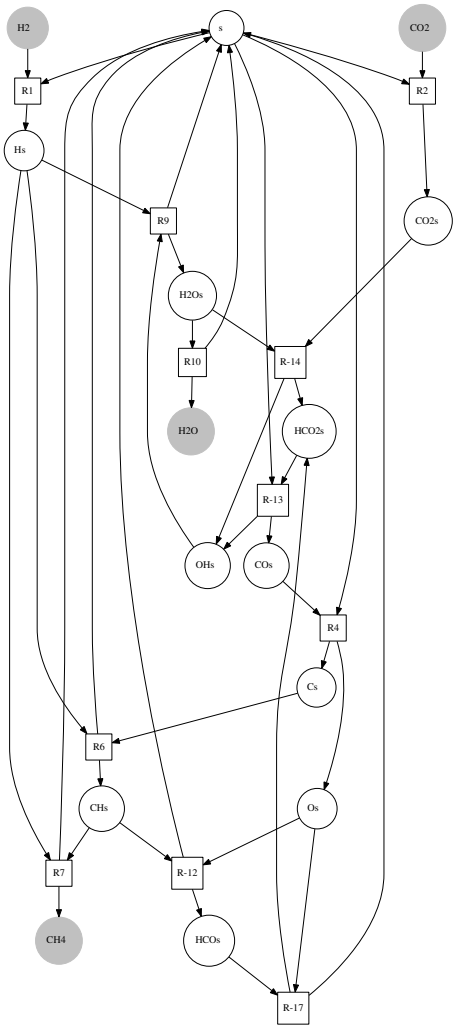

Figure 56: P-graph N.53.

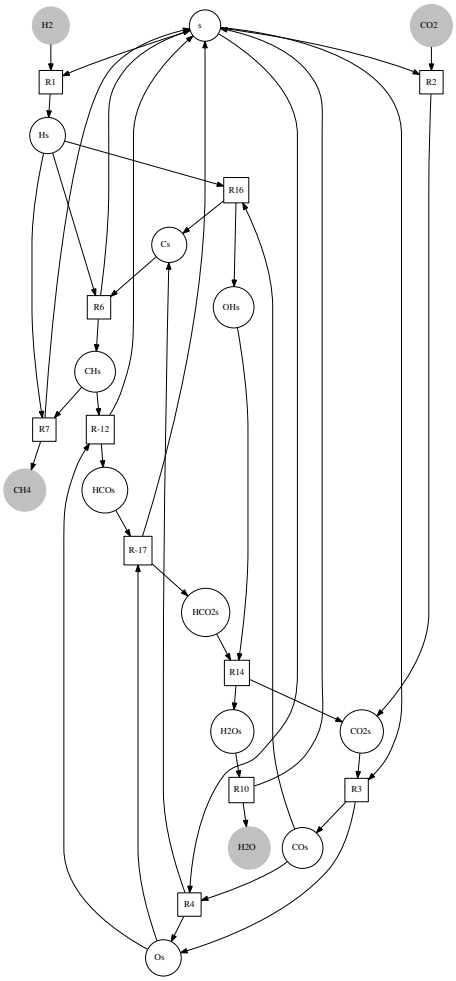

Figure 57: P-graph N.54.

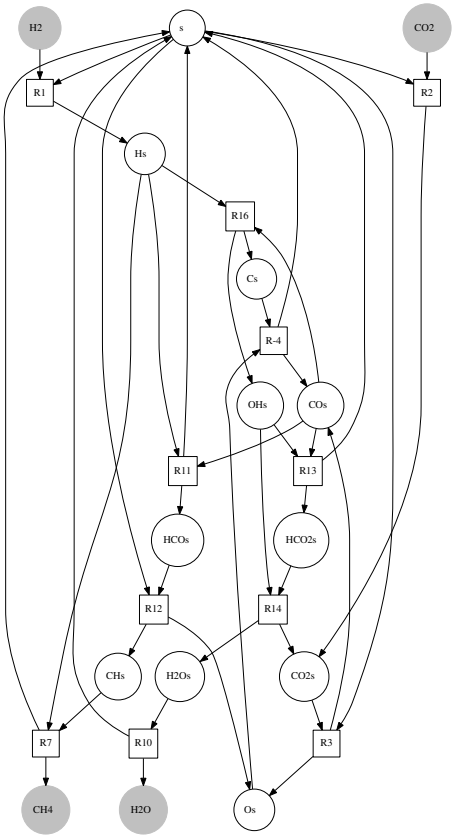

Figure 58: P-graph N.55.

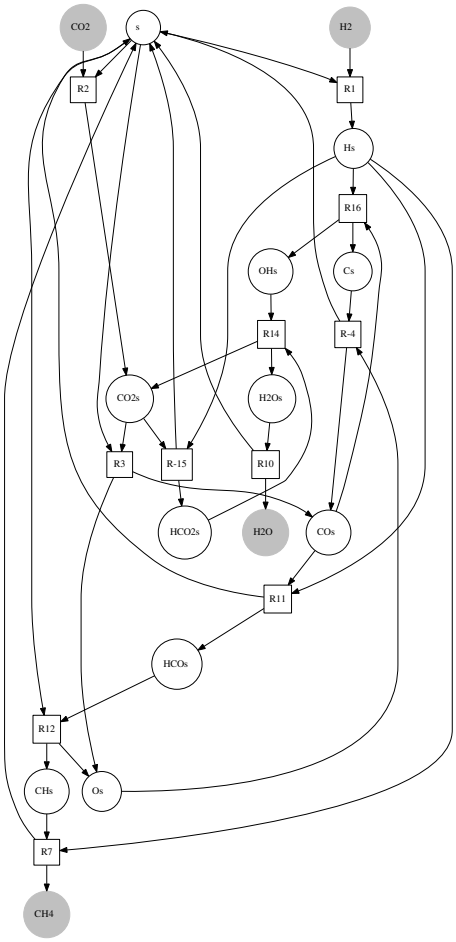

Figure 59: P-graph N.56.

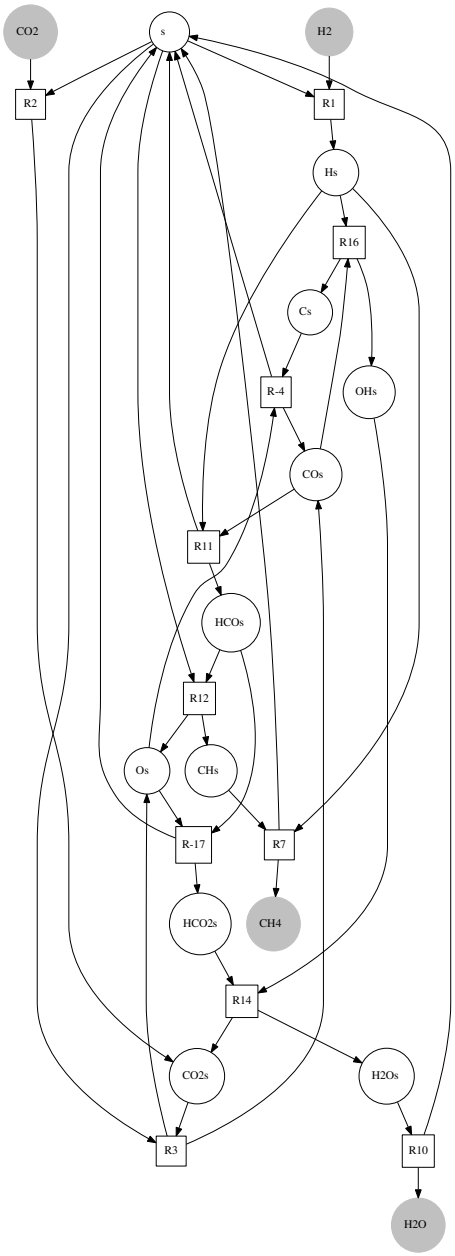

Figure 60: P-graph N.57.

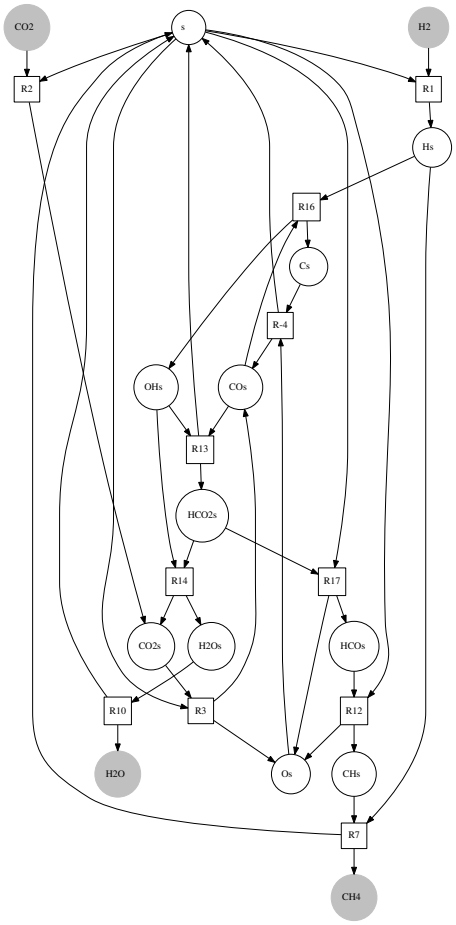

Figure 61: P-graph N.58.

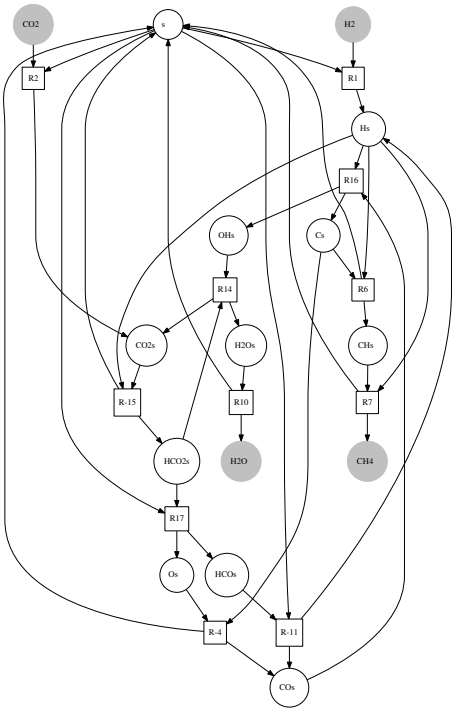

Figure 62: P-graph N.59.

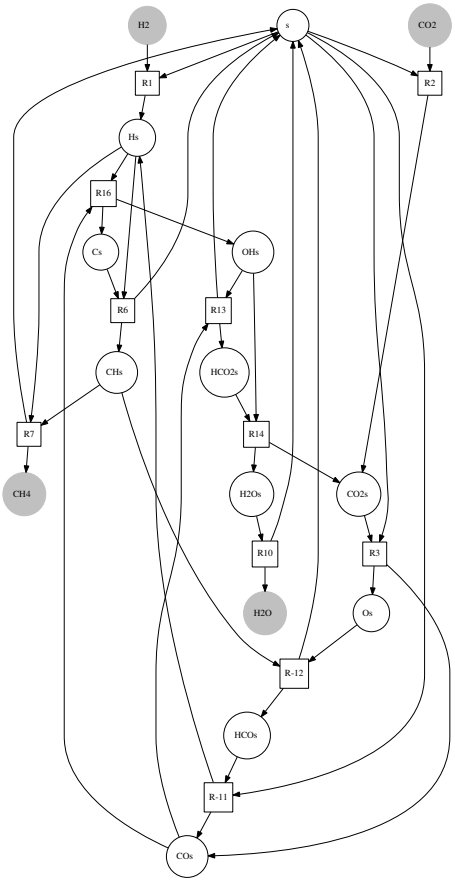

Figure 63: P-graph N.60.

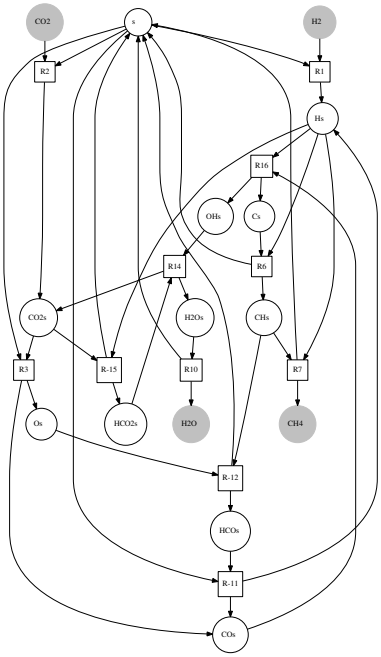

Figure 64: P-graph N.61.

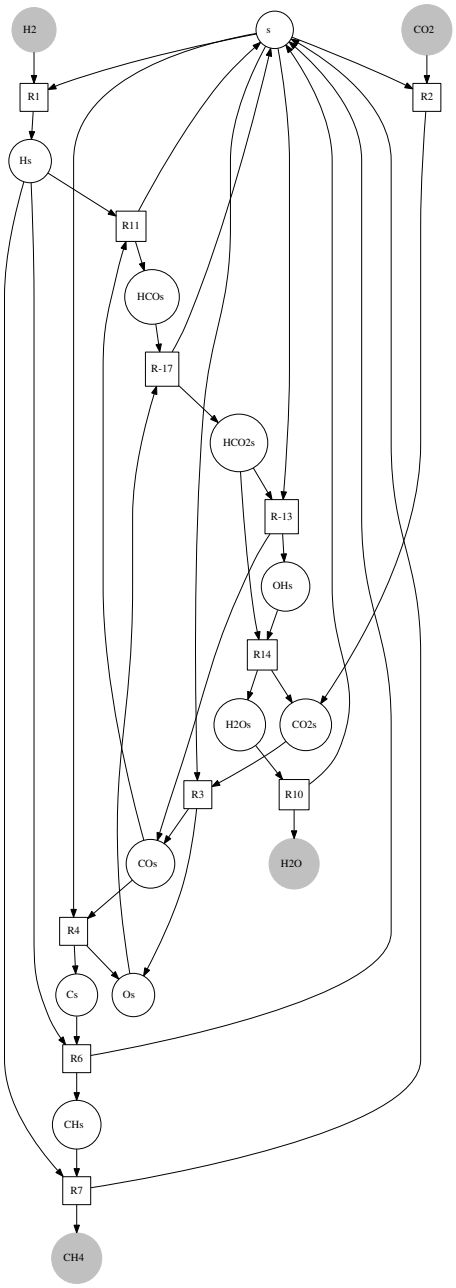

Figure 65: P-graph N.62.

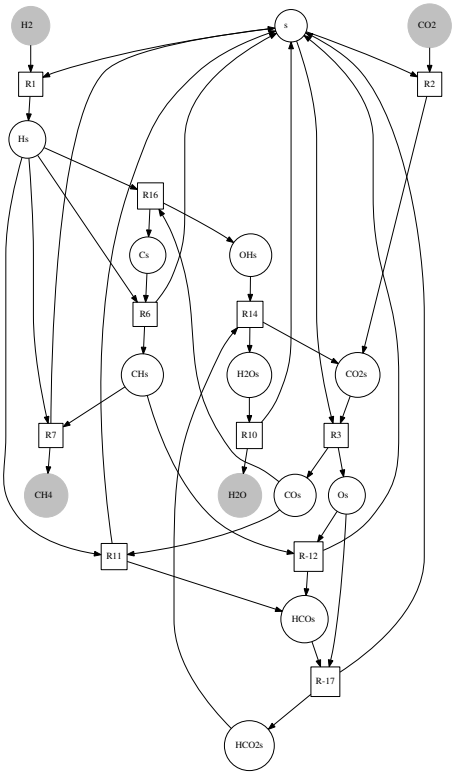

Figure 66: P-graph N.63.

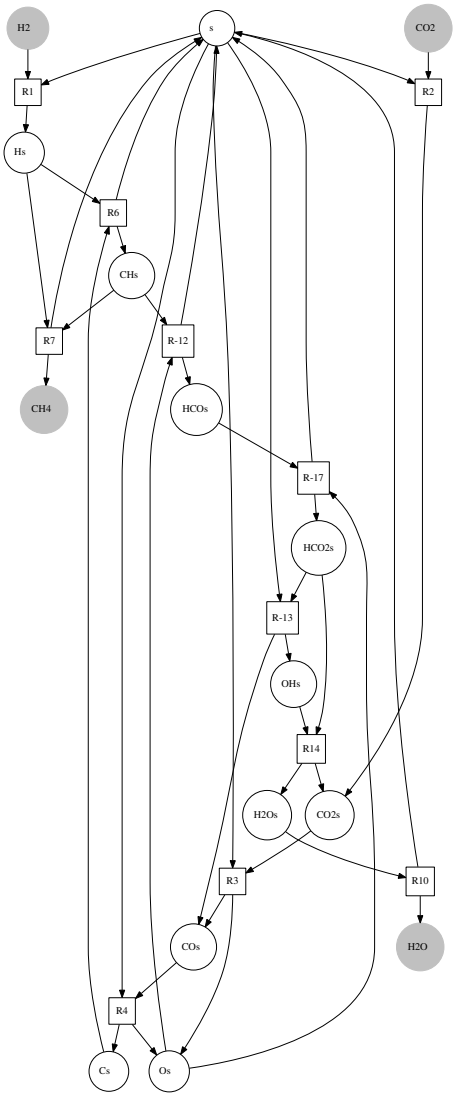

Figure 67: P-graph N.64.

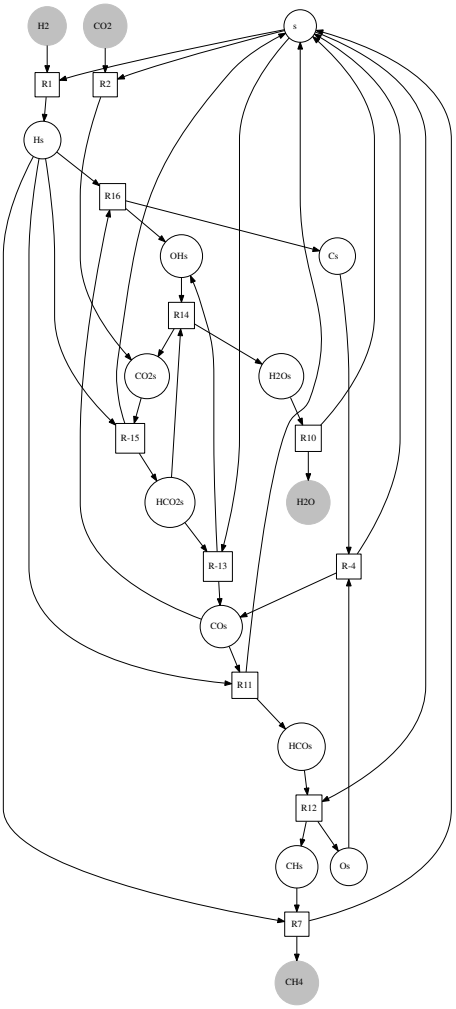

Figure 68: P-graph N.65.

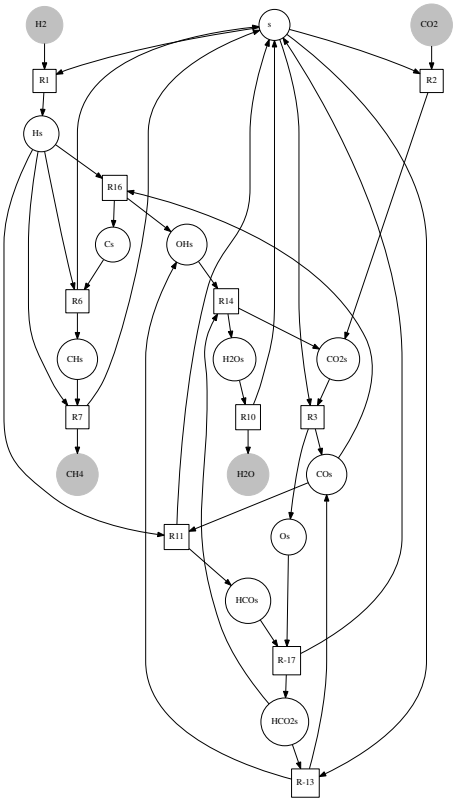

Figure 69: P-graph N.66.

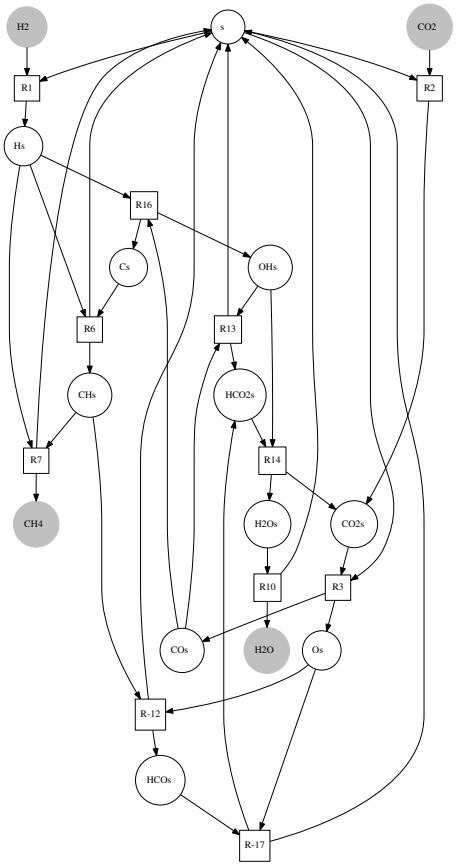

Figure 70: P-graph N.67.

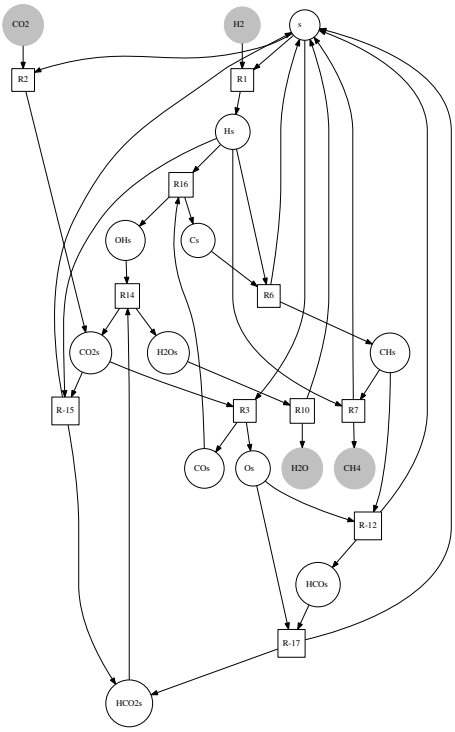

Figure 71: P-graph N.68.

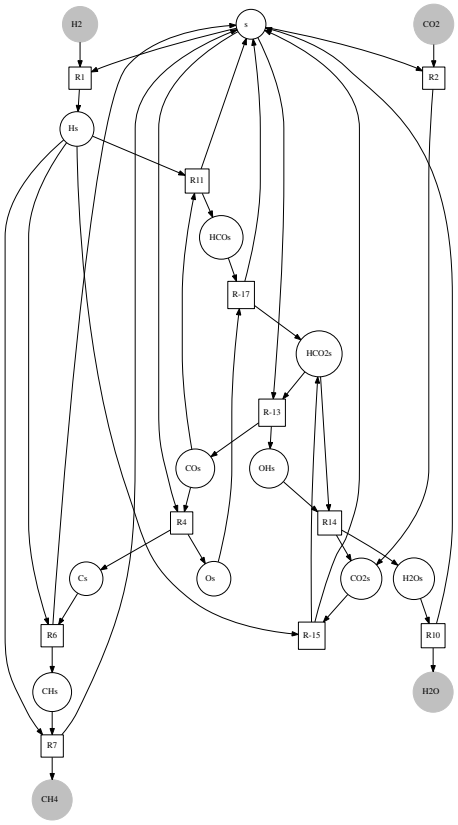

Figure 72: P-graph N.69.

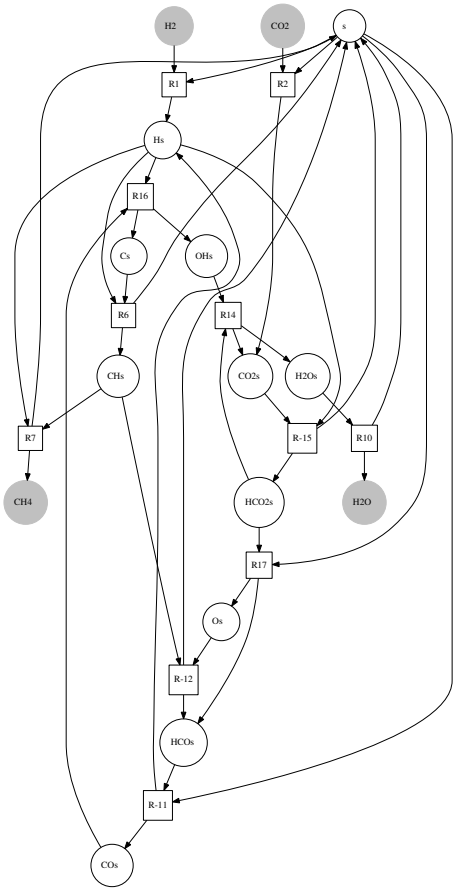

Figure 73: P-graph N.70.

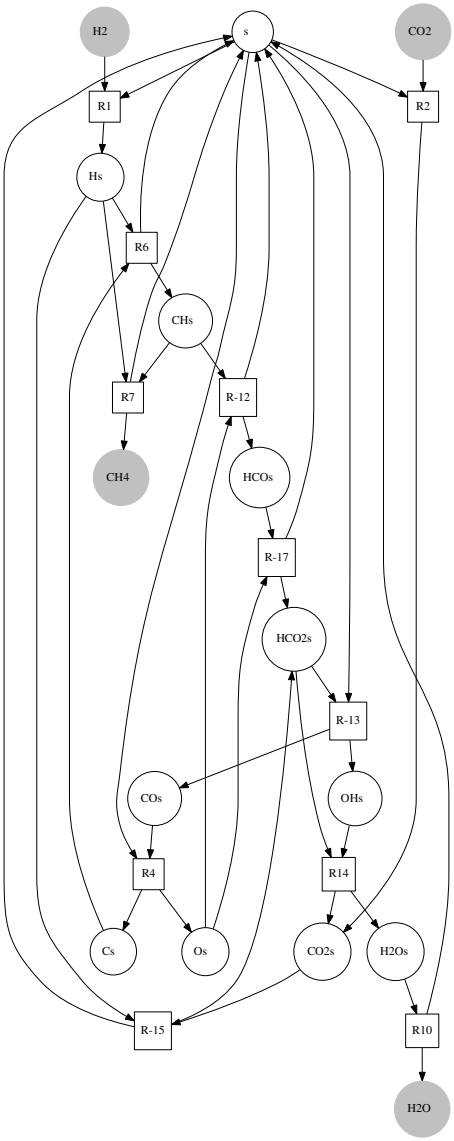

Figure 74: P-graph N.71.