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ORIGINAL PAPER

Search for reaction pathways with P-graphs and reaction blocks: 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, and the methanation of carbon dioxide with hydrogen provides a promising option. Nevertheless, the reaction mechanism of this system is under discussion. The proposal of new pathways and the discussion of their feasibility can be structured with the application of P-graphs, 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 pathways are 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.

Keywords Methanation · P-Graph · Reaction pathways · Hydrogen · Carbon dioxide

List of symbols

E	A global reaction
O	A set of feasible reactions in a chemical system
M	A set of feasible species in a chemical system

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R	A set of global reactants
P	A set of global products
o	A subset of feasible reactions within O
m	A subset of feasible species within M
(m, o)	A P-graph with nodes for species and reactions. Can represent a mechanism
$mec[O]$	The set of all feasible mechanisms within O. It has been found with PBT algorithm [10]
o_{RB}	A reaction block. It is a set of reactions within O
m_{RB}	The set of species within M participating in the reactions included in o_{RB}
r_{RB}	Reactants of a reaction block. It is a set of species within M
i_{RB}	Intermediaries of a reaction block. It is a set of species within M
p_{RB}	Products of a reaction block. It is a set of species within M
y_i	A reaction within O
S_{RB}	An aggregate reaction for the block o_{RB}
$f_{S_{RB}}$	An aggregate reaction function, relating o_{RB} and $\{S_{RB}\}$
$mec[O]^{\underline{o_{RB}}}$	The set of all feasible mechanisms within O including the reactions in o_{RB}. It has been found with PBT algorithm [10]
$mec[O]^{\overline{o_{RB}}}$	The set of all feasible mechanisms within O not including the reactions in o_{RB}. It has been found with PBT algorithm [10]
O^R	A reduced set of reactions equal to $(O \backslash o_{RB}) \cup \{S_{RB}\}$

1 Introduction

The climate effects of atmospheric CO_2 has been the subject of study in the last 3 decades [16,23] and many efforts has been directed to its capture from industrial gas streams, mainly by absorption in amines [25] and adsorption on solids [7]. After separation, different downstream processes could be implemented for mitigating global climate change, as reuse, geological storage or ocean storage [15]. Despite the huge potential of the last two options, the net cost of reuse is far more attractive [18].

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 [5]. 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, [19]) has been performed on different catalysts [36], but the reaction mechanism is subject of debate [9].

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

Even though the decomposition of CO_2 to adsorbed CO is widely accepted as an intermediate step [9] and the participation of formate-like species has been reported [4,24,32], the mechanism on the catalyst surface is still not clear.

In other contexts, the P-graph theoretic method [10,13,14] has been adopted to explore the mechanisms of catalytic [22] and biochemical reactions [28]. P-graphs have also been used to synthesize process networks [12], to optimize industrial complexes [31], to optimize regional energy [21] and biomass supply chains [20], to optimize renewable energy systems [30], to select technologies for reducing carbon emissions [34], to design sustainable supply chains [33], and to economically allocate resources [1].

Within the context of reaction pathway identification, P-graphs show a wide set of attractive properties when compared with other methods such as linear algebraic methods [17,29], convex methods [2,26], combinatorial analysis [27], and reaction route graphs [11]. These properties include the following [3]: 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. These pathways 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). It is important to note that the real mechanism to explain the overall reaction can be a combination of more than one structural minimal pathway obtained in step 1. Therefore, theoretical pathways obtained in the first step can be excluded if they cannot contribute to form the overall reaction in combination with other structural minimal pathways.
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 [10,13,14] and a reduction of the domain presented in this work.

The number of combinatorial candidates for a mechanism grows exponentially with the number of reactions. If the set of proposed feasible reactions is in the tens, the number of combinatorially possible mechanisms can grow to the billions. Question is whether it is possible to reduce the search without excluding feasible solutions. Furthermore, another question is whether it is possible to aggregate elementary reactions without losing information from the mechanism during the search.

This paper defines a reaction block as a set of reactions that can be treated as a single reaction during the search of pathways in silico. With the use of reaction blocks, the search space of feasible pathways can decrease by millions without excluding feasible mechanisms. Even though this method is based on lumping, it has not been formalized in the field of P-graphs to reduce the search domains.

The aim is to apply the first two stages of the aforementioned strategy in the methanation of CO_2. We also present definitions and theorems for the use of reaction blocks in the search of reaction pathways with P-graphs, allowing a significant reduction of the search space.

Pointing to the third stage, the stoichiometrically feasible mechanisms reported herein are a guide for further experiments and future demonstration of the reaction mechanism. The set of 71 feasible pathways for the CO_2 methanation system has not been reported before.

2 Methodology

2.1 Searching reaction pathways with P-graphs

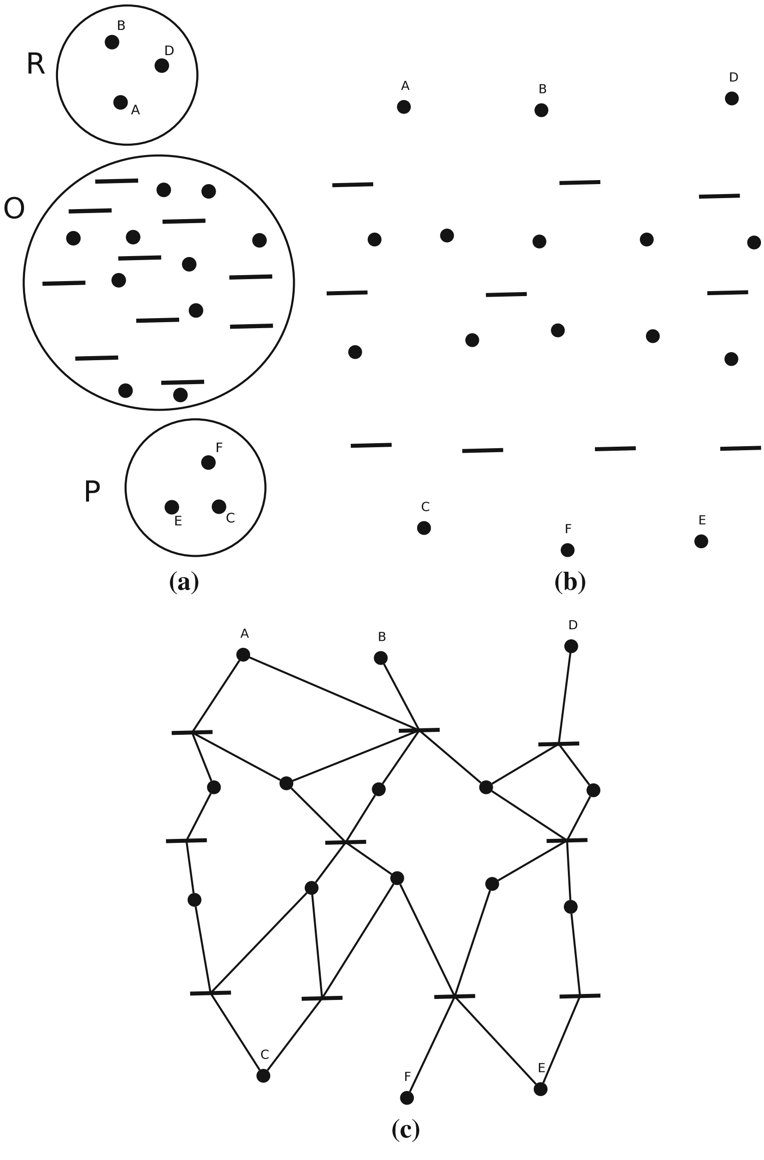
To search for candidate mechanisms it is necessary to consider each feasible alternative. Therefore, a non-ambiguous and systematic representation is required. The use of P-graphs is proposed for this purpose. P-Graphs were originally introduced by Friedler et al. for process synthesis [13] and have been used to propose reaction pathways [10,22]. This representation is close to Species-Reaction graphs (SR graphs) [6], but without labels on edges.

P-graphs consist of two sets of nodes: operations (or reactions) and species. These nodes are linked by arcs, which state a relationship. P-graphs allow an accurate representation of reactions or processes when compared with conventional graphs (digraphs and signal flow graphs) [13].

The search for reaction mechanisms in a reaction network has been addressed in previous works [10,13,14,22]. A global reaction (E) is needed to define global reactants (R) and products (P) of a reaction system (Fig. 1). These species must be included in all feasible P-graphs. A set of feasible reactions has to be defined, called O (from operations). This set summarizes all the feasible reactions discussed by the scientific community (Fig. 1a). The set of reactions imposes intermediates. While the set O is a list of reactions, the set M is a set of the included species (reactants, intermediates and products) [13].

After the definition of sets, a Maximal Structure is generated through an algorithm, the Maximal Structure Generation (MSG) presented by Friedler et al. [10,14]. This structure contains all the combinatorial pathways [14], so that all relations within the set O are included in the Maximal Structure (Fig. 1b, c).

A mechanism has to meet the mass balance within the network, which can be evaluated either in forward or backward direction. A procedure is also necessary to connect global reactants and products through the reaction network for searching feasible mechanisms. A general algorithm (PBT) was published for this purpose [10]. This algorithm generates all pathways within a maximal structure represented by a P-graph. In this strategy, the mechanisms with a correct mass balance are distinguished through the feasibility of a Linear Programming problem for deciding stoichiometric factors [10]. The chemical species are classified as active or inactive through the process, in order to ensure the feasibility of the concluded pathways. The activation also allows to explore feasible solutions by enumeration. The algorithm is composed



(a) (b)

(c)

Fig. 1 Maximal structure generation (MSG). **a** Sets, **b** all elements, **c** maximal structure

by three types of steps: synthetic, to consume the active species; retro-synthetic, to produce the active species; and back-tracking steps, invoked when the LP subproblem to find stoichiometric factors is infeasible. The process is combinatorially complete. However, the search is not exhaustive since the infeasibility of a LP subproblem justifies the exclusion of the set of reactions steps triggering the infeasibility. As a consequence, an infeasible subproblem is not solved repeatedly.

Table 1 Reactions considered in the system

Label	Reaction	Reported by
1	$H_2 + 2s \rightleftarrows 2Hs$	[35]
2	$CO_2 + s \rightleftarrows CO_2s$	[24]
3	$CO_2s + s \rightleftarrows COs + Os$	[24]
4	$COs + s \rightleftarrows Cs + Os$	[35]
5	$COs \rightleftarrows CO + s$	[35]
6	$Cs + Hs \rightleftarrows CHs + s$	[35]
7a	$CHs + Hs \rightleftarrows CH_2s + s$	[35]
7b	$CH_2s + Hs \rightleftarrows CH_3s + s$	[35]
7c	$CH_3s + Hs \rightleftarrows CH_4s + s$	[35]
7d	$CH_4s \rightleftarrows CH_4 + s$	[35]
8	$Os + Hs \rightleftarrows OHs + s$	[35]
9	$OHs + Hs \rightleftarrows H_2Os + s$	[35]
10	$H_2Os \rightleftarrows H_2O + s$	[35]
11	$COs + Hs \rightleftarrows HCOs + s$	[9]
12	$HCOs + s \rightleftarrows CHs + Os$	[9]
13	$COs + OHs \rightleftarrows HCO_2s + s$	[32]
14	$HCO_2s + OHs \rightleftarrows CO_2s + H_2Os$	[32]
15	$HCO_2s + s \rightleftarrows CO_2s + Hs$	[32]
16	$COs + Hs \rightleftarrows Cs + OHs$	[24]
17	$HCO_2s + s \rightleftarrows HCOs + Os$	[24]
18	$CO_2s + OHs \rightleftarrows HCO_3s$	[4]
19	$HCO_3s + Hs \rightleftarrows HCO_2s + OHs$	[4]

The free sites on catalyst surface are denoted by s. Accordingly, the adsorbed species are identified with an s suffix

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 be evaluated either 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: 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 combinatorial enumeration of pathways. The number of combinatorial candidates for 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 justifying its selection. All these reactions have been identified 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 are presented in the following section.

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, as demonstrated below. This theoretical reduction of the system infers 19 reactions, and therefore ≈ 1 billion of combinatorially feasible mechanisms.

The routines for the Maximal Structure generation and the search for candidate mechanisms with P-graph theory were adapted from previous developments [10,14] and implemented in GNU Octave [8].

2.2 Definitions and theorems

This section presents the definitions, lemmas and a theorem for the creation and use of reaction blocks. The proofs of lemmas and the theorem have been included in the Appendices.

2.2.1 Definition 1

A *feasible pathway* is a p-graph (m, o) with mass balance satisfaction. It connects reactants and products of a global reaction (E) with reactions $(o \subseteq O)$ from a defined set (O). This p-graph has been founded in the Maximal Structure by the PBT algorithm [10]. The set m is a subset of predefined species M and covers all species that participate in reactions belonging to o. The set of all feasible pathways within the Maximal Structure is denoted by $mec\,[O]$.

2.2.2 Definition 2

A *reaction block* (o_{RB}) is a subset of the reactions set $(o_{RB} \subseteq O)$. Its reactions are connected in series, allowing branches. o_{RB} covers a set of species (m_{RB}) divided in reactants (r_{RB}), intermediates (i_{RB}) and products (p_{RB}) of the reaction block. The set o_{RB} is such that no species in i_{RB} participate in reactions belonging to $O \backslash o_{RB}$. In this way, no intermediate in i_{RB} is present outside the reaction block. A reaction block can be summarized as an aggregated reaction S_{RB} (see *Definition 3* and Fig. 2).

2.2.3 Lemma 1

Let y_i be a reaction belonging to o_{RB} a reaction block in O. Let (m, o) be a feasible pathway in $mec\,[O]$. If y_i participates in the pathway $(y_i \in o)$, then all reactions in the reaction block have to be in the pathway $(o_{RB} \subseteq o)$. The proof of this lemma has been included in "Appendix A".

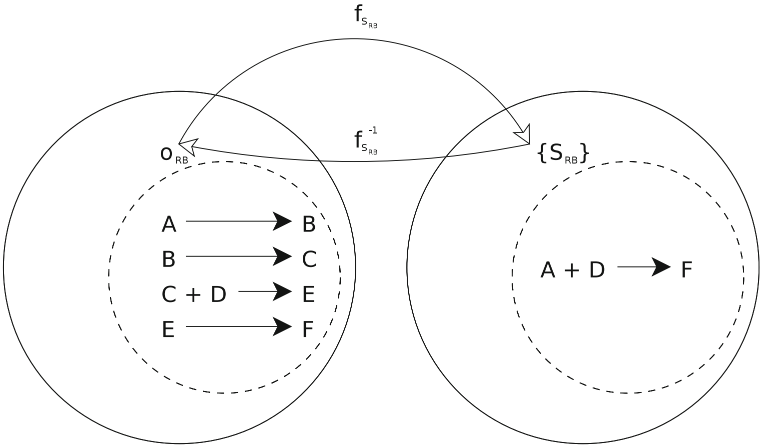


Fig. 2 Example: construction of reaction S_{RB} from reaction block o_{RB}. A construction function $f_{S_{RB}}$ is defined between sets

2.2.4 *Definition 3*

An *aggregate reaction* (S_{RB}) for the block o_{RB} is a composition of all the reactions in the block. It is constructed as a summation:

$$S_{RB} := \sum_{i \in \{1,2,\ldots,|o_{RB}|\}} \gamma_i \cdot y_i \qquad\qquad y_i \in o_{RB} \tag{2}$$

In this equation, the γ_i factors are such that:

- The reactants of S_{RB} are r_{RB}.
- The products of S_{RB} are p_{RB}.
- All intermediates of the reaction block (i_{RB}) are not in S_{RB}.
- The same mass balance is satisfied between r_{RB} and p_{RB} through the p-graph (m_{RB}, o_{RB}) and S_{RB}.

As an example, the block in the left hand side of Fig. 2 can be condensed into an aggregate reaction as shown in the right hand side of the same figure.

2.2.5 *Definition 4*

After the construction of S_{RB} two functions are defined between the sets o_{RB} and $\{S_{RB}\}$: an *aggregate reaction function* ($f_{S_{RB}}(o_{RB}) := \{S_{RB}\}$) and its inverse ($f^{-1}_{S_{RB}}(\{S_{RB}\}) := o_{RB}$). Note that by construction $f_{S_{RB}}$ is a bijective function (Fig. 2).

2.2.6 Definition 5

A feasible pathway (m, o) can include reactions in o_{RB} or not. The sets of pathways in each case can be defined as follows:

$$\begin{aligned} mec\,[O]^{\underline{o_{RB}}} &= \{(m, o)\ a\ feasible\ pathway\ | \\ & m \subseteq M\ \wedge\ o \subseteq O\ \wedge\ o \cap o_{RB} \neq \emptyset\} \end{aligned} \tag{3}$$

$$\begin{aligned} mec\,[O]^{\overline{o_{RB}}} &= \{(m, o)\ a\ feasible\ pathway\ | \\ & m \subseteq M\ \wedge\ o \subseteq O\ \wedge\ o \cap o_{RB} = \emptyset\} \end{aligned} \tag{4}$$

Since the last condition in the definition of $mec\,[O]^{\underline{o_{RB}}}$ and $mec\,[O]^{\overline{o_{RB}}}$ only has two possibilities, those sets establish a partition on $mec\,[O]$, as stated in Lemma 2.

2.2.7 Lemma 2

Let $o' \subseteq O$. The collection $\{mec\,[O]^{\underline{o'}}, mec\,[O]^{\overline{o'}}\}$ partitions $mec\,[O]$. The proof of this lemma is presented in "Appendix B".

2.2.8 Theorem 1

Given a set of reactions (O) with a reaction block (o_{RB}), there is a bijective function (F) relating the pathways obtained from O and the pathways obtained from $O^R := (O \backslash o_{RB}) \cup \{S_{RB}\}$.

The proof of this theorem is presented in "Appendix C".

Theorem 1 can be used for obtaining feasible pathways with an aggregated set of reactions. If a reaction block is created within a reaction set, then every pathway found by the PBT algorithm [10] in the reduced set of reactions has a connection with a pathway in the disaggregated set of reactions through the F function. The pathways constructed by the PBT algorithm [10] in the aggregated set of reactions can include the reaction S_{RB} or not. When it is included, the pathway can be rewritten through $f_{S_{RB}}^{-1}$ substituting S_{RB} by elementary reactions; if it is not included, both pathways are identical in the reduced and the original space of reactions.

The reaction mechanisms are constructed with elementary reactions for explaining the molecular changes step by step. The use of elementary reactions allows to postulate a rate limiting step, and create a kinetic expression supported by these hypotheses. In this context, Theorem 1 allows to use the PBT algorithm [10] in non-elementary reaction sets. In this strategy, the constructed pathways can be translated to elementary reaction sets with the aforementioned conversion through $f_{S_{RB}}^{-1}$.

The next section illustrates the use of reaction blocks on a methanation system and the subsequent search for feasible mechanisms. In this paper, Theorem 1 is necessary in order to perform the search of feasible pathways in a reduced space of reactions and convert back the mechanisms in terms of elementary reactions. No pathway is lost in this process, as demonstrated herein.

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, 92 feasible mechanisms were found. Further filtration was performed looking for reported intermediates on catalyst surface: COs and HCOs, reported by Eckle et al. [9]. 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 D".

Figure 3 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 (→) and reverse (←) ways have been classified in a single reaction. Reactions 1, 2, 7, and 10 are present in the complete set of filtered pathways. Since Reaction 7 is a reaction block, all filtered pathways should include reactions 7a to 7d from Table 1.

Figure 4 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. 3: 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 can 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. 4 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 assumed 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 the Methodology. The confirmed reactions and species have been marked with gray in Fig. 4. The inclusion of all other reactions and species have to be proved through

Table 2 Feasible mechanisms for CO_2 methanation expressed as reaction sets

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

Table 2 continued

Number	Reaction set										
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

The participation of COs and HCOs is imposed, because they have been identified as well known intermediates [9]

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

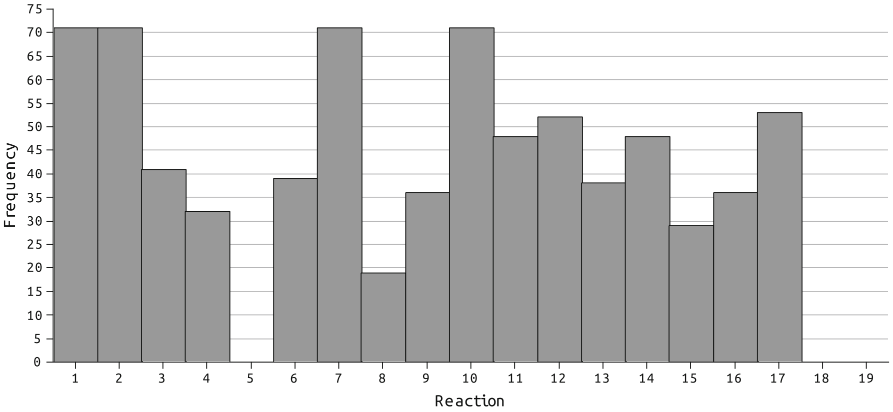


Fig. 3 Histogram for the appearance of each reaction within the 71 filtered pathways represented in Table 2 and “Appendix D”

3. Structure the answers to the last question: No (0) or Yes (1). Within the Fig. 4 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 feasibility of each scenario: (0) or (1) will be true. Impose the respective logic consequences on Fig. 4 and Table 2.
5. If all species are confirmed, stop. Else, return to step 1 with the new information.

With this algorithm, 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 can finish 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. These experiments are different from the molecular characterization of intermediates. To confirm or discard the remaining free reactions a causality relation is necessary among species: the demonstration of a transition.

Taking into account the Fig. 4, 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.

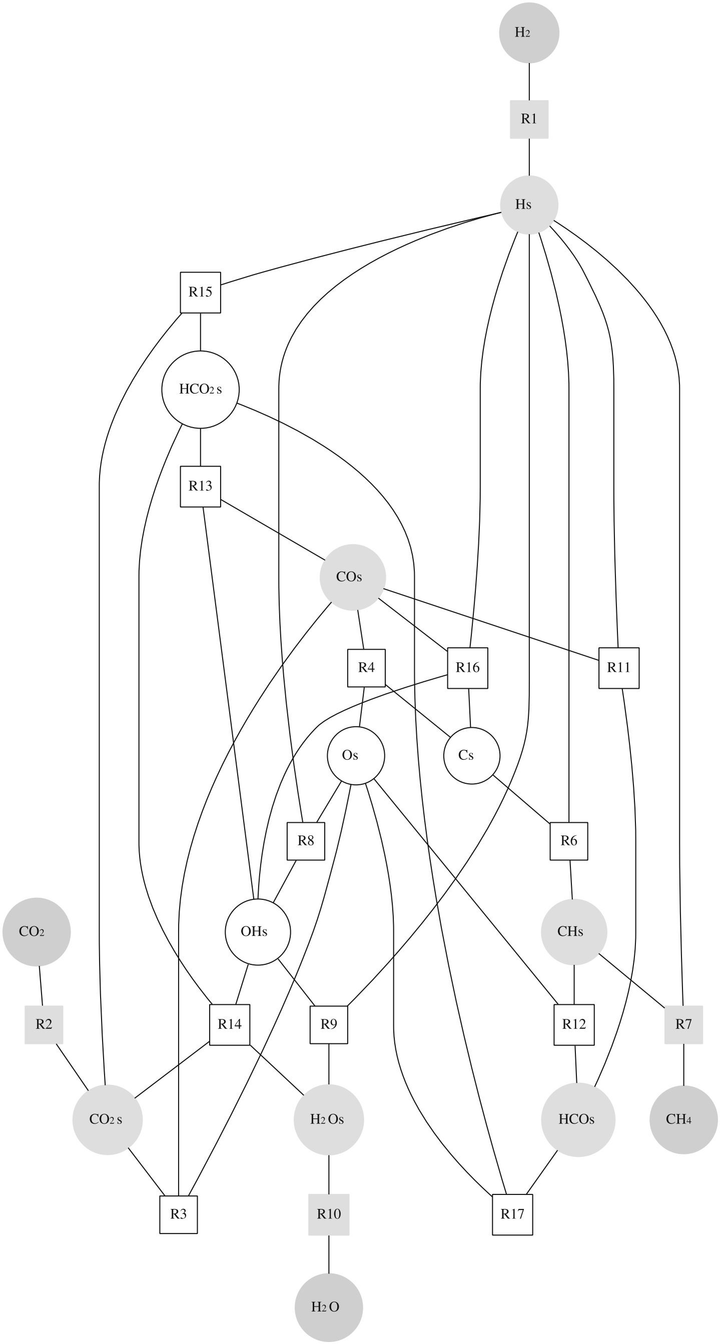


Fig. 4 Maximal structure after pathway filtration. The participation of COs and HCOs is imposed, because they have been identified as well known intermediates [9]. Species and reactions marked with gray are present in all filtered pathways (Table 2). The active site on surface (*s*) has been omitted in this representation to ease the reading

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 Table 2, 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:
   (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. Then, this scenario is infeasible.
   (1) Yes. *OHs* is confirmed. It 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 D", Fig. 6.

It is important to highlight the termination 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.

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

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

5 Conclusions

This work introduces the use of reaction blocks for reducing the domain of feasible reactions in a reaction system. The aforementioned reduction maintains the number of feasible pathways, as a consequence of Theorem 1. This theorem establishes a bijective function between the sets of feasible pathways within the original and the reduced space of reactions. The use of reaction blocks is also based on lemmas and definitions herein presented.

The main use of Theorem 1 is the validation of the search of feasible pathways in a reduced space of reactions, while no feasible mechanism is lost. This theorem also formalizes a way for converting back the mechanisms found in the reduced set of reactions in terms of the original set of elementary reactions. Theorem 1, the lemmas, and definitions provide a basis for further theorems, in order to improve the search of reaction mechanisms within a Maximal Structure of feasible reactions.

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

Acknowledgements Felipe A. Díaz-Alvarado wants to thank the FCFM Grant *Apoyo a la Inserción Académica* 2016; University of Chile. This project was financed by *CONICYT/FONDECYT de Iniciación en Investigación/2017-11170042*. The authors acknowledge the loan of *eowyn* cluster by J.C. Salgado from University of Chile.

Appendix A: Proof of Lemma 1

If (m, o) is a feasible pathway, it has been found within the Maximal Structure by the PBT algorithm [10]. Then, theorems R1 to R6 [10] are valid for this pathway. Since theorem R3 is valid, all intermediates in a feasible pathway have to be completely consumed. Taking into acount the definition of o_{RB}, the intermediates in the reaction block (i_{RB}) are not included in other reactions outside the block. Then, the reactions for consuming these intermediates belong to the reaction block o_{RB}. By Theorem R3 and Axiom T4 [10], all reactions in o_{RB} have to be included in o. Otherwise, there exists an intermediate $i^* \in i_{RB}$ which is not completely consumed, violating Theorem R3 [10].

Appendix B: Proof of Lemma 2

- No intersection: Let (m^*, o^*) be a feasible mechanism belonging to $mec\,[O]^{\underline{o'}}$. Then $o^* \cap o' \neq \emptyset$. By definition of $mec\,[O]^{\overline{o'}}$, $(m^*, o^*) \notin mec\,[O]^{\overline{o'}}$. Similarly, an element in $mec\,[O]^{\overline{o'}}$ cannot be in $mec\,[O]^{\underline{o'}}$, so $mec\,[O]^{\underline{o'}} \cap mec\,[O]^{\overline{o'}} = \emptyset$.
- Covering: Let (m^*, o^*) be an element in $mec\,[O]^{\underline{o'}} \cup mec\,[O]^{\overline{o'}}$. Then:

  $$\begin{aligned} mec\,[O]^{\underline{o'}} \cup mec\,[O]^{\overline{o'}} = \{&(m^*, o^*)\ a\ feasible\ pathway\ | \\ &\left[m^* \subseteq M \wedge o^* \subseteq O \wedge o^* \cap o' \neq \emptyset\right] \vee \left[m^* \subseteq M \wedge o^* \subseteq O \wedge o^* \cap o' = \emptyset\right]\} \end{aligned}$$

  With a distribution of *or* over *and* we have:

  $$\begin{aligned} mec\,[O]^{\underline{o'}} \cup mec\,[O]^{\overline{o'}} = \{&(m^*, o^*)\ a\ feasible\ pathway\ | \\ &m^* \subseteq M\ \wedge\ o^* \subseteq O\ \wedge \left[\ o^* \cap o' \neq \emptyset\ \vee\ o^* \cap o' = \emptyset\right]\} \end{aligned}$$

  Since the term in parenthesis [ ] is a tautology, we have:

  $$\begin{aligned} mec\,[O]^{\underline{o'}} \cup mec\,[O]^{\overline{o'}} = \{&(m^*, o^*)\ a\ feasible\ pathway\ | \\ &m^* \subseteq M\ \wedge\ o^* \subseteq O\} \end{aligned}$$

  The last statement is the definition of a feasible pathway in O, so $(m^*, o^*) \in mec\,[O]$. Then $mec[O] = mec[O]^{\underline{o'}} \cup mec[O]^{\overline{o'}}$.

Appendix C: Proof of Theorem 1

- The function: Let $(m^*, o^*) \in mec[O]$. Let F be a piecewise function defined as follows:

  $$F\left[(m^*, o^*)\right] = \begin{cases} F_1[(m^*, o^*) \in mec[O]^{\underline{o_{RB}}}] = (m^{*2}, o^{*2}) \in mec[O^R]^{\underline{S_{RB}}} \\ F_2[(m^*, o^*) \in mec[O]^{\overline{o_{RB}}}] = (m^{*2}, o^{*2}) \in mec[O^R]^{\overline{S_{RB}}} \end{cases}$$

  The functions F_1 and F_2 are defined as follows (see Fig. 5):

  $$\begin{aligned} F_1[(m^*, o^*)] &:= (m^{*2}, o^{*2}) \mid m^{*2} = m^* \backslash i_{RB}\ \wedge\ o^{*2} = (o^* \backslash o_{RB}) \cup \{S_{RB}\} \\ F_2[(m^*, o^*)] &:= (m^{*2}, o^{*2}) \mid m^{*2} = m^*\ \wedge\ o^{*2} = o^* \end{aligned}$$

  By Lemma 2, the collection $\{mec\,[O]^{\underline{o_{RB}}}, mec\,[O]^{\overline{o_{RB}}}\}$ partitions $mec\,[O]$. Also the collection $\{mec\left[O^R\right]^{\underline{\{S_{RB}\}}}, mec\left[O^R\right]^{\overline{\{S_{RB}\}}}\}$ partitions $mec\left[O^R\right]$. Both partitions are represented in Fig. 5. Therefore, the next steps in this proof will be demonstrated for F_1 and F_2 separately.

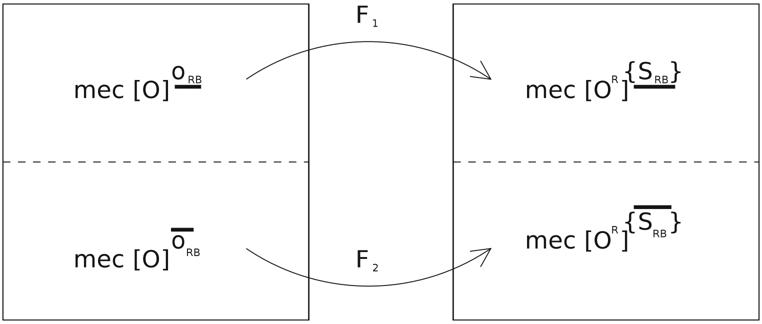


Fig. 5 Function F between sets of pathways. The subfunctions F_1 and F_2 are represented relating the elements into each partition

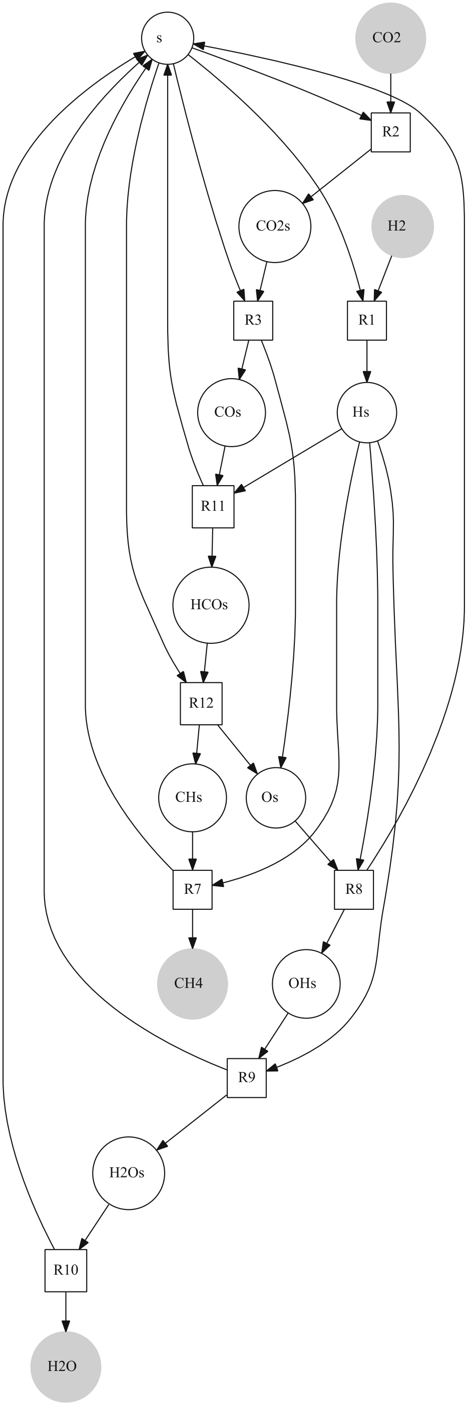
- Every pathway in $mec[O]$ has an image in $mec[O^R]$:
  - For F_1: It is possible to create o^{*2} since both $o_{RB} \subseteq o^*$ and $\{S_{RB}\}$ exist. The latter has been constructed with the function $f_{S_{RB}}$, which is feasible to apply because S_{RB} exists by definition of o_{RB}. The set $m^{*2} = m^* \backslash i_{RB}$ exists, because $(m^*, o^*) \in mec\,[O]^{\underline{o_{RB}}}$ and then $i_{RB} \subseteq m^*$.
    Is (m^{*2}, o^{*2}) a feasible pathway? (m^*, o^*) is a feasible pathway, because $(m^*, o^*) \in mec\,[O]^{\underline{o_{RB}}}$. Let y^* be a reaction in o_{RB}. By Lemma 1, if y^* belongs to the pathway then all $y \in o_{RB}$ belongs to the pathway. By definition of o_{RB}, all its intermediates are absent from other reactions outside the reaction block. The remotion of o_{RB} lets the pathway incomplete. Since reactions in o_{RB} have been removed, the intermediates i_{RB} are no longer necessary. Without o_{RB} the reactants r_{RB} and products p_{RB} are not linked through the pathway. They can be connected by the reaction S_{RB}. By definition of S_{RB}, it respects the same local mass balance than o_{RB}. Then, the new pathway has a feasible mass balance.
    In this statement, the sets m^{*2} and o^{*2} have been constructed, so every pathway in $mec\,[O]^{\underline{o_{RB}}}$ has an image in the pathways set $mec\left[O^R\right]^{\underline{\{S_{RB}\}}}$.
  - For F_2: It is possible to create o^{*2} and m^{*2}, because both definitions are equalities in F_2. (m^{*2}, o^{*2}) is a feasible pathway since (m^*, o^*) is also a feasible pathway. Then, every pathway in $mec\,[O]^{\overline{o_{RB}}}$ has an image in the pathways set $mec\left[O^R\right]^{\overline{\{S_{RB}\}}}$.
- The image of any pathway in $mec[O]$ is unique:
  - For F_1: Let (m^{*2}, o^{*2}) and (m^{*3}, o^{*3}) pathways in $mec\left[O^R\right]^{\underline{\{S_{RB}\}}}$ such that $F_1[(m^*, o^*)] = (m^{*2}, o^{*2})$ and $F_1[(m^*, o^*)] = (m^{*3}, o^{*3})$. As $m^{*2} = m^* \backslash i_{RB}$ and $m^{*3} = m^* \backslash i_{RB}$, then $m^{*2} = m^{*3}$. On the other hand $o^{*2} = (o^* \backslash o_{RB}) \cup \{S_{RB}\}_2$ and $o^{*3} = (o^* \backslash o_{RB}) \cup \{S_{RB}\}_3$. But $\{S_{RB}\}_2 = \{S_{RB}\}_3$ because $f_{S_{RB}}$ is bijective by Definition 4. Then, $(m^{*2}, o^{*2}) = (m^{*3}, o^{*3})$, so the image of (m^*, o^*) through F_1 is unique.
  - For F_2: Let (m^{*2}, o^{*2}) and (m^{*3}, o^{*3}) pathways in $mec\left[O^R\right]^{\overline{\{S_{RB}\}}}$ such that $F_2[(m^*, o^*)] = (m^{*2}, o^{*2})$ and $F_2[(m^*, o^*)] = (m^{*3}, o^{*3})$. As $m^{*2} = m^*$ and $m^{*3} = m^*$, then $m^{*2} = m^{*3}$. On the other hand $o^{*2} = o^*$ and $o^{*3} = o^*$, so

$o^{*2} = o^{*3}$. Then, $(m^{*2}, o^{*2}) = (m^{*3}, o^{*3})$, so the image of (m^*, o^*) through F_2 is unique.

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

See Figs. 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, and 76.

Fig. 6 P-graph N.1



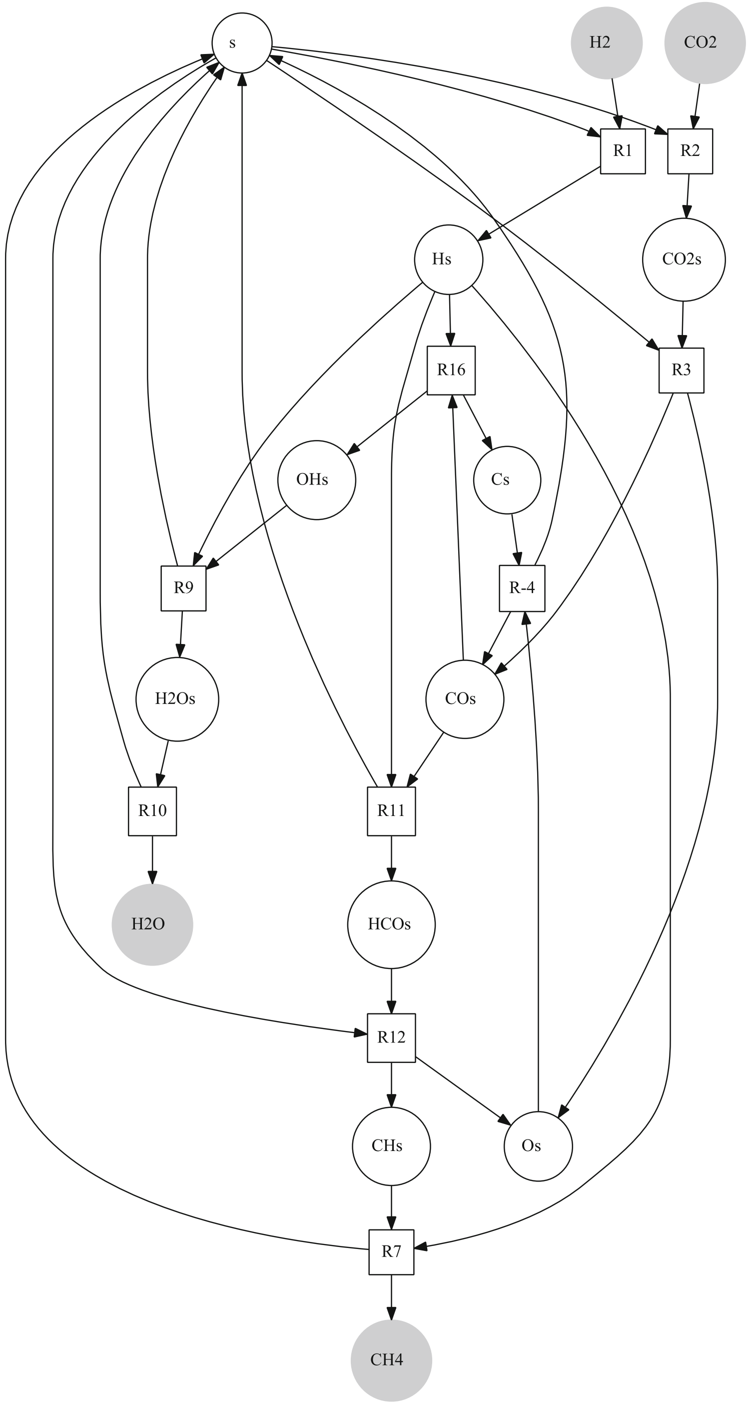


Fig. 7 P-graph N.2

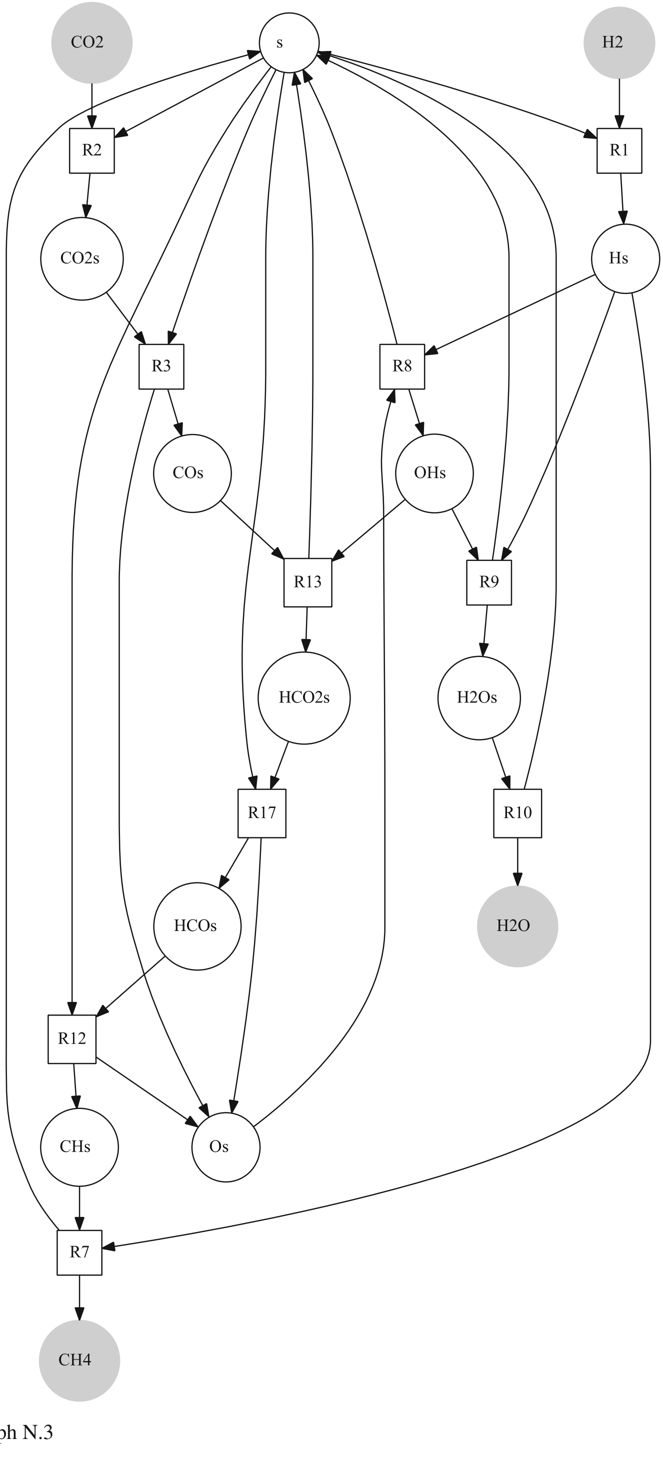


Fig. 8 P-graph N.3

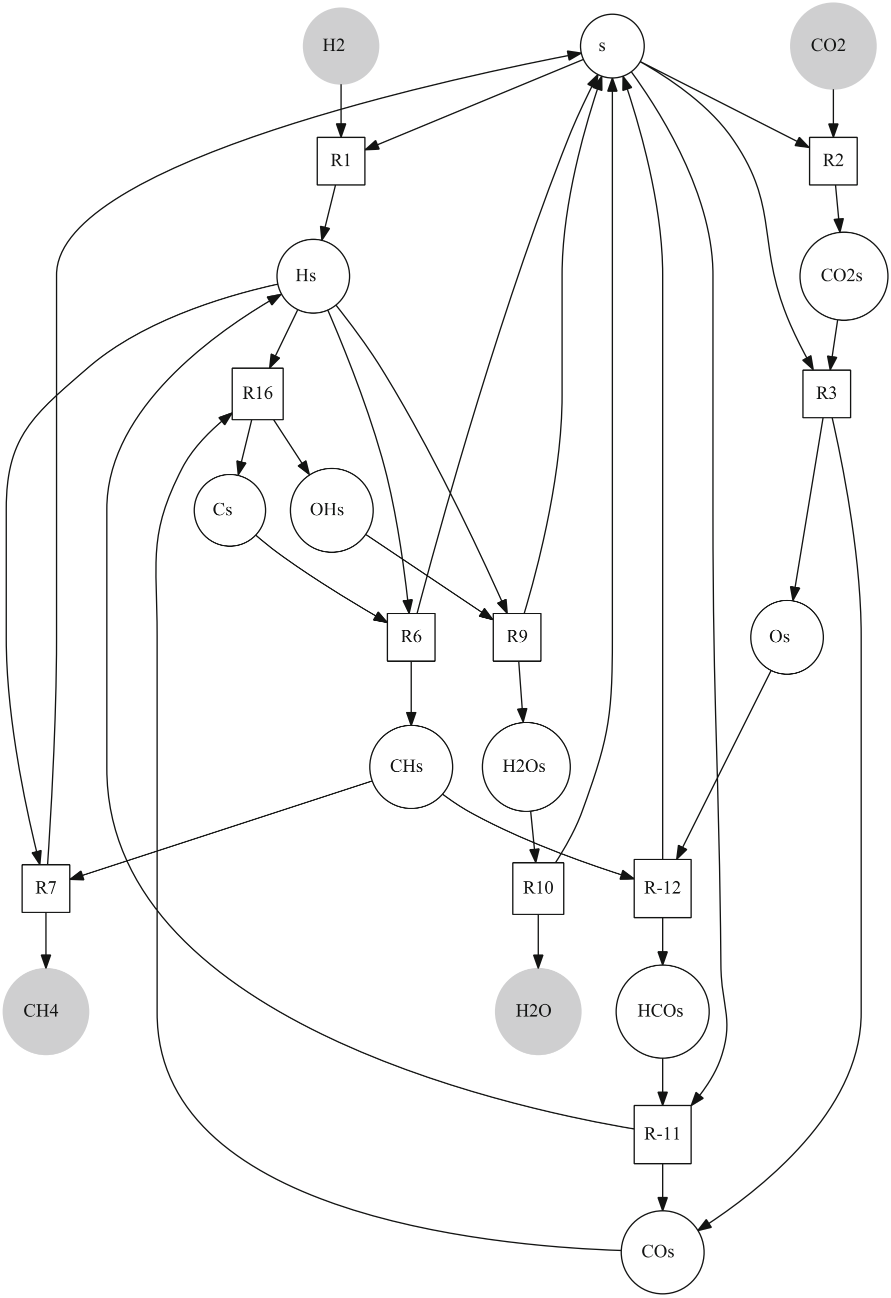


Fig. 9 P-graph N.4

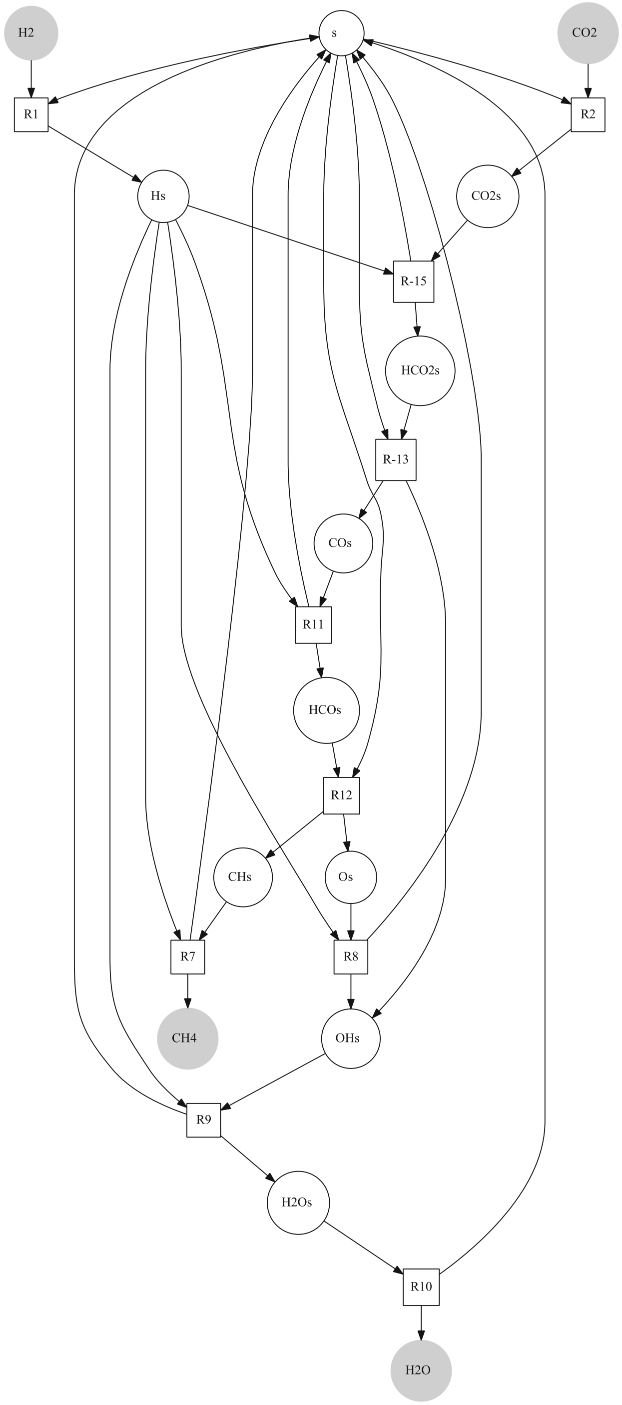


Fig. 10 P-graph N.5

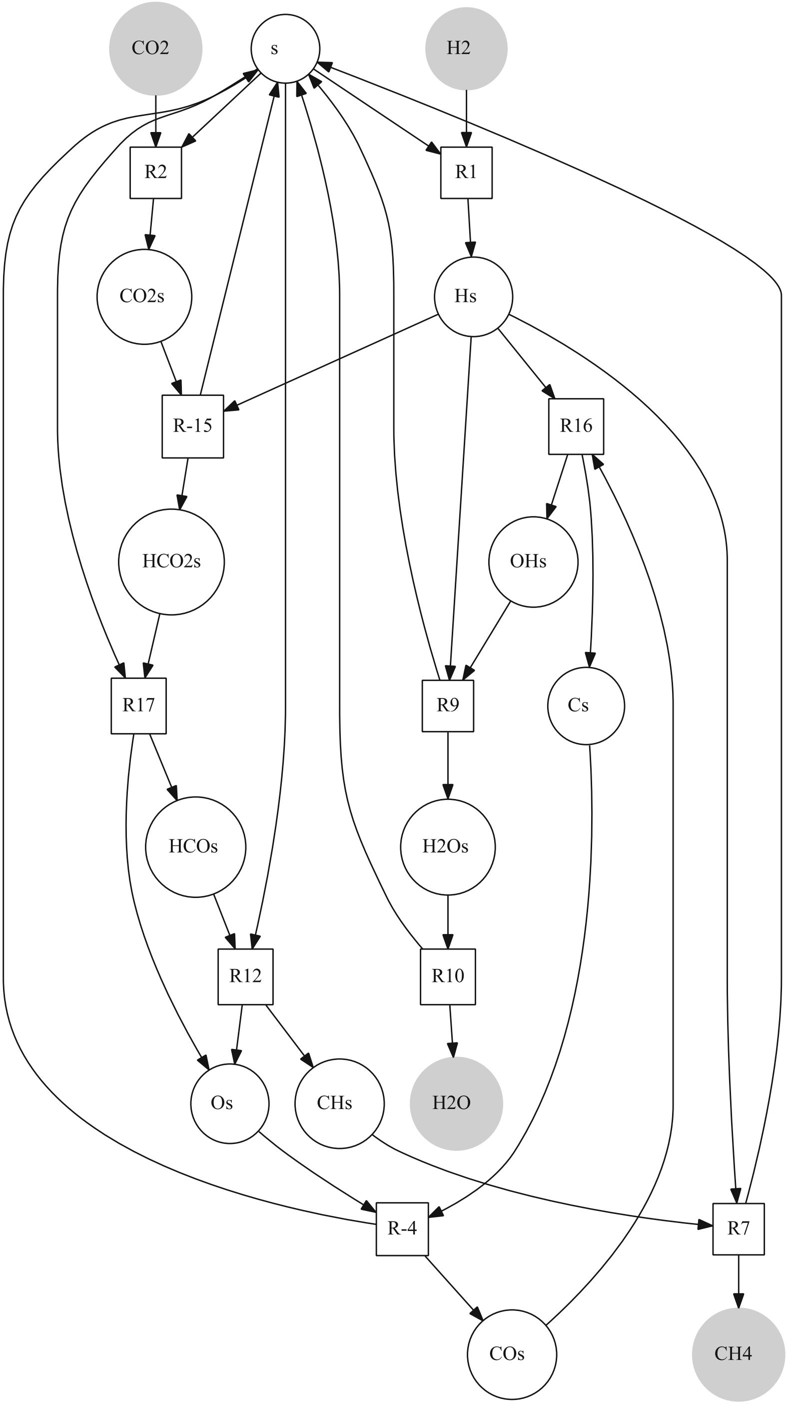


Fig. 11 P-graph N.6

Fig. 12 P-graph N.7

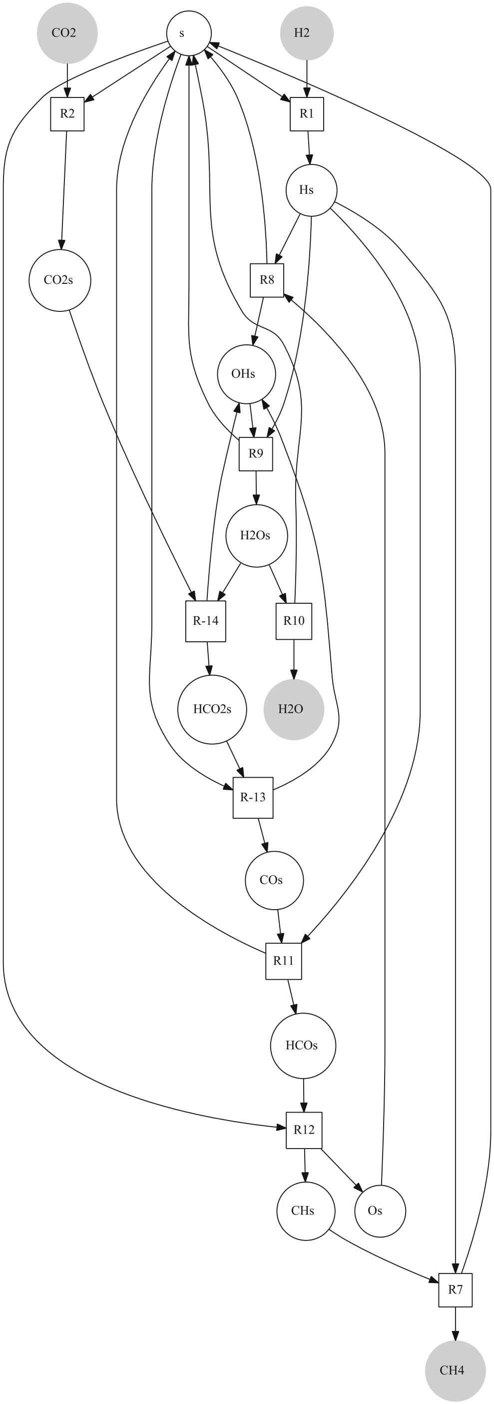


Fig. 13 P-graph N.8

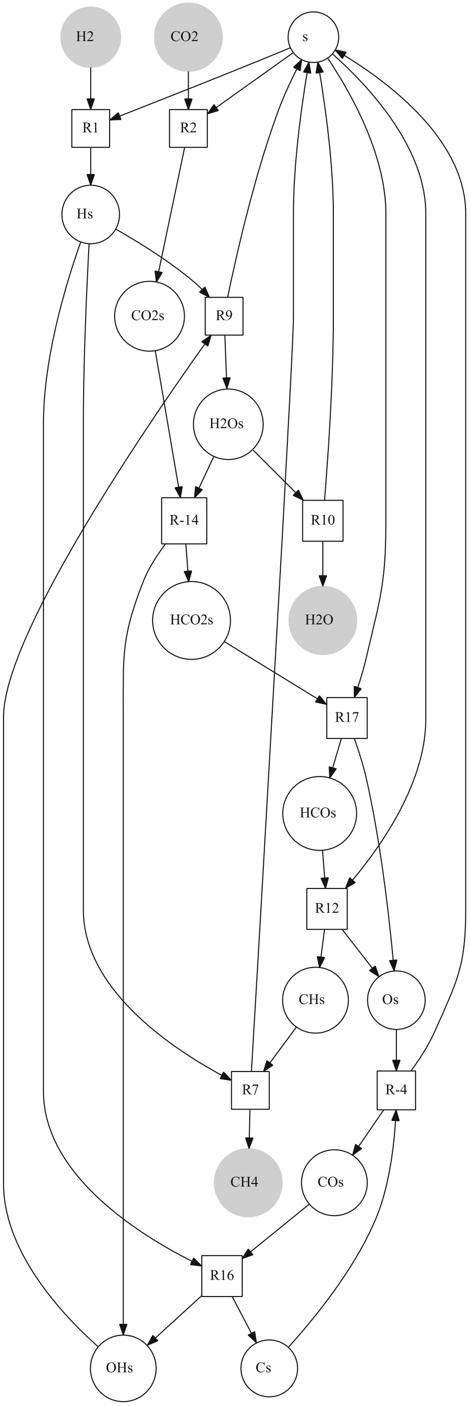


Fig. 14 P-graph N.9

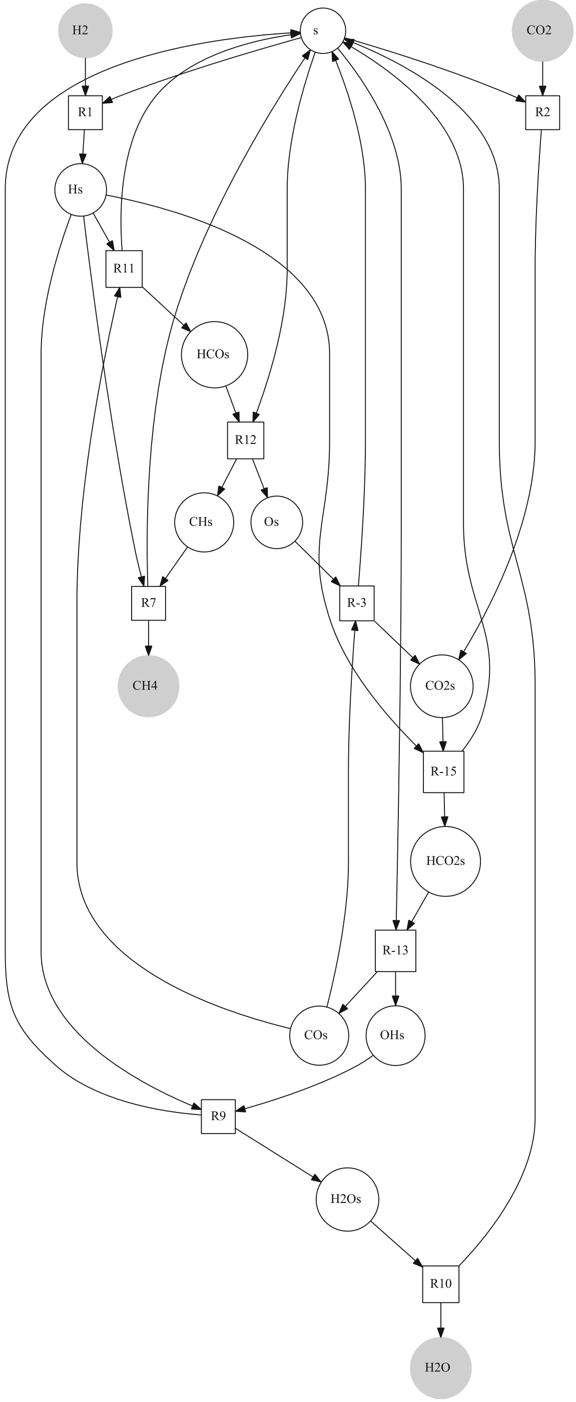


Fig. 15 P-graph N.10

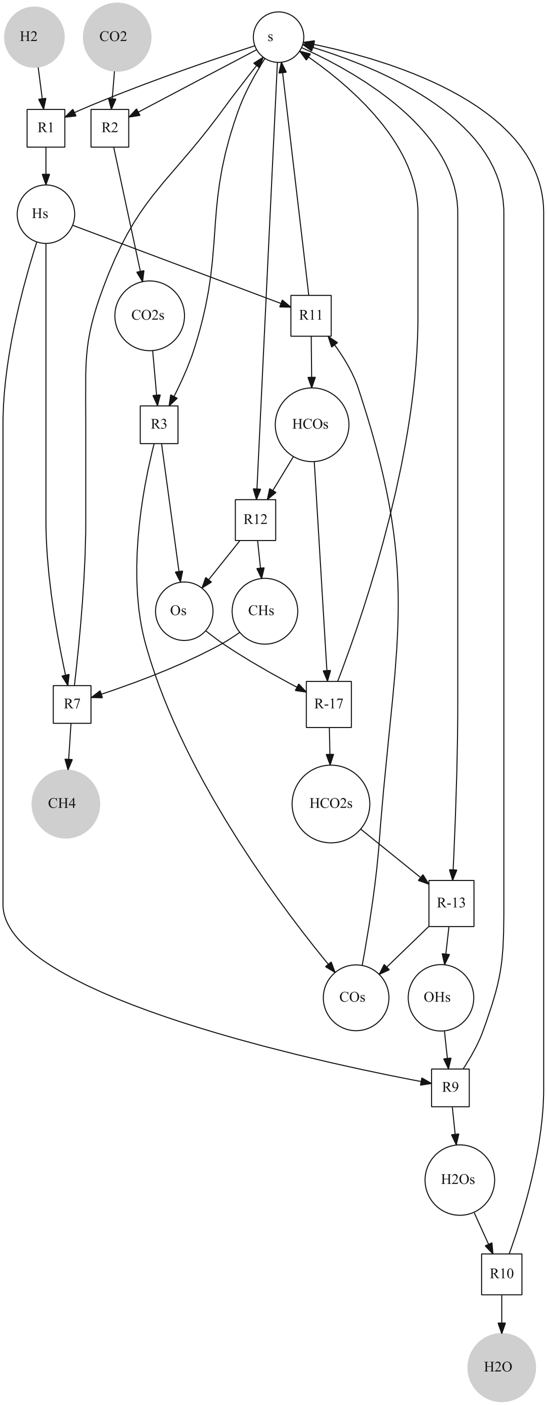
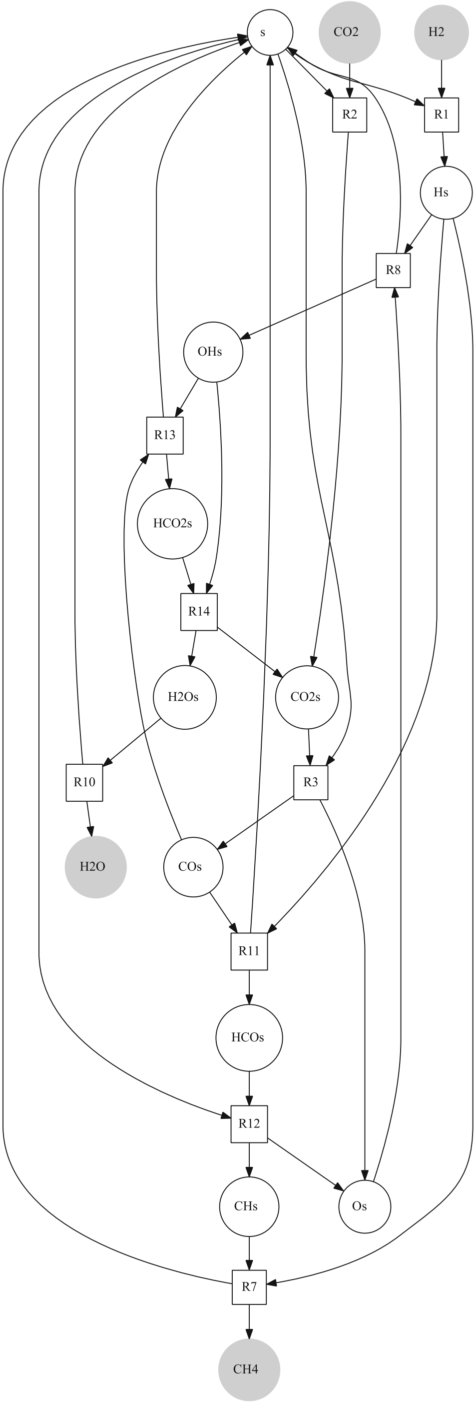


Fig. 16 P-graph N.11



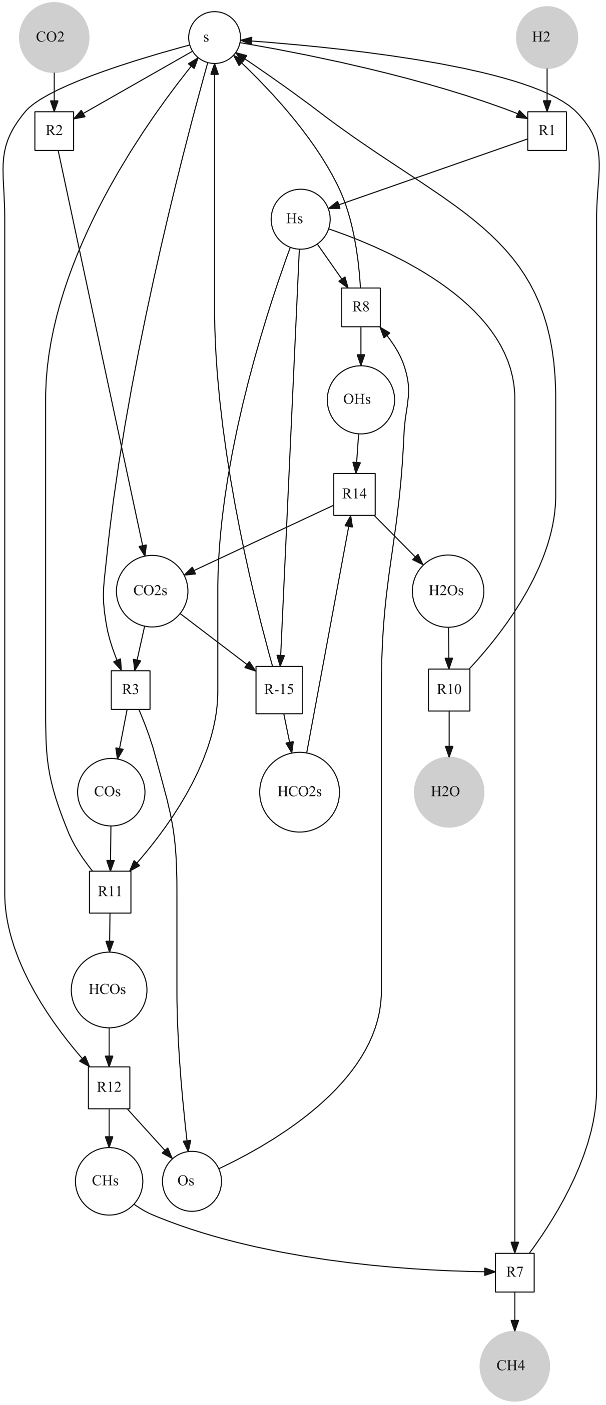


Fig. 17 P-graph N.12

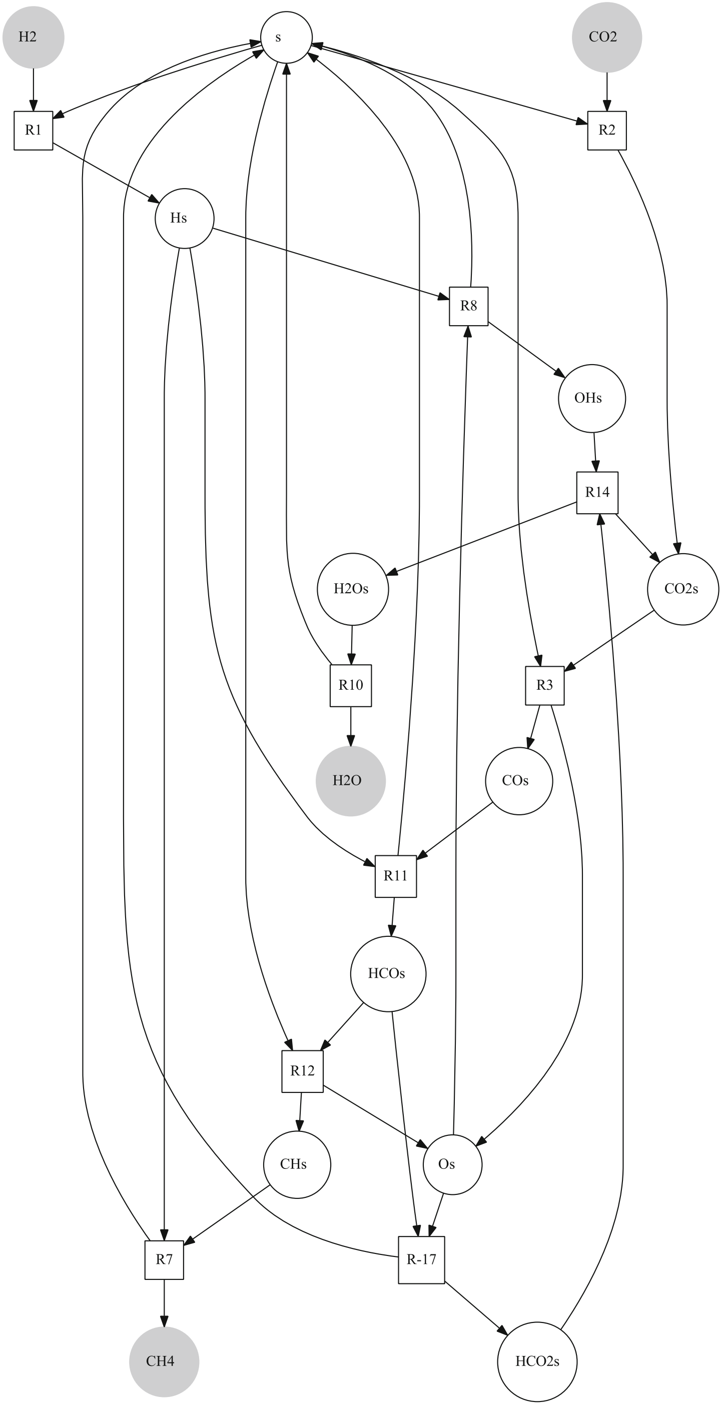


Fig. 18 P-graph N.13

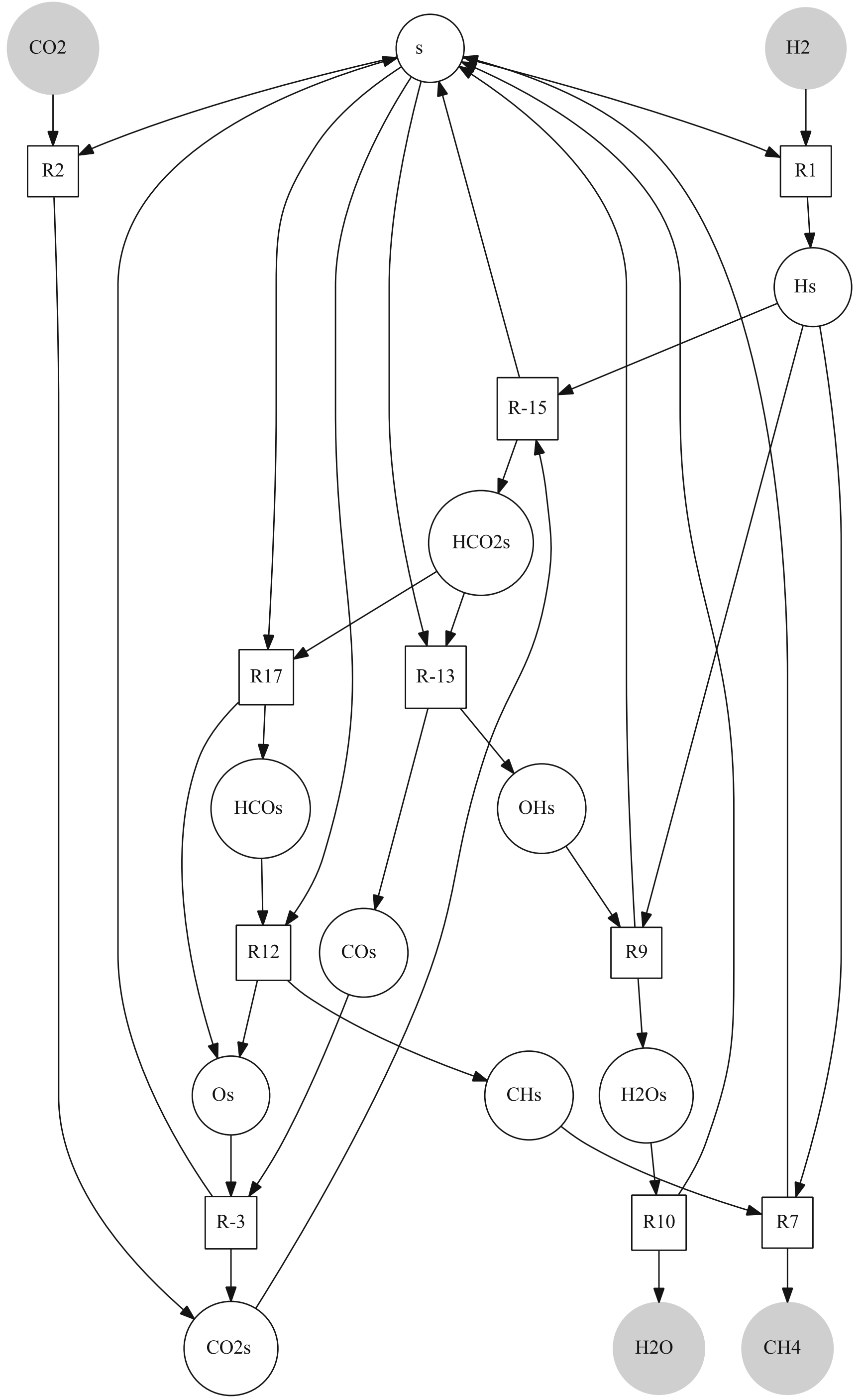


Fig. 19 P-graph N.14

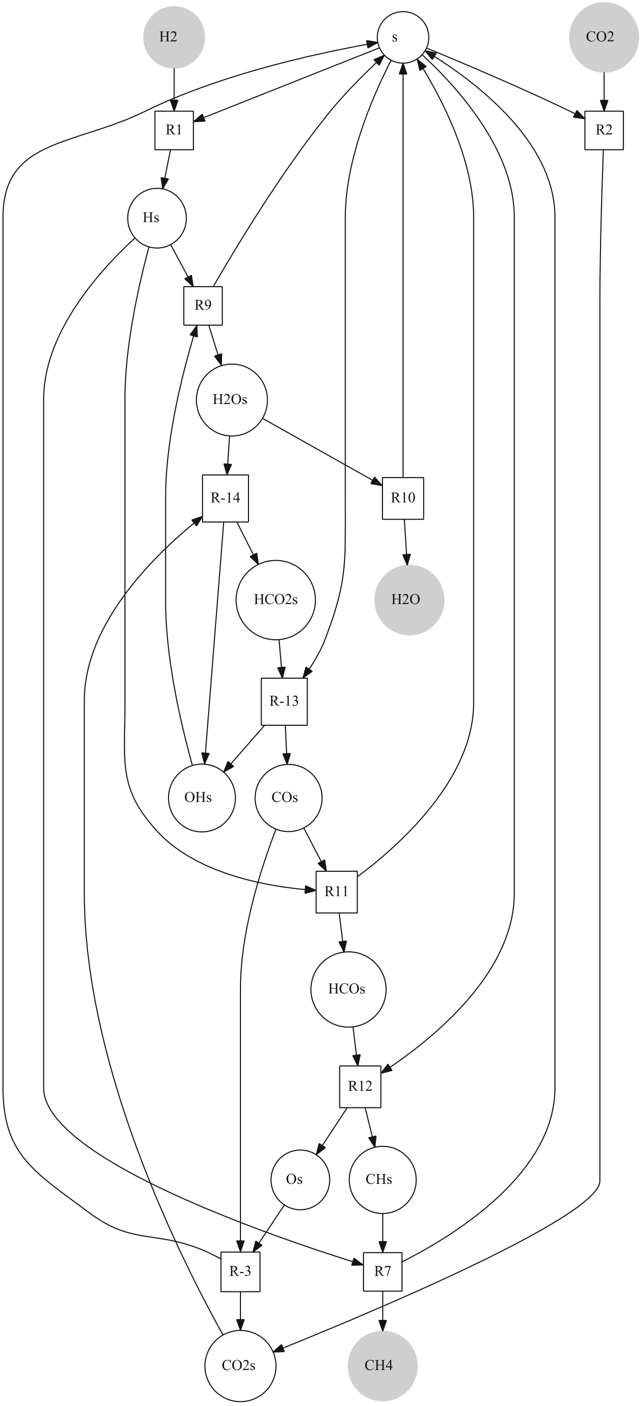


Fig. 20 P-graph N.15

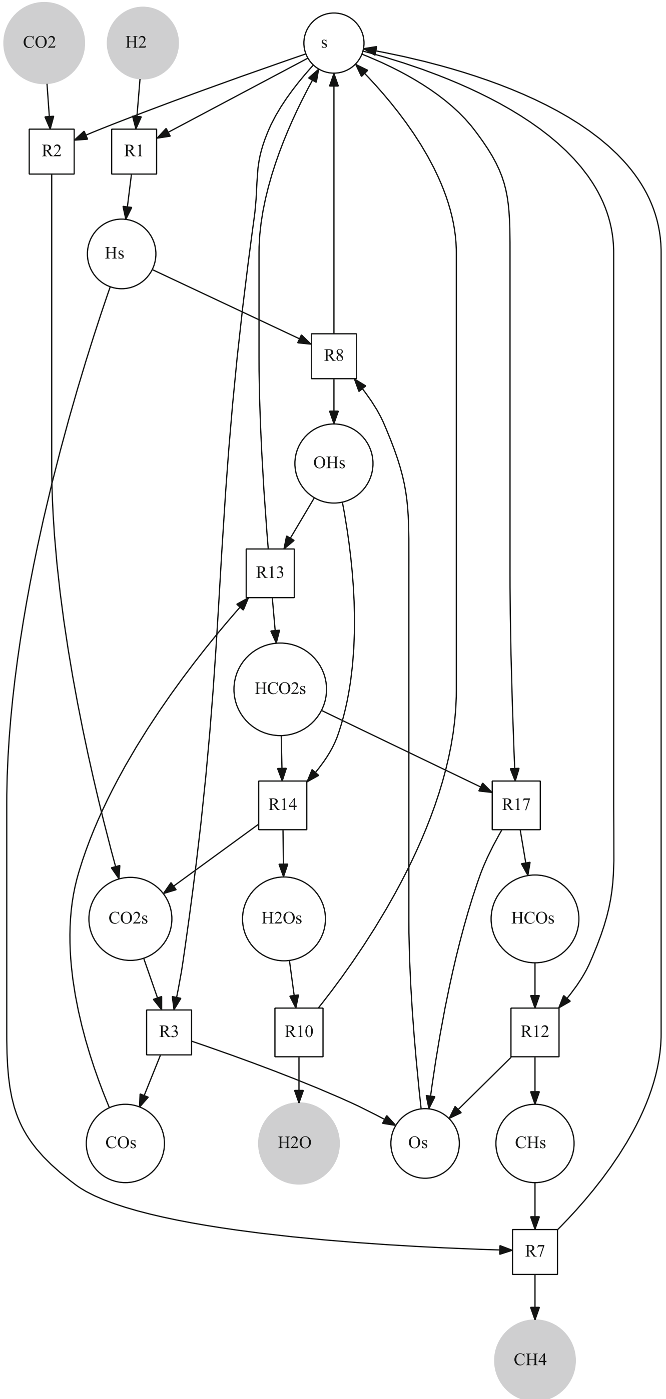


Fig. 21 P-graph N.16

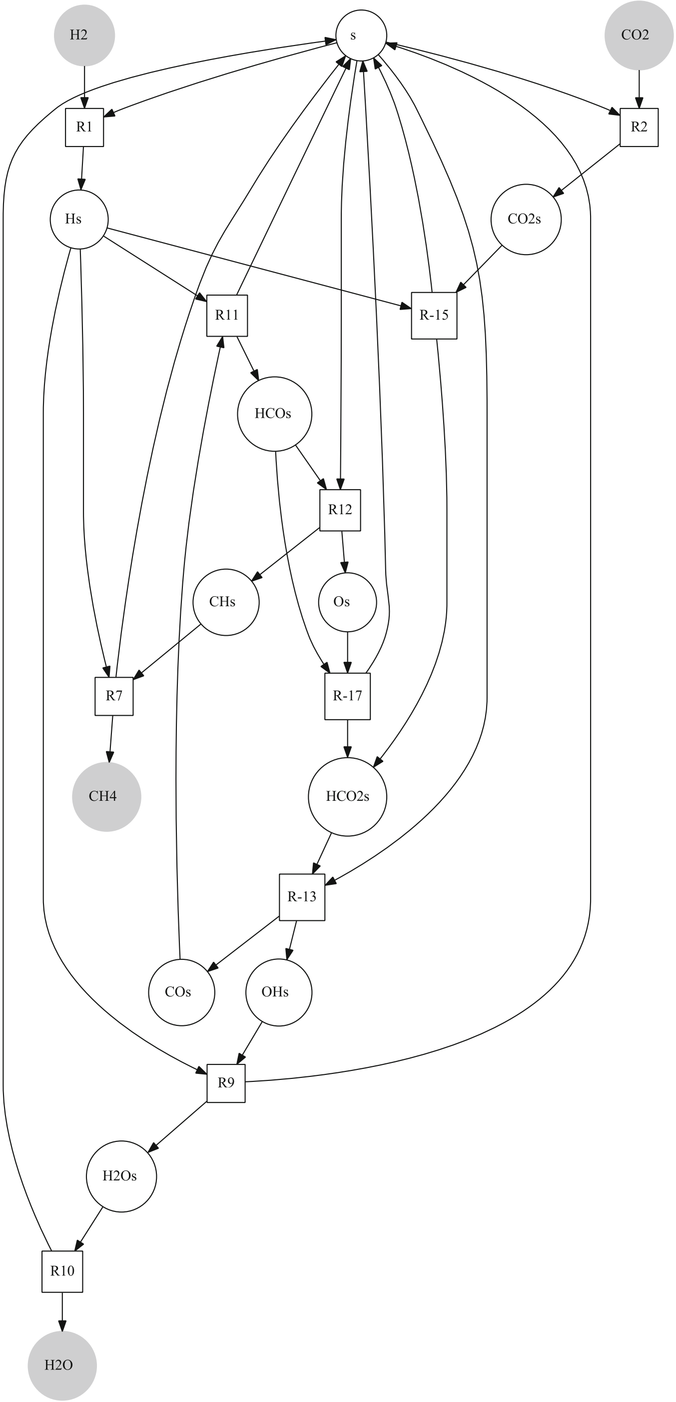


Fig. 22 P-graph N.17

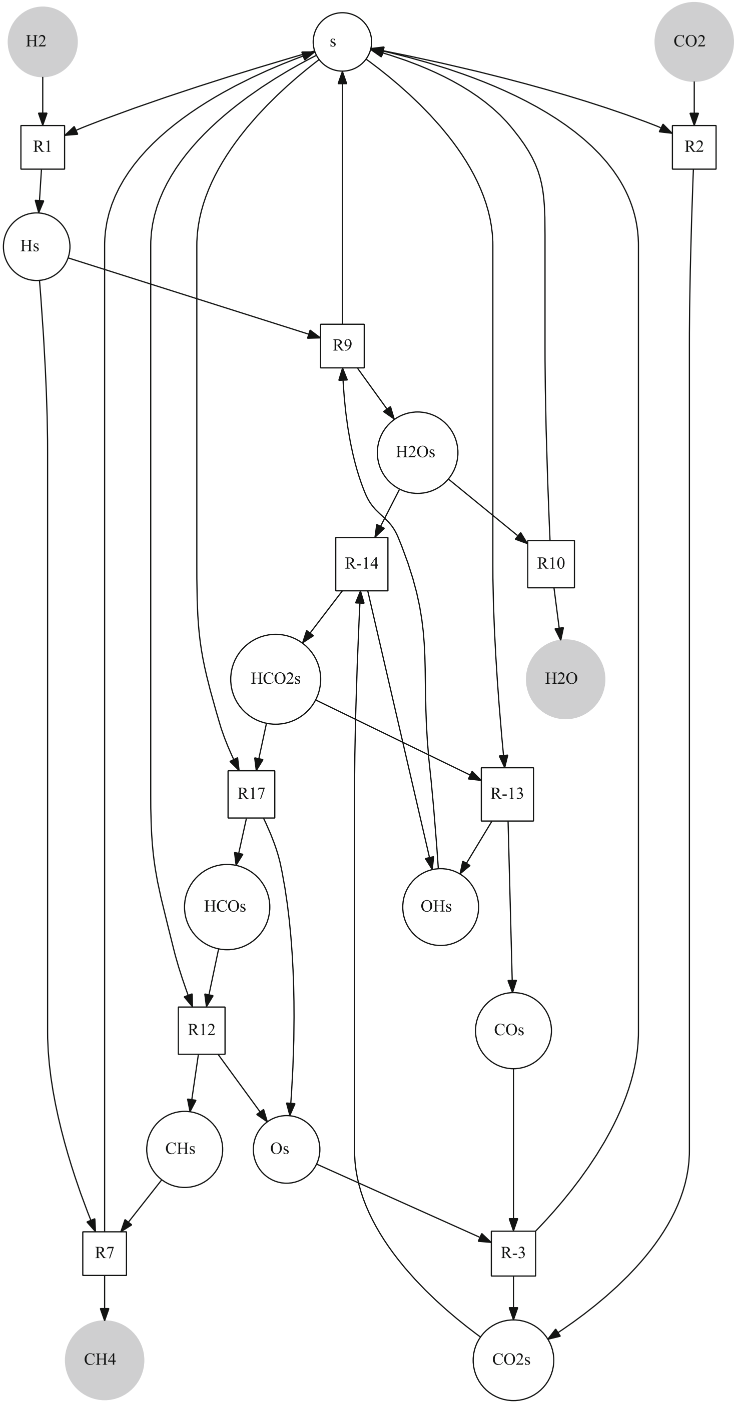
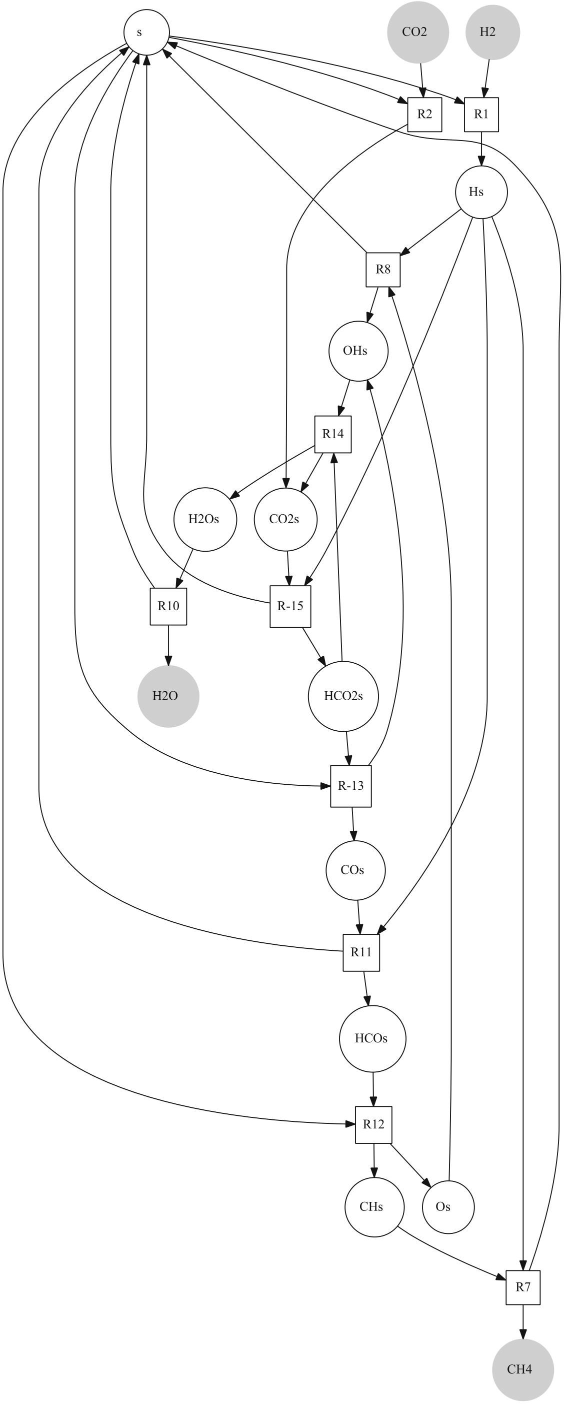


Fig. 23 P-graph N.18

Fig. 24 P-graph N.19



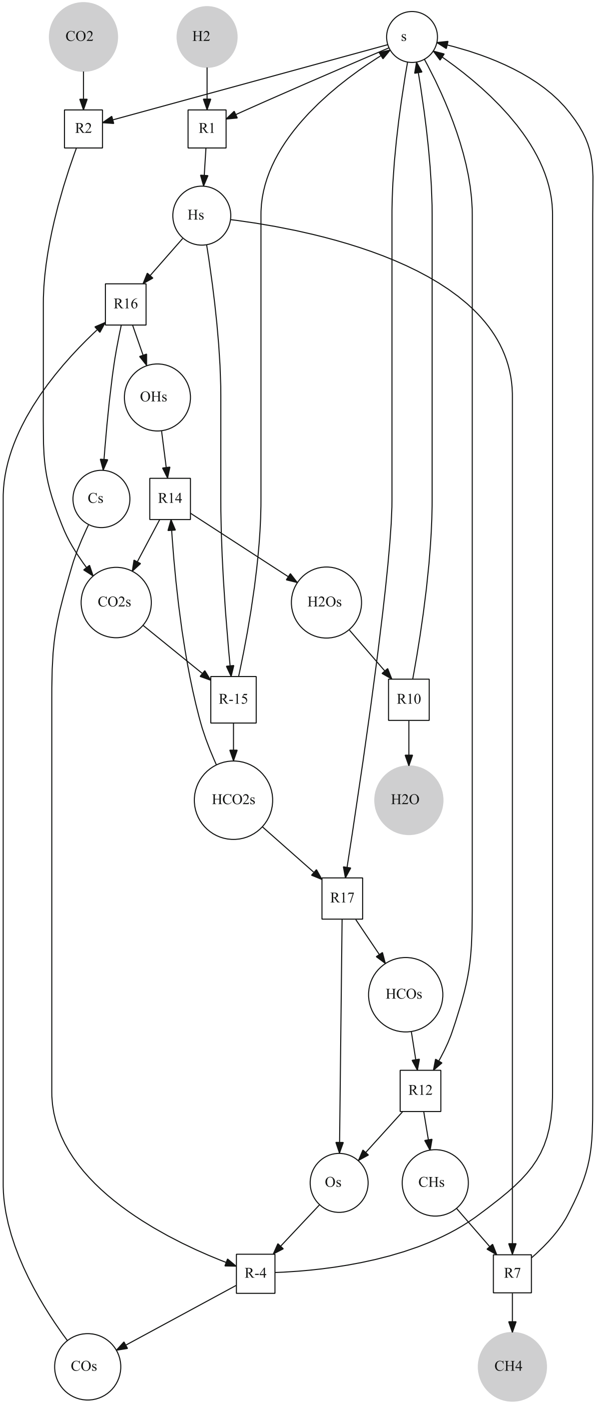


Fig. 25 P-graph N.20

Fig. 26 P-graph N.21

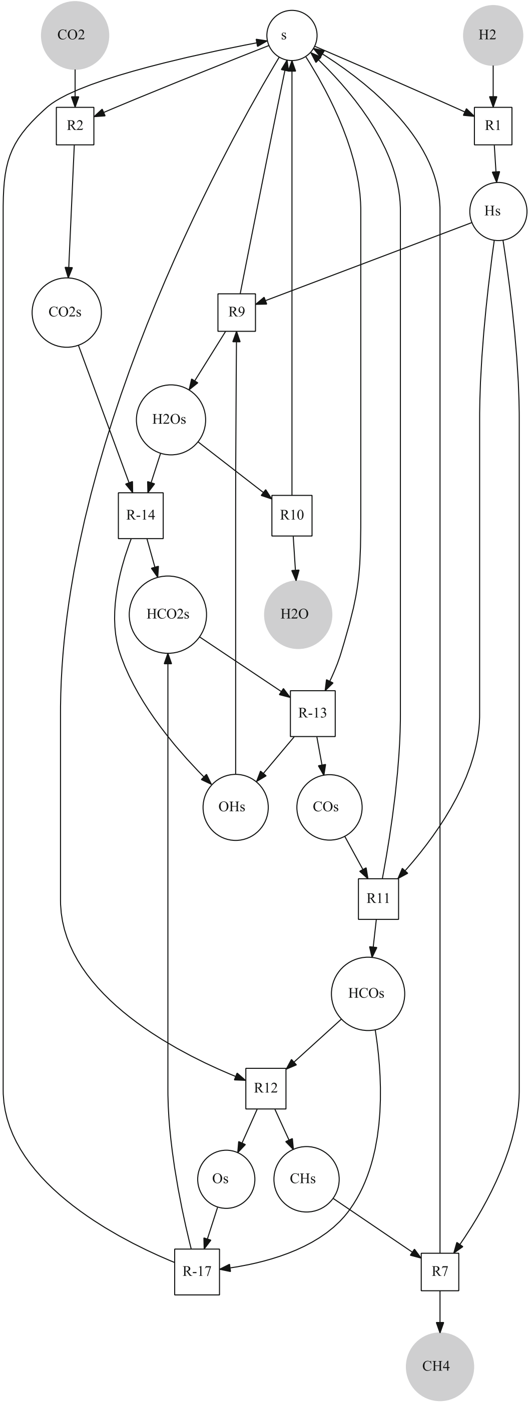
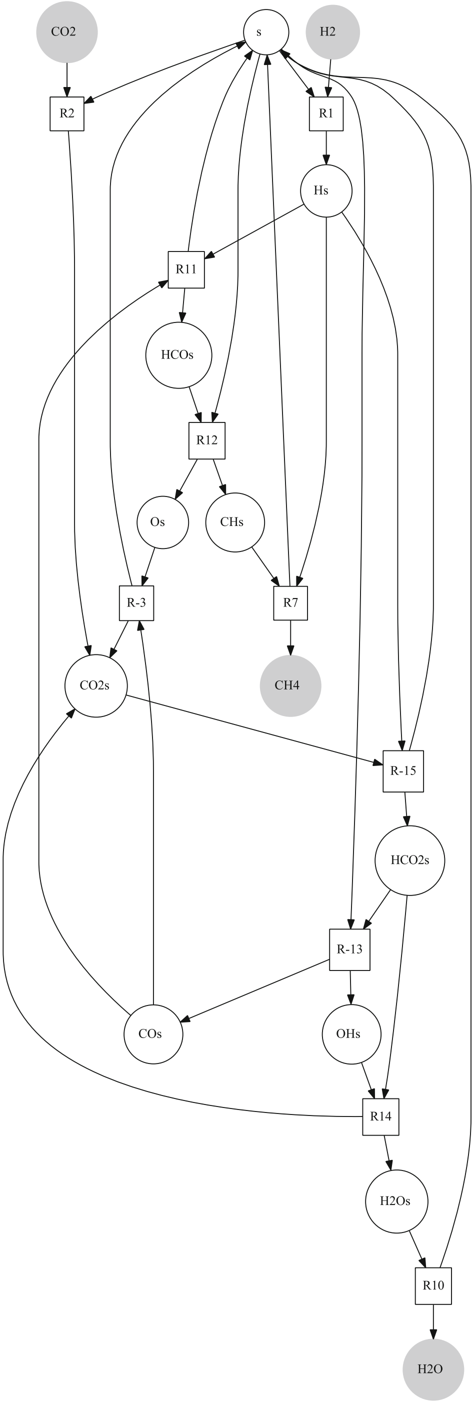


Fig. 27 P-graph N.22



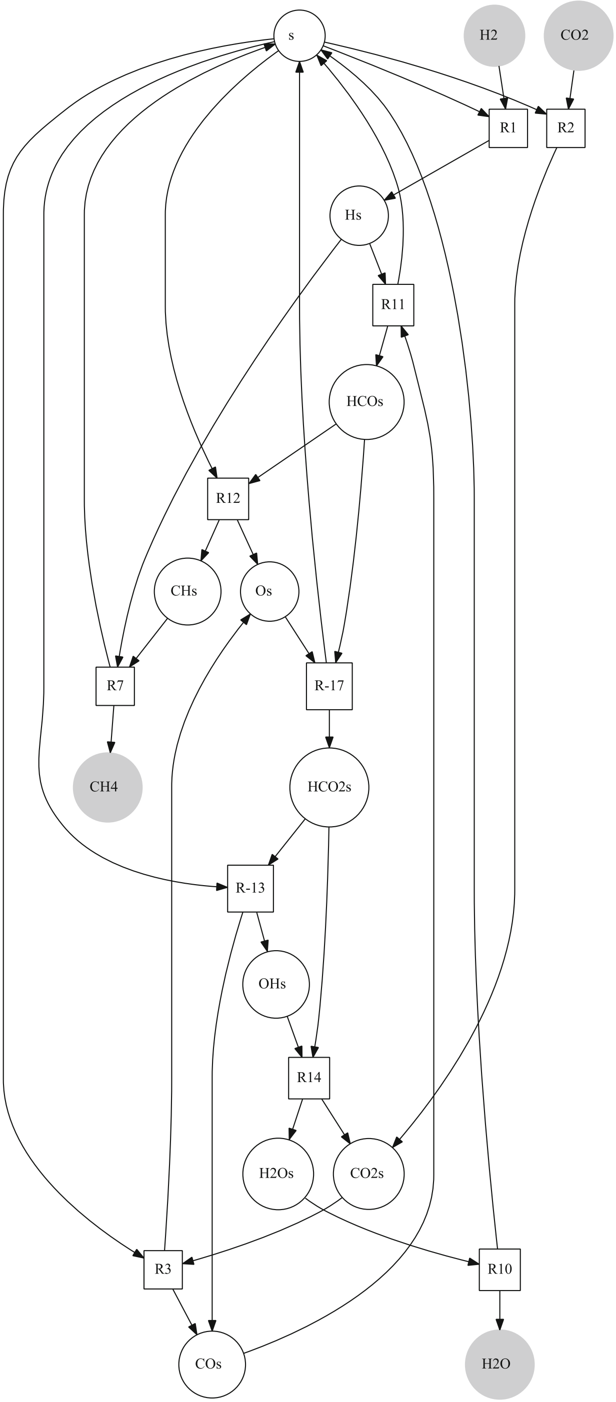


Fig. 28 P-graph N.23

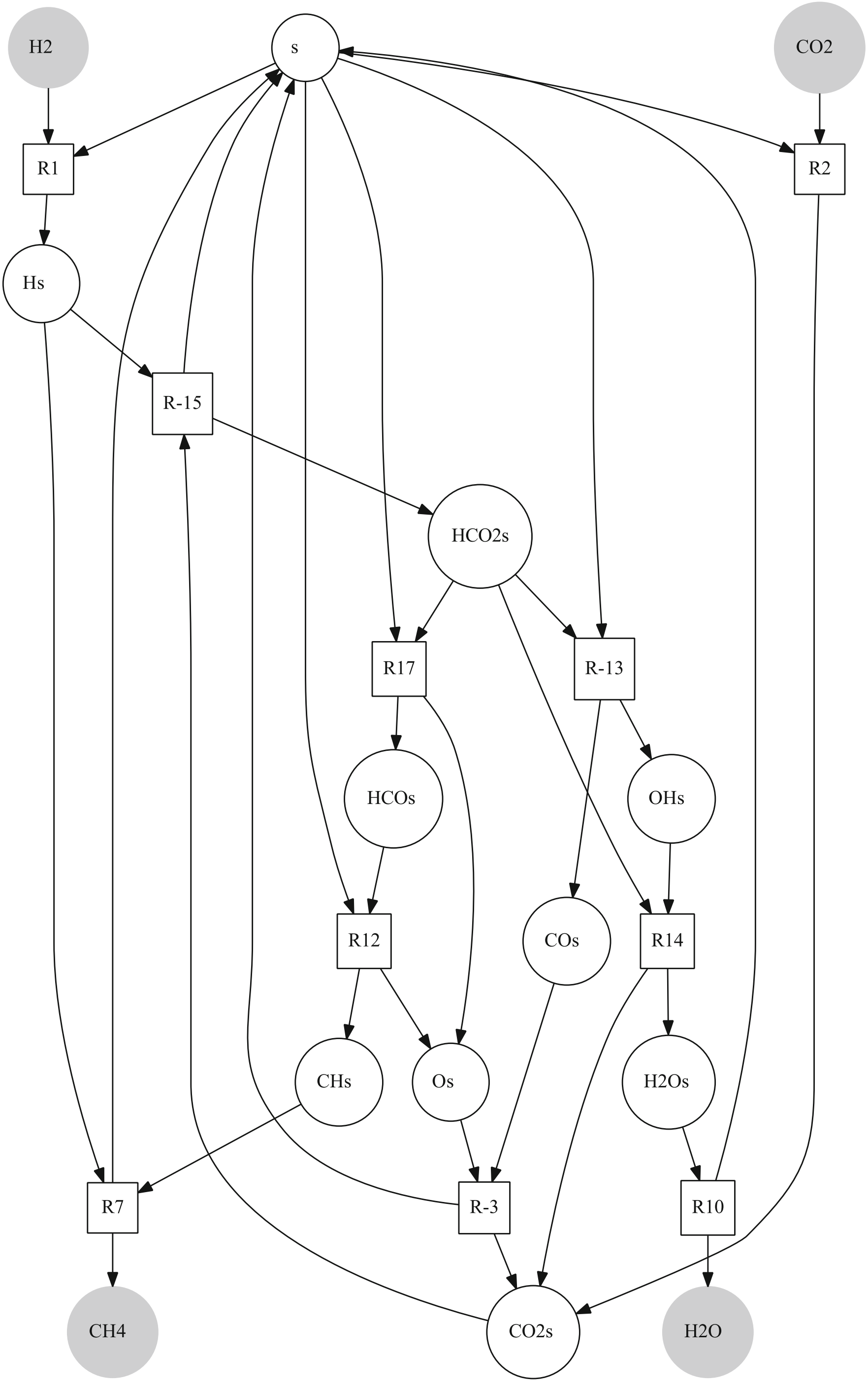


Fig. 29 P-graph N.24

Fig. 30 P-graph N.25

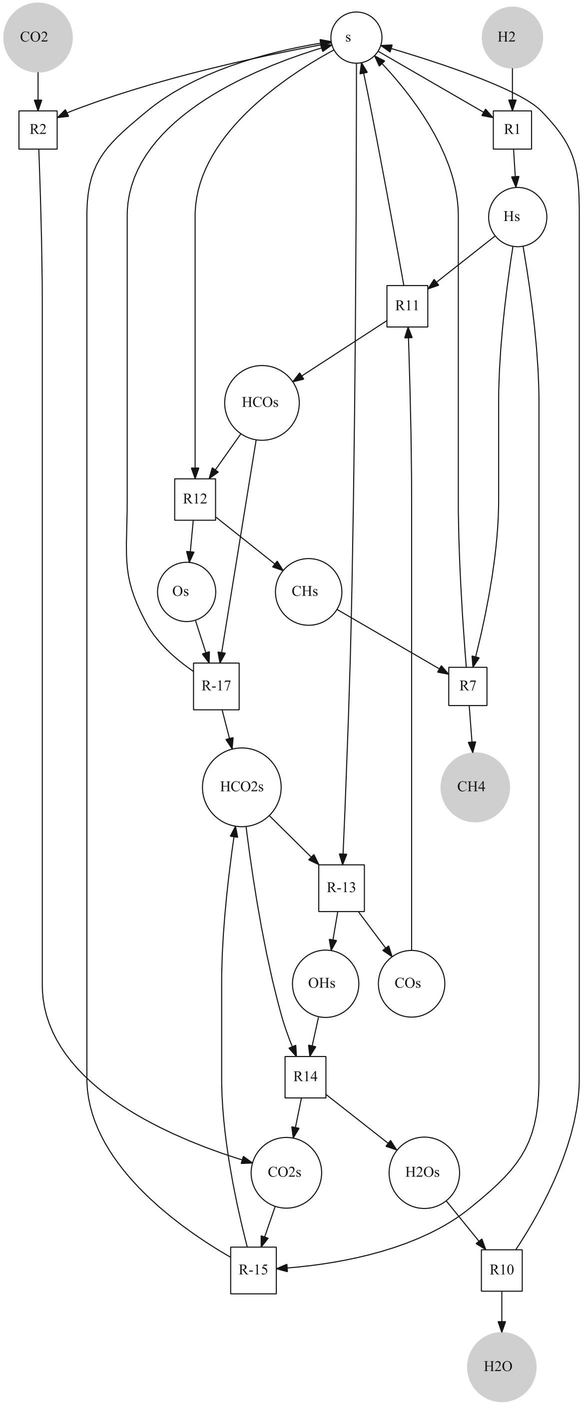
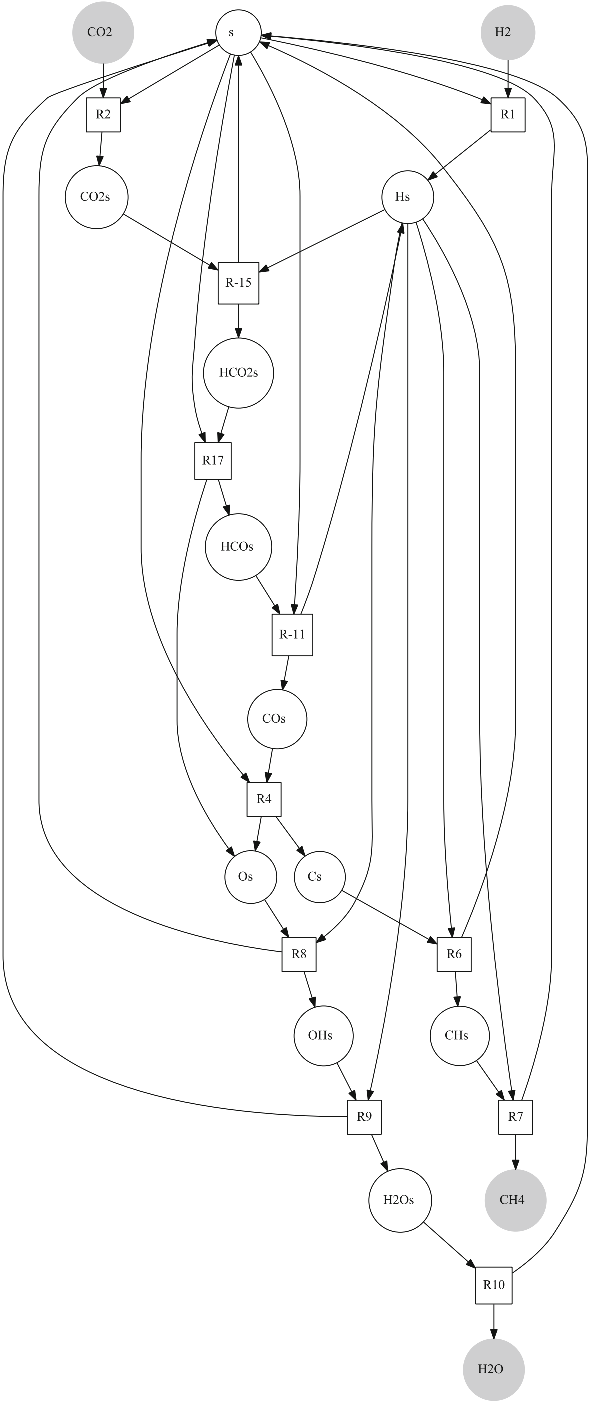


Fig. 31 P-graph N.26



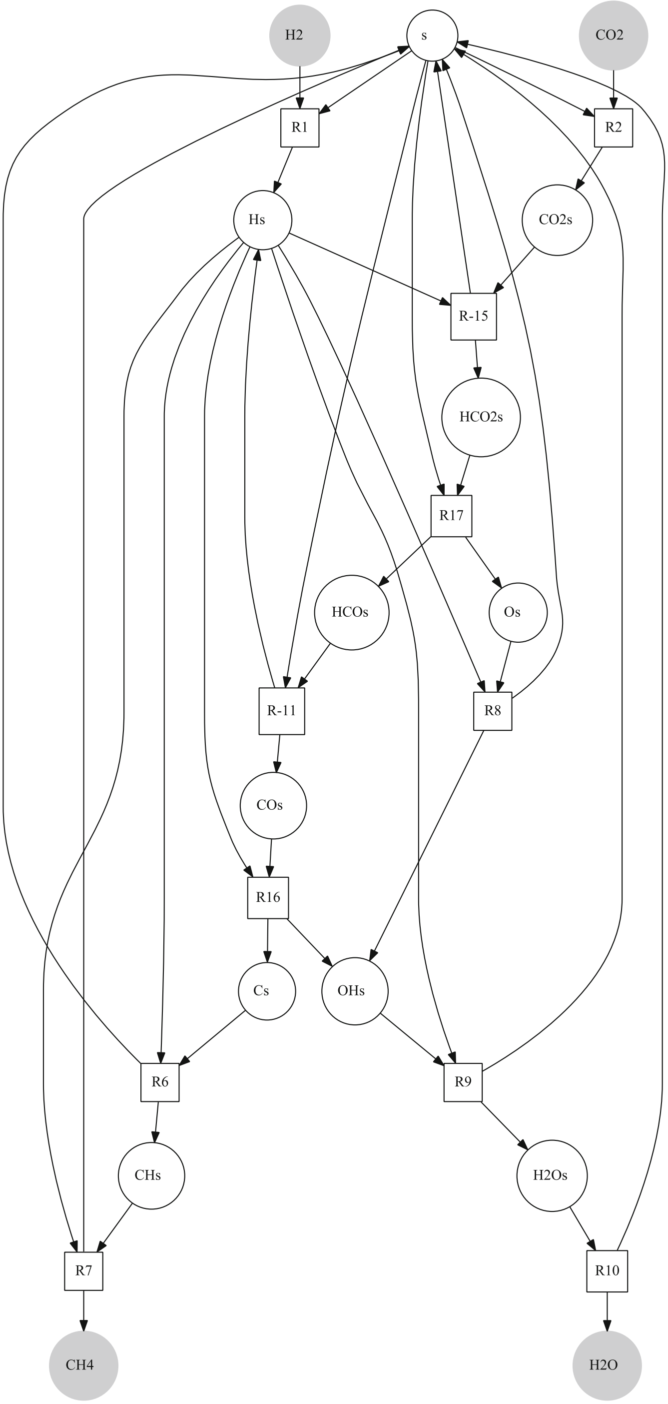


Fig. 32 P-graph N.27

Fig. 33 P-graph N.28

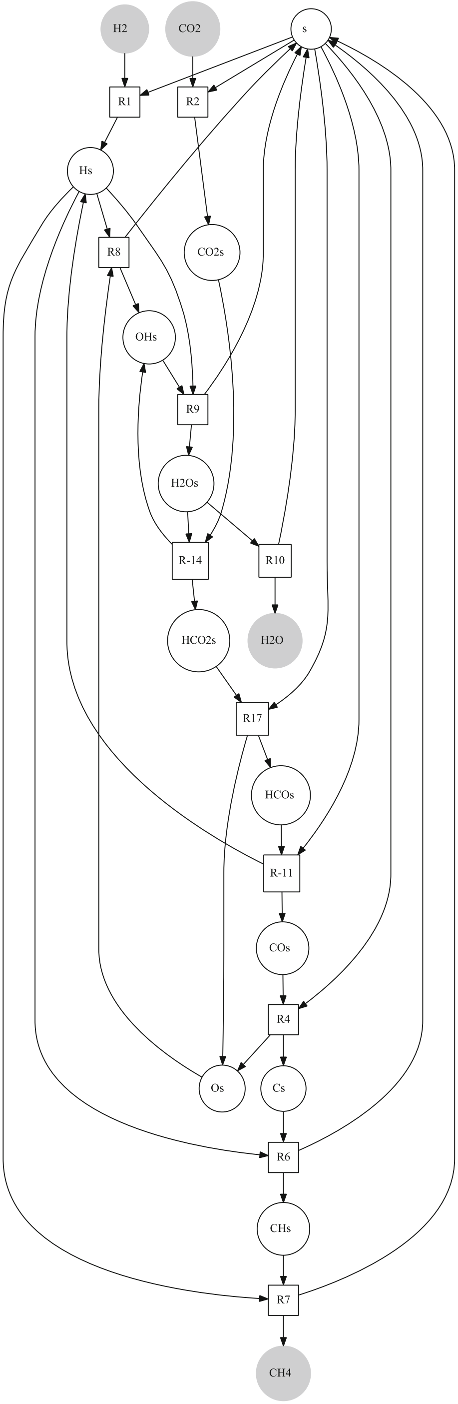
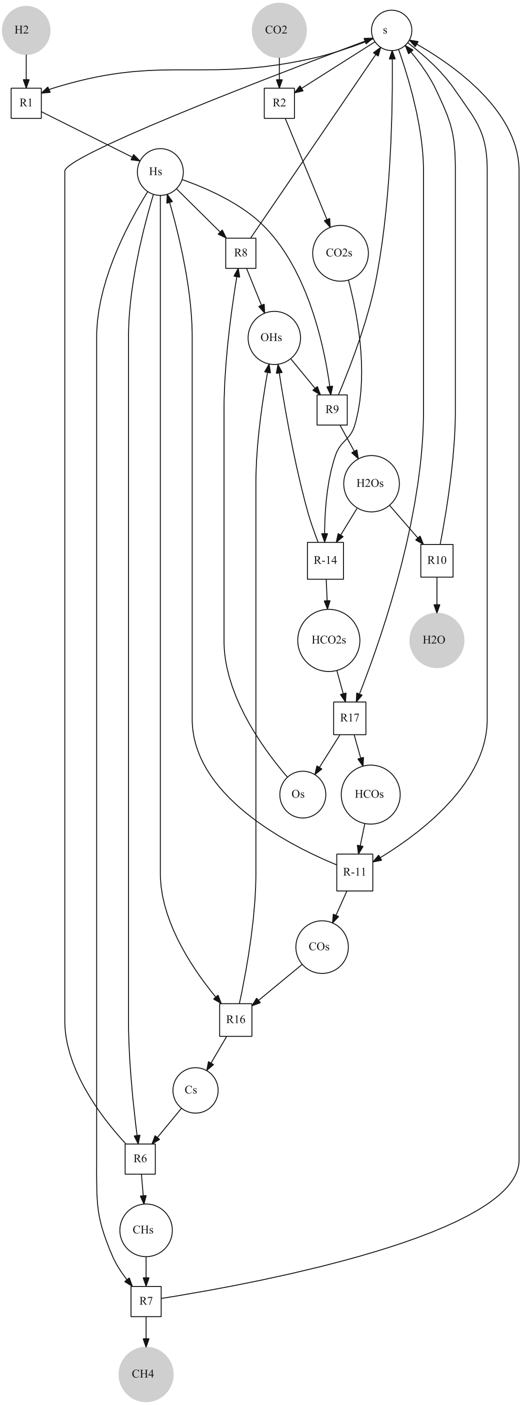


Fig. 34 P-graph N.29



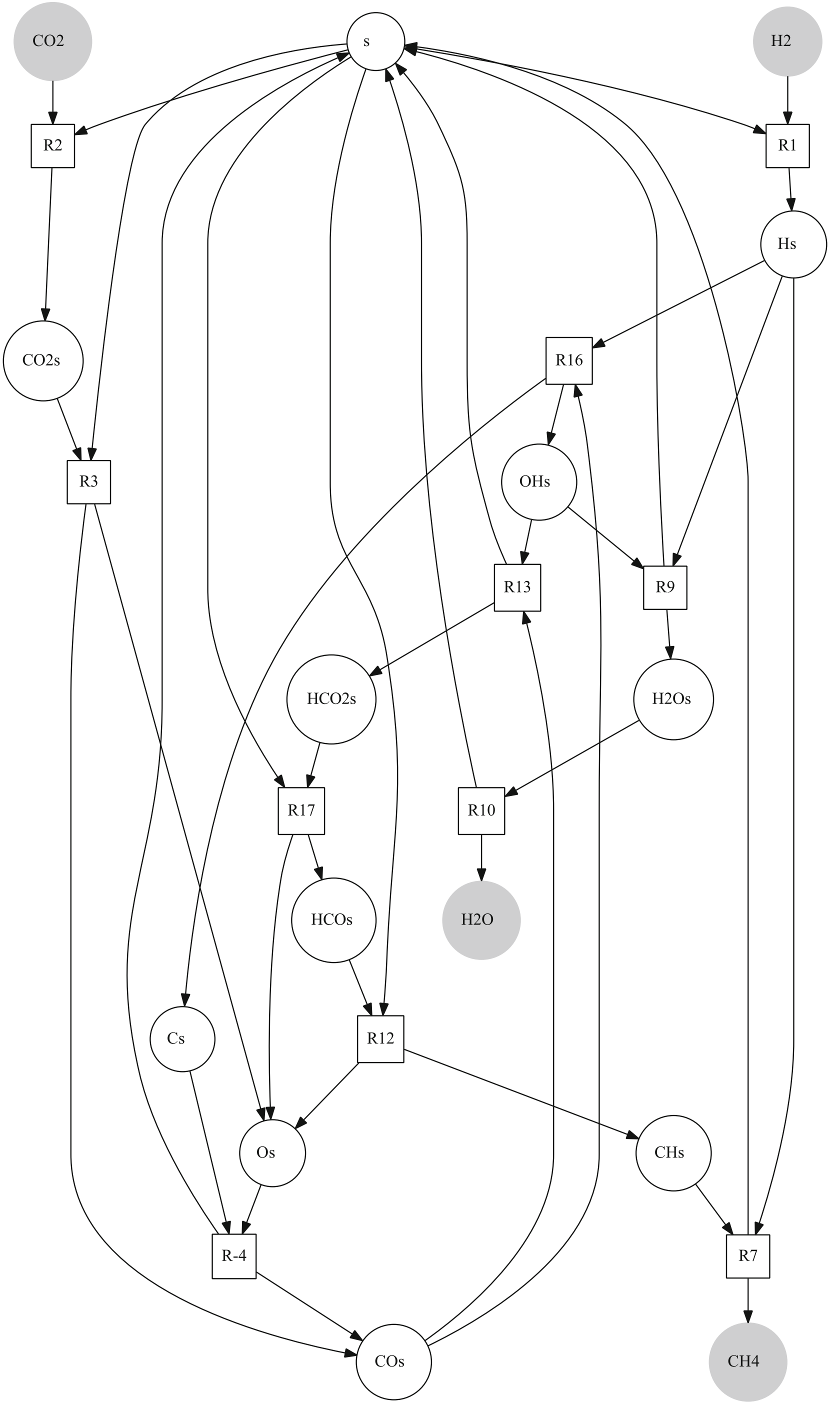


Fig. 35 P-graph N.30

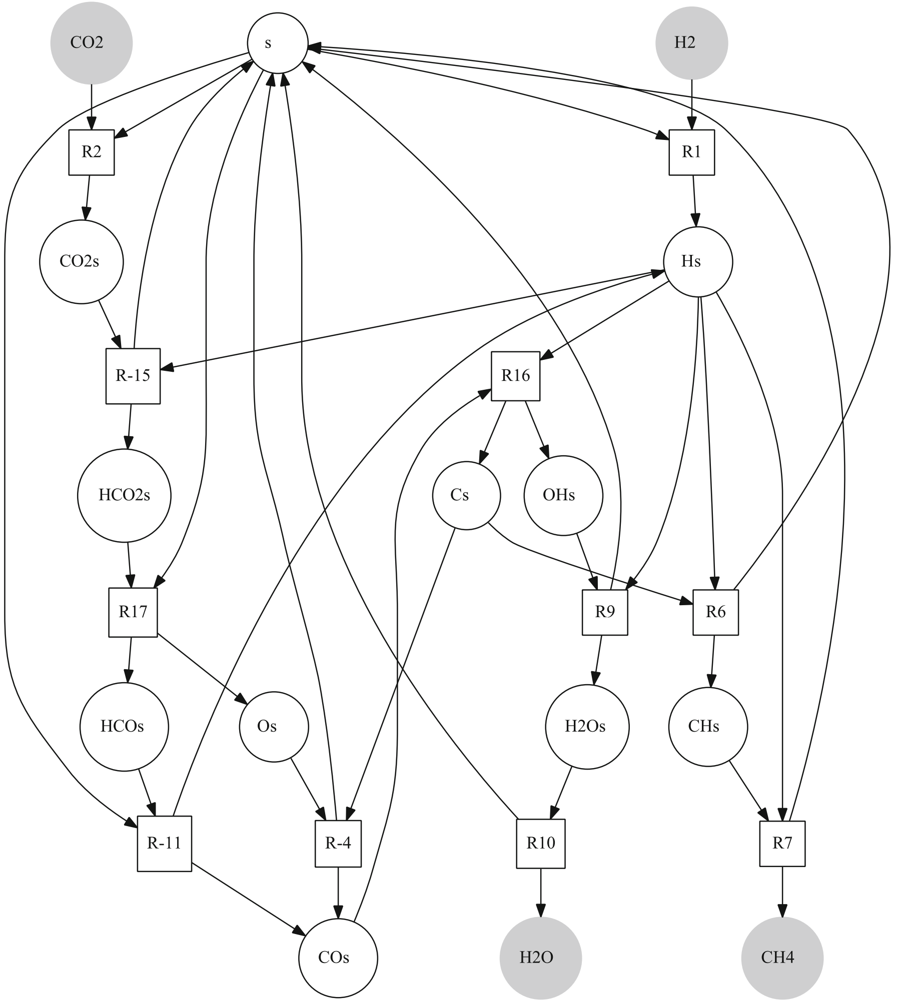
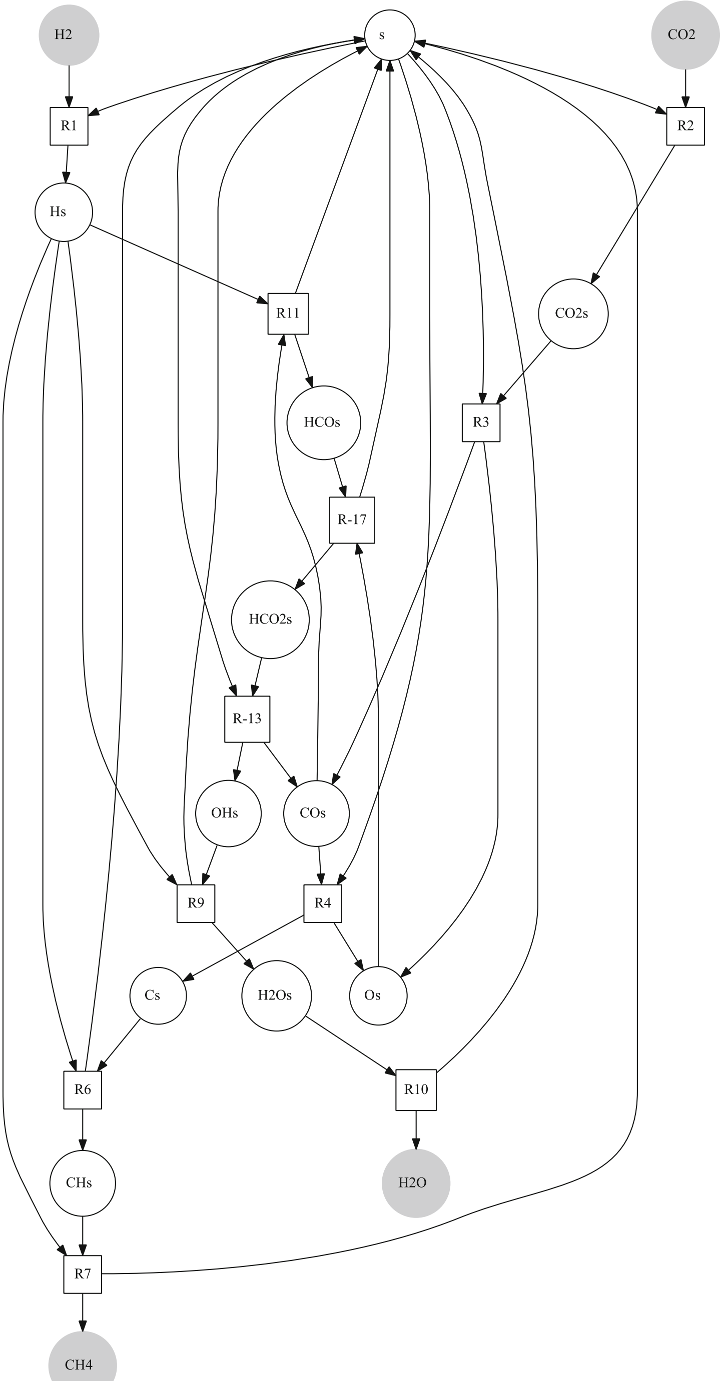


Fig. 36 P-graph N.31



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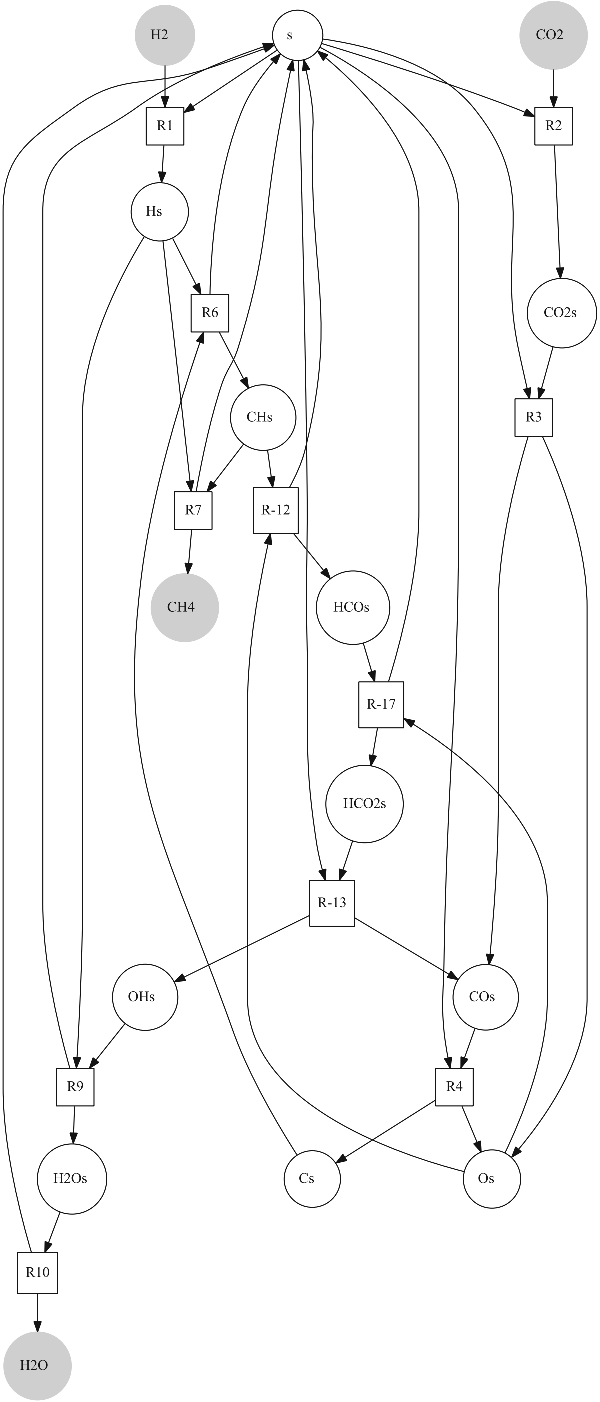

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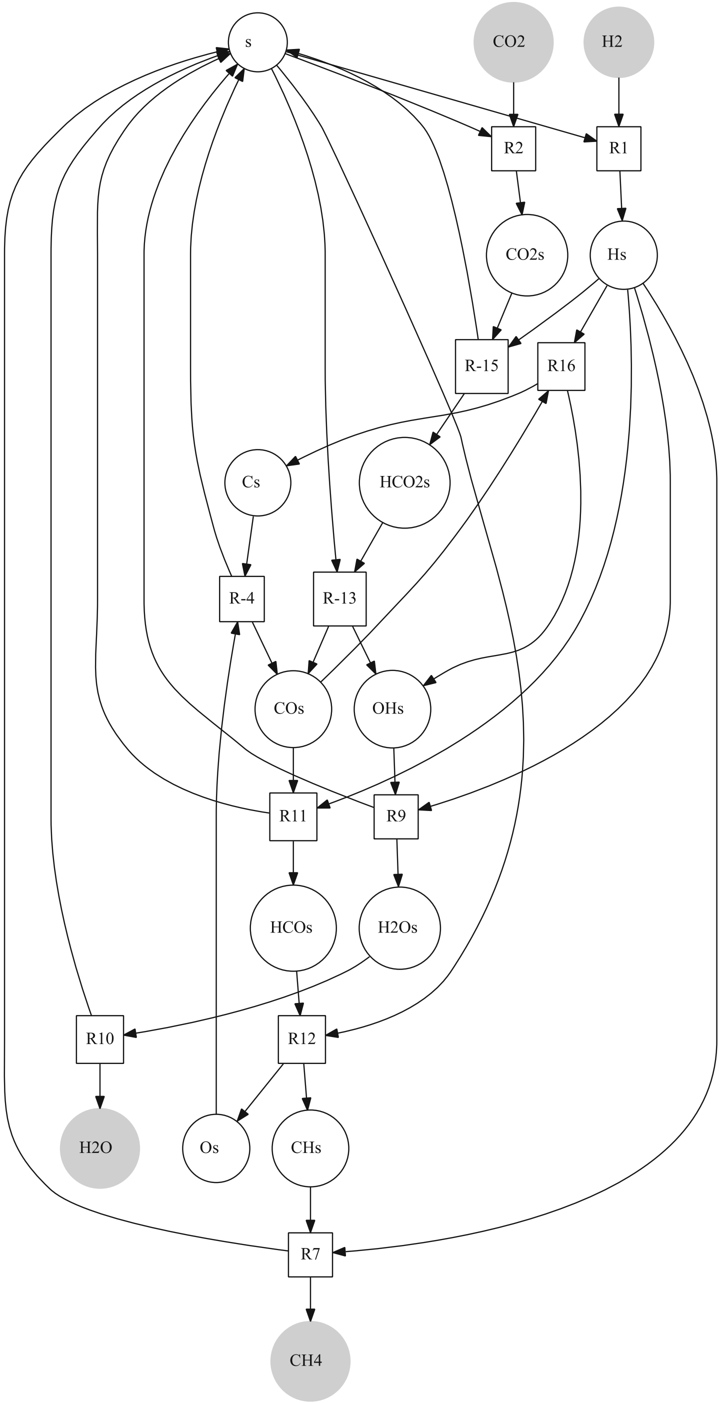

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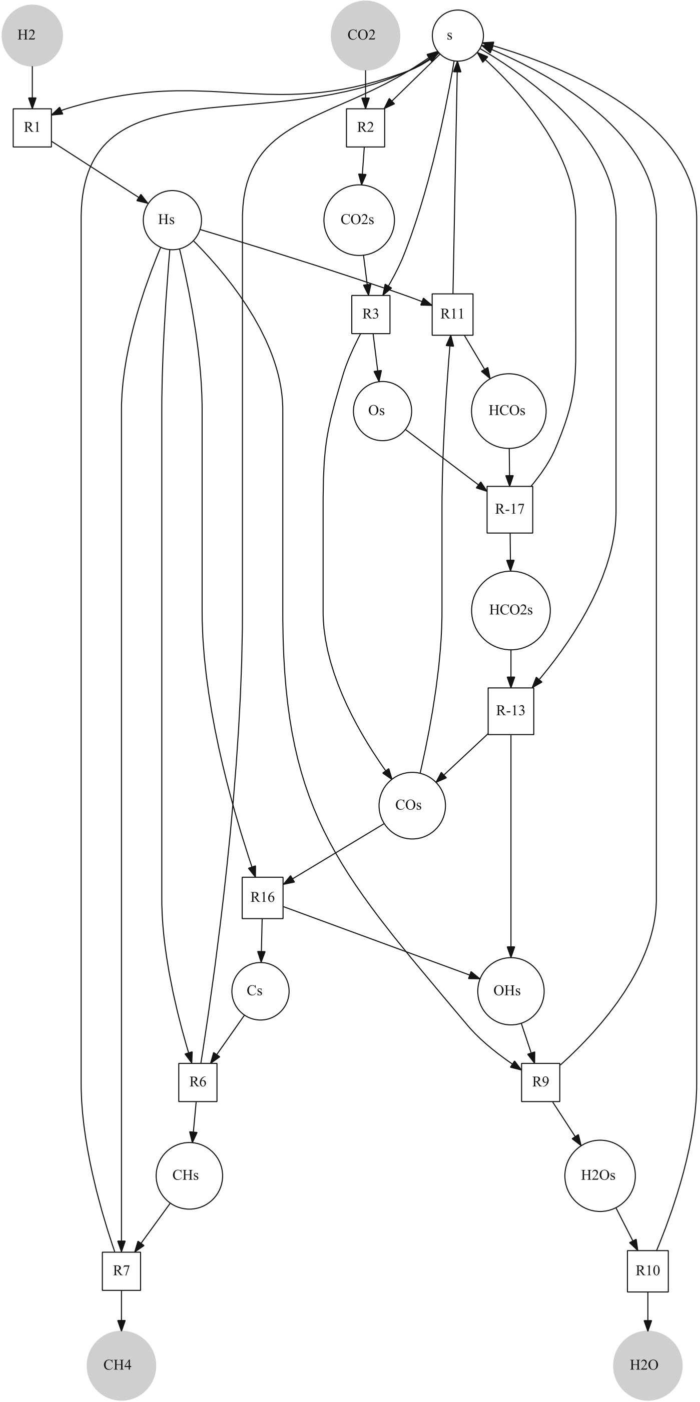

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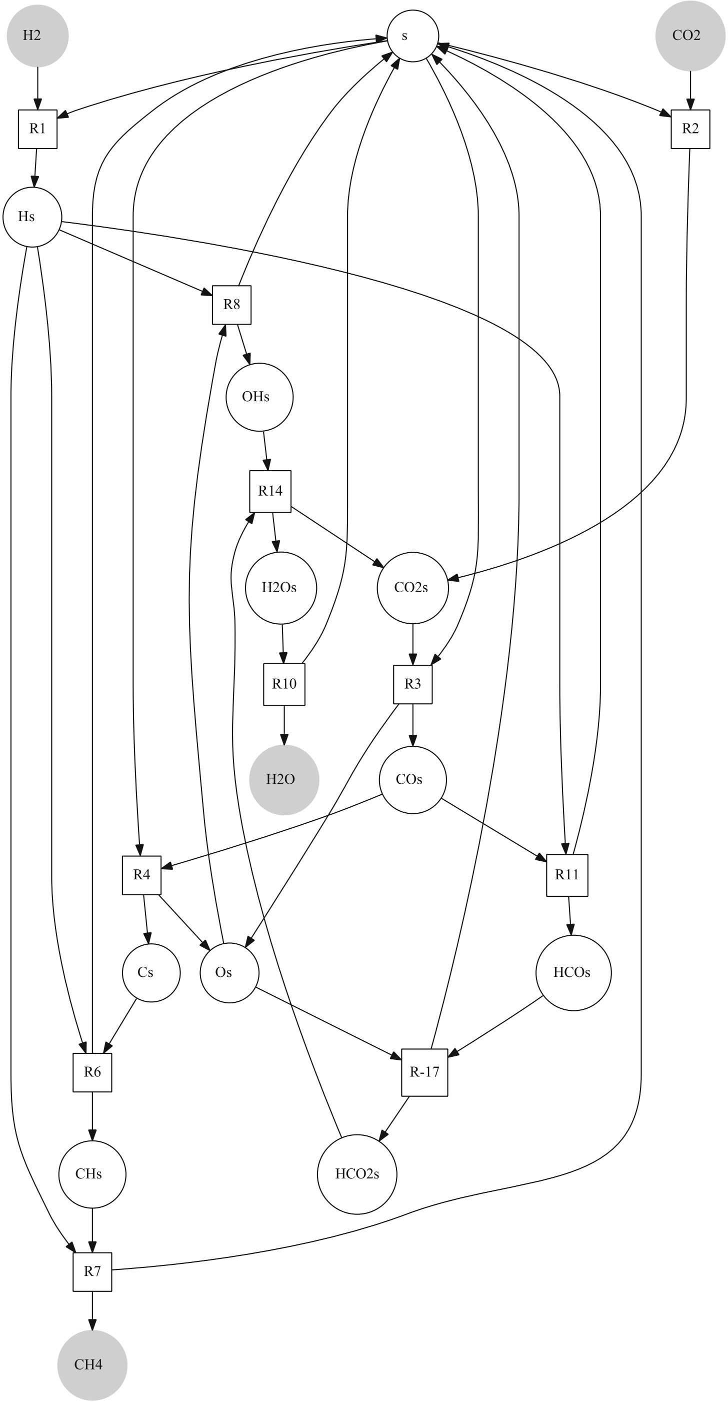

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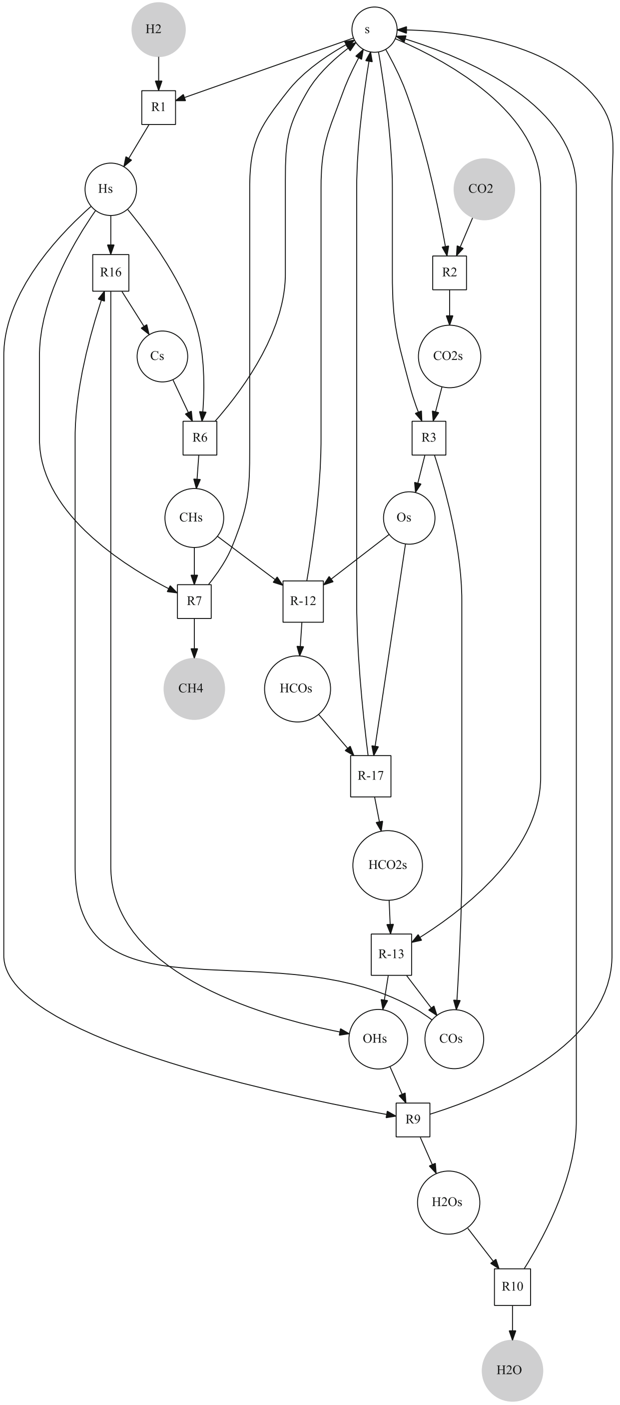
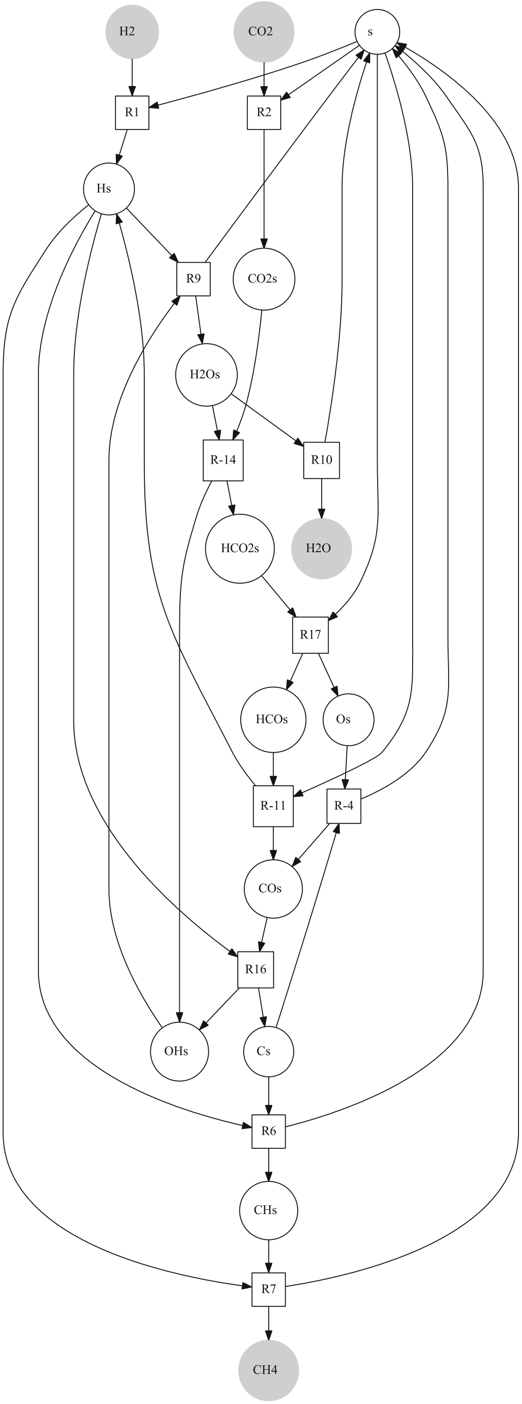
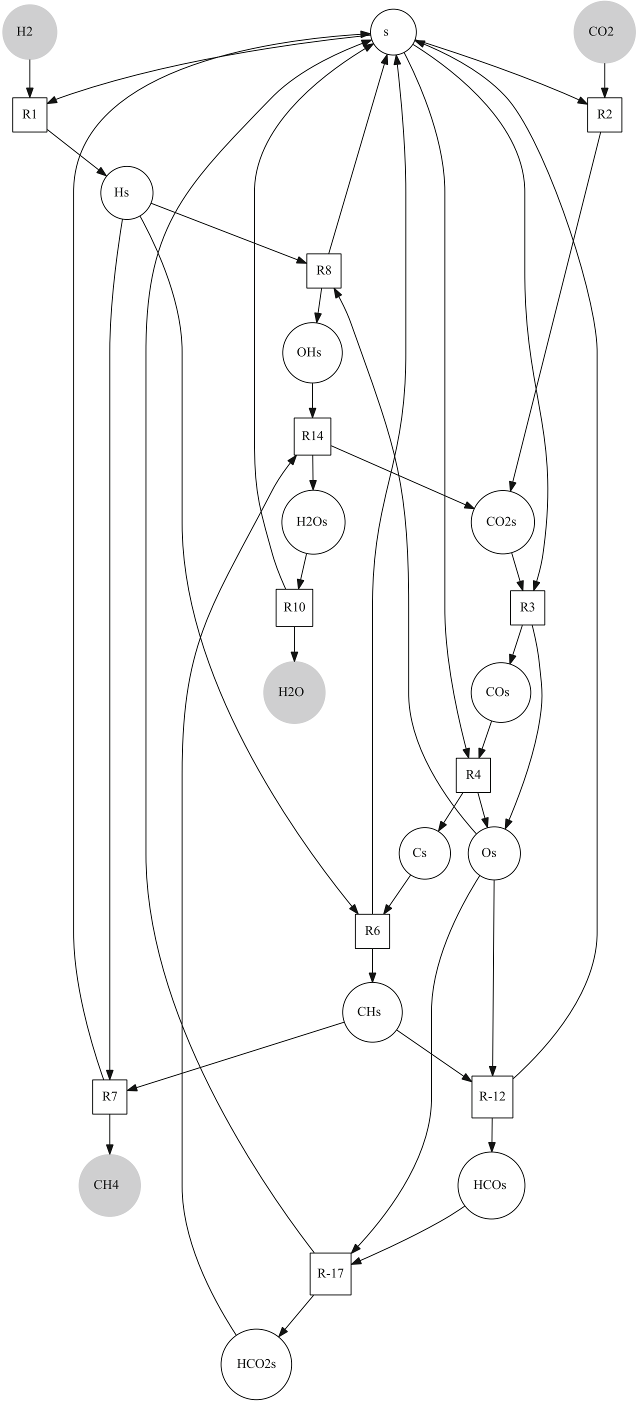


Fig. 42 P-graph N.37

Fig. 43 P-graph N.38





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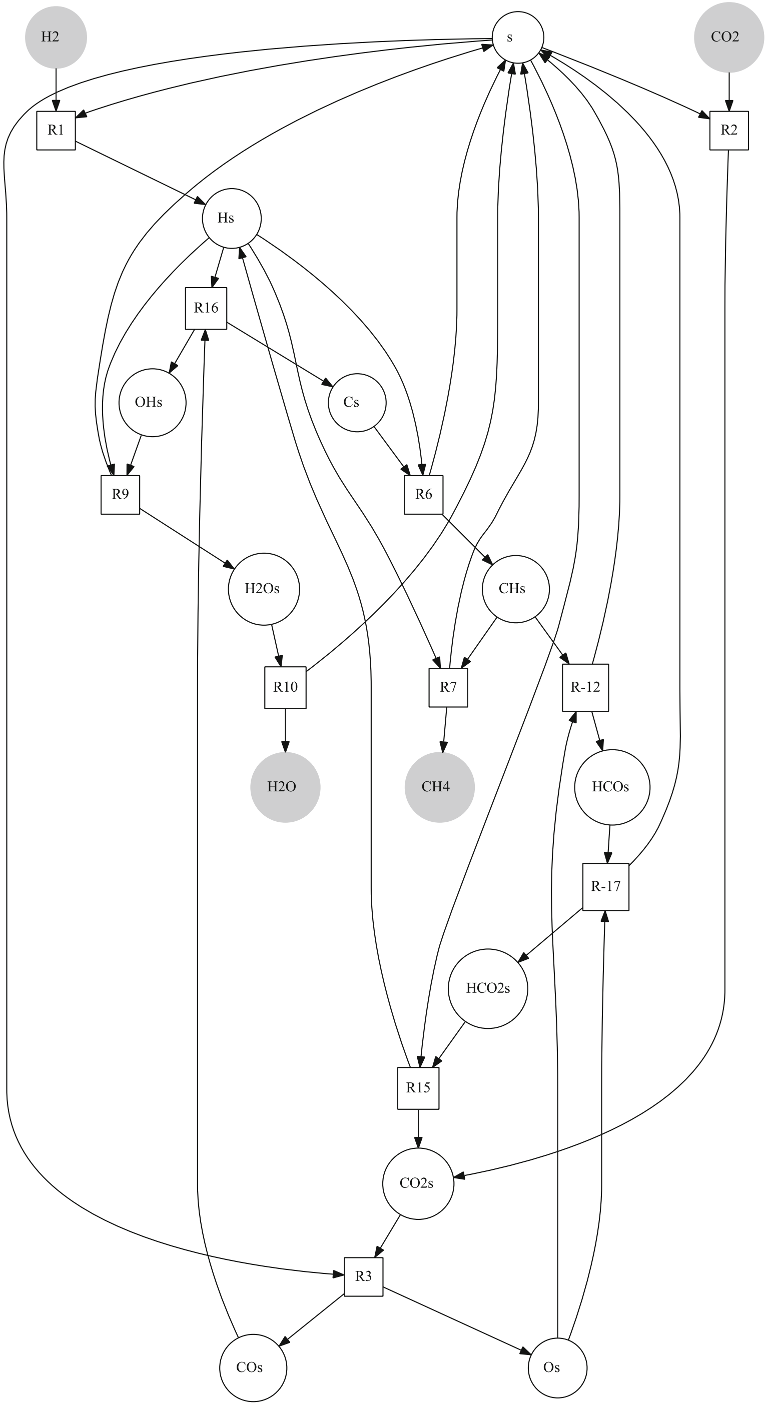

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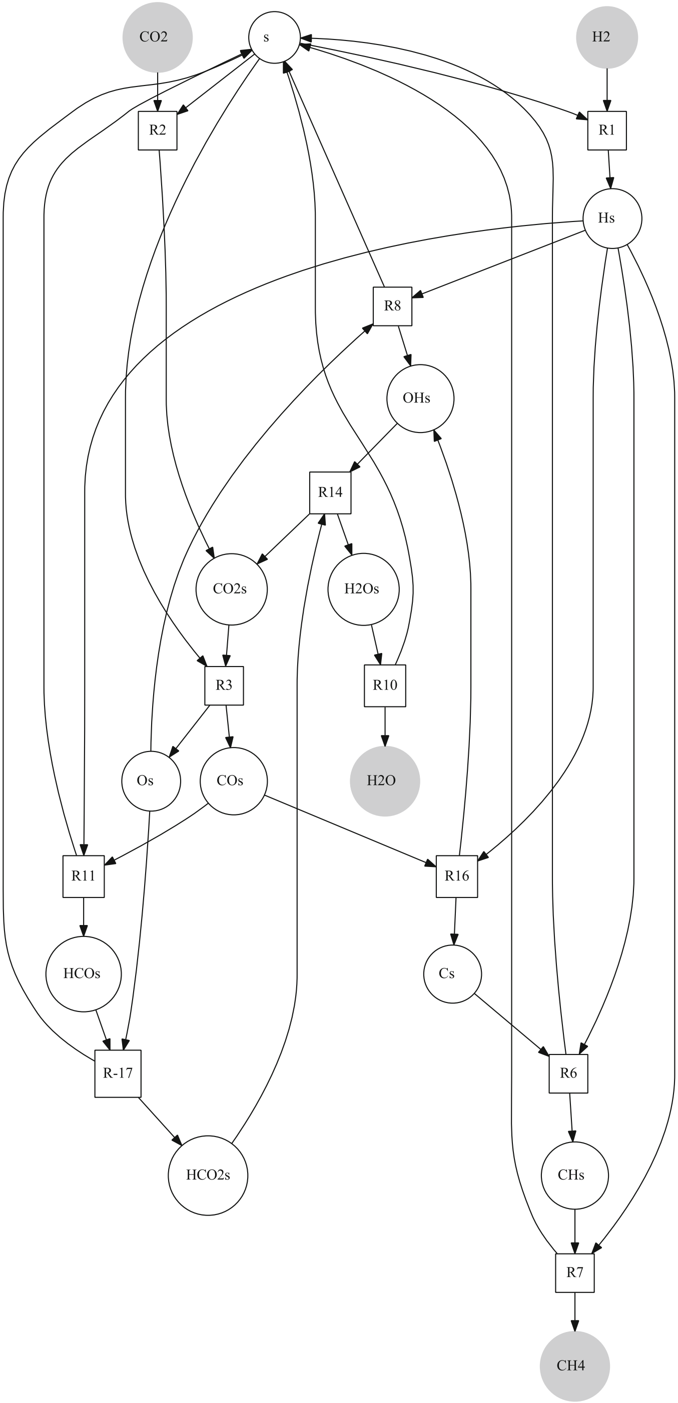

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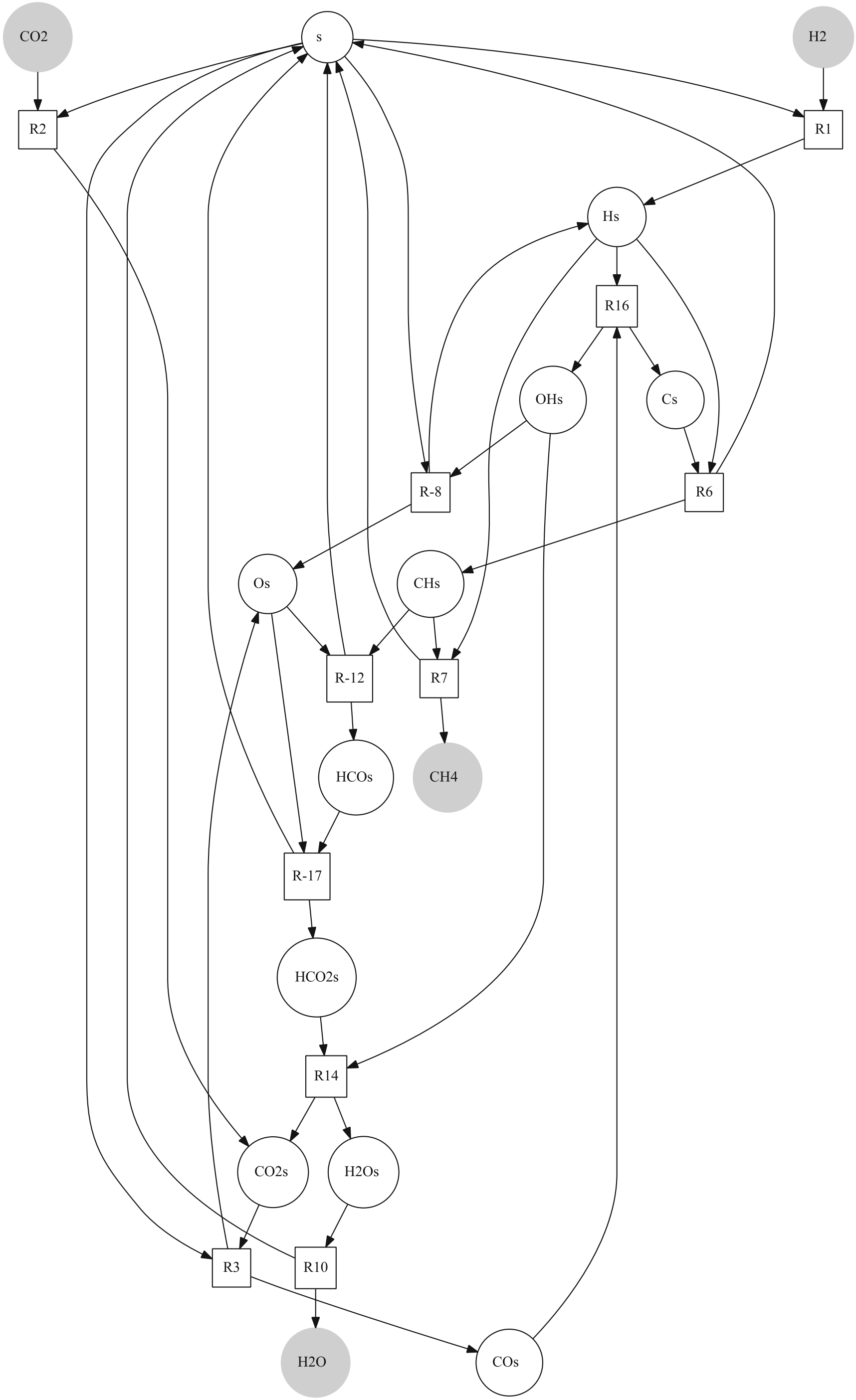
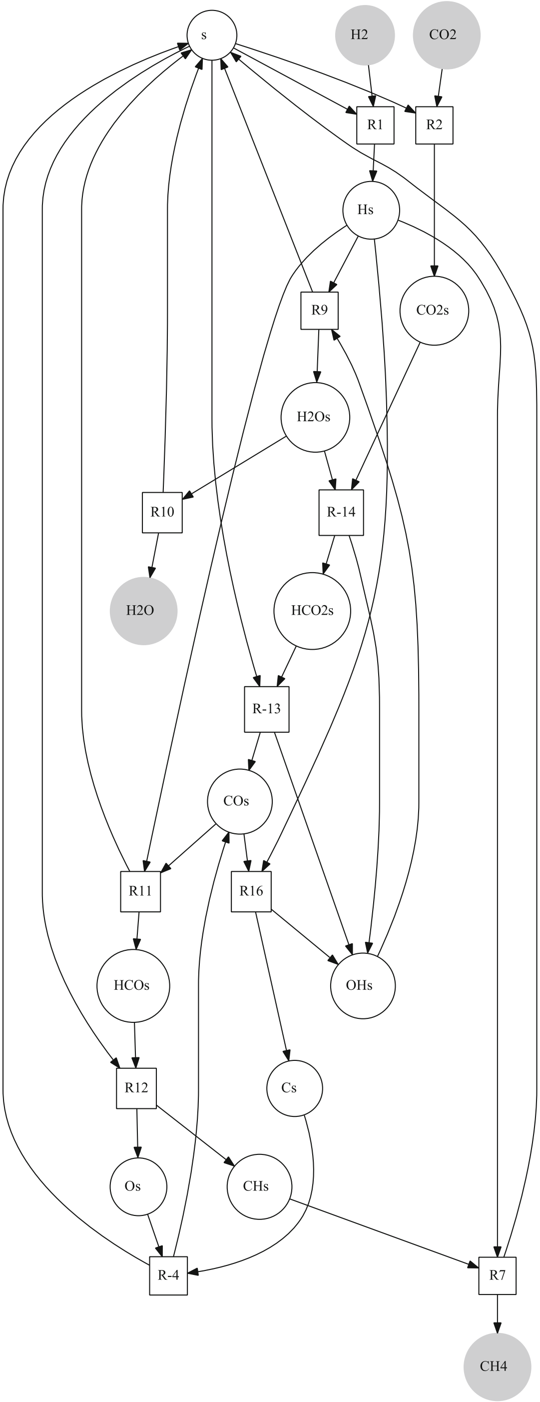
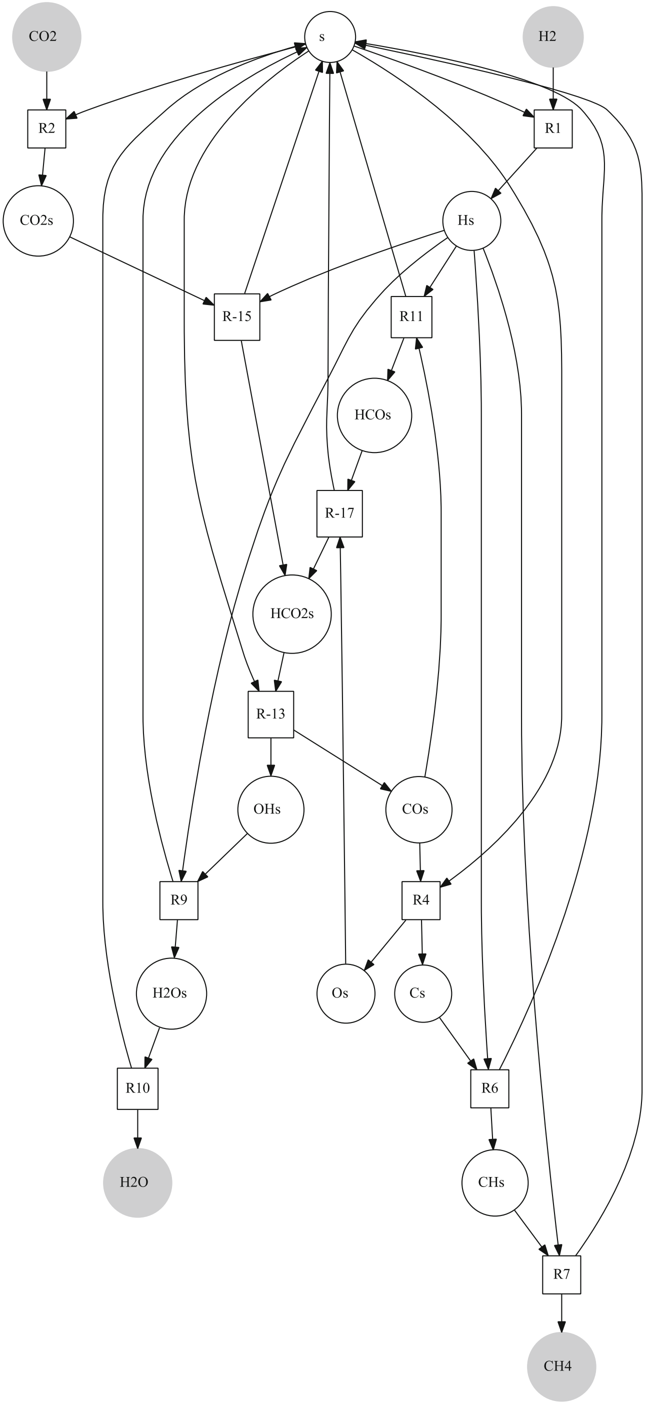


Fig. 47 P-graph N.42

Fig. 48 P-graph N.43





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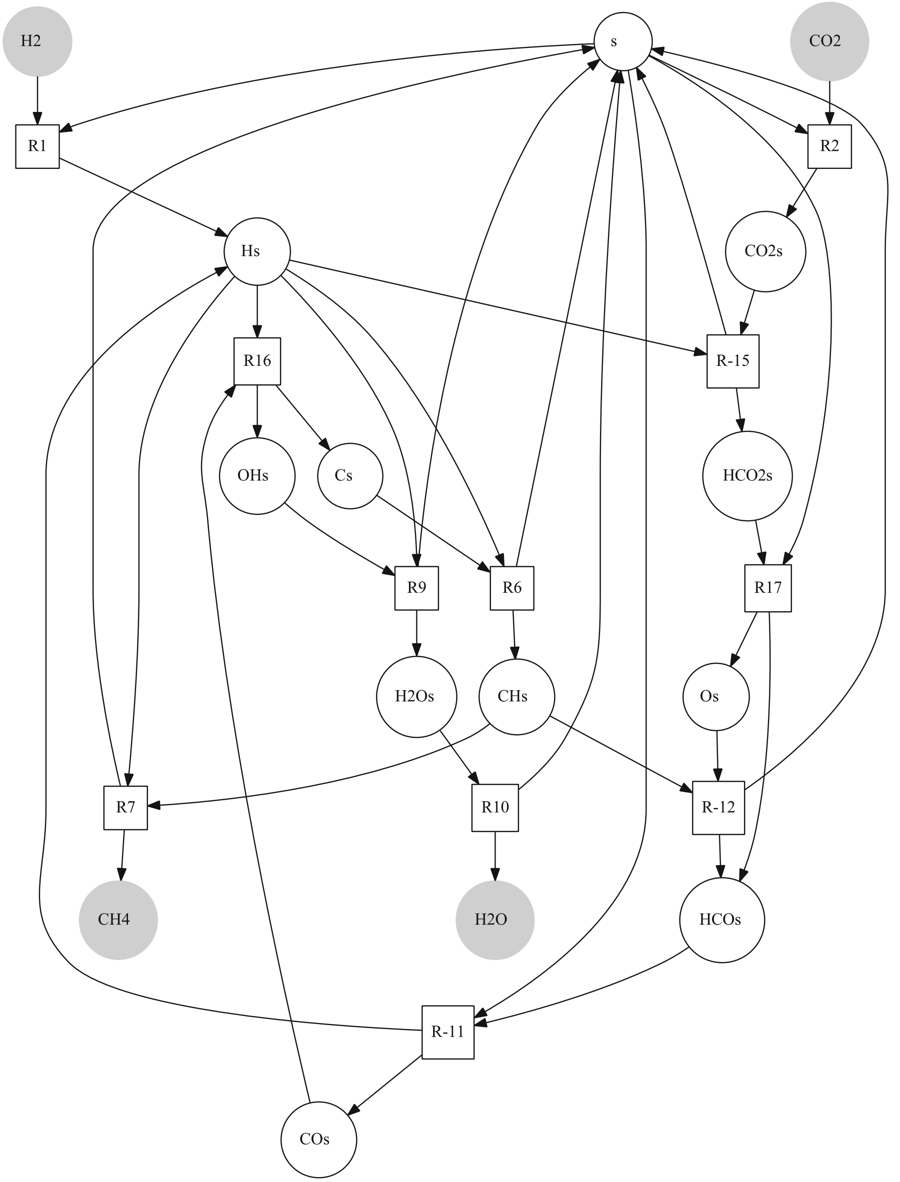

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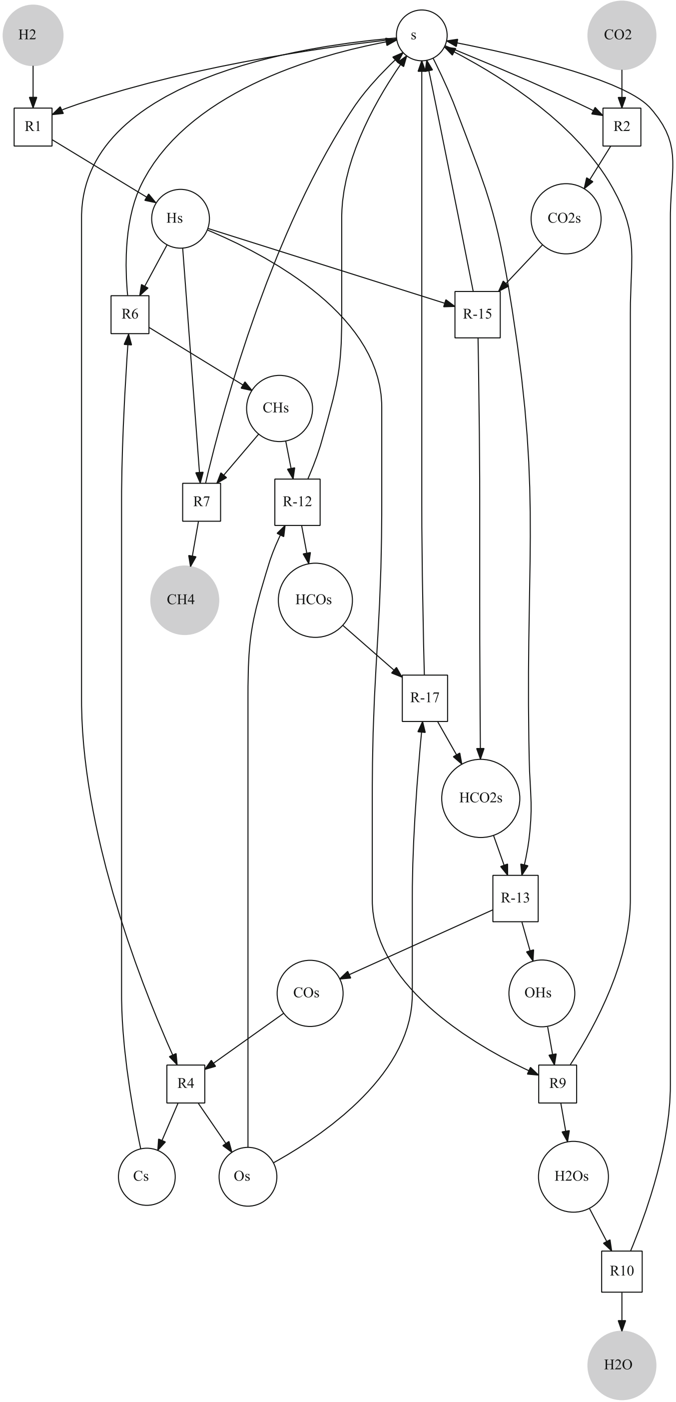

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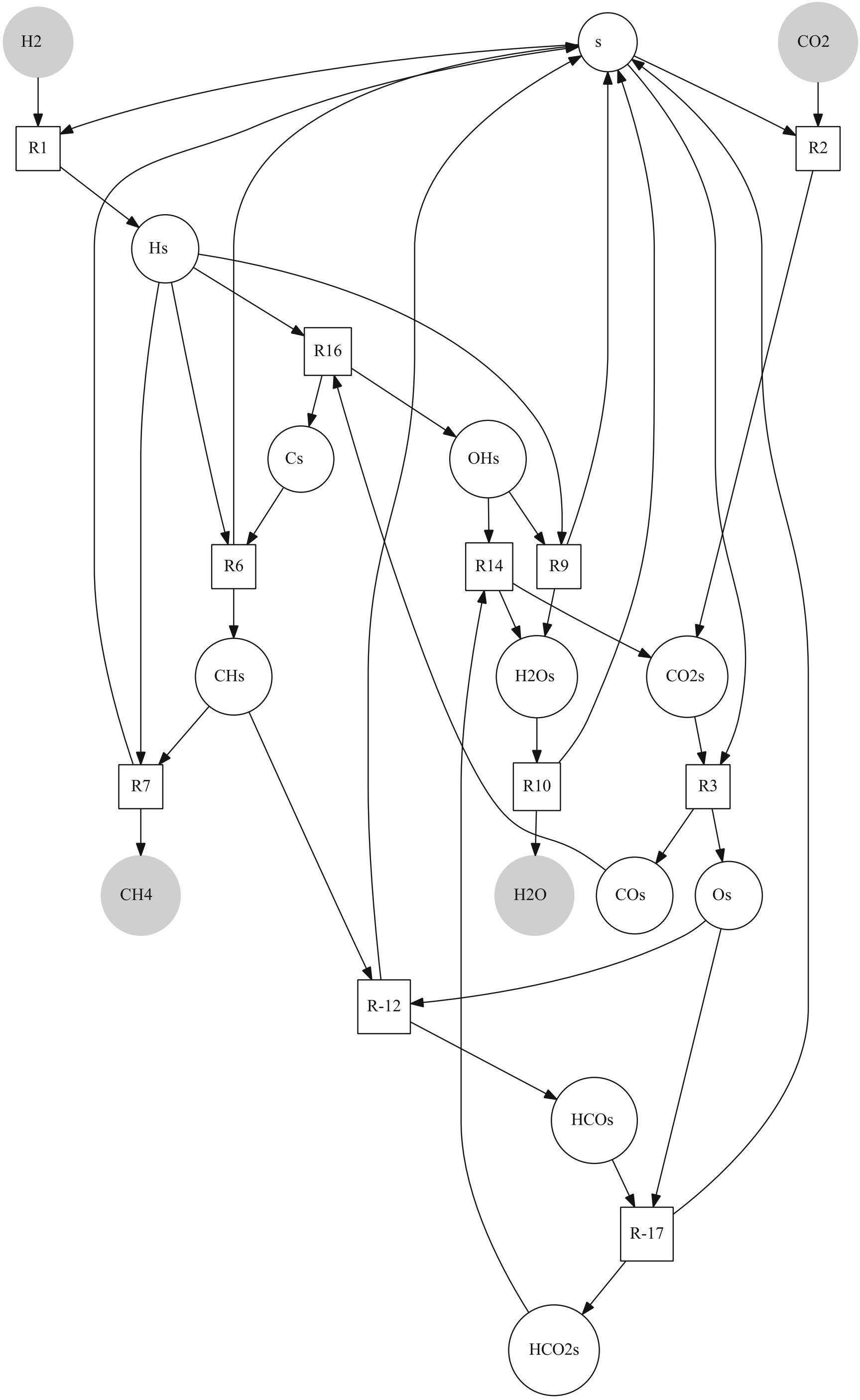
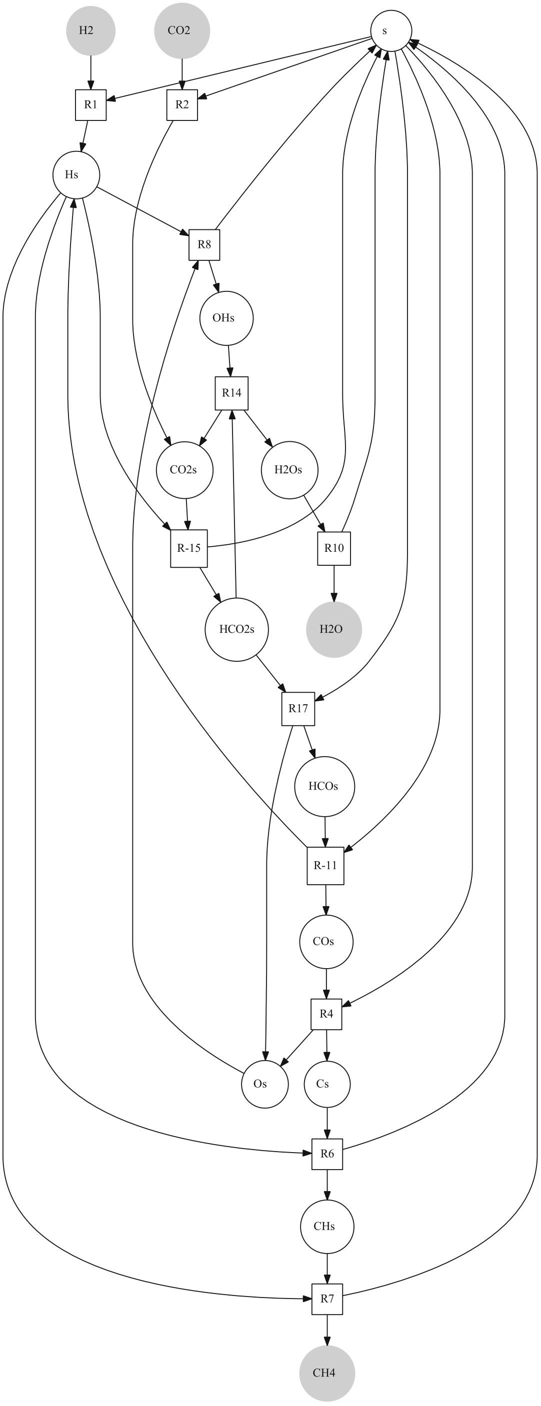


Fig. 52 P-graph N.47

Fig. 53 P-graph N.48



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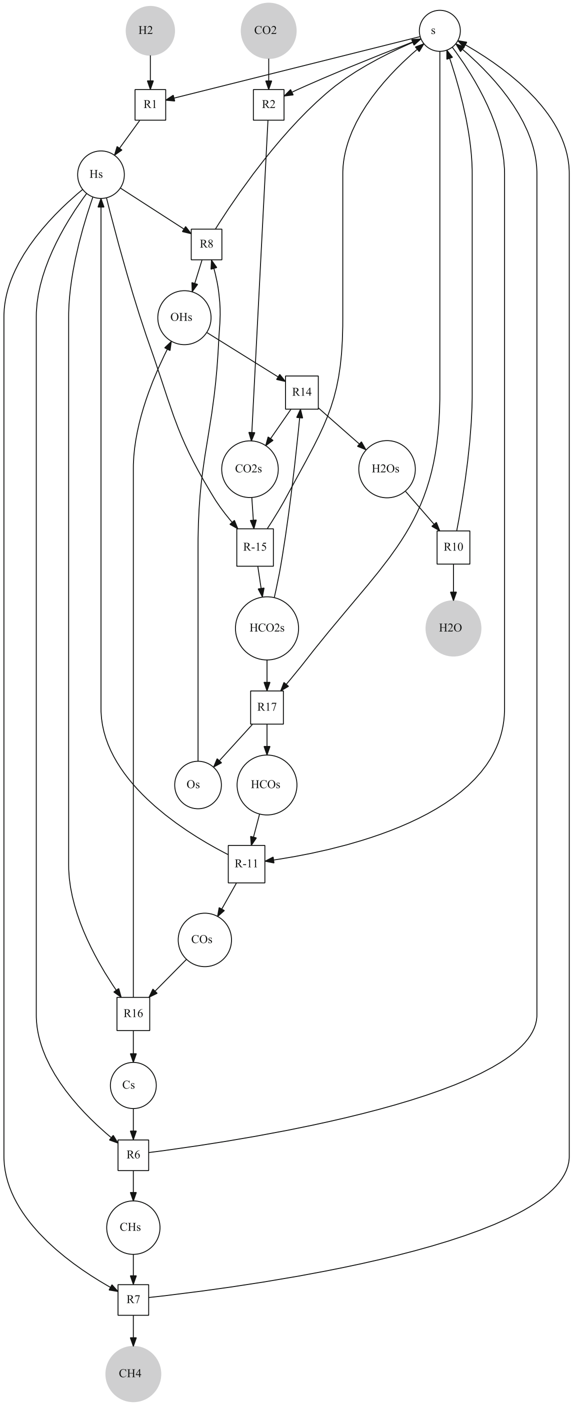

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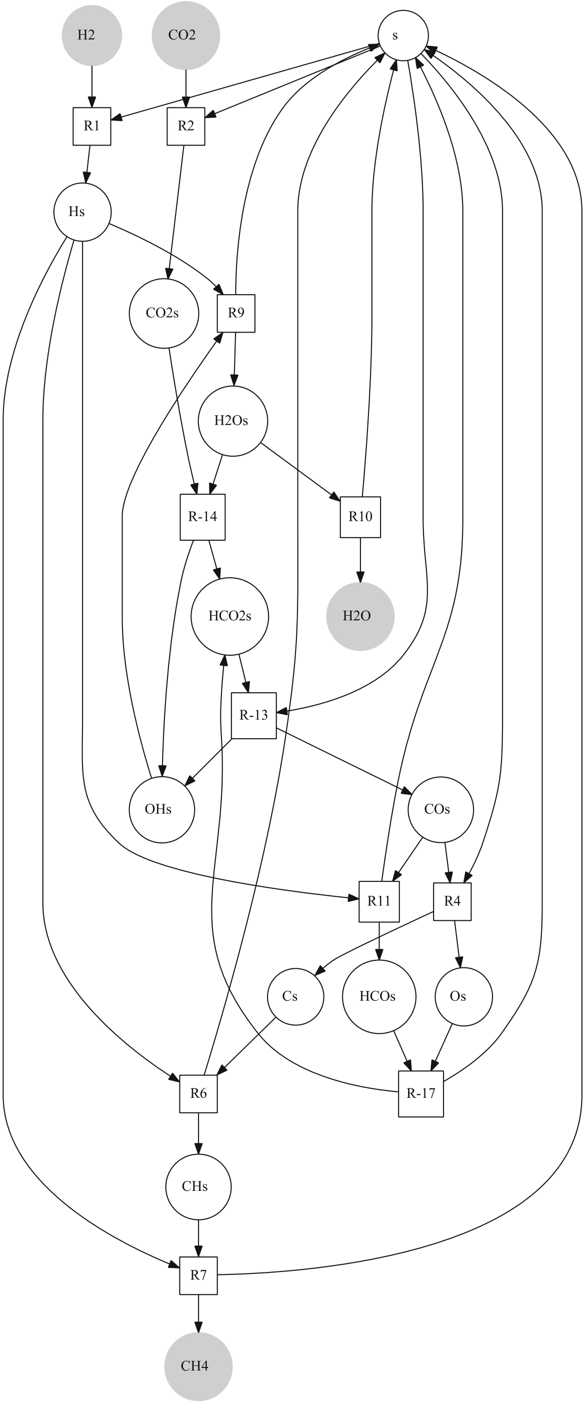

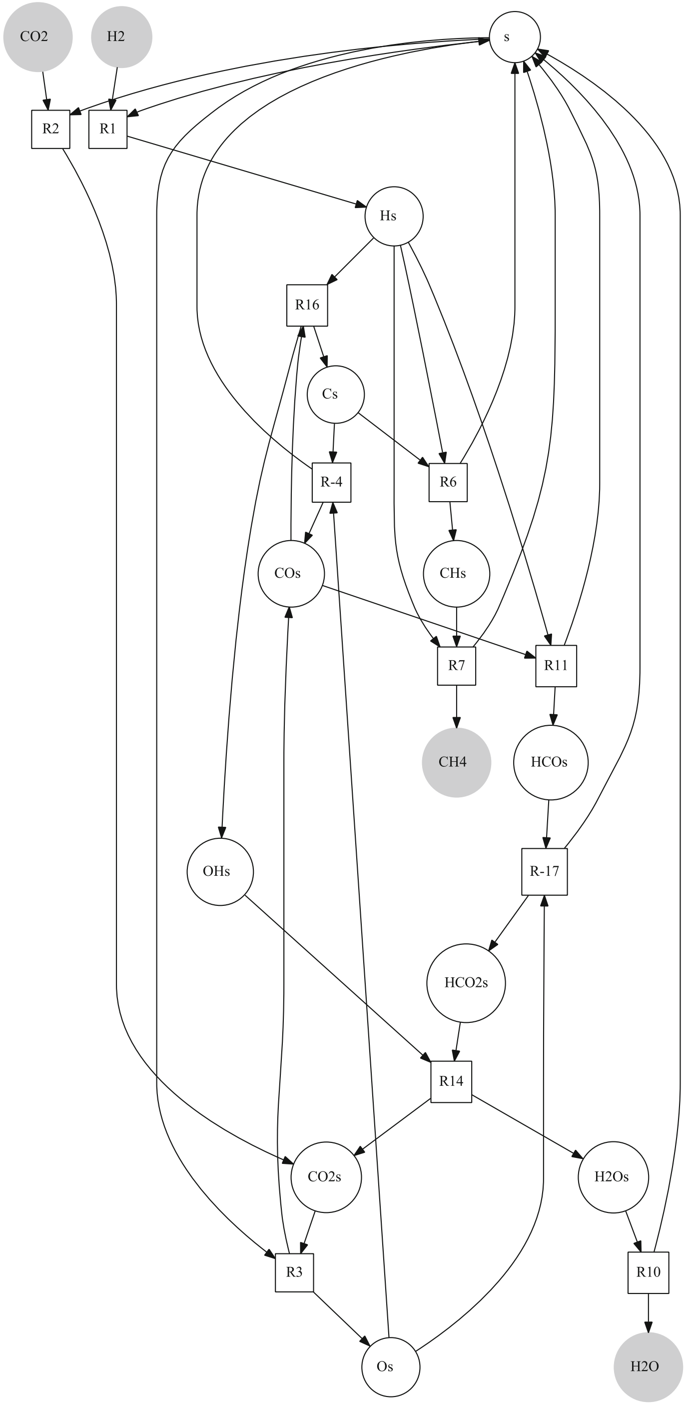

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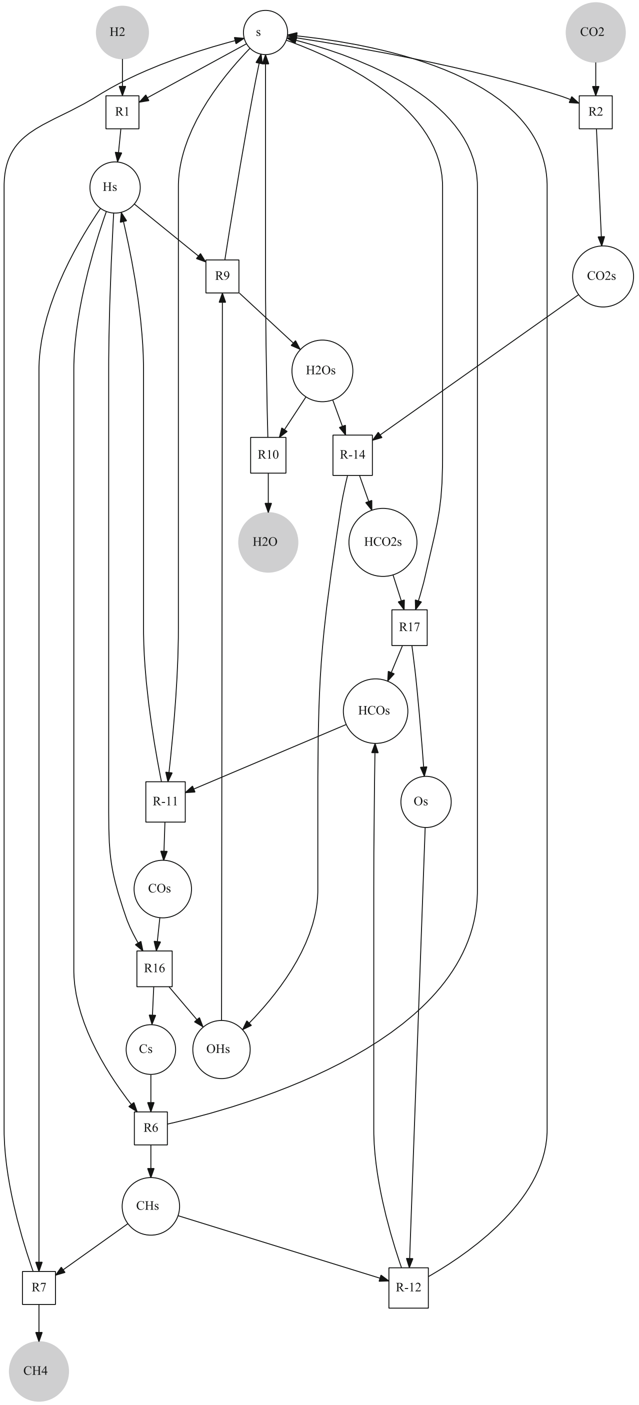

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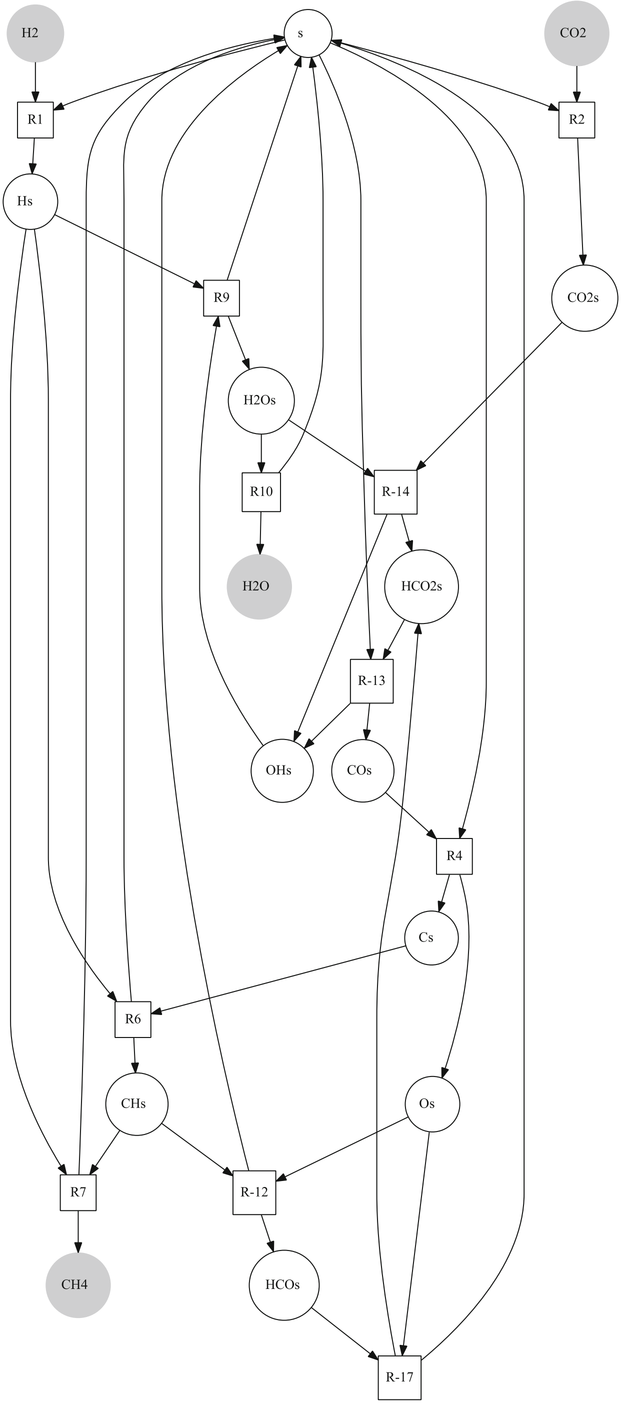

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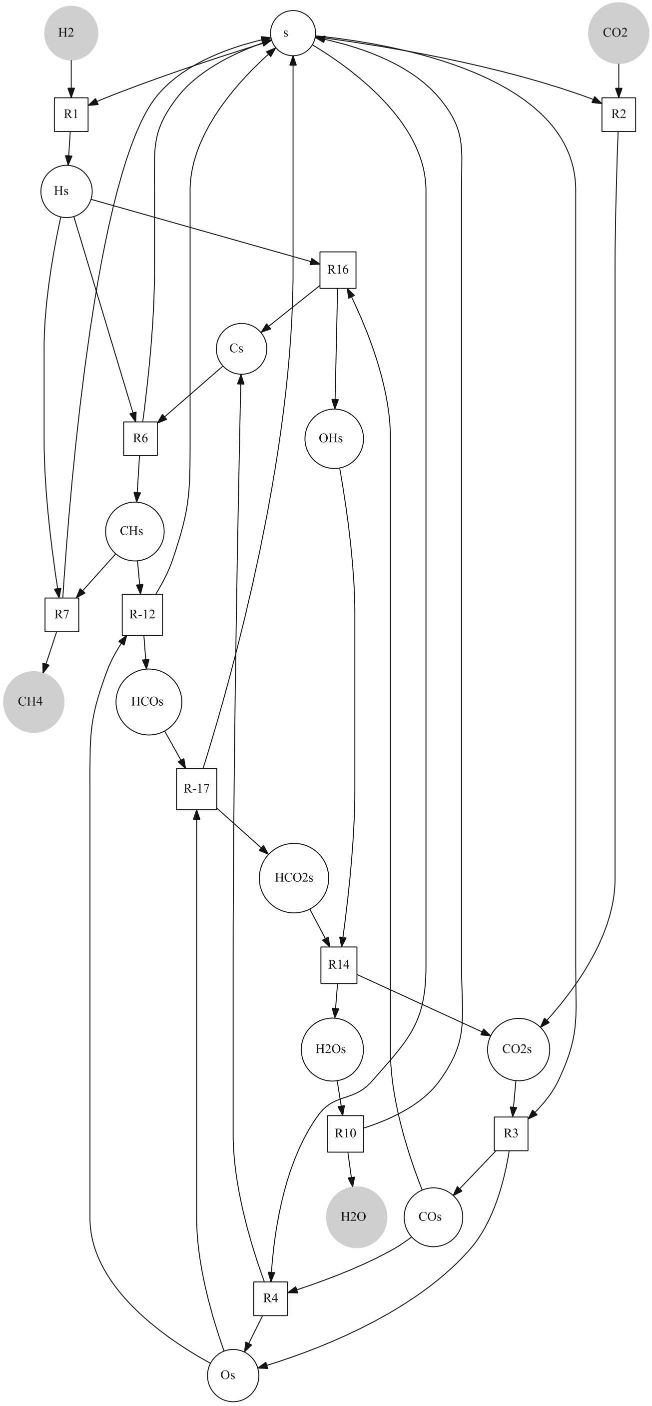

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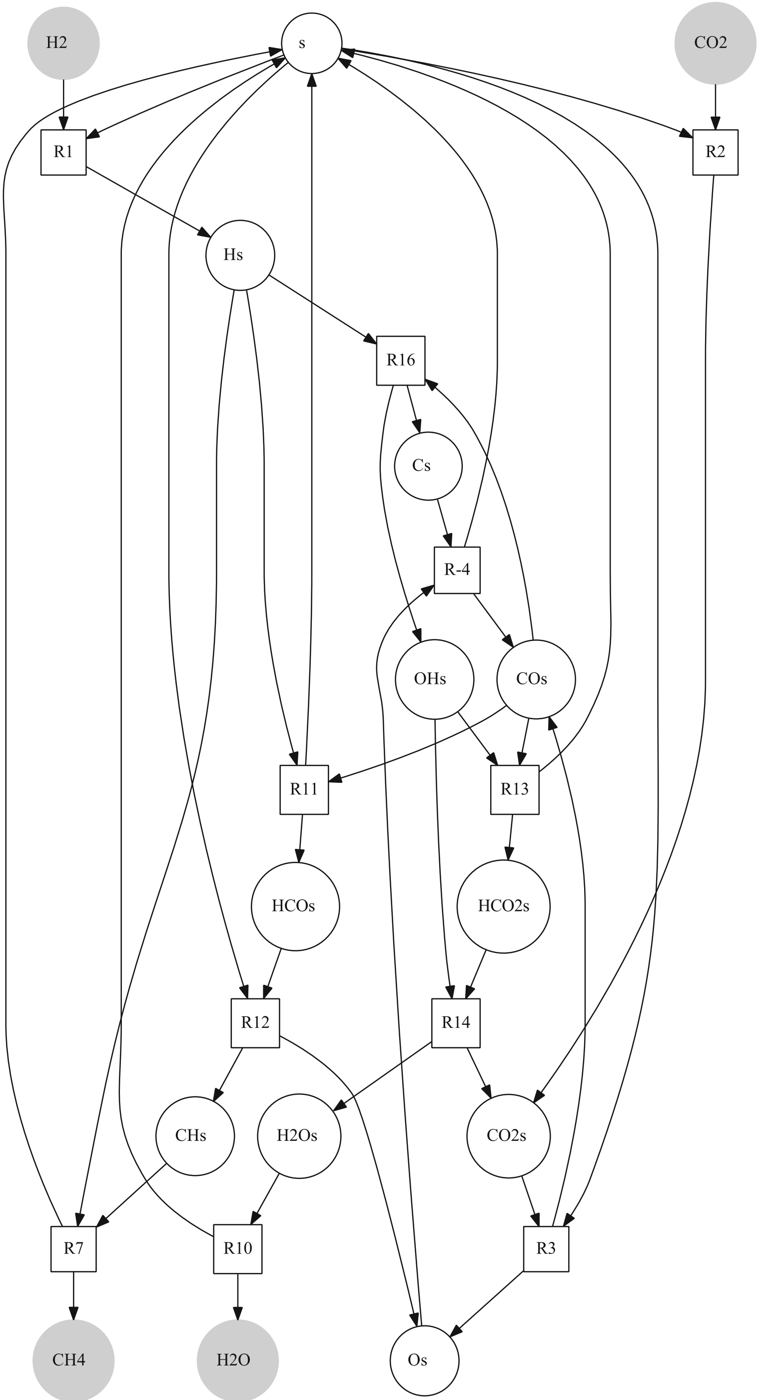

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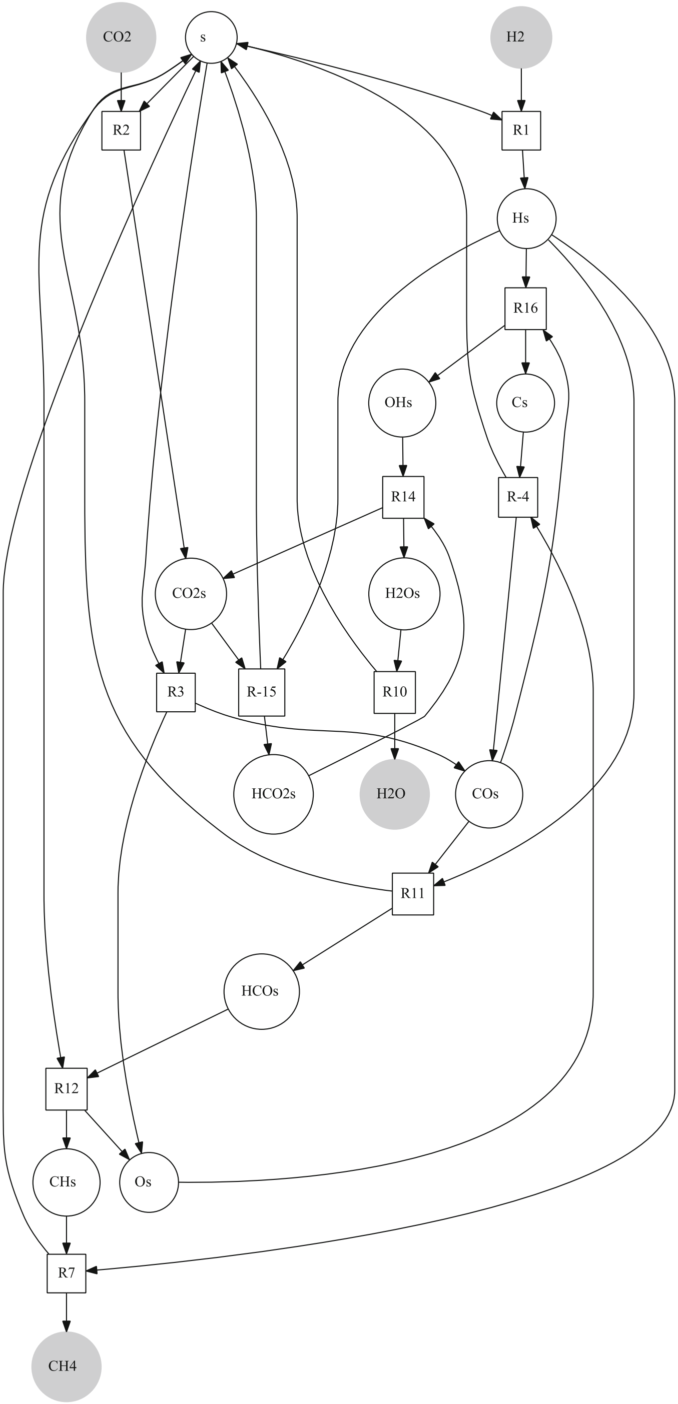
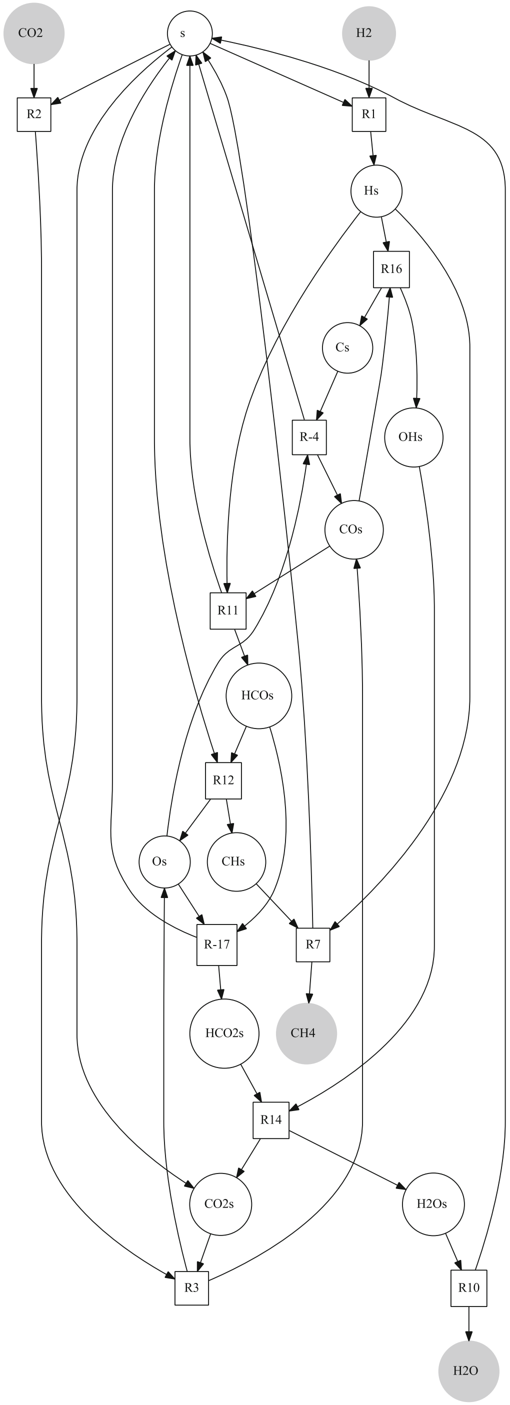
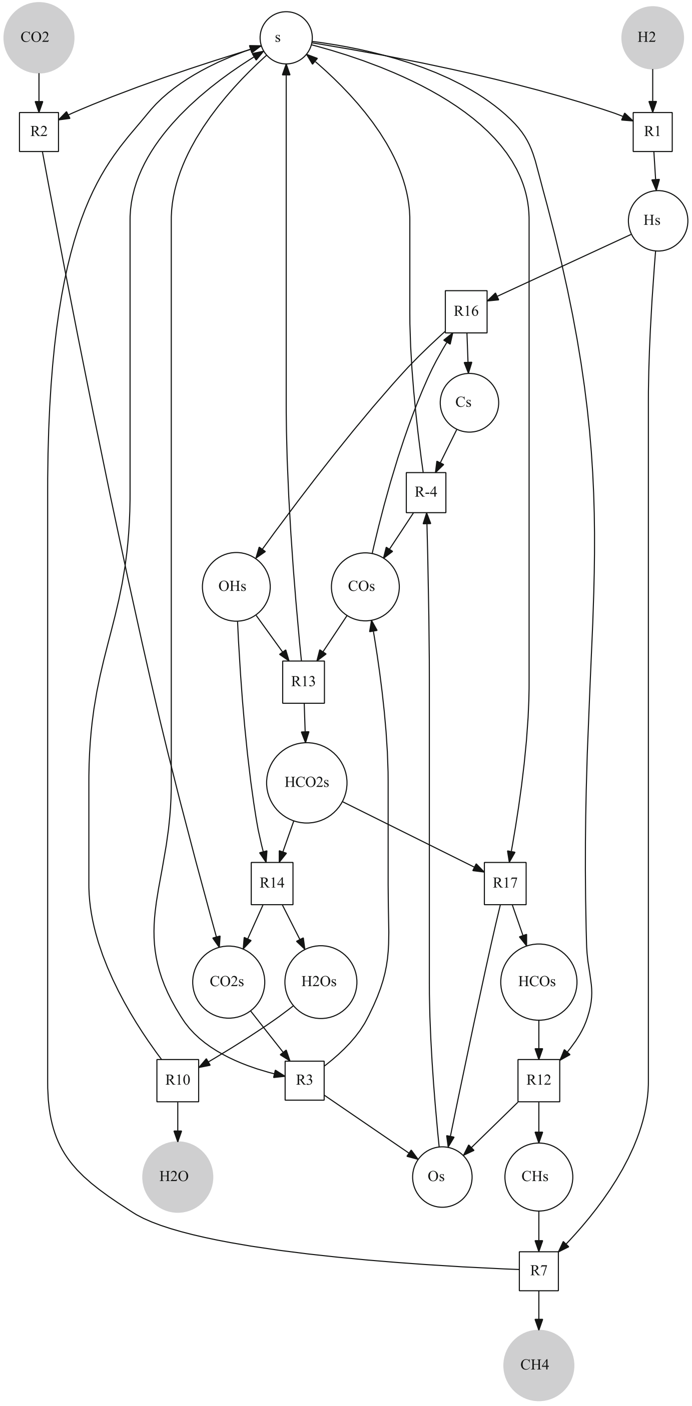


Fig. 61 P-graph N.56

Fig. 62 P-graph N.57





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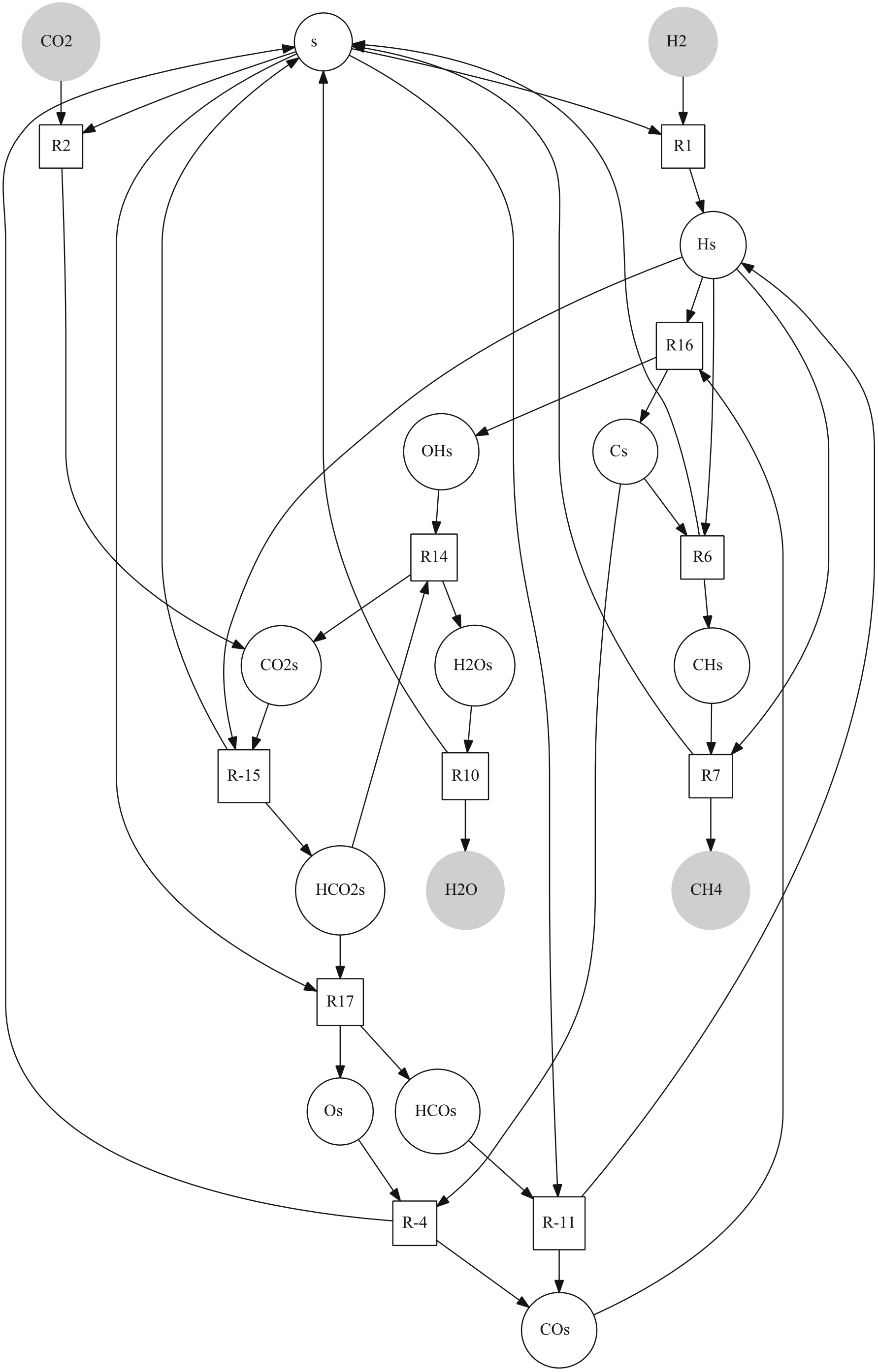

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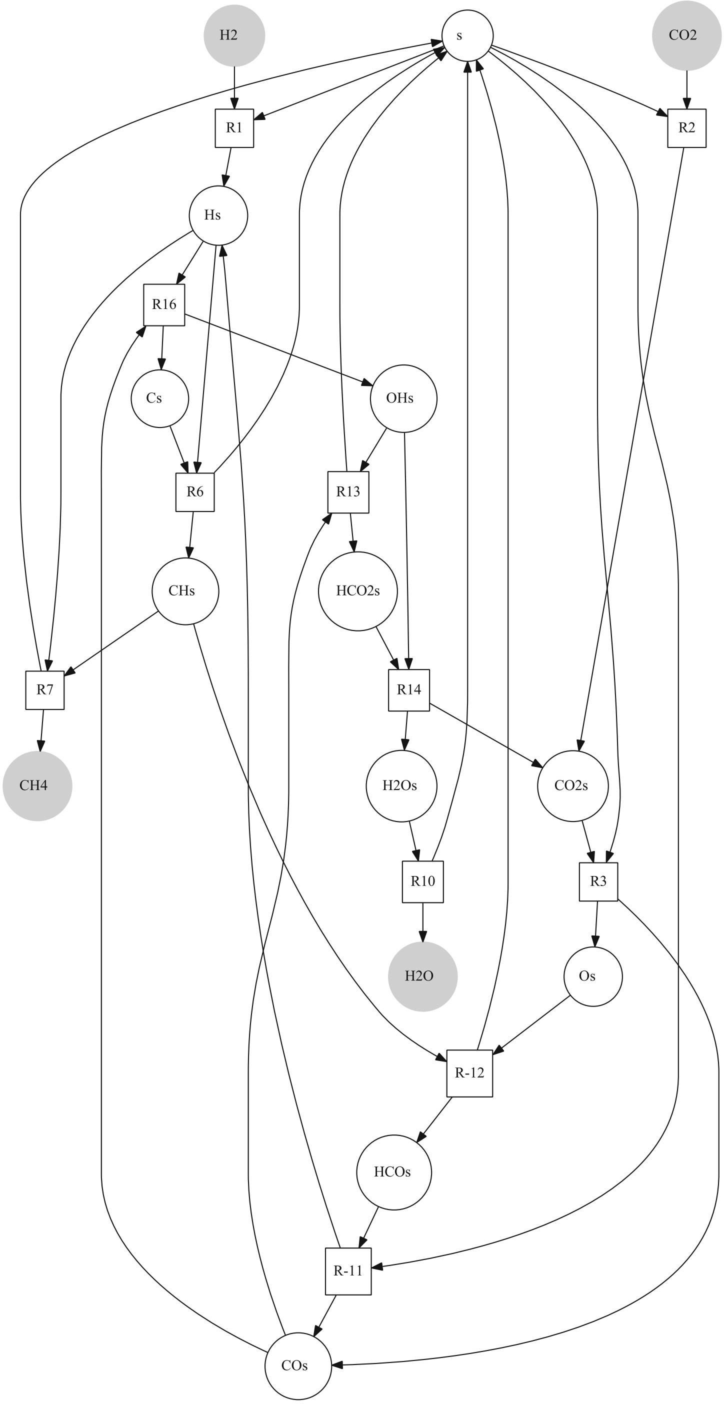

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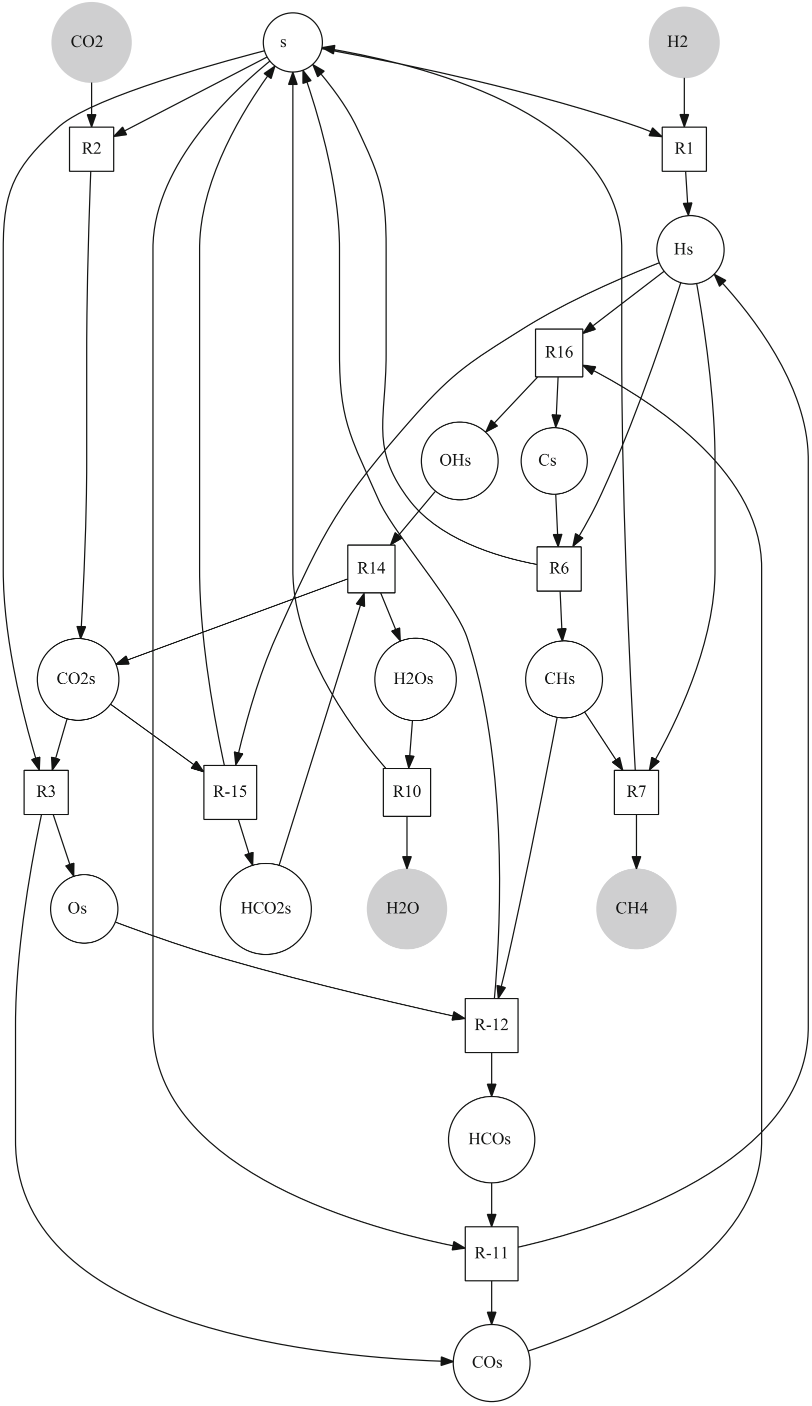
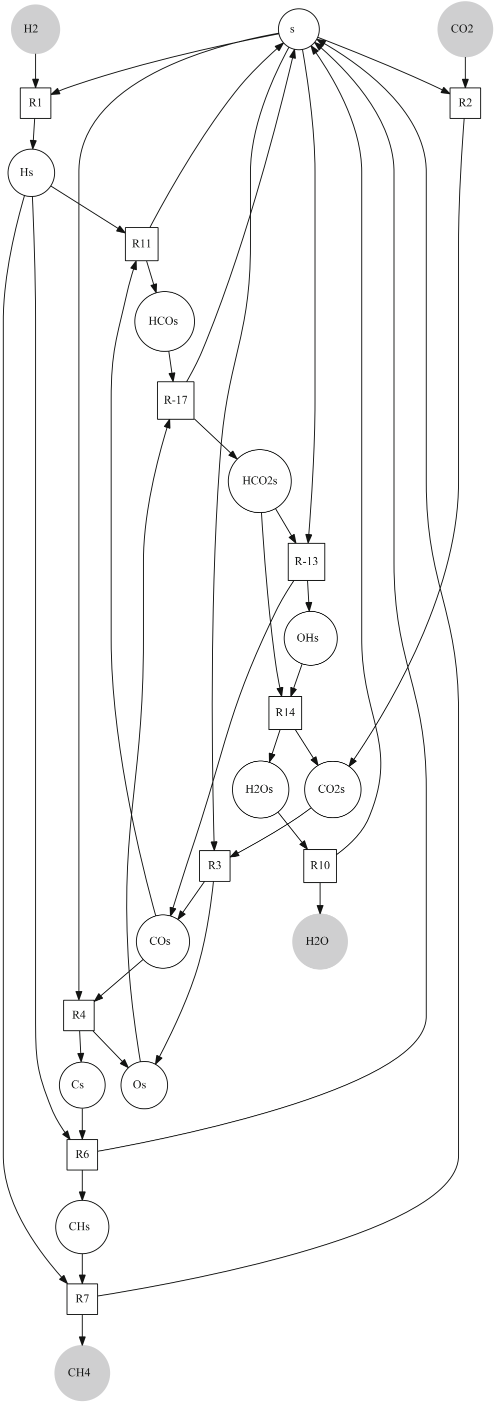


Fig. 66 P-graph N.61

Fig. 67 P-graph N.62



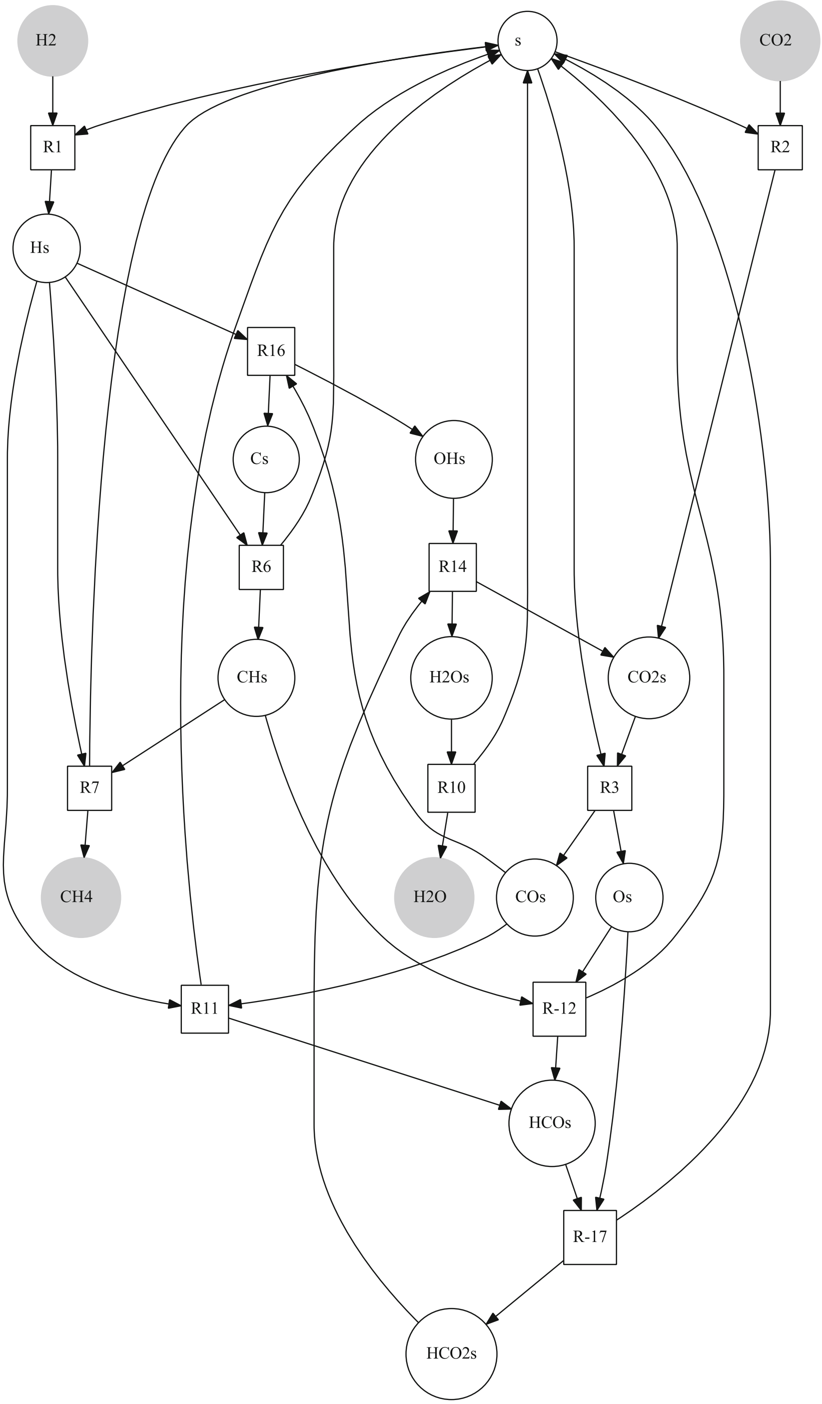
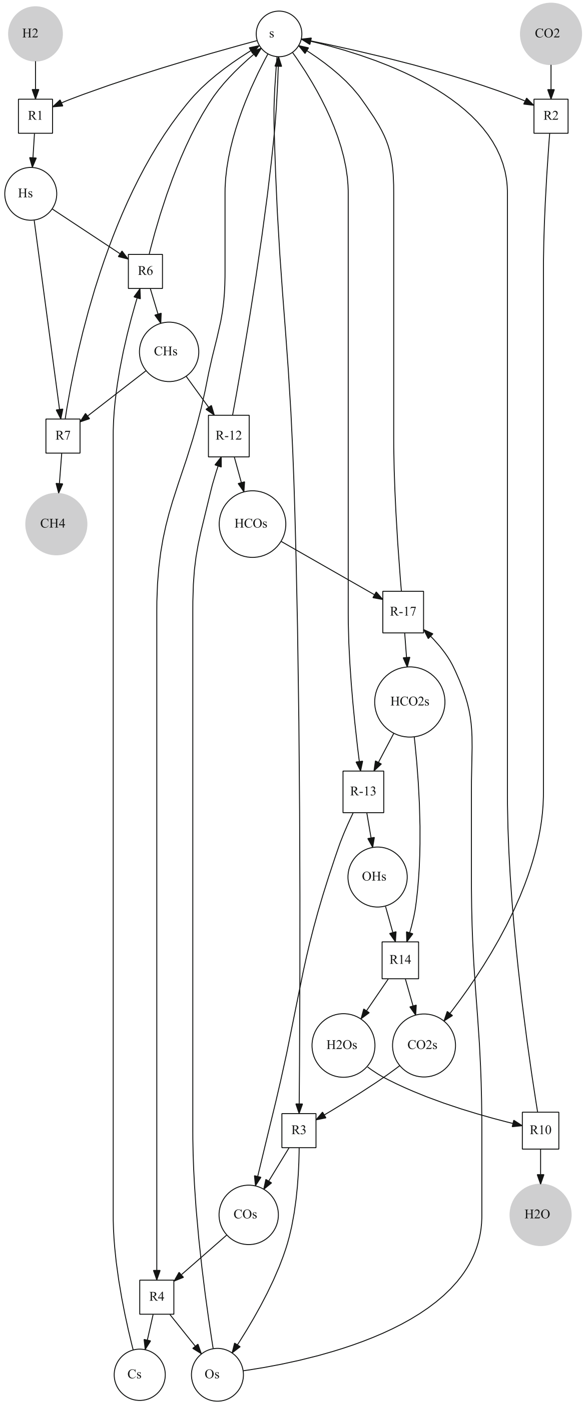
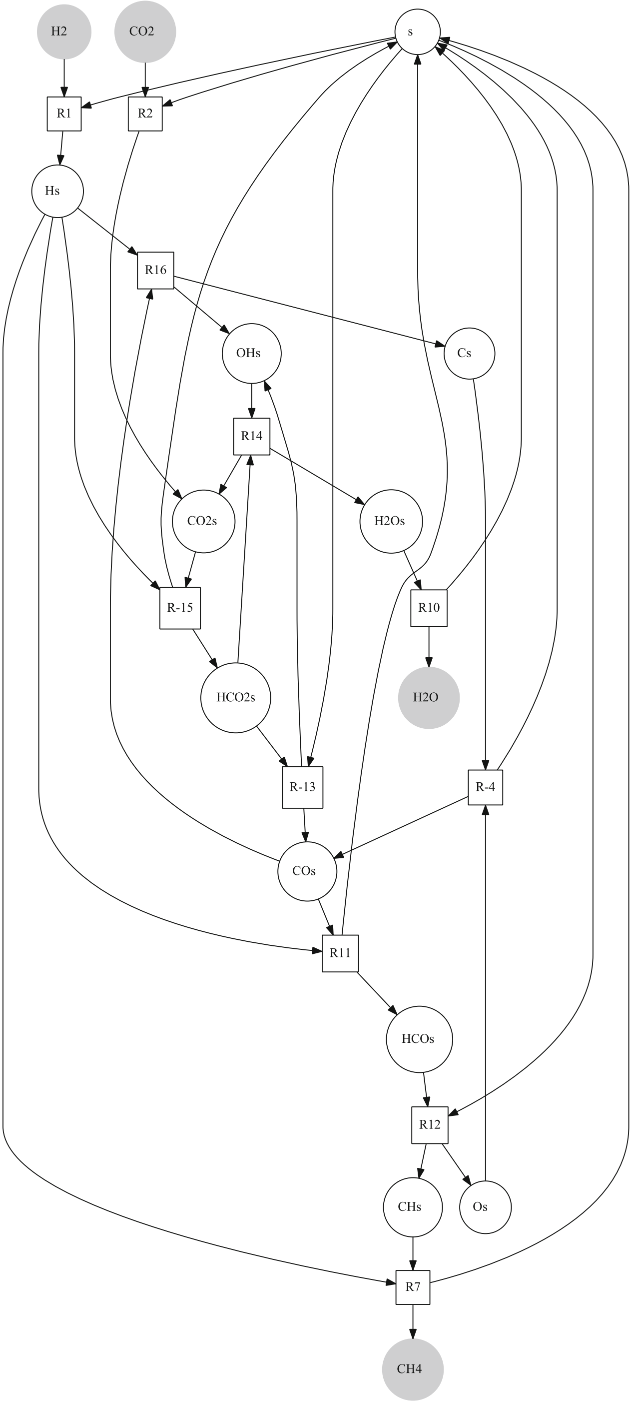


Fig. 68 P-graph N.63

Fig. 69 P-graph N.64





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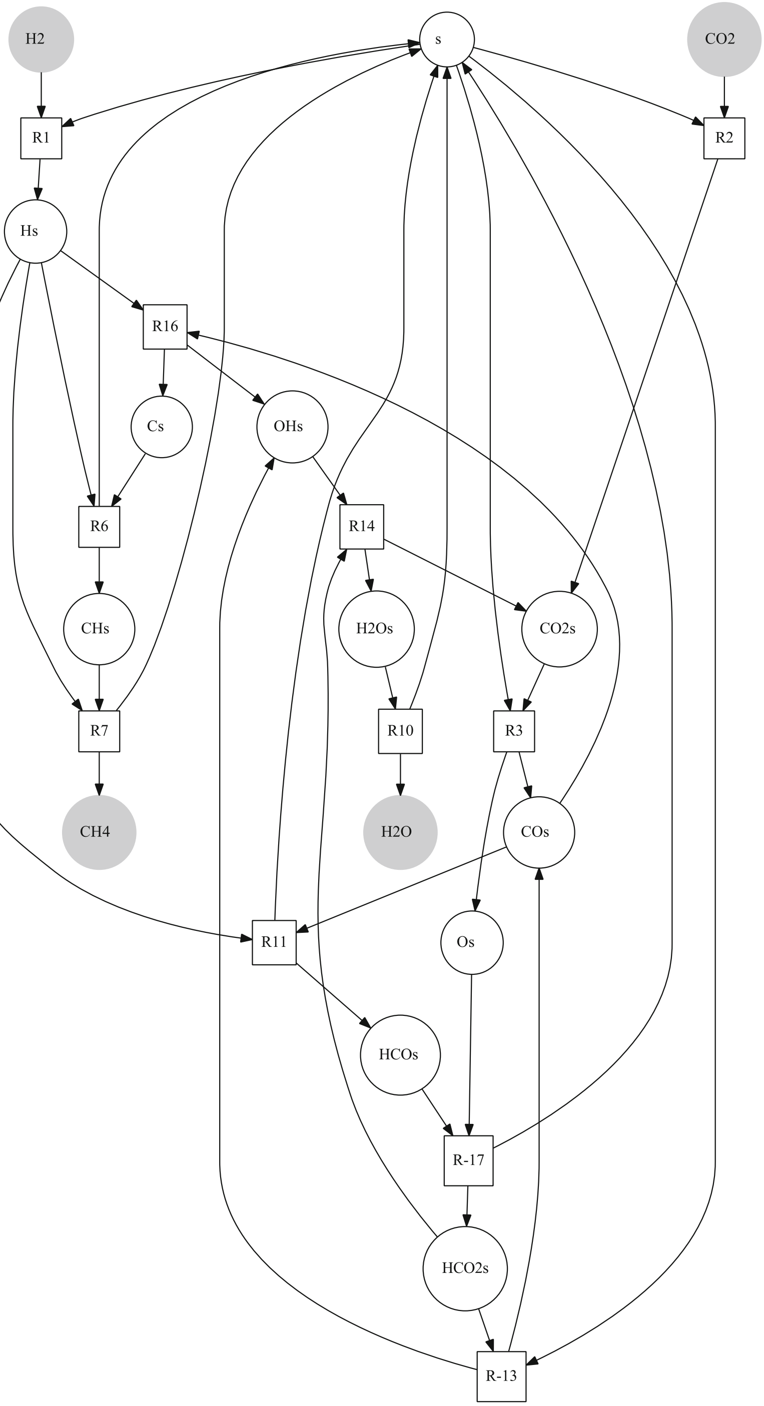

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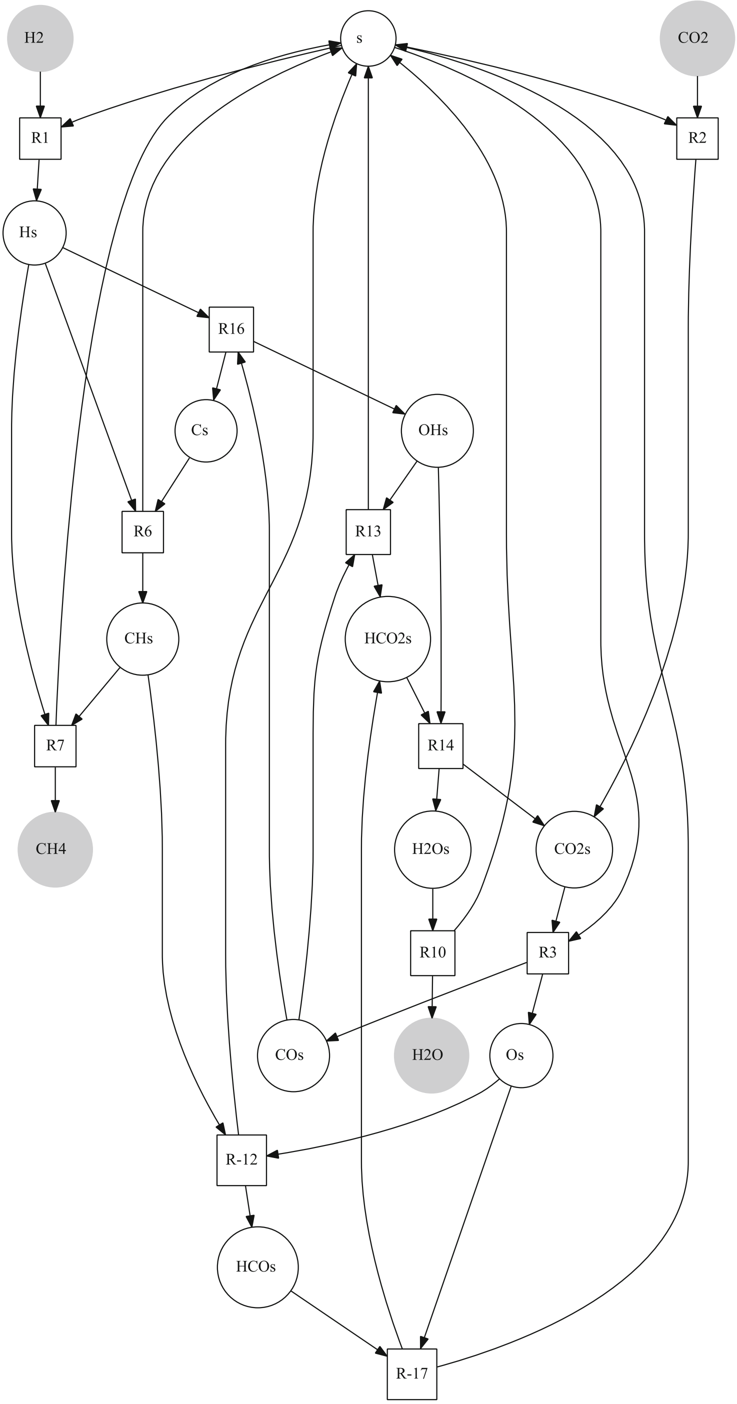

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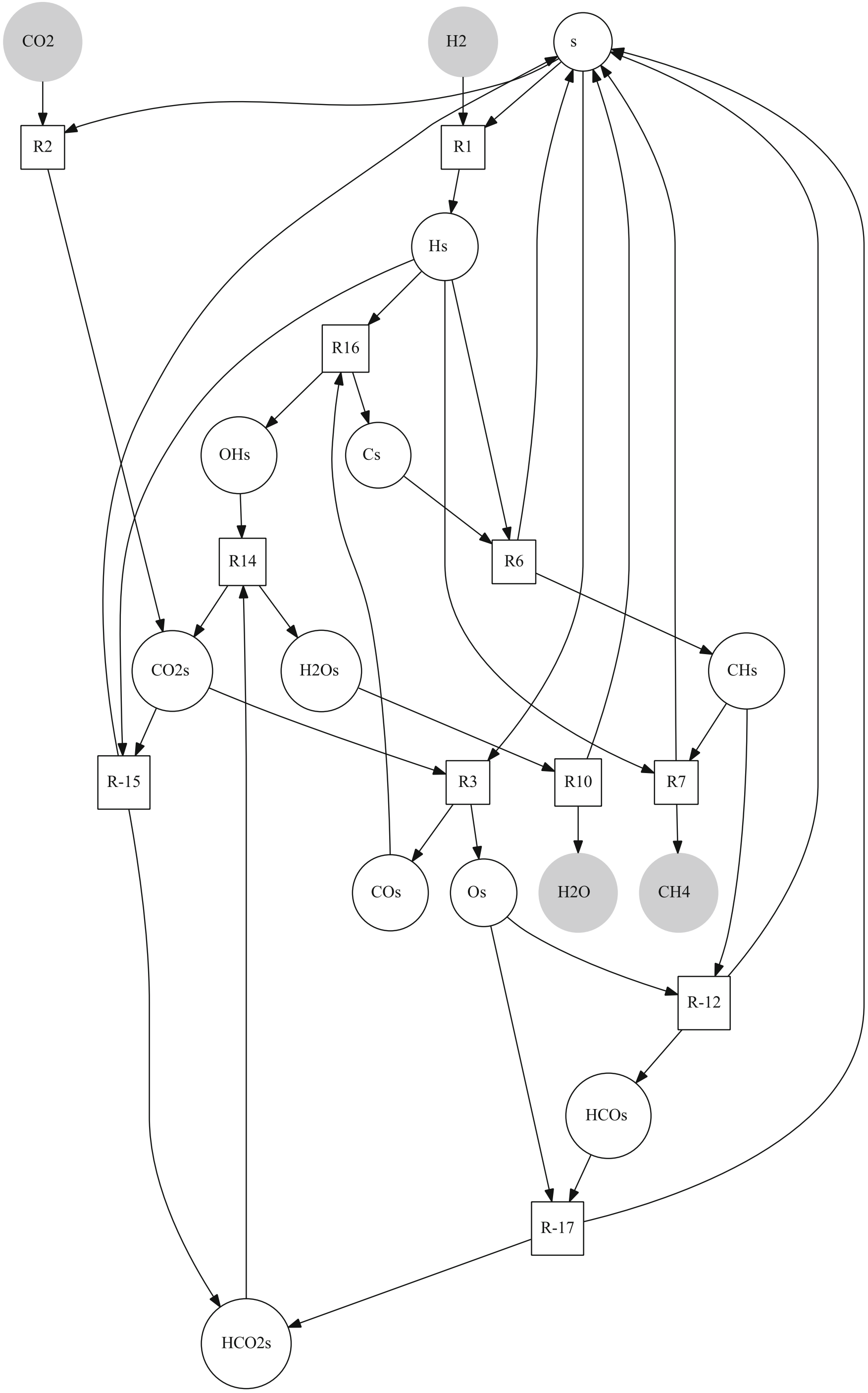

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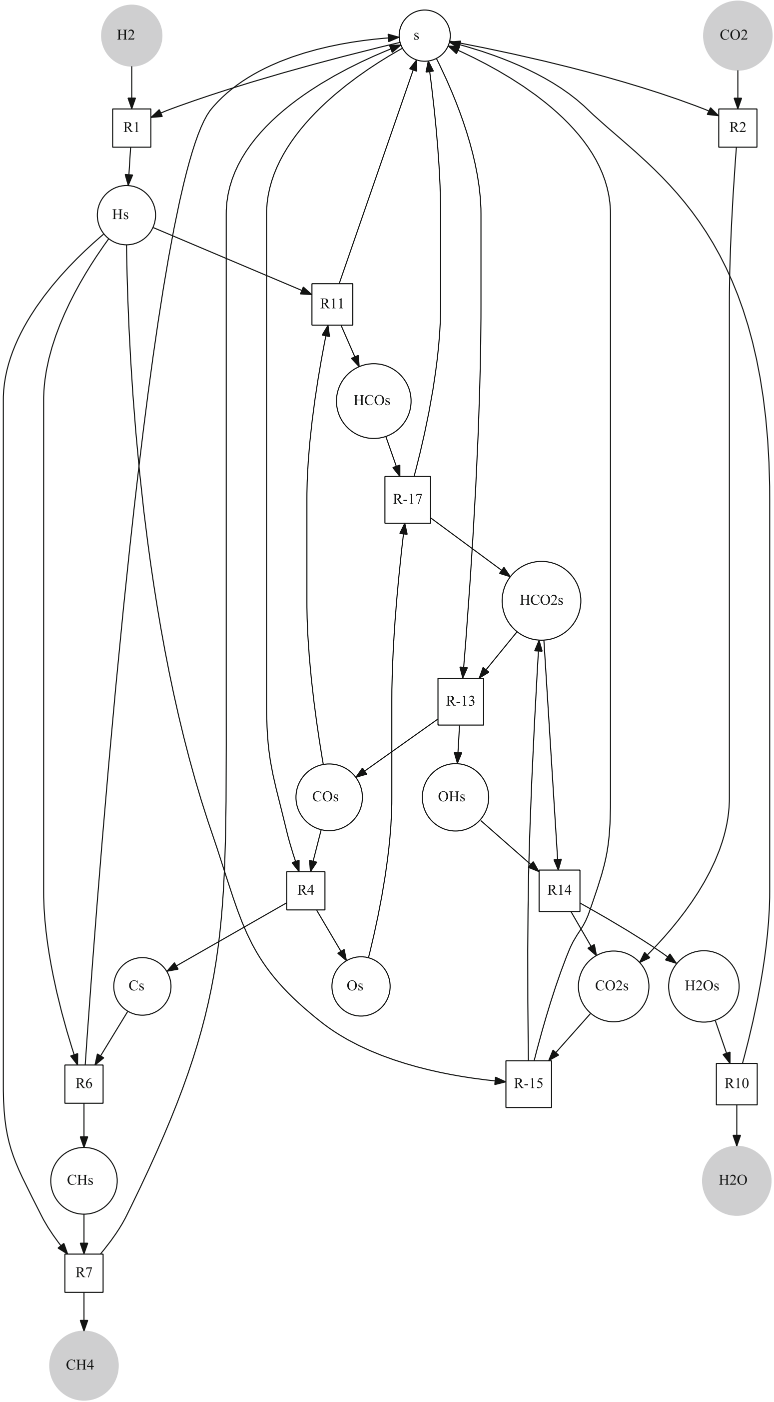

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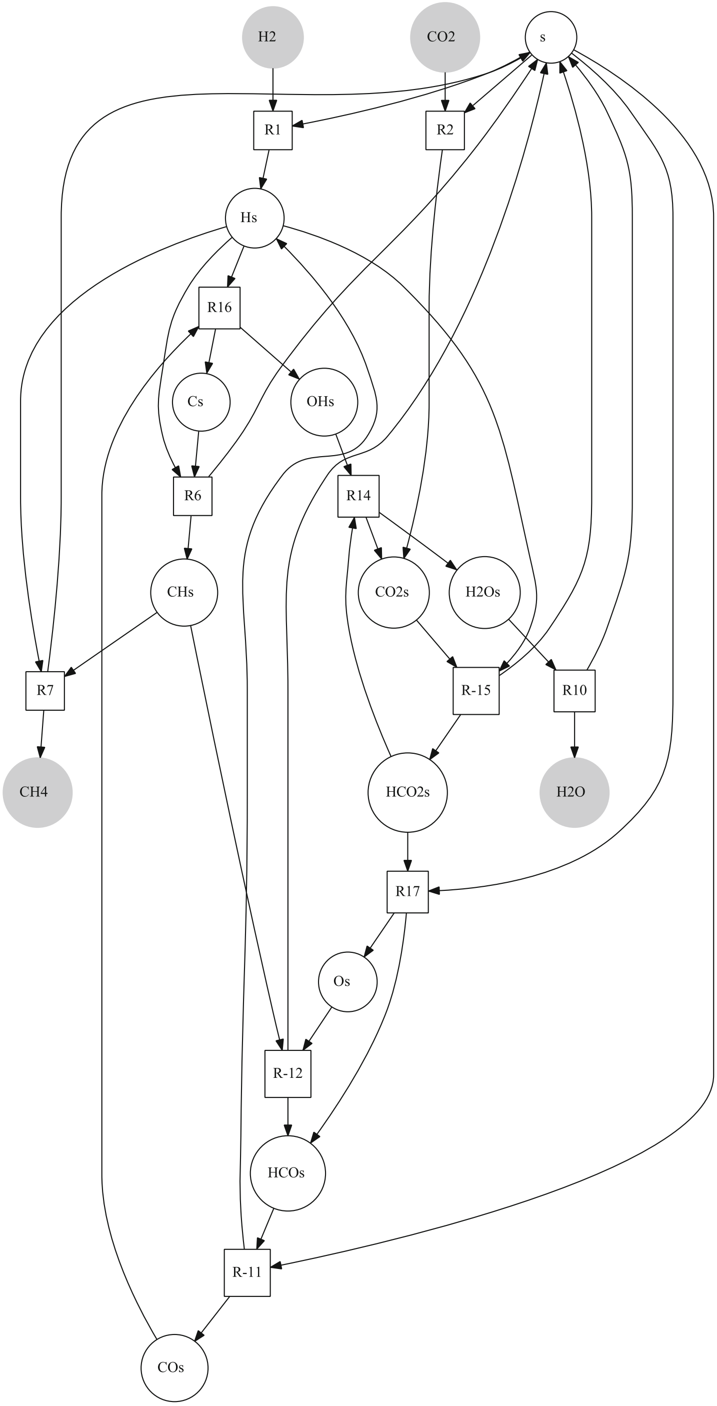

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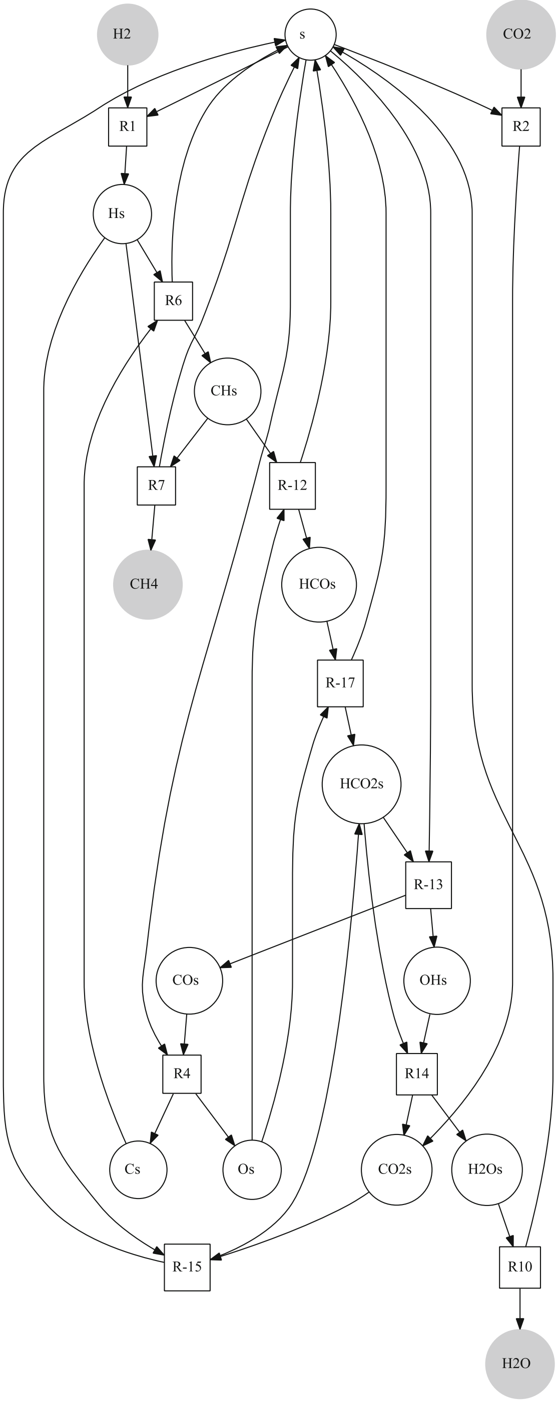
Fig. 76 P-graph N.71



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