

Search for reaction pathways with P-graphs: theoretical base for domain reduction with reaction blocks

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Abstract

The proposition of new kinetic expressions for a reaction system starts with the postulation of feasible reaction pathways. An ordered and combinatorially complete search of feasible mechanisms would focus the efforts of the expert groups on the selection of likely mechanisms and the creation of kinetic laws.

The search of feasible pathways can be addressed with algorithms based on P-graphs. This article proposes the definition of reaction blocks as a set of reactions with exclusive intermediaries, within a Maximal Structure. Two lemmas and a theorem are proposed to formalize the use of reaction blocks during the search of reaction pathways with the PBT algorithm. These reaction blocks allow a reduction of the search space when applied on a Maximal Structure of reactions. An example is presented to illustrate this reduction: the combinatorial number of feasible pathways in the methanation of carbon dioxide with hydrogen is 31.38 billion; and this search domain is reduced to 1.16 billion with the application of reaction blocks. No feasible pathway is lost in this process, as stated by the theorem

herein proposed.

Keywords: P-Graph, Reaction pathways

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1. Introduction

The determination of reaction mechanisms plays a key role in the kinetic description of reactive systems. A reaction mechanism consists of a set of reactions occurring in series, parallel, or combinations thereof, which describe molecular modifications of the reactants and intermediate species to generate the products of a chemical system. The sequence of steps in a mechanism determines the rate of the overall reaction, which depends on a rate limiting step: the slowest step involved in the mechanism [1].

The kinetic description of an overall reaction is developed in three major stages, namely:

- The postulation of feasible mechanisms.
- Selection of the most likely mechanism supported on physicochemical information.
- The postulation and validation of a kinetic law assuming a rate limiting step in the mechanism.

Usually, the emphasis of the groups working on kinetics and catalysis is placed on the second and third phases. The first phase is covered by proposing several alternatives, and determines the results of the following phases [2].

An ordered and combinatorially complete search of feasible mechanisms would focus the efforts of the expert groups in catalysis on the selection of likely mechanisms (phase 2) and the proposition of kinetic laws (phase 3). The execution of a complete search in phase 1 would support more robust analyses and would increase the speed of the overall kinetic study.

To search for candidate mechanisms is necessary to analyze each feasible alternative, so a non-ambiguous representation is required. The use of P-graphs is proposed for this purpose. P-graphs were originally introduced by Friedler et al for process analysis [3] and have been used to propose reaction pathways [4, 5]. 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) [3].

The search for reaction mechanisms in a reaction network has been addressed in previous works [3, 7, 4, 5]. 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 intermediaries. While the set O is a list of reactions, the set M is a set of the included species (reactants, intermediaries and products) [3].

After the definition of sets, a Maximal Structure is generated through an algorithm: the Maximal Structure Generation (MSG) presented by Friedler et al [7, 4]. This structure contains all the combinatorial pathways [7], so all relations within the set O should be included in the Maximal Structure (Figs. 1b and 1c).

A mechanism has to meet the mass balance within the network, which can either be evaluated in forward or backward overall direction. A

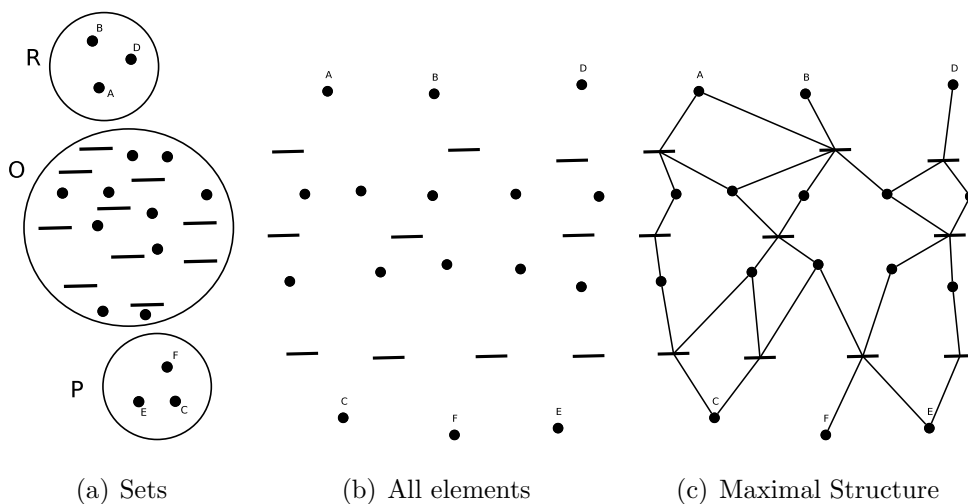


Figure 1: Maximal structure generation (MSG).

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 [4]. In this strategy, the mechanisms with a correct mass balance are distinguished through the feasibility of a Linear Programming problem for deciding stoichiometric factors.

Within the Maximal Structure, the number of combinatorial candidates for being a mechanism is $3^n - 1$, with n the number of reactions in set O, since every reaction can participate or not in a pathway [4]. This value is sustained in the following ideas: If it is included, a reaction can participate in a direct or reverse way. Thus, there are three possible participation options for each reaction in a pathway: direct (\rightarrow), reverse (\leftarrow), or no participation. As a pathway with no reaction is not a pathway, we need to remove this configuration from the counting.

The number of combinatorial candidates for a mechanism grows exponentially with the number of reactions. If the proposed feasible

reactions in the system are elementary, the number of reactions populating the set O can be tens, so the number of combinatorially possible mechanisms can grow to 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 article defines a reaction block as a set of reactions that can be treated as a single reaction during the execution of the PBT algorithm. With the use of reaction blocks, the search space of feasible pathways can decrease by millions without excluding feasible mechanisms. An example is presented to illustrate this point. The aim of this work is to 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.

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 Appendixes.

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 [4]. 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. 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}), intermediaries (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 $O \setminus o_{RB}$, so no intermediary 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).

2.3. Lemma 1

Let y_i a reaction belonging to o_{RB} a reaction block in O . Let (m, o) 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.

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:

$$S_{RB} := \sum_{i \in \{1, 2, \dots, |o_{RB}|\}} \gamma_i \cdot y_i \quad y_i \in o_{RB} \quad (1)$$

γ_i factors are such that:

- The reactants of S_{RB} are r_{RB} .
- The products of S_{RB} are p_{RB} .

- All intermediaries 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 in an aggregate reaction, as shown in the right hand side of the same figure.

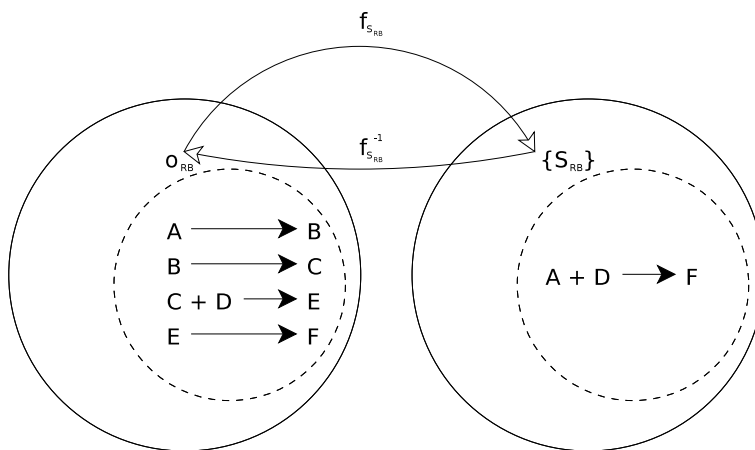


Figure 2: Example: construction of reaction S_{RB} from reaction block o_{RB} . A construction function $f_{S_{RB}}$ is defined between sets.

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 ($f_{S_{RB}}^{-1}(\{S_{RB}\}) := o_{RB}$). Note that by construction $f_{S_{RB}}$ is a bijective function (Fig. 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:

$$\begin{aligned} mec [O]^{o_{RB}} &= \{(m, o) \text{ a feasible pathway} \mid \\ &\quad m \subseteq M \wedge o \subseteq O \wedge o \cap o_{RB} \neq \emptyset\} \end{aligned} \quad (2)$$

$$\begin{aligned} mec [O]^{\overline{o_{RB}}} &= \{(m, o) \text{ a feasible pathway} \mid \\ &\quad m \subseteq M \wedge o \subseteq O \wedge o \cap o_{RB} = \emptyset\} \end{aligned} \quad (3)$$

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

2.7. Lemma 2

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

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 $O^R := (O \setminus o_{RB}) \cup \{S_{RB}\}$.

The proof of this theorem is available in Appendix C. Theorem 1 can be

used while 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 [4] 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 [4] 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 on these hypotheses. In this context, Theorem 1 allows to use the PBT algorithm [4] 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. The search for feasible mechanisms in this system is presented in other work of the same authors [8]. In this article, 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.

3. Application of reaction blocks on a reaction system for CO₂ methanation with hydrogen

The CO₂ methanation has been signed as an alternative for cycling anthropogenic CO₂ [9]. In this reaction the carbon dioxide is converted to methane, which could be used as fuel. While anthropogenic CO₂ is mainly generated by combustion, it can be converted back to a fuel by methanation. In this cycle, both the source of H₂ and the energy source for the process determine the carbon footprint calculated by LCA [10]. The methanation

of CO_2 through hydrogenation is summarized by Sabatier's reaction (Eq.4, [11]):



Table 1 shows all species and reactions included in the CO_2 methanation system. All these reactions have been signed as elementary and will be understood as feasible reactions in the methanation system. Taking all of these reactions, the combinatorial number of feasible mechanisms is $3^{22} - 1 \approx 31.38$ billion.

In this case, the reactions R7 to R10 in Table 1 can be considered a reaction block because they are connected in series and there is no reaction outside the block including these intermediaries. This reaction block is consistent with Definition 2, and it is summarized by (R7a) in Table 2. The set of reactions has 19 elements after the reduction using a reaction block, so the search domain decreases to $3^{19} - 1 \approx 1.16$ billions. The new set of reactions is listed in Table 2. Theorem 1 allows to state a relation between each feasible mechanism in the original set of reactions and a feasible mechanism in the reduced space, so this reduction maintains the number of feasible mechanisms from the disaggregated reaction set.

As mentioned before, the search of pathways within the reduced set of reactions is presented in other work of the same authors [8]. In this context, the use of reaction blocks allow a significant reduction of the search domain.

Name herein	Reaction	Reported by
R1	$H_2 + 2s \rightleftharpoons 2Hs$	[12]
R2	$CO_2 + s \rightleftharpoons CO_2s$	[13]
R3	$CO_2s + s \rightleftharpoons COs + Os$	[13]
R4	$COs + s \rightleftharpoons Cs + Os$	[12]
R5	$COs \rightleftharpoons CO + s$	[12]
R6	$Cs + Hs \rightleftharpoons CHs + s$	[12]
R7	$CHs + Hs \rightleftharpoons CH_2s + s$	[12]
R8	$CH_2s + Hs \rightleftharpoons CH_3s + s$	[12]
R9	$CH_3s + Hs \rightleftharpoons CH_4s + s$	[12]
R10	$CH_4s \rightleftharpoons CH_4 + s$	[12]
R11	$Os + Hs \rightleftharpoons OHs + s$	[12]
R12	$OHs + Hs \rightleftharpoons H_2Os + s$	[12]
R13	$H_2Os \rightleftharpoons H_2O + s$	[12]
R14	$COs + Hs \rightleftharpoons HCOs + s$	[14]
R15	$HCOs + s \rightleftharpoons CHs + Os$	[14]
R16	$COs + OHs \rightleftharpoons HCO_2s + s$	[15]
R17	$HCO_2s + OHs \rightleftharpoons CO_2s + H_2Os$	[15]
R18	$HCO_2s + s \rightleftharpoons CO_2s + Hs$	[15]
R19	$COs + Hs \rightleftharpoons Cs + OHs$	[13]
R20	$HCO_2s + s \rightleftharpoons HCOs + Os$	[13]
R21	$CO_2s + OHs \rightleftharpoons HCO_3s$	[16]
R22	$HCO_3s + Hs \rightleftharpoons HCO_2s + OHs$	[16]

Table 1: Reactions considered in the system.

Name herein	Reaction	Reported by
R1a	$H_2 + 2s \rightleftharpoons 2Hs$	[12]
R2a	$CO_2 + s \rightleftharpoons CO_2s$	[13]
R3a	$CO_2s + s \rightleftharpoons COs + Os$	[13]
R4a	$COs + s \rightleftharpoons Cs + Os$	[12]
R5a	$COs \rightleftharpoons CO + s$	[12]
R6a	$Cs + Hs \rightleftharpoons CHs + s$	[12]
R7a	$CHs + 3Hs \rightleftharpoons CH_4 + 4s$	S_{RB} , this work
R8a	$Os + Hs \rightleftharpoons OHs + s$	[12]
R9a	$OHs + Hs \rightleftharpoons H_2Os + s$	[12]
R10a	$H_2Os \rightleftharpoons H_2O + s$	[12]
R11a	$COs + Hs \rightleftharpoons HCOs + s$	[14]
R12a	$HCOs + s \rightleftharpoons CHs + Os$	[14]
R13a	$COs + OHs \rightleftharpoons HCO_2s + s$	[15]
R14a	$HCO_2s + OHs \rightleftharpoons CO_2s + H_2Os$	[15]
R15a	$HCO_2s + s \rightleftharpoons CO_2s + Hs$	[15]
R16a	$COs + Hs \rightleftharpoons Cs + OHs$	[13]
R17a	$HCO_2s + s \rightleftharpoons HCOs + Os$	[13]
R18a	$CO_2s + OHs \rightleftharpoons HCO_3s$	[16]
R19a	$HCO_3s + Hs \rightleftharpoons HCO_2s + OHs$	[16]

Table 2: Reactions considered in the system after reduction.

4. Concluding remarks

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 sustained on lemmas and definitions herein presented.

The application of reaction blocks has been exemplified in the methanation of CO_2 with H_2 . In this context, the reduction of the feasible reaction space implies a decrease in the number of combinatorial pathways within the Maximal Structure, from 31.38 billion to 1.16 billion.

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.

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Notation

E	A global reaction.
O	A set of feasible reactions in a chemical system.
M	A set of feasible species in a chemical system.
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 [4].
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 $\{S_{RB}\}$
$mech [O]^{o_{RB}}$	The set of all feasible mechanisms within O including the reactions in o_{RB} . It has been found with PBT algorithm [4].
$mech [O]^{\overline{o_{RB}}}$	The set of all feasible mechanisms within O not including the reactions in o_{RB} . It has been found with PBT algorithm [4].
O^R	A reduced set of reactions equal to $(O \setminus o_{RB}) \cup \{S_{RB}\}$

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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 [4]. Then, theorems R1 to R6 [4] are valid for this pathway. Since theorem R3 is valid, all intermediaries in a feasible pathway have to be completely consumed. Taking into account the definition of o_{RB} , the intermediaries in the reaction block (i_{RB}) are not included in other reactions outside the block. Then, the reactions for consuming these intermediaries belong to the reaction block o_{RB} . By Theorem R3 and Axiom T4 [4], all reactions in o_{RB} have to be included in o . Otherwise, there exist an intermediary $i^* \in i_{RB}$ which is not completely consumed, violating Theorem R3 [4].

Appendix B: Proof of Lemma 2

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

$$mec [O]^{o'} \cup mec [O]^{o'} = \{(m^*, o^*) \text{ a feasible pathway} \mid [m^* \subseteq M \wedge o^* \subseteq O \wedge o^* \cap o' \neq \emptyset] \vee [m^* \subseteq M \wedge o^* \subseteq O \wedge o^* \cap o' = \emptyset]\}$$

With a distribution of or over and we have:

$$mec [O]^{o'} \cup mec [O]^{o'} = \{(m^*, o^*) \text{ a feasible pathway} \mid m^* \subseteq M \wedge o^* \subseteq O \wedge [o^* \cap o' \neq \emptyset \vee o^* \cap o' = \emptyset]\}$$

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

$$mec [O]^{\underline{O}} \cup mec [O]^{\overline{O}} = \{(m^*, o^*) \text{ a feasible pathway} \mid m^* \subseteq M \wedge o^* \subseteq O\}$$

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 a piecewise function defined as follows:

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

The functions F_1 and F_2 are defined as follows (see Fig. 3):

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

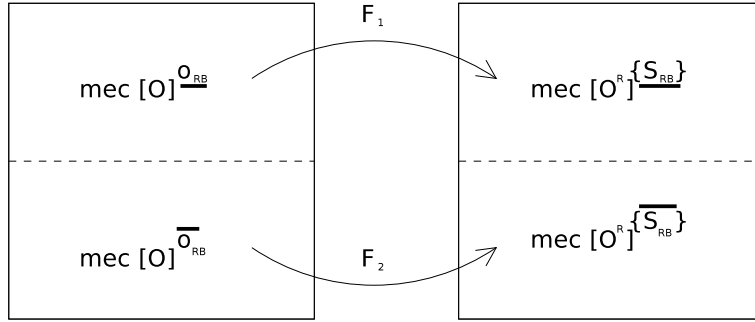


Figure 3: Function F between sets of pathways. The subfunctions F_1 and F_2 are represented relating the elements into each partition.

By Lemma 2, the collection $\{mec [O]^{\underline{O}_{RB}}, mec [O]^{\overline{O}_{RB}}\}$ partitions $mec [O]$. Also the collection $\{mec [O^R]^{\underline{S}_{RB}}, mec [O^R]^{\overline{S}_{RB}}\}$

partitions $mec[O^R]$. Both partitions are represented in Fig. 3. Therefore, the next steps in this proof will be demonstrated for F_1 and F_2 separately.

- 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 $m^{*2} = m^* \setminus i_{RB}$ exists, because $(m^*, o^*) \in mec[O]^{o_{RB}}$ and then $i_{RB} \subseteq m^*$.

Is (m^{*2}, o^{*2}) a feasible pathway? (m^*, o^*) is a feasible pathway, because $(m^*, o^*) \in mec[O]^{o_{RB}}$. Let y^* 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 intermediaries 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 intermediaries 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 $mec[O]^{o_{RB}}$ has an image in the pathways set $mec[O^R]^{\{S_{RB}\}}$.

- 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 $mec [O^R]^{\overline{\{S_{RB}\}}}$.

- 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 $mec [O^R]^{\overline{\{S_{RB}\}}}$ such that $F_1[(m^*, o^*)] = (m^{*2}, o^{*2})$ and $F_1[(m^*, o^*)] = (m^{*3}, o^{*3})$. As $m^{*2} = m^* \setminus i_{RB}$ and $m^{*3} = m^* \setminus i_{RB}$, then $m^{*2} = m^{*3}$. On the other hand $o^{*2} = (o^* \setminus o_{RB}) \cup \{S_{RB}\}_2$ and $o^{*3} = (o^* \setminus o_{RB}) \cup \{S_{RB}\}_3$. 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 $mec [O^R]^{\overline{\{S_{RB}\}}}$ 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.