

Conservation Laws

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1 Introduction

Autocatalytic networks typically involve internal species which make more of themselves and external species which play the role of fuel or waste. While autocatalytic networks lack conservation law, there are still conservation laws for the total mass and conserved fragments of molecules called moieties. These moieties are arranged differently after the reactions so that autocatalytic species manage to make more of themselves. The question we address here is: could these conservation laws for moieties actively rule the production of autocatalytic species?

2 Type 1 with fuel and waste

We start considering the type 1 example with F (fuel) and W (waste) to allow for mass conservation. Using two different fuels for the different reactions, we can write the reactions as:



The stoichiometric matrix is in terms of F_1 , F_2 , W , A and B :

$$S = \begin{pmatrix} -1 & 0 \\ 0 & -1 \\ 0 & 1 \\ -1 & 2 \\ 1 & -1 \end{pmatrix} \tag{2}$$

This matrix has a left nullspace of dimension 3, since 3 out of 5 rows are linearly dependent from the other two. A possible basis of the nullspace is then:

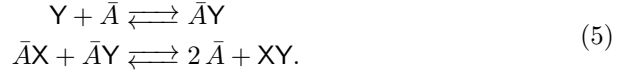
$$\bar{A} = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 1 \\ 1 \end{pmatrix} \quad X = \begin{pmatrix} 0 \\ 1 \\ 1 \\ 0 \\ 0 \end{pmatrix} \quad Y = \begin{pmatrix} 1 \\ 0 \\ 1 \\ 0 \\ 1 \end{pmatrix} \quad (3)$$

\bar{A} , X , Y can be seen as the moieties that the system is conserving, indeed, written as the following, their value must remain constant throughout the dynamics of the reactions. We find that

$$\begin{aligned} \bar{A} &= F_2 + A + B \\ X &= F_2 + W \\ Y &= F_1 + W + B. \end{aligned} \quad (4)$$

Based on this, all the species can be expressed as combinations of these moieties: $A = \bar{A}$, $B = \bar{A}Y$, $F_1 = Y$, $F_2 = \bar{A}X$, $W = XY$.

Reactions ?? then become, in terms of singular compounds:



We can identify then, 3 stoichiometric matrices for each of the moieties, taking into account in which reaction they are consumed and produced

$$S_{\bar{A}} = \begin{pmatrix} 0 & 0 \\ 0 & -1 \\ 0 & 0 \\ -1 & 2 \\ 1 & -1 \end{pmatrix} \quad S_X = \begin{pmatrix} 0 & 0 \\ 0 & -1 \\ 0 & 1 \\ 0 & 0 \\ 0 & 0 \end{pmatrix} \quad S_Y = \begin{pmatrix} -1 & 0 \\ 0 & 0 \\ 0 & 1 \\ 0 & 0 \\ 1 & -1 \end{pmatrix} \quad (6)$$

This means that the conservation of the moiety \bar{A} is hidden in the two reactions



The conservation law for the moiety X is instead hidden in the reaction



whereas for the moiety Y :



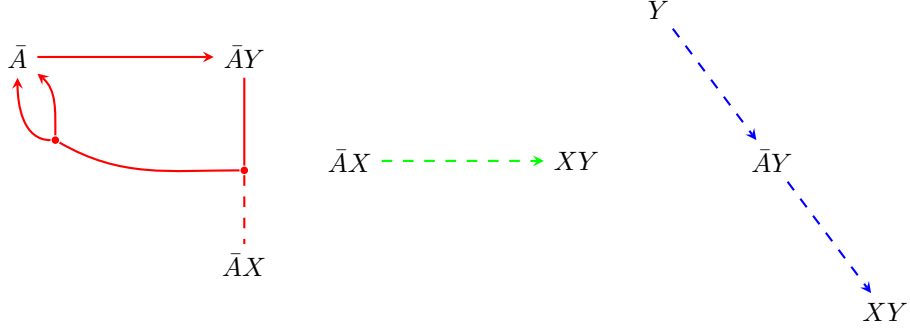


Figure 1: Moieties conservation representation. Only moiety \bar{A} contains an autocatalytic pattern (loop). Moieties \bar{X} and \bar{Y} represents only pure fluxes

We notice that the autocatalytic behavior of the network (autocatalysis of A) is actually hidden in just one of the the conservation laws, while the others are "fueling" the system to keep the moieties concentration constant. Note that just because we are taking the reactions once, when we look at the overall one, we end up with the autocatalysis of A, whereas taking twice the first reaction and once the second, we end up with the autocatalysis of B. This shows that the autocatalytic modes \mathbf{g}_i still play a role to define the autocatalytic behavior.

3 Type 2 with fuel and waste

Let's consider now the generic reactions for a type 2 core that allow for mass conservation:



Assuming as rows, respectively species F_1 , F_2 , F_3 , W , A , B and C , the stoichiometric matrix S will appear

$$S = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \\ 0 & 0 & 1 \\ -1 & 0 & 1 \\ 1 & -1 & 1 \\ 0 & 1 & -1 \end{pmatrix}
 \tag{11}$$

The nullspace has dimension 4, and a possible basis for it can be

$$H = \begin{pmatrix} 1 \\ 1 \\ 1 \\ 2 \\ 0 \\ 1 \\ 2 \end{pmatrix} \quad X = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 1 \end{pmatrix} \quad Y = \begin{pmatrix} 0 \\ 0 \\ 2 \\ 1 \\ 1 \\ 1 \\ 1 \end{pmatrix} \quad Z = \begin{pmatrix} 1 \\ 0 \\ 1 \\ 1 \\ 0 \\ 1 \\ 1 \end{pmatrix} \quad (12)$$

So that the conservation laws for the moieties H, X, Y, Z can be written as

$$H = F_1 + F_2 + F_3 + 2W + B + 2C \quad (13)$$

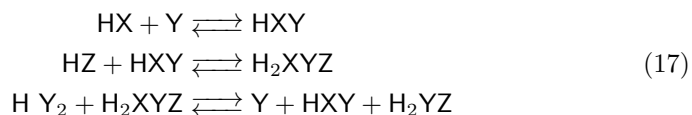
$$X = F_1 + B + C \quad (14)$$

$$Y = 2F_3 + W + A + B + C \quad (15)$$

$$Z = F_2 + W + C \quad (16)$$

Based on this, all species must then be combinations of these four moieties:
 $A = Y, B = HXY, C = H_2XYZ, F_1 = HX, F_2 = HZ, F_3 = HY_2, W = H_2YZ$.

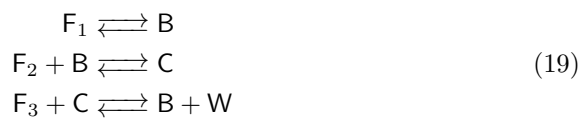
Reactions ?? then become, in terms of these compounds:



The stoichiometric matrix for moiety H then, following ??, will be

$$S_H = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \\ 0 & 0 & 2 \\ 0 & 0 & 0 \\ 1 & -1 & 1 \\ 0 & 2 & -1 \end{pmatrix} \quad (18)$$

Describing the set of reactions



These reactions can be shown from the point of view of the moieties through the following graph:

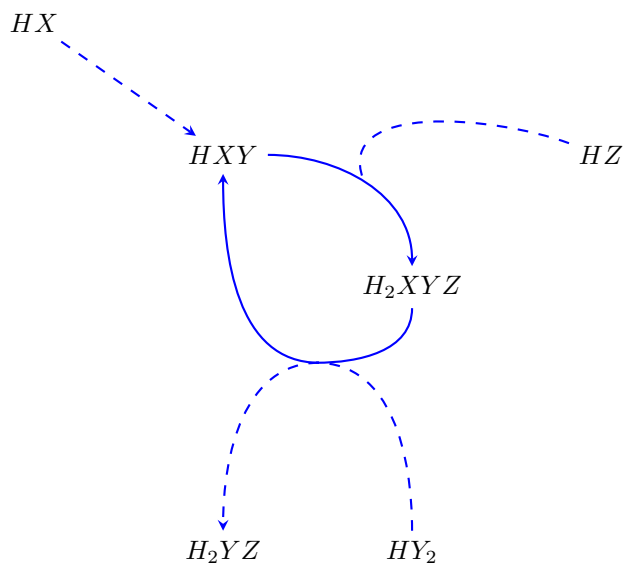


Figure 2: Moiety H conservation representation. One autocatalytic cycle is present

One can analyse the overall reaction, taking each reaction once, to see that it contains the autocatalysis of B:

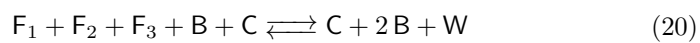


Figure ?? contains three different processes combined:

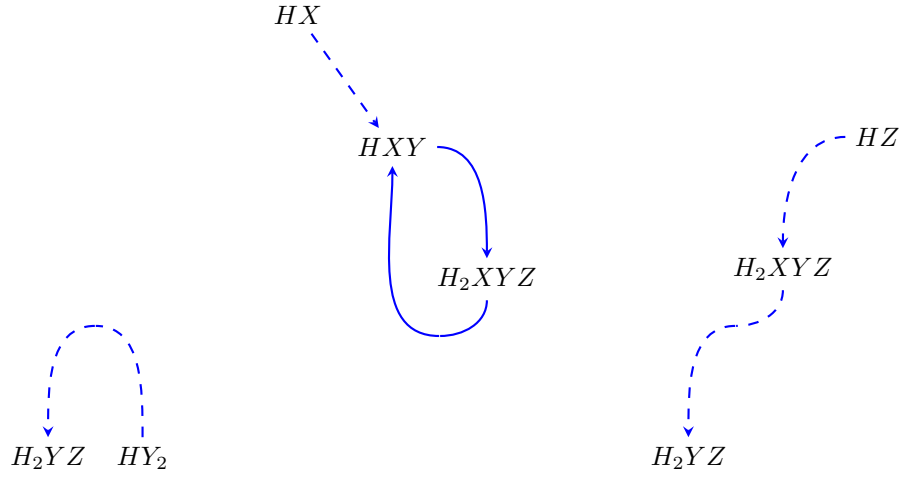


Figure 3: We can see that the conservation of moiety **H** is split into three different processes: two pure fluxes and one autocatalytic cycle

Next, the stoichiometric matrix for moiety **X** then ,following ??, will be

$$S_X = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 1 & -1 & 1 \\ 0 & 1 & -1 \end{pmatrix} \quad (21)$$

Describing the set of reactions



This reactions can be represented as:

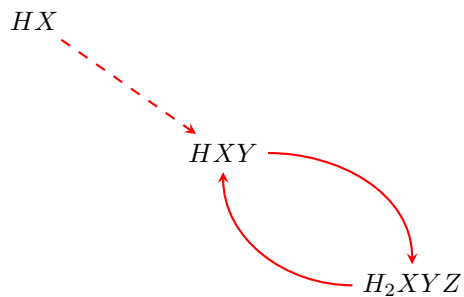
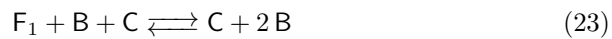


Figure 4: Moiety X conservation representation. One autocatalytic cycle is present

Again, taking each reaction once, we can see the explicit autocatalysis of B:

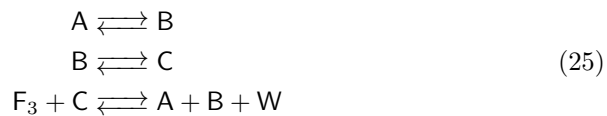


We notice that the cycle in Figure ?? is the same we encountered in Figure ??. We will refer to common processes as **patterns**. Hence, this particular cyclic pattern is shared between conservation of moieties H and X .

Continuing, the stoichiometric matrix for moiety Y will be

$$S_Y = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -2 \\ 0 & 0 & 1 \\ -1 & 0 & 1 \\ 1 & -1 & 1 \\ 0 & 1 & -1 \end{pmatrix} \quad (24)$$

Describing the set of reactions



We can plot these reactions on a graph:

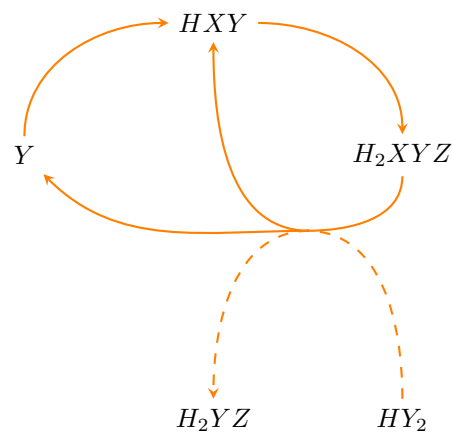


Figure 5: Moiety Y conservation representation. One autocatalytic cycle is present

The overall reaction, taking each reaction once, contains the autocatalysis of B again:

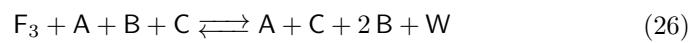


Figure ?? contains 2 different processes combined:

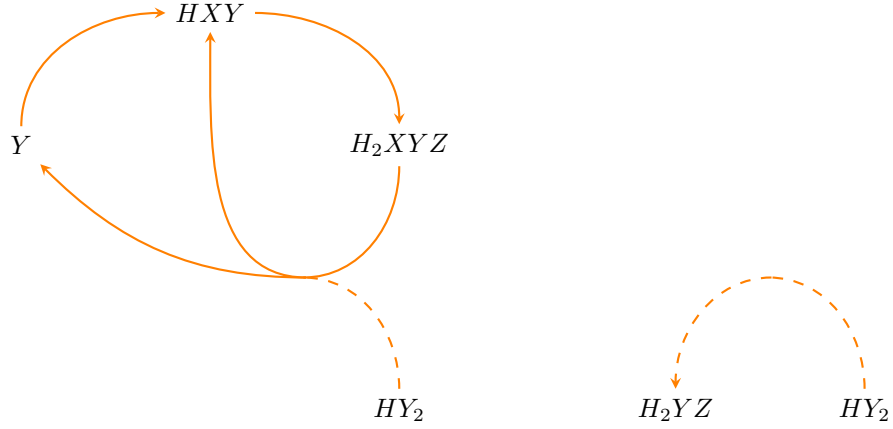


Figure 6: We can see that the conservation of moiety **Y** is split into two different processes: one pure flux and one complex autocatalytic cycle

We notice that the flux in Figure ?? is the same we encountered in Figure ?. Hence, this particular non-cyclic pattern is shared between conservation of moieties **Y** and **H**.

Lastly, for the moiety **Z**

$$S_Z = \begin{pmatrix} 0 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 1 & -1 \end{pmatrix} \quad (27)$$

Describing the set of reactions



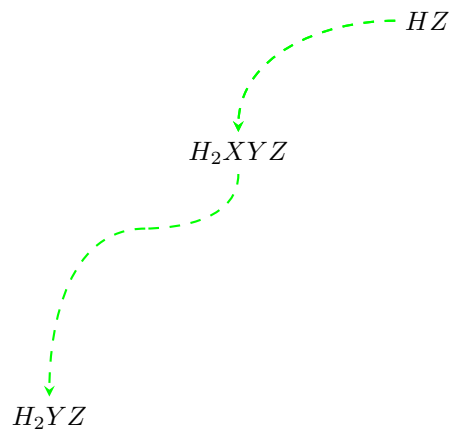


Figure 7: Moiety Z conservation representation. No autocatalytic cycle is present

Meaning that the overall reaction, taking each reaction once, contains the only the consumption of F_2 through C as catalyst



From all the moiety conservations we can then identify 4 different patterns, shared among the conservation processes

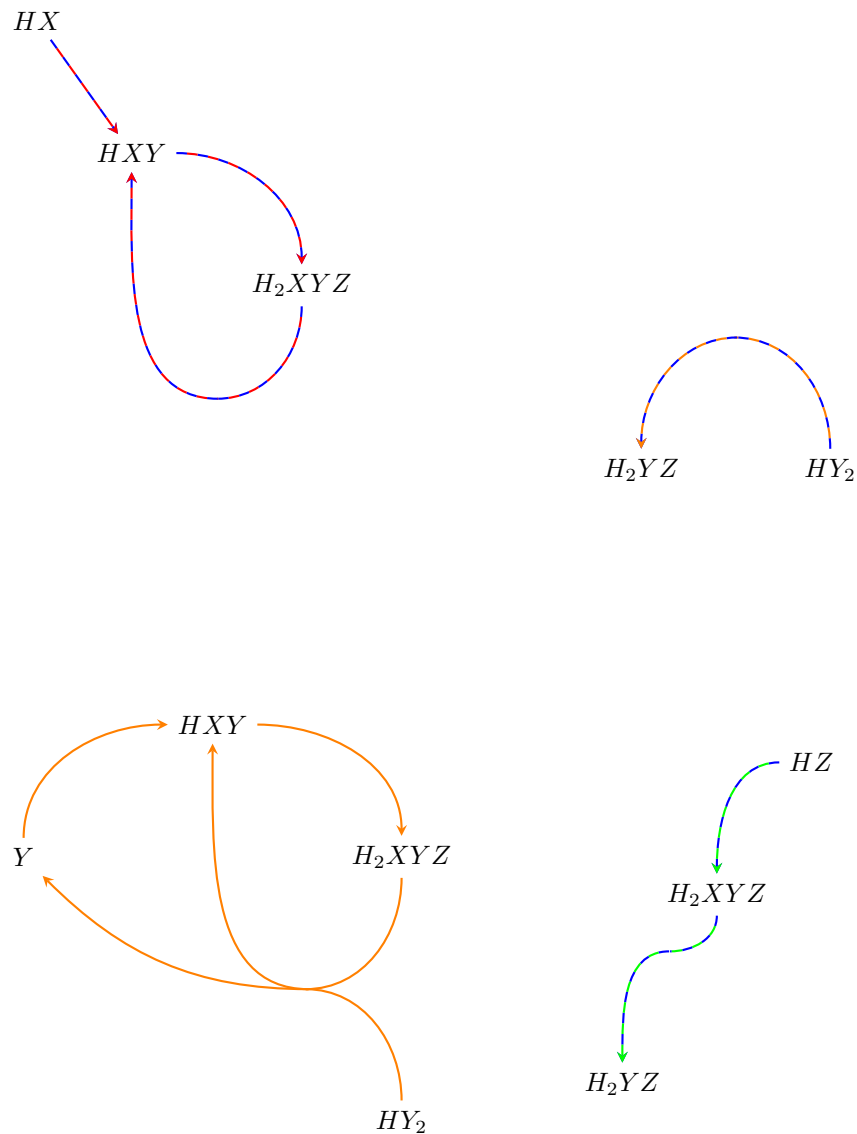


Figure 8: Conservation laws showed the appearance of 4 possible patterns: a simple autocatalytic cycle, a complex autocatalytic cycle and two simple fluxes

Studying the moiety conservations, we ended up having a new level of understanding of the network:

- Moiety **H** hides a simple autocatalytic cycle and two simple fluxes

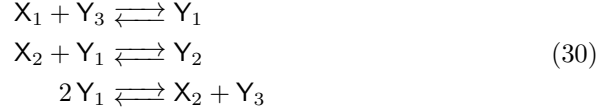
- Moiety **X** hides the same autocatalytic cycle of **H**
- Moiety **Y** hides a complex autocatalytic cycle and one of the simple fluxes seen in **H**
- Moiety **Z** hides a simple flux, being the other one hidden in **H**

Overall, 4 different patterns are shared among the conservation paths for the moieties.

In this case, we notice that the autocatalysis of species B is hidden in 3 out of 4 of the conservation laws (3 are the moieties conservations that contain a loop), last one being instead a "fuel reaction". Note again that we end up with the catalysis of just one species when analyzed the overall reaction, even though all the species in a core should present autocatalysis. This is because we're considering an overall reaction as the weighted sum with weight 1 of all the single reactions, which is indeed as taking the autocatalytic mode \mathbf{g}_B for type 2. Thus, depending what species i we want to look at, we should take into account different combinations of the three reactions, according to the autocatalytic mode vector \mathbf{g}_i .

4 Invaders' example

An interesting network that shows a 3x3 autocatalytic core is



Where X_1, X_2 are constant quantities. The stoichiometric matrix for respectively species X_1, X_2, Y_1, Y_2, Y_3 reads

$$S = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 1 \\ 1 & -1 & -2 \\ 0 & 1 & 0 \\ -1 & 0 & 1 \end{pmatrix} \tag{31}$$

Two conservation laws show up:

$$\begin{aligned} A &= X_1 + 2X_2 + Y_1 + 3Y_2 \\ B &= X_2 + Y_1 + 2Y_2 + Y_3 \end{aligned}$$

Such that we can further decompose our species in elementary compounds:

$$\begin{aligned}
X_1 &= A \\
X_2 &= BA_2 \\
Y_1 &= BA \\
Y_2 &= A_3B_2 \\
Y_3 &= B
\end{aligned}$$

Moiety A is conserved through the set of reactions



This can be seen from the following path

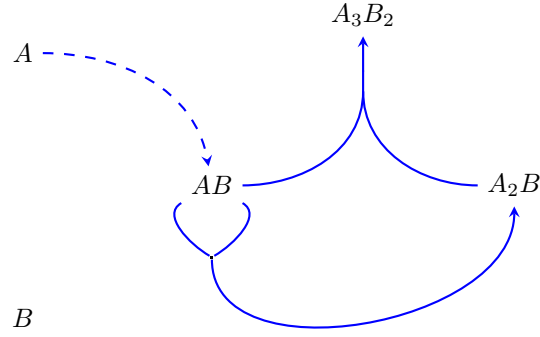
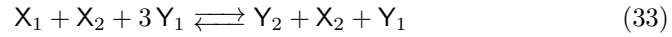
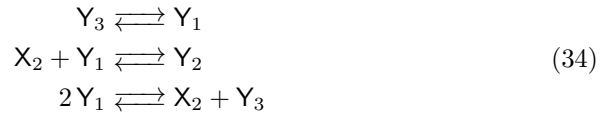


Figure 9: Moiety A conservation representation. One autocatalytic cycle is present

Leading to the overall reaction



Moiety B is conserved through the set of reactions



This can be seen from the following path

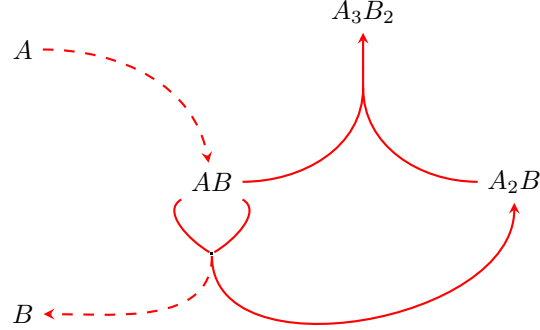
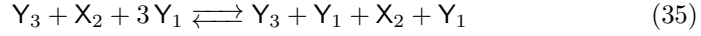


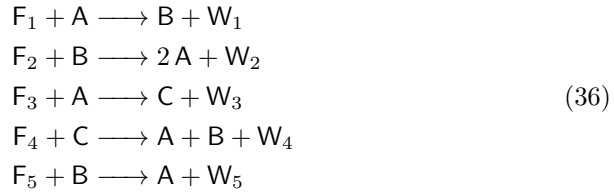
Figure 10: Moiety B conservation representation. One autocatalytic cycle is present

Leading to the overall reaction



5 Interaction between type 1 and 2

We focus now on the possible conservation laws that arise in the most elementary network that presents a type 1 core and a type 2 one. Reactions will here be taken irreversibly and for the sake of generality, fuel and waste will be different for each of the reactions:



The stoichiometric matrix being, respectively for F_1 , F_2 , F_3 , F_4 , F_5 , W_1 , W_2 , W_3 , W_4 , W_5 , A , B and C

$$S = \begin{pmatrix} -1 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ -1 & 2 & -1 & 1 & 1 \\ 1 & -1 & 0 & 1 & -1 \\ 0 & 0 & 1 & -1 & 0 \end{pmatrix} \quad (37)$$

This matrix has a left nullspace of dimension 8, since 8 out of 13 rows are linearly dependent from the other two. A possible basis of the nullspace is made be the independent vectors:

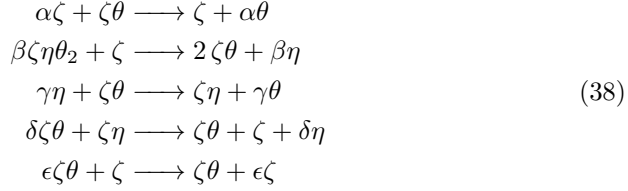
$$\begin{aligned} \alpha &= \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} & \beta &= \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} & \gamma &= \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} & \delta &= \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} \\ \epsilon &= \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \end{pmatrix} & \zeta &= \begin{pmatrix} 1 \\ 1 \\ 0 \\ 1 \\ 1 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 1 \\ 1 \\ 1 \end{pmatrix} & \eta &= \begin{pmatrix} 0 \\ 1 \\ 1 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 1 \\ 0 \\ 1 \\ 0 \\ 0 \\ 1 \end{pmatrix} & \theta &= \begin{pmatrix} 0 \\ 2 \\ 0 \\ 1 \\ 1 \\ 1 \\ 0 \\ 1 \\ 0 \\ 1 \\ 0 \\ 0 \\ 1 \\ 0 \end{pmatrix} \end{aligned}$$

So that the conservation laws for the moieties $\alpha, \beta, \gamma, \delta, \epsilon, \zeta, \eta$ and θ can be written as

$$\begin{aligned}
\alpha &= F_1 + W_1 \\
\beta &= F_2 + W_2 \\
\gamma &= F_3 + W_3 \\
\delta &= F_4 + W_4 \\
\epsilon &= F_5 + W_5 \\
\zeta &= F_1 + F_2 + F_4 + F_5 + W_5 + A + B + C \\
\eta &= F_2 + F_3 + W_2 + W_4 + C \\
\theta &= 2F_2 + F_4 + F_5 + W_1 + W_3 + A
\end{aligned}$$

Based on this, all species must then be combinations of these eight moieties: $A = \zeta\theta, B = \zeta, C = \zeta\eta, F_1 = \alpha\zeta, F_2 = \beta\zeta\eta\theta_2, F_3 = \gamma\eta, F_4 = \delta\zeta\eta, F_5 = \epsilon\zeta\theta, W_1 = \alpha\theta, W_2 = \beta\eta, W_3 = \gamma\theta, W_4 = \delta\eta, W_5 = \epsilon\zeta$

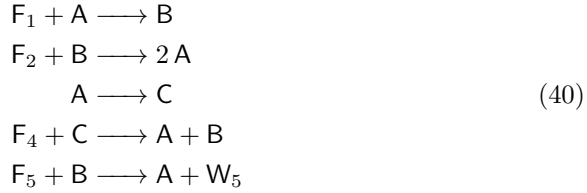
Reactions ?? then become, in terms of singular compounds:



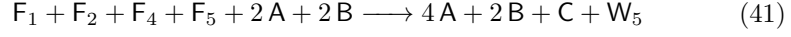
The moieties $\alpha, \beta, \gamma, \delta, \epsilon$ are conserved through their respective fuel consumption processes:



The conservation of moiety ζ relies on the processes:



Leading to the overall reaction

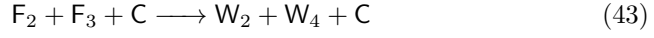


Which explicitly concerns the autocatalysis of A.

The conservation of moiety η relies on the processes:



Leading to the overall reaction

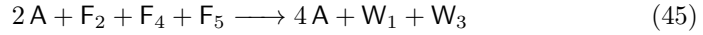


Again, not concerning the autocatalysis of A.

The conservation of moiety θ relies on the processes:



Leading to the overall reaction



This conserved quantity takes again part in the autocatalytic production of A.