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BRIEF COMMUNICATION

Returnability as a criterion of disequilibrium in atmospheric reactions networks

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Abstract The concept of network returnability is reformulated as an equilibrium constant for a reaction network. Using this concept we study the atmospheric reaction networks of Earth, Mars, Venus and Titan. We found that the reaction network in the Earth's atmosphere has the largest disequilibrium, followed by that of Titan which is still far from the most returnable atmospheres of Mars and Venus. We find that the chemical species with null or very low returnability are those in the highest disequilibrium in their respective atmospheres mainly due to physical, biogenic and/or anthropogenic mechanisms.

Keywords Reaction networks · Equilibrium · Graph theory · Retrunability · Planetary atmospheres

1 Introduction

The study of structural characteristics of reaction networks was pioneered by the works of a few mathematical chemists in the 1970s and 1980s, which is compiled in the reviews of Balaban [1], Temkin et al. [2] and Koca et al. [3]. The field has expanded today by the availability of new data on chemical and biochemical reactions [4]. One interesting field in which this analysis is very promising is that of atmospheric reaction networks. Atmospheres are the gaseous envelopes around planets and satellites, which are present in our solar system in Venus, Earth, Jupiter, Saturn, Uranus, Neptune and Saturn's largest satellite, Titan [5]. The atmosphere of the Earth, which is fundamental for the existence of life in our planet, has some peculiar characteristics, which appears

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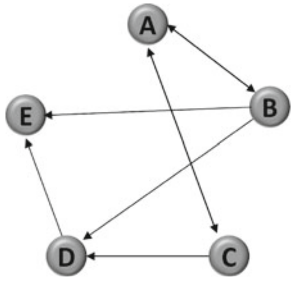
Reactions	Reaction network
A $\longrightarrow$ B + C B + C $\longrightarrow$ A B + C $\longrightarrow$ D B + D $\longrightarrow$ E	

Fig. 1 Illustration of a series of hypothetical reactions (*left*) and the corresponding reaction network (*right*) in which chemical species are the nodes and directed links exist between a reactant and a product

to defy the laws of chemistry and physics. For instance, the Earth is located between Venus and Mars in the solar system. These two planets have a chemical composition which is basically formed by oxidised compounds, such as carbon dioxide. The concentration of CO_2 in Venus and Mars is almost 3, 000 times larger than that on the Earth. In contrast, the concentration of oxygen in our planet is 160 times larger than that in Mars and more than half a million larger than that in Venus. Oxygen is a very reactive gas. It reacts with hydrogen, nitrogen, methane, etc. to form a variety of other chemicals, which include water, nitrate, carbon dioxide, among others [5]. Some of these molecules react with each other as well as with radiation to form new molecules giving rise to a complex network of chemical transformations.

The reaction networks of the atmospheres of the Earth, Mars, Venus and Titan were analyzed by Solé and Munteanu [6]. In a reaction network we start by representing the system of chemical reactions by a directed network $D = (V, A)$ [4]. In this reaction network, nodes $v_i \in V$ represent chemicals (reactants and products) and a directed link or arc $(p, q) \in A$ indicates that p is a reactant in a chemical reaction that produces among others, the product q. For instance, in Fig. 1 we illustrate a system of hypothetical chemical reactions and its network representation. In the case of reversible reactions, here represented by two reactions A→B+C and B+C→A, the links between the corresponding reactants and products have arrows in both directions (see Fig. 1).

According to the results of Solé and Munteanu [6] the largest network is that of the Earth and it is also the most sparse. All networks display small-worldness in the sense that the average path length $\bar{l}$ scales as $\bar{l} \sim \ln n$, where n is the number of chemicals. They also display larger average Watts-Strogatz clustering coefficient [7] than random analogues, in particular $\overline{C}$ for the Earth network is more than 10 times larger than that of a random graph. All networks are degree disassortative [8], with the Earth network displaying the largest disassortativity among all networks. Solé and Munteanu [6] have also found that the only atmospheric reaction network that display modularity is that of the Earth.

A characterization of small cycles in these four atmospheric reaction networks was carried out by Gleiss et al. [9]. It was observed that all these networks have significantly more triangles and a smaller number of large cycles than random graphs. In determining the number of cycles, Gleiss et al. [9] considered these networks as undirected and unweighted ones. However, we know that some important information can be contained in the directionality of these reactions. Here we study these four atmospheric reaction networks by considering them as directed graphs. We analyze how far from equilibrium the network of chemical reactions in a given atmosphere is. This analysis is carried out by means of the concept of network returnability which is reformulated here as an equilibrium constant between the physical system of reactions in an atmosphere and a hypothetical reference system. We find that the Earth's atmosphere has the network of reactions with the largest departure from equilibrium, i.e., the least returnable one, which may be a consequence of the biogenic and antropogenic activity on our planet. The second least returnable atmospheric reaction network is that of Titan, which has some resemblances to the Earth, followed by those of Venus and Mars, respectively. The individual role of some of the most important chemical species in these atmospheres is also analyzed by means of the node returnability concept.

2 Methods

Here we start by reformulating the concept of network returnability which was introduced by using combinatorial reasoning by Estrada and Hatano [10]. We formulate this concept here in terms of the equilibrium of a directed reaction network and its hypothetical reference system. This will allow us to interpret the results of this work in terms of the disequilibrium existing in atmospheric reaction networks. We start by considering that for every reaction network there is a hypothetical reference system in which all reactions are reversible. This means that a system of chemical reactions has a reference system consisting of the underlying undirected network of the corresponding reaction network (see Fig. 2). This reference system considers that all reactions are reversible and can be seen as an ideal equilibrium. We note that a network in which all links are reversible is represented as an undirected graph.

In order to determine how far from this ideal equilibrium a hypothetical reaction network is, we consider the free energy difference between the real physical and its

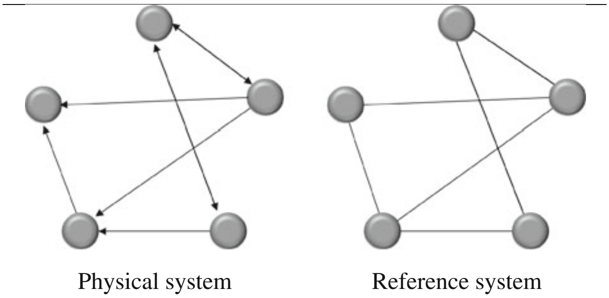


Fig. 2 Reaction network (*left*) and its reference system (*right*) consisting of the same set of nodes but with every link being undirected

reference system. Let F^{phys} and F^{ref} be the free energies of the reaction and reference networks, respectively. Then,

$$\Delta F = F^{\text{phys}} - F^{\text{ref}} = -\beta^{-1} \ln \frac{Z^{\text{phys}}}{Z^{\text{ref}}}, \tag{1}$$

where Z^{type} is the partition function of the corresponding (physical or reference) system and $\beta = 1/kT$ is the inverse temperature (k is the Boltzmann constant and T is the temperature). The system in which all reactions are reversible (reference system) is more stable than the one in which some reactions are not reversible. Thus, we can determine the relative returnability [10] of a reaction network with respect to its hypothetical reference system. This is given by the ratio of the two partition functions

$$K = \frac{Z(D)}{Z(\text{G})} = e^{-\beta \Delta F}, \tag{2}$$

where we have used the fact that the physical system is represented by the digraph $D = (V, A)$ and the reference one by the corresponding underlying graph $G = (V, E)$.

Estrada and Hatano [11] have previously shown that the partition function of an undirected network is given by

$$Z(G) = tr\left(e^{\beta \mathbf{A}}\right), \tag{3}$$

where $\mathbf{A}$ is the adjacency matrix of the graph. Several of the mathematical properties of this index have been studied in the literature and the reader is referred to the reviews [12,13] and the references therein. Numerical analysis of this index and related quantities are found in [14]. By expanding the exponential into its Taylor series we have

$$Z(G) = tr\mathbf{I} + \beta tr\mathbf{A} + \beta^2 \frac{tr\mathbf{A}^2}{2!} \cdots + \beta^k \frac{tr\mathbf{A}^k}{k!} + \cdots, \tag{4}$$

where $\mathbf{I}$ is the identity matrix. It is known that $tr\mathbf{A}^k$ counts the number of closed (self-returning) walks of length in k the graph. That is, $tr\mathbf{A}^k > 0$ for any network that contains at least one cycle. Thus, the partition function $Z(G)$ is a weighted sum over all closed walks (CWs) in the undirected network, in which longer CWs are penalized more heavily due to the factor $1/k!$.

Now, by following similar arguments to those used above $Z(D)$ can be defined as

$$Z(D) = tr\left(e^{\beta \mathbf{D}}\right) = tr\mathbf{I} + \beta tr\mathbf{D} + \beta^2 \frac{tr\mathbf{D}^2}{2!} \cdots + \beta^k \frac{tr\mathbf{D}^k}{k!} + \cdots, \tag{5}$$

Here, $tr\mathbf{D}^k$ measures the number of returnable walks of length k starting and ending at the same node. Thus, $tr\mathbf{D}^k > 0$ if, and only if the network has a returnable cycle of length k. Because $tr\mathbf{I} = n$ is the number of nodes in the network and we are not interested in the influence of the size of the network in the relative 'returnability' of a reaction network we simply remove this term from the partition functions. Hence, we have the rectified ratio of partition functions as

$$K_r(\beta) = \frac{Z(D,\beta) - n}{Z(\mathrm{G},\beta) - n}. \tag{6}$$

We call K_r the returnability of a directed network. The returnability of a directed network is bounded as $0 \leq K_r(\beta) \leq 1$. The lower bound is obtained for a network containing no cycles and the upper bound is reached for symmetric directed networks. For a directed cycle of n nodes C_n, $K_r \to 0$ for $n \to \infty$ [10]. Note that when $\beta \equiv 0$, $Z(D,\beta) = Z(G,\beta) = 0$. This situation represents a network at an infinite temperature in which every node is isolated. For the sake of simplicity in the analysis we define the index $pK_r = -\log K_r$. Large values of this index correspond to those networks which are far from the ideal reference state in which every reaction is reversible, or in other words, those reaction networks that are least returnable. There are substantial differences between the returnability and the reciprocity [15] of a network. The last is the fraction of links in a network which are reciprocal (bidirected). It is straightforward to realize that a network with null reciprocity can have non-zero returnability, i.e., a directed cycle. On the other hand, the existence of reciprocal links does not guaranty a high returnability in the network. For such kind of differentiations the reader is directed to the reference [10].

The returnability of a given chemical (reactant or product) in a reaction network is defined here in a similar way as for the global network. That is, for the chemical p we define

$$K_r(p) = \frac{\left(e^{\beta \mathbf{D}}\right)_{pp} - 1}{\left(e^{\beta \mathbf{A}}\right)_{pp} - 1}, \tag{7}$$

as the returnability of all chemical reactions in which this chemical takes place. For the sake of simplicity in this work we set up $\beta \equiv 1$ for all the calculations.

3 Results and discussion

We calculated the values of pK_r for the four reaction networks studied by Solé and Munteanu [6]. The results are displayed in Table 1 for $\beta = 1$ together with the number of chemical species n and reactions m for the four atmospheric reaction networks.

As can be seen the Earth has the least returnable reaction network, followed by that of Titan, while the most returnable reaction network is that of Mars. The reciprocity of the Earth atmospheric reaction network is also the smallest of the four networks indicating that it has the least number of reversible reactions. It is followed by Titan, then Mars and finally Venus, which has the atmosphere with the largest number of reversible reactions. This order is different from the one introduced by the returnability (see Table 1) and highlights the differences between these two network measures. In order to understand the details of the returnability of atmospheric reactions in these networks we have calculated the values of $K_r(p)$ for every chemical species in the four

Table 1 Returnability of atmospheric reaction networks together with their number of chemical species *n* and reactions *m*

Atmosphere	n	m	pK_r
Earth	248	778	3.627
Titan	71	396	2.796
Venus	42	175	1.955
Mars	31	144	1.787

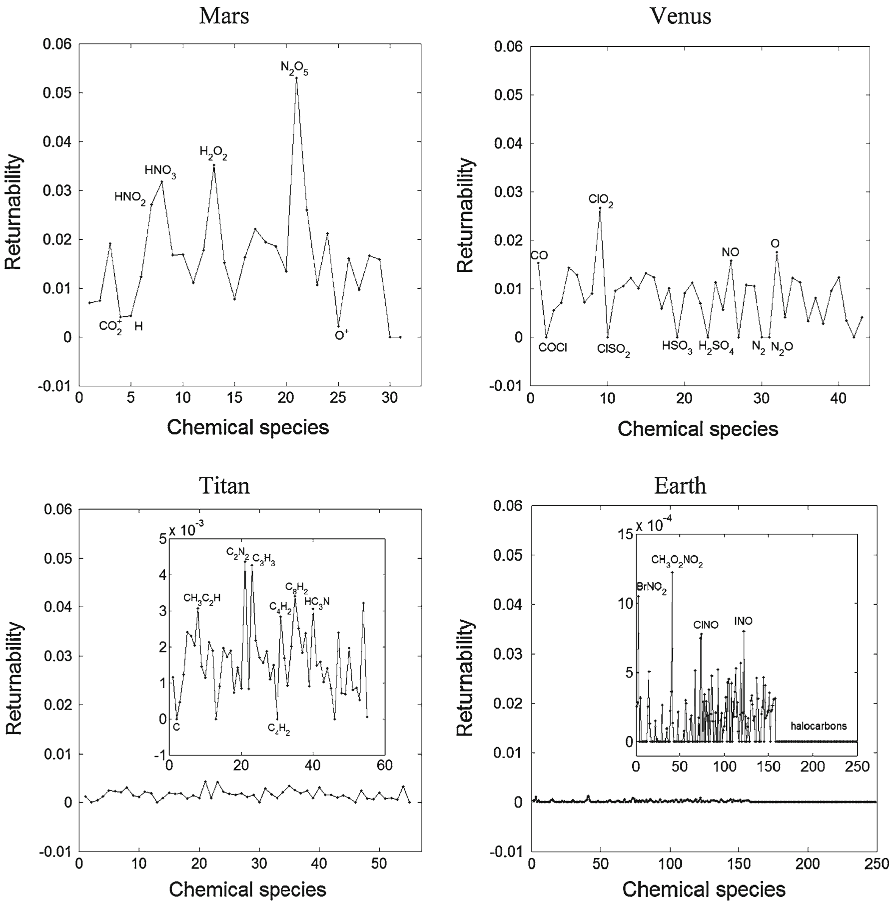


Fig. 3 Returnability of every chemical species in the reaction networks of Mars, Venus, Titan and the Earth. The four plots are displaying the same scale for returnability in order to remark the difference among the four reaction networks. For the networks of Titan and the Earth an inset is used to enlarge the scale of returnability. Some of the most and least returnable compounds are identified for each network

networks (see Fig. 3). The most remarkable finding is that in the Earth atmosphere 170 out of 249 species have $K_r(p) = 0$, which represents almost 70% of the total number of species. Even more interesting is the fact that the majority of those species having null returnability in the Earth's atmosphere are injected into the atmosphere from the Earth's surface. In general, they are of natural, biogenic or man-made origin. For instance, 62% of the compounds having $K_r(p) = 0$ are halocarbons, which are man-made chemicals of tremendous importance for understanding the atmospheric chemistry of ozone depletion [5]. Another interesting observation is that the species with the largest returnability within the Earth's atmosphere are those intermediate species produced and consumed naturally in the atmosphere through diverse chemical reactions. The most returnable species in the Earth atmosphere is methyl peroxynitrate $CH_3O_2NO_2$, which is formed and decomposed in the atmosphere by the reversible reaction $RO_2 + NO_2 + M \leftrightarrow RO_2NO_2 + M$, where M represents any species that dissipate energy, such as N_2 or O_2 on the Earth [16]. Methyl peroxynitrate is degraded by the following reactions [17]: $RO_2NO_2 + h\gamma \rightarrow RO_2 + NO_2$ or $\rightarrow RO + NO_3$ as well as $RO_2NO_2 + OH \rightarrow H_2O + NO_2 + O_2$. Other species with large relative returnability in the Earth atmosphere are: $BrNO_2$, INO, $ClNO_2$, ClNO, H_2O_2, etc. We have verified that the information contained in the returnability of species is not reproduced by other network measures like the in- and out- degree. For instance, the Pearson correlation coefficients between in- and out-degree vs. returnability of species do not exceed 0.3 indicating no significant relationship between them.

The analysis of those chemical species having null returnability within the Earth's atmosphere provides insight about the meaning of the low global returnability of this reaction network. Among the species with $K_r(p) = 0$ which are not halocarbons we find several volatile hydrocarbons (C_2H_2, C_2H_4, C_2H_6, C_3H_7, C_3H_8) which are mainly injected into the atmosphere from anthropogenic sources [5,17]. Other compounds in this category are methane CH_4, ammonia NH_3, methyl iodine CH_3I and bromine CH_3Br, methanol CH_3OH, acetonitrile CH_3CN, among others which are all of biogenic origin. For instance, methane can be injected naturally into the atmosphere from wetlands, termites and oceans apart from anthropogenic sources which include enteric fermentation, rice paddies, biomass burning, petroleum industry, etc. [5]. Because these compounds are injected into the atmosphere from different sources but mainly due to biogenic and anthropogenic activities it is plausible that the low returnability of the Earth's atmosphere is an indication of the large disequilibrium existing within it. This disequilibrium has been identified as evidence of the close interrelation between the atmosphere and the biosphere of our planet. For instance, Lovelock and Margulis [18] have compared the actual and equilibrium concentrations of several constituents of the Earth's atmosphere, which are produced by biological sources. We reproduce partially these results in Table 2 together with the returnability of the corresponding chemical species, were it can be seen that the departure from equilibrium expectations is correlated with the returnability of the species. Also note that the two species with non-zero returnability are the ones which also appear naturally in the atmosphere.

In complete contrast with these findings are those observed for the atmospheres of Venus and Mars. In Mars, which has the most returnable atmospheric reaction network of the four studied here (see Table 1), there is no one chemical species with null returnability (see Fig. 3). In Venus there are 7 chemical species which have zero returnability: COCl, $ClSO_2$, HSO_3, H_2SO_4, NOCl, N_2 and N_2O. Both atmospheres are characterized by the predominant presence of CO_2 (96.5% in Venus and 95.5% in Mars) followed by nitrogen (3.5% in Venus and 2.7% in Mars). However, there are several differences that can account for the larger departure from equilibrium of Venus atmosphere in comparison with that of Mars. One important aspect is the

Table 2 Concentration of different chemical species within the Earth's atmosphere and the concentration expected for them if the atmosphere was a thermodynamic equilibrium

Species	$K_r(p)$	Present fractional concentration	Expected fractional equilibrium concentration	Departure from equilibrium	Source
N_2	0.000155	0.78	$<10^{-10}$	10^{10}	Denitrifying bacteria
N_2O	0.000185	3.1×10^{-7}	$<10^{-20}$	10^{13}	Denitrifying bacteria
CH_3I	0.0	10^{-12}	$<10^{-35}$	10^{23}	Marine algae
NH_3	0.0	10^{-9}	$<10^{-35}$	10^{27}	Nearly all organisms
CH_4	0.0	1.7×10^{-6}	$<10^{-35}$	10^{29}	Anaerobic fermenting bacteria

The ratio between both concentrations gives the departure from equilibrium of the Earth's atmosphere. Some of the sources for these gases in the Earth's atmosphere are given. All data according to Lovelock and Margulis [18] and updated according to Wayne [5]

possible existence of lightning discharges in Venus which occurs at a rate of at least half of that on the Earth [19]. This lightning may produce the pyrolisis of CO_2 and more importantly the production of NO. It is known that oxides of nitrogen may play an important role in the oxidation of SO_2 to SO_3 and sulphuric acid [5]. These findings may explain why N_2O, COCl, $ClSO_2$, HSO_3, H_2SO_4 are among the least returnable species in Venus atmosphere and make the network of reactions in this atmosphere slightly more similar to the one on the Earth [20] than that of Mars (see Table 1).

We now turn our attention to Titan, which has the atmosphere with the second least returnable reaction network. This satellite has some characteristics that place it in a unique position in our solar system [21]. It has liquid at the surface, a thick atmosphere, energy sources such as energetic electrons and solar UV, has complex chemical reactions, precipitation, erosion, volcanism, impact processing, etc. All of which makes it similar to the primitive Earth. It has an atmosphere with a reaction network which is 10 times more returnable than that of the Earth, but still 10 times less returnable than those of Venus and Mars. Despite this relative low returnability there are only two chemical species which have null returnability: atomic carbon C (formed by electronic impact on CO) and butane C_4H_{10} (see Fig. 3). Butane is a sink compound which is formed in Titan's atmosphere by three different routes but not degraded by any. This compound has been found in higher concentrations in Titan surface than in its troposphere, which may be an indication of the fact that it can be injected into the atmosphere by physical processes as well as returning to the surface by means of precipitation. Because of the presence of hydrocarbon oceans in Titan (mainly formed by ethane, methane and nitrogen, but that can dissolve atmospheric constituents and their photochemical products) these processes are also plausible for other analogues of butane [22]. In fact, we have found that C_2H_4 (ethene), C_2H_6 (ethane) and C_3H_2 (diacetylene) are among the least returnable chemical species in this atmosphere. The other species are radicals (OH, CH, NH, O, N) and molecules like H_2O, which is also found forming pools in the surface probably as a consequence of meteor impacts. Water is 100 times less returnable in Titan's atmosphere that in those of Mars and Venus and its returnability is comparable to that of this molecule in the Earth's atmosphere. Curiously, the remaining of the chemical species have returnabilities of approximately the same order of magnitude, which is 10 times larger than those of ethane, ethene and diacetylene. As can be seen in Fig. 3 these reurnabilities are still very low in comparison to those of Mars and Venus. In other words, the returnabilities of most chemical species in Titan atmospheric reaction network are very low, which may be indicative of the out of equilibrium of this atmosphere. The influence of cosmic radiation, like in the reaction $CO + e^{-} \rightarrow C + O + e^{-}$, or evaporation/precipitation processes from a hydrocarbon ocean, and the impacts of meteorites, which may be responsible for the existence of liquid water pools, are major contributors to the out-of-equilibrium state of the atmospheric reaction network of Titan [22–25]. This is in some way confirmed by the very low returnability of species like carbon, ethane, ethene, butane and water, and a general low returnability for all species in this atmosphere.

4 Conclusions

We have seen here that the returnability of an atmospheric reaction network can give an indication of the departure from equilibrium of that system. Similar analysis can be done by considering the returnability of the different chemical species in the reaction network. Using these concepts we have found that the Earth has an atmospheric reaction network 100 times less returnable than those of Mars and Venus. This agrees with the consensus that the Earth's atmosphere "maintains a steady-state disequilibrium composition with the fuel being continuously replenished" [5], (see also [26]). The atmosphere of Titan has a reaction network that occupies an intermediate place between that of the Earth and those of Mars and Venus. It is ten times more returnable than that on the Earth but still far from the returnabilities of Mars and Venus. The analysis of individual chemical species in these atmospheres reveals that their returnability or lack of it is mainly related to the existence of physical, biogenic and/or anthropogenic mechanisms altering the 'natural' equilibrium of reactions in the atmospheres. Thus, the study of returnability of global systems or of their individual components can be a useful tool for understanding how far from equilibrium these systems are.

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