

Interactive comment on “Quantifying drivers of chemical disequilibrium in the Earth’s atmosphere” by E. Simoncini et al.

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Interactive Discussion

Discussion Paper

Reply to Referee # 2

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The authors thank Referee # 2 for his helpful review, which represents a good piece of non-equilibrium science and gives the possibility to underline the aims of the manuscript and the relevance of the adopted assumptions.

In the revised manuscript, we will provide a more detailed clarification about our aims, and a specific section about non-equilibrium thermodynamics (NET). We have chosen to use the language of traditional chemistry rather than NET because the former is better suited to our intended readership. In the updated manuscript we will underline that although we have chosen to use the language of chemical potentials rather than thermodynamic forces, this does not imply that we have made any unnecessary near-equilibrium assumptions. Specifically, we plan to outline the NET approach at the beginning of Section 3, and to include an appendix with more details, particularly regarding its relationship to the approach we have taken.

In the following, we provide a short discussion about our aims and a justification of the thermodynamic approximations and tools used in the manuscript.

1. **Aim of the manuscript and assumptions.** With this paper we want to provide a thermodynamic analysis of the power given to the Earth's atmosphere by fluxes

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of material from its surface. This analysis is useful in the perspective of analyzing the effect of biological activity on the thermodynamic conditions of the Earth. Due to the subject under study, we make particular assumptions, fully explained in details in the text. The given approximations allow us to provide a first level of analysis, useful for the above mentioned purpose. In particular:

- In the right time scale material fluxes can be considered constant.
- Since we are handling the Earth's atmosphere as a steady state system, we do not need to consider kinetics.
- As typical in biogeochemical cycles sciences, we consider the change in Gibbs free energy of the system equal to the sum of the Gibbs free energy added to the system and of the one dissipated in the system.

In this light, the tools presented work correctly and are entirely consistent with non-equilibrium thermodynamics.

2. **Simplification of the NET formulations.** Let us go a bit more into details. In our simplified scheme, free energy power is introduced into the system by material fluxes and dissipated by chemical reactions. The presented topic of the study is the CH_4/O_2 disequilibrium in Earth's atmosphere, thus the *driven* process is the maintenance of the present concentrations of CH_4 and O_2 against what equilibrium conditions would predict for the (very simplified) reaction: $\text{CH}_4 + 2 \text{O}_2 \rightleftharpoons \text{CO}_2 + 2 \text{H}_2\text{O}$. Assuming the steady state, generation and dissipation of free energy must be equal. We can then use the flux analysis to study the disequilibrium of our simplified system. In particular, using the nomenclature given by the Referee, the entropy production by the considered (simplified) reaction can be calculated by:

$$\frac{d_i S}{dt} = J \cdot X = \frac{d\xi}{dt} \cdot \left(-\frac{\partial \Delta_R G}{\partial \xi} \right)_{P,T} \cdot \frac{1}{T} = -\frac{1}{T} \cdot \left(\frac{\partial \Delta_R G}{\partial t} \right)_{P,T} \quad (1)$$

In our manuscript we assume that temperature is fixed. This is very well justified in the Earth's atmosphere since the chemical reactions do not contribute much heat in comparison to purely physical processes, absorption, phase transitions, transport. One must also consider the influence of kinetics on Radiative Transfer; however, since the reaction is assumed in steady state, no change in concentration is happening and no effect on the Radiative Transfer is produced. Thus in the case of a steady state the term $\left(\frac{\partial \Delta_{RG}}{\partial t}\right)_{P,T}$ in eq. 1 is zero, because either the chemical reaction is changing the species concentrations. Conclusively, we can correctly approximate the entropy produced by the net change in free energy due to material flow into the system. We will add in the manuscript an appendix in which we give the details about the link between NET and the classical thermodynamics analysis used in this work.

3. **Exoplanets habitability.** Regarding the analysis of the habitability of exoplanets, we agree with the arguments given by Referee # 2. In the next version of the manuscript, we will discuss the exoplanet topic only in the section "*Implications and future prospects*", clarifying the aim of the present work.

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