Reply to Robert Niven’s Review

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We thank Professor Niven for his insightful review, which reveals a number of issues that we will clarify in the revised manuscript.

One particularly important point that we must make in response to this review is that the model in section 3 of our paper was never intended as a serious model of an atmosphere. We will revise the paper to make it even more explicit that this model is only meant as an illustration of the general qualitative behaviour of chemical systems maintained out of equilibrium, and as an introduction to the calculations to be performed in Section 4. Indeed, a central point of our paper is that one does not need to analyse the kinetics of the dissipating reactions in order to calculate the power needed to maintain disequilibrium.

This is the reason for the assumptions of uniform $T$ and $p$ and unit fugacities of the reactants in this model, as well as the unrealistically simple single-step reaction $A \leftrightarrow B$. When we apply these ideas to the real atmosphere in Section 4, we do not model the atmosphere as a single box of gas but instead calculate the flux of Gibbs energy (or equivalently, separate fluxes of entropy and first-law energy) across the boundary between the surface and the atmosphere. Consequently we do not require any of the simplifying assumptions that are made in Section 3.

We now respond to the reviewer’s numbered points.

1.

We are very sympathetic to the reviewer’s position that entropy production (or negative entropy flux) is a technically better measure of the amount of disequilibrium than power. Indeed, during the production of the manuscript there was much discussion about this issue among the authors. Eventually the idea of using power won out due to its greater familiarity to the intended readership. However, due to comments from several of the reviewers we will revise the manuscript so that it tells the entropy story as well. We plan to include an appendix in the revised version, showing how the same ideas can be expressed more formally in the entropy-centric language of non-equilibrium thermodynamics.
However, having said that, we do not believe there is anything fundamentally incorrect about using the power as we have calculated it. The power and the entropy production measure different things. The power figure we calculate represents the minimum rate at which work must be done in order to bring about a chemical transformation. This figure is not independent of temperature (because chemical potentials typically decrease as $T$ increases) but depends upon it in a different way than the entropy production. The power is a biologically relevant thing to calculate, because plants effectively extract work from sunlight, and we wish to know how much of this work eventually contributes to driving the methane-oxygen disequilibrium.

The point about local variations in entropy production is an important one, but not one we feel we have overlooked. As Professor Niven writes, the total rate of at which negentropy must be supplied to maintain disequilibrium can be written

$$\dot{\sigma} = \iiint_V \dot{\sigma} dV,$$

where $\dot{\sigma}$ is the local rate of depletion of negentropy. But in steady state this can also be written as a surface integral,

$$\dot{\sigma} = \oint_{\Omega} \vec{j} \cdot d\Omega,$$

where $\vec{j}$ is the local negentropy flux. In our paper we calculate only one component of this negentropy flux, and we calculate it over only one part of the system’s boundary, as represented by the dotted line in Figure 4. In addition we calculate one component of the flux of first-law energy over this boundary.

This puts a lower bound on the entropy that must be produced inside the atmosphere. The actual entropy production is of course much higher than this lower bound, since the entropy produced by methane oxidation is dwarfed by that produced by heat transport, the water cycle, photochemistry and the thermal absorption of Solar photons. Nevertheless it is useful to quantify the extent to which this one particular exchange process contributes to the disequilibrium, and this is the reason for focusing on it in our paper. A similar argument can be made for calculating the flux of first-law energy across this boundary. These two fluxes can be combined to give the rate at which energy must be supplied in the form of work in order to maintain the disequilibrium, as discussed above.

Since we are calculating a flux of entropy across a boundary rather than the entropy produced in the volume of the system, we only need to worry about nonuniformities in temperature near the surface we’re integrating over. In our case this means that variations in surface temperature can affect our result in principle, but the much larger variations in temperature over the height of the atmosphere are irrelevant. $T$ in our equations represents only the surface temperature, and our results are very insensitive to
its value (we will quantify this in the updated manuscript). This justifies our use of a constant surface temperature approximation.

We appreciate the reviewer’s criticism of the Gibbs energy density as a measure of disequilibrium. This is part of the illustrative model in Section 3, and we intended it only as an illustrative demonstration of the principles at work; we realise that it has problems as a measure of disequilibrium, especially when the simplifying assumptions of constant $T$ and $p$ are relaxed. However, we agree that it would make more sense conceptually to use the local Planck potential, and will update the manuscript to reflect this.

2.

We will change the manuscript to make the units of [A] and [B] clearer. They were intended as mole fractions, although it is not entirely uncommon to see volume fractions specified in atmospheric chemistry, usually in the form of ppmv (parts per million by volume). Note that since these are assumed to be ideal gases, the volume fraction is numerically equal to the mole fraction.

We used unit fugacities to fit the general spirit of the model as the simplest possible example. However, we agree that failing to mention them altogether might be a simplification too far, so we will change the equations to include the fugacities, and explicitly state that we have set them to 1.

We will change the equations in Section 3 to specify the kinetics in terms of partial pressures rather than mole fractions.

3.

We agree that an extension to non-unit stoichiometry would be more general. However, this would be unrealistic unless we also included multi-step reactions, with addition equations for the concentration of intermediates. To become a generally useful model of atmospheric chemistry kinetics, the model would also have to include the transport of species between layers of different temperature and pressure, as well as the possibility of photochemical reactions.

However, we feel that including such a model would greatly increase the length of our paper without adding any significant novelty. Such complex kinetic models of atmospheric chemistry already exist. Rather than adding such features to our model (which would risk yet further obscuring its purpose as a simple motivating example) we will add some citations to more detailed models that can already be found in the literature.

Replies to the minor comments

1. For the sake of generality, in this paragraph we wish to remain agnostic about who is controlling whom. We agree that this wording is awkward, however, and we will re-examine this sentence.
2. We will remove this claim.

3. We will clarify these lines. The focus on equilibrium chemistry in this paragraph is quite deliberate. We are considering what would happen if the exchange fluxes were somehow set to zero and the reaction allowed to come to equilibrium. For methane oxidation Earth’s atmosphere this would result in not a single molecule of CH$_4$, as Lippincott et al. point out, but for other reactions this may not be the case. The only purpose of this argument is to justify the choice of the ratio between the parameters $k_f$ and $k_r$ of our toy model.

4. At this point we are not talking about O$_2$ and CH$_4$ but about the fictional species A and B in our toy model. The justification for assuming constant concentrations of O$_2$ and CH$_4$ is given at the point where we make this assumption, on lines 7–13 of page 1305, in Section 4. However, we will edit the text to refer to this argument in Section 3 as well.

5. We will make this suggested change.

6. We will correct this error.

7. We will endeavour to remove any redundant information from Section 5.

8. We will consider replacing the net-reaction arrows in Figure 1 with double arrows. The driving process is shown as a conversion process rather than as a source and a sink in order to illustrate the conceptual “power supply”, whose magnitude we calculate.