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Review of:

Quantifying drivers of chemical disequilibrium in the Earth's atmosphere

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Reviewer: Elbert Branscomb

General Comments

This paper addresses questions of significant general interest, namely how to estimate the power needed to maintain atmospheric chemical disequilibria, what the magnitude of that power is in the important case of the CH_4/O_2 disequilibrium found in the earth's atmosphere, and the issue of whether the result, and in particular the general approach, might aid in detecting life on other planets. The thermodynamic approach taken to estimating the power is presented as the paper's main contribution. The manuscript seems clearly within the scope of ESD.

However, in my judgment the manuscript does not rise above the threshold sufficient to justify publication either with regard to significance or original contribution. At the same time, I do not view the shortfall as being so great, or beyond reasonable dispute, that I would object to being overridden on this judgment by other reviewers or editors.

In summary, my reasons for this negative decision come down to two points. First, to my mind the case is not made that power calculations of the type considered could in any practical case assist in deciding whether some distant planet was 'metabolizing'. The analysis presented in effect argues against this idea - as the authors themselves essentially acknowledge with commendable candor; the powers predicted are too small and, more importantly, no practical strategy seems to exist for determining, for a distant planet, either the needed production fluxes (required to estimate the power by the proposed method) or what fraction of the power involved could not be explainable as due to abiotic processes. Admittedly, on the other hand, some real value attaches to this "negative" conclusion.

Second and more importantly, as I explain in some detail below, I feel the thermodynamic analysis presented, which is really the paper's main point, is to be faulted on several grounds and is not, as it stands at least, a significantly useful contribution.

However, before launching on a discussion of that point I first note what I view as the paper's strengths and following that present a short list of specific points keyed to locations in the text.

Notable strong points

1. The very detailed and informative general discussion of atmospheric disequilibria presented in section 2 “Disequilibrium and its drivers”.
2. The analysis of the issues involved in estimating the chemical flux rates, and the value of ΔG , in the CH_4/O_2 system (in section 4), which to my mind is quite carefully done, informative, and a noteworthy contribution in its own right.
3. The detailed discussion of the limitations of the approach taken and of its applicability (section 5.1) which I also find impressively careful and commendably candid.

Specific comments keyed to the text

1. p 1291, line ~15 “The tectonic forces themselves are driven by the flow of heat from the Earth’s interior to its exterior. The temperature difference between the two is another form of disequilibrium. This disequilibrium is partially driven by radioactive decay, but is primarily the result of left-over heat from the Earth’s formation. The transport of this heat to the exterior brings the planet closer to equilibrium, but it happens at such a slow rate that the Earth is still far from its equilibrium state 4.5 billion years after its creation.”
The last two sentence are, I believe, incorrect. While the fraction of the heat generation in the earth that is radiogenic is evidently poorly determined (estimates apparently range from 45 to 90%) something like 2/3 is likely a best estimate (e.g. 30TW radiogenic vs 44TW total). In part for this reason, that the planet is still out of thermal equilibrium is not, primarily, because the “transport of this (i.e. “left over”) heat to the exterior . . . happens at such a slow rate” (and if it was Kelvin’s famously false argument about the age of the earth would have been conceptually correct and not too far wrong quantitatively – in fact an overestimate of sorts since he was unaware, I believe, of the role of convection in the process – and tectonic activity would have ceased several billion years ago). It is instead in the main due to the fact that the earth’s radionuclide endowment is still far out of equilibrium with respect to it’s decay products (the dominant nuclides having billion year half lives).
2. p 1291, line 20: “Chemical systems tend over time toward a unique equilibrium state.” My point here is a phrasing quibble; since (as the authors fully understand and entirely rely on) only “isolated” systems, and not just isolated chemical systems so tend - I would prefer a different wording of this point.
3. p 1294,.line 10; “In this paper we will show that one need not model the kinetics in order to calculate the power required to drive the disequilibrium.” As I discuss in some detail below, I claim that both this statement

as well as the paper’s key result (an expression for the power in terms of the reaction flux and the extent of the chemical disequilibrium produced), are not novel contributions of this paper; see, e.g. the cited papers by Stucki analyzing a thermodynamically ‘identical’ problem).

Critique of the thermodynamic analysis:

The criticisms made here derive from the fact that the phenomenon under study is fundamentally one of non-equilibrium (indeed far from equilibrium) thermodynamics. As a result, I argue, analyzing it within the concept structure of classical equilibrium theory is, at best, misleading and in some points problematically so. In particular, seen from a NET perspective, the key result obtained (a formula for the power in terms of the reaction flux producing the disequilibrium and the strength of the disequilibrium produced) is neither non-trivial nor novel. In my view, the present analysis obscures these important and simple insights while also ignoring relevant precedent work and essential literature; and is for that reason not a positive contribution.

In defense of the author’s approach, however, I want to acknowledge the likelihood that almost all readers would recognize it as being not only the correct and expected way to approach a thermodynamic problem of this (indeed any) type, but would likely not be aware that any fundamentally different approach exists or is called for. Therefore, given that I do not take issue with the key result of the analysis, I can see an argument - based on reader intelligibility - for the approach taken (putting the claims of novelty aside).

The argument that the derivation of the formula for the power needed to sustain the CH_4/O_2 disequilibrium, when done in NET terms, is neither novel nor ‘non-trivial’. The main points (elaborated on below) are that:

1. it follows immediately from the NET description of the thermodynamics of a free energy converting process that the power involved in the necessarily endergonic (i.e. “driven”) reaction producing a non-equilibrium state for a chemical reaction, i.e. a state’s whose affinity “ A ” is positive: “ $A > 0$ ”, (note: $A = 0$ at equilibrium, and is positive for a reaction whose products are at higher concentration w.r.t. its reactants than would be the case at equilibrium) is $P_{driven} = v A$ where v is the reaction’s velocity: $v = d\xi/dt$ (ξ is the “extent of reaction”). In the manuscript under review, both v and ΔG are taken as known quantities.

The affinity A is the thermodynamically correct measure of a reaction’s distance from equilibrium (see the Stucki reference cited below). Under the special conditions assumed: i.e. the system in steady state and having constant (and uniform) p and T , a Gibb’s free energy can be defined, which then bears a simple numerical relationship to the reaction’s affinity, namely $A = \Delta_x G$ (where I have here followed the author’s notation and convention of considering the necessarily positive change in Gibb’s free energies “ $\Delta_x G$ ” that would be involved in raising a mole of reagents from

equilibrium to the non-equilibrium state under consideration). Thus, we can rewrite the expression for the power involved in the reaction flux as $P_{driven} = v \Delta G$ (the paper’s key result).

2. by the second law, the power of the necessarily exergonic reaction(s) that must be driving the driven/endergonic reaction, by being mechanistically coupled to it, cannot be less than this: $P_{driver} \geq P_{driven}$.

That this conclusion follows directly, and most naturally, from the formalism of NET, is because that formalism respects and conforms to the fact that the problem under study is inherently a non-equilibrium *dynamic, finite rate, on-going process* (in fact a far-from-equilibrium one; not, even approximately to be represented as a static Gibbsian ‘difference’ between equilibrium, or quasi-equilibrium, states). It is moreover a process that is of the particular type termed “free energy conversion”, in which two processes are “coupled”, thereby forming one spontaneous compound process in which one exergonic process drives an endergonic partner. Such systems are not (properly) within the domain of classical equilibrium thermodynamics.

Moreover the NET analysis of the problem is also inherently more general than one based on equilibrium thermo concepts. From a conceptual and methodological point of view the difference is substantial. In particular, NET does not require that the system under study have a uniform or constant temperature, nor that it be operating in steady state. And it treats such finite velocity, inherently irreversible processes naturally, including most importantly systems involving pairs of coupled, irreversible processes producing free energy conversion, as I will attempt to suggest in the discussion below.

I note that the authors cite (for other purposes) perhaps the best available general introduction to NET (Kondepudi & Prigogine, *Modern Thermodynamics*, 1998); which discussion is, arguably, the book’s main purpose. I highly recommend that source, but also suggest for the author’s consideration two others: Caplan and Essig, *Bioenergetics and linear nonequilibrium thermodynamics; the steady state*, 1999, a standard text on free energy conversion systems: and, perhaps especially, a series of papers by Jorge Stucki published in the 1980’s considering the problem of oxidative phosphorylation and the driving of an ATP vs ADP + Pi disequilibrium by a redox cascade - a problem that, in thermodynamic terms, is formally analogous to the one considered (see in particular: J. Stucki, *The Optimal Efficiency and the Economic Degrees of Coupling of Oxidative Phosphorylation*. Eur. J. Biochem, 109, 269-283, 1980; though I note that in the analysis there presented the assumption is made, following Onsager, that fluxes depend only linearly on forces).

But in the interest of clarifying and supporting my opening assertion on this point, I offer next a brief summary of the relevant aspects of an NET analysis of problems of the present type.

The general expression for the entropy production within a spatially bounded system (potentially open to both material and energy fluxes across the boundary) within which a number n of “irreversible” processes (those effecting, at a finite rate, changes in entropy content) are taking place is of the form:

$$\frac{d_i S}{dt} = \sum_{j=1}^n J_j X_j \geq 0$$

where the symbol ' $d_i S$ ' refers to entropy production by irreversible processes, J_j is the flux, and X_j the "force", for the j 'th process; and where I note that X_j in this notation is just the rate of entropy production per unit flux by the j 'th process; see K+P, op cit., pp 88 (note: a commonly adopted convention, followed, e.g. by Stucki in the cited refs, multiplies the above expression by temperature, conferring "energy" units on both sides and replacing the terms X_j by $\bar{X}_j = T X_j$ - i.e. the "forces" then have units of energy change per unit flux; but this, in my view, obscures the important point that, physically, thermodynamic forces are just changes in entropy density and are in no valid sense "energies"). The inequality on the r.h.s. of the above formula is an expression of the 2nd law.

For chemical reactions (following De Donder) the flux of the reaction is the rate of change of the so-called "extent of reaction ξ " (i.e. the reaction "velocity", v): $J = v = d\xi/dt$, and the force is the "distance from equilibrium" as measured (also following De Donder), by the reaction's "affinity" $A(\xi)$, i.e. " $X(\xi) = A(\xi)/T$ ", where $A(\xi) \equiv \sum_k \nu_k \mu_k$, and ν_k is the stoichiometric coefficient (positive for products, negative for reactants), and μ_k the chemical potential (here expressed in energy units, as originally defined by Gibbs) respectively of the k 'th reagent.

The general connection between affinity and Gibb's free energy, in the situation where the latter is defined, is given by $A(\xi) = -(\partial G/\partial \xi)_{p,T}$, with the consequence that the change in a reaction's Gibbs free energy ΔG (here necessarily negative) upon relaxing it from a non-equilibrium state $A(\xi)$ to equilibrium ($A = 0$) is numerically equal to $-A(\xi)$: $A(\xi) = -\Delta G$ (see K&P p111, including a discussion of why this is only a numerical equivalence).

In general, the fluxes may depend not just on their cognate force, but on all of the forces in the system: $J_j(\{X_l\}; \forall l)$. Therefore, if more than one process is operating in the system, one of more of them can be "endergonic" (i.e. running up hill against its natural gradient, so that for these processes $J_j X_j < 0$ since their forces are negative: $X_j < 0$) - no offense being given to the 2nd law thereby as long as the sum over all processes is still positive: $\sum_j J_j X_j \geq 0$. But, of course, a process can be endergonic only if it is "driven" by being coupled mechanistically to one or more other exergonic processes with the consequence that the coupled processes act as a single, spontaneous (net entropy producing) thermodynamic process.

In the simplest such case of just two processes:

$$\frac{d_i S}{dt} = J_1 X_1 + J_2 X_2 \geq 0$$

and taking one process, say the first, to be endergonic: $X_1 < 0$, then that process must be coupled to, and driven by, the second one; that is, we must have

that each of the fluxes depend on both forces: $J_1(X_1, X_2)$ and $J_2(X_1, X_2)$, and also that these dependencies are such that entropy is produced in the system by process 2 faster than it is being ‘consumed’ by process 1: $J_1 |X_1| \leq J_2 X_2$. The rate at which “work” is produced by this free energy conversion system is the endergonic term $J_1 |X_1|$ (in entropy flux units); see Stucki, op. cit..

Correspondingly, the efficiency of the conversion of the free energy of the driving (free energy dissipating = entropy increasing) process to that of the driven (free energy creating = entropy reducing) process is:

$$\eta = \frac{-J_1 X_1}{J_2 X_2}$$

(Stucki, op. cit.) which, by the 2nd law, necessarily satisfies $0 \leq \eta \leq 1$ - reflecting that the work output of the system (expressed again in entropy flux units) is necessarily a lower bound on the work input ($J_2 X_2$) needed to drive the process. And the point is made explicit that systems driving endergonic processes are just dynamically trading entropy production in the driving process for a lesser rate of entropy reduction in the driven process - the latter being the system’s work output.

If it is desired to follow history’s convention and express the work output in units of power (i.e. energy per unit time) it is trivial to do so (when, as in the model under study, the temperature is assumed to be uniform and constant) by multiplying the rate of entropy reduction in the output channel by temperature: $Power - out = -T J_1 X_1 = -T v A_1 = v \Delta_x G$ which is the key formula used in the paper to compute the lower bound on the power required.

However, it is an important conceptual implication of the NET analysis of free energy converting systems (i.e. “engines”) that physically, the work performed is always, and (in terms of the underlying physics, the expression of), reducing the entropy density of the substance (energy and/or mater) that is the flux of a driven, endergonic, process. This is true even in the case of engines in which the output is mechanical work, i.e. motion in a single dimension; in this case, in which the flux emerging as work has only one degree of freedom ($W_{work} = 1$), $S_{work-out} = k \ln W_{work} = 0$; thus for example, in the canonical case of the heat engine the entropy of the heat energy Q_w that is converted to mechanical energy is reduced, from Q_w/T_w (where T_w is the effective temperature at which the conversion takes place) to zero - and the situation is formally analogous to chemical free energy conversion although in systems producing chemical work the entropy reduction of the driven flux is never so complete.

It is also important to note that the above NET analysis, based on computing rates of entropy change, applies even when the system is not characterized by a uniform, or constant, temperature - nor does it require any steady state or quasi-equilibrium assumptions. The only required assumption is that of “local equilibrium” - the substance of which is that a reasonably well defined Boltzmann distribution - and thus a “local” temperature, can be attributed to the volume neighborhood of each point in the system (see discussion in K&P, Ch 1 and p87).

Finally, the total entropy budget should also be considered. The rate of change of the entropy of a bounded system dS/dt is the sum of the rate due to the irreversible processes taking place within it ($d_iS/dt \geq 0$) plus the rate due to the movement of matter and/or energy across the system's boundary, conventionally called d_eS/dt , which can be of either sign; that is, $dS/dt = d_iS/dt + d_eS/dt$. In steady state, clearly, the system's total entropy is constant, i.e. $dS/dt = 0$, so that $d_eS/dt = -d_iS/dt$, i.e. there must be a net export of entropy from the system which just balances that produced by its irreversible processes.

This implies, as is explicitly laid out in the cited Stucki paper, that for a non-equilibrium steady state to be maintained in a free energy converting ("driver-driven") system such as the one under consideration (and operating at a conversion efficiency less than one), the system must have a third process functioning as a "load" or a "relaxation path" (the existence of which is also discussed at length in the manuscript under review). That is, we must have (at least) three processes:

$$\frac{d_iS}{dt} = J_1X_1 + J_2X_2 + J_3X_3 \geq 0$$

where as before process 1 is taken to be a driven/endergonic ($X_1 < 0$) process, process 2 the exergonic process ($X_2 > 0$) that is coupled to, and driving, process 1, and where process 3 is also exergonic ($X_3 > 0$). In the simplest form of this model (adopted by Stucki) $X_3 = -X_1$ and $J_3 = J_3(X_3)$; that is, the thermodynamic force produced by the free energy converting couplet comprising processes one and two, is now, in magnitude, the positive force for the exergonic relaxation path; and the relaxation flux depends only on that force.

In this model, the steady state assumption implies

$$\begin{aligned} -\frac{d_eS}{dt} &= \frac{d_iS}{dt} \geq 0 \\ &= (J_1 - J_3)X_1 + J_2X_2 \\ &= (J_3 - J_1)|X_1| + J_2X_2 \end{aligned}$$

which is the rate at which entropy is being exported from the system, and, I note, corresponds to the "enthalpy" part of the (dynamic) entropy budget, i.e. we can write, $dH/dt = T d_eS/dt = -T d_iS/dt$; which term can be considered, in equilibrium thermo terms, as the "enthalpy" export rate (per mole reaction progress) needed to hold the system in steady state. In steady state, we must also have $J_3 = J_1$ (no net accumulation of the driven product) so that in that case $d_eS/dt = -J_2X_2$ (the net export of entropy from the system is equal to the entropy flux of the driving process).