

# Review of Quantifying drivers of chemical disequilibrium in the Earth's atmosphere, by E. Simoncini, N. Virgo, and A. Kleidon

(Dated: 13 Jan 2013)

## 1. SUMMARY

The authors present an interesting work on the calculation of chemical disequilibrium in planetary atmospheres, which could be used to identify the presence of biotic processes. The manuscript, however, contains several misconceptions and/or oversights in its theoretical analysis, which require further consideration and modification before it will be suitable for publication.

I apologise for the lateness of this review: summer holidays intervened, and I needed to check the calculations. This review was written without reference to the other reviews; inspecting them now, I note that item 2 below is examined in more detail by reviewer 2. I am happy for my identity to be known to the authors.

## 2. MAJOR COMMENTS

1. The problem with oversimplified box models is that they oversimplify the physics, to the extent that important features can be overlooked. In this study, a planetary atmosphere is represented as a single box with a single temperature  $T$ , with input and output chemical fluxes. A real planetary atmosphere, of course, is not in thermodynamic equilibrium (unless very far from its star) and so exhibits a multitude of local temperatures; this indeed is a characteristic feature of "thermal disequilibrium".

So, firstly, is the power consumption (8) an appropriate measure of disequilibrium? A well-established line of reasoning suggests it is not, since we must also account for the quality of the energy degraded: 1 kW dissipated at 300 K is quite different to 1 kW dissipated at 10 K or 1000 K. A more appropriate variant of the power consumption is the local entropy production or - putting it another way - the negentropy flux required to maintain the disequilibrium:

$$\hat{\sigma} = -\frac{J_A \Delta_r G}{T} \quad (1)$$

The effect of locality is then accounted by integration over the atmospheric volume  $V$ , allowing for  $\Delta_r G$  as a function of  $T$ :

$$\dot{\sigma} = \iiint_V \hat{\sigma} dV = -\iiint_V \frac{J_A \Delta_r G}{T} dV \quad (2)$$

Of course, the authors know this! Power calculations are useful and, to many audiences, more readily understood, but the entropy production is more fundamental and should not be omitted.

Secondly, the authors use the Gibbs energy volumetric density  $g$  as a measure of disequilibrium. Yes, the Gibbs free energy is minimised at equilibrium, but does it truly represent non-equilibrium conditions and so can be used to determine the distance from equilibrium? Here the authors have stumbled into a long-standing controversy between the Belgian school, who maintain that only the affinity serves this purpose, and the rest of the world (led by Lewis and Randall), who consider the Gibbs free energy to be quite adequate. Without wading too deeply into this controversy (noting the much longer comment by reviewer 2), three matters should be pointed out:

- (a) The Gibbs free energy is generally used to assess the distance between chemical composition states which lie on the equilibrium "manifold"; i.e. it is used to calculate the distance between the observed chemical composition state - which is otherwise in physical equilibrium - and the final state of chemical equilibrium. Putting it another way, all disequilibrium states must correspond to some other equilibrium state with a different composition. The set of possible disequilibrium states is therefore tightly restricted. Variations in  $T$  and  $P$  can be examined (e.g. graphically or analytically), but the process is usually considered to take place at constant  $T$  and  $P$ ; it is not usually considered to be "driven" to the  $(T, P)$  conditions with lowest free energy (in fact this would lead to spurious conclusions).
- (b) In symbols, small  $g$  is usually taken to represent the specific free energy  $G/m$ , where  $m$  is the fluid mass. Due to variations in density, it is much less common to consider the free energy per volume  $G/V$ . See also comment 2 below, on the definitions of  $[A]$ ,  $[B]$ .

- (c) Regardless of the comments in (a), the Gibbs free energy cannot capture the disequilibrium associated with temperature variations. For this, a more appropriate measure is the local Planck potential:

$$\Psi = \frac{G}{T} \quad (3)$$

or specific Planck potential:

$$\psi = \frac{G/m}{T} = \frac{G}{Tm} \quad (4)$$

where  $m$  is the fluid mass. (Sometimes the negative quantity is used.) This again yields a quantity expressed in entropic units (or entropy per unit mass), not simply in energetic units. The effect of locality can again be accounted by integration over the atmospheric volume  $V$ , allowing for  $\psi$  as a function of  $T$ :

$$\iiint_m \frac{G}{Tm} dm = \iiint_V \psi \rho dV \quad (5)$$

This would serve the authors' purpose much more than their quantity  $g$ .

2. There are two problems in the formulation in part 3:

- (a) What do the symbols  $[A]$ ,  $[B]$  represent? If A and B are gaseous species,  $[A]$  and  $[B]$  would usually be partial pressures (in atm); if A and B are in solution, they would typically be molar concentrations (mol/L or mol/kg). Sometimes one sees mole fractions (mol/mol) for gases or in solution. It is not common to use molar or volumetric concentrations (mol/m<sup>3</sup> or m<sup>3</sup>/m<sup>3</sup>) for gases. To distinguish the meaning clearly, it is preferable to use  $[A]$  and  $[B]$  (or some other symbol) exclusively to represent concentrations, and a separate symbol such as  $P_A, P_B$  for partial pressures.
- (b) The authors have overlooked the importance of fugacity or activity coefficients.

The kinetic equations (2)-(4), based on conservation laws, are correct (at least they are usually written this way), provided  $[A]$  and  $[B]$  strictly represent molar concentrations. However, the equilibrium constant in (1), based on thermodynamics, requires fugacities or activities. Assuming gaseous species, it should be written:

$$K_{eq} = \frac{f_B}{f_A} = \frac{\gamma_B P_B}{\gamma_A P_A} \quad (6)$$

where  $f_A, f_B$  are fugacities,  $\gamma_A, \gamma_B$  are fugacity coefficients, and  $P_A, P_B$  are partial pressures. The variation in fugacity coefficients can alter the observed pressures substantially; perhaps not on Earth, but certainly for denser atmospheres such as on Venus or on gas giants. They cannot be neglected.

Thus two sets of corrections are needed:

- (a) The fugacity coefficients enter into all equilibrium constants and free energy equations. For example, it is incorrect to write  $K_{eq} = P_B/P_A = k_f/k_r$  (or the form based on concentrations, page 1294), even though this is found in most textbooks. This brings a correction term into the second part of (5) and into (6),(7),(8) etc.. but curiously not into (9).
- (b) An ideal gas (or non-ideal gas) conversion factor is needed to convert the concentrations in the kinetic equations (2)-(3) into partial pressures. This flows through into both parts of (5) and into (7),(8), etc ... but also not into (9).
3. The analysis in part 3 also only examines a chemical reaction with unit stoichiometric coefficients, and assumes first-order kinetics for each species. A more general treatment would allow for non-unitary stoichiometric coefficients and non-first-order reactions. Thus for the reaction



the equilibrium constant is

$$K_{eq} = \frac{f_C^c f_D^d}{f_A^a f_B^b} \quad (8)$$

and the kinetic law, written in terms of concentrations, becomes:

$$\dot{\xi} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt} = k[A]^\alpha [B]^\beta [C]^\gamma [D]^\delta \quad (9)$$

where  $\xi$  is the extent of reaction,  $[A]$  to  $[D]$  are molar concentrations, and  $\alpha$  to  $\delta$  are the reaction orders, which are a priori unknown (must be determined by experiment). The molar balance equations corresponding to (2)-(4) can be assembled accordingly.

Bringing these equations together would considerably complicate the authors' analysis. However, this extension is essential if the authors wish to analyse planetary chemical reaction kinetics in general. Indeed, given the non-unit stoichiometry in the example in part 4, this exercise would certainly be immediately useful, and would present a more general formulation of their analysis.

### 3. MINOR COMMENTS

1. page 1289 line 14: perhaps "controlled by a biosphere" better captures the meaning
2. page 1291 line 15: I might be wrong, but I believe the Earth's geothermal energy arises predominantly from radioactive decay, especially of K-40. This could be checked.
3. page 1295 lines 8-12: The analysis here is simplistic, since it considers only the equilibrium constant (thermodynamics) and not the kinetics.
4. page 1296 line 1: For species such as  $O_2$  and  $CH_4$ , I'm not sure the authors can maintain that the total concentration  $c$  will be constant. At steady state, yes, but this is a weak condition. In fact, the derivation of (R4) suggests otherwise. A more sophisticated argument is needed here.
5. page 1296 eq (6): Since the argument of a logarithm must be dimensionless, a purist would write these equations relative to the fugacity of the species at standard state, ie:

$$\mu_A = \Delta_f G_A^\circ + RT \ln f_A/f_A^\circ \quad (10)$$

Since  $f_A^\circ = 1$  by definition, these terms vanish, but the units are accounted correctly. See Atkins 1982, pp 168-174.

6. page 1298 line 13-22: The definition of Gibbs energy density assumes  $[A]$ ,  $[B]$  are molar concentrations rather than pressures; this should be made consistent with the responses to major point 2.
7. Section 5 is extremely long, and could be shortened significantly without loss of information.
8. Fig 1: At risk of confusion, the authors might consider representing the chemical reaction using doubleheaded arrows, with the rate constant explicit on each. Also, the "driving process" might involve conversion of B to A, or merely a pair of sources and sinks.

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### 4. REFERENCES\*

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[1] P.W. Atkins, Physical Chemistry, 2nd ed., Oxford Univ. Press, Oxford, 1982.