



# Quantifying drivers of chemical disequilibrium: theory and application to methane in the Earth's atmosphere

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Received: 29 October 2012 – Published in Earth Syst. Dynam. Discuss.: 23 November 2012

Revised: 6 June 2013 – Accepted: 25 July 2013 – Published: 11 September 2013

**Abstract.** It has long been observed that Earth's atmosphere is uniquely far from its thermochemical equilibrium state in terms of its chemical composition. Studying this state of disequilibrium is important both for understanding the role that life plays in the Earth system, and for its potential role in the detection of life on exoplanets. Here we present a methodology for assessing the strength of the biogeochemical cycling processes that drive disequilibrium in planetary atmospheres. We apply it to the simultaneous presence of CH<sub>4</sub> and O<sub>2</sub> in Earth's atmosphere, which has long been suggested as a sign of life that could be detected remotely. Using a simplified model, we identify that the most important property to quantify is not the distance from equilibrium, but the power required to drive it. A weak driving force can maintain a high degree of disequilibrium if the residence times of the compounds involved are long; but if the disequilibrium is high and the kinetics fast, we can conclude that the disequilibrium must be driven by a substantial source of energy. Applying this to Earth's atmosphere, we show that the biotically generated portion of the power required to maintain the methane–oxygen disequilibrium is around 0.67 TW, although the uncertainty in this figure is about 10% due to uncertainty in the global CH<sub>4</sub> production. Compared to the chemical energy generated by the biota by photosynthesis, 0.67 TW represents only a very small fraction and, perhaps surprisingly, is of a comparable magnitude to abiotically driven geochemical processes at the Earth's surface. We discuss the implications of this new approach, both in terms of enhancing our understanding of the Earth system, and in terms of its impact on the possible detection of distant photosynthetic biospheres.

## 1 Introduction

More than 40 yr ago, Lovelock (1965) suggested that, before looking for life on other planetary bodies, we would first need to appreciate what life has done on the Earth. He proposed that an unambiguous sign of the widespread presence of life on Earth is the high degree of chemical disequilibrium associated with Earth's atmospheric composition. A particularly noticeable aspect of the atmosphere's disequilibrium is the coexistence of methane and oxygen, which would be depleted by chemical reactions to carbon dioxide and water if they were not continuously replenished. The high concentration of these compounds, among others, makes the thermodynamic state of the Earth's atmosphere unique when compared to other planets and moons.

Previous work by Lovelock and others (e.g. Lovelock, 1965; Lippincott et al., 1966; Lovelock and Margulis, 1973; Sagan et al., 1993) has focused on quantifying the degree of disequilibrium in the atmosphere. One potential application of this is the detection of life on exoplanets. The idea is that, with advanced spectroscopic methods that will likely be available in the relatively near future, we should be able to detect the presence of strong chemical disequilibrium in distant planets' atmospheres. Such a disequilibrium may have abiotic causes, such as photochemistry, but if these can be eliminated it may be possible to conclude that the atmosphere's composition is being controlled by a biosphere.

Using a simple conceptual model, we argue that quantifying the degree of disequilibrium in itself only gives part of the picture. A given chemical system may lie far from equilibrium because it is held there by an energetically powerful driving process, or simply because the chemical species

involved have very long residence times. We present a way to quantify the strength of the biogeochemical processes that drive chemical disequilibrium, taking into account both the amount of disequilibrium in the system and the magnitudes of the fluxes that drive it. Our analysis results in a figure with the units of power, which allows the strength of chemical cycling processes to be compared to that of other Earth system processes, such as the atmospheric circulation, the water cycle, and geological processes.

We then apply this methodology to the coexistence of methane and oxygen in Earth's atmosphere. The atmospheric methane cycle results primarily from the production of CH<sub>4</sub> due to anaerobic digestion, and the production of O<sub>2</sub> and uptake of CO<sub>2</sub> and H<sub>2</sub>O by photosynthesis. These processes form a small part of the carbon cycle. We show that the power required to drive this disequilibrium is around 0.7 TW. This power ultimately comes from the energy that the biota extracts from sunlight through photosynthesis; a small fraction of this power is funnelled into driving the atmosphere's methane–oxygen disequilibrium.

Our analysis paves the way toward quantifying the strength of biogeochemical cycling in general, by tracing the global flows of available energy from its ultimate sources in sunlight and geothermal gradients to physical and chemical cycles.

The concept of thermodynamic disequilibrium, particularly in respect to atmospheric chemistry, is introduced in Sect. 2. Then, in Sect. 3 we present a simplified “toy” model of a generic chemical system held out of disequilibrium by exchange fluxes across the system boundary. We use this model to show that the amount of disequilibrium in a system depends both on the fluxes that drive the system and the kinetics of the reactions that take place within it, and to show why the power involved in driving the disequilibrium is a useful measure to calculate.

In Sect. 4 we apply this reasoning to the addition of CH<sub>4</sub> and O<sub>2</sub> to the atmosphere by the biosphere, to give a figure for the power involved in driving the atmospheric methane cycle. This figure depends only on the fluxes of four compounds to and from the surface, as well as their concentrations in the atmosphere and their thermodynamic properties. A detailed model of the reactions' kinetics is not required, and consequently the calculations in Sect. 4 are rather simpler than those in Sect. 3.

Finally, in Sect. 5 we discuss the limitations of our approach, the wider context of our results, and the prospects for further applications in biogeochemistry and the search for life on exoplanets, before briefly concluding in Sect. 6.

## 2 Disequilibrium and its drivers

An isolated physical system is said to be in thermodynamic equilibrium when its entropy is at a maximum. For systems that are not isolated but are instead held at a constant

temperature by being connected to a heat bath, this translates into a minimum of the Helmholtz energy; for systems whose temperature and pressure are both held constant, the relevant potential is the Gibbs energy. The second law states that all systems must eventually approach such an equilibrium state, but it says nothing about how rapidly this must occur. The thermodynamic arguments used to establish this apply equally to chemical and physical systems.

To describe a physical system in disequilibrium and identify its drivers, we need to consider the entropy balance of the system in addition to its energy, mass, and momentum balances. The entropy balance describes how the entropy of a system,  $S$ , changes in response to the exchange fluxes across the system's boundary. Following the notation of Prigogine (Kondepudi and Prigogine, 1996), this change may be written as

$$\frac{dS}{dt} = \frac{d_i S}{dt} + \frac{d_e S}{dt}, \quad (1)$$

where  $d_i S/dt$  is the rate at which entropy is produced by the dissipative processes within the system that bring the system closer to thermodynamic equilibrium, while  $d_e S/dt$  is the rate at which entropy is exchanged with the system's surroundings by the exchange of energy and mass.  $dS/dt$  and  $d_e S/dt$  may be positive or negative, as long as  $d_i S/dt \geq 0$ , as required by the second law of thermodynamics.

If the system is in steady state on the relevant timescale then its state is not changing over time, and hence  $dS/dt = 0$  and the rate of net entropy export balances the rate of entropy production, i.e.  $d_e S/dt = -d_i S/dt$ . As pointed out by Tykodi (1967) and emphasised by Jaynes (1980), this must be true even if parts of the system are so far from equilibrium that its entropy cannot easily be measured or even defined. As long as we define the system in such a way that the entropy flux can be calculated at every point on its boundary then we can apply thermodynamic reasoning to steady-state systems no matter how far from equilibrium they are. This observation is crucial when applying thermodynamics to Earth system processes. It implies that we can quantify the drivers of disequilibrium within the system by evaluating the thermodynamic properties of the fluxes at the system boundary.

There are many examples of physical and chemical disequilibria in the Earth system (Dyke et al., 2011; Kleidon, 2012). Most of the important disequilibria in the Earth system are ultimately driven by the difference in the radiative temperature between the incoming, solar radiation at around 6000 K, which corresponds to an import of radiative energy of low entropy, and the radiative temperature of the radiation emitted from Earth at around 255 K, which corresponds to an export of radiative energy of high entropy. In steady state, the mean absorption of solar radiation balances the mean emission of terrestrial radiation, and this radiative exchange is associated with a net entropy export,  $d_e S/dt$ , of the whole Earth system. It is this net entropy export by radiative exchange with space that ultimately allows for the maintenance

of dissipative activity on Earth (as  $d_i S/dt = d_e S/dt$  in steady state) and drives most of the disequilibria found in the Earth system.

States of disequilibrium do not necessarily involve life. As an example, the continental landscape would be flat if it were in equilibrium. Minimising Gibbs energy in this case is equivalent to minimising the gravitational potential under the constraint of mass conservation of the continental crust (see e.g. Kleidon et al., 2013). Erosion, being driven by gradients in height, acts to reduce these gradients, bringing the system closer to equilibrium. This is offset by plate-tectonic forces, which create new sources of gravitational potential, preventing erosion from bringing the landscape to equilibrium entirely. We say that the tectonic forces are the driver of the landscape height disequilibrium. 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 and partially by the 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.

Chemical disequilibrium is in many ways similar to this kind of physical disequilibrium. Chemical systems tend over time toward a unique equilibrium state that is typically described by a minimum in Gibbs energy within the system. The concentrations of species in the chemical equilibrium state can in general be determined from their thermodynamic properties; by chemical "disequilibrium" we simply mean the contemporaneous presence of compounds whose concentrations are different from these equilibrium values. In the atmosphere, disequilibrium persists in part because of fluxes of various chemical species to and from the surface, as well as by photochemical reactions. These fluxes push the system further from chemical equilibrium, while reactions within the atmosphere tend to drive the state closer to equilibrium. Over very long timescales the two approximately balance, resulting in a persistent state of disequilibrium.

For the atmosphere we may write

$$\frac{d_e S}{dt} = \frac{d_{e,\text{surface}} S}{dt} + \frac{d_{e,\text{photo}} S}{dt}, \quad (2)$$

with  $d_{e,\text{surface}} S$  and  $d_{e,\text{photo}} S$  representing changes in entropy due to surface fluxes and radiative fluxes involved in photochemistry respectively. Since our focus in this paper is on the surface fluxes, we will not calculate the photochemical entropy flux. However, the above expression implies that  $d_{e,\text{surface}} S/dt$  puts a lower bound on  $d_e S/dt$ .

This chemical disequilibrium is characterized by the system's entropy balance. This is associated with the exchange of heat (or, more precisely, enthalpy,  $H$ ) which is taken up or released by the reactions, as well as the mass exchange of chemical compounds of different entropies across the system

boundary. If we denote the mass fluxes of reactants and products by  $J_A$  and  $J_B$ , the rate of entropy exchange is given by

$$\frac{d_{e,\text{surface}} S}{dt} = S_B^\circ J_B - S_A^\circ J_A - \frac{J_H}{T}, \quad (3)$$

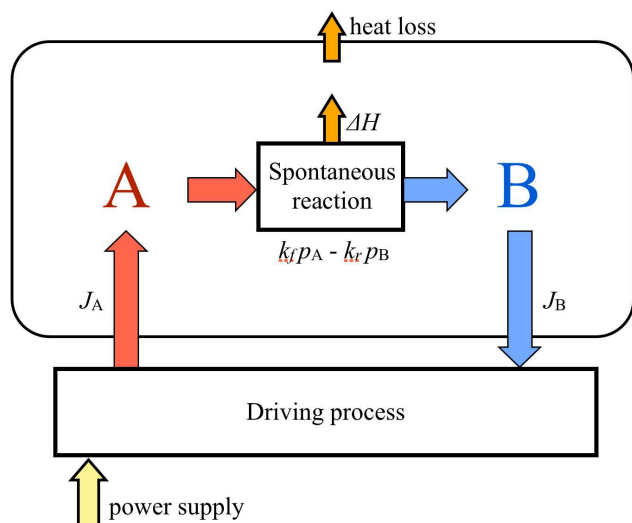
where  $S_A^\circ$  and  $S_B^\circ$  denote the standard molar entropies of reactants and products and  $J_H$  the enthalpy exchange. Together with the radiative entropy exchange associated with photochemistry, this balances the total entropy production by chemical reactions and other processes within the system. If a single reaction is considered, this dissipation of Gibbs energy can be expressed by the common description of  $\Delta_r G = \Delta_r H - T \Delta_r S$ , where  $\Delta_r G$ ,  $\Delta_r H$  and  $\Delta_r S$  are the Gibbs energy, enthalpy and entropy of the reaction. With this notation, the internal entropy production by the chemical reaction within the system can be expressed by

$$\frac{d_i S}{dt} = \nu \frac{\Delta_r G}{T} = \nu \frac{\Delta_r H}{T} - \nu \Delta_r S, \quad (4)$$

where  $\nu$  is the reaction velocity (see e.g. Kondepudi and Prigogine, 1996). In principle, the variables in the above expression (including  $T$ ) are functions of position and would have to be integrated over the whole atmosphere in order to calculate the total entropy production. In the steady state,  $d_e S/dt = d_i S/dt$ . Then, the change in enthalpy within the system is balanced by the enthalpy exchange,  $\nu \Delta_r H = J_H$  (which ultimately leaves the Earth system as a small contribution to its emitted thermal radiation), and the change in molar entropies during the reactions is balanced by the entropy exchange associated with the mass fluxes at the system boundary  $\nu \Delta_r S = S_B^\circ J_B - S_A^\circ J_A$ . Effectively, this allows us to replace a difficult volume integral with a much easier surface integral. It is easier to derive an approximate value for this surface integral because the temperature and chemical concentrations are fairly constant at the Earth's surface, whereas they vary quite substantially with height if the entire volume of the atmosphere is considered.

In the context of non-equilibrium thermodynamics,  $-\Delta_r G$  is sometimes called the affinity,  $A$ , with the difference in terminology serving to emphasise that a non-equilibrium process is being considered (this notation is used, for example, by Kondepudi and Prigogine, 1996). Although we prefer the  $\Delta_r G$  notation, it should be noted that its use does not imply any near-equilibrium assumption in our work.

In this paper we apply this approach to the simultaneous presence of  $O_2$  and  $CH_4$  in the Earth's atmosphere. Numerically characterising the amount of disequilibrium is not straightforward. However, the magnitude of the forces required to drive the disequilibrium is fairly straightforward to calculate, and in many ways such a figure tells us more than a static quantification of the disequilibrium would. The driver of the atmosphere's disequilibrium is composed of many processes, which include photochemical and vertical transport effects as well as the mass exchange at the surface. However,



**Fig. 1.** A diagrammatic representation of our simple, illustrative model. A single “box” contains a mixture of two ideal gases, A and B, at standard conditions. A “driving process” uses a source of work to convert B into A at a rate  $J_A = -J_B$ , while a spontaneous chemical reaction converts A into B at a net rate  $k_f p_A - k_r p_B$ . In steady state the rates of consumption and production of the two species by the two processes will balance. Both the driving process and the chemical reaction may release (as shown) or absorb heat.

it is useful to separately quantify the contributions from individual processes. In this paper we show how to calculate the contribution from an exchange of mass fluxes at the surface. The magnitude of such a driver of disequilibrium can be determined directly from the mass fluxes of the compounds together with standard chemical properties. In the next section we illustrate the analysis using a simple artificial example. In Sect. 4 we apply it to the addition of  $\text{CH}_4$  to the atmosphere by biotic processes, and the associated addition of  $\text{O}_2$  and removal of  $\text{H}_2\text{O}$  and  $\text{CH}_4$ .

### 3 An illustration of a flux-driven chemical disequilibrium

We begin our analysis with a simple, abstract model of a chemical system held out of equilibrium by fluxes of chemical species across its boundary. The aim of this model is not to directly represent the atmosphere or any another specific system. Instead it is a conceptual model whose purpose is to make clear the relationship between thermodynamic disequilibrium and the power required to drive the exchange fluxes, and consequently to provide an illustration of the general qualitative behaviour of chemical systems maintained out of equilibrium. This model includes a number of simplifying assumptions that we make for purely illustrative purposes; these assumptions will not be used when we apply these concepts to the  $\text{CH}_4$  chemistry in Earth’s atmosphere in Sect. 4.

(a)

		speed of kinetics $k_f, k_r$	
		low	high
mass flux $J_A$	low	intermediate disequilibrium	low disequilibrium
	high	high disequilibrium	intermediate disequilibrium

(b)

		speed of kinetics $k_f, k_r$	
		low	high
mass flux $J_A$	low	low power	lowest power
	high	highest power	high power

**Fig. 2.** Tables summarising some of the qualitative results illustrated by our conceptual model. The labels  $J_A$ ,  $k_f$  and  $k_r$  refer to parameters of our model, discussed in the text. (a) The amount of disequilibrium in a flux-driven system (according to any measure that takes account of only the concentrations) depends upon both the magnitude of the fluxes and on the kinetic rates of the chemical reactions that deplete them. The disequilibrium may generally be expected to be highest when the fluxes are fast and the kinetics slow, and at its lowest when the fluxes are slow and the kinetics fast. However, measures based on the concentrations alone cannot distinguish between the cases where the fluxes and the kinetics are both high from the cases where they are both low. This is important because the timescales of planetary processes vary over tens of orders of magnitude. (b) Similarly to disequilibrium, the power depends both on the fluxes and the kinetics, but the power is also proportional to the overall timescale, allowing it to distinguish the cases that disequilibrium alone cannot.

Broadly speaking, we are concerned with systems that are held out of chemical equilibrium by some externally driven process that continuously adds some chemical species to the system and removes others. These exchange fluxes are balanced by chemical reactions that take place within the system.

The kinetics of atmospheric chemistry are in general very complex, with models containing from hundreds up to thousands of species and reactions.

In this paper we will show that one need not model the kinetics in order to calculate the power required to drive the disequilibrium. However, in spite of this, it is instructive to begin by considering a highly simplified, conceptual model that explicitly includes the kinetics of the dissipating reaction. The simplified physical set-up of this conceptual model is shown in Fig. 1, and some of the issues that it illustrates are summarised in Fig. 2.

In this toy model, a “driving process” uses work to turn a single species B into another species A, and the atmospheric chemistry is represented by a single one-step reaction,  $A \rightleftharpoons B$ . In the interests of simplicity we will also let the “atmosphere” be represented by a single “box” of gas of volume  $V$ , at constant temperature and pressure. None of these assumptions are necessary in order to perform the calculations in Sect. 4; we make them only for the purposes of presenting a tractable illustrative model.

We also assume that fluxes and reaction kinetics maintain constant concentrations for A and B, i.e. there are no fluctuations in the concentrations over time, or long-term changes in the concentrations; this approximation is reasonable for our purpose of calculating an order-of-magnitude figure for the free energy flux.

In this simplified model, the gas phase reaction  $A \rightleftharpoons B$  consumes A and produces B at a rate  $k_f \gamma_A p_A / RT - k_r \gamma_B p_B / RT$ , where  $p_A$ ,  $p_B$  are the partial pressures, and  $\gamma_A$ ,  $\gamma_B$  are the fugacity coefficients of A and B, respectively. Since this model is intended as a simple illustrative example, we henceforth assume unitary fugacity coefficients. The net rate is then  $(k_f p_A - k_r p_B) / RT$ . If there are no surface fluxes (i.e. there is no driving process) then the reaction will proceed until the net rate of change equals zero, i.e.  $p_B / p_A = k_f / k_r$ . At this point the system has reached chemical equilibrium. In this state the forward and backward reactions both occur, but they do so at the same rate.

The ratio  $k_f / k_r$  is known as the equilibrium constant, denoted  $K_{eq}$ . Its value can be determined from the thermodynamic properties of the reactants A and B through the relation

$$K_{eq} = e^{-\Delta_r G^\circ / RT} = \frac{p_B}{p_A}, \quad (5)$$

where  $\Delta_r G^\circ$  is the difference in Gibbs energies of formation between the reactants and the products. For the reaction  $\text{CH}_4 + 2 \text{O}_2 \rightleftharpoons \text{CO}_2 + 2 \text{H}_2\text{O}$ , the equilibrium constant is around  $1.7 \times 10^{145}$ , implying that an atmosphere in equilibrium would not contain a single molecule of  $\text{CH}_4$ , as pointed out by Lippincott et al. (1966). However, this need not be the case for every example of chemical disequilibrium in a planetary system, so for the sake of illustration we will give our hypothetical  $A \rightleftharpoons B$  reaction a reaction constant of  $K_{eq} = 4$ , implying that there is 4 times as much B as A when the system is in equilibrium.

We now consider the situation in which a driving process consumes B and produces A. We assume, somewhat arbitrarily, that the process always consumes B and produces A at the same rate, which is assumed to be constant over time and not to depend upon the concentrations of A and B. In general the driving process will require a power source in order to perform this transformation. We denote the total flux of A from the driving process (in moles per unit time)  $J_A$ , and the total flux of B by  $J_B = -J_A$ . It is convenient to normalise these by the volume of the system, so we will write  $j_A = J_A / V$  and

$j_B = J_B / V$ . These quantities can be thought of as the fluxes of A and B into and out of a unit-volume sized part of the system.

Since  $p_a = p \cdot n_A / n$ , we can rescale the fluxes and obtain the dynamics

$$\frac{dp_A}{dt} = j_A RT - k_f p_A + k_r p_B \quad (6)$$

$$\frac{dp_B}{dt} = j_B RT + k_f p_A - k_r p_B = -\frac{dp_A}{dt}. \quad (7)$$

Since the total number of moles of A and B is constant we can write  $p_B = p - p_A$ , where  $p$  is the total pressure in the system. This allows us to reduce Eqs. (6) and (7) to the one-dimensional differential equation

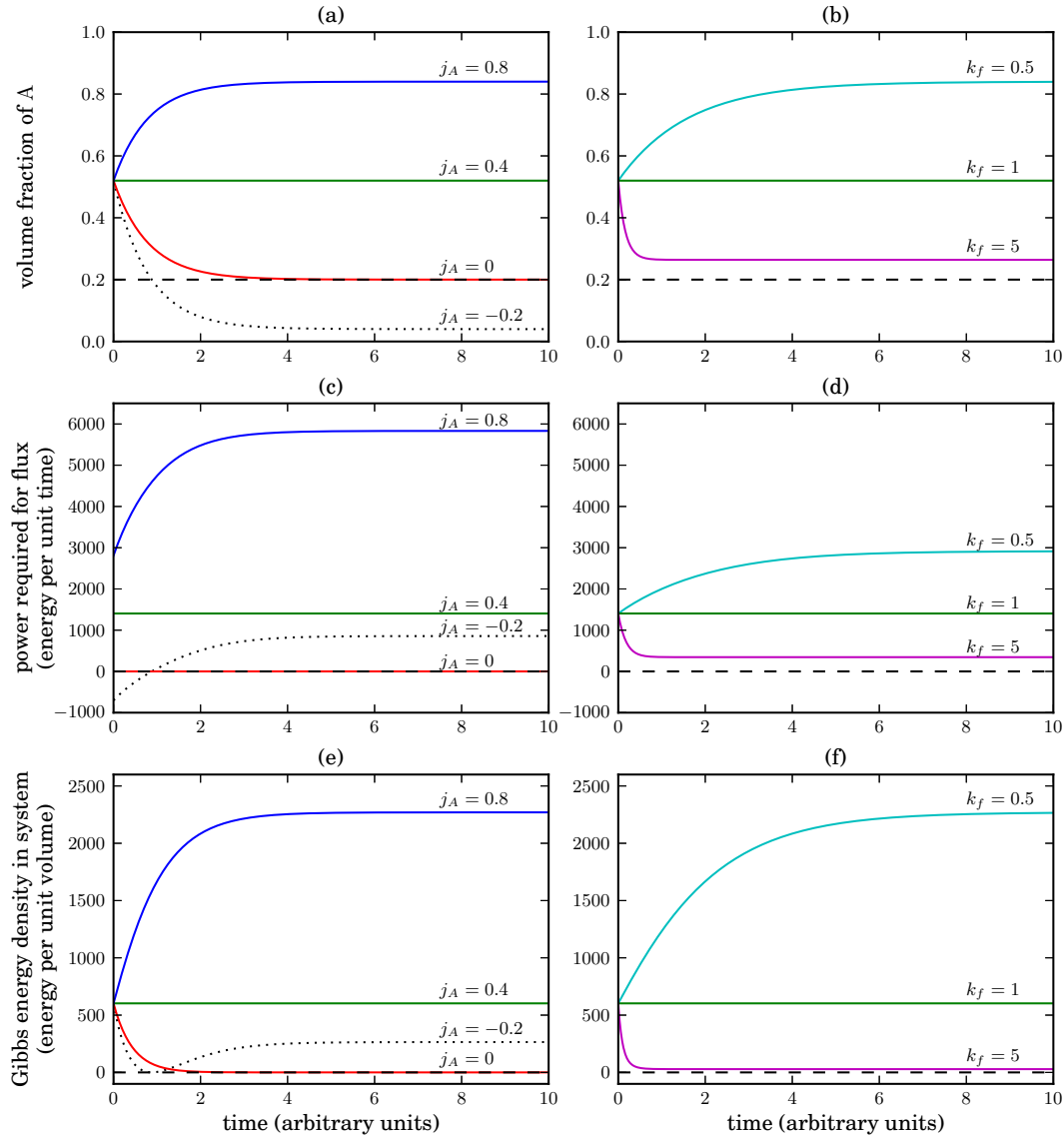
$$\frac{dp_A}{dt} = j_A RT + p k_r - (k_f + k_r) p_A. \quad (8)$$

Some example solutions of Eq. (8) can be seen in Fig. 3a and b. In all cases the concentration of A converges toward the steady-state value

$$\hat{p}_A = \frac{j_A RT + p k_r}{k_f + k_r} = \frac{P + j_A RT / k_r}{1 + K_{eq}}, \quad (9)$$

which can be derived by setting the right-hand side of Eq. (8) to zero (the precise value of this steady-state concentration depends upon the more-or-less arbitrary details of our model; its linear dependence on the flux  $j_A$  is a consequence of the reaction kinetics being first order). The analytical solution of Eq. (8) for initial conditions  $p_A(0) = p_A^0$  is given by  $p_A(t) = (p_A^0 - \hat{p}_A) e^{-(k_f + k_r)t} + \hat{p}_A$ .

We now wish to analyse this system from an energetic point of view. There are two options for how this reasoning may be expressed. The first would be to calculate the entropy production due to the reaction and note that in steady state this must be balanced by the entropy exchange across the system’s boundary, as outlined in Sect. 2. However, another way to think about it is in terms of the power (in the form of work) that must be used by the driving process in order to maintain the disequilibrium. In many ways these are simply two ways to express the same concept, since for an isothermal system one may obtain the entropy production simply by dividing the power dissipated by  $T$ . However, the power is a physically meaningful quantity in its own right, with slightly different properties to the entropy exchange. We choose to use power rather than entropy production in this study for two reasons. Firstly, power units allow a more convenient comparison with other Earth system processes; and secondly, we wish to emphasise that the  $\text{CH}_4$  disequilibrium in the atmosphere is ultimately driven by photosynthesis, in which power is extracted from sunlight. Expressing our results in power units tells us what proportion of this photosynthetically generated power ultimately contributes to driving atmospheric disequilibrium.



**Fig. 3.** Evaluation of the role of exchange fluxes and chemical kinetics in shaping chemical disequilibrium in the simple system explored in Sect. 3. **(a)** shows some example solutions to Equation 8, showing the volume fraction of A over time. In this plot we fix the parameters  $k_f=1$  and  $k_r=0.25$ , and vary the rate  $j_A$  of the driving process.  $V$  and  $c$  are set to 1. The initial value of  $[A]=0.52$  is such that a flux of 0.4 will maintain this value as a steady state. Fluxes higher or lower than this result in the system converging to a different steady state. If the flux is zero the system converges to the chemical equilibrium state (dashed line), whereas the greater the rate of the driving process, the further away the final steady state is from thermodynamic equilibrium. The dotted line shows what happens if the flux has the opposite sign (B added and A removed): the system converges to a steady state that is away from equilibrium in the opposite direction. **(b)** is similar, except that we hold  $j_A$  constant at 0.4, and vary both  $k_f$  and  $k_r$  so as to keep  $K_{eq}=k_f/k_r$  equal to 4 (i.e. the thermodynamic properties are kept constant but the overall speed of the kinetics is changed). The steady-state concentration of A depends on both the flux and the kinetics; systems with fast kinetics ( $k_f=5$ ) converge to a state closer to equilibrium than those with slow kinetics ( $k_f=0.5$ ), as well as approaching their steady-state value more rapidly. **(c)** and **(d)** show the same trajectories as **(a)** and **(b)**, except that we plot the power required to drive the flux  $j_A$ , according to Eq. (12). Note that in plot (c), the flux with the negative sign initially has a negative power. This is because A is initially in excess, and hence work could in principle be extracted by converting it to B. However, once the system reaches a steady state, A is no longer in excess and the power required is positive. In **(d)** one can see that when the kinetics of the dissipating reaction are fast, less power is required to maintain the flux. This is because the steady states of these systems are closer to equilibrium. Finally, **(e)** and **(f)** show the total amount of Gibbs energy,  $G$ , resident in the system, according to Eq. (16). This can be considered a measure of disequilibrium. When the flux is 0 in **(e)**, the Gibbs energy approaches its minimum value of zero, indicating that the system is in equilibrium. Fluxes with a higher magnitude generally push the system toward higher Gibbs energies. The dotted line reaches the minimum and then increases again because the concentration of A passes through its equilibrium value. In **(f)** we can see that the system with fast kinetics rapidly moves very close to the minimum  $G$  value, whereas those with slow kinetics move further away.

We begin by considering the Gibbs energy change for the reaction  $A \rightleftharpoons B$ . This is given by  $\mu_B - \mu_A$ , where  $\mu_A$  and  $\mu_B$  are the chemical potentials of the two species. If we assume for the sake of this illustrative model that the reaction takes place under standard conditions then these are given by

$$\mu_A = \Delta_f G_A^\circ + RT \ln \frac{p_A}{p_0} \quad \text{and} \quad \mu_B = \Delta_f G_B^\circ + RT \ln \frac{p_B}{p_0}, \quad (10)$$

where  $\Delta_f G^\circ$  represents the Gibbs energy of formation of a substance and  $p_0 = 1 \text{ atm}$  is the standard pressure (see Eq. 20 below for the case where the reaction does not take place under standard conditions). Inverting Eq. (5), we can see that the difference in the Gibbs energies of formation,  $\Delta_r G^\circ = \Delta_f G_B^\circ - \Delta_f G_A^\circ$ , is given by  $-RT \ln K_{\text{eq}}$ . We therefore have that, under these assumptions,

$$\Delta_r G = \Delta_r G^\circ + RT \ln \frac{p_B}{p_A} = RT \ln \frac{p - p_A}{K_{\text{eq}} p_A}. \quad (11)$$

This equation represents the amount of Gibbs energy lost when the gas phase reaction converts one mole of A into B, and its negative,  $-\Delta_r G$ , represents the Gibbs energy gained by the system as the driving process converts one mole of B back into A. Later we will show that  $-\Delta_r G$  can also be seen as a lower bound on the amount of work that the driving process must use in order to convert one mole of B into A.

We therefore have that the power required by the driving process is given by

$$P = -J_A \Delta_r G = J_A RT \ln \frac{K_{\text{eq}} p_A}{p - p_A}. \quad (12)$$

Figure 3c and d show how this quantity changes over time for the example fluxes shown in Fig. 3a and b.

The calculations in Sect. 4 below are based on a generalisation of Eq. (12). We use measured values of the fluxes and the concentrations in order to calculate the power, and this means that we have no need to consider the very complex kinetics of the methane oxidation reactions that balance the fluxes of  $\text{CH}_4$ ,  $\text{O}_2$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

However, in the context of this simple model, we may note that the steady-state value of  $[A]$  is in itself a function of  $j_A$ . Therefore, if we assume that  $j_A$  has been fixed at a given value for long enough for any transient behaviour to die out, we may substitute  $p_A$  by  $\hat{p}_A$  using Eq. (9) to derive

$$P = J_A RT \ln \frac{p + j_A RT/k_r}{p - j_A RT/k_f}. \quad (13)$$

This equation predicts the steady-state power requirements given only the parameters of our conceptual model, namely the kinetic constants  $k_f$  and  $k_r$ , and the flux per unit volume  $j_A RT$ .

We note that  $j_A RT$  cannot be greater than  $p k_f$  or less than  $-p k_r$ , otherwise the argument of the logarithm would be negative. This expresses the fact that the flux  $J_B$  of B out

of the system cannot be greater than the fastest rate at which the reaction can produce B, and similarly for A. As the fluxes approach these limits, the power required to drive them approaches infinity.

We may also see from this equation that if the kinetic constants  $k_f$  and  $k_r$  are increased while holding the flux rate  $j_A$  and the equilibrium constant  $K_{\text{eq}} = k_f/k_r$  constant, the term inside the logarithm becomes closer to 1, and therefore the magnitude of  $P$  becomes smaller. This is because systems with faster kinetics reach steady states closer to equilibrium, and closer to equilibrium less power is needed to sustain  $j_A$ . This is also illustrated in Fig. 3b and d.

Next we will consider the distance of our system from equilibrium. There are many possible ways to define disequilibrium; we shall do it by considering the density of Gibbs energy  $g$  in the system, which is here defined as  $g = \sum_i p_i \mu_i$ .

The power may be thought of as a flux of Gibbs energy into the system. This Gibbs energy is dissipated by the gas phase reaction  $A \rightleftharpoons B$ . In steady state the influx and the dissipation must balance, but during transients the density of Gibbs energy changes at a rate given by  $P - v_r \Delta_r G$ , where  $v_r = k_f p_A/(RT) - k_r p_B/(RT)$  is the velocity of the dissipating reaction. The density of Gibbs energy approaches its minimum value as the system approaches chemical equilibrium, and consequently it can be seen as a measure of the system's disequilibrium.

The density of Gibbs energy in the system is given by  $g = p_A \mu_A + p_B \mu_B$ . We must define  $\mu_A$  and  $\mu_B$  such that their difference  $\mu_B - \mu_A$  is given by Eq. (11). This can be done in many ways, with the different choices changing  $g$  by an additive constant. We choose

$$\mu_A = RT \ln \frac{1 + K_{\text{eq}}}{p} + RT \ln p_A \quad (14)$$

and

$$\mu_B = RT \ln \frac{1 + K_{\text{eq}}}{p K_{\text{eq}}} + RT \ln p_B, \quad (15)$$

which corresponds to a scale on which  $g=0$  at chemical equilibrium. This results in the following expression for the Gibbs energy density:

$$g = p_A RT \ln \frac{1 + K_{\text{eq}}}{p} p_A + (p - p_A) RT \ln \frac{1 + K_{\text{eq}}}{p K_{\text{eq}}} (p - p_A). \quad (16)$$

The Gibbs energy density in our conceptual model is plotted over time in Fig. 3e and f, showing that the system's distance from equilibrium can be the result of either a fast flux, or slow kinetics, or both.

This point may be made clearer by substituting the expression for the steady-state value of  $p_A$  (Eq. 9) to obtain the steady-state value of  $g$  as a function of the model's parameters:

$$g = \frac{p}{1 + K_{\text{eq}}} \left( 1 + \frac{j_A R T}{p k_r} \right) R T \ln \left( 1 + \frac{j_A R T}{p k_r} \right) + \frac{K p}{1 + K_{\text{eq}}} \left( 1 - \frac{j_A R T}{p k_f} \right) R T \ln \left( 1 - \frac{j_A R T}{p k_f} \right). \quad (17)$$

One can see from this equation that as  $j_A R T/k_f$  and  $j_A/k_r$  become small, the steady-state  $g$  approaches its minimum value of zero. This can happen either if  $j_A$  is small (a low flux), or if  $k_f$  and  $k_r$  are large (fast kinetics). Conversely, a high flux and slow kinetics will result in a large value of  $g$ .

Although the precise form of Eq. (16) depends on the details of our illustrative model, we can expect this last result – that a given degree of disequilibrium can be achieved by either a fast driving process and fast kinetics, or by a slow driving process and slow kinetics – to apply to any chemical reaction model, no matter how complex. This is because changing every flux and every kinetic constant in the same proportion is equivalent to changing the timescale of the dynamics. Consequently, making such a change will not affect the steady-state concentrations, meaning that the distance from equilibrium must remain the same. This will be true regardless of what measure of disequilibrium is used, as long as it depends only upon the concentrations and not on the fluxes.

On the other hand, the power,  $P$ , does depend on the overall rate at which the driving process and the kinetics operate. This can be seen, for example, in Eq. (13), where the expression within the logarithm is independent of the overall timescale in the same way that  $G$  is, but this is multiplied by  $J_A = V j_A$ , and will therefore increase if  $j_A$ ,  $k_f$  and  $k_r$  are all increased in the same proportion. This result is summarised in Fig. 2.

Finally, we complete our analysis by showing that  $P$  can be seen as a lower bound on the rate at which the driving process must consume its power supply. In what follows we consider the Gibbs energy change of the driving process, i.e. for the conversion of B into A. We denote this  $\Delta_x G$ , with the “x” indicating that we are considering the exchange fluxes. This quantity has the opposite sign from  $\Delta_r G$ , the Gibbs energy change of the  $A \rightleftharpoons B$  reaction discussed above. That is,  $\Delta_x G = -\Delta_r G$ .

This difference in Gibbs energies may be expressed as  $\Delta_x G = \Delta_x H - T \Delta_x S$ . For gases under atmospheric conditions,  $\Delta_x H$  is a constant depending on the thermodynamic properties of the reactants. In our illustrative model it is given by  $\Delta_f H_A^\circ - \Delta_f H_B^\circ$ . The  $T \Delta_x S$  term is not a constant but rather a function of the concentrations. It may readily be calculated from  $T \Delta_x S = \Delta_x H - \Delta_x G$ .

We now imagine that the driving process has access to a supply of energy in the form of work. We suppose that, as it converts one mole of B into A it uses an amount  $W$  of work and gives off an amount  $Q$  of heat. Applying the first law, we see that  $W = Q + \Delta_x H$ , i.e. some of the input energy must be taken up by the enthalpy change, with the rest being given off as heat (it is in principle possible for  $\Delta_x H$  to be

negative, in which case  $Q > W$ ). The second law states that the driving process must produce entropy at a non-negative rate. The total change in entropy per mole of B converted into A is  $\Delta_x S + Q/T$ , with the first term representing the change in material entropy as B is converted into A, and the second being due to the release of heat.

We thus have that  $\Delta_x S + (W - \Delta_x H)/T \geq 0$ , or  $W \geq \Delta_x H - T \Delta_x S$ . The quantity  $\Delta_x G$  can therefore be seen as a lower bound on the amount of work that must be used per mole to convert B into A. Since the driving process converts B into A at a rate of  $\nu$  mol s<sup>-1</sup>, we have that  $P = \nu \Delta_x G$  is a lower bound on the rate at which work must be consumed by the driving process. Any additional work consumed will be converted into other forms of energy, so we can interpret  $P$  as the component of the driving process’s input power that goes into driving the disequilibrium.

We may also note that  $P = \nu \Delta_x G = \nu \Delta_x H - \nu T \Delta_x S$ . The  $\nu \Delta_x H$  term may be seen as a flux of first-law energy from the driving process into energy associated with the chemical system (or in the opposite direction if  $\Delta_x H$  is negative), whereas  $\nu T \Delta_x S$  is a lower bound on the heat that must be given off by the driving process.

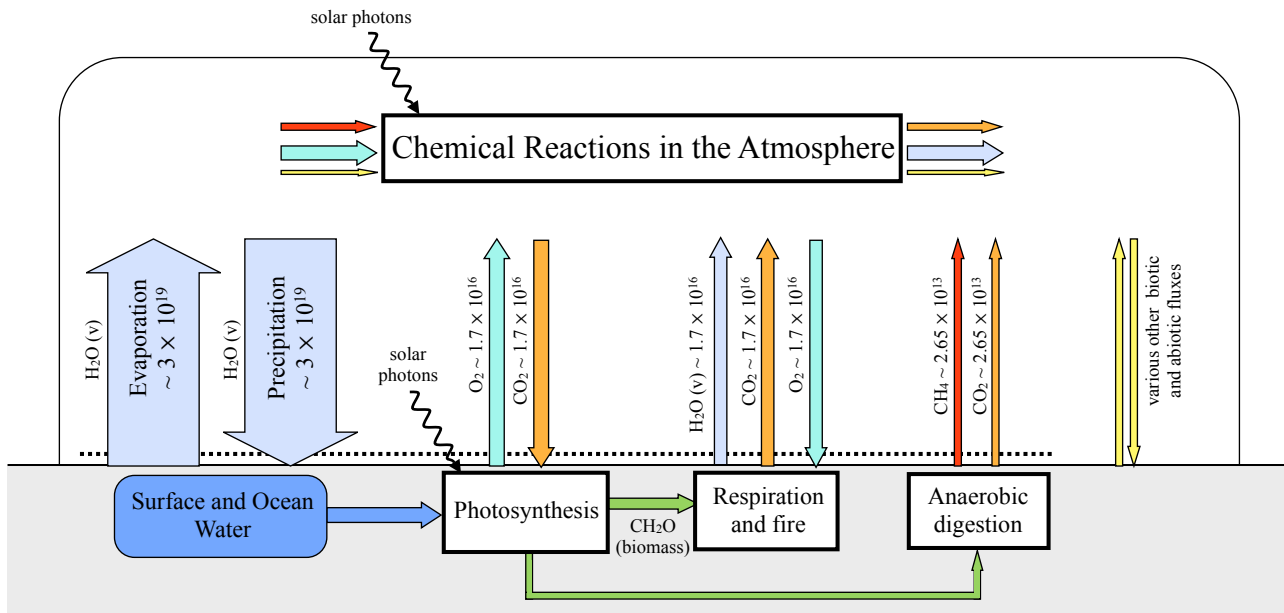
In this section we have used a simple illustrative model to demonstrate the properties of power as a measure of disequilibrium. The power required to drive disequilibrium in a system depends upon the chemical potentials of the species involved, and also upon the fluxes needed to maintain them. All drivers of disequilibrium in a planetary system must have a power source, and our analysis allows this to be quantified. In the following section we will apply these ideas to a practical example, the chemistry of methane in Earth’s atmosphere.

It is worth noting that although we have used the Gibbs energy as a measure of disequilibrium in this illustrative example, this would not be a good measure of disequilibrium in general, because the Gibbs energies of two spatial regions cannot meaningfully be added unless their temperatures are equal. For a more general system, such as a planet’s atmosphere, a better measure of disequilibrium could be constructed based on the local Planck potential,  $\Psi = G/T$ , which is expressed in entropic units. We do not pursue this idea further, however, because it is not necessary to measure the disequilibrium of the atmosphere in order to calculate the power involved in maintaining it.

#### 4 Application to CH<sub>4</sub> chemistry in the atmosphere

We now apply these ideas to the disequilibrium noted by Lovelock, whereby the atmosphere contains both CH<sub>4</sub> and O<sub>2</sub> in substantial concentrations. Our aim is to calculate the power required to drive this disequilibrium, which we will quantify using data on the concentrations and fluxes of the gases CH<sub>4</sub>, O<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O(vapour). We will also subdivide the Gibbs energy flux into its  $\Delta H$  and  $T \Delta S$



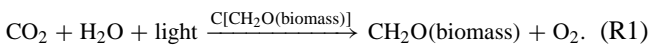


**Fig. 4.** A graphical illustration of the fluxes of various gases in and out of the atmosphere. All figures are taken from Schlesinger (1997), updated with Ehhalt et al. (2001) and EPA (2010), and have been converted to  $\text{mol a}^{-1}$ . There is a large amount of uncertainty in these figures; in particular, the uncertainty in the methane fluxes is of the order of 10 %. The largest fluxes are associated with the water cycle; evaporation adds  $\text{H}_2\text{O}(v)$  to the atmosphere at a rate of around  $3 \times 10^{19} \text{ mol a}^{-1}$ , which is almost exactly balanced by its removal due to precipitation. Much smaller fluxes of  $\text{O}_2$  and  $\text{CO}_2$  are produced by photosynthesis, which also requires liquid water and a power source, in the form of sunlight. These fluxes are almost balanced by respiration and fire, with only a small fraction of biomass being consumed by anaerobic digestion, which adds  $\text{CH}_4$  and  $\text{CO}_2$  to the atmosphere at a rate of the order  $3.5 \times 10^{13} \text{ mol a}^{-1}$ , of which around  $1.2 \times 10^{13} \text{ mol a}^{-1}$  is from natural sources and the rest is anthropogenic. Abiotic sources, primarily fossil fuel burning, add an additional  $8 \times 10^{12} \text{ mol a}^{-1}$  of methane to the atmosphere. The influx of methane is balanced by a complex network of chemical reactions in the atmosphere, one of whose net effects is to convert  $\text{CH}_4$  and  $\text{O}_2$  into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The thick dotted line indicates which fluxes are included in our analysis. We calculate the net fluxes of energy and entropy passing through this surface, excluding the radiative fluxes.

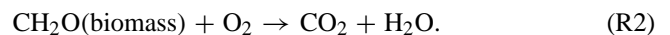
components, and show that the enthalpy plays a much greater role than the  $T \Delta S$  term.

The relevant material fluxes are summarised in Fig. 4. By far the largest fluxes are those associated with the water cycle: evaporation (including transpiration) and precipitation add and remove water vapour from the atmosphere at a rate of around  $3 \times 10^{19} \text{ mol a}^{-1}$ . Since these fluxes are more or less balanced, most of the free energy entering the atmosphere through evaporation is balanced by the free energy leaving the atmosphere through condensation. Nevertheless, the water cycle plays an important role in maintaining the  $\text{CH}_4$  disequilibrium.

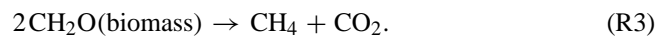
As an extremely coarse approximation, biomass has the chemical formula  $\text{CH}_2\text{O}$ , and photosynthesis can be seen as the following chemical reaction:



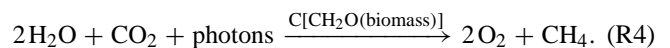
Photosynthesis adds  $\text{O}_2$  and removes  $\text{CO}_2$  from the atmosphere at a rate of around  $1.7 \times 10^{16} \text{ mol a}^{-1}$ . This is almost balanced by respiration and fire, which (again to a very rough approximation) are essentially the reverse of photosynthesis:



These processes also add  $\text{H}_2\text{O}$  vapour to the atmosphere, although the rate at which this happens is very small compared to the amount of water that enters the atmosphere through evaporation and transpiration (some  $\text{H}_2\text{O}$ , such as that produced by respiration in roots, probably becomes surface water rather than entering the atmosphere directly). However, not all biomass is oxidised by respiration or fire. Some is consumed by anaerobic digestion instead, which, again very roughly approximated, can be seen as



If we assume that the total amount of biomass stays roughly constant, we can combine Reactions (R1), (R2) and (R3) to give the net reaction

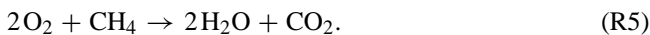


Thus, life's net effect upon the atmosphere in terms of the methane–oxygen disequilibrium is to continually remove  $\text{CO}_2$  and add  $\text{O}_2$  and  $\text{CH}_4$  (Russell, 2007). The rate at which this occurs can be determined by estimating the rate at which

CH<sub>4</sub> is produced biotically. Schlesinger (1997, p. 373) gives a budget of global CH<sub>4</sub> emissions, including both natural and anthropogenic sources, with a total flux into the atmosphere of 535 Tg a<sup>-1</sup> CH<sub>4</sub>. If we exclude the 10 Tg a<sup>-1</sup> CH<sub>4</sub> due to geological emissions and the 100 Tg a<sup>-1</sup> CH<sub>4</sub> associated with fossil fuel use, we end up with a figure of 425 Tg a<sup>-1</sup> CH<sub>4</sub>, or  $2.65 \times 10^{13}$  mol a<sup>-1</sup>, for the biotically generated flux of methane on the modern Earth.

We will denote the biotically generated flux of methane on the modern Earth with  $\nu$ . This may be thought of as the absolute net rate at which Reaction (R4) occurs, expressed in mol a<sup>-1</sup>. So the driving process puts CH<sub>4</sub> into the atmosphere at a rate  $\nu$  and O<sub>2</sub> at  $2\nu$ , while removing CO<sub>2</sub> and H<sub>2</sub>O at  $\nu$  and  $2\nu$ , respectively.

From time to time, for the sake of exposition, we will find it convenient to imagine that these fluxes are balanced by the following spontaneous net reaction taking place in the atmosphere:



However, we stress that this is not really the case. In reality these fluxes are balanced by a complex network of chemical reactions that take place at many different altitudes in the atmosphere. These reactions do consume O<sub>2</sub> and CH<sub>4</sub> and produce H<sub>2</sub>O and CO<sub>2</sub> but they also interact with many other surface fluxes, particularly ones relating to the nitrogen cycle. Additionally, many of the reactions in this network are not spontaneous but are instead driven by photochemistry. For example, the dominant process consuming CH<sub>4</sub> is its oxidation by OH into formaldehyde, which is then broken up into products by photodissociation (Hobbs, 2000). Since temperature and pressure vary with height these reactions take place under a wide variety of conditions. Finally, the system is not currently in a steady state, since human activity has increased the rate of biotic methane production and its concentration in the atmosphere is increasing at a rate of around  $1.9 \times 10^{12}$  mol a<sup>-1</sup> (Schlesinger, 1997, p. 373). However, there is no need to consider the details of these processes in order to calculate the power added to the atmosphere by the net driving process shown in Eq. (R4).

Reaction (R4) represents the net fluxes supplied by the biota to the atmosphere, to a rough approximation (more precisely, since H<sub>2</sub>O vapour is removed by precipitation, it reflects the combined net effect of the biota and the water cycle). Thus, for every mole of CH<sub>4</sub> added to the surface layer of the atmosphere, two moles of O<sub>2</sub> are added, and two moles of H<sub>2</sub>O and one mole of CO<sub>2</sub> are removed. We make the simplifying approximation that the surface layer of the atmosphere has an approximately constant uniform temperature, pressure, humidity and CH<sub>4</sub> concentration. We may then calculate that for every mole of CH<sub>4</sub> added by this process, the atmosphere's Gibbs energy changes by

$$\Delta_x G = \mu_{\text{CH}_4} + 2\mu_{\text{O}_2} - \mu_{\text{CO}_2} - 2\mu_{\text{H}_2\text{O}}, \quad (18)$$

**Table 1.** Thermodynamic data for the four species we consider, in gas phase, tabulated at unit pressure and  $T_0=298$  K (taken from Atkins, 1994); the surface concentrations we assume in our calculation; and the species' chemical potentials in the gas phase near the surface, calculated using Eq. (20) with  $T=288$  K. These figures lead to a  $\Delta_x G$  of 799 kJ mol<sup>-1</sup> for the non-spontaneous conversion of CO<sub>2</sub> and H<sub>2</sub>O into O<sub>2</sub> and CH<sub>4</sub>.

Species	$\Delta_f G^\circ$ (kJ mol <sup>-1</sup> )	$\Delta_f H^\circ$ (kJ mol <sup>-1</sup> )	Concentration (mole fraction)	Potential $\mu$ (kJ mol <sup>-1</sup> )
O <sub>2</sub>	0	0	0.209	-3.748
CH <sub>4</sub>	-50.72	-74.81	$1.75 \times 10^{-6}$	-83.27
CO <sub>2</sub>	-394.36	-393.51	$3.6 \times 10^{-4}$	-413.3
H <sub>2</sub> O	-228.57	-241.82	0.02	-238.4

where  $\mu$  represents the chemical potential of a given species (as in the previous section, the subscript "x" indicates that we are considering the Gibbs energy due to exchange fluxes rather than a reaction within the system). Under atmospheric conditions these species are well approximated by ideal gases. For ideal gases close to standard conditions the chemical potential of each reactant can be calculated from (Kondepudi and Prigogine, 1996, p. 138),

$$\mu_i(p_i, T) = \mu_i^\circ + RT \ln \frac{p_i}{p_0} \quad (19)$$

where  $\mu_i^\circ = \Delta_f G_i^\circ$  is the  $i$ -th compound's Gibbs energy of formation,  $p_i$  is its partial pressure and  $p_0 = 1$  atm is the standard pressure at which  $\mu_i^\circ$  is tabulated. For ideal gases at conditions further from the standard ones, a more detailed formula is

$$\mu_i(p_i, T) = RT \ln \left( \frac{p_i}{p_0} \right) + \frac{T}{T_0} (\mu_i^\circ - \Delta_f H_i^\circ) + \Delta_f H_i^\circ, \quad (20)$$

where  $T_0$  is the standard temperature (Simoncini et al., 2012).

We use present-day values of [O<sub>2</sub>]=20.946 %, [CO<sub>2</sub>]=360 ppmv, [CH<sub>4</sub>]=1.75 ppmv (Schlesinger, 1997) and  $T=288$  K for the surface temperature. The concentration of H<sub>2</sub>O varies typically between 1 and 4 % at the Earth's surface; using a value of 2 % gives us a value for  $\Delta_x G$  of 799 kJ (see Table 1). This figure is positive because we are considering the effect of the driving process: the addition of CH<sub>4</sub> and O<sub>2</sub> and the removal of O<sub>2</sub> and CO<sub>2</sub> cannot occur spontaneously.

Assuming constant concentrations for H<sub>2</sub>O and CH<sub>4</sub> is a crude approximation, but a reasonable one given our purpose of calculating an order-of-magnitude figure for the free energy flux. The figure for  $\Delta_x G$  is not particularly sensitive to these concentrations, in that either of them may be changed by a factor of 10 without changing  $\Delta_x G$  by more than 1.5 %. This also justifies our use of a single one-box model for the atmosphere, since it implies that local variations in the chemical potentials will be small.

Multiplying  $\Delta_x G$  by the rate at which CH<sub>4</sub> is added to the atmosphere due to biotic processes (quoted above), we arrive

at a figure of  $P = \nu \Delta_x G = 0.67$  TW for the total net flux of free energy from the surface to the atmosphere associated with this driving process. The uncertainty in this figure is of the order of 50 %, due to the uncertainty in the CH<sub>4</sub> flux figure. This Gibbs energy flux may also be seen as the power that the biosphere puts into the atmosphere's CH<sub>4</sub> disequilibrium. It is worth mentioning that it is only meaningful to calculate the *net* Gibbs energy flux in this way. This is because the Gibbs energies of formation are defined on scales whose zero point is a matter of convention. Because of this, it is not possible to assess (for example) the contribution of the O<sub>2</sub> flux by calculating  $\nu \mu_{O_2}$  alone, since this figure does not have a physical meaning.

The Gibbs energy flux may be subdivided into a flux of enthalpy and a  $T \Delta_x S$  term. The enthalpy change of the driving process (Reaction R4) is given by  $\Delta_x H = \Delta_f H_{CH_4}^\circ + 2 \Delta_f H_{O_2}^\circ - \Delta_f H_{CO_2}^\circ - 2 \Delta_f H_{H_2O(v)}^\circ = 802$  kJ, with  $\Delta_f H^\circ$  denoting the standard enthalpy of formation of a compound (see Table 1 for the values used). We can turn this into a flux by multiplying  $\Delta_x H$  by the rate  $\nu$  of the driving process, which gives us an enthalpy flux of  $\nu \Delta_x H = 0.67$  TW that differs by only a small amount from the Gibbs energy flux.

In general, enthalpy can be further subdivided into an internal energy term and a term relating to the volume change (i.e.  $\Delta_x H = \Delta_x U + p \Delta_x V$ ), but for Reaction (R4),  $\Delta_x V = 0$ , meaning that  $\Delta_x H$  can be seen as purely a change in internal energy.  $\nu \Delta_x H$  can therefore be seen as a flux of energy stored in chemical bonds.

This energy comes ultimately from sunlight, from which it is transformed by photosynthesis into bond energy in sugars, a small fraction of which eventually becomes the  $\nu \Delta_x H$  term in the free energy flux. If we imagine, temporarily, that the fluxes are balanced by the hypothetical Reaction (R5), we may see that the dissipating reaction must have the opposite  $\Delta H$ , turning bond energy into heat at a rate that balances the rate at which it is added to the system. This heat will then form a very small fraction of the heat lost to space by thermal radiation by the atmosphere. We may safely assume that this is the ultimate fate of most of the bond energy added to the real atmosphere, although a small amount of it may return to the surface in other fluxes. We note that 0.67 TW is a very small flux of heat in comparison to the energy fluxes associated with absorption and emission of radiation in the atmosphere, and should not be expected to affect its temperature directly (CH<sub>4</sub>, CO<sub>2</sub> and H<sub>2</sub>O do affect the atmosphere's temperature due to being greenhouse gases, but this is a separate issue).

We now turn to the contribution of  $-T \Delta_x S$ , which is given by  $\Delta_x G - \Delta_x H = -0.30$  kJ. Its contribution to the Gibbs energy flux is  $-\nu T \Delta_x S = -0.0025$  TW. Its magnitude is very small compared to the contribution of the enthalpy. Its negative sign means that the enthalpy flux is slightly greater than the Gibbs energy flux, implying that a driving process of the maximum possible efficiency would actually absorb heat at a

low rate, rather than releasing it. This figure corresponds to a flux of material entropy ( $\nu \Delta_x S$ ) of about  $8.8 \times 10^6$  J K<sup>-1</sup> s<sup>-1</sup> in the direction from the driving process to the atmosphere. This entropy is absorbed by the reactions in the atmosphere. This is nevertheless consistent with the second law, because those reactions are exothermic and produce more entropy by giving off heat than they absorb in the form of material entropy.

To summarise, we have shown in this section that the power used by the biosphere to maintain the simultaneous presence of CH<sub>4</sub> and O<sub>2</sub> in Earth's atmosphere is of the order 0.67 TW, although there is a lot of uncertainty in this figure due to the uncertainty in measurements of the CH<sub>4</sub> flux. This power may be seen as a flux of Gibbs energy from the surface to the atmosphere; almost all of this Gibbs energy flux is accounted for by the term relating to the internal energy, i.e. energy stored in chemical bonds.

## 5 Discussion

In this section, we discuss the limitations of our methodology, and the interpretation and wider context of the 0.67 TW estimate. Finally, we discuss the implications and future prospects of this work, both in terms of furthering our understanding of biogeochemical cycles on Earth, and in terms of its implications for the detection of photosynthetic biospheres on distant exoplanets.

### 5.1 Limitations

A primary result of this paper is the figure of 0.67 TW for the power put into maintaining the atmosphere's CH<sub>4</sub> disequilibrium by the biosphere. The error in this figure is around 10 % due to uncertainty in the global CH<sub>4</sub> emissions. In particular, although recent literature had a very high uncertainty on methane emissions (of the order of 50 % in Schlesinger, 1997), new data gives a better estimate. While human-related emissions can be relatively easily estimated, the natural (biological and non-biological) are more difficult to estimate. The IPCC gives four different data references, with a whole average natural emission of 209.25 TgC a<sup>-1</sup>, and a maximum uncertainty of the order of 29 % (Ehhalt et al., 2001). The US EPA 2010 reports an average of 208 TgC a<sup>-1</sup>; in this case, data ranges are quite large for each single source, but the relative contributions of emissions from each source to the total budget are not independent of each other (EPA, 2010). Thus, the ranges cannot be summed, yielding in a whole uncertainty of 29 % for natural emissions. The data about human-related emissions are on average 336 TgC a<sup>-1</sup> with a maximum uncertainty of 6 %. The total present uncertainty on methane emission rates is of the order of 10 %. This allows us to conclude that the power needed to maintain the atmosphere's CH<sub>4</sub> disequilibrium is about  $(0.67 \pm 0.07)$  TW.

In order to produce our primary result, we have relied on some fairly crude assumptions: our model of the net driving process (Reaction R4) is highly simplified, and we have used a one-box global model with constant values for the temperature and for the concentrations of CH<sub>4</sub> and H<sub>2</sub>O, which in reality vary over time and space. The errors introduced by these simplifications are likely to be small compared to the uncertainty in the CH<sub>4</sub> flux.

Our figure only applies to the biotically driven component of the methane–oxygen disequilibrium, and is very far from being a full budget of Gibbs energy in atmospheric chemistry. For that one would need to consider biotically and abiotically driven fluxes of many other compounds, and in particular ones relating to the nitrogen cycle. Photochemistry is also a substantial source of chemical power in the atmosphere, quite likely dwarfing that due to the surface fluxes. One of the major advantages of a thermodynamic approach is that these other factors do not need to be taken into account in order to produce a figure for one particular driving force, as we have done.

Although we see the 0.67 TW figure as being primarily due to the action of the biosphere, it is worth reiterating that the water cycle also plays an important role. If there were no water cycle then the atmosphere would come into vapour pressure equilibrium with the oceans, leading to a much higher water vapour content than observed. The water cycle prevents this by acting as an “atmospheric dehumidifier” (Paulius and Held, 2001), removing water vapour from the air. Maintaining the vapour pressure disequilibrium requires a source of power, which in the case of the water cycle comes ultimately from the radiative heating of the surface. The water cycle is thus associated with a substantial disequilibrium of its own. Since the magnitude of the water cycle is dominated by physical processes, particular evaporation from the world’s oceans, the direct role of the biosphere on the water cycle and due to the small contribution that is involved in the CH<sub>4</sub> disequilibrium can safely be neglected. There may, however, be substantial indirect effects of biotic activity on the water cycle through changes in the atmospheric composition and the atmospheric greenhouse effect that would need to be further evaluated.

In order to quantify the biotically generated fraction of the power needed to maintain the CH<sub>4</sub>/O<sub>2</sub> disequilibrium, we have considered only the processes that are entirely due to biological activities. In particular, the methane oxidation would not take place if it were not for the biotically generated influx of methane; on the other hand the removal of the byproduct water vapour from the atmosphere by the water cycle is a physical process that would occur regardless of the methane flux. Thus we include the power associated with the oxidation reaction in our figure, but not the power involved in removing the resultant water vapour from the atmosphere which is likely to be minute.

It should be noted that our thermodynamic approach is complementary to approaches based on Earth system

feedbacks. The figure we calculate tells us how much power is required to maintain the concentrations of CH<sub>4</sub> and O<sub>2</sub> in the atmosphere, but by itself it says nothing about how sensitive these concentrations are to perturbations of the system. For this one would need a detailed model of the kinetics of methane oxidation in the atmosphere, which depends not only on the concentrations of CH<sub>4</sub>, O<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub> but also on many other factors, including the concentrations of ions such as OH, which in turn depend on biotically generated fluxes of nitrogen compounds. It would also be necessary to take into account the effect of the atmospheric composition on photosynthesis, both directly and through feedbacks relating to albedo and the greenhouse effect. In general, considering feedbacks would be required in order to account for any change in the system over time. The advantage of a thermodynamic approach is that it allows a quantitative figure to be derived even when such dynamical details are unknown, and it is for this reason that we believe it should form an important component of biogeochemists’ tool boxes.

We were able to use a single one-box model to obtain the methane-disequilibrium figure because of the insensitivity of the chemical potentials to the concentrations in this particular case. This is likely not to be the case for every instance of chemical disequilibrium in the Earth system. If the chemical potentials have a high degree of spatial or temporal variation then an analysis along these lines will still be possible, but the calculation will be more complex. In such cases we envisage the use of global models, in which the power is calculated locally and then integrated over time and space. Such an approach would also allow the local variations to be visualised, but it would require more input data, since the spatial and temporal variation of both the concentrations and the fluxes would have to be known or modelled.

## 5.2 Chemical disequilibrium and life

To relate our estimate of the power involved in maintaining the methane disequilibrium back to the original question of whether chemical disequilibrium is a sign of life, we first place this estimate into the context of biotic activity and then discuss the relationship between chemical disequilibrium and life more broadly.

To associate our 0.67 TW figure to biotic activity, it can be roughly subdivided into a natural and an anthropogenic component. According to Schlesinger’s atmospheric methane budget, about 35 % of the CH<sub>4</sub> flux comes from natural systems, corresponding to a power of around 0.24 TW. The remaining 0.43 TW consists of emissions by biotic processes associated with human activity, the largest contributors being due to enteric fermentation by animals (0.13 TW) and to rice paddies (0.09 TW).

To compare these numbers into the work associated with processes within a broader, Earth system context (Kleidon, 2010), we note that the 0.67 TW is a minute fraction of the total energy flux supplied by solar radiation of around

175 000 TW, and also in relation to the total, photosynthetic productivity of about 215 TW. Yet, when compared to the chemical energy that is made available by precipitation for the dissolution of the continental crust on land of less than 1 TW, this power associated with atmospheric chemical disequilibrium is comparable in magnitude to other geochemical processes at the land surface.

Nevertheless, given that the 0.67 TW of power associated with the methane–oxygen disequilibrium represents only a fraction of about 0.3 % of the total photosynthetic activity, it would seem that the associated disequilibrium is a poor indicator of the actual, overall activity of the Earth's biosphere. However, a more detailed analysis that includes other processes might result in a higher figure.

In fact, there are also other types of process that contribute toward disequilibrium. On Earth, atmospheric chemical disequilibrium can be seen in the concentrations of oxygen, ozone, methane and nitrous oxide concentrations, among other small components (Lovelock, 1965, 1975; Lederberg, 1965; Lippincott et al., 1966; Lovelock and Margulis, 1973; Sagan et al., 1993; Lenton, 1998). Disequilibrium by itself is not an unequivocal indicator of life, since it can also be caused by abiotic processes such as photochemistry or geothermally driven surface chemistry. In particular, photochemistry can produce substantial amounts of O<sub>2</sub> and O<sub>3</sub>, as found in the Earth's stratosphere as well as on Venus and Mars, and as can be expected in Venus-like exoplanets (Segura, 2007; Montessin et al., 2011; Schaefer and Fegley, 2011). These forms of chemical disequilibrium, however, result directly through the interaction of radiation and atmospheric chemistry and do not involve exchange fluxes between the surface and the atmosphere.

Sagan et al. (1993) suggest a step-by-step method in which all drivers of a planet's atmospheric disequilibrium are identified, with the aim of ruling out abiotic explanations: “once candidate disequilibria are identified, alternative explanations must be eliminated. Life is the hypothesis of last resort”. The advantage of this type of methodology for life-detection over the search for oxygen (or its photochemical product, ozone) is that exoplanetary biospheres may operate using different chemistry from that of Earth's biota, resulting in a different atmospheric composition. In such a case we may still be able to infer the presence of life by identifying a strong disequilibrium that has no abiotic explanation.

The detection of chemical disequilibrium in exoplanets' atmospheres is not an easy challenge. In recent years it has become possible to detect and characterise atmospheres of giant planets, by using the Hubble Space Telescope (HST), Spitzer Space Telescope, and from the ground (Madhusudhan and Seager, 2011). Of particular interest from the habitability point of view is the detection of rocky planets, which can be also called “terrestrial planets” for the similarity with Earth and with other rocky planets of our Solar System. The formation of the atmosphere of these planets is presently under studied (Miguel et al., 2011). However, spectra can

provide the profile for only some species and not for all the species given by a complete atmospheric chemical model. A methodology is then needed to combine the available spectra with simpler chemical models, which can still simulate adequately the real conditions.

Although their composition is very close to thermochemical equilibrium, in warm atmospheres like the ones of giant planets and brown dwarfs, disequilibrium processes are known (Visscher and Moses, 2011). Ultraviolet irradiation drives photochemistry, as for terrestrial planets, and eddy and molecular diffusion produce a very fast vertical transport which can drive chemical composition out of its equilibrium due to the dependence of the equilibrium constant on the temperature. Models have been developed that compare the timescales of vertical mixing and of chemical kinetics (Prinn and Barshay, 1977; Visscher et al., 2010; Moses et al., 2011). This kind of model has been used to explain some species' disequilibrium present in Jupiter, Saturn, Uranus and Neptune (Visscher and Moses, 2011). A good evaluation of the significance of both photochemistry and vertical mixing in hot planets is given in Kopparapu et al. (2012).

Because our method calculates only the contribution due to surface fluxes, it could in principle help us to separate this from the contribution associated with abiotic photochemistry. The contribution from surface exchange fluxes may result from purely abiotic fluxes, e.g. from the interior, but can also result from biotic activity that takes place at the planetary surface. Hence, it would seem that our methodology could provide a useful contribution to separating out the abiotic contributions to chemical disequilibrium in the planetary atmosphere as proposed by Sagan et al. (1993).

### 5.3 Implications and future prospects

In this paper we have focused on accounting for the power required to sustain the atmosphere's concentrations of CH<sub>4</sub> and O<sub>2</sub>. However, our aim has also been to set out a methodology whereby sources of chemical disequilibrium in general can be quantified. We see the application of this methodology to other biogeochemical cycles as a major future benefit of this work. We hope that tracing the sources and sinks of chemical energy in the Earth system will allow the chemical cycling in the atmosphere, biosphere, oceans and lithosphere to be expressed in a common unifying language. A thermodynamic analysis will allow these disparate processes to be directly compared to one another, despite the huge differences in timescales involved. Tracing how much of this power is provided by biotic processes will increase our understanding of the effect life has upon the Earth system as a whole.

It is interesting to consider how the power involved in driving methane oxidation by O<sub>2</sub> has changed over the history of the Earth. In the Archean period the situation was quite different from today, with the biosphere being dominated by methanogens. Before the evolution of oxygenic

photosynthesis, the only source of O<sub>2</sub> would have been volcanoes, with this O<sub>2</sub> being depleted by the oxidation of reduced organic gases (Kump et al., 2011). In such a situation the flux of O<sub>2</sub> would have been much smaller than the flux of CH<sub>4</sub>, and so we must use the O<sub>2</sub> flux rather than the CH<sub>4</sub> flux in our calculation. Kharecha et al. (2005) give figures for the concentrations and O<sub>2</sub> flux on the Archaean Earth, which we summarise in Table 2.

Using this data, we arrive at a figure of  $3.6 \times 10^{-2}$  TW for the power involved in reducing O<sub>2</sub> by CH<sub>4</sub>, two orders of magnitude below the figure for the modern Earth. However, this figure does not take into account oxidation of CH<sub>4</sub> by other reducing agents that would also have been emitted from volcanoes, and by slower processes like mantle iron oxidation and weathering. It should be noted that the atmospheric residence times are also very different in this situation than for the modern Earth. From the figures in Table 2 we calculate that the methane residence time would have been of the order three million years, rather than the present-day value of around 12 yr (Ehhalt et al., 2001), and the oxygen residence time would have been much lower than the present-day value. Nevertheless, this rough estimate would suggest that it required considerably less power to sustain the high CH<sub>4</sub> concentrations in the Earth's past.

This work also has implications for the search for life on exoplanets. The disequilibrium of Earth's atmosphere is largely caused by biotic activity, and chemical disequilibrium in the atmosphere of an exoplanet has long been proposed as a potential indicator of life. As other authors have pointed out (Sagan et al., 1993), disequilibrium is not a foolproof indicator of biotic activity, since it may also have abiotic causes as explained above. Our work contributes to this by helping us to understand which disequilibria are most in need of explanation. A high degree of disequilibrium may be the result of slow kinetics and a low-power driving process, and in this case it becomes more plausible that the driving fluxes could be caused by abiotic surface chemistry, powered (for example) by geothermal gradients. On the other hand, a power of a higher magnitude would require a more powerful source of energy, making it more likely that its ultimate source is light. The next step in such an analysis would be to attempt to eliminate abiotic photochemistry as an explanation for the disequilibrium, as well as geological causes; this would require detailed modelling of the chemistry involved. The identification of a chemical disequilibrium requiring a high-power driving force would not be an unambiguous sign of life on an exoplanet, but it would certainly mark it out as an important target for further study.

However, in order to calculate the power of a driver of disequilibrium, one must be able to estimate the influxes and outfluxes as well as the concentrations of the species involved. It is unlikely that these could be directly measured for an exoplanet, meaning that they would instead have to be estimated by building a detailed model of the kinetics of planets' atmospheric chemistry, and then working backwards

**Table 2.** Data used for an estimate of the lifetime of methane and its disequilibrium or present Earth conditions and before the Great Oxidation Event, when the biosphere was dominated by methanogens. The CH<sub>4</sub> lifetime is calculated as the ratio of atmospheric concentration to flux into the atmosphere. In the case of the present atmosphere, the limiting flux is methane, whilst prior to the Great Oxidation Event the oxygen flux was likely to be much smaller than the methane flux and thus the limiting flux. Atmospheric concentrations and methane flux estimates are taken from Kharecha et al. (2005).

	Present earth	Prior to great oxidation	Units
[CH <sub>4</sub> ]	$7.38 \times 10^{-8}$	$1.00 \times 10^{-3}$	mol L <sup>-1</sup>
[O <sub>2</sub> ]	$8.61 \times 10^{-5}$	$8.61 \times 10^{-17}$	mol L <sup>-1</sup>
[CO <sub>2</sub> ]	$1.65 \times 10^{-7}$	$1.65 \times 10^{-7}$	mol L <sup>-1</sup>
[H <sub>2</sub> O]	$1.65 \times 10^{-4}$	$1.65 \times 10^{-4}$	mol L <sup>-1</sup>
O <sub>2</sub> flux	$3.53 \times 10^{-16}$	$1.08 \times 10^{-17}$	mol L <sup>-1</sup> s <sup>-1</sup>
CH <sub>4</sub> lifetime	6.63	$2.92 \times 10^6$	yr
Power	0.67	0.04	TW

to determine what fluxes would be needed to support the measured concentrations. This is not an easy task, but it is a necessary one if a photosynthetic alien biosphere is to be unambiguously identified through this method.

## 6 Conclusions

In this paper we have discussed the general properties of systems held in a non-equilibrium steady state of chemical disequilibrium by externally driven fluxes of chemical species across their boundaries. We have shown how to calculate the power required to drive such fluxes, and argued for its use as a tool in biogeochemistry. We have demonstrated this by applying it to the methane–oxygen disequilibrium in Earth's atmosphere. As a general but central result we have shown that an analysis of the kinetics of the dissipating reactions is not always needed for the calculation of the power to maintain disequilibrium. We have discussed the implications of this work for the detection of life on exoplanets. In future work, we believe that this methodology of assessing the strength of biogeochemical cycling by quantifying the global flows of energy involved will lead to important insights into the functioning of the Earth system and life's role within it.

*Acknowledgements.* The authors thank the Helmholtz Gemeinschaft for funding through the Helmholtz Alliance "Planetary Evolution and Life". E. S. thanks the Agreement ASI/INAF I/025/10/0 for further support and Dr. S. Schymanski for the discussion about chemical potential.

Edited by: J. Lelieveld

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