Disequilibrium in planetary atmospheres and the search for habitability

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Overview of this talk

• What is chemical disequilibrium

• How to calculate disequilibrium in chemical processes

• Atmospheric Disequilibrium of Earth

• Further applications
Introduction

What is chemical disequilibrium, and why should we use it?
Titania may produce abiotic oxygen atmospheres on habitable exoplanets

Norio Narita, Takafumi Enomoto, Shigeyuki Masaoka & Nobuhiro Kusakabe

The search for habitable exoplanets in the Universe is actively ongoing in the field of astronomy. The biggest future milestone is to determine whether life exists on such habitable exoplanets. In that context, oxygen in the atmosphere has been considered strong evidence for the presence of photosynthetic organisms. In this paper, we show that a previously unconsidered photochemical mechanism by titanium (IV) oxide (titania) can produce abiotic oxygen from liquid water under near ultraviolet (NUV) lights on the surface of exoplanets. Titania works as a photocatalyst to dissociate liquid water in this process. This mechanism offers a different source of a possibility of abiotic oxygen...
"The general struggle for existence of animate being is struggle for entropy, which becomes available through the transition of energy from the hot sun to the cold earth" (Boltzmann, 1886)

"Life feeds of high quality energy gradient" (Schrödinger, 1944)
The emergence of life allowed the use of more degrees of freedom associated to geological and atmospheric cycles, and consequently the generation of more free energy from the same initial energy sources.


Co-evolution of Earth geochemical cycles and life [ Grenfell et al., 2010. Lammer et al., 2010 ]

“Once candidate disequilibria are identified, alternative explanations must be eliminated. Life is the hypothesis of last resort” (Sagan et al., 1993)
Atmospheric Chemical Disequilibrium

A PHYSICAL BASIS FOR LIFE DETECTION EXPERIMENTS

By Dr. J. E. LOVELOCK

Assumptions of Life

It is a relatively simple matter to distinguish between living and non-living systems. In order to understand the experiments that have been designed for the detection of life, it is necessary to consider some of the assumptions that underlie them. These assumptions include:

1. All life processes are based on the conservation of energy and mass.
2. Life processes are characterized by specific chemical reactions.
3. Life processes are not influenced by external factors such as temperature or pressure.
4. Life processes are capable of self-replication.

Experiments for Detection of Life

The distinguishing features of a living system, as observed in experiments, include:

1. Order and regularity.
2. Reproducibility.
3. Self-organization.

The results of these experiments are used to evaluate the possibility of life on other worlds. The diagrams illustrate the composition of the atmospheres of Earth, Venus, and Mars, as well as a sterile Earth.

*INAF - Arceto*
The contemporaneous presence of O\(_2\) and CH\(_4\) into the Earth’s atmosphere is maintained by a power of ~ 0.67 TW.

About 0.43 TW are given by living processes (animal enteric fermentation, 0.13TW; rice paddies 0.09TW).

Atmospheric Chemical Disequilibrium

$$\rm{CO}_2 + H_2O \rightarrow CO + 3\ H_2$$

$$\alpha(f_i, P) = \frac{f_{CH_4} f_{H_2O}}{f_{CO} f_{H_2}^3 P^2} = K_{eq}(T)$$

$$K_{eq}(T) = e^{-\Delta G/RT} = e^{-(\Delta H/RT - \Delta S/R)}$$


How to calculate (and compare) disequilibrium in chemical processes
Atmospheric Chemical Disequilibrium

The extent of chemical disequilibrium

In order to measure the extent of disequilibrium, we have to deal with the thermodynamics of non-equilibrium (irreversible) processes.

The distance of a system from its equilibrium condition (i.e. the measure of its irreversibility) is given by the entropy production within a system:

\[
\frac{d_iS}{dt}
\]

The extent of chemical disequilibrium

\[ \frac{d_i S}{dt} = J \cdot X = \frac{d\xi}{dt} \cdot \frac{\alpha}{T} \]

Extent of reaction:
\[ \xi(t) = \frac{[A]_0 - [A](t)}{\nu_A} \]
Chemical Affinity
\[ \alpha(t) = -\left(\frac{\partial \Delta_r G(t)}{\partial \xi}\right)_{T,p} \]

It can be also written as:
\[ \frac{d_i S}{dt} = R \cdot (R_f - R_r) \cdot \ln \left( \frac{R_f}{R_r} \right) \]
\( R_f = \) forward rate
\( R_r = \) backward rate

\[ A + B \rightleftharpoons C + D \]
\[ \frac{d_i S}{dt} = R(k_f[A]_t[B]_t - k_r[C]_t[D]_t)ln \left( \frac{k_f[A]_t[B]_t}{k_r[C]_t[D]_t} \right) \]

Caplan and Essig, Bioenergetics and linear nonequilibrium thermodynamics; the steady state, 1999
- Python pre-processor provides Fortran routines
- Creates modules from chemical network
- Dust evolution, cooling heating photoionization
- Large test suite
- Highly optimized, fast solvers
- Open source, bitbucket community

www.kromepackage.org
Atmospheric disequilibrium of the Earth
Earth Atmospheric Chemical Disequilibrium

- 64 layers (~1km each);
- Eddy diffusion;
- Entropy production and the power dissipation:

\[ \sigma = \frac{d_i S}{dt} \]

\[ \frac{\sigma \times T}{A_{Earth}} \sim W m^{-2} \]

Simoncini, Brucato, Grassi, sub. to OLEB
S. O. Danielache, E. Simoncini, Y. Ueno, Archean Atmospheres Modeled with the KROME Chemistry Package, JPGU 2014
Angerhausen D., Sapers H., Simoncini E., and coworkers. An astrobiological experiment to explore the habitability of tidally locked M-Dwarf planets, IAU 2013 Proceedings.
Earth Atmospheric Chemical Disequilibrium
Earth Atmospheric Chemical Disequilibrium

\( \text{O}_3 \) (cm\(^{-3}\))

\( \text{O}_3 \) (cm\(^{-3}\))
Earth Atmospheric Chemical Disequilibrium

- full model
- no photochemistry

CO, O₃, CO₂, O₂, N₂

Graphs showing altitude vs. concentration for various gases at different altitudes.
Oxygen reactions in the K-80 network
Earth Atmospheric Chemical Disequilibrium

The energetic structure

Present Earth

Present Earth without photochemistry
Earth Atmospheric Chemical Disequilibrium

\[ \text{TC + PC + PS} \]

\[ \text{TC + PS} \]
Earth Atmospheric Chemical Disequilibrium

Simoncini, Brucato, Grassi, sub. to OLEB
Kasting, J. F., Scientific American Magazine; 80 2004

From the schematic evolution of abundances shown in Fig. 4, we chose 6 epochs that reflect significant states in the chemical composition of the atmosphere. These epochs and the corresponding ages and tropospheric mixing ratios are listed in Table 1. Following standard practice, we use the term mixing ratio to mean the fractional number density of a species. With...
Earth Atmospheric Chemical Disequilibrium

Life origin and development
The weight of photochemistry

Simoncini, Brucato, Grassi, in preparation
Atmospheric extent of disequilibrium

Further studies

-> Earth + fluxes (steady state)
-> Earth + simplified biosphere (not stable LV model)
-> Analysis of reaction pathways
-> Deeper analysis of sulfur chemistry
-> Influence of Sun luminosity variability

basis for habitability studies

-> Atmospheric spectra
-> Mars atmosphere
-> Rocky and warm/hot exoplanets (new models)
-> Other Solar System planets and moons
Modeling exoplanets with KROME

+ Y. Miguel

Observatoire de Côte d’Azur, Nice, France
Hot rocky exoplanet

* $M = 10 \cdot M_e$
* Star = Sun ($T_{\text{surf}} = 5777 \text{ K}$)
* $T \sim 2200 \text{ K}$ (temperature profile by Ito et al., *ApJ* 801 144, 2015)
* 30 species from accretion (Y. Miguel code)
  —> part of them condensates

* Build-up abundances and pressure profile using the Scale Height:

$$H = \frac{k_b T}{M g}$$

* Using the $T, p$ conditions, take out not gaseous species
* $K_{zz} = 10^6$ (low Martian atmosphere)
* Build-up the network: NIST, KIDA, exoplanets literature, Mercury atmosphere

=> 45 reactions

Miguel, Y, Simoncini, E., *in prep.*
Hot rocky exoplanet: effect of diffusion

$K_{zz} \sim \text{cm}^2 / \text{s}$

$O_2$

$Na$

Miguel, Y., Simoncini, E., in prep.
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