Sustainability: Principles and Practices
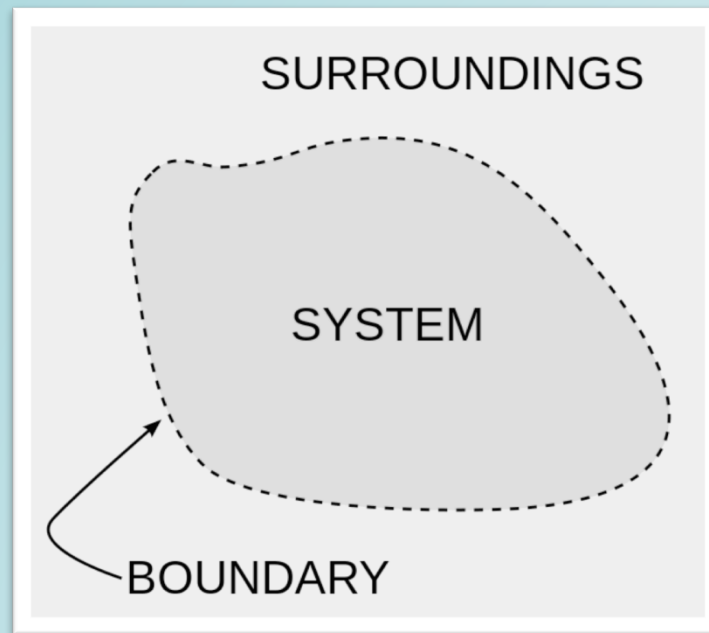## Spring 2014

PPT Set 4
Professor Anthony Serianni

Driving Forces for Biogeochemical Cycles

Energy and Energy Flow:
Thermodynamics

Thermodynamics involves the study of <u>energy exchange</u> between a <u>system</u> and its environment (the <u>surroundings</u>); it is a area of study within the general field of physical chemistry.

Thermodynamics is a <u>quantitative</u> science.

Thermodynamics is the study of equilibrium states;
it does not address the rate at which a particular
equilibrium state is reached, only what the equilibrium
state will look like once it is reached.

Thermodynamics gives reasonably accurate predictions
of what a particular equilibrium state will look like
based on the calculation of the change in the free energy
that occurs as an initial state is converted into a final state.

A fundamental principle of thermodynamics

For the universe in which we exist, energy
cannot be created or destroyed, but can
change forms or flow from one place to another.
This energy transfer can occur in the form of
heat or work.

Types of Thermodynamic Systems

Energy transfer is studied in three types of systems:

Open systems	*Open systems can exchange both matter and energy with an outside system.* They are portions of larger systems and in intimate contact with the larger system. Your body is an open system.
Closed systems	*Closed systems exchange energy but not matter with an outside system.* Though they are typically portions of larger systems, they are not in complete contact. The Earth is essentially a closed system; it obtains lots of energy from the Sun but the exchange of matter with the outside is almost zero.
Isolated systems	*Isolated systems can exchange neither energy nor matter with an outside system.* While they may be portions of larger systems, they do not communicate with the outside in any way. The physical universe is an isolated system; a closed thermos bottle is essentially an isolated system (though its insulation is not perfect).

Heat can be transferred between open systems and between closed systems, but not between isolated systems.

Our System and Surroundings

The Milky Way is a spiral galaxy comprised of 200 billion stars.

It is 90,000 light years in diameter.

(The speed of light is 186,000 miles per second!)

Our star is located in the fourth spiral (Orion).

**The Earth is a <u>closed</u> system.
The Universe is an <u>isolated</u> system.**

First Law of Thermodynamics

In an isolated system, the total amount of energy is conserved.

The **First Law** can be stated in other ways:

- Energy cannot be created or destroyed, only changed from one form to another.
- When heat flows to or from a system, the system gains or loses an amount of energy equal to the heat transferred.
- You cannot get more energy out of a system than the energy you put in plus the energy of the system.

Second Law of Thermodynamics

It is not possible to convert one form of energy into another with 100% efficiency.

Isolated systems become more disordered with time.

The <u>entropy</u> of an isolated system remains constant or increases.

The rule that "entropy always increases" only applies to isolated systems. The Earth, and the surface ecosystems of the Earth in particular, are not isolated systems. Individual parts of a system, even an isolated one, can decrease their own entropy at the expense of a larger increase somewhere else within the system.

Free energy is energy available to do some type of work; it is denoted *G* (Gibbs free energy).

Thermodynamic studies are essentially studies of the free energies associated with a particular process and how these free energies determine whether a particular process is favored or unfavored.

In most cases, it is not possible to determine the precise value of G in the initial and final states of some process, but you can determine how much G changes when the initial state is converted into the final state; that is, you can measure ΔG, the change in free energy, accurately.

Two quantities determine the magnitude (how big) and the sign (negative or positive) of ΔG.

1) the change in internal energy (ΔE) or enthalpy (ΔH), and
2) the change in entropy (ΔS)

that occur as the initial state is converted into the final state.

Change in internal energy (ΔE) or enthalpy (ΔH)

Changes in energy (heat) as the initial state converts to the
final state under conditions of constant volume (ΔE)
or constant pressure (ΔH); in the former case, no
work can be done because the volume of the system is constant.

In our studies, we care mainly about ΔH: it has a <u>positive</u> (+) sign when energy (heat) is *required* to go from the initial to final state, and it has a <u>negative</u> (-) sign if energy (heat) is *released* during the same process.

Change in entropy (ΔS)

This is a measure of the change in the *degree of disorder*
of the system as the initial state converts to the final state.
Is the final state more or less ordered than the initial state?

If the final state is <u>less</u> ordered, then entropy has <u>increased</u> and ΔS is <u>positive</u>.
If the final state is <u>more</u> ordered, then entropy has <u>decreased</u> and ΔS is <u>negative</u>.

All else being equal, systems tend to move towards decreasing order; *i.e.*, increasing entropy.

It costs energy to oppose this natural tendency towards increasing disorder.

Systems can increase their order, but only at
the expense of increasing the disorder in their
surroundings (giving an overall positive value to ΔS).

This is how living systems oppose the intrinsic and relentless
drive towards increasing disorder in the universe.

An important equation relating ΔG, ΔH and ΔS

$$\Delta G = \Delta H - T\Delta S$$
(the Gibbs free energy equation)

Consider some process, A $\longrightarrow$ B

ΔG is <u>always</u> negative when ΔH is (-) and ΔS is (+).
ΔG is <u>always</u> positive when ΔH is (+) and ΔS is (-).

ΔG is negative for processes that are favorable.
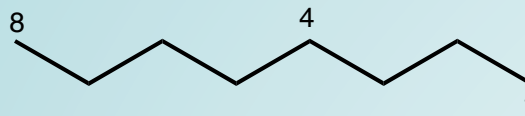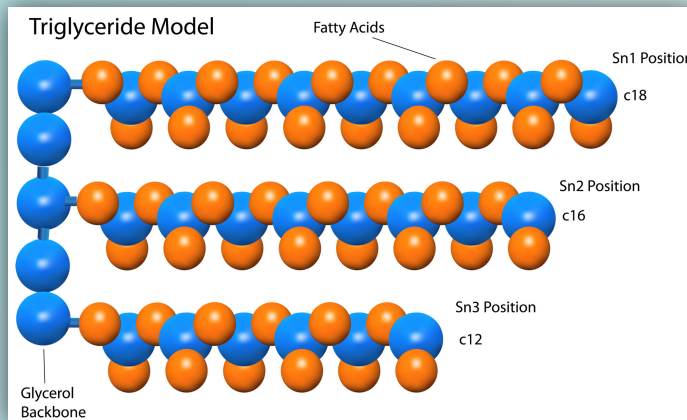
Combustion (oxidation) of a Fatty Acid

$$CH_3(CH_2)_{14}COOH \ (s) + 23 \ O_2 \ (g) \longrightarrow 16CO_2 \ (g) + 16H_2O \ (l)$$
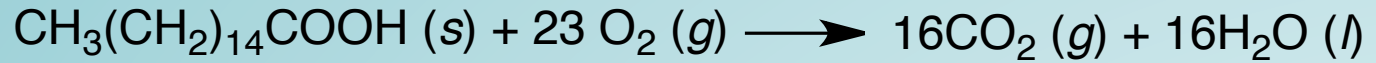
palmitic acid:
a sixteen-carbon (C_{16}) saturated fatty acid
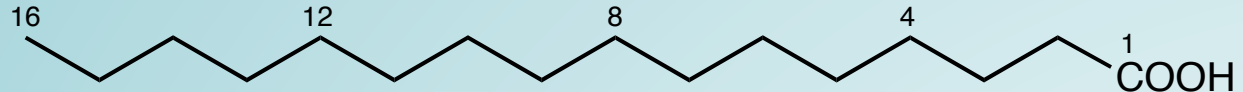
chemical structure of palmitic acid

chemical structure of *n*-octane (eight carbons)

Triglyceride Model   Fatty Acids

Sn1 Position
c18

Sn2 Position
c16

Sn3 Position
c12

Glycerol
Backbone

Ball-and-stick model of a triglyceride (fat cell)

On the exchange between heat and work
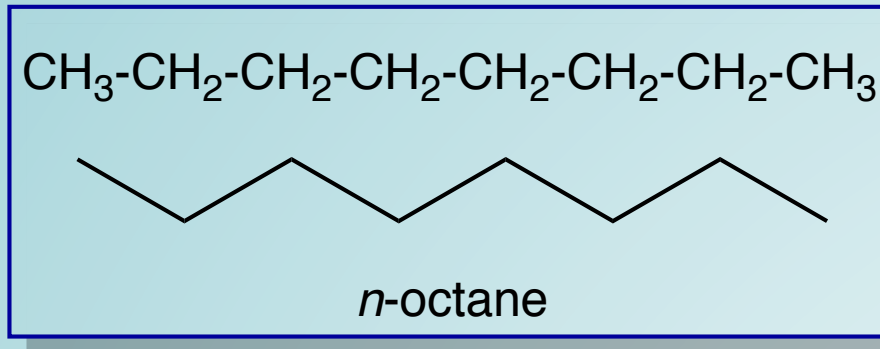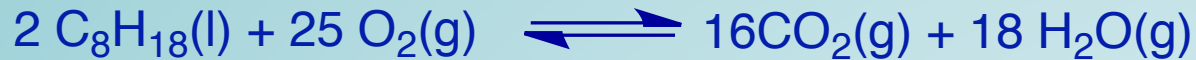## Burning (combusting) palmitic acid (a fatty acid)
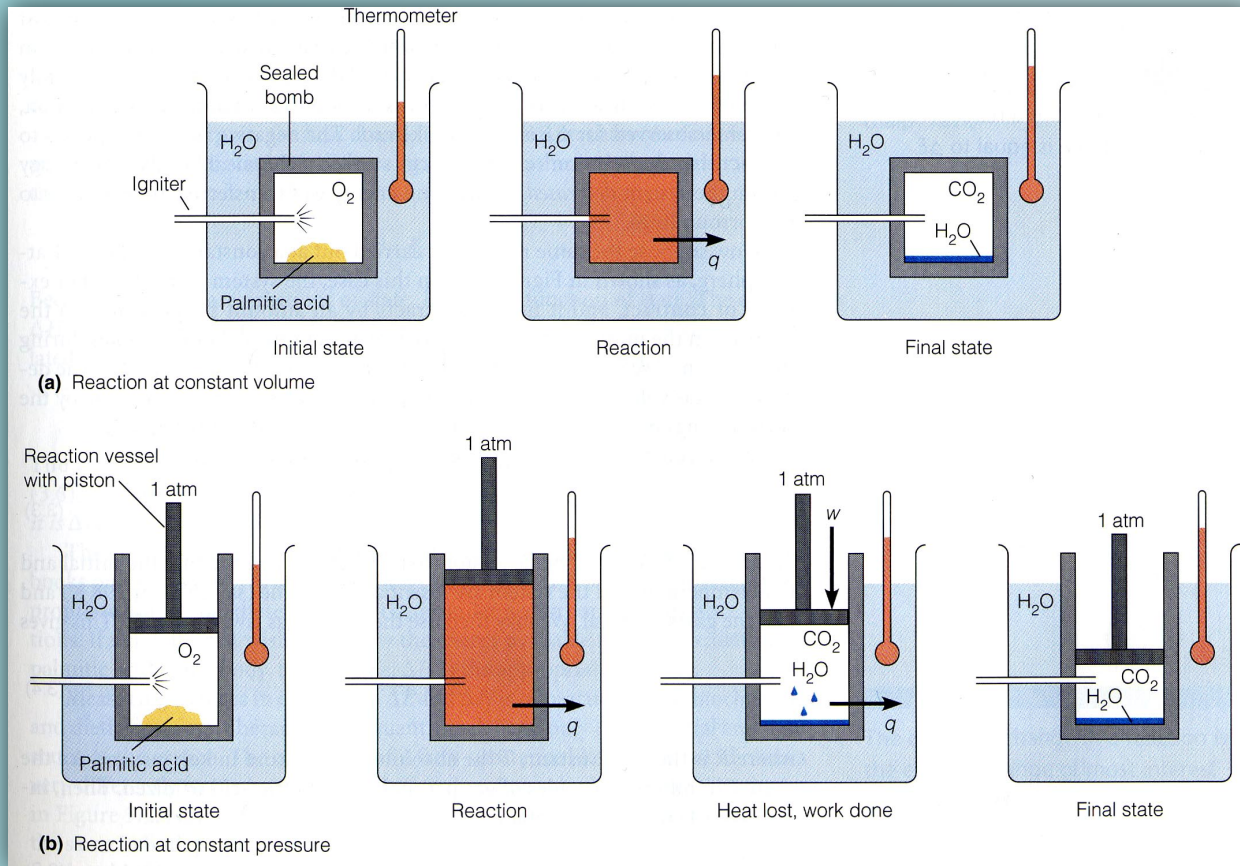
Heat released under constant <u>volume</u>

Heat released under constant <u>pressure</u>

The amounts of released heat are different! Work is involved in the constant pressure case but not in the constant volume case.
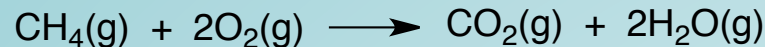
Combustion of gasoline (*n*-octane)

$$2\ C_8H_{18}(l) + 25\ O_2(g) \rightleftharpoons 16CO_2(g) + 18\ H_2O(g)$$

CH$_3$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_3$

n-octane

One gallon of gasoline produces about 19.4 lbs (8.8 kg) of CO_2 (a greenhouse gas).

The ratio of H to C determines the energy content of a given fossil fuel; natural gas (CH_4) has a higher H/C ratio (4) than does *n*-octane (2.25), and thus when equal amounts of both are combusted, CH_4 produces more heat per carbon atom released than does *n*-octane (*i.e.*, less CO_2 is emitted per quantity of energy produced).

Thermodynamics of Fossil Fuel Combustion

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$$

For methane
ΔG^o = -801 kJ/mol
ΔH^o = -802 kJ/mol
ΔS^o = -5 J/K/mol
802 kJ/mol/carbon

$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(g)$$

For propane (LPG)
ΔG^o = -2074 kJ/mol
ΔH^o = -2044 kJ/mol
ΔS^o = +101 J/K/mol
681 kJ/mol/carbon

$$2C_8H_{18}(l) + 25O_2(g) \longrightarrow 16CO_2(g)\ 18H_2O(g)$$
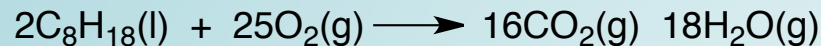
For octane (gasoline)
ΔG^o = -5218 kJ/mol
ΔH^o = -5075 kJ/mol
ΔS^o = +487 J/K/mol
634 kJ/mol/carbon

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$
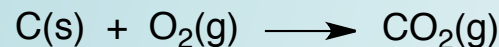
For carbon
ΔG^o = -394 kJ/mol
ΔH^o = -393 kJ/mol
ΔS^o = +3 J/K/mol
393 kJ/mol/carbon

A. G. Lappin

Oxidation state is defined as the charge an atom might be imagined to have when electrons are counted according to an agreed-upon set of rules:

1. the oxidation state of a free element (uncombined element) is zero
2. for a simple (monatomic) ion, the oxidation state is equal to the net charge on the ion
3. hydrogen has an oxidation state of 1 and oxygen has an oxidation state of –2 when they are present in most compounds.
4. the algebraic sum of oxidation states of all atoms in a neutral molecule must be zero, while in ions the algebraic sum of the oxidation states of the constituent atoms must be equal to the charge on the ion.
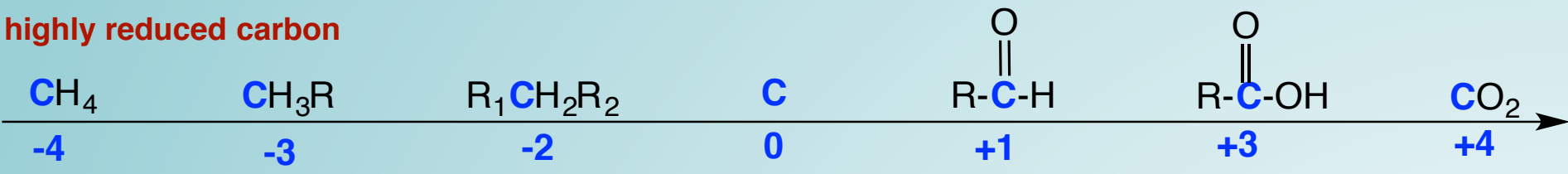
Figure 3.5. Energy Flows through the Biosphere
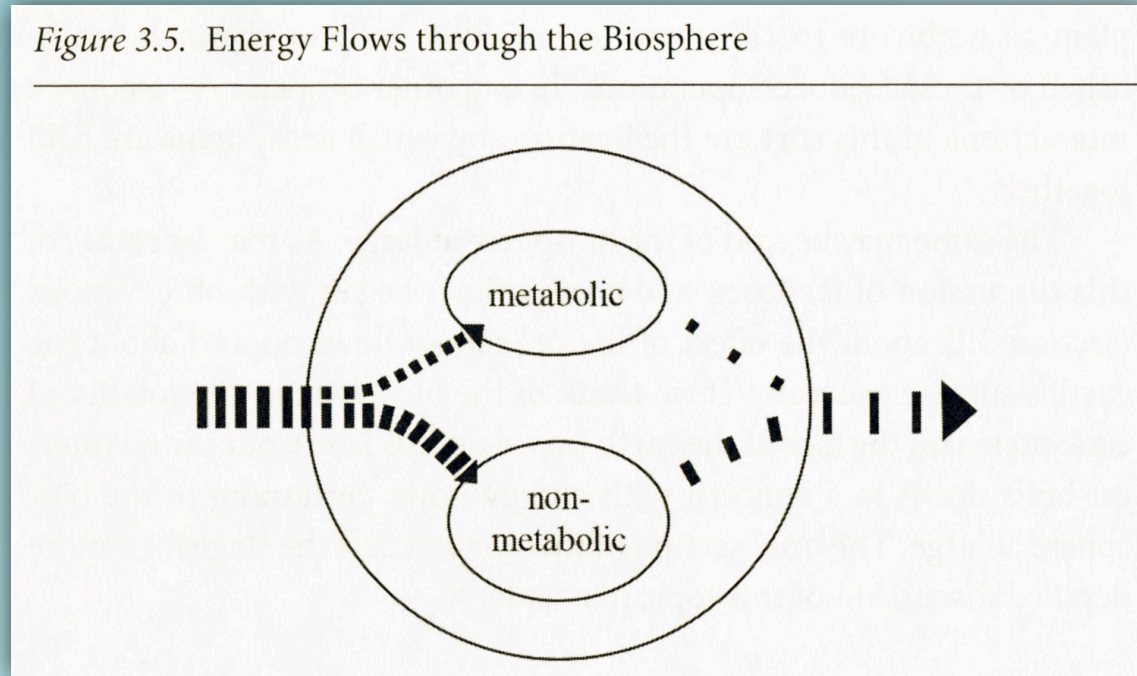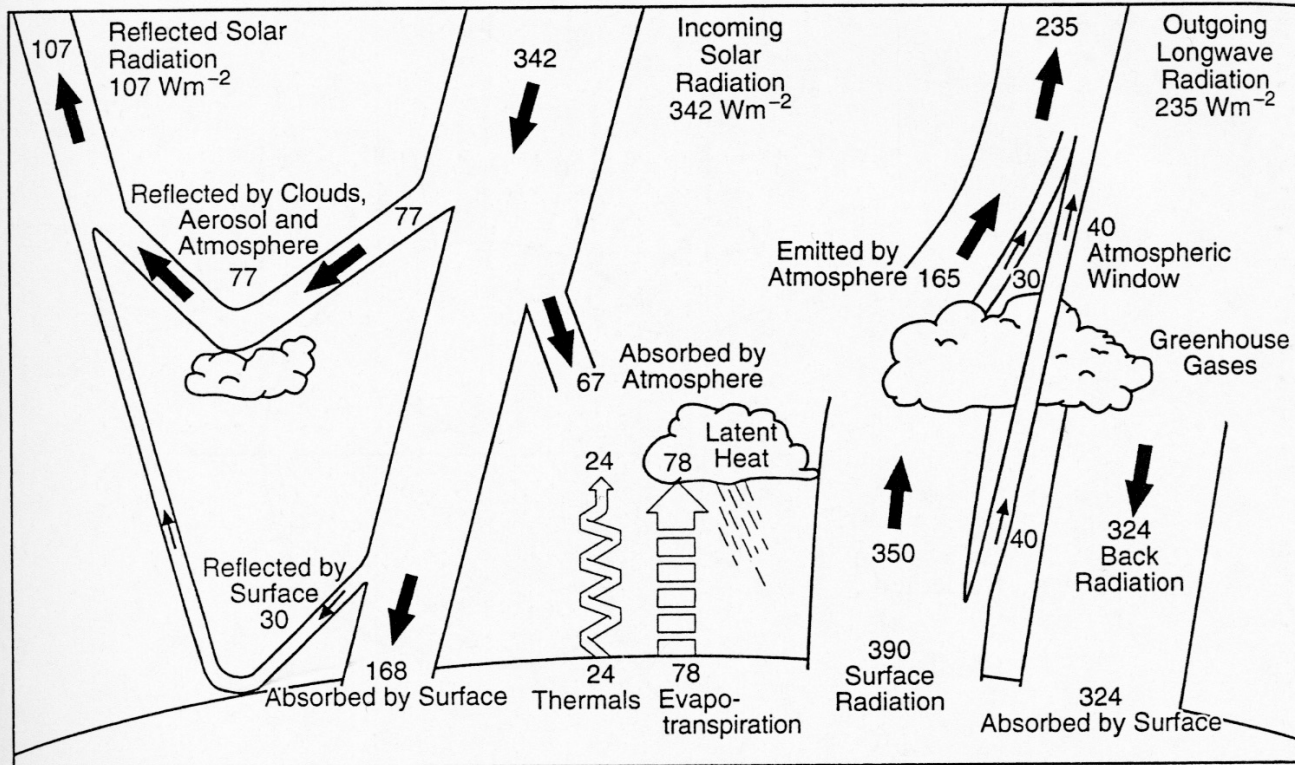
Densely-packed arrows: incoming solar radiation (high-grade energy)
Loosely-packed arrows: outgoing radiation (low-grade heat)

Note the different amplitudes of incoming radiation: ~1/4 of solar wavelengths are useful for photosynthesis, and about 1% of these contribute to biomass production.

K. M Sayre, *Unearthed*, UND Press, 2010

Earth: Energy Balance

FIGURE 4.4   The Earth's annual and global mean energy balance (Kiehl and Trenberth 1997). Of $342\,\text{W}\,\text{m}^{-2}$ incoming solar radiation, $168\,\text{W}\,\text{m}^{-2}$ is absorbed by the surface. That energy is returned to the atmosphere as sensible heat, latent heat via water vapor, and thermal infrared radiation. Most of this radiation is absorbed by the atmosphere, which, in turn, emits radiation both up and down. (Reprinted by permission of the American Meteorological Society.)
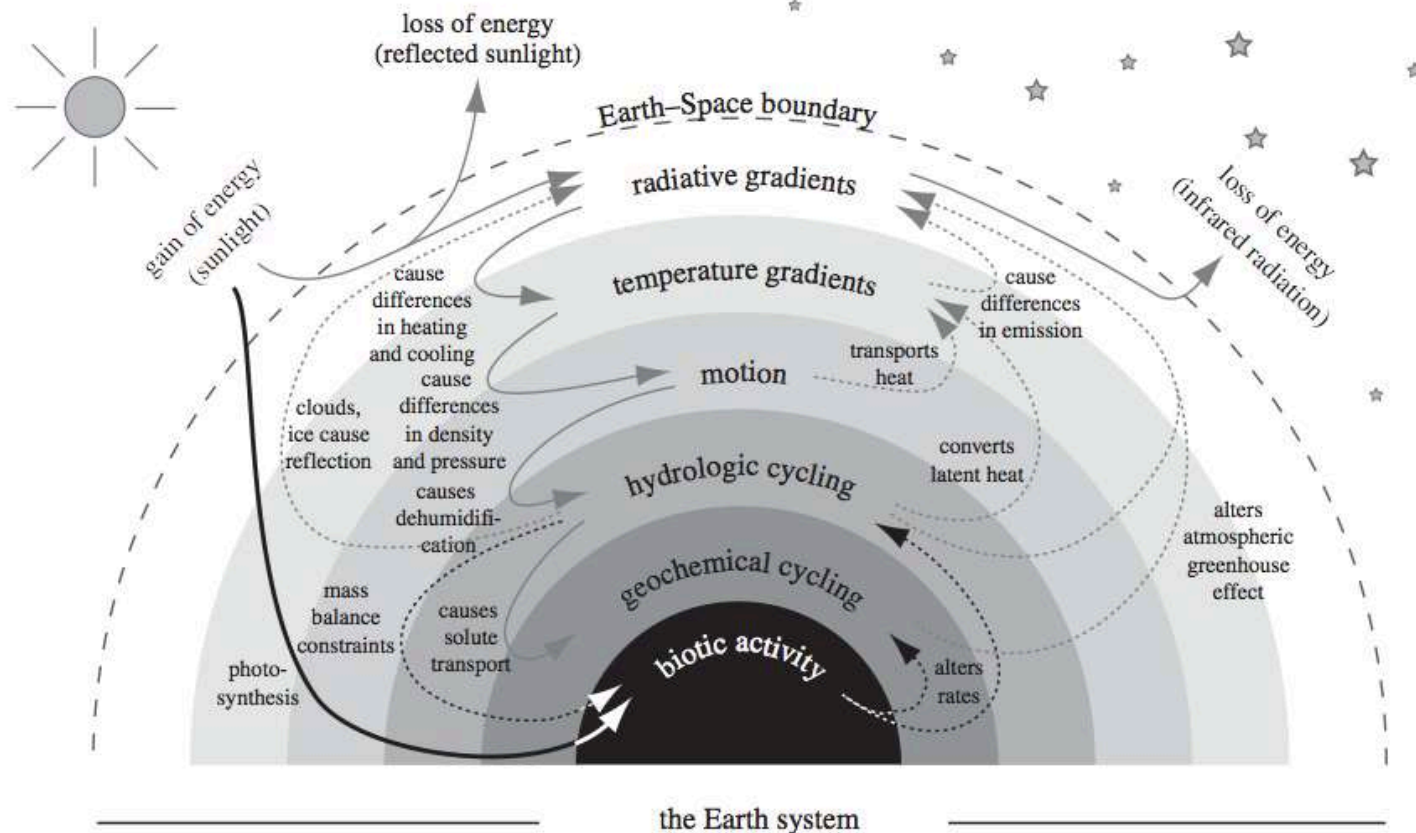
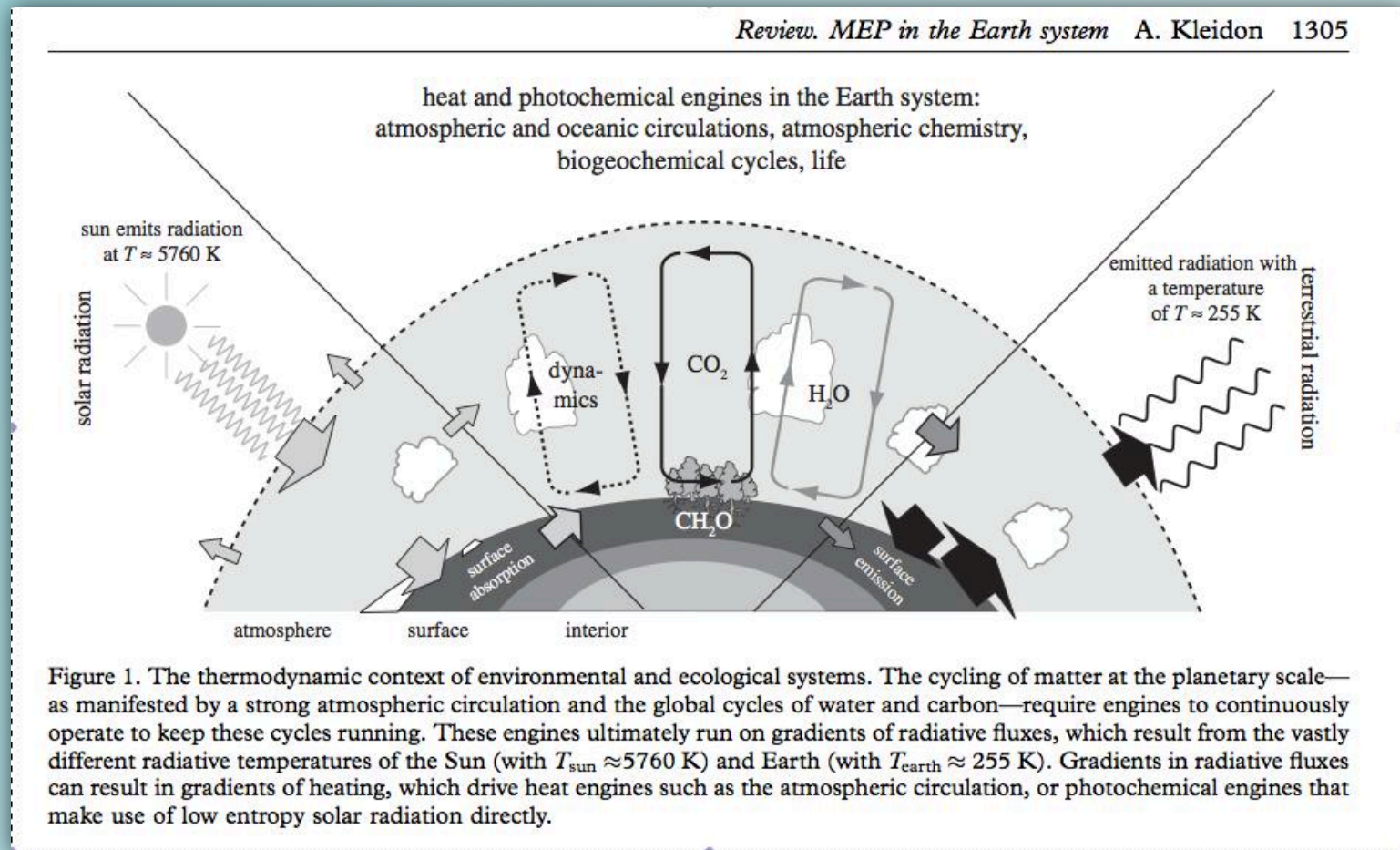# Some irreversible Earth processes

Figure 5. Simplified diagram to illustrate the main interactions of different irreversible processes within the Earth system and the place of biotic activity in these interactions. (Adapted from Kleidon (2009b).)
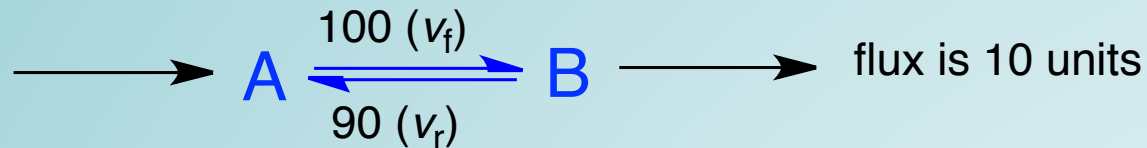
One additional wrinkle……

Earth operates far from thermodynamic equilibrium
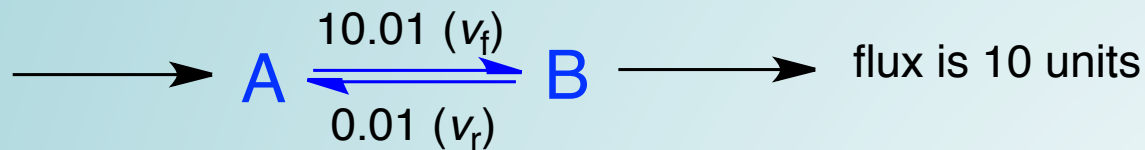(non-equilibrium thermodynamics; Earth is not an isolated system).

Review. MEP in the Earth system   A. Kleidon   1305

Figure 1. The thermodynamic context of environmental and ecological systems. The cycling of matter at the planetary scale—as manifested by a strong atmospheric circulation and the global cycles of water and carbon—require engines to continuously operate to keep these cycles running. These engines ultimately run on gradients of radiative fluxes, which result from the vastly different radiative temperatures of the Sun (with $T_{sun} \approx 5760$ K) and Earth (with $T_{earth} \approx 255$ K). Gradients in radiative fluxes can result in gradients of heating, which drive heat engines such as the atmospheric circulation, or photochemical engines that make use of low entropy solar radiation directly.