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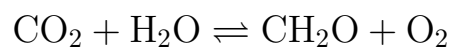
1 Origin of biogeochemical cycles

Reference: Morowitz [1]

1.1 The carbon cycle

1.1.1 The biological cycle

The carbon cycle may be viewed in various ways. In its most familiar manifestation, one has the reaction



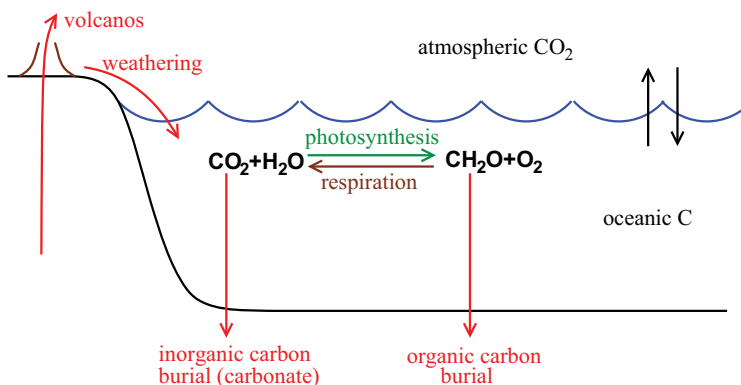
Photosynthesis goes to the right, respiration to the left. CH_2O is shorthand for organic carbon, i.e., a carbohydrate “fixed” by photosynthesis from CO_2 .

Roughly half this reaction takes place on land, the other half at sea. But nearly all of the CO_2 in the atmosphere and oceans is in the oceans.

This is the essence of the *biological* carbon cycle, which is nearly a closed system: about 99.9% of the carbon fixed by photosynthesis returns back to the oceans and atmosphere via respiration.

1.1.2 The rock cycle

The other 0.1% of the organic carbon which is fixed is eventually buried. Some (inorganic) CO_2 is also buried, as carbonate. A rough picture looks like this:



If CO_2 in the atmosphere and oceans is not to be depleted, there must be a source to counter the sink of burial. The source is volcanism (and related metamorphic and hydrothermal processes).

Weathering processes (i.e., erosion) provide a means, via the so-called “Urey reactions,” of extracting CO_2 from the atmosphere and transporting some of it to the oceans. Then, assuming no other changes, it is eventually buried again. This is the geochemical, or “rock” cycle.

Schematically, CO_2 concentrations evolve as

$$\frac{d[\text{CO}_2]}{dt} \simeq \text{volcanism} - (\text{weathering} + \text{burial})$$

If there were no volcanic source, weathering and burial would deplete the CO_2 in the oceans and atmosphere in about 10^5 – 10^6 years. So it turns out that we owe our existence to mantle convection and plate tectonics!

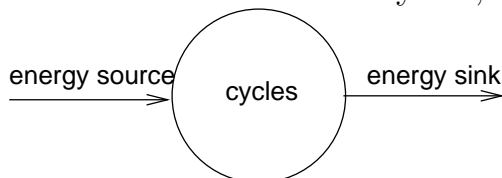
The field of (bio)geochemical cycles is devoted to the study of *all* elemental cycles, not just that of carbon. Prominent among them are the oxygen, nitrogen, sulfur, and phosphorous cycles. In detail they differ from the carbon cycle but the basic theme—cycling through organisms at fast time scales and rocks at slow time scales—remains the same.

The various cycles are not independent: they are instead *coupled* into a kind of “supercycle,” with prominent subcycles, like that of carbon, oxygen, and sulfur, identifiable within the supercycle.

1.2 Energy flow

The existence of biogeochemical cycles such as the carbon cycle raises a natural question: *Why do cycles exist?*

Morowitz proposes an answer: the flow of energy through a chemically reacting system requires the existence of chemical cycles, i.e.,



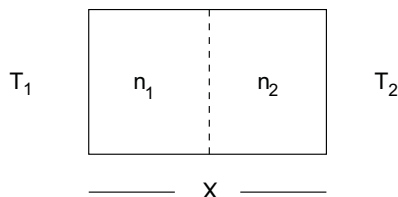
The cycles occur in any intermediate system. The Earth is one such example: the energy source is (dominantly) solar radiation; the energy sink is outer space.

The “energy flow” may be generalized to any flow from a higher to lower potential (e.g., rock movement, or chemical diffusion).

Morowitz’s theory is essentially an application of fundamental principles in irreversible thermodynamics as they apply to non-equilibrium stationary states.

1.3 Two-reservoir model

We start with a very simple model and proceed to somewhat less simple (but still highly idealized) systems. Consider a gas placed in a box between two reservoirs, one side of which is held at temperature T_1 and the other at T_2 :



The gas has average number density Ψ .

The barrier is at the midpoint and contains pores that are small compared to the mean-free-path of the particles so that the residence times within the reservoirs are much longer than the time it takes to traverse the barrier.

In steady state, there is a flow of heat from the hotter to the colder side. We assume each side is perfectly mixed and in equilibrium with their respective reservoirs. Then the steady state is characterized by

$$\begin{aligned} n_1, n_2 &= \text{number density of atoms on sides 1 and 2} \\ T_1, T_2 &= \text{temperature on sides 1 and 2} \end{aligned}$$

In steady state the mass fluxes in each direction must be equal. These fluxes are proportional to

$$\langle mv^2/2 \rangle^{1/2} \propto \sqrt{T},$$

leading to Prigogine's solution

$$n_1 \sqrt{T_1} = n_2 \sqrt{T_2}.$$

As expected, the density is inversely related to temperature. The sum of the densities is constrained by mass conservation:

$$n_1 + n_2 = 2\Psi$$

We thus have the (obvious) result that the flow of heat through the system results in a concentration difference.

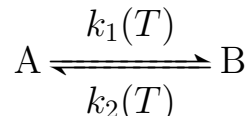
Now imagine that the system were entirely isolated by adiabatic (insulating) walls. Then the system would come to an equilibrium state characterized by

$$n_1 = n_2.$$

Consequently the non-equilibrium state is more ordered (i.e., it has lower entropy). The order is maintained by the flow of energy through the system.

1.4 Reactive species

We now replace the perfect gas by two chemical species A and B which react as:



The system is therefore characterized by concentrations

$$[A_1], [B_1], [A_2], [B_2]$$

The evolution of the system follows the kinetic equations of the form

$$\begin{aligned} \frac{d[A_1]}{dt} &= \text{reactions } B_1 \rightarrow A_1 \\ &- \text{reactions } A_1 \rightarrow B_1 \\ &+ \text{flow of } A_2 \text{ to box 1} \\ &- \text{flow of } A_1 \text{ from box 1.} \end{aligned}$$

The flow rate through the barrier is proportional to the thermal velocity of the molecules. Take the transfer rates to be

$$\begin{aligned} \nu_{12} &\propto \sqrt{T_1} && \text{flow } 1 \rightarrow 2 \\ \nu_{21} &\propto \sqrt{T_2} && \text{flow } 2 \rightarrow 1 \end{aligned}$$

The explicit equations for $[A_1]$ and $[B_1]$ are then

$$\frac{d[A_1]}{dt} = k_2(T_1)[B_1] - k_1(T_1)[A_1] + \nu_{21}[A_2] - \nu_{12}[A_1] \quad (1)$$

$$\frac{d[B_1]}{dt} = -k_2(T_1)[B_1] + k_1(T_1)[A_1] - \nu_{12}[B_1] + \nu_{21}[B_2] \quad (2)$$

along with similar equations for $[A_2]$ and $[B_2]$.

We proceed to the following points:

1.4.1 No equilibrium solution

In the absence of flow, thermal equilibrium would predict

$$k_1(T_1)[A_1] = k_2(T_1)[B_1]$$

or

$$\frac{[B_1]}{[A_1]} = \frac{k_1(T_1)}{k_2(T_1)} \equiv K(T_1)$$

where $K(T_1)$ is the equilibrium constant of the reaction.

A similar result must hold for box 2:

$$\frac{[B_2]}{[A_2]} = \frac{k_1(T_2)}{k_2(T_2)} \equiv K(T_2)$$

But

- A_1 and B_1 each flow from side 1 to 2 at rate ν_{12} .
- A_2 and B_2 each flow from side 2 to 1 at rate ν_{21} .

If there were no thermal gradient (i.e., if $T_1 = T_2$), the steady-state ratios $[B]/[A]$ would be equal on each side:

$$\frac{[B_1]}{[A_1]} = \frac{[B_2]}{[A_2]}.$$

But these ratios cannot be equal in general, because $T_1 \neq T_2$ and, in general,

$$K(T_1) \neq K(T_2).$$

Thus there is no thermal equilibrium, and non-equilibrium concentrations are expected.

1.4.2 Cycles

We now show the existence of cycles. Adding (1) and (2) in steady state, we obtain

$$\nu_{21}([A_2] + [B_2]) = \nu_{12}([A_1] + [B_1])$$

As expected, there is

no net flow of $([A] + [B])$ across the boundary.

Consequently any flow of A must be balanced by an equal and opposite flow of B.

Because there is no thermal equilibrium, we have

$$k_1(T_1)[A_1] - k_2(T_1)[B_1] \neq 0$$

From equation (1), we have that in steady state, the quantity above must balance the flow of A:

$$k_1(T_1)[A_1] - k_2(T_1)[B_1] = \nu_{21}[A_2] - \nu_{12}[A_1]$$

But the RHS above must also be non-zero, requiring

$$\nu_{21}[A_2] \neq \nu_{12}[A_1]$$

Consequently

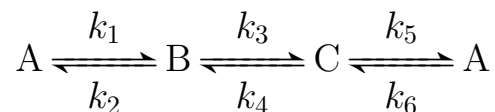
- There must be a finite net flow of A in one direction.
- This flow must be balanced by an equal and opposite flow of B.

We therefore find a *cycle*. We conclude that

- The steady state is out of equilibrium.
- Energy flow leads to internal organization.
- The organization includes a cyclic flow of material.

1.5 Cycles and the breaking of detailed balance

Consider a vat in contact with a isothermal reservoir, with the chemical reactions



The equilibrium concentrations satisfy

$$k_1[A] = k_2[B]$$

$$k_3[B] = k_4[C]$$

$$k_5[C] = k_6[A]$$

The specific equilibrium concentrations $[A]$, $[B]$, $[C]$ follow from the condition that mass is conserved:

$$[A] + [B] + [C] = \text{const.}$$

Equilibrium follows from *microscopic reversibility*: each process must have the same probability as the reverse process.

Thus there must be no flow (or cycle) around the system in equilibrium.

Note, however, that we could maintain a steady state but still have a net flow \mathcal{F} around the system, such that

$$k_1[A] - k_2[B] = k_3[B] - k_4[C] = k_5[C] - k_6[A] = \mathcal{F}.$$

This is one example of a cycle. We proceed to provide a general condition for such a cycle to exist.

Consider a (canonical ensemble of) system(s) at equilibrium. Define

$$f_i = \text{Prob}(\text{system is in state } i)$$

$$t_{ij} = \text{Prob}(\text{system in state } i \text{ will change to state } j \text{ in unit time})$$

In equilibrium we have *detailed balance*:

$$f_i t_{ij} = f_j t_{ji}$$

Assume that the system is in contact with an isothermal reservoir, and irradiate the system with a constant flux of electromagnetic radiation, such that there is *net absorption* of radiation.

The steady state will be characterized by a flow of heat to the reservoir:

$$\text{radiation} \rightarrow \text{system} \rightarrow \text{heat to reservoir.}$$

The steady state will be characterized by new occupation numbers and transition probabilities

$$f'_i \quad \text{and} \quad t'_{ij}.$$

If detailed balance were to hold, for every transition involving absorption of radiation, a reverse transition would exist in which the system would radiate a photon.

But there would then be no net absorption of energy and flow of heat. Consequently detailed balance does *not* hold *in general* for the steady state:

$$f'_i t'_{ij} \neq f'_j t'_{ji} \tag{3}$$

In the steady state the occupation numbers are time independent. Therefore “incoming” transitions balance “outgoing” transitions:

$$\frac{df'_i}{dt} = 0 = \sum_j \left(\text{Prob}(j \rightarrow i) - \text{Prob}(i \rightarrow j) \right) \tag{4}$$

$$= \sum_j \left(f'_j t'_{ji} - f'_i t'_{ij} \right) \tag{5}$$

For at least for one f'_i, f'_j pair, the term above in parentheses must be non-zero due to the relation (3). On the other hand, the requirement that the sum vanish means that other terms in the sum must also be non-zero.

We therefore identify cycles: For at least some states i, j , the paths from i to j and from j to i are not equal; i.e., states leave by one path and return by another.

We thus obtain Morowitz’s *cycling theorem*:

In steady state systems, the flow of energy through the system from a source to a sink will lead to at least one cycle in the system.

1.6 Summary

These general considerations refer to molecular organization, but we expect that they should apply to ecosystems at all scales, and perhaps even the

evolution of life. In summary:

- The Earth's surface receives energy from a source (the Sun) and gives it up to a sink (outer space).
- Energy flow causes a cyclic flow of matter; and a cyclic flow of matter requires an energy flow.
- Energy flow led to life and biogeochemical cycles. “Thus the problem of the origin of life and the development of the global ecosystem merge into one and the same problem” (Morowitz, p. 120).

References

- [1] Morowitz, H. J. *Energy Flow in Biology* (Ox Bow Press, Woodbridge, CT, 1979).

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