A primer of Quantitative Reasoning—PROCESS MATTERS

In biogeochemistry, models consist of boxes and arrows are used in common practices. This period of our class provides an initial set of concepts and conventions often used in literatures of biogeochemistry and environmental studies. Key terms in this group are:

steady-state,

residence time,

turnover time,

first-order kinetics, and

donor-controlled flows.

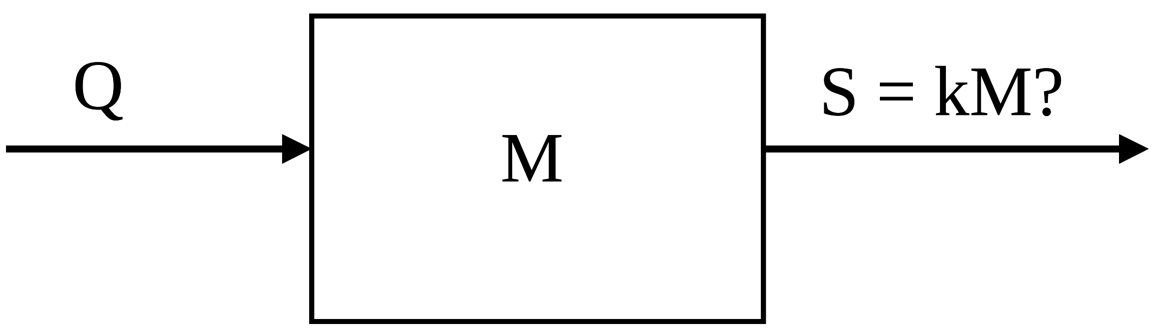
While box-and-arrow models are frequently used in studying material cycles, energy budgets can also be modeled using this kind of approaches based on the two important **thermodynamic laws**, i.e., the first and the second law.

Chemical equilibrium equations usually provide essential mechanisms for the understanding of concentration relationships among related compounds in the Earth system. For example, the distribution of various forms of **carbonates** in the environment is mostly determined by **their chemical equilibria**.

1. Turnover Time and Residence Time

Consider a single reservoir (**M**) and with the inflow rate (**Q**) and the outflow rate (**S**), the turnover time ($\boldsymbol{\tau}_o$) of the reservoir system is the ratio between the content (M) and the outflow rate (**S**):

$$\boldsymbol{\tau}_o = \mathbf{M}/\mathbf{S}.$$



If the relationship between the outflow rate (**S**) and the reservoir content (**M**) follows a linear first-order kinetics, e.g., $\mathbf{S} = \mathbf{kM}$; and, $\boldsymbol{\tau}_o = \mathbf{M}/\mathbf{S} = \mathbf{k}^{-1}$.

Turnover time sometimes is also called “renewal time” or “flushing time” in practice.

The residence time is the time spent in a reservoir by an individual molecule or a kind of material. It is also the age of a molecule when it leaves the reservoir. Normally, for a single chemical substance, different molecules or ions will have different resident times in a given reservoir. Our interest is often in the average residence time of all molecules of the substance. It is fairly common that the word "average" is implicit in our communication and is simply referred as residence time.

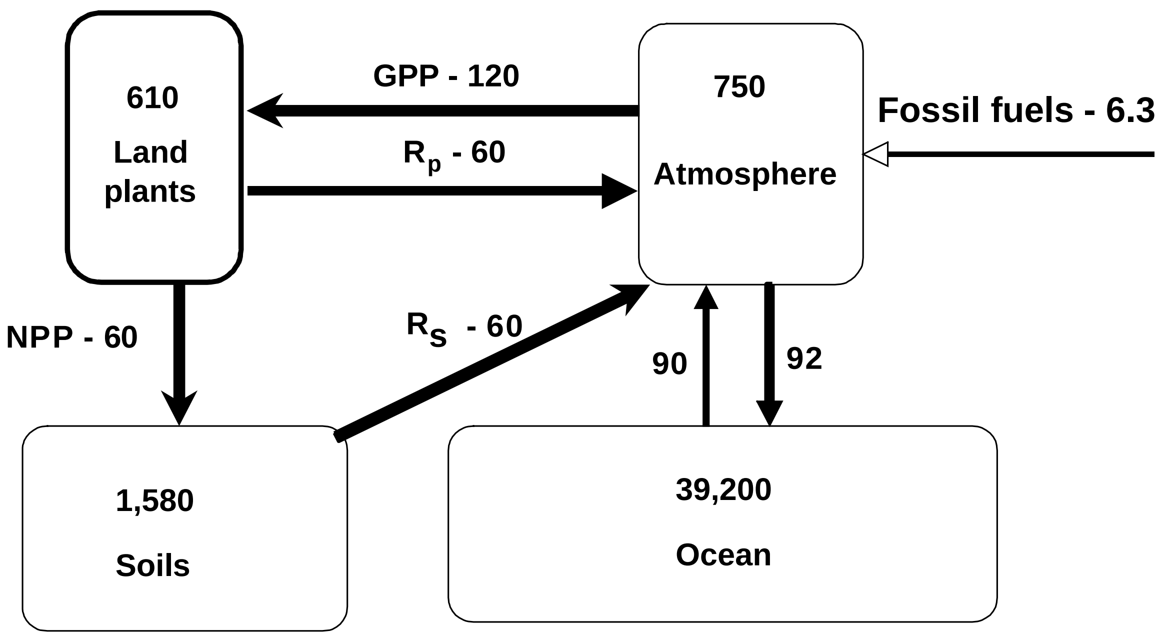
In a single reservoir system, if the outflow rate (**S**) is the same as the inflow rate (**Q**), the system is said at its steady-state or equilibrium, the residence time ($\boldsymbol{\tau}_r$) is the same as the turnover time ($\boldsymbol{\tau}_0$), equals to the ratio of the content (**M**) and the outflow rate (**S**) or the inflow rate (**Q**):

$$\boldsymbol{\tau}_r = \boldsymbol{\tau}_o = \mathbf{M}/\mathbf{S} = \mathbf{M}/\mathbf{Q}$$

If the system is not at steady-state, a meaningful residence time cannot and should be determined.

Both the path pattern in the reservoir and the mixing of the substance in question influence the frequency distributions of turnover time, residence time, and the age of the substance in the reservoir. Examples of applying this formulation are given in the assigned reading.

The global carbon cycle:



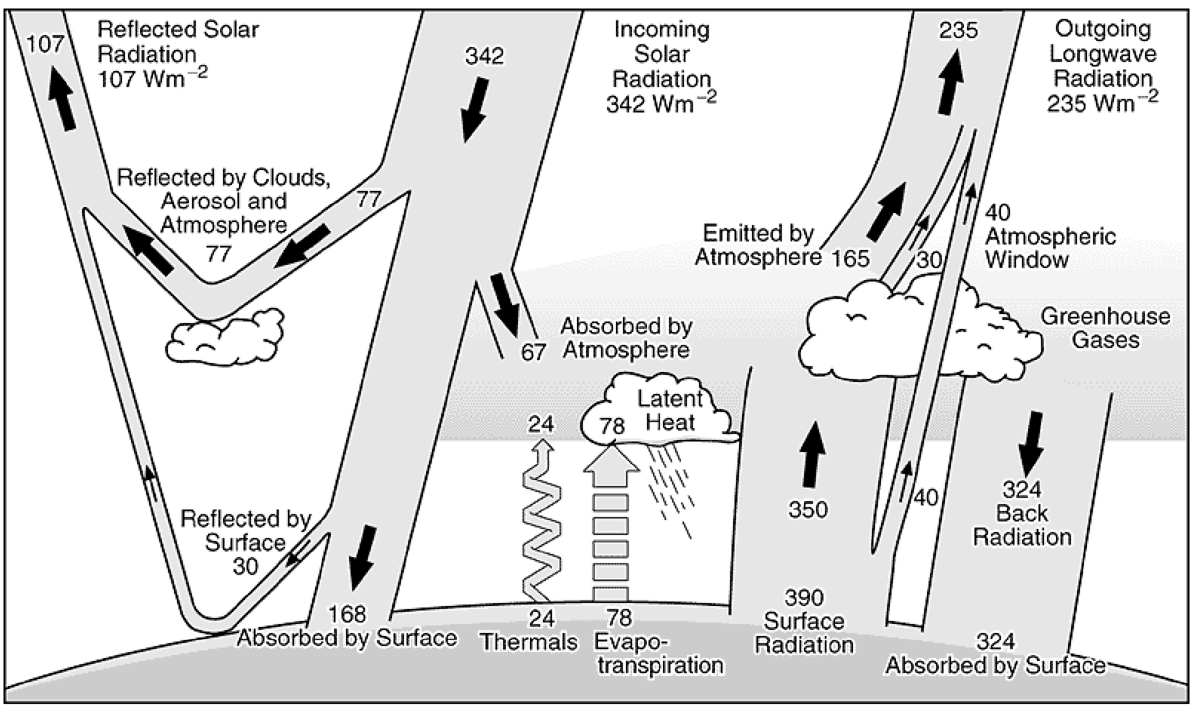
Based on Schimel et al. 1995 and IPCC 2001

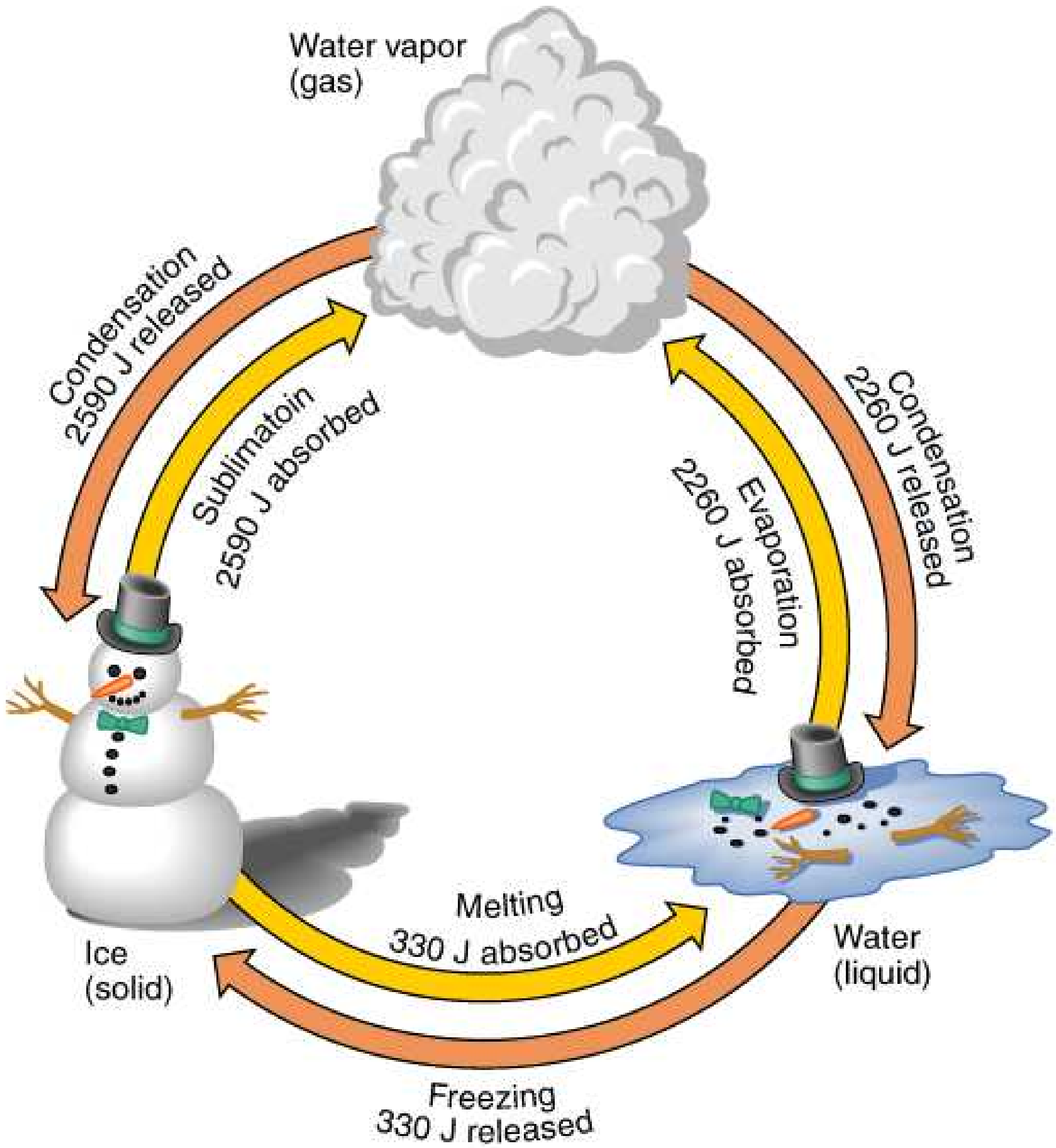
2. The Laws of Thermodynamics

The first law of thermodynamics states ………

The second law of thermodynamics states………

Examples of using the two laws of thermodynamics are given in the assigned reading.





Water vapor
(gas)
Condensation
2590 J released
Sublimatoin
2590 J absorbed
Condensation
2260 J released
Evaporation
2260 J absorbed
Ice
(solid)
Melting
330 J absorbed
Water
(liquid)
Freezing
330 J released

3. Chemical equilibrium equations

Example-1: a hunk of $CaCO_3$ (limestone) in an open container

Example-2: pH in rainwater

$$CO_2 \rightleftarrows H_2CO_3 \rightleftarrows HCO_3^- \rightleftarrows CO_3^{2-} \rightleftarrows CaCO_3\downarrow$$

$[CO_2]$ in the atmosphere

pH of the ocean water

$[Ca^{2+}]$ or the like

temperature

water mixing

[salts]

etc.