Energy Flow in Marine Ecosystem

Introduction

- Marin ecosystem is a functional system and consists of living groups and the surrounding environment
- It is composed of some groups and subgroups
 - 1. The physical environment: seawater and dissolved salts and suspended particles
 - 2. Bottom sediments
 - 3. Living organisms
 - **1.** Animals
 - 2. Plants
 - 3. Microorganisms (saprobe)

According to their way of living and their environment, living groups are classified as:

- Intertidal (littoral)
- Sublittoral (up to 200 m depth)
- Pelagic (open water)
- Constituents of the marine ecosystem are also classified according to their function:
 - Abiotic substances: (all chemicals present in solution or in bottom sediments
 - Producers (autotrophs): (photosynthetic organisms, marine plants)
 - Consumers (heterotrophs): organisms feeding on marine plants and prefabricated organic matter

• Decomposers/reduces: organisms feeding on dead organisms and recycle the organic matter These components are linked together in a closed cycle (Fig. 1)



- From Fig.1 we can deduce the following points:
 - 1. In some ecosystems, the cycle could be completed with only three components (odd system)
 - 2. It is clear that the composition of the environment controls the biological activity of all the living organisms. However, living organisms greatly determine concentrations and distribution the abiotic material. Living organisms influence and determine the distribution of nutrients, precipitation of carbonates, reduction of sulphate ions, distribution of dissolved oxygen and carbon dioxide in water and the atmosphere.
 - 3. The presence of forces and counter forces that act against any significant compositional variability and keep the chemical composition almost constant. However, human interference may force these changes
 - 4. Activity of the living organisms depends on:
 - 1. Recycling of the abiotic material
 - 2. Flow of energy inside the system

What is energy?

Energy is the capacity of a physical system to perform <u>work</u>. Energy exists in several forms such as <u>heat</u>, <u>kinetic</u> or mechanical energy, light, <u>potential energy</u>, electrical, or other forms.

Energy is either:

- Stored or potential (chemical potential energy, gravitational potential energy)
- Energy in transition (heat, work)
- Heat: transitional energy which transfers between bodies or among particles in the same body
 - Heat passes from the hot body (source) to the cold body (sink)
 - Heat transfer by:
 - Conduction
 - Convection
 - Radiation
- Work: mechanical work is the amount of <u>energy</u> transferred by a <u>force</u> acting through a distance
- In <u>thermodynamics</u>, work is the quantity of <u>energy</u> transferred from one system to another without an accompanying transfer of <u>entropy</u>
- <u>Thermodynamics</u>: is the study of the conversion of heat energy into different forms of <u>energy</u> (in particular, mechanical, chemical, and electrical energy); different energy conversions into heat energy



What is a thermodynamic system?

<u>a thermodynamic system</u>, originally called a working substance, is defined as that part of the universe that is under consideration. A real or imaginary <u>boundary</u> separates the system from the rest of the universe, which is referred to as the environment or <u>surroundings</u>.



<u>a phase</u> is a region of space (a <u>thermodynamic system</u>), throughout which all physical properties of a material are essentially uniform. Examples of physical properties include <u>density</u>, <u>index of refraction</u>, and chemical composition. A simple description is that a phase is a region of material that is chemically uniform, physically distinct, and (often) mechanically separable. In a system consisting of ice and water in a glass jar, the ice cubes are one phase, the water is a second phase, and the humid air over the water is a third phase. The glass of the jar is another separate phase.

First law of thermodynamics

 "Energy can be transformed (changed from one form to another), but it can neither be created nor destroyed."

$$\mathbf{E}_2 - \mathbf{E}_1 = \Delta \mathbf{E} = \mathbf{q} - \mathbf{w} \tag{1}$$

q is positive when the system absorbs heat (endothermic reactions)

q is negative when the system radiates heat (exothermic reactions)

w is positive when work is done by the system

W is negative when work is done on the system



Any thermodynamic system in an equilibrium state possesses a state variable called the internal energy (E). Between any two equilibrium states, the change in internal energy is equal to the difference of the heat transfer into the system and work done by the system.

CH₂(CH₂)₁₄COOH (solid) + 23O₂ (gas) → 16CO₂ (gas) + 16H₂O (liquid)

Palmitic acid

Figure 3.1

Two ways of studying the heat evolved in combustion. In (a) the reaction occurs in a sealed vessel, or "bomb," at constant volume. During the reaction, heat (q) is transferred to the surrounding water bath, which experiences a small increase in temperature. No work is done because the system is at constant volume. In (b) the reaction vessel is fitted with a piston held at 1 atm pressure. During the reaction the temporary heating of the gas in the vessel causes the piston to be pushed up, but the contraction in total gas volume in the reaction has the result that after the vessel and gas have cooled to the water temperature the final volume is actually smaller than the initial volume. Thus, net work is done on the system, and the total amount of heat delivered to the bath is slightly different from that in (a).



Chemical reactions may take place either:

- 1. Under constant pressure (reactions in the ocean)
- 2. Under constant volume (in closed system)

In the first case , if the volume changes, work is done and equals P∆V, where P is the constant pressure (atmospheric pressure) and ∆V is the change in volume Change in internal energy :

 $\Delta \mathbf{E} = \mathbf{q} - \mathbf{w} = \mathbf{q} - \mathbf{P} \Delta \mathbf{V}$ (2)

Since most of the reactions takes place under constant pressure,

$$\mathbf{q}_{\mathbf{p}} = \Delta \mathbf{E} + \mathbf{P} \Delta \mathbf{V} = \Delta \mathbf{H} \qquad (3)$$

 ΔH is called enthalpy change or heat of reaction

Under constant volume, ΔV equals zero, and P ΔV will be zero, therefore

$$\Delta \mathbf{E} = \mathbf{q}_{\mathbf{v}}$$

 ΔE and ΔH , depend only on the initial and the final state of the reactants and not by any mean on the intermediate steps between the two states.

Uses of $\Delta \mathbf{H}$

- 1. Indication of spontaneous reactions:
 - Exothermic reactions (ΔH -ve) are spontaneous
 - while endothermic (\Delta H +ve)reactions are not

2. Measure of stability:

When the ∆H of the products of the dissociation of a substance is negative, the reaction is most probably spontaneous

- This means that the substance is unstable with respect to the specific products and under the specific conditions of the reaction.
- For example, it is not exact if we say that hydrogen peroxide (H₂O₂) is unstable without précising the products of the dissociation and the conditions of the reaction:

At 25 °C and one atm, H₂O₂ is stable and does not dissociate easily to its constituents

$$\mathbf{H}_{2}\mathbf{O}_{2(1)} \qquad \longrightarrow \qquad \mathbf{H}_{2(g)} + \mathbf{O}_{2(g)} \qquad \qquad \Delta \mathbf{H} = 44.8 \text{ kcal}$$

However it is unstable when it dissociates according to the reaction:

 $H_2O_{2(l)} \longrightarrow H_2O_{(l)} + 1/2 O_{2(g)} \Delta H = -23.4 \text{ kcal}$

3. Δ H is used for the determination of other thermodynamic properties such as Δ G.....

Determination of ΔH

1- The experimental method

- It is possible to measure the heat absorbed or radiated during any chemical reaction using a *microcalorimeter*
- Since in a closed system we measure q_v
- To obtain ΔH , the value of q_v should be corrected for the work done by the system Suppose the reaction:

 $CH_{4(g)} + 2O_2 \longrightarrow CO_{2(g)} + 2H_2O_{(l)} \quad q_v = -211$ kcal The value of q_v could be corrected by adding the value of P ΔV at 25° C and one atm.

$$P \Delta V = 1$$
 atm. X -2 x 24.5 = -49 l atm

1 l atm = 24.2 cal

$$P \Delta V = -49 \ge 24.2 = -1.2 \ \text{kcl}$$

 $\Delta H = -211 - 1.2 = -212.2 \ \text{kcal}$

By calculation:

This method is based on the Hess's, which indicates that ΔH and ΔE depend on the state of reactants and products of the reaction and not on steps of the reaction. In multistep reactions the final ΔH is the sum of the ΔH ($\Sigma \Delta H$) of the individual steps:

Consider the oxidation of methane to carbon monoxide

$$\mathbf{CH}_{4(g)} + 1.5\mathbf{O}_2 \longrightarrow \mathbf{CO}_{(g)} + 2\mathbf{H}_2\mathbf{O}_{(l)}$$

This reaction could be regarded as two step reaction:

- 1. $CH_{4(g)} + 2O_2 \longrightarrow CO_{2(g)} + 2H_2O_{(l)} \qquad \Delta H = -212 \text{ kcal}$ (1)
- 2. $CO_{2(g)} \longrightarrow CO + 0.5 O_2$ $\Delta H = 68.3 \text{ kcal}$ (2)
- **3.** Adding equation 1 to equation 2 we get

$$\Delta H = -212 + 68.3 = -144.7 \text{ kcal} \tag{3}$$

The free energy of the system

- It is the part of the total energy that determines the ability of any substance to exchange energy (chemical reaction)
- the term thermodynamic free energy refers to the amount of <u>work</u> that can be extracted from a <u>system</u>,
- It is a subtraction of the <u>entropy</u> of a system multiplied by a reference temperature (giving the "unusable energy") from the total energy, yielding a <u>thermodynamic state</u> <u>function</u> which represents the "<u>useful energy</u>".

H = G + TS Total energy free energy organization energy

T = absolute temperature ^OK

S = entropy

Changes in free energy of any reaction is a measure of how possible it can take place

 $\Delta \mathbf{H} = \Delta \mathbf{G} + \mathbf{T} \Delta \mathbf{S}$ $\Delta \mathbf{G} = \Delta \mathbf{H} - \mathbf{T} \Delta \mathbf{S}$

Spontaneous reactions are those that high and negative ΔG and ΔH and positive T ΔS values.

Example of entropy increasing

in a small 'universe', a thermodynamic system consisting of the 'surroundings' (the warm room) and the 'system' of glass, ice, cold water which has been allowed to reach <u>thermodynamic equilibrium</u>.

- Entropy : $\Delta S = \Delta q/T$
- In this universe, some <u>heat</u> energy δQ from the warmer room at 298 K (25°C) will spread out to the cooler system of ice and water at its temperature *T* of 273 K (0°C), the melting temperature of ice. Thus, the entropy of the system, increases by $\delta Q/273$ K. (The heat δQ for this process is the energy required to change water from the solid state to the liquid state, and is called the <u>enthalpy of fusion</u>, i.e. the ΔH for ice fusion.)
- the entropy of the surrounding room decreases less than the entropy of the ice and water increases: δQ/298 is < δQ/273: the final net entropy after such an event is always greater than was the initial entropy.



Second law of thermodynamics

- Every system will tend to change to a condition of maximum stability
- You can't get out of it as much as you put in (except at absolute zero)
 - A perpetual motion machine can not be made
- It is impossible to convert heat completely into work in a cyclic process

Examples in the marine system:

- 1. Oxidation of organic matter
- 2. Flow of chemicals from concentrated to diluted solutions
- 3. Flow of heat from high temperature water masses (surface water) to low temperature water masses (subsurface layers)
- 4. Tendency of chemical reactions to pass from an initial state to the state of equilibrium (pH buffering by the carbonate/borate systems)

Free energy and equilibrium constant

- $\Delta G^0 = -RT \ln K$
- R = universal gas constant 1.985 cal k⁻¹ mol⁻¹
- T = absolute temperature °k
- When ΔG^0 is high and negative, K will be high and positive
- When ΔG^0 is high and positive, K will be high and negative

Ex: if $K = 10^{10}$ $\Delta G^0 = -13.7$ kcal mol⁻¹ (spontaneous reaction until reaching equilibrium)

if $K = 10^{-10}$ $\Delta G^0 = +13.7$

Reaction will never take place spontaneously and appreciably.

Energy flow in the ecosystem







Representation of the interaction of a biogeochemical cycle (scipled circle) and a unidirectional energy-flow system. N.P., nutrient pool; <u>A</u>, autotrophs; <u>H</u>, heterotrophs; P_g, gross production; P_n, net production that may be consumed; (**R**), stored or exported. (After Odum¹)

Energy flow and cycle of elements







Representation of the interaction of a biogeochemical cycle (scipled circle) and a unidirectional energy-flow system. N.P., nutrient pool; A, autotrophs; H, heterotrophs; P_g, gross production; P_n, net production that may be consumed; (R), stored or exported. (After Odum¹)

The sulfur cycle

- 1. Reduction of sulphate to organic sulfur
- 2. Oxidation of organic S to sulfate
- 3. Transformation of organic sulfur to hydrogen sulphide
- 4. Bacterial oxidation of hydrogen sulfide to sulfate
- 5. Sulfate ions are reduced anaerobically to hydrogen sulfide in sediments
- 6. Aerobic oxidation of hydrogen sulfide to sulfate in sediments
- 7. In the presence of H₂S, iron phosphate is transformed to iron sulfide (precipitate) and phosphate ions are liberated in overlying water



The solfur cycle (after Odum¹). (See text for explanation of numbers).