

THE ENERGETICS OF LIFE

Thermodynamics and Bioenergetics:

Thermodynamics is the study of energy and its effects on matter

Bioenergetics is the quantitative analysis of how organisms gain and utilize energy, a special part of thermodynamics

A special part of the general science of thermodynamics

1. The sun is the source of all energy: the energy of a green photon is 57 kcal/mole
2. ATP hydrolysis yields ~12 kcal/mole in vivo
3. Breaking of covalent bond requires considerable energy to break C-C ~ 83 kcal/mole
4. Thermal energy from one vibrational degree of freedom is 2.51 kJ/mole, so covalent bonds are stable
5. Noncovalent bonds require only a few kJ/mole to make or break

BIOENERGETICS

1. Review first and second laws of thermodynamics
2. Discuss the use of the concept of free energy change in predicting direction of reactions
3. Discuss the coupling of energy yielding and energy utilizing reactions through the often employed energy rich compound ATP

•All kind of things are going on in a cell

It's a dynamic structure: it moves, it synthesizes complex macromolecules, it selectively shuttles substances in and out and between compartments

All requires energy-- must be obtained from the environment and expended as efficiently as possible

Plants get it from sun; we eat plants and other animals that ate plants or ate other animals that ate plants etc

Energy processing is much of what BC is abt; that's the purpose of all that structure

Because of the central role of energy in life, we're going to spend some time talking abt it

ENERGY, HEAT, AND WORK

1. What is a system?

Any part of the universe you choose to study

bacterial cell

petri plate full of cells

mouse

mouse and room where mouse is hiding

earth

entire universe

2. What are the surroundings?

Surroundings are what's outside your system

3. System can be either *closed* (isolated) or *open*

•Closed:

no exchange of either matter or energy with surroundings

•Open:

matter and energy can pass in and out

•What are biological systems??

Biological systems are open

Internal energy:

1. Every system contains a specific amount

- called **U** or **E**

2. Where does it come from?

- kinetic energy of motion, vibration and rotation of atoms and molecules
- energy stored in chemical bonds

3. It is a property (or function) of the state of the system

Can the internal energy of a system change?

1. No, if it's closed--yes if it's open

2. Bioenergetics involves all energy that can change in biochemical processes (energy in atomic nucleus doesn't change)

3. How can the energy change in an open system? 2 ways:

- heat transfer in or out
- work done by the system or done to the system

4. Since **E** is a function of state, it depends only on the initial and final state, not on the path

First law of thermodynamics

- Energy (U or E) is conserved in a closed system**

Energy is conserved between the system and the surroundings in an open system

$$\Delta E = q - w$$

If $\Delta E = 0$

Then $q = w$

1. Changes in heat and work do depend on the path (they define the path...)

What are heat and work?

- They are not properties of the system

energy in transit

•Heat is called **q**

+ means heat absorbed

- means heat is lost

•Work is called **w**

+ means system did work

- means surroundings did work on system

•Change in **E** , since E is a fn of state, depends only on the initial and final state, not on the path

•**What describes the absorption or discharge of heat that occurs when a (constant volume or pressure) system exchanges heat with its surroundings? Fig 3.1**

3.1a Constant volume, $\Delta E = q$

3.1b Constant pressure, $w = P\Delta V$

•At the end of the rxn, did the system gain or lose heat?

Enthalpy

called **H**

H = the heat content of the system

a property of the system

ΔH = how much heat was gained or lost

$$\Delta H = \Delta E + P\Delta V$$

In biochemistry, $\Delta H \sim \Delta E$

because very little change in pressure or volume, so

$$\Delta H = q - w$$

ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

1. First law does not explain direction of reaction

Why does ice melt in RT water? It requires energy, ΔH is positive, but it is clearly thermodynamically favorable

Why does lit match burn paper, to CO_2 and water, but can't make paper from them?

These are both irreversible processes...

Reversible: ice cube into 0°C water, add a little heat, cube melts, lower temp a little and some of the water freezes.

The irreversible examples are far from equilibrium, the reversible process is close to equilibrium

The direction of processes

- Favorable processes are spontaneous in certain directions

Why?

Is it the lowest energy state? No, remember the ice cube in RT water. Also see **Table 3.1** for examples of low and high entropy states

- All closed systems tend to approach a state of maximum randomness**

Entropy

Disorder (randomness) is defined as **entropy**

called **S**

Everything melts in a fridge if energy supply turned off...

$S = 0$ only for a perfect crystal at absolute 0 (Third law)

$$S = k_B \ln W$$

k_B = Boltzmann constant (R divided by Avogadro's number)

W = number of energetically equivalent ways of arranging the components of a system

S varies with temperature, units are $J \cdot K^{-1}$

FREE ENERGY: THE SECOND LAW IN OPEN SYSTEMS

Straight thermo not so useful in BC

GIBBS FREE ENERGY, G

1. Biological systems not closed, and need to be described with a function of state that includes H and S

- Energy and Entropy changes important in living systems
- Gibbs Free Energy, called **G**, is a function of state that includes both S and E (independent of path like H and E)

$$\Delta G = \Delta H - T\Delta S$$

- lower energy (negative ΔH) or more disorder (positive ΔS) and both can make a reaction favorable: they both can make ΔG negative

see **Fig 3.4** Contribution of enthalpy and entropy to several processes

2. What is the thermodynamic criterion for a "spontaneous" process?

- favorable is a better term because spontaneous can be thought to imply "fast" and spontaneous/favorable does not have anything to do with speed

3. The standard for a favorable process (spontaneous) in an open system at constant P and T is that ΔG be negative

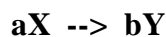
- a positive ΔG means the reaction is not favorable

4. ΔG is a measure of the maximum useful work obtainable from any reaction.

FREE ENERGY AND CHEMICAL REACTIONS

Determination of change in free energy (ΔG) of a reaction

For any reaction:



$$\Delta G = \Delta G^\circ + RT \ln \frac{[Y]^b}{[X]^a}$$

ΔG° is the standard free energy change = the difference in the free energy of the products and reactants when both are present at 1M concentration at 25°C. or the change in free energy when the reaction proceeds under conditions such that the reactants and products are all at 1M concentration at 25°C

Relationship between K_{eq} and ΔG°

•if $\Delta H = T\Delta S$, then $\Delta G = 0$ and the reaction is not favored to go either forward or backward.

The rate of the forward reaction = the rate of the reverse reaction **$V_f = V_r$**

•The system is at equilibrium

$$\text{so } 0 = \Delta G^\circ + RT \ln K_{eq}$$

and

$$\Delta G^\circ = -RT \ln K_{eq}$$

$$R = 8.31451 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

•if $K_{eq} = 1$, then $\Delta G^\circ = 0$

•if $K_{eq} > 1$, then ΔG° is negative and the reaction is exergonic

if $K_{eq} < 1$, then ΔG° is positive and the reaction is endergonic

Living systems are not at equilibrium. Rather, they maintain a **steady state** such that the amount of energy that is extracted from food is approximately equal to the amount of energy needed to maintain the organism.

Conventions in Biochemistry:

1. ΔG°

ΔG° is the standard free energy change at pH 0

$\Delta G^{\circ'}$ is the standard free energy change at pH 7

$\Delta G^{\circ'}$ applies to biological systems

2. The activity of water is assigned a value of 1 even though its concentration is 55.5 M so the $[H_2O]$ term is ignored

Calculations of $\Delta G^{\circ'}$

1. From $K_{eq} = \frac{[Y]^b}{[X]^a} = e^{-\Delta G^\circ / RT}$

2. From the summation of $\Delta G^{\circ'}$ if an overall reaction can be expressed in terms of several reactions with a common intermediate

3. From the standard free energies of formation (ΔG°_f) of the products and reactants

$$\Delta G^{\circ'} = \Delta G^\circ_{f, \text{products}} - \Delta G^\circ_{f, \text{reactants}}$$

*in this method the error can be large since ΔG° is a small difference between 2 large numbers

What does all this have to do with enzymes?

Enzymes do not alter the equilibrium of a reaction because they alter V_f and V_r equally

Enzymes alter the path of the reaction

The reaction takes an easier, faster path, and therefore less activation energy (ΔG^\ddagger) is required

FREE ENERGY AND CONCENTRATION

Chemical potential or partial molar free energy = the contribution of each component in a reaction to the total free energy. For example G_A is the chemical potential of component A.

Activity measures the effective concentration of a component. It is primarily affected by high concentrations, and is due to interactions between the molecules that affects their chemical potential so that $\Delta G_A = \Delta G_A^\circ + RT \ln a_A$ where **a** is the activity of A

We ignore the above and assume molar concentration = chemical potential, as is the case in very dilute solution when molecules do not interact with each other much.

Fig 3.5 shows that diffusion will occur until concentrations (and chemical potentials) are equal.

HIGH-ENERGY PHOSPHATE COMPOUNDS: FREE ENERGY SOURCES IN BIOLOGICAL SYSTEMS

Structure of ATP

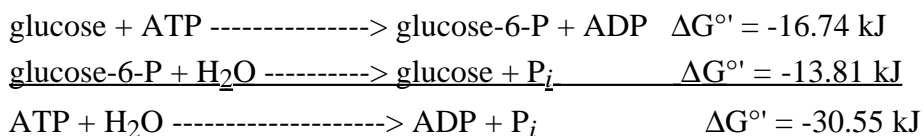
Fig 3.8

- at pH 7, 3 of the 4 protons of ATP are completely ionized and 1 is 50% ionized
- both ATP and ADP exist as 1:1 Mg^{++} complexes
 - affinity of ATP for Mg^{++} is 10x greater than of ADP

ΔG° of hydrolysis of ATP

- under physiological conditions the reaction is too much in favor of ATP hydrolysis (to ADP and P_i) to meas. K_{eq} directly
- so it's measured through coupled reactions

example:



--the difference in the free energy of ADP and P_i and of ATP is 30.55 kJ/mole

--the products are considerably more stable than ATP

- usually reactions liberating 30 kJ or more are said to involve a high energy bond

energy NOT in bond

- why are ADP and P_i so much more stable than ATP?

several explanations of why ATP is an unstable compound compared to ADP and P_i

orthophosphate is more stable than the phosphate at the end of ATP because of resonance of stabilization (**Fig 3.9**)

in ATP, P is hooked to another P

Electrostatic repulsion: negative charges on phosphates of ATP create instability due to charge repulsion

ΔG° of other phosphorylated intermediates

- anhydrides, enols and guanidine phosphates are high energy compounds

- esters are low energy

- many important reactions of intermediary metabolism have phosphorylated compounds occurring either as substrates or products

- 2 classes of compounds: (see **Fig 3.7**)

lower ΔG° than ATP

higher ΔG° than ATP

what is ΔG° of ATP?

- ATP can donate its terminal phosphate to a large number of compounds

- ATP can be formed from certain phosphorylated intermediates

- depends on the ΔG° of hydrolysis of the phosphorylated intermediate

This is often called the phosphate group transferring potential **PGTP** (it's the ΔG° with the "sign" reversed, also see **Fig 3.7**)