Without Energy, There Is No Life
You Matter
until you multiply yourself times the speed of light squared
Then you Energy
1. The chemistry of life is organized into metabolic pathways

• What is **metabolism**??

• Metabolic pathways alter molecules in a series of steps, sometimes occurring in a cycle.
• Catabolic pathways are often emissive reactions.

• Anabolic pathways are often absorptive reactions.

• The energy released by emissive rxns is used to drive absorptive rxns, and/or is converted into heat.
2. Organisms transform energy

- What kind of energy is in a chemical?

- Where, exactly, is it?

- Exactly, exactly where do we get most of the energy from our food molecules?
• A central property of living organisms is the ability to transform energy.

• What are the *forms* that kinetic and potential energy are found in?

• Eg – What form of energy is in a battery?
3. There are two laws of thermodynamics

- **Thermodynamics** is the study of energy transformations.
- In this field, the term *system* indicates the matter under study and the *surroundings* are everything outside the system.
- A *closed system*, like liquid in a thermos, is isolated from its surroundings (to a great degree).
- In an *open system*, energy (and often matter) can be transferred between the system and surroundings.
• Are you open or closed???

• The **first law of thermodynamics** states that you can’t get something for nothing.

• The second law says you can’t even break even.
  
  • \( E = mc^2 \) represents one of the most fundamental transformations in the universe, that of mass to energy, and vice-versa.

• What transformations are you making right now??
TODAY'S SPECIAL

Buy one Fish & Chips for the price of two and receive a second Fish & Chips ABSOLUTELY FREE!
• The second law of thermodynamics states that every energy transformation must make the universe as a whole more disordered.

• **Entropy** is a quantity used as a measure of disorder, or randomness.

• 5 minutes, if time. [Entropy song](#)
• In most energy transformations, ordered forms of energy are converted at least partly to heat.

• Heat is energy in its most random state.

• Combining the two laws, the *quantity* of energy in the universe is constant, but the *quality* (its ability to do work) is not.
So how DO you stay so organized and alive?

Organisms are islands of low entropy in an increasingly random universe. (Profound statement, eh? Probably written on a bathroom wall somewhere.)

2.A.1.a.3. Describe how increased disorder and entropy are offset.

2.A.1.b. Explain how Living systems do not violate the second law of thermodynamics, which states that entropy increases over time.
• **Spontaneous** processes are those that can occur without outside help at normal temperatures.

• Spontaneous doesn’t mean fast. Rusting is spontaneous but slow.
Learning Objectives

Explain how biological systems use free energy based on empirical data that all organisms require constant energy input to maintain organization, to grow, and to reproduce. [LO 2.1, SP 6.2]

Justify a scientific claim that free energy is required for living systems to maintain organization, to grow, or to reproduce, but that multiple strategies exist in different living systems. [LO 2.2, SP 6.1]

Predict how changes in free energy availability affect organisms, populations, and ecosystems. [LO 2.3, SP 6.4]
FREE Energy!!!!!!!
• Is energy ever free?

• Free energy is the portion of a system’s energy that is able to perform work when temperature is uniform throughout the system.
Essential knowledge 2.A.1: All living systems require constant input of free energy.
2.A.1.a. Explain what is meant by: life requires a highly ordered system.
2.A.1.a.1. Why is free energy required to maintain order in a system.
2.A.1.a.2. explain why the loss of free energy flow results in death.
The free energy (G) in a system is related to the total energy (H) and its entropy (S) by this relationship:

\[ G = H - TS, \]  

where \( T \) is temperature in Kelvin units.

Here is young Josiah at Yale.
• For a reaction to be spontaneous, the system must either give up energy (decrease in H), give up order (increase in S), or both.

• Delta G must be negative for a reaction to be spontaneous.

• Nature runs “downhill”.

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• Let’s understand these graphs…

• An **exergonic reaction** has a net release of free energy, delta G is negative. They are catabolic.

![Exergonic Reaction Diagram](image-url)
Here is an example:

- \( \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O} \)
- \( \Delta G = -686 \text{ kcal/mol} \)
- Through this reaction 686 kcal have been made available to do work in the cell.
- The products have 686 kcal less energy than the reactants.
- This is catabolic, because a bigger molecule is broken into smaller ones. It is exergonic because the forming of the bonds of the products releases more energy than it takes to break the bonds of the reactants.
• **An endergonic reaction** is one that absorbs free energy from its surroundings. Anabolic? Why?
5. ATP powers cellular work by coupling exergonic reactions to endergonic reactions

- A cell does three main kinds of work:
  - *Mechanical work*, beating of cilia, contraction of muscle cells, and movement of chromosomes, vesicles, etc.
  - *Transport work*, pumping substances across membranes against the direction of spontaneous movement
  - *Chemical work*, driving endergonic reactions such as the synthesis of polymers from monomers.

- In most cases, the immediate source of energy that powers cellular work is ATP.
2.A.1.b.1. Describe how order is maintained by coupling cellular processes that increase with those that decrease entropy.
2.A.1.b.2. Explain what must occur to energy input to maintain order and power cellular processes.
2.A.1.b.3. Explain why energetically favorable exergonic reactions, such as ATP→ADP, that have a negative change in free energy can be used to maintain or increase order in a system by being coupled with reactions that have a positive free energy change.
• ATP (adenosine triphosphate) – let’s break it down…

(a) Structure of adenosine triphosphate

Fig. 6.8a
• The bonds between phosphate groups can be broken by ?????

• ATP -> ADP + P_i + energy
• The phosphate bonds are weak because each of the three phosphate groups has a negative charge.

• Why, then, are they called “energy rich” bonds???

• Why is weak good, though??

• Structure determines function.
• In the cell the energy from the hydrolysis of ATP is coupled directly to endergonic processes by transferring the phosphate group to another molecule.

• This molecule is now phosphorylated.

• This molecule is now more reactive.

• This is how ATP provides the energy to make reactions happen.

• What enzymes catalyze this???
Fig. 6.9 The energy released by the hydrolysis of ATP is harnessed to the endergonic reaction that synthesizes glutamine from glutamic acid through the transfer of a phosphate group from ATP.

(a) Without ATP

\[ \text{Glu} + \text{NH}_3 \rightarrow \text{Glu} - \text{NH}_2 \quad \Delta G = +3.4 \text{ kcal/mol} \]

(b) With ATP

1. \[ \text{Glu} + \text{ATP} \rightarrow \text{Glu} + \text{P} \quad \Delta G = -7.3 \text{ kcal/mol} \]
2. \[ \text{Glu} - \text{P} + \text{NH}_3 \rightarrow \text{Glu} - \text{NH}_2 + \text{P}_i \]

(c) Free energy change with ATP

\[ \text{Glu} + \text{NH}_3 \rightarrow \text{Glu} - \text{NH}_2 \quad \Delta G = +3.4 \text{ kcal/mol} \]

\[ \text{ATP} \rightarrow \text{ADP} + \text{P}_i \quad \Delta G = -7.3 \text{ kcal/mol} \]

Net \[ \Delta G = -3.9 \text{ kcal/mol} \]
• ATP is like a battery that is continually recharged by adding a phosphate group to ADP.

• Where does the energy to recharge come from?

• In a working muscle cell the entire pool of ATP is recycled once each minute, over 10 million ATP consumed and regenerated per second per cell.
A catalyst is a chemical agent that changes the rate of a reaction without being consumed by the reaction.

- An enzyme is a catalytic protein; their name often ends in -ase.

Chemical reactions between molecules involve both bond breaking (catabolic) ones and bond forming (anabolic) ones.

- Catabolic rxns are usually exergonic (energy from the formed bonds of the products is released).
- Anabolic rxns are usually endergonic (and the energy is stored in the bonds that are formed).
• Chemistry is all about collisions; chemicals must collide to form bonds and collisions break bonds.

• Anything that increases the number or force of collisions will help make a reaction happen faster.

• What kinds of things could do that?
• Activation energy is the amount of energy necessary to push the reactants over an energy barrier, after which they react on their own.

• At the summit, the molecules are at an unstable point, the transition state.

• Heat is one thing that can provide activation energy.

Note that delta G is negative in this reaction.

Fig. 6.
• In the temperatures typical of the cell, there is not enough energy for most molecules to make it over the hump of activation energy.

• Heat would speed reactions, but it would also denature proteins and kill cells.

• Hmmm...how can these reactions happen at the relatively low temperatures inside most cells?
• Enzyme speed reactions by lowering $E_A$.
  • The transition state can then be reached even at moderate temperatures.
• Enzymes do not change delta G.
  • It hastens reactions that would occur eventually, but too slowly to do the cell any good.
  • Know this graph of an exergonic reaction.

Fig. 6.13
Essential knowledge 4.B.1: Interactions between molecules affect their structure and function.
4.B.1.a. Explain how molecular structure and function are linked.
4.B.1.b. The shape of enzymes, active sites and interaction with specific molecules are essential for basic functioning of the enzyme.
4.B.1.b.1. Explain what is meant by: the substrate must fit into the enzyme’s active site.
2. Enzymes are substrate specific

• A **substrate** is a reactant which binds to an enzyme.

• When a substrate or substrates binds to an enzyme, the enzyme catalyzes the conversion of the substrate to the product. How, exactly, do you think it works?
  
  • Sucrase is an enzyme that binds to sucrose and breaks the disaccharide into fructose and glucose.

\[
\text{Sucrase} \quad \text{Sucrose} + \text{H}_2\text{O} \rightarrow \text{Glucose} + \text{Fructose}
\]
• The **active site** of an enzymes is ???
• The **specificity** of an enzyme is due to ???
• As the substrate binds, the enzyme changes shape leading to a tighter **induced fit**, bringing chemical groups in position to catalyze the reaction.  
  [Link](http://web.chem.ucsb.edu/~molvisual/ABLE/induced_fit/index.html)
3. Specificity is also due to attractions between parts of the enzyme and parts of the substrate.

- In most cases substrates are held in the active site by weak interactions, such as hydrogen bonds and ionic bonds.
- So it is both shape and charge match-ups which make each enzyme specific for catalyzing the reaction involving only a particular substrate.
Fig. 6.15

1. Substrate binds to enzyme.
2. Substrate is converted to products.
3. Products are released.
4. Active site is available for another molecule of substrate.
Enzymes use two basic mechanisms to lower activation energy and speed a reaction by allowing it to happen at a lower temperature.

- For anabolic reactions, the active site and shape changes during induced fit orients substrates in the correct position for the bond to be formed with the help of a gentler collision (at a lower activation energy).

- For catabolic reactions, when the enzyme-substrate complex changes shape, it may put stress on bonds that must be broken, making it easier for a lesser collision to break them.
A single enzyme molecule can catalyze thousands of reactions a second. **Turnover # = rxns/sec**

*Enzymes are unaffected by the reaction* and are reusable. Here’s a good example:

In a litter box, urea is hydrolyzed in this way:

$$\text{H}_2\text{N-CO-NH}_2 + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{NH}_3$$

urea       ammonia

Bacteria from the air produce urease in the litter box. Urease has a turnover # of 30,000 rxns/sec. Without urease, it would take 3 million years to break down the urea from one day of kitty pee.
The rate that a specific number of enzymes catalyzes reactions depends in part on **substrate concentration**.

As substrate concentration increases, collisions between enzyme and substrate increase, increasing the rate of reactions.

However, there is a limit.

At or above a certain substrate concentration, the active sites on all enzymes are engaged and working as fast as they can.

The only way to increase productivity at this point is to add more enzyme molecules.

What would a graph of enzyme action depending on substrate concentration look like?
• Temperature has a major impact on reaction rate.

• As temperature increases, collisions between substrates and active sites occur more frequently as molecules move faster.

• However, at some point (often 40°C) thermal agitation begins to disrupt the weak bonds that stabilize the protein’s active conformation and the protein **denatures**.

• Each enzyme has an optimal temperature.
• Because pH also influences shape and therefore reaction rate, each enzyme has an optimal pH too.
• This falls between pH 6 - 8 for most enzymes.
• However, digestive enzymes in the stomach are designed to work best at pH 2 while those in the intestine are optimal at pH 8, both matching their working environments.
• This is an often used example.
• Now for practice…

Fig. 6.16b
Tips

• Grid LEFT to right
• Use the formula sheet
• Don’t round until the end
• Look at HOW the answer should be given

“round to nearest…”

.123
The 1 is in the **tenths** place
The 2 is in the **hundreds** place
The 3 is in the **thousandths** place
Q5: Rate

Hydrogen peroxide is broken down to water and oxygen by the enzyme catalase. The following data were taken over 5 minutes. What is the rate of enzymatic reaction in mL/min from 2 to 4 minutes? Round to the nearest hundreds

<table>
<thead>
<tr>
<th>Time (mins)</th>
<th>Amount of (O_2) produced (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.3</td>
</tr>
<tr>
<td>2</td>
<td>3.6</td>
</tr>
<tr>
<td>3</td>
<td>4.2</td>
</tr>
<tr>
<td>4</td>
<td>5.5</td>
</tr>
<tr>
<td>5</td>
<td>5.9</td>
</tr>
</tbody>
</table>
Q5

- Rise/run = rate = 5.5 - 3.6 / 4 - 2
- Rise/run = rate = 1.9 / 2
- Rise/run = rate = .95
• Many enzymes require nonprotein helpers, **cofactors**.
  
  • Some inorganic cofactors include zinc, iron, and magnesium, which is a cofactor in all phosphate transfer reactions.

• **Organic cofactors**, **coenzymes**, include vitamins or molecules derived from vitamins. Eg.- NAD, FAD, NADP
4.B.1.b.2. Describe how cofactors and coenzymes affect enzyme function.

4.B.1.c. Explain how enzyme activity can be enhanced or inhibited.

4.B.1.d. Explain the following: The change in function of an enzyme can be interpreted from data regarding the concentrations of product or substrate as a function of time. These representations demonstrate the relationship between an enzyme’s activity, the disappearance of substrate, and/or presence of a competitive inhibitor.
• Binding by some molecules, inhibitors, prevent enzymes from catalyzing reactions.

• If the inhibitor binds to the same site as the substrate (the active site), then it blocks substrate binding via **competitive inhibition**. Mercury, eg.

• In some bacteria, sulpha drugs competitively inhibit an enzyme involved in folic acid synthesis.
• If the inhibitor binds somewhere other than the active site, it blocks substrate binding via **noncompetitive inhibition**. Lead and cyanide disable enzymes in this way.

• Binding by the inhibitor causes the enzyme to change shape, rendering the active site unreceptive at worst or less effective at catalyzing the reaction.

• *Reversible* inhibition of enzymes is a natural part of the regulation of metabolism.

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**Fig. 6.17c**

(c) A noncompetitive inhibitor

Noncompetitive inhibitor
1. Metabolic control often depends on allosteric regulation

- In many cases, the molecules that naturally regulate enzyme activity behave like reversible noncompetitive inhibitors for enzymes with quaternary structure.

- These molecules often bind weakly to an allosteric site, a specific receptor on the enzyme that is not the active site. These molecules are thus called allosteric inhibitors.

- Binding by these molecules can either inhibit or promote enzyme activity.
Many enzymes show COOPERATIVITY

- When one or more substrates fit into their active sites, the site in a different subunit of the enzyme changes shape to fit the next substrate better.

- Watch. 5+ minutes, but may need to watch only the first two or three. But, there is a kind of a “what’s wrong with this picture” lesson in the last couple minutes.
• One common method of metabolic control is **feedback inhibition** in which a metabolic pathway is turned off by its end product. Mucho important!!!

• The end product inhibits an enzyme in the pathway, usually early.

• When the product is abundant the pathway is turned off, when rare the pathway is active.

2. The localization of enzymes within a cell helps order metabolism

- Structures within the cell bring order to metabolic pathways.
- A team of enzymes for several steps of a metabolic pathway may be assembled together as a multienzyme complex.
- The product from the first can then pass quickly to the next enzyme until the final product is released.
• Some enzymes and enzyme complexes have fixed locations within the cells as structural components of particular membranes.

• Others are confined within membrane-enclosed eukaryotic organelles.

• Both methods concentrate enzymes for efficiency.

Fig. 6.21
Word for the day…

• If these regulatory mechanisms hadn’t evolved, the chemistry in a cell would be forever caddywhompus.