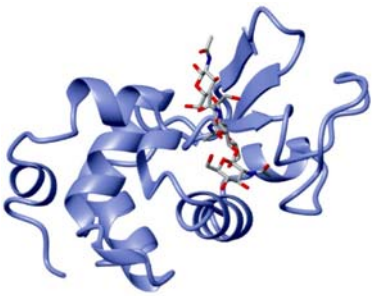
Elements of Biochemistry I

CHEM 2770 & MBIO 2770



Hélène Perreault
Tel: 204-474-7418
550 Parker Building
Helene.Perreault@umanitoba.ca

Office Hours: Tues, Thurs, 2-4 pm

Lectures: Mon, Wed, Fri, 12:30-1:20 in Room 223 Wallace.

Textbook: "*Principles* of *Biochemistry, 5th edition*" by: Moran *et al*.

Available in the Bookstore and also used for CHEM / MBIO 2780.

Course site:
http://home.cc.umanitoba.ca/~perreau/CHEM2770/Main.htm
Contains old exams. Course notes will be posted here.

Laboratory: The laboratory manual is available in the bookstore today.

Lab coats and safety glasses are required.

Laboratory information will be available on the web site.

Monday Afternoon Lab please report to any Biochemistry lab in Parker (406, 416, 422, 428).

Tuesday Morning Lab please report to either room 422 or 428 Parker.

Friday Afternoon Lab please report to room 406 Parker.

Evaluation:

Laboratory:	15%
Mid-term exam Wed. Oct. 29 6:00–7:00 PM:	25%
Final exam set by Student Records:	60%

About 25% of the final exam will consist of questions from the lab.

All lecture material is examinable.

Study the old exams.

Read and Study!

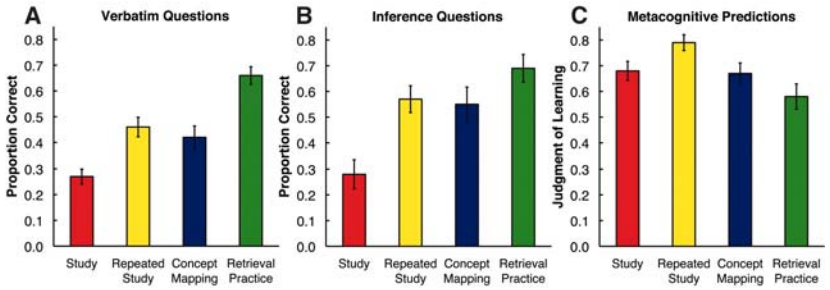
You will find some advice on "*studying*" in the following article:

"Retrieval Practice Produces More Learning than Elaborative Studying with Concept Mapping"

Jeffrey D. Karpicke, *et al.* *Science* **331**, 772 (2011);

The article suggests that memorizing is an effective way to learn.

Fig. 1 Results of Experiment 1.



J D Karpicke, J R Blunt Science 2011;331:772-775

Science
AAAS

Published by AAAS

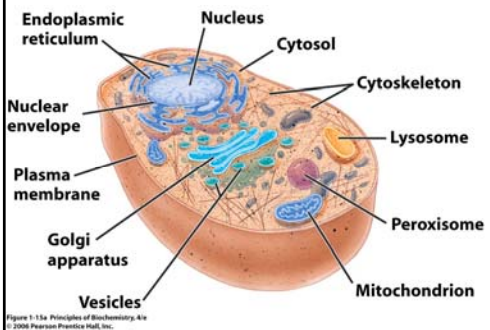
http://www.scienceinseconds.com/blog/The-Funnies

Chapter 1

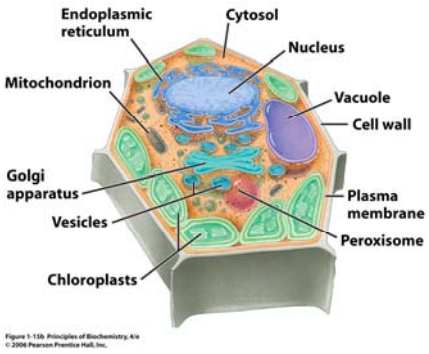
The nature and structure of cells.

Unifying principles of Biochemistry – for you to review.

Animal Cell



Plant Cell



We will address **what** is known and **how** we know it. The latter is one purpose of our laboratory.

Rat muscle cell actin.

Human endothelial cell microtubules.

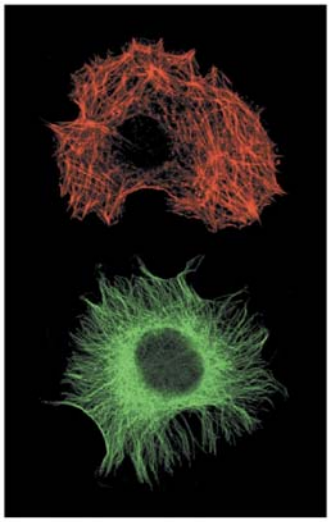


Figure 1-16 Principles of Biochemistry, 4/e
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http://mrsec.wisc.edu/

Biochemistry

Bios = life – Greek *al kimya* = the transmutation – Arabic

Chemistry explains "*change*" using **atoms**.

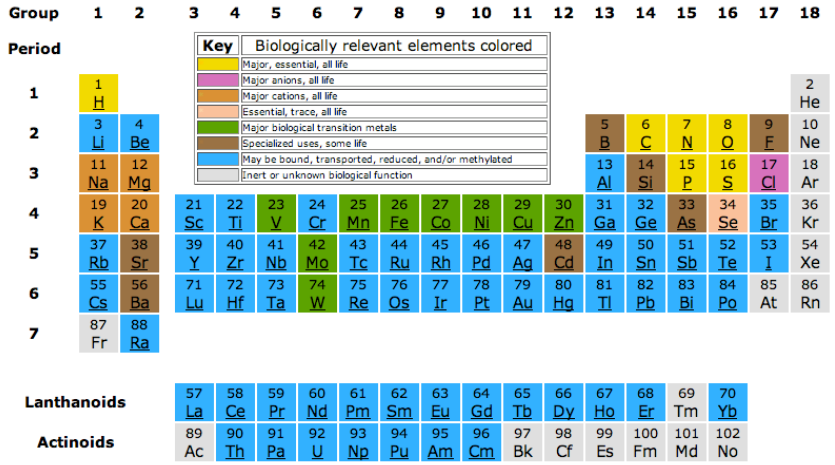
All chemical change involves rearrangements of **electrons**.

Biochemistry explains *life* in terms of the **atomic structures** of biological molecules and their reactions.

	Size
Redwood Tree	110 m
Human	2 m
Ant	$4x10^{-3}$ m
Human Skin	$5x10^{-4}$ m
Red Blood Cell	$6x10^{-6}$ m
Largest Virus	$5x10^{-7}$ m
Cell Membrane	10^{-8} m
Thickness of DNA	$3x10^{-9}$ m
Water Molecule	$2.8x10^{-10}$ m
C-atom	$7x10^{-11}$ m
Atomic nucleus	10^{-14} m
Proton	10^{-15} m
Electron	10^{-18} m

See *scaleoftheuniverse.com*

The Biochemical Periodic Table:



http://umbbd.msi.umn.edu/periodic/elements/sn.html

Biomolecule	% in *E. coli*
Protein	15
Nucleic Acid	7
Carbohydrate	3
Lipid	2
Water	70
Other	3

The Biosphere contains about 10 x10^6 different species ranging from single cells to complex animals.

New Species of Mammal Discovered in 2013

Olinguito – a relative of the racoon was identified in the Andes.

It is arboreal, nocturnal, omniverous.

http://www.nature.com/news/cute-mammal-is-first-carnivore-discovered-in-western-hemisphere-for-35-years-1.13565

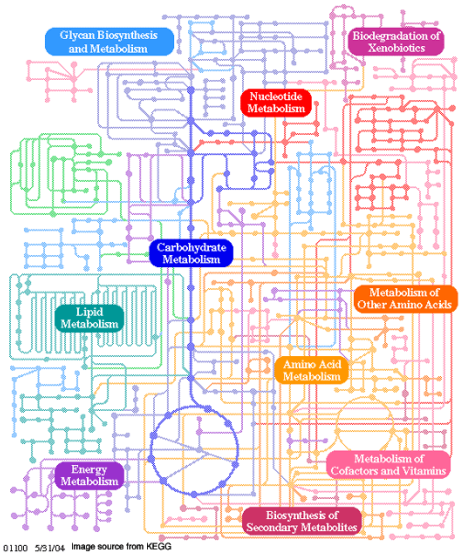
All life uses the same types of biomolecules and all share some common metabolic features. This suggests a **common ancient ancestor**.

"Variations on a Theme"

Change = **Chemical Reactions**

Synthesis and degradation of biomolecules and other transformations associated with life.

Metabolism: An organized network of reactions occurring in cells.



E. coli contains about 1000 metabolites interconverted by about 2000 enzymes.

http://www.manet.uiuc.edu/pathways.php

Catabolism: Reactions that degrade nutrient molecules yielding energy.

Anabolism: Reactions in which cell components are assembled from small molecules and energy.

There are 5 different types of biochemical transformation involving bond formation or breakage:

1. Group Transfer
2. Internal Rearrangement
3. Cleavage
4. Condensation
5. Oxidation-Reduction

Bond strength depends on the properties of the atoms including:

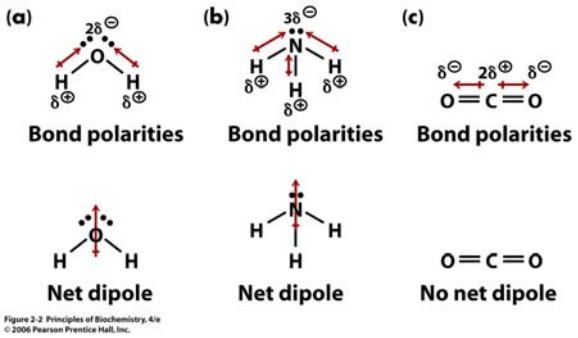
Electronegativity: A measure of the ability of an atom in a molecule to attract electrons to itself.

H	2.1	C	2.5
N	3.0	O	3.5
P	2.1	S	2.5

Saturated Hydrocarbons – molecules with mostly C–H and C–C bonds. They are also called "**aliphatic**". They are **non-polar** or only slightly polar because they share electrons equally.

In contrast, the covalent C–O bond is **polar**. $\overset{\delta^+}{C}—\overset{\delta^-}{O}$

Recall that covalent bonds involve sharing pairs of electrons.

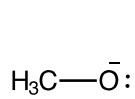


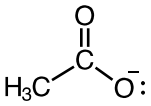
Biomolecule reactivity is found in **functional groups** that have polar bonds.

C=O	Carbonyl, Carboxyl	H–S	Thiol = Sulfhydryl
H–O	Alcohol, Hydroxyl	P–O	Phosphate, phosphoryl
H–N	Amino		

Biochemical Functional Groups

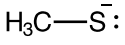
Nucleophiles:


alkoxide

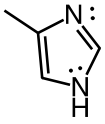

carboxylate


Carbanion


Hydroxide

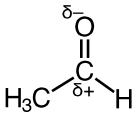

Thiolate

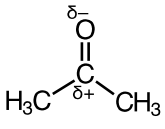

Amine

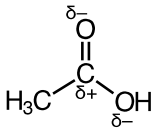

Imidazole

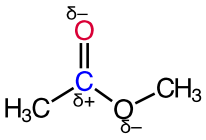
Biochemical Functional Groups

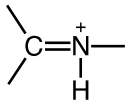
Electrophiles:

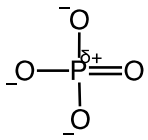

Aldehyde


Ketone


Carboxylic Acid


Ester

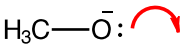

Protonated Imine

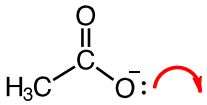

Phosphate

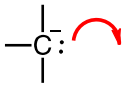

Proton

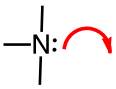
Nucleophile Reactivity

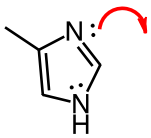
Nucleophiles:

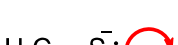

alkoxide

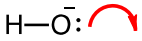

carboxylate


Carbanion


Amine

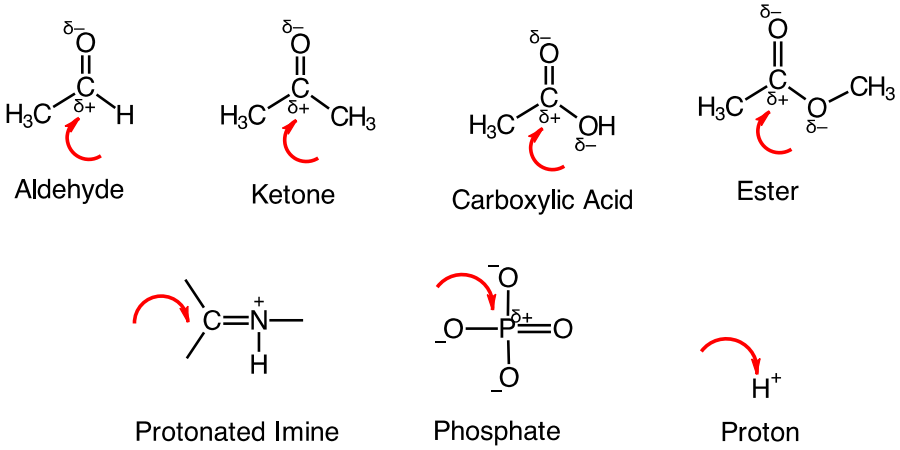

Imidazole


Thiolate

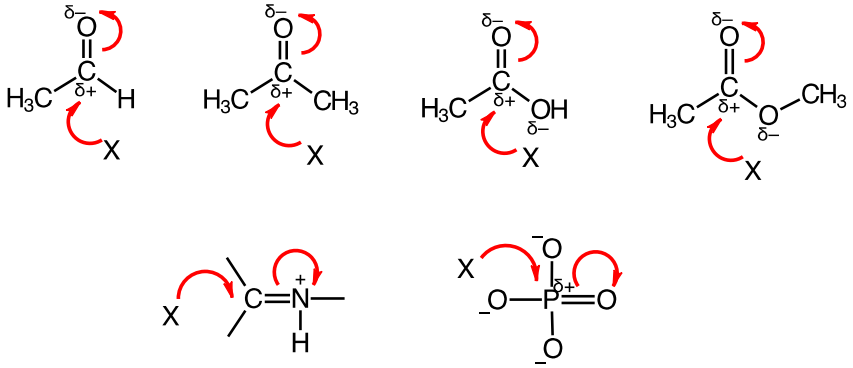

Hydroxide

Electrophile Reactivity

Electrophiles:

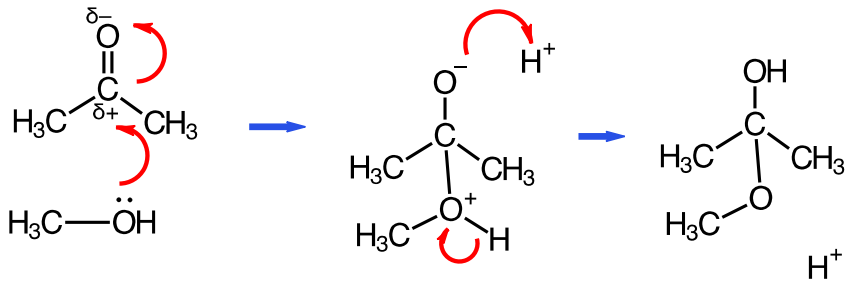


A lot of biochemistry happens when nucleophiles meet electrophiles.



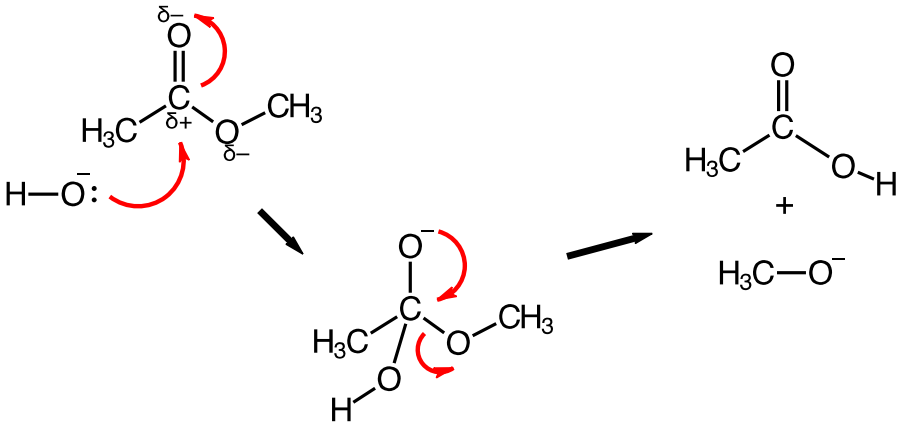
"Arrow Pushing"

Nucleophilic Addition



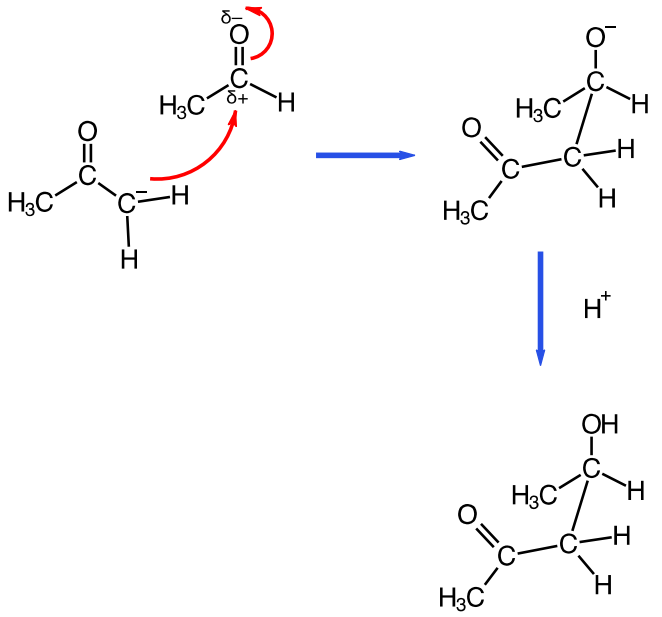
This is a Group Transfer.

Nucleophilic Substitution



Another Group Transfer.

Condensation



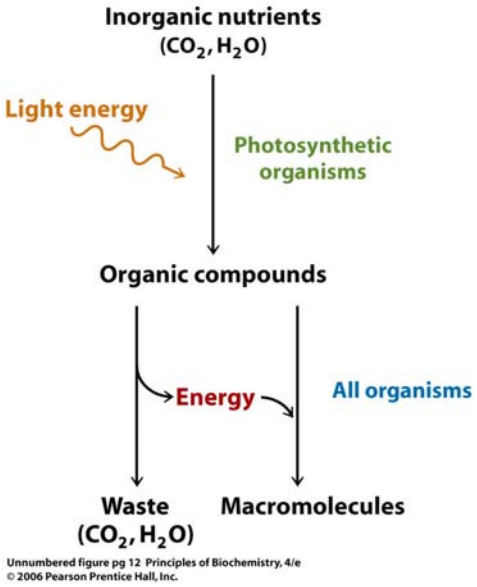
Thermodynamics

All living organisms require a source of **energy** to live and grow.

1st Law of Thermodynamics: The energy of the universe is constant.

Energy is the capacity of a system to do **work** or release **heat**.

The units for energy are Joules.



Unnumbered figure pg 12 Principles of Biochemistry, 4/e
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There are many forms of energy:

Kinetic Energy is the energy an object has owing to its motion.

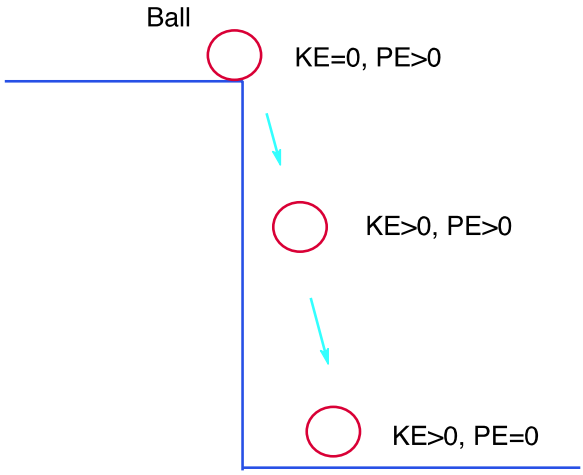
Potential Energy is the energy an object has owing to its position in a field; *e.g.* gravity, electric, magnetic.

H is **enthalpy**, the **heat** energy of material at constant pressure.

Heat is the transfer of energy from a region of high temperature to a region of low temperature and associated with the motions of atoms or molecules.

Even though energy cannot be created or destroyed, during a physical or chemical change, energy may **change its form**.

In the picture below, the ball at rest has zero kinetic energy and lots of gravitational potential energy.



The falling ball converts its potential energy into kinetic energy.

When it strikes the ground, the ball converts its kinetic energy into heat, warming the ball and the ground and the air around it. It might also do work *e.g.* squish a bug.

At rest, all the potential energy and kinetic energy have been lost as heat.

The **total energy** in the whole system (ball, air, bug, table, ground, *etc.*) is **unchanged** but it can interconvert from one form to another.

PE + KE = constant.

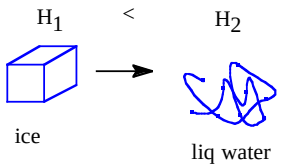
2nd Law of Thermodynamics:

The entropy of the universe increases.

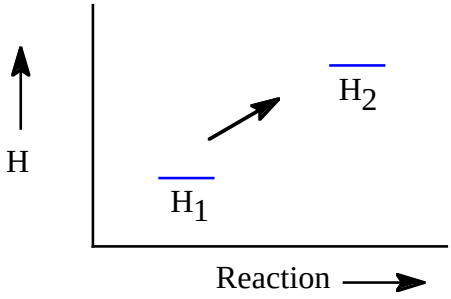
Entropy S, is a measure of the disorder of a system. It is the tendency of energy to spread out over time.
Units are Joules/Kelvin ($J \cdot K^{-1}$).

A hot frying pan **spontaneously** cools when placed in cold water, and the water heats up. This is because the heat is more **randomly** distributed between the frying pan and the water afterwards.

Another example: At room temperature, ice spontaneously melts, obeying all the Laws of thermodynamics.



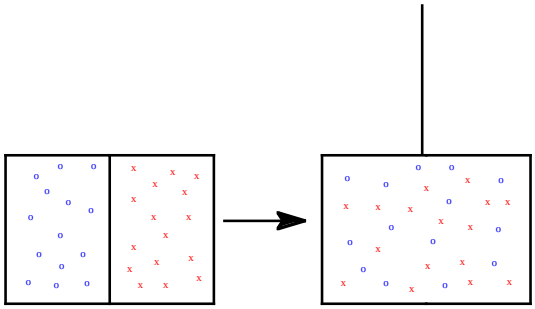
Energy Level Diagram



$\Delta H = H_2 - H_1 \sim +6$ kJ / mole

Clearly, ΔH is not a good predictor of spontaneity.

Consider a spontaneous change in which $\Delta H = 0$.



The gases mix spontaneously and irreversibly but there is no change in the energy of the atoms.

The degree of **disorder**, **entropy** increases spontaneously.

By combining the 1st and 2nd Laws we can predict **spontaneous** change.

$$G = H - TS$$

Gibb's Free Energy, **G**, is the **energy available to do work** at constant temperature and pressure.

Think of H as the ***total energy*** of the system and TS as the "***wasted energy***" then ΔG is the "***useful energy***".

The greater is H, the more work can be done.

The smaller is S, the greater is the order, the more work can be done.

How much work is available in transforming a system from G_1, H_1, S_1 to G_2, H_2, S_2?

e.g. glucose → water and carbon dioxide

$$G_2 - G_1 = H_2 - H_1 - T(S_2 - S_1)$$

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

In a chemical change: $A + B \longrightarrow C + D$

$$\Delta H = H_C + H_D - (H_A + H_B)$$

If ΔH is +, heat is absorbed – **Endothermic**. (ice melts)

If ΔH is – , heat is evolved – **Exothermic**. (glucose oxidation)

$\Delta S = S_C + S_D - (S_A + S_B)$

If ΔS is +, disorder has increased.

If ΔS is –, order has increased.

$\Delta G = G_C + G_D - (G_A + G_B)$

If ΔG is +, free energy is absorbed: **Endergonic**. G must have been added to the system. This will not occur spontaneously.

If ΔG is –, free energy is released: **Exergonic**. The reaction is spontaneous.

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

ΔH	ΔS	ΔG	
–	+	–	spont.
+	–	+	non-spont.
+	+	?	?
–	–	?	?

The 2nd Law states that $\Delta S_{universe} > 0$

But, as cells grow $\Delta S_{cell} < 0$

Do living cells defy the laws of thermodynamics ?????

No!

Cells remove G from sunlight / nutrients in their surroundings, decreasing the order in their surroundings, increasing the order within themselves. So all laws are obeyed.

$\Delta S_{univ} = \Delta S_{cell} + \Delta S_{surr} > 0$

But where is the energy in glucose?

Molecules contain "**internal energy**". This includes kinetic energy of vibrations, rotations, and translations of the molecules and the potential energy of the electrons in **chemical bonds**.

For the reaction $A + B \longrightarrow C + D$

in a closed system, the reaction will proceed until "***equilibrium***" is reached, after which, no change will occur.

This is the **Law of Mass Action**.

Equilibrium can be described by the ***equilibrium constant***.

$$K_{eq} = \frac{[C]*[D]}{[A]*[B]}$$

The reactants and products are driven to equilibrium by **free energy changes**. They spontaneously fall down the free energy hill toward equilibrium which is their lowest free energy state.

The relationship between free energy change and equilibrium is given by:

$$\Delta G = -R * T * \ln(K_{eq})$$

R = Gas Constant = 8.31 J / mol · K. T = Temp in K.

If K_{eq} = 19 at 25°C then, $-RT\ln(K'_{eq})$ =

– (8.315 J/mol K)(298 K)(ln19) = – 7,296 J/mol = – 7.3 kJ/mol

We will discuss this realtionship again later in the course.