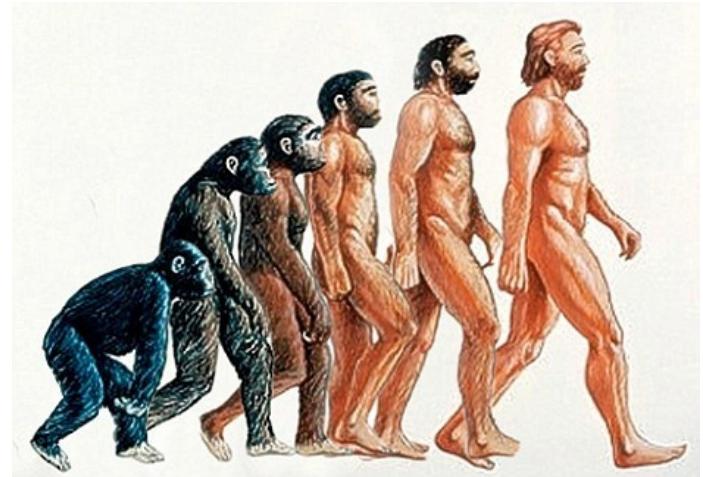
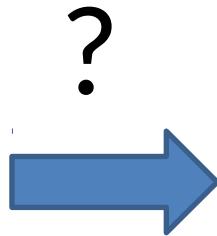
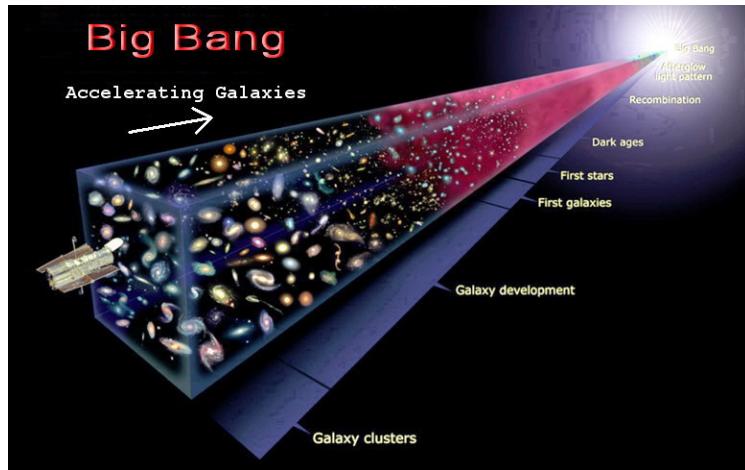


# Natural order from disorder?

Can nature **spontaneously** create order/complexity?

# Natural order from disorder?

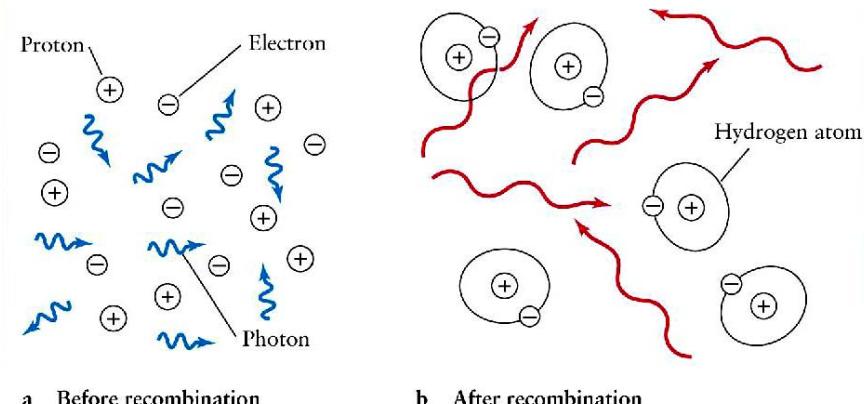
Obviously, YES. The entire history of the universe is FILLED with precisely this process.



# Cooling

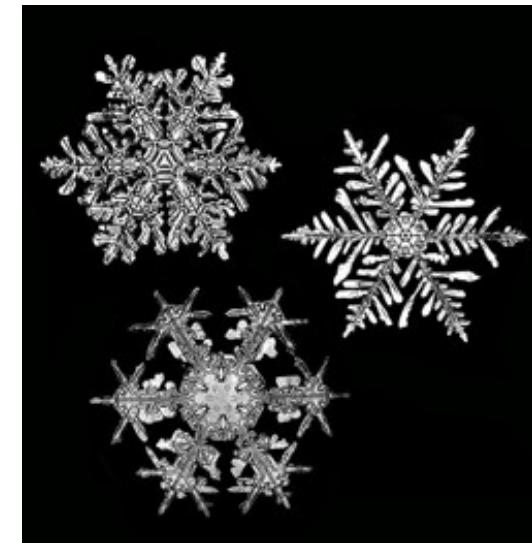
- Let's start by thinking about **cooling**:

- ✓ The universe began in a hot dense state (Big Bang) with (almost) no structure. Ever since then it has been **expanding and cooling**, causing various structures to “**condense out**”.
- ✓ E.g., at one time, all of space was filled basically with hot protons, neutrons, electrons, and photons (particles of light). As these gasses **cooled**, the electrons combined with the protons, resulting in **neutral hydrogen atoms condensing out**
- ✓ Because the electrons and protons were now together as hydrogen atoms (fewer possible arrangements), this condensation represented a **decrease in entropy/increase in order**. However, the energy released in this process, carried away and spread out as photons, represented **at least as great an increase in entropy/increase in disorder**.



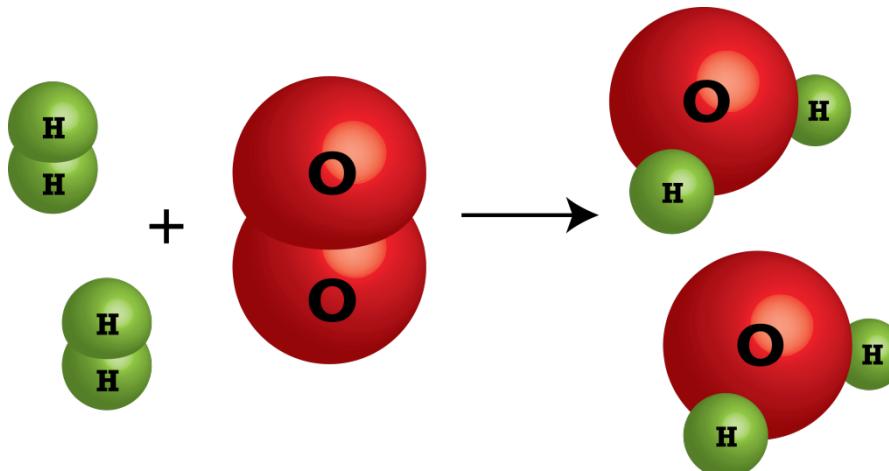
## Cooling

- The same thing happens when water molecules **condense** into snowflakes:
  - ✓ Ice is a **more ordered** structure than water vapor (less ways for the H<sub>2</sub>O molecules to be spread out, analogous to the [electron + proton  $\rightarrow$  hydrogen] condensation), so the condensation of water molecules into snowflakes **reduces their entropy**.
  - ✓ But as discussed before, when water freezes, **energy is released** (analogous to the energy released as a photon when a hydrogen atom forms).
  - ✓ This energy warms the surrounding, cooler air molecules, which then take it away (like the dispersing photons). This **dispersal of thermal energy** represents a greater entropy increase than the water-to-ice entropy decrease  $\Rightarrow$  **net entropy increase**.
  - ✓ Aside: The 6- (or 3- or 12-) sided symmetry is a result of the underlying symmetry of the water molecule (quantum...)



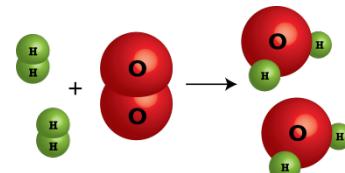
## Cooling

- Chemical reactions are the same: they are just a **type of cooling** (dispersal of energy).
- Example of **exothermic reaction**: the burning of hydrogen and oxygen gas:



# Cooling

- Chemical reactions are the same: they are just a **type of cooling** (dispersal of energy).
- Example of **exothermic reaction**: the burning of hydrogen and oxygen gas:
  - ✓  $2\text{H}_{2(\text{g})} + \text{O}_{2(\text{g})} \rightarrow 2\text{H}_2\text{O}_{2(\text{g})} + (\text{Energy released})$
  - ✓ Number of gas particles (per reaction) has decreased from 3 to 2. Fewer gas particles  $\Rightarrow$  fewer ways of arranging them  $\Rightarrow$  decrease in entropy (more order, like water-to-ice)
  - ✓ The electric field energy released (when the bonds change) goes into thermal energy (random KE) of the water molecules, then environment. This **increase in entropy**, by  $\Delta S = E/T$ , is **greater than the above decrease** (many ways of dispersing this energy)
  - ✓ This reaction is like water-to-ice cooling, except that the energy released is initially dispersed amongst the reaction products themselves (and then the environment)
  - ✓ Aside: Like many chemical reactions, an *activation energy* ("spark") is required...



# Cooling

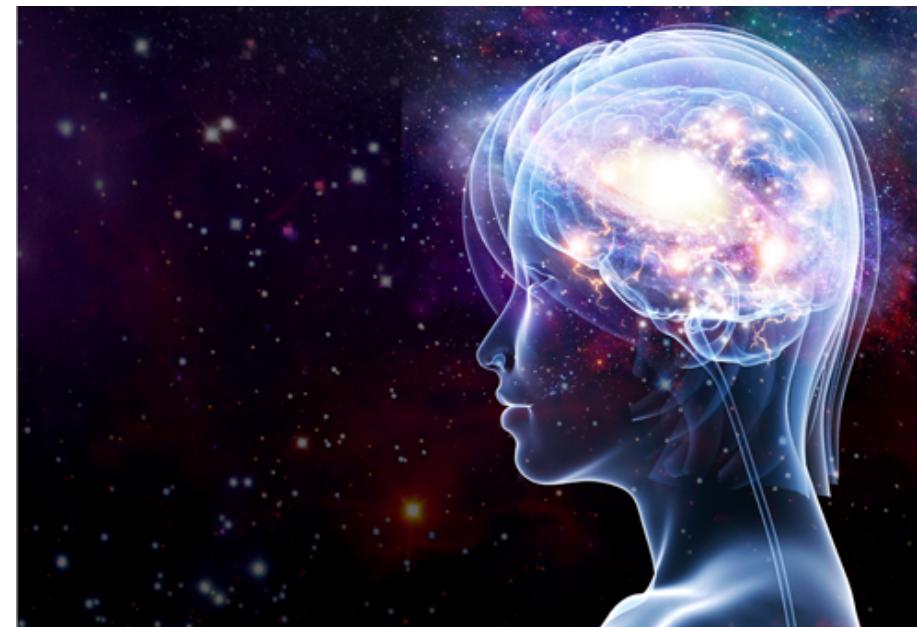
- Key points:

- ✓ Chemical reactions happen **not** because the energy in the bonds decreases. (E.g., in **endothermic** reactions, energy must be *supplied*, and the energy in bonds **increases**.) Energy is always **conserved**, so reactions don't occur because of a “lowering of energy”.
- ✓ Chemical reactions are driven by the **dispersal of energy**, i.e., a reduction in the **quality** of the energy, **not the quantity**. More generally, the driving force of *any* natural process in the universe is the random, purposeless dispersal of energy—analogous to “cooling”.
- ✓ There are many chemical (and physical\*) reactions in which more structured (lower-entropy) products emerge **spontaneously** from less structured (higher-entropy) reactants, provided a compensating disorder is created in the surrounding environment.

\*E.g., Carnot cycle: reactant = hot source; product = ordered KE of piston; compensating disorder created in cold sink

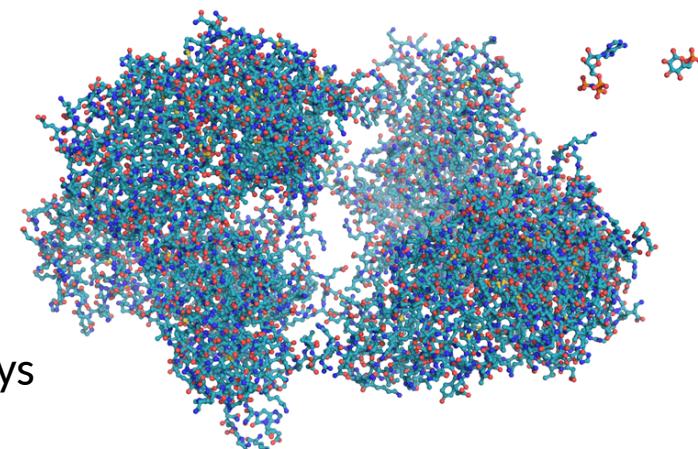
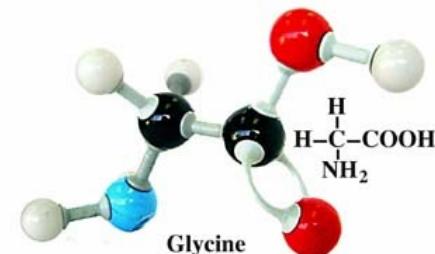
# Cooling

- So, assuming that life is just (complex) chemical reactions:
  - ✓ Could nature **spontaneously create**, as products of chemical “cooling”, the complex structures (machinery) of life, from less structured reactants?
  - ✓ Would the very same “cooling” **animate** these machines?
  - ✓ Is **human consciousness** just a (marvelous) form of “cooling”—just another way in which the universe cools as it expands?



# Proteins

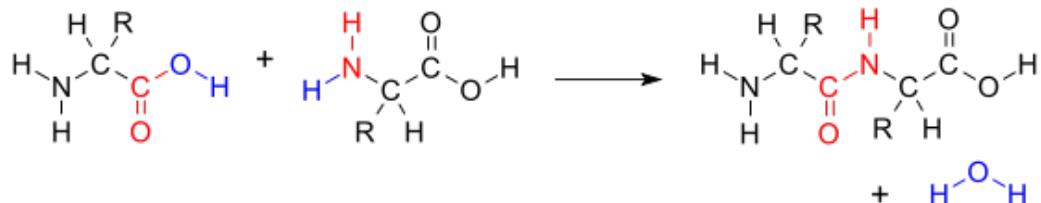
- Recall: **amino acids** are the building blocks of life. The human body uses 20 of them to construct **proteins**, the bulk of living stuff. The simplest amino acid is glycine.
- The **origin** of amino acids on the early Earth is not a big mystery. (Recall: Miller-Urey experiment, chemical reactions near deep-sea vents, material from space.)
- The bigger question is, how can amino acids **spontaneously** come together in the form of proteins? Two steps:
  - ✓ Amino acids link together in **long chains**
  - ✓ These chains **coil** and **fold/intertwine** in complex ways



typical protein

# Formation of Amino Acid Chains

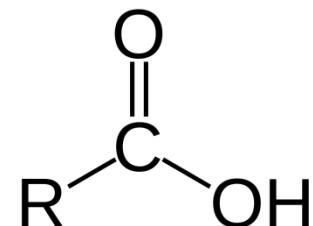
- Amino acids (e.g., glycine) have two key parts:
  - ✓ An  $\text{NH}_2$  *amine group*
  - ✓ A  $\text{COOH}$  *carboxylic acid group*
- Two amino acids join when the **amine group** in one approaches the **acid group** in the other, resulting in a **peptide bond** and the expulsion of a water molecule:



- This **consumes energy**, and is a big reason why we need to eat (more later...). But assuming we *have* a long chain of amino acids (a *peptide chain*), let's see how it **coils**.



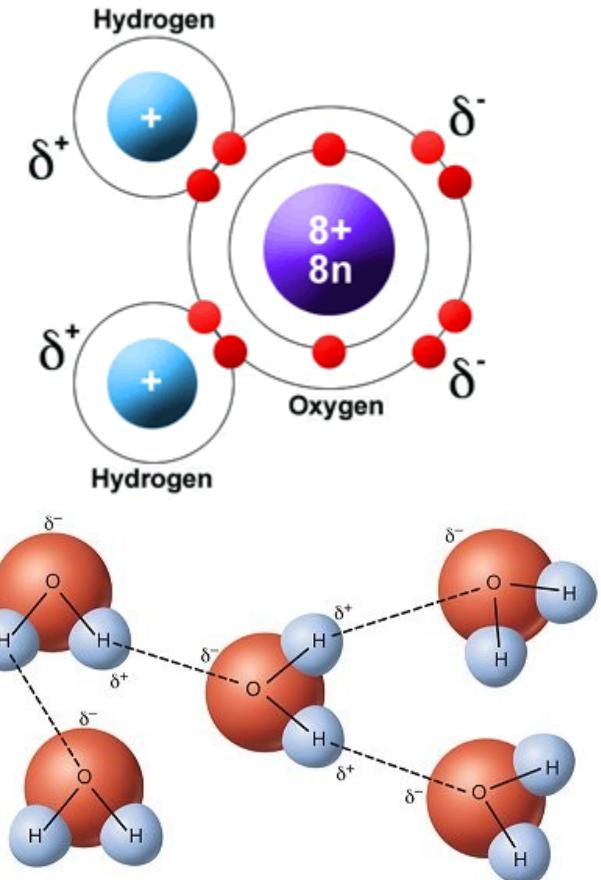
N=blue, C=black, O=red, H=white



carboxylic acid (note the OH)

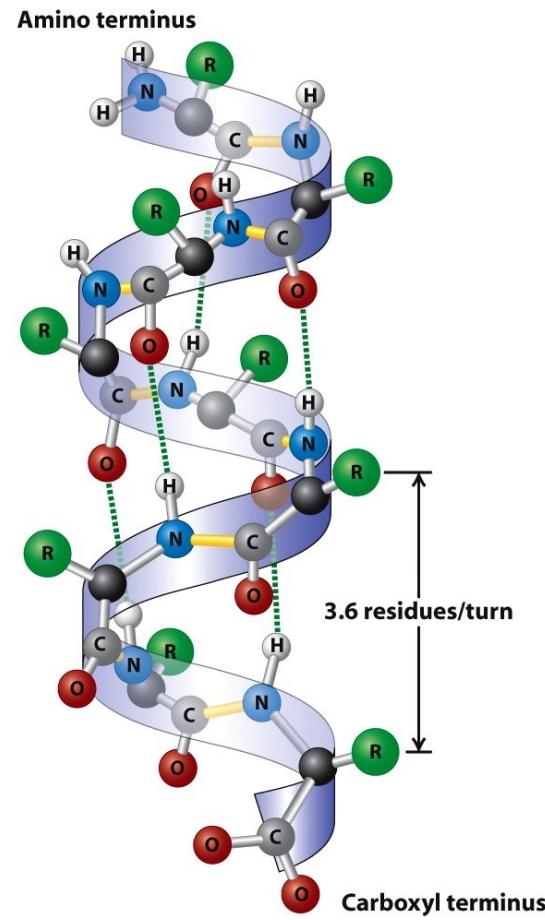
# Coiling of an Amino Acid Chain into a Helix

- The water molecule,  $\text{H}_2\text{O}$ , is a **polar molecule**: Each H shares its electron with the O, making the protruding Hs **positive**. Also, the O has four more unshared electrons, opposite the Hs, making the side of the O opposite the Hs **negative**.
- In **liquid water**, the positive Hs of one molecule attract the negative Os in neighboring molecules. This **hydrogen bond** is stronger than van der Waals interaction, and weaker than covalent or ionic bonds, and is responsible for various “magical” properties of water that make it integral to life.
- It’s also responsible for the **coiling** of amino acid chains into the very important **alpha helix**. The H attached to the N of one peptide bond **hydrogen-bonds** with the O attached to the C of a neighboring peptide bond. This bond is strong enough to hold the helical structure in place.



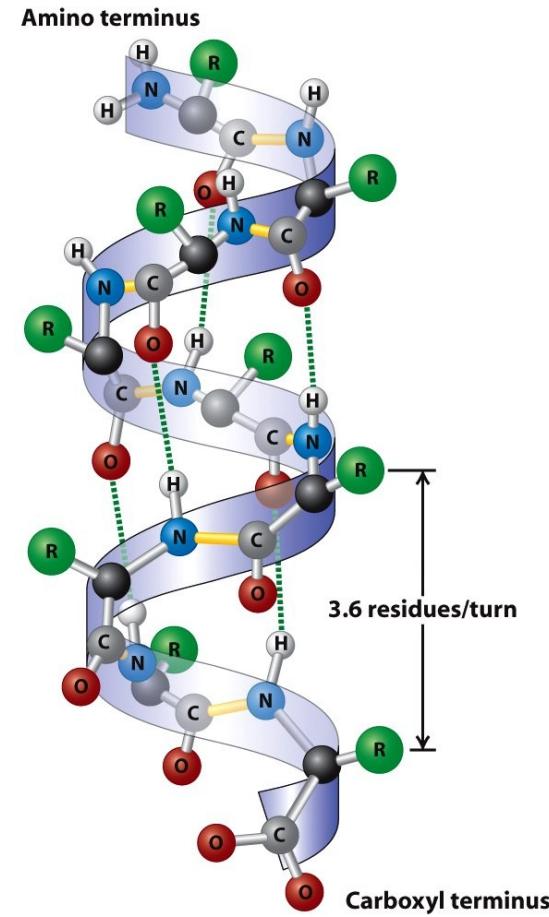
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# Coiling of an Amino Acid Chain into a Helix

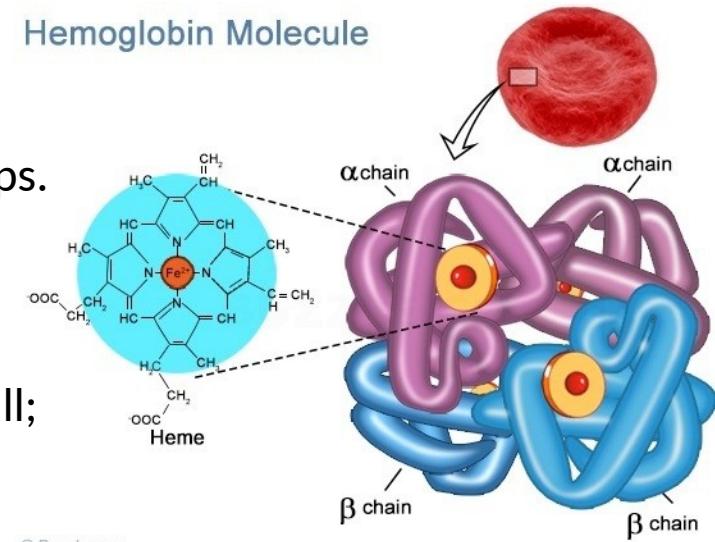
- The rigid alpha helix is a **more ordered** form of the amino acid chain, than just a random, floppy, linear chain. How can this order arise **spontaneously** (via the Second Law)?
- The O—H hydrogen bonds are sufficiently strong that, when they form, enough (electrostatic field) energy disperses into the environment (as thermal energy) that the resulting **increase in disorder** exceeds the increase in order off the alpha helix. The universe as a whole is **more disordered!!**
- Moreover, the formation of the helix is **irreversible**: once the energy disperses, there's not enough concentrated energy around to break the bonds. (When you cook an egg, you're unzipping the helix.) This form of **local order** has "**condensed out**" of the universe's inexorable ratcheting towards **greater overall disorder!**  $\Delta S > 0$ .



# Folding and Intertwining of Helices

- **Hemoglobin molecules** (making up 96% of the non-water in red blood cells) carry **oxygen** to all the cells in your body.
- Each molecule is made of two alpha and two beta helices, bent and twisted in such a way as to hold four **heme** groups. Each heme group has one **iron atom** that oxygen binds to. (Blood is red because iron oxide is rust. So eat your iron!)
- The bending and twisting of the helices is not random at all; it is very precise. Each red blood cell contains zillions of **identical** hemoglobin molecules. Hemoglobin is a **highly ordered** structure. Can such order emerge **spontaneously**?
- Yes, in part for the same reason oil and water don't mix...

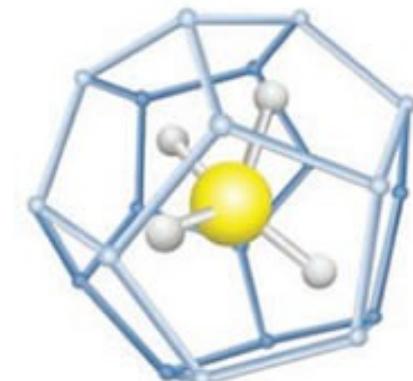
Hemoglobin Molecule



© Buzzle.com

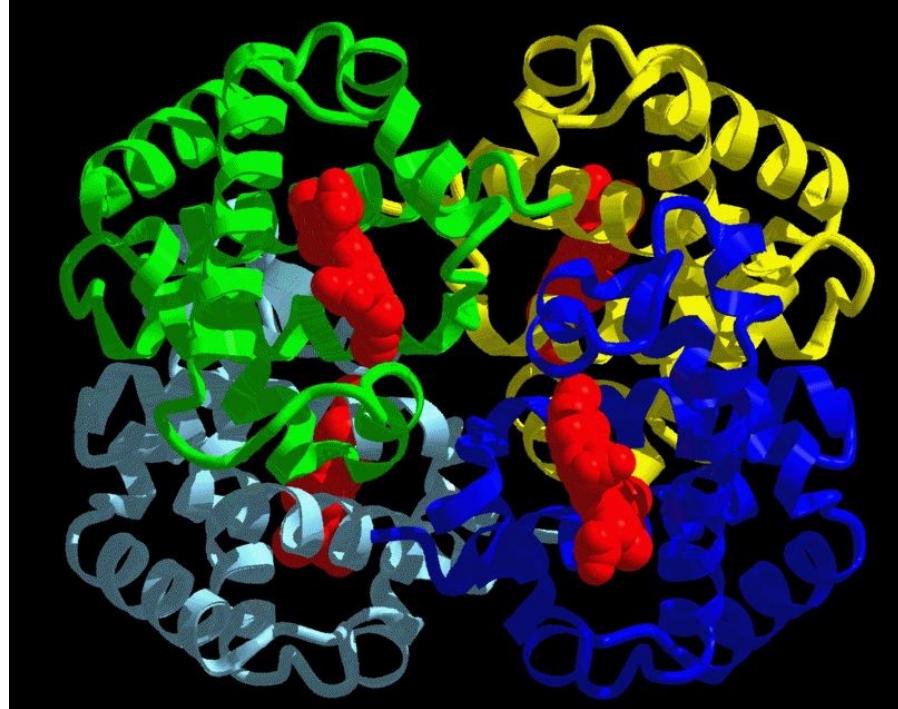
# Folding and Intertwining of Helices

- Why doesn't oil **disperse** in water, like a drop of ink? Surely this would **increase the entropy** of the universe, and so be spontaneous? Why does it do the **opposite**: clump together after we try to mix it?
- Hydrocarbons (like oil) are made of only C & H atoms, and are **hydrophobic**: when a hydrocarbon molecule is put in water, the surrounding (polar) water molecules interact with its H atoms and form a **highly structured** cage around it. (E.g., methane =  $\text{CH}_4$ .)
- The resulting **increase in order** would outweigh the **decrease in order** caused by the spreading out of the oil molecules (and their energy). Oil molecules clump together to show as few of the themselves to the water as possible: hydrophobic = water-hating.
- What does this have to do with folding & intertwining of helices?



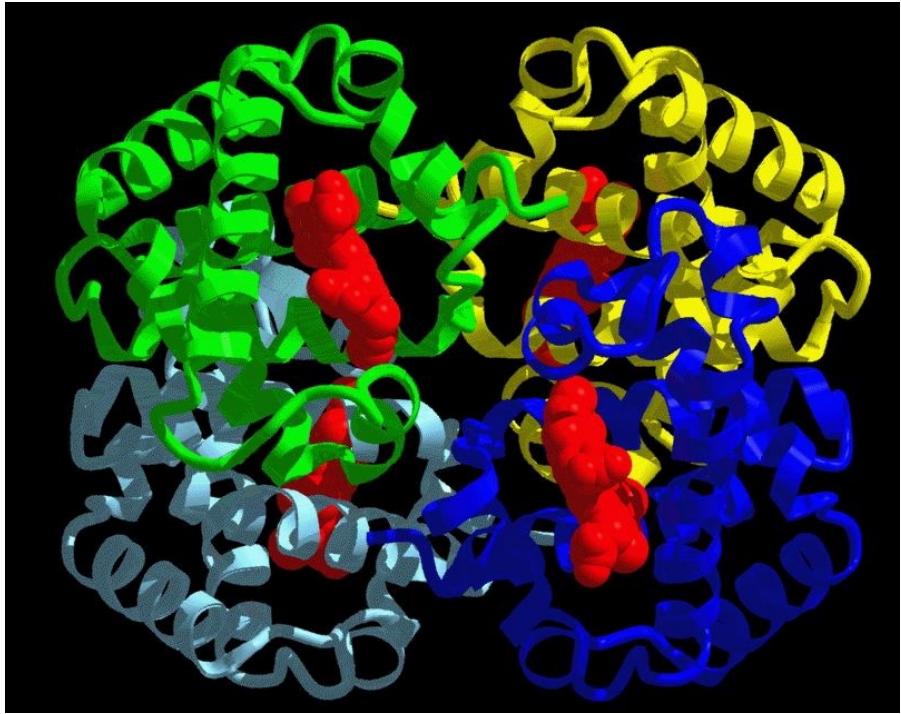
# Folding and Intertwining of Helices

- Many of the amino acids in the helices have **hydrocarbon parts**, and so **behave like oil** (hydrophobic).
- Water molecules would form **intricate cages** around any hydrocarbon parts sticking out into the surrounding water, **increasing the order** in the universe.
- The helices fold in ways that tend to **minimize** exposure of hydrocarbon parts to the water, and thus **minimize order (maximize disorder)**.
- The same effect probably plays a role also in the four helices **intertwining** in hemoglobin.



The formation of this complex structure increases the disorder of the universe

# Folding and Intertwining of Helices

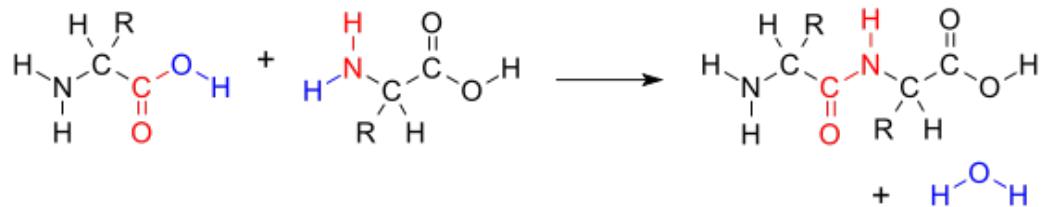


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# Formation of Amino Acid Chains

- But how are amino acid chains formed **in the first place?**
- Recall that forming the peptide bonds between the amino acids in a chain **consumes energy**.



- So the short answer is obvious:  
**We eat food that provides this energy.**
- But the long answer is more interesting...



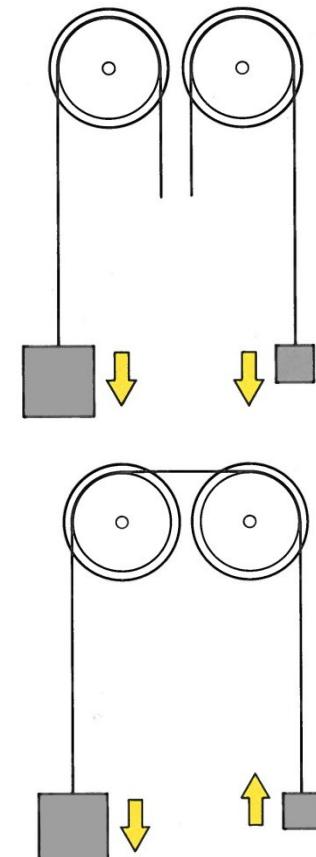
# Formation of Amino Acid Chains

- The ordered chain has more structure (**lower entropy**) than the scattered amino acids it was made from. Thus, there must be a **compensating disorder** created elsewhere. **How?**
- We eat, in part for the energy, but more importantly: we take in **high quality** (low entropy) energy, and allow it to **decay to low quality** (high entropy) energy, which we expel as body heat and excrement. This **spontaneous order-to-disorder** process *drives non-spontaneous disorder-to-order* processes in our bodies, sustaining our relatively low entropy bodies against decay, and thus staving off death.
- This **low entropy energy** ultimately comes from the **Sun**, or more ultimately, from the **Big Bang** itself. Life is **intimately connected** with the very *dynamics of the universe itself*. Life is **not** an *isolated* phenomenon. “**Biosphere**= Universe!



# Coupling Spontaneous to Non-Spontaneous Processes

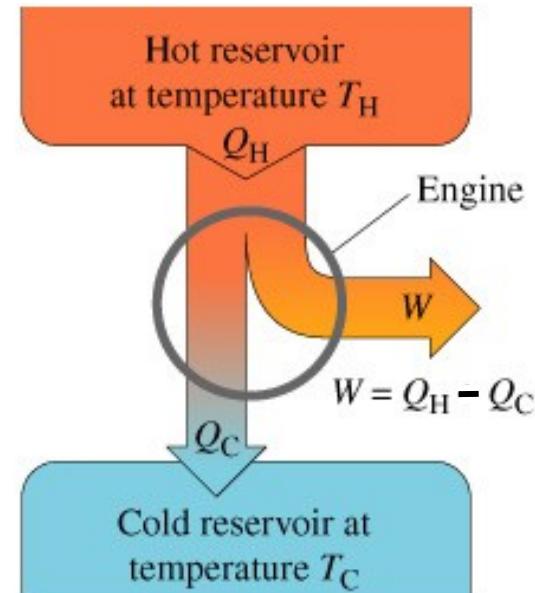
- “This spontaneous order-to-disorder process drives non-spontaneous disorder-to-order processes in our bodies.”  
**HOW??**
- Analogy:
  - ✓ **Top Picture:** Both masses will spontaneously fall.
  - ✓ **Bottom Picture:** When **coupled together**, the heavier mass will raise the lighter. A **stronger** spontaneous reaction can **drive** a weaker spontaneous reaction in the **reverse (non-spontaneous or unnatural) direction**.
- Questions:
  - ✓ How do we assess the “**driving power**” of a reaction?
  - ✓ What are the “gears and wheels” that **couple** life’s chemical reactions?



# Driving Power of a Reaction

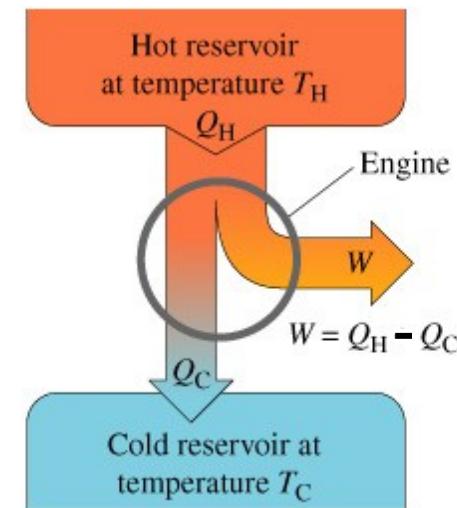
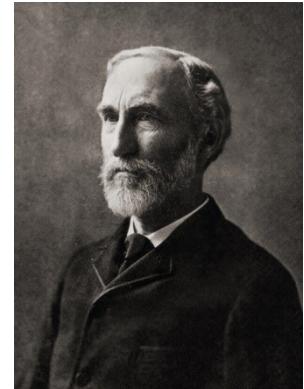
- Recall:

- ✓ In a heat engine, the **spontaneous** flow of thermal energy from hot to cold is **harnessed** to do **useful work**, which can be used to **create structure and order**. “Order from disorder”.
- ✓ But not all of  $Q_H$  is converted into useful work. A minimum amount of it has to be “wasted” as **heat energy** (absolute energy) instead of being converted into **useful work** (increasing its **usefulness**) giving entropy to **entropy increase** for the universe.
- ✓ The amount of energy that is **free to do work** (create structure and order) is called the **free energy**. For a heat engine, the free energy available goes **down** as it does work:  $\Delta$ What about in the case of chemistry?



# Driving Power of a Reaction

- Josiah Gibbs (1839–1903), in Boltzmann's generation, was the first person to apply thermodynamics to chemistry, and hence make thermodynamics more readily applicable to life.
- E.g., we can think of an exothermic chemical reaction as a heat source with total energy  $Q_H$ . When the system liberates energy  $Q_H$ , its entropy goes down, and its entropy is reduced:  $\Delta S = -Q_H/T_H$ .
- In order for this to happen spontaneously, a minimum of "waste heat" ( $Q_C$ ) must be dumped into the environment (at temp  $T$ ), increasing its entropy by  $(Q_C/T)$  at least the same amount like the heat engine, the free energy of the system goes down as it does work:  $\Delta F = -W = -Q_H + Q_C = \Delta U - T\Delta S$ .



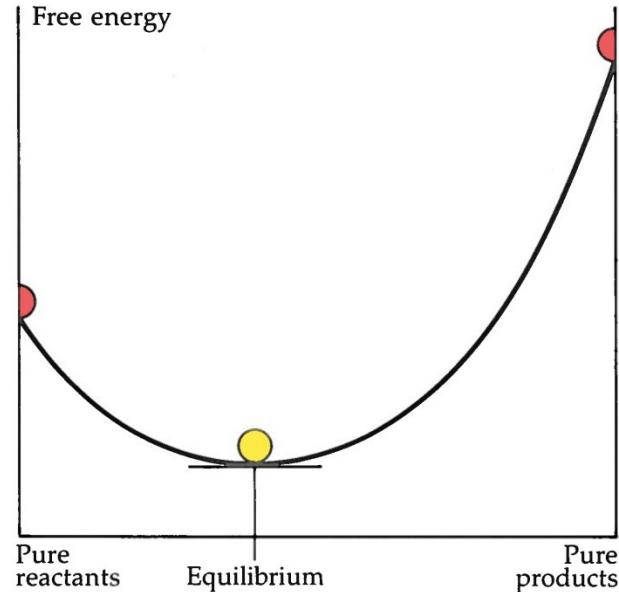
# Driving Power of a Reaction

- All chemical reactions spontaneously move towards lower free energy:

$$\Delta F = \Delta U - T\Delta S < 0$$

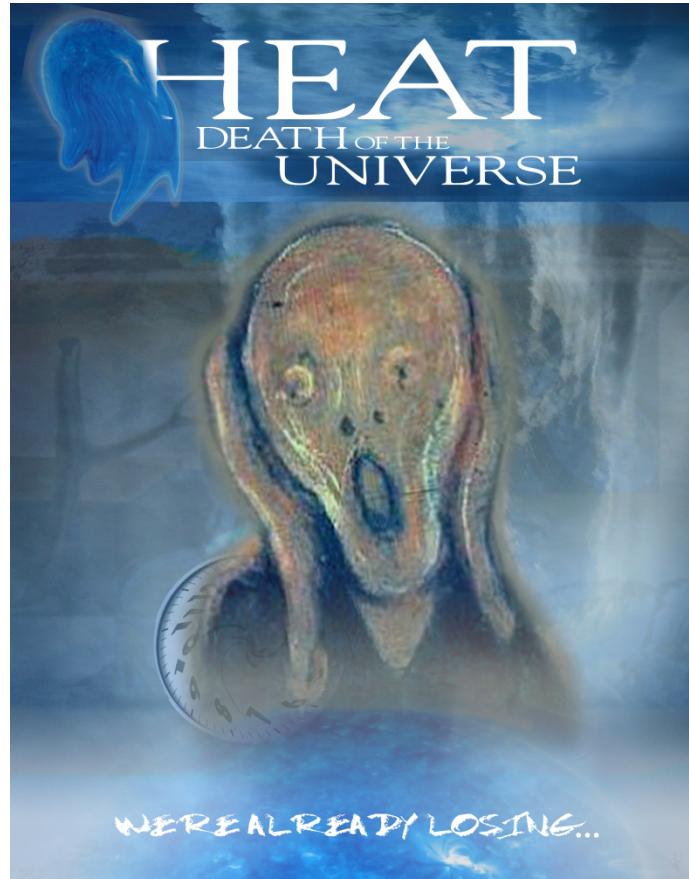
- This is the “driving power” of the reaction: the greater the “fall” in free energy, the more **useable energy (“work”)** is liberated to create structure and order elsewhere.
- This applies to all natural processes in the universe:

- ✓ Systems do not spontaneously move to **lower energy** (e.g., When you heat a gas).
- ✓ Systems spontaneously move to **lower free energy**. This drives all process, including animating life.
- ✓ Systems fall down in free energy, as the universe falls up in total entropy.



# The End of Free Energy

As the total entropy of the universe steadily ratchets up, we are not running out of energy (energy is **conserved—eternal**). We are running out of **free** energy. **Useful** energy. Energy that can be used to **create structure and order, and animate life.**

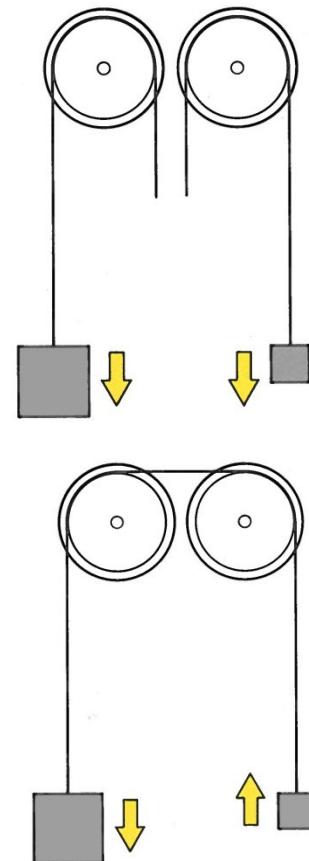
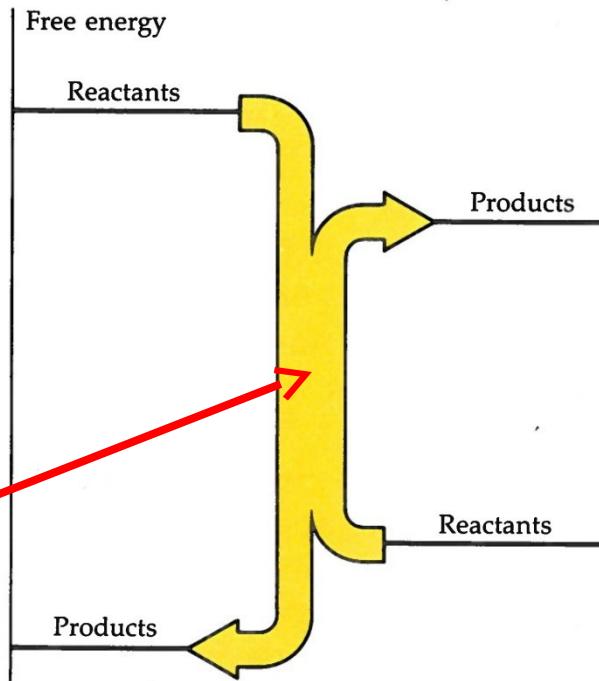


# Coupling Reactions

- How does this inexorable slide into disorder animate life?

When **coupled** together, a reaction that **falls further** in free energy (a more vigorous slide into disorder) can **drive** one that **falls less** in free energy (less vigorous slide into disorder) in the **reverse direction**.

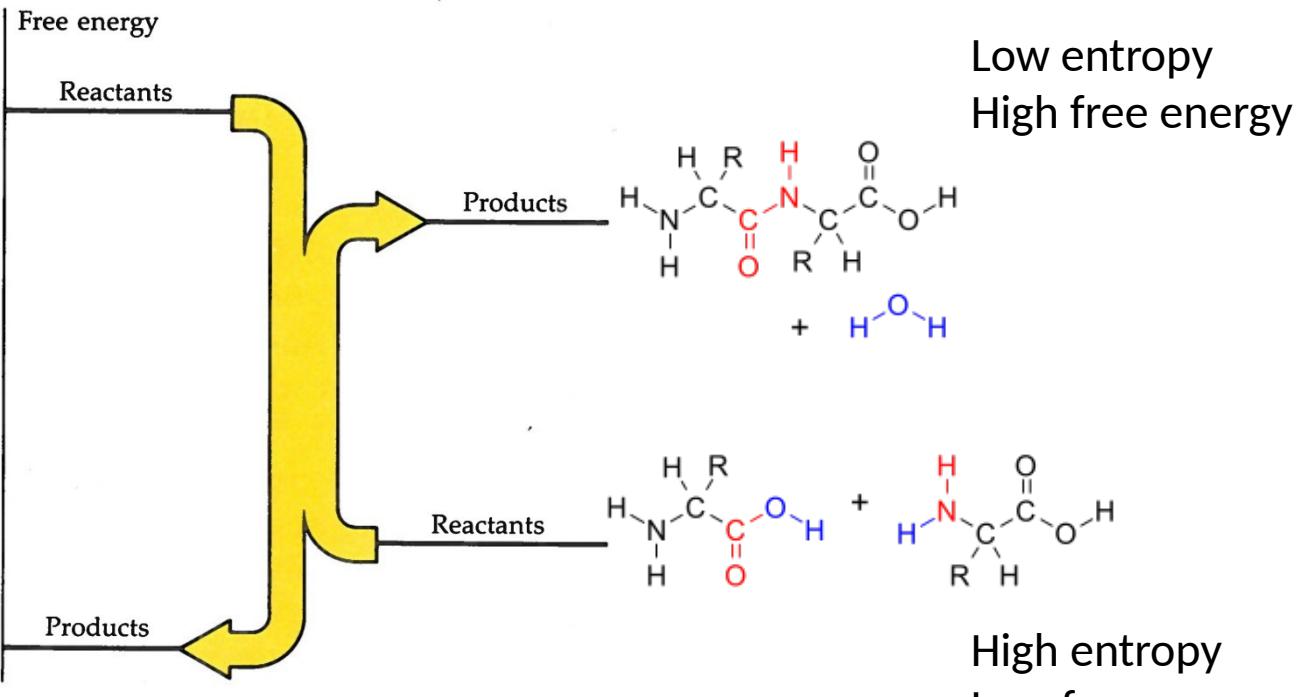
Life's "gears and wheels"



# Example: Bioenergetics Coupled to Biosynthesis

Bioenergetics (LEFT: degradation of food) **coupled** to Biosynthesis (RIGHT: linking amino acids)

Low entropy  
High free energy



# The Gears of Biosynthesis

Let's first look at some of the “gears” of Biosynthesis (RIGHT)



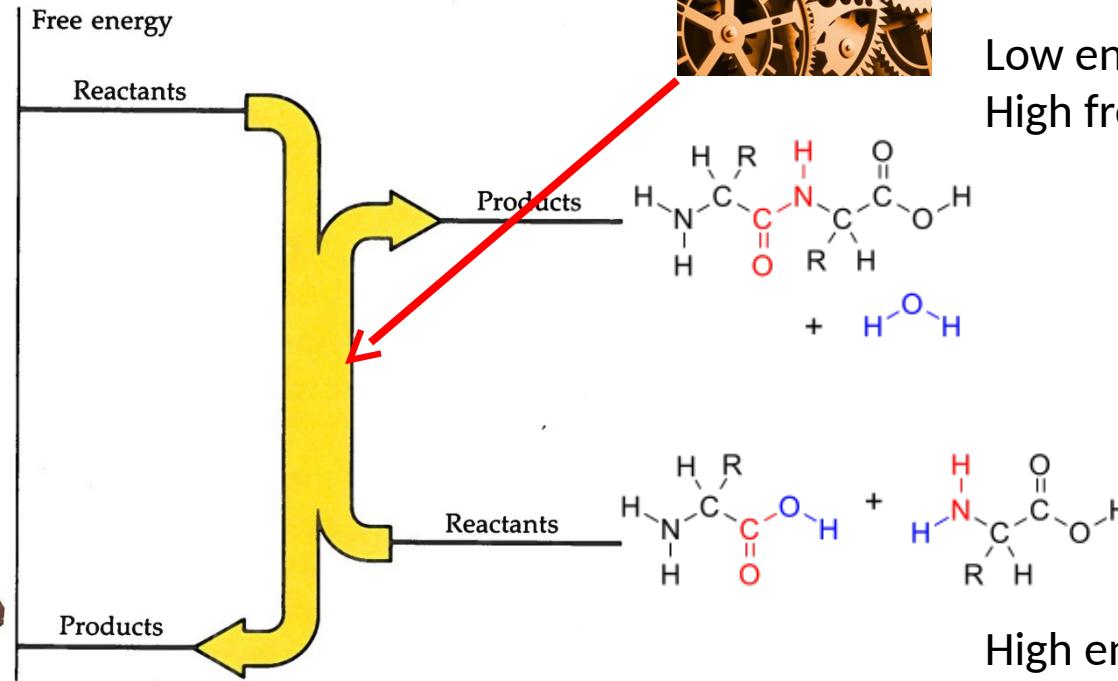
Low entropy  
High free energy



Low entropy  
High free energy

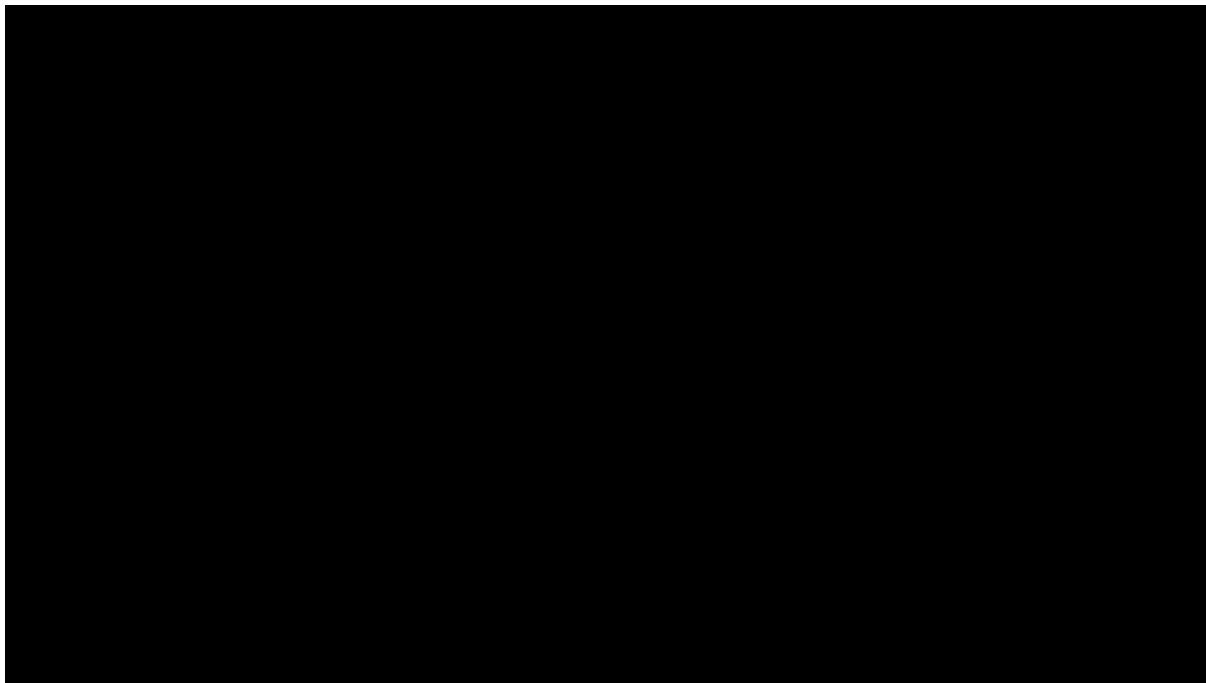


High entropy  
Low free energy



# The Gears of Biosynthesis

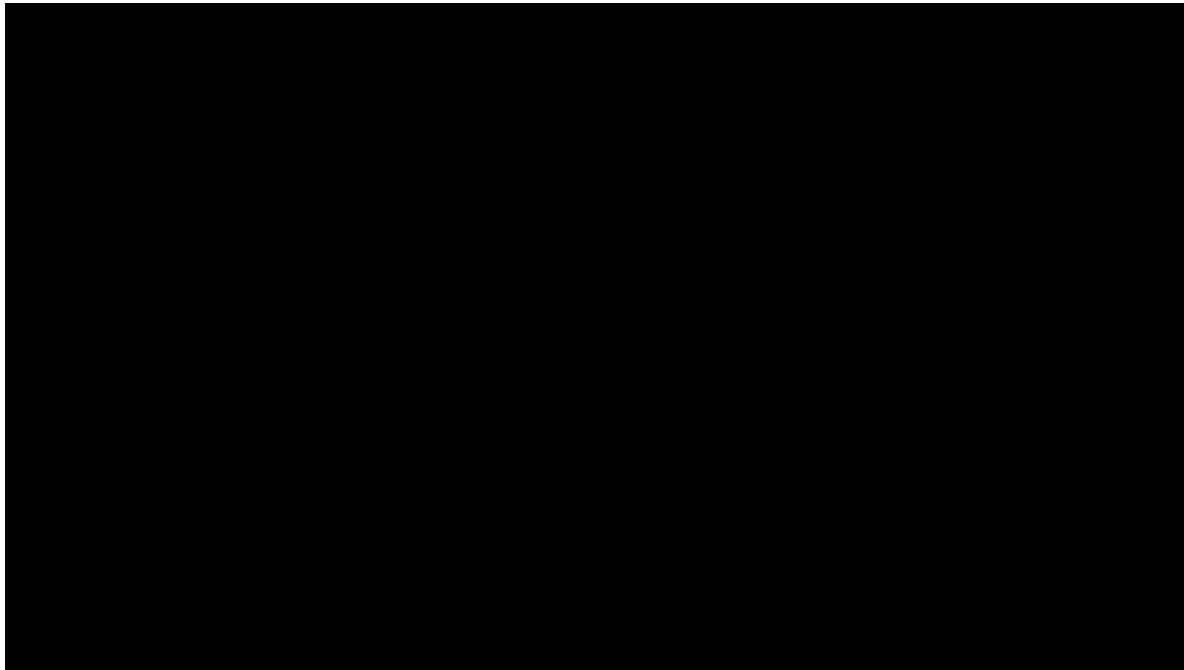
**It's complicated...**



<https://www.youtube.com/watch?v=gG7uCskUOrA>

# The Gears of Biosynthesis

**It's complicated...**



<https://www.youtube.com/watch?v=WFCvkDSfIU>

# The Gears of Biosynthesis

**It's complicated...**

**Other similar animations, emphasizing different aspects:**

<https://www.youtube.com/watch?v=D3fOXt4MrOM>

<https://www.youtube.com/watch?v=lpb5s2F1pyM>

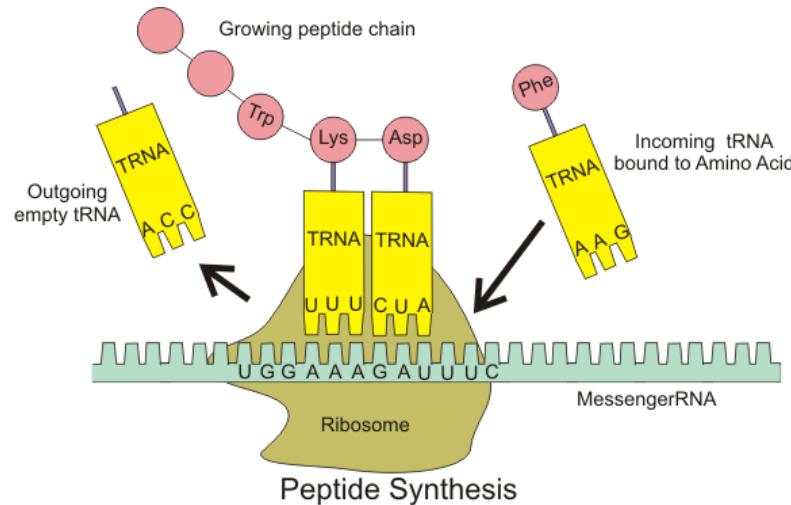
<https://www.youtube.com/watch?v=28mgfg8nRT4>

<https://www.youtube.com/watch?v=JX2MdZX6Bys>

[https://www.youtube.com/watch?v=B\\_zD3NxSsD8](https://www.youtube.com/watch?v=B_zD3NxSsD8)

# The Gears of Biosynthesis

The “gears” of biosynthesis are **highly complex, microscopic machines!**



**How could they possibly arise spontaneously?**

We'll return to this question later...

First we'll look at some “gears” (microscopic machines) of bioenergetics

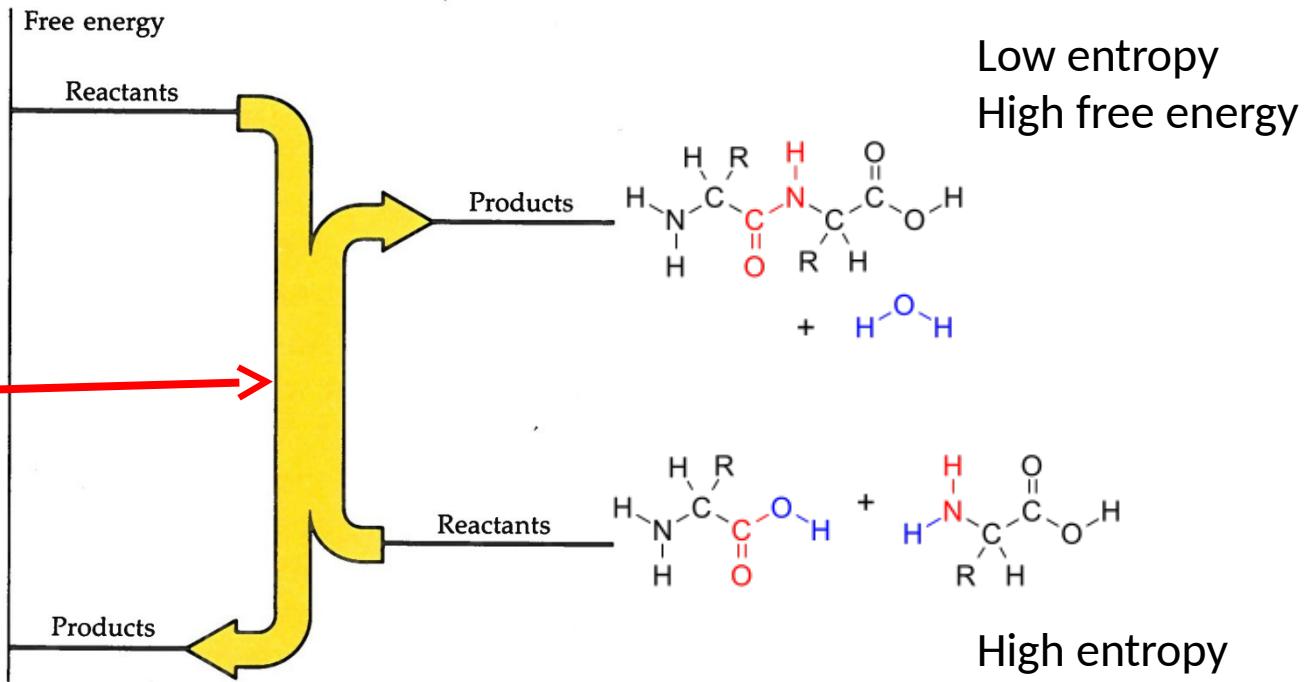
# The Gears of Bioenergetics

Let's now look at some of the "gears" of Bioenergetics (LEFT)

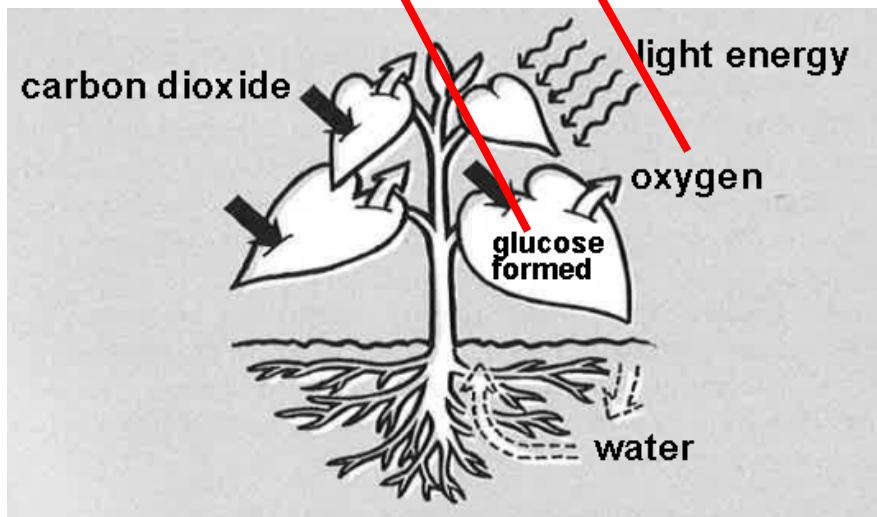
Low entropy  
High free energy



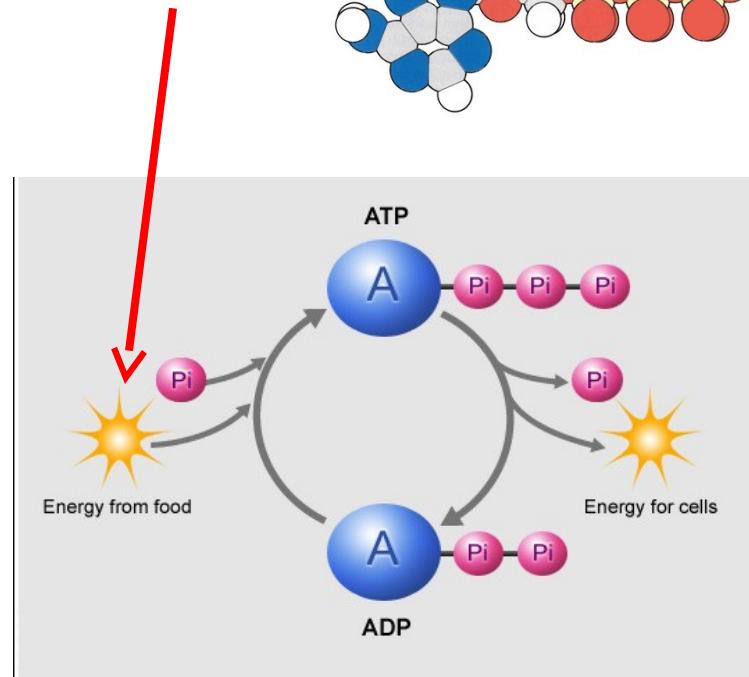
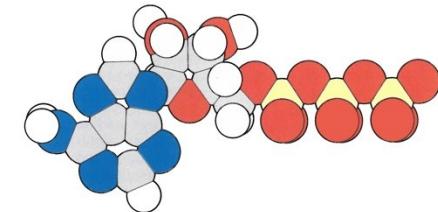
High entropy  
Low free energy



# The Gears of Bioenergetics

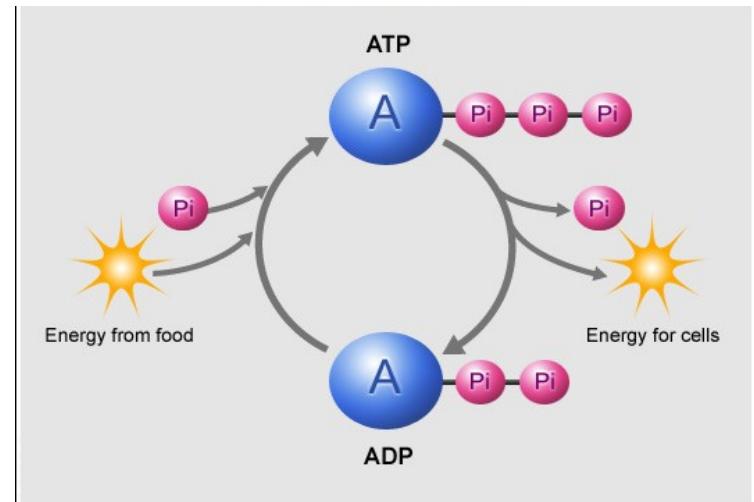
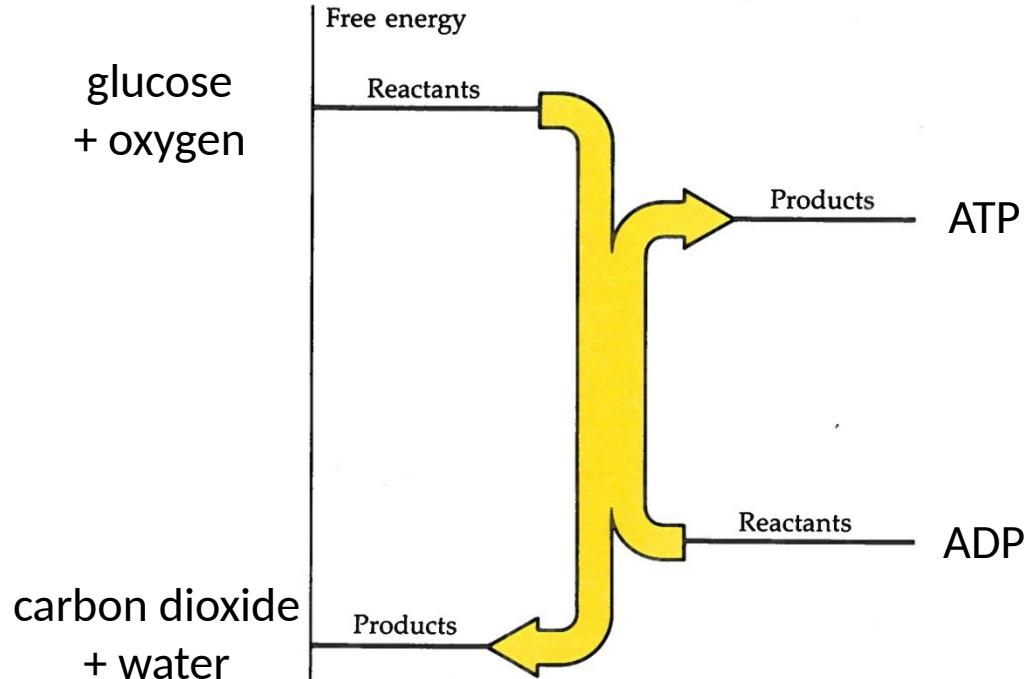


photosynthesis (more later...)



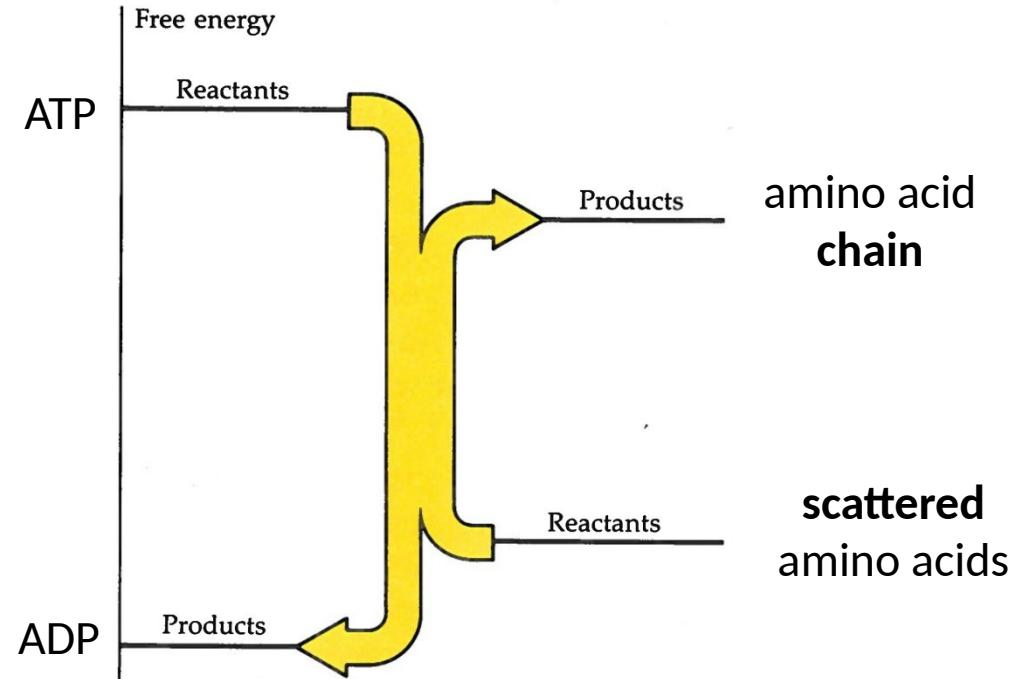
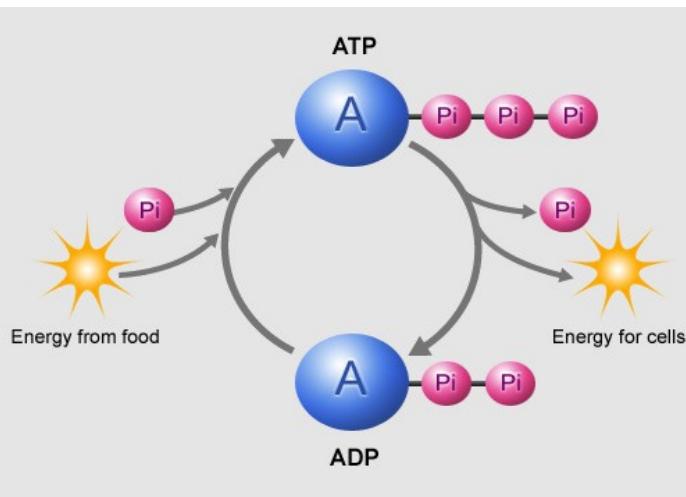
adenosine diphosphate  $\rightleftharpoons$  triphosphate ( $\text{PO}_4$ )

# The Gears of Bioenergetics



This is a **spontaneous** process that increases the entropy of the universe

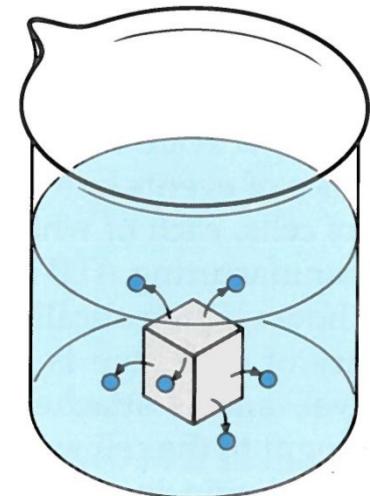
# The Gears of Bioenergetics



This is a **spontaneous** process that increases the entropy of the universe

# The Gears of Bioenergetics

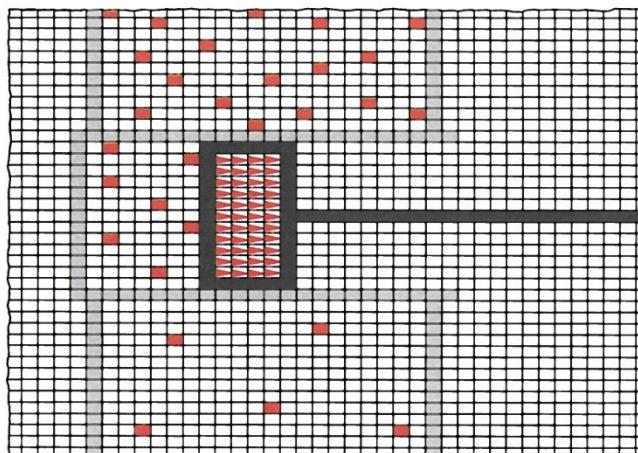
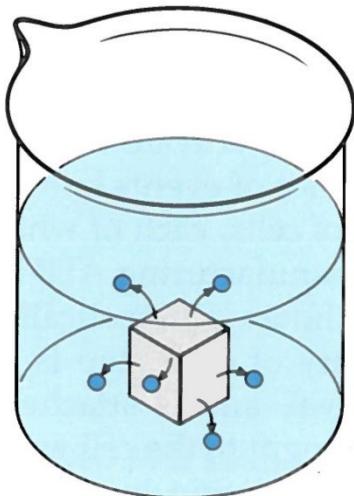
- ADP & ATP are the **life blood of bioenergetics**
- The energetic “charging” of ADP to ATP is done by an **electrochemical battery**
- **Example** of electrochemical battery:
  - ✓ Drop a cube of **iron** (Fe) into a **copper** (Cu) sulfate solution
  - ✓ The **Cu<sup>2+</sup> ions** in the water have a **strong affinity** for electrons
  - ✓ When they touch the cube, the **Fe atoms** give up 2 electrons to the **Cu<sup>2+</sup> ions**. The Fe atoms become **Fe<sup>2+</sup> ions** in solution, & the Cu<sup>2+</sup> ions become neutral **Cu atoms** that deposit on the cube
  - ✓ **Net result:** the **copper precipitates** and the **iron dissolves**



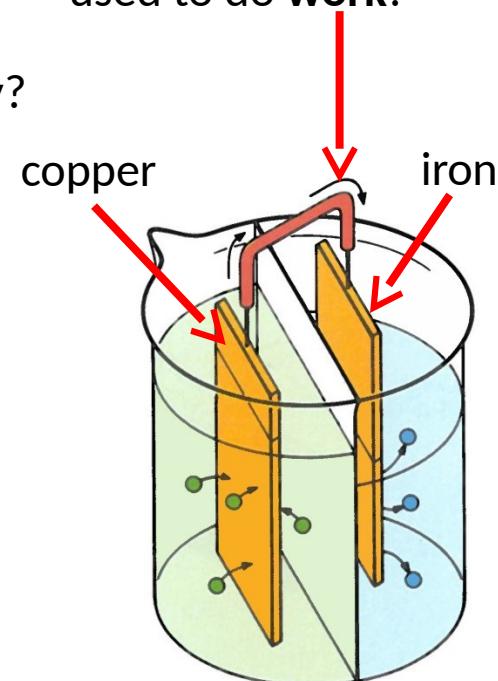
# The Gears of Bioenergetics

- Key Idea:

- ✓ As it stands, the **spontaneous flow** of electrons from the **Fe atoms** to the **Cu<sup>2+</sup> ions** is in **random directions**.
- ✓ What if we force the electrons to flow in **one direction only**?  
(Exactly like we extracted **ordered KE** in the heat engine!)



Electric current (opposite electron flow) can be used to do **work!**

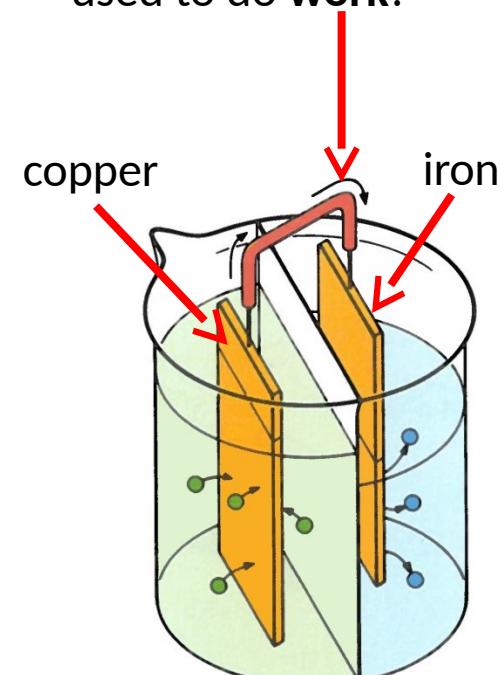


# The Gears of Bioenergetics

- **Aside:**

- ✓ Where does the energy released by such a copper-iron battery actually come from?
- ✓ The nuclear furnaces in long-dead stars, which created the elements heavier than hydrogen, up to iron.
- ✓ Fission reactors today use uranium, which is created when stars explode as supernovae.
- ✓ Fusion reactors being developed today will use hydrogen, which was created by the Big Bang itself. **It is the most ancient (and abundant) of all fossil fuels.**

Electric current (opposite electron flow) can be used to do **work!**



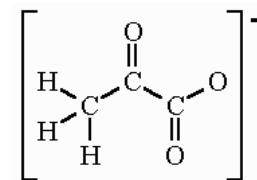
ignoring “salt bridge”...

# The Gears of Bioenergetics

- Nature has evolved a similar battery, in which glucose & oxygen are “burned” to charge ADP to ATP:

✓ Like Cu<sup>2+</sup> ions, **oxygen** has a **strong affinity** for electrons; it likes to become O<sup>2-</sup>

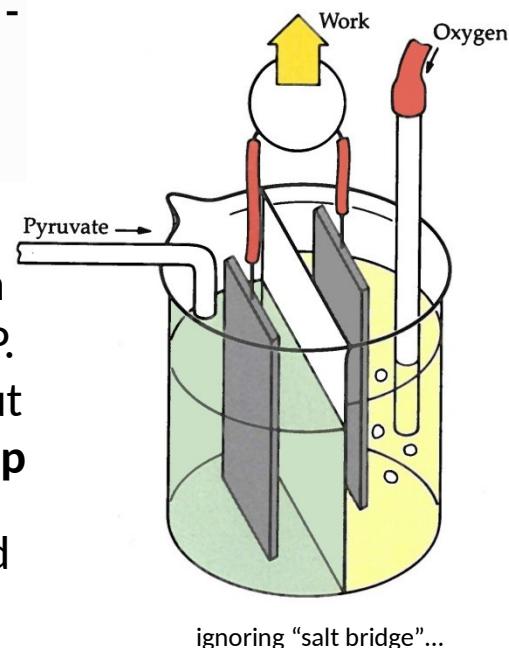
✓ Glucose gets “snipped” into two **pyruvate** ions:  
(which can easily give up their extra electron)  
...and two **protons** (H<sup>+</sup> ions) are produced



✓ The **spontaneous flow** of electrons from pyruvate to oxygen (the “burning of sugar”) does the work to charge ADP to ATP. The ATP have higher order (**lower entropy**) than the ADP, but with everything else, the **net entropy** of the universe **goes up**

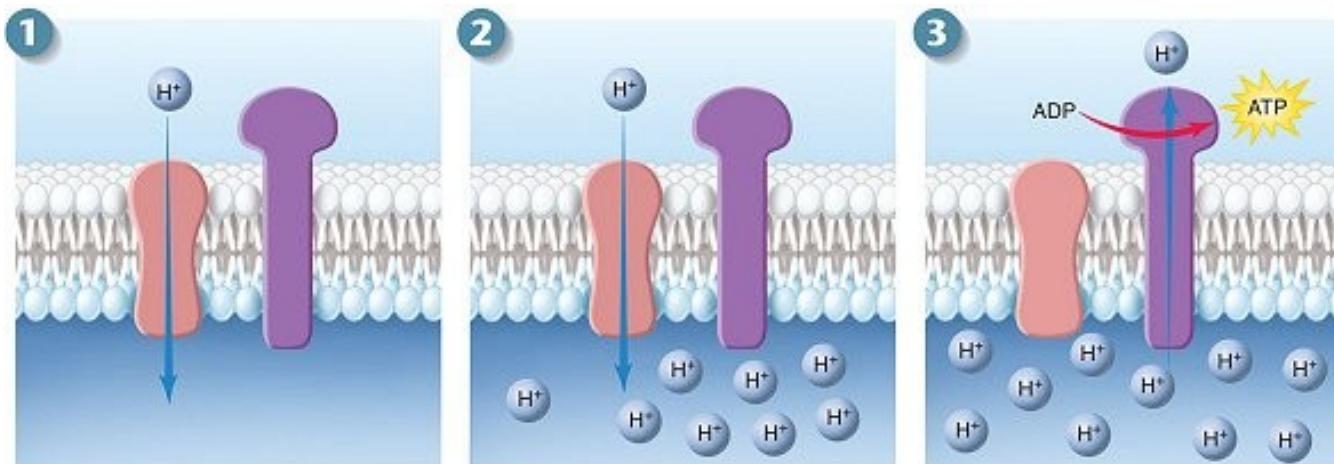
✓ The pyruvate falls apart into carbon dioxide (we exhale), and each O<sup>2-</sup> picks up two **protons** to become water...

IA		IIA		IVA		VIA		VIIA		0	
13	14	15	16	17	18	19	20	21	22	23	24
Boron 10.811	Carbon 12.011	Nitrogen 14.007	Oxygen 15.999	Fluorine 18.998	Neon 20.180						
Aluminum 13.00	Silicon 14.00	Phosphorus 15.00	Sulfur 16.00	Chlorine 17.00	Argon 18.00						



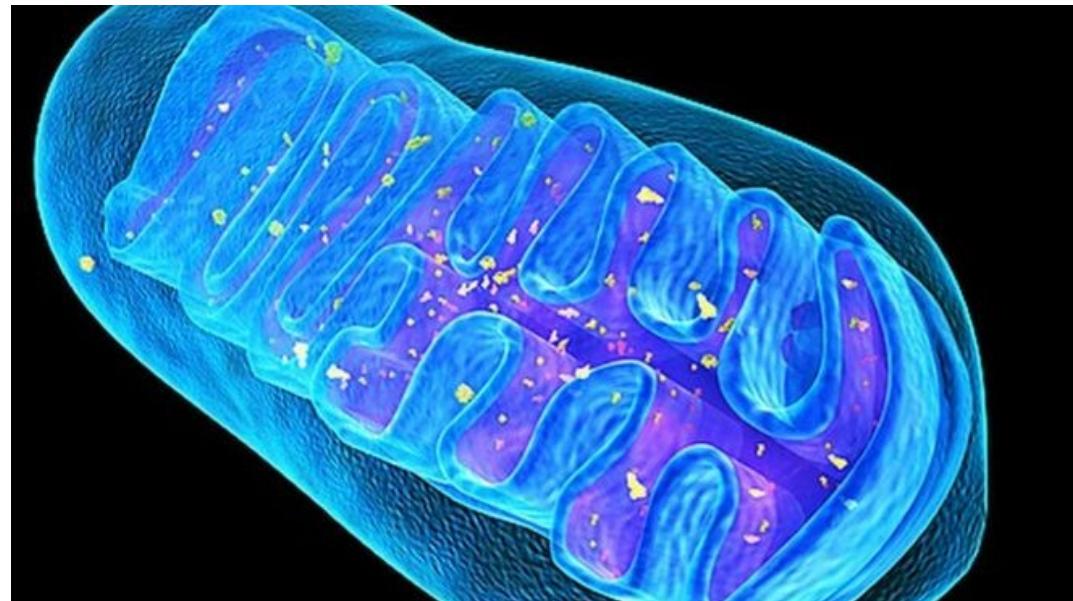
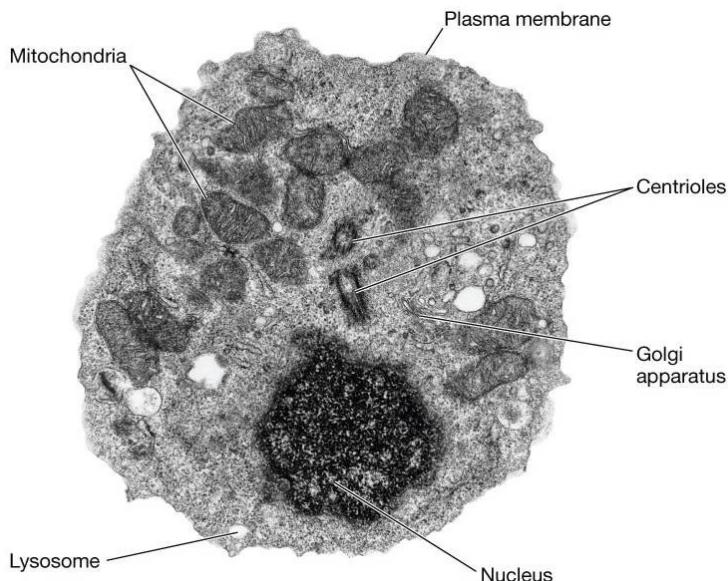
# The Proton Gradient

- The **spontaneous flow** of electrons **does not directly** charge the ADP to ATP. Instead:
  1. It drives a **proton pump** that forces protons across a membrane
  2. This creates a **proton gradient** that stores potential energy across the membrane (in an **electric field**).
  3. This **store of energy** can be tapped by allowing protons to flow back across the membrane through a protein called **ATP synthase**. The **electric field accelerates the protons**, and this extra **kinetic energy** is used to charge ADP to ATP.



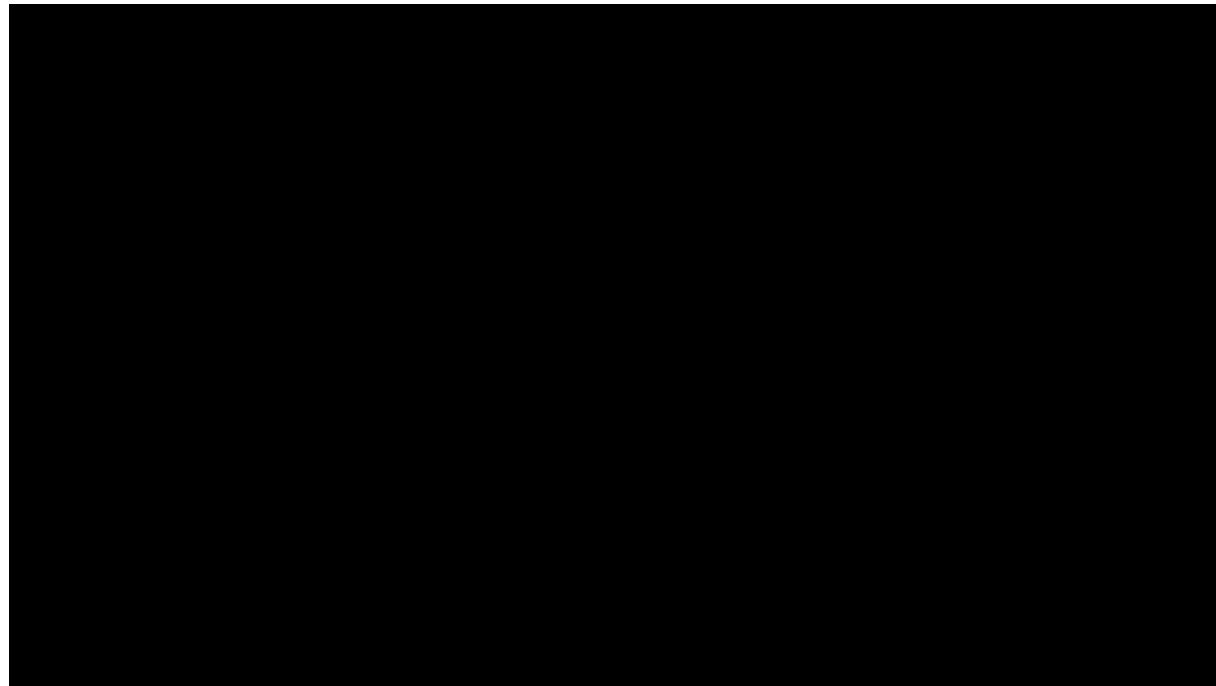
# The Proton Gradient

- All of this takes place in **mitochondria** inside cells:



# The Proton Gradient

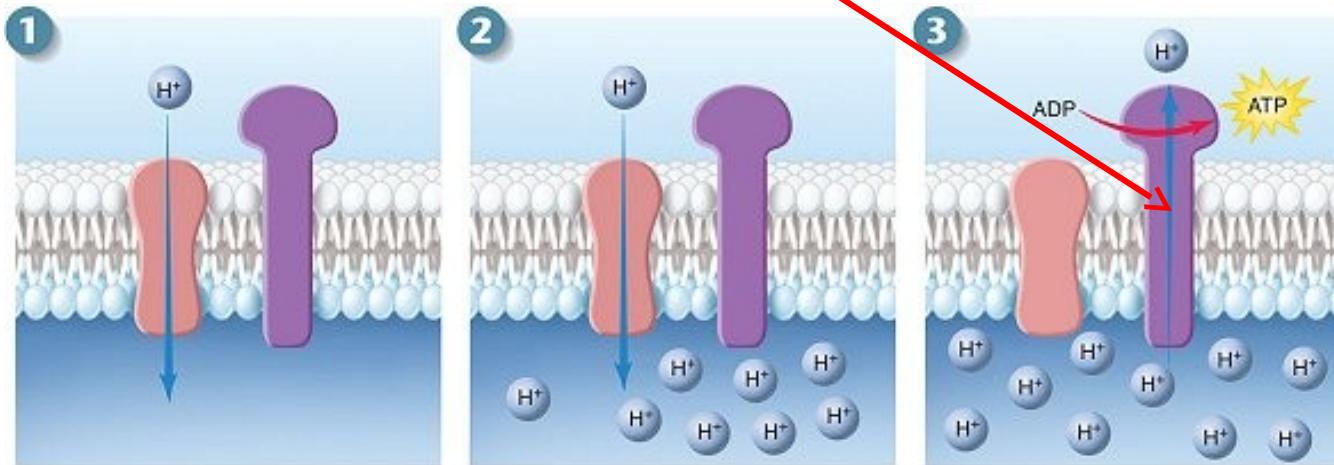
- All of this takes place in **mitochondria** inside cells:



<https://www.youtube.com/watch?v=nD9fyuisMkg>

# The Proton Gradient

- Let's look at how **ATP synthase** actually works...

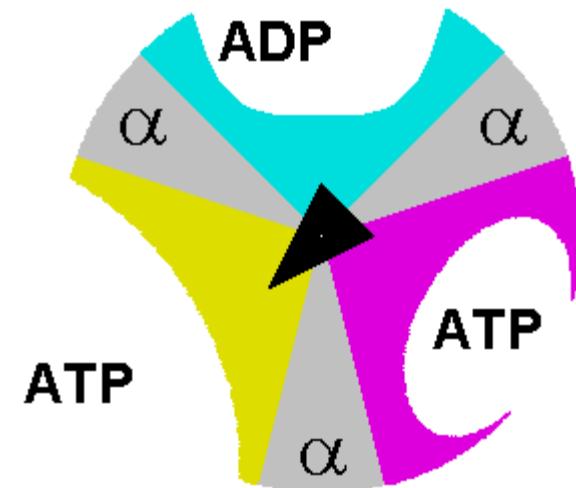
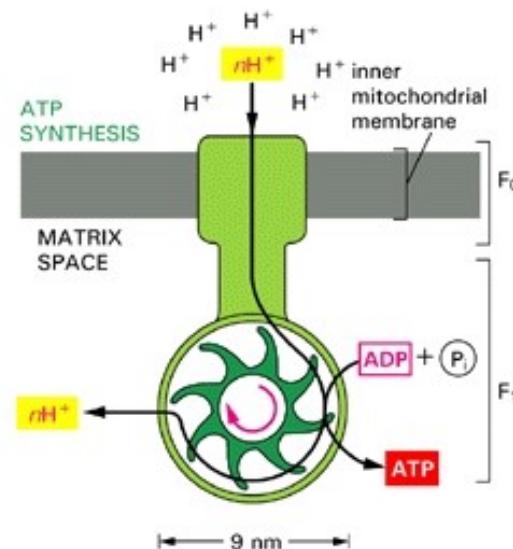


# The Proton Gradient

The **proton gradient** creates an **electric field** that **accelerates** the protons let back across the membrane.

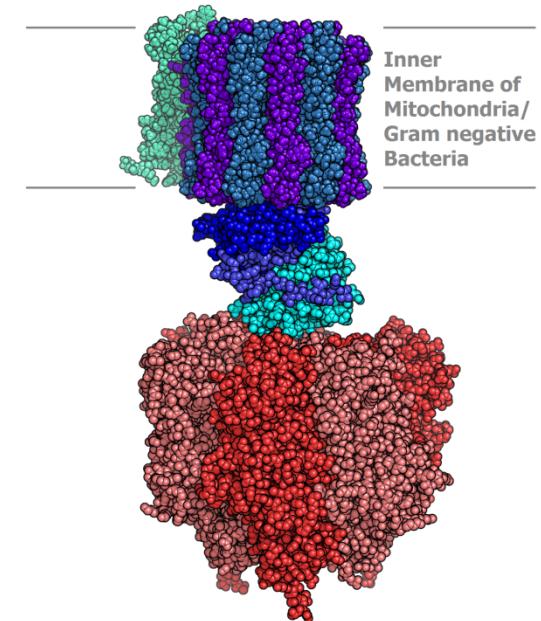
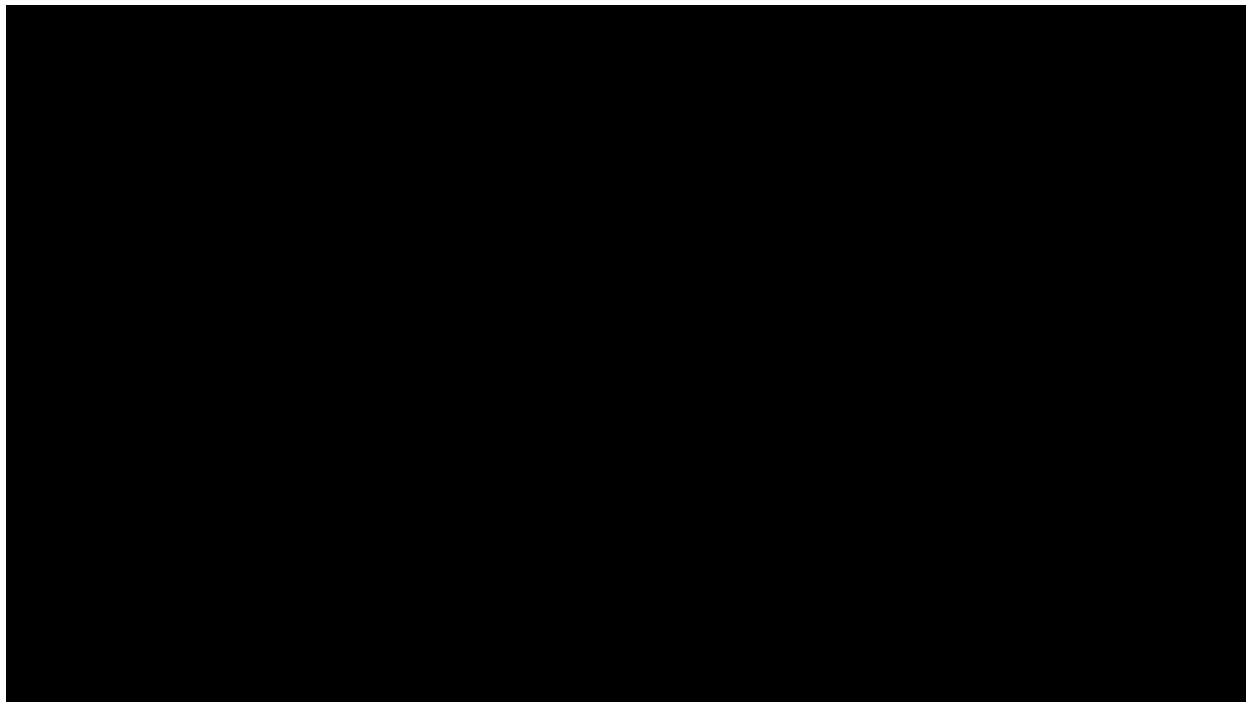
These accelerated protons push on a **rotary mechanical motor**, which converts ADP to ATP (it's a **physical machine**, not what one usually thinks of as "chemistry"!)

About 3 protons need to pass through to charge one ATP (100 charges per second).



# The Proton Gradient

- The ATP synthase machine:



<https://www.youtube.com/watch?v=XI8m6o0gXDY>

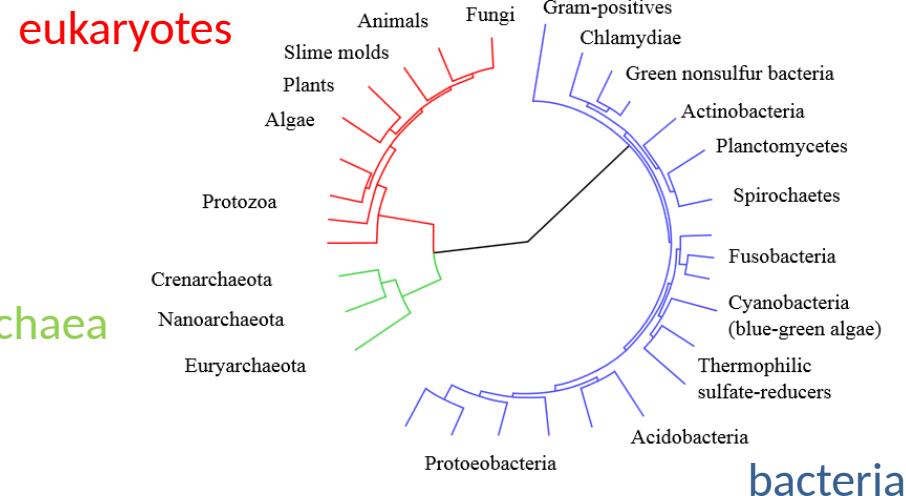
**intelligent design?**

# The Proton Gradient

**proton gradient...so what?**

# The Proton Gradient

- Today, **all** energy that living organisms use ultimately comes from **generating and tapping a proton (or other ion) gradient**.
- It is the **universal “battery” that powers all life on Earth**, as universal as the genetic code itself. Thus, it is an important clue to the **origin of life**.
- For example, the **ATP synthase** (the machine that **taps** energy from the gradient) is as **universal** as the **ribosome** (the protein synthesis machine), and it displays the same deep “phylogenetic” split between archaea and bacteria ⇒ **it was present in the last universal common ancestor (LUCA)**, and must have “evolved” prior to this. (How? More later...)

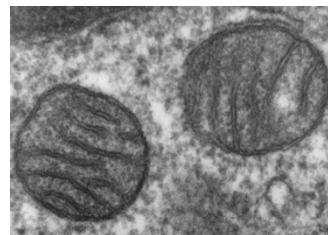


# The Proton Gradient

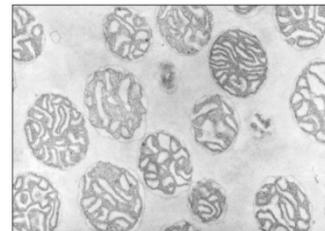
- In eukaryotes (like us), this proton gradient “battery” is inside **mitochondria**. The mitochondria across all eukaryotes have the **same general structure** (see pictures)
- These bacteria-sized organelles may have originally been **aerobic bacteria** that **invaded and colonized** early eukaryotic cells (they have an independent bacteria-like genome!)



examples of eukaryotes



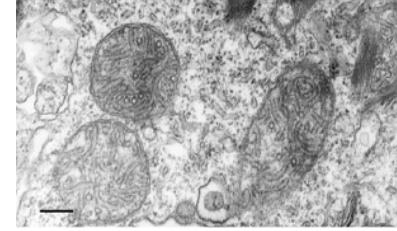
mammalian lung



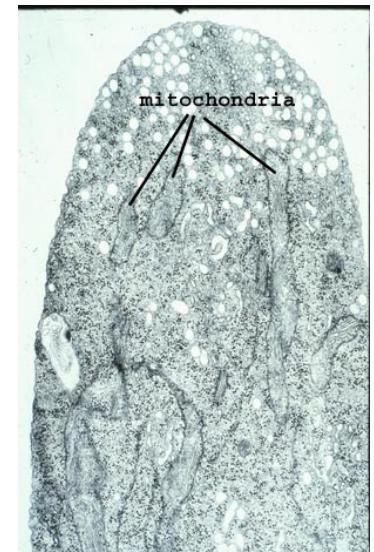
mung bean



bat pancreas



paramecium



fungus

# The Proton Gradient

- Okay, so ion gradients are the universal battery of life. But this raises a **severe evolutionary chicken-and-egg problem:**
  - ✓ Proteins are used to generate and tap ion gradients (e.g., the ATP synthase is used to tap the proton gradient and convert ADP to ATP)
  - ✓ But **energy** is needed to build proteins (like ATP synthase) in the first place (protein synthesis consumes 75% of a cell's ATP budget)

**Proteins are required to generate energy, but energy is needed to build those proteins.** So

- *where did the energy come from that built the first proteins?*
  - This has long been a **deep mystery**, but recently progress has been made: **Naturally occurring** proton gradients at **deep-sea hydrothermal vents** have been shown to **spontaneously synthesize amino acids** (building blocks of proteins) and **nucleotides** (building blocks of RNA & DNA), and may have been the **initial spark of life**. **We are one step closer to understanding how it *might* have been possible for rocks to “come to life”!**

# The Proton Gradient

- See: The Origin of Membrane Bioenergetics (Lane & Martin 2012).  
Also: [Nature News](#). Martin: “There are lots of theories [of the origin of life] but ours is the first to **start with the cell.**” (Most scientists assume that **self-replicating molecules** or proteins came first.)
- Rocks of deep-sea thermal vents contain labyrinths of tiny thin-walled pores, which could have acted as ‘**proto-cells**’, the first life-forms:
  - ✓ **(CO<sub>2</sub>- and H<sup>+</sup>-rich) acidic** ocean water on the outside and **(H<sub>2</sub>- and OH<sup>-</sup>-rich) alkaline** vent water on the inside, separated by a thin mineral (iron sulfide, FeS) wall, sets up a natural proton gradient of magnitude & orientation used by modern cells;
  - ✓ Powered by the proton gradient, the FeS wall can **catalyse** conversion of **CO<sub>2</sub>** and **H<sub>2</sub>** into organic carbon-containing molecules, and **concentrate** them inside, enabling them eventually to generate **genes, proteins and a proto-membrane**.

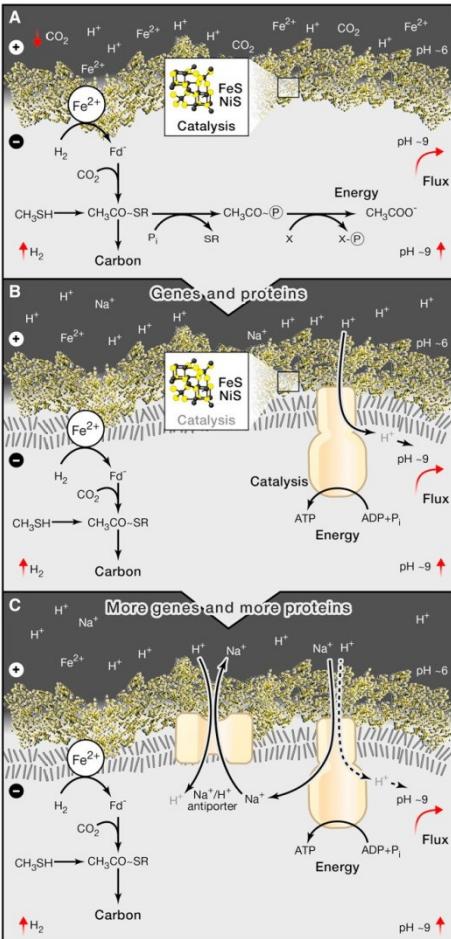


Iron sulphide (FeS) honeycomb: “a fertile environment.”

# The Proton Gradient

Some details are shown in diagrams A and B:

- A. In the presence of the proton gradient, **catalysis** catalyzes  $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{Carbon Energy} (\text{CH}_3\text{COO}^-)$  (glucose). Note! Modern microbacteria near vents, that similarly live off  $\text{CO}_2$  and  $\text{H}_2$ , use enzymes (protein catalysts) also based on FeS and Fe(Ni)S (a hint this may be right...) catalysts) also based on FeS and Fe(Ni)S (a hint this may be right...)
- B. The carbon, plus this relatively **low entropy** energy inside the proto-cell, allows the formation of **complex** organic carbon structures like amino acids, RNA bases, sugars, lipids, and possibly (?) even **ATP synthase** (a very efficient coupling to the proton gradient).  
[Note that the  $\text{H}^+$  (acid) passing through the ATP synthase is neutralized by continuous supply of  $\text{OH}^-$  (base) in the vent water.]



The proto-cell evolves towards **ever more efficient** coupling to the proton gradient, since this increases the rate at which energy is dissipated (and the universe moves to a state of **higher entropy**).  
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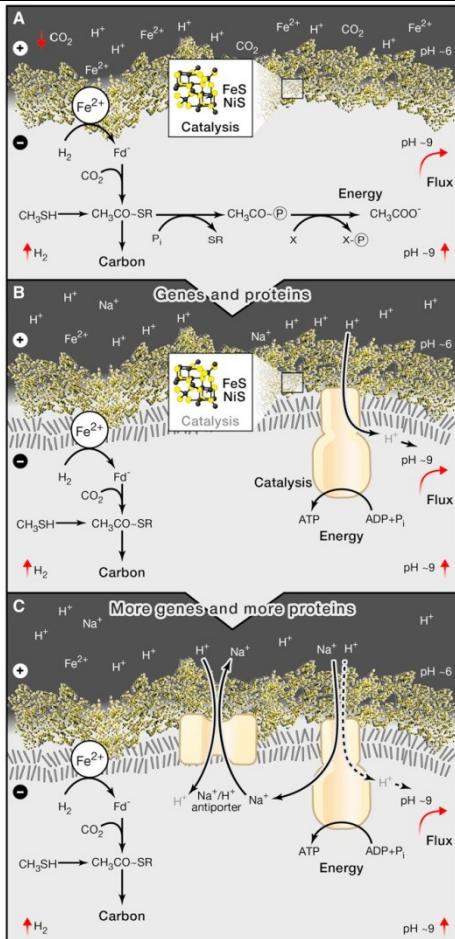
# The Proton Gradient

Such proto-cells could **tap** the naturally occurring proton gradient, but how could they evolve to **generate** their own gradient, and become **free-living** cells, floating around in the ocean?

Three things would be needed:

- ✓ A completely sealed **organic cell wall** (to replace the FeS rock wall)
- ✓ A **proton pump** (to pump out the protons that enter through the ATP synthase, which are no longer neutralized by vent water  $\text{OH}^-$ )
- ✓ An **energy source** to drive the pump

**Idea:** The FeS wall was **leaky** to  $\text{H}^+$ , reducing efficiency. Lipids (fats) may have naturally formed an organic cell wall (more later...), which would help reduce the leakiness, and would **improve efficiency**.



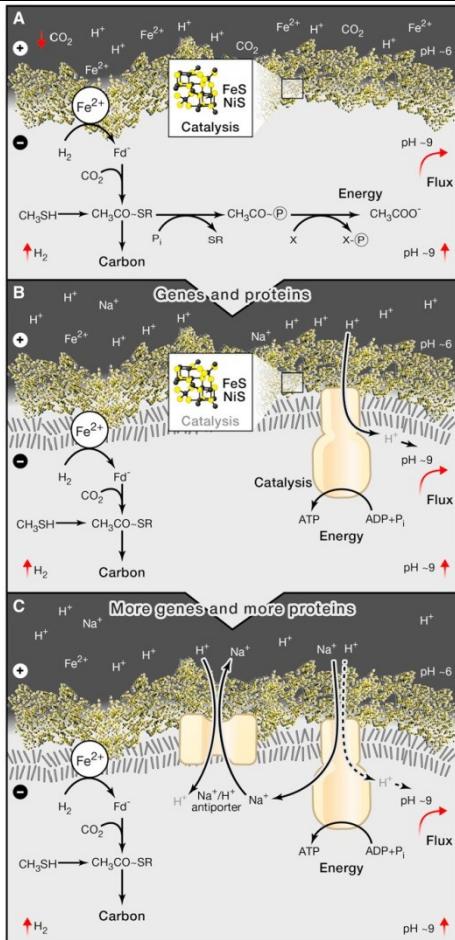
# The Proton Gradient

Assuming the evolving organic cell wall tightened up slowly: was **first** impermeable to **large** ions like  $\text{Na}^+$ , then to **small** ions like  $\text{H}^+$  (protons)...

C. ...there would have been a long transition time during which a  $\text{Na}^+$  gradient would have been **more efficient** than a  $\text{H}^+$  gradient. This could explain **why** modern vent microbes have a very simple  $\text{Na}^+/\text{H}^+$  “**antiporter**”, which runs for **free**, converting  **$\text{H}^+$  bioenergetics** to  **$\text{Na}^+$  bioenergetics**. In such a transition-stage proto-cell, the natural proton gradient is still used ( $\text{H}^+$  passing through the antiporter is still neutralized by the continuous supply of  $\text{OH}^-$  in the vent water).

This suggests a **plausible** path to an **organic cell wall** and a  $\text{Na}^+$  pump. What **drives** it? Just switch from proton gradient to **energy from metabolizing  $\text{CO}_2 + \text{H}_2$** . The newly “living” cell could then detach from the rock and become a free-living cell floating in the ocean.

Many details are **still mysterious**, but we are **one step closer!**



# Summary

## Summary:

- We **may never be certain** how life on Earth began. The further back we push the question, the less direct evidence survives.
- Nevertheless, scientists are making **stunning progress** towards a variety of possible/plausible ways that life **may** have begun.
- But we still have a long way to go, which is good in the sense that **science thrives on mystery**, and **dies as knowledge becomes complete**.