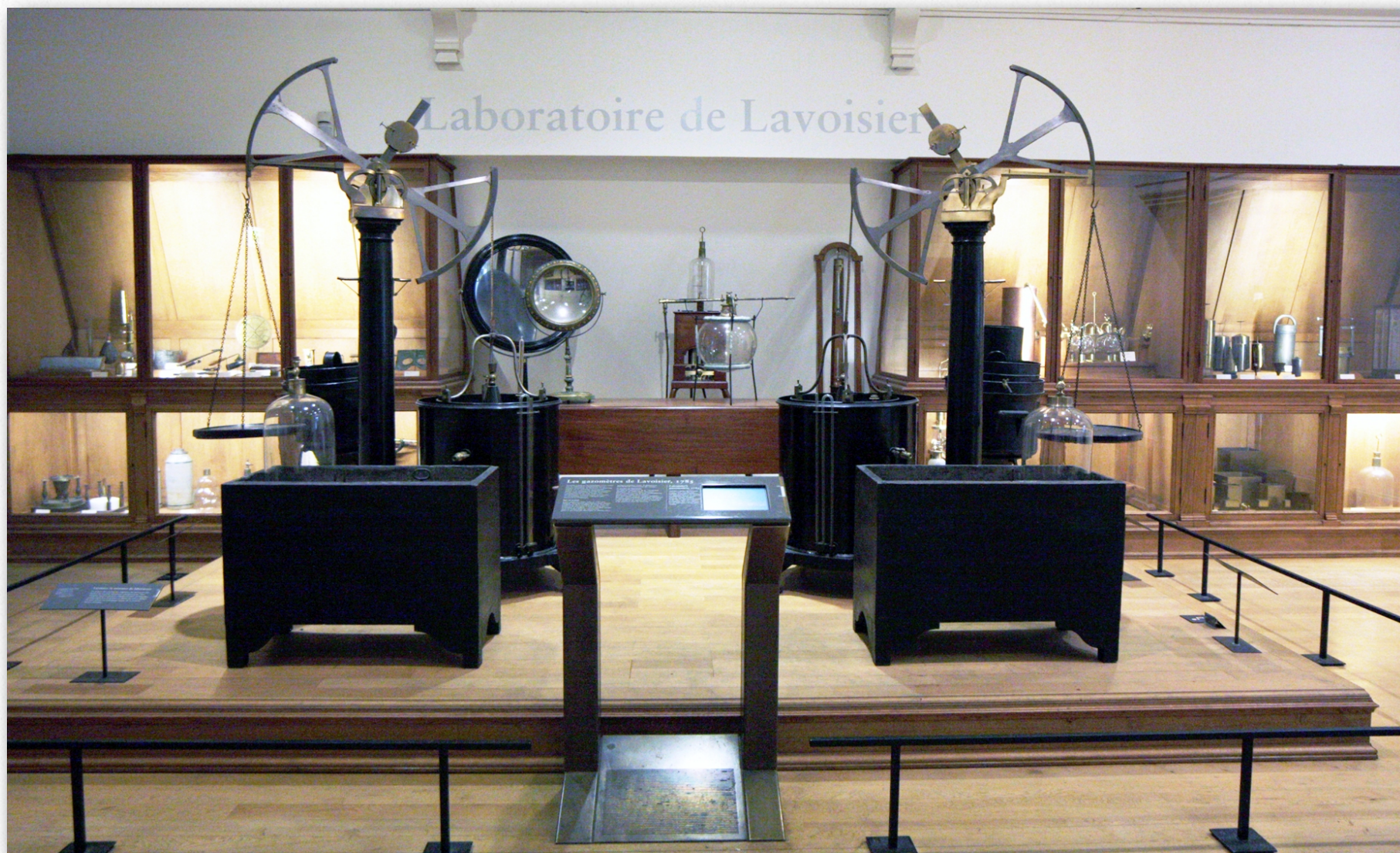


Introduction: Basic Chemistry



Certain chemistry

"Organic chemistry is the chemistry of carbon compounds. Biochemistry is the chemistry of carbon compounds that crawl"

-Michael Adams.

To understand biochemistry, one must possess at least a basic understanding of organic and general chemistry. In this brief section, we will provide a rapid review of the simple concepts necessary to understand cellu-

lar chemistry. Chemistry is chemistry, whether in a cell or outside it, but biological chemistry is a particular subset of organic chemistry that often involves enormous macromolecules, and that happens in the aqueous environment of the cell.

Figure 1.18 shows the various organic functional groups common in biochemistry. You will encounter these functional groups as you study the biosynthetic and breakdown pathways that build and recycle the

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chemical compounds of which cells are made. In addition to knowing the names and struc-

tures of these groups, students need a basic understanding of covalent and ionic bonds.

Class	General Structure	Name	Functional Group
Alkenes	$RCH=CHR$	Double Bond	$C=C$
Alcohols	ROH	Hydroxyl	$-OH$
Ethers	ROR	Ether	$-O-$
Amines	RNH_2 R_2NH R_3N	Amino	$-N$ (with two bonds)
Thiols	RSH	Sulfhydryl	$-SH$
Aldehydes	$R-\overset{\overset{O}{\parallel}}{C}-H$	Carbonyl	$-\overset{\overset{O}{\parallel}}{C}-$
Ketones	$R-\overset{\overset{O}{\parallel}}{C}-R$	Carbonyl	$-\overset{\overset{O}{\parallel}}{C}-$
Carboxylic Acids	$R-\overset{\overset{O}{\parallel}}{C}-OH$	Carboxyl	$-\overset{\overset{O}{\parallel}}{C}-OH$
Amides	$R-\overset{\overset{O}{\parallel}}{C}-NR_2$	Amide	$-\overset{\overset{O}{\parallel}}{C}-N$ (with two bonds)
Esters	$R-\overset{\overset{O}{\parallel}}{C}-OR'$	Ester	$-\overset{\overset{O}{\parallel}}{C}-OR$
Phosphoric Acid Esters	$R-O-\overset{\overset{O}{\parallel}}{P}(OH)_2$	Phosphoric Ester	$-O-\overset{\overset{O}{\parallel}}{P}(OH)_2$
Phosphoric Acid Anhydrides	$R-C-\overset{\overset{O}{\parallel}}{P}(OH)_2-O-\overset{\overset{O}{\parallel}}{P}(OH)_2$	Phosphoric Anhydride	$-\overset{\overset{O}{\parallel}}{P}(OH)_2-O-\overset{\overset{O}{\parallel}}{P}(OH)_2-$

Figure 1.18 - Important functional groups in biochemistry

Image by Aleia Kim

Covalent bonds, as you know, are the result of sharing of electrons between two atoms. Ionic bonds, by contrast, are formed when one atom donates an electron to another, such as in the formation of sodium chloride.

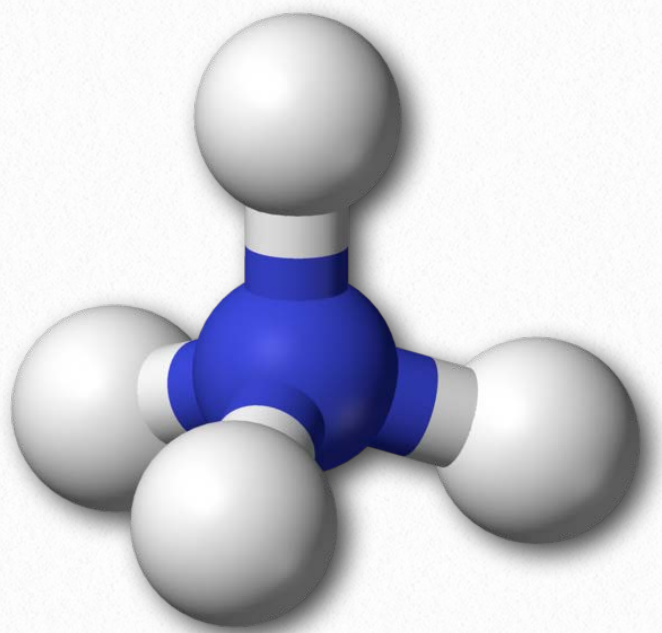


Figure 1.19 - Tetrahedral structure
Wikipedia

Single covalent bonds can rotate freely, but double bonds cannot. Single bonds around a carbon atom are arranged in a tetrahedron with bond angles of 109.5° relative to each other, with the carbon at the center (Figure 1.19). Double bonded carbons create a planar structure with bond angles typically of about 120° .

Electronegativity

Electronegativity is a measure of the affinity a nucleus has for outer shell electrons (Table 1.2). High electronegativity corresponds to high affinity. Elec-

trons in a covalent bond are held closer to the nucleus with a greater electronegativity compared to a nucleus with lower electronegativity.

For example, in a molecule of water, with hydrogen covalently bonded to oxygen, the electrons are “pulled” toward the oxygen, which is more electronegative. Because of this, there is a slightly greater negative charge near the oxygen atom of water, compared to the hydrogen (which, correspondingly has a slightly higher positive charge). This unequal charge distribution sets up a dipole, with one side being somewhat negative and the other somewhat positive. Because of this, the molecule is described as polar.

Hydrogen bonds between water molecules are the result of the attraction of the partial positive and partial negative charges on different water molecules (Figure 1.20). Hydrogen bonds can also form between hydrogens

Table 1.2
Electronegativities of Various Atoms

Atom	Electronegativity
Oxygen	3.5
Nitrogen	3.0
Sulfur	2.6
Carbon	2.5
Phosphorous	2.2
Hydrogen	2.1

Image by Aleia Kim

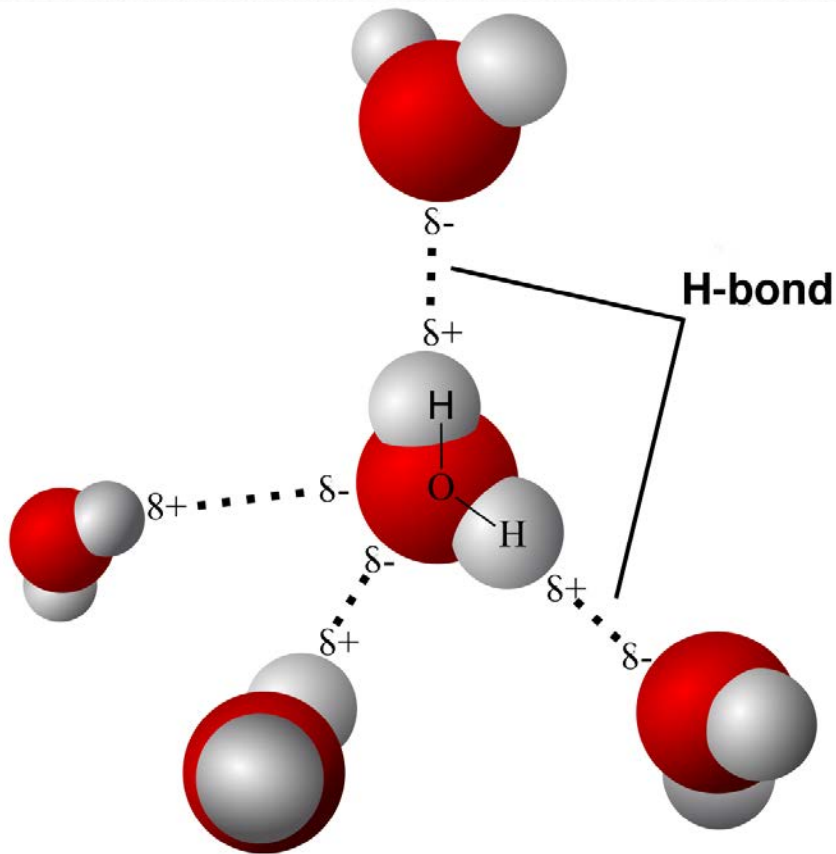


Figure 1.20 Hydrogen bonds (dotted lines) between water molecules

Wikipedia

with a partial positive charge and other strongly electronegative atoms, like nitrogen, with a partial negative charge. It is important to remember that hydrogen bonds are interactions between molecules (or parts of molecules) and are not bonds between atoms, like covalent or ionic bonds.

Bonds between hydrogen and carbon do not form significant partial charges because the electronegativities of the two atoms are similar. Consequently, molecules containing many carbon-hydrogen bonds will not form hydrogen bonds and therefore, do not mix well with water. Such molecules are called hydrophobic. Other compounds with the ability to make hydrogen bonds are polar and

can dissolve in water. They are called hydrophilic. Molecules possessing both characteristics are called amphiphilic.

Weak interactions

Hydrogen bonds are one kind of electrostatic (i.e., based on charge) interaction between dipoles. Other forms of electrostatic interactions that are important in biochemistry include weak interactions between a polar molecule and a transient dipole, or between two temporary dipoles. These temporary dipoles result from the movement of electrons in a molecule. As electrons move around, the place where they are, at a given time, becomes temporarily more negatively charged and could now attract a temporary positive charge on another molecule. Since electrons don't stay put, these dipoles are very short-lived.

Thus, the attraction that depends on these dipoles fluctuates and is very weak. Weak interactions like these are sometimes called van der Waals forces. Many molecular interactions in cells depend on weak interactions. Although the individual hydrogen bonds or other dipole-dipole interactions are weak, because of their large numbers, they can result in quite strong interactions between molecules.

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Oxidation/reduction

Oxidation involves loss of electrons and reduction results in gain of electrons. For

every biological oxidation, there is a corresponding reduction - one molecule loses electrons to another molecule. Oxidation reactions tend to release energy and are a source of bioenergy for chemotrophic cells.

Ionization

Ionization of biomolecules, by contrast does not involve oxidation/reduction. In ionization, a hydrogen ion (H^+) leaves behind its electron as it exits (leaving behind a negative charge) or joins a group (adding a positive charge). Biological ionizations typically involve carboxyl groups or amines, though phosphates or sulfates can also be ionized. A carboxyl group can have two ionization states - a charge of -1 corresponds to the carboxyl without its proton and a charge of zero corresponds to the charge of the carboxyl with its proton on. An amine also has two ionization states. A charge of zero corresponds to a nitrogen with three covalent bonds (usually in the form of $C-NH_2$) and a charge of +1 corresponds to a nitrogen making four covalent bonds (usually $X-NH_3^+$).

Stereochemistry

A carbon has the ability to make four single bonds (forming a tetrahedral structure) and if it bonds to four different chemical groups, their atoms can be arranged around the carbon in two different ways, giving rise to stereochemical "handedness" (Figure

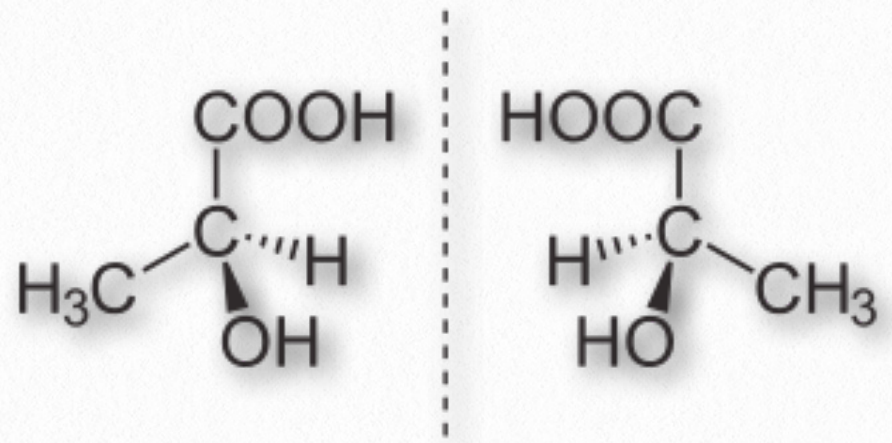


Figure 1.21 - Mirror images of lactic acid

1.21). Each carbon with such a property is referred to as an asymmetric center. The property of handedness *only* occurs when a carbon has four different groups bonded to it. Enzymes have very specific 3-D structures, so for biological molecules that can exist in different stereoisomeric forms, an enzyme that synthesizes it would make only one of the possible isomers. By contrast, the same molecules made chemically (not using enzymes) end up with equal amounts of both isomers, called a racemic mix.

Gibbs free energy

The Gibbs free energy calculation allows us to determine whether a reaction will be spontaneous, by taking into consideration two factors, change in enthalpy (ΔH) and change in entropy (ΔS).

The free energy content of a system is given by the Gibbs free energy (G) and is equal to the enthalpy (H) for a process minus the absolute temperature (T) times the entropy (S)

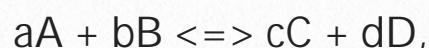
$$G = H - TS$$

For a process, the change in the Gibbs free energy ΔG is given by

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

A ΔG that is negative corresponds to release of free energy. Reactions that release energy are exergonic, whereas those that absorb energy are called endergonic.

The biological standard Gibbs free energy change ($\Delta G^{\circ'}$) corresponds to the ΔG for a process under standard conditions of temperature, pressure, and at pH = 7. For a reaction



the equilibrium constant, K_{eq} is equal to

$$K_{eq} = \frac{[C]^{c_{eq}}[D]^{d_{eq}}}{[A]^{a_{eq}}[B]^{b_{eq}}}$$

where a,b,c,and d are integers in the balanced equation. Large values of K_{eq} correspond to favorable reactions (more C and D produced than A and B) and small values of K_{eq} mean the opposite. At equilibrium,

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

If a process has a $\Delta G = Z$ and a second process has a $\Delta G = Y$, then if the two processes are linked, ΔG and $\Delta G^{\circ'}$ values for the overall reac-

tion will be the sum of the individual ΔG and $\Delta G^{\circ'}$ values.

$$\Delta G_{total} = \Delta G_1 + \Delta G_2 = Z + Y$$

$$\Delta G^{\circ'}_{total} = \Delta G_1^{\circ'} + \Delta G_2^{\circ'}$$

Catalysis

Catalysis is an increase in the rate of a reaction induced by a substance that is, itself, unchanged by the reaction. Because catalysts remain unchanged at the end of a reaction, a sin-

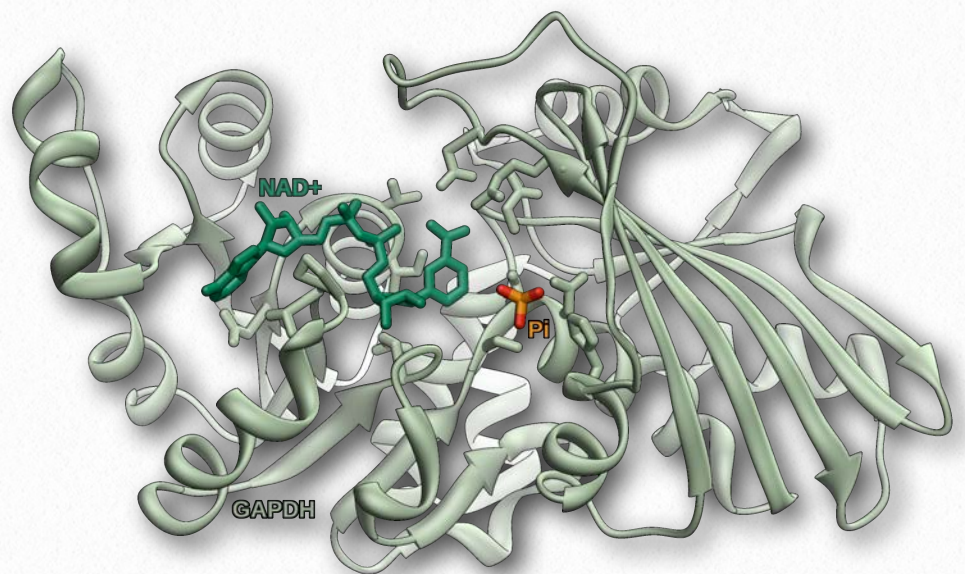


Figure 1.22 - Glyceraldehyde-3-phosphate dehydrogenase in the midst of catalysis

Wikipedia

gle catalyst molecule can be reused for many reaction cycles. Proteins that catalyze reactions in cells are called enzymes, while ribozymes are RNA molecules that act as catalysts.

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The Number Song

To the tune of "Everybody Loves Somebody Sometime"

Metabolic Melodies Website [HERE](#)

Avogadro's number is a huge one
Boltzmann's constant's rather miniscule
Values differing enormously
As we learned in school

Science numbers need to have dimensions
Size is not the most important thing
Units give the yardsticks needed
For under-STAN-ding

Bridge

It's taught in the ivory towers
By professors it's so ballyhooed
Values can have such diff'rent powers
That to know them we must have their magnitudes

One light year's a really lengthy distance
Grams define the masses high and low
The ohm can measure the resistance
If current should flow

Bridge

One set of factors you SHOULD know
The roots of seven and of three et al
Cannot be expressed as a ratio
Oh these numbers all are quite irration-al
Three point one four one five nine two six five
No end to Pi's digits it's absurd
Endlessly reminding me that I've
BEEN SO OUT-num-bered

*Recording by David Simmons
Lyrics by Kevin Ahern*

Elemental Learning

To the tune of "*Sentimental Journey*"

Metabolic Melodies Website [HERE](#)

Gonna do
Some elemental learning
Studying for my degree

Elevate
My supplemental earnings
With atomic chemistry

Learning 'bout
The subatomic units
In an atom's nucleus

Balance charge
With all of the electrons
Or an ion you'll possess

Neutrons
They're the chargeless bits in
Atoms
Protons sometimes wish they had 'em
Gotta have an a-dequate supply
In nuclei

If you don't
There'll be a price for payin'
For the instability

'Cuz you'll get
The nucleus decaying
Radi-o-activity

*Recording by Heather Pearson Boren and Eric Hill
Lyrics by Kevin Ahern*