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F01 29.1.2013

Lecture plan - chemistry

- Atoms - chemical bond
- Carbon chemical bond
- Atoms and molecules in space;
  Information derived from spectroscopy
  - Molecules in the universe;
  - Existence and formation
  - Interactions between light and matter;
    photochemistry, photoionization, photofragmentation
- Thermochemistry in the universe
- Biochemistry

The atomic model

Atoms are made of nuclei, which consist protons($p^+$) and neutrons($n$), and electrons($e^-$).
The diameter of an atom is on the scale of $0.1\,\text{nm} \approx 1\,\text{angstrom}$. The simplest atom is the Hydrogen atom, $1\,e^-$ and $1\,p^+$.

Niels Bohr’s atomic model suggests that the electron has a wave property. Waves have a function, $\Psi$ and so the electron should also have its function. By taking the square of $\Psi$ one gets the probability distribution. If the electron has this wave property it will have a probability distribution around the nucleus and therefore different probabilities of finding the electron.

If two waves are out of phase they will cancel each other out. Out of phase orbits are therefore not possible because if there is no wave there is no electron. If the waves are on the other hand in phase, they get bigger and form a standing wave, „giving” the electron an orbit.

(a) Electron’s wave function and prob. distribution

(b) Waves out of phase, deconstructive interference

(c) Waves in phase creating a standing wave

Wave properties of electrons
By expanding this model to atoms bigger than hydrogen, a standing wave forms for each orbit. In between the waves they cancel due to deconstructive interference. This explains why only certain orbits are allowed and others not, making the orbits quantized.

(a) Standing waves in an extended atomic model  
(b) Allowed/Quantized orbits

Extended atomic model

The energies of orbits are

$$E = -\frac{R}{n^2}$$

where \(n\) take positive integer values and \(n = 1\) represents the closest orbit. The criteria for quantum energy levels are the standing waves.

Energies of orbits

But how to consider all this in three dimensions? By looking at the probability distribution of the electron the 2D orbit is approximately where the maximum probability of finding the \(e^-\) is. But in theory, the \(e^-\) could be essentially everywhere because of the prob. distribution. Now, by extending this distribution around the nucleus the orbit is acquired from all the maxima of the distributions. This creates a so called probability space and the probability of finding the \(e^-\) is the same on the space’s boundary. The \textit{s} orbitals form a spherical probability space.

By searching for points with the same probabilities, \(\Psi^2(r, \theta)\), one gets the \(p\), \(d\) and \(f\) orbitals. These orbitals however don’t form a spherical space. They form a sort of „balloon-ee” orbitals. These orbitals are the basis of the periodic table.

One familiar with the Pauli exclusion principle knows that two electrons can not occupy the same quantum state. Each orbital can therefore only contain two electrons, with spins \textit{up} and \textit{down}. 

2
Forming the orbitals

(a) Shapes of the orbitals
(b) Spins of electrons

Screening

The electrons "want" to be in the lowest energy state.

\[
\begin{align*}
H & : 1s^1 & \text{ground state} \\
H^* & : > 1s^1 & \text{excited state} \\
C & : 1s^2 2s^2 2p^2 & \text{ground state} \\
C^* & : 1s^2 2s^2 2p^1 3s^1 & \text{exapmlary excited state}
\end{align*}
\]

The valence electrons are the highest energy electrons. Inner/core electrons have lower energy and are closer to the core. Valence \(e^-\) can "go everywhere" and are usually outside the core \(e^-\). \(s \rightarrow p \rightarrow d\); \(e^-\) moves further away from core \(e^-\) and distorts the energy diagram of the hydrogen atom. Elements are grouped in the periodic table by valence electrons.
Relationship between atoms and valence electron orbitals

Molecules

Let's take the bonding of two hydrogen atoms as an example. It is possible to either add or subtract the wave functions and then take the square to find the probability distribution of the electrons. The two atom orbitals become two molecular orbitals.

\[
2(\Psi_{1s}^2) \Rightarrow \begin{cases} 
(\Psi_{1s} - \Psi_{1s})^2 \\
(\Psi_{1s} + \Psi_{1s})^2 
\end{cases}
\]

(a) Net repulsion forces: antibonding
(b) Net attraction forces: bonding (Chemical bond)

Molecular orbits by subtracting/adding wave functions

By adding the wave functions the system becomes more stable to make a molecule (lower energy tendencies). The molecular energies (orbitals) become quantized.

\[A^*, AB^* \rightarrow \text{High energy electron configuration - excited states}\]
\[A, AB \rightarrow \text{Low energy electron configurations - ground states}\]
Chemical bonds

Let’s look at the four elements associated with life in the universe

$$H, C, N, O$$

Carbon has four valence electrons. It is impossible to distinguish between electrons. The core electrons are not needed for consideration, only valence electrons are important. The conventional energy diagram gets distorted a bit, creating four $sp^3$ orbitals instead of one $s$ and three $p$. Because electrons repel each other, the valence electrons try to be as far from each other as possible.

Nitrogen has three valence $e^-$ and therefore one paired $sp^3$ orbital and three unpaired. Oxygen has two valence $e^-$ and two unpaired $sp^3$ orbitals. By combining carbon, nitrogen and oxygen with hydrogen one gets: $CH_4$ - methane, $NH_4$ - ammoniak and $H_2O$ - water.

Valence electrons

<table>
<thead>
<tr>
<th></th>
<th>$H$</th>
<th>$O$</th>
<th>$N$</th>
<th>$C$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
</tr>
</tbody>
</table>
Molecules made from $H$, $C$, $N$ and $O$

Here an emphasis will be on carbon chemistry, because of its importance for life on earth. Also, energies of the atoms will be related to the periodic table.

In the universe there are mostly atoms in the 1st and 2nd line of the periodic table.

$$H \sim 75\%$$
$$He \sim 25\%$$
$$\text{rest} < 1\%$$

Most of the „rest” part are elements in the 2nd line of the periodic table.

As mentioned before, carbon has four valence electrons. This fact is a very important and interesting one, especially on hybridization (forming the $4xsp^2$ orbitals).

In chemistry, hybridization is the concept of mixing atomic orbitals to form new hybrid orbitals suitable for the qualitative description of atomic bonding properties. Hybridised orbitals are very useful in the explanation of the shape of molecular orbitals for molecules. It is an integral part of valence bond theory.

Valence electrons in molecules will try to be as far away from each other as possible. As a result a maximum angle will be between them.

In chemistry, pi bonds ($\pi$ bonds) are covalent chemical bonds where two lobes of one involved atomic orbital overlap two lobes of the other involved atomic orbital. Pi bonds are usually weaker than sigma bonds. From the perspective of quantum mechanics, this bond’s weakness is explained by significantly less overlap between the component p-orbitals due to their parallel orientation. ($2p$ orbitals with unpaired electrons form a molecular orbital.)
(a) Angle

(b) Molecule

(c) Simple schematic

Angle and hybridization of \( \text{C}_2\text{H}_4 \)

(a) Orbitals

(b) Schematic

Angle and hybridization of \( \text{C}_2\text{H}_2 \)

More examples

Lazy, but convenient notation
Chirality

A chiral molecule is a type of molecule that has a non-superposable mirror image. The feature that is most often the cause of chirality in molecules is the presence of an asymmetric carbon atom. The term chiral in general is used to describe an object that is not superposable on its mirror image. Achiral (not chiral) objects are objects that are identical to their mirror image. Human hands are perhaps the most universally recognized example of chirality. Chiral isomers/chirality - left/right hand molecules. Only differ in terms of symmetry but can have completely different properties. Amino acids have chiral isomers, for example tryptophane (basic unit in proteins/enzymes)
Carbon containing molecules have a very large variety in structure because of carbon’s ‘flexibility’. Carbon-chemistry: organic- and bio-chemistry. Adenine is a good example. It is a building block of DNA, along with bla, ble and blu. Carbon also plays a big role in Bio-compounds and macromolecules in life.
Forces, potentials and energies

Atoms have an attraction force acting between them. It grows stronger and stronger as the atoms get closer to each other.

\[ F = -\frac{dU}{dr} \]

When the electron clouds start overlapping, the huge repulsion force starts to have effect.

Net force with respect to atomic distance

Instead of the regular energy levels of a single atom, molecular energy levels are not really levels, but form potential wells at each level. With rising energy the energy levels become denser.

Molecular potential wells at energy levels
The molecule vibrates inside the potential well, it is restricted within the potential. The particles are moving and have a wave property. From this quantum energy levels are derived (similar to orbital quantum energy levels). Standing waves are necessary to form quantum energy levels. Out of phase waves will only cancel each other out. Faster vibrations higher in potential well.

Spacing between rotational levels get bigger and bigger with increasing energy levels. Faster rotations with rising energy levels.

Rotational energy levels
Molecules form and get „more stable”, i.e. they have lower energy levels than atoms. As mentioned earlier, molecular energy levels are not levels, but potentials. The bottom of those potential wells is approximately the energy level. Each potential curve has vibrational levels and vibrational levels have rotational levels. This gets more and more complex with rising energy.

Energy levels: Atomic, molecular, vibrational, rotational

Different types of light (radiation) excite different energy levels.

<table>
<thead>
<tr>
<th>Type</th>
<th>Energy Level</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blue/ultraviolet</td>
<td>$E(n)$</td>
<td>Molecule gets excited</td>
</tr>
<tr>
<td>Infrared</td>
<td>$E(v)$</td>
<td>Vibrations get excited</td>
</tr>
<tr>
<td>Microwaves</td>
<td>$E(J)$</td>
<td>Excite rotations</td>
</tr>
</tbody>
</table>

Each factor has its characteristic parameters. These parameters are acquired from excitation of different energies and compared with databases to determine molecules. This is what spectroscopy is all about.

Characteristic parameters

<table>
<thead>
<tr>
<th>Type</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atoms</td>
<td>$R_A$</td>
</tr>
<tr>
<td>Molecules</td>
<td>$R_{AB}$, $\delta_{AB}$</td>
</tr>
<tr>
<td>Vibrations</td>
<td>$C_{AB}$</td>
</tr>
<tr>
<td>Rotations</td>
<td>$B_{AB}$</td>
</tr>
</tbody>
</table>

Absorbtion and emission

A beam of light from a distant object passes through numerous intervening gas clouds in galaxies and intergalactic space. These clouds subtract specific colors from the beam. The resulting absorption spectrum is used to determine the distances and chemical composition of the invisible clouds. If there are for example three clouds, it will not be able to determine from which cloud the absorption lines belong.
Exemplary absorption spectrum

For emission it is different. Molecules are in excited states due to vibrational/rotational/electronic energy and go down an energy level or many energy levels, emitting energy while doing so. Electronic level emission $(E_n)$ emits ultraviolet light $(\lambda \sim \text{nm})$, vibrational $(E_v)$ emits infrared light $(\lambda \sim \mu\text{m})$ and rotational $(E_J)$ emits microwaves $(\lambda \sim \text{cm})$.

Molecular clouds in space absorb light (ultraviolet photons) from light sources and can then emit themselves visible light (optical photons).

At first, prisms were used to deviate light to some sort of a screen which revealed the spectrum. Today electronic devices are used for this.

Lets look at the hydrogen atom. Emission lines are at different wavelengths depending on the energy transition. The same goes for the absorption lines.
Carbon monoxide, $CO$, is a key molecule. It is seen a lot from clouds in space. The emission lines are plotted versus frequency. The bigger the molecule is, the spectrum becomes more complex. Here are a few examples, all in the microwave spectra, that is, rotational emission lines.

![CO emission spectrum (microwave)](image)

More complex spectra

**Problems with detection**

i) Cloud problem mentioned above

ii) Absorption/Emission:
If we have a rotational molecule and an electromagnetic (EM) wave $\rightarrow$ only absorption if frequency of EM waves is the same as rotational frequency. Also, the molecule has to be polar. Hence, EM wave, made of Electric field, grabs pole of molecule and starts to rotate it. Same goes for vibrations.

![Absorption if frequencies are the same](image)
However, $H_2$ is nonpolar and doesn’t absorb according to this. How does detection work?

H nonpolar $\rightarrow$ no absorption due to rotational or vibrational excitations

Absorption in the vacuum UV region $\rightarrow$ affected by the atmosphere. i.e. molecules in atmosphere absorb and therefore distort measurements from space. Better to measure spectra from space.

The solution to the hydrogen problem is that the proton and the electron are spinning. The $H$ atom has an excited state where spins are in the same direction. It jumps to the ground state which has antiparallel spins and emits a photon. This can be detected because of abundances of $H$ and solves the space detection problem.

If we look again at the $CO$ spectrum. Are qualitative and quantitative analysis possible? The peak heights for the same compound differ. That is because number of molecules in different quantum energy levels is different. This distribution of molecules gives the spectrum. This spectrum is temperature dependent and the distributions become different with varying temperatures. These kind of measurements are used to determine the temperature. A good fit of measured vs. calculated values gives the temperature after comparing with databases. The kinetic energy is in contrast with the temperature.
Comparing spectra with different temperatures

Large temperature variations in space: giant molecular clouds (GMC). Hot molecular clouds are in the vicinity of stars/light energy. Cold molecular clouds are far away from stars/light energy.

(a) Hot MC  
(b) Cold MC

(c) How cold MC work

Giant molecular clouds
In space, if 2 atoms collide they will not stick together and form a molecule. They will collide and bounce away from each other. The atoms need to go down in energy to make a molecule. Their energy consists of potential energy and kinetic energy

\[ E_{\text{tot}} = E_{\text{pot}} + E_{\text{kin}} \]

The atoms need to lose energy in order to „go down” into the molecular potential energy well, as described before. How is this achieved?
A third body is needed. While colliding the atoms during their collision, it jumps away with more energy and the atoms lose energy and get trapped in the potential well. This third body can be another atom or something else, a solid particle (crystal/dust particle).

This third body can be a surface (dust particle ~ $\mu m$), where the atoms get stuck on surface, diffuse on surface, combine and give away energy to the dust. They then go away as a molecule. Therefore the dust acts as a catalyst for molecular formation. This dust is approximately 1% of compounds in interstellar medium (ISM) and is typically of the order of $0.1 - 1 \mu m$. This dust is like a cold cloud, it has solid states compounds with carbonaceous(C) or silicate(Si) core. These are normally cold particles so other atoms can diffuse and combine on its surface.
Dust surface

This is not the only way for molecules to form in space. Two molecules can collide and form by transferring energy to rotational/vibrational energy. Two colliding molecules can also lose energy as photon in order to form a molecule.

![Diagram of reactions in the interstellar medium](image)

Figure 5.9  Reactions in the interstellar medium. (Adapted with permission from Fraser, 2002)

Reactions in intersellar medium

This can be summarized in a pretty simple way:

\[
\text{atom + atom } \rightarrow^C_{M(s)} \text{ Molecule}
\]

but

\[
\text{atom + molecule } \rightarrow \text{ molecules}
\]

\[
\text{molecule + molecule } \rightarrow \text{ molecules}
\]

Two examples of reactions are

Exchange reaction: \( A + H_3CB \rightarrow ACH_3 + B \)

Addition reaction: \( H_2C=CH_2 + AB \rightarrow H_2AC-CH_2B \)
There have been 12 different atoms detected in space in molecular clouds. The most common are: H, C, N and O ("CHON").

Let's now look at the molecular difference in GMC, ISM and Earth’s surface.

Collisions between particle needed for reactions:

Collision frequency:

\[
\begin{align*}
A + B/Z_{AB} \\
A + A/Z_{AA}
\end{align*}
\]

(no. of collisions per sec per volume unit)

\[
\begin{align*}
Z_{AA} &\propto \text{size}/d^2_A \\
Z_{AA} &\propto \text{velocity} A = v(T, m_A) \\
Z_{AB} &\propto [A][B] \\
Z_{AA} &\propto [A]^2 \\
T, m_A \text{ const. } : Z_{AA}' = [A]^2
\end{align*}
\]

Above, \(d\) is the diameter of the atom. \([A]\) is the concentration of \(A\), and \(Z\) is number of collisions per second per volume. The collision frequency parameters are size, speed, temperature and mass.

<table>
<thead>
<tr>
<th>Temperature ([K])</th>
<th>GMC</th>
<th>ISM ([10 - 20])</th>
<th>Earth/surface ([300])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molec. density (A = \text{molec./cm}^3)</td>
<td>(10^6)</td>
<td>1</td>
<td>(10^{19})</td>
</tr>
<tr>
<td>Collision freq. (Z_{AA}' = A^2)</td>
<td>(10^{12})</td>
<td>1</td>
<td>(10^{38})</td>
</tr>
</tbody>
</table>

Rate \(\propto Z_{AB}\), Rate \(\propto f \Rightarrow\) Rate \(\propto f Z_{AB}\)

\(f\): High enough energy to break bonds and form new ones. Number of molecules with enough energy to exceed activation energy.

**Probability of collision**

The moving atom, \(A\), will hit the stationary atom, \(B\), if \(A\)'s center is within a circle with \(B\)'s diameter as radius (see fig). \(A\)'s center needs to be within the cross section

\[
\sigma = d^2 \pi
\]

\(R_{\text{dotted}} = D_{\text{blue}}\)
For ions this is a bit different.
A moving particle containing charge creates an electric field.
The attraction force is, \( F \propto \frac{1}{r^2} \).
A and B start attracting each other. Atoms with charge tend to deviate from their straight line of movement to collide with neutral atoms. This increases collision frequency drastically, and the collision cross section greatly increases, \( \sigma \gg d^2 \pi \).
\( f \): energy barrier

**Ionized collisions**

Thermal equilibrium \( \rightarrow \) fewer particles with high energy (Boltzmann distribution).
Higher temperature increases energy of particles \( \rightarrow \) more more can overcome energy barrier.

Energy barriers, \( E_a \): activation energy

Dust can help in breaking of bonds. Molecule(AB) attaches to dust and gets split into atoms A and B. Another molecule arrives and bonds with A and B, then leaves the dust.
Dust acts as a catalyst

The dust decreases the energy barrier/activation energy $\rightarrow$ catalysis effect. This makes the dust particles important, key to forming molecules. This catalysis effect increases $f$.

**Radicals**

Atom/molecular fragments with unpaired electrons. They are reactive because $e^{-}$ want to pair, i.e. reactivity determined by electron pairing. Unpaired electrons enhance reactivity. Radicals therefore tend to pair. The energy barrier is very small.
Cosmic rays

Ions and radicals?

Created by radiation:
- Cosmic rays: $p^+ 84\%, \text{He}^{2+}/\alpha 14\%$, cores 2%. Cosmic rays are made of particles. Cosmic rays can also dissociate molecules.
- Electromagnetic waves from stars Waves carry energy

Ions:

\[
\begin{align*}
\text{radiation} + \text{AB} & \rightarrow \text{AB}^+ + e^- \\
h\nu^+ \text{AB} & \rightarrow \text{AB}^+ + e^- \\
p^+ + \text{AB} & \rightarrow \text{AB}^+ + e^- \\
\text{He}^{2+} + \text{AB} & \rightarrow \text{AB}^+ + e^-
\end{align*}
\]

Radicals:

\[
\begin{align*}
\text{radiation} + \text{AB} & \rightarrow \text{A} + \text{B} \\
h\nu^+ \text{AB} & \rightarrow \text{A} + \text{B} \\
p^+ + \text{AB} & \rightarrow \text{A} + \text{B} \\
\text{He}^{2+} + \text{AB} & \rightarrow \text{A} + \text{B}
\end{align*}
\]

→ Energy can be transferred to molecules (excite molecules)
→ Electrons can go away, leaving the molecule as an ion: Photoionization.

Ionization energy differ from various atoms/molecules.

<table>
<thead>
<tr>
<th>Atom or molecule</th>
<th>Ionisation energy (eV)</th>
<th>Ionisation wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H I</td>
<td>13.6</td>
<td>90.73</td>
</tr>
<tr>
<td>He</td>
<td>24.59</td>
<td>50.48</td>
</tr>
<tr>
<td>He$^+$</td>
<td>54.51</td>
<td>22.8</td>
</tr>
<tr>
<td>Li</td>
<td>5.32</td>
<td>233.3</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>75.63</td>
<td>16.4</td>
</tr>
<tr>
<td>C</td>
<td>11.26</td>
<td>110.2</td>
</tr>
<tr>
<td>C$^+$</td>
<td>24.38</td>
<td>50.91</td>
</tr>
<tr>
<td>O</td>
<td>13.62</td>
<td>93.19</td>
</tr>
<tr>
<td>O$^+$</td>
<td>35.11</td>
<td>35.53</td>
</tr>
<tr>
<td>H$_2$</td>
<td>15.43</td>
<td>80.45</td>
</tr>
<tr>
<td>CO</td>
<td>14.01</td>
<td>88.60</td>
</tr>
<tr>
<td>C$_2$</td>
<td>12.0</td>
<td>103.4</td>
</tr>
<tr>
<td>CN</td>
<td>13.8</td>
<td>89.9</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>12.6</td>
<td>98.5</td>
</tr>
</tbody>
</table>

Table 5.2 Bond energies and photodissociation wavelengths

<table>
<thead>
<tr>
<th>Chemical bond and bond order$^a$</th>
<th>Bond energy (kJ mol$^{-1}$)</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=O (s)</td>
<td>1075</td>
<td>105</td>
</tr>
<tr>
<td>N=N (s)</td>
<td>943</td>
<td>120</td>
</tr>
<tr>
<td>C=C (s)</td>
<td>754</td>
<td>149</td>
</tr>
<tr>
<td>C=C (d)</td>
<td>838</td>
<td>134</td>
</tr>
<tr>
<td>C=C (c)</td>
<td>612</td>
<td>184</td>
</tr>
<tr>
<td>C-C (s)</td>
<td>348</td>
<td>323</td>
</tr>
<tr>
<td>C-H (s)</td>
<td>415</td>
<td>271</td>
</tr>
<tr>
<td>H-H (s)</td>
<td>436</td>
<td>274</td>
</tr>
</tbody>
</table>

$^a$ Bond order: (s) triple; (d) double; (c) single.

(b) Bond energies, $10^2 \text{nm} \sim \text{UV}$

Table 5.3 Ionisation energies and wavelengths

(a) Ionization energy. Middle column: energy needed, right column: max $\lambda$
Electron-ion and electron-molecule reactions

\[ \text{C}_2\text{H}_2 \text{ being radiated} \]
\[ \rightarrow \text{dissociate} \]
\[ \rightarrow \text{form big molecules... life?} \]

This is considered a possible reason for the creation of big organic molecules in space.
Laser experiment

Ground state of $C_2H_2$ is inert and linear. Excited state (valence $e^-$ in higher energy orbitals) behaves much differently. It dissociates and forms radicals.

(a) Radicals from $C_2H_2$

(b) Excitation of ground state of $C_2H_2$

$C_2H_2$

Radiation excites molecules $\rightarrow$ dissociates $\rightarrow$ forms radicals

Ionized fractions with high enough energy form organic molecules. These fractions/radicals formed from dissociated $C_2H_2$ because of cosmic rays.

![Figure 5.11 Hydrocarbon reactions leading to PAH synthesis. (Adapted with permission from Fraser, 2002)](image)

Hydrocarbon reactions

$H_3^+$ hot stuff today!
Entropy and free energy

The entropy, $S_{total}$ of the Universe increases, i.e. $\Delta S_{total} > 0$ for an isolated system. Let’s look at the Universe as our isolated system. Is a system is an isolated system, it will reach a maximum in entropy, $S_{tot}(max)$ is not necessarily possible in the Universe. Entropy as a whole in the universe is increasing.

If $S \uparrow$, some changes/evolutions are occurring within the system.

Equilibrium: changes/evolutions do not occur.

Entropy in the Universe as an isolated system. The path can be a reaction, evolution of a galaxy etc. (NOT time)

Forming a solar system results in a negative entropy change $\Delta S_{solar\ system} < 0$. Other entropy change has to be bigger for a positive total entropy change

$$\rightarrow \Delta S_{tot} = \Delta S_{solar\ system} + \Delta S_{other} > 0.$$

Other examples can be where two liquids form a crystal in an isolated system:

$$\Delta S_{reaction} < 0, \Delta S_{other} > 0, \rightarrow \Delta S_{total} = \Delta S_{reaction} + \Delta S_{other} > 0.$$ 

or the creation of life, where molecules are gathered to form bigger things, whether it is small, or a human being:

$$\Delta S_{life} < 0, \Delta S_{other} > 0, \rightarrow \Delta S_{total} = \Delta S_{life} + \Delta S_{other} > 0.$$

$G$ is the free energy and is proportional to the entropy in the following way:
\[ \Delta G \propto -\Delta S \]

The free energy, \( \Delta G \) is the maximum work that can be extracted from a reaction (100% efficiency)

Entropy and Free energy of an isolated system

Equilibrium/Inequilibrium in the universe?

In space and interstellar medium the chemistry is slow. To measure whether a system is in equilibrium or not, chemists use an equilibrium constant. This constant is calculated by the ratio of chemical concentration of the products and the reagents from a process:

\[
A + B \rightarrow \rightarrow C + D \\
\frac{[C][D]}{[A][B]} = K
\]

Measurements imply that there is inequilibrium in the Universe.

Particles with high energy become less frequent \( \rightarrow \) Boltzmann distribution.

By passing the energy barrier and increasing concentration on right side, until there are equal numbers of molecules above the energy barrier on each side results in equilibrium (See Fig). In equilibrium, the free energy is equal to zero, \( \Delta G = 0 \), but in inequilibrium, it is negative, \( \Delta G < 0 \).
System in equilibrium

(a) Equilibrium

(b) Inequilibrium in ISM:

HNC $\rightarrow$ HCN
Equilibrium vs. inequilibrium

The first law of thermodynamics:

\[ \Delta U = \text{internal energy} = w + q \]

There is an instance where the work can be used again to get the reagents (by adding some heat). That is a state of equilibrium between system and surroundings.

\[ w_{max} + q_{min} \Rightarrow \Delta G = w_{\text{reversible}} \]
Inequilibrium is the driving force for things to happen.

In the human body a lot of chemical reactions occur. Lets look more closely at carbohydrates. They are broken down to smaller units, glucose. The glucose is an „energy storage” which is stored in the cytoplasm.

\[ \text{Glucose} : C_6H_{12}O_6 \]

Glucose + oxygen \( \rightarrow \) products + Energy

Glucose comes from the cytoplasm and oxygen from the air. The products are water, which leaves as urea and sweat, and carbon dioxide, which goes through breathing. The energy is for keeping the body temperature and for the body to perform actions.

Reagent energy is higher than the products’
Glycogen is a macromolecule of glucose. ADP/ATP is important for energy storing. The net process of glucose is

\[
C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O; \Delta G = -2870 \text{kJ (per mol/glucose)} \\
36ADP + 36P_i \rightarrow 36ATP + 36H_2O; \Delta G = +1080 \text{kJ}
\]

Net negative $\Delta G$

$\Delta G > 0$ is unfavourable. In the ATP process, something with a higher $|\Delta G|$ and a negative $\Delta G$ is needed to make the overall process negative. That is achieved with the glucose process. ADP take energy and store it in ATP. Enzymes help with reaction steps

\[
S + E \rightleftharpoons SE \rightarrow P + E
\]

Biopolymers are macromolecules

DNA is a double helix, sort of like a wound up zipper. The DNA bases are Cytosine and Thymine (small units) and Adenine and Guanine (bigger units). The possible combinations of those are A—T and G—C. They are combined by Hydrogen bonds and are „flat” molecules.
RNA is a single stream of molecules, while DNA are double streams. The fundamental difference between DNA and RNA is that RNA have Uracil while DNA have Thymine.
DNA & RNA

With the help of enzymes, RNA is made from information from DNA. RNA string is like one half of the DNA double helix.

RNA has hidden information on how to make proteins. mRNA attaches to ribosome (a "factory") and produces enzymes/proteins with tRNA (small units with 3 bases).
Protein construction

TABLE 4.1 Specification of the Amino Acids by RNA

<table>
<thead>
<tr>
<th>Second Base</th>
<th>Uracil (U)</th>
<th>Cytosine (C)</th>
<th>Adenine (A)</th>
<th>Guanine (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>First Base</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UUU</td>
<td>phenylalanine</td>
<td>UCU serine</td>
<td>UAU tyrosine</td>
<td>UGU cysteine</td>
</tr>
<tr>
<td>UUC</td>
<td>phenylalanine</td>
<td>UCC serine</td>
<td>UAC tyrosine</td>
<td>UGC cysteine</td>
</tr>
<tr>
<td>UUA</td>
<td>leucine</td>
<td>UCA serine</td>
<td>UAA stop</td>
<td>UGA stop</td>
</tr>
<tr>
<td>UUG</td>
<td>leucine</td>
<td>UCG serine</td>
<td>UAG stop</td>
<td>(UGA selenocysteine)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>UGG tryptophan</td>
</tr>
<tr>
<td>CUU</td>
<td>leucine</td>
<td>CUC proline</td>
<td>CAU histidine</td>
<td>CGU arginine</td>
</tr>
<tr>
<td>CUC</td>
<td>leucine</td>
<td>CCC proline</td>
<td>CAC histidine</td>
<td>GCG arginine</td>
</tr>
<tr>
<td>CUA</td>
<td>leucine</td>
<td>CCA proline</td>
<td>CAA glutamine</td>
<td>GCA arginine</td>
</tr>
<tr>
<td>CUG</td>
<td>leucine</td>
<td>CCG proline</td>
<td>CAG glutamine</td>
<td>AGG arginine</td>
</tr>
<tr>
<td>AUU</td>
<td>isoleucine</td>
<td>ACU threonine</td>
<td>AAU asparagine</td>
<td>AGU serine</td>
</tr>
<tr>
<td>AUC</td>
<td>isoleucine</td>
<td>ACC threonine</td>
<td>AAC asparagine</td>
<td>AGC serine</td>
</tr>
<tr>
<td>AUA</td>
<td>isoleucine</td>
<td>ACA threonine</td>
<td>AAA lysine</td>
<td>AGA arginine</td>
</tr>
<tr>
<td>AUG</td>
<td>methionine</td>
<td>ACG threonine</td>
<td>AAG lysine</td>
<td>AGG arginine</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GUU</td>
<td>valine</td>
<td>GCU alanine</td>
<td>GAU aspartic acid</td>
<td>GGU glycine</td>
</tr>
<tr>
<td>GUC</td>
<td>valine</td>
<td>GCG alanine</td>
<td>GAC aspartic acid</td>
<td>GGC glycine</td>
</tr>
<tr>
<td>GUA</td>
<td>valine</td>
<td>GCA alanine</td>
<td>GAA glutamic acid</td>
<td>GGA glycine</td>
</tr>
<tr>
<td>GUG</td>
<td>valine</td>
<td>GCG alanine</td>
<td>GAG glutamic acid</td>
<td>GGG glycine</td>
</tr>
</tbody>
</table>

Notes:
1 Leftmost column specifies the first base, and the top row the second base, in the codon.
2 In some organisms.

RNA amino acids
Protein synthesis