Sample: Inorganic Chemistry - Water Project

Water

Project paper

Introduction

As early as in 6th century BC Greek philosopher Thales of Miletus stated that the originating principle of nature was a single material substance: water. Of course, he was wrong but undoubtedly water is the most important compound in the world.

Water is one of the most plentiful substances on Earth. Total amount of water on the Earth is estimated to be $1.39 \cdot 10^{18}$ tons. There are about $1.3 \cdot 10^{13}$ tons of water in the atmosphere [1]. Water is a component of minerals and rocks. Water is part of the composition of planets, satellites and comets of the solar system. Its molecules are present in interstellar space [2].

Water is the main substance of living organisms including humans. It fills our cells, which are two-thirds water by volume. If you count every single molecule in a human body, 99% of them will be water molecules [3]. Water is central to life and without it there could be no life. Realizing this truth, the father of modern biochemistry Albert Szent-Györgyi once said: “Life is water dancing to the tune of solids” [3]. And water makes life possible due to its unique, sometimes anomalous properties.

Main discussion

1. History

Everyone knows that H_2O is the formula of water. Undoubtedly, it is the most widely known chemical formula. But until the middle of 18th century it was unknown. It was Henry Cavendish who first determined water composition. He discussed it in his work “On Factitious Airs” published in 1766. Later it was proved by the first decomposition of water into hydrogen and oxygen, by electrolysis done in 1800 by W. Nicholson. J.L. Gay-Lussac and A. Humboldt definitely proved that water consists of two portions of hydrogen and one portion of oxygen in 1805.

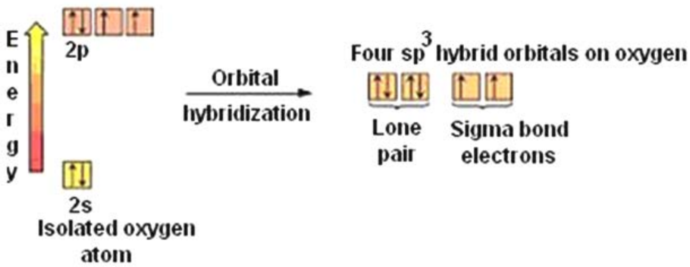
The next important milestone in water science, which allowed to explain its unique properties, was the discovery of hydrogen bonding. The hydrogen bond was first mentioned in 1912 by Moore and Winmill. The description of hydrogen bonding in terms of water came some years later, in 1920, from Latimer and Rodebush [4].

Ascertainment of water molecule geometry became possible thanks to Linus Pauling, who developed the orbital hybridisation theory in 1928 [4].

Despite the subject may seem to be simple and completely studied, research of water was carried out uninterruptedly throughout the 20th century and is still carried out in 21st.

2. Structure and geometry

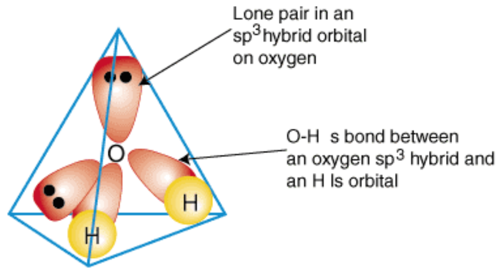
Isolated oxygen atom has six outer-shell electrons, forming one s- and three p-orbitals. When forming a water molecule these four orbitals are transformed into four uniform sp^3 hybrid orbitals.



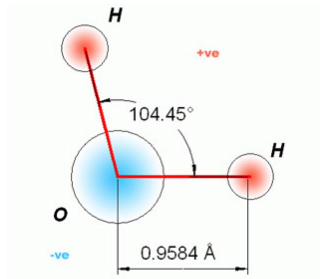
Two of the sp^3 hybrid orbitals contain bonding pairs, and the two contains lone pairs [5].

Each O–H covalent bond is formed by the overlap of a 1s orbital of a hydrogen atom with one of the singly occupied sp^3 hybrid orbitals of the oxygen atom. So, two of the six outer-shell electrons of oxygen form covalent bonds with hydrogen atoms.

To minimize repulsion between the four orbitals surrounding the oxygen they tend to arrange themselves as far from one another as possible. So, electron pair geometry of water is tetrahedral. Molecular geometry is bent (or angular):



Electron pair geometry



Molecular geometry

The maximum possible angle between orbitals in tetrahedron is 109.5°. However, the lone pairs are closer to the oxygen atom, and consequently the repulsion between them is stronger than that between the two covalent bonding pairs. As a result, the two hydrogen atoms are pushed closer together, and the H—O—H angle is 104.45° [5].

3. Isotopes

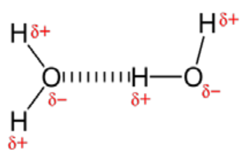
Any water is a mixture of isotopic species. There are two stable isotopes of hydrogen (^{1}H and ^{2}H often denoted by D) and three stable isotopes of oxygen (^{16}O, ^{17}O and ^{18}O), which give rise to nine stable isotopic species of water. Their relative abundances are as follows: $H_2{}^{16}O$ – 99.78%, $H_2{}^{18}O$ – 0.20%, $H_2{}^{17}O$ – 0.03%, $HD^{16}O$ – 0.015%, $D_2{}^{16}O$ – 0.02 ppm, the other four species are trace amounts. Isotopic species containing heavy protons (deuterium) – $^{2}H_2O$ (or D_2O) is called heavy water. Besides stable isotopic species, water contains some trace amount of radioactive $^{3}H_2O$ (or T_2O) and HTO [6].

4. Phase behaviour

Water is the sole compound on earth naturally occurring in all three states: solid, liquid and gas. Many physical properties of water distinguish it from other molecules of similar mass, and it has remained mystery for a long time.

The molar mass of water is only 18 g/mol. Most substances with such low mass are gases under ambient conditions, but water is a liquid. Moreover, water boils at an extremely high temperature for its size, and the freezing point is much higher than expected. All this is caused by one effect – hydrogen bonding.

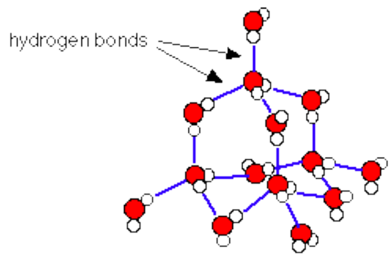
The water molecule is polar. The partially negative charge is concentrated at the oxygen due to its high electronegativity. Hydrogen atoms have partially positive charge. This charge displacement constitutes an electric dipole. Electrostatic force between partially positive hydrogen atom on one molecule and partially negative oxygen of a neighbouring molecule results in intermolecular attraction.



This process is called hydrogen bonding. Thus, in liquid state water molecules are connected to each other by hydrogen bonding, and due to this force water is liquid under ambient conditions [8, 9].

Another important result of the hydrogen bonding network is that water has a very high specific heat [8, 9].

There are very few substances whose liquid form is denser than the solid and water is one of them. The density of ice is smaller than that of water, because due to hydrogen bonds water molecules in solid state form regular arrangement. In this arrangement every hydrogen atom is involved in hydrogen bond and every oxygen atom is involved in two hydrogen bonds:



The hydrogen bonds around each oxygen atom form a tetrahedral structure similar to that between carbon atoms in diamond (thus, ice and diamond are somewhat topologically related). The tetrahedral coordination opens up the space between molecules resulting in less density than in liquid state [8, 9].

A special and interesting form of solid water is clathrate hydrates (or gas hydrates). Clathrate hydrates are crystalline solids forming cages built of hydrogen bonded water molecules, in which small non-polar molecules are trapped. Usually trapped molecules are gases. The lattice structure of gas clathrates cannot exist without trapped molecules. Without them, clathrate hydrates would turn into conventional ice or liquid water [10].

In recent years, some scientists began to distinguish the fourth phase of water (so-called exclusion zone) arising on a surface and being intermediate between solid and liquid state [3]. But this opinion has no unanimous acceptance in the scientific world.

As we can see, water does not exist without hydrogen bonding. But it was interesting to study water properties without any hydrogen bonds. This was a challenge of great daring and complicacy but of doubtful utility. This aim was has been reached by isolation of a single H_2O molecule by encapsulation it into fullerene C_{60} [11].

5. Electrical properties

The conductivity of pure (deionized) water is negligibly small, however, the presence of small amounts of salts in the potable water dramatically increases water conductivity [9].

In liquid state water is partially auto-ionized. This equilibrium process results in hydroxide anion and hydronium cation [8, 9]:

$HOH + HOH \leftrightarrow H_3O^+ + OH^-$

When an electric current passes through water (electrolysis), the latter is split into hydrogen and oxygen. Electrode half reactions of electrolysis are following:

Cathode (–): $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (reduction)

Anode (+): $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$ (oxidation)

Overall reaction: $2H_2O \rightarrow 2H_2 + O_2$

This process is used to obtain hydrogen of high purity [7].

6. Chemical properties

First of all, water is a very good solvent. It dissolves more substances than any other solvent. Being polar itself, it dissolves only polar substances. When an ionic or polar compound enters water, it is surrounded by water molecules. The relatively small molecule size allows more intensive interactions between the solute and solvent. The partially negatively charged oxygen atoms of water molecules are attracted to positively charged components of the dissolved substance, and conversely for the positively charged hydrogen atoms [8].

Chemically, water is amphoteric: it can act either as an acid or as a base:

$HCl(acid) + H_2O(base) \leftrightarrow H_3O^+ + Cl^-$

$NH_3(base) + H_2O(acid) \leftrightarrow NH_4^+ + OH^-$

Some substances react with water when dissolving. Dissolution of most salts leads to their hydrolysis of salts, dissolution of oxides leads to acid and base formation [5, 9].

Water is a reactive substance.

It is oxidized by atomic oxygen resulting in hydrogen peroxide:

$H_2O + [O] \rightarrow H_2O_2$

When interacting with F_2 the whole range of products, including HF, O_2, O_3, H_2O_2, F_2O etc. is formed [5, 8]. When reacting with other halogens, water forms mixture of two acids:

$H_2O + Cl_2 \rightarrow HCl + HClO$

Under elevated temperature chlorine and bromine decompose water, e.g:

$H_2O + Br_2 \xrightarrow{T,^\circ C} HBr + O_2$

When passing through hot coal, water is decomposed by the following reaction:

$H_2O + C \xrightarrow{T,^\circ C} CO + H_2$

Under elevated temperatures in the presence of a catalyst water reacts with CO, CH_4 and other hydrocarbons [8]:

$H_2O + CO \xrightarrow{Fe} CO_2 + H_2$

$H_2O + CH_4 \xrightarrow{Ni\ or\ Co} CO + 3H_2$

The two above reactions are used in industry to obtain hydrogen.

Water reacts with a lot of metals with formation of H_2 and corresponding hydroxide [5, 8]. With alkaline and alkaline-earth metals (except Mg) the reaction goes at room temperature:

$2K + 2H_2O \rightarrow 2KOH + H_2$

Less active metals react with water at elevated temperatures, for example, Mg and Zn – higher than 100°C, Fe –higher than 600°C

$2Fe + 3H_2O \rightarrow Fe_2O_3 + 3H_2$

Interaction of water with oxides of non-metals gives corresponding acids, e.g.

$3H_2O + P_2O_5 \rightarrow 2H_3PO_4$

$H_2O + SO_3 \rightarrow H_2SO_4$

Interaction of water with oxides of metals gives corresponding bases, e.g.

$Li_2O + H_2O \rightarrow 2LiOH$

When a salt of a weak acid or weak base (or both) is dissolved in water, hydrolysis reaction occurs resulting in corresponding acid and base formation [5, 8], e.g.

$NH_4Cl + H_2O \rightarrow NH_4OH + HCl$

Short ionic form: $NH_4^+ + H_2O \rightarrow NH_4OH + H^+$

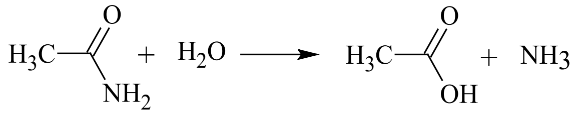
$NaNO_2 + H_2O \rightarrow NaOH + HNO_2$

Short ionic form: $NO_2^- + H_2O \rightarrow HNO_2 + OH^-$

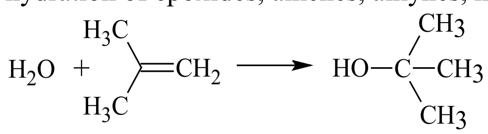
Some amounts of water may be coordinated with a salt forming a crystalline hydrate, e.g.

$\underset{white}{CuSO_{4(s)}} + 5H_2O_{(l)} \rightarrow \underset{blue}{CuSO_4 \cdot 5H_2O_{(s)}}$ – blue copperas (crystalline hydrate) [5, 8]

In organic chemistry water participates in reactions of hydrolysis of ethers, esters, amides and corresponding polymers [12], e.g.



and hydration of epoxides, alkenes, alkynes, nitriles etc. [12], e.g.



Water is worth extended papers and books to be written about it. Many have already been written, and even more will be written. It is impossible to embrace a whole range of questions in a thumbnail sketch.

7. Application

It is a bit weird to speak about water application: everyone knows it is used everywhere. We need it for living, because we are made of it, we need it in industry, we need it in agriculture, we need it in everyday life (for washing, for cooking, for recreation etc.), we use it for transportation and so on and so forth.

Conclusion

Importance of water can hardly be exaggerated. Water molecule is very simple and has bent geometry. Properties of water are unique. Anyway, scientists managed to understand and explain these anomalous properties. The key point in all of them is hydrogen bonding. And the latter takes place, because the water molecule is polar. Chemical properties of water are manifold and diverse. There hardly is a substance participating in such great number of chemical reactions. There is also no substance having such wide application as water.

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