LECTURE 2 -
STRUCTURE AND BONDING IN WATER

Lect02, slide 2 here

Water, known chemically as dihydrogen oxide, consists of two hydrogen atoms and one oxygen atom. The formula is written H_2O and may be represented diagrammatically in several ways, a few of which we will examine. Each hydrogen atom is bonded to the oxygen. Since each hydrogen atom has one valance electron and the oxygen atom has six valance electrons (see Figure 2-1), the traditional picture of bonding in water is that of two strong covalent bonds between the individual hydrogens and the oxygen. In covalent bonding an electron from each atom is shared with the other atom. This would give the hydrogens each two electrons, and give the oxygen eight electrons. These numbers complete the 1s shells for the hydrogen and the 2s shell for the oxygen. This should lead to a very stable molecule. Figure 2-2 represents such a molecule.

Lect02, slide 3 here

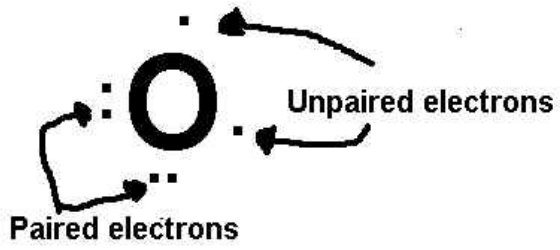

Figure 2-1

Lect02, slide 4 here

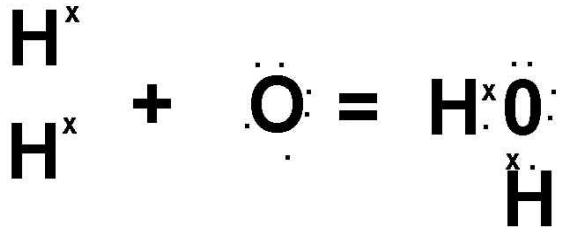

Figure 2-2

Covalent bonding therefore represents an equal sharing of electrons between two atoms. If the two atoms are identical, for example oxygen in O_2 or hydrogen in H_2 we should expect that the sharing is equal. However, if the atoms are not identical, we might expect that one atom will attract electrons more strongly than the other and that the sharing will be unequal. In the extreme case we could get a compound like sodium chloride, usually written Na^+Cl^-. This indicates that the chlorine atom attracts the electron much more strongly than the sodium atom. In effect sodium donates an electron to chlorine. This type of bonding is of course known as ionic bonding, which may be defined as bonding between ions created when one atom donates one or more electrons to another atom. It is known that atoms that are far apart on the periodic table have predominantly ionic bonding while atoms that are close together have dominantly covalent bonding.

This leads us to ask, "Is the traditional picture of pure covalent bonding in water correct?" Linus Pauling used the concept of electronegavity to help answer this question. Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons. It is the difference in the electronegativities of the atoms that is significant.

Lect02, slide 5 here

The most commonly used scale of electronegativity was created by Pauling.

Lect02, slide 6 here

Pauling (1960, p.90) lists the electronegativity of hydrogen as 2.1 and of oxygen as 3.5. Here, the difference is 1.4.

Lect02, slide 7 here

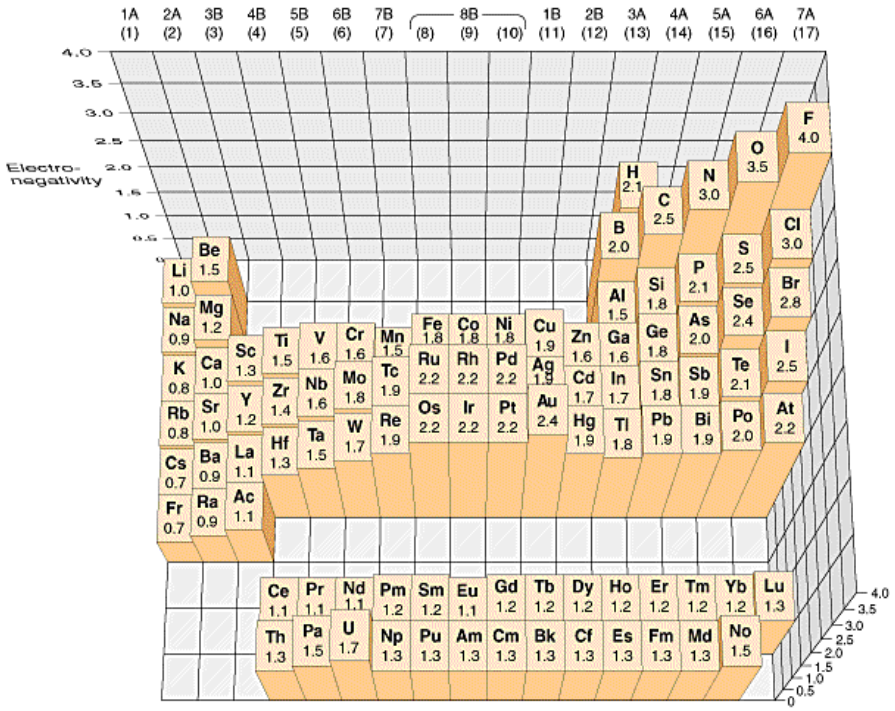

Figure 2-3

Pauling (1960, p. 99) represents graphically the amount of ionic character versus the difference in electronegativity (Figure 2-4). From his graph, a difference in electronegativity of 1.4 corresponds to about a 39% ionic character in the bond. More exact work indicates that the true percent ionic character is closer to 33%. The bonding in water is thus not purely covalent as it is often described but is actually a resonant bond, with resonance between covalent and ionic types. The covalent type is dominant. This resonant bonding has extremely important consequences for the properties of water and the influence of water on geology and on life itself.

Lect02, slide 7 here

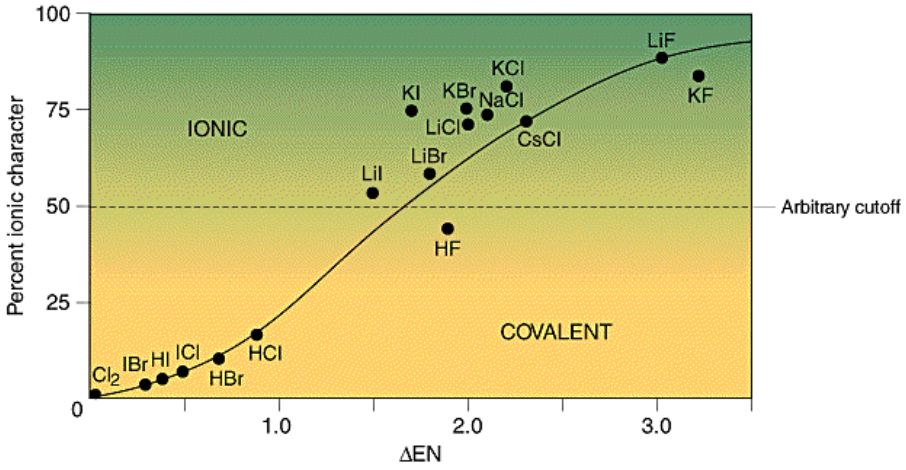

Figure 2-4

The oxygen atom surrounds itself with eight electrons that are in a 2s orbital and in three 2p orbitals. These orbitals hybridize into four sp^3 orbitals, each capable of holding two electrons. In a perfect sp^3 hybrid the orbitals would point to the corners of a tetrahedron and the H-O-H bond and would be that of the tetrahedron, 109.5°. The observed angle in water is 104.5°. The orbitals not involved in bonding to hydrogen are called "lone pairs" and exhibit large repulsion because of the unshielded electric charges. Thus the lone pair orbitals spread farther apart than the tetrahedral angle and force the hydrogen ions closer together. If the bonds in water involved standard 2p orbitals, the bond angle should be that of the p orbital or 90°. The larger the degree of hybridization, the larger the bond angle, as Table 2-1 shows.

Lect02, slide 8 here

Table 2-1

COMPOUND	BOND ANGLE
H_2Se	91°
H_2S	92°
PH_3	93°
H_2O	104.5°
NH_3	107°

Lect02, slide 9 here

One result of the resonant bond in water is that the hydrogen-oxygen bond is an electric dipole with the oxygen being negative while the hydrogen is positive. The dipole character of water accounts for many other properties and needs to be examined in more detail.

Water's dipole moment is 1.86 Debye units (1 Debye unit = 1 D = 10^{-18} statcoulomb cm). This can be determined by putting water between plates and seeing how much voltage needs to be put on the plates to put a given charge on the plates. The voltage required is directly proportional to the dielectric constant of the medium surrounding the plates. P.P. Debye developed this technique in 1914. Using this, and other techniques, the dipole moment may be evaluated. The dipole moment for water corresponds to a charge of +0.33 units on each hydrogen and -0.66 units on the oxygen. (Pauling, 1964, p.276-277).

From the point of view of bonding, the dipolar character of water leads to the formation of hydrogen bonds. A hydrogen bond can be thought of as a weak ionic bond. In water each hydrogen ion carries a partial positive charge. The electron on hydrogen has been partially donated to the oxygen. In quantum mechanical terms the wave function for the donated electron has more density near the oxygen and less near the hydrogen. The oxygen anion carries a double

partial negative charge. Hydrogen ions on one molecule may form a long, ionic type bond to an oxygen anion on another molecule. This is the hydrogen bond. It must be remembered that the bond strength for ionic type bonds is given by a Coulomb type force law as shown in equation 2-1:

Lect02, slide 10 here

Here e_1 and e_2 represent the charge on the first and second ions,

$$f \approx \frac{e_1 \bullet e_2}{r^2} \qquad (2\text{-}1)$$

respectively and r^2 represents the square of the distance between the ions. In water the hydrogen-oxygen bond distance is 0.096 nm. Since the charges are only partial charges and the distance r is long compared with a regular ionic bond, the hydrogen bond is much weaker than the normal ionic bond. Nevertheless, the hydrogen bond is significant. It is much stronger than a Van der Walls bond, for example. The hydrogen bond in water is somewhere between 2 and 10% as strong as the hydrogen-oxygen resonant bond. For another example, hydrogen bonds hold the amino acid base pairs together in DNA and allow the DNA molecules to unzip and rezip to reform the double helix. They also account for some of the most significant properties of water.

Lect02, slide 11 here

In ice the hydrogen bonds are strong enough to hold the molecules together as a solid. In ordinary ice the water molecules are arranged around hydrogen bonds in tetrahedral coordination. As temperature increases, the random thermal vibrations become stronger. Eventually the vibrations are strong enough to begin to break some hydrogen bonds. The ice melts. Even in liquid water some hydrogen bonding is still present. As the bonds are broken, the rigid structure of the ice collapses. The water molecules can pack closer together. The average number of nearest neighbors increases to 4.4, rather than 4.0 in ice. (Narten *et al.*, 1967). This is responsible for the increase in density

when ice melts, or expressed in another manner, for the fact that ice floats.

Lect02, slide 12 here

Water is unique in many ways. The physical properties of water are, without exception, anomalous. No other liquid has so many peculiarities. Water's deviation from normal behavior is also marked, the deviations often being much larger than any other structure. We will discuss the physical properties of water in the next lecture. It is the "strange" behavior of water that, more than any other single factor, makes the earth the unique planet it is. (Horne, 1978, pp.236-239).

Lect02, slide 13 here

As Figure 2-5 demonstrates, the melting and boiling points of water are clearly different from those of other column VI B elements in the periodic table. The high transition temperatures that water exhibits clearly demonstrate that a strong "glue" present in water is not present in the other compounds. That glue is hydrogen bonding. Why is the hydrogen bonding so much stronger in water? The electronegativities of sulfur, selenium, and tellurium are respectively 2.5, 2.4, and 2.1. The critical difference in electronegativity between hydrogen and these elements is then 0.4, 0.3, and 0.0. Such differences indicate that the percent ionic character of the bonds ranges from about four down to zero. Since the bonds are almost totally covalent, it follows that little or no hydrogen bonding exists. Similar differences exist with other hydrides, as shown in figure 2-5.

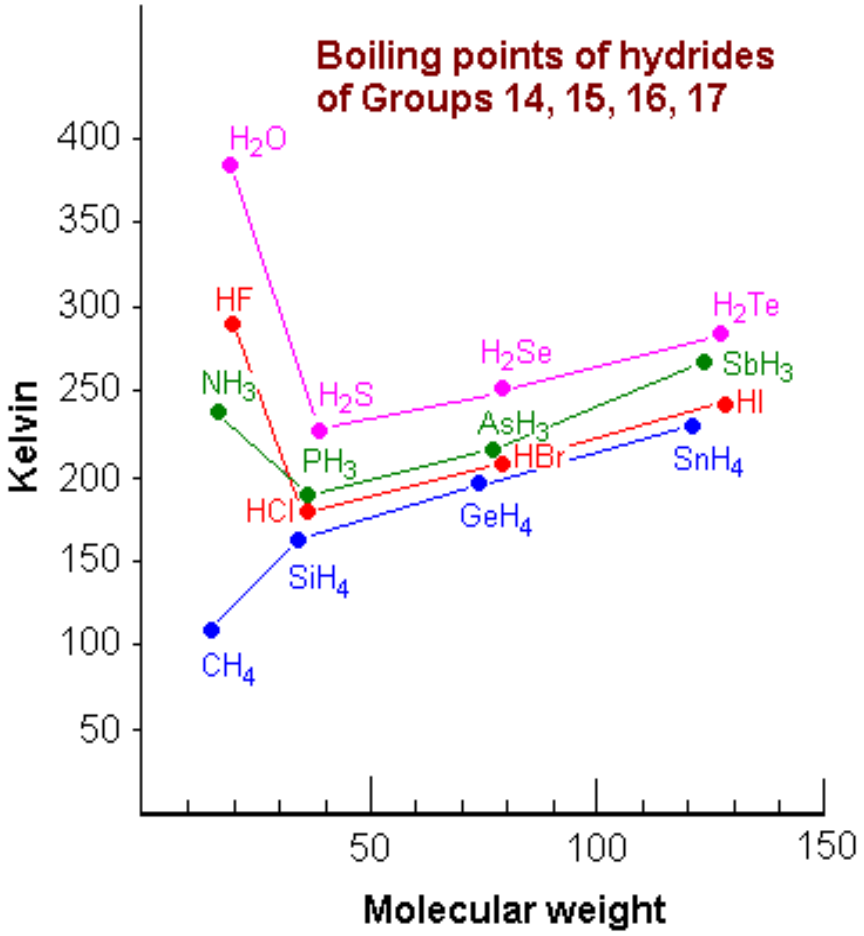

Figure 2-5

Lect02, slide 14 here

Another way of looking at water is to examine iso-electronic compounds with ten electrons. We will use methane (CH_4), ammonia (NH_3), water (H_20), hydrogen fluoride (HF), and neon. Table 2-2 presents relevant data. Water has only two bonds, both of which are resonant covalent-ionic bonds. However, the presence of the additional hydrogen bonding holds the water together, giving it substantially higher melting and boiling points than the other iso-electronic compounds. Ammonia has only one lone pair of electrons, so can form only one hydrogen bond. Hydrogen fluoride has three lone pairs, but only one hydrogen ion. Water is the "perfect" mix, two lone pairs and two hydrogen ions, so it can form two hydrogen bonds.

Table 2-2 Properties of Iso-electronic Compounds with ten electrons

Compound	Methane	Ammonia	Water	Hydrogen Fluoride	Neon
Molecular weight	16.04	17.02	18.02	20.01	20.18
Bond Electronegativities	0.45	0.94	1.34	1.88	NA
Number of bonds	4	3	2	1	0
Melting Point, K	90.7	194.5	273.2	190.5	24.6
Boiling Point, K	111.6	239.8	373.2	293.0	27.1

Modified from a table in Water, chemical bonds, and macromolecular structure, 2008.

References

Ralph Albert Horne, The Chemistry of Our Environment, John Wiley & Sons, New York, 1978.

A.H. Narten, M.D. Danford, and H.A. and Levy, X-Ray diffraction study of liquid water in the temperature range 4-200°C, Discussion Faraday Soc., 43, 97-107, 1967.

Linus Pauling, The Nature of the Chemical Bond, third edition, Cornell University Press, Ithaca, New York, 1960.

Linus Pauling, College Chemistry, third edition, W.H. Freeman and Company, San Francisco, 1964.

Virtuallaboratory.net, Water, chemical bonds & macromolecular structure, last revised August 25, 2008, http://virtuallaboratory.colorado.edu/Biofundamentals/lectureNotes/Topic2AB_Water.htm, last seen January 8, 2010.

Figure References

2.1 Fordham Preparatory School., (June 1, 2004). Scientific Help on Chemistry: Lewis Dot Diagrams http://www.fordhamprep.com/gcurran/sho/sho/lessons/lesson38.htm (August 18, 2004).

2.2 Fordham Preparatory School., (June 1, 2004). Scientific Help on Chemistry: Lewis Dot Diagrams http://www.fordhamprep.com/gcurran/sho/sho/lessons/lesson38.htm (August 18, 2004).

2.3 General Chemistry 1, University of Florida, (1999). http://server.chem.ufl.edu/~itl/2045_s99/lectures/lec_12.html (January 5, 1999 no longer available).

2.4 General Chemistry 1, University of Florida, (1999). http://server.chem.ufl.edu/~itl/2045_s99/lectures/lec_13.html (January 5, 1999 no longer available).

2.5 The Basic Language and Vocabulary of Chemistry : Section 4, CHEMICAL BONDS (July 28, 2002) http://members.optushome.com.au/scottsoftc/chapter04/Hydrogenbond.html (August 18, 2004).

\6246\\lect\6246lect02_S10.wpg
January 8, 2010