

## PHYS4xx Supplement - Chemical bonds and geometry

Bound states of atoms, ions and molecules have a common origin in the electromagnetic interactions among the charged constituents of atoms, namely the atom's electrons and nuclei. A useful benchmark for gauging molecular binding is provided by the binding energy of an electron in an atom, which is usually a few electron-volts or eV, where  $1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$ . It is often useful to compare binding energies with the kinetic energy scale  $k_B T$  of particles in thermal equilibrium at a temperature  $T$ , where  $k_B$  is Boltzmann's constant ( $1.38 \times 10^{-23} \text{ J/K}$  or  $8.6 \times 10^{-5} \text{ eV/K}$ ). Thus, the thermal energy scale of a system at  $T = 300 \text{ K}$  is  $0.026 \text{ eV}$  or  $4 \times 10^{-21} \text{ J}$ , which is more than an order of magnitude less than an eV. This means that some bound states, such as atoms with binding energies of  $\sim 100k_B T$ , will be stable at room temperature, whereas other states, say weakly associated molecules with binding energies of a few  $k_B T$ , will be subject to breakup by thermal motion.

### *Ionic binding*

If two different atoms, each of which can gain or lose electrons relatively easily, are placed in a conducting environment, then it is possible that a transfer of electrons will take place, changing the atoms into ions. By virtue of their net charge, ions with opposite signs are attracted to each other and may form a bound state. As you recall, the Coulombic potential energy  $V(r)$  between charges  $Q_1$  and  $Q_2$  separated by a distance  $r$  is  $V(r) = k_{\text{coul}} Q_1 Q_2 / r$ , where  $k_{\text{coul}}$  is a constant with the value  $8.99 \times 10^9 \text{ Jm/C}^2$ . To determine the strength of ionic binding, then, we need to know the charges of the ions and the distance between them.

The radii of atoms is a slowly varying function of atomic number, as can be seen from Table S.1. For example, even though the number of electrons changes by a factor of 5 over the sequence Ne, Ar, Kr and Xe (10, 18, 36 and 54 electrons, respectively), the atomic radii only change by 40%. The radii of ions, on the other hand, may vary markedly with the net ionic charge even if there is little change in the nuclear charge. For example, the sequence  $\text{F}^-$ , Ne,  $\text{Na}^+$  have radii of 0.14, 0.15 and 0.10 nm,

Table S.1. Selected radii of ions and noble gases, quoted in nm. [In part, from L. Pauling, *The Nature of the Chemical Bond*]

<i>Ion</i>	<i>Radius</i>	<i>Atom</i>	<i>Radius</i>	<i>Ion</i>	<i>Radius</i>
$\text{F}^-$	0.136	Ne	0.154	$\text{Na}^+$	0.095
$\text{Cl}^-$	0.181	Ar	0.188	$\text{K}^+$	0.133
$\text{Br}^-$	0.195	Kr	0.201		
		Xe	0.216		

respectively, even though each of the ions has 10 electrons and the nuclear charge varies by only one unit between successive ions in the sequence. Given that the charge on the ions is just a few times the electron charge, and the distances between ions are similar to that between an electron and a nucleus in a single atom, we might expect ionic binding energies to be in the range of a few eV, like the binding energy of the hydrogen atom. An accurate sum over the charges of ions in a crystal lattice gives a binding energy of 6 - 10 eV per unit cell for singly charged ion pairs such as NaCl. These energies are high enough that a temperature of thousands of degrees would be needed for the thermal energy  $k_B T$  to approach the binding energy of an ionic crystal and cause it to boil, an estimate that is confirmed by the boiling points of ionic compounds like CsCl (B.P. = 1290 °C) and LaO (B.P. = 4200 °C).

### *Covalent bonds*

Neutral atoms also can form electromagnetic bound states with each other because there is a charge separation between the nucleus and its surrounding electrons. For example, two neutral hydrogen atoms can combine to form a hydrogen molecule  $H_2$  with the release of 4.75 eV. X-ray scattering data show that the atoms in  $H_2$  share electrons, in the sense that electrons are likely to be found in a spatial region between the protons, a different behavior from the charge separation of ionic binding. The sharing of electrons between atoms is referred to as *covalent* binding; for example, two carbon atoms can have covalent bonds which contain 2 (single bond), 4 (double bond) or 6 (triple bond) electrons. Table S.2 displays some representative covalent bonds demonstrating how the bond strength increases with the number of shared electrons. The table also shows that covalent binding energies are not dissimilar to ionic binding energies - it would take several eV to completely extract a given atom from its covalently bound neighbors.

Table S.2. Some typical covalent bond strengths, each quoted in three sets of units with the conversions:  $1 \text{ kJ/mol} = 1.04 \times 10^{-2} \text{ eV/bond} = 0.40 \text{ } k_B T/\text{bond}$  at  $T = 298\text{K}$ . [From T.L. Cottrell, *The Strengths of Chemical Bonds*]

<i>Bond</i>	<i>Energy</i>		
	(kJ/mol)	(eV/bond)	( $k_B T/\text{bond}$ )
C - C	350	3.6	140
C - O	310	3.2	124
C - H	415	4.3	166
H - H	436	4.5	176
O - H	463	4.8	186
C = C	610	6.3	244
C = O	740	7.7	299
C $\equiv$ C	836	8.7	338

When two atoms are linked by a covalent bond, the average separation between their nuclei is less than the sum of the atomic radii of the isolated atoms. Table S.3 displays some typical covalent radii, found by taking a known bond length between two atoms in a molecule and apportioning it between the atoms. A comparison of Tables S.1 and S.3 shows that ionic radii can be double the size of covalent radii. Notice also that the radii *decrease* with *increasing* number of shared electrons in going from single to double to triple bonds.

### *Interactions of neutral molecules*

The forces between neutral molecules often are loosely referred to as *van der Waals forces*. One category of van der Waals forces are *London* or *dispersive forces*, which arise even in neutral molecules with no permanent dipole moment. Group IV halides such as  $\text{CF}_4$  and  $\text{CCl}_4$  have no permanent dipole moment, yet their melting points and boiling points are similar to the group V halides which have permanent dipole moments; for example,  $\text{CF}_4$  (no dipole) boils at  $-128\text{ }^\circ\text{C}$  while  $\text{PF}_3$  (permanent dipole) boils at  $-102\text{ }^\circ\text{C}$ . Thus, the interaction between neutral, symmetric molecules may be on the same order of magnitude as the dipole-dipole interactions. In the case of molecules without permanent dipole moments, the fluctuations in the charge distribution of one molecule induce fluctuations in the charge distribution of a neighbor, resulting in an attractive force at moderate separation.

A second category of these forces is the electromagnetic interaction between molecules with permanent dipole moments. For example, simple group V compounds such as  $\text{PF}_3$  are shaped like trigonal pyramids with the group V atom (P) at the apex, giving them a permanent dipole moment. Such molecules exhibit a dipole-dipole interaction, sometimes referred to as the Keesom interaction, although its strength is much weaker than the strictly ionic interaction found in common ionic salts. This effect

Table S.3. Radii of covalent bonds formed by a selection of atoms, quoted in nm.  
[From J. Israelachvili, *Intermolecular and Surface Forces*]

<i>Bond and Atom</i>	<i>Covalent radius</i>	<i>Bond and Atom</i>	<i>Covalent radius</i>
- H	0.03	- C	0.077
- F	0.064	= C	0.067
- Cl	0.099	≡ C	0.060
- O	0.066	- N	0.070
= O	0.062	= N	0.062
		≡ N	0.055

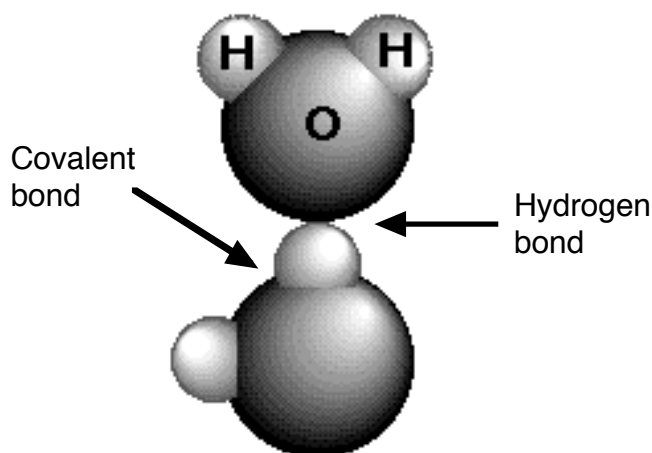


Fig. S.1 Comparison of hydrogen and covalent bonds in water molecules ( $\text{H}_2\text{O}$ ).

can be illustrated using melting points as crude measures of binding strength:  $\text{NaCl}$  has a melting temperature of  $901\text{ }^\circ\text{C}$ , while  $\text{PF}_3$  melts at  $-152\text{ }^\circ\text{C}$ .

*Hydrogen bonding* refers to a specific interaction between certain molecules containing hydrogen atoms. Consider the boiling points for the following sequence of structurally similar molecules:  $\text{H}_2\text{O}$  ( $100\text{ }^\circ\text{C}$ ),  $\text{H}_2\text{S}$  ( $-60\text{ }^\circ\text{C}$ ),  $\text{H}_2\text{Se}$  ( $-42\text{ }^\circ\text{C}$ ) and  $\text{H}_2\text{Te}$  ( $-2\text{ }^\circ\text{C}$ ). The general trend is for the boiling point to increase with molecular mass, but water has an anomalously high boiling point compared to other related compounds, an effect which is attributed to the hydrogen-bonding present between water molecules.

Hydrogen bonding takes place between a hydrogen nucleus (proton) of one molecule and the "unbonded" electrons of the other. To be more specific, X-ray scattering shows that the water molecule is bent like a V, with excess electron density

Table S.4. Selected hydrogen bond energies in neutral molecules. The hydrogen bonds are indicated by  $\cdots$ . [From B. E. Douglas and D. H. McDaniel, *Concepts and Models of Inorganic Chemistry*]

<i>Hydrogen bond</i>	<i>Energy</i>		
	(kJ/mol)	(eV/bond)	( $k_B T$ /bond)
C - H $\cdots$ N	12 - 20	0.13 - 0.21	5 - 8
C - H $\cdots$ O	24	0.25	10
N - H $\cdots$ O	16 - 24	0.17 - 0.25	6 - 10
O - H $\cdots$ O	20 - 28	0.21 - 0.29	8 - 11
F - H $\cdots$ O	44	0.46	18
F - H $\cdots$ F	28	0.29	11

at the apex of the V, giving the molecule a permanent dipole moment with a negative charge at the apex (oxygen atom) and a positive charge at the hydrogens. The hydrogen bond is then between a hydrogen on one atom and the oxygen on another, as illustrated in Fig. S.1. From the hydrogen bond energies quoted in Table S.4, one can see that typical hydrogen bond strengths are about 20 times weaker than single covalent bonds, as quoted in Table S.2. Thus, systems of hydrogen-bonded molecules can be expected to boil at much lower temperatures than ionic compounds, an expectation that can be verified by comparing the boiling point of water (100 °C) with that of a few thousand degrees typical of ionic compounds.

Lastly, some mention should be made of van der Waals radii. When two molecules are near each other in a liquid, their distance of closest approach is significantly greater than the sum of their covalent radii. For example, the distance between two chlorine atoms in Cl<sub>2</sub> is 0.20 nm, but the steric resistance between chlorine atoms on two different Cl<sub>2</sub> molecules is strong at separations less than 0.36 nm. The van der Waals radius is then a measure of the size of the atom in a molecule as experienced by an atom in a different molecule. Again using Cl<sub>2</sub> as an example, the 0.36 nm distance between the Cl<sub>2</sub> molecules may be used to assign a van der Waals radius of 0.18 nm to a chlorine atom. Some typical van der Waals radii are summarized in Table S.5.

Table S.5. Selected van der Waals radii of atoms, quoted in nm. [From J. Israelachvili, *Intermolecular and Surface Forces*]

<i>Atom</i>	<i>van der Waals radius</i>	<i>Atom</i>	<i>van der Waals radius</i>
H	0.11	C	0.17
F	0.14	N	0.15
Cl	0.18	O	0.15