**APPENDIX 2. Modified/Enriched Text on Chemical Bonding**

AUTHOR: Georgios Tsaparlis  
Translated from Greek by Georgios Tsaparlis. English text checked by Bill Byers.

1. **OVERVIEW OF THE CHEMICAL BOND**  
- Factors determining the chemical behavior of atoms  
- Types of chemical bonding (covalent - ionic)

**Electric forces and electric potential energy in chemistry**

At an atomic or molecular level, electrical forces (electrical interactions) outweigh* gravitational forces.** Central to any description of these electrical interactions is Coulomb's law. According to this law, a force $F_C$ is exerted between two point electric charges $q_1$ and $q_2$. This force is attractive when we have electric charges of opposite sign, but repulsive when we have electrical charges of the same sign. The magnitude/measure of this force becomes larger (in absolute value) as the charges increase, but smaller if the distance between them increases.*** Fig. 1 shows the vectors for the Coulomb forces acting between two same-sign and two opposite-sign electrical charges.

A similar relationship also applies to the (electric potential) energy that corresponds to the Coulomb force, with potential energy being positive for repulsive forces, and negative for attractive forces. The magnitude and sign of the energy is very important as a criterion for determining the direction of changes in nature, with change always being spontaneous towards reducing energy (principle of minimum energy).

- Coulomb's law and the principle of minimum energy apply to both macroscopic bodies and to submicroscopic particles, such as molecules, atoms, atomic nuclei, and electrons.

- The atomic model used here considers electrons to be "placed" in (electron) shells around the nucleus (and constantly moving around it). **** We distinguish these shells as either inner shells or the outer shell. The latter plays a decisive role in the formation of chemical bonds and the chemical properties of molecules and it is called the valence shell. Furthermore, electrons in this shell are called valence electrons.

![Figure 1. Coulomb force between two electric charges showing repulsive forces (top) and attractive forces (bottom)](image)

* The ratio of the electric force to the gravitational force between two electrically charged atoms (ions) is $\sim 1000$.

** The magnitude of the gravitational force increases as the masses of the bodies increase, and as the distance between them decreases.

*** The magnitude of the Coulomb force, $|F_C|$, is proportional to the product of the interacting charges $q_1$ and $q_2$, and inversely proportional to the square of the distance $r$ between them:

$$|F_C| = \frac{k|q_1q_2|}{r^2}$$

where $k$ is the proportionality constant, the value of which depends on the material in which the charged particles are embedded.

**** According to the modern quantum mechanical picture of atoms and molecules, instead of discrete electrons that move in orbits/shells, we have an electron cloud.
Factors that determine the chemical behavior of atoms

The chemical behavior of atoms is determined primarily by two parameters. These are:
1. the valence electrons
2. the size of the atom (atomic radius)

Valence electrons

Table 1 shows the valence electrons for selected elements. Note that valence electrons up to 4 are single (lone electrons), while for 5 and above pairs begin to form: with 5 electrons, one electron pair is formed plus 3 unpaired/lone electrons; with 6 electrons, we find two pairs plus 2 unpaired; with 7 electrons, we have three pairs plus one unpaired; and finally, with eight electrons, we have four pairs. Based on this table we can determine electronic formulas for compounds formed (see below).

<p>| TABLE 1: Valence electrons for elements belonging to main groups (groups A) of the periodic table |
|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|</p>
<table>
<thead>
<tr>
<th>IA</th>
<th>IIA</th>
<th>IIIA</th>
<th>IVA</th>
<th>VA</th>
<th>VIA</th>
<th>VIIA</th>
<th>Noble Gases (0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H·</td>
<td>He·</td>
<td>Li⁺</td>
<td>Be·</td>
<td>B·</td>
<td>C·</td>
<td>N·</td>
<td>O·</td>
</tr>
<tr>
<td>Na⁺</td>
<td>Mg·</td>
<td>Al·</td>
<td>Si·</td>
<td>P·</td>
<td>S·</td>
<td>Cl·</td>
<td>Ar·</td>
</tr>
<tr>
<td>K·</td>
<td>Ca·</td>
<td>Sc·</td>
<td>Ti·</td>
<td>V·</td>
<td>Cr·</td>
<td>Mn·</td>
<td>Fe·</td>
</tr>
<tr>
<td>Rb·</td>
<td>Sr·</td>
<td>Y·</td>
<td>Zr·</td>
<td>Nb·</td>
<td>Mo·</td>
<td>Tc·</td>
<td>Ru·</td>
</tr>
<tr>
<td>Cs·</td>
<td>Ba·</td>
<td>Hg·</td>
<td>Tl·</td>
<td>Pb·</td>
<td>Po·</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Atomic radius (the size of the atom)

The size of an atom is one of the most smoothly varying properties throughout the periodic table.

- Across a period, the atomic radius decreases from left to right.
This is because as we go from left to the right, the atomic number increases, thus increasing the positive charge on the nucleus, and thereby reducing the radius, because of greater attraction of the electrons by the nucleus. Also,
- Within a group, the atomic radius increases from top to bottom.
As we go down a group, new shells are added and the distance of valence electrons from the nucleus increases because the net attraction is reduced, and, consequently, the atomic radius increases (see Fig. 2).

The size of an atom determines the force with which the electrons in the outer shell are held by the nucleus, because forces of electrostatic nature (Coulomb forces) are exerted between the positively charged nucleus and the negatively charged electron. Therefore, the smaller the atom, the more difficult it is to lose electrons, but the more readily the atom can gain electrons (more strongly attracted by the nucleus). Conversely, the larger an atom, the more easily it loses electrons but the harder it will be to gain electrons (weaker attraction by the nucleus).

- An atom that tends to gain electrons is called electronegative, while an atom that tends to lose electrons is called electropositive.

**Electronegativity**

The **electronegativity** of an atom is a property used to indicate the atom’s capacity to attract electrons. The electronegativity of an atom cannot be measured directly but it is calculated from other atomic properties.

Various ways of calculating the electronegativity have been proposed, with the **Pauling scale** being most widely used. Table 2 is a periodic table of the (dimensionless) electronegativity values of atoms according to the Pauling scale. The scale is relative and the values range from 0.7 for francium (Fr) to 3.98 for fluorine (F). For hydrogen, the value is 2.20.

- Note that, strictly speaking, the electronegativity (based on the way its value is calculated), is not a property of the atom, but rather a property of the atom in a molecule.
- In general, electronegativity increases, from the left to right, across a period in the periodic table (C < F), while within a group of the periodic table it decreases from top to bottom (F > Cl).

Following from this, it is apparent that cesium (Cs) will lose an electron more easily than sodium (Na). Similarly, a chlorine (Cl) atom will gain an electron more readily than will an iodine (I) atom (Fig. 2).

**EXERCISE**

Compare the atoms of lithium (Li) and sodium (Na) with regard to: (a) their atomic number and (b) their radius. Use this information and Coulomb’s law to predict which is the more electronegative of the two elements, lithium or sodium, and, correspondingly, which will be the more electropositive element of the two. Use the Pauling electronegativity values to confirm your conclusion.

![Figure 2. The atomic radii of halogens in picometers (pm)](image)
2. THE CHEMICAL BOND / COVALENT BOND (Part I)

What really makes atoms form chemical bonds? Generally speaking, we can accept that in a molecule, nuclei of the atoms are held together (they are linked with a chemical bond) because of nuclei-electrons attractions; a simple application of Coulomb's law.* The stability of the molecule, and thus the equilibrium distance between the nuclei (the length of the chemical bonds), is directly linked to attaining minimum energy. All chemical bonds (regardless of their type) can be explained on the basis of the need for achieving stability, that is, minimum energy.

Covalent bonding between atoms of the same chemical element

We begin with the study of chemical bonding in diatomic molecules composed of atoms of the same element (homonuclear molecules), such as H₂, F₂, Cl₂, O₂ and N₂.

* NOTE: In this periodic table, the modern IUPAC continuous numbering system is used for the groups. For instance, group 1 stands for the group IA of the earlier system, while 17 stands for VIIA. (IUPAC: International Union of Pure and Applied Chemistry)
NOTE: The formulas $\text{H}_2$, $\text{F}_2$, $\text{Cl}_2$, $\text{O}_2$, and $\text{N}_2$, which show the type and number of atoms that are present in a molecule, are called **molecular formulas**.

For reasons that will become apparent below, the bond in such molecules is named **covalent** and the molecules **covalent molecules** (and the corresponding compounds are named **covalent compounds**).

Fig. 3 shows graphically the difference in energy between two separate hydrogen atoms (H) (top) and the hydrogen molecule (H$_2$) (below). We clearly observe that the hydrogen molecule has lower energy than the total energy for the two isolated hydrogen atoms, thus the molecule is more stable than the two separated atoms.

![Energy Diagram](image)

**FIGURE 3** The formation of a covalent bond results in the system acquiring a lower energy, as shown schematically for the case of formation of a hydrogen molecule from two isolated hydrogen atoms. On the other hand, energy will be required to break the bond (bond energy). The stronger the bond, the greater the energy that will be needed.

- In 1916 Lewis proposed his ingenious model of **an electron pair** shared between the two bonded atoms of e.g. hydrogen, fluorine, etc. The bonds are justified by the concept of **an electron pair**, because of the contribution of electrons and the overlap of the *valence electron clouds*.

- The rule of eight electrons (octet rule) helps to predict: (a) the number of covalent bonds formed by any atom, and (b) the stoichiometry of a molecule of the resulting compound.

**EXAMPLE: Formation of a covalent bond in the molecule H$_2$**

Let us now consider how two hydrogen atoms might be combined to form a hydrogen molecule. Each hydrogen atom can contribute its single electron to produce a common shared electron pair, that is, a pair that now belongs to both atoms. In this way each of two atoms will acquire the electronic structure of the noble gas 'helium' (He):

$$ \text{H}^- + \text{H}^+ \rightarrow \text{H} : \text{H} $$

Fluorine gas: the first element in the group of halogens is the most electronegative of all chemical elements.

The metal cesium (Cs), the penultimate element of the group of alkali metals is the most electropositive of all the naturally occurring chemical elements. (The element francium, Fr, the heaviest of the alkali metals is in fact more electropositive than Cs, but is radioactive and unstable and must be synthesized artificially - artificial chemical element.)

**The Octet Rule**

Atoms tend to fill their valence shell with eight electrons to obtain a noble gas structure - unless the outer shell is the K shell, where only two electrons are needed to obtain such a structure.
The formula \( H : H \) showing all valence electrons of the atoms involved in the chemical bond is called an **electronic formula** or **Lewis structure**.

We can similarly account for the covalent bonding in the molecules \( F_2 \) and \( Cl_2 \). We observe that the molecules \( H_2, F_2 \) and \( Cl_2 \) all have a shared electron pair and we say that we have a **SINGLE BOND**, which is denoted by a single *dash* between the two atoms: \( H─H, F─F \) and \( Cl─Cl \).

**NOTE:** The formulas \( H─H, F─F, \) and \( Cl─Cl \) that show the chemical bonds in a molecule (how the atoms of the molecule are linked by chemical bonds) are called **structural formulas**. For \( F_2 \) and \( Cl_2 \) the corresponding **electronic formulas** (Lewis structures) are:

![Lewis Structures](image)

Using similar reasoning we find that in \( O_2 \) we have a **DOUBLE BOND** (two shared electron pairs) (structural formula: \( O═O \)), while in \( N_2 \) we have a **TRIPLE BOND** (structural formula: \( N≡N \)) (three shared electron pairs). The corresponding **electronic formulas** are:

![Covalent Bonding](image)

**Covalent bonding between atoms of different chemical elements**

In the case of homonuclear diatomic molecules, the two bonded atoms are identical, have the same electronegativity and therefore the same capacity to attract the common electron pair. We can now study the bond that will be formed between atoms of different elements (a **heteronuclear bond**), where the atoms can have different though not very different electronegativities. In fact both elements will be nonmetals, e.g. \( HCl \) (hydrogen chloride), \( H_2O \) (water), and \( NH_3 \) (ammonia).

**EXAMPLE: Formation of a hydrogen chloride molecule (HCl) from a \( ^1H \) atom and a \( ^17Cl \) atom**

Here both atoms contribute their single (unpaired) electron to form a **covalent bond**. In this way both atoms are able to acquire a noble gas structure. On the basis of the electronic formula, we observe that in the \( HCl \) molecule we have three non-bonding electron pairs (that is, electrons not participating in the formation of bonds) and one bonding pair, which constitutes the covalent bond:
The above representations, showing the distribution of the valence electrons in the molecule, and the formation of covalent bonds, are called **electronic formulas** or **Lewis structures**. The covalent bond may be represented with a dash (H—Cl, **structural formula**).

- The nature of the chemical bond in this case is also covalent and is indeed similar to that for the case of homonuclear molecules. The basic difference is that the two atoms now have different, but not very different, electronegativities. This results in **bond polarization**, which we will study later.

It is evident from the above that the octet rule can help our understanding of: (a) the number of covalent bonds formed between two atoms, and (b) the stoichiometry of a molecule of the resulting compound [e.g. (H)$_2$(Cl)$_2$, (H)$_2$(O)$_2$, (H)$_2$(N)$_2$]. But note that there are many covalent compounds for which this rule does not apply (e.g., BF$_3$).

**EXERCISE:** Confirm that in the case of the molecule BF$_3$, the octet rule does not apply.

### 3. IONIC BONDING

We begin now to study a second type of chemical bond, the **ionic bond**, from the experimental observation that the melts of certain compounds (e.g. NaOH, NaCl) (as well as the aqueous solutions of electrolytes - ACIDS, BASES AND SALTS) are conductors of **direct electric current** (while a pure liquid or liquefied covalent compound, e.g. Br$_2$, is not). This leads to the conclusion that in the **electrolytes** [melts (see Fig. 4) and aqueous solutions*] there exist mobile electric charges, which we call **ions**. In contrast, in the solid state of these compounds there is no mobility, so we do not have conduction of electricity.

- The overall system (melt or solution of the electrolyte) is electrically neutral, leading to the assumption of the existence of **positive** and **negative ions**, which overall in the electrolyte have equal but opposite electric charges.
- These experiments suggest that for substances where the melts are electrical conductors, **ions must preexist in the crystal lattice**.
- In the crystal lattice oppositely charged ions will attract each other, while ions with charges of the same sign will repel each other, through Coulombic interactions. These forces are exerted between **any two ions** in a crystal lattice, but become stronger as the ions lie closer to each other (see Fig. 5).

Chemical analysis is able to show the ratio of positive to negative ions in an ionic compound, e.g. (Na)$_2$(Cl)$_2$, (Ca)(Cl)$_2$, (Fe)$_2$(Cl)$_2$, (Fe)$_3$(Cl)$_3$, (Na)$_2$(O)$_2$, (Ca)$_2$(S)$_2$. Moreover, experimental data can quantify the electric charge of any specific ion, Na$^+$, Cl$^-$, Ca$^{2+}$, Fe$^{2+}$, Fe$^{3+}$, O$^{2-}$.

* Dissolution of NaCl(s) in water results in dissociation of the crystal, so that the ions are now able to move freely (a conductor of electricity).
These charges then explain the ratio of positive and negative ions in any ionic compound.

To explain the charges on these ions, we use the MODEL of electron transfer from the atom of the more electropositive element to the atom of the more electronegative element, resulting in a cation and an anion, which obey the **octet rule**.

**Formation of ionic compounds**

An atom of any element of the alkali metal group (e.g., sodium, Na) contains only a single electron in its outer shell. The sodium ion, Na⁺, has lost this valence electron and has thereby acquired a noble gas (Ne) structure. Furthermore, the atom of any element of the halogens group (e.g., chlorine, Cl) has seven electrons in its outer shell. The chlorine ion, Cl⁻, has gained an electron and thereby acquired a noble gas structure (Ar).

- In general, elements where the atoms have "few" electrons in their outer shell have a tendency to lose electrons to form cations (**electropositive elements**). This usually happens with the elements from the first three main groups (IA, IIA, IIIA) of the periodic table.
- Conversely, elements where the atoms have "many" electrons in their outer shell have a tendency to gain electrons to form anions (**electronegative elements**). This usually happens with the elements of the last three groups (not counting the noble gases group) on the right-hand side of the periodic table (groups VA, VIA and VII).

Let us now look at another example of ionic compound formation, that of lithium fluoride, LiF, from the metallic element lithium (3Li) and the nonmetallic element fluorine (9F). The electronic structure of the atoms are: 3Li(2,1) and 9F(2,7). Accordingly, in LiF we have: Li⁺(2) and F⁻(2,8).
In an analogous manner, the ionic compound NaCl is formed from sodium (\(_{11}\text{Na}\)) and chlorine (\(_{17}\text{Cl}\)). The electronic structure of the sodium atom is: \(_{11}\text{Na}(2,8,1)\) and the electronic structure of the chlorine atom is: \(_{17}\text{Cl}(2,8,7)\). Therefore, in NaCl we have: Na\(^+(2,8)\) and Cl\(^-(2,8,8)\).

**IMPORTANT NOTE 1:** Ionic compounds have a *crystalline structure*, in which the ions are located so that, in NaCl for example, each cation is surrounded by six anions and each anion is surrounded by six cations (see Fig. 6). This arrangement ensures that minimum energy and hence maximum stability is achieved. Moreover, it is apparent that in the crystal of an ionic compound, such as NaCl, the *Coulomb forces are exerted in all directions, between each pair of Na\(^+\) and Cl\(^-\).*

**IMPORTANT NOTE 2:** In ionic compounds there is no concept of *molecules*, but the chemical formulas simply show the simplest *integer ratio* of positive and negative ions in the crystal.

**IMPORTANT NOTE 3:** Let us consider the formation of crystalline NaCl(s) from the chemical reaction between *elemental sodium metal*, Na(s) and *elemental chlorine gas*, Cl\(_2\)(g). This is quite a complex process, involving far more than the formation of individual Na\(^+(g)\) ions and Cl\(^-(g)\) ions from individual atomic gaseous Na(g) and Cl (g), with loss and gain of an electron, respectively. In fact an isolated Na\(^+(g)\) ion together with an isolated Cl\(^-(g)\) ion are not energetically more stable than an individual Na(g) atom together with an individual Cl(g) atom. As mentioned above (Important Note 1), the achieved crystalline state ensures minimum energy, that is maximum stability, for the system. We conclude that it is NOT the octet rule that “imposes” the formation of an *ionic bond*; however, the octet rule is able to explain the charges on the ions and the stoichiometry of ionic compounds.

Fig. 5 shows a two-dimensional representation of the crystal structure (of the crystal) of NaCl, in which each cation is surrounded by four anions, and each anion is surrounded by four cations. The fifth and the sixth counter ions are found in the parallel ion layers above and below the plane of the paper. (See also the three-dimensional representation of the NaCl crystal structure in Fig. 6.)

- Therefore, **in ionic compounds there is no concept of a molecule**. (Compare with the case of the covalent bond in the molecule H-H or the case of water in Fig. 7). The chemical formula, for example NaCl, merely shows the simplest integer ratio of cations and anions in the crystal.

**Electronic formulas of ionic compounds**

As we did for covalent/molecular compounds, we can also write *electronic formulas* (Lewis structures), for ionic compounds, showing in this case all valence electrons of the two ions.
NOTE 1: In the electronic formulas for ionic compounds, the anion with its valence electrons is placed within square brackets, with its electronic charge as a right-hand superscript outside the brackets.

NOTE 2: As a metal atom loses all its valence electron(s) (these electrons having been gained by the nonmetal atom), cations are shown without electrons in the electronic formulas.

**Features of ionic compounds**

The key features of ionic compounds are:

1. They are mostly metal oxides (e.g., Na₂O, CaO), metal hydroxides (e.g., NaOH, Ca(OH)₂), and salts (e.g., NaCl, CaCl₂).

2. As a general rule (but with exceptions as we will see below) the bond between a metallic atom (e.g. Li, Na, Ca) and the atom of a nonmetallic element (e.g. O, F, Cl) is ionic; therefore, the bond is between ions Li⁺, Na⁺, Ca²⁺, O²⁻, F⁻, Cl⁻ and not between neutral atoms.

3. Molecules do not exist in ionic compounds; rather a crystal is formed in which the ions are the structural units.

4. They have high melting points because strong Coulomb forces hold the ions in the crystal. For example, common salt (sodium chloride) melts at about 800°C.

5. Their crystals are hard and brittle, not malleable and ductile, as is the case with the crystals of metals.

6. Unlike the crystals of metals (metallic crystal lattices, see Fig. 8), ionic compounds are poor conductors of electricity in the solid state. However, their melts and aqueous solutions do conduct electricity.

7. Many ionic compounds are soluble in water.

---

*Ionic compounds: Lewis structures*

- NaCl → Na⁺ + [Cl⁻]
- MgBr₂ → Mg²⁺ + 2[Br⁻]
- K₂S → 2K⁺ + [S⁺]
- Al₂O₃ → 2Al³⁺ + 3[O²⁻]

*The formulas of ionic compounds may be written so as to show clearly the ions:

\[(\text{Na}^+)_2\text{O}^{2-}\]
\[\text{Ca}^{2+}\text{O}^{2-}\]
\[\text{Na}^+(\text{OH})^-\]
\[\text{Ca}^{2+}[(\text{OH})^-]_2\]
\[\text{Na}^+\text{Cl}^-\]
\[\text{Ca}^{2+}(\text{Cl}^-)_2\]
Melting points of ionic compounds

We noted previously that ionic compounds have high melting points. But how do melting points vary? The first table in the right-hand column below lists the melting points of ionic compounds (salts) with a constant cation (Na⁺) but different anions from the VIIA group of the periodic table (halogens). We note a decrease in melting point from top to bottom. This can be explained on the basis of the increasing size of the anions from top to bottom: the larger the anion, the larger the cation-anion distance, thus diminishing the attractive Coulomb forces between the cation and anion.

Similarly the second table in the right-hand column below lists melting points for ionic compounds (salts), where the anion (Cl⁻) has been kept constant but the cation is varied down the first group of the periodic table (alkali metals, group IA). The decreasing melting points can again be explained by the increasing size of the cations from top to bottom.

4. COVALENT BOND (Part II)

Features of covalent (or molecular) compounds

1. Covalent (or molecular) compounds are significantly different from ionic ones; they occur as discrete clusters of atoms (molecules), rather than as extensive aggregates (crystals). Moreover, the attractive forces between molecules are weak, compared to those between the ions in the crystal lattice. Therefore, molecular compounds tend to occur as soft solids with low melting points, liquids with low boiling points, or gaseous substances. Of course, there are cases in which the atoms are linked together by COVALENT BONDS to form macromolecules/ giant structures, such as in the case of diamond or graphite, two carbon macromolecules (see, Fig. 9): diamond is characterized by extreme hardness, while both have very high melting points.

2. Covalent compounds are mostly compounds between non-metals: H₂O HCl, NH₃, CH₄, CCl₄. Oxides of non-metals (e.g., H₂O, CO, CO₂, SO₂) is a broad category here.

3. They are poor conductors of electricity when pure, but the aqueous solutions of some covalent compounds (e.g. acids) do conduct electricity.

<table>
<thead>
<tr>
<th></th>
<th>m.p. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaF(s)</td>
<td>+993</td>
</tr>
<tr>
<td>NaCl(s)</td>
<td>+801</td>
</tr>
<tr>
<td>NaBr(s)</td>
<td>+747</td>
</tr>
<tr>
<td>NaI(s)</td>
<td>+661</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>m.p. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl(s)</td>
<td>+801</td>
</tr>
<tr>
<td>KCl(s)</td>
<td>+770</td>
</tr>
<tr>
<td>RbCl(s)</td>
<td>+718</td>
</tr>
<tr>
<td>CsCl(s)</td>
<td>+645</td>
</tr>
</tbody>
</table>

FIGURE 8. Representation of the chemical bond in metals (metallic bond).

Observe that cations of the metal form a solid metallic lattice. The electrons released by the formation of metal cations (each metal atom has lost one electron) do not belong to any specific cation, but are free to move throughout the lattice. The electrical conductivity of the metal can be attributed to this mobility of the electrons.

FIGURE 9. Graphite (left) and diamond (right) are examples of crystalline solids where atoms are linked by covalent bonds (covalent crystals).
Boiling points of covalent compounds

As mentioned previously, covalent compounds usually occur as soft solids with low melting points, liquids with low boiling points, or as gases. We will now consider how their boiling points vary. The adjacent table gives the boiling points for covalent (molecular) compounds, containing a constant nonmetallic element (H) and different atoms from the VIIA group of the periodic table (halogens). With the exception of HF, which has an anomalously high and positive b.p. (it is a gas only at temperatures above about 19°C), we observe an increase in the boiling point as we move to heavier halides. The complete explanation for both the HF anomaly and the trend for the other compounds cannot be given on the basis of our knowledge to date, but requires an understanding of the forces between molecules ("intermolecular forces" or more correctly "intermolecular bonds").

<table>
<thead>
<tr>
<th>Compound</th>
<th>b.p. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF(g)</td>
<td>+19.5</td>
</tr>
<tr>
<td>HCl(g)</td>
<td>-85</td>
</tr>
<tr>
<td>HBr(g)</td>
<td>-67</td>
</tr>
<tr>
<td>HI(g)</td>
<td>-35</td>
</tr>
</tbody>
</table>

Variation of energy in a covalent bond

Fig. 10 shows the change in potential energy as the distance between the two hydrogen atoms ($R_{HH}$) in the hydrogen molecule ($H_2$) is varied. We note that at a particular internuclear distance $R_o$, the energy reaches a minimum. This is the most stable arrangement and $R_o$ is referred to as the length of the chemical bond.

Nonpolar and polar covalent bonds

In the case of a diatomic homonuclear covalent molecule (such as $H_2$), the atoms forming the bond have the same capacity to attract electrons, since they have the same electronegativity. The shared electron pair is therefore equidistant from each of the two atoms. Such a bond is called nonpolar. However, in the case of a diatomic heteronuclear covalent molecule, the electron pair will be closer to the more electronegative of the two bonded atoms. The molecule now has the characteristics of a dipole: the more electronegative atom being partially negatively charged and the less electronegative atom being partially positively charged. Such a covalent bond is called polar.
Let us consider, as an example, molecules of the hydrogen halides, HF, HCl, HBr and HI. The difference in electronegativity is 1.9 for HF, 0.9 for HCl, 0.7 for HBr and 0.4 for HI. Therefore, in HF we have a more polar covalent bond, while in HI the covalent bond is less polar.

An analogy for the chemical bond: the chemical bond as a tug-of-war game

Imagine two friends playing a game of tug-of-war. They hold a thick rope at both ends and compete to see who can pull the rope stronger and move the friend towards himself/herself. Imagine further that the weather is cold, and that a source of heat (a heater) is fixed, in the middle of the rope, so both the friends are trying to bring the heater closer so as to warm themselves.

Usually the stronger player will be able to draw the rope and heater closer to him or her, but will be forced to hold it at a certain distance so as not to be burned. If it should happen that the two players are of exactly equal strength, the heater will be maintained at an equal distance from both. While, a player may momentarily displace the heater to his/her side, the other will quickly bring it back to the “equilibrium position”. Our conclusion is that both players will be held together by their efforts to claim the heater for themselves, justifying the analogy with the chemical bond.

Provide mappings in the table below to illustrate the relationship between the two players and the atoms (the two "players") of the chemical bond:

<table>
<thead>
<tr>
<th>Tug-of-war game</th>
<th>Chemical bond</th>
</tr>
</thead>
<tbody>
<tr>
<td>Players</td>
<td>↔</td>
</tr>
<tr>
<td>The player’s strength</td>
<td>↔</td>
</tr>
<tr>
<td>Heater</td>
<td>↔</td>
</tr>
<tr>
<td>Players with same strength</td>
<td>↔</td>
</tr>
<tr>
<td>Players with differing strengths</td>
<td>↔</td>
</tr>
</tbody>
</table>

Therefore, the ionic bond can be regarded as an extreme case of a polar covalent bond, with bond polarity even larger for an ionic bond.

Shapes of molecules with polar covalent bonds*

\[
\begin{align*}
H & \quad (\delta+) \quad Cl & \quad (\delta-) \\
\text{O} & \quad (2\delta-) & \quad (\delta-) \quad (2\delta+) \quad (\delta-) \\
\text{H(\delta+)} & \quad \text{H(\delta+)} & \quad \text{O} = \text{C} = \text{O}
\end{align*}
\]

* The value of $\delta$ varies, depending on the difference in electronegativity of the two atoms forming the bond. The larger the difference, the more polar the bond will be.
5. CHEMICAL BONDS - NOT TWO EXTREME CASES, BUT A CONTINUOUS GRADATION

As noted above, the difference in electronegativity between the two atoms involved in forming a chemical bond can vary significantly, giving rise to a variety of polarity of bonds. The difference in electronegativity between the two atoms participating in the bond and the resulting polarity of the bond allows us to assign a percentage ionic character and a percentage covalent character to the bond.

- In principle, a purely ionic bond does not really exist, and each ionic bond has to a greater or lesser extent some degree of covalent character. The larger the electronegativity difference between two atoms, the more ionic the bond will be. Thus, while the bond in Si-O is ~50% ionic and ~50% covalent, the bonds in Na-Cl and Mg-O have a smaller proportion of covalent character.

- According to Pauling, a difference of 1.7 in electronegativity between the bonded atoms (on the Pauling scale) corresponds to 50% ionic character, so a difference of more than 1.7 corresponds to a bond that is primarily ionic.

The continuum between ionic and covalent bonding is illustrated by the variety of values observed for the melting points of different halogen compounds (see table below). Identify the compounds that are solids at room temperature and those that are liquids. Note, also, which of the halogen compounds are composed of a metal and a nonmetal and which are composed of two nonmetallic atoms. The first five compounds have more ionic character, the last three have more covalent character, while AlCl₃ (although a compound between a metal and a nonmetal) has a larger covalent than ionic character.

### Melting points of various halogen compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>m.p. °C</th>
<th>MgCl₂(s)</th>
<th>AlCl₃(s)</th>
<th>SiCl₄(l)</th>
<th>SCl₂(l)</th>
<th>PCl₅(l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaF(s)</td>
<td>+902</td>
<td>+714</td>
<td>+190</td>
<td>−70</td>
<td>−78</td>
<td>−112</td>
</tr>
<tr>
<td>NaCl(s)</td>
<td>+801</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaBr(s)</td>
<td>+755</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaI(s)</td>
<td>+651</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

EXERCISE 1. Compare the electronegativity differences between the atoms forming the compounds in the above table.

EXERCISE 2. Compare the electronegativity differences between oxygen and the other atom in the following compounds (oxides) Na₂O, MgO, SiO₂, and H₂O.

EXERCISE 3. Compare the electronegativity differences for the atoms making up the hydrogen halides, HF, HCl, HBr and HI.
For the molecules HF, HCl, HBr and HI, the percentage ionic character, calculated using an accurate method, was found to be 41, 18, 12 and 6% respectively, in agreement with the electronegativity differences. The case of HF, where the electronegativity difference of 1.9 would be expected to result in a mainly ionic bond, is interesting: HF is a gas at temperatures above 19ºC, so it appears that here the covalent character must dominate.

- In conclusion, the electronegativity difference is not the only criterion for the prediction of the type of bond formed. Indeed, there are cases of bonds between atoms with large electronegativity difference (such as HF), which experimentally demonstrate a covalent nature.

**EXERCISE 4.** The following table gives the percentage ionic character in several common covalent bonds. Compare these values with the corresponding differences in electronegativity.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Ionic character (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H</td>
<td>33</td>
</tr>
<tr>
<td>N-H</td>
<td>27</td>
</tr>
<tr>
<td>C-H</td>
<td>8</td>
</tr>
<tr>
<td>C-F</td>
<td>23</td>
</tr>
<tr>
<td>C-Cl</td>
<td>18</td>
</tr>
<tr>
<td>C-O</td>
<td>13</td>
</tr>
<tr>
<td>C-N</td>
<td>7</td>
</tr>
</tbody>
</table>

**Conclusions**

- We consider a chemical bond to be ionic when the ionic character is greater than the covalent character. The larger the electronegativity difference between the two bonded atoms, the more ionic the bond is likely to be.
- Chemical bonds between atoms of different elements are polar, with a partially ionic and a partially covalent character. If the covalent character is dominant, we have a **polar covalent bond**, if the ionic character dominates, we have **ionic bonding**.
- In the general case, a chemical bond (covalent or ionic) shows a **partial covalent** and a **partial ionic** character, and thus we are not restricted to the extreme types of bonds (covalent at one end and ionic at the other), but a **continuous variation between these two extremes**.
Examples

In silica (SiO$_2$), a compound between a semi-metallic element, silicon, and a non-metal, oxygen we have approximately 50% ionic character and approximately 50% covalent character. In ionic compounds such as sodium chloride (NaCl) and magnesium oxide (MgO) we have a smaller percentage of covalent character,* while in covalent compounds such as hydrogen bromide (HBr) and hydrogen iodide (HI) we have a higher percentage of covalent character (88 and 94% respectively).

Exercises and Problems

Chemical bonds

From the school textbook, pp. 74-77. (See end of APPENDIX 1)

NOTES

1. Part of the present text has been taken from the official Greek chemistry textbook:

Liodakis S., Gakis D., Theodoropoulos D., Theodoropoulos P., & Kallis A., Chemistry for the 10$^{th}$-grade general education, Student’s Book (pp. 52-61).

PUBLISHER: Greek Ministry of Education and Religious Affairs / Institute of Educational Policy / Diophantos, Institute of Technology, Computers, and Publications.

Accessible openly at:

http://ebooks.edu.gr/modules/ebook/show.php/DSGL111/476/3148,12654/

2. A number of the illustrations (Table 1 and some figures, see Appendix 1) have been taken from the above textbook, while many others have been taken from the Internet.

* The estimated percentage ionic character for NaCl, using an accurate approach is 68%, so even for NaCl we have approximately 1/3 covalent character.