Electronic Supplementary Material (ESI) for Chemistry Education Research and Practice.

APPENDIX 1. Material on chemical bonding from the standard Greek textbook*, **

* ***Chemistry for the 10th-grade general education*** (Student's Book, in Greek, pp. 52-61). AUTHORS: Liodakis S., Gakis D., Theodoropoulos D., Theodoropoulos P., & Kallis A. 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/

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

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

What is a bond? When and why is it created?

Most, if not all, of the world's material wealth that surrounds us derives from compounds formed by combining the elements of the periodic table. The hundred or so known chemical elements can give rise to millions of different combinations (compounds) in the same way that the relatively small number of phonemes that make up a language can produce countless words. Atoms are linked to form compounds by means of chemical bonds. Simply put, the **chemical bond** is the "glue" that binds the atoms (or other building blocks of matter, for example ions) together, to form associations or even other groups of atoms, such as polyatomic elements e.g. S_8.

.

- A chemical bond is created when the structural units of matter (atoms, molecules, or ions) come close enough together, so that the **attractive forces** that are developed between them (e.g., between the nucleus of one atom and the electrons of another atom) overcome the **repulsive forces** involved (i.e. between the nuclei and between their electrons). ***Connections of atoms are made through their valence electrons, that is, the electrons of the outermost electron shell***. Remember that the electronic structure of atoms exhibits periodicity, which is expressed through the arrangement of the elements in the periodic table. This structure is reflected in the type and strength of the bonds that develop between the atoms of the elements. Finally, it should be emphasized that the creation of a chemical bond results in a lowering of energy, making the system more stable**.**

• Approximately 600,000 compounds are synthesized every year.

• The chemical bond is the force that holds the atoms (or other structural units of matter, e.g., ions) together.

• Valence electrons, the "influential" electrons, those which have the capacity to make chemical bonds.

Factors that determine the chemical behavior of atoms

The chemical behavior of an element is primarily determined by two parameters:

1. the valence electrons
2. the size of the atom (*atomic radius)*

These fundamental characteristics of an atom will be addressed separately, and will be associated with the chemical behavior and consequently the type of chemical bonding that they are causing.

• Since the mid-1960s a number of noble gas compounds, e.g. XeF_2, XeO_4, have been successfully synthesized in the laboratory under specific conditions.

Valence electrons

It is known that the electronic structure, especially the outer (v*alence*) electrons, is responsible for the chemical behavior of an atom. Elements that possess a completed outer shell of eight electrons (except the K shell, which is filled with two electrons) do not tend to form compounds. The noble gases belong to this category. Atoms of these elements exist in a very stable energy state, and this stability can be attributed to their filled outer shell.

Atoms of the other elements are not "in the same boat", that is, they do not have an octet of electrons in their outer shell (or a dyad of electrons in the case of the K shell) but try to acquire this structure, that is, to "look like" the noble gases. They can achieve this chemically by losing, gaining or sharing electrons to acquire the stable electronic structure of the noble gases (***octet rule***). Note that for up to 4 valence electrons, the electrons are single (unpaired), but for 5 or more electrons they begin to form pairs. Using the data in TABLE 2.2 below we can predict the electronic formulas of compounds likely to be formed.

• **Octet Rule:**
Atoms tend to fill their valence shell with eight electrons (unless it is the K shell which requires two electrons to be filled) to acquire a noble gas structure.

TABLE 2.2: Valence electrons of elements that belong to main groups (groups A) of the periodic table

IA	IIA	IIIA	IVA	VA	VIA	VIIA	Noble gases
H·							He:
Li·	·Be·	·B·	·C·	:N·	:O·	:F·	:Ne:
Na·	·Mg·	·Al·	·Si·	:P·	:S·	:Cl·	:Ar:
K·	·Ca·				:Se·	:Br·	:Kr:
Rb·	·Sr·				:Te·	:I·	:Xe:
Cs·	·Ba·						

For example an element of the IA group in the periodic table (the alkali metals) has a single electron in its outer shell, which it seeks to lose, so that it can attain a noble gas structure. In this way it is charged positively (electropositive element). In an analogous manner, an element of the VIIA group in the periodic table, which has seven electrons in its outer shell, seeks to gain an electron to obtain a noble gas structure, and so becomes negatively charged (electronegative element). We can conclude that elements that have "few" electrons in their outer shell have a tendency to lose electrons; this usually happens with the elements of groups IA, IIA, and IIIA in the periodic table. On the other hand, elements with "many" electrons in their outer shell have a tendency to gain electrons; this usually happens with the elements of the VA, VIA and VIIA groups in the periodic table.

Atomic radius (the size of the atom)

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

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

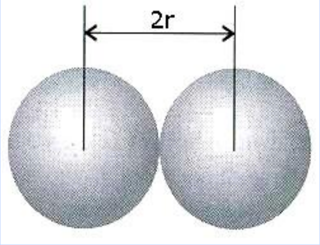
- Across a period, the atomic radius decreases from left to right.

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,

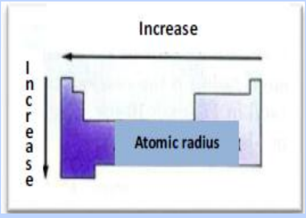
- Within a group, the atomic radius increases from top to bottom.

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.

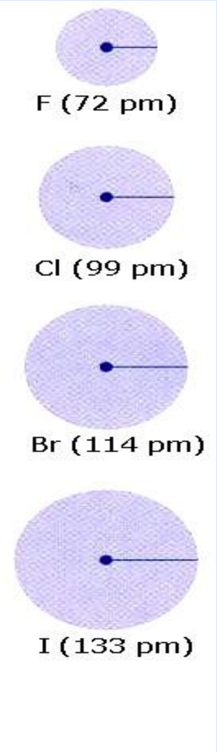
It follows from this that a cesium (Cs) atom will lose an electron more easily than a sodium (Na) atom. Similarly, a chlorine (Cl) atom can gain an electron more easily than an iodine (I) atom.



The atomic radius is defined as half the distance between the nuclei of two adjacent atoms of an element, which are in the solid crystalline state.



The atomic radius of the elements in the periodic table increases from right to left and from top to bottom.



The atomic radii of the halogens

Types of chemical bonding

There are two main types of chemical bonding, **ionic bonding** and **covalent bonding**. In addition to these, there are other types of bonds, such as the metallic bond (occurring in metals or alloys), the Van der Waals bonds (developed between molecules), etc.

Ionic bonding

- Ionic bonding usually occurs between a metal (that is, an element that tends to lose electrons) and a nonmetal (an element that tends to gain electrons). The bond derives from the attraction of oppositely charged ions, the cations (which are positively charged) and the anions (which are negatively charged). These ions are formed by electron transfer, e.g. from the metal to the nonmetal.

In other words, during the formation of an ionic bond between two atoms, one atom loses 1-3 electrons, thus taking the form of a cation (positive ion) and the other atom gains 1-3 electrons, thus taking the form of an anion (negative ion).

The ions formed are attracted to each other by electrostatic Coulomb forces and are arranged in space in regular geometrical shapes to form ionic crystals.

Let us now consider how the ionic compound LiF can be formed, from the metallic element lithium ($_3Li$) and the nonmetallic element fluorine ($_9F$). The electronic structure of the atoms are: $_3Li(2,1)$ and $_9F(2,7)$. When the two atoms come close to one another, an electron is transferred from the Li atom to the F atom, and in this way they both obtain a noble gas structure, changing into oppositely charged ions, that is, we have: $Li^+(2)$ and $F^-(2,8)$, as shown schematically below:

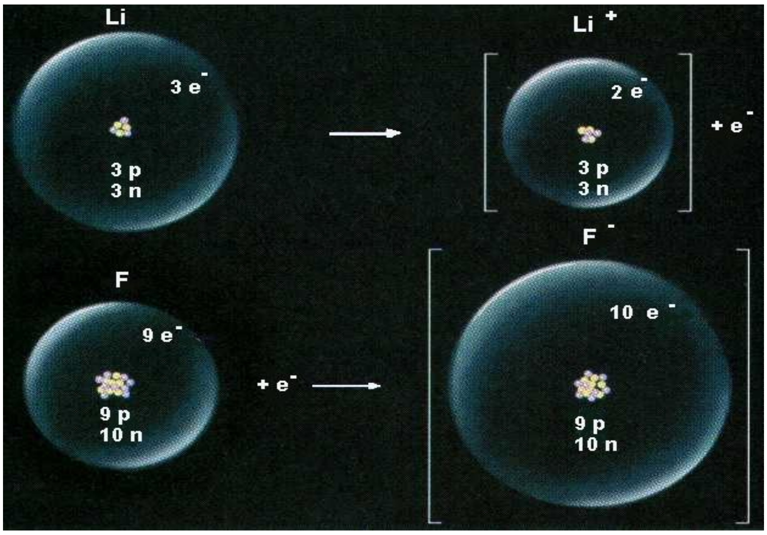
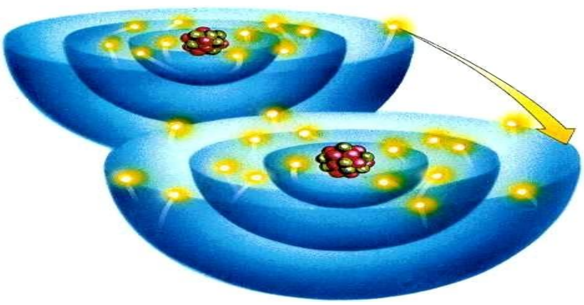


FIGURE 2.3 Schematic drawing showing the formation of the ionic compound LiF by Li and F.

Observe that in the figure above, expulsion of an electron from the Li atom leads to a reduction of its atomic radius. So cations are always smaller than the corresponding neutral atoms. Alternatively, the gaining of an electron by a neutral fluorine atom results in an increase in the atomic radius, which is why the anions are always larger than the corresponding neutral atoms.

Similarly, the ionic compound NaCl is formed from sodium ($_{11}Na$) and chlorine ($_{17}Cl$). The electronic structure of the sodium atom is: $_{11}Na(2,8,1)$. By losing the valence electron, the Na atom acquires the structure (2,8), that is the noble gas structure of neon. In this way, the sodium cation is formed: $Na \rightarrow Na^+ + e^-$.

The electronic structure of the chlorine atom is: $_{17}Cl$ (2,8,7). By gaining the electron lost by the Na atom, the Cl atom acquires the structure (2,8,8), that is, the noble gas structure of argon. Hence the chlorine anion is formed: $Cl + e^- \rightarrow Cl^-$



As the atomic radius increases, and the number of valence electrons decreases, the capacity of the atom to lose electrons increases. That is, the electropositive (metallic) character of the element increases

• On the contrary, as the atomic radius decreases, and the number of valence electrons increases, the capacity of the atom to gain electrons increases. That is, the electronegative (nonmetal) character of the element increases.

• Ionic bond is the forces of electrostatic nature that hold together the cations and anions in ionic compounds

FIGURE 2.4 Schematic drawing showing the formation of the ionic compound NaCl by electron transfer from Na to Cl

Finally, the ions that are formed are held together in fixed positions within a NaCl crystal by means of electrostatic forces. In the crystal, these Coloumb forces are exerted in all directions. In this way, the ions are accommodated so that each cation is surrounded by six anions and each anion is surrounded by six cations. This arrangement ensures that the system attains minimum energy, that is, maximum stability. Therefore, ***for ionic compounds there is no concept of a discrete molecule***; the chemical formula, e.g. NaCl, merely shows the simplest integer ratio of positive and negative ions in the crystal.

FIGURE 2.5 Schematic representation of the formation of solid sodium chloride (common table salt) from solid sodium metal and chlorine gas.

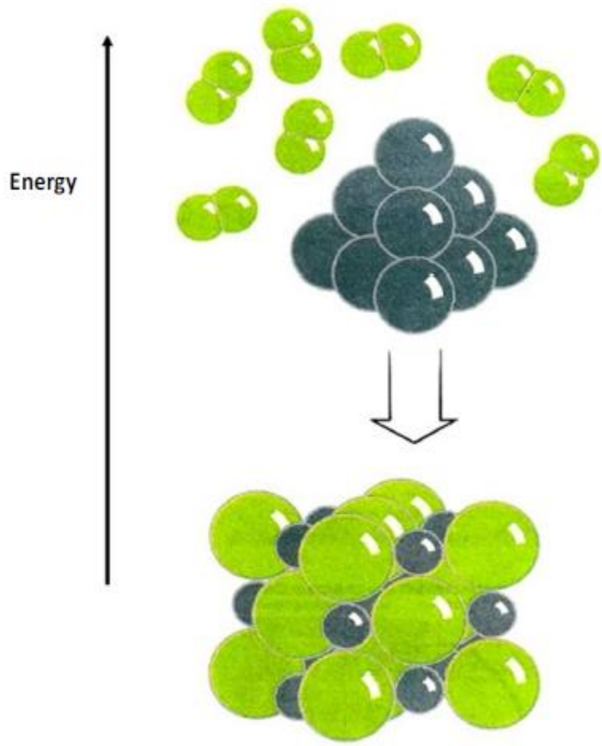
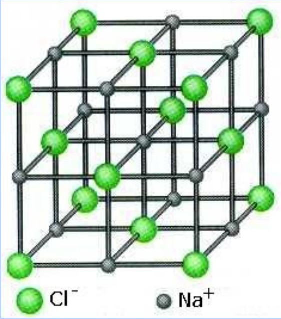
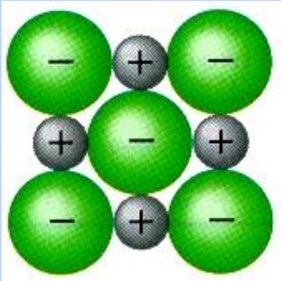


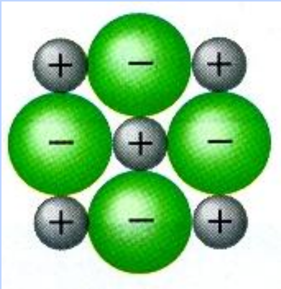
FIGURE 2.6 Crystal formation of NaCl from Na(s) and Cl_2(g). Notice that the Na^+ ions, resulting from loss of electrons, have a smaller size than the Na atoms (silvery spheres), while the Cl^- anions, resulting from the gain of electrons, have a larger size than the Cl atoms (yellow-green spheres). Also remember that an ionic bond leads the system to lower energy, as is shown graphically in the figure.



Repesentation of the NaCl crystalline lattice (expanded form).



Vertical cross-section of the crystal (first layer).



Vertical cross-section of the crystal (second layer).

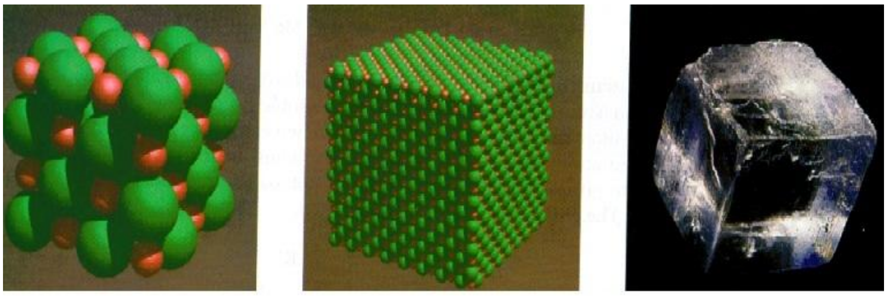
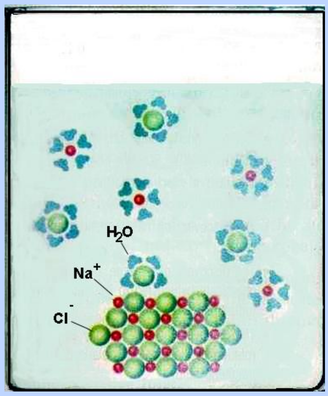


FIGURE 2.7 Representation of the crystal of NaCl (solid form). The photo on the right is a photo of a NaCl crystal, as it looks macroscopically.

Features of ionic compounds

The key features of ionic compounds are:

1. Ionic compounds are mostly metal oxides, metal hydroxides, or salts.
2. Discrete molecules do not exist in ionic compounds, rather a crystal (an ionic crystal) is formed, in which the ions constitute the structural units.
3. Ionic compounds have high melting points because of the strong Coulomb forces, which hold the ions in the crystal; for example, common salt (sodium chloride) melts at about 800°C.
4. Their crystals are hard and brittle, not malleable and ductile, as is the case with the crystals of metals.
5. Unlike the crystals of metals (metallic crystal lattices), ionic compounds in the solid state are poor conductors of electricity. However, their melts and their aqueous solutions do conduct electricity (see the figures below and on the right).
6. Many ionic compounds are soluble in water.



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)

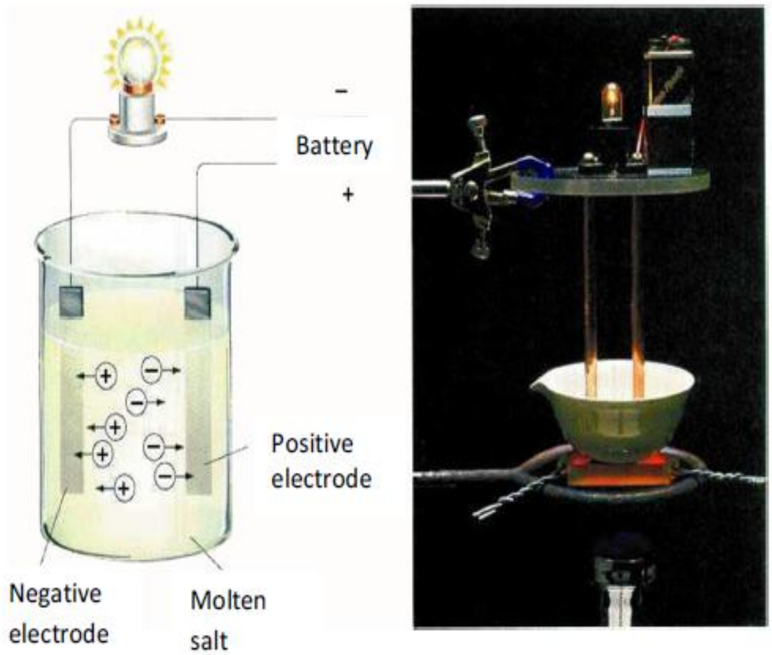


FIGURE 2.8. Melting a crystal of NaCl breaks up the lattice so that the ions can move freely (a conductor of electricity).

Covalent bonding

Let us now consider how a covalent bond may be formed. When a compound does not contain a metallic element, the amount of energy required to expel electrons tends to be very large, and therefore formation of an ionic compound is not possible. The best that can happen in this case, is that the atoms, while essentially retaining their own electrons, simultaneously enter into an “agreement of co-ownership", that is, they share common electron pairs between themselves.

➢ *When two neighboring atoms are held together by a pair of electrons, we say that they are linked by a covalent bond.*

This common electron pair is not limited to one atom, but spreads like a net, surrounding both atoms. It is also possible for atoms to share more than two electrons. Consequently, atoms may be linked by a single bond (one shared electron pair), a double bond (two shared electron pairs) or a triple bond (three shared electron pairs).

➢ *A covalent bond can connect atoms of the same element (nonmetals) or of different elements (usually nonmetals).*

Do not forget that, as in the case of ionic compounds, covalent bonds are formed only when the system is driven to a lower energy state to produce a more stable structure.
Let us now see how two hydrogen atoms can be connected to form a hydrogen molecule. Each of the hydrogen atoms contributes its single electron, resulting in the formation of a common electron pair, that is, a pair that belongs to both atoms. In this way both of the atoms acquire a noble gas (helium) structure:

$$H^{\cdot} + {}^{\cdot}H \longrightarrow H:H$$

In an analogous manner, we can consider the formation of a hydrogen chloride molecule (HCl) between one ${}_{1}H$ atom and one ${}_{17}Cl$ atom. The two atoms each contribute an unpaired electron to form a covalent bond. In this way both atoms are again able to acquire a noble gas structure:

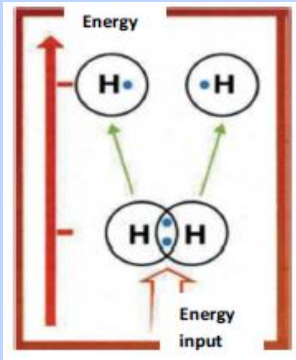
$$H^{\cdot} + {\cdot}\ddot{\underset{\cdot\cdot}{Cl}}: \longrightarrow H:\ddot{\underset{\cdot\cdot}{Cl}}: \qquad H-Cl$$

The above representations, showing the distribution of the valence electrons in the molecule, as well as the formation of covalent bonds, are called ***electronic formulas***. From the electronic formula for the HCl molecule we can observe that there are three non-bonding electron pairs (electrons that do not participate in bonding) and one bonding pair, the covalent bond. This covalent bond can also be represented by a hyphen.

At this point it is appropriate to make brief reference to the notion of electronegativity. ***The electronegativity of an element refers to the tendency of an atom of the element to attract electrons, when it participates in the formation of polyatomic units***.

Where the atoms forming a covalent bond are identical as e.g. in the H_2 molecule, the common pair of electrons of the covalent bond is attracted equally by both nuclei, in which case we have a uniform distribution of the shared electron pair between the two atoms and ***a nonpolar***

• A coordinate bond (or *dative covalent* bond) occurs when both the shared electrons are provided by only one of the two bonded atoms.



The formation of a covalent bond leads to a lowering of energy, as shown schematically above for the case of the formation of the hydrogen molecule. In contrast, to break a bond will require that energy (the bond energy) is provided. The stronger the bond, the larger the energy required.

• In general, the atoms of non-metals are joined by covalent bonds.

• The electronic formulas for molecules give us the same information as do the molecular formulas (that is, which atoms and in what proportions make up the molecule), but in addition, they also show the distribution of the valence electrons of the atoms.

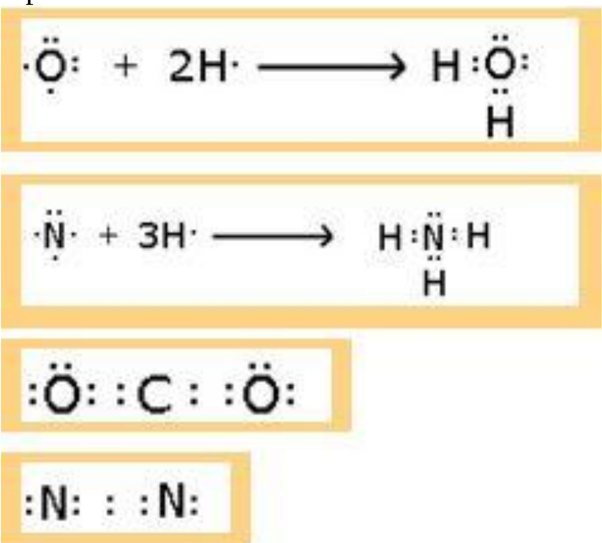
• The electronegativity of an atom indicates the force with which it attracts electrons in molecules of the compounds that it forms with other atoms. Note that as the atomic radius decreases and the number of valence electrons increases, the electronegativity value increases.

covalent bond is produced.

However, this will not be the case when the atoms forming a covalent bond are different, e.g. in the HCl molecule. In this case, the shared pair of electrons will be attracted more strongly by the more electronegative atom. Thus, there will be an uneven distribution of the shared electron pair with a greater proportion toward the more electronegative atom (in this case, Cl). Such a bond is called ***a polar covalent bond***. Clearly the greater the electronegativity difference between the two atoms, the more polar the covalent bond will be.

FIGURE 2.9 The polar covalent bond (*in the middle*) is an intermediate state between the nonpolar bond (*left*) and the ionic bond (*right*).

Electronic formulas for the polyatomic molecules water (H_2O) and ammonia (NH_3), and molecules with multiple covalent bonds: carbon dioxide (CO_2) and nitrogen (N_2) are given below. Note that in all cases, except for N_2, the covalent bonds are polar. Also note that a double and a triple bond consist of two or three shared electron pairs, respectively.



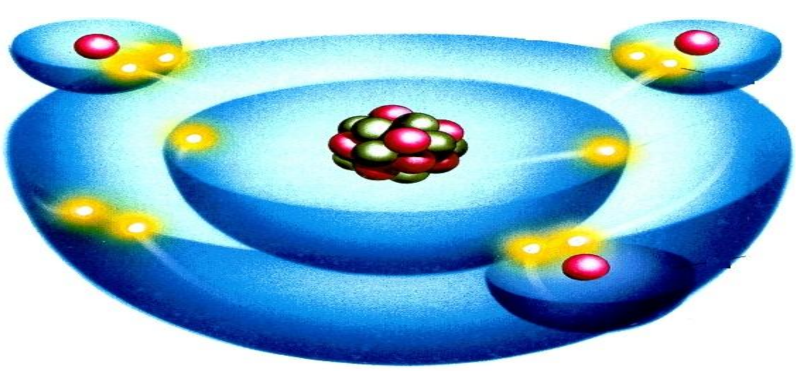


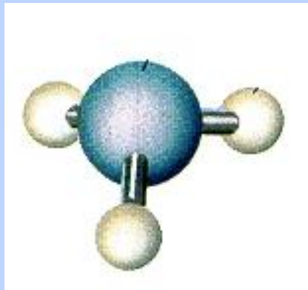
FIGURE 2.10 Schematic representation of the covalent compound NH_3

• Purely covalent or purely ionic bonds represent extreme cases. Most bonds are intermediate in nature.

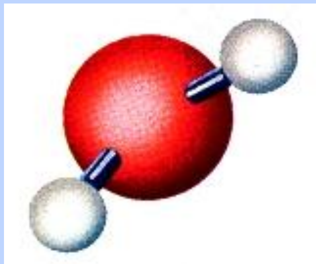
• A polar covalent bond indicates the existence of ionic character in the covalent bond.

Molecular models of covalent compounds

The HCl molecule



The NH_3 molecule



The H_2O molecule

The CO_2 molecule

Features of covalent or molecular compounds

1. Covalent (or molecular) compounds show significant differences from ionic ones. In particular, 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 existing between the ions in a crystal lattice. Therefore molecular compounds tend to occur as soft solids with low melting points, liquids with low boiling points, or as gases. Of course, there are cases in which atoms are covalently linked together to form macromolecules, as in the case of diamond and graphite, which can lead to extreme hardness and high melting points.

2. Covalent compounds are usually formed between nonmetals, e.g., acids, oxides of nonmetals, etc.

3. Covalent compounds in their pure state tend to be poor conductors of electricity, but aqueous solutions of some of these compounds (e.g. acids) do conduct electricity.

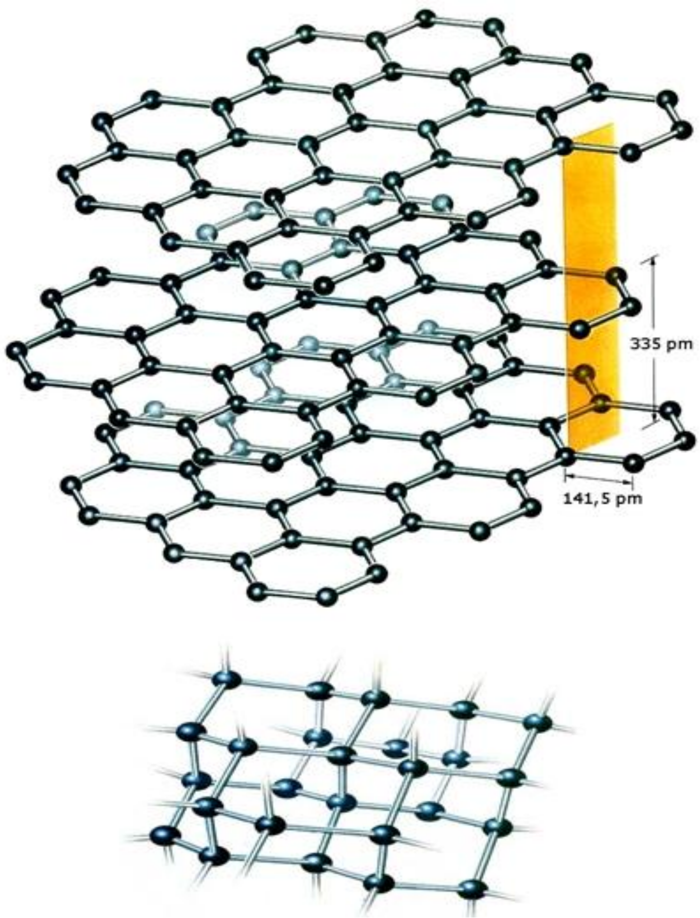


FIGURE 2.11 Graphite (above) and diamond (below) are examples of crystalline solids where atoms are linked by covalent bonds (covalent crystals).

EXERCISES AND PROBLEMS (pp. 74-77 in original Greek text)

Chemical bonds

38.[1] Complete the following sentences:
a) The noble gases have in their outer shell .... electrons, except .... which has .... electrons in .... shell.

b) Chlorine (Cl), which is an element in group VIIA of the periodic table, has .... electrons in its outer............. and .... or contributes ………… electron to obtain a .... gas structure.
c) Sodium (Na), which is an element in group IA of the periodic table, with the electron structure (2,8,1), must ……….. one electron in order to obtain a .... gas structure.
d) The atomic radius determines the .... of the ....

39. Explain why the concept of the molecule should not be used in the case of $CaCl_2$ (calcium chloride). What exactly does the chemical formula for an ionic compound show?

40. What is the difference between the covalent bond formed between atoms of the same element and that formed between atoms of different elements? Justify your answer.

***41.**[2] You are given the elements A and B. Element A belongs to group IIA and is from the first period, while element B belongs to group VIIA and is found in the third period of the periodic table. Explain what kind of bond can be formed between these elements. What is the molecular formula for the resulting compound? What does this formula show?

***42.** You are given the elements C and D. Element C belongs to group IA and is from the first period, while element D belongs to the VIIA group and is found in the second period of the periodic table. Explain what kind of bond can be formed between these elements. What is the molecular formula for the resulting compound? What does this formula show?

***43.** Describe the way in which the formation of ionic compounds between the following takes place:
a) potassium ($_{19}K$) and fluorine ($_{9}F$).
b) magnesium ($_{12}Mg$) and sulfur ($_{16}S$).
c) calcium ($_{20}Ca$) and hydrogen ($_{1}H$).

***44.** Write electronic formulas for the covalent compounds: a) phosphorus trichloride: PCl_3, b) methane: CH_4, c) chloroform: $CHCl_3$. The atomic numbers of the elements P, Cl, C, H are respectively: 15, 17, 6, 1.

45. Is the compound NaCl (sodium chloride) covalent or ionic?

---

[1] The numbering is according to the original Greek text.
[2] A **red star** before the **numbe**r denotes a more *demanding* exercise/problem.

It is ……............ because (CHOOSE THE CORRECT ANSWER):

a) under normal conditions it occurs in the solid state.
b) it is formed by transfer of electrons from the chlorine atoms to sodium atoms.
c) it consists of molecules each having two dissimilar poles.
d) it consists of molecules each having two identical poles.
e) it is formed by electron transfer from the sodium atoms to the chlorine atoms.

***46.** In the table below fill in the cells with:
a) The letter C, if the compound formed by the corresponding elements is covalent,
b) the letter I if the corresponding compound is ionic, and
c) the letter X if the respective elements do not form a chemical compound at all.

	$_{17}Cl$	$_{16}S$	$_{20}Ca$
$_{1}H$			
$_{11}Na$			
$_{6}C$			
$_{10}Ne$			

Also write in each cell the formula for any compound that forms.

***47.** Describe the bonds in the molecule of ethane, which has the chemical formula C_2H_6, given that the carbon atoms in this molecule are joined together by a single covalent bond. Also write the electronic formula for this compound. How many covalent bonds occur in a molecule of C_2H_6? Explain your answer. The atomic numbers for carbon and for hydrogen are Z=6 and Z=1 respectively.

***48.** Label with C the sentences below, that you assume to be correct and with W those you assume to be wrong, and explain your choices.
a) Na with structure (2,8,1) loses electrons more easily than K with structure (2,8,8,1).
b) F with structure (2,7) gains electrons more easily than Cl with structure (2,8,7).
c) Ca with structure (2,8,8,2) forms chemical compounds as easily as Kr with structure (2,8,18,8), with a third element e.g. Cl having the structure (2,8,7).
d) Na with structure (2,8,1) has a larger atomic radius than Al with structure (2,8,3).
e) Ca with structure (2,8,8,2) has a larger atomic radius than Mg with structure (2,8,2).

***49.** You are given the atomic numbers of carbon (C): Z = 6 and hydrogen (H): Z = 1. These two elements form three covalent compounds, compound A with formula C_2H_X, compound B with formula C_2H_Y and compound B with formula C_2H_W. If it is known that compound A has a single covalent bond between

the carbon atoms, that compound B has a double covalent bond between the carbon atoms, and that compound C has a triple covalent bond between the carbon atoms, suggest electronic formulas for compounds A, B and C, describing how the bonds are created. How many and what types of bonds are present in the compounds A, B and C?

50. For an ionic compound, explain which of the following statements is correct:
a) The concept of the molecule applies to this bond.
b) Forces of an electromagnetic nature are exerted between the atoms.
c) All ionic compounds are gaseous.
d) Oppositely charged ions exist in the crystal lattice.

***51.** Classify the following molecules into covalent polar and covalent nonpolar: a) HCI ; b) N_2 ; c) d NH_3; e) Cl_2
Give reasons for your answers.

52. Which of the following bonds are present in the oxygen molecule? For oxygen: $Z = 8$.
a) A polar covalent double bond.
b) A non-polar covalent triple bond.
c) A non-polar covalent double bond.
d) An ionic bond.
ε) No bond is formed because it is a monoatomic element.