6.1 The Development of the Periodic Table

Warm Up

1. Can you suggest the meaning of the word "periodic" in the term "periodic table"?

2. On what basis are the elements arranged in the modern periodic table?

3. What is true about chemical elements that appear in the same vertical column in the table?

Discovering an Elemental Order

Science in general and chemistry in particular exist because our human species has always had an insatiable desire to make sense of the world around us. We have relentlessly sought to explain nature's phenomena, to solve her mysteries, and to discover her order and logic by deciphering the events and objects we encounter.

One of the most important and successful examples of such efforts is the development of the periodic table of the elements. This single document is arguably more valuable to chemists, and perhaps even society itself, than any piece of equipment, wonder drug, or process ever invented.

The periodic table had its beginnings in the early part of the 1800s. By 1817, 52 elements had been discovered. Although some had been known since ancient times, many new elements were being discovered using the energy available from the electric battery invented by Volta in 1800. Researchers saw the need to organize those elements and the enormous amount of information gathered about them into some kind of meaningful form. German scientist Johann Dobereiner noticed similarities within several groups of three elements such as chlorine, bromine, and iodine, which he called "triads." These similarities gave chemists some evidence that an organizational scheme was at least possible.

In 1857, English chemist William Odling proposed that the elements could be divided into groups based on their chemical and physical properties. Many of those groups actually resemble the vertical columns in the periodic table today.

In 1862, French geologist Alexandre-Emile de Chancourtois arranged the elements by increasing atomic mass. He noted that elements with similar properties seemed to occur at regular intervals. He devised a spiral graph with the elements arranged onto a cylinder such that similar elements lined up vertically. When his paper was published, however, it was largely ignored by chemists. Unfortunately, de Chancourtois had left out the graph, which made the paper hard to understand. As well, he had written the paper from a geologist's rather than from a chemist's perspective.

In 1864, English chemist John Newlands noticed that similar properties seemed to repeat every eighth element in much the same way that the notes of a musical scale repeat every eighth tone. Newlands called this the "law of octaves" and it resulted in several similar elements being grouped together, but with limited success.

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The Periodic Law

The most successful organization of the elements was arrived at independently and almost at the same time by the German chemist Julius Lothar Meyer and the Russian chemist Dmitri Ivanovich Mendeleev. The chemical community, however, ultimately awarded Mendeleev the majority of the credit.

In a paper submitted to the Russian Chemical Society in March 1869, Mendeleev arranged the elements into a **periodic table** and proposed the **periodic law**, which can be stated as follows:

> If elements are arranged in order of increasing atomic mass, a pattern can be seen in which similar properties recur on a regular or *periodic* basis.

Notice that this is called a "law" rather than a "theory." Theories attempt to explain *why* relationships or phenomena exist, whereas laws simply identify *that* they exist. We will see if we can supply the "why" by the end of this section.

Dmitri Mendeleev received most of the credit for several reasons. First, Mendeleev's work was published a year before Meyer's. Second, Mendeleev chose to concentrate on the chemical properties of the elements, while Meyer focused mainly on physical properties. Third, and most importantly, Mendeleev chose to leave several blank spaces in his table where he predicted as-yet-undiscovered elements with specific properties would eventually be placed. Because he had arranged similar elements vertically in his table, the location of those blank spaces effectively identified the properties that those elements would have upon being discovered. When the elements were eventually discovered, the predictions turned out to be extremely accurate.

A version of Mendeleev's table, published in 1872 and showing 65 elements is shown in Figure 6.1.1.

Reiben	Gruppo I. — R^2O	Gruppo II. — RO	Gruppo III. — R^2O^3	Gruppo IV. RH^4 RO^2	Gruppo V. RH^3 R^2O^3	Gruppo VI. RH^3 RO^3	Gruppo VII. RH R^2O^7	Gruppo VIII. — RO^4
1	Il = 1							
2	Li = 7	Bo = 9,4	B = 11	C = 12	N = 14	O = 16	F = 19	
3	Na = 23	Mg = 24	Al = 27,8	Si = 28	P = 31	S = 32	Cl = 35,5	
4	K = 39	Ca = 40	– = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fo = 56, Co=59, Ni = 59, Cu=63.
5	(Cu = 63)	Zn = 65	– = 68	– = 72	As = 75	So = 78	Br = 80	
6	Rb = 86	Sr = 87	?Yt = 88	Zr = 90	Nb = 94	Mo = 96	– = 100	Ru = 104, Rh=104, Pd = 106, Ag=108.
7	(Au = 199)	Cd = 112	In = 113	Sn = 118	Sb = 122	To = 125	J = 127	
8	Cs = 133	Bs = 137	?Di = 138	?Ce = 140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er = 178	?La = 180	Ta = 182	W = 184	—	Os = 195, Ir=197, Pt = 198, Au=199.
11	(Ag = 108)	Hg = 200	Tl = 204	Pb = 207	Bi = 208	—	—	
12	—	—	—	Th = 231	—	U = 240	—	— — — —

Figure 6.1.1 *The blank spaces marked with lines for elements with atomic masses 44, 68, 72, and 100 represent Mendeleev's belief that those elements would eventually be discovered and fit in the spaces. The symbols at the top of the columns (e.g.,* R^2O *and* RH^2*) are molecular formulas written in the style of the 1800s. The letter "R" represents any element in the family and the formulas represent the probable hydrogen and oxygen compounds.*

An example of the accuracy of one of Mendeleev's predictions (and thus support for his periodic table) can be seen in Table 6.1.1. The table displays the properties predicted in 1871 for the element with atomic mass 72, compared to the actual properties for that element, called germanium, which was discovered in 1886.

Table 6.1.1 *Predicted and Observed Properties of Germanium*

Properties of Germanium	Predicted Properties in 1871	Observed Properties in 1886
Atomic mass	72	72.3
Density	5.5 g/cm^3	5.47 g/cm^3
Melting point	very high	960°C
Specific heat	0.31 J/g °C	0.31 J/g °C
Oxide formula	RO_2	GeO_2
Oxide density	4.7 g/cm^3	4.70 g/cm^3
Chloride formula	RCl_4	$GeCl_4$

Using the oxide formulas that he had proposed as a guide, Mendeleev also corrected the atomic masses of the elements beryllium, indium, and uranium.

Because of its obvious usefulness, Mendeleev's periodic table gained widespread acceptance among chemists. We should remember that the periodic table was constructed prior to any discoveries about the inner structure of the atom. The similarities of various elements were eventually explained based on the quantum mechanical description of their electron arrangements, but the table identified those regularities more than 50 years before they were understood!

Quick Check

1. Who was the first person to arrange the chemical elements into groups?

   ____

2. How did Newland's analogy to music apply to elemental properties?

   ____

3. How did blank spaces in Mendeleev's periodic table help it eventually gain acceptance?

   ____

   ____

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The Modern Periodic Table — By the Numbers

Since its creation, the periodic table has undergone several changes. Many new elements have been discovered or synthesized since 1872, but the most significant modification occurred in 1913. Data gathered by the young British chemist Henry Moseley, combined with the discovery of isotopes, resulted in the elements of the periodic table being re-ordered according to their *atomic numbers* rather than their atomic masses.

If elements are arranged in order of increasing atomic number, a pattern can be seen in which similar properties recur on a regular or periodic basis.

The Modern Periodic Table

With the inclusion of element 117 in April 2010, the periodic table includes 118 elements, 92 of which occur naturally. Each element is assigned its own box in the table containing that element's one- or two-letter symbol, atomic number and sometimes, but not always, atomic mass. The boxes are arranged in order of increasing atomic number beginning at the top left with hydrogen and proceeding horizontally left-to-right. Because elements 113 to 118 have not yet been assigned permanent names, their temporary names simply reflect their atomic numbers. Figure 6.1.2 shows a simplified periodic table.

The horizontal rows in the periodic table are called **periods** and these are numbered beginning at the top from 1 down to 7. Each vertical column is called a **family** or **group** and these are labeled using one of two schemes. Many chemists prefer an older system, which assigns each column a number from 1 to 8 combined with either the letter A or B.

A newer system adopted by the international governing body of chemistry called IUPAC (International Union of Pure and Applied Chemistry) simply numbers each group from 1 through 18 and uses no letters. For ease of reference, we will use the IUPAC numbering system.

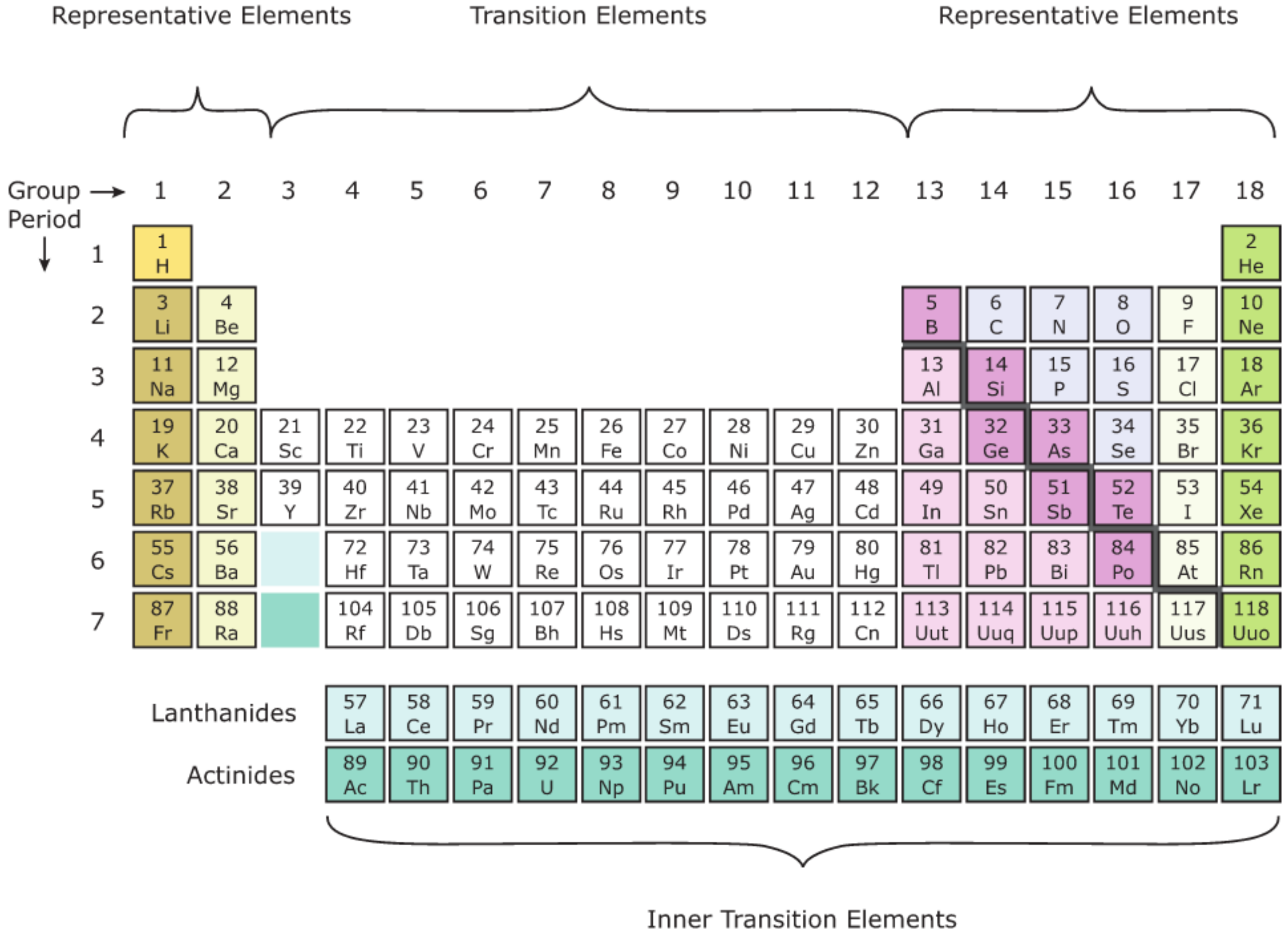
Because each element is a member of both a horizontal period and a vertical group, its position on the table can be specified in much the same way as a geographic location on a map can be identified using lines of longitude and latitude.

The two most important things to know about the periodic table are:

1. Elements in the same chemical family have similar chemical properties because they have similar outer electron configurations. (This is among the most important of all chemical concepts.)
2. As we move down a chemical family or across a period, there are regular changes in these properties called periodic trends. (These will be discussed in detail in the next section.)

Groups 1 and 2 on the left, and 13 through 18 on the right contain the **representative** or **main group elements**. Groups 3 through 12 are the **transition elements**. Within the transition elements are two horizontal series collectively called the **inner transition elements**. The first series, known as the **lanthanides**, fits between elements 56 and 72 in the 6th period and the second series, called the **actinides**, fits between elements 88 and 104 in the 7th period.

Consider the periodic table in Figure 6.1.2.



Group → Period ↓	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
Lanthanides				57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides				89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Figure 6.1.2 *This periodic table shows only the element's symbols and their atomic numbers.*

The first distinction among the elements relating to their properties that we will discuss is their classification as metals, non-metals, or semi-metals. The "staircase" line descending from group 13 down to group 16 separates metals on the left side from non-metals on the right.

About three-quarters of the elements are metals, including some main group elements and all of the transition and inner transition elements. Properties of **metals** include:

- solids at room temperature, except for mercury, which is a liquid
- generally shiny or lustrous when freshly cut or polished
- good conductors of heat and electricity
- generally malleable, which means they can be rolled or hammered into thin sheets
- generally ductile, which means they can be rolled or stretched into wires
- generally flexible as thin sheets or wires
- during chemical changes, tending to give up electrons relatively easily to form cations

The **non-metals** are located in the upper right portion of the table. Properties of non-metals include:

- usually gases or brittle solids at room temperature, except for liquid bromine
- solid non-metals ranging in appearance from dull or lustrous and translucent to opaque
- poor conductors of heat and electricity
- during chemical changes, tending to gain electrons from metals to form anions or share electrons with other non-metals.

Along the staircase line are several **semi-metals** (also called **metalloids**). These solid elements are semiconductors, which mean they are poor electrical conductors at room temperature, but become better conductors at higher temperatures. This is opposite to how metal conductivity varies with temperature. Metals become less conductive as temperature increases.

As we move right-to-left across a period and down a chemical family, the elements become more metallic. These changes involve both physical and chemical properties, and those and other trends will be discussed in the next section.

Quick Check

1. Fill in the missing spaces in the table below:

Element Name	Element Symbol	Group Number	Period Number	Metal/Non-metal/ Semi-metal
	Si			
Osmium				
		6	4	
	Mt			
Antimony				semi-metal
		17	5	

2. (a) Rearrange the following alphabetical list in order of least metallic to most metallic.
aluminum, cesium, chromium, fluorine, gallium, oxygen, sulphur, zirconium

____

(b) Based on your answer to (a) above, which of the eight elements would you expect to have the:

- greatest tendency to gain an electron? ______________________________
- greatest tendency to lose an electron? ______________________________

A Closer Look at the Periodic Table

It is the number and type of outermost electrons that are primarily responsible for an atom's chemistry. The members of a chemical family have similar numbers and types of outermost electrons. The outermost electrons that participate in chemical bonding are known as **valence electrons**. We will be discussing chemical bonding in more detail in a later section. For now, this section will introduce some families in the periodic table and the corresponding electron arrangements that will influence the bonding behaviour of their elements.

Group 1 — The Alkali Metals

Alkali metals are located on the far left side of the periodic table. This group includes lithium, sodium, potassium, rubidium, cesium, and the rare and radioactive francium. Alkali metals are all soft, silvery solids and the most reactive of all metals. The name of the group is based on the fact that the oxide compounds of the alkali metals dissolve in water to produce strongly basic solutions. They all corrode rapidly in air to a dull gray appearance, react vigorously with water to produce hydrogen gas, and readily form compounds with non-metals.

Alkali metal atoms have one valence electron in the s sublevel with the general electron configuration [noble gas]ns^1 where "n" represents the outer energy level. In their chemical reactions, they readily lose that outer electron to form 1+ cations and so assume the electron configuration of previous noble gas. Notice in Table 6.1.2 that each of the alkali metals has the same number and type of valence electrons. Note also, that as we move down the group and the value of "n" increases, the outermost electron spends most of the time farther and farther from the nucleus so the atoms become larger.

Table 6.1.2 *Alkali Metal Electron Configurations*

Alkali Metal	Core Notation Configuration
Li	[He] $2\mathbf{s}^1$
Na	[Ne] $3\mathbf{s}^1$
K	[Ar] $4\mathbf{s}^1$
Rb	[Kr] $5\mathbf{s}^1$
Cs	[Xe] $6\mathbf{s}^1$
Fr	[Rn] $7\mathbf{s}^1$

Group 2 — The Alkaline Earth Metals

These elements are also silver-coloured reactive metals. Although they are not as reactive as the alkali metals, they readily form compounds with non-metals. Their oxides are also alkaline but unlike alkali compounds, some group 2 compounds have a low solubility in water. They have two valence electrons and have the general electron configuration [noble gas]ns^2. They will readily form 2+ cations by losing those two valence electrons and so will achieve the identical electron configuration of the nearest noble gas. Chemists call this becoming **isoelectronic** with the noble gas.

Group 17 — The Halogens

This family contains the most reactive elements and is the only one in which all three states of matter are represented. At room temperature, fluorine and chlorine are gases, bromine is a liquid, and iodine and the very rare and radioactive astatine are solids.

The elemental halogens exist as diatomic molecules and readily form compounds with metals, and also hydrogen, carbon, and other non-metals. The halogens possess seven valence electrons with two electrons in the outer s sublevel and five electrons in the p sublevel. They therefore have the general ns^2np^5 outer electron configuration. In their reactions with metals, halogens will typically gain a single electron forming 1– anions and acquiring a noble gas electron configuration. When they react with non-metals, they will often share valence electrons.

Group 18 — The Noble Gases

As the name suggests, this family of gases is generally unreactive, although compounds of argon, krypton, xenon, and radon have been prepared.

All of the noble gases, except helium, have filled s and p sublevels. As the s and p sublevels are an atom's outermost orbitals, atoms of neon down to radon have eight electrons in their outer charge clouds with the ns^2np^6 configuration. They are said to possess "stable octets." This particularly stable electron configuration explains the low reactivity of the noble gases. It also explains the electron configuration achieved by

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many cations and anions. For example, consider Table 6.1.3, showing elements from four different families. Note that the stable ion of each element has the same electron configuration as the noble gas nearest to it in periodic table.

Table 6.1.3 *Electron Configurations of Noble Gases and Nearby Elements*

Element	Electron Configuration for Atom	Nearest Noble Gas	Symbol and Electron Configuration for Stable Ion	
oxygen	$[He]2s^22p^4$	argon	O^{2-}	$[He]2s^22p^6$
calcium	$[Ar]4s^2$	neon	Ca^{2+}	$[Ne]3s^23p^6$
selenium	$[Ar]4s^23d^{10}4p^4$	krypton	Se^{2-}	$[Ar]4s^23d^{10}4p^6$
cesium	$[Xe]6s^1$	xenon	Cs^+	$[Kr]5s^24d^{10}5p^6$

Transition Elements

The transition elements include groups 3 through 12 in the periodic table. All are metals and most are hard solids with high melting and boiling points. An explanation of their chemical behaviour is beyond the scope of this course, but it differs from the representative elements. For example, the transition elements show similarities within a given period as well as within a group. In addition, many transition elements form cations with multiple charges and those cations often form complex ions. A number of transition metal compounds have distinct and recognizable colours. The differences occur mainly because the last electrons added for transition metals are placed in inner d orbitals. Electrons in these orbitals are usually closer to the nucleus than in the outer s or p orbitals filled for the representative elements.

Quick Check

1. Identify the family number and name to which each of the following properties best apply:

Property	Family Number	Family Name
(a) reactive non-metals possessing seven valence electrons		
(b) reactive solids that form 2+ cations during reactions		
(c) invisible gases that are almost totally unreactive		
(d) soft, very reactive silvery solids with one valence electron		

2. Elements in the same family demonstrate similar chemical behaviour. Consider the following chemical formulas: $LiBr$, K_2O, Sr_3N_2, AlF_3, CaO, H_2S. Write chemical formulas for:

   (a) sodium iodide ___________
   (b) barium sulphide ___________
   (c) gallium chloride ___________
   (d) rubidium sulphide ___________
   (e) magnesium phosphide ___________
   (f) hydrogen selenide ___________

3. Which two families contain the most reactive elements? Can you suggest a possible reason for this given their location on the periodic table?

____

____

A Quantum Mechanical View of the Periodic Table (Extension)

Let us look a little more closely at the organization of the periodic table from a quantum mechanics perspective. First we'll look at three different aspects of the elements in the periodic table.

(1) Consider Figure 6.1.3 showing the chemical families separated into the four main blocks of the table. Notice that each block corresponds to one of the four different electron sublevels. Notice also that the number of columns or families in each block exactly matches the number of electrons that occupy that sublevel. (This diagram also includes both the older and newer numbering schemes employed for the chemical families.)

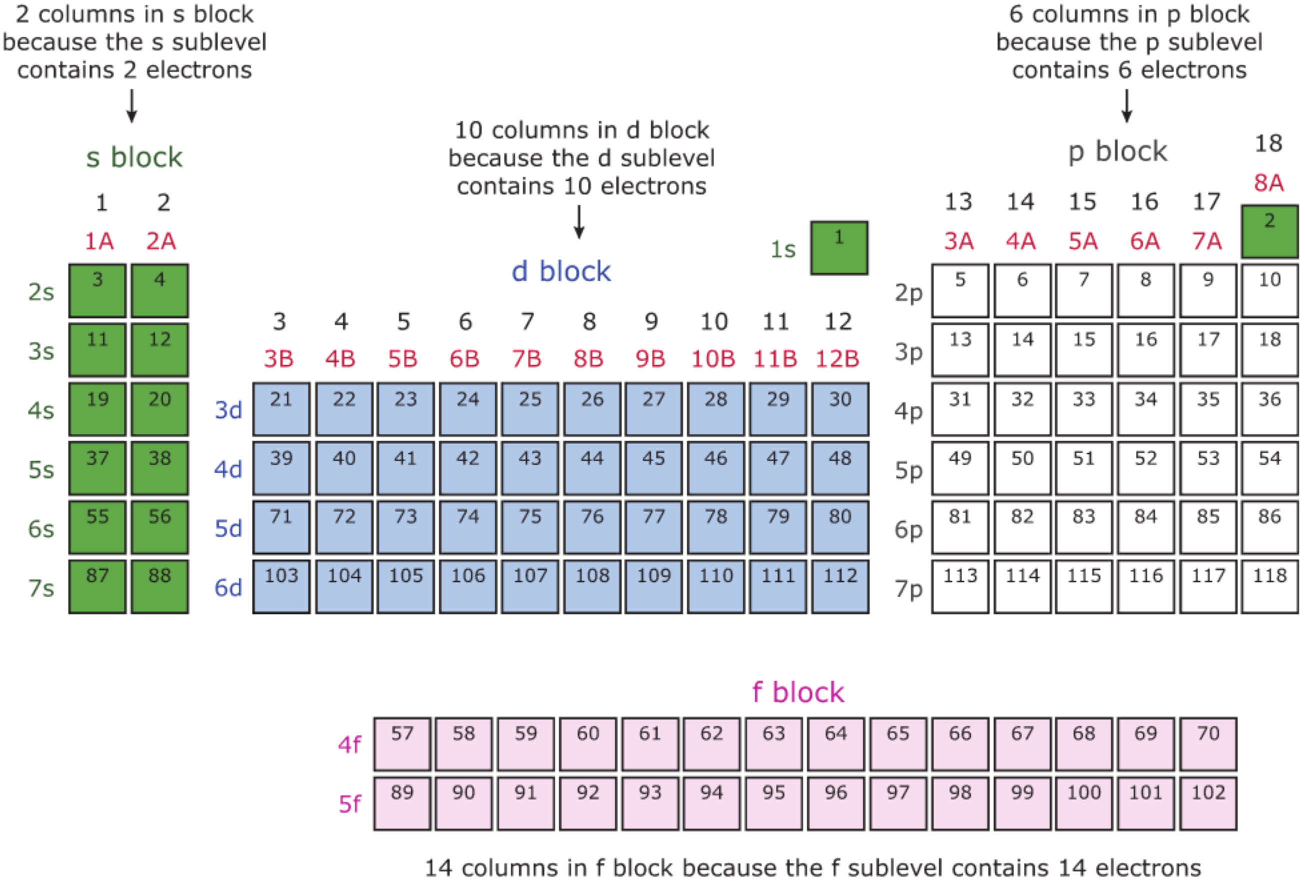

Figure 6.1.3 *The periodic table separated into its four main blocks*

Table 6.1.4 *Order of Filling Sublevels*

1s →
2s → 2p
3s → 3p
4s → 3d → 4p
5s → 4d → 5p
6s → 4f → 5d → 6p
7s → 5f → 6d → 7p

(2) Consider in Figure 6.1.3 the sublevels associated with each of the chemical periods in the table. Notice that as we "read" the sublevels from left to right like the words on a page, we follow exactly the order of filling sublevels specified by the Aufbau principle and summarized by the diagonal diagram in the previous chapter. That order is shown again in Table 6.1.4.

Note also that as we reach each noble gas at the end of a period, we move down and begin a new period. Each new period number specifies the value of the next energy level as we start filling the s orbital for elements on the left side of that period. Thus every new period represents a larger charge cloud or electron "shell" in which electrons spend most of their time farther from the nucleus.

(3) Finally, consider Figure 6.1.4, showing the extended form of the periodic table with the f block lanthanides and actinides inserted after barium and radium respectively. Note the consistent order and the obvious connection of electron configuration to element location in the periodic table.

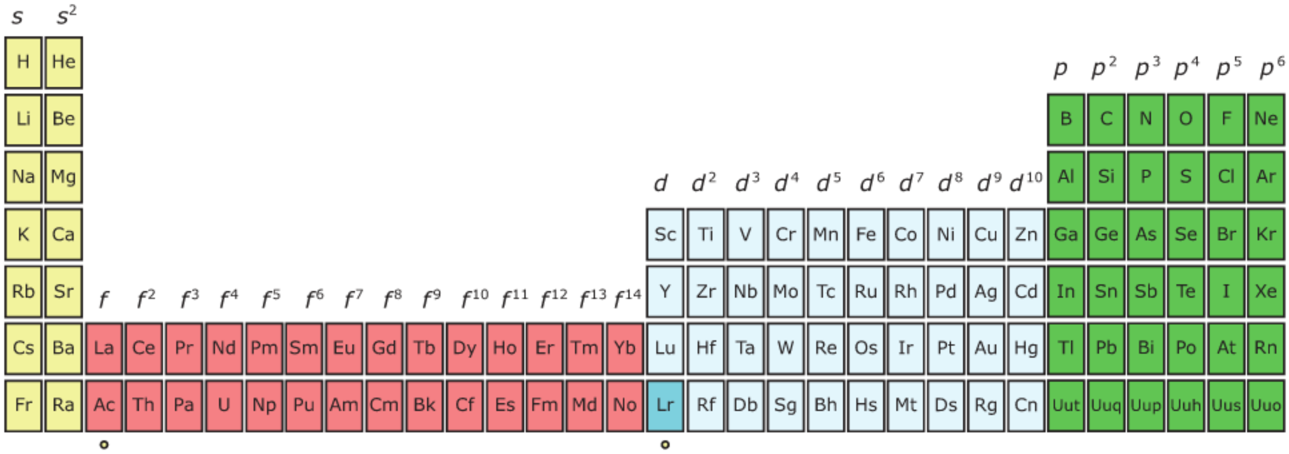

Figure 6.1.4 *Periodic table showing pattern of electron configuration*

Chemists, like all scientists, don't really believe in coincidences. We have discussed that the structure of the periodic table is based firmly on experimentation. The organization of the periods and chemical families results from and summarizes an enormous amount of empirical data gathered about the elements. It is truly amazing that this arrangement of the elements in the periodic table was essentially in place *before* the development of the quantum mechanical model of the atom! The fact that the electron configurations of the elements specified by quantum mechanics exactly matches their organization in the periodic table is one of the greatest successes in the history of science.

Far from being a coincidence, the exact correlation exists precisely because quantum mechanics provides the theoretical foundation for the experimentally derived periodic table. Stated another way, the quantum mechanical view of the atom is the "why" behind the "what" stated in the periodic law. Of course, it can also be said that the structure of the periodic table is arguably the best piece of supporting evidence for the quantum mechanical model of the atom.

Perhaps John Newlands wasn't far off the mark when he used a musical analogy in referring to elemental properties. Think of the millions of chemical reactions happening around us as symphonies played out by the instruments we call the chemical elements in nature's orchestral arrangement that is the periodic table.

6.1 Activity: The Elements of PowerPoint®

Question

How much information about an element can you present in a 10-minute PowerPoint® presentation?

Procedure

1. Choose any one of the naturally occurring elements in the periodic table. Confirm the selection with your teacher to avoid duplicate selections among class members.
2. Using any and all resources available online or in print, produce a PowerPoint® presentation no longer than 10 minutes that includes as much information about your element as you can discover. Make sure to include the following: symbol, atomic number and mass, location on the periodic table, electron configuration, melting point, boiling point, common compounds, and uses. The presentation can include any videos showing reactions or compounds or any interesting properties of the element.

Results and Discussion

1. Be prepared to answer questions about from your classmates and your teacher for a few minutes after your presentation.

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6.1 Review Questions

1. What is the most important thing to know about the periodic table?

2. What significant modification to the periodic table occurred just before World War I?

3. Why do elements in the same chemical family have similar chemical properties?

4. (a) Where are the most metallic elements located on the periodic table?

   (b) Where are the most non-metallic elements located on the periodic table?

5. Consider the properties listed for eight different elements. Match each element on the left to its property on the right by writing the element's chemical symbol next to its property.

Element	Properties	Symbol
(a) chlorine	found in carbohydrates and an elemental gas in 21% of the atmosphere	
(b) silver	soft conductor that reacts explosively with water producing H_2 gas	
(c) neon	less than 1 ounce of this solid radioactive nonconductor exists on Earth	
(d) cesium	waxy yellow solid non-metal found in match heads, fertilizers, and detergents	
(e) oxygen	blue-gray metalloid used extensively in the computer industry	
(f) phosphorus	very reactive green gas used in the trenches in World War I	
(g) silicon	shiny solid that is the best conductor of heat and electricity	
(h) astatine	invisible unreactive gas used in lasers and some electric street signs	

6. Six different elemental properties are listed below corresponding to family numbers 1, 2, 6, 14, 17, and 18 in the periodic table. Write the appropriate family number next to each of the properties listed below. Each family number may be used only once.

Element Properties	Family Number
unreactive gas used in electric street signs and comprising 0.93% of the atmosphere	
shiny multivalent solid, good conductor, forms coloured compounds	
soft silvery solid, good conductor, reacts vigorously with water	
gray-white metalloid predicted by Mendeleev and discovered in 1886	
reactive metal present in bones and teeth possessing two valence electrons	
yellow-green gaseous non-metal and the most reactive of all the elements	

7. State four properties of elements classified as metals.

8. State four properties of elements classified as non-metals.

9. State a general rule for predicting the ion charges of many of the representative or main group elements.

10. Use your answer to question 8 above and write the formulas for the stable ions of the following:

(a) Be ____ (b) Te ____ (c) Cs ____ (d) Ra ____ (e) Ga ____ (f) Se ____ (g) In ____

11. Identify three properties of the elements belonging to each of the following chemical families:

(a) alkali metals

(b) alkaline earth metals

(c) halogens

(d) noble gases

12. Extension: Complete the following table by writing in the missing electron configurations. Highlight the outermost electrons in your answers. (Completed answers show outermost electrons in bold type.)

Group 2	Core Notation	Group 17	Core Notation	Group 18	Core Notation
Be		F	$[\mathrm{He}]\mathbf{2s^2\ 2p^5}$	He	
Mg		Cl		Ne	
Ca	$[\mathrm{Ar}]\mathbf{4s^2}$	Br		Ar	
Sr		I		Kr	$[\mathrm{Ar}]\mathbf{4s^2}\ 3d^{10}\ \mathbf{4p^6}$
Ba	$[\mathrm{Xe}]\mathbf{6s^2}$	At	$[\mathrm{Xe}]\ \mathbf{6s^2}\ 4f^{14}5d^{10}\mathbf{6\ p^5}$	Xe	
Ra				Rn	$[\mathrm{Xe}]\mathbf{6s^2}\ 4f^{14}5d^{10}\ \mathbf{6p^6}$

6.2 Periodic Trends — Regular Changes in Elemental Properties

Warm Up

1. What attractive force is responsible for holding the cloud of electrons in place in atoms?

   ____

2. What effect would a strengthening of that force have on the sizes of atoms?

   ____

3. What might cause a strengthening of that force?

   ____

4. What might contribute to a weakening of that force?

   ____

The Second Key Concept — Periodic Trends

All of the chemical and physical behaviour of the elements is really a result of their electron configurations. In the last section, we discussed how similar outer-electron configurations explained the similar properties of elements within the chemical families of the periodic table. We will now concentrate on a second key concept associated with the organization of the elements in the table.

> As we move across a period or down a chemical family, there are regular changes in elemental properties.

These consistent and predictable changes in elemental properties are known as **periodic trends.** Identifying and explaining them can be a great benefit when describing chemical interactions between atoms.

Periodic Trends in Atomic Size

In the quantum mechanical model, the outer boundaries of an atom depend on the size of a charge cloud in which electrons spend approximately 90% of their time. This means that the sizes of individual atoms cannot be determined in the same way as we might, for example, measure the size of objects such as marbles or grapefruits. In these cases, the object's boundaries are hard and definite, unlike those of atoms.

However, we can estimate the sizes of atoms based on how close they get to one another when bonds form between them. This can be done by measuring the distance between the nuclei of identical adjacent atoms in an element sample and dividing that distance by two.

The two common definitions of atomic size stem from the classification of elements into metals and non-metals. Non-metal elements commonly occur as diatomic molecules. For these elements, atomic size is defined as the **covalent radius**, which represents one half the distance between the two identical nuclei in the molecule.

Although the nature of bonding between metal atoms is beyond the scope of this course, the process of estimating their atomic size is very similar to that for non-metals. Metal atoms pack together in the solid state to form a crystal lattice much like ions in a salt. In a sample of a metal element, half the distance between the identical nuclei of adjacent metal atoms in the crystal is defined as the **metallic radius**.

Both of the above techniques for estimating atomic size involve determining half the bond length between identical atoms in element samples as shown in Figure 6.2.1.

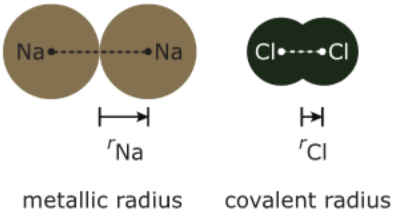

Figure 6.2.1 *Estimating atomic size involves determining bond length.*

Factors Influencing Atomic and Ionic Size

Let's consider for a moment what might influence the size of an atom. Because an atom's volume is really the result of a cloud of electrons, this question is really the same as asking: What affects the size of an atom's electron cloud? Seen from that perspective, it makes sense that two opposing factors influence atomic size:

1. The number of energy levels present. As the number of energy levels (n) increases, the probability that outer electrons will spend more time further from the nucleus increases and so the atoms become larger.
2. The amount of nuclear charge "felt" or "seen" by the outer electrons. As this effective nuclear charge increases, the outer electron cloud is pulled closer to the nucleus and the atom becomes smaller. Chemists use the symbol "Z_{eff}" to refer to the effective nuclear charge.

Of these two opposing factors, the one that predominates as we move across a period or down a chemical family will most influence how the sizes of those atoms change.

Consider Figure 6.2.2, showing the relative atomic radii of the elements. The actual sizes range from the smallest, helium, at 31 pm to the largest, cesium, at 270 pm. How those sizes change across periods and down families shows a clear pattern.

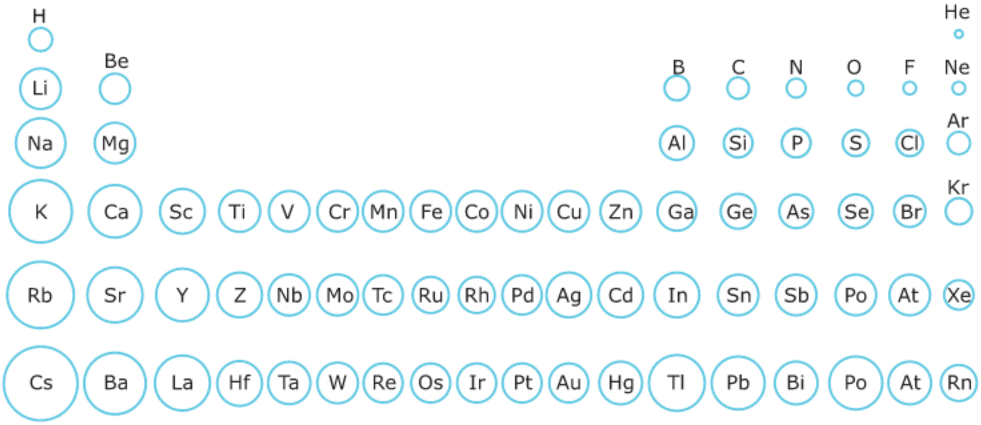

Figure 6.2.2 *Periodic table showing atomic radii*

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Two definite periodic trends are evident:

As we move down a family or group, the sizes of the atoms generally increase.
As we move across a period, the sizes of the atoms generally decrease.

As we move down a chemical family and the value of n increases for each new element, a new inner electron level is added between the nucleus and the atom's outer electron cloud. Even though the positive charge on the nucleus is increasing, each additional inner level of electrons *effectively shields* the outer cloud from the attractive force of that nucleus, and the electron cloud increases in size. The additional inner electron clouds also repel each other, which further contributes to the increasing size of atoms as the group as we move lower in the table. This clearly shows that as the number of energy levels present in the atom increases, the size of the atom also increases.

As we move left-to-right across a period, the electrons are being added to the same outer level. This means that the level of shielding by the inner electrons remains the same. It also means that the added electrons are *ineffective at shielding each other* from the increasing positive charge on the nucleus. The result is that Z_{eff} on those outer electrons increases and the charge cloud is pulled closer and closer to the nucleus so the size of the atom decreases.

Consider Figure 6.2.3, which shows the periodic changes in atomic radii as we move from period 1 through period 6. The alkali metals are the largest members of each period and then the radii generally decrease to a minimum at the noble gases. Down each family, the atomic radii generally increase.

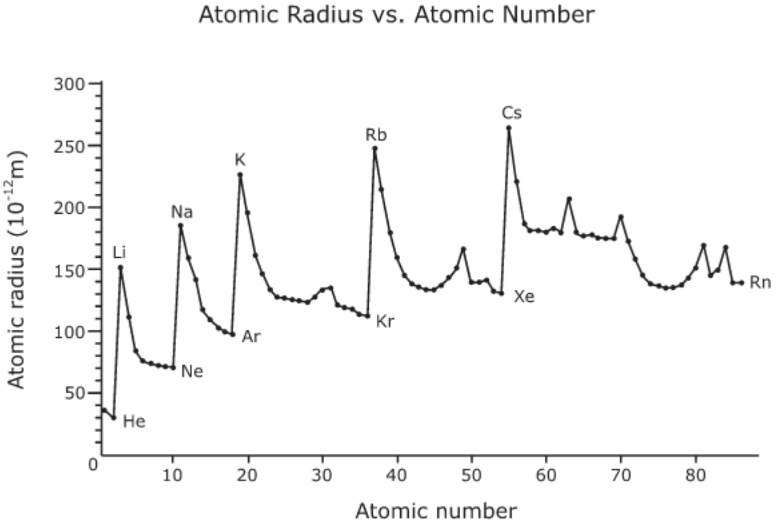


Figure 6.2.3 *Periodic changes in atomic radii as we move from period 1 through period 6*

There are exceptions to the general trends stated above and they can be explained by considering the electron configurations of the atoms and the electron sublevels being filled in each case.

For example, as we move across period 4, we start filling the 4th energy level at potassium and the atomic sizes shrink as expected for the first two elements. But when we arrive at the transition elements and begin filling the 3d sublevel, the sizes remain relatively constant as we move across to zinc.

To understand this, remember that n = 3 electrons spend most of their time *closer to the nucleus* than those electrons in the n = 4 charge cloud. We would therefore expect electrons in the 3d sublevel to be capable of shielding the outer 4s electrons from the increasing nuclear charge as we move across the period. This would reduce Z_{eff}. Consider the elements vanadium and zinc. The electron configuration for V is $[Ar]3d^{3}4s^{2}$ and the electron configuration for Zn is $[Ar]3d^{10}4s^{2}$. Even though zinc has a nucleus with 7 more protons than vanadium, the extra shielding provided by zinc's 10 electrons in the 3d sublevel is such that zinc's atomic radius is equal to vanadium's!

This shows how effective inner electrons can be at shielding outer electrons from the "pull" of an increasingly positive nucleus and significantly influence atomic size. A number of other examples can be found throughout the periodic table.

Quick Check

1. Which of the two opposing factors that influence atomic size predominates as we move across a chemical period? What is the general result?

   ____

2. Which of the two opposing factors that influence atomic size predominates as we move down a chemical family? What is the general result?

   ____

3. In general, is "effective shielding" most evident going across a period or down a family? How can you tell?

   ____

Forces Affecting Ion Size

The same forces that influence the sizes of atoms also influence the sizes of ions and in the same way. Let's consider these forces and rank the following species in order of size from largest to smallest: Al^{3}, F^{-}, Mg^{2+}, N^{3-}, Na^{+}, Ne, O^{2-}.

Note that all of the ions have 10 electrons and are therefore isoelectronic with neon. Since each species has the same number of electrons, we can assume that the amount of shielding is also the same for each. This means that the attractive force from each nucleus is the only factor influencing the size of each species. The greater the number of protons present, the stronger the attractive force on the electron cloud and therefore the smaller the atom or ion. This tells us that ranking the species in order of atomic number (positive charge on the nucleus) will also represent the order of decreasing size. Therefore, the answer is:

$$N^{3-} > O^{2-} > F^{-} > Ne > Na^{+} > Mg^{2+} > Al^{3+}$$

Periodic Trends in Ionization Energy

Ionization energy (IE) is defined as the minimum energy required to remove an electron from a gaseous atom or ion. The term is often used to mean the "first" ionization energy (IE_1) whereby a neutral atom becomes a 1^{+} cation according to the following equation:

$$\text{atom}\,(g) \;+\; IE_1 \;\rightarrow\; \text{ion}^{+}\,(g) \;+\; e^{-}$$

Ionization energy tells us how strongly an atom holds onto its outermost electrons. This is an important property because an element with a low IE_1 will be more likely to lose electrons and form cations during chemical changes. A high IE_1 might signal an element's tendency to gain electrons and form anions or perhaps not forms ions at all.

We might expect that a large atom, whose outer electrons are held less tightly, would have a lower IE_1 than a smaller atom whose outer electrons are held much more strongly. Said another way, as atomic size decreases, ionization energy should increase. This is, in fact, the general trend, as shown in Figure 6.2.4.

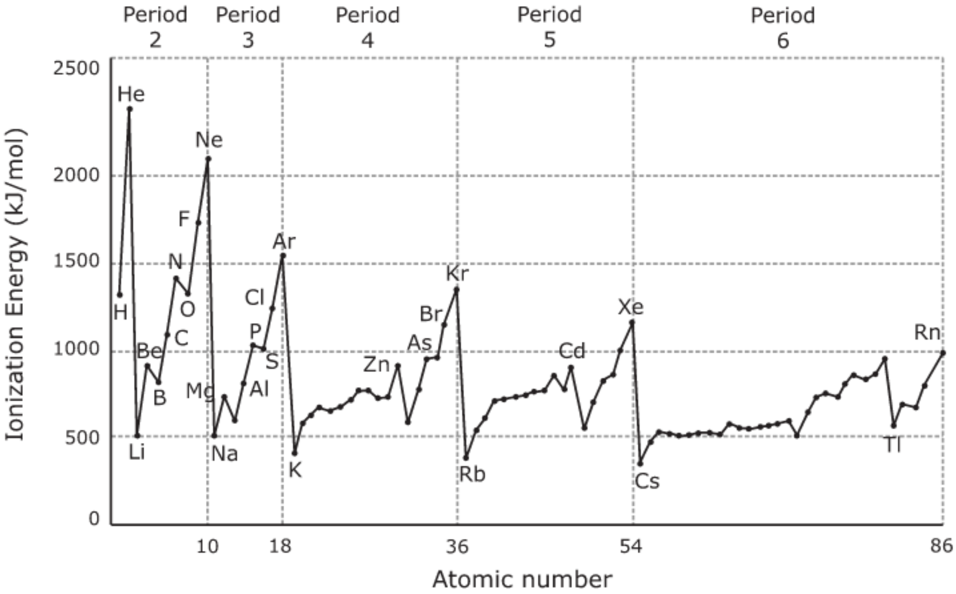


Figure 6.2.4 *As atomic size decreases, ionization energy increases.*

We can see that the lowest IE_1 values are associated with the largest atoms, which are located in the lower left corner of the periodic table. Conversely, the highest IE_1 numbers correspond to the smallest atoms, located in the upper right portion of the table.

At the beginning of each period, the largest atoms are the alkali metals, which have the lowest ionization energies. As we progress across the period and the sizes of the atoms decrease, we see a corresponding general increase in ionization energy until we reach the maximum value at each noble gas. At the beginning of the next period, the dramatic drop in ionization energy reflects the significant increase in size of that next alkali metal. As we move down a chemical family, the increase in atomic size results in a general decrease in ionization energy. The periodic trends are clearly evident up to the end of the 6th period.

The diagram shows that lower ionization energies are associated with elements nearer the left side of the periodic table, namely the metals. This tells us that metals generally tend to lose electrons when they are involved in chemical reactions. Non-metals, on the other hand, with relatively high ionization energies, have a tendency to gain or even share electrons rather than lose them. Of course, noble gases do neither of the above.

Exceptions to Ionization Energy Trends — One Example

As with atomic radii, there are several exceptions to the general trends in ionization energy, which we can explain by analyzing electron configurations. One example of this occurs with nitrogen and oxygen. Even though oxygen is a smaller atom than nitrogen, oxygen has a lower first ionization energy. Nitrogen has a single electron in each of its three 2p orbitals and a half-filled p sublevel that is quite stable. Oxygen, however, has a pair of electrons in one of its 2p orbitals (Figure 6.2.5). The increased electron-electron repulsion associated with that pairing makes it easier for oxygen to lose one of those electrons when first ionized.

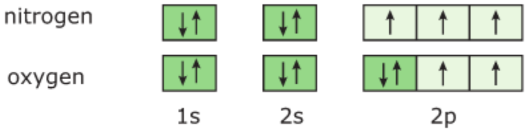


Figure 6.2.5 *Electron configurations in nitrogen and oxygen*

This reminds us that the repulsive forces between electrons, as well as the attractive forces affecting them from the nucleus, have a role to play in determining properties such as size and ionization energy.

Studying ionization energies allows us to do more than predict which elements might tend to lose or gain electrons during chemical changes. Investigating ionization energies also helps us identify which electrons are likely to be associated with those changes.

As we might expect, after removing one electron from an atom, further ionization energies increase. This occurs because each successive electron removed is being separated from an increasingly positive ion. However, those increases are *not regular*. Whenever the last outer or valence electron is removed, the next ionization requires significantly more energy because inner or "core electrons" are now involved. This can be seen using beryllium as an example. The atom has two valence electrons and the electron configuration is $1s^2 2s^2$. Table 6.2.1 shows the first three ionization energies for beryllium.

Table 6.2.1 *First Three Ionization Energies of Beryllium*

Species	Electron Configuration	Ionization Energy (kJ/mol)
Be^{o}	$1s^2 2s^2$	$IE_1 = 900$
Be^{1+}	$1s^2 2s^1$	$IE_2 = 1\,756$
Be^{2+}	$1s^2$	$IE_3 = 14\,860$

After the second (and last valence) electron is removed, the dramatic increase in energy required to remove the third electron reflects the fact that it is an inner or "core" electron. This shows us that core electrons are bound much more tightly to the nucleus, and thus do not take part in chemical reactions. This holds true for all of the elements in the periodic table.

Sample Problem – Trends in Ionization Energy

Using only the periodic table, rank each of the following alphabetical lists of elements in order of increasing first ionization energies.
(a) argon chlorine phosphorus sodium sulphur
(b) antimony arsenic bismuth nitrogen phosphorus

What to Think about	How to Do It
1. Ionization energy increases left-to-right across a period and moving up a chemical group.	
2. The elements listed in (a) are members of period 3. List the elements in the order they appear from left-to-right in period 3.	$Na < P < S < Cl < Ar$
3. The elements listed in (b) belong to group 15 of the periodic table. List the elements in the order they appear from bottom-to-top in group 15.	$Bi < Sb < As < P < N$

Practice Problems — Trends in Ionization Energy

1. Using only the periodic table, rank the following alphabetical list of elements in order of decreasing first ionization energy.

   aluminum argon cesium magnesium rubidium silicon sodium sulphur

2. Using the periodic table, write the correct number in the space after each statement below:

   Members of this chemical family have the highest IE_1 in their period. _________
   Members of this chemical family have the lowest IE_1 in their period. _________
   Members of this chemical period have the highest IE_1 in their family. _________
   Members of this chemical period have the lowest IE_1 in their family. _________

3. Extension: The nature of the 2s sublevel is such that 2s electrons have a higher probability of being found closer to the nucleus than electrons in the 2p sublevel. Consider this and the following electron configurations:

   beryllium: $1s^2\,2s^2$ boron: $1s^2\,2s^2\,2p^1$

   Suggest a reason why boron's first ionization energy is less than beryllium's, even though boron is a smaller atom.

   ____

An Introduction to Electronegativity

Our discussions so far have focused on the electron configurations, properties, and periodic trends associated with *individual atoms* of the elements. This has been directed towards an eventual understanding of how these atoms behave when they form chemical bonds.

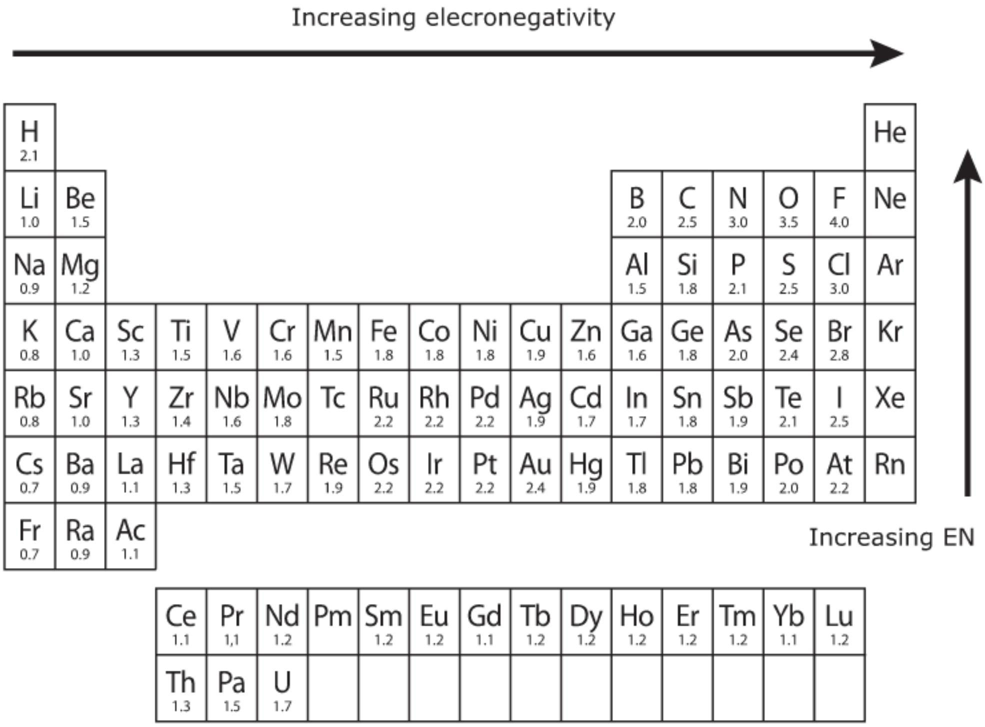
Chemical bonding begins when the valence electrons in a region of space between two atoms are attracted by or "shared" between the adjacent nuclei. Each nucleus exerts an influence on those electrons, which ultimately determine the nature of the resulting bond.

To begin to describe this effect and the nature of the resulting bonds, let's look at an elemental property associated with bonded atoms. It is one of the most important properties in chemical bonding.

Electronegativity is defined as the relative ability of a bonded atom to attract shared electrons to itself. Atoms with relatively high electronegativities (EN) tend to pull bonded electrons closer to their nuclei. Atoms with lower EN values have their bonded electrons pulled further away. As we'll see in section 6.3, this will dictate not only the nature of the chemical bonds that form, but also the properties of the compounds containing those bonds.

We might expect that smaller atoms would have higher EN values since their nuclei would be closer to bonded electrons than the nuclei of larger atoms. We might also expect that larger atoms would therefore tend to have lower EN values. This is indeed the case, and because atomic size shows periodic trends, we shouldn't be surprised that electronegativity does as well. In fact, the general trends in electronegativity are similar to those seen in ionization energy.

We can see a clear resemblance to the trends in ionization energy, namely that EN increases going across a period and increases moving up a group (Figure 6.2.6). (The noble gases don't have EN values because they don't generally form chemical bonds.)



H 2.1																	He
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr
Rb 0.8	Sr 1.0	Y 1.3	Zr 1.4	Nb 1.6	Mo 1.8	Tc	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe
Cs 0.7	Ba 0.9	La 1.1	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn
Fr 0.7	Ra 0.9	Ac 1.1															

Ce 1.1	Pr 1,1	Nd 1.2	Pm	Sm 1.2	Eu 1.2	Gd 1.1	Tb 1.2	Dy 1.2	Ho 1.2	Er 1.2	Tm 1.2	Yb 1.1	Lu 1.2
Th 1.3	Pa 1.5	U 1.7											

Figure 6.2.6 *Periodic table showing trends in electronegativity*

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The electronegativity values are numbers ranging from a low of 0.7 for cesium to 4.0 for fluorine (Figure 6.2.7). The values were determined by the great American chemist Linus Pauling.

For our purposes, we will only be interested in the relative magnitudes of the numbers.

The trends indicate that metal atoms, which are large with low ionization energies, also have relatively low EN values. Smaller non-metal atoms tend to have higher ionization energies and electronegativities. The consequences of these properties with respect to chemical bonding are coming up in the next section, so stay tuned!

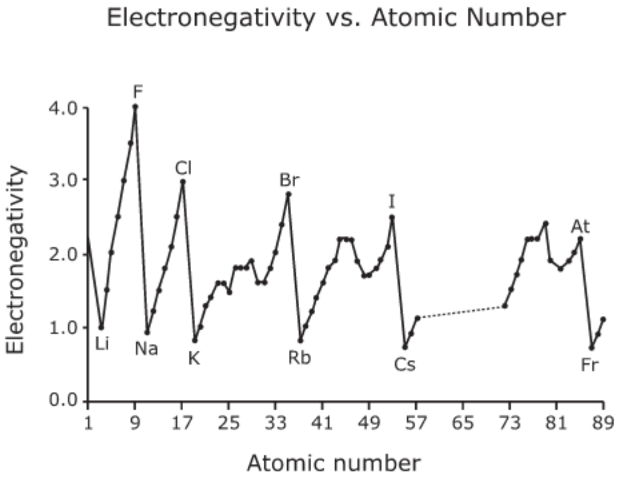

Figure 6.2.7 *Graph showing electronegativity values*

6.2 Activity: A Summary Diagram of Periodic Trends

Question

How can we summarize the three periodic trends discussed in this section using one periodic table?

Materials

Periodic table, a ruler or straight edge

Procedure

1. Consider each of the three periodic trends listed below and complete the following table by writing in either the word "increases" or "decreases" for each of the properties listed in the spaces available.

	Moving Across a Period	Moving Up a Chemical Family
Atomic Size		
Ionization Energy		
Electronegativity		

2. Print a full page version of the periodic table of the elements from whatever website you wish.

3. Using a ruler, draw three parallel vertical arrows facing up on the left margin of the periodic table. Draw three parallel horizontal arrows facing to the right across the top of the table.

4. Label each of the three arrows on the left and across the top with the terms: "Atomic Size," "Ionization Energy," and "Electronegativity." Next to each term, write the appropriate words from the table that you filled in above.

5. Using a ruler, draw a long diagonal arrow beginning at the bottom left corner of the table and extending and pointing to the top right corner. Along the top side of that arrow, write in how each of the three terms listed above changes as you move from the bottom left corner of the periodic table to the top right corner. Save this table because we will refer to it in Section 6.3.

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6.2 Review Questions

1. What is meant by the term "periodic trends"?

2. Why is it difficult to measure the sizes of individual atoms?

3. Two of the elemental properties discussed in this section show similar trends when moving across a period and up a chemical family. Identify these and the trend observed.

4. One of the three properties discussed shows periodic trends when moving across a period or up a family opposite to the other two properties. Identify this property and the trend observed.

5. Briefly explain why fluorine is a smaller atom than lithium. Consider which factor is predominating across a period.

6. Where are the largest atoms located on the periodic table? Where are the smallest atoms located on the periodic table?

7. The attraction of electrons to the nucleus and repulsion of the electrons between each other both influence the size of an atom or ion. Use this to complete the following statements.
   (a) A cation will always be _________________ (smaller or larger) than its parent neutral atom because of __________________ (increased or decreased) attraction of the outer electrons for the nucleus and __________________ (increased or decreased) repulsion of the electrons for each other.
   (b) An anion will always be _________________ (smaller or larger) than its parent neutral atom because of __________________ (increased or decreased) attraction of the outer electrons for the nucleus and __________________ (increased or decreased) repulsion of the electrons for each other.

8. What role do inner or core electrons play in determining atomic size and ionization energy?

9. Complete the following table by filling in the words "lower left" or "upper right" in the appropriate spaces.

Where on Periodic Table Elements Show:	
Largest atomic radii	
Smallest atomic radii	
Lowest ionization energy	
Highest ionization energy	
Lowest electronegativity	
Highest electronegativity	

10. Consider the first two ionization energies for lithium:

    $IE_1 = 519$ kJ/mol $\qquad IE_2 = 7\,285$ kJ/mol

    Explain why lithium's second ionization energy is more than 10 times its first.

11. Elements with low ionization energies tend to have relatively low electronegativities. What might this indicate about how they will behave when reacting with high IE and EN elements?

12. Elements with high ionization energies tend to have relatively high electronegativities. What might this indicate about how they will behave when reacting with low IE and EN elements?

13. What do you think might occur if two non-metal atoms, each with high EN and IE values reacted together? (Hint: Will either have a tendency to give away electrons?)

14. Extension: Write the electron configuration for nickel and zinc. Use these to explain why an atom of zinc is larger than an atom of nickel.

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6.3 Describing Chemical Bonding

Warm Up

1. What term do we give to an atom's outer electrons that take part in chemical bonding?
   ____

2. Define electronegativity.
   ____

3. In which region of the periodic table are elements located that tend to
   (a) lose outer electrons most easily during chemical changes?
   ____

   (b) gain outer electrons most easily during chemical changes?
____

An Introduction to Chemical Bonding

All matter is composed of atoms, and those individual atoms are far too small to see. From that, it seems reasonable to conclude that matter must be made up of large numbers of atoms connected or bonded together. In this section, we will investigate the nature of the bonds between atoms and how those bonds determine important properties in compounds.

Atoms are electrical species with a negative cloud of electrons surrounding and attracted to a positive nucleus. As you have learned, the electrostatic forces of attraction and repulsion within atoms influence properties such as atomic size, ionization energy, and electronegativity. Those same forces and properties also play a role whenever atoms bond together.

When two atoms approach each other, all of the electrostatic interactions associated with equally and oppositely charged particles occur. The negative electron clouds of the atoms exert repulsive forces on each other, as do the positive nuclei of each atom. This repulsion slows the approaching atoms and converts some of their kinetic energy to potential energy. In addition, each nucleus also begins to attract the approaching atom's outer electron cloud. These attractive forces are most intense in the region of space where the electron clouds "overlap" between the adjacent nuclei. If the attractive forces between the atoms are stronger than the repulsive forces, the two atoms together are in a state of lower energy than when they were apart. Thus, a chemical bond forms between them.

Types of Chemical Bonds

The events described above apply to the formation of all chemical bonds. But recall that we have classified elements as metals and non-metals based on a number of physical and chemical properties that correlate to different positions on the periodic table. These properties and the three possible ways that these two varieties of elements can combine give rise to three different *types* of chemical bonds, which are listed in Table 6.3.1. In this course, we will cover ionic and covalent bonds.

Table 6.3.1 *Types of Chemical Bonds*

Atoms Involved in Chemical Bond	Type of Chemical Bond
1. metal bonded to non-metal	ionic bond
2. non-metal bonded to non-metal	covalent bond
3. metal bonded to metal	metallic bond

Table 6.3.1 is a simplified summary of chemical bonds because the bonds between atoms in most chemical compounds have varying proportions of both ionic and covalent characteristics. We will begin with clear examples of each type of bond to introduce the concepts involved.

Ionic Bonds

Ionic bonds form between two atoms with large differences in their ionization energies and electronegativities. Recall from Section 6.2 that such combinations typically occur when relatively large metal atoms located on the far left side of the periodic table in groups 1 or 2 combine with smaller non-metal atoms on the far right side of the table belonging to groups 16 or 17.

Look again at the table of electronegativities introduced in section 6.2 (Figure 6.2.6). Imagine a "collision," for example, between an alkali metal atom such as sodium and a halogen atom such as chlorine. These elements are located at opposite ends of the 3rd period of the periodic table and therefore exhibit significant differences in size, ionization energy, and electronegativity.

Compared to an atom of sodium, a chlorine atom is smaller with a higher ionization energy and electronegativity. As a result, when the outer electron clouds of these two atoms encounter each other, sodium's lone valence electron will be closer to chlorine' nucleus than to its own. It will therefore feel a stronger attraction from chlorine's nucleus than from its own. In fact, because the difference in the electronegativities of these two elements is *greater than 1.7*, the probability of finding sodium's outer electron near chlorine's nucleus is so great that the sodium atom can be considered to *transfer* that valence electron to the chlorine atom. Electronegativity difference is often abbreviated as **Δ**EN.

The large sodium atom, having lost the only electron in its 3rd energy level, is now a much smaller positively charged sodium cation (Na^+). The relatively small chlorine atom, having gained an extra electron, becomes a larger negatively charged chloride anion (Cl^-). These two oppositely charged ions are now bound together by an electrostatic attraction called an **ionic bond**.

An **ionic bond** is the electrostatic attractive force between the oppositely charged ions produced when a metal atom transfers one or more electrons to a non-metal atom.

The electron transfer from sodium to chlorine and the resulting ionic bond is shown in Figure 6.3.1.

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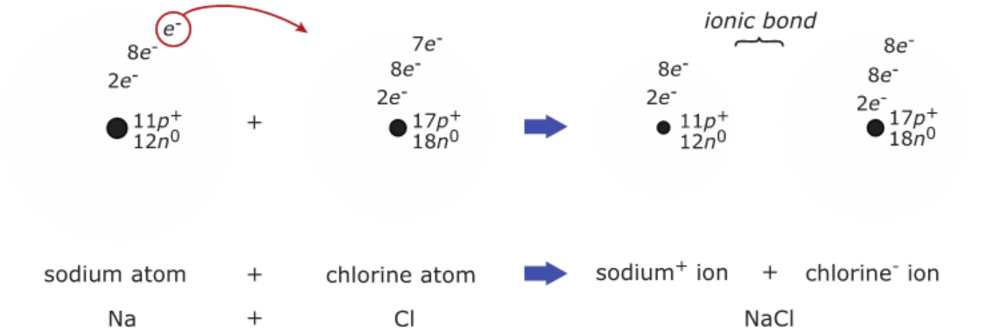

Figure 6.3.1 *An electron transfers from sodium atom to a chlorine atom, resulting in the formation of an ionic bond between the ions.*

The Ionic Crystal Lattice

Obviously, when any macroscopic sample of chlorine gas and sodium metal react together, countless atoms will transfer electrons to form countless oppositely charged ions. These oppositely charged species being produced in close proximity are drawn together into an ordered, solid, three-dimensional array of cations and anions called a **crystal lattice** (Figure 6.3.2). The smallest whole number cation-to-anion ratio in this structure represents the chemical formula for the ionic compound, in this case, NaCl.

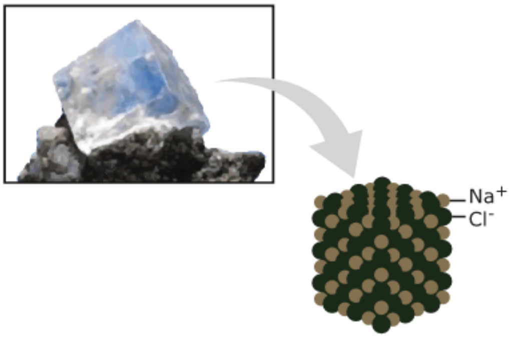

Figure 6.3.2 *NaCl crystal lattice*

The vast number of interionic forces present in a crystal lattice locks all of the ions into place. This helps explain why all ionic compounds are solids with high melting temperatures (e.g., sodium chloride melts at 801°C.)

Ionic compounds form a number of different crystal structures depending on the relative sizes and ratios of their ions. Those ratios in turn depend on the charges on the ions in the compound.

Recall from section 6.1 that the representative elements in groups 1, 2, 13, 15, 16, and 17 of the periodic table tend to form stable ions by losing or gaining sufficient electrons to become isoelectronic with the nearest noble gas. This results in the common ion charges shown in Table 6.3.2 for those groups.

Table 6.3.2 *Common Ion Charges in Groups 1, 2, 13, 15, 16, and 17*

Group Number	1	2	13	15	16	17
Most Common Ion Charge	1+	2+	3+	3-	2–	1–

We can think of ionic bond formation as a case of *extremely unequal electron sharing*. Both metal and non-metal nuclei attract the valence electrons between them when their atoms meet. However, the non-metal pulls those electrons so close to its own nucleus that it effectively captures the metal's valence electrons and forms the metal cation and non-metal anion. An accurate analogy might be a grossly mismatched tug-of-war, except that in this case, the smallest competitor wins.

Several important points should be mentioned when summarizing ionic bonding:

1. Ionic compounds form between metals and non-metals whose ΔEN exceed 1.7. They typically form when metals from groups 1 or 2 react with non-metals from groups 16 or 17 of the periodic table.

2. During the formation of an ionic bond, metal atoms will transfer one or more valence electrons to the more electronegative non-metal atoms. This occurs because of the metal's relatively low ionization energies and electronegativities. In the process, metal cations and non-metal anions form and are attracted to each other by ionic bonds.

3. Ionic compounds form structures known as crystal lattices. The vast number of attractive forces present in such lattices account for the high melting temperatures of ionic compounds.

4. The formulas for ionic compounds represent the smallest whole number ratios of cations-to-anions that are electrically neutral.

Quick Check

1. What event occurs when atoms of metals and non-metals react to become cations and anions?

   ____

2. Identify the three types of chemical bonds based on the different elements involved.

   ____

   ____

   ____

3. Which chemical families in the periodic table are typically associated with ionic bond formation?

   ____

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Sample Problem — Ionic Bond Formation

Write formulas for the compounds formed when the following elements combine and justify that the bonds present are ionic by determining the ΔEN in each case.
(a) Ca and Br (b) Al and O (c) Be and O (d) Rb and N (e) Ba and Cl

What to Think about

1. Write the element symbols with their charges and criss-cross the numbers.
2. Reduce formulas to smallest whole number ratios
3. Determine ΔEN values using the table above. Values above 1.7 represent ionic bonds.

How to Do It

(a) $Ca^{2+}\ Br^{1-} \rightarrow CaBr_2$ $\Delta EN = 1.8$ (ionic bond)
(b) $Al^{3+}\ O^{2-} \rightarrow Al_2O_3$ $\Delta EN = 2.0$ (ionic bond)
(c) $Be^{2+}\ O^{2-} \rightarrow BeO$ $\Delta EN = 2.0$ (ionic bond)
(d) $Rb^{1+}\ N^{3-} \rightarrow Rb_3N$ $\Delta EN = 2.2$ (ionic bond)
(e) $Ba^{2+}\ Cl^{1-} \rightarrow BaCl_2$ $\Delta EN = 2.1$ (ionic bond)

Practice Problems — Ionic Compounds

1. Write formulas for the ionic compounds formed when the following elements combine:

   (a) Ba and Br
   (b) Be and O
   (c) Sr and N
   (d) Mg and Cl
   (e) Fr and F

2. Justify that the bonds in the following compounds are ionic by calculating the ΔEN values for each.

   (a) RbF
   (b) $RaCl_2$
   (c) KBr
   (d) Na_2O

3. Write formulas for the ionic compounds formed when the following elements combine. Using the ΔEN values, arrange the compounds in order of the increasing ionic character of the bonds in each compound.
   (a) Na and N (b) Sr and Br (c) Li and Cl (d) Cs and F (e) Rb and O

Covalent Bonds

Now let's look at the formation of a bond between two atoms of the same non-metal element, such as hydrogen (Figure 6.3.3). Obviously, the electronegativities of these or any two identical atoms would be the same.

As mentioned above, bond formation begins with atoms "colliding." As the two hydrogen atoms approach each other, their kinetic energy increases as each electron cloud is attracted to the other's approaching positive nucleus. The two atoms continue moving together until the repulsive forces of the two negative electron clouds and the two positive nuclei slow the atoms and convert their kinetic energy into potential energy.

As the atoms get close to each other, their electron clouds may overlap enough to cause attractive forces to exceed repulsive ones. The two valence electrons will move into the region of space between the adjacent nuclei because this is where they experience the most attractive force from those two centres of positive charge. The two atoms will settle into a position next to each other with the pair of valence electrons in a cloud of negative charge between the two nuclei. As the electron clouds of each hydrogen atom overlap, the two valence electrons experience the maximum attractive force between the two adjacent nuclei. This force of attraction of a pair of valence electrons between two adjacent nuclei constitutes a single **covalent bond**. In our example, the result of this covalent bond is a molecule of hydrogen, H_2

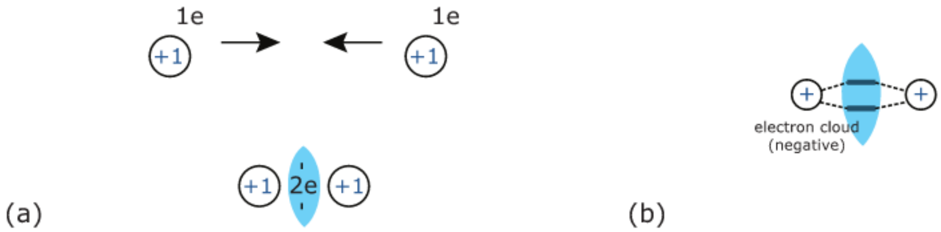

Figure 6.3.3 *(a) Two hydrogen atoms collide and two valence electrons move into the space between the nuclei. (b) The valence electrons experience a force of attraction from the two nuclei. This attraction holds the two atoms together to form* H_2.

Because this bond has formed between two atoms of hydrogen, the electronegativity difference associated with the atoms in the bond must be zero. This tells us that, on average, the pair of bonded electrons will spend the majority of their time equidistant between the two hydrogen nuclei. Stated another way, this means that the density of the electron charge cloud is greatest in the region of space halfway between the two adjacent nuclei. This is true whenever two atoms of the same element form covalent bonds. The "equal sharing" of valence electrons is sometimes referred to as a "pure covalent" or non-polar covalent bond.

Although both ionic and covalent bond formation involves only valence electrons, there are several important differences between the two events:

1. Covalent bonds typically form between two non-metal atoms rather than between metal atoms and non-metal atoms.
2. Because no electron transfer occurs and no ions form, all of the species prior to and following covalent bond formation between two atoms are electrically neutral.
3. The force of attraction in a covalent bond is between a pair of electrons and two adjacent positive nuclei, rather than between a cation and an anion as in an ionic bond. Electrons in covalent bonds are *always associated into pairs*.
4. Covalent compounds often exist as independent molecules rather than large crystal structures.

Polar Covalent Bonds

We have discussed above the two extreme cases of bonding: complete electron transfer and completely equal electron sharing. Between these extremes are covalent bonds involving *unequal* electron sharing.

When atoms with different electronegativities form covalent bonds, those ΔEN values may be minimal or significant. If ΔEN is less than 0.4, the bonding electrons between the two atoms spend no more of their time nearer one nucleus than the other. Such bonds are designated as being mostly covalent because ΔEN appears to be insignificant. Another way to characterize this is to say that these bonds have very little "ionic character."

However, as ΔEN increases beyond 0.4, the pair of bonding electrons will be drawn closer and closer to the nucleus of the atom with the higher electronegativity. This unequal distribution of electron density will give that end of the bond a partially negative "pole" and the other a partially positive "pole." A bond "dipole" is said to exist and the bond itself is known as a **polar covalent bond**.

As the ΔEN increases and the bonds become more and more polar, we could say that the amount of ionic character in those bonds increases (Table 6.3.3).

Table 6.3.3 *Relationship of ΔEN and Bond Designation*

ΔEN	Bond Designation
0	non-polar covalent
< 0.4	mostly covalent
0.4 – 1.7	polar covalent
> 1.7	ionic

Let's look at an example of a polar covalent bond. When a hydrogen atom having an electronegativity of 2.1 bonds to a chlorine atom with an electronegativity of 3.0, the ΔEN = 0.9. The electron density will be concentrated near chlorine giving that end of the bond a partial negative charge and leaving the hydrogen end with a partial positive charge. The bond dipole is said to be in the direction of chlorine and we can designate this polar covalent bond in several ways. One is shown in Figure 6.3.4. The lower case Greek deltas (δ) indicate that there are slight or *partial* charges associated with each end of the HCl molecule. Note also that more electron density is associated with chlorine. Another depiction of this polar covalent bond simply shows the hydrogen chloride bond as a straight line between the element symbols. Beneath this is an arrow facing in the direction of the highest electron density or the negative end of the bond dipole.

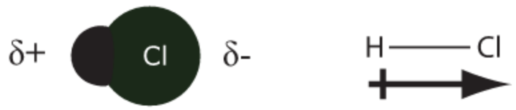

Figure 6.3.4 *Polar covalent bonds depictions. The bond dipole is in the direction of the chlorine.*

Atoms That Form More Than One Bond

So far we have considered the formation of only one bond per atom in two different molecules, namely H_2 and HCl. Notice that hydrogen and chlorine each require a single electron to become isoelectronic with their nearest noble gas. In hydrogen's case, one more electron will complete its first energy level. When chlorine acquires another electron it achieves a stable octet in its valence shell.

In each example, the sharing of a pair of valence electrons, whether equal or not, gives each atom in the bond the benefit of that extra electron in its valence shell. The bond also allows both atoms to have *all of their valence electrons paired,* which is a very stable configuration from a quantum mechanical perspective.

Of course, non-metals sometimes require more than one electron to achieve a stable outer electron shell and have all of their valence electrons paired. Consider several non-metals in groups 14, 15, and 16. To achieve a stable octet containing four electrons pairs in each of their valence shells, carbon requires four electrons, nitrogen needs three, and oxygen needs two.

> This tells us that the number of electrons required by an atom to achieve the stable outer electron configuration of the nearest noble gas also represents the number of covalent bonds that the atom must form.

We can use Table 6.3.4 to predict formulas for compounds formed between elements in these families. For example, when phosphorus and chlorine react together, phosphorus requires three electrons to complete its octet, while chlorine requires only one.

Table 6.3.4 *Electrons Needed to Achieve a Stable Octet for Non-metals*

Periodic Table Group Number	14	15	16	17
Electrons Needed to Achieve Stable Octet	4	3	2	1

The element with the lower electronegativity, in this case phosphorus, normally requires the most electrons and is written first in a chemical formula. Place the number of electrons it requires above its symbol on the right (similar to a charge without the sign). Then do the same for chlorine as follows: P^3 Cl^1 Now criss-cross those numbers to give the formula: PCl_3.

The process is similar to writing ionic formulas except no charges exist and you don't always reduce the formula to the smallest ratio of atoms. This is because a covalent formula does not represent a ratio. Rather, it tells us the actual number of atoms that exist in the molecule. Assume at this point, however, that you *can* reduce covalent formulas unless told otherwise by your teacher.

There are also numerous examples where more than one pair of electrons is shared between the same two atoms. Two pairs of shared valence electrons results in a double covalent bond and three pairs will produce a triple covalent bond. We will discuss multiple bonds in detail in the next section. For now, we will only mention that as the number of electron pairs shared between two adjacent nuclei increases, so does the strength of the covalent bond.

Sample Problem — Covalent Bond Formation

Predict the formulas for the compounds formed when the following elements combine and determine whether the bonds present are non-polar covalent or polar covalent.

(a) N and F (b) C and H (c) Si and N (d) C and S (e) O and O

What to Think about	**How to Do It**
1. Determine how many electrons each atom requires to complete its valence shell and write that number above the symbol. 2. Criss-cross those numbers and reduce ratios if possible (for now). 3. Determine the ΔEN for each and classify the bonds present.	(a) $N^3 F^1 \rightarrow NF_3$ $\Delta EN = 1.0$ (polar covalent) (b) $C^4 H^1 \rightarrow CH_4$ $\Delta EN = 0.4$ (polar covalent) (c) $Si^4 N^3 \rightarrow Si_3N_4$ $\Delta EN = 1.2$ (polar covalent) (d) $C^4 S^2 \rightarrow CS_2$ $\Delta EN = 0$ (non-polar covalent) (e) $O^2 O^2 \rightarrow O_2$ $\Delta EN = 0$ (non-polar covalent)

Practice Problems — Comparing Types of Chemical Bonds

1. Consider the ΔEN values and pair up the elements Al, Cl, N, and Na to write the formula for the types of compounds identified below. Justify each choice by showing the appropriate ΔEN value next to each formula.
   (a) A compound with an ionic bond

   (b) A compound with a polar covalent bond

   (c) A compound with a non-polar covalent bond

2. Calculate the ΔEN values for the bonds in the following compounds. Then arrange the compounds in order from those containing bonds in which the electrons are shared most equally to those in which the electrons are shared most unequally.
   (a) H_2O (b) PCl_3 (b) CI_4 (d) SiO_2 (e) AlN

3. Complete the following table:

Elements Present	Formula	ΔEN Value	Nature of Bonds	Atom Possessing Greater Electron Density
C and S				
B and Cl				
Al and O				
N and I				
Ca and F				

The Strength of Ionic vs. Covalent Bonds

Remember that ionic compounds are solids at room temperature and have high melting points. This results from the vast number of interionic forces locking all of the ions together in place in the crystal lattice. As mentioned earlier, the common ionic compound NaCl melts at 801°C.

Covalent compounds, however, usually exist as individual molecules and in any of the three states of matter: solid, liquid, or gas. We shouldn't conclude from this, however, that covalent bonds are any weaker than ionic bonds. Consider, for example, the molecule methane, CH_4, the main component of natural gas.

Although the melting point of methane (–182°C) is very low compared to sodium chloride, this physical property does not reflect the strength of the C – H bonds in methane or indicate that the bonds are weak compared to those in NaCl.

This is because no chemical bonds are broken when methane or any molecular covalent compound melts. Instead, weak intermolecular forces *between* the molecules are overcome. The result is that molecules are separated *from each other* rather than breaking the bonds between the atoms within those molecules.

The energy required to separate the bonded carbon and hydrogen atoms within the molecules from each other is far more than that required to simply pull the molecules apart. In the final section of this chapter, we will discuss the different forces that hold molecules together. Although some of those forces are stronger than others, *none are as strong as chemical bonds*.

Compelling evidence of the strength of covalent bonds can be seen by studying compounds called **network covalent solids**. Rather than consisting of individual molecules, these substances are held together by covalent bonds that extend throughout the entire sample. In the same way that melting an ionic solid requires overcoming all of the attractive forces between the oppositely charged ions in the crystal lattice, melting a network covalent solid involves breaking all of the covalent bonds within what is effectively a giant molecule literally as big as the sample.

Consider quartz, for example, which is a network covalent solid having the formula SiO_2 (Figure 6.3.5). The fact that no separate molecules exist in a quartz crystal means that the melting point is very high: 1550°C. The melting point does reflect the strength of the bonds in the compound. It shows us that covalent bonds can be as strong as ionic bonds.

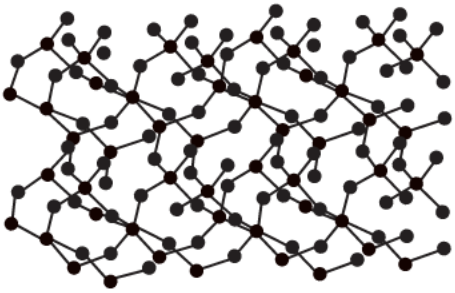

Figure 6.3.5 *A quartz crystal*

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6.3 Activity: The Colours of Chemical Bonds

Question

Can one primary colour blending into another be used to depict the transition from pure covalent bonding to ionic bonding?

Materials

Either blue, green, and yellow coloured pencils or blue, green, and yellow watercolour paint and brushes.

Procedure

1. Use the three grids below, (A), (B), and (C). In each of the blank spaces, write the correct formula for the compound resulting from the combination of the two elements that intersect at that space. Remember to write the least electronegative atom symbol first.

2. Consult the electronegativity table given earlier (Figure 6.2.6). Determine the electronegativity difference for each pair of elements to determine the type of bonds present in those compounds. Then shade in the spaces around each formula according to these directions: Shade in the spaces around the compounds containing ionic bonds yellow, covalent bonds blue and polar covalent bonds green.

(A)

	Li	**Be**	**B**	**C**	**N**	**O**	**F**
F							

(B)

	Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**
Cl							

(C)

	K	**Ca**	**Ga**	**Ge**	**As**	**Se**	**Br**
Br							

Results and Discussion

1. Does every metal-non-metal combination result in an ionic bond?

6.3 Review Questions

1. For a chemical bond to form between two atoms, how must the energy associated with the bonded atoms compare to the energy when the atoms are apart? What does this tell us about the attractive forces compared to the repulsive forces between them?

2. What is an ionic crystal lattice and how does it explain the high melting points of ionic compounds?

3. Use your answer to question 2 to explain why formulas for ionic compounds do not represent neutral independent molecules of those compounds.

4. Identify the attractive forces associated with
   (a) ionic bonds

   (b) covalent bonds

5. (a) Identify two similarities between ionic and covalent bonds.

   (b) Identify two differences between ionic and covalent bonds.

6. Complete the following table by writing in the formulas of the compounds formed from the pairs of elements. Determine the ΔEN value for each and then classify the bonds as non-polar covalent, polar covalent, or ionic.

Elements	Compound Formula	ΔEN Value	Nature of Bonds Present
(a) rubidium and oxygen			
(b) strontium and bromine			
(c) carbon and sulphur			
(d) silicon and chlorine			

7. Magnesium is a metal and sulphur is a non-metal. Compare the ΔEN value for these elements in the compound MgS to the ΔEN value for the non-metals hydrogen and oxygen in water, H_2O. Which of the two compounds possesses a greater amount of ionic character in its bonds?

8. Glucose is a covalent compound with the molecular formula $C_6H_{12}O_6$. This and many other covalent formulas aren't reduced to the smallest whole-number ratios of atoms in the compound. Why not?

9. Many covalent compounds have much lower melting points than ionic compounds. Why does this not mean that covalent bonds are weaker than ionic bonds?

10. Diamond is a form of pure carbon containing only covalent bonds. It is the hardest substance known and has a melting point of about 3550°C. What name do we give to this type of covalent substance? Suggest a reason for its very high melting point.

11. Consider the nature of the covalent bonds present in HCl and in N_2. Which substance would you expect to have the higher melting point? Give a reason for your answer.

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6.4 Lewis Structure Diagrams

Warm Up

1. Why do elements in the same chemical family display similar chemical behaviour?

   ____

2. How can you determine the number of valence electrons in each of the representative or main group elements?

   ____

3. Define the term "stable octet."

   ____

Depicting Atoms, Ions, and Molecules in Two Dimensions

As you learned earlier, an atom's valence electrons are the outermost electrons. These are the electrons involved in chemical bonding. This means that, in chemical behaviour, the valence electrons of an atom are really the only electrons that matter.

In 1916, the American chemist Gilbert N. Lewis devised a system of representing the atoms of the elements based on the number of valence electrons they possess. This notation system uses each element symbol to represent the nucleus and all of the inner electrons of an atom (Lewis called this the "kernel" of an atom). It then surrounds that symbol with a series of dots representing that atom's valence electrons.

The notation is a simple and useful way to represent atoms and serves as a foundation to help us understand and predict chemical behaviours and compound structures without the need for sophisticated bonding theories. Our discussion of Lewis structures and diagrams will be confined to the representative or main group elements in the periodic table, that is, groups 1, 2, 13, 14, 15, 16, 17, and 18.

We will begin by discussing Lewis structures for individual atoms and ions, and then expand that discussion to include Lewis diagrams for molecular compounds and polyatomic ions.

Lewis Structures for Atoms

To write a Lewis structure for an atom, you need only determine the number of an atom's valence electrons. Recall from our discussion of the periodic table that this process is straightforward for the main group elements. For any period, beginning at the alkali metals, we see that atoms of this family have one valence electron. As we move across the period, each main group family has atoms with one additional valence electron up to the stable octet of four electron pairs present in each noble gas (except helium) (Table 6.4.1).

Table 6.4. *Valence Electrons in Main Group Atoms*

Main Group Number	1	2	13	14	15	16	17	18
Valence Electrons	1	2	3	4	5	6	7	8
Valence Electron Configuration	ns^1	ns^2	$ns^2\,np^1$	$ns^2\,np^2$	$ns^2\,np^3$	$ns^2\,np^4$	$ns^2\,np^5$	$ns^2\,np^6$

To write Lewis structures for the atoms, follow these steps:

1. Write the element symbol.
2. For hydrogen place a single dot next to the symbol. For helium place a pair of dots.
3. For 2nd period elements and beyond: for each valence electron present, place one dot around that symbol at one of the four positions of the compass: west, east, north, or south.
4. If more than four valence electrons are present, begin pairing the dots only after the four compass positions are filled.

The relative placement of the paired and unpaired dots isn't as important as how many of each is present. Figure 6.4.1 shows the Lewis structures for the main group elements of the first three periods.

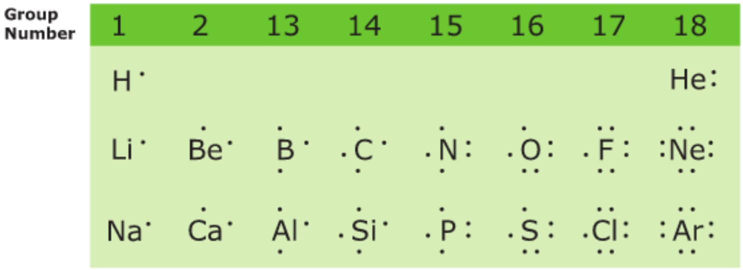


Figure 6.4.1 *Lewis structures for main group elements of the first three periods*

As you view Figure 6.4.1, consider the following important points:

1. As each element in a family has the same number of valence electrons, the Lewis structure for those elements has the same number of dots.
2. For the metals, the *total number of dots* represents the number of electrons that each atom loses when forming a cation.
3. In a correctly drawn Lewis structure for a non-metal, the number of *unpaired* dots shown represents either the number of electrons that atom *must gain* when forming an anion, or the number the electrons the atom *must share* to complete its octet when forming covalent bonds.

Lewis Structures for Monatomic Ions

From points 2 and 3 above, we can see that writing Lewis structures for monatomic ions is straightforward.

For the metals in groups 1, 2, and 13, the Lewis structure for their *stable ions* does not include any dots. The element symbol is usually enclosed in square brackets with the cation's charge written outside the brackets on the upper right. The magnitude of that positive charge simply equals the number of dots (which represent electrons) that were removed from the neutral atom's Lewis structure. Remember that because the number of protons in the nucleus has not changed, a loss of any number of electrons will result in that amount of positive charge on the cation.

For the non-metals in groups 15, 16, and 17, the Lewis structures for their anions all include four pairs of dots surrounding the element symbol enclosed in square brackets with the appropriate negative charge written outside the brackets on the upper right. The magnitude of the negative charge written outside the brackets equals the number of *unpaired* dots that were originally present in the parent atom's Lewis structure. This also equals how many electrons were required to generate the four pairs resulting in a stable octet.

The Lewis structures are shown for the sodium and chloride ions in Figure 6.4.2. Note that the chlorine atom originally had one unpaired dot. This required one electron for four pairs resulting in the charge of 1– on the anion. The sodium has had its one dot removed to form a 1+ cation.

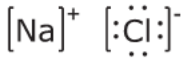


Figure 6.4.2 *[CAPTION TO COME]*

Quick Check

1. What do the "dots" in a Lewis structure for an atom or an ion represent?
   ____

2. What do the total number of dots present in the Lewis structures for the metals in groups 1, 2, and 13 tell us about the cations these atoms will form during a chemical change?
   ____

3. The Lewis structures for nitrogen, phosphorus, and antimony include one pair of dots and three unpaired dots. How many electrons do these atoms require to form a stable octet?
   ____

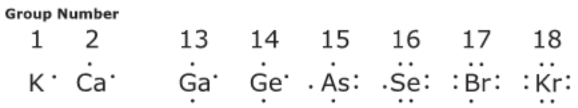
Sample Problem — Drawing Lewis Structures

Draw the Lewis structures for the representative elements belonging to period 4 of the periodic table.

What to Think about

1. Elements in the same chemical family have the same number of valence electrons.
2. Those electrons are represented by placing dots around each element symbol.
3. Consider Figure 6.4.1. Begin at group 1 and give potassium 1 valence electron. Continue to the right placing the same number of dots around each symbol in the same way that the dots appear for the other members of each group.

How to Do It



Practice Problems — Building Lewis Structures

1. Write the Lewis structures for the main group elements in period 5 of the periodic table.

2. Write the Lewis structures for the following atoms and ions.

   (a) Ba (b) Al^{3+} (c) Bi (d) I^- (e) Te

3. Convert the following atomic symbols to the Lewis structures for the ions of those elements:

   (a) Ca (b) Se (c) Ga (d) As

Lewis Structures for Molecules

Each of the pages in this book is a flat surface and any diagrams or images that you see on these pages can only be two-dimensional representations of the real three-dimensional world. Of course, the ionic and molecular compounds that make up that world are also three-dimensional. Understanding their shapes is a very important part of explaining and predicting their behaviour.

Recall that ionic compounds normally exist as ordered, three-dimensional arrays of cations and anions called crystal lattices. The arrangement of ions in these crystals maximizes the attractions between the oppositely charged ions within the lattices and minimizes the repulsions between ions with the same charges. The diagram of an NaCl crystal lattice in section 6.3 helped with visualizing such a structure.

When molecules form, their three-dimensional shapes are also governed by the attractive and repulsive forces that exist within them. The first step toward visualizing the three-dimensional shape of a molecule is to convert its molecular formula into a two-dimensional Lewis structure.

One of the simplest examples of a Lewis structure is a diatomic halogen molecule such as Cl_2 (Figure 6.4.3). The single line between the atoms represents one pair of shared electrons. The other pairs of electrons are referred to as non-bonding or **lone pairs** of electrons. Note that all 14 of the valence electrons possessed by the 2 chlorine atoms are accounted for in the Lewis structure. Note also that each chlorine atom now has the benefit of an extra valence electron and thus has a stable octet.

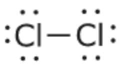


Figure 6.4.3 *Lewis structure of* Cl_2

As with any new procedure, learning to draw Lewis diagrams for molecules is easier if you follow a series of steps. Let's begin with a simple example: the Lewis structure for a molecule of nitrogen trichloride, NCl_3.

Step 1: Determine the total number of valence electrons in the molecule.

A correctly drawn Lewis structure must account for all of the valence electrons present. In this case, nitrogen has five valence electrons and each chlorine atom has seven. Therefore the total number of valence electrons is given by: $5 + (3 \times 7) = 26$.

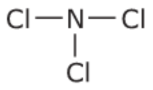
Note that this is an even number, which will be true for all of the examples you will see. There are a few cases where odd numbers of electrons exist, but the vast majority of molecules (and polyatomic ions) possess even numbers of valence electrons. All bonding electrons exist in pairs.

Step 2: Construct the "skeleton" of the molecule using lines to indicate single covalent bonds between the atoms.

To generate the most likely skeleton of the molecule, the following set of guidelines will be of great help. The guidelines are based on numerous empirical observations and hold true for the vast majority of molecules. They also correspond to what we would expect given the electron configurations and electronegativities of the atoms involved. They may seem difficult to remember at first, but you won't need to use all of them for every molecule you draw. As with any new skill, the steps will become more familiar with practice.

Guidelines for Generating Molecule "Skeletons"

1. If the general formula for the compound is of the form "AX_n," then the central atom "A" will be the one with the lower group number, which also usually corresponds to the lower electronegativity. Obviously, if only two atoms exist in the molecule, then no central atom exists.
2. Hydrogen atoms form only one bond and so do not achieve an octet of electrons.
3. Fluorine atoms always form only one bond, and the other halogen atoms *usually* form only one bond. Exceptions to this occur if those halogens are central atoms and are bonded to other smaller halogens or to oxygen.
4. (a) Oxygen atoms normally form two bonds and don't often bond to each other in compounds with other elements. (An exception to this is hydrogen peroxide.)
   (b) Nitrogen atoms normally form three bonds.
   (c) Carbon atoms normally form four bonds.
5. Avoid creating rings or cyclic structures when you draw skeletons.



$$Cl - \underset{\underset{Cl}{|}}{N} - Cl$$

Figure 6.4.4 *Molecular skeleton for NCl_3*

Using the above rules, we see that a central atom exists and that nitrogen is most likely that central atom. We can therefore sketch the molecular skeleton for NCl_3 shown in Figure 6.4.4. The relative orientation of each chlorine atom around the nitrogen atom isn't that important because Lewis structures do not depict shape or 3-D geometry. All the matters at this stage is that nitrogen is in the centre and each chlorine atom is a peripheral or surrounding atom.

Step 3: Subtract the number of valence electrons used to construct the skeleton from the total number of valence electrons available from step 1 to determine the number of valence electrons remaining.

Consider that each line drawn in the skeleton represents a pair of bonding valence electrons, so, in this case, the number of valence electrons remaining is: $26 - (3 \times 2) = 20$.

Step 4: Assume that all of the atoms in the molecule obey the octet rule (except hydrogen). Determine the number of additional valence electrons required (beyond those already present as a result of the bonds drawn) to give all of those atoms the required eight valence electrons.

In this case, because each peripheral chlorine atom has one bond and is therefore associated with two valence electrons, each chlorine atom needs six more electrons to complete its octet. The central nitrogen has three bonds and so has the benefit of six valence electrons. This means that the nitrogen atom needs only two more valence electrons to complete its octet. The calculation to determine the total number of required valence electrons is: $(3 \times 6) + 2 = 20$

Step 5: Compare the number of valence electrons available (from step 3) to the number of valence electrons needed to complete the octets of the atoms (from step 4). If those two numbers match, pair up the electrons. Beginning with the peripheral atoms and ending with the central atom, place those electron pairs where they're needed to satisfy the octets. In this case, the two numbers do indeed match and so the resulting Lewis structure is shown in Figure 6.4.5. If the numbers don't match, there is a procedure we'll discuss later.

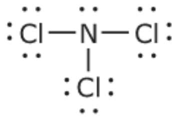


Figure 6.4.5 *Lewis structure for NCl_3*

At this point, consider the:

Criteria Governing the Octet Rule in a Lewis Structure

(a) A peripheral or surrounding atom must not violate the octet rule in a Lewis structure. If an atom does violate the octet rule, then it must be a central atom in the molecule. This doesn't apply to hydrogen, which is associated with only two electrons in molecules.

(b) ***Exception (i)*** Atoms belonging to the second period in the periodic table will not have expanded octets in Lewis structures. An expanded octet (more than eight valence electrons) is only possible for elements belonging to the 3rd period or higher because only those atoms have access to d orbital electrons. These electrons are unavailable below the third energy level.
Exception (ii) The atoms Be, B, and Al will often have incomplete octets such that only two or three pairs of valence electrons will be associated with these central atoms in Lewis structures for molecules.

Step 6: If the numbers in step 5 above agree, then as a final step, check that the total number of valence electrons represented in the diagram matches the total number of valence electrons you began with in step 1.

In this example, the number of valence electrons in the diagram matches the number in the molecule.

Quick Check

1. Suggest a reason why the elements Be, B, and Al are not able to achieve a valence octet when they form covalent compounds.

   ____

2. Hydrogen sulphide, H_2S, is a poisonous, foul-smelling, and flammable gas. Why is the molecular skeleton "S – H – H" incorrect for this molecule?

   ____

3. Determine the total number of valence electrons present in each of the following molecules:

   (a) H_2Se ______ (b) CCl_4 ______ (c) NF_3 ______ (d) PCl_5 ______ (e) SF_6 ______

Sample Problem — Drawing a Lewis Structure for a Molecule

Draw the Lewis structure for a molecule of water, H_2O.

What to Think about	**How to Do It**
1. Each hydrogen atom will form one bond and the oxygen will form two. The oxygen must therefore be the central atom even though it has a higher electronegativity than hydrogen. Oxygen has six valence electrons and hydrogen has one.	
2. Use the steps listed above: **Step 1**: Determine the total number of valence electrons in the molecule. **Step 2**: Construct the "skeleton" of the molecule.	6 + (2 × 1) = 8 valence electrons present in molecule
Step 3: Determine the number of valence electrons remaining.	The skeleton must be: H – O – H
Step 4: Assume that all of the atoms in the molecule obey the octet rule (except hydrogen).	Electrons available: 8 Electrons used in skeleton: 4 Electrons remaining: 8 – 4 = 4
Step 5: Compare the number of valence electrons available to the number of valence electrons needed to complete the octets of the atoms.	Electrons required to complete oxygen's octet: 4
Step 6: Available electrons match electrons in the diagram. Note that in the final structure, oxygen is associated with two bonding pairs and two non-bonding (or lone pairs).	Pair up remaining electrons and place them where needed to satisfy oxygen's octet. $H - \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} - H$

Practice Problems – Drawing Lewis Structures for Molecules

1. Construct the Lewis structure for a molecule of carbon tetrachloride, CCl_4.

2. (a) Draw the Lewis structure for a molecule of ammonia, NH_3.

   (b) When you're finished drawing the structure, determine how many bonding pairs and how many lone pairs of electrons are associated with the central atom.

3. (a) Draw the Lewis structure for a molecule of boron trichloride, BCl_3.

   (b) Consider the central atom in your structure. Does it possess a stable octet of eight electrons?

Drawing Lewis Structures for Molecules Containing Multiple Bonds

We have seen that one pair of valence electrons shared between two adjacent nuclei constitutes a single covalent bond. There are also many cases where the covalent bonds between two atoms involve more than one pair of shared electrons. These are known as **multiple bonds**. If two pairs of electrons are shared between the same two atoms, the bond is called a double bond and if three pairs exist, the bond is a triple bond.

As you might expect, as multiple bonds involve more attractive forces between two atoms than single bonds do, multiple bonds are stronger. Bond strengths are usually measured by the amount of energy required to break a mole of those bonds and are thus represented by the unit kJ/mol. The greater attraction between the atoms in a multiple bond also draws those bonded atoms closer together, which means that multiple bonds are also shorter than single bonds. Table 6.4.2 compares some single and multiple bond strengths and lengths.

Table 6.4.2 *Single and Multiple Bond Strengths and Lengths*

Bond	Bond Energy (kJ/mol)	Bond Length (pm)
C – C	347	154
C = C	614	134
C ≡ C	839	120
N – N	160	145
N = N	418	125
N ≡ N	941	110
C – O	358	143
C = O	799	123
C ≡ O	1072	113

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Let's follow the steps outlined above to draw the Lewis structure for a molecule that contains double bonds, such as carbon dioxide, CO_2.

Step 1: The total number of valence electrons is given by: $4 + (2 \times 6) = 16$

Step 2: Carbon has the lower group number and electronegativity, and oxygen doesn't usually bond to itself in compounds with other elements. Therefore the following skeleton is likely:

O – C – O

Step 3: As four electrons were used to construct the above skeleton, 12 of the original 16 electrons remain to complete each atom's octet.

Step 4: Each of the oxygens in the skeleton requires six electrons and the carbon atom requires four electrons to complete their valence shells. This gives a total of: $(2 \times 6) + 4 = 16$ electrons.

Step 5: Notice that 16 electrons are required but only 12 electrons are available to complete the octets of the atoms. We are therefore lacking four electrons. This means that we must return to step 2 and re-draw the molecular skeleton such that we incorporate one *multiple bond* for each pair of electrons that we lack to complete the octets._

Because we are four electrons short, we can consider either of the following modified skeletons:

skeleton 1: **O = C = O** or skeleton 2: **O ≡ C – O**

Although both skeletons above show carbon forming a total of 4 bonds, as oxygen normally forms two bonds, we would choose skeleton 1, showing each oxygen atom participating in a double bond as being the most likely skeleton. Note also the symmetry associated with this choice as opposed to skeleton 2. Molecules will often possess a high degree of symmetry and that also makes this choice more likely: **O = C = O**

Now we again return to following the steps:

Step 3: Each line in the skeleton represents a pair of shared electrons, so each double bond indicates two electron pairs or four electrons. Therefore eight electrons have been used in constructing the skeleton, so the number of electrons remaining is given by: $16 - (2 \times 4) = 8$

Step 4: The two oxygen atoms each need four more electrons to complete their octets, but the carbon atom now has the benefit of eight valence electrons and so requires no more. This means that only eight electrons are needed to complete the octets of the atoms in the skeleton.

Step 5: As the number of electrons we need now matches the number available, we pair up those electrons to give the Lewis structure for carbon dioxide. Figure 6.4.6 shows two possible ways of representing that structure.

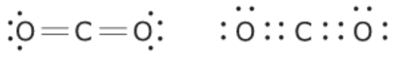

Figure 6.4.6 *Lewis structures for* CO_2

As a final step we see that all 16 valence electrons have been accounted for in the Lewis structure. The construction of this molecule can be understood by considering how the valence electrons present in each individual atom are reorganized as the two double bonds form:

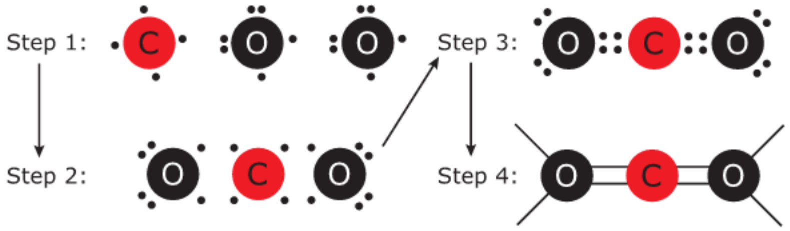

Figure 6.4.7 *Constructing the molecule from the Lewis structures*

Extension: Drawing Lewis Structures Containing Atoms With Expanded Octets

Sometimes we discover that fewer electrons are available than needed to complete the octets of the atoms in a molecule. At other times, we might encounter situations where more electrons are available than needed. This normally results in **expanded octets** associated with the central atom in a Lewis structure. Remember that an expanded octet is only possible for an atom if d orbital electrons are available. That is only possible for elements belonging to period 3 or higher in the periodic table.

Let's investigate this by drawing the Lewis structure for one of the few compounds involving noble gases, namely XeF_4. To do this, we follow the steps below:

Step 1: Total number of valence electrons $= 8 + (4 \times 7) = 36$

Step 2: Molecular skeleton: See Figure 6.4.8.

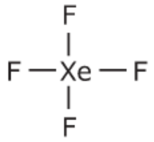

Figure 6.4.8 *Molecular skeleton for XeF4*

Step 3: Electrons used in skeleton: $4 \times 2 = 8$
Electrons remaining: $36 - 8 = 28$

Step 4: Electrons required to complete octets: $4 \times 6 = 24$

Note that xenon needs no electrons but each fluorine atom needs six electrons to complete its octet.

Step 5: We have 28 electrons available but only need 24. At this point, we first place the 24 electrons where they're needed in pairs around each peripheral fluorine atom. We then place the remaining two pairs of electrons around the central xenon. The orientation of the lone pairs on the central atom is not important. Simply placing two pairs at any two locations available on xenon is all that matters. Note that xenon has an "expanded octet" of 12 valence electrons.

Step 6: All 36 valence electrons are accounted for in the Lewis structure (Figure 6.4.9).

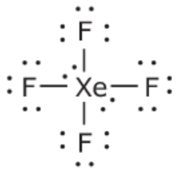

Figure 6.4.9 *Lewis structure for XeF_4*

Sample Problem — Drawing a Lewis Structure Containing a Multiple Bond

Draw the Lewis structure for a molecule of hydrogen cyanide, HCN.

What to Think about	How to Do It
1. Calculate the total valence electrons present in the molecule.	Total of 10 valence electrons available
2. Determine the molecular skeleton.	Most likely skeleton: $H-C-N$
3. Determine electrons used in skeleton and those remaining.	As 4 electrons were used to construct the skeleton, there are 6 remaining.
4. Determine electrons needed to complete octets.	The carbon needs 4 more electrons and the nitrogen needs 6 to complete their respective octets.
5. Compare the number of valence electrons available to the number of valence electrons needed to complete the octets of the atoms.	As only 6 electrons are left, we are 4 electrons short.
6. Adjust the skeleton, if needed.	This means that the original skeleton must be changed to incorporate multiple bonds.
7. Hydrogen only forms one bond and so cannot be the central atom. Of the remaining two atoms, carbon has the lower group number and electronegativity. Carbon is therefore the most likely central atom. Carbon normally forms four bonds and nitrogen forms three.	Hydrogen can only form one bond so the two extra bonds must be added between the nitrogen and carbon atoms in the form of a triple bond. The new skeleton is therefore: $H-C\equiv N$
8. We see that 8 valence electrons (4 × 2) have been used in this new skeleton, leaving only 2 of the original 10.	As carbon's octet is now satisfied and nitrogen only needs 2 more electrons, the number of available electrons matches the number required. Pairing up those final two electrons and placing them on nitrogen gives: $H-C\equiv N:$ A final check shows us that all 10 valence electrons are accounted for.

Practice Problems – Lewis Structures Containing Multiple Bonds and Expanded Octets

1. Formaldehyde is used as a disinfectant, an embalming agent, and as a component in many organic synthesis reactions. Draw the Lewis structure for a molecule of formaldehyde, CH_2O.
(Hint: Carbon is the central atom.)

2. Carbon monoxide is an invisible, odorless, and toxic gas that renders hemoglobin unable to transport oxygen to body tissues. Draw the Lewis structure for a molecule of CO.

3. Extension: Bromine trifluoride is a very reactive and toxic liquid that explodes on contact with water and organic compounds. Draw the Lewis structure for a molecule of BrF_3.

Drawing Lewis Structures for Polyatomic Ions

Many polyatomic ions contain non-metal atoms bonded covalently to each other. To draw a Lewis diagram for a polyatomic ion, we follow the same steps discussed above but must be careful to count the correct number of valence electrons present when we begin. Remember that the magnitude of the charge on a cation equals the number of valence electrons *removed* from the original neutral species. The amount of negative charge on an anion represents the number of electrons *added*.

Consider the ammonium cation, NH_4^+. The positive charge tells us that one valence electron has been removed from the total number of valence electrons possessed by the five neutral atoms. To begin this Lewis structure, we therefore count a total of $5 + (4 \times 1) - 1 = 8$ valence electrons. Following the above steps, we eventually arrive at the Lewis structure in in Figure 6.4.10. We normally enclose Lewis structures for both monatomic and polyatomic ions in square brackets, as shown.

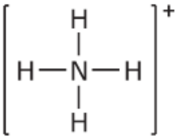

Figure 6.4.10 *Lewis structure for the ammonium cation, NH_4^+*

Extension: The Curious Case of Resonance

When a molecule or ion contains double bonds next to single bonds, there are often several different and equally correct Lewis structures that we can draw. Consider the case of the carbonate anion, CO_3^{2-}. This ion has a total of: $4 + (3 \times 6) + 2 = 24$ valence electrons. (Note the extra two electrons due to the charge.)

Following the steps learned earlier, we realize that we are short two electrons when completing the octets of all the atoms. We therefore incorporate one double bond into the skeleton. The final Lewis structure therefore becomes the one shown n Figure 6.4.11.

If this represented the actual structure, we would expect that the two single carbon – oxygen bonds would prove to be longer and weaker than the double bond. Experimental data indicates, however, that all three bonds are equal in strength and length. They appear to be stronger than a single C – O bond, but weaker than a double bond. They are also slightly shorter than a single bond, but slightly longer than a double bond. It is as if the two electrons in the multiple bond have been shared equally or "averaged" between the central carbon and each of the three oxygen atoms.

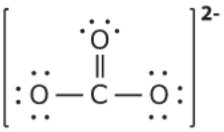

Figure 6.4.11 *Lewis structure for the carbonate anion, CO_3^{2-}*

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Chemists call these electrons "delocalized" because they're not associated with any one pair of bonded atoms, but are rather "spread out" equally between all three pairs. Lewis structures cannot properly show delocalized electrons. They represent this phenomenon by depicting the double bond in each of the possible locations in a series of diagrams and connecting each diagram with a set of double arrows. The diagrams are called **resonance structures**. It must be emphasized, however, that the pair of electrons *does not* move around between pairs of atoms as the diagrams might suggest. The three diagrams in Figure 6.4.12 are simply the only way to depict delocalized bonding electrons using Lewis structures. The phenomenon of resonance is evident in an important organic compound called benzene.

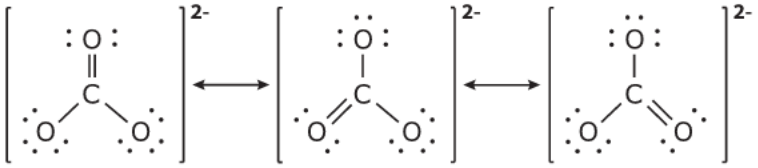

Figure 6.4.12 *Resonance structures for a carbonate ion*

Lewis Structures for Molecules with More than One Central Atom

Molecules and ions can be much more complicated than we have discussed above. Lewis structures are not often used to depict such species, but we can still employ the process when several central atoms exist in relatively simple molecules and ions. In these examples, you will be given the basic skeleton and can then proceed with the remaining steps to generate the correct Lewis structure.

Consider a simple organic acid called formic acid whose formula is CH_2O_2 (or HCOOH). Recall that carbon, oxygen, and hydrogen normally form four bonds, two bonds, and one bond respectively. In Figure 6.4.13, note that both a carbon atom and an oxygen atom are between other atoms in different locations in the structure.

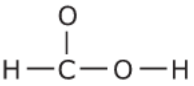

Figure 6.4.13 *Skeleton for formic acid, CH_2O_2 (or HCOOH)*

You should now be able to complete the diagram following the remaining steps. The final Lewis structure you arrive at should be the one shown in Figure 6.4.14. You will encounter many such molecules when discussing organic chemistry.

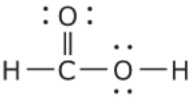

Figure 6.4.14 *Lewis structure for formic acid, CH_2O_2 (or HCOOH)*

6.4 Activity: Making the Leap to Three Dimensions

Question

How can we use Lewis structures to predict the three-dimensional shapes of molecules or polyatomic ions?

Materials

modelling clay
Popsicle® sticks or wooden splints

Procedure

1. Consider the Lewis structures discussed in this section: NCl_3, H_2O, CO_2, NH_4^+, XeF_4, and CO_3^{2-}. Review each as you fill in the following table. The first one is done for you.

1. Chemical Formula	**2. Number of Atoms Bonded to Central Atom**	**3. Number of Lone Pairs on Central Atom**	**4. Sum of Columns 2 and 3**
NCl_3	**3**	**1**	**3 + 1 = 4**
H_2O			
CO_2			
NH_4^+			
XeF_4			
CO_3^{2-}			

2. Obtain some modeling clay and wooden splints or Popsicle® sticks. Using the clay, make a small sphere about the size of a lemon. This will represent the central atom in each of the above species.

   In any chemical species, each pair of bonding or lone pair of electrons represents regions of negative charge. It follows, then, that when these are attached to a central atom in a molecule or polyatomic ion, they will attempt to minimize the repulsive forces between them. They accomplish this by assuming positions in three-dimensional space around the central atom such that they are as far away from each other as possible, while still remaining bonded to that central atom.

3. To represent this, consider each molecule and ion listed above. Look at the total number in column 4 for each species and select that number of sticks. Now insert them into the clay such that they are all as far away from each other as possible in three-dimensional space.

4. Sketch the shapes that you construct for each species in the appropriate space in the table below.

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Chemical Formula	Sketch of 3-D Shape
NCl_3	
H_2O	
CO_2	
NH_4^+	
XeF_4	
CO_3^{2-}	

5. Are all of the shapes different? If not, which ones look similar? How do the numbers in column 4 compare for those shapes that might look similar?

6.4 Review Questions

1. Consider the following list of elements. Place each in the appropriate column in the table below depending on whether it obeys the octet rule, likely has an incomplete octet, or could potentially have an expanded octet in a Lewis structure.

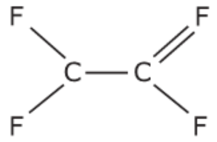
   H, Be, B, C, N, O, F, Al, Si, P, S, Cl

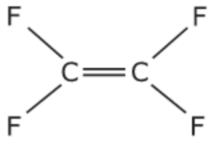
Incomplete Valence Octet	**Valence Octet**	**Expanded Valence Octet**

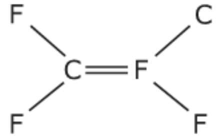
2. Helium and neon are in the same chemical family but yet have different numbers of dots in their Lewis structures. What is the reason for this? Explain why neither element ever forms chemical compounds.

3. Consider the following pairs of elements in the table below. If each pair was part of a molecule or polyatomic ion, which of the two would most likely be the central atom and which would be the peripheral or surrounding atom? Place each element of each pair in the appropriate column in the table.

4. The molecule tetrafluoroethene is a building block of the synthetic material known as Teflon®. Tetrafluoroethene has the formula C_2F_4. Consider the following molecular skeletons for this molecule. Complete the Lewis structure for the most likely skeleton.







5. Draw Lewis structures for each of the following molecules in the space provided.

   OF_2

   H_2S

Element Pair	**Probable Central Atom**	**Probable Peripheral Atom**
(a) phosphorus and chlorine		
(b) nitrogen and oxygen		
(c) carbon and sulphur		
(d) nitrogen and hydrogen		
(e) oxygen and fluorine		

PCl_3

CCl_2F_2

6. Draw Lewis structures for each of the polyatomic ions in the space provided.

OH^-

AlH_4^-

CN^-

7. Extension: Draw Lewis structures for each of the following. Each central atom in the molecules or ions has an expanded octet.

SF_6

PCl_5

Cl_4^-

$SeBr_4$

8. Draw Lewis structures for each of the following containing multiple bonds.

CS_2

SCO (C is central)

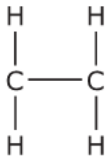
O_3 (Extension: Draw two resonance structures)

NO_3^-(Extension: Draw three resonance structures)

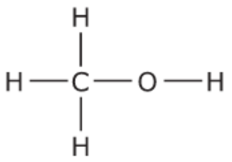
9. Convert the following molecular skeletons into complete Lewis structures.

$H-C-C-H$

$H-O-O-H$



$\underset{\displaystyle H}{\overset{\displaystyle H}{C}}-\underset{\displaystyle H}{\overset{\displaystyle H}{C}}$



$H-\underset{\displaystyle H}{\overset{\displaystyle H}{C}}-O-H$

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6.5 Extension: The Shape and Behaviour of Molecules

Warm Up

1. What does an element's electronegativity tell us?

   ____

2. Use your answer to question 1 to define the term "polar covalent bond."

   ____

3. If a substance contains polar *molecules*, how might that affect its melting and boiling points?

   ____

Converting Lewis Structures into Three Dimensions — VSEPR Theory

Drawing Lewis structures serves an important purpose beyond indicating connectivity of atoms in molecules and polyatomic ions. The two-dimensional collections of symbols, lines, and dots often allow us to deduce the three-dimensional shapes of the chemical species they represent. Determining the shapes of those chemical species is an essential part of understanding and predicting their physical and chemical behaviour.

The process of inferring a three-dimensional shape from a Lewis structure is based on a very simple premise: Valence electrons represent regions of negative charge that repel each other.

Any group of valence electrons associated with a central atom will tend to orient themselves in three-dimensional space around that atom so as to minimize the repulsion between them. Examples of such groups of valence electrons include a lone pair, bonding pair, or multiple pairs involved in a double or triple bond.

In short, while remaining attached to the central atom, these groups of electrons will position themselves as far away from each other as possible. This is the fundamental principle behind the **valence shell electron pair repulsion (VSEPR) theory,** which chemists use whenever they convert Lewis structures into molecular shapes.

Let's imagine a central atom in three-dimensional space and apply the above principle to distribute two, three, four, five, and six electron groups around that centre. When we do, we discover that a different spatial arrangement results for each number of electron groups. Each arrangement minimizes the repulsive forces between the groups by occupying the maximum amount of space around the central atom.

We can show these five arrangements using balloons attached together to represent the electron groups. Just as the balloons will fill up all the available space around their centre of attachment, so too will electron groups fill up the available space around a central atom (Figure 6.5.1).

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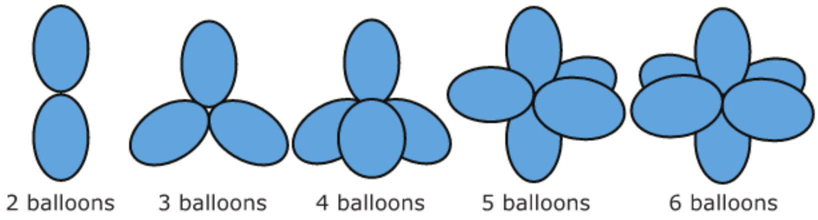


Figure 6.5.1 *Balloons in different arrangements around a central attachment*

If the electron groups are *bonding electrons*, then the peripheral atoms they bind to the central atom adopt that same arrangement and produce a *molecular shape*.

Several experimental tools exist that allow us to determine molecular geometry. X-ray crystallography as well as neutron and electron diffraction are employed for compounds in the solid phase. For molecules in the gaseous phase, gas electron diffraction is used.

Electron groups and their repulsive effects ultimately determine where and how the nuclei of the atoms in a molecule or polyatomic ion arrange themselves in three-dimensional space. And it's the resulting *shapes of those species* that we really care about.

We will consider each of the five electron group arrangements separately. Let's begin by assuming that each electron group is a bonding group connecting the central atom (with single or multiple bonds) to the peripheral atoms. We'll then expand our discussion to include lone-pair electron groups on the central atom. As a general notation, the central atom is "**A**," a peripheral or surrounding atom is "**X**," and a lone-pair of electrons on the central atom is "**E**."

Two-Bonding Electron Groups: AX_2

When two groups of bonding electrons connect the central atom to two peripheral atoms, the notation "$\mathbf{AX_2}$" applies. The surrounding atoms are as far as possible from each other on opposite sides of the central atom. The shape is *linear* with the X–A–X bond angle being 180° (Figure 6.5.2).

Figure 6.5.2 *The shape of two-bonding electron groups is linear.*

The shape is the same whether the two-bonding groups are the shared electrons in two single bonds, two double bonds, or a single and a triple bond. For example, consider the following three molecules. Note that all are AX_2 molecules with the same linear shape and that any lone-pairs attached to the surrounding atoms do not affect their orientation around the central atom.

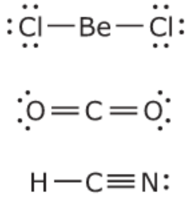


Figure 6.5.3 *AX_2 molecules have the same linear shape whether the shared electrons form two single bonds, two double bonds, or a single and a triple bond.*

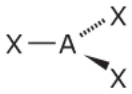
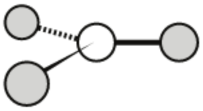
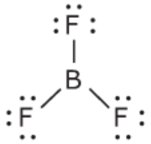
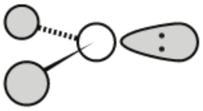
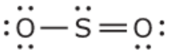
Three-Electron Groups: AX_3 and AX_2E

When three groups of electrons orient around a central atom, two shapes are possible. If all the electron groups are bonding, then an **AX_3** arrangement gives rise to a *trigonal planar* (or flat triangle) molecule with X–A–X bond angles of 120°. The bonding electron group interactions are called "*bond-pair* **–** *bond-pair*" (BP-BP) interactions.

If one of the three electron groups is a lone-pair rather than a bonding pair, we use the notation **AX_2E**. The molecule that we see is *bent* or *angular* with the lone-pair occupying one of the three corners of the triangle. As lone-pair electrons are attracted to only one atomic nucleus, they are held less tightly than bonding electron groups. Their electron clouds therefore occupy more space and exert more repulsive force on bonding electron groups than those groups exert on each other. These more intense "*lone-pair* **–** *bond-pair*" (LP-BP) interactions force the bonded atoms closer together in an AX_2E molecule and so reduce the X–A–X bond angle to less than 120°.

Similar to lone-pairs, we would also expect that larger peripheral atoms would exert *more repulsive forces* than smaller ones, and thus affect bond angles in a molecule. In Table 6.5.1, a solid triangle represents an atom or lone electron pair projecting out of the page, while a dashed line means the atom or lone-pair goes into the page.

Table 6.5.1 *Shapes of Three-Electron Groups: AX_3 and AX_2E*

AX_mE_n Notation	**Molecular Shape**	**Sample Lewis Structure**
 AX_3	 trigonal planar	 boron trifluoride
 AX_2E	 bent or angular	 sulphur dioxide (1of 2 resonance structures)

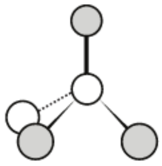
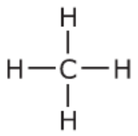
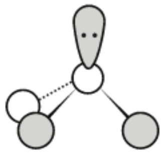
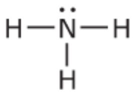
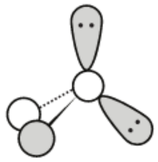
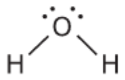
Four-Electron Groups: AX_4, AX_3E, and AX_2E_2

Four electron groups will occupy the four corners of a regular tetrahedron and may result in three different molecular shapes. If all the electron groups are bonding, then the molecule is labeled as **AX_4** and adopts a tetrahedral (four-sided or four-faced) shape with each of the X–A–X bond angles at 109.5°. An example of this is methane gas, CH_4.

If one of the four electron groups is non-bonding, the molecule is considered **AX_3E** and the lone-pair occupies one of the four corners of the tetrahedron. The molecule we see is called a trigonal pyramid. Once again, the more intense LP-BP interactions will push the bonded atoms closer together than they would be in an AX_4 molecule. Evidence of this is seen in an AX_3E molecule such as ammonia in which the H–N–H bond angles are only 107° rather than 109.5°.

When two of the four groups of electrons are lone-pairs, the designation **AX_2E_2** applies. Two of the four corners will be occupied by the two bonded atoms and the remaining two corners by the lone-pairs. The molecule will be an angular shape similar to AX_2E, although the X–A–X bond angle will be smaller. In such an arrangement, not only will each of the two lone-pairs force the bonded atoms closer together via LP-BP interactions, but they will also exert a repulsive force on each other called a *lone-pair – lone-pair* (LP-LP) interaction. This is the most intense of the electron group repulsive interactions. The combined result of the additional repulsive forces is an even smaller X–A–X bond angle. In water, for example, the H–O–H bond angle is found to be only 104.5°. Table 6.5.2 below shows the molecular shapes of four-electron groups.

Table 6.5.2 *Shapes of Four-Electron Groups: AX_4, AX_3E, and AX_2E_2*

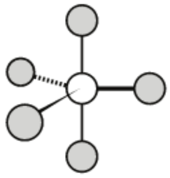
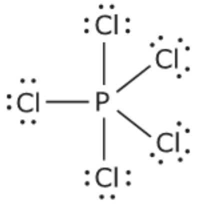
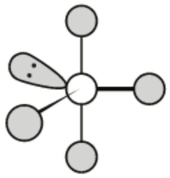
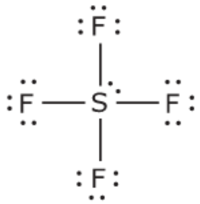
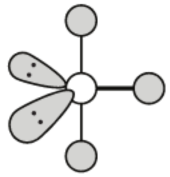
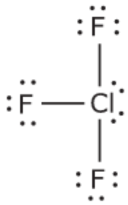
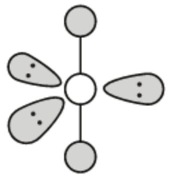
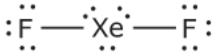
AX_mE_n Notation	Molecular Shape	Sample Lewis Structure
 AX_4	 tetrahedral	 methane
 AX_3E	 trigonal pyramidal	 ammonia
 AX_2E_2	 bent or angular	 water

Five-Electron Groups: AX_5, AX_4E, AX_3E_2, and AX_2E_3

If more than four electron groups surround a central atom, that atom will have an expanded octet so it must belong to period 3 or higher in the periodic table. Expanded octets are only possible if d orbitals are available and none exist below the third energy level.

When five electron groups are present, two distinct sets of positions are occupied by those groups. One set of three positions lies in a trigonal plane, and the electron groups are referred to as *equatorial groups*. A second set of two positions places each group of electrons above and below the trigonal plane. These are called *axial groups*. The equatorial electron groups are separated by 120° bond angles, and the axial and equatorial groups are separated by 90°. Once again, LP-BP and LP-LP interactions play a role in reducing X–A–X bond angles as the number of lone-pairs attached to the central atom increases. Table 6.5.3 shows the molecular shapes of five-electron group systems.

Table 6.5.3 *Shapes of Five-Electron Groups: AX_5, AX_4E, AX_3E_2, and AX_2E_3*

AX_mE_n Notation	Molecular Shape	Sample Lewis Structure
 AX_5	 trigonal bipyramidal	 phosphorus pentachloride
 AX_4E	 seesaw	 sulphur tetrafluoride
 AX_3E_2	 T-Shaped	 chlorine trifluoride
 AX_2E_3	 linear	 xenon difluoride

Six-Electron Groups: AX_6, AX_5E, and AX_4E_2

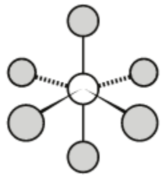
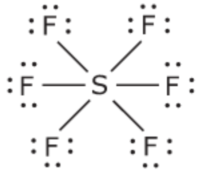
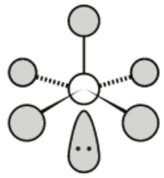
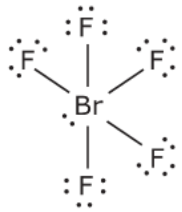
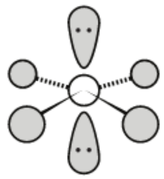
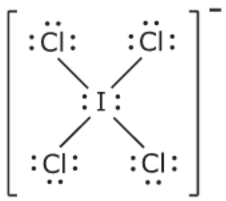
The final major electron group arrangement has six electron groups around the central atom. Unlike the five-electron group system, all six vertices are equivalent and point towards the corners of an octahedron as shown in Table 6.5.4.

If all of the electron groups are bonding, then the molecule is labeled as **AX_6**. The shape adopted by the molecule is octahedral (eight-faced) and all of the X–A–X bond angles are 90°.

When one of the six-electron groups is a non-bonding pair, it doesn't matter which of the six locations that lone-pair occupies around the central atom because all locations are identical. The molecule is classified as **AX_5E** and the molecular shape is square pyramidal. The lone pair is directed downward at the bottom centre of the four-based pyramid as Table 6.5.4 shows.

If two of the six-electron groups are lone-pairs, there are two orientations available in an octahedral shape. They could lie adjacent to each other with a separation of 90°, or lie opposite each other separated by 180°. As the diagram shows below, the two lone-pairs will always be as far away from each other as possible and separated by 180°. This minimizes the significant LP-LP repulsive interaction between them.

Table 6.5.4 *Shapes of Six-Electron Groups:* AX_6, AX_5E, *and* AX_4E_2

AX_mE_n Notation	Molecular Shape	Sample Lewis Structure
 AX_6	 octahedral	 sulphur hexafluoride
 AX_5E	 square pyramidal	 bromine pentafluoride
 AX_4E_2	 square planar	 tetrachloroiodate ion

Quick Check

1. What is the fundamental principle associated with VSEPR Theory?

____

2. Consider the electron group interactions: LP-BP, BP-BP, and LP-LP. Arrange these in order from least intense to most intense.

____

3. Although methane, ammonia, and water each have four electron groups associated with the central atom, the bond angles between the atoms in each molecule are 109.5°, 107°, and 104.5° respectively. Explain why.

____

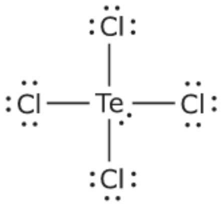
Molecular Formulas to Molecular Shapes

We are now in a position to combine the information from this and the previous section to predict molecular shapes starting with a molecular formula. The steps will guide you through this process:

Step 1 →	**Step 2** →	**Step 3** →	**Step 4**
Beginning with the formula, determine the Lewis structure using the steps outlined in Section 6.4.	Consider the central atom in the completed Lewis structure. Note the number of bonded atoms and lone pairs associated with that atom.	Assign an AX_mE_n notation to the molecule or polyatomic ion. (Note any bond angles affected by the presence of one or more lone pairs.)	Refer to the appropriate electron group arrangement category given in the tables above to determine the shape of the molecule. (You're done!)

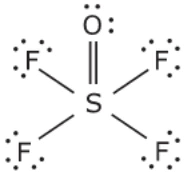
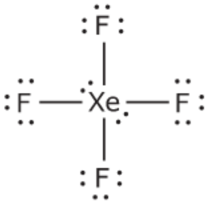
Sample Problem – Deducing a Molecular Shape

Determine the shape of the molecule tellurium tetrachloride, $TeCl_4$

What to Think about	**How to Do It**
1. Refer to the steps listed in Section 6.4 to determine the Lewis structure for the molecule.	Tellurium has the lower electronegativity and so is the central atom. All of the chlorine atoms will therefore obey the octet rule and form only one bond.
2. Note that tellurium is a member of the 5th period in the periodic table and is therefore capable of having an expanded octet.	There are five electron groups around the central atom. Four are bonding groups and one is a lone-pair of electrons. The molecule is therefore classified as AX_4E. An AX_4E molecule will have a "seesaw" shape. 

Practice Problems

1. Complete the following table for each of the chemical species.

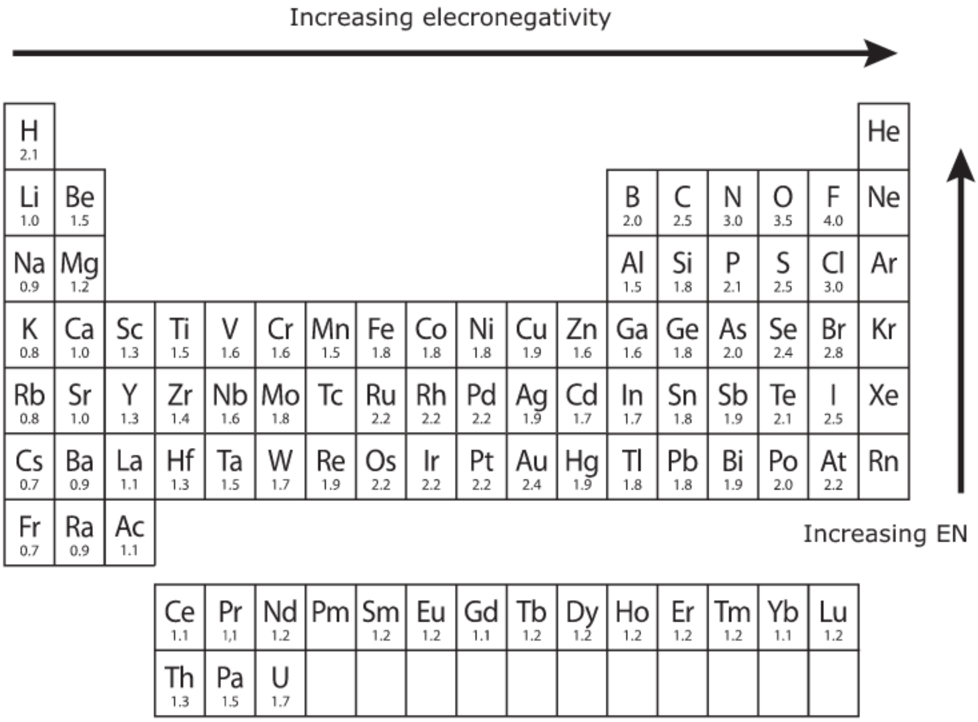
Lewis Structure	AX_mE_n Notation	Molecular Shape (Name and Diagram)
(a) 		
(b) 		

2. Complete the following table for each of the chemical species.

Chemical Formula	Lewis Structure	AX_mE_n Notation	Molecular Shape (Name and Diagram)
(a) CCl_4			
(b) PF_3			
(c) SCl_2			

From Polar Bonds to Polar Molecules

Recall the concept of electronegativity and the table of electronegativity values, which you saw in section 6.2 (Figure 6.5.4).



H 2.1																	He
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr
Rb 0.8	Sr 1.0	Y 1.3	Zr 1.4	Nb 1.6	Mo 1.8	Tc	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe
Cs 0.7	Ba 0.9	La 1.1	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn
Fr 0.7	Ra 0.9	Ac 1.1															

Ce 1.1	Pr 1,1	Nd 1.2	Pm	Sm 1.2	Eu 1.2	Gd 1.1	Tb 1.2	Dy 1.2	Ho 1.2	Er 1.2	Tm 1.2	Yb 1.1	Lu 1.2
Th 1.3	Pa 1.5	U 1.7											

Figure 6.5.4 *Periodic table showing electronegativity values*

As stated at the beginning of this section, an essential part of understanding and predicting the chemical and physical properties of substances is determining the shapes of their molecules. Among the most *significant consequences* of molecular shape is the *polarity of molecules*.

Molecular polarity not only affects physical properties such as melting point, boiling point, and solubility, but also influences a substance's chemical reactivity in both synthetic and biological processes.

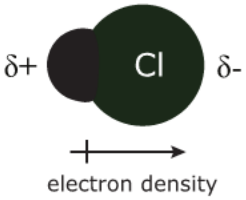


Figure 6.5.5 *HCl is a diatomic molecule containing a polar bond.*

Recall that a chemical bond is considered to be polar if electron-sharing in the bond is unequal enough due to the electronegativity differences of the atoms involved. If a diatomic molecule contains a polar bond, then the *molecule itself* must also be polar, as in a compound such as HCl (Figure 6.5.5).

However, if a molecule contains *more than two atoms*, the shape of the molecule as well as the polarity of its bonds will play a role in determining if the entire molecule will be polar. Stated another way, if the bonds within the molecule are polar, the molecule itself may or may not be, depending on its shape. Let's consider an example of each.

In carbon dioxide, each of the two C==O double bonds is quite polar because the two atoms have a $\Delta EN = 1.0$. However, because the molecule itself is AX_2 and therefore linear, each of those identical bond dipoles is pointing in a direction exactly opposite to the other because of the 180° O – C – O bond angle. This means that the molecular shape is such that the bond dipoles *effectively cancel each other out* resulting in a non-polar molecule. You can compare this to two evenly matched tug-of-war teams pulling in opposite directions on a rope — neither team wins because they are equally strong.

In water, just as in CO_2, a central atom is bonded between two identical peripheral atoms and each of those two bonds has a significant and identical dipole. However, because H_2O qualifies as an AX_2E_2 molecule, it is bent or V-shaped. This means that the molecular shape is such that the bond dipoles point in the same general direction and so reinforce each other. This results in a polar molecule.

Chemists can detect and measure a molecule's polarity in an electric field. They assign a magnitude to that polarity expressed as a "dipole moment." Water is very polar and has a significant dipole moment, but the dipole moment of non-polar carbon dioxide is zero. As Figure 6.5.6 shows, the water molecule has a net dipole, while the carbon dioxide molecule does not. The importance of the polarity of water molecules cannot be overstated as we will soon see.

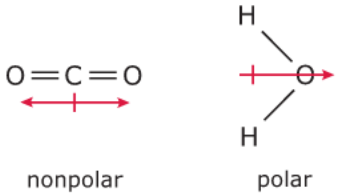


Figure 6.5.6 *The V-shape of a water molecule results in a significant dipole moment.*

In the above example, two *different molecular shapes* were the reason that bond dipoles in one molecule cancelled out, but didn't cancel in another molecule. There is also a possibility that two molecules having the *same shape* and containing polar bonds could be either polar or non-polar. We can use two AX_4 molecules to demonstrate this.

In Figure 6.5.7, carbon tetrachloride on the left is a symmetric molecule with four chlorines situated at the corners of a tetrahedron. Each C – Cl bond is polar in the direction of chlorine because carbon and chlorine have electronegativities of 2.5 and 3.0 respectively. The four bond dipoles, however, cancel out as they point in opposite directions in the symmetric molecule and so the molecular itself is non-polar. Carbon tetrachloride is a liquid used as a solvent for other non-polar substances. As you will soon see, one non-polar substance will usually mix well with another.

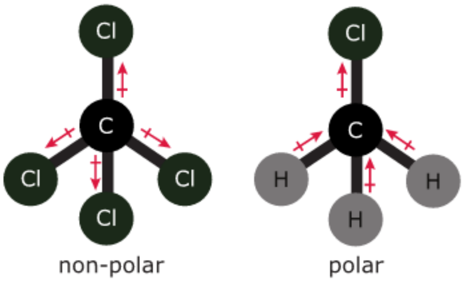


Figure 6.5.7 *Two molecules having the same shape can have different polarities. Carbon tetrachloride, on the left, is non-polar; chloromethane, on the right, is polar.*

The molecule on the right in Figure 6.5.7 is called chloromethane. All of its bond dipoles point in the same general direction. Each C – H bond is polar towards the carbon due to carbon's higher EN value (2.5 vs. 2.1), and the C – Cl bond polarity points in a similar direction towards chlorine. Now, as was the case with water above, the bond dipoles reinforce each other and so the entire molecule is polar.

In this example, molecular composition rather than molecular shape determined whether a molecule was polar or non-polar. In all cases, however, the key question is the same.

Does the molecule contain polar bonds and, if so, do the bond dipoles cancel each other or not?

If bond dipoles exist but cancel each other, then the molecule is non-polar. If bond dipoles don't cancel or if they reinforce each other, then the molecule is polar. Answering this question often involves attempting to visualize and even manipulate a three-dimensional shape based on a diagram drawn on a flat page. Although that might seem difficult at first, it will become easier with practice. Remembering the simple guidelines below will also help.

Guidelines for Determining If a Molecule Is Non-polar or Polar

1. When the peripheral atoms in a molecule are identical and arranged symmetrically around a central atom, any bond dipoles that exist will cancel out and the molecule will be non-polar.
2. When the molecule is asymmetric (not symmetric) either due to its shape or its composition, any bond dipoles that exist will usually not cancel out and the molecule will be polar.

If you review all the shapes listed in the tables given earlier, you will notice that several shapes have the peripheral atoms arranged *symmetrically* around the central atom. "Symmetrical" means balanced or evenly arranged.

In most cases, symmetrical molecules are AX_m molecules in which no lone pairs exist on the central atom. All such molecules containing identical peripheral atoms will be non-polar, regardless of the bond dipoles that exist.

Can you discover any shapes where lone pairs *do exist* on the central atoms that include symmetrically arranged peripheral atoms? If so, then those molecules will also prove to be non-polar as long as the peripheral atoms are all the same.

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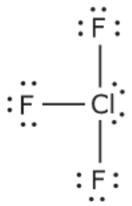
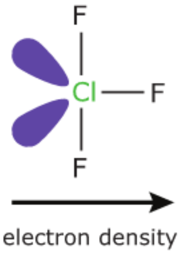
Sample Problem

Consider the Lewis structure shown here for the compound chlorine trifluoride:
Determine the shape of the molecule and if the molecule is polar.



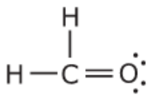
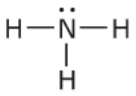
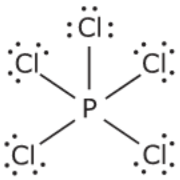
What to Think about	**How to Do It**
1. To determine if the bonds are polar, find the ΔEN from the electronegativity table.	$\Delta EN = 4.0 - 3.0 = 1.0$ The bonds are therefore polar in the direction of fluorine.
2. To determine if the molecule is polar, assign an AX_mE_n label and find the molecular shape.	The molecule has an AX_3E_2 designation and so adopts a "T-shaped" structure.
3. Considering the molecular shape, decide if the molecule is symmetric or asymmetric and therefore either polar or non-polar.	The bond dipoles therefore do not cancel and so the molecule is polar. 

Practice Problems

1. Complete the following table by listing the AX_mE_n notations and their shapes in the appropriate columns for all the symmetric and asymmetric molecules that you can find. Assume that all the peripheral atoms in the molecules are the same. The first entries are done for you.

***Symmetric* Molecules**		***Asymmetric* Molecules**	
AX_mE_n Notation	**Shape of Molecule**	**AX_mE_n Notation**	**Shape of Molecule**
AX_2	linear	AX_2E	bent or angular

2. Complete the following table.

Lewis Structure	AX_mE_n Notation	Molecular Shape (Name and Diagram)	Polar Molecule? (Yes / No)
(a) 			
(b) 			
(c) 			

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Intermolecular Forces

We have seen that opposite charges are ultimately responsible for all chemical bonds. Electron-deficient positive ions are attracted to electron-abundant negative ions in ionic bonds. Pairs of negative electrons are attracted to adjacent positive nuclei in covalent bonds.

The chemical bonds within molecules are called **intramolecular** forces. ("Intra" means "within.") Attractive forces between molecules and between ions and molecules are called **intermolecular forces.**

Intermolecular forces are as dependent on electrostatic attraction as intramolecular forces are. However, because they typically involve smaller charges and/or greater distances between the chemical species, they aren't as strong as chemical bonds. Yet these forces are so important that without them, life itself could never exist on this tiny "blue marble" in space we call Earth.

Our final discussion of this chapter will focus on the various types of intermolecular forces that exist. We will begin with the forces that act between neutral molecules, and then consider a force that acts between molecules and ions. Let's start where our previous discussion ended by revisiting polar molecules.

Dipole-Dipole Forces — Attractions Between Polar Molecules

Within any substance containing polar molecules, each molecule has a positive and a negative pole — a **molecular dipole**. Because of these partial charges, the molecules in the liquid and solid phases will naturally orient themselves so that the positive pole of one molecule will be next to and attract the negative pole of an adjacent molecule. This force of attraction is called a **dipole-dipole force**. This network of dipole-dipole forces will result in higher melting and boiling points because more energy will be required to overcome the attractions between the molecules.

The more polar those molecules are, the stronger the dipole-dipole forces. Figure 6.5.8 shows two depictions of polar HCl molecules with the dipole-dipole force acting between them.

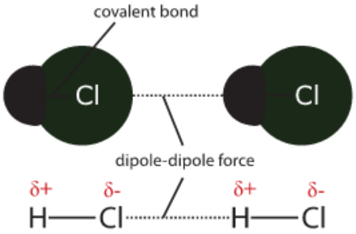

Figure 6.5.8 *One way to show dipole-dipole forces is to draw the actual molecule shapes (top diagram). Another way is to use the element symbols only (bottom diagram).*

Hydrogen Bonds — Special Dipole-Dipole Forces

A much stronger example of a dipole-dipole force exists between polar molecules that contain a hydrogen atom bonded to either nitrogen, oxygen, or fluorine. The atoms of these 2nd period elements are each small, highly electronegative, and have lone electron pairs. All of these properties are significant.

The H – **N**, H – **O**, and H – **F** bonds in each of these molecules will be *very polar* due to hydrogen's low electronegativity resulting in a large ΔEN. This means that a significant amount of electron density will be removed from hydrogen, leaving it with a large partial positive charge. This will also leave its nucleus almost unshielded because hydrogen has no core electrons. The other end of the molecule will gain that electron density and thus acquire a large partial negative charge.

The partially positive hydrogen in one molecule will then be attracted to the lone electron pair of the partially negative atom of another molecule. That attractive force will be particularly strong not only because of the extremely polar bonds within the molecules, but also because *all of the atoms involved are small*. This allows the tiny electropositive hydrogen to get very close to the lone pairs on the partially negative nitrogen, oxygen, or fluorine atoms of the other molecules. This intense intermolecular force is known as a **hydrogen bond**.

It is not an exaggeration to state that hydrogen bonds make life on Earth possible. For example, consider that most of our Earth and most of our bodies are composed of water. Water molecules have a relatively low mass and the vast majority of substances composed of such molecules have very low boiling points, even if those molecules are polar. Look at Figure 6.5.9 showing the boiling points of the binary (two element) hydrides of groups 14 to 17 of the periodic table.

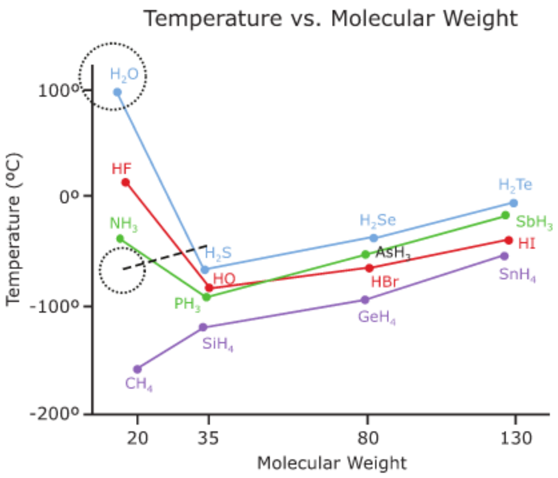

Figure 6.5.9 *Boiling points of binary hydrides of groups 14 to 17*

The group 14 hydrides are all symmetric AX_4 molecules and non-polar, so we would expect those substances (SnH_4 , GeH_4, SiH_4, and CH_4) to have low boiling points, and they do. Note that the boiling points of these compounds decrease with decreasing molar mass. The binary hydrides of the remaining groups, however, are asymmetric polar molecules. Their dipole-dipole forces contribute to higher boiling points than seen in group 14.

Something very interesting occurs, however, with the heaviest hydrides in groups 15, 16, and 17. Look at how the boiling points change for these substances as we move up each group. Consider the group 16 binary hydrides for example: H_2Te, H_2Se, H_2S, and finally H_2O (water). As the mass of each polar AX_2E_2 molecule decreases, the boiling point drops, but not consistently. After H_2S, if the trend were consistent, we would expect water to have a boiling point of approximately –90°C (see dashed line in Figure 6.5.9). The fact that the actual boiling point is almost 200°C higher than that is clear evidence of the strength of the hydrogen bonds in water (Figure 6.5.10a). Life as we know it would be very unlikely if water became a gas at –90°C! Even the fact that ice floats is due to hydrogen bonding. That characteristic of water is of great importance to aquatic life during cold temperatures.

The significance of hydrogen bonds is further demonstrated by the fact that the three-dimensional structure of many proteins and even the base-pairing in the double helix of DNA molecules depend on the existence of these essential forces. These are hydrogen bonds involving an oxygen or nitrogen atom (Figure 6.5.10b).

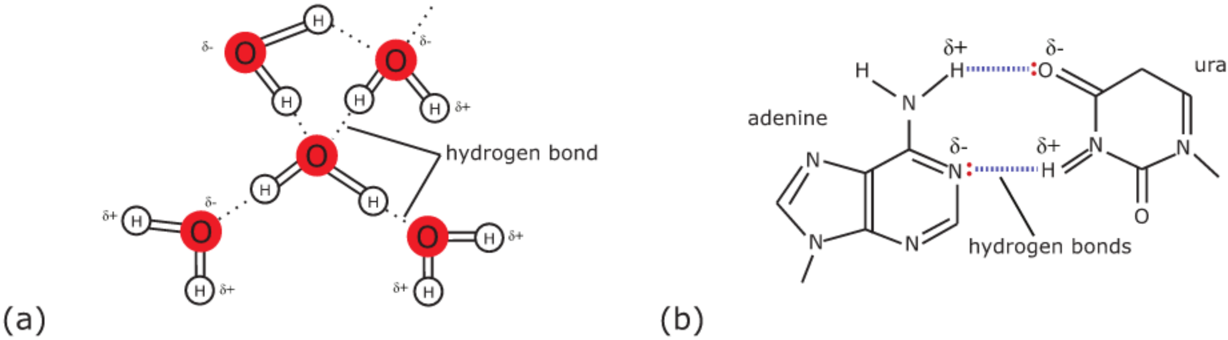

Figure 6.5.10 *(a) Hydrogen bonds in water; (b) Hydrogen bonds in DNA base-pairing*

Dispersion (London) Forces — A Growing Attraction

For a molecular substance to exist as a liquid or solid, the molecules must be close together. This means some kind of intermolecular attractive force must exist between those molecules.

So far, we have discussed two of these intermolecular forces. Dipole-dipole forces and hydrogen bonds act to cause polar molecules to "stick" together and maintain a molecular substance in the liquid or solid state of matter.

However, we might expect that substances composed of non-polar molecules might never exist as liquids or solids since they have no particular reason to attract each other. That is definitely not the case. Many molecular substances composed of non-polar molecules exist as liquids or even solids at room temperatures. Those that don't can usually be condensed or solidified under the right conditions. The obvious question would be: What intermolecular force would cause non-polar molecules to attract each other?

The explanation of this force relies on the quantum mechanical description of the atom and the force itself is named for the physicist, Fritz London, who used quantum mechanics to explain the basis of the attraction. We'll use a non-polar molecule as an example.

Consider a sample of chlorine gas, Cl_2. As the $\Delta EN = 0$, the molecules are non-polar and the electron density in the negative cloud surrounding this diatomic molecule is evenly distributed. This means that *on average*, the electrons will spend no more of their time nearer one chlorine nucleus than the other, and so the probability distribution is even throughout the orbital cloud.

However, at any instant, there is a *possibility* that there may be more electron density on one side of the molecule than the other, resulting in an instantaneous molecular dipole. This dipole will have little effect on any other Cl_2 molecules that are far away. But if those molecules are in close proximity, even a short-lived dipole in one molecule will distort or polarize the electron cloud of a neighbouring molecule. This happens because the negative pole of the instantaneous dipole will repel electron density in the nearby electron cloud to the opposite side of that molecule. As well, the positive pole will pull electron density to the near side of another neighbouring molecule. Each induced dipole results in an intermolecular attraction between the newly polarized molecules and induces more dipoles in surrounding molecules. As a result, the dipoles *disperse* throughout the sample, causing the molecules to attract each other. These intermolecular forces of attraction are called **dispersion forces** or **London dispersion forces**.

Figure 6.5.11 shows an instantaneous dipole in the non-polar molecule on the left inducing a dipole in the neighbouring molecule on the right. The dispersion force then exists between the two molecules.

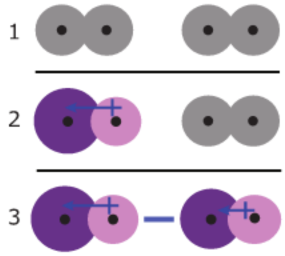

Figure 6.5.11 *An instantaneous dipole in the non-polar molecule on the left (2) induces a dipole in its neighbouring molecule on the right (3).*

Although London forces are the *only* forces acting between non-polar molecules, they exist between the particles of *all* substances. Except in the case of strong hydrogen bonds, they may be the dominant intermolecular force even for polar molecules.

The strength of dispersion forces will increase as the size of the molecules involved increases. This is because large electron clouds are more loosely held than smaller clouds. Thus they are more easily deformed or polarized by a nearby dipole than compact tightly held clouds are.

Even molecular shape can play a role in dispersion forces. Molecules with more surface area have electron clouds that are spread out and so are more easily distorted by neighboring dipoles.

Consider the melting and boiling points of diatomic halogens of group 17. The higher temperatures required for these phase changes as we descend the group is evidence of the increasing strength of the London forces between the molecules.

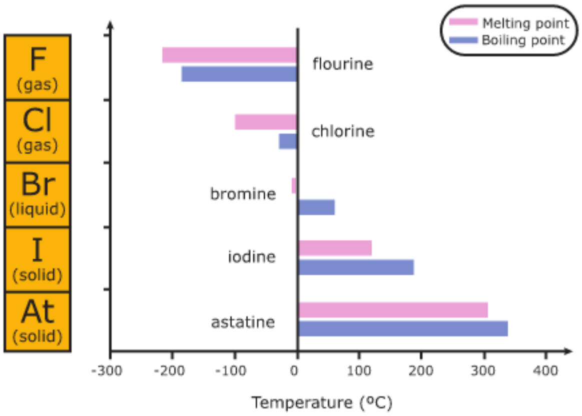

Figure 6.5.12 *Melting and boiling points of diatomic halogens of group 17*

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Ion-Dipole Forces — Surround and Separate

We will conclude our discussion of intermolecular forces by focusing on an important interaction that occurs when an ionic compound dissolves in water.

The ionic bonds holding a crystal lattice together are strong. However, when the surface of that lattice is in contact with water, each ion on that surface will attract the oppositely charged end of polar water molecules near them. That attraction between an ion and a polar molecule is called an **ion-dipole force.** These attractive forces soon overcome those between the ions themselves, so the crystal structure begins to break down. As the ions move away from the lattice surface, they immediately become surrounded or enclosed in what chemists call a **hydration shell.**

At the centre of one type of hydration shell, the negative oxygen ends of water molecules orient themselves next to and surround a cation. At the centre of another shell, an anion is engulfed by water molecules oriented with their positive hydrogens next to the ion's negative charge. Figure 6.5.13 shows the ion-dipole forces acting between water and Na^+ and Cl^- ions in an aqueous solution. Ion-dipole forces are the primary force responsible for the solubility of ionic compounds in water and aqueous solutions of some ionic compounds are almost as necessary for life as water itself.

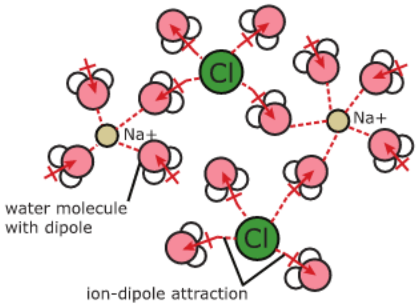

Figure 6.5.13 *Ion-dipole forces between water molecules and Na^+ and Cl^- ions in an aqueous solution*

6.5 Activity: Modeling the AXmEn Molecules

Question

How can building the various AX_mE_n shapes help us to determine molecular polarities?

Materials

modelling clay
Popsicle® sticks or wooden splints
small spherical balloons
(Note: A good quality molecular model kit can be used in place of the above items.)

Procedure

1. Using the modelling clay, make a small sphere about the size of a lemon as you may have done in the activity at the end of section 6.4. This sphere will represent the central atom (**A**) for each AX_mE_n category you construct.
2. You will need a total of nine sticks. Trim three of the sticks to a length of about 4 cm. Blow up three small spherical balloons until they are about 12 cm long and tie the ends. Tape the tied ends of the balloons to the ends of shortened sticks. The regular sticks will represent bonded electron groups attached to peripheral atoms (**X**). The balloons taped to the trimmed sticks will represent lone-pair electrons (**E**).
3. The modelling clay, sticks, and balloons will allow you to construct each of the AX_mE_n molecules discussed in this section and listed in the table below. After you build one, simply take the structure apart to build the next.

Build each of the shapes listed in the table below, but before you take each apart, look at each structure and ask yourself the following question: If each of the bonds in these molecules were polar and all of the peripheral atoms were the same, would the *molecule* be polar or non-polar?

Complete the following table below as you construct each shape:

AX_mE_n Notation	Sample Molecule	Name of Shape	Polar Molecule? Yes/No
AX_2	CO_2		
AX_3	BF_3		
AX_2E	SO_2		
AX_4	CH_4		
AX_3E	NH_3		
AX_2E_2	H_2O		
AX_5	PCl_5		
AX_4E	SF_4		
AX_3E_2	BrF_3		
AX_2E_3	XeF_2		
AX_6	SF_6		
AX_5E	BrF_5		
AX_4E_2	XeF_4		

4. Note that an electronegativity value is not listed for xenon in the table shown earlier in this section. In spite of this, you are still able to determine if the two molecules above containing Xe as the central atom are polar or not. Why?

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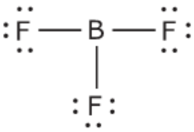
6.5 Review Questions

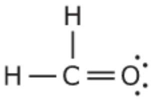
1. (a) What do the letters: V S E P and R in the term "VSEPR theory" stand for?

   (b) What does the theory allow us to do?

2. Why do non-bonding or lone-pair electrons attached to a central atom occupy more space than bonding electron pairs?

3. Consider the following Lewis structures. Would you expect these molecules to have the same shape or a different shape? Explain.



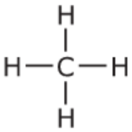


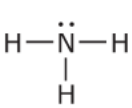
4. For each pair of columns, draw lines to connect the AX_mE_n notation on the left to the correct shape listed on the right. (The first one is done for you.)

AX_mE_n Notation	**Molecular Shape**	**AX_mE_n Notation**	**Molecular Shape**
AX_3	angular	AX_4E	T-shaped
AX_2E_3	trigonal bipyramidal	AX_2E	octahedral
AX_4	trigonal pyramidal	AX_3E_2	square pyramidal
AX_3E	trigonal planar	AX_6	square planar
AX_2E_2	tetrahedral	AX_5E	angular
AX_5	linear	AX_4E_2	seesaw

5. Consider the Lewis structures for methane and ammonia.

   (a) Which molecule will have the smaller X–A–X bond angle and why?





   (b) Identify the main intermolecular force acting between the molecules of methane and between the molecules of ammonia in pure samples of each compound.

6. Assume that all of the peripheral atoms are the same for each AX_mE_n category listed below and complete the following table. (Note that two different bond angles exist in for AX_5.)

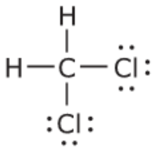
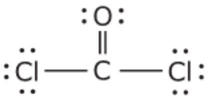
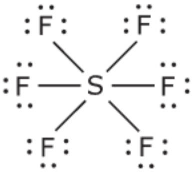
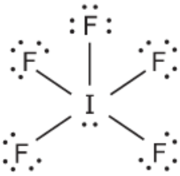
AX_mE_n Category	**AX_2**	**AX_3**	**AX_4**	**AX_5**		**AX_2E_3**	**AX_6**	**AX_4E_2**
X–A–X Bond Angle								

7. Consider the following group 15 binary hydrides: SbH_3, AsH_3, PH_3, and NH_3. Which should have the highest boiling point and why?

8. The industrial production of ammonia, NH_3, from H_2 and N_2 is called the Haber process, named for Fritz Haber, the German chemist who developed it just before World War I. During the process, in a gaseous mixture of all three substances, NH_3 must be separated from H_2 and N_2. This is done by cooling the gaseous mixture so as to condense only the NH_3. This leaves the elemental nitrogen and hydrogen as gases to be recycled and produce more ammonia. Why does only the ammonia liquefy upon cooling, but not the H_2 or N_2?

9. Identify two examples of how hydrogen bonding between molecules makes life on Earth possible.

10. Complete the following table:

Lewis Structure	AX_mE_n Notation	Shape of Molecule (Name and Diagram)	Type of Intermolecular Force Acting Between Molecules
(a)  dichloromethane			
(b)  phosgene			
(c)  sulphur hexafluoride			
(d)  iodine pentafluoride			

10. Iodine is a non-polar diatomic molecule, yet its molecules have enough attraction for each other that the element exists as a solid at room temperature. Identify the attractive force and explain why it is strong enough to keep the molecules of I_2 attached to each other even at room temperature.

11. Ionic compounds such as NaCl have very high melting points because a great deal of energy is required to overcome the many attractive forces between the oppositely charged ions in an ionic crystal lattice. NaCl melts at 801°C, yet its ions will readily separate from each other at room temperature when the solid is added to water. Explain this by discussing the predominant force that allows an ionic compound to dissolve in water.

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