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Ionic Compounds

Applications of Chemistry to Mineralogy



Claude H. Yoder

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Franklin and Marshall College

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Preface

This introduction to ionic compounds is designed for the reader who wants a better understanding of the concepts that are used by the chemist and mineralogist in their attempts to unravel the mysteries of nature. The emphasis on the relationship of structure at the atomic level to the symmetry and properties of crystals will be of particular interest to those interested in mineralogy. The book requires no knowledge of chemistry or mineralogy beyond that obtained in a typical secondary school curriculum. It is designed to appeal to the mineralogy student who wants to delve more deeply into the relationships between structure and bonding at the atomic level and the macroscopic properties of minerals. It should also appeal to the serious mineral collector who wants to learn more about the chemical and crystallographic properties of his collection. Finally, the author hopes that the book will be of value to those students of geology who want to bolster their understanding of chemistry.

The author believes that learning is enhanced by the reader's active participation in the material. Consequently, brief segments of information are followed by a question that the reader should grapple with *before* looking at the answer. In most cases, the questions are not difficult and can be answered with minimal effort. However, even this amount of reflection, in the author's experience, increases understanding of the subject material.

The author has made considerable use of the excellent computer program Crystal-Maker3 (written by David Palmer), for illustrations throughout this book. Information about this program can be obtained from the web site <http://www.crystallmaker.co.uk>. The program Kristall2000 (written by Klaus Schilling), was used for drawings of crystal forms.

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Chapter 1

Bonding and Composition

The way in which atoms in compounds are held together is one of the major concerns of the chemist. Atoms differ in the number of protons and neutrons in their nuclei, the very tiny center of the atom that contains all of the positive charge contributed by the protons. For example, atoms of carbon contain 6 protons, while atoms of silicon contain 14 protons. Although every atom of carbon must contain 6 protons, the number of neutrons, which have no charge, can vary. Two atoms of the same element that have different numbers of neutrons are called **isotopes**. The predominant isotope of carbon, carbon-12, contains 6 protons and 6 neutrons. The mass number, the sum of the number of protons and neutrons, is used to designate the isotope. About 1% of naturally occurring carbon is carbon-13, which has 6 protons and 7 neutrons in the nucleus. Each neutral atom must also have electrons equal in number to the number of protons. If the atom gains electrons to become a negative ion, the number of electrons exceeds the number of protons. Thus, a neutral sodium atom contains 11 negatively charged electrons, but a sodium atom with a single negative charge, Na^- , contains 12 electrons, and the common Na^+ ion contains only 10 electrons.



How many protons are there in an atom of magnesium?



12. The number of protons in the nucleus is called the atomic number and is given above the symbol of the element in the periodic table shown in Figure 1.



How many electrons are there in an atom of calcium that has a plus two charge?



18. The atomic number of calcium is 20, which means that the nucleus contains 20 protons. If the atom were electrically neutral, 20 electrons would be required to balance this positive charge. When two electron are removed, the atom has two more protons than electrons and therefore has a plus two ($2+$) charge.

All of the known elements are shown in the periodic table of the elements (Figure 1), which was developed by chemists over many years. Most of the credit for the

arrangement of the elements is given to the Russian chemist Dimitri Mendeleev and the German Lothar Meyer, although it was the British physicist Henry Mosley who realized that the elements should be arranged according to their atomic number.

Main Group =		I	II											III	IV	V	VI	VII	VIII																
1																			1	2															
	H																			H	He														
3	Li	4	Be											5	6	7	8	9	10																
														B	C	N	O	F	Ne																
11	Na	12	Mg	Transition Elements										13	14	15	16	17	18																
														Al	Si	P	S	Cl	Ar																
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
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
55	Cs	56	Ba	57	La	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
87	Fr	88	Ra	89	Ac	104	Rf	105	Db	106	Sg	107	Bh	108	Hs	109	Mt																		

Figure 1 The periodic table (excluding the rare earth elements). The metals, found primarily to the left of Group IV, tend to form ionic compounds with the non-metallic elements to the right of Group IV.

The basic organizational scheme of the table was based, however, on the similarities of the chemical properties of the elements. For example, the elements in the first column on the left, referred to as Group I (columns are called “groups,” whereas rows are “periods”), are reactive metals. All metals have a characteristic shininess or luster, are malleable (can be shaped), and conduct electricity in the solid state. However, the elements in Group I are so reactive that their surfaces, unless they are freshly exposed, are covered with a white coating that conceals their luster. This coating is due to the reaction of the metal with oxygen and water vapor in the air. When these elements react with water they form hydrogen gas (which frequently bursts into flame due to its reaction with the oxygen in the air) and hydroxide ion. As we will see in Chapter 8, hydroxide ion is a strong base or alkali, and, consequently, the Group I elements are frequently called the alkali metals. They also react with many other non-metals: the elements on the right-hand side of the periodic table. These non-metallic elements include the halogens, the elements of Group VII.

Over the years two different modes of interaction between atoms have been proposed. These two different modes can be seen in the melting points ($^{\circ}\text{C}$) of compounds formed between chlorine atoms and atoms of the elements of the third row of the periodic table:

Table 1 Melting points ($^{\circ}\text{C}$) of the chlorides of the third row elements

NaCl	MgCl ₂	AlCl ₃	SiCl ₄	PCl ₃	SCl ₂	Cl ₂
801	708	190	-70	-91	-78	-101

The elements on the left of the periodic table (the metals) appear to form compounds with considerably higher melting points than those on the right-hand side. In fact, it appears that the change from one mode of interaction to the other occurs at aluminum chloride.

1.1 TYPES OF BONDING

The interaction between the atoms in sodium chloride (NaCl) and magnesium chloride (MgCl₂) is referred to as ionic “bonding” or **ionic interactions**. The interaction between the other elements and chlorine is called **covalent bonding**. The **ionization energy**, which is the energy required to remove an electron from an atom, increases considerably from left to right on the periodic table. Sodium, which is at the left side of the periodic table, has an ionization energy of 498 kJ/mol (this is the amount of energy necessary to remove an electron from a gaseous sodium atom). Chlorine, which is on the right of the periodic table, has a much higher ionization energy of 1255 kJ/mol.



Which atom—Na or Cl—will lose an electron most easily?



Sodium, of course, because it has the lower ionization energy.

We must also consider the ability of atoms to accept an electron. This ability is measured by their **electron affinity** or their electro-negativity, both of which increase from left to right on the periodic table. The **electronegativity** of an atom was first defined by Linus Pauling, one of the great American chemists, as the *power of an atom in a molecule to attract electrons to itself* (Pauling, 1960). Pauling assigned a value of 4.0 units to fluorine, the most electronegative atom. The electronegativity scale is given in Appendix 2.

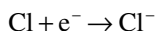


Which atom—Na or Cl—will be most likely to accept an electron?

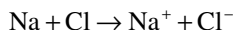


Chlorine, because it has the higher electronegativity.

Given that sodium loses an electron rather easily and chlorine readily accepts an electron, we can certainly predict that when an atom of sodium meets an atom of chlorine, an exchange of an electron will occur. We can symbolize this with the equations:



The products of the first equation are the sodium ion and the electron, symbolized by e⁻. (The minus sign is given to remind us that an electron has a negative charge.) We can summarize the electron exchange with the equation



The ions on the right-hand side of this equation are oppositely charged and are strongly attracted to one another. Therefore, at room temperature, these ions are tightly packed in the solid state. In other words, the compound NaCl, common table salt and the mineral halite, consists of ions. Many of the compounds that exist in nature are ionic compounds. For example, galena (PbS), sphalerite (ZnS), and magnetite (Fe₃O₄) are all ionic compounds.

We will not spend much time on the other mode of interaction, the one that occurs in compounds such as PCl₃, CCl₄, or H₂O. For the moment, we can think of the covalent interaction between the atoms in these compounds as a *sharing* of electron density. This mode occurs between atoms that have relatively similar electronegativities. For example, the difference in the electronegativities of phosphorus and chlorine is not sufficient to cause an exchange of electrons. Instead, some of the electron density of the phosphorus is shared with the chlorine and *vice versa*.

There are two types of covalent compounds. The first, **molecular** covalent compounds, contain groups of atoms that we call **molecules**. For example, in water, there are molecules that contain two hydrogen atoms attached to an oxygen atom. These molecules are the smallest unit, or building block, in the compound. Moreover, molecules are not ruptured (destroyed) by melting or boiling (Figure 2). Ice, liquid water, and steam all consist of molecules that have two hydrogens attached to oxygen by covalent bonds. Molecular compounds generally have fairly low melting and boiling points.

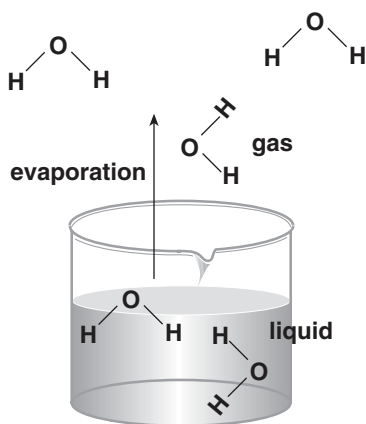


Figure 2 Boiling of water. Molecules remain intact during changes in phase.

There are also covalent compounds that have very high melting and boiling points. Quartz (SiO₂) has a very high melting point and has covalent bonds between silicon and oxygen atoms. These compounds are generally **network covalent** compounds; they do not contain molecules. In quartz, for example, each silicon is attached to four oxygen atoms and each oxygen is attached to two silicon atoms. These covalent bonds extend in three dimensions throughout the entire crystal. A small portion of this network is shown in Figure 3.

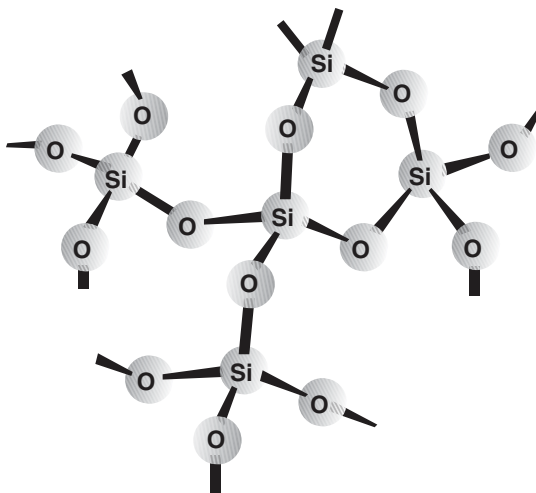


Figure 3 A portion of the network covalent bonding in SiO_2 .



Can you explain why network covalent compounds have much higher melting points than molecular covalent compounds?



Melting involves a change from the rigid solid state to the mobile, fluid liquid state. In the liquid state, particles must be able to move independent of other particles. In a covalent molecular compound, this can happen easily because molecules are attracted to one another by rather weak forces. It does not take much energy to break these weak forces and allow the molecules to move independently of one another. (Notice again that melting of a molecular substance does not break the covalent bonds within the molecule. These bonds are usually very strong.) In a network covalent solid there are no molecules. In order to create mobility, covalent bonds must be broken to allow atoms or groups of atoms to move independently. These covalent bonds are extremely strong and their rupture requires much energy. Thus, the temperature required for melting a covalent network compound is much higher than that required for the melting of a molecular compound.

1.2 IONIC COMPOUNDS

1.2.1 Types of Ions

We now return to our discussion of *ionic* compounds. You will recall that the atoms (or groups) in an ionic compound are charged; that is, each contains either an excess of electrons or a deficiency of electrons. Ions with an excess (more than the neutral atom) of electrons are called **anions**. Ions with a deficiency of electrons are called **cations**.



Classify each of the following as likely to form a cation or an anion—K, Fe, O.



Potassium almost always forms a cation because it has a low ionization energy. Iron, a transition element, also has a low ionization energy and forms cations. Oxygen has a high electronegativity and, therefore, attracts electrons and forms an anion.

The ions formed by atoms need not have just unitary charge ($1+$ or $1-$). Some atoms can attain two or three additional electrons and others can lose two or three electrons. Usually, the number of electrons lost or gained can be predicted by the inert gas rule:

Atoms tend to form ions with the electron configuration of the nearest inert gas.

The potassium atom has one more electron than argon, which is the closest inert gas (see Group VIII in the periodic table in Figure 1). Potassium will therefore lose one electron to chlorine, which has one less electron than argon. This means that the compound KCl contains potassium cations and chlorine anions.



What charge will the atoms of the alkali metals, Li to Fr, adopt in ionic compounds?



$1+$, because each of them can lose one electron to obtain the same number of electrons as the nearest inert gas.



Write the symbol for the ion formed by calcium.



Ca^{2+} . The amount of positive charge is indicated by the superscript $2+$, which means that the ion has two more protons in the nucleus than the number of electrons. Calcium is a member of the alkaline earth metal elements, all of which lose two electrons when they form ions.



The group VI elements, O to Po, are sometimes referred to as the chalcogens. What charge will the atoms of these elements adopt in ionic compounds?



$2-$. They require two additional electrons to achieve the same number of electrons as the closest inert gas. For example, sulfur, with 16 electrons in the neutral atom, will gain two electrons to reach the 18 electrons of argon.



The common mineral fluorite (Figure 4) forms beautiful cubic crystals. This mineral is mainly calcium fluoride. What ions are present in this mineral?



Ca^{2+} and F^- . The fluoride ion, F^- , is the first member of the halogen group of elements adjacent to the inert gas elements.

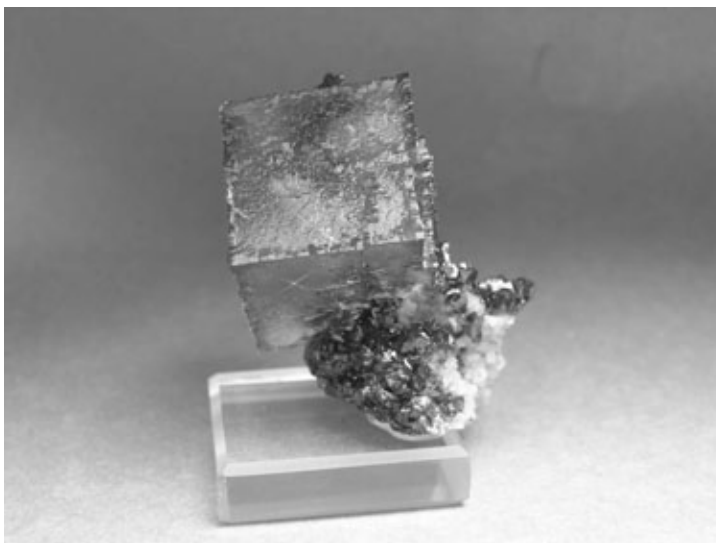


Figure 4 A sample of fluorite (Elmwood Mine, Tennessee).

The transition elements (see Figure 1) form cations, but because they are far removed from the inert gases, the inert gas rule cannot be used to predict the charge on the cations. Many of the elements also form more than one type of cation. For example, iron forms two common cations— Fe^{2+} and Fe^{3+} . Table 2 shows the cations formed by each of the important elements.

Table 2 Charges on transition metal cations

Cr	2+, 3+
Mn	2+
Fe	2+, 3+
Co	2+, 3+
Ni	2+
Cu	1+, 2+
Zn	2+
Cd	2+
Ag	1+
Au	1+, 3+
Hg	2+

There are also two other common main group elements, whose cation charges are not obvious. Tin and lead, both members of Group IV, form cations that have a 2+ charge. The position of the Group IV elements in the periodic table suggests that either gain or loss of four electrons should be possible. As we will see later, cations with charges greater than 3+ do not exist as ions and anions with charges greater than 3− probably do not exist in ionic form.



In the compound FeO, what is the charge on the cation?



2+. Because oxygen forms only a 2⁻ anion, iron must have a 2+ charge to balance the 2⁻ charge of the anion.

The question above uses a very important principle:

Every compound must be electrically neutral.

That is, the positive charge in the compound must be exactly counterbalanced by negative charge. This is why the formula for the compound calcium fluoride is CaF₂, rather than CaF, Ca₂F₃, or CaF₄. The calcium ion has a charge of 2+, the fluoride ion has a charge of 1⁻, and therefore two fluoride ions must be present for every calcium ion in order to make the compound electrically neutral.



If a very small sample of a compound contains 120 Fe³⁺ ions, how many S²⁻ ions must also be present?



180. 120 ions, each of which have a 3+ charge, produce a total charge of +360. A total negative charge of -360 is required to counterbalance this. Each sulfur supplies a 2⁻, and therefore 360/2 = 180 sulfur ions.



How do you write the formula of this compound?



Fe₂S₃, which tells us that for each Fe³⁺ ion there are one and one half S²⁻ ions (180/120 = 3/2). Or, for every 2 iron ions there are 3 sulfur ions.

1.2.2 Names of Ions

Next we need to learn how to name some simple compounds. There are two parts to the name of any binary (two element) ionic compound: the name of the cation and the name of the anion.

Let us start with the name of the anion. For monatomic (one atom) anions, simply take the name of the element, remove the last couple of letters and add *-ide*. For example, the Br⁻ ion is bromide. The O²⁻ ion is a little tricky in that we might suspect that it should be called oxygide but, in fact, it is the oxide ion. The rest of the anions are easy: S²⁻ is sulfide, As³⁻ is arsenide, I⁻ is iodide, and so on.



Name the following anions: F⁻ and Se²⁻.



Fluoride and selenide.

Many minerals contain anions that have more than one element covalently bonded to one another. Most of these anions are **oxy anions**; that is, they contain some central element that is attached to one or more oxygen atoms. The entire group of atoms is a charged molecule. The names of these anions are given in Table 3.

Table 3 The formulas and names of oxy anions important in minerals

Formula	Name
NO_3^-	nitrate
CO_3^{2-}	carbonate
SO_4^{2-}	sulfate
CrO_4^{2-}	chromate
WO_4^{2-}	tungstate
MoO_4^{2-}	molybdate
PO_4^{3-}	phosphate
AsO_4^{3-}	arsenate
VO_4^{3-}	vanadate
BO_3^{3-}	borate
SiO_4^{4-}	silicate (ortho or nesu)

Notice that all have names that end in *-ate*. The first part of the name is derived from the name of the central element.

The structures of several oxy anions are shown below. The lines between the central atom and the oxygens are covalent bonds. The dotted lines represent the structure of the anion. The tetrahedral anions have the central atom at the center of the solid geometric figure with four triangular faces (see Figure 5). The oxygens occupy the corners or apices of the tetrahedra. The trigonal planar anions have the central atom at the center of a triangle.

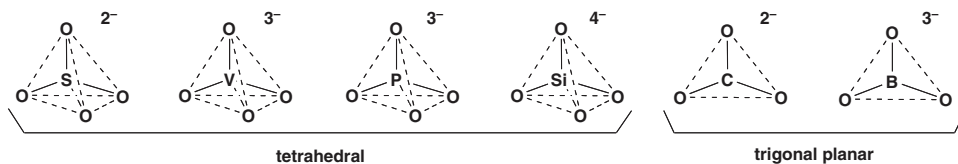


Figure 5 Tetrahedral and trigonal planar oxy anions. In the tetrahedral anions the central atom sits in the middle of the tetrahedron and the oxygen atoms are located at the corners of the four faces of the tetrahedron.



Name each of the ions in Figure 5.



From left to right: sulfate, vanadate, phosphate, silicate, carbonate, borate.

Now for the cation names. There are two ways to name the cation. In the International Union of Pure and Applied Chemistry (IUPAC) nomenclature we simply add a Roman numeral for the charge to the name of the element. Fe^{3+} is iron(III). Notice that the charge goes inside parentheses. The older (common) nomenclature is a little more complicated. In this method, the ion of any element that forms only one common ion is given the name of the element. For example, zinc only forms one common cation. Zn^{2+} is called the zinc ion. Likewise, Cs^+ is the cesium ion.

If the element forms two common ions, we add the suffix *-ic* to the Latin (or Greek) root of the symbol of the element for the ion that has the higher charge. We add the suffix *-ous* to the root of the symbol of the element for the ion that has the lower charge. Consider the two common ions of the element iron: Fe^{2+} and Fe^{3+} . The root of the symbol for this element is *ferr* (that's where the symbol Fe comes from). Fe^{3+} has the higher charge so we add *ic* to *ferr* to get ferric. Fe^{2+} has the lower charge so we add *ous* to *ferr* to get ferrous. Thus, Fe^{3+} is the ferric ion and Fe^{2+} is the ferrous ion. The Latin roots are given in Table 4 below:

Table 4 Some root names of the elements

Element	Symbol	Root
chromium	Cr	chrom
cobalt	Co	cobalt
copper	Cu	cupr
iron	Fe	ferr
gold	Au	aur
mercury	Hg	mercur
tin	Sn	stann



Give the IUPAC name for the copper ion with the higher charge.



Copper(II). Table 2 tells us that copper forms two ions: Cu^+ , and Cu^{2+} . The IUPAC name for the ion with the higher charge is copper(II).



Provide the older (common) name for the same ion.



Cupric. The root name for copper is *cupr*, to which we add *ic* to designate the higher charge.

We can now put the cation and anion names together to form compound names.

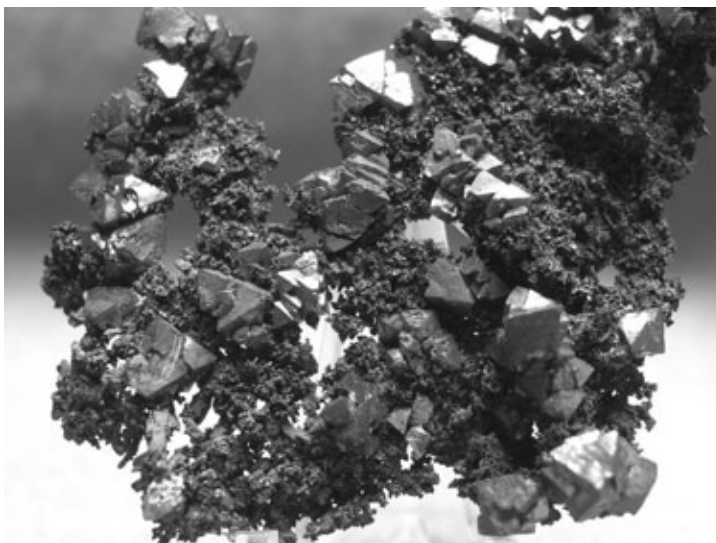


Figure 6 A sample of cuprite on native copper from the Ray Mine, Arizona. This is the octahedral habit for cuprite.



See if you can name the common mineral cuprite, Cu_2O , in the common system. For a picture of a sample of cuprite see Figure 6.



Cuprous oxide. The compound contains the oxide ion, O^{2-} , and therefore the copper must have a +1 charge. Cu^+ is the copper ion that has the lower charge and therefore we add *ous* to the root *cupr* to get cuprous.



Use the common system to name the following compounds: NiS , FeCO_3 , and PbSO_4



Nickel sulfide, ferrous carbonate, and lead sulfate.

We now know what ions the elements form when they combine to form ionic compounds and we know how to name simple binary ionic compounds.

1.3 PERCENT COMPOSITION AND EMPIRICAL FORMULA

The composition of all compounds, whether they are ionic or covalent, is expressed in two main ways. First, we can designate the percentage of each element in the compound. The determination of these percentages is frequently one of the first analyses performed on a compound. For example, pure SiO_2 has a percent composition of 46.7% Si and 53.3% O. Although we will not discuss the methods that are used to determine these numbers, we do want to know what they mean and how they can be used.



If we have a 100 g sample of pure quartz; that is, pure SiO_2 , how many grams of silicon are present?



46.7 g. In order to get the weight of the element we need only multiply the weight of the sample (100 g) by the percentage expressed as its decimal equivalent (0.467). Thus,

$$0.467 \times 100 \text{ g} = 46.7 \text{ g}$$



Calcite is primarily calcium carbonate (minerals usually contain small amounts of other compounds). Calcium carbonate has a percentage composition of 40.0% Ca, 12.0% C, and 48.0% O. Determine the weight of carbon in a 12 g sample of calcite.



1.44 g

Percent composition data is frequently used to determine the **empirical formula** of a compound. The empirical formula of a compound provides information about: a) what elements are present, and b) the ratios of the atoms of those elements. Let us take an example. The formula for calcium carbonate is CaCO_3 .



What elements are present in calcium carbonate?



This is obvious, but notice that we do have to know that Ca is the symbol for calcium, C is carbon, and O is oxygen.

The subscripts that appear after each symbol represent the relative number of atoms of each element. If there is no subscript, it is understood to be a one, thus CaCO_3 could also be written as $\text{Ca}_1\text{C}_1\text{O}_3$. The formula CaCO_3 should be interpreted as follows: for every one atom of calcium there is one atom of carbon and three atoms of oxygen.



Write a similar sentence for the formula for ferric oxide, Fe_2O_3 .



For every two iron atoms there are three oxygen atoms in ferric oxide.

Notice that we could divide the subscripts in the formula for Fe_2O_3 by 2 and get $\text{FeO}_{1.5}$, which would reveal the same ratio (1 to 1.5) of iron to oxygen. We could also multiply the subscripts by 2 (or any other number) to get Fe_4O_6 . However, the *empirical formula should reveal the simplest whole number ratio of atoms in the compound*. This means that the formula Fe_2O_3 , which contains the smallest whole numbers, is the preferred empirical formula.

Although the interpretation of the empirical formula given above is perfectly correct, we should really modify it slightly to take advantage of a concept widely used by both

chemists and geologists. Because scientists usually deal with gram amounts of materials, we frequently express the empirical formula in terms of a much larger number of atoms.

1.3.1 The Mole

We need to digress to define the mole, which is just a number, in the same way that a gross is 144 or a ream is 500 sheets of paper. First, we need to review atomic weight. The atomic weights in the periodic table (see Appendix 1) represent the average mass of an atom of the element in atomic mass units. Some atomic weights are given below in Table 5:

Table 5 Some atomic weights (amu)

hydrogen	carbon	oxygen	silicon	titanium
1.008	12.01	16.00	28.09	47.88

These numbers tell us the relative weights of the atoms.



How much heavier is an average atom of titanium than an average atom of hydrogen?



47.5 times heavier ($47.88/1.008 = 47.5$).



What mass of titanium will contain the same number of atoms as 1.0 g of hydrogen?



48 g. Atoms of titanium are 47.5 times heavier than those of hydrogen. Therefore, 48 g (we are rounding off to two significant figures) of titanium will contain the same number of atoms as 1.0 g of hydrogen.



What mass of carbon will contain the same number of atoms as 2 g of hydrogen?



24 g. Because an average atom of carbon is 12 times heavier than an atom of hydrogen we need just multiply 2 g by 12, or $2\text{ g} \times (12/1) = 24\text{ g}$.

We can easily see that the atomic weight of an element expressed in grams, pounds, tons, or any unit we would like to use, contains the same number of atoms as the atomic weight of some other element expressed in the same units. For example, 16 tons of oxygen contains the same number of atoms as 12 tons of carbon. Because we so often work in gram amounts, it would be nice to know the *actual number of atoms in an amount of an element equal to its atomic mass in grams*. In other words, how many atoms are present in 12.01 grams of carbon, in 1.008 grams of hydrogen, or in 32.04 grams of sulfur? We know, of course, that the number of atoms in each of these quantities is the same. But what is the number? This number has been determined experimentally in a number of different ways and turns out to be an extremely large number— 6.022×10^{23} .



How many atoms are present in 24 grams of carbon?



1.2×10^{24} atoms. There are 6.0×10^{23} atoms in 12 g of carbon. In 24 grams there are

$$\frac{24 \text{ g}}{12 \text{ g}} \times 6.0 \times 10^{23} \text{ atoms} = 1.2 \times 10^{24} \text{ atoms}$$

This number— 6.022×10^{23} —is also called **Avogadro's number**, in honor of the Italian chemist Amedeo Avogadro, who did much of the work necessary to determine the number. This number— 6.022×10^{23} —is also called a **mole**.



How many moles of atoms are there in 24 grams of carbon?



2 moles.



How many grams of calcium must be weighed out in order to obtain a sample containing 3 moles of atoms?



120 g. The atomic mass of calcium is 40 and therefore a mole of calcium weighs 40 grams. Three moles of calcium is $3 \text{ mole} \times 40 \text{ g/mole} = 120 \text{ g}$.



How many moles of calcium are present in a 20 g sample of calcium?



0.50 mole. The mass of an element is always converted to moles by dividing by the atomic mass of the element (expressed in grams per mole). Thus,

$$\frac{20 \text{ g}}{40 \text{ g/mol}} = 0.50 \text{ mole.}$$

Now we are ready to get back to formulas. The formula Fe_2O_3 can be expressed in terms of moles: for every two moles of iron atoms (that's $2 \times 6 \times 10^{23}$ atoms) there are three moles of oxygen atoms (that's $3 \times 6 \times 10^{23}$ atoms).



Brucite is $\text{Mg}(\text{OH})_2$. The OH^- ion is called the hydroxide ion and the parentheses are used to indicate that the subscript 2 applies to everything inside the parentheses. How many moles of hydroxide ion would be found with 0.1 mole of magnesium ions?



0.2 mole. The formula tells us that for every mole of magnesium, we have two moles of hydroxide.

Molar Mass (Formula Weight)

We can now calculate the **molar mass** (sometimes also called the **formula weight**) of a compound. This is the mass of one mole of the compound and can be determined by simply adding the atomic masses of each of the elements (taking into account the number of each) in the compound. For brucite, we need to add the atomic weight of magnesium, two times the atomic weight of oxygen and two times the atomic weight of hydrogen (notice that $\text{Mg}(\text{OH})_2$ is equal to MgO_2H_2). So, this would be $24 + (2 \times 16) + (2 \times 1) = 58$ g per mole.



How many moles of oxygen are there in 58 g of $\text{Mg}(\text{OH})_2$?



Two. Because 58 grams is the weight of one mole of $\text{Mg}(\text{OH})_2$ and one mole of $\text{Mg}(\text{OH})_2$ contains two moles of oxygen, 58 grams must contain two moles of oxygen.

The molar mass is important in the determination of the percent composition of a compound from its empirical formula. For example, suppose that we want the percent of iron in pyrite, FeS_2 . The molar mass of FeS_2 is $56 + (2 \times 32) = 120$ g per mole. In this mass of FeS_2 there is 56 g of iron. Thus, the percentage of iron is

$$\frac{56 \text{ g Fe/mole}}{120 \text{ g/mole}} \times 100 = 47\% \text{ Fe}$$



Determine the percentage of titanium in rutile, TiO_2 .



59.9%. The molar mass is 79.9 g per mole. That molar mass contains 47.9 g of Ti. Thus, the percentage is

$$\frac{47.9 \text{ g Ti/mole}}{79.9 \text{ g/mole}} \times 100 = 59.9\% \text{ Ti}$$

1.3.2 Calculation of Empirical Formula from Percent Composition

The conversion of experimental composition data to empirical formula is an important step in determining the identity of a substance. Suppose that we have a sample of a heavy, pale yellow, crystalline material that has the composition: 59.0% Ba, 13.5% S, and 27.4% O. We need to convert this percent composition data to an empirical formula, which will

tell us the relative number of moles of barium, sulfur, and oxygen in the substance. The key to this conversion lies in the understanding of the phrase “relative number of moles of barium, sulfur, and oxygen in the substance.” If we want the number of moles of each we must know the mass of each element in some amount of the substance and then we must convert each of those masses to moles.

We could choose any amount of the substance and convert it to the mass of each of the elements. If we choose 100 grams of the substance, it makes the problem a little easier because we can do the first part of the math in our heads. For example, if we have a 100 g sample of the substance and it contains 59.0% barium, the mass of barium present is

$$100 \text{ g} \times 0.590 = 59.0 \text{ g}$$

Likewise, in this same sample we have 13.5 g sulfur and 27.4 g oxygen. In order to convert these masses to moles we divide each by their atomic mass:

$$\text{Ba} \frac{59.0 \text{ g}}{137.33 \text{ g/mol}} = 0.430 \text{ mol}$$

$$\text{S} \frac{13.5 \text{ g}}{32.07 \text{ g/mol}} = 0.421 \text{ mol}$$

$$\text{O} \frac{27.4 \text{ g}}{16.00 \text{ g/mol}} = 1.71 \text{ mol}$$

We could at this point write the empirical formula as $\text{Ba}_{0.430}\text{S}_{0.421}\text{O}_{1.71}$, but we know that the empirical formula should be expressed in whole numbers. Consequently, we divide each of the subscripts by the smallest one (0.421), which gives us subscripts of 1.02, 1.00, and 4.06. These still are not whole numbers, but because these numbers have been derived from experimental data, which contain errors, we cannot expect the numbers to come out to exact whole numbers. The numbers appear close enough to 1, 1, and 4 to allow us to safely round them off. Hence, the empirical formula of the substance is BaSO_4 .

In some cases the numbers will not come close to whole numbers and we must then multiply each by some number that will produce a set of whole numbers. The following is such a case.



Determine the empirical formula of a compound with percent composition data of Fe, 69.9%, O, 30.1%.



Fe_2O_3 . In a 100 g sample there will be 69.9 g Fe, and 30.1 g O. The number of moles of each is

$$\text{Fe} \frac{69.9 \text{ g}}{55.85 \text{ g/mol}} = 1.25 \text{ mole Fe}$$

$$\text{O} \frac{30.1 \text{ g}}{16.0 \text{ g/mol}} = 1.88 \text{ mole O.}$$

When we divide both numbers by the smaller, we get 1.00 and 1.50. Certainly, 1.50 is nowhere close to a whole number and so we must multiply both numbers by the smallest possible number to convert both to a whole number. If we multiply both of the mole amounts by 2, we will obtain the formula Fe_2O_3 .

1.3.3 Use of Oxide Data

Mineralogists frequently report percent composition data for minerals that contain oxygen in terms of the oxides of the metals (and sometimes some of the non-metals, see below). For example, the data for spinel would be reported as MgO 28.2%, Al₂O₃ 71.8%. This does not mean that spinel is a mixture of these oxides.

In order to calculate the empirical formula from oxide data, we need to know what anion is present and we must convert the oxide percentages to moles of each cation. Spinel is an oxide, which means that we can assume that the anion is the O²⁻ ion.



Now, convert the percentages of MgO and Al₂O₃ to relative numbers of moles of Mg and Al.



First, we assume our usual 100 g sample, which would contain 28.2 g of MgO and 71.8 g Al₂O₃. Next, we determine the number of moles of each of these oxides by dividing each mass by the molar mass of the oxide:

$$\text{MgO} \quad \frac{28.2 \text{ g}}{40.3 \text{ g/mol}} = 0.700 \text{ mole}$$

$$\text{Al}_2\text{O}_3 \quad \frac{71.8 \text{ g}}{102.0 \text{ g/mol}} = 0.704 \text{ mole}$$

Finally, we convert these mole amounts to the number of moles of Mg and Al. Because one mole of MgO contains one mole of Mg, 0.700 mole of MgO must contain 0.700 mole of Mg atoms. One mole of Al₂O₃ contains two moles of aluminum per mole of Al₂O₃, and therefore 0.704 mole of Al₂O₃ is equivalent to $2 \times 0.704 = 1.408$ mole Al.

$$\text{moles Mg} = 0.700$$

$$\text{moles Al} = 1.408$$

Thus, we know that Mg and Al are present in a one to two ratio ($1.408/0.700 = 2.0$). But, what about the rest of the compound? The rest of the compound is the anion O²⁻.



If spinel contains two Al³⁺ ions for every one Mg²⁺ ions, how many O²⁻ ions must it contain for every one Mg²⁺ ion?



Four O²⁻ ions. If we have a sample that contains one Mg²⁺ and two Al³⁺ ions, the total positive charge in that sample is $2 \times 3 + 2 = 8$. The only anion present is O²⁻ and consequently there must be four of these to balance the 8+ charge and make the compound electrically neutral.



What is the empirical formula of spinel?



MgAl₂O₄.

1.3.4 Formulas for Solid Solutions



As our next example, we consider a sample of olivine that has the analysis: MgO, 26.2%, FeO, 37.1%, and SiO₂, 35.0%. Olivine contains the nesosilicate ion SiO₄⁴⁻. Determine the empirical formula of this sample.



Assuming a 100 g sample, we convert percentages to mass, and then convert the masses to moles by dividing by the molar mass.

$$\text{MgO} \quad \frac{26.2 \text{ g}}{40.3 \text{ g/mol}} = 0.650 \text{ mol}$$

$$\text{FeO} \quad \frac{37.1 \text{ g}}{71.8 \text{ g/mol}} = 0.517 \text{ mol}$$

$$\text{SiO}_2 \quad \frac{35.0 \text{ g}}{60.1 \text{ g/mol}} = 0.582 \text{ mol}$$

All of the silicon must be present in the SiO₄⁴⁻ ion, so we can use it as our standard; that is, because we know that the sample contains the SiO₄⁴⁻ ion we can say that 0.582 mol represents the silicate ion. The mole amounts of magnesium and iron must be calculated relative to the anion. Thus, we divide the other mole amounts (notice that MgO and FeO have one mole of cation per mole) by 0.582:

$$\text{Mg} \quad \frac{0.650}{0.582} = 1.12$$

$$\text{Fe} \quad \frac{0.517}{0.582} = 0.888$$

$$\text{Si} \quad \frac{0.582}{0.582} = 1.00$$

It is tempting to think that all of these numbers are really 1.00; that, in other words, there is considerable experimental error in the measurements. However, if the error were that large, the numbers should not be reported to three significant figures. Thus, it is unlikely that we can assign both Mg and Fe the value of 1.00.

Our next thought should be: Can we find a number that we can multiply each of the three numbers by to get whole numbers? Multiplication by 8, for example, gives 8.96 for Mg, 7.10 for Fe, and 8 for Si. These numbers are now reasonably close to whole numbers, and we could probably give Mg₉Fe₇(SiO₄)₈ as the empirical formula for the sample. In fact, olivine is an example of a mineral that forms a **solid solution**. A solid solution occurs when one or more cations (or anions) can exchange places in the crystal structure. This means that a particular olivine may not have a whole number composition on the macroscopic scale (we sometimes use the word **nonstoichiometric** composition to mean the same thing). So, we can give the formula as Mg_{1.12}Fe_{0.888}SiO₄. This formula cannot be exactly correct because the charges are not balanced. The number of positive charges is 2 × 1.12 + 2 × 0.888 = 4.02; the number of negative charges is -4.00. Hence, there must be some experimental error in the percent composition data.

Because solid solutions exist for many minerals, let us briefly digress and consider a very small sample of olivine that contains 100 silicate ions, 118 magnesium cations, and 82 iron cations. (Notice that the number of 2+ cations must be twice the number of 4- anions, in order to achieve electrical neutrality.) The empirical formula of this sample is

definitely $\text{Mg}_{1.18}\text{Fe}_{0.82}\text{SiO}_4$. A sample obtained from a different location, where the olivine was formed under different conditions, contains 100 silicate ions, 93 magnesium cations, and 107 iron cations. This sample definitely has an empirical formula of $\text{Mg}_{0.93}\text{Fe}_{1.07}\text{SiO}_4$. Both are samples of olivine, both contain roughly equal amounts of magnesium and iron cations, but each has different properties. Moreover, the empirical formula for each could (mistakenly) be written as MgFeSiO_4 . In fact, a whole range of magnesium and iron ratios can be obtained. The end members of this range of solid solutions are Mg_2SiO_4 (forsterite) and Fe_2SiO_4 (fayalite). The composition of a compound anywhere in the solid solution range is sometimes indicated by the formula $(\text{Mg,Fe})_2\text{SiO}_4$, where it is understood that the magnesium and iron substitute for one another and that the sum of the subscripts of Mg and Fe must add up to 1.00.

The principle used to determine these empirical formulas is sufficiently important to state it more concisely:

Electrical neutrality must be maintained at both short ranges (over a small number of atoms) and at long ranges (the macroscopic level).



Determine the empirical formula for pyromorphite (which contains the phosphate (PO_4^{3-}) anion) with a composition of PbO 82.2%, P_2O_5 15.7%, Cl 2.6%.

$$\begin{array}{l} \text{PbO} \frac{82.2 \text{ g}}{223.2 \text{ g/mol}} = 0.368 \text{ mol} \qquad \text{moles Pb} = 0.368 \\ \text{P}_2\text{O}_5 \frac{15.7 \text{ g}}{141.94 \text{ g/mol}} = 0.111 \text{ mol, but each mole of P}_2\text{O}_5 \\ \qquad \qquad \qquad \text{contains 2 moles of P, so} \qquad \qquad \text{moles of P} = 0.222 \\ \text{Cl} \frac{2.6 \text{ g}}{35.45 \text{ g/mol}} = 0.0733 \text{ mol} \qquad \qquad \text{moles Cl} = 0.0733 \end{array}$$

Based on one phosphate ion (which contains one phosphorus), we have $0.368/0.222 = 1.66$ moles Pb and 0.330 moles Cl. Notice that if we multiply each number, including the number for phosphate, by 3 we will get whole numbers— $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$.

1.4 COVALENT CHARACTER IN IONIC COMPOUNDS

Before we go on to discuss the interactions between the ions in ionic compounds, it is important to realize that there is a whole spectrum of bonding interactions in compounds. In a particular compound, the bonding is not necessarily completely ionic or covalent. When the electronegativities of the atoms are very different, the bonding is generally primarily ionic. Compounds of metals with very low electronegativities (for example, potassium or cesium) with non-metals with high electronegativities (for example, fluorine, chlorine, or oxygen), are generally considered to be nearly 100% ionic. On the other hand, a compound formed from two non-metals with similar electronegativities (for example, NCl_3) is generally considered to be nearly 100% covalent. But what about compounds such as Al_2O_3 , (corundum) or Sb_2S_3 (stibnite)? In these compounds, the difference in electronegativities is considerable but not extreme; the compounds are, therefore, neither completely ionic nor completely covalent. We say they have a certain amount of ionic character. Thus, Al_2O_3 might have bonds with about 40% ionic character. This certainly implies that some electron density is transferred from one atom to another but, at the same time, some of the electron density is shared.



Which compound in each of the following pairs is more ionic?

a) KF or KI

b) As_2S_3 or Sb_2S_3



a) KF,

b) Sb_2S_3

In general, electronegativity decreases going down a group. Thus, iodine has a lower electronegativity than fluorine and the difference in electronegativity between potassium and fluorine is therefore greater. The same is true for arsenic and antimony, but not by much because they are closer within the group.

Now consider FeO and Fe_2O_3 . In this case, the ionic character cannot be easily assessed by looking at the electronegativities of the elements. Even though the iron in FeO is the Fe^{2+} ion, whereas in Fe_2O_3 it is the Fe^{3+} ion, there is no easy way to determine the electronegativity of an ion. A model that is particularly convenient for this situation, and in many other bonding problems, was proposed by Kazimierz Fajans, a Polish-American chemist.

Fajans' model works as follows: We first assume that the compound of interest is ionic. Second, we consider the effect of the cation on the electron density of the anion. The more the cation distorts the electron density of the anion, the more covalent the compound. In other words, the more the cation pulls electron density into the region between the atoms, the more electron density is available for sharing.

Let us consider as an example the bonding in FeO and Fe_2O_3 . First, we imagine that each compound is ionic. (It doesn't matter whether the bonding is actually ionic or not; this is just a first step in the model.) Thus, FeO is imagined to contain the Fe^{2+} and O^{2-} ions, whereas Fe_2O_3 is imagined to contain the Fe^{3+} and O^{2-} ions. If we want to compare the bonding in the two compounds we must ask which ion— Fe^{2+} or Fe^{3+} —distorts the electron density of the oxide ion more.



Which ion— Fe^{2+} or Fe^{3+} —distorts the electron density of the anion to the greater extent?



Fe^{3+} , because of its higher charge and, consequently, its greater attraction for the electron density.

Let us look at this idea a little more carefully. The cation distorts the electron density by virtue of its electrostatic "pull" on the electrons. The magnitude of this attraction is proportional to the *charge density* of the cation. The charge density in turn depends on the magnitude of the charge per unit volume of the cation. Or, in simpler terms, the greater the charge and the smaller the size of the cation, the more the cation distorts the electron density. So, which cation— Fe^{2+} or Fe^{3+} —is smaller, which is more highly charged? Clearly, Fe^{3+} has a higher charge, but which ion is smaller?

The size of the ion depends on the attraction of the protons in the nucleus for the electron density surrounding the nucleus. The greater the attraction the more the nucleus pulls the electron density toward it and the smaller the ion becomes. The Fe^{3+} ion has one less electron than Fe^{2+} , which means that there are fewer electrons to shield the outer most

electrons from the nuclear charge. Thus, the attraction between the nucleus and the electrons of Fe^{3+} is greater than the attraction in the Fe^{2+} ion. Therefore, the Fe^{3+} ion is smaller.

Because Fe^{3+} is both smaller and has a higher charge, the amount of positive charge per volume (the charge density) must be greater than that of the Fe^{2+} ion. Consequently, the Fe^{3+} ion distorts the electron density of the oxide ion more effectively. There is a greater build-up of electron density in the region between the “ions” and Fe_2O_3 is more covalent (see Figure 7).

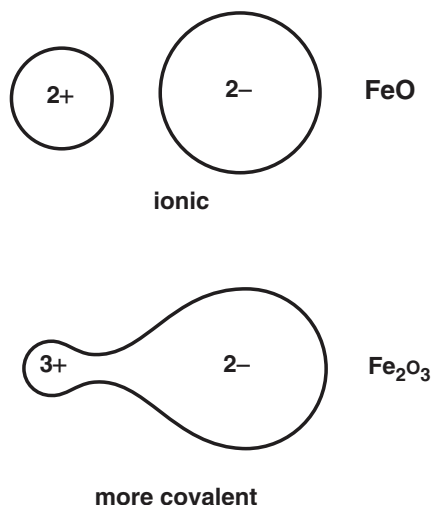


Figure 7 Distortion of electron density by cations of high charge and small size.



Now use Fajans' model to predict whether SiO_2 or SnO_2 is more covalent.



SiO_2 . When we imagine the Si^{4+} and Sn^{4+} ions, we immediately recognize that both have the same charge, but Sn^{4+} is the larger ion because it contains more electrons (it is lower on the periodic table). Thus, the charge density of Si^{4+} is higher and the distortion of electron density is greater in SiO_2 . Of course, we have mentioned earlier that $4+$ ions do not exist and both SiO_2 and SnO_2 are predominantly covalent.



Next, apply the model to two compounds that have different anions— CaO and CaS —to predict the degree of covalent bonding.



CaS is more covalent. In this case the cation is the same in both compounds, but the anions are different. Both have the same charge, but the sulfide ion is larger. Larger ions generally have a greater number of electrons and are more polarizable. The sulfide ion is more distortable, the electrons are more delocalized into the region between the nuclei, and CaS is therefore more covalent. (The same conclusion could, of course, also have been reached using the difference in electronegativities.)

There is one more valuable aspect of Fajans' model. Because transition metal ions have d-electrons that are relatively close to the "surface" of the atom, these ions themselves have somewhat distortable electron density. In other words, the electron density of transition metal cations can be distorted by the anion, causing mutual polarization of the ions. Thus, compounds that contain transition metal cations generally have more covalent character than compounds that do not have transition metal cations.



Which is more covalent—CaS or CuS?



CuS, because copper is a transition metal and therefore has d-electrons which result in mutual polarization of the ions.



Mineralogists frequently represent the silicon in the silicate ion SiO_4^{4-} as the Si^{4+} ion. Comment on this strategy.



This strategy is sometimes useful in describing the structure of silicates, but it is not an accurate portrayal of the bonding in the silicate ion. The silicon-oxygen covalent bond is a very strong bond. It does have some ionic character, but it is not accurate to think of the SiO_4^{4-} ion as containing an Si^{4+} ion and four oxide ions. Fajans' rules reveal that any highly charged, small ion cannot survive; it distorts the electron density of the "anions" and covalency results.

1.5 INTERACTIONS BETWEEN IONS

Now that we have several ways to determine the covalency of a compound, let us return to our ionic compounds. We want to inquire at this point about the interactions that exist between ions. We also want to know something about what factors influence the magnitude of these interactions.

1.5.1 Some Laws of Electrostatics

It is a fundamental law of physics, first put on a quantitative basis by the French physicist Charles Augustin Coulomb, that

oppositely charged particles attract one another and like charged particles repel one another.

Because this simple statement and its quantitative expression are so important, we must be absolutely clear about it.



What will happen if we position a cation and an anion next to one another as shown on the next page?



The two particles will attract one another and will move toward one another until they are touching.



Coulomb determined that the magnitude of the force of the attraction (or repulsion if the charges have the same sign) is proportional to the magnitude of the charge on each particle (q_1 and q_2) and inversely proportional to the square of the distance (r) between them. Mathematically, this is expressed as

$$F = \frac{kq_1q_2}{r^2}$$

where k is a proportionality constant. The force between the ions determines many of the properties of ionic compounds, including their stability.

Potential Energy of Charged Particles

Actually, stability is related more directly to the energy of the compound. You will probably remember that energy is the ability to do work and that work is accomplished when a force is exerted through a distance.



What are the two kinds of energy?



Kinetic energy, which is the ability of an object to do work by virtue of its motion, and potential energy, the ability of an object to do work by virtue of its position.

A boulder perched on the top of a cliff has no kinetic energy because it is not moving. However, it could fall at any moment and then its motion could be harnessed to do work (for example, if attached to a rope and pulley it could lift a weight). Thus, this motionless boulder has the potential to do work; that is, it has potential energy.

Of course, our ions are not boulders, but they also have the potential to move (if they are oppositely charged they can move toward one another) and thus have potential energy. They also have a small amount of kinetic energy because they vibrate back and forth in their positions in the solid. The potential energy (V) is expressed mathematically by an expression that is very similar to that derived by Coulomb for the force:

$$V = \frac{kq_1q_2}{r}$$

Notice that the difference between the two expressions is that the force has r^2 in the denominator, while the potential energy has r in the denominator. The important point is that the energy of an ionic compound, which is primarily electrostatic potential energy, depends on the charge on each ion and the distance between the ions.



Consider the following arrangement of chloride ions. Is this arrangement likely to be stable?



No, this arrangement will not be stable because the ions are negatively charged and will repel one another.



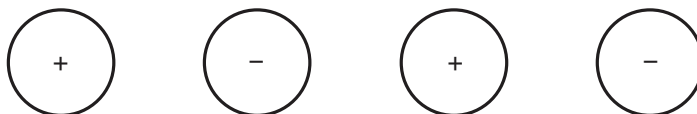
What is the sign of the potential energy of these ions?



Positive. Notice that when q_1 and q_2 have the same sign the potential energy will be positive.

We must keep in mind then that usually a stable ionic compound will have a negative potential energy. The kinetic energy will always be positive, but it makes only a small contribution to the total energy because there is little movement of the ions in the solid state.

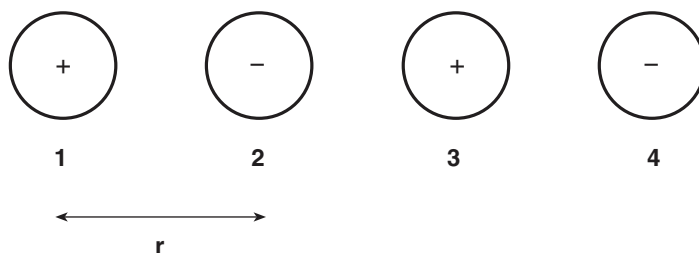
Now, let us look at the following arrangement of ions, which represents a portion of a row of ions in solid sodium chloride.



What is the sign of the potential energy for these four ions?



Negative. In order to answer this question we must consider the interaction of each ion with all of the others. To facilitate this, we will number the ions and also assume that



the distance between each pair of adjacent ions is the same. We will call this distance r .

We start with the left-hand ion, number 1. It is attracted to ion number 2 and the energy of this interaction is given by

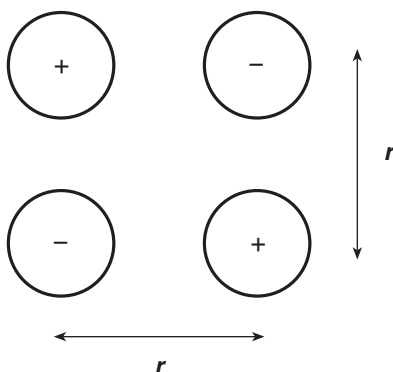
$$V = \frac{kq_1q_2}{r}$$

It is repelled by ion number 3 because ions 1 and 3 have the same charge. The magnitude of this repulsion will be less than that of the attraction between 1 and 2 because 3 is farther away (a distance of $2r$). Ion 1 is also attracted to ion 4, but that attraction is much smaller (because of the greater distance) than the attraction between 1 and 2. Thus, we can conclude that the potential energy of the interaction of ion 1 with all the others is negative.

Now consider ion 2. It will be attracted to ions 1 and 3 by the same amount and repelled by 4, although this repulsion will be only half (because the distance is $2r$) that of the attraction between 2 and one of its neighbors. Thus, we can conclude that the potential energy of ion 2 must also be negative.

The same arguments can be made for ion 3, which is just like 2 but with opposite charge, and ion 4 (just like 1 but with opposite charge). The potential energy of all four ions must therefore be negative; that is, the attractions outweigh the repulsions. To put this another way, the attractions lower the potential energy more than the repulsions raise the potential energy.

Take a look at another arrangement of four ions:



In this arrangement the ions occupy the corners of a square. How will the potential energy of this arrangement compare with the potential energy of the linear arrangement of the ions?



This arrangement will have a lower potential energy. Each ion is attracted to two other ions and repelled by one. All of the repulsions are at a distance of $\sqrt{2}r$ (the distance of the diagonal, d , can be calculated using the Pythagorean theorem — $d = \sqrt{r^2 + r^2}$). Although we should really go through all of the interactions mathematically (being careful not to count the interaction between a given set of ions more than once), we can be reasonably sure of our conclusion because there are 4 attractions at a distance of r in this arrangement, but 3 attractions at a distance of r and one at a distance of $3r$ in the previous example. Both arrangements have 2 repulsions and in the square arrangement the repulsions are more significant because the ions are closer— $\sqrt{2}r$ rather than $2r$. Although the repulsions are important, the number of attractions at the nearest neighbor

distance in this case produces a lower potential energy for the square arrangement.

We have just demonstrated an important point:

The stability of a set of ions depends upon their geometric arrangement. Thus, ions will tend to arrange themselves to maximize attractions and minimize repulsions.

Before we go on to look at ways that ions can arrange themselves in three dimensions, let us take a few minutes to see how the potential energy of ionic compounds is affected by charge and distance.

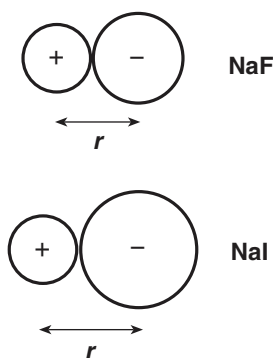


Which of the following compounds—NaF or NaI—has the lower potential energy?



NaF. We need to consider three things: the charges on the cation and anion, the distance between the cation and anion, and the arrangement of the ions in the solid ionic compound. At this point we know nothing about the arrangement of the ions in the solids, so we must ignore this factor. (It turns out that the charge and distance factors are generally more important than difference in arrangement.)

The charge on the cation is clearly the same in both compounds because the cation is the same (Na^+). The charge on the anion is also the same because both are halide ions with a charge of $1-$. The only difference between the compounds is the distance between the cation and anion. This distance can be obtained experimentally by X-ray diffraction, but we do not need to resort to this in order to answer the question. In general, the size of atoms increases as we go down the periodic table (see Appendix 1). Thus, the iodide ion is larger than the fluoride ion. Moreover, we can assume that in the solid the ions are “touching.” Thus, we can think of the distances as shown in the following diagram:



The distance r between the neighboring ions in NaF is smaller and will lead to a more negative potential energy for NaF. Remember that r is in the denominator of the expression for potential energy, and a smaller number in the denominator produces a larger quotient. (Because the ions have opposite charges, the number is negative.)



How does a more negative potential energy affect the properties of the two compounds? Consider properties such as melting point and hardness.



The more negative the potential energy the greater the amount of work required to separate the ions and therefore the greater the stability of the compound. The greater the stability of the compound, the more energy is required for melting or boiling, or moving ions past one another when the surface is perturbed by scratching (hardness).

1.5.2 Lattice Energy and Its Effect on Properties

The negative potential energy of an ionic compound is sometimes referred to as its **lattice energy**, which can also be defined as the **amount of work required to separate the ions from the solid state into the gaseous state**. Thus, for NaF, the lattice energy is the energy required for the process



To make sure that you see that the lattice energy and the negative of the potential energy are the same, consider what happens to the potential energy when we move the ions to a large separation (such as occurs in the gas state).



The potential energy is close to zero. From the equation

$$V = \frac{kq_1q_2}{r}$$

you can see that when r is infinity, $V = 0$. Thus, the potential energy is really the negative of the work required to separate the ions to infinity. The separation in the gaseous state is not infinite, but it is very large. Thus,

$$\text{lattice energy} = -\text{potential energy}$$



Which compound has the greater lattice energy— K_2O or CaO ?



CaO . CaO has the most negative potential energy because the calcium ion has a 2+ charge, whereas the potassium ion has a 1+ charge. Notice that the fact that there are two potassium ions per oxide ion has nothing to do with the analysis. The analysis of potential energy considers only two neighboring, adjacent ions of opposite charge. The Ca^{2+} ion is also slightly smaller than the K^+ ion, but this difference in size is a much smaller factor than the difference in charge (Ca^{2+} has twice the charge of K^+).



Which has the greater hardness—cuprite (Cu_2O) or chalcocite (Cu_2S)? **Hardness** is the **relative resistance to abrasion** and is measured on a scale devised by the German mineralogist, Friedrich Mohs, in 1812. On this scale, various

minerals are assigned values from 1 to 10. Very soft talc is assigned the value of 1, quartz is 7, and diamond is at the top of the scale with a value of 10.



Cuprite is harder because of the smaller size of the oxide ion and consequent higher lattice energy. The hardness of cuprite is 3.5–4, whereas chalcocite has a hardness of 2.5–3.



Which has the greater hardness—chalcocite (Cu_2S) or covellite (CuS)?



We would predict that CuS would have the greater hardness, because the cation Cu^{2+} has a higher charge than the cation Cu^+ in chalcocite. The potential energy of CuS should be more negative (greater lattice energy) and the ions should be more tightly constrained in the lattice, thereby making the compound harder to scratch. However, chalcocite has a hardness of 2.5–3, whereas covellite has a hardness of 1.5–2 on the Mohs hardness scale. This difference is probably associated with the unusual arrangement of ions in the covellite structure. This structure is probably also associated with the greater covalent character of the interaction between the ions in covellite, as predicted by Fajans' rules.

Chapter 2

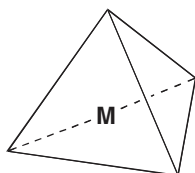
The Structure of Ionic Compounds: Closest Packing

Although many of the compounds of greatest interest to mineralogists contain both ionic and covalent bonding, the structures of most minerals can be analyzed primarily in terms of the ionic model. As we have seen, this model assumes that simple electrostatic attractions provide the stability of ionic compounds and that these interactions account for many of the properties, such as melting point and hardness, of minerals.

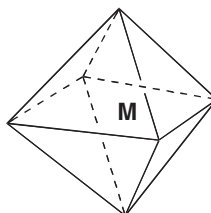
Generally, ionic compounds attempt to reach a state of lowest potential energy by increasing the number of attractions between oppositely charged ions, while minimizing the repulsions between charges of the same sign. The number of attractions per ion can be increased by increasing the number of oppositely charged ions surrounding the ion, and by having the ions as close as possible.



Which of the following arrangements of anions around a cation (M) provides the greater number of attractions? The anions are positioned at the corners of the tetrahedron (a) and the octahedron (b).



(a)



(b)



Arrangement (b), because there are six anions surrounding the cation, whereas in arrangement (a), there are only four anions around the cation.

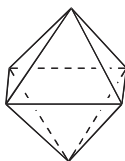


But, does not arrangement (b) also have more repulsions between the anions?



Yes, but usually the attractions outweigh the repulsions because the anions are closer to the cation than they are to each other. However, there are arrangements that force the anions very close to one another and the repulsions then begin to outweigh the attractions.

The **number of nearest neighbor anions surrounding a cation** is called the cation's **coordination number**. The same is true for an anion. Thus, the coordination number in arrangement (a) above is 4 and in (b) it is 6. As we have seen before, the geometrical figure adopted by the anions in (a) is called a tetrahedron because the geometric figure has four sides. (Many of the words used to describe structures have Greek or Latin origins. The ending *-hedron* comes from the Greek meaning “seat” or, more aptly, “face.”) The geometrical figure in (b) is an octahedron because it is 8 faces. Be sure to take a close look at the octahedron redrawn below, because it is a common polyhedron.



How many corners and how many faces are there in an octahedron?



6 corners and 8 faces.

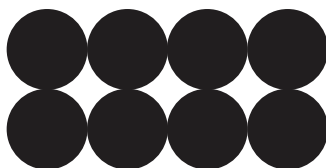
2.1 CLOSEST PACKING OF IONS

Because it is generally favorable to keep the distance between the cation and anion as small as possible, ions frequently pack together as closely as possible. These closest-packed arrangements are very important in understanding the structure of solids.

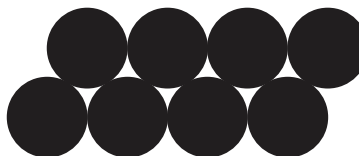
We will first consider the most efficient way to pack spherical objects, such as ping-pong balls.



Which of the arrangements of spheres shown below is the most efficient use of space (and therefore makes the objects as close as possible)?



(a)



(b)

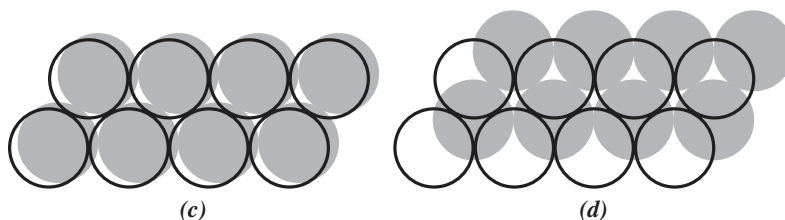


Arrangement (b) makes the most efficient use of space.

The arrangements (a) and (b) represent just one layer of spheres. We must now add another layer on top of (b).



Which of the following arrangements provides for the closest contact of spheres?
Note: The “empty” spheres are sitting on top of the bottom layer.



In case you need to look at these two from a different perspective, here is a side view:



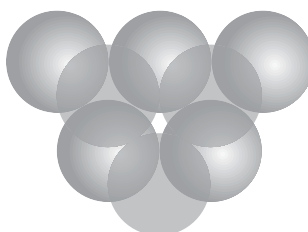
Arrangement (d). Arrangement (c) places each sphere in the second layer directly above a sphere in the first layer. That is, (c) has identical layers placed one above the other. Arrangement (d) places the spheres of the top layer in the depressions of the bottom layer. It therefore uses the space available most effectively and brings the spheres in closer contact to one another.

2.1.1 The Holes Between the Layers

Before we go on to add another layer of close-packed spheres to arrangement (d), let us look more closely at the voids (empty spaces) between the two layers of spheres.



In the representation below, the darker spheres are on top of the lighter spheres. Can you find two different types of voids between the layers?





In the diagram below, **x** marks two identical voids. Each of these “holes” is surrounded by four spheres, three on the bottom layer and one from the top layer. These holes are called tetrahedral holes because the spheres surrounding each hole are located at the corners of a tetrahedron as shown in Figure 8 (with the spheres moved apart somewhat to make the void more obvious). The tetrahedral shape has been emphasized by connecting the spheres with lines.

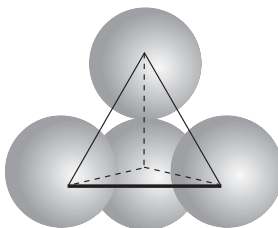
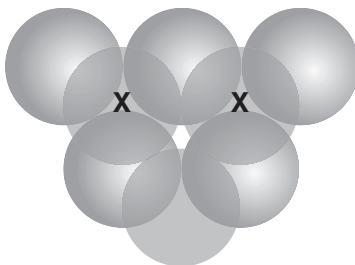


Figure 8 The tetrahedral hole.

The other kind of hole between the two layers is shown in Figure 9.

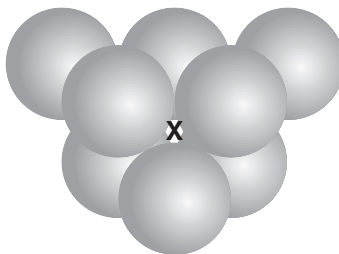


Figure 9 The octahedral hole. Looking down through two layers.

Notice that the void shown in Figure 9 is located between three spheres in the top layer and three in the bottom layer. Figure 10 shows a side view of just the six spheres spread apart to better show the void.

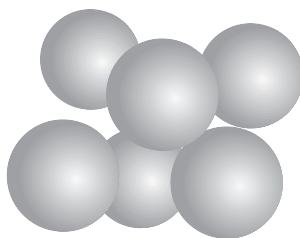


Figure 10 An expanded side view of the octahedral hole.

The same view is shown again in Figure 11 with the spheres in the top layer designated with a **t** and the ones in the bottom layer with a **b**. Lines are drawn between adjacent spheres and the octahedral shape of the spheres can be seen:

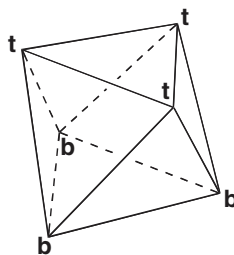


Figure 11 Another view of the octahedral hole. Spheres in top and bottom layers are designated **t** and **b**, respectively.

It is more common to see the octahedron as shown in Figure 12, where the polyhedron in Figure 11 is tilted up until two spheres from the top layer and two from the bottom layer are perpendicular to the plane of the paper.

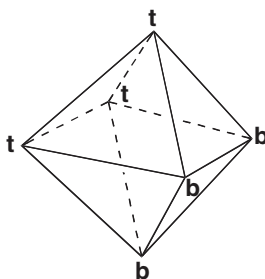


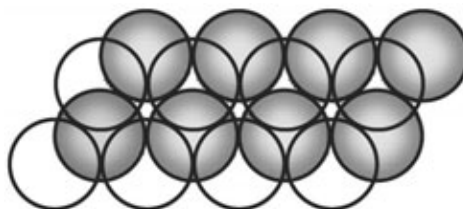
Figure 12 The more conventional view of the octahedron.

2.1.2 Stacking Sequences

We have established that there are two different types of voids between the spheres of two adjacent layers of closest-packed spheres. We are therefore ready to add another layer of closest-packed spheres to our stack.



Take a careful look at the two-layer stack shown below and see if you can determine that there are two ways to position the third layer.



There are two ways to position the third layer. In the first, the spheres are stacked directly over the position of the spheres in the bottom layer, as shown in Figure 13, where the third layer is shown with dotted circles (which are directly above the spheres in the first layer).

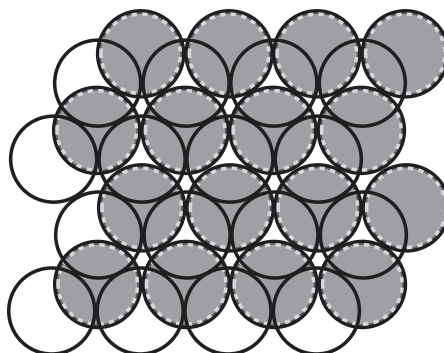


Figure 13 AB stacking of spheres (hexagonal closest packing). The bottom layer is shown as solid grey spheres, the middle layer as empty circles, and the top layer as dotted circles with a grey fill.

Or, the third layer can sit directly over the depressions in the bottom layer, as shown in Figure 14.

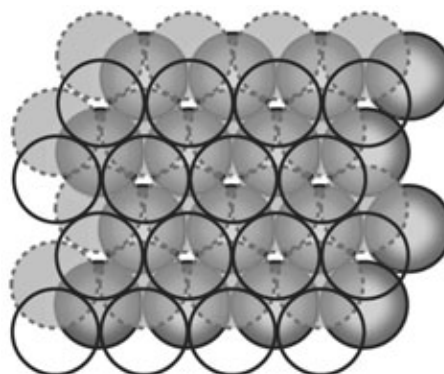


Figure 14 ABC stacking of spheres (cubic closest packing). The bottom layer is shown as solid grey spheres, the middle layer as empty circles, and the top layer as dotted circles with a grey fill.

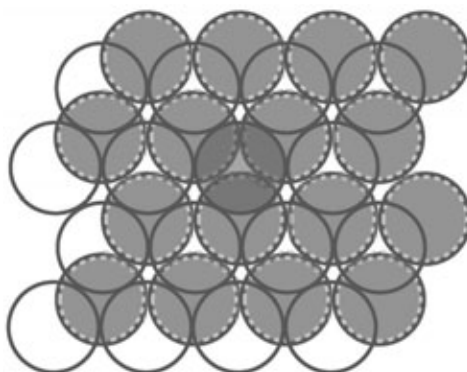
The first sequence of layers (Figure 13) is sometimes referred to as AB packing, which indicates that every third layer has exactly the same orientation as the first layer. Of course, as the three-dimensional solid is built up the layers repeat ABABAB . . . The second sequence of layers (Figure 14) is referred to as ABC packing to indicate that every fourth layer is the same as the first. So the solid has the sequence ABCABC . . .

These diagrams are difficult to visualize and require some effort to understand the difference between the two packing schemes. There is no difference in utilization of space; both schemes make equally effective use of space. However, there is a difference in geometry. The AB sequence has a different symmetry than the ABC sequence. To emphasize this difference, the former is called **hexagonal closest packing**; the latter is **cubic closest packing**. We will discuss the meaning of these terms later.

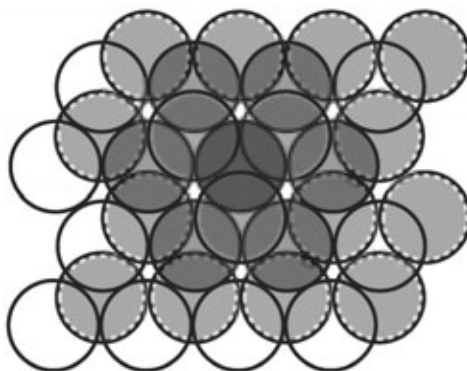
Before we apply these closest-packing schemes to ionic compounds, let us take a look at the number of equidistant nearest-neighbor spheres around a given sphere in both the hexagonal and cubic schemes.



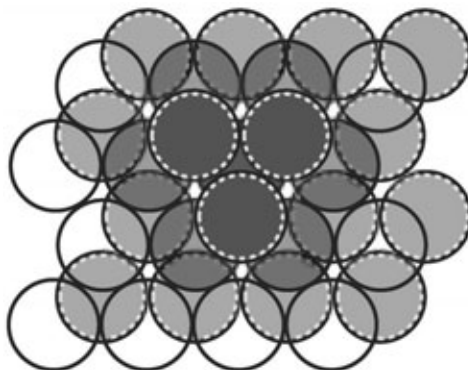
Take a look at the darker sphere in the middle layer of the hexagonal scheme shown below and count the number of nearest neighbors. (The top layer, shown as dotted circles with a grey fill, is difficult to distinguish from the bottom layer, shown as solid grey spheres.)



There are 12 nearest-neighbor spheres; six of these surround the sphere within its own middle layer, three surround it in the layer below, and three surround it in the layer above. In the diagram below, the six neighbors in the *same* layer are darkened.



In the diagram below, the three nearest neighbor spheres in the top layer are darkened. Of course, it is impossible to show the three nearest neighbors in the bottom layer using this top view of the packing.



Thus, the coordination number of each sphere is 12. The same is true for cubic closest packing.



Can you imagine what types of substances would crystallize in either of these closest-packing schemes? Hint: Because we have been talking about spheres of identical size, the substances are not ionic compounds. Compounds contain more than one element and therefore have more than one size atom.



The inert gases, which exist as closest-packed atoms in their solid elemental forms, and metals (sodium, copper, iron, and so on), which have no directionality in the bonding between the atoms and therefore behave as spheres in the solid state.

2.1.3 Closest Packing for Ionic Compounds

We can now tackle ionic compounds. In simple binary ionic compounds there are two types of spheres: the cation spheres and the anion spheres. The cation spheres are almost always smaller than the anion spheres. The problem, then, is how do we pack two sets of spheres that are of different sizes and try to maximize the coordination number of each ion so that the electrostatic attractions can be maximized? For many compounds the answer is relatively simple. The *anions are larger* and can be arranged in a closest-packed arrangement—either the AB (hexagonal) or ABC (cubic) scheme.



If the anions are closest packed, where do the cations go?



In the voids between the anions. The cations can go either into a tetrahedral void or an octahedral void.

Although it may not be obvious from our diagrams, the tetrahedral and octahedral voids are different in size. The octahedral void has six spheres touching one another at the corners of an octahedron, whereas the tetrahedral void is surrounded by only four spheres. Without doing some simple geometrical calculations, we can get an idea of the relative size of the two voids by observing that in a tetrahedron the void is enclosed by triangles of spheres (Figure 15 (a)) whereas, in an octahedron, the void is bound by a square (Figure 15 (b)).

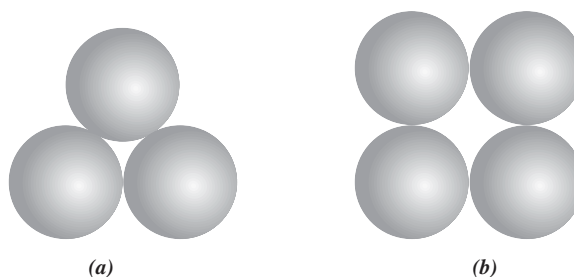


Figure 15 A part of the spheres enclosing tetrahedral (a) and octahedral (b) voids.

Notice that to complete the tetrahedron, we need just add one sphere above the center of the triangle in Figure 15 (a). To complete the octahedron we must add one sphere above the center of the square and one below the center in Figure 15 (b). These diagrams show that the void in the octahedron contains more empty space.



What factor do you suppose determines what type void the cation will occupy?



The size of the cation relative to the size of the anion.

If the cation is fairly small it will fit more easily into the tetrahedral holes; if it is larger it will occupy the octahedral holes.

The ideal size of the cation *relative to the size of the anion* for each of the voids can be determined by trigonometry. For example, a cation will fit snugly into an octahedral void if it is 0.41 times the size of the anion. If it is significantly larger than that, it may not be possible to fit the cation into the closest-packed array. This is the case for compounds such as cesium chloride, where the cation has an ionic radius of 1.67 \AA and the anion has a radius of 1.84 \AA (thus, the ratio is 0.91). In this solid, the chloride ions “open up” to form the simple cubic packing shown in Figure 16.

Notice that the chloride ions are not closest-packed, but instead are stacked in a square arrangement within a layer and in a neat cubic arrangement in 3-dimensions. This means that the voids between the layers are cubic, with eight chloride ions forming the corners of the cube. The large cesium ion occupies these voids.



Can you see what factor, other than size, may favor this type of packing, even though it is not closest packing?

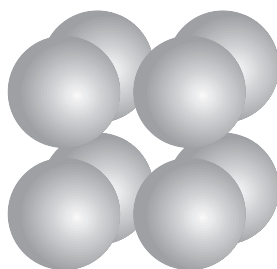


Figure 16 Simple cubic packing.



The greater number of attractions between the cation and the anions. The coordination number of the cations (and the anions) is eight and there are therefore eight nearest neighbor anions to which the cation is attracted.

But, you might ask, is it not true that the solid will always maximize the electrostatic interactions to make the potential energy as low as possible? And, if that is the case, why do not all compounds use this type of packing? To answer these questions, imagine that we have a very small ion occupying the cubic void in the cesium chloride structure (see Figure 17).

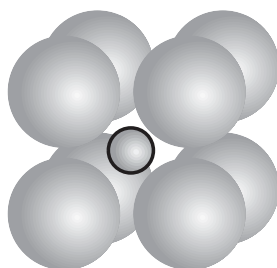


Figure 17 Small cation occupying the cubic hole in the CsCl structure.



What happens to the anions in this case?



The anions can get closer because the cation in the center of the void is not sufficiently large to keep them “opened up.” As the anions get closer, the repulsions between them increase and the potential energy goes up (that is, the compound becomes less stable). It then becomes energetically more favorable for the compound to adopt an arrangement that has fewer anions around the cation. Both the repulsions and attractions will decrease, but the decrease in the repulsions will be greater and the new closest-packed arrangement will be more stable.

The relationship between structure and the relative size of the cation and anion was summarized by Pauling (1960): “A coordinated polyhedron of anions is formed about each cation, the cation-anion distance being determined by the radius sum and the ligancy (coordination number) of the cation by the radius ratio.”

2.1.4 Relationship of Formula to Occupation of Voids

In order to analyze the structure of ionic compounds more carefully we need to know the number of tetrahedral and octahedral voids in the closest-packed structures. Figure 18 shows all of the tetrahedral voids surrounding one sphere between two layers of closest-packed spheres. Of course, each of these voids is shared by four spheres.

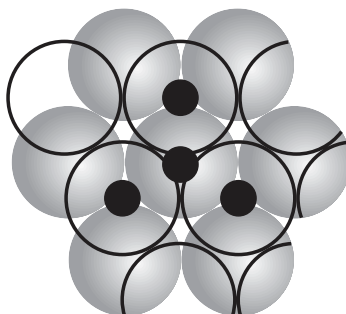


Figure 18 Tetrahedral holes surrounding one sphere.



On average, then, how many voids are there per sphere in the diagram?



One. Each void is shared by four spheres, but there are four voids per sphere.

Figure 18 shows only two adjacent layers of closest-packed spheres. In order to determine the total number of tetrahedral voids per sphere, we must also consider the layer below the sphere in question. This layer is just like the layer above the sphere (imagine hexagonal packing, so that the layer below looks just like the layer shown with the empty circles) and contains another four voids around the sphere. Thus, the total number of tetrahedral voids per sphere is two. The same sort of analysis shows that there is one octahedral void per sphere.

Thus, regardless of the type of closest packing, there are two tetrahedral voids and one octahedral void per sphere (anion).



If a solid contains closest-packed anions (X) and all of the octahedral holes are filled with cations (M), what is the formula of the solid?



MX. There is one cation per anion.



If an ionic compound has the formula MX_2 and the cations occupy the octahedral voids, what fraction of the octahedral voids are occupied?



One-half.



What is the formula of a compound that has closest-packed cations (not usually the case) and all of the tetrahedral voids filled with anions?



MX_2 . Fluorite (CaF_2) is an example of a solid that can be described as closest-packed cations with anions in the tetrahedral voids (see page 78 for another description of the structure of fluorite). There are two anions per cation.

Chapter 3

The Symmetry of Crystals

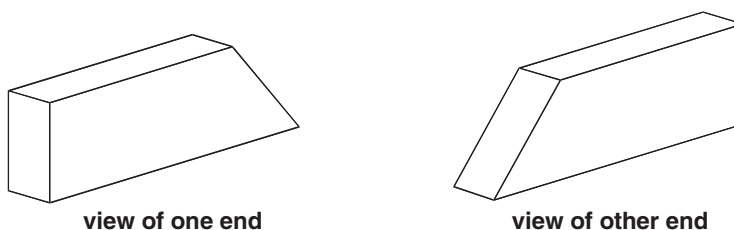
Before we continue our discussion of the packing of ions we must examine one of the most important characteristics of compounds: the symmetry of the crystals that they form. Consider the crystals in Figure 19.

The crystals of wulfenite appear to be shaped like barrels with square sides; crystals of vanadinite have a hexagonal form; the crystals of the magnetite specimen are cubic. These differences are a result of differences in the compounds at the atomic level; that is, they are produced by the particular arrangements of the atoms. Those arrangements are reproduced as the crystal grows.

These differences in crystal shape are described in terms of the symmetry characteristics or elements that are present in the crystal. We will now take a look at these symmetry elements.

3.1 SYMMETRY ELEMENTS

First, consider the block of wood shown below:



At one end the block is squared off; at the other end it is sawed at an angle.



Certainly, this is not a very symmetric object. Does it have any symmetry?



The block has a **plane of symmetry**; that is, an imaginary plane that cuts through the block as shown on page 43. The part of the block on the right side of the plane is exactly the same as that on the left side. In fact, we could cut

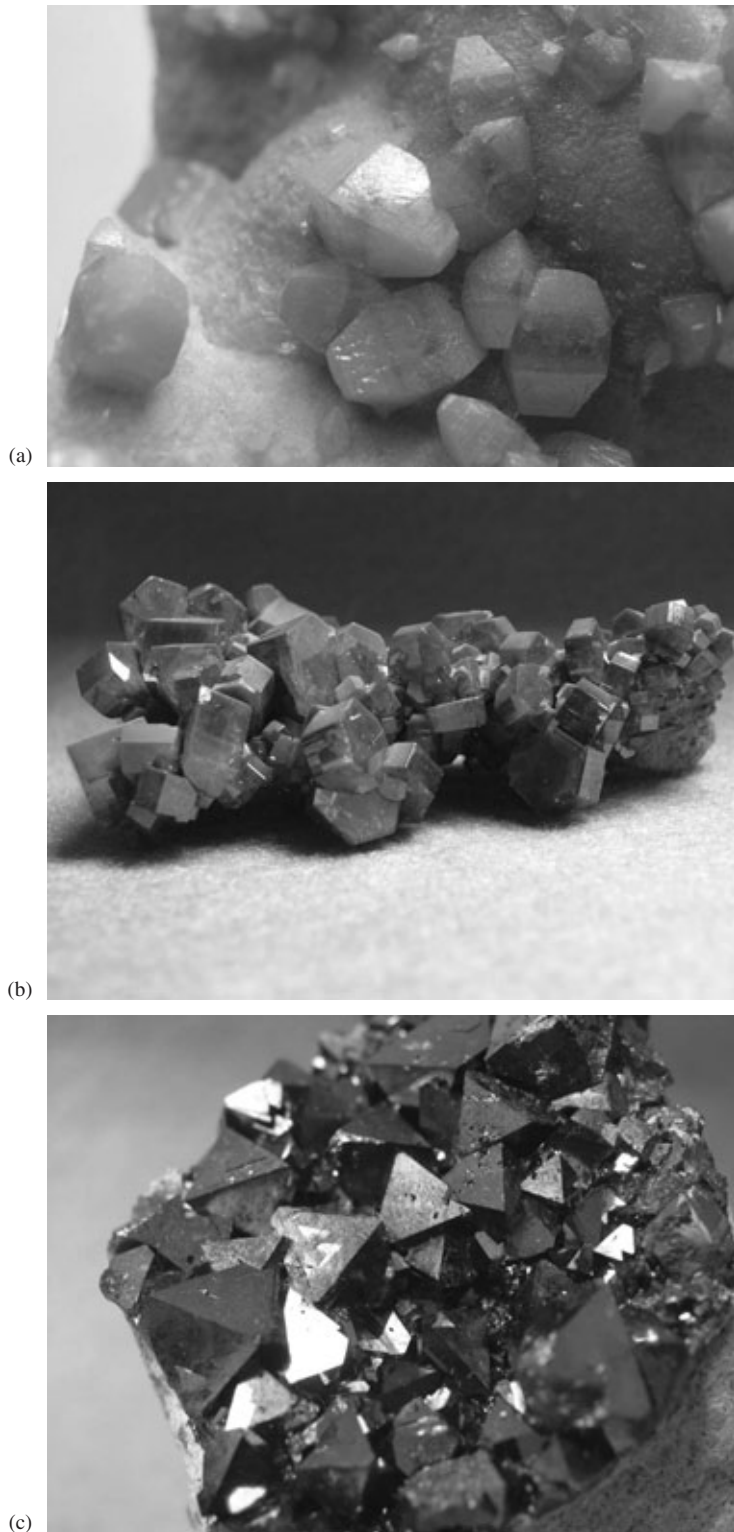
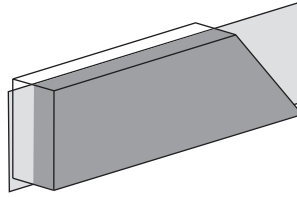
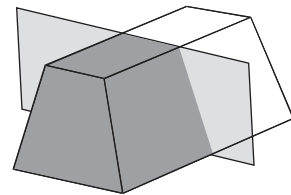
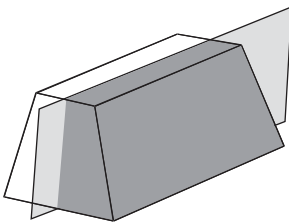
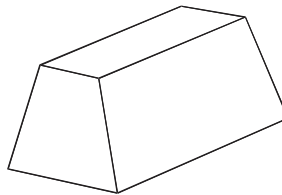


Figure 19 Crystals of (a) wulfenite (Los Lamentos, Chihuahua, Mexico), (b) vanadinite (Mibladen, Morocco), (c) magnetite (Mina Huaguino, Potosi, Bolivia).

the block through the plane and produce two thinner blocks with the same symmetry.



Can you find the two planes of symmetry in the object shown below? Each end of this block is identical and shaped like a regular trapezoid, which has two parallel sides with equal angles at the other two sides.

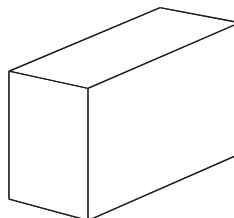


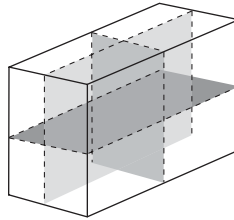
Notice that each plane slices the block into two identical halves.

Another way to view these planes is as **mirror planes**. If the plane were a mirror, the image seen in the mirror would be the image of the object on the other side of the mirror.



Sketch the planes for the following block:

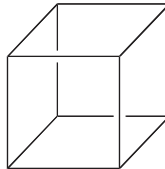




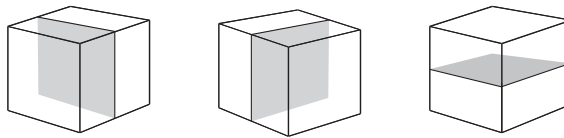
There are three planes.



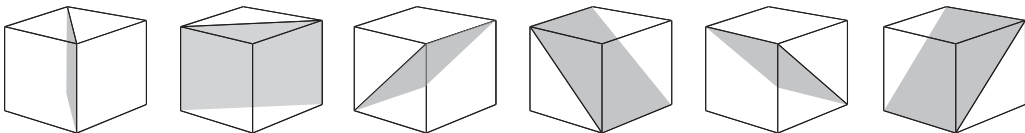
Now determine the planes in a block with a great deal of symmetry—a perfect cube.



Here is one set of mirror planes:



There are also planes that cut across the diagonal:



Now we are ready for an **axis of symmetry**. If we place a rod through the center of the rectangular block in Figure 20 we can rotate the block through 180° and the new orientation will look the same as the original orientation. In fact, if you close your eyes while a friend does the rotation you would be unable to tell whether the rotation had

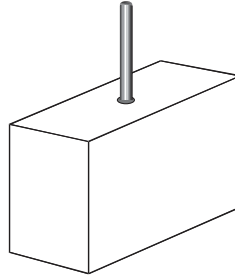


Figure 20 An axis of symmetry.

actually occurred, unless the block was marked in some way. In Figure 21 we show the block with a small dot on the top, followed by clockwise rotation of 180° , and then further rotation of another 180° to bring the block back to its original position.

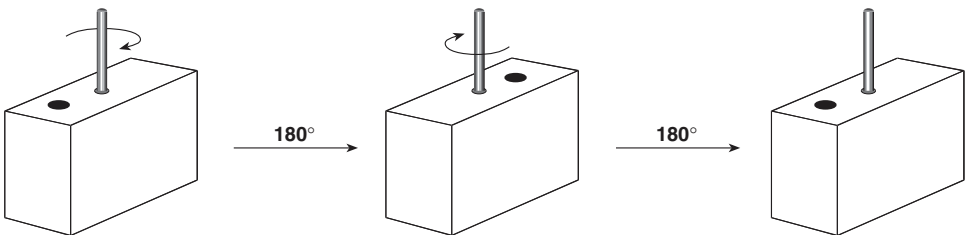


Figure 21 A two-fold axis of rotation. If the marker dot were not present, the orientation of the block after a rotation of 180° would be indistinguishable from its original state.

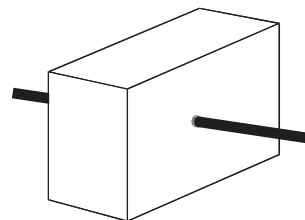
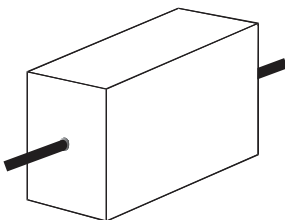
This rod is called an **axis of rotation**. In this case it is called a two-fold axis because we must rotate the block twice before it returns to its original position. Or, to put it another way, rotation by $360^\circ/n$, where $n = 2$ produces an equivalent, or indistinguishable, orientation. n is also called the **order** of the axis. Thus, a four-fold axis, which requires rotation by $360^\circ/4 = 90^\circ$, has an order of 4.



Are there other rotational axes in the block?

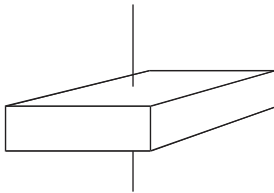
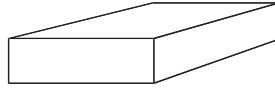


Yes, the two shown below:

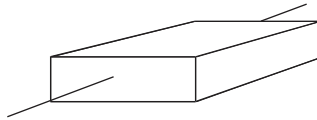




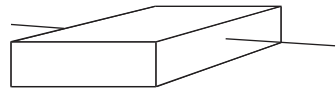
What type of rotational axes are present in the square block shown below?



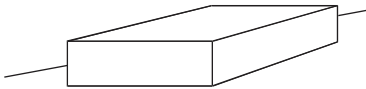
4-fold



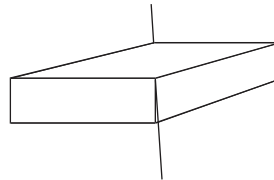
2-fold



2-fold



2-fold through corner



2-fold through corner

The four-fold axis is the highest order (n is largest) axis and is considered the principle axis. The highest order axis plays an important role in distinguishing one crystal system from another.



What is the principle rotational axis in the crystals of vanadinite shown in Figure 22?



The six-fold axis. Careful examination of the crystals shows that they do not have perfect hexagonal symmetry. Compare for example, the crystal in the lower part of the figure with the smaller one in the middle and the larger one at top. This is a result of the fact that different faces of a crystal will grow at different rates, depending on conditions and the surroundings of the crystal. Generally, even in a distorted (non-perfect) crystal the symmetry will be clear. It will always be true that

the angles between equivalent faces of crystals of the same substance are constant.

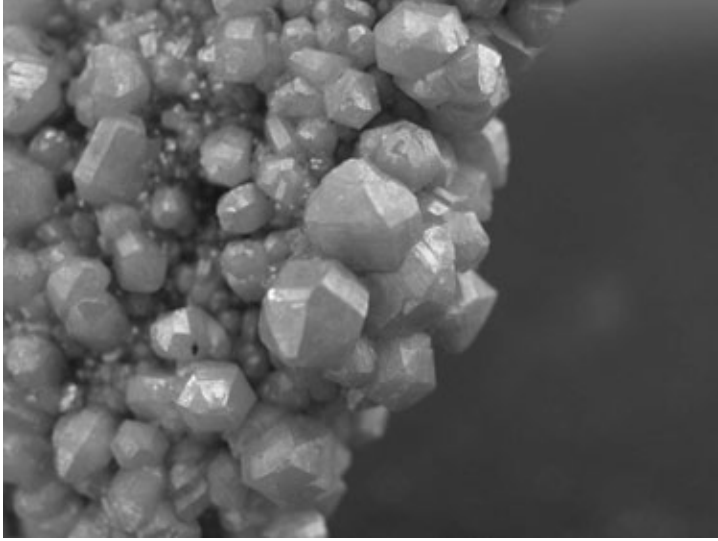
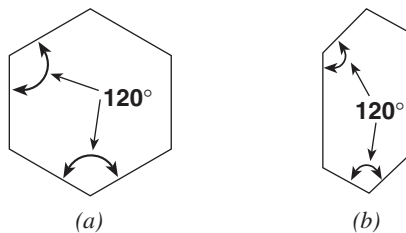


Figure 22 Vanadinite (J.C. Holmes Claim, Patagonia, Santa Cruz Co., Arizona).

This is known as Steno's law (Nicolas Steno, Danish scientist and priest) and is illustrated in Figure 23 for two different hexagonal crystals, one with a perfect hexagonal cross section, the other highly distorted.



Steno's Law

Figure 23 Illustration of Steno's law: the constancy of interface angles: (a) a regular hexagon; (b) a distorted hexagon.

The third symmetry element is the **inversion center**. A square contains an inversion center. The inversion center is always at the center of the object. If a line is drawn through the inversion center, a point on the line at any given distance from the center will have an equivalent, indistinguishable point the same distance from the center but on the other side of the line (see Figure 24).

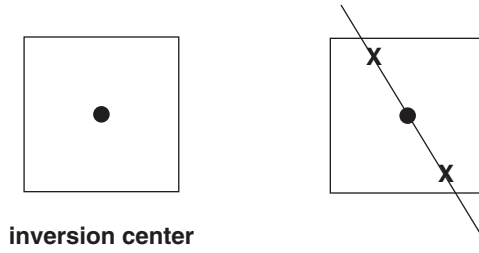
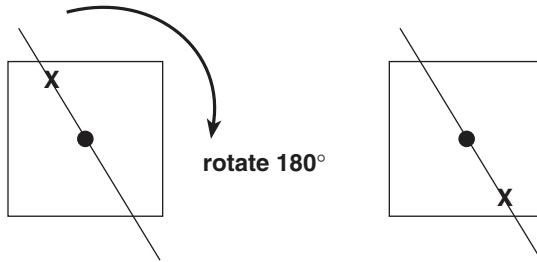
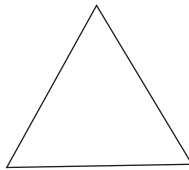


Figure 24 The inversion center.

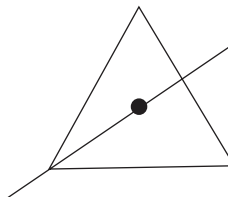
The two points (x) can be shown to be indistinguishable by rotation through 180° .



Is there an inversion center in an equilateral triangle?



No. A line drawn through the center and an apex does not intersect another apex at any distance from the center.



The final symmetry element is a rotation/inversion axis (or **rotoinversion axis** or **improper rotation axis**). (Here we are using the convention used by geologists. Chemists define the improper rotation axis as a rotation followed by a reflection through a plane at right angles to the axis.) This symmetry element is really a combination of the rotation axis and the inversion center. A tetrahedron has a four-fold rotation/inversion axis bisecting each edge and extending through the center of the tetrahedron (Figure 25).

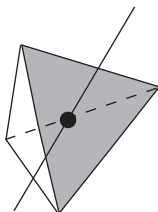


Figure 25 The 4-fold rotoinversion axis in the tetrahedron.

Figure 26 shows how the rotoinversion symmetry operation (an operation is the use of a symmetry element) regenerates the original orientation.

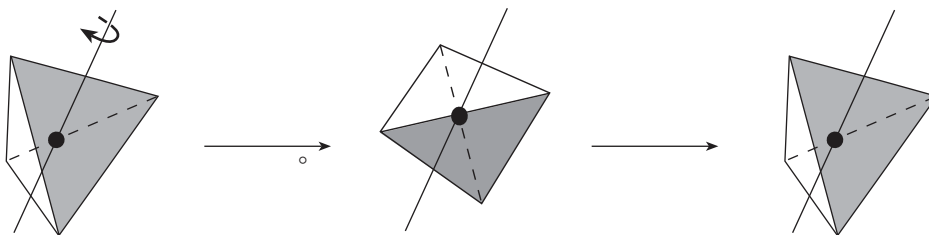


Figure 26 Rotation followed by inversion.

This sequence of operations is actually difficult to understand without the use of a mechanical model. Follow the position of apex 1 as you first rotate 90° clockwise around the axis and then invert the new position of 1 through the center of the tetrahedron. As you can see, an equivalent and indistinguishable (if the marker 1 were not present) orientation is produced by this set of operations.

In crystallography, the rotational axis, the plane of symmetry, and the rotoinversion axis are given special designations. Axes are designated by a number that indicates the order of the axis. A rotoinversion axis is given a number to indicate the order with a line above; for example, $\bar{4}$ (pronounced bar four) would indicate the axis shown above. Alternatively, this axis is designated with a minus sign; for example, -4 . A plane of symmetry is designated by the letter *m*.

3.2 HERMANN-MAUGUIN NOTATION (POINT GROUPS)

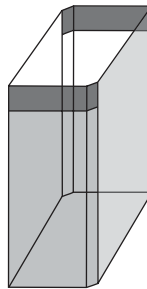
A set of symbols, called the **Hermann-Mauguin** (German crystallographer, Carl Hermann, and French mineralogist Charles-Victor Mauguin) designation, is used to unambiguously designate the symmetry of a crystal. For example, the designation 222 indicates

that there are three two-fold axes at right angles to one another. The designation $2m$ indicates that there is one two-fold axis and a mirror plane that includes the axis in its plane. The designation $2/m$ (read 2 over m) indicates that there is a two-fold axis and a mirror plane that is perpendicular to the axis.

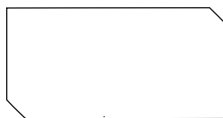
The complete designation of the symmetry of a crystal requires the correct assignment of axes and identification of the symmetry elements. There are a total of 32 different combinations of symmetry elements. Each of these has a unique Hermann-Mauguin notation or **point group** and is called a **crystal class**. The 32 crystal classes can be divided into six **crystal systems**. We will try to give you an appreciation of point groups and crystal classes, but our main emphasis will be on the more general crystal systems.



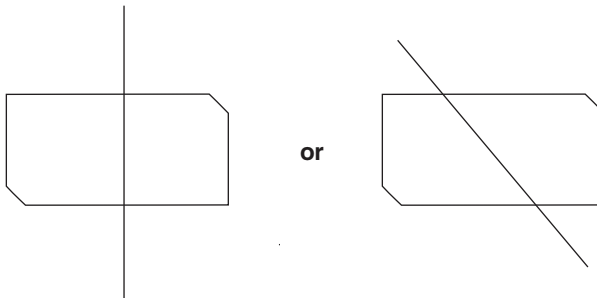
Take a careful look at the object below (notice that two of the top edges have a dark band), locate all of the symmetry elements, and give the point group classification of the object.



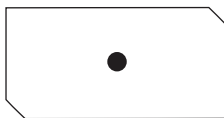
A look at the top view (with the figure rotated 90° clockwise)



shows that there are no mirror planes such as



There is also no horizontal mirror plane and no center of symmetry because of the presence of the black band. There is a two-fold rotational axis, indicated as a dot to designate protrusion toward the reader.



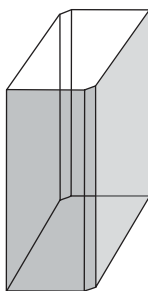
Rotation of 180° brings one corner over to the opposite corner and produces an equivalent and indistinguishable (without the label) orientation.



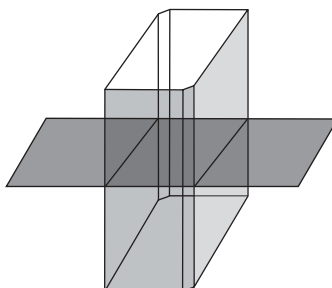
The correct Hermann-Mauguin designation is therefore 2.



Identify all of the symmetry elements and give the Hermann-Mauguin classification for a similar object without the band at the top.



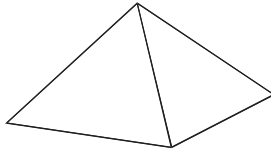
The top view is the same as shown before and therefore the object has a two-fold axis and no vertical mirror planes. Because the band has been removed, it now also has a horizontal mirror plane, as shown below, and a center of symmetry (inversion center):



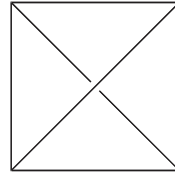
The symmetry designation is therefore $2/m$.



Give the symmetry designation of the following pyramidal crystal:



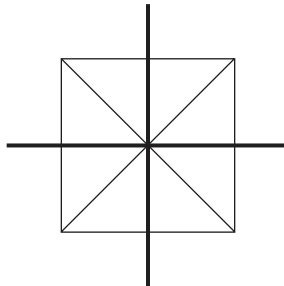
side view



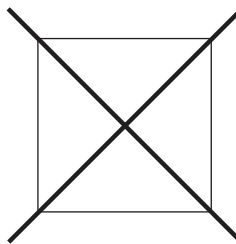
top view



4mm. The crystal has a four-fold axis and two sets of vertical mirror planes. One set cuts the crystal in halves as shown below:



The other set cuts the crystal along its edges:



Notice that the two planes within a set are converted into one another by rotation about the four-fold axes. That means that if we draw one mirror plane and the crystal has a four-fold axis, the other plane must exist. The four-fold axis does not convert one set of planes into the other set.

3.3 CRYSTAL SYSTEMS

The symmetries of crystals can be divided into six basic types or crystal systems (Table 6):

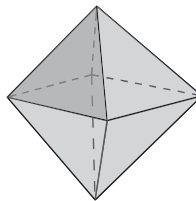
Table 6 The six crystal systems

Type	Symmetry
1. triclinic	no planes, and only a one-fold rotational axis or a one-fold rotoinversion axis
2. monoclinic	a mirror plane or a two-fold rotational axis or a two-fold rotational axis with a perpendicular mirror plane
3. orthorhombic	more than one perpendicular mirror plane, or three perpendicular two-fold rotational axes, or three perpendicular two-fold axes each with a perpendicular mirror plane
4. tetragonal	one four-fold rotational axis and, possibly, one or more mirror planes and/or two-fold rotational axes. The two-fold axes must be perpendicular to the four-fold axis.
5. hexagonal	one six-fold or three-fold rotational axis and, possibly, one or more mirror planes and/or two-fold rotational axes. The two-fold axes must be perpendicular to the 6-fold axis.
6. isometric (cubic)	four three-fold axes that intersect at a diagonal with three four-fold or two-fold rotational axes or mirror planes. The three four-fold or two-fold rotational axes are mutually perpendicular.

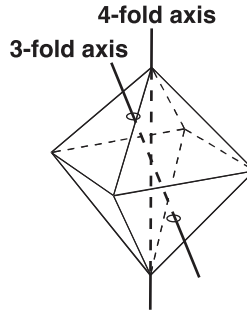
The symmetry increases from the triclinic system to the cubic system.



Identify the crystal system to which the following octahedral crystal belongs:



Isometric. The crystal has three four-fold rotational axes that run from an apex to its opposing counterpart and four three-fold axes that run from the center of each face to the center of the opposite face. One of the four-fold axes and one of the three-fold axes are shown on the next page:



In order to give the *point group designation* of this crystal, it is necessary to identify all of the symmetry elements in the crystal and to understand the relationship of these elements to the crystallographic axes.

3.3.1 Crystallographic Axes

For each crystal system, three axes (four in the hexagonal system) are assigned that coincide with the symmetry axes or are perpendicular to mirror planes. In the isometric system, these axes coincide with the four-fold rotation or rotoinversion axes or the two-fold rotational axes. They are mutually perpendicular and are labeled a_1 , a_2 , and a_3 , rather than the conventional labels of a , b , and c , because they are identical in every respect other than orientation. By convention, the positive end of the a_1 axis is toward the reader, the positive end of the a_2 axis is to the right in the plane of the paper, and the positive end of the a_3 axis is up in the vertical direction. The axes are shown for the octahedron in Figure 27.

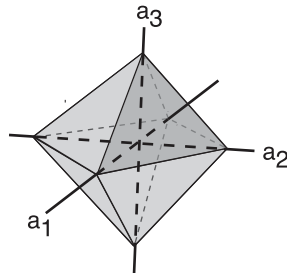


Figure 27 The crystallographic axes for the isometric system shown for an octahedron.



Carefully identify all of the symmetry elements of the octahedron in Figure 27.



Each crystallographic axis is a four-fold rotational axis and each axis has a mirror plane perpendicular to it that contains the other two axes. There are four three-fold rotoinversion axes that run through the top faces of the octahedron and emerge through the opposing bottom faces. These intersect the crystallographic axes at an angle of $54^\circ 44'$. There is a center of symmetry and there are six two-fold axes that extend from one edge to the opposing edge and bisect

two of the crystallographic axes. Perpendicular to each of these two-fold axes is also a mirror plane. There are also three mirror planes each of which cuts through four edges and two axes (there are a total of 12 edges in an octahedron).

In the isometric system, the first part of the point group designation indicates the order of the rotational or rotoinversion axis at the a_1 axis (and therefore also at the a_2 and a_3 axes). The second number refers to the axis along the diagonal and is always 3 or $\bar{3}$ (-3) in the isometric system. The third part of the designation refers to any symmetry elements—a two-fold axis, a mirror plane, or a two-fold axis with a perpendicular mirror plane ($2/m$)—between the edges of the cube (bisecting the crystallographic axes).



Give the point group designation for the octahedron.



$4/m\bar{3}2/m$. This point group has the greatest number of symmetry elements of any of the isometric classes. The class with the most symmetry is sometimes referred to as the **holohedral class** (from the Greek *holos* meaning complete).

In most of the other crystal systems, the axis with the highest order rotational symmetry is designated the z -axis, which is more commonly called the c -axis. The order of this axis is given first in the point group designation. In the monoclinic system, the b -axis is taken as the two-fold axis or as perpendicular to the mirror plane.



Examine the crystal in Figure 28 and give the point group designation.

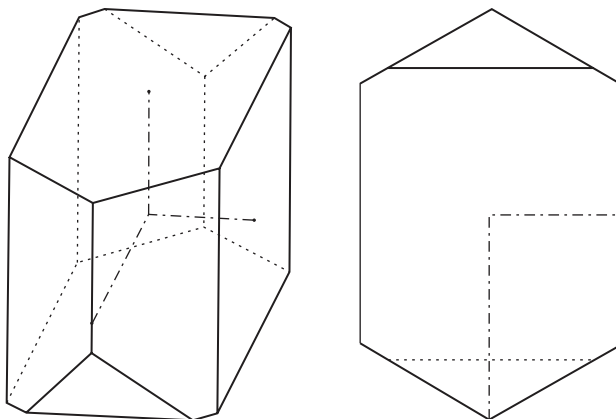


Figure 28 An orthoclase crystal. Top view on the right.



$2/m$.

In the orthorhombic system, the two-fold axes are taken as the crystallographic axes. If there is only one two-fold axis it is designated the c -axis. The symmetry elements are listed in order of the three axes— a , b , c .



Examine the crystal in Figure 29 and give the point group designation.

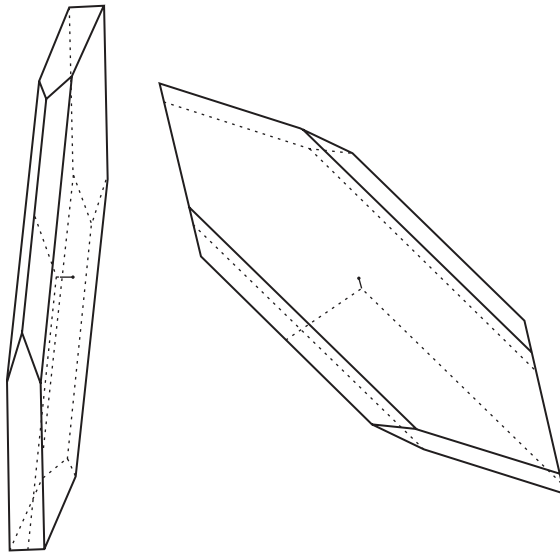


Figure 29 A barite crystal. A side view on left, top view on right.



$2/m2/m2/m$

In the hexagonal system the single 6 , $\bar{6}$, 3 , or $\bar{3}$ axis is defined as the c -axis and three additional axes in a plane perpendicular to the c -axis coincide with two-fold axes or planes. These axes are 120° apart and are designated a_1 , a_2 , and a_3 because the operation of the principal rotational axis makes them identical except for orientation. By convention, the a_2 axis is in the plane of the paper to the reader's right hand. The first part of the point group designation gives the symmetry of the c -axis and any plane perpendicular to it, the second part provides the symmetry along the a -axes, and the third part indicates symmetry elements that bisect the angles between the a -axes. If the symmetry of the c -axis is 3 or $\bar{3}$, the crystal is said to be in the **trigonal** subsystem of the hexagonal system.



Examine the crystal in Figure 30 and give the point group designation.

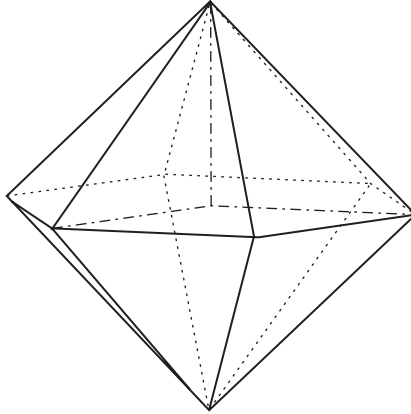


Figure 30 A crystal of beryl (not a typical habit for beryl).



$6/m\bar{2}/m\bar{2}/m$.

Chapter 4

The Structure of Some Simple Closest-packed Compounds

4.1 SYMMETRY OF THE AB AND ABC CLOSEST-PACKED ARRANGEMENTS

We return now to our discussion of the difference in symmetry between the hexagonal (AB) and cubic (ABC) closest-packing arrangements. Take another look at just two layers (A and B) of the hexagonal closest-packing arrangement (Figure 31):

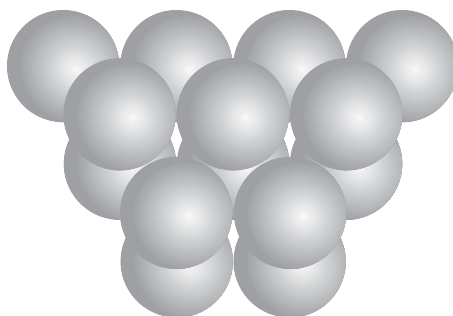


Figure 31 The hexagonal closest-packed arrangement of spheres.

A portion of this arrangement is redrawn in Figure 32, which shows the three-fold axis of symmetry extending down through the hole in the middle.

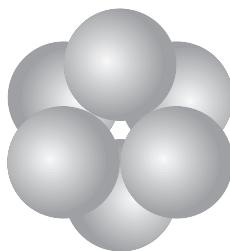


Figure 32 The 3-fold axis of symmetry in the hexagonal closest-packed arrangement.



Refer to Table 6 and determine the symmetry of this arrangement.



Table 6 reveals that a three-fold or six-fold principal axis is necessary for hexagonal symmetry.

The cubic symmetry of the ABC arrangement of spheres (cubic closest packing) is more difficult to visualize. A portion of four layers of the ABC arrangement is shown in Figure 33.

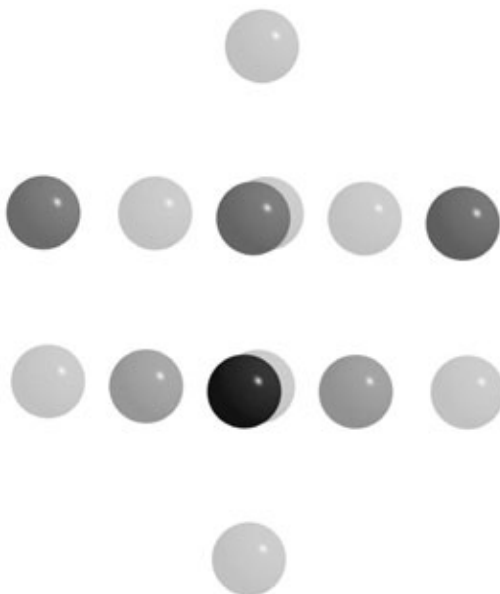


Figure 33 The ABC packing of spheres. The more intense the color of the sphere the closer in space to the reader. Unlike figure 31, this is a side view of four layers.

If we rotate this Figure, we begin to get a pattern that has a more symmetrical appearance and is shown in Figure 34 with a cube outline (two more spheres have also been added).

Because the spheres are present at the corners *and* at the center of each face, this is usually referred to as a **face-centered** arrangement.

4.2 THE UNIT CELL

By now we can see that the examination of a fairly large set of spheres (ions) is a bit tedious, and we begin to look for the smallest unit of atoms that represents the entire compound. This smallest unit must have the same elements of symmetry as the macroscopic crystalline material and it must repeat itself throughout the crystal. That is, it must be the building block used to form the entire crystal. This unit is called the **unit cell**.

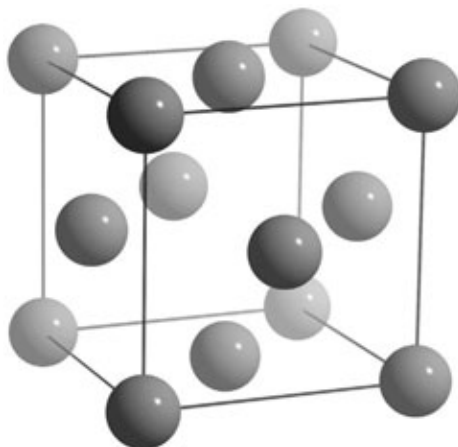


Figure 34 The cubic structure of the ABC packing of spheres.

In the pattern shown in Figure 35, the rectangle can be used as the building block to create the entire pattern.

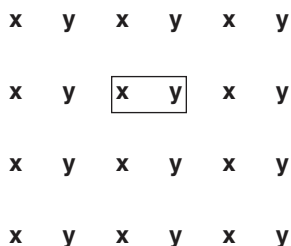
x	y	x	y	x	y
x	y	x	y	x	y
x	y	x	y	x	y
x	y	x	y	x	y

Figure 35 A possible unit cell for the pattern.

The shaded areas below represent the movement of the same rectangle in all four directions parallel to the edges of the block. Notice that when the block is moved there can be no space between blocks.

x	y	x	y	x	y
x	y	x	y	x	y
x	y	x	y	x	y
x	y	x	y	x	y

For example, the following is not a building block for the pattern:



because movement in all four directions does not fill all of the space of the pattern. On the other hand, there are a number of other building blocks or unit cells that could be chosen.

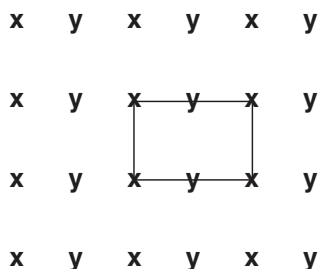


Figure 36 Another possibility for the unit cell.

The unit cell in Figure 36 encloses a quarter of each x and a half of each y . Notice that movement of it in all four directions will eventually reproduce the entire pattern. One other possibility for the unit cell in this pattern is shown in Figure 37.

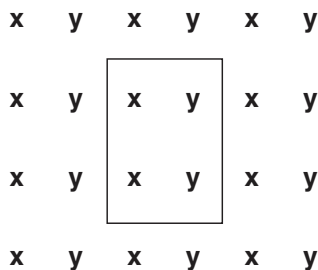


Figure 37 A third possibility for the unit cell.

This grouping of two x 's and two y 's and the space surrounding them will also reproduce the entire pattern.

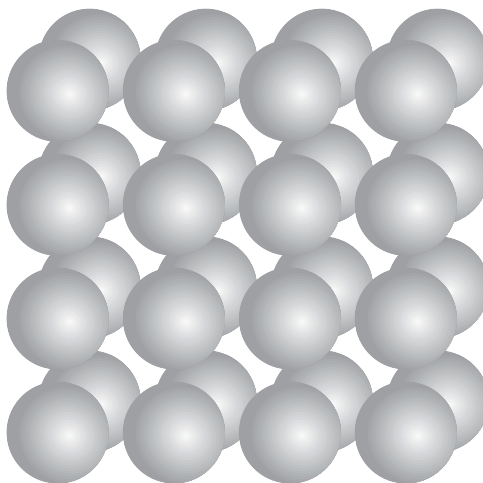
So, which unit cell should we choose? Usually, the simplest, most symmetric unit cell is favored. In this case, we should therefore favor the first (Figure 35).

We also need to be able to count the number of items (atoms or ions) in each cell. In Figure 35 there is clearly one x and one y per unit cell. In the second unit cell (Figure 36), the cell cuts the corner of each x , thereby taking a quarter of it. The cell includes half of each y . Thus, there are $4 \times 1/4 = 1$ x and $2 \times 1/2 = 1$ y . So both of these choices of unit

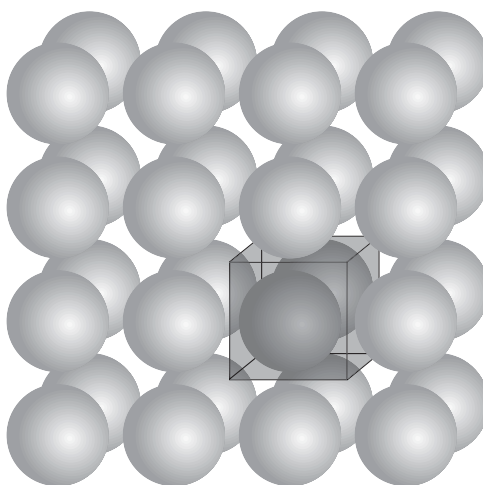
cells produce the same numbers of x and y . On the other hand, the last choice of unit cell (Figure 37) contains twice as many x 's and y 's ($2x$ and $2y$). In all cases, the ratio of x to y is the same (1 to 1). It is this ratio that determines the formula of the compound.



Can you provide at least one unit cell for the simple cubic packing shown previously?



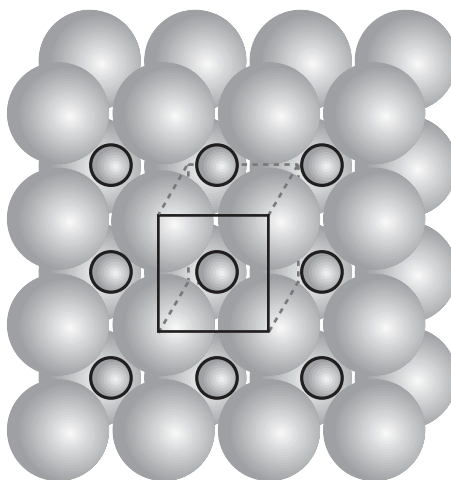
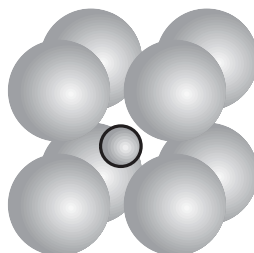
One possibility is a cube surrounding a sphere, as shown below:



By analogy with what we did in two dimensions, we can see that another choice of unit cell would include one-eighth of each of eight spheres at the corners of a cube. This is actually the preferred unit cell and is referred to as a simple cubic unit cell.



Shown below is the same view of the CsCl structure shown in Figure 17. Choose a unit cell for it.



This is essentially the same unit cell with a cation in the center and an eighth of a chloride ion at each of the corners of a cube. The front part of the cube extends through the center of the four front spheres surrounding the cation and back to the centers of the four rear spheres surrounding the cation.



Count the number of ions of Cs^+ and Cl^- in the unit cell.



One Cs^+ ion, and $1/8 \times 8 = 1 \text{ Cl}^-$ ion.

4.3 THE NaCl STRUCTURE

We return now to the NaCl structure, which contains sodium ions in the voids of a cubic closest-packed array of chloride ions. The cubic closest-packed array of ions was illustrated previously in Figures 14 and 34. The unit cell shown in Figure 38 is based on a face-centered arrangement of sodium ions, which is equivalent to the face-centered cubic structure of the chloride ions. The lines between adjacent ions in Figure 38 are not covalent bonds; they merely represent ionic interactions between adjacent ions.

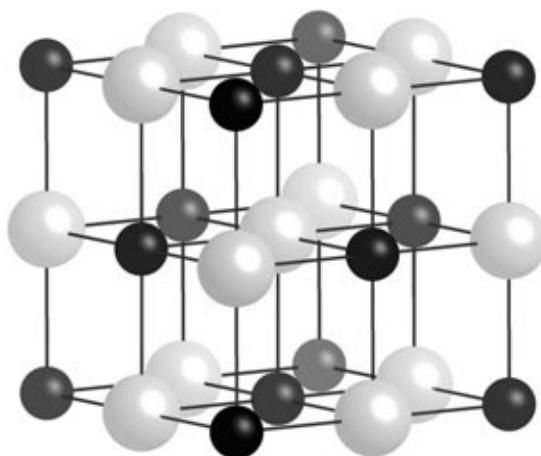


Figure 38 The unit cell of NaCl.



Examine Figure 38 and determine how many nearest-neighbor sodium ions surround the chloride ion at the center of the unit cell.



Six. One above the chloride, one below the chloride, and four in the middle horizontal plane.



Although all of the ions surrounding any one sodium ion are not shown, how many chloride ions must surround each sodium ion?



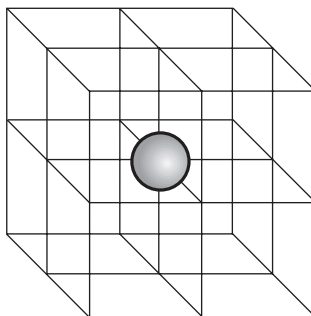
Six. There is a one-to-one ratio of sodium ions to chloride ions and therefore the coordination numbers of each must be the same. The coordination number of six for the sodium ion in NaCl should also be obvious because we know that the sodium ions are present in the octahedral holes of the closest packed chloride ions.



How many sodium ions and chloride ions are in the unit cell?

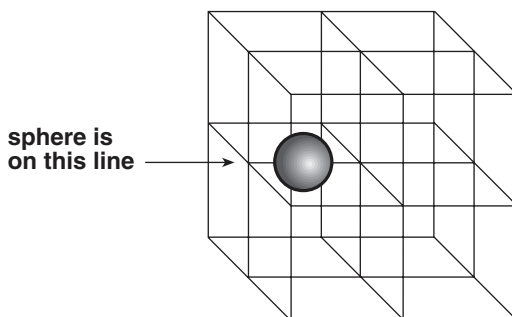


There are four sodium ions and four chloride ions. The sodium ion on a particular corner is shared by eight cubes. This is shown below, where a sodium ion is at the center of eight cubes, each of which represents a unit cell. Thus, each of the corner sodium ions contributes one-eighth of an ion to the unit cell. There are eight of these; thus, $8 \times 1/8 = 1$.



sphere shared by eight unit cells

The sodium ion on each face is shared by two adjacent cubes. Thus, each face sodium ion contributes $1/2$ to the cell. There are six of these; thus, $6 \times 1/2 = 3$. This gives a total of 4 sodium ions. The chloride ions can be counted in the same way. Notice that there is one complete chloride ion in the center of the cube and there are 12 chloride ions on the edges. The edge chloride ions contribute $1/4$ of an ion to the unit cell (see below). Hence, $12 \times 1/4 = 3$, giving a total of $1 + 3 = 4$ chloride ions.



sphere on edge, shared by four unit cells

Because this unit cell contains more than one of each ion, it may appear to be larger than the simplest unit cell. In fact, there are several other choices for the unit cell of NaCl, but the one shown in Figure 38 is preferred.

This cell contains four vertical planes of symmetry that run through the corners and middle, such as the ones shown in Figure 39. Figure 40 shows a three-fold axis.

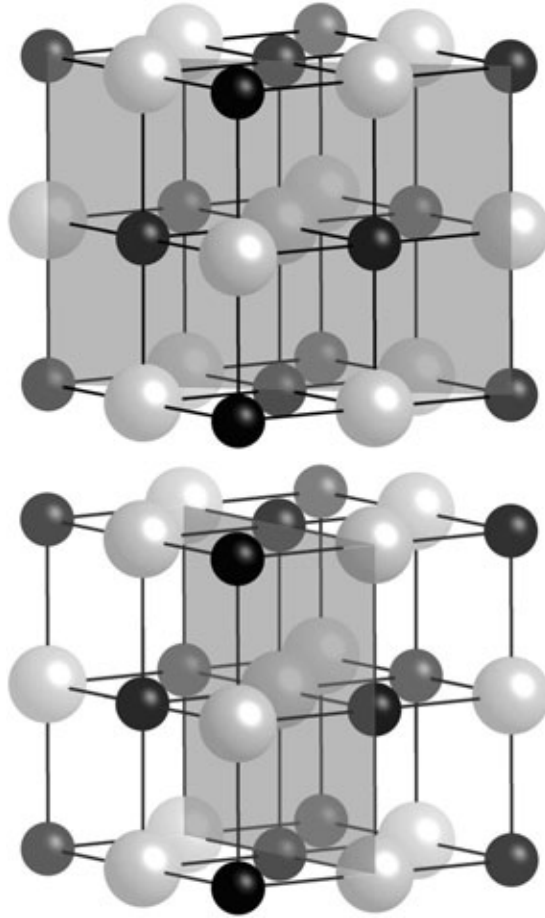


Figure 39 Two of the vertical planes in the NaCl unit cell.

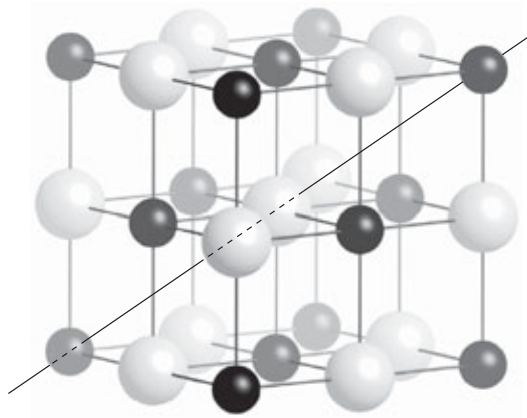


Figure 40 One of the 3-fold axes.

There is also a center of symmetry. Although it is probably not obvious, there are also three-fold *rotoinversion* axes coaxial with the three-fold axes (a hand-held model is almost essential to see this). The highest order axes are the three four-fold axes that run through the middle of each face. (The axis goes through the sodium ion at the center of the face in Figure 41 below.)

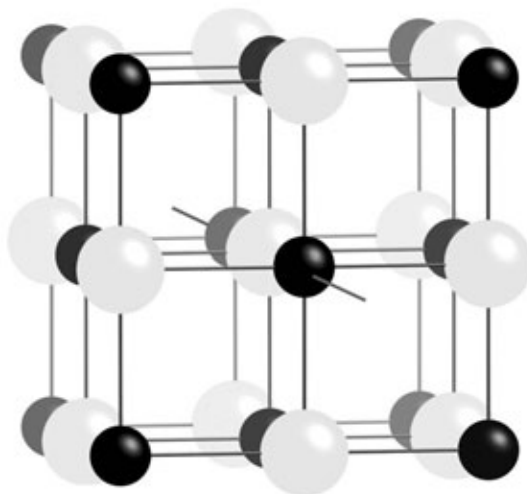


Figure 41 One of the 4-fold axes in the unit cell of NaCl.

The point group designation for the unit cell is $4/m\bar{3}2/m$.

4.4 THE SPHALERITE STRUCTURE

We now take a look at a common mineral, sphalerite. This mineral is also called zinc blende and the unit cell shown below is frequently referred to as the zinc blende structure. The larger spheres in Figure 42 are sulfide ions, the smaller ones are zinc ions.



Can you determine what type of unit cell this is?



Face-centered cubic.



What is the coordination number of the zinc ions and which voids do the zinc ions fill?



The coordination number is 4 and therefore the zinc ions fill tetrahedral sites.

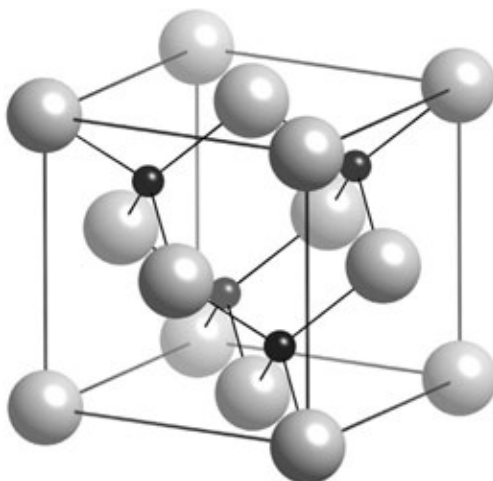


Figure 42 The unit cell of sphalerite, ZnS.



What percent of the available tetrahedral voids are filled by zinc ions?



Fifty percent. Remember that there are two tetrahedral and one octahedral voids per closest-packed sphere. The formula of zinc sulfide is ZnS and therefore there must be one zinc cation per sulfide anion. If there is one cation per anion, but two tetrahedral voids per anion, only one of the two voids can be filled.

Make sure that you can see that the sulfide ions are closest packed by taking a look at the view of the unit cell in Figure 43 with some of the sulfide ions removed.

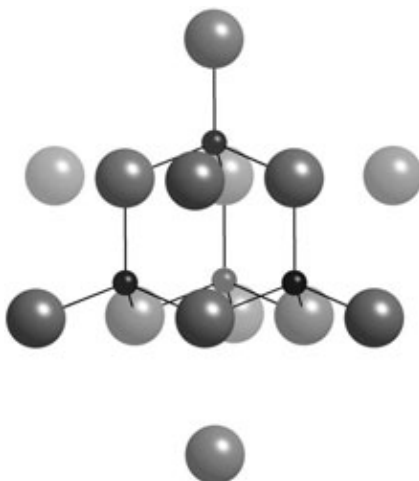


Figure 43 Layers of sulfide ions in sphalerite.



What type of packing—AB or ABC—do the sulfide ions utilize?



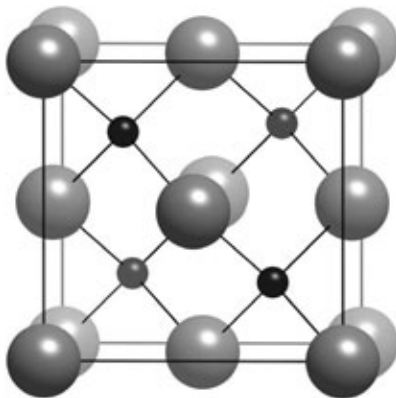
ABC. Notice that in Figure 43 there are six ions in the two middle layers, one in the top, and one in the bottom layer. The shading (darkness) of the bottom sphere shows that it is aligned with a sphere in the top layer. Hence, sphalerite is a face-centered, cubic closest-packed substance with the zinc cations located in the tetrahedral sites.



Can you determine if a unit cell of this substance has the same symmetry as the NaCl unit cell (which is also face-centered cubic)?



The front view of a face given below shows that the four-fold axis running through the center of each face for NaCl does not exist here. This is a result of the fact that the four zinc ions surrounding the center of the cell (there is no sphere at the center) are not at the same depth.



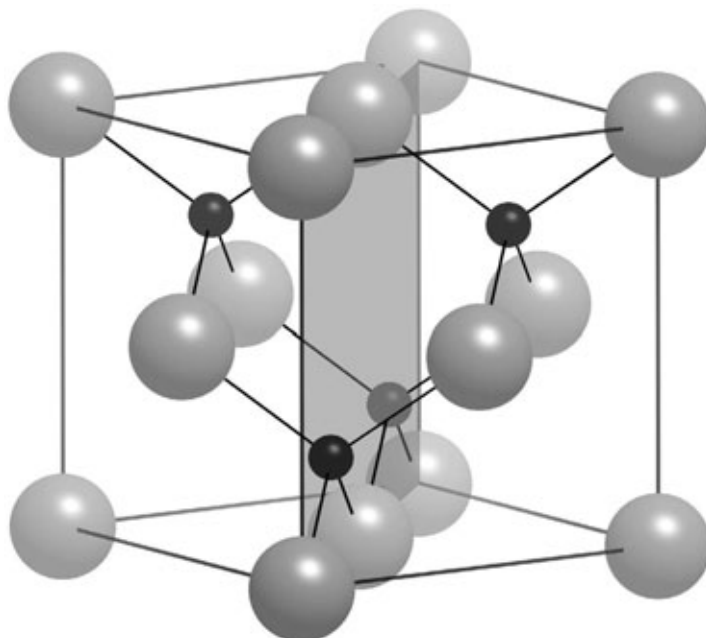
As indicated by the brightness of these ions, two are at the same level (from front to back), and the other two are farther back but at the same level. This means that there is a two-fold axis through the center of the face. There are also no vertical mirror planes that cut through the centers of opposite edges.



Are there any vertical mirror planes?



Yes, they extend through the diagonals as shown below:



Now look at the illustration above more closely. Perform a four-fold rotation about an axis through the center of the face and then an inversion through the center of the unit cell (it may be helpful to watch the zinc ions). You should observe that there is a four-fold rotation-inversion axis.



Is there a center of symmetry?



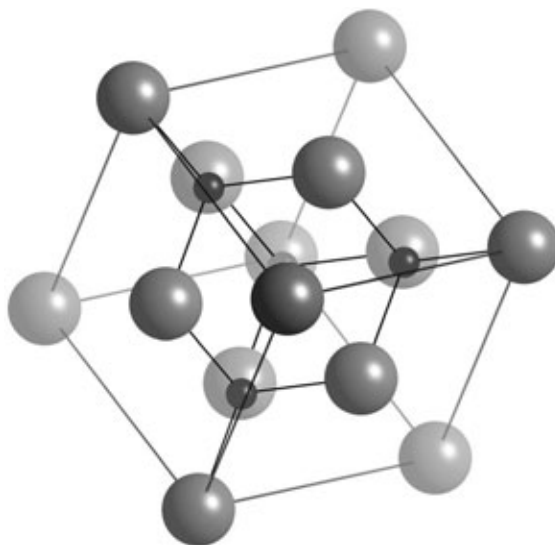
No.



Are the diagonal three-fold axes still present?



Yes, as shown by the following view of the cell diagonal.



The unit cell is therefore still cubic. Can you determine its point group designation?



$\bar{4}3m$. The NaCl structure has a point group of $4/m\bar{3}2/m$ and is therefore more symmetrical, but both are in the isometric system.

If we compare the point group designations for the NaCl structure and the sphalerite structure ($4/m\bar{3}2/m$ vs $\bar{4}3m$), we immediately notice the greater symmetry of the NaCl structure. For example, the perpendicular mirror planes present in the NaCl structure are not present in the sphalerite structure.



Both the NaCl and sphalerite structure contain anions in the ABC closest-packing arrangement. What causes the difference in symmetry?



The location of the cations. In NaCl, all of the octahedral sites are filled. (In fact, the NaCl structure is basically a set of two closest-packed sets of ions.) In sphalerite only half of the tetrahedral sites are occupied.

4.5 AXIAL RELATIONSHIPS

We have previously discussed the crystallographic axes. In the isometric system, the axes extend through the centers of each face of a crystal and intersect in the center as shown in Figure 44.

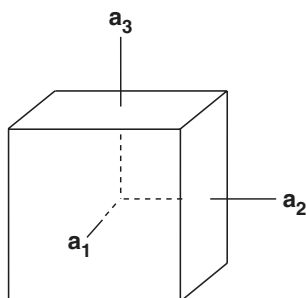
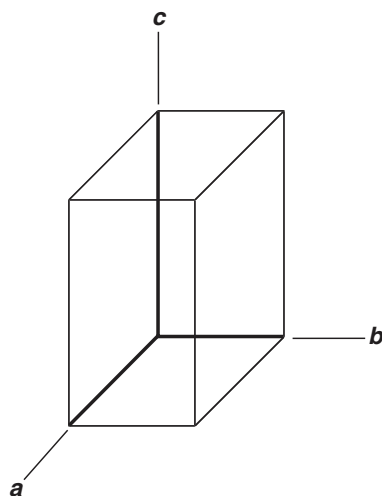


Figure 44 The perpendicular axes for a crystal in the isometric system.

The axes are labeled a_1 , a_2 , and a_3 , which correspond to the x , y , z coordinates in the Cartesian coordinate system. The axis a_1 is assumed to extend toward the reader, a_2 is perpendicular to a_1 but in the same plane, and a_3 is the vertical axis. For a cubic *unit cell* the distance from the corner of the cell to each face of the cell is the same along each of the axes. Thus, a_1 , a_2 , and a_3 are equal in length in the cubic system (the lines representing the extension of the axes are drawn longer for convenience). The fact that the axes have the same length is emphasized in another name for the cubic system—*isometric* (*iso* means same or constant, *metros* means measure).



for barite:
 $a = 8.87 \text{ \AA}$
 $b = 5.45 \text{ \AA}$
 $c = 7.14 \text{ \AA}$

**These are the lengths
of the bold lines
along the inside edges
of the unit cell.**

Figure 45 The axes for an orthorhombic unit cell.

Figure 45 shows the axes for the *unit cell* of an orthorhombic crystal. In the orthorhombic system, the axes are perpendicular to one another, but each has a different length. The lengths of the edges of the unit cell (which are the lengths of the axes) for barite are given in the figure.

Table 7 lists some generalizations about the lengths of the unit cell axes and the angles between them for each of the crystal systems.

We must now add a slight complication. We have not discussed several other symmetry elements. These elements involve translation (movement) of the unit cell within the

Table 7 Relationships of axes in the six crystal systems

Crystal System	Length of Axes	Angles
isometric (cubic)	all three of equal length	90° angles between axes
hexagonal	three axes of equal length in one plane, principal axis perpendicular to plane	120° angles between three axes in plane. Principal axis at right angles to others
tetragonal	two axes of equal length in plane perpendicular to principal axis, which is of different length	90° angles between all axes
orthorhombic	axes all of different lengths	90° angles between all axes
monoclinic	axes all of different lengths	two angles of 90°
triclinic	axes all of different lengths	no angles of 90°

crystal, whereas the symmetry elements involved in the point group designations of crystals involve no translation. The repetition of the unit cell throughout the crystal can be thought of as following a series of hypothetical points, which together are referred to as **lattice points**. The French crystallographer, Auguste Bravais, showed that the construction of an entire crystal can be described by the repetition of the unit cell in only 14 different types of lattices (referred to as the **Bravais lattices**). For isometric unit cells, there are only three Bravais lattices: the **primitive** lattice in which each unit cell has lattice points at its eight corners, the **body-centered** lattice in which each unit cell has lattice points at its eight corners and one at the center of the cell, and the **face-centered** lattice in which each unit cell has lattice points at the eight corners and at the center of each of the six faces of the unit cell. The NaCl and sphalerite structures are examples of the face-centered lattice, while the CsCl structure is an example of the primitive lattice.

A complete listing of the internal, atomic symmetry of a mineral is given by its **space group**, which includes all of the symmetry elements (primarily a designation of the point group designation of the unit cell *and* the type of lattice). We will continue to point out, where appropriate, various symmetry elements in the unit cell, but we will increasingly resort to the dimensions and shape of the unit cell to designate only the *crystal system*.

4.6 WURTZITE, A POLYMORPH OF SPHALERITE

Before we take a look at a mineral in which all of the tetrahedral sites are occupied, let us look at the polymorph of sphalerite, called wurtzite, which has AB closest packing of the sulfide ions. The word **polymorph** is derived from *poly*, meaning more than one, and *morph*, meaning form. Polymorphs are **two or more compounds that have the same composition but a different arrangement of atoms**. A portion of the structure is shown in Figure 46.



How many layers of closest-packed sulfide ions are shown?



5. Notice that the layers alternate in the hexagonal closest-packed sequence ABAB . . . The zinc ions occupy, as they did in sphalerite, one-half of the tetrahedral voids.

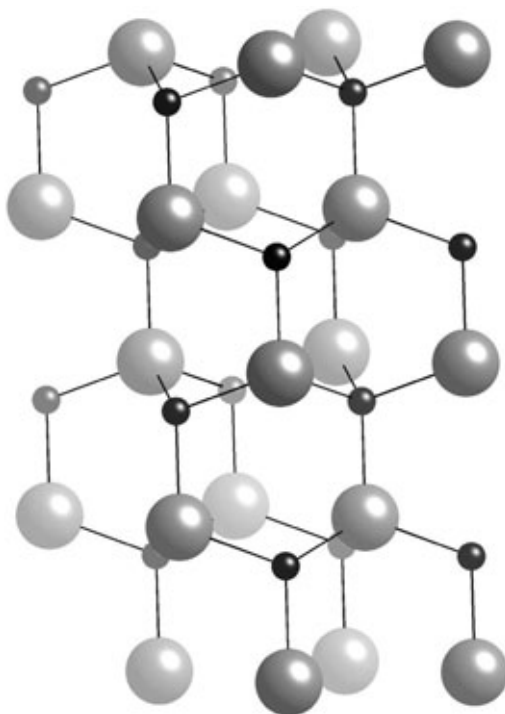


Figure 46 A portion of the wurtzite structure.

The symmetry (crystal system) of wurtzite becomes more obvious when four unit cells are examined, as shown in Figure 47 (we show just the top view). In fact, the larger internal angles of the cell shown in the top view are 120° and the smaller angles are 60° .

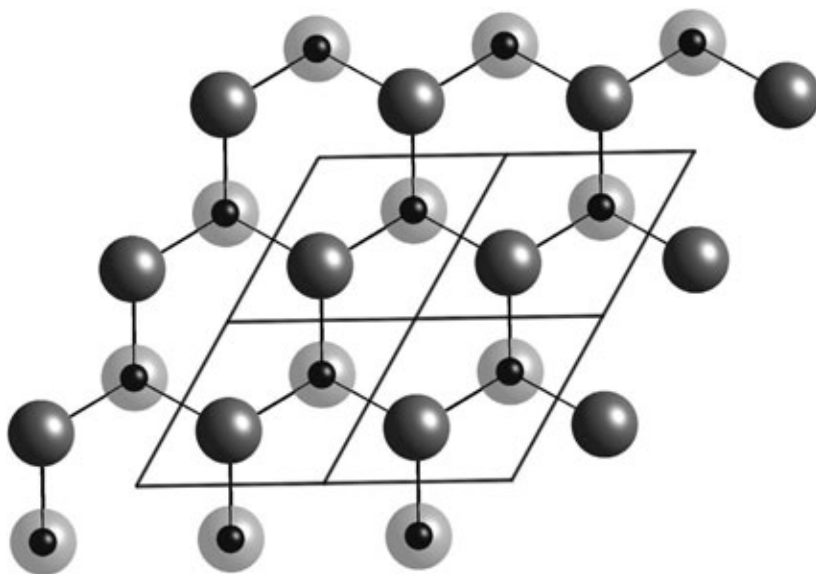


Figure 47 The hexagonal symmetry of wurtzite.

This set of unit cells shows that there is no six-fold rotational axis along the c -axis (remember that the top view looks down the c -axis). However, there is a three-fold rotational axis, and this is sufficient to place wurtzite in the hexagonal system.

4.7 THE FLUORITE STRUCTURE

Let us return to the cubic closest-packing arrangement and take a look at a mineral that contains ions in all of the tetrahedral voids. The unit cell of fluorite, CaF_2 , is shown in Figure 48.

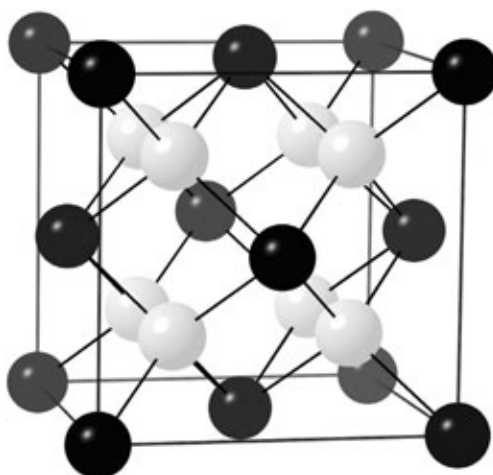


Figure 48 The unit cell of fluorite.



Which ion must be located in the tetrahedral sites?



The fluoride ion. There are two tetrahedral sites per closest-packed ion. If all the tetrahedral sites are occupied, the formula must be either MX_2 or M_2X . Normally, we expect the anion to be closest packed because generally anions are larger than the cations. In the case of CaF_2 the fluoride ion, with an ionic radius of 1.33 \AA , is larger than the calcium ion ($r = 1.00 \text{ \AA}$), but the structure can be analyzed by assuming that the Ca^{2+} ions are closest-packed. Thus, in the illustration above (and in those below), the lighter spheres are F^- and the black spheres are Ca^{2+} .

Figure 49 shows another view of the unit cell that shows only the calcium ions. The similarity to the face-centered NaCl and ZnS structures should be obvious.

Remember that cubic closest packing occurs with the ABC sequence.

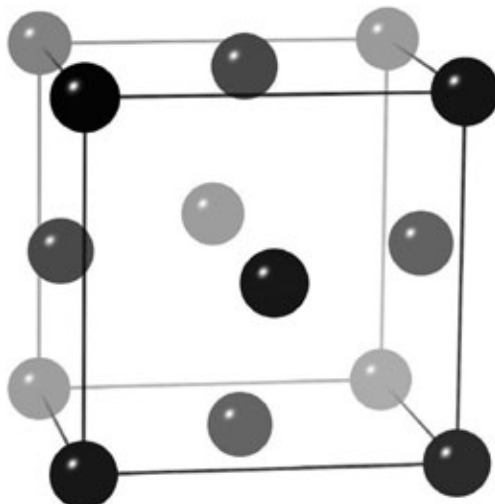


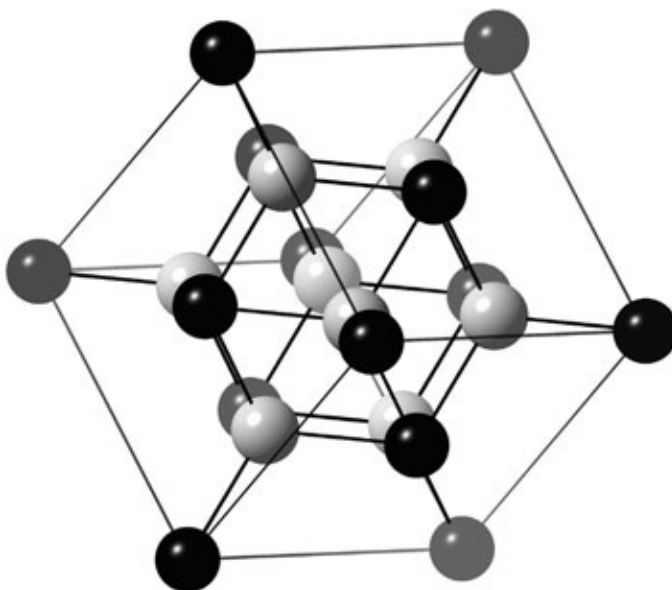
Figure 49 The face-centered arrangement of calcium ions in fluorite.



Try to determine all of the symmetry elements in Figure 48 and give the point group designation.



$4/m\bar{3}2/m$. If you have trouble seeing the diagonal rotoinversion axes, you might want to examine the diagonal view below, tilted just slightly to the left of one of the axes.



Thus, rotation of 120° around the diagonal, followed by inversion through the center of symmetry, would produce an equivalent image (you may need a model to fully appreciate this).



Before we leave this beautifully symmetric species, can you determine the coordination number of the cation and anion?



The fluoride ion is obviously four-coordinate because it fills the tetrahedral voids. The ratio of cation to anion is 1 to 2. So, the cation must have twice as many anion nearest neighbors, giving it a coordination number of eight.

Let us try one more way of looking at the coordination of the fluoride ions in fluorite. Figure 50 shows the coordination polyhedra for each of the fluoride ions in the unit cell.

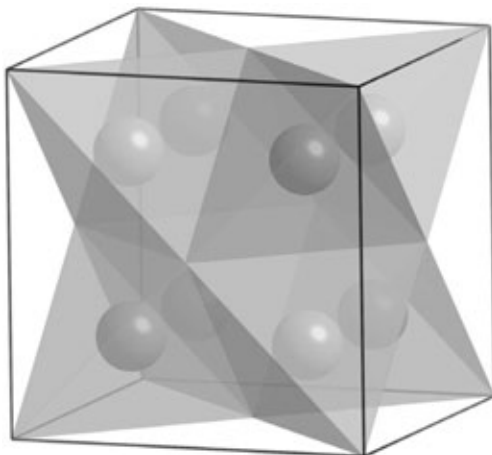


Figure 50 The coordination polyhedra surrounding the fluoride ions in fluorite.

Of course, these polyhedra are tetrahedra. At the corners of the tetrahedra are calcium ions (which are not shown in Figure 50).

Fluorite provides an excellent example of the fact that there are frequently several ways to visualize a structure. Instead of looking at the positions of the calcium ions as closest packed, let us now look at the fluoride ions as *cubic packed*; that is, at the corners of a cube. Figure 51 shows an array of cubic cells containing fluoride ions. At the centers of alternate cubes are the calcium ions. The staggering of the ions both in the vertical and horizontal direction minimizes the repulsions between the cations.

When the structure is visualized as cubic closest packing of the cations, it is the position of the cations that is emphasized, but in fact the cations cannot be at tangents to one another. The distance between the calcium ions in fluorite is 3.8 \AA , which is almost twice the distance between two calcium ions touching at a distance of 2.0 \AA (twice the ionic radius of Ca^{2+}). Thus, it is probably more correct to think of the structure as cubic packing of the fluoride ions with calcium ions in the cubic holes. This also has the advantage of illustrating Pauling's third rule that *highly charged cations prefer to maximize their separation*. [The rule as it appears in the *Nature of the Chemical Bond* is: "The presence of shared edges and especially of shared faces in a coordinated structure decreases its stability; this effect is large for cations with large valence and small liganacy." Pauling (1960)]

A picture of a sample of fluorite is shown in Figure 52.

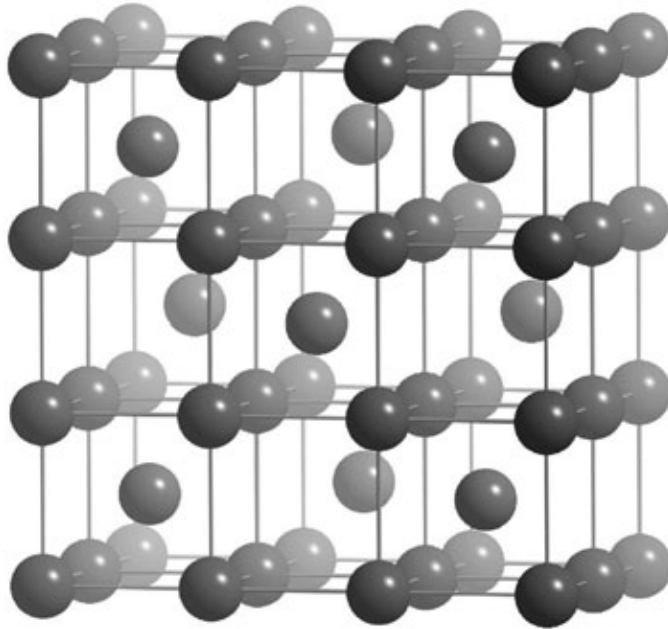


Figure 51 The structure of fluorite visualized as cubic packing of fluoride ions. The calcium ions are located at the centers of cubes, staggered in both the vertical and horizontal directions.



Figure 52 Fluorite (Rosiclare Level, Gov Royalty Ore, Minerva Mine #1, Hardin Co., Illinois)

4.8 THE RUTILE STRUCTURE, POLYHEDRAL COORDINATION MODELS

The use of the polyhedral view of a structure becomes more and more useful as the structure becomes more complex. For example, rutile (TiO_2) can be thought of as hexagonal closest packing of oxide ions with Ti^{4+} ions in half of the octahedral sites. The views in Figure 53 along the three axes show that the unit cell is definitely not cubic.

The cross-section along one axis is square, but along the other two axes it is rectangular. This is our first example of a tetragonal unit cell. In the tetragonal system, the axes are perpendicular to one another, but one is different in length than the other two. The view along the c -axis shows that the a - and b -axes must have the same length, but the c -axis is shorter.



Can you determine the point group designation from these three views?



$4/m2/m2/m$. Notice that each axis has a perpendicular plane of symmetry. Perhaps this plane will be more apparent from a polyhedral view (Figure 54).

From this view, we find that each of the Ti^{4+} ions is surrounded by six oxygens at the corners of octahedral polyhedra. If we look carefully at several other views, we find that some of the corner octahedra are linked to the central octahedron at an apex. This means that they share the oxygen that is at the apex. The view in Figure 55 shows that four of the corner octahedra share one apex each with the central octahedron.

The other four octahedra form two sets. The set of two in the lower left of the figure is probably easier to see than the other set in the upper right of the figure. In each set, the two adjacent octahedra share an apex with one another and with the central octahedron. The oxygen at this apex, then, is shared by three titanium ions. From Figure 56 we can see that vertically adjacent octahedra at each corner of the unit cell share an edge. By including more atoms in our view we can see that the octahedra are stacked along the c -axis.

Each octahedron in a stack shares an edge with an octahedron above it and an opposite edge with an octahedron below it. Each stack of octahedra is surrounded by four other stacks. The stacks are connected by sharing apices.



Do you remember what ion is at the corner of each octahedron?



An oxide ion. We have not yet looked at the polyhedra surrounding each oxygen.

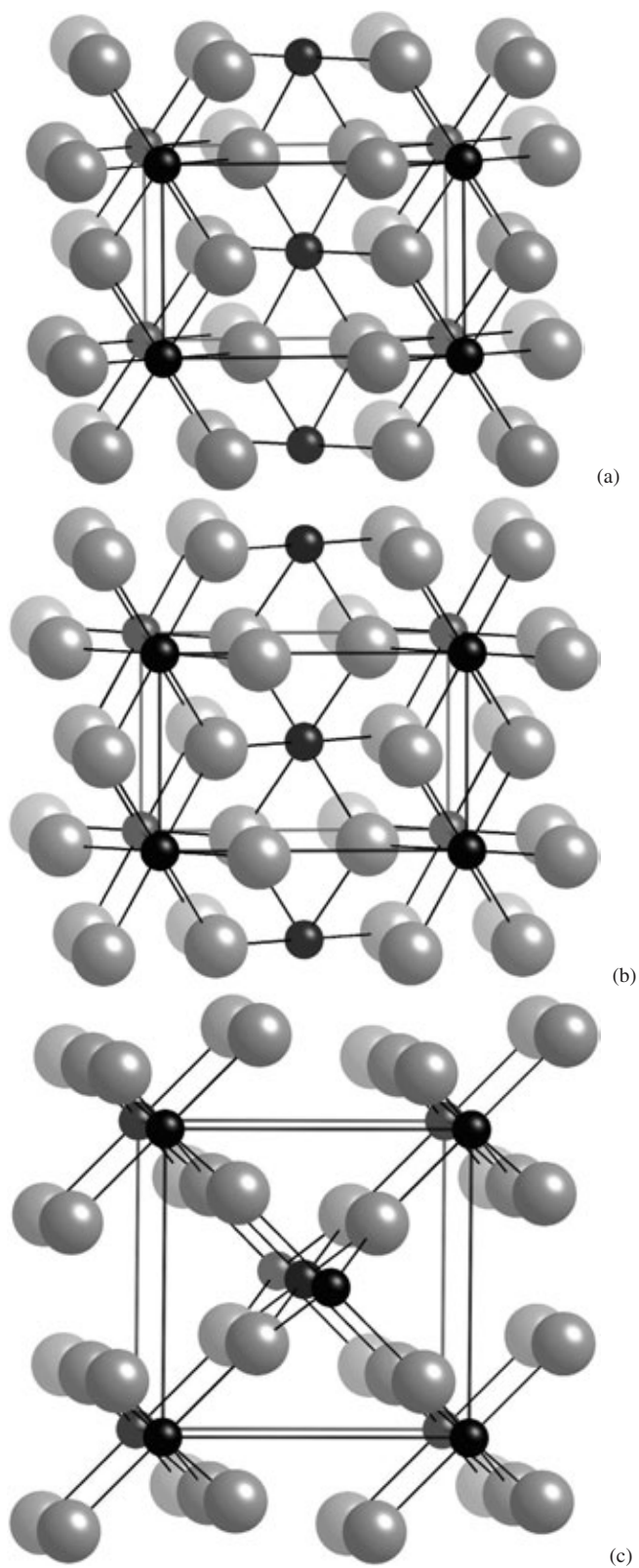


Figure 53 The rutile structure: (a) view down a -axis; (b) view down b -axis; (c) view down c -axis.

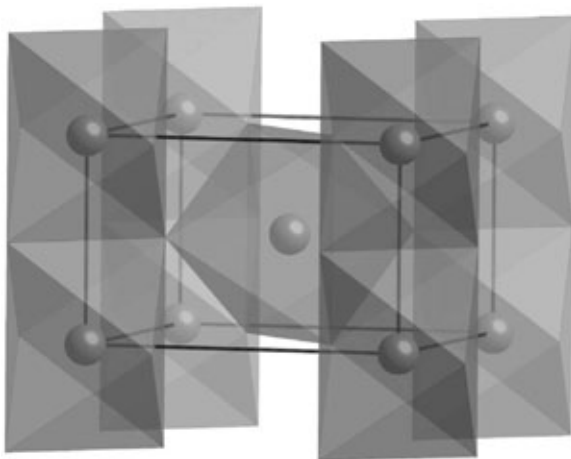


Figure 54 A view of the rutile structure showing the coordination polyhedra surrounding titanium. The c -axis is vertical.

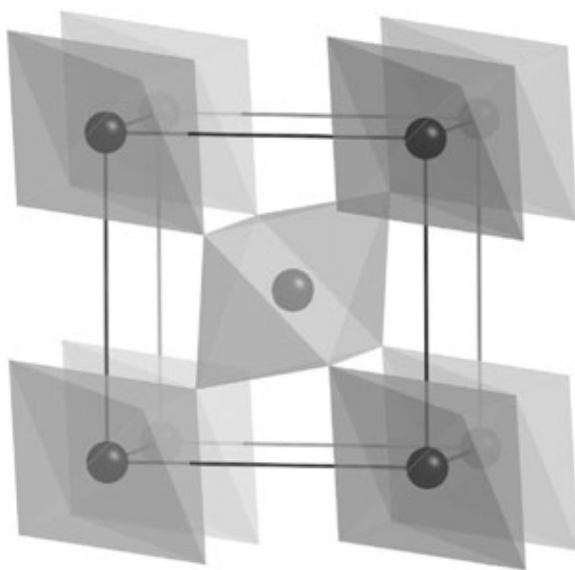


Figure 55 Sharing of oxygens by adjacent titanium atoms in the rutile structure.

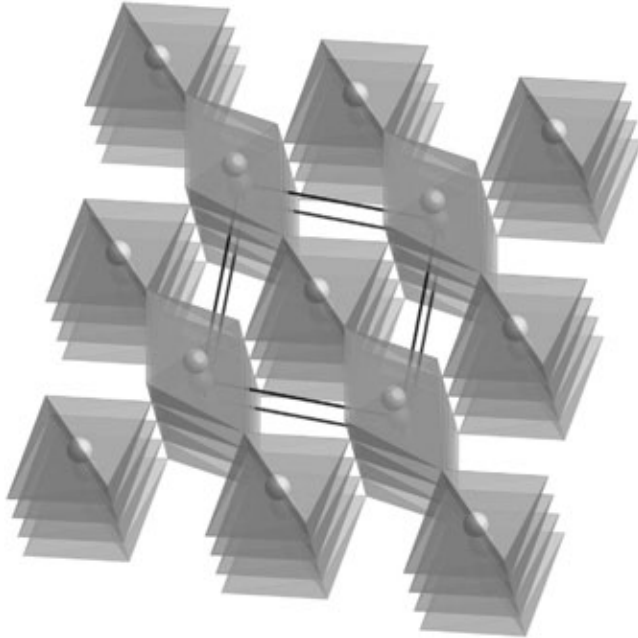
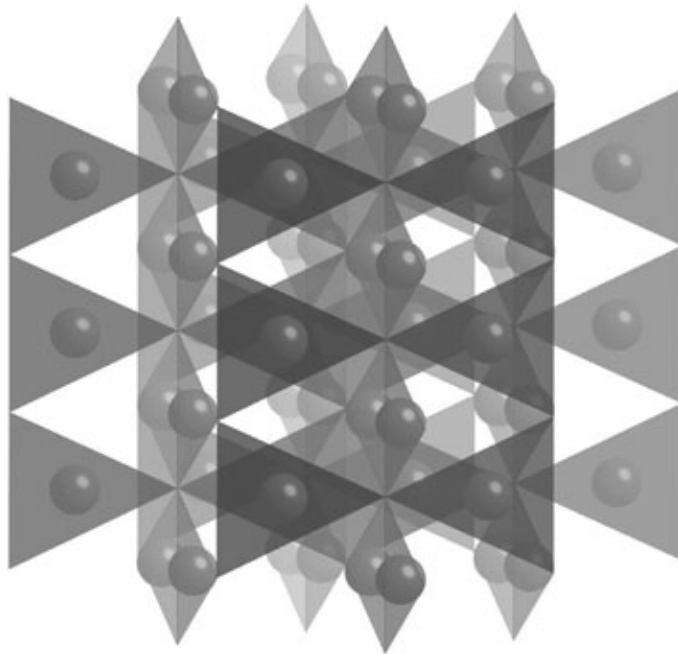


Figure 56 Octahedra stacked along c -axis in the rutile structure (looking down the c -axis).



Can you interpret the picture below?



These are the triangular polyhedra surrounding each oxide ion. Thus, each oxide ion is surrounded by three titanium ions.

Finally, Figure 57 shows both sets of polyhedra looking down the c -axis.

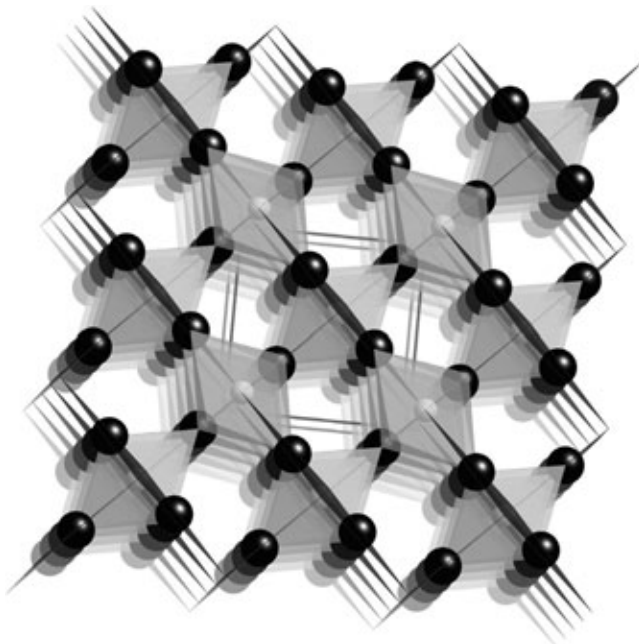


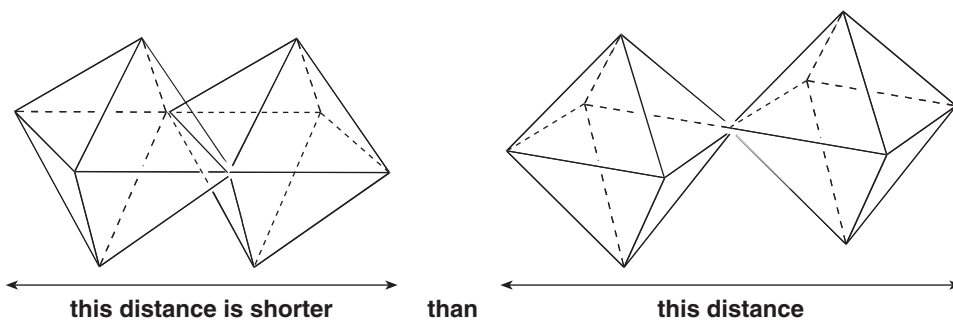
Figure 57 Both sets of coordination polyhedra in rutile.



Do these polyhedral representations help you to understand why TiO_2 is tetragonal rather than isometric?



Because the *edges* of the octahedra are shared along the c -direction, whereas *corners* are shared along the a - and b -axes, the unit cell is shorter in the c -direction. To be sure you understand this, take a look at the following:





Before we conclude our discussion of rutile, we must also comment on the bonding between the titanium and oxygen. Do you remember Fajans' rules?



Fajans' rules indicate that covalent bonding is favored by high charge and small size of the cation and high charge and large size of the anion. Remember that it is really the density of the charge on the cation; that is, charge per unit volume that is important in polarizing the charge of the anion and creating shared electron density (covalent bonding).



To get some idea of the charge density of the Ti^{4+} ion compared with that of a Ca^{2+} ion, use the following ionic radii— 0.40 \AA (Ti^{4+}) and 1.00 \AA (Ca^{2+})—to determine the volume of each ion and then the charge/volume ratio.



The formula for volume is $V = \frac{4}{3}\pi r^3$, which produces volumes of 0.3 \AA^3 and 4 \AA^3 for Ti^{4+} and Ca^{2+} , respectively. Now, dividing the charge by the volume produces: $\frac{4}{0.3 \text{ \AA}^3} = 10$ charges per \AA^3 for Ti^{4+} and $\frac{2}{4 \text{ \AA}^3} = 0.5$ charges per \AA^3 for Ca^{2+} .

If we compare the charge densities of the two ions, we see that the Ti^{4+} has 20 times the charge density of the Ca^{2+} ion. In fact, the polarizing power of the Ti^{4+} ion is so great that the covalent character in any compound containing the Ti^{4+} ion is very large. So great that, in fact, it is probably more accurate to speak of the bonding as being primarily covalent. To put this another way, the Ti^{4+} ion probably does not exist (the value used above for the ionic radius is an estimate), but we retain the ionic model because it is much simpler to use than the covalent model.

Chapter 5

Factors that Affect the Symmetry of the Unit Cell

Now we are ready to tackle another type of question. How is the symmetry of the unit cell affected by the nature of the cation and anion, as well as other factors such as temperature and pressure? Our answers to these questions will help us to understand the structures of compounds at the atomic level and, consequently, the reasons that crystals of a particular compound have a specific shape.

5.1 EFFECT OF CATION

We will first take a simple case: a comparison of sphalerite with galena. As you know, sphalerite is ZnS and galena is PbS .



What factor is most likely to influence the unit cell for these two compounds?



The size of the cation. Zn^{2+} has an ionic radius of 0.74 \AA , whereas Pb^{2+} has a radius of 1.19 \AA (see Appendix 3).

You should remember that sphalerite has a cubic closest-packed (face-centered) arrangement of sulfide ions with zinc cations occupying half of the tetrahedral voids.



What do you think is the effect of substituting Pb^{2+} for Zn^{2+} ?



Because the Pb^{2+} is larger, it can more easily occupy the octahedral voids. Thus, in galena all of the octahedral sites are occupied by lead ions. We have seen this structure before; it is the NaCl structure.



Are the symmetries of crystals of sphalerite and galena different?



Yes. Galena has the full isometric symmetry of $4/m\bar{3}2/m$, while sphalerite has a slightly lower symmetry of $\bar{4}3m$. Both belong to the isometric crystal system.

5.1.1 The Chalcopyrite Structure and Solid Solution

A different kind of change in cation occurs in the common mineral chalcopyrite. The formula of chalcopyrite is usually given as CuFeS_2 , from which we can assume that there are two cations, Cu^{2+} and Fe^{2+} , and one anion, S^{2-} (of course, there are two anions for every copper or iron cation). The anion packing is cubic closest packing, giving a sphalerite type structure.

Assume that the structure of chalcopyrite is the sphalerite structure with either Cu^{2+} or Fe^{2+} in place of the Zn^{2+} ion. Moreover, assume that the cations are placed randomly in the tetrahedral voids. In other words, on average, there is a 50% chance that a particular void is occupied by Cu^{2+} and a 50% chance that it is occupied by Fe^{2+} .



Would the symmetry of this randomized structure be the same as that of sphalerite?



Yes, because, on average, half of the tetrahedral voids are occupied by an “average” cation. This produces the cubic symmetry of sphalerite.

In fact, at room temperature chalcopyrite has a structure that consists of very precisely ordered cations (Figure 58).

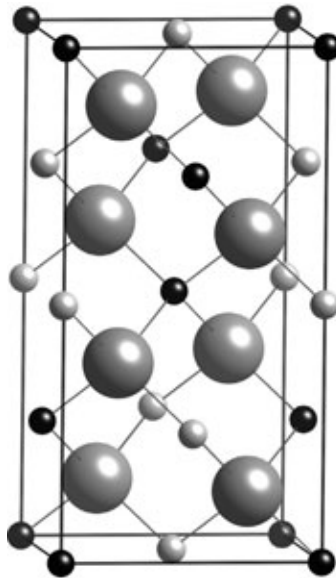


Figure 58 The structure of chalcopyrite. The small dark spheres are copper ions, the small light spheres are iron ions, and the large light spheres are sulfide ions.

For the moment, ignore the sulfide ions and concentrate on the cations. Starting at the top of the unit cell, there are four copper cations at the corners and one iron cation in the center. In the next layer of cations there are two copper ions on opposite faces and two iron cations on the other set of faces. Then, in the middle layer there is a layer similar to the top layer, but the ions are reversed (iron at the corners, copper in the middle). The next to bottom layer is a repeat of the second layer from the top, except that the ions are reversed. The bottom layer is, of course, a repeat of the top layer.



How does this unit cell compare to the sphalerite unit cell?



The sphalerite unit cell has the same dimensions in all three directions and is therefore isometric. The chalcopyrite unit cell is longer in the c -direction because there are four distinct layers of cations to accommodate before the sequence begins to repeat. The a - and b -directions are equal in length, but c is longer.



To what crystal system does this unit cell belong?



Tetragonal.



Determine the symmetry of the principal axis.



It is a four-fold rotation-inversion axis. If you have trouble seeing this, look down the c -axis, rotate 90° , look at the new position of the atoms, and then invert them through the center. The new configuration of atoms will be indistinguishable from the original one.

You are probably wondering why the copper and iron ions adopt this particular arrangement. As far as we know, there is no good answer for that question.



Do you think the random order arrangement is more likely at high or low temperatures? Why?



The ordered (tetragonal) arrangement is the lowest possible energy for chalcopyrite. If we increase the energy available by increasing the temperature, the ions can move from position to position and, at high enough energy, the random arrangement will exist.

In looking at the formula of chalcopyrite, you may also have wondered whether this structure could accommodate more or less copper (or more or less iron). This process of substituting one cation or anion for another we have seen before and know it as solid solution.



Write a formula for a solid solution member of chalcopyrite.



$\text{Cu}_{1.2}\text{Fe}_{0.8}\text{S}_2$, or $\text{Cu}_{0.8}\text{Fe}_{1.2}\text{S}_2$, or $\text{Cu}_{1.3}\text{Fe}_{0.7}\text{S}_2$, etc. Electrical neutrality must always be maintained and therefore if the solid solution contains only Cu^{2+} , Fe^{2+} , and S^{2-} , the subscripts of Cu and Fe must add up to the subscript of sulfur.

Partly because of the tendency to form solid solutions, the chemical composition of most minerals cannot be represented by a simple formula. The next time you pick up a piece of chalcopyrite and think, “Oh, this is CuFeS_2 ,” remember that this is only approximately its composition. A sample of chalcopyrite is shown in Figure 59.

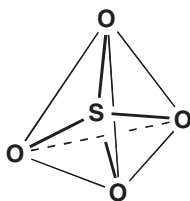


Figure 59 Chalcopyrite (Pachapaque, Peru). This habit is not typical. Sphenoidal (elongated tetrahedral) crystals are more common.

5.2 EFFECT OF THE ANION

5.2.1 Some Oxy Anions

We can now consider the effect of the size and shape of the anion on the symmetry and dimensions of the unit cell. For minerals, the anion can vary widely. So far, we have talked only about monatomic (single atom) anions, but many minerals contain polyatomic anions such as carbonate, sulfate, phosphate, vanadate, and, of course, silicates. These are all **oxy anions**; that is, they contain some central atom surrounded by oxygens. It is important to understand that in these anions the oxygens are attached to the central atom by covalent bonds (the bonds may, of course, contain some ionic character). The sulfate, phosphate, vanadate, and nesosilicate ions are tetrahedral in shape. For example, the sulfate ion contains a sulfur at the center of a tetrahedron, as shown below (remember the entire species has a charge of $2-$, which is not shown in this structural representation):



Can you predict whether each of the sulfur–oxygen bonds is primarily covalent or considerably ionic?



Primarily covalent. The electro-negativity of oxygen is 3.5 and the value for sulfur, which is immediately below oxygen in the periodic table, is 2.5 (see Appendix 2). Thus, the difference is 1.0, which suggests that the bonds are mainly covalent. By comparison, the difference between the electro-negativities of oxygen and sodium is 2.6.

The sulfate ion has a charge of 2⁻. Because oxygen is more electronegative than sulfur, we can assume that most of the 2⁻ negative charge resides on the oxygens (this distribution of electron density is convenient but only approximate). Because the ion is symmetrical (all of the bonds have the same length), we can also assume that these two electrons are evenly distributed over four oxygens.

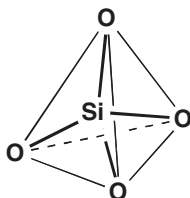


How much charge do each of the oxygens of the sulfate ion carry?



1/2 of an electron (2 electrons/4 oxygens = 0.5 electrons per oxygen).

The simplest silicate ion is the nesosilicate ion, SiO₄⁴⁻. It, too, is tetrahedral.



How does the ionic character of the Si—O bond compare with that of the S—O bond, and how much charge resides on each oxygen?



Because the electro-negativity of silicon is 1.8, the Si—O bond is more ionic than the S—O bond. If we assume that the charge of four electrons is evenly distributed around the four oxygens, each oxygen will have one full electron of charge.

It is important to realize that although the Si—O bond has some ionic character, it is still mainly covalent. This means that in a crystal, the bonds around the silicon will remain pretty much the same as in an isolated SiO_4^{4-} ion. They will have about the same bond length and the same tetrahedral angle of approximately 109° between bonds. There are many different types of silicate anions that are important in the rocks that form most of the Earth's crust. These anions are formed (on paper) by taking the basic SiO_4 unit and linking it with other SiO_4 units in various ways. We will return to this later.

Because carbonates are also important as ores, we should also mention the carbonate ion. The carbonate ion has a triangular geometry (also referred to as trigonal planar) with carbon at the center of the triangle (see Figure 5).

Before we tackle several of these oxy anions, let us try a much simpler diatomic anion, the S_2^{2-} ion. This ion contains two sulfur atoms, covalently bonded to one another. The ion has a 2- charge.

5.2.2 The Pyrite Structure

Suppose that we take ferrous oxide (FeO), which has the NaCl structure, and replace the oxide ion with the disulfide ion (S_2^{2-}). The structure in Figure 60 shows each S_2^{2-} ion aligned along the c -axis. Make sure that you can see that this is indeed the NaCl structure with the S_2^{2-} ions replacing the chloride ions and Fe^{2+} replacing the sodium ions.

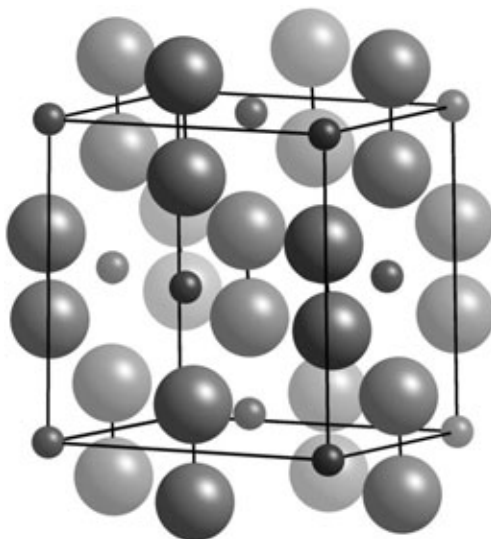


Figure 60 The high-temperature form of pyrite.



Is the unit cell isometric?



No, the alignment of the disulfide ions along the c -axis extends or elongates the unit cell in the c -direction and makes it tetragonal rather than isometric.

Actually, this is not the structure of the common mineral pyrite (FeS_2). However, it is the structure of compounds with similar anions such as carbide (C_2^{2-}) and azide (N_3^-). The actual structure of pyrite is shown in Figure 61.

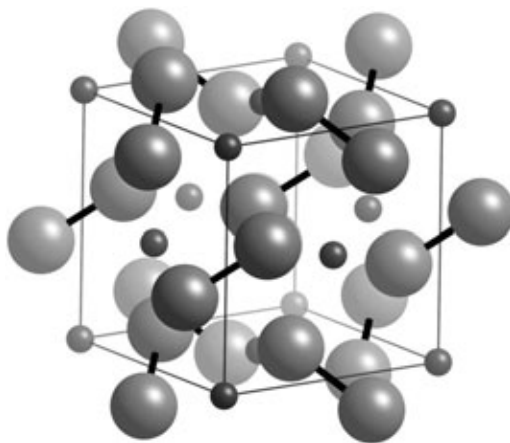


Figure 61 The structure of pyrite.

There are three sets of four disulfide ions. In the middle layer we see one set, each member of which has the same orientation. Although it is not obvious, this arrangement of disulfide ions retains the isometric symmetry of the NaCl structure. A sample of pyrite is shown in Figure 62.



Figure 62 Pyrite (Ambasaquass, Logono Region, Spain).

Another variation on the NaCl structure occurs with sodium cyanide. There are several forms of the compound that are stable in different temperature ranges. At low temperatures, the form depicted in Figure 63 (CN^- ions are represented as white ellipses) is stable.

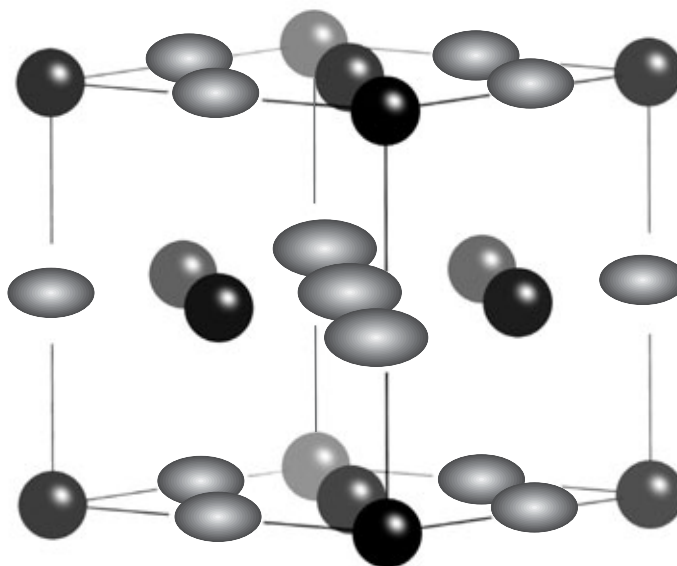


Figure 63 The structure of NaCN.

The CN^- ions are all orientated in the same direction and we might therefore expect the unit cell to be elongated in the c -direction (or the a - or b -directions, since all directions are equivalent in the isometric system). This would result, as we have seen above for high-temperature FeS_2 , in a tetragonal unit cell. In fact, the unit cell shown above is elongated along the direction in which the ellipses are orientated, but also compressed in the perpendicular direction. This gives rise to a unit cell that has a top view shown in Figure 64.

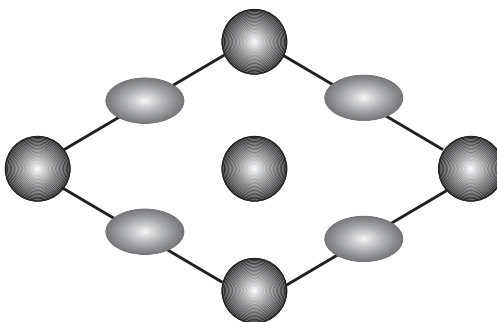


Figure 64 The top view of the NaCN unit cell.

This is a unit cell that has two angles that are not 90° . (Remember that the isometric and tetragonal unit cells have 90° angles, and the hexagonal unit cell has a 120° angle and a three-fold axis.)



See if you can determine the symmetry elements in this unit cell.



There are three perpendicular two-fold rotational axes. There are also mirror planes that contain each of the axes, and a center of symmetry.



Based upon your identification of symmetry elements, give the crystal system and the point group designation.



Orthorhombic, $2/m2/m2/m$. The orthorhombic system contains at least one two-fold axis and vertical mirror planes or perpendicular two-fold axes. Notice that it is not necessary for all of the angles between the axes to be 90° in order to have an orthorhombic crystal. The symmetry elements are the necessary determinants of the classification.



At higher temperatures, NaCN adopts the NaCl cubic form. Can you rationalize this?



In order to obtain the necessary symmetry, the anion must either attain spherical symmetry or must have orientations similar to those in pyrite. At higher temperatures, it is not likely to be less symmetrical, and therefore the anion presumably gains spherical symmetry. It does this by rotating about its lattice point, so that, on average, the rest of the ions “see” a sphere.

5.2.3 The Calcite Structure

Calcite, CaCO_3 , provides another variation on the NaCl structure. It can be thought of as the NaCl structure with trigonal planar carbonate ions replacing chloride ion. As shown in Figure 65, the triangular carbonate ions have their planes perpendicular to the three-

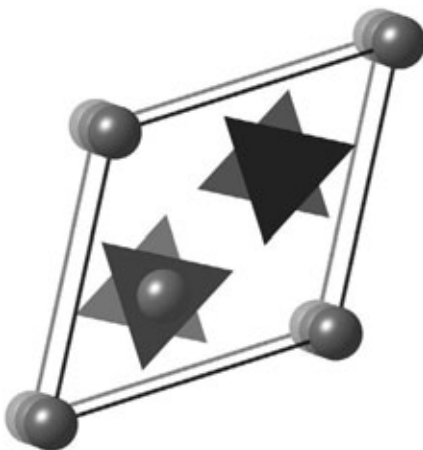


Figure 65 The calcite structure looking down a 3-fold axis.

fold axis. This allows the structure to compress in the direction of the three-fold axis and it becomes hexagonal, rather than isometric. A side view of the unit cell, as shown in Figure 66, shows that the cations are sandwiched directly between the carbonate ions, forming rows of alternating cations and anions. Within each row down the three-fold axis, the triangular carbonate ions are staggered. It is tempting to attribute the staggering of the carbonate ions to their attempt to minimize repulsions between the negatively-charged oxygens, but it is more likely that the arrangement is due to the geometry required for the coordination of the calcium ions to the carbonate oxygens.

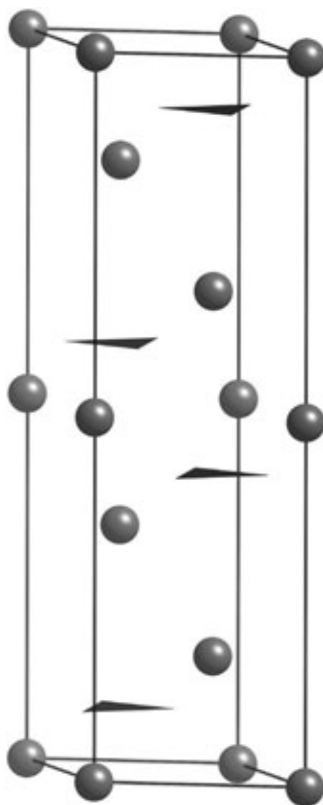


Figure 66 A side view of the calcite unit cell (perpendicular to the 3-fold axis).

The calcium ion is six-coordinate, which would be expected based on the similarity of the structure to that of NaCl (the calcium ions are essentially in the octahedral voids). The coordination number of an oxygen in an oxy anion can be easily determined if the coordination number of the cation is known. For example, the calcium ion in CaCO_3 has a charge of 2+ and is six-coordinate. Every one of the six nearest neighbors therefore must “neutralize” $2/6 = 1/3$ of a positive charge. The neutralizing ability of the carbonate ion

comes from the electron density on the oxygens. Each oxygen of a carbonate ion has two-thirds of an electron (remember that carbonate has a $2-$ charge). Thus, one oxygen of one carbonate ion has too much electron density to “neutralize” the charge of one calcium ion; in fact, it has twice the $1/3$ needed. Therefore, each oxygen is coordinated to two calcium ions.

This determination of the coordination number of the ion is predicated on the electrical neutrality principle given earlier (see page 19). This principle is also called the electrostatic valence principle and is part of Pauling’s second rule: “In a stable ionic structure the valence of each anion, with changed sign, is exactly or nearly equal to the sum of the strengths of the electrostatic bonds to it from the adjacent cations.” (Pauling, 1960)

A picture of a calcite crystal is shown in Figure 67.



Figure 67 Calcite (Reynolds Co., Missouri), a view of the three-fold symmetry.



Try this same reasoning with sphalerite, remembering that the zinc ions are four-coordinate.



Zinc is $2+$ and because it is four-coordinate, $2/4 = 1/2$ charge must be “neutralized” by the S^{2-} anions. Each anion has a full two electron charge and therefore each anion must be coordinated to four cations ($-2/4 = -1/2$).

5.2.4 Aragonite, A Polymorph of Calcite

Now let us take a look at a polymorph of calcite—aragonite. A view down the c -axis is shown in Figure 68.

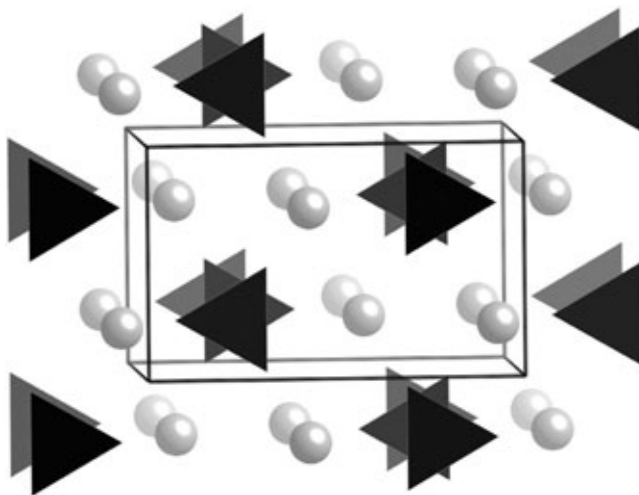


Figure 68 A view of the aragonite structure down the c -axis.

Figure 69 contains a view along the a -axis:

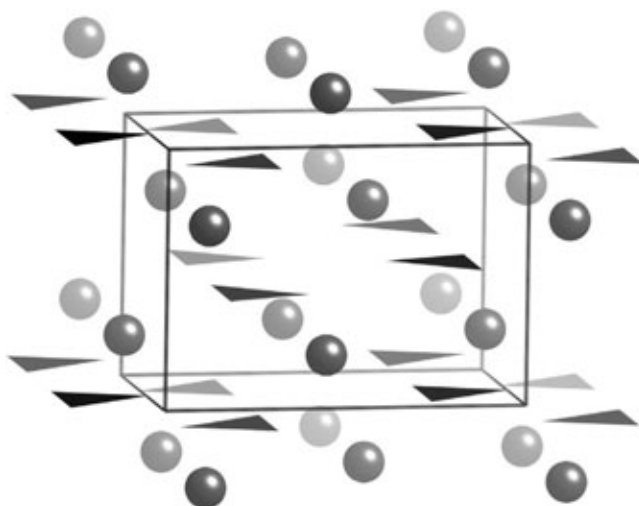


Figure 69 A view of the aragonite structure along the a -axis.



First look at the calcium ions in Figure 69. Would you say they are approximately cubic closest-packed or hexagonal closest packed?



Because the layers have an AB sequence, they are roughly hexagonal closest packed.

The anions are also almost closest packed, but notice that they exist in two slightly different planes between layers of cations.

Now look at the view down the c -axis (Figure 68). The carbonate ions are stacked on top of one another in the same staggered formation that existed in calcite. The arrangement of both cations and anions produces a unit cell that is orthorhombic.

Figure 70 shows one cation surrounded by carbonate ions in two layers. If we look just at the top triangles (the three that are darkest in color), we notice that two of the triangles have a corner pointing toward the calcium ion, while the other triangle has two corners (one edge) directed toward the calcium ion. In the lower layer, two triangles have two corners (one edge) pointing at the calcium ion and one triangle has only one corner toward the calcium ion. If we count up the number of nearest-neighbor corners (oxygens), we find that it is 4 (top layer) + 5 (lower layer) = 9. Thus, the coordination number of calcium is 9.

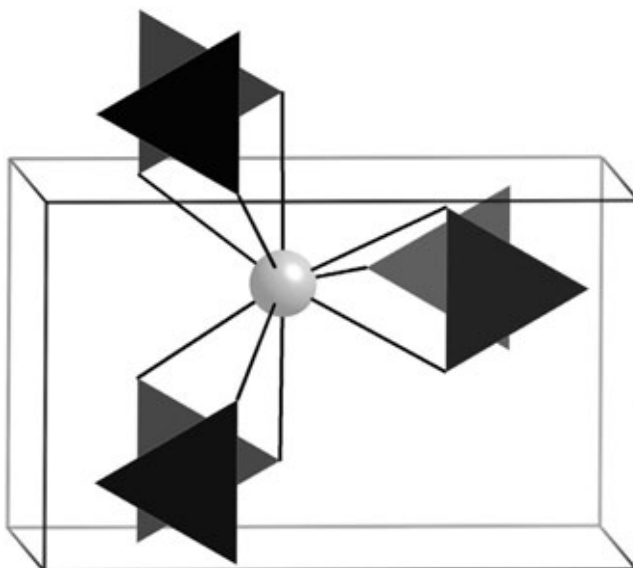


Figure 70 9-coordination of calcium ions in aragonite.



Now, determine the coordination number of each oxygen.



Three. There is a positive charge of 2 distributed among 9 oxygens, and each oxygen has a negative charge of $2/3$ ($6/9$). Therefore, each oxygen must be shared with three calcium ions ($\frac{2/3}{3} = 2/9$).

Aragonite can be formed from calcite by high pressures. In fact, continued grinding of calcite in a mortar and pestle will produce aragonite. However, at room temperature and pressure, calcite is the more stable polymorph.



Is the difference in coordination numbers any indication of the effect of pressure?



Yes, aragonite, which is formed at higher pressures, has a more compact structure. This gives rise to a decreased distance between the calcium ions and carbonate ions and the greater coordination number of the calcium ions and oxygen atoms. Aragonite consequently has a higher density.



Given that calcium carbonate can adopt two fairly common forms—calcite and aragonite—what type structure do you suppose MgCO_3 (magnesite) and SrCO_3 (strontianite) adopt?



The type structure depends on the size of the cation: smaller cations lead to lower coordination numbers (as we have seen before). MgCO_3 has the calcite structure, whereas SrCO_3 has the aragonite structure.

5.2.5 Several Sulfates, Anhydrite and Barite

We continue our investigation of the affect of the anion on structure with several sulfates—*anhydrite* (CaSO_4) and *barite* (BaSO_4). The tetrahedral sulfate ion is shown in Figure 71 (a) sitting on its base (a face) and oriented on an edge in Figure 71 (b).

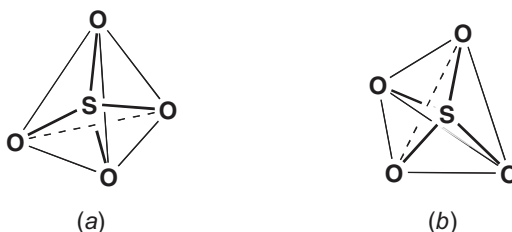


Figure 71 Two orientations of a tetrahedron: (a) sitting on face; (b) sitting on edge.

It may not be obvious from this drawing but the edges at the top and bottom of Figure 71 (b) are perpendicular. Of course, at each corner there is an oxygen that has an average electron density of one-half of an electron.

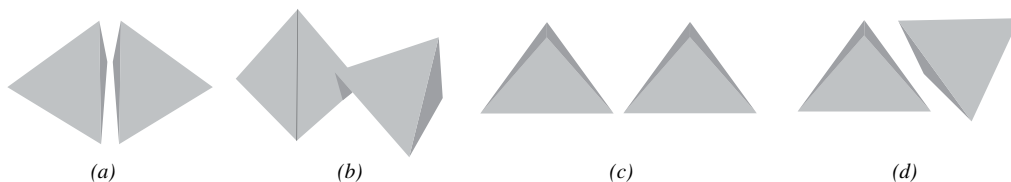
If we just consider the packing of the anions, we are concerned with three factors:

1. How to pack tetrahedral units in the most efficient way.
2. How to pack anions that are tetrahedral with negative charges at their corners in a way that will minimize repulsions between the anions.
3. How to pack the anions to maximize the attractions between the cations and the negative charges at the corners of the anions.

The last two factors are sufficiently important that they outweigh the first. This means that we no longer can use simple closest-packing models to predict the arrangement of the ions (although sometimes the arrangement is approximately closest packing). Prediction of how the second and third factors combine to determine the structure is very difficult. However, we can make some generalizations.



Examine the following ways of arranging adjacent sulfate ions and determine which is energetically the most favorable.



Arrangement (a) is not favorable because the negative charges on the corner oxygens are very close at the three corners of the two opposing faces (the tetrahedra are drawn in perspective; actually, the two faces are parallel). Thus, the repulsions are high in (a). The repulsions are lower in (b), but the negative charge of the right-hand sulfate is close to the three oxygens on the face of the left-hand sulfate. Arrangements (c) and (d) show the edge-down arrangement of the sulfate ions. Arrangement (d) has the lowest repulsions because the oxygens are further apart.

In anhydrite, CaSO_4 , the sulfate ions exist in vertical stacks along the c -axis. In each stack the tetrahedra are orientated in the same way with edges perpendicular to the c -axis. Neighboring stacks have edges orientated in the same way along one axis while stacks running along the other axis have their edges staggered. The view in Figure 72 is down the c -axis.

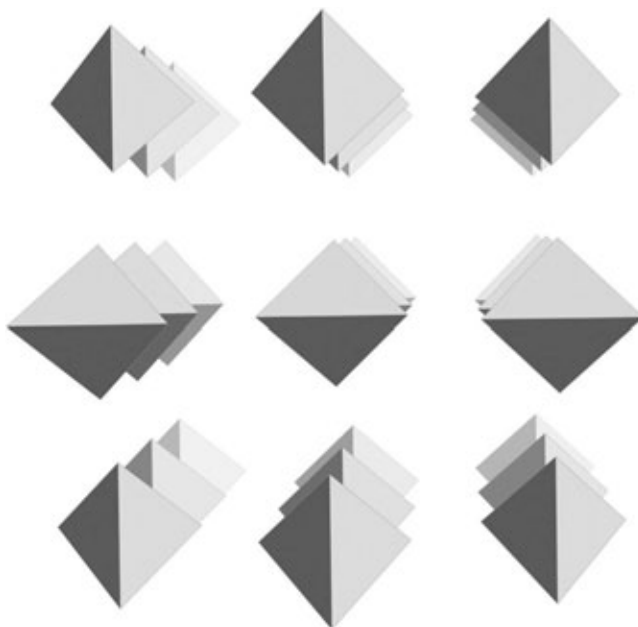


Figure 72 Anhydrite, sulfate ions only, looking down the c -axis.

Because the stacks of oppositely orientated tetrahedra are staggered, the calcium ions are also staggered (Figure 73).

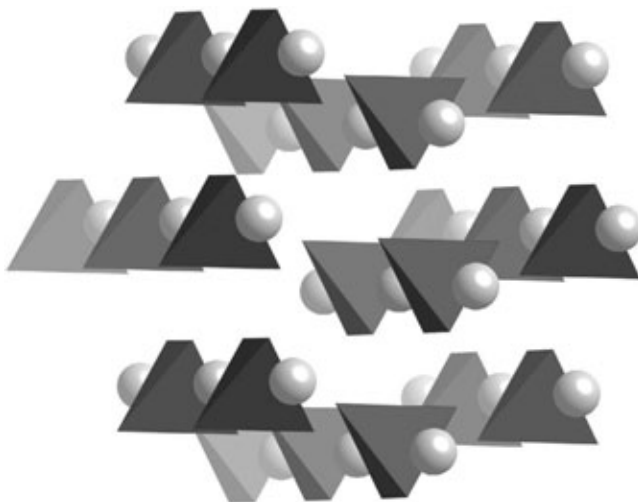


Figure 73 Anhydrite. Sulfate ions as tetrahedra, calcium ions as spheres.

Figure 74 shows the eight-coordination of the calcium to nearest neighbor oxygens.

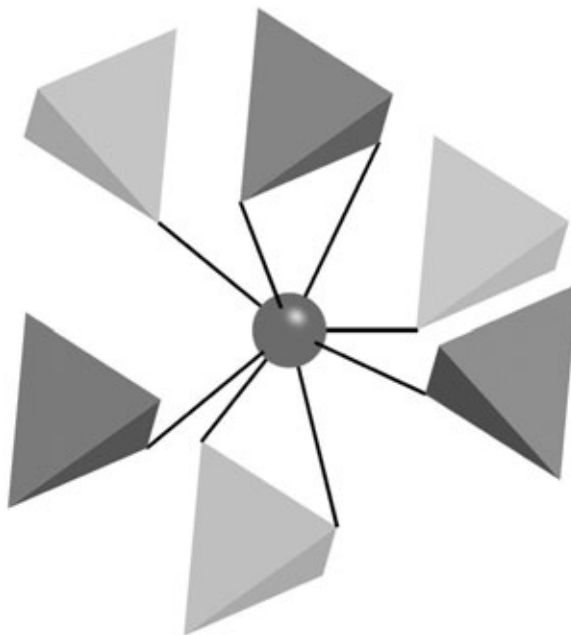


Figure 74 Anhydrite. 8-coordination of calcium ions.



Determine how many calcium ions are coordinated to each oxygen.



Because of the eight coordination, each oxygen must neutralize a charge of $2/8 = 1/4$. But each oxygen has a charge of $1/2$ and must therefore be coordinated to two calciums.

The unit cell is shown in Figure 75 looking down the c -axis:

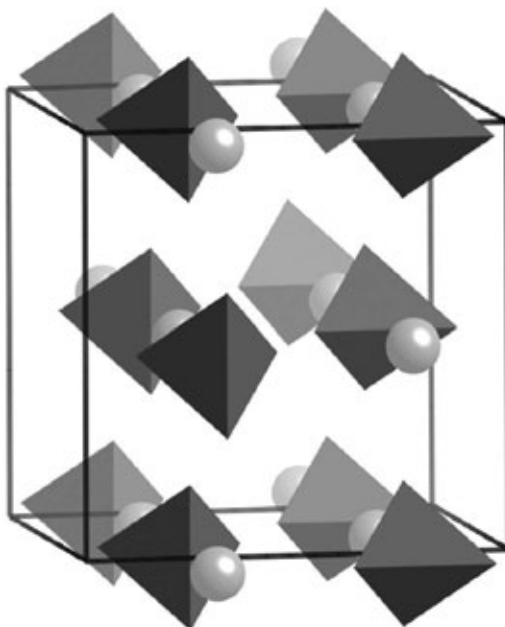


Figure 75 Anhydrite unit cell, looking down c -axis (rotated slightly to the right).



What is the symmetry of the unit cell?



Although it is not obvious from Figure 75, there are four CaSO_4 units in the unit cell. The angles between the a -, b -, and c -axes are 90° . The disposition of cations and anions is slightly different in each direction and therefore the unit cell lengths are unequal. The unit cell belongs to the orthorhombic system.

In barite (BaSO_4) we might expect the coordination number of the barium to be higher due to the larger size of the barium ion. The unit cell should also have a greater volume. In Figure 76 (looking down the c -axis) the sulfate tetrahedra can be seen to be staggered along the a -direction (horizontal).

Figure 77 shows that the tetrahedra in adjacent layers are offset (staggered).

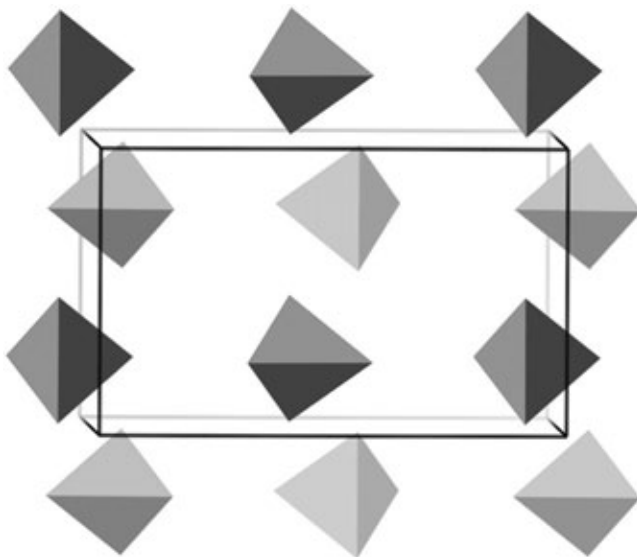


Figure 76 Barite, sulfate ions only; looking down the *c*-axis.

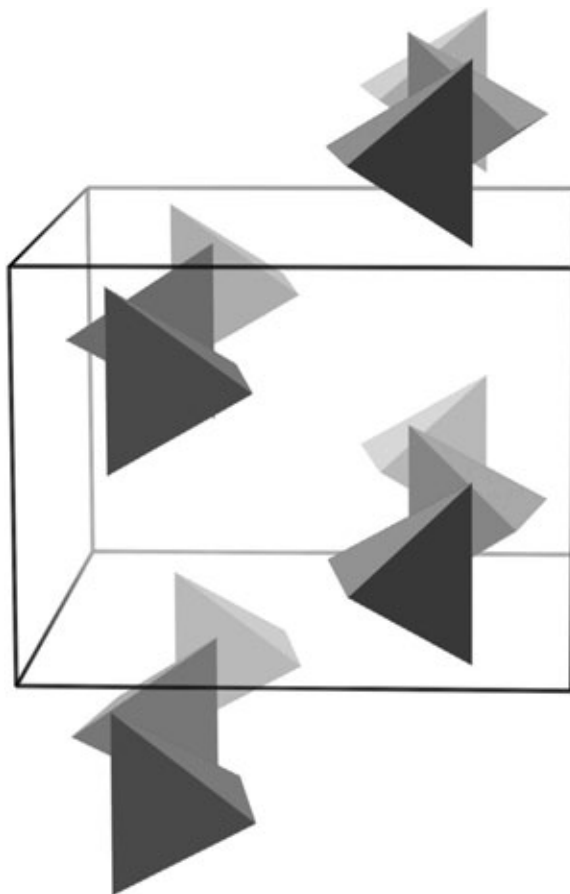


Figure 77 Barite, sulfate ions only. Looking down the *a*-axis.

The barium ions are positioned between the sulfate ions such that the barium ions and sulfate ions lie on planes of symmetry along the a -axis. Each barium ion is coordinated to the two oxygens on the edge of each of five tetrahedra and to two corners of two other tetrahedra, resulting in twelve-coordination for barium (Figure 78).

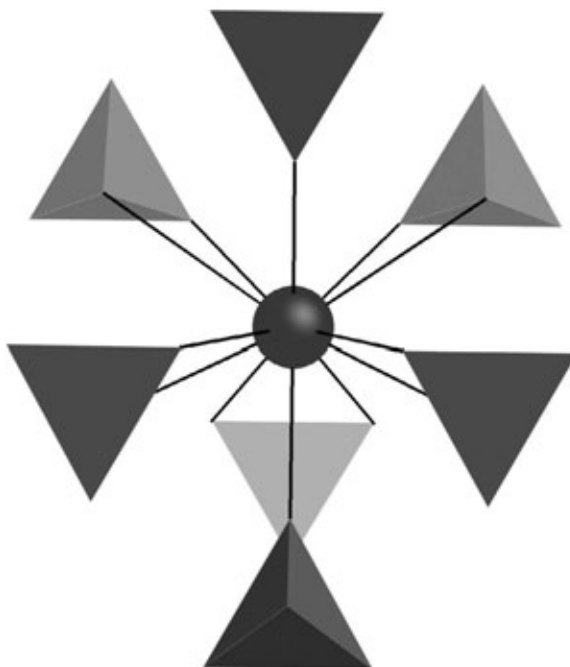


Figure 78 Coordination of Ba^{2+} in barite.



Determine how many barium ions are the nearest neighbors of each oxygen of each sulfate ion.



3.

Finally, let us take a look at the unit cell parameters for the two sulfates (each unit cell contains four MSO_4 units):

$$\text{BaSO}_4 \quad a = 8.884 \text{ \AA}, \quad b = 5.458 \text{ \AA}, \quad c = 7.153 \text{ \AA}$$

$$\text{CaSO}_4 \quad a = 6.993 \text{ \AA}, \quad b = 6.995 \text{ \AA}, \quad c = 6.245 \text{ \AA}$$

Anhydrite has nearly equal a - and b -axes, almost producing tetragonal symmetry. The barite unit cell is considerably more elongated in both the a - and c -directions, which generally results in crystals that are more tabular than those of anhydrite.



Calculate the volume of the unit cells for each mineral.



$V = 346.8 \text{ \AA}^3$ for BaSO_4 , $V = 305.5 \text{ \AA}^3$ for CaSO_4 .

As predicted, the unit cell for the sulfate with the larger cation has the greater volume. Both sulfates are orthorhombic. A sample of barite is shown in Figure 79.



Figure 79 Barite (XiChang, SiChuan Province, China).

5.2.6 Several Silicates, Zircon, and Beryl

We conclude our discussion of the affect of the anion on the unit cell by examining two silicates. The nesosilicates are the simplest of a very large category of compounds that form most of the rock-forming minerals. The nesosilicate ion SiO_4^{4-} is **isostructural** (has the same structure) with the sulfate ion. Both are tetrahedral ions with covalent bonding between the central atom and the oxygen atoms positioned at the corners of the tetrahedra. The ions *differ primarily in their charge*—sulfate is 2−, nesosilicate is 4−. Zircon (ZrSiO_4) contains SiO_4^{4-} ions and Zr^{4+} “ions.” As we have seen previously, cations with a charge of 4+ do not exist; their compounds are at least partly covalent. However, it is useful to visualize the interactions in ZrSiO_4 as primarily ionic interactions.

We have already discussed CaSO_4 , and it should come as no surprise to find that the structures of zircon and anhydrite are similar. A look down the *c*-axis of the zircon unit cell (Figure 80) shows that the silicate ions are staggered in both directions; that is, along

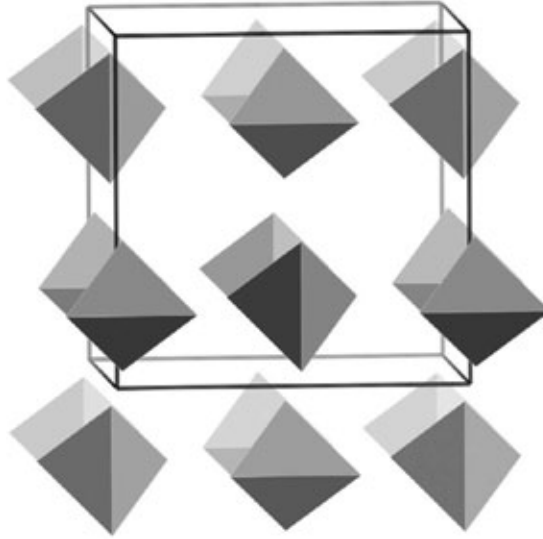


Figure 80 Zircon structure, silicate ions only. Looking down the c -axis.

both the a - and b -axis. In anhydrite, a similar view (Figure 72) shows staggering in only one direction. This difference has an important consequence: in zircon the unit cell has equal a - and b -axes. This is more apparent if we reposition the unit cell as shown in Figure 81:

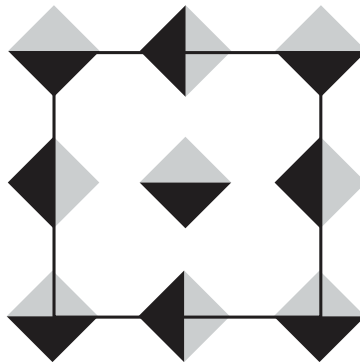


Figure 81 Zircon unit cell, silicate ions only.

A simple count of the number of corner to corner distances across the tetrahedra in the x -direction (horizontal) is $1/2 + 1 + 1/2 = 2$. The count in the y -direction (vertically) is the same. Hence, the a - and b -axes are equal in length, but not equal to the c -axis.



Give the crystal system of zircon.

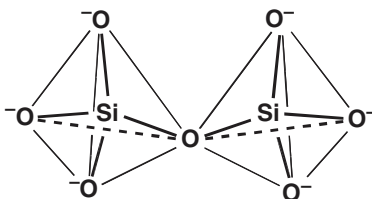


Tetragonal.

Our final example of the effect of the anion on the symmetry of the unit cell (and consequently the symmetry of the crystals that are formed) is the mineral beryl. Beryl contains a cyclosilicate ion.

The Silicates

We need to digress briefly to examine the structures of some of the ions that are formed by the “condensation” of the **nesosilicate** ion, SiO_4^{4-} (the word *neso* is from the Greek *nesogaeon* meaning “island.” The nesosilicates are sometimes also referred to as insular silicates). Two SiO_4^{4-} ions can combine by sharing one oxygen to form the **sorosilicate** ion. This ion is shown below with two tetrahedra joined by one corner.



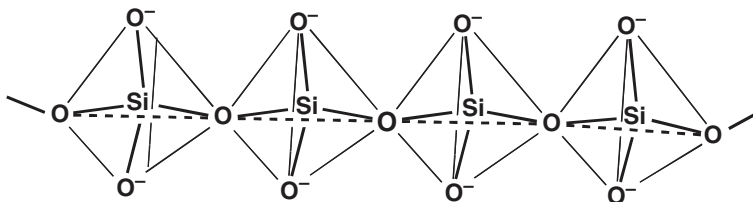
The thicker lines represent covalent bonds. The formula for this ion is $\text{O}_3\text{Si—O—SiO}_3^{6-}$, or $\text{Si}_2\text{O}_7^{6-}$. Each oxygen that is not shared has a negative charge. There are six of these oxygens and therefore the charge on the ion is 6–.

This “condensation” or combination of tetrahedra can be written as



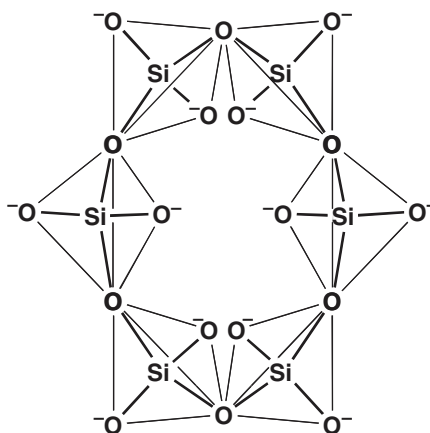
Although this equation is primarily of pedagogical value, it does reveal that the silicon content (percent silicon) of the sorosilicate ion is higher than that of the nesosilicate ion. It is generally true that the first silicates to crystallize from magmatic processes are the nesosilicates, followed by sorosilicates and so on, with the feldspars and quartz (with their high silicon to oxygen ratio) being the last to crystallize.

It is also possible for *two* oxygens of each silicate tetrahedron to be shared with other tetrahedra. This can occur in two ways. The **inosilicates** (from the Greek *ino* meaning “thread”) form long chains. A portion of such a chain is shown below. The empirical formula for this anion is SiO_3^{2-} (each silicon “owns” two oxygens plus a half share in two others). Another way to think about this is that this unit (SiO_3^{2-}) repeats itself until the entire chain is complete.



Each non-shared oxygen carries a negative charge. This type of chain, along with sufficient cations to neutralize the charge of the anions, is found in the pyroxene family of minerals. These chains can also combine with another chain by sharing oxygens between the chains. This double chain arrangement is found in the amphibole family of minerals.

The second arrangement that generates two shared oxygens occurs when short chains form rings; for example, the $\text{Si}_3\text{O}_9^{6-}$, or $\text{Si}_6\text{O}_{18}^{12-}$ ions. These anions are called **cyclosilicates**. The $\text{Si}_6\text{O}_{18}^{12-}$ ion is shown below.

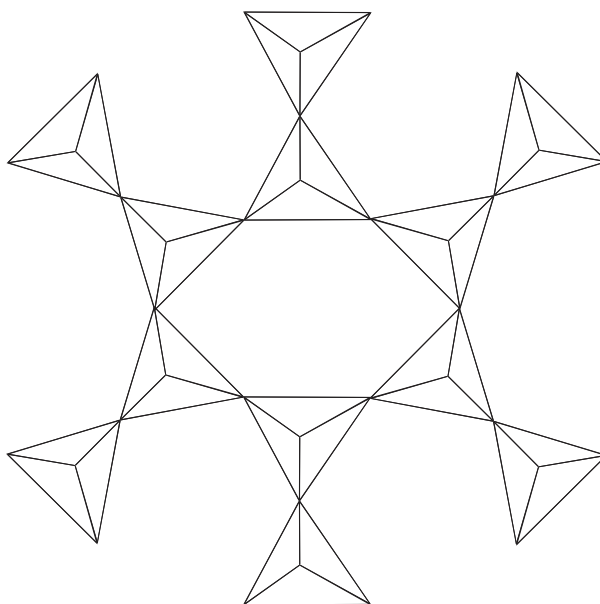


What is the repeat unit in the cyclosilicates?



The SiO_3^{2-} group. Thus, the $\text{Si}_6\text{O}_{18}^{12-}$ ion can be written as $(\text{SiO}_3^{2-})_6$.

When *three* oxygens of each tetrahedron are shared, the chains or rings turn into sheets, with each silicon containing one unshared oxygen that carries a negative charge. A small section of an essentially infinite sheet of these **phyllosilicates** (from the Greek *phyllo* for “sheet”) is shown below. These anions are responsible for the layered structure of the mica family of minerals.



Finally, *all* of the oxygens of each tetrahedron can be shared with other tetrahedra. This produces a three-dimensional network of Si—O bonds (see Figure 3), which contain only covalent bonds (no ions) and are called **tectosilicates**. Quartz is probably the best-known example of this family. In quartz, each silicon is surrounded at the corners of a tetrahedron by oxygen atoms. Each oxygen is shared by two silicons. Thus, one half of each oxygen “belongs” to a given silicon, thereby producing the empirical formula SiO_2 .

Aluminum can substitute for silicon in many of the silicates. Up to 50% of the SiO_4 tetrahedra can be replaced by AlO_4 tetrahedra in the feldspar family of tectosilicates. Each AlO_4 tetrahedron carries a 1– charge and therefore the feldspars require cations to neutralize the charge. For example, the feldspar albite has one fourth of the SiO_4 tetrahedra replaced by AlO_4 tetrahedra and therefore has the formula $\text{NaAlSi}_3\text{O}_8$.



Rewrite this formula to more clearly show the charge on the aluminum tetrahedra and the sodium ion.



$\text{Na}^+[\text{AlO}_2^-][\text{SiO}_2]_3$ This formula should not be interpreted as indicating two separate sets of three-dimensional networks, one for silicon and one for aluminum. The aluminum takes the place of one fourth of the silicon atoms in the quartz structure. Remember that in quartz, which contains only SiO_4 tetrahedra, each Si shares four oxygens with other silicons. Thus each Si “owns” only $4 \times 1/2 = 2$ oxygens.

Beryl contains the $\text{Si}_6\text{O}_{12}^{12-}$ ion. It also contains Be^{2+} ions, Al^{3+} ions, and Na^+ ions. Many samples, including the one that we will examine, also contain other ions such as Cs^+ . The cancellation of this large number of negative charges in the anion involves a considerable number of cations in a complicated structure. Figure 82 reveals $\text{Si}_6\text{O}_{12}^{12-}$ ions stacked in a staggered fashion down the *c*-axis.

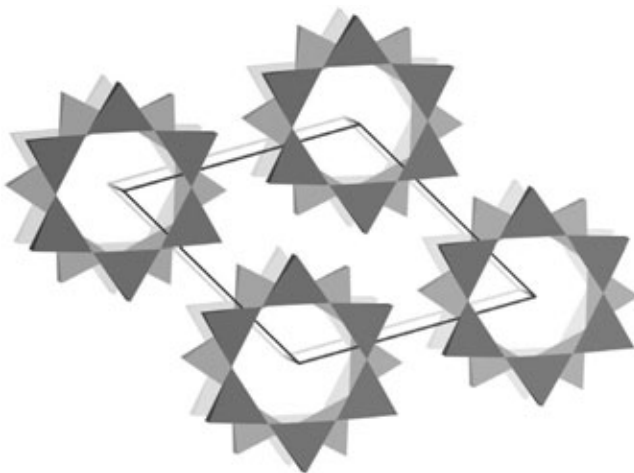


Figure 82 Beryl, cyclosilicate ions only, view down *c*-axis.

This is made clearer in Figure 83, where layers of cyclosilicate ions are shown. Alternate layers minimize repulsions by staggering the rings. Thus, what may appear in Figure 82

to be single 12-cornered rings is actually three layers of 6-cornered rings. The first two layers are clearly visible, but the third is barely visible as what appears to be a shadow on the left side of the rings. Within a layer, the rings are arranged in what is essentially a closest-packed arrangement. This results in a hexagonal unit cell. The three layers of anions in Figure 83 also reveal a horizontal plane of symmetry.

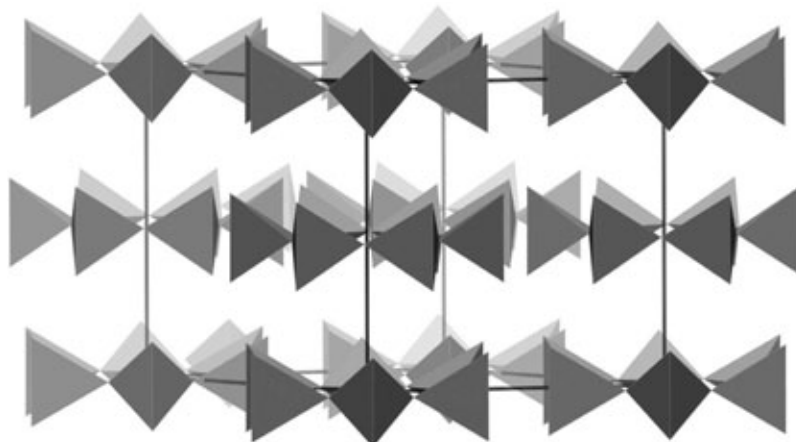


Figure 83 Beryl, cyclosilicate ions viewed perpendicular to c -axis.

Of course, the cyclosilicate rings are not really closest packed. There are many cations arranged between the rings. Figure 84 shows a side view of the three layers and the octahedral polyhedra of the aluminum ions.

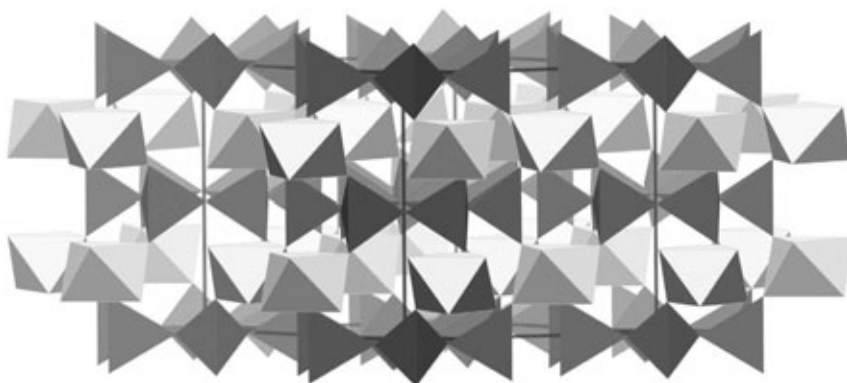


Figure 84 Beryl, side view of cyclosilicate and Al^{3+} ions.

Figure 85 shows the addition of the Al^{3+} ions with their octahedral coordination, the Be^{2+} ions with their tetrahedral coordination, and the sodium ions in the centers of the rings.



Figure 85 Beryl, Na^+ , Be^{2+} , Al^{3+} , and cyclosilicate ions.

The six-coordination of the sodium ions can be seen more clearly in Figure 86, which shows just the anions and the sodium ions.

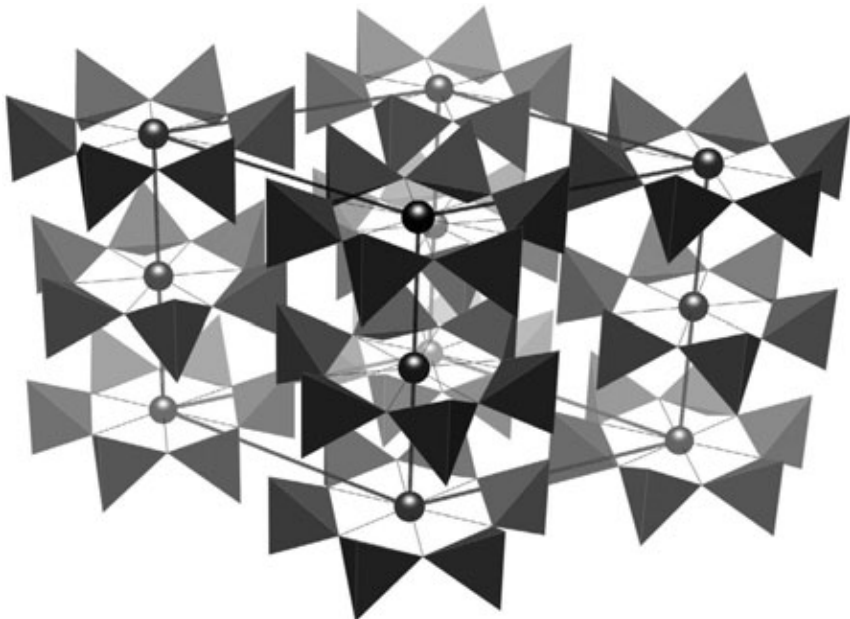


Figure 86 Beryl, cyclosilicate ions and Na^+ ions. The 6-coordination of the sodium to the shared oxygens in the 6-membered rings is shown. The unit cell is shown with lines connecting the sodium ions.



Can you explain why the aluminum and sodium ions have six-coordination, whereas the beryllium ions have only four-coordination?



This question can be answered in two ways. If we assume that the ions interact strictly through their Coulombic “ionic” interactions, we can rationalize the coordination number on the basis of size. The Be^{2+} ion is simply too small to accommodate 6 atoms or groups around it. The second explanation assumes that the ions use some amount of covalent bonding through the use of their atomic orbitals (we will discuss orbitals in Chapter 7). Beryllium appears in the second row of the periodic table, where the atoms utilize orbitals in the second quantum level. This level has a total of four orbitals—one 2s- and three 2p-orbitals. Sodium and aluminum, on the other hand, are in the third row, where the atoms have access to one 3s-, three 3p-, and five 3d-orbitals. Sodium and aluminum, therefore, can utilize more than four orbitals. Each orbital provides for a covalent interaction and consequently the number of orbitals available is equivalent to the maximum number of covalent bonds that can be formed.

In general, then, the structure of the unit cell depends on the relative sizes and charges of the cation and anion, and the shape of the anion. The ions are arranged to produce the lowest potential energy. These arrangements maximize attractions, minimize repulsions, and generally maintain electrical neutrality over even very short distances. The presence of significant covalent bonding and the existence of hydrogen bonding (relatively weak interactions between the hydrogen of hydroxyl group (OH^-) and sites with excess electron density) also affect the structure and properties of minerals. Polymorphs differ in their potential energies but, even though one polymorph is always more stable than the others at a given temperature and pressure, reorganization of the structure to the more stable form is usually (but not always) sufficiently slow that most polymorphs are stable mineral species.

5.3 EFFECT OF TEMPERATURE AND PRESSURE

We have alluded to the effect of temperature and pressure at several points during our discussion. We conclude this section by summarizing the effects of these two variables. An increase in temperature:

- a) increases the energy available for rotation of anions in their lattice sites and generally leads to an increase in symmetry of the unit cell.
- b) increases the energy available for random ordering of cations, which also leads to an increase in symmetry of the unit cell.
- c) increases the energy available for diffusion of cations of other elements throughout the crystal structure, thereby leading to solid solution (particularly when the sizes and charges of the cations are similar).

An increase in pressure generally leads to a decrease in the volume of the unit cell and an increase in coordination number. In addition to the examples already given, we should also mention the high pressure form of SiO_2 (stishovite), where silicon has a coordination number of 6, as opposed to its normal coordination number of 4.

Chapter 6

Physical Properties: Morphology

6.1 CRYSTAL MORPHOLOGY

The shape of the crystals that are formed by a particular compound is determined by the symmetry of the unit cell of the compound and by conditions such as ion concentrations, temperature, pressure, and the space available for the formation of the crystals. The shapes of crystals are described by their forms, such as cube, tetrahedron, etc., and by the symmetry of the crystals. In the sections that follow, we will first develop a system of designating the relationship of the faces of a crystal to the crystallographic axes and then use this system to develop the general idea of a crystal form.

6.2 MILLER INDICES

The relationships between the faces of a crystal and the axes that define the crystal system are generally described by **Miller indices** (devised in 1839 by the British crystallographer William Miller). Consider two general faces orientated as shown in Figure 87. The larger face MNO is tilted toward the *c*-axis at a less severe angle than the smaller face MPO. Both faces intercept the *a*- and *b*-axes at the same point, but the larger face intercepts the *c*-axis at twice the distance of the smaller face. When there are two or more faces that intercept all three axes (when they are fully extended so that they *can* intercept the axes), the larger face is called the unit face. The Miller indices are obtained by first determining the position on each axis where the face intercepts the axis. For the unit face these positions are by definition given the value of one unit on each axis. Next, the Miller indices are obtained by taking the reciprocal of each intercept. Thus, for the unit face the Miller indices are designated in parentheses as (111), listing them in order of the *a*-, *b*-, and *c*-axes. The indices are read as “one one one.”

For the smaller face, the intercepts are determined relative to the reference face. Thus, the MPO face intercepts the *a*- and *b*-axes at the same positions as the reference face and therefore the intercepts are one unit. On the *c*-axis the intercept is half of the distance to N, which was taken as one unit (notice that the units are relative). Thus, the intercept of MPO on the *c*-axis is $\frac{1}{2}$. The reciprocal of $\frac{1}{2}$ is 2 and the Miller indices for the face MPO therefore are (112). It is helpful to recognize that the larger the value of the index of the *c*-axes, the smaller the inclination of the face toward the axis.

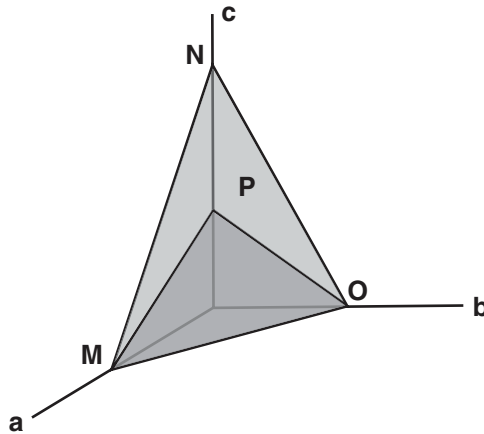


Figure 87 Two faces of a crystal relative to the axes.



Now examine Figure 88 and determine the Miller indices for the face shown there.

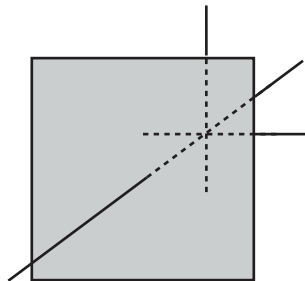


Figure 88 A face of a crystal relative to the axes.



This face intercepts the a -axis at what we will designate as one unit distance and does not intercept (that is, runs parallel to) the b - and c -axes. The Miller indices are therefore $1/1$, $1/\infty$, and $1/\infty$. Since anything divided by infinity is zero, the indices are (100) .

Figure 89 shows the (111) face in two different crystals. The shape of the face of the isometric crystal is clearly different from the (111) face of the tetragonal crystal. Thus, the same designation of the face does not indicate that the shape of the face is the same in different crystal systems. Indeed, the different shapes are a result of the different shaped unit cells: in the isometric system the unit cells are cubes, in the tetragonal system the unit cells are shortened (in this case) in the c -direction. When the unit cell parameters for a substance are known, the length of the cell axes can be used as unit distances to derive the Miller indices.

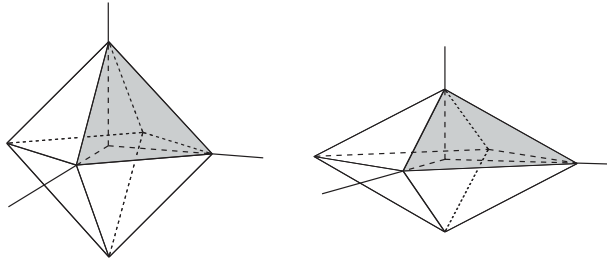


Figure 89 The (111) face in an isometric (left) and a tetragonal crystal.

Now consider a crystal in the isometric system with corner faces, only one of which is shown in Figure 90.

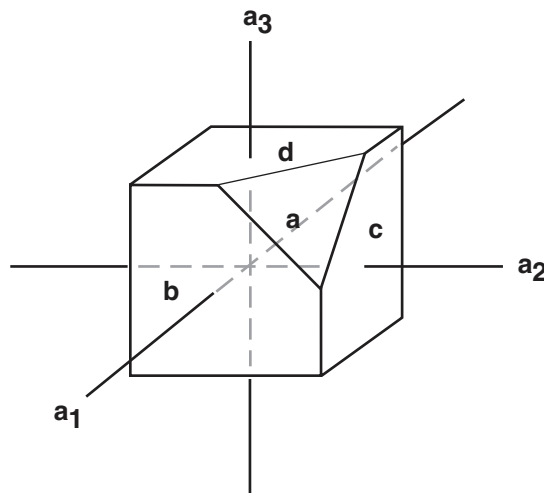


Figure 90 Several faces of a crystal in the isometric system. As drawn the crystal does not have isometric symmetry. A real isometric crystal containing face **a** would have seven other faces, one at each corner of the cube. These other faces are not shown.



Look at the face labeled **a** and determine how it would intersect the axes if the face were extended until it was large enough to meet the axes.



The face would intersect each axis the same distance from the origin. We will arbitrarily call these distances $1a_1$, $1a_2$, and $1a_3$. The Miller indices for this face are (111).

Next examine the face labeled **b**. This face intersects axis a_1 at a shorter distance than $1a_1$ from the origin, but because we are only interested in the relative intersections of a given face with the three axes we will also call this intersection $1a_1$. Face **b** clearly runs parallel to axis a_2 and to axis a_3 and therefore intersects with these only at infinity. Thus, the Miller indices for face **b** are (100).

Now let us try a slight variation on our isometric crystal by adding a third type of face. This face **e** is shown in Figure 91. This face clearly intersects the axes a_1 and a_3 , but runs parallel to axis a_2 . It therefore has intercepts of $1a_1$ and $1a_3$ and infinity a_2 . The reciprocals of these are 1, 0, and 1, listing them in order of the axes. Face **e** then is given the indices (101).

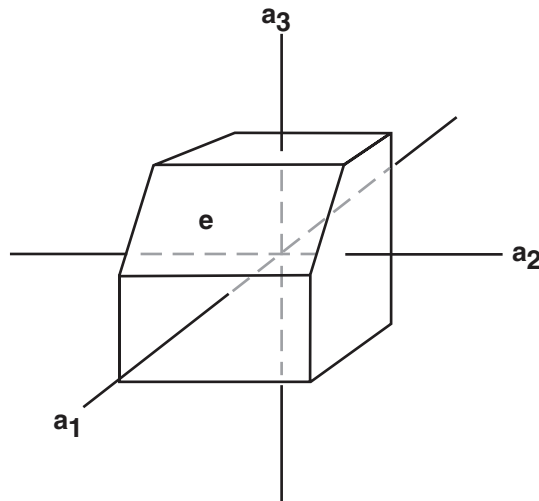


Figure 91 Another face of a crystal.

6.3 FORMS

Now let us try an experiment with the (111) face in an isometric crystal in the point group $4/m\bar{3}2/m$. The object of our experiment will be to see what set of faces is formed by operating on the (111) face with the symmetry elements of this point group.



Take face **a** in Figure 90 and operate on it with the four-fold a_3 axis, followed by reflection in the plane perpendicular to this axis. What geometric form is produced?



With this face, the four-fold a_3 axis and a reflection perpendicular to this generate the closed form—the octahedron shown in Figure 92. A completely enclosed crystal or form is said to be **euohedral** (from the Greek root *eu-* meaning “well” or “finely”). This form is indicated by the Miller indices of the face that was used to generate it enclosed in curly brackets.



Begin with the (100) face (see Figure 88 and 90) and determine what form will be generated by using rotation through the a_3 four-fold axis, followed by rotation about the a_1 four-fold axis.

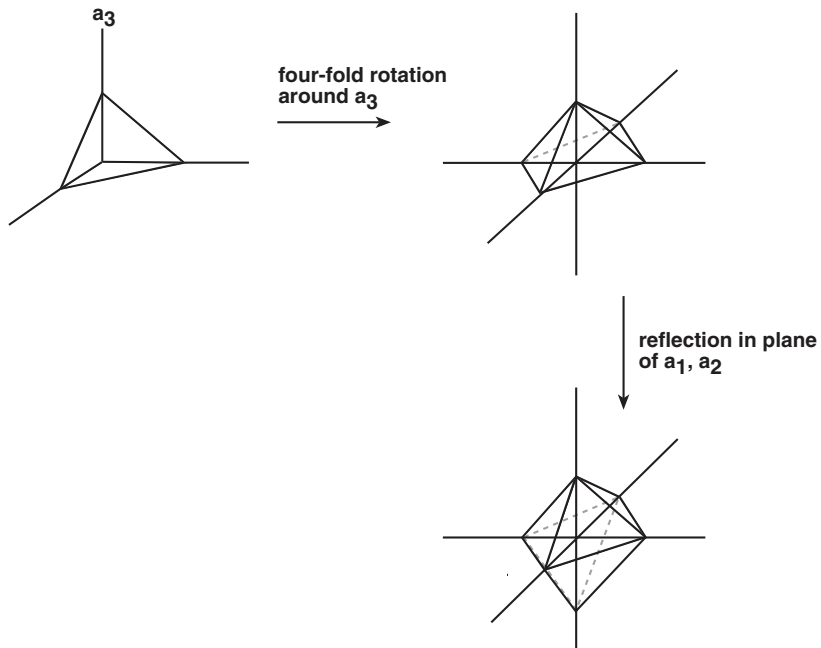


Figure 92 The octahedron $\{111\}$ generated from the (111) face.



Rotation of the (100) face about the a_3 axis produces a four-sided box without the top and bottom. Rotation of this box through a_1 then generates the top and bottom of the box. In other words, the symmetry of this class produces a cube—the $\{100\}$ form.

When the same procedure is applied to the (101) face, the closed form shown in Figure 93 is produced. This is known as the dodecahedron because it has a total of twelve faces.

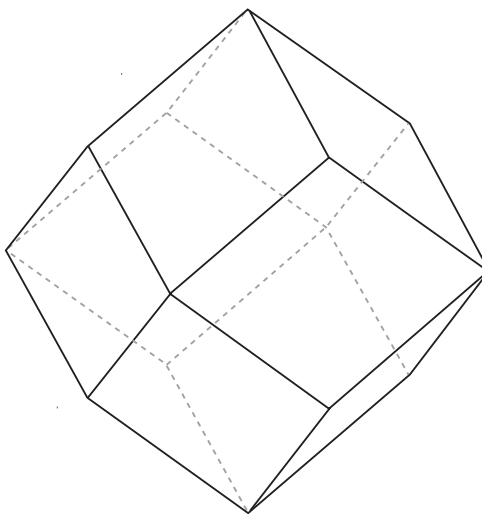


Figure 93 The dodecahedron formed by symmetry operations in the isometric system on the (101) face.



The dodecahedron above is shown again below with several of the faces lettered. Assign the Miller indices to these faces.

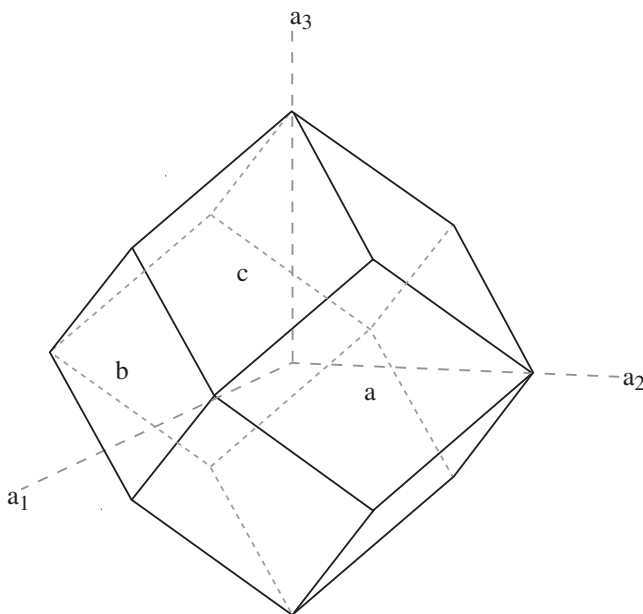


Figure 94 The dodecahedron with several faces labeled. Notice that the a_1 axis extends through the intersection of face **a** with face **b**, and that the negative end of the a_2 axis extends through the opposite corner of face **b**.



Face **a** intersects a_1 and a_2 and runs parallel to a_3 and therefore is the (110) face. Face **b** intersects a_1 and the negative end of a_2 and is parallel to a_3 ; it is the (1-10) face. Face **c** intersects a_1 and a_3 and is parallel to a_2 and is the original (101) face.

We will continue to explore the isometric system by choosing a point group of lower symmetry—the $\bar{4}3m$ group. In this symmetry, the planes perpendicular to the four-fold axes are not present and therefore forms like the octahedron with the greater symmetry due to the perpendicular plane are not formed. Probably the most common form in this class is the tetrahedron, formed from the (111) face. A tetrahedron could also have been generated by starting with the (1-11) face; this tetrahedron has a different orientation relative to the first. The one generated from the (111) face is called the positive tetrahedron, while the other is referred to as the negative tetrahedron. The two are indistinguishable unless they are present in the same crystal. For example, a combination of a small amount of one with the other produces the combination form shown in Figure 95. If they combine in equal forms, a crystal with the shape of an octahedron is formed. When this happens it is often the case that the faces of the two tetrahedra will have different striations or luster.

Finally, in the $2/m\bar{3}$ point group, the perpendicular plane is present and forms more similar to those in the $4/m\bar{3}2/m$ group are produced. The pyritohedron, named for the mineral that frequently adopts the form (though pyrite also shows cubes and octahedra, and many combinations), is shown in Figure 96.

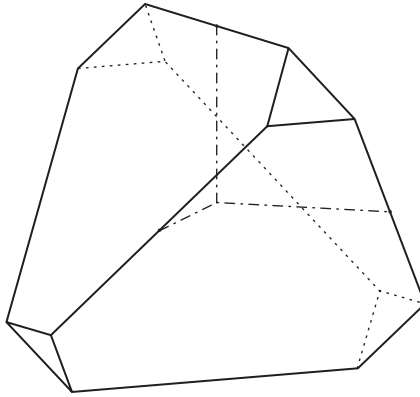


Figure 95 A form composed of both a positive and negative tetrahedron.

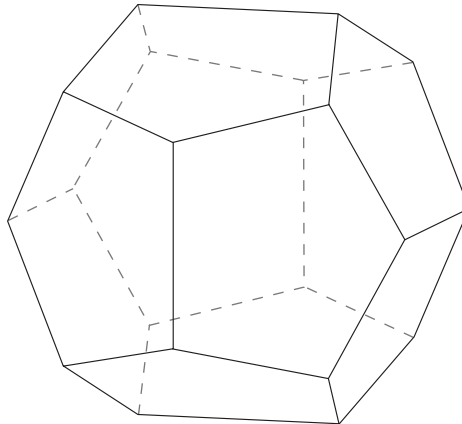


Figure 96 The pyritohedron.



The pyritohedron above is shown in Figure 97 with one of the faces lettered. Assign the Miller indices to this face.



This face clearly cuts the a_1 -axis and is parallel to a_3 . It is also inclined toward a_2 but does not intersect it at the same distance from the origin as the intersection with a_1 (this can be seen by recognizing that the axis a_2 extends through the center of the edge adjoining the two neighboring faces). We can reasonably assume that the intersection with a_2 is at twice the distance of the intersection with a_1 . Thus, the intersections are 1, 2, infinity. The reciprocals are 1, 1/2, and 0. Because Miller indices never involve fractions, we multiply each number by two to get the face (210). In general, the most common faces of crystals have the simplest Miller indices. That is, faces with indices such as (561) are generally rare.

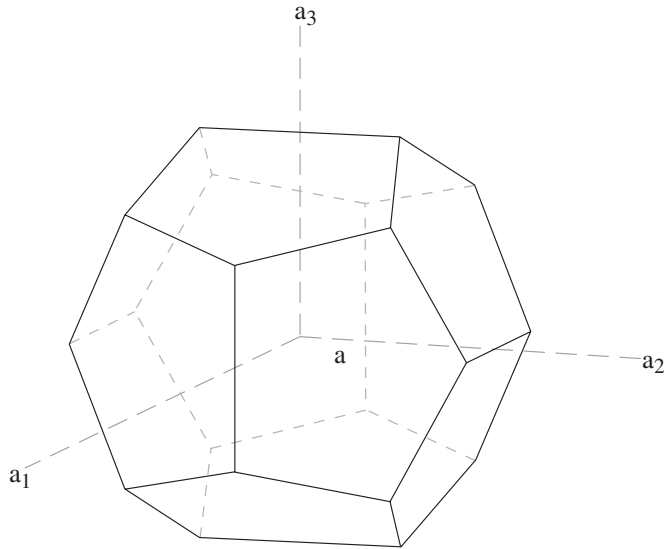


Figure 97 The pyritohedron with one face labeled.

All of the isometric point groups form the cube and dodecahedron, but only two of the five classes form the tetrahedron, two form the pyritohedron, and three form the octahedron. As we have implied, many crystals also exist as combinations of more than one form. This is shown in Figure 98 where the cube/octahedron and cube/dodecahedron combinations are seen.

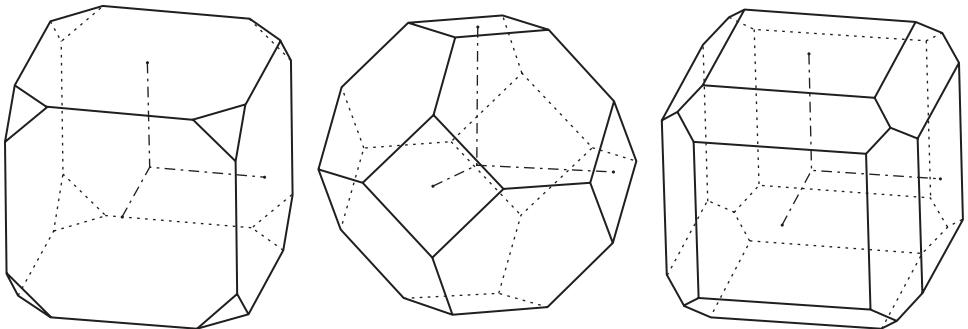
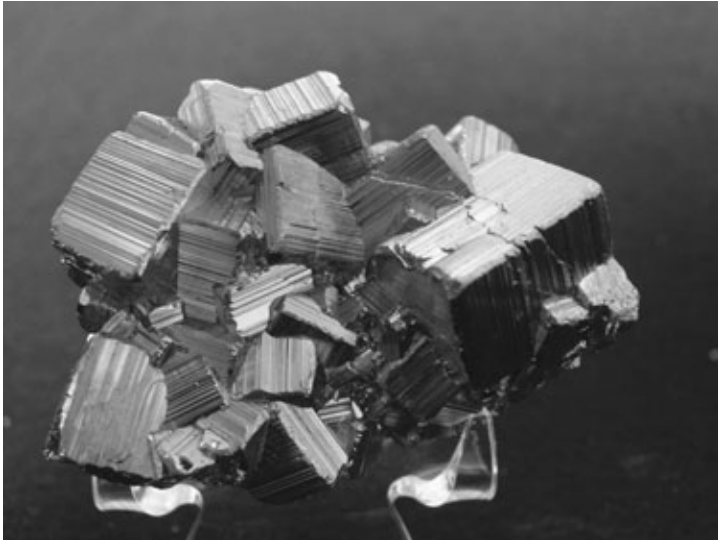
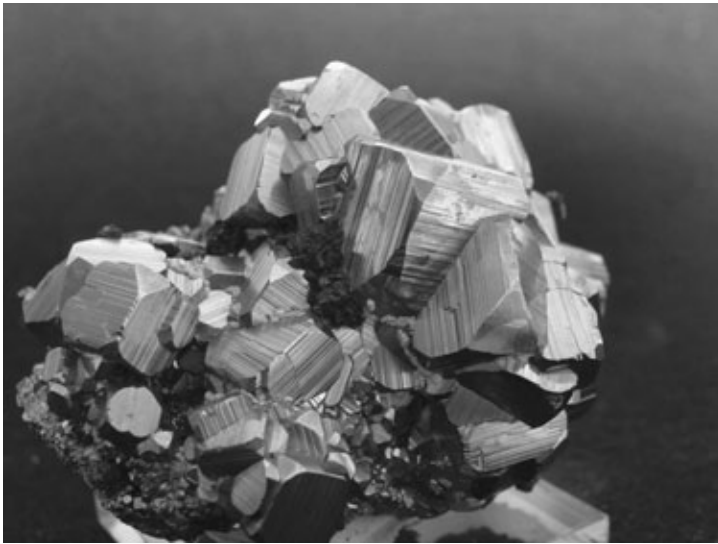


Figure 98 Some isometric combination forms. From left to right: the cube slightly modified by the octahedral form, the cube modified to a greater extent by the octahedral form, and the cube modified by the dodecahedron.

In Figure 99, we also show photographs of some pyrite crystals. As you can see, these crystals are considerably distorted from the idealized symmetries that we have discussed. Notice also that the faces of some of the cubic crystals have striations in a direction perpendicular to the striations on neighboring faces. This is a result of the lower symmetry of the $2/m\bar{3}$ class, where, for example, the four-fold axes that would generate identical cube faces, are absent.



(a)



(b)

Figure 99 Some pyrite crystals: (a) cubes showing striations in different directions on adjacent faces (Huanzala, Peru); (b) cubes modified by octahedral faces (Huanzala, Peru); (c) cubes modified by dodecahedral faces (Nanisivik Mine, Northwest Territory, Canada); (d) octahedra (Huanzala, Peru).



(c)



(d)

Figure 99 *Continued*

Although an elaboration on all of the forms adopted by crystals is beyond the scope of this text, a number of others deserve mention. In the hexagonal system, the trapezohedron, the scalenohedron, and the rhombohedron are common forms (Figure 100). In the systems of lower symmetry there are also open forms, that is, forms that do not by themselves produce a complete crystal. These forms are also used in other systems to describe portions of the crystal. Figure 101 shows the pedion, the pinacoid (two parallel faces), a prism form (three or more parallel, connected faces), and a pyramid form.

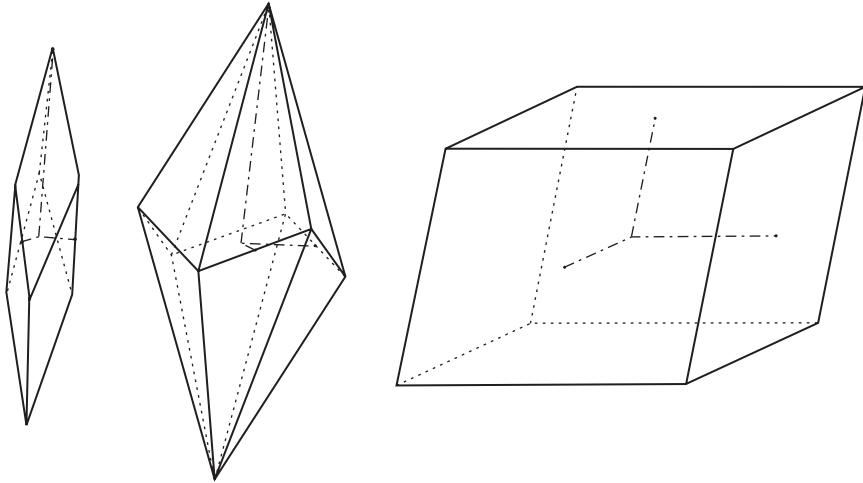


Figure 100 The trapezohedron (trigonal), scalenohedron, and rhombohedron.

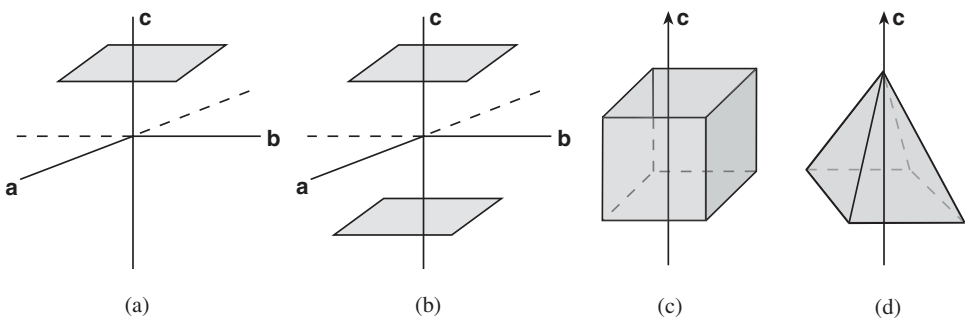
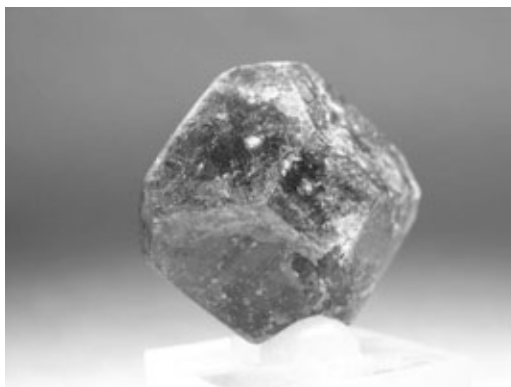


Figure 101 Some open forms: (a) the pedion; (b) the pinacoid; (c) prism; (d) pyramid.



Describe the crystal system and the crystal form of the following crystal. The opposite side has a similar appearance:





The crystal has a four-fold axis and a horizontal plane of symmetry (perpendicular to the four-fold axis). It also has four two-fold axes perpendicular to the four-fold axis and four mirror planes along those axes. The crystal therefore belongs to the tetragonal system. The form can be described as ditetragonal bipyramidal and the “slanted” faces are referred to as pyramid faces.

The specific form of the crystal is controlled by how rapidly various faces are developed (grow) and this depends on the internal forces in the unit cell, the environment in which the crystal grows, the concentration of the ions in solution, and the temperature and pressure. Figure 102 shows a cubic stacking of isometric unit cells, as well as three other symmetries that result from stacking of the same isometric unit cell in different directions. The different rates of growth of different faces are also shown in Figure 103 where a cube-

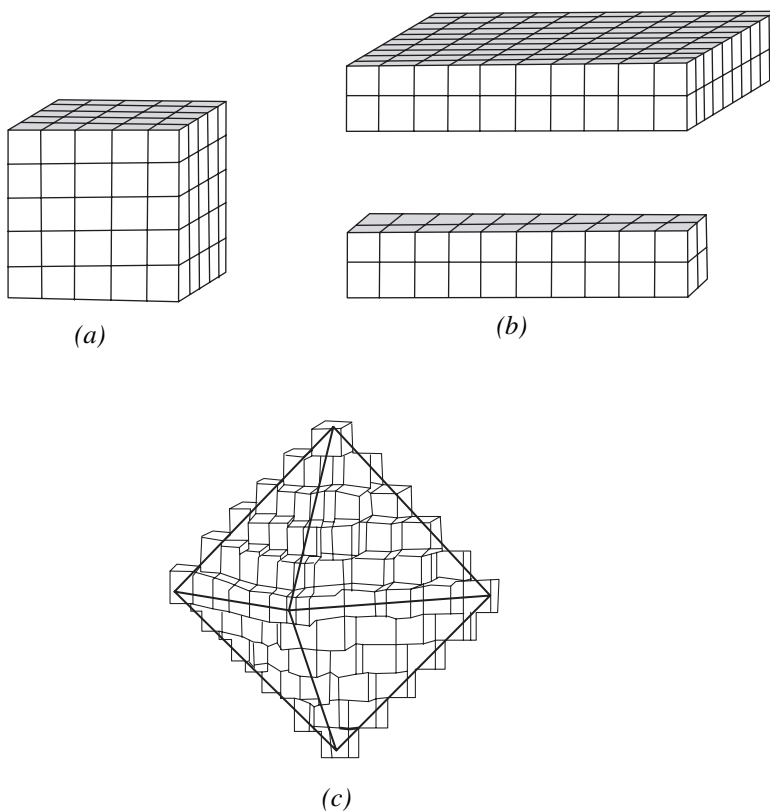


Figure 102 The packing of cubic unit cells: (a) packing equally in three directions produces a cube; (b) acceleration of packing in the x - and y -directions; (c) packing along the 3-fold axis. (Reproduced by permission from Klein, C. and Hurlbut, C. S., Jr., *Manual of Mineralogy*, 21st edn, John Wiley, NY, 1993, Figure 2.3 page 20.)

octahedron form of NaCl is portrayed. The (111) face, for example, has only chloride ions (or only sodium ions) exposed to the solution, whereas faces such as the (001) face have both sodium ions and chloride ions exposed. For those faces with both ions exposed, the face is essentially electrically neutral and is less likely to attract sodium or chloride ions from the surrounding solution. The (111) face, as it appears to the solution, is negatively charged and therefore attracts sodium ions quite rapidly. (Another way to analyze this is to realize that there are more places for a sodium ion to be attracted on the (111) face than on the (001) face.) The (111) octahedral face therefore grows more rapidly until it disappears, leaving only the cube faces (as shown in the bottom of the figure). This rationalization helps to account for the high percentage of cubic crystals in those classes of the isometric system that can form both cubic and octahedral forms.

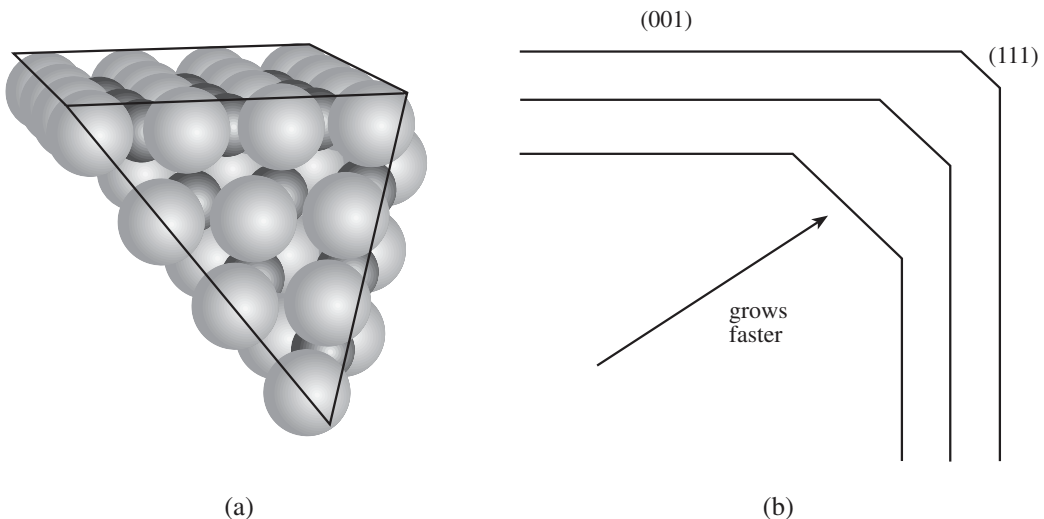


Figure 103 Rate of growth of different faces in an isometric crystal. Strong attractions for ions in solution increases the rate of growth of the (111) face (a) until eventually it disappears (b).

6.3.1 Habit

The particular shape of crystals as determined by the relative growth of their faces is called the crystal habit. Long thin crystals are called acicular (needle-like), whereas tabular crystals develop most rapidly in two dimensions. Equant crystals, on the other hand, develop pretty much equally in three directions. Figure 104 shows a schematic classification of these descriptions of habit. Of course, some crystals exist in easily recognized forms, such as the ones described in the previous section—cubic, octahedral, tetrahedral, etc.

Crystals can also aggregate in masses that have less easily recognized crystalline forms. These masses include shapes such as botryoidal (grape-like), oolitic (pea-shaped), globular (nearly spherical), stalactitic, lamellar (platy), and dendritic (finely extended structures). Figure 105 shows botryoidal forms of both goethite and lepidolite.

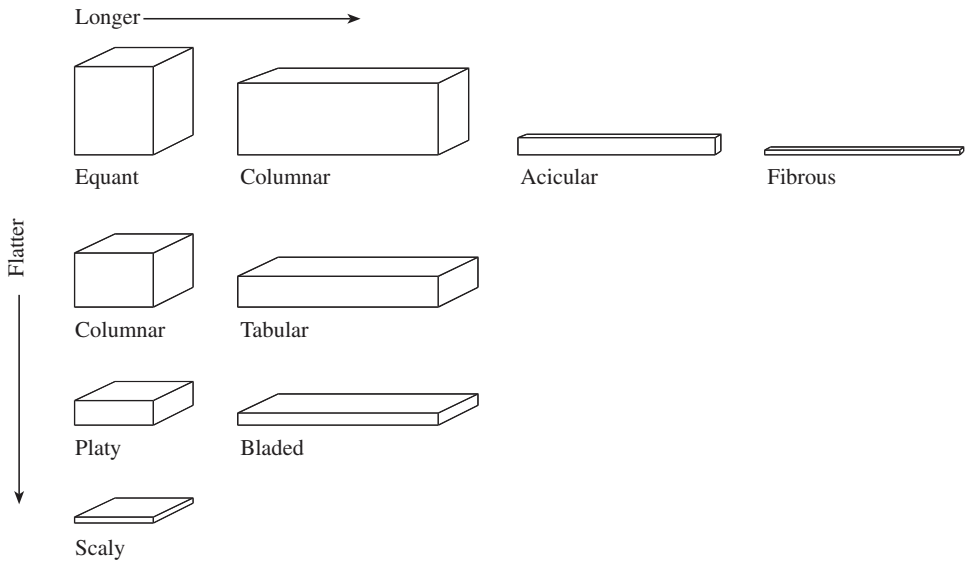
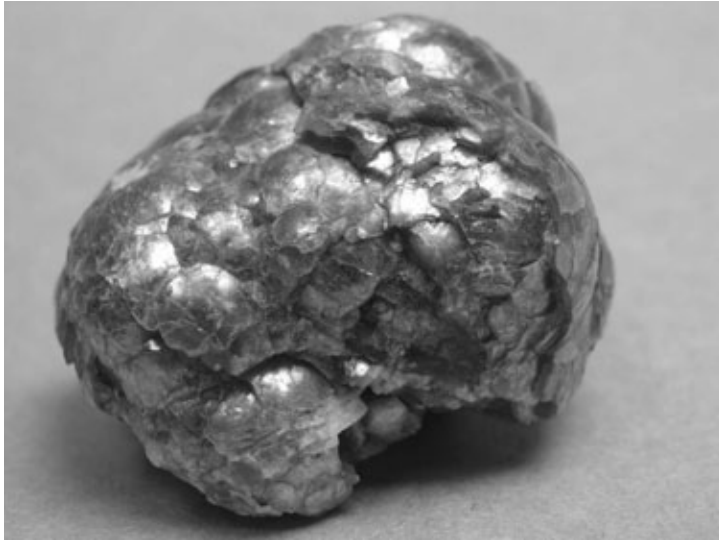


Figure 104 Classification of habits.



(a)

Figure 105 Botryoidal goethite (Mina Buena Tierra, Santa Eulalia, Chihuahua, Mexico) (a) and lepidolite (Lavra da Taqueral, Itinga, Minas Gerais, Brazil) (b).



(b)

Figure 105 *Continued*

6.4 DEVIATIONS IN CRYSTAL GROWTH

Crystals frequently do not grow in perfect single crystals that contain one or more crystal forms. There are many deviations from such normality, only four of which will be discussed here: parallel growth, twinning, epitaxy, and pseudomorphism. The first two involve crystals of the same compound, whereas in the latter two another compound is involved.

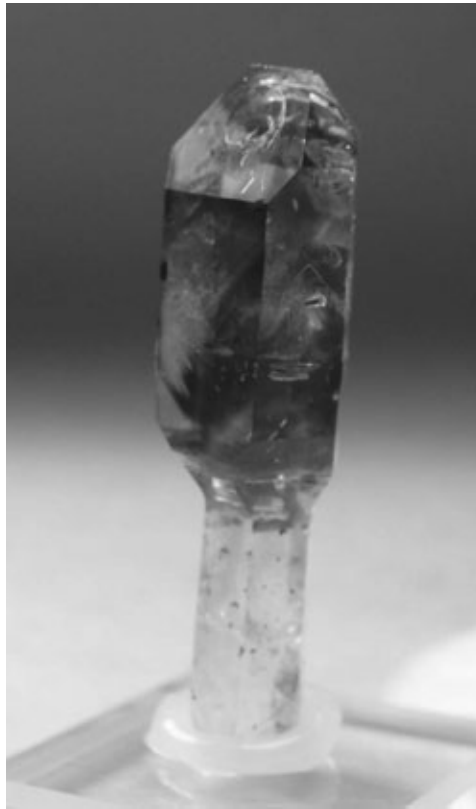
6.4.1 PARALLEL GROWTH

Parallel growth occurs when two or more crystals have their axes parallel to one another. Two examples of this phenomena are shown in Figure 106, where a “scepter” and a “plate” of quartz are shown. The top part of the scepter presumably formed because the growth of the stem was altered by conditions that favored slower growth and therefore larger faces. In the smoky quartz, an aggregate of crystals have grown side by side. However, in both cases, the aggregate consists of the same array of atoms and so each represents, at the atomic level, only one crystal.

6.4.2 Twinning

Twinning occurs when two or more different crystals of the same compound grow in specific symmetric relationships to one another. Consider a two-dimensional schematic of an orthorhombic crystal as shown in Figure 107.

The crystals contact one another along the x -axis and share the atoms or groups that exist on the points along this line. The two orthorhombic arrays continue on their own from that contact point. Because this point of contact involves shared points, the relationship between the two crystals is determined by the lattice parameters and therefore



(a)



(b)

Figure 106 An amethyst scepter (Brandberg, South Africa) (a) and an example of parallel growth in smoky quartz (Galileia, Minas Gerais, Brazil) (b).

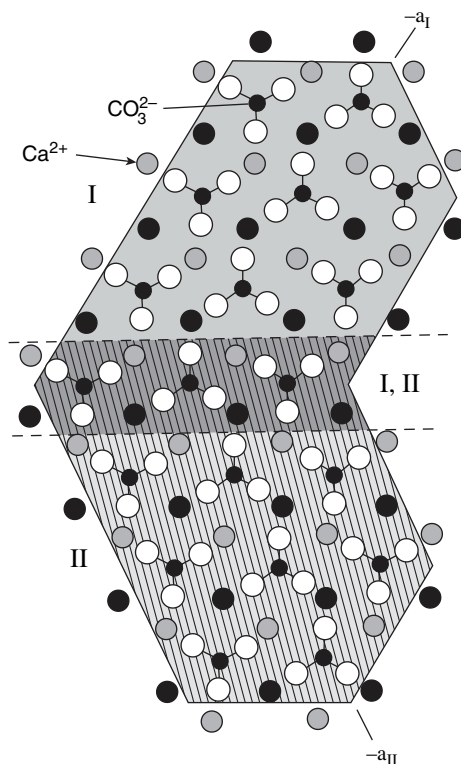


Figure 107 Twinning in an orthorhombic crystal. The twinning of aragonite ($CaCO_3$) is shown. The intersection of crystal I with crystal II occurs in the section labeled I,II, where coordination of the ions differ only slightly from those in the individual crystals. (Reproduced by permission from Bloss, F. D., *Crystallography and Crystal Chemistry*, Mineralogical Society of America, Washington, DC, 1994, Figure 10-25C, p. 329.)

will have a particular angle for a particular mineral. Although twinning is a distortion of the arrangement of the ions (atoms) in the lattice, the increase in potential energy due to this distortion is small because it generally involves relatively small changes in the surroundings of the ions along the contact plane. Hence, twins are only slightly less stable than their individual crystals and are therefore fairly common. Of course, once formed they are stable for very long periods of time because the rate of their devolution to a single crystal is extremely low. Twins can also be formed by rotation around an axis or inversion through a center of symmetry. Generally, rotational twins are penetration twins rather than contact twins and the appearance of the two types is quite different. Figure 108 shows a contact twin of quartz known as a Japan law twin, in which the two crystals have inter-crystal angles of $84^\circ 33'$. Part (b) of the figure shows a penetration twin of pyrite, and in part (c) a common twin type of the feldspar orthoclase (the Carlsbad twin).

6.4.3 Epitaxis and Pseudomorphism

When a crystal is influenced by another compound, either epitaxis or pseudomorphism may occur. If the new compound shares some of the lattice points with the original crystal, it may grow in the same direction and is referred to as an **epitaxial** overgrowth. When the

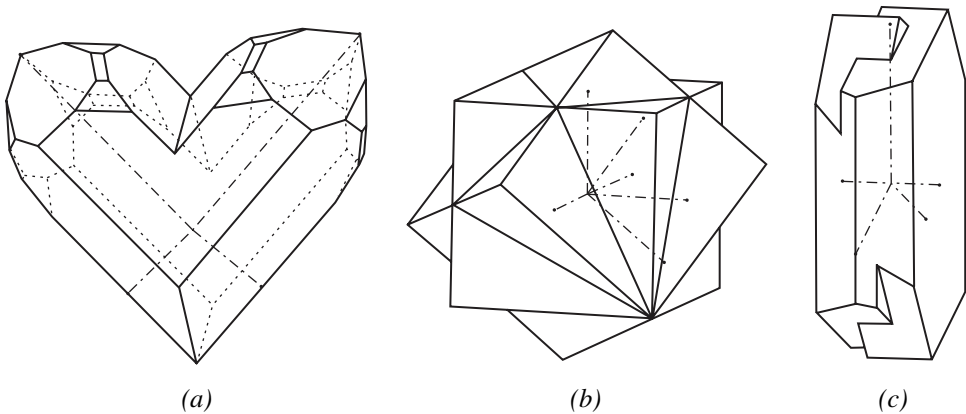


Figure 108 Several twinning forms: (a) a Japan law twin of quartz; (b) a penetration twin of pyrite; (c) a Carlsbad twin of orthoclase.

second compound simply grows over the first mineral and takes the shape of the original mineral an **encrustation pseudomorph** or **epimorph** forms. (The word pseudomorph comes from the Greek *pseudo* meaning false and *morph* meaning form. The prefix *epi* means on top of or outside of.) After the encrustation is formed, the original mineral may be dissolved as shown in Figure 109.



Figure 109 An epimorph of manganocalcite after calcite (Pachapaqui, Peru).

When the new compound substitutes, even partially, for the original compound, the pseudomorph is called a **substitutional pseudomorph**. Usually the new compound has an ion in common with the original, as is the case of goethite pseudomorph after pyrite (both contain iron: as Fe^{3+} in goethite and as Fe^{2+} in pyrite) and the malachite pseudomorph after azurite (both contain Cu^{2+} , CO_3^{2-} , and OH^-) shown in Figure 110. The malachite pseudomorph is particularly interesting, because the two minerals differ only in the stoichiometry (mole ratio) of the ions present.



(a)



(b)

Figure 110 Pseudomorphs: (a) goethite after pyrite (Pelican Point, Utah); (b) malachite after azurite (Tsumeb, Namibia).



Examine the crystals in Figure 110 closely and determine to what crystal system the original mineral belongs.



The goethite pseudomorph is an easy one—the original pyrite is in the isometric system. Incidentally, these particular pseudomorphs are sometimes referred to as limonite. The term limonite is not an accepted mineral name and is used when the composition of the iron oxide is uncertain. The names of minerals are

frequently derived from either the location in which they were first found or from the name of an individual who has made an important contribution to mineralogy. Of course, some names, such as hematite (from the Greek *haimatitis* for the color red) and sphalerite (from the Greek for treacherous, because of its similarity to galena) were derived from the appearance of the mineral or have some classical historical connection. Mineral names are approved by the Commission on New Minerals and New Mineral Names of the International Mineralogical Association and new minerals are summarized in the journal *American Mineralogist*.

The original azurite appears to have a two-fold symmetry axis and belongs to the monoclinic system. Malachite belongs to the same system, but very rarely forms large crystals (it is usually massive or forms thin fibrous needles).

Chapter 7

Physical Properties: Color

The color of minerals is one of their most fascinating properties and is frequently the first thing that draws attention to the mineral. Color can originate in a number of ways: from the presence of a cation or anion that is colored, from the presence of an “impurity” that is colored, or from a defect in the arrangement of the ions in the solid. The color is always a result of the transition of electrons in the ions or the crystal lattice from one energy level to another. Before we explain this “movement” of electrons we need to review the nature of light and the electromagnetic spectrum.

7.1 LIGHT AND THE ELECTROMAGNETIC SPECTRUM

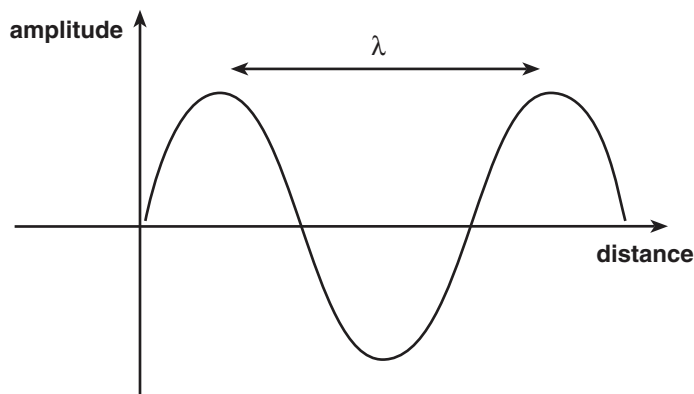
At one time, light was believed to be a stream of particles that, upon hitting the retina of the eye, induces sight. In the early part of the twentieth century the wave model of light became popular, and we now attribute most properties of light to its wave motion. The oscillatory motion is a result of changes in electric and magnetic fields associated with light. The rate at which the wave moves up and down is called its frequency and the distance between waves is called the wavelength.



Draw a wave and show how to determine its wavelength.



The wavelength is the distance from crest to crest or from trough to trough.



The wavelength and the frequency are inversely related; that is, as the frequency increases, the wavelength decreases, and this relationship is given by the equation

$$\lambda\nu = c$$

where the Greek letters λ and ν stand for wavelength and frequency, respectively, and c is the speed of light.

Another important relationship for light was discovered by the German physicist Max Planck. The energy of light is proportional to its frequency, with the proportionality constant, the Planck constant h , having a value of 6.6×10^{-34} J-s:

$$E = h\nu$$

The fact that “light” can exist with a number of different frequencies and wavelengths is shown by the electromagnetic spectrum given in Figure 111 below.

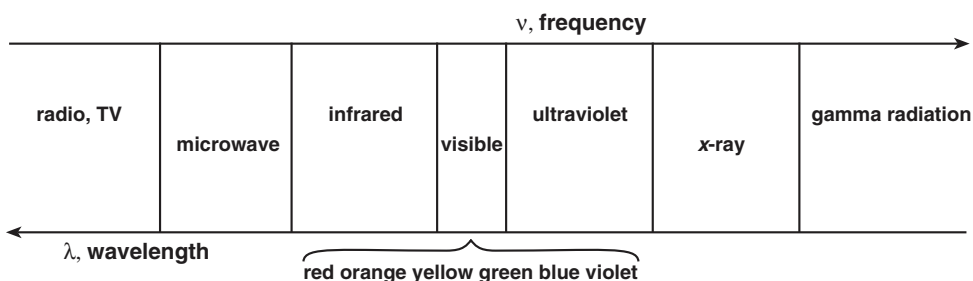


Figure 111 The electromagnetic spectrum. Notice that the visible portion of the spectrum is only a small fraction of all possible wavelengths of electromagnetic radiation.

The visible region of the spectrum is particularly pertinent to our discussion of color. These are the frequencies of light that our retinas respond to and they vary from the high frequency violet to the lower frequency red. When we “see” red, our retinas are responding to light with a wavelength of about 700 nm. The object that looks red in most cases does not generate red light, it merely reflects or transmits red light that originated from another source.



If you are sitting in a library, the light source is either fluorescent or incandescent light. This white light contains all of the frequencies in the visible range. What, then, causes you to see your shirt as red?



If you see red, only the red frequencies of light are striking your retina. The other frequencies in the white light, like the violet, blue, green, and yellow, are being absorbed by your shirt and are therefore not reflected.

7.2 THE NATURE OF ELECTRONS

Before we can answer the question of why some ions are colored and what determines the color, we must discuss the nature of the electron. When the electron was first discovered, it was thought to be a particle. Later work revealed that electrons exhibit many of the same properties as light and therefore can also be thought of as having wave properties. This idea led to the development of wave mechanics, also called quantum mechanics.

In order to understand the wave properties of an electron, consider the following very unrealistic situation. Imagine that an electron is confined to a line, designated as $x = 0$ to $x = 1$ in Figure 112 below. Assume, moreover, that all of the important properties of the electron can be explained by describing it as a wave, just like the wave obtained by stretching a rubber band between your hands and then having a friend pull up the middle of the band and release it. The band will undergo a variety of wave-like vibrations, one of which is shown on our line in Figure 112 (a) and designated with $n = 1$. Notice that because we insist on restricting the motion of the rubber band by holding it, the amplitude of the wave must be zero at our fingers; that is, at $x = 0$ and $x = 1$. The wave shown in Figure 112 (a) is particularly simple, but two slightly more complex waves are shown in Figure 112 (b) and (c). There are many more complex waves that can exist between $x = 0$ and $x = 1$, but they are all constrained by the condition that they have zero amplitude at the boundaries ($x = 0$ and $x = 1$).

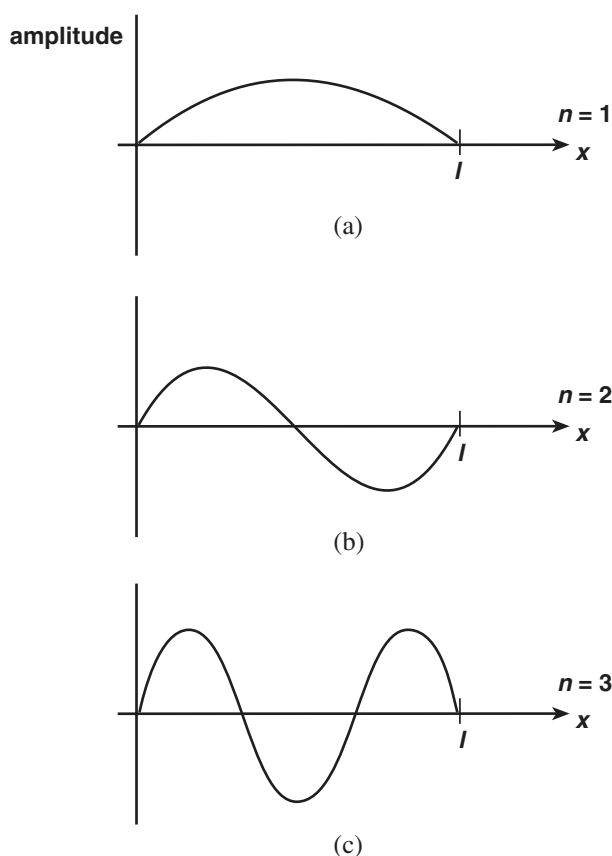


Figure 112 The wave nature of an electron confined to a line extending from zero to an x value of 1 (the tic mark): (a) the wave with the longest wavelength; (b) the wave with the next longest wavelength; (c) the wave with third longest wavelength.



Determine the wavelengths of the $n = 2$ and $n = 3$ waves.



The wavelength is the distance between two crests or two troughs of the wave. The wavelength of the $n = 2$ wave is therefore 1 and the wavelength of the $n = 3$ wave is two-thirds 1.

Of course, you must be wondering about the advantage of treating something as a wave that you had previously thought of as a solid particle. Wave mechanics informs us that each wave reveals two things about the electron: its *energy* and the *probability of finding the electron at a certain point on the line*.



Now that you know something about the wavelength of the $n = 1, 2,$ and 3 waves, can you speculate on how the energy of these waves might vary? (Keep in mind what we said about the energy of light.)



The wavelength of light is inversely proportional to its frequency; that is, the higher the wavelength, the lower the frequency. The Planck relationship tells us that the energy of light is proportional to its frequency. By analogy, the wave with the longest wavelength will have the lowest frequency and therefore the lowest energy.

Because only waves with certain wavelengths (and frequencies) will fit on the line, only certain energies can exist for the electron on the line. This is one of the most interesting aspects of wave mechanics—the *energy of an electron can have only certain values*. This very strange feature of matter at the atomic level is similar to buying a new car and finding that when you step on the accelerator the car immediately goes 20 miles per hour, a further push on the pedal produces 40 miles per hour, then 70 miles per hour. But as hard as you try you cannot produce a speed of say 35 or 60 miles per hour. This aspect of energy is called **quantization** from the Latin *quantus* meaning “how much.” The jumps from one energy level to another are often referred to as quantum jumps. Figure 113 shows the energy levels for the $n = 1, 2,$ and 3 waves.

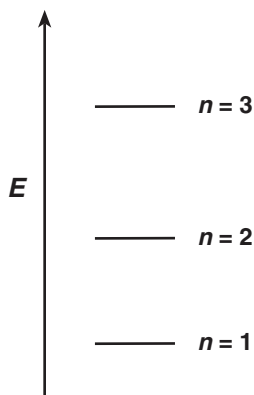


Figure 113 The three lowest energy levels for an electron confined to a line.



If the energies of the $n = 1, 2,$ and 3 waves are $10, 30,$ and $60,$ respectively, in some unit of energy such as joules, how much energy must be expended in order to make the quantum jump from the $n = 1$ to the $n = 3$ wave?



The difference in energy is $60 - 10 = 50$ units.

The wave property of the electron is also related to the position of the electron on the line. The German physicist Max Born proposed that the square of the amplitude of the wave is proportional to the probability of the electron being at that point. Figure 114 shows the wave and the square of the wave for the $n = 1$ and $n = 2$ waves. For the $n = 1$ wave, the square of the amplitude is largest in the middle of the line and this is where the electron is most likely to be. The use of a *probable* position rather than a definite position is the second strange aspect of all matter at the quantum level. It is a bit like watching a friend dive into murky water and swim underwater for a distance. Because his swimming ability is familiar to you, you can estimate his position with probabilities. Based on the strength of his kick and stroke, he is probably about at the mid-point now, you might say after 20 seconds.

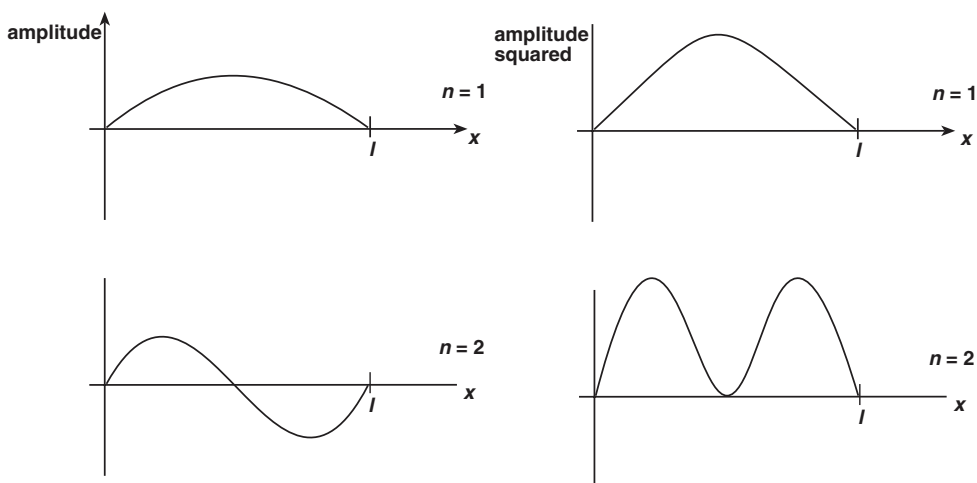


Figure 114 The probability of finding an electron. On the left are the wave functions and on the right are the square of the amplitude functions that describe the relative probability of finding the electron on the line. For $n = 1$ the maximum probability of finding the electron is at $x = 1/2$ because the square of the amplitude of the wave is greatest at this point.



Examine Figure 114 and determine the probability of finding the electron at the mid-point of the line when $n = 2$.



Because the square of the amplitude of the wave is zero at the mid-point of the line, the probability of finding the electron there is zero.

Of course, electrons are usually “inside” of a three-dimensional atom and our simple one-dimensional analogy won’t work in three dimensions, although the basic principles are the same. In three dimensions, three numbers, rather than one, are required to specify

the waves. These numbers, called **quantum numbers**, are given the letters n , l , and m , and each specifies something about the energy and position of an electron. The principal quantum number, n , is one of the major determinants of the energy and the probable distance of the electron from the nucleus. The angular momentum quantum number, l , helps to determine the energy and specifies the shape of the electron density. The magnetic quantum number, m , specifies the energy in a magnetic field, and determines the orientation of the electron density relative to an external reference. Wave mechanics indicates that only certain combinations of these three numbers are possible and that each different combination gives a complete description of the energy and the position probability of an electron. Each one of these unique combinations of n , l , and m is called an **orbital**. In specifying the orbitals, the numerical value of n is used, but the letters s, p, d, and f are used for values of l , and symbols related to the Cartesian coordinate system are used for the values of m .

The relative energies of the orbitals up to the 3d-orbitals are shown in Figure 114. The lowest-energy orbital is the 1s-orbital (for this orbital the values of n , l , and m are 1, 0, 0, respectively) and the electron density in this orbital is spherically symmetric as shown in Figure 116. The orbital of next lowest energy is the 2s, which also has spherical symmetry. Indeed, all s-orbitals have the same angular position probabilities; the electron is

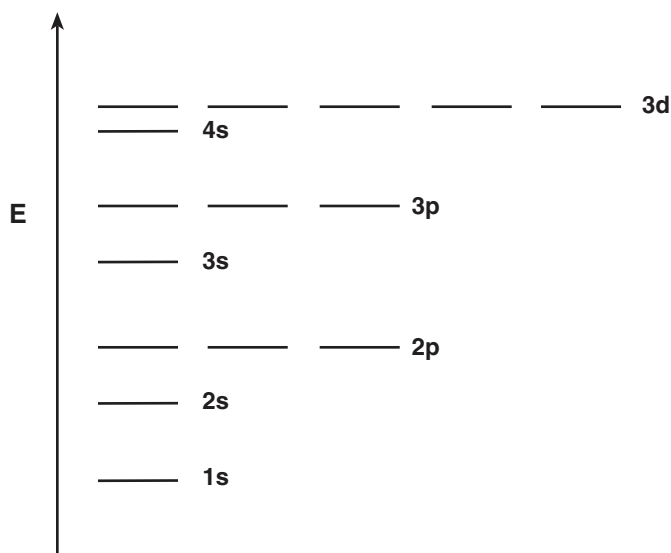


Figure 115 Energy diagram for electrons in an atom. Each line represent an orbital. Only the orbitals up to the 3d-orbitals are shown. The 4s-orbital is slightly lower in energy for some atoms, but higher than the 3d-orbitals in ions.

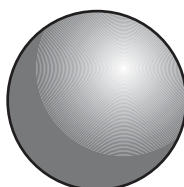


Figure 116 The angular probability pattern for any s-orbital. The sphere indicates that the probability of finding an s-electron is the same at any point on a sphere with a given radius. The nucleus of the atom is at the center of the sphere.

equally likely to be at any one of a set of equally spaced points on a sphere surrounding the nucleus. An electron in a 2s-orbital is more likely to be farther from the nucleus than an electron in a 1s-orbital.

In order of increasing energy, the three 2p-orbitals now appear, each with a dumbbell probability pattern, as shown in Figure 117. The three p-orbitals have the same energy and differ from one another only in their orientation on the x -, y -, and z -axes. As n increases to the value of 3, another set of s- and p-orbitals appear and then a set of d-orbitals. There are five d-orbitals for each value of n equal to or greater than three. These five d-orbitals have the same energy in an isolated atom and the angular probability patterns are shown in Figure 118.

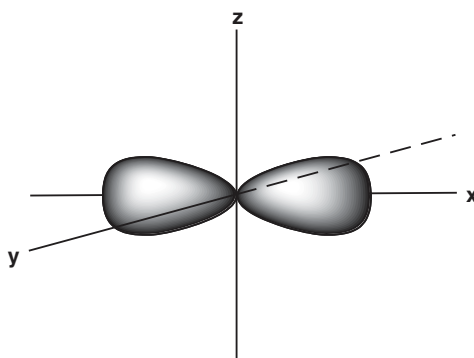


Figure 117 The angular location probability pattern for a $2p_x$ -orbital. The pattern indicates that the electron is most likely to be found on either side of the nucleus along the x -axis. There is no chance of finding the electron at the nucleus or on the y - or z -axes.

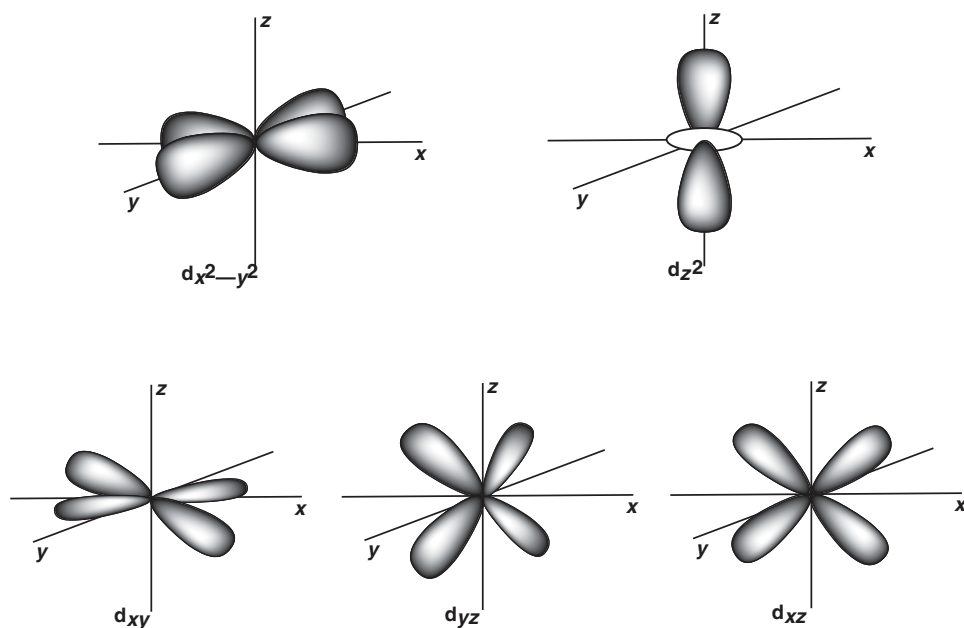


Figure 118 The angular location probability patterns for the d-orbitals. The lobes of the d_{xy} -orbital are located between the x - and y -axes; the lobes of the d_{yz} -orbital are between the y - and z -axes perpendicular to the x -axis; and the lobes of the d_{xz} -orbital are between the x - and z -axes perpendicular to the y -axis.



Based on Figure 118, which of the d-orbitals has the greatest probability of having electron density on the x - and y - axes? Which has the greatest probability of having electron density on the z -axis?



An electron in the $d_{x^2-y^2}$ orbital has the greatest probability of being on the x - and y -axes, whereas an electron in the d_z is most likely to be on the z -axis. The other three d-orbitals all have a zero probability of having the electron density on the axes and therefore have electron density between two of the three axes. For example, the d_{xy} has the greatest probability of having electron density between the x - and y -axes. The d-orbitals will play a critical role in our discussion of the color of ions.

Each orbital has the energy shown in Figure 115 and two electrons can be housed in each orbital if their values of a fourth quantum number are different. This fourth quantum number, the spin quantum number s , has only two possible values— $+1/2$ and $-1/2$. The spin quantum number is interpreted as indicating that the electron also has properties associated with spin and the two values of s indicate either clockwise or counterclockwise spin. Thus, if two electrons are to be described by the same orbital, their s values must be different: one electron must have a value of $+1/2$, the other must have an s value of $-1/2$. Another way to phrase this is that *no two electrons in an atom can have the same set of four quantum numbers*. This is known as the **Pauli Exclusion principle** (Austrian physicist, Wolfgang Pauli).

7.3 ELECTRON CONFIGURATIONS

We are now able to provide a description of the energy and location probability of every electron in an atom. This description is called the **electron configuration** of an atom and it is obtained by placing electrons in orbitals, with no more than two electrons in each orbital. We are usually interested in the most stable form of the atom, called the ground state, and therefore we must be sure to place the electrons in the lowest energy orbitals.



Follow the energy levels in Figure 115, and write the electron configuration of iron.



The electron configuration can be expressed with a diagram such as that in Figure 119, using arrows to represent the spins of the electrons, or it can be written on a line with superscripts to indicate how many electrons are in each orbital. For Fe, there are 26 electrons to distribute. Even though the 4s-orbital has a slightly lower energy than the 3d-orbitals, we write the electron configuration as shown at the bottom of the figure, keeping all of the orbitals with the same value of n together.

Iron is a member of the transition metals, located between Group II and Group III on the periodic table (see Appendix 1). For these elements, the d-orbitals are the last to be filled with electrons when writing the electron configuration. In fact, the electron configurations correlate nicely with the position of the elements in the periodic table. The elements that have their most energetic electrons in s-orbitals are the s-fillers and these appear

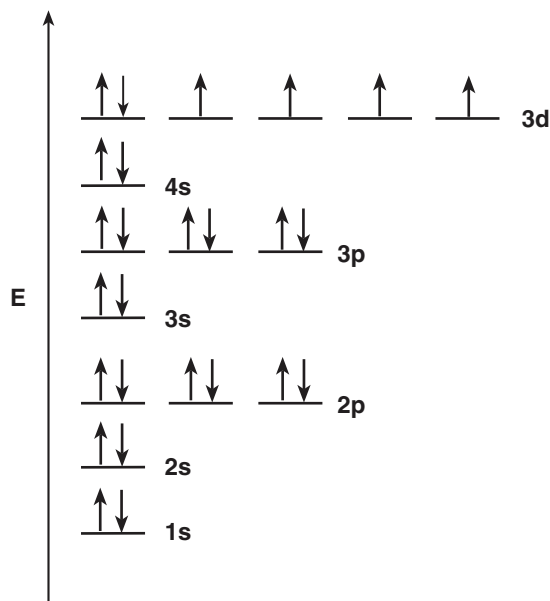
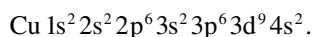


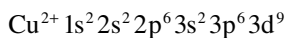
Figure 119 The electron configuration of iron presented in terms of the relative energies of the electrons (top) and, in more abbreviated form, in terms of the orbitals occupied (bottom).

on the left side of the table in Groups I and II. The p-fillers are on the right-hand side of the periodic table, and the d-fillers are in between the two.

We are now finally ready to tackle the question of why copper sulfate is blue. We begin by writing the electron configuration of copper:



Because copper is present in copper sulfate as the plus two ion, we next remove the two most energetic electrons from the copper atom. These electrons are the 4s electrons (the 4s-orbital has a higher energy than the 3d-orbitals in ions). (When the electron configuration is written in order of increasing n value, we always remove the electrons from the “outermost” orbital as written in order to form the ion.) So, the electron configuration of the copper plus two ion is:



Because the d-electrons are the outermost electrons in the ion they are most likely to be responsible for bonding or color. In general, the outermost electrons are known as the **valence electrons**. We must now focus our attention on them.

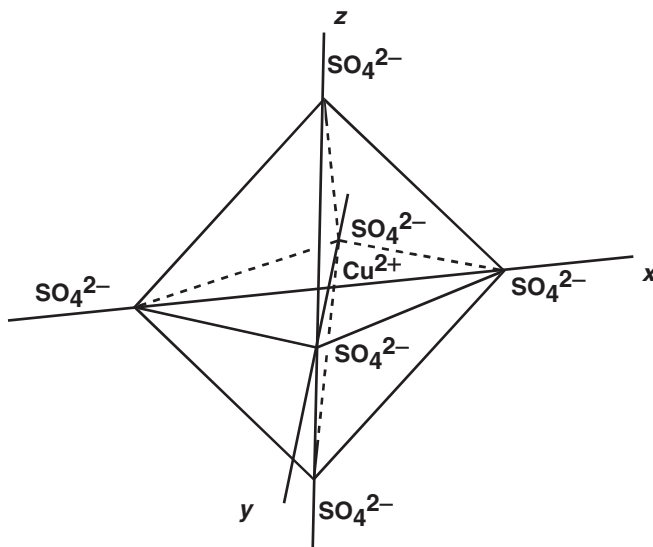
7.4 THE CRYSTAL FIELD MODEL

The electron configuration written above is the appropriate description of the electrons in the isolated ion; for example, an ion in the gaseous phase where it is not close to any other ion. But in the solid, the d-orbitals will have somewhat different energies. Let us assume

that in copper sulfate the sulfate ions are closest packed and that the copper ions fill the octahedral holes. In order to simplify things, we can also assume that the sulfate ion is a spherical ion with a minus two charge.



Provide a diagram of the surroundings of a copper ion in solid copper sulfate.



Now consider the effect of the anions on the energies of the electrons in the d-orbitals.



First determine whether the anions will increase or decrease the energies of electrons in the d-orbitals, relative to their energies in an isolated ion.



Because the anions have a negative charge, as do the d-electrons, the electrons will be repelled by the anions and their energies will increase. In fact, the closer the anions are to the electrons, the more the energy of the electrons will increase.



Next, examine the orientation of the $d_{x^2-y^2}$ orbital and the d_{xy} orbital (see Figure 118) and determine which will be affected more by the negative charge of the anions.



Figure 118 shows that the $d_{x^2-y^2}$ orbital has its areas of maximum electron density directly on the x - and y -axes, which is also where the anions are located. The d_{xy} orbital, on the other hand, has its electron density between the x - and y -axes. The energy of an electron in the $d_{x^2-y^2}$ orbital will therefore be increased more by the presence of the anions at the corners of the octahedron.

In fact, two of the d-orbitals, the $d_{x^2-y^2}$ and the d_{z^2} , are pointed directly at the anions and the electrons in these orbitals will therefore be repelled rather strongly. The electrons in the other three orbitals are directed into the regions of space between the anions and so they will also be repelled, but not as strongly as the other two. Thus, two of the d-orbitals will be higher in energy than the other three, as shown in the energy level diagram given in Figure 120, which also shows the energies of the d-orbitals in the isolated ion. For this isolated ion the d-orbitals have the same energy—they are said to be degenerate. When the ion is placed in the electric field of the crystal, the energies of the degenerate d-orbitals all increase but two go up more than the others. This model of what happens to the orbitals as they are surrounded by anions is called the **Crystal Field theory**.

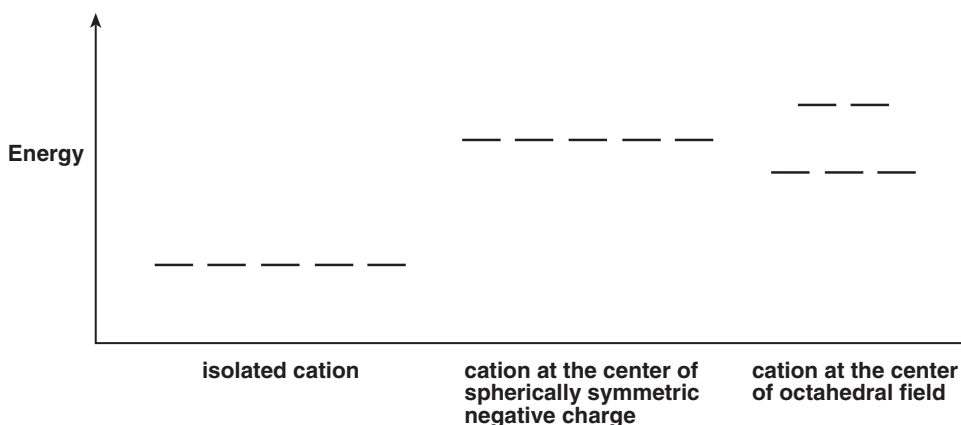


Figure 120 The splitting of the d-orbitals in an octahedral field. In an isolated ion, the d-orbitals have the same energies (left), but as the ion begins to be surrounded by six anions the energies of all of the orbitals increase. If the charge of the anions were somehow dispersed over a sphere, the energies of the d-orbitals would still be degenerate (middle). When the anions are positioned at the corners of an octahedron, the degeneracy of the orbitals is broken and two sets of energy levels are formed.

The consequence of this crystal field splitting of the degeneracy of the d-orbitals is that one electron from the lower set of energy levels (called the t_{2g} set, for reasons that we will not discuss) can make a jump (more properly called a **transition**) to an orbital in the e_g set. In order to make this transition, an amount of energy exactly equal to the difference in energies of the two sets of orbitals is required. This amount of energy for a copper ion in copper sulfate is provided by light in the red region of the visible part of the electromagnetic spectrum. Copper sulfate in white light is exposed to all of the frequencies of the visible region of the spectrum, including the red frequencies. The red frequencies are absorbed by the copper ions in order to excite an electron from one d-orbital to another. The copper sulfate transmits the remainder of the white light, which is the blue portion. When these remainder frequencies strike the retina we perceive the color blue. After the copper ion has been excited, it relaxes and the electron drops back to the t_{2g} orbitals.

Of course there are many facets to the crystal field model. It predicts, for example, that the extent of the splitting of the d-orbitals will depend on what anions surround the cation, the nature of the cation, and the distance between the cation and anion. It also predicts that the splitting of the d-orbitals is different if the cation is surrounded by the anions in a different geometry. For example, if the cation is in a tetrahedral hole, three of the

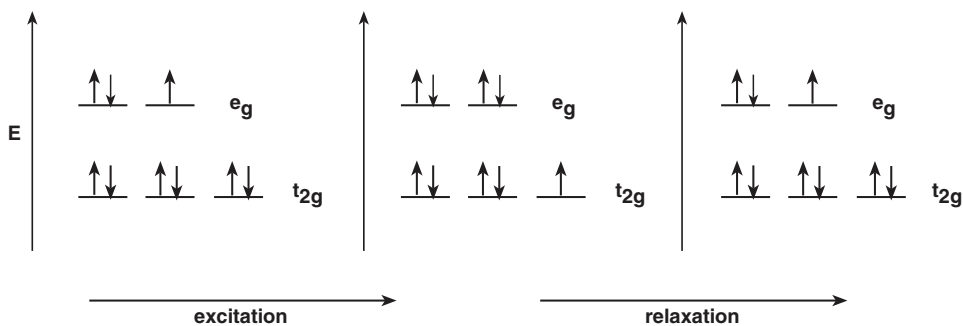


Figure 121 Excitation of an electron in the copper ion. Each electron is designated by an arrow that represents the direction of the spin of the electron.

d-orbitals are at higher energy than the other two (just the reverse of the octahedral splitting).



The minerals malachite and azurite both contain Cu^{2+} , CO_3^{2-} , and OH^- ions, but in different ratios. Malachite is green, whereas azurite is blue. Provide a rationalization for this observation.



It would be tempting to attribute the colors to the occupation by the copper ions in the two minerals of sites with different coordination numbers. In fact, in each mineral, there are two different copper ion sites, and both of these sites have approximately **square planar** geometry. That is, each copper is surrounded by oxygens at the corners of a square. The crystal field diagram for a square planar arrangement of ions is shown below.



The energy required for the electronic transition from the second highest energy level to the highest energy level is approximately the same as it would be if copper were in an octahedral environment. It is not surprising therefore that both azurite and malachite have colors in the green to blue region, similar to that of CuSO_4 where the copper is an octahedral environment. The difference between the surroundings of the copper ions in azurite relative to the surroundings in malachite is very subtle. In both minerals, two of the oxygens around each copper ion belong to a carbonate ion and two oxygens are a part of

two hydroxide ions. However, in azurite each hydroxide ion interacts with three copper ions, whereas in malachite each hydroxide ion interacts with only two copper ions. This difference is sufficient to make the surroundings of each copper ion in malachite slightly different from that in azurite. The energies required for the transition from the second highest to the highest energy levels are different, and therefore the colors are different.

Although cations such as Zn^{2+} , Cd^{2+} , and Ag^+ are transition metal cations and contain d-electrons, in these cations the d-orbitals are completely filled. The only electronic transitions that could occur would be from a d-orbital to a much higher energy orbital such as an s- or p-orbital. These transitions require light in the ultraviolet region. These ions therefore do not absorb visible light, and their salts are colorless (unless the anion is colored).

7.5 COLORED CATIONS

Now that we understand why cations such as Cu^{2+} , Fe^{2+} , and Cr^{3+} are colored and why their colors are dependent on their surroundings in the crystal structure, let us look at a few minerals that contain colored cations. Rhodochrosite (MnCO_3) is pale to deep pink, similar to the color of the Mn^{2+} ion in aqueous solution. The pale pink color is typical of octahedrally coordinated Mn^{2+} . (Tetrahedral Mn^{2+} is generally green-yellow in color.) Vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) is almost colorless when it is first mined, but rapidly turns blue to green due to the oxidation of the Fe^{2+} ion to Fe^{3+} . Most hydrated ferrous salts are pale green. In siderite (FeCO_3), the color that the Fe^{2+} ion imparts ranges from tan to brown. On the other hand, in almandine ($\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3$, a member of the garnet group), the Fe^{2+} ion is eight-coordinate and produces a deep red color. The Cu^{2+} ion provides a color of blue to green in almost all of its minerals such as malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$, green), azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$, blue), and brochantite ($\text{Cu}_4\text{SO}_4(\text{OH})_6$, blue-green). However, tenorite (CuO) is black, while cuprite (cuprous oxide, Cu_2O) is red. Covellite (CuS) is blue, while chalcocite (cuprous sulfide, Cu_2S) is dark lead gray.

The true colors of some minerals can only be seen when the sample is finely powdered. Rather than grinding up a specimen, a small area is rubbed against a hard porcelain surface until a **streak** of the mineral is obtained. The color obtained in this streak test can be quite different from the appearance of the sample itself. For example, samples of specular hematite (the word specular refers to the mirror-like surface) have a very shiny black appearance due to the reflective nature of the naturally polished surface. The streak test reveals the true color of hematite—a red-brown.

Although most anions are colorless, a few such as chromate (orange-red) are colored. The color of this oxy anion (CrO_4^{2-}) cannot be explained by the crystal field model because the bonding in the ion is predominantly covalent and requires the use of the **molecular orbital** model. This model is the molecular analog of the wave mechanical treatment of orbitals in atoms. It assumes that there are orbitals that extend over all of the atoms in the molecule or ion. Each orbital has an energy and a probability distribution, analogous to the orbitals for atoms. The color of the anion is the result of an electronic transition that is produced by light in the visible region of the electromagnetic spectrum.

Some anions, particularly ones that are more polarizable, may impart a covalent character to the compound and produce color. The sulfide ion, colorless in simple Group I salts such as Na_2S , produces considerable covalent character in combination with the heavier and more polarizable transition metals, such as in yellow grenockite (CdS) and reddish acanthite (Ag_2S), as well as in the cuprous and cupric sulfides mentioned above.

7.6 ION IMPURITIES

In many cases, a mineral has a color that is not a result of the major cation or anion that is present. The color of the sample is due to the presence of a cation that is either incorporated into the crystal lattice in very small amounts by substituting for the original cation of the same charge, or in a solid solution, or is part of a compound that occurs with the main compound, perhaps as an inclusion, as a mixture, or as a surface coating. For example, most lithium-containing minerals, such as lepidolite or spodumene (both are silicates) are pale violet in color, yet lithium compounds such as lithium sulfate are colorless in solution (white as powders). Although it is not impossible that the color in the silicates could be due to covalent interaction between the cation and the anion (silicate anions are colorless), the fact is that these minerals almost always contain small amounts of the Fe^{2+} or Fe^{3+} ions, which produce the violet color. In beryl ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$), small amounts of Cr^{3+} substitute for Al^{3+} and produce the green color of the emerald, whereas in corundum (Al_2O_3), the chromium produces the red of the ruby.



Smithsonite, ZnCO_3 , contains two colorless ions. Yet many samples of smithsonite are very nicely colored. What cation is present in samples that are green-blue or rose colored?



The green-blue color could be due to either Cu^{2+} or Ni^{2+} ions. (Nickel is a relatively unusual cation in minerals.) The rose smithsonite probably contains Co^{2+} .

7.7 CRYSTAL DEFECTS

Color can also be produced when a deviation from the regular orderly arrangement of ions occurs in the crystalline structure. Actually, these defects occur in every crystalline material. Many types of defects are known, but the one that is most often associated with the color of certain minerals is known as the **Frenkel defect** (Jacov Frenkel, Russian physicist) in which an ion is displaced from its normal position in the structure. As is the case with all types of defects, electrical neutrality must always be maintained, even over short ranges. In the case of a displaced fluoride ion in fluorite (CaF_2), the hole left behind must contain an electron. This electron is not bound to a nucleus as in an atom, but is trapped within the electrostatic field provided by the neighboring Ca^{2+} ions and the F^- ions. It therefore behaves very much like an electron in an atom, with its own set of energy levels. These energy levels have spacings that allow fluorite to absorb energy in the visible region and impart a purple color to the crystal. This kind of color center (sometimes called an F-center, from the German word, *Farbe*, for color) can be produced by high energy radiation such as X-rays. The purple color of amethyst and the dark color of smoky quartz are a result of the ejection of an electron from an oxygen in the vicinity of an iron or aluminum atom that has substituted for the silicon in SiO_2 . In smoky quartz, for example, the aluminum imparts a negative charge to the covalent network that must be neutralized. Irradiation, either natural or artificial, ejects an electron from an oxygen close to the aluminum, thereby producing electrical neutrality. The unpaired electron on the oxygen has a set of energy levels that allow for an electronic transition by visible light. These color centers can often be destroyed by heating the crystal.

Chapter 8

Chemical Properties

8.1 SOLUBILITY

One of the characteristics attributed to ionic compounds is solubility in water. In fact, many ionic compounds are not very soluble in water and, indeed, were it not for our familiarity with compounds like sodium chloride, ionic compounds would probably be thought of as insoluble. However, ionic compounds are more soluble in water than they are in less polar compounds such as hydrocarbons. And the converse is generally true for covalent compounds: they are usually more soluble in organic solvents than in water. The solubility of some ionic compounds in water can be attributed to the interaction of the ions with the water molecules. To understand this interaction, we need to examine the electron density in the water molecule.



Which atom is more electronegative—hydrogen or oxygen?



Oxygen is more electronegative. In fact, it is the second most electronegative atom in the periodic table (see Appendix 2), being immediately to the left of the most electronegative atom, fluorine.

The high electronegativity of oxygen removes some electron density from both hydrogen atoms in water and creates an uneven distribution of electrons in the molecule. We frequently represent additional or excess electron density with a delta minus sign and a deficit of electron density as a delta plus sign. The electron density can therefore be represented as shown in Figure 122. Because the hydrogen atoms are on the same side of the molecule, this side is electron deficient. The oxygen side is electron rich. The molecule is said to have two poles, a **dipole**, or a dipole moment, that is represented with an arrow.

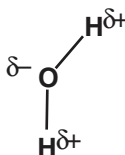
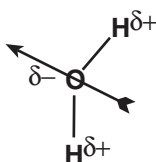


Figure 122 The uneven distribution of electron density in the water molecule.



Draw an arrow through the water molecule, using the head of the arrow to show excess electron density and the tail of the arrow to show partial positive charge.



The arrow is pointed toward the oxygen with the tail directly between the two hydrogens.

Now consider a cation in the midst of water molecules. The positive charge of the cation will cause some of the water molecules to orientate themselves so that the negative side (the head of the arrow) is pointed toward the cation. In this way there is the same lowering of potential energy due to adjacent opposite charges that we have seen in our discussion of lattice energy. Figure 123 shows six water molecules surrounding a cation with their dipoles pointed toward the cation.

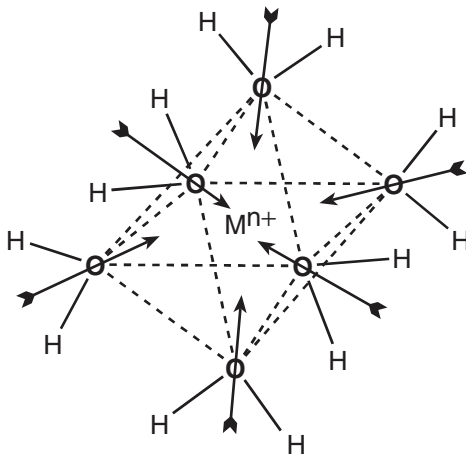


Figure 123 A cation surrounded by water molecules with the negative end of their dipoles closest to the positive charge.



How would a diagram for the interaction of water molecules with an anion differ from the one above?



Because an anion has a negative charge, it will attract the positive end of the water dipole. Each water molecule in the figure above will be reversed. The potential energy of the system will be lowered relative to random orientations

of water molecules or orientations that place the negative end of each water dipole closest to the anion.

The attraction of the cation or anion for the negative or positive end of the dipole lowers the potential energy of the ion relative to the ion in the gaseous state. We can contrast this situation with a cation in the solvent hexane, a typical organic solvent not too different from the hydrocarbons that make up the mixture we call gasoline. Hexane is a covalent molecular compound that consists of six carbon atoms attached together in a row, with each of the carbons also attached to two or three hydrogen atoms. Because carbon and hydrogen have similar electronegativities, there is very little separation of electron density between carbon and hydrogen (and none between adjacent carbons). Consequently, hexane has a very small dipole.



Which has the lower energy—a cation in hexane or a cation in water?



Remember that the attraction of an ion for a dipole lowers the energy. Thus, the cation in water is stabilized by the charge–dipole interaction and therefore has the lower energy. If you are confused by the idea that stabilization is accompanied by a lowering of energy, remember that many phenomena move to a state of lower energy: water flows downhill, batteries run down, and so on. In fact, this tendency of a system to go to a lower energy is embodied by the first law of thermodynamics.

8.1.1 Energetics of Dissolution (and a bit of thermodynamics)

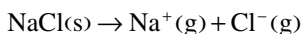
The greater solubility of most ionic compounds in water (rather than solvents that have little or no dipole moment) is due to the stabilization of the ions by water molecules. Does this mean that all ionic compounds are soluble in water? No, there is another factor that must be taken into account—the lattice energy.



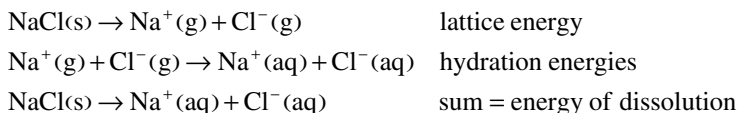
Can you write an equation that represents the lattice energy of NaCl?



The lattice energy, you will recall, is the energy required to remove the ions from the solid and disperse them into the gaseous state.



If the lattice energy is greater than the energy liberated when the ions enter the water and are surrounded by water molecules, then it is usually the case that the compound will be insoluble. In other words, in order for dissolution to occur, energy would have to be added to the sodium chloride/water system. In fact, the equations for the lattice energy and the hydration of the ions add up to the equation for the dissolution:



When equations add together to give a third equation it is also true that their energy changes will add to give the energy change of the third equation. This is known as **Hess's Law** (Germain Henri Hess, Swiss-Russian chemist).

Let us see if we can use a combination of the lattice energy and the hydration energy to understand why a compound like CaCO_3 (calcite) is not very soluble in water.



Calcite contains the ions Ca^{2+} and CO_3^{2-} . Is the lattice energy of calcite greater than that of sodium chloride?



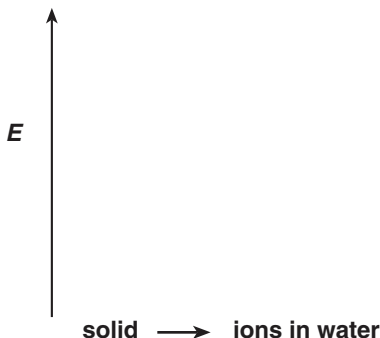
It certainly is because of the fact that the cation in calcite has a 2+ charge while the cation in sodium chloride has only a 1+ charge. Moreover, the carbonate ion has twice the charge of the chloride ion. The greater charge on the cation and anion causes the lattice energy of calcite to be greater than that of NaCl (in fact, it takes almost four times as much energy to separate the ions in calcite).

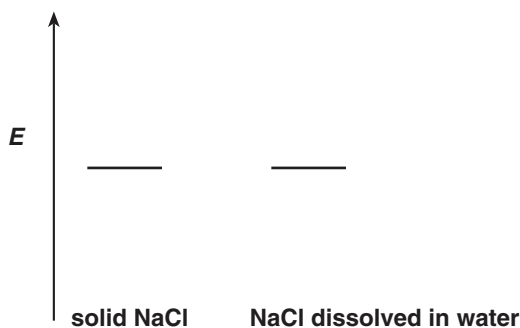
You are probably thinking, “Yes, but isn’t the hydration energy of the Ca^{2+} ion also going to be greater than that of the Na^+ ion, and the Ca^{2+} ion will therefore be more stabilized by the water molecules?” It is true that the calcium and the carbonate ions are more stabilized by water molecules than the sodium and chloride ions because they are more highly charged. But, it is generally true that the lattice energy is the dominant factor. That is, the greater hydration energy (greater stabilization) of the ions in calcite is outweighed by the greater amount of energy required to separate the ions. The upshot of this is that calcite is not very soluble. In fact, *it is generally true that compounds that contain ions that have charges greater than 1+ or 1- are insoluble.* (Of course, solubility is relative: some compounds are more insoluble than others, meaning that a smaller number of moles of the compound dissolve in a given amount of water, usually one liter.)

Before we discuss the exceptions to this rule, let us refine our discussion of solubility. For the dissolution of NaCl, the energy of hydration is almost exactly equal to the lattice energy, which means that no energy needs to be added to dissolve NaCl.

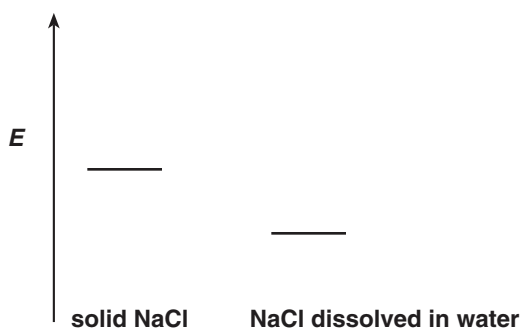


On the energy diagram below, draw two short horizontal lines to indicate the relative energies (energies are impossible to measure in an absolute sense and therefore are given as energy changes or relative energies) of solid NaCl and the ions in water.





This diagram indicates that the energies of the solid and the hydrated ions are about equal. If the hydrated ions were more stable relative to the solid, the diagram would appear as:



In general, the lower the energy of the ions relative to the solid, the more likely the solid is to dissolve. It is also helpful to know that this difference in energy is called the energy of dissolution and when the ions have a lower energy than the solid, the energy “flows downhill.” When a solid with this kind of energy profile dissolves, the difference in the energy between the hydrated ions and the solid must be given off and the solution becomes warm due to that liberated energy. This is another consequence of the **First Law of Thermodynamics**, which in this case states that energy cannot be lost (we usually say that it is conserved).

For NaCl, then, the change in energy upon dissolution is about zero. For many solids the change in energy upon dissolution is positive; that is, the energy of the hydrated ions is greater than that of the solid plus water.



Given that the energy change is positive when the ions are at a higher energy than the solid, is the energy change defined as

$$\Delta E = E(\text{products}) - E(\text{reactants}), \text{ or as}$$

$$\Delta E = E(\text{reactants}) - E(\text{products})?$$



If ΔE is positive it must be defined as $E(\text{products}) - E(\text{reactants})$. If you do not see this, try calculating ΔE when the energy of the hydrated ions is 400 kJ and the energy of the solid plus water is 300 kJ (on some arbitrary scale). When ΔE is positive and therefore heat must be added to the system, the reaction is said to be **endoergic**. If ΔE is negative and energy is liberated, the reaction is said to be **exoergic**. (You may recognize the prefixes *endo* and *exo* as the Latin words that mean “into” and “out of”).

For the dissolution of NaCl, the ΔE of zero means that we are not sure if sodium chloride will dissolve or not. Of course, as mentioned before, we know from experience (experimentally) that NaCl is reasonably soluble in water (6 moles of NaCl dissolve in a liter of water). As you may have guessed, there is another factor that must be considered for dissolution and, indeed, for all processes. This other factor is the change in disorder or **entropy** (designated by the symbol S) in the system. According to the **Second Law of Thermodynamics**, *an increase in disorder helps to make the process favorable*.



Does the disorder increase or decrease when solid NaCl dissolves to form the hydrated ions?



In the solid, the ions are systematically and neatly organized, whereas in the solution they are moving randomly throughout the water. On the other hand, many of the water molecules are more organized in the solution due to the orientation of some of them around the ions. In general, the size and charge of the ions determines whether the orientation of the water molecules is more important than the increase in disorder due to the motion of the ions. This change in disorder is also measured as a change in entropy, ΔS , and is *positive when the disorder increases*. For the dissolution of NaCl the entropy change is positive and it is this factor that, when combined with the difference in energy, makes NaCl soluble.

Mathematically, the two factors, energy and entropy, are combined into a new variable, the **free energy** (G) or Gibbs' energy (Josiah Willard Gibbs, American physicist):

$$\Delta G = \Delta H - T \Delta S$$

In this equation, H stands for **enthalpy**, which for our purposes is equal to energy. (The exact relationship between the enthalpy and energy is expressed as $H = E + PV$, where P and V are pressure and volume. For most purposes, the PV term can be ignored.) We can now make our analysis a bit more quantitative. Thermodynamics tells us that *a process is favorable when the ΔG is negative* and the more negative the ΔG , the more favorable the process.



Is ΔG positive or negative for the dissolution of NaCl?



Because NaCl is soluble, ΔG at room temperature (notice the T in the equation) is negative.

Thus, we conclude that both factors—energy and entropy—must be considered in evaluating the extent of any process, but it is frequently the case that the energy is the more important factor. This is the reason that we considered only the lattice energy and the hydration energy in arriving at our generalization for solubility.

8.1.2 Solubility Rules

The exceptions to our generalization about solubility are most easily given in the form of solubility rules for simple compounds containing anions that are important in minerals:

Table 8 Solubility rules

-
1. All nitrates are soluble.
 2. All alkali metal salts are soluble.
 3. All chlorides, bromides, and iodides are soluble except those of silver, lead(II), and mercury(I). All fluorides are insoluble except those of silver and the alkali metals.
 4. All hydroxides are insoluble except those of the alkali metals. Barium hydroxide is moderately soluble.
 5. All oxides and sulfides are insoluble except those of the alkali metals and the bottom members of the alkaline earth metals. (The soluble oxides and sulfides generally react with water to form hydroxides, or, in the case of sulfides, hydrogen sulfides.)
 6. All sulfates are soluble except those of barium, lead(II), and silver. Calcium and strontium sulfate are moderately soluble.
 7. All carbonates are insoluble except those of the alkali metals (other than lithium).
 8. All phosphates are insoluble except those of the alkali metals (other than lithium).
-



Use these rules to predict the solubility of the following minerals in water: galena (PbS), barite (BaSO₄), and fluorite (CaF₂).



Galena contains the sulfide ion and because lead (II) is not an alkali metal (rule 5), PbS is insoluble. Barite contains the sulfate ion and BaSO₄ is one of the few simple sulfates that is insoluble. Fluorite contains the fluoride ion and because it also contains an alkaline earth metal cation (rule 3), CaF₂ is insoluble.

Notice that these solubility rules are in good agreement with our generalization that the lattice energy controls the solubility. Only when the lattice energy is relatively low, due to a 1+ or 1− charge on at least one of the ions, will the lattice energy be small enough to allow the hydration of the ions to provide the stability necessary to dissolve the compound. The major exceptions to this rule occur with the sulfate anion: compounds such as Fe₂(SO₄)₃ (the hydrated version Fe₂(SO₄)₃·9H₂O is coquimbite) or CuSO₄ (the hydrated version CuSO₄·5H₂O is chalcantite) are soluble.

When some ionic compounds precipitate from aqueous solution, they form a hydrate. For example, CuSO₄ precipitates from a concentrated aqueous solution as CuSO₄·5H₂O. This formula indicates that every mole of CuSO₄ contains five moles of water of hydration. This water of hydration is incorporated into the crystal structure primarily as a result of the charge-dipole attraction between the ions and the water molecules. The water can be removed from most hydrates by heating to temperatures in the range of 100–200°C.

Many minerals containing oxy anions, other than silicates, form primarily in sedimentary conditions; that is, in aqueous solution. Minerals containing the carbonate or sulfate ions are not likely to be formed at the high temperatures of igneous processes because both anions decompose at high temperatures. For example, calcium carbonate decomposes to CaO and CO₂. The solubility rules can provide a rationalization for observations such as the fact that halite (NaCl) is formed mainly in evaporated lakes with high concentrations of sodium and chloride ions, or the relatively infrequent occurrence of chalcantite in copper mines, except where aqueous solutions may be concentrated and/or evaporated.

The rules can also be useful in cleaning specimens. Many iron sulfides decompose in the presence of moist air. This is primarily a result of oxidation (reaction with oxygen) of the S₂²⁻ or S²⁻ ions to SO₄²⁻.



How can you remove FeSO₄ from a partially decomposed sample of marcasite (FeS₂)?



Because the sulfate will be soluble in water (rule 6), you can wash the sample thoroughly with water. The sulfide (rule 5) will not be soluble.

8.1.3 Double Salts

Many of the minerals in the Earth's crust are not simple ionic compounds consisting of one type of cation such as Cu²⁺ and one type of anion such as carbonate, CO₃²⁻. These more complex compounds can be classified as **double** (or triple or quadruple) **salts**. (These salts are also referred to as **ternary** or **quaternary**.) That is, they contain more than one type of cation and/or more than one type of anion. For example, one of the common ores of copper is malachite, which has the formula Cu₂CO₃(OH)₂. This is an ionic compound that contains the Cu²⁺ ion and both the carbonate and hydroxide anions. Double salts can be thought of as combinations (but not mixtures) of two or more simple salts. Malachite can be visualized as CuCO₃ + Cu(OH)₂. Malachite is frequently found with azurite, which has the formula Cu₃(CO₃)₂(OH)₂. Azurite simply has a different ratio of the two simple salts: 2 CuCO₃ + Cu(OH)₂.



Another copper mineral, brochantite, has the formula Cu₄SO₄(OH)₆. Into what simple salts can you mentally dissect this compound?



CuSO₄ + 3 Cu(OH)₂

Brochantite is particularly interesting from the standpoint of its solubility. Copper sulfate is certainly soluble in water, but copper hydroxide is not. Of course, brochantite is not a mixture of CuSO₄ and Cu(OH)₂; the Cu²⁺, SO₄²⁻, and OH⁻ have very different positions in the structure of brochantite than they do in the individual simple salts. Nevertheless, it is useful to predict the water solubility of double salts from the solubilities of the simple salt components. A good general rule is that the double salt will have a solubility similar

to the simple salt that is less soluble. Because $\text{Cu}(\text{OH})_2$ is insoluble, we would predict that brochantite would not be very soluble, which is, in fact, the case.

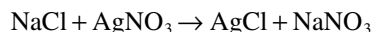
8.2 REACTIONS WITH ACIDS

Some minerals will react with acids and actually dissolve in them if they are finely powdered. In order to understand this phenomenon, we need to delve into some basics of chemical reactions.

8.2.1 Types of Chemical Reactions

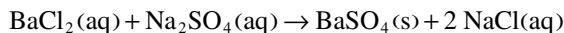
It will be helpful as we go along to keep in mind that most chemical reactions can be characterized as one of four major types:

1. Ion combination reactions. In these reactions, ions simply change partners. In the reaction of NaCl with AgNO_3 , the products are AgCl and NaNO_3 .

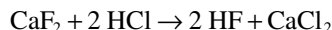


The products of many of these reactions' can be predicted by using the solubility rules. Ion-combination reactions that form precipitates (water-insoluble compounds) are known as **precipitation reactions**. In the reaction above, only AgCl is insoluble (solubility rule 3) and precipitates as soon as the reactants are mixed in water.

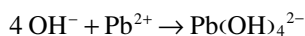
Barium sulfate precipitates (solubility rule 6) when a solution of barium chloride reacts with a solution of sodium sulfate. The other product of the reaction, NaCl , is soluble and does not precipitate:



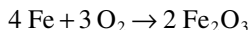
2. Hydrogen ion transfer reactions. In these reactions, also known as **Bronsted–Lowry acid–base reactions**, a hydrogen ion is transferred from one species to another. Fluorite (CaF_2) is etched by acids because a hydrogen ion is transferred from the acid to the fluoride ion and forms the molecule HF .



3. Electron sharing reactions. These reactions are also known as **Lewis acid–base reactions** (Gilbert Newton Lewis, American chemist) and involve the donation of electrons from an electron-rich species like the hydroxide ion to an electron deficient species like the lead ion. The product of these reactions are referred to as adducts or complexes.

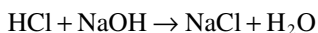


4. Electron transfer reactions. These reactions are most commonly called **oxidation–reduction reactions**, but if you remember the category as electron transfer you will know that in every “redox” reaction one species gives up electrons (is oxidized), which are then accepted by another species (is reduced). A familiar example of this is the rusting of iron by moist air. In this reaction the iron is converted to Fe^{3+} and the oxygen in the air is reduced to the oxide ion, O^{2-} .



Although it is true that in aqueous solution the Fe^{2+} ion is readily converted to Fe^{3+} and Cu^+ is easily oxidized to Cu^{2+} , there are many important minerals that contain the Fe^{2+} and Cu^+ ions. The solubility of the mineral containing these cations of lower charge is usually a factor in their stability. For example, cuprite (Cu_2O) is very insoluble and therefore not easily oxidized to tenorite (CuO).

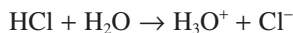
Now let us return to acids and bases (category 2). The alchemists knew that acids have a bitter taste (today we realize that no chemical should be tasted because of the potential toxicity of the compound), change the color of the plant dye litmus, and react violently with bases. Bases were known to have a slippery feel, to turn litmus blue, and to react violently with acids. The reaction of an acid with a base is now called **neutralization** and generally results in the production of a salt and water. For example, the reaction of hydrochloric acid with sodium hydroxide produces sodium chloride and water:



The definition of acids and bases that is most commonly used in mineralogy is that *an acid is a species capable of donating a hydrogen ion, H^+* , and a *base is a species capable of accepting a hydrogen ion*. This definition was proposed independently by the Danish chemist Johannes Bronsted and the British chemist Thomas Lowry. In the reaction of HCl with NaOH, HCl is the acid because it donates a hydrogen ion and hydroxide ion is a base because it accepts the hydrogen ion. This reaction and most other acid–base reactions are carried out in water. Water itself can act as both an acid and a base and is said to be **amphiprotic** (this word is much like ambidextrous—it denotes action possible in two different ways).



Write an equation that shows HCl, a very good hydrogen ion donor, donating a hydrogen ion to water.



Here the water acts as a base and accepts the hydrogen ion from the HCl, thereby forming the species H_3O^+ , called the hydronium ion.



Is the hydronium ion capable of donating a hydrogen ion?

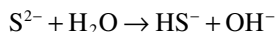


It certainly is. It contains three hydrogens, it is positively charged, and is strongly attracted to any species that is electron-rich. Indeed, the hydronium ion will react with the electron rich chloride ion (a base) in the reverse of the equation above.

Actually, every Bronsted–Lowry equation contains two acids and two bases. Each acid–base reaction can be thought of as two competing reactions; in the case of the reaction of HCl with water, the competition is between the transfer of a hydrogen ion from HCl to water (the reactants) and the transfer of a hydrogen ion from the hydronium ion

to the chloride ion (the products). Both of these reactions occur continuously in water and an equilibrium is established that favors the formation of the products. In other words, the HCl more effectively donates hydrogen ions to water than the hydronium ion does to chloride ion.

Sulfide ion, present in many ores, can react with water as a base (it cannot possibly be an acid because it contains no hydrogen):



In this equation there are also two acids and two bases. Water functions as an acid, as does the HS^- ion, while the S^{2-} and OH^- ions behave as bases. The equilibrium in this case lies on the reactant side; that is, there are more transfers of protons from HS^- to OH^- than there are from H_2O to S^{2-} and therefore, at equilibrium, only a small amount of the sulfur is present as HS^- .

8.2.2 Water as Both Acid and Base



Write an equation that shows a water molecule transferring a hydrogen ion to another water molecule.



This reaction shows that both hydronium ion and hydroxide ion will be present in all aqueous solutions. However, the equilibrium for the reaction lies on the reactant side and, consequently, the amount of hydronium ion present in pure water is very small, 1×10^{-7} moles per liter of water. The number of moles of hydroxide ion present in pure water is the same (1×10^{-7} moles per liter) because each transfer of a hydrogen ion from one water molecule to another produces one hydronium ion and one hydroxide ion.

The concentrations of hydronium ion and hydroxide ion in aqueous solutions are so important that a special mathematical function is used to express them. The **pH** of a solution is defined as:

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

The brackets indicate the unit of solution concentration known as molarity. **Molarity** (M) is defined as the number of moles of a substance in one liter of solution. Notice that the symbol p simply stands for the negative logarithm to the base 10.



Calculate the pH of pure water.



In pure water the hydrogen ion concentration is 1×10^{-7} mole/liter and thus the pH is $-\log[1 \times 10^{-7} \text{M}] = 7$. Although hydrogen ions in water are covalently attached to oxygen in the hydronium ion, it is common to use the terms hydrogen ion and hydronium ion interchangeably.

In pure water the hydronium ion and hydroxide ion concentrations are the same. When an acid such as HCl is added to water it reacts with the water to form more hydronium

ions, some of which then react with a small amount of hydroxide ion in the water to form a small amount of additional H_2O . Thus, addition of an acid increases the hydronium ion concentration and decreases the hydroxide ion concentration.



Calculate the pH of a 0.1 M HCl solution.



Because HCl is a very strong hydrogen ion donor, 0.1 mole of HCl will donate essentially all of its hydrogen ions to water, thereby forming 0.1 mole of hydronium ions. The pH is

$$-\log[1 \times 10^{-1} \text{ M}] = 1.$$

It is important to recognize that when the hydronium ion concentration is greater than that of the hydroxide ion, the solution is said to be acidic and the pH will be less than 7.

8.2.3 Strong and Weak Acids

There are a great many substances that can donate hydrogen ions. However, only six of the common acids are **strong acids**; that is, very good hydrogen ion donors—HCl, HBr, HI, HClO_4 , HNO_3 , H_2SO_4 . The other acids, such as carbonic acid (H_2CO_3), phosphoric acid (H_3PO_4), acetic acid (CH_3COOH), and H_2S are weak acids. To illustrate the difference, suppose that we add 0.1 mole of nitric acid to one liter of water in one beaker and 0.1 mole of acetic acid to one liter of water in another beaker. When we measure the pH of the two solutions, we find that the pH of the nitric acid solution is 1.0 while the pH of the acetic acid solution is 2.9. Although this difference in pH of only two units may not seem like much, it actually corresponds to almost a hundred-fold difference in the amount of hydronium ion present in the two solutions. Only about 1% of the acetic acid molecules donate a hydrogen ion to water, whereas almost 100% donation occurs with nitric acid.

8.2.4 Conjugate Bases

Of greater importance to the mineralogist than the acid itself is the anion derived from the acid when the acid loses a hydrogen ion. This anion is called the **conjugate base** of the acid.



Give the conjugate base of each of the following acids: HNO_3 , H_2CO_3 .



The conjugate base of HNO_3 is the nitrate ion, NO_3^- . There are two conjugate bases related to carbonic acid (H_2CO_3) because there are two hydrogens that it can donate. Therefore, the hydrogen carbonate ion (HCO_3^-) and the carbonate ion (CO_3^{2-}) are both conjugate bases. Many of the anions in minerals are the conjugate bases of common acids. The hydroxide ion is the conjugate base of water, the sulfate ion is the conjugate base of H_2SO_4 , and the phosphate ion is the conjugate base of phosphoric acid.



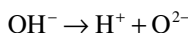
Many minerals contain oxide or sulfide ions. Are these ions conjugate bases?



Indeed they are. Remember that water has two hydrogen atoms (the same is true of H_2S) and can donate both of them, as hydrogen ions, to a base. When it transfers one hydrogen ion it forms the hydroxide ion, the conjugate base of water.



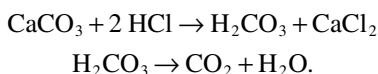
and then the OH^- ion can also transfer a hydrogen ion to form the oxide ion.



Formally, the oxide ion is the conjugate base of the hydroxide ion, but it is also considered the conjugate base of water when two hydrogen ions are transferred.

An anion that is the conjugate base of a strong acid has very little affinity for hydrogen ions; that is, the strong hydrogen ion donor ability of the acid produces a very weak hydrogen ion acceptor tendency in the conjugate base. Compounds that contain these anions therefore do not react with acids. On the other hand, compounds that contain *anions that are the conjugate bases of weak acids will react with acid*.

A common method of identifying calcite and many other (but not all) carbonates is to add a drop of hydrochloric acid to the mineral. If it is calcite, the fizzing that occurs is due to the evolution of carbon dioxide, which results from the decomposition of the carbonic acid that is formed. This sequence of reactions can be written as:



The reaction of atmospheric carbon dioxide with water (the reverse of the second equation) is important in the weathering of rocks, and the formation of large carbonate deposits such as calcite, dolomite ($\text{CaMg}(\text{CO}_3)_2$), and siderite (FeCO_3).



Which of the following minerals will react with HCl or another strong acid—barite (BaSO_4), brucite ($\text{Mg}(\text{OH})_2$), malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$)?



Barite will not react because it contains the anion (SO_4^{2-}) of a strong acid (H_2SO_4). Brucite will react because the hydroxide ion is the conjugate base of water, a weak acid. Malachite will react and fizz because it contains both the carbonate ion, the conjugate base of the weak acid carbonic acid, and the hydroxide ion.

Why then do not *all* carbonates react readily with acid? If the compound containing the carbonate ion is very insoluble, there will not be enough carbonate ion present in the aqueous solution to form carbonic acid when acid is added. For example, dolomite ($\text{MgCa}(\text{CO}_3)_2$) reacts slowly with acid at room temperature.



Why is dolomite ($\text{MgCa}(\text{CO}_3)_2$) less soluble than CaCO_3 ?



Dolomite can be thought of as a double salt of MgCO_3 and CaCO_3 . Double salts usually have a solubility similar to the solubility of the least soluble simple salt constituent. Because MgCO_3 is less soluble than CaCO_3 , dolomite is less soluble than calcite.

It is also important to note that the silicates are generally not soluble in acids. At one time it was believed that silicic acid ($\text{Si}(\text{OH})_4$) was the species from which the nesosilicate anion could be derived. There is now evidence that suggests that silicic acid does not exist as a molecular species and that hydrated SiO_2 is formed when strong acids are added to compounds such as Na_4SiO_4 . However, minerals containing the nesosilicate ion are generally very insoluble and will react with concentrated acids only with heat.



Explain the insolubility of the garnet family of minerals, all of which have the formula $\text{M}_3\text{Z}_2(\text{SiO}_4)_3$; for example andradite, $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$.



Notice first that these compounds are double salts. Second, the anion has a minus four charge and the cations have plus two and plus three charges. Consequently, the lattice energy of these compounds is very high and is not compensated by the heats of hydration of the ions.

8.3 USE OF CHEMICAL REACTIONS FOR IDENTIFICATION

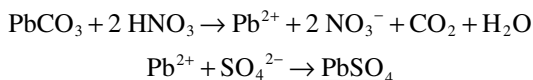
Although X-ray diffraction or analysis of the X-rays emitted by electron microscopy are the preferred methods of identification of minerals, fast and relatively secure identifications can be made by using chemical reactions. Precipitation reactions and acid–base reactions are two of the most common types of reactions used in chemical identifications.



Design a chemical method to distinguish between cerussite (PbCO_3) and smithsonite (ZnCO_3).



The solubility rules indicate that Pb^{2+} reacts with the sulfate ion to form insoluble PbSO_4 , whereas the zinc ion will not react with sulfate ion because ZnSO_4 is soluble. Before a source of sulfate ion can be added to the mineral, the mineral must be dissolved so that the lead or zinc ions can enter the solution. This dissolution can be accomplished by adding an acid such as nitric acid, which is ideal because the anion (the nitrate ion) does not form insoluble salts with almost all cations (solubility rule 1). If the cation is easily oxidized, as would be the case with Fe^{2+} , then nitric acid may cause oxidation. After the mineral is dissolved, either sulfuric acid or sodium sulfate, both of which will provide sulfate ion, can be added to the solution. If the mineral is cerussite, a precipitate of PbSO_4 will form as shown in the equations



The underline of PbSO_4 reveals that this compound precipitates out of solution. Notice also that the first reaction is an acid–base reaction and the second is an ion combination reaction. The addition of sulfate ion to the dissolved smithsonite would not produce a precipitate.



How would you identify a mineral believed to be either smithsonite (ZnCO_3) or hemimorphite ($\text{Zn}_3\text{Si}_2\text{O}_7$)?



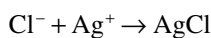
The carbonate will react with hydrochloric acid, “fizz” and eventually dissolve if enough acid is added, whereas the silicate (hemimorphite contains the sorosilicate ion, $\text{Si}_2\text{O}_7^{6-}$) will not readily react with acid.



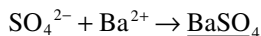
A mineral specimen is believed to be malachite, but a friend thinks that the distinct blue-green, needle-like crystals are more characteristic of atacamite or brochantite. An onlooker, obviously familiar with copper minerals, suggests that the sample, which was found in the 79 Mine in Arizona, is more likely to be aurichalcite. You proceed to search for the minerals in Fleischer’s Glossary of Minerals or on the web at sites such as www.mindat.org and find the following formulas: malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$), atacamite ($\text{Cu}_4\text{Cl}_2(\text{OH})_6$), brochantite ($\text{Cu}_4\text{SO}_4(\text{OH})_6$), and aurichalcite ($(\text{Zn,Cu})_5(\text{CO}_3)_2(\text{OH})_6$). The designation (Zn,Cu) in the formula for the aurichalcite means that the compound may exist as a solid solution containing a variable amount of zinc and copper. Of course, the charge of the cations must always add up to the charge on the anions. For example, a particular sample of aurichalcite might have a formula of $(\text{Zn}_{0.7}\text{Cu}_{0.3})_5(\text{CO}_3)_2(\text{OH})_6$. Can you distinguish between these three minerals using chemical reactions?



Because malachite and aurichalcite are carbonates, they will fizz when a bit of nitric or hydrochloric acid is added, due to the formation of carbonic acid and the subsequent evolution of CO_2 . Atacamite can be identified by treating a solution of the mineral in nitric acid with silver nitrate. The chloride ion will react with the silver ion to form insoluble silver chloride (Table 8, solubility rule 3).



Brochantite can be identified by treating a solution of the mineral with a solution of barium nitrate. A precipitate of BaSO_4 (Table 11, solubility rule 6) will form if the sulfate ion is present.

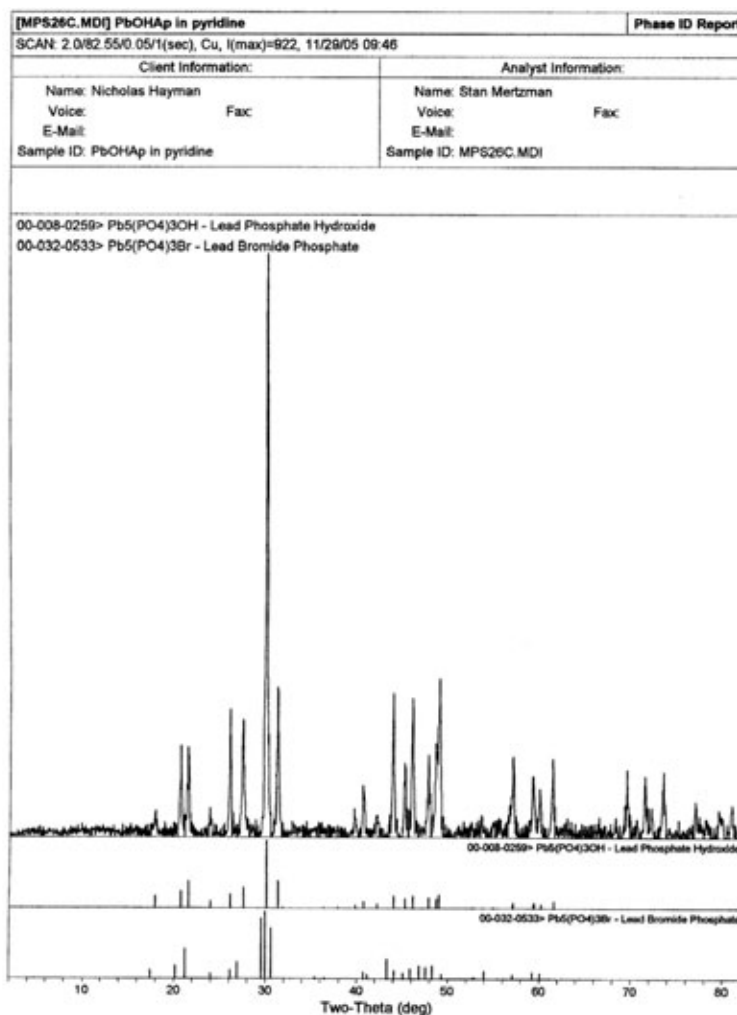


Malachite and aurichalcite cannot be distinguished by using only precipitation reactions and Bronsted-Lowry acid–base reactions. Another type of acid–base reaction, the Lewis reaction (reaction category 3), is necessary. Zinc ion will react with hydroxide ion to form insoluble zinc hydroxide (solubility rule 4), which will then react with excess hydroxide ion as a Lewis acid to form the soluble Lewis adduct $\text{Zn}(\text{OH})_4^{2-}$. Although the copper ion will react with hydroxide ion to form insoluble $\text{Cu}(\text{OH})_2$, this hydroxide does not act as a Lewis acid and will not dissolve in excess hydroxide ion.



The X-ray diffraction pattern shown below was obtained for a compound believed to be the bromide analog of pyromorphite, a member of the apatite family. The XRD line pattern serves as a fingerprint of the compound. The two

compounds that have line patterns most similar to that of the possible $\text{Pb}_5(\text{PO}_4)_3\text{Br}$ are shown at the bottom of the figure. Can you think of a simple chemical procedure that would distinguish between the two?



Franklin and Marshall College

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Figure 124 An X-ray diffraction (powder) of a compound believed to be $\text{Pb}_5(\text{PO}_4)_3\text{Br}$. The simulated patterns at the bottom are generated by the instrument's computer from patterns stored in the database.



If the compound is $\text{Pb}_5(\text{PO}_4)_3\text{Br}$, the addition of nitric acid to a small sample will dissolve the compound but leave a precipitate of PbBr_2 (Table 8, solubility rule 3). If the compound is $\text{Pb}_5(\text{PO}_4)_3\text{OH}$, the compound will dissolve and leave no residue.

A comparison of the XRD line pattern with the lines shown at the bottom for $\text{Pb}_5(\text{PO}_4)_3\text{OH}$ and $\text{Pb}_5(\text{PO}_4)_3\text{Br}$, clearly shows that the compound is the hydroxide.

Appendix 1

The Periodic Table

Periodic Table

Main Group =	I	II	— Transition Elements —										III	IV	V	VI	VII	VIII	
	1	4	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	
	H	Be	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
	1.00794	9.01218	44.95591	47.88	50.9415	51.9961	54.9380	55.847	58.9332	58.69	63.546	65.39	69.723	72.59	74.9216	78.96	79.904	83.80	
	3	12	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	
	Li	Mg	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
	6.941	24.305	88.9059	91.224	92.9064	95.94	(98)	101.07	102.9055	106.42	107.8682	112.41	114.82	118.710	121.75	127.60	126.9045	131.29	
	11		57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	
	Na		La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
	22.98977		138.9055	178.49	180.9479	183.85	186.207	190.2	192.22	195.08	196.9665	200.59	204.383	207.2	208.9804	(209)	(210)	(222)	
	19		89	104	105	106	107	108	109										
	K		Ac	Rf	Db	Sg	Bh	Hs	Mt										
	39.0983		226.0254	227.0278	(261)	(266)	(264)	(269)	(268)										
	37		87	Fr	Ra														
	Rb		(223)	(223)															
	85.4678																		
	55																		
	Cs																		
	132.9045																		
	5																		
	B																		
	10.811																		
	13																		
	Al																		
	26.98154																		
	6																		
	C																		
	12.011																		
	14																		
	Si																		
	28.0855																		
	7																		
	N																		
	14.0067																		
	15																		
	P																		
	30.97376																		
	8																		
	O																		
	15.9994																		
	9																		
	F																		
	18.998403																		
	17																		
	Cl																		
	35.453																		
	18																		
	Ar																		
	39.948																		
	2																		
	He																		
	4.002602																		
	1																		
	H																		
	1.00794																		
	70																		
	Yb																		
	173.04																		
	69																		
	Tm																		
	168.9342																		
	100																		
	Fm																		
	(257)																		
	99																		
	Es																		
	(252)																		
	98																		
	Cf																		
	(251)																		
	97																		
	Bk																		
	(247)																		
	96																		
	Cm																		
	(247)																		
	95																		
	Am																		
	(243)																		
	94																		
	Pu																		
	(244)																		
	93																		
	Np																		
	(237.0482)																		
	92																		
	U																		
	(238.0289)																		
	91																		
	Pa																		
	(231.0359)																		
	102																		
	No																		
	(259)																		
	101																		
	Md																		
	(258)																		
	103																		
	Lr																		
	(260)																		

Lanthanides

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
140.12	140.9077	144.24	(145)	150.36	151.96	157.25	158.9254	162.50	164.9304	167.26	168.9342	173.04	174.967

Some common group names:

- I.** The alkali metals
- II.** The alkaline earth metals
- VI.** The chalcogens
- VII.** The halogens
- VIII.** The inert or noble gases

Summary of general trends in properties:

- 1.** Size of atoms. Atoms increase in size as a group is descended (for example, Ba is larger than Mg), and decrease slightly in size as a period (row) is traversed from left to right (F is smaller than Li).
- 2.** Ionization energy. Ionization energy decreases down a group and increases across a period from left to right.
- 3.** Electronegativity. Electronegativity decreases down a group and increases across a period from left to right.
- 4.** Metallicity (the tendency of an element to be a metal). Metallicity increases down a group and decreases across a period from left to right. For example, carbon has no metallic elemental forms, whereas lead, the element at the bottom of group IV, exists only in a metallic form. Astatine, the bottom member of the halogens, has no metallic forms.

Appendix 2

The Elements: Symbols, Melting Points, Boiling Points, Densities, and Electronegativities

170 Appendix 2 The Elements

Element	Symbol	mp	bp	Density	χ^P	χ^{AR}	Element	Symbol	mp	bp	Density	χ^P	χ^{AR}
Actinium	Ac	1050	3200	10	1.1	1.00	Mercury	Hg	-38.87	356.9	13.546	1.9	1.44
Aluminum	Al	660.2	(2400)	2.702	1.5	1.47	Molybdenum	Mo	2610	5560	10.22	1.8	1.30
Americium	Am	995	(2600)	11.7	1.3		Neodymium	Nd	1024	3027	7.00	1.1	1.07
Antimony	Sb	630.5	(1380)	6.68(25°)	1.9	1.82	Neon	Ne	-248.6	-246	0.900(0°)		
Argon	Ar	-189.2	-185.8	1.7824			Neptunium	Np	640		20.45	1.3	1.22
Arsenic	As	817	613(s)	5.72	2.0	2.20	Nickel	Ni	1455	(2730)	8.90	1.8	1.75
Astatine	At				2.2	1.96	Niobium	Nb	2468	4930	8.57	1.6	1.23
Barium	Ba	(725)	(1140)	3.51	0.9	0.97	Nitrogen	N	-209	-195.8	1.25(0°)	3.0	3.07
Berkelium	Bk				1.3		Nobelium	No				1.3	
Beryllium	Be	1278	(2970)	1.848	1.5	1.47	Osmium	Os	(3000)	(5000)	22.5	2.2	1.52
Bismuth	Bi	271.3	1560	9.80	1.9	1.67	Oxygen	O	-218.8	-183.0	1.429	3.5	3.50
Boron	B	(2200)	(3800)	2.34	2.0	2.01	Palladium	Pd	1550	(2927)	12.02	2.2	1.39
Bromine	Br	-7.2	58.78	3.119	2.8	2.74	Phosphorus	P	44.2	280	1.82	2.1	2.06
Cadmium	Cd	320.9	764.9	8.65	1.7	1.46	Platinum	Pt	1769	(3800)	21.45	2.2	1.44
Calcium	Ca	850	1490	1.55	1.0	1.04	Plutonium	Pu	640	3235	19	1.3	1.22
Californium	Cf				1.3		Polonium	Po	254	962	9.3	2.0	1.76
Carbon	C	3500(s)	4830	3.51	2.5	2.50	Potassium	K	63.7	774	0.862	0.8	0.91
Cerium	Ce	795	3468	6.67	1.1	1.06	Praseodymium	Pr	935	3127	6.77	1.1	1.07
Cesium	Cs	28.7	690	1.873	0.7	0.86	Promethium	Pm	1035	2730		1.1	
Chlorine	Cl	-101.0	-34.6	3.214	3.0	2.83	Protactinium	Pa				1.4	1.14
Chromium	Cr	(1900)	(2500)	7.19	1.6	1.56	Radium	Ra	700		(5)	0.9	0.97
Cobalt	Co	(1493)	(2900)	8.9	1.8	1.70	Radon	Rn	-71	-61.8	9.73(0°)		
Copper	Cu	1083	2595	8.96	1.9	1.75	Rhenium	Re	3180	(5625)	21	1.9	1.46
Curium	Cm		7		1.3		Rhodium	Rh	1966	(3800)	12.4	2.2	1.45
Dysprosium	Dy	1407	2600	8.536	1.1	1.10	Rubidium	Rb	38.9	688	1.53	0.8	0.89
Einsteinium	Es				1.3		Ruthenium	Ru	(2400)	(3900)	12.2	2.2	1.42
Erbium	Er	1497	2900	9.05	1.1	1.11	Rutherfordium	Rf					
Europium	Eu	826	1439	5.259	1.1	1.01	Samarium	Sm	1072	1900	7.54	1.1	1.07
Fermium	Fm				1.3		Scandium	Sc	1539	2727	3.0	1.3	1.20
Fluorine	F	-219.6	-188.1	1.696(0°)	4.0	4.10	Selenium	Se	217	685	4.79	2.4	2.48
Francium	Fr				0.7	0.86	Silicon	Si	(1410)	2355	2.33(25°)	1.8	1.74
Gadolinium	Gd	1312	3000	7.895	1.1	1.11	Silver	Ag	960.8	2212	10.5	1.9	1.42
Gallium	Ga	29.78	(2400)	5.907	1.6	1.82	Sodium	Na	97.8	890	0.971	0.9	1.01
Germanium	Ge	937.4	(2830)	5.32(25°)	1.8	2.02	Strontium	Sr	770	1384	2.6	1.0	0.99
Gold	Au	1063	2966	19.32	2.4	1.42	Sulfur	S	119	444.6	2.07	2.5	2.44
Hafnium	Hf	(2150)	5400	13.2	1.3	1.23	Tantalum	Ta	2997	(5425)	16.6(0°)	1.5	1.33
Helium	He	-269.7	-268.9	0.178			Technetium	Tc	(2200)			1.9	1.36
Holmium	Ho	1461	2600	8.80	1.1	1.10	Tellurium	Te	450	990	6.24	2.1	2.01
Hydrogen	H	-259.2	-252.7	0.0899	2.1	2.20	Terbium	Tb	1356	2800	8.27	1.1	1.10
Indium	In	156.17	2000	7.31	1.7	1.49	Thallium	Tl	304	1457	11.85	1.8	1.44
Iodine	I	113.6	184.35	4.93	2.5	2.21	Thorium	Th	(1700)	(4000)	(11.7)	1.2	1.11
Iridium	Ir	(2410)	4500	22.42	2.2	1.55	Thulium	Tm	1545	1727	9.33	1.1	1.11
Iron	Fe	1535	3000	7.86	1.8	1.64	Tin	Sn	231.9	2270	7.31	1.8	1.72
Krypton	Kr	-157	-153	3.708			Titanium	Ti	(1675)	3260	4.5	1.5	1.32
Lanthanum	La	920	3470	6.15	1.1	1.08	Tungsten	W	(3400)	(5900)	19.3	1.7	1.40
Lawrencium	Lr						Uranium	U	1132	3818	18.9	1.5	1.22
Lead	Pb	327.4	(1744)	11.34	1.8	1.55	Vanadium	V	(1890)	(3000)	6.1	1.6	1.45
Lithium	Li	180.5	(1326)	0.534	1.0	0.97	Xenon	Xe	-111.9	-108	5.88		
Lutetium	Lu	1652	3327	9.85	1.2	1.14	Ytterbium	Yb	824	1427	6.98	1.1	1.06
Magnesium	Mg	650	1107	1.738	1.2	1.23	Yttrium	Y	(1500)	2927	4.47(0°)	1.2	1.11
Manganese	Mn	1245	(2097)	7.4	1.5	1.60	Zinc	Zn	907	419.5	7.14	1.6	1.66
Mendelevium	Md				1.3		Zirconium	Zr	1852	(4000)	6.4	1.4	1.22

^aMelting points and boiling points in °C at 760 torr, densities in g/cc or g/L for gases. χ^P and χ^{AR} are Pauling and Allred-Rochow electronegativities, respectively.

Appendix 3

Metallic, Covalent, and Ionic Radii

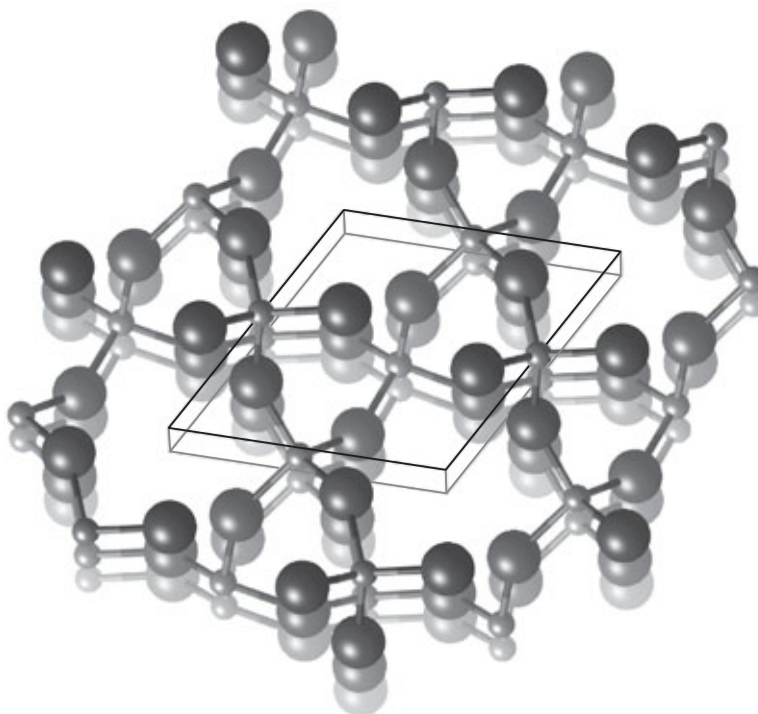
Atom/Ion	<i>r.</i> pm	Atom/Ion	<i>r.</i> pm	Atom/Ion	<i>r.</i> pm
Ag	144	Fe ³⁺	60	Pd ²⁺	86
Ag ⁺	115	Ga	153	Po	153
Al	143 (140)	Ga ³⁺	62	Pt	139
Al ³⁺	53	Ge	139 (122)	Pt ²⁺	80
Ar	(95)	H	(37)	Pt ⁴⁺	77
As	(122)	He	(32)	Rb	250
As ³⁺	58	Hf	159	Rb ⁺	152
Au	144	Hg	155	Rh	134
Au ⁺	137	Hg ²⁺	102	Rn	(145)
B	(90)	I	(133)	Ru	134
Ba	224	I ⁻	220	S	(102)
Ba ²⁺	135	In	167	S ²⁻	184
Be	112 (125)	In ³⁺	80	Sb	161(143)
Be ²⁺	45	Ir	136	Sb ³⁺	76
Bi	182	Ir ³⁺	82	Sc	164
Bi ³⁺	103	K	235	Sc ³⁺	75
Br	114	K ⁺	138	Se	(117)
Br ⁻	196	Kr	(110)	Se ²⁻	198
C	(77)	La	188	Si	(118)
Ca	197	La ³⁺	103	Sn	158(140)
Ca ²⁺	100	Li	157	Sn ²⁺	118
Cd	152	Li ⁺	76	Sr	215
Cd ²⁺	95	Lu	172	Sr ²⁺	118
Ce	182	Lu ³⁺	86	Te	(135)
Ce ³⁺	102	Mg	160	Te ²⁻	221
Cl	(99)	Mg ²⁺	72	Th	180
Cl ⁻	184	Mn	137	Ti	147
Co	125	Mn ²⁺	70	Ti ³⁺	67
Co ²⁺	70	N	(75)	Tl	171
Co ³⁺	69	Na	191	Tl ⁺	150
Cr	129	Na ⁺	102	Tl ³⁺	88
Cr ³⁺	62	Ne	(69)	U	156
Cs	272	Ni	125	V	135
Cs ⁺	167	Ni ²⁺	70	V ²⁺	79
Cu	128	O	(73)	W	141
Cu ⁺	77	O ²⁻	140	Xe	(130)
Cu ²⁺	73	Os	135	Y	182
F	(71)	P	(110)	Y ³⁺	90
F ⁻	133	Pb	175	Zn	137
Fe	126	Pb ²⁺	119	Zn ²⁺	74
Fe ²⁺	70	Pd	137	Zr	160

Appendix 4

Quartz

Quartz is one of the most common and fascinating minerals. Unlike the minerals that we have concentrated on in the text, quartz is not an ionic compound. It is a three-dimensional covalent network compound that contains Si–O covalent bonds. The Si–O bond is one of the strongest covalent bonds with a bond energy of 450 kJ/mole, which can be compared to other covalent single bonds such as the C–O (360 kJ/mole) and the P–O (340 kJ/mole) bonds. Because the electronegativity of silicon is about 1.8 while oxygen is 3.5, the difference in electronegativity between the two atoms is large enough to give the bond significant ionic character, which is one of the factors that makes the bond so strong.

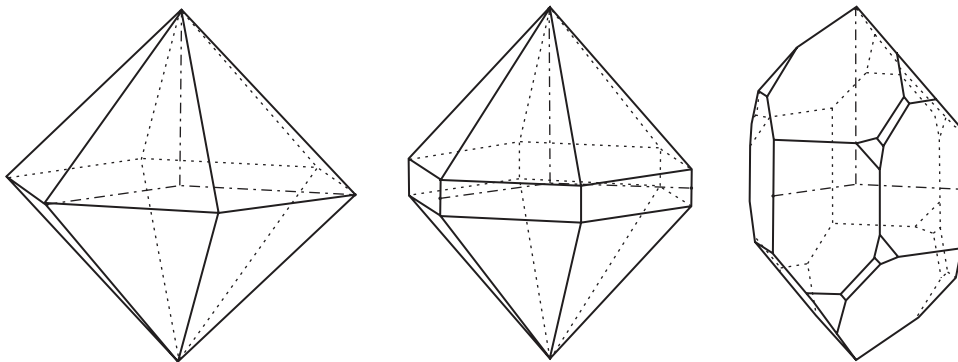
Quartz exists as two polymorphic forms: alpha-quartz (or low quartz), stable at room temperature and pressure, and beta-quartz (or high quartz), stable only at temperatures above about 600°C. The structure of alpha-quartz is shown below:



The structure contains what appear to be both 6- and 12-membered rings of silicons and oxygens. Although it is not easy to see from the illustration above, both sets of “rings”

actually spiral down through the structure along the c -axis. The structure of beta-quartz is very similar but slightly more symmetric. The two polymorphs differ by slight distortions in the crystal lattice and are called displacive polymorphs.

Alpha quartz belongs to the point group 32, whereas the more symmetric beta quartz has 622 symmetry. Alpha quartz has a variety of different crystal habits, several of which are shown below:



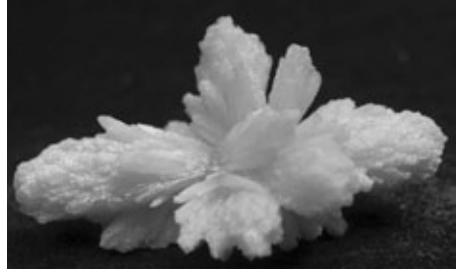
The two forms on the left are formed by beta quartz, but are also formed, although not commonly, by alpha quartz. Quartz forms a large number of colored varieties, including rose quartz, amethyst, smoky quartz, citrine (light-yellow), and milky quartz. Inclusions such as rutile and hematite are fairly common. It also exists in a large number of varieties that exhibit no macroscopic crystalline structure. These include chalcedony, agate, flint, chert, and jasper.

Compounds with the formula SiO_2 also include tridymite and cristobalite, both formed at high temperatures. Each of these polymorphs of SiO_2 are reconstructive polymorphs of quartz: bond breaking is required for transitions from one to another, a process that requires considerable energy. Thus, these polymorphs can be found at room temperature and pressure because of the low rate at which they convert to quartz, which is more stable at room temperature and pressure. Both tridymite and cristobalite also have alpha and beta displacive polymorphs. Alpha tridymite is orthorhombic, beta tridymite is hexagonal, alpha cristobalite is tetragonal, and beta cristobalite is isometric. Finally, two more polymorphs, coesite (monoclinic) and stishovite (tetragonal), are formed only at very high pressures. Both have been found at Meteor Crater in Arizona, presumably formed by the high pressure (and temperature) produced upon impact of a meteor.

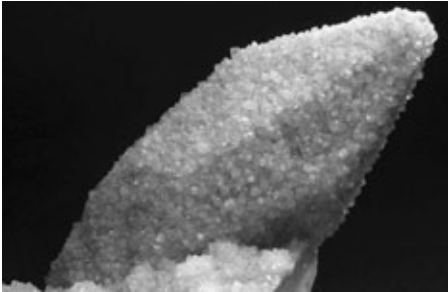
The following page presents photographs of a few of the many forms that crystalline quartz can adopt.



Quartz, Cactus Amethyst (Magaliesberg, South Africa)



Quartz, Artichoke (Shangbao, Leiyang Hunan Province, China)



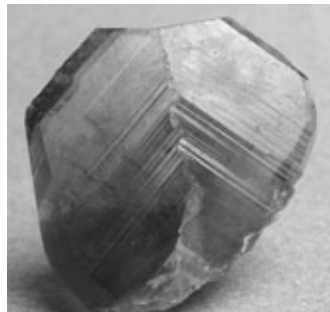
Quartz ps Calcite (Rio Grande do Sul, Brazil)



Quartz ps Calcite (Irai, Rio Grande do Sul, Brazil)



Quartz, var. Morion (Fazenda Recruta Vitoria da Conquista, Bahia, Brazil)

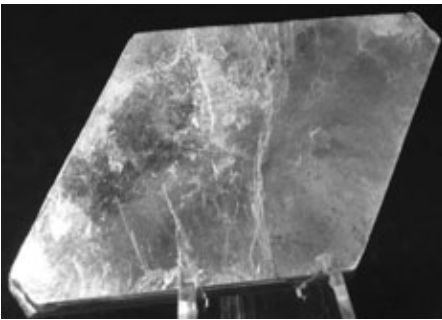


Smoky Quartz, Japan Law Twin (Lincoln Co., New Mexico)

Appendix 5

Crystal System Identification Practice

Answers can be found in most mineral field guides (see Appendix 7).



Muscovite (Diamond Mica Mine, Keystone, Pennington, South Carolina)



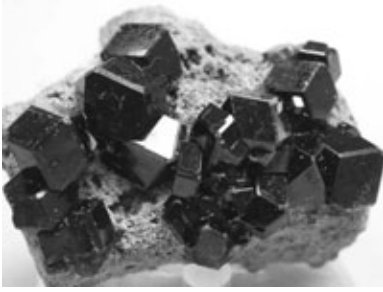
Orthoclase (Maroon Bells, Colorado)



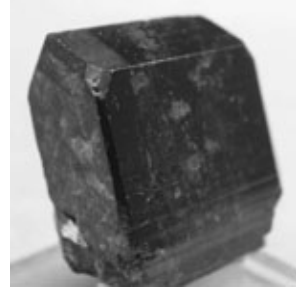
Tetrahedrite (The Judge Tunnel, Park City, Utah)



Vanadinite (Acif Mine, Mibladen, Morocco)



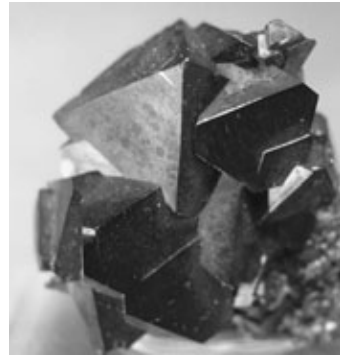
Grossular (near Sadiola Gold Mine, Kanzs, Mali)



Epidote (Green Monster Mt., Prince Of Wales Island, Alaska)



Barite (Niobec Mine, Chicoutimi, Quebec, Canada)



Cuprite (Mashamba West Mine, Shaba Province, Zaire)



Wulfenite (Rowley Mine, Maricopa Co., Arizona: George Godas specimen and photo)

Appendix 6

Crystal Systems and Classes

System	Class
triclinic	$\bar{1}$
monoclinic	2 m $2/m$
orthorhombic	222 mm^2 $2/m^2/m^2/m$
tetragonal	$\frac{4}{2}$ $\frac{4}{2}$ $4/m$ 422 $4mm$ $\bar{4}2m$ $4/m^2/m^2/m$
hexagonal	$\frac{6}{2}$ $\frac{6}{2}$ $6/m$ 622 $6mm$ $\bar{6}m^2$ $6/m^2/m^2/m$ $\frac{3}{2}$ $\frac{3}{2}$ 32 $3m$ $\bar{3}2/m$
isometric	23 $2/m\bar{3}$ 432 $\bar{4}3m$ $4/m\bar{3}2/m$

Appendix 7

Additional Reading and Resources

MINERALOGY TEXTS:

- Bloss FD, *Crystallography and Crystal Chemistry*. Washington, DC: *Mineralogical Society of America*; 1994.
- Klein C, *Manual of Mineral Science.*, 22nd edn. New York: John Wiley; 2002.
- Gainkav R, Skinner HCW, Foord EE, Mason B, and Rozenzweig A, *Dana's New Mineralogy*. 8th edn., New York: John Wiley; 1997.
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- Anthony JW, Bideaux RA, Bladh KW, Nichols MC, *Handbook of Mineralogy*. Tucson, AZ: Mineral Data Publishing; 1990.
- Bernard JH, Hyrsl J, *Minerals and Their Localities*. Czech Republic: Granit; 2004.
- Wenk H-R, Bulakh A, *Minerals, Their Constitution and Origin*. Cambridge: Cambridge University Press; 2004.
- Putnis A, *Introduction to Mineral Sciences*. Cambridge: Cambridge University Press; 1995.
- Deer WA, Howie RA, and Zussman J, *Introduction to Rock-Forming Minerals*. 2nd edn, London: Longman; 1996

CHEMISTRY TEXTS:

- Pauling L, *The Nature of the Chemical Bond*. 3rd edn, Ithaca, NY: Cornell University Press; 1960.
- Wells AF, *Structural Inorganic Chemistry*. 5th edn, Oxford: Oxford University Press; 1986.

FIELD GUIDES:

- Pough, FH, *Rocks and Minerals*. 5th edn, Peterson Field Guide, Boston: Houghton Mifflin; 1988.
- Johnsen, O, *Minerals of the World*. Princeton Field Guides, Princeton, NJ: Princeton University Press; 1994.

MINERALOGY MAGAZINES:

- The Mineralogical Record*, P. O. Box 35565, Tucson, AZ
www.MineralogicalRecord.org
- Lapis International*, LLC, East Hampton, CN
www.lapisint.com
- Rocks and Minerals*, Heldref Publications, Washington, DC
www.rocksandminerals.org

WEB RESOURCES:

- The Mineral Database
www.mindat.org
- Amethyst Galleries
<http://mineral.galleries.com>
- webmineral.com
- www.webmineral.com
- The Wired Chemist
<http://wulfenite.fandm.edu>

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Pyrrhotite (Fe_{1-x}S , $x = 0 - 0.17$) with Quartz (Dalnegorsk, Russia. 5.0×7.0 cm, mon)



Chalcopyrite (CuFeS_2) (Pachapaqui District, Peru. 3.0 cm view, tet)



Marcasite (FeS_2) (White Desert, Egypt. 4.5×4.0 cm, orth)



Marcasite, botryoidal (FeS_2) (Olkusz Mine, Silesia, Poland. 7.8×3.5 cm, orth)



Galena (PbS), cubic and octahedral habit (Viburnum Trend, Sweet-water Mine, Reynolds Co., Missouri. 3.7×4.4 cm, iso)



Realgar on Calcite (AsS) (Hunan, China. 3.4×8.0 cm, mon)



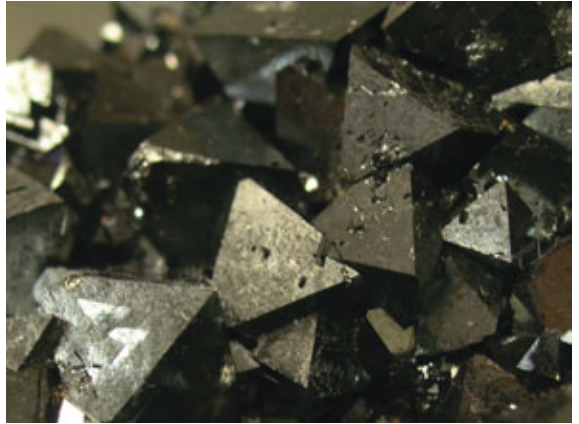
Stibnite with Dolomite (Sb_2S_3) (Bela Spira, Maramures, Romania. 5.3×4.5 cm, orth)



Hematite, Kidney Ore (Fe_2O_3) (Egremont, Cumbria, England. 4.5×2.8 cm, hex. Lee Tori specimen)



Hematite ps Magnetite (Fe_2O_3) (Chubut, Patagonia, Argentina. 5.5×3.2 cm, hex)



Magnetite (Fe_3O_4) (Mina Huaguno, Potosi, Bolivia. 2 cm view, iso)



Magnetite, cubic habit (Fe_3O_4) (Zinc Co. of America, 2500' level, Balmat, New York. 2.0×2.7 cm, iso)



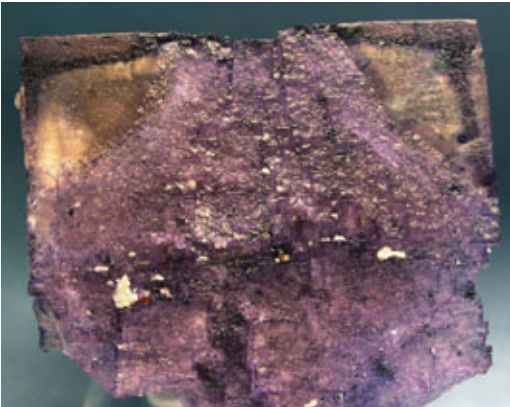
Cuprite on Copper (Cu_2O) (Ray Mine, Arizona. 6.3×5.2 cm, iso)



Fluorite, octahedral habit (CaF_2) (Oatman, Arizona. 3.5×5.0 cm, iso)



Fluorite, botryoidal (CaF_2) (Huaron District, Peru. 5.5×3.0 cm, iso)



Fluorite, etched "optical" corners (CaF_2) (Elmwood Mine, Elmwood, Tennessee. 5.9×5.2 cm, iso)



Malachite ps Azurite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$) (Seabra Bahia, Brazil. 7.0×6.0 cm, mon)



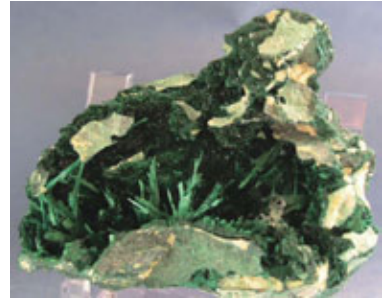
Azurite and Malachite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$) (Copper Queen Mine, Bisbee, Arizona. 7.7×6.8 cm, mon)



Malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$) (Kakanda Mine, Democratic Republic of the Congo. 4.5×3.6 cm, mon)



Azurite and Malachite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$) (Anging Copper Mine, Anhui Province, China. 9.3×3.8 cm, mon)



Malachite, fibrous ($\text{Cu}_2\text{CO}_3(\text{OH})_2$) (Luithia Mine, Democratic Republic of the Congo. 5.0×2.1 cm, mon)



Rhodochrosite (MnCO_3) on Manganite (N'Chwaning Mine, Kuruman, South Africa. 4.1×2.7 cm, hex)



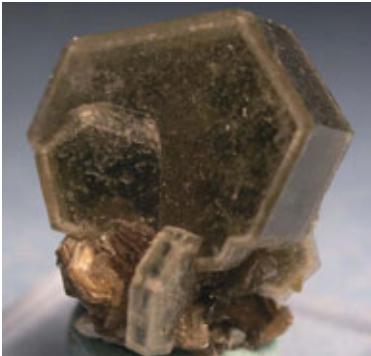
Rhodochrosite (MnCO_3) (N'Chwaning Mine, Kuruman, South Africa. 3.3×1.4 cm, hex)



Gypsum Twins ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) (Red River Floodway, Winnipeg, Manitoba, Canada. 6.5×7.5 cm, mon)



Vanadinite on Barite ($\text{Pb}_5(\text{VO}_4)_3\text{Cl}$ on BaSO_4) (Acif Mine, Morocco. 5.2×5.6 cm, hex)



Apatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) (Panasqueira, Portugal. 2.5×2.7 cm, hex)



Pyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{Cl}$) (Zvezdel Mine, S. Rhodope Mts., Bulgaria. 3.3×5.5 cm, hex)



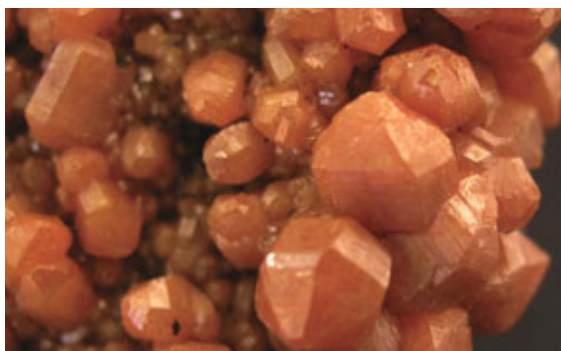
Scheelite on Wulframite with Quartz (CaWO_4 on $(\text{Fe},\text{Mn})\text{WO}_4$) (Chungju, S. Korea. 3.0×3.7 cm, tet)



Vanadinite ($\text{Pb}_5(\text{VO}_4)_3\text{Cl}$) (Mibladen, Morocco. 8.0×2.5 cm, hex)



Vanadinite, hopped
($\text{Pb}_5(\text{VO}_4)_3\text{Cl}$) (Pure Potential Mine, La Paz Co., Arizona. 2.4×1.7 cm, hex)



Vanadinite (J.C. Holmes Claim, Santa Cruz Co., Arizona. 1 cm view, hex)



Wulfenite (PbMoO_4) (Los Lamentos, Chihuahua, Mexico. 1.3 cm view, tet)



Wulfenite (PbMoO_4) on Hemimorphite with Quartz druse (Barking Spider Mine, Arizona. 5.0×4.4 cm, tet)



Wulfenite (PbMoO_4) on Goethite (Whim Creek Mine, Whim Well, Australia. 4.5×5.1 cm, tet)



Wulfenite (PbMoO_4) with Mimetite (Rowley Mine, Maricopa Co., Arizona. 1.8×3.2 cm, tet. George Godas Collection and photo)



Spessartine ($\text{Mn}_3\text{Al}_2(\text{SiO}_4)_3$) (Sanshuishan, Guangdong Province, China. 8.2×7.0 cm, iso)



Rhodonite ($(\text{Mn,Fe,Mg,Ca})\text{SiO}_3$) (Franklin, New Jersey. 6.5×5.0 cm, tri)