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Chapter 3

Stoichiometry

Stoichiometry, the study of the quantitative aspects of composition and chemical reactions, is traditionally taught from a nonstructural basis using molecular formulas consisting of easily countable numbers of atoms in small integer relationships. Calculations involve the determination of empirical and molecular formulas, mass–mole relationships, and concentrations, using equations balanced with integer coefficients.

Another aspect of stoichiometry involves the determination of empirical formulas for compounds having extended structures. However, before the stoichiometry of extended structures is addressed, we should ask the following questions: How can the existence of an extended structure be predicted, and how prevalent are extended structures?

Chemists divide the periodic table into two main regions—the metals and the nonmetals—using a staircase-like diagonal line that runs through the table. Elements that are in contact with this line are sometimes called metalloids. Table 3.1 summarizes the structural properties of combinations of these classes of elements. Compounds formed between nonmetals and other nonmetals tend to be relatively small, discrete molecules. In contrast, compounds formed between metals and nonmetals

Table 3.1. Combinations of Classes of Elements

Element Combination	Likely Structure	Examples
Nonmetal and nonmetal	Discrete molecule	CO_2, PCl_3, NO
Metal and metal	Extended (alloys)	CuZn (brass), NiTi
Metal and nonmetal[a]	Extended (salts)	NaCl, ZnS, $CaTiO_3$
Metalloid combinations	Extended or discrete	Si, BN (extended) $SiCl_4$, $AsCl_3$ (discrete)

[a] Some combinations of transition metals, in high oxidation states, with nonmetals can produce discrete molecules. For example, OsO_4 and $TiCl_4$ are generally considered to be discrete molecules rather than salts.

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or between metals and other metals usually form solids with extended structures. Pure metals themselves also form solids with extended structures. These extended-structure solids include many metals, minerals, and salts that are commonly encountered.

Determining Stoichiometry from Unit Cells

Many of the solids discussed in this book are properly described as extended solids, because they comprise patterns of atoms that continuously repeat until the boundaries of the solid are reached. This section discusses the common formalism for describing the repeating patterns—the construction of unit cells—and illustrates the connection between unit cells and stoichiometric formulas.

The unit cell of an extended solid is a collection of its atoms, and sometimes fractions of its atoms, that can be systematically translated through space to create the entire solid. The size and shape of a unit cell are described by the lengths of three edges (a, b, and c) and the angles (α, β, and γ) between them. The edges connect points in the solid that have identical environments.

Unit cells are parallelograms in two dimensions and parallelepipeds in three dimensions. The procedure for translating the cell is to move the cell and its contents the length of its edge along the direction in which that edge points. When carried out in all directions defined by the edges of the unit cell (and when repeated from each newly produced cell), this process will leave no gaps between unit cells, and will generate the entire array or crystal.

Figure 3.1 illustrates a two-dimensional example of a unit cell on a square array of identical dots that could represent, for example, a layer of atoms in the metallic element chromium. The square is a unit cell; its edges connect identical points that lie at the centers of squares formed by the dots. When the unit cell is translated parallel to its edges by the length of the edge, in each of the four possible directions, an identical set of four unit cells results, as outlined by the dashed lines. By continuing this process, the entire structure will be produced, as demanded for a unit cell.

In contrast, Figure 3.2 shows a square (formed by the solid lines) that is not a unit cell. Its edges do not connect points with identical environments, and it will not generate the correct array if it is replicated along its edges, since this test unit cell requires the dots to have a closer repeat distance.

The selection of a unit cell is not unique; its corners can be placed anywhere within a crystal. For example, using the same pattern of dots, another kind of square, shown as solid lines in Figure 3.3, would also serve as a unit cell. In this case, the corners are placed at the centers of the dots. Again, translating the square leads to identical unit cells, as shown by dashed lines on the figure.

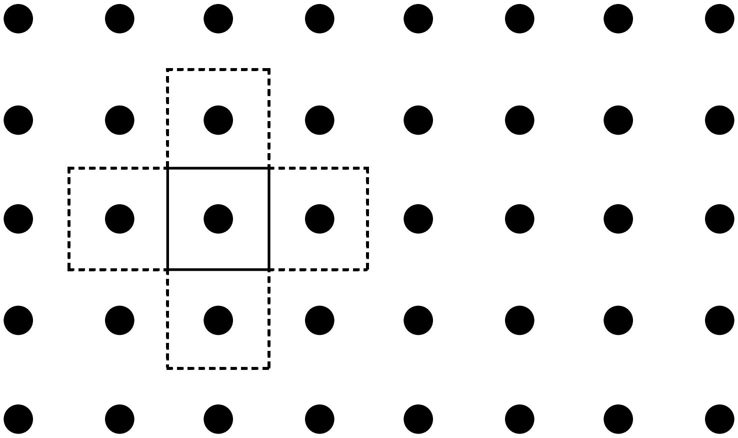

Figure 3.1. An array of dots with a square unit cell superimposed on it. Translation of the unit cell in any direction (represented by the dashed squares) will generate identical cells that, as the process continues through space, will produce the entire structure.

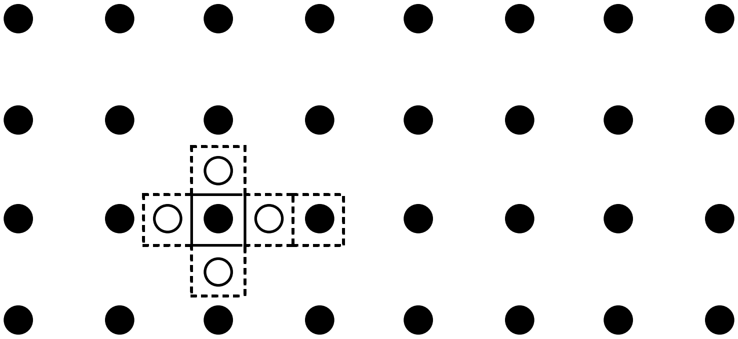

Figure 3.2. If a unit cell is not chosen properly, translation of that cell will not generate the desired array. In this picture translation of the original unit cell (dark outline) produces some dots that do not belong to the array (white circles).

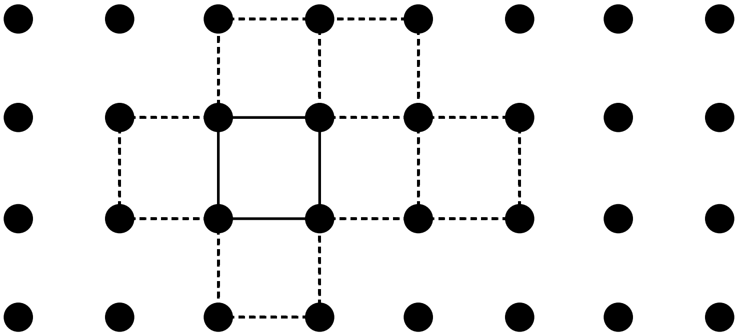

Figure 3.3. Selection of several different unit cells is possible for the same structure. This one differs from Figure 3.1 in that the atoms are at the corners of the unit cell rather than in the middle. However, translation of this unit cell will still generate the complete structure.

Once a unit cell has been determined, the number of atoms in the unit cell can be identified. In Figure 3.1, there is one dot contained entirely within the unit cell and no others associated with the unit cell, leading to a count of one dot (atom) per unit cell. The count should be unaffected by the choice of the unit cell if their areas are the same: In Figure 3.3, no dots are contained entirely within the unit cell, but each of those at the corners of the unit cell is partly within the unit cell. In the expanded view in Figure 3.4, it is apparent that one-quarter of each dot lies within the bounds of the unit cell, and, because there are four such dots (one at each corner), there is 4 × 1/4 = 1 dot associated with the unit cell. Another way to think of this condition is that if any dot (atom) is shared by four unit cells, such as the situation here, then it will contribute one-fourth of its total area to each of the cells (one-fourth to any given cell).

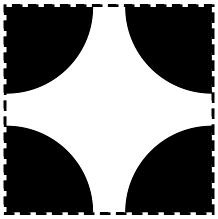

Figure 3.4. Only one-fourth of each corner atom is actually within the unit cell shown in Figure 3.3.

Although it is conventional practice to choose a unit cell with the highest possible symmetry, many different parallelograms could be employed as unit cells. Figure 3.5 shows a unit cell without right angles on the same array of dots. In this case four points lying at the corners of a “squashed” parallelogram are used to define the unit cell. Translation in each of four directions as described above yields identical unit cells (outlined with dashed lines) that can be further replicated to produce the entire structure. In this case, too, a “stoichiometry” of one dot per unit cell is found. Geometric arguments can be used to show that each adjacent pair of dots accounts for a total area of one-half of a dot, and there are two such pairs for a total area of one dot; alternatively, the portions of the four dots defining the parallelogram that are contained within the unit cell can be cut out with scissors and, when pasted together, will be seen to form one complete dot. The sharing formalism can again also be applied: With each dot participating in four unit cells, *on average* it contributes one-fourth of its area to any one of these unit cells.

Moving to an example involving a solid with two different types of atoms, consider a pattern with two different sizes of dots (Figure 3.6). This pattern could represent a layer from the NaCl structure, with the small circles being Na^+ ions and the large circles Cl^- ions. A square with its four corners in the centers of a square of four Na^+ ions may be selected as a unit cell. It contains one Cl^- ion entirely within its bounds and 4 × 1/4 = 1 total Na^+ ion, from the collective contributions of the four corner Na^+ ions, for a 1:1 Na^+:Cl^- stoichiometry, corresponding to the empirical formula NaCl.

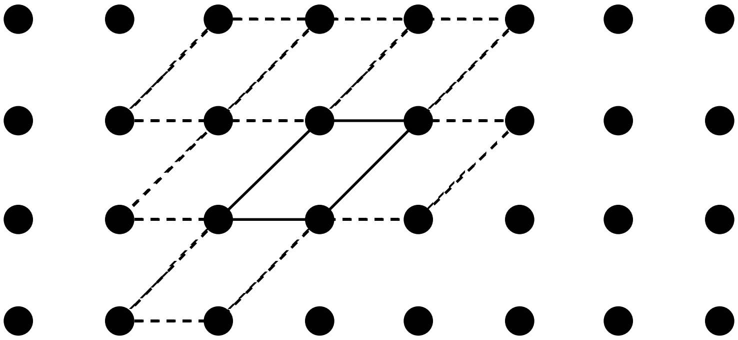

Figure 3.5. Unit cells need not be squares or rectangles; here, a tilted parallelogram serves as a unit cell.

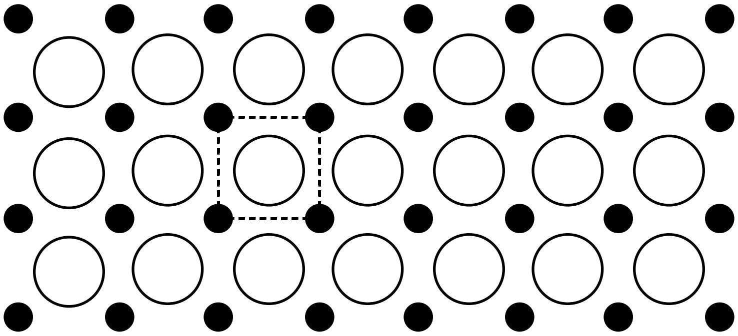

Figure 3.6. A two-dimensional model for a solid such as NaCl, with small circles representing the Na^+ ions and the large circles representing the Cl^- ions. One possible unit cell is indicated by the dashed lines.

A larger unit cell for the same pattern is shown with dashed lines in Figure 3.7. In this case the corners have been placed in the center of the Cl^- ions, and a square that is larger than the square in Figure 3.6 has been selected as the unit cell. This unit cell contains four Na^+ ions entirely within its bounds and none at the edges or corners. To count the number of Cl^- ions within the unit cell, one is in the center (counts as 1); four are at the corners (counts as $4 \times 1/4 = 1$); and four are on the edges (counts as $4 \times 1/2 = 2$; each of these four ions is half in the unit cell or, alternatively, is shared by two unit cells and thus contributes one-half to this particular unit cell). This gives a total of four Cl^- ions to go with the four Na^+ ions, resulting once again in a 1:1 NaCl stoichiometry.

A variety of two-dimensional patterns, suitable for practice in finding unit cells, are found in wallpapers, tile floors, and Escher prints. The Escher print shown in Figure 3.8 has two possible unit cells outlined upon it.

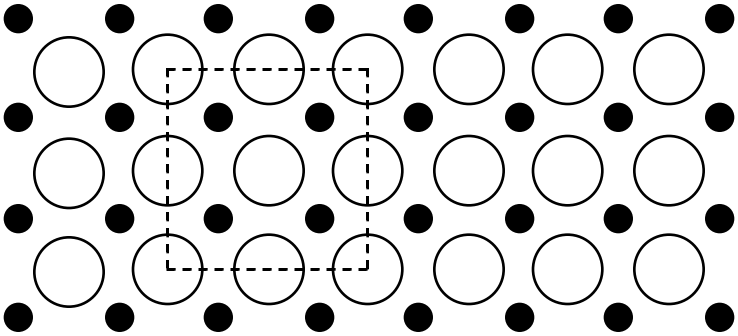

Figure 3.7. A larger unit cell for the structure shown in Figure 3.6.

Figure 3.8. Unit cells may be identified in Escher prints. The top unit cell contains one black and one white bird, and the lower unit cell contains two black and two white birds. The notations at the edges of the figure are Escher's own marks.

The concepts articulated for two dimensions are readily extended to three dimensions[1]. Although all crystalline solids have unit cells that are parallelepipeds in three dimensions, many simple compounds (and some not-so-simple compounds) have cubic symmetry and unit cells that are cubes. One metal (polonium) crystallizes with a simple cubic (sc) structure: the metal atoms sit only at the unit cell corners. Shifting the cube in all three mutually perpendicular directions, by the length of a side of the cube, will generate six identical unit cells, which can be further replicated to create the entire structure. The unit cell of polonium is sketched in Figure 3.9 but is most easily seen with a model kit: From the cut-away view shown, each sphere contributes one-eighth of its total volume to the indicated unit cell. The total sphere volume from the eight spheres defining the cube is 8 × 1/8 = 1 sphere. Alternatively, extending the structure makes it apparent that any given sphere is shared by eight unit cells and thus contributes one-eighth of its volume to any particular unit cell.

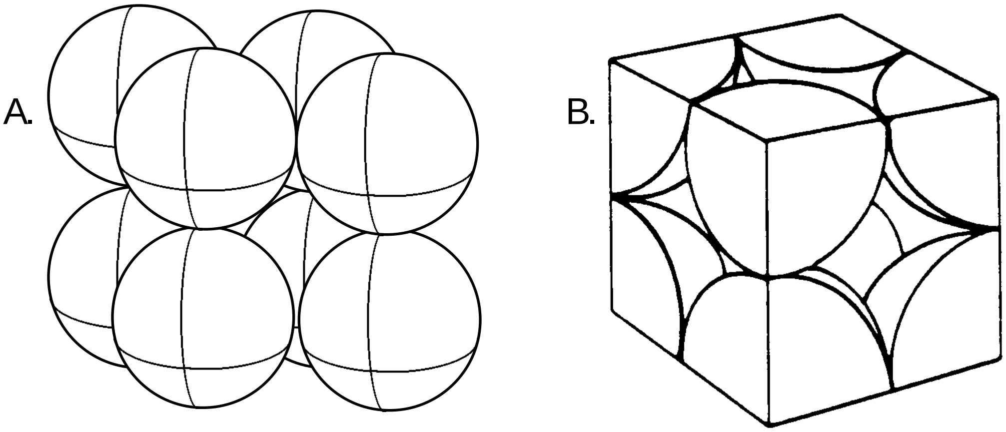

Figure 3.9. A: A simple cubic unit cell showing the eight atoms that are part of the unit cell. B: Only one-eighth of the volume of each of the eight spheres contributing to the unit cell is contained within it.

Demonstration 3.1. Corner-Shared Atoms in a Simple Cubic Unit Cell

Materials

Knife
Orange or apple
Toothpicks (optional)

Procedure

---

[1] A copy of the ICE Crystal Structure Solid-State Model Kit (SSMK) or a similar kit or software is recommended as an aid to visualizing structural features.

- In front of the class, cut the piece of fruit into eighths.
- Arrange four pieces on a flat surface as shown for the bottom layer of a simple cubic unit cell (Figure 3.9B).
- Hold the remaining four pieces in place as the second layer or fasten them in place with toothpicks. This will show that the eight eighths form the corners of a cube.

Variation

A similar procedure may be used to show that one-fourth of the volume of an edge atom is within a given unit cell, and one-half of a face-centered atom is within a given unit cell (see below).

A more common structure for metallic elements is the body-centered cubic (bcc) structure (Figure 3.10), with a cubic unit cell having atoms at the corners of the cube and an atom in the center of the cube (the body center). The corners and the center of a bcc unit cell have the same environment. The count in this case will be two atoms per unit cell: now one atom is entirely enclosed by the unit cell by virtue of being in its center, and again the 8 × 1/8 = 1 atom results from the contributions of the eight atoms at the corners of the cube.

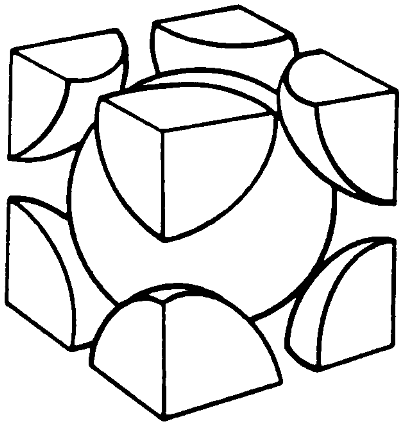

Figure 3.10. A body-centered cubic unit cell showing a full sphere within the unit cell in addition to the eight one-eighth sphere volumes from the corner spheres

Figure 3.11 shows that the body-centered cubic structure is adopted by many elements, including all the alkali metals and a number of transition elements, including V, Cr, Mo, W, and Fe.

Aluminum, copper, silver, gold, and nickel are common examples of the elements that adopt a face-centered cubic (fcc) structure (Figure 3.12). In addition, all of the solid noble gases adopt this same structure. The unit cell of this structure may be described with the help of a model kit as having atoms at each corner of the cube as well as atoms in the center of each face (hence the term face-centered, for which the corners and face-centered positions possess identical environments). The count in this case will be four atoms per unit cell: the corner atoms make their usual contribution of a single atom (8 × 1/8 = 1); and each of the remaining six atoms, one lying in the center of each cube face, contributes one-half its volume to the unit cell (each of these atoms is shared by two unit cells, thus contributing one-half to the unit cell of interest), making 6 × 1/2 = 3 atoms, for a total of four atoms.

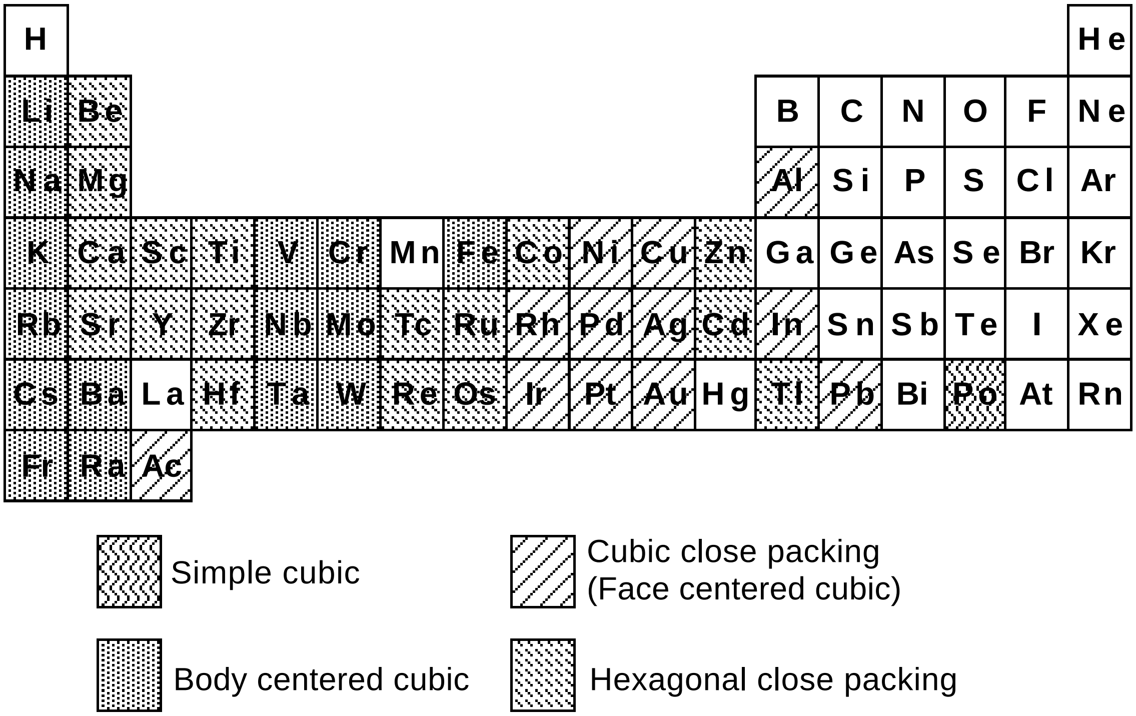

Figure 3.11. Periodic table showing the metallic elements that have one of the four indicated packing arrangements. (Data from reference 1.)

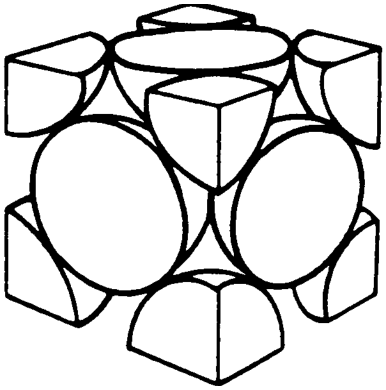

Figure 3.12. A face-centered cubic unit cell, showing the half-sphere volumes on the six faces of the cube in addition to the eight one-eighth sphere volumes from the corner spheres.

Demonstration 3.2. The FCC Structure Videotape.

A videotape showing different viewing perspectives of the FCC structure is available. For information on obtaining a copy, write Professor Nathan S. Lewis, Dept. of Chemistry, California Institute of Technology, Pasadena CA 91125.

The stoichiometry of solid compounds can also be determined by counting the atoms in their unit cells. Calcium titanate, which is found to occur naturally as the mineral perovskite, is a good example. The stoichiometry of perovskite and its structure are the basis for a variety of important solids ranging from high-temperature superconductors to piezoelectric materials. The perovskite structure can be described with the simple cubic unit cell shown in Figure 3.13 and in the model kit. In the picture of the structure, the layer sequence describes the arrangement of the atoms in cross sections at various heights (z) from the base of the unit cell. At the bottom of the unit cell, $z = 0$; and halfway up, $z = 1/2$. The top layer ($z = 1$) must be identical to the bottom layer: It is connected to the bottom layer by unit cell edges that connect points with identical environments, and it serves as the bottom layer for the unit cell above it.

There are Ca^{2+} ions at the corners of the cube, a Ti^{4+} ion centered in the cube, and O^{2-} (oxide ions) in the middle of each face of the cube. This arrangement corresponds to a stoichiometry of one Ca^{2+} ion ($8 \times 1/8 = 1$), one Ti^{4+} ion (completely contained in the cube), and three O^{2-} ions (each of the oxide ions is shared by two unit cells, so that $6 \times 1/2 = 3$ oxide ions belong to this unit cell). The resulting formula of $CaTiO_3$ is thus readily established from the unit cell.

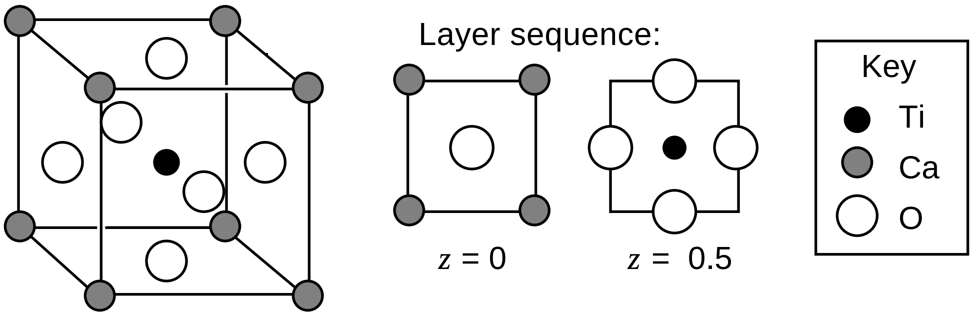

Figure 3.13. One unit cell of the perovskite ($CaTiO_3$) structure. The layer sequence shown next to the unit cell represents cross sections of the unit cell that would be seen if planes were passed through the cubic unit cell parallel to the base. Thus, at $z = 0$ the base of the unit cell contains an oxide ion at its center and the four bottom corner Ca^{2+} ions. At $z = 0.5$, the plane passes through the four face-centered oxide ions and the center Ti^{4+} ion. The $z = 1$ view is identical to the $z = 0$ view, because the top face of the unit cell is the bottom face of the unit cell above it.

Solid Solutions

As already noted, discrete molecules have easily countable numbers of atoms, and small integer relationships exist between the numbers of different kinds of atoms composing the molecule. Extended crystalline solids provide far broader stoichiometric vistas than discrete compounds. An analogy might be that moving from discrete molecules to extended solids is somewhat akin to discovering fractions after having dealt exclusively with positive integers. In addition to the discussion of metallic and ionic solids presented earlier, two classes of extended crystalline solids—substitutional and variable stoichiometry solid solutions—are particularly interesting complements to introductory discussions of stoichiometry. These materials are the basis of commonly encountered solids such as the semiconductors used in light-emitting diodes and diode lasers, metal alloys like brass[2] and bronze, and battery electrodes.

Substitutional Stoichiometry

As will be seen in Chapter 7, the ability to continuously tune physical properties using solid solutions can be thought of as a means of effectively expanding the periodic table. For example, the number of molecular compounds of silicon and hydrogen is presently limited to about a dozen, including SiH_4, Si_2H_6, and Si_3H_8. In contrast, a vast number of extended solids of formula Si_xGe_{1-x} ($0 \le x \le 1$) exists. Both silicon and germanium have the structure of diamond (Chapter 5), as do all of the Si_xGe_{1-x} solid solutions. As x varies in this stoichiometric formula, many of the properties of this family of solids are continuously tunable between the extremes of pure silicon and pure germanium. This tunability is extremely important in the semiconductor industry, in which, for example, the colors of light absorbed and emitted by these solids can be tuned with their composition, that is, with the value of x (*see* Chapter 7).

Solids like Si_xGe_{1-x} often form disordered substitutional solid solutions; that is, germanium atoms randomly replace silicon atoms in elemental silicon (or vice versa). Thus, we can speak only of the probability of finding a substituting germanium atom at sites in the crystal structure where the exchangeable silicon atoms would usually be found: A formula like $Si_{0.283}Ge_{0.717}$ means that at any site where a silicon or germanium atom could be found in the crystal structure, there is a 28.3% chance that the atom is silicon and a 71.7% probability that the atom is germanium; the number of significant figures reflects the quality of the analytical data. The formula weight for stoichiometric purposes would be the weighted average,

---

[2] As the ratio of zinc to copper changes, the structure of brass changes. Consequently, the name brass actually represents a number of phases that can have different structures. Within a given range of compositions, however, brass is a solid solution. *See* reference 2.

calculated as [(0.283) × (atomic weight of Si)] + [(0.717) × (atomic weight of Ge)] = 60.00 g/mol. An analogy can be drawn between this calculation and the determination of the atomic weight for an element with two isotopes.

Figure 3.14 shows two-dimensional solid solutions of elements A and Z of varying stoichiometries, along with the "pure" A and "pure" Z structures from which the solid solutions are derived.

Demonstration 3.3. Disordered Binary Solid Solutions

Materials

Coins or sets of objects (marbles or identical sheets of paper, for example) that are distinguishable by having one of two colors.
Opaque bag or container, one for each student
Solid-State Model Kit (SSMK) (optional)

Procedure

- Individual students are assigned an atomic site in, for example, an fcc structure for which they will decide the identity of the atom at that site. If a disordered binary solid solution of composition $A_{0.5}Z_{0.5}$ is to be modeled, have each student flip a coin. A toss of "heads" puts an A atom at that student's atomic position, and a "tails" puts a Z atom at that position. To model other stoichiometries, have students place two types of visually distinguishable but otherwise identical objects in an opaque container in the stoichiometric ratio to be modeled: for example, to model $A_{0.25}Z_{0.75}$, three marbles of one color (Z atoms) and one of another color (A atoms) are placed in the container, and one marble is drawn at random by the student. After the drawings, the total number of A and Z atoms selected can also be counted to compare the agreement with the theoretical probability of three Z atoms to one A atom.
- To model a two-dimensional solid, draw a grid on the board with an arbitrary number of rows and columns. As each coin is tossed or marble is drawn by the student assigned to a particular atom, place a symbol (one representing A; one representing Z) in one of the boxes in the grid. A single row could be used to model a one-dimensional structure in the same way.

Variation for SSMK

- As noted in the kit's instructions, a Sharpie permanent marker can be used to color some of the large spheres in the SSMK (the color can later be removed with 95% ethanol). This step permits three-dimensional disordered solid solutions to be built for a variety of structures such as fcc and diamond (other structures amenable to forming solid solutions are described later): The choice of what color sphere to place at a site is again dictated by the results of student coin tosses or draws, as described.

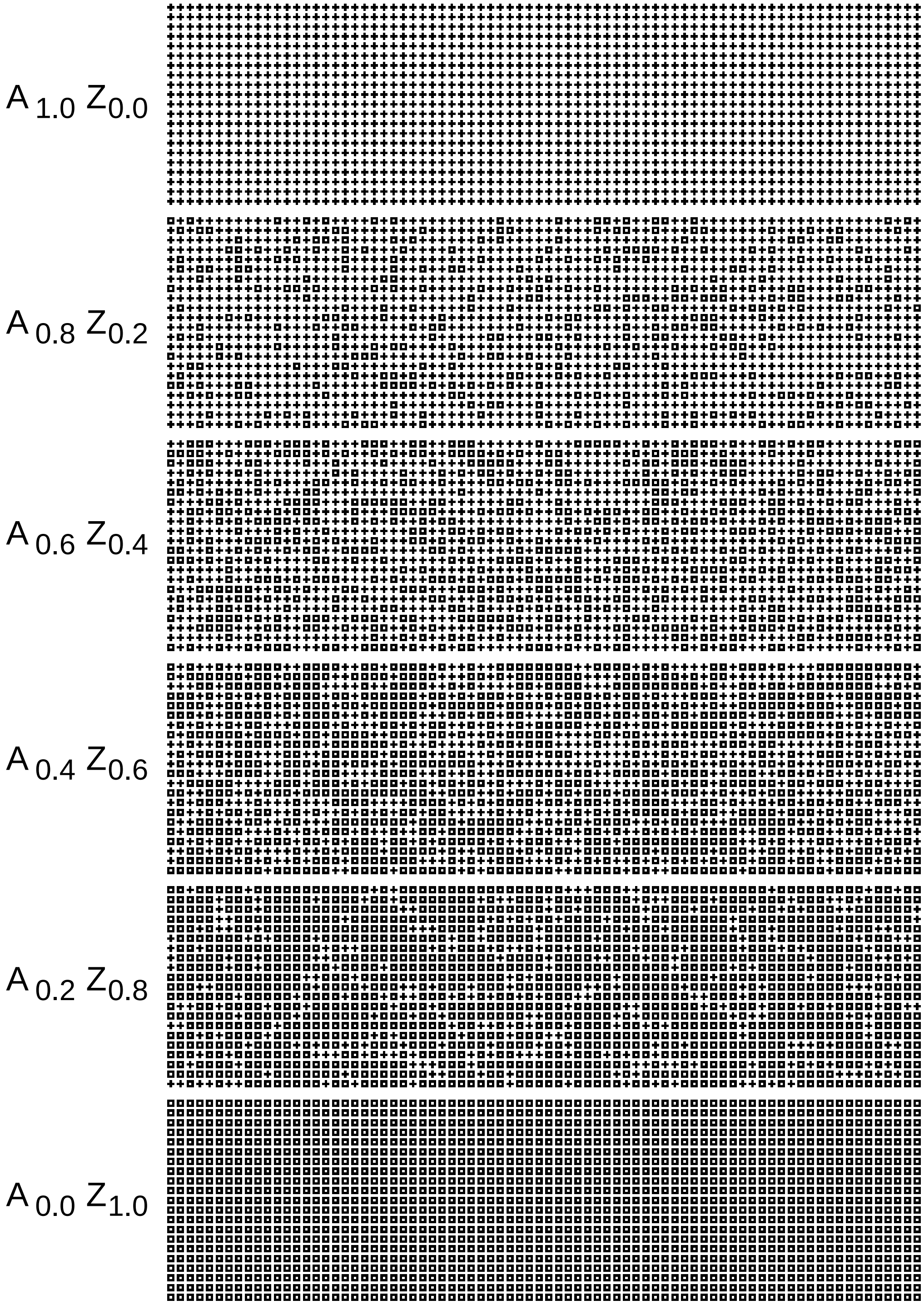

Figure 3.14. Substitutional solid solutions $A_{1-x}Z_x$ with varying stoichiometries (varying values of x). Diamonds represent atom A and squares represent atom Z.

Two other examples of disordered solid solutions come from metal alloys and salts. In general, two solids are most likely to be completely miscible in one another (x taking on any value from 0 to 1, that is, from no substitution to complete substitution) if the substituting atoms or ions are similar in chemistry and size (radii usually within about 15% of one another) and if the end members of the series have the same structure. An example of a solid solution that permits any degree of substitution is cupronickel, Cu_xNi_{1-x}: both Cu and Ni have the face-centered cubic structure (Figure 3.12), and the atomic radii are within 3% of one another (1.246 and 1.278 Å for Cu and Ni, respectively). An example in which only limited substitution is possible because of size differences is that only up to about 20% of the copper atoms can be replaced by aluminum in the fcc structure.

Salts like CdS and CdSe can form solid solutions in which the anion positions in the crystal (Chapters 5 and 7) are filled with S or Se anions with probabilities of x and $(1 - x)$, respectively, based on the stoichiometric formula CdS_xSe_{1-x} ($0 \le x \le 1$). Likewise, salts in which cations are randomly distributed onto cation sites in the crystal can be formed, as illustrated by the combination of MgO and FeO, and these salts form solid solutions of stoichiometry $Mg_xFe_{1-x}O$ ($0 \le x \le 1$), having the structure of NaCl, rock salt (Chapter 5). These three-element or ternary solid solutions can be extended to four-element or quaternary solid solutions in some compounds like $Ga_xAl_{1-x}P_yAs_{1-y}$ ($0 \le x \le 1$; $0 \le y \le 1$; zinc blende structure discussed in Chapters 5 and 7), in which simultaneous, unlimited substitution for the Groups 13 and 15 elements is possible.

In geology, some minerals form partial or complete solid solutions. In the mineral olivine, Mg^{2+} and Fe^{2+} can be completely substituted for each other. Consequently, the formula for olivine is written as $Mg_xFe_{2-x}SiO_4$ ($0 \le x \le 2$) or more commonly as $(Mg,Fe)_2SiO_4$. Thus, the limiting formulas range from Mg_2SiO_4 (the mineral forsterite) to Fe_2SiO_4 (the mineral fayalite) *(3)*.

The mineral hydroxyapatite, $Ca_5(PO_4)_3OH$, is the principal component of tooth enamel. Addition of fluoride in water or from toothpaste causes the formation of fluorapatite, $Ca_5(PO_4)_3F$, which is more resistant to cavity formation. Substitution of fluoride for hydroxide is tunable over the complete range of formulations $Ca_5(PO_4)_3(OH)_xF_{1-x}$ ($0 \le x \le 1$). This substitution is also true in geological samples of the minerals hydroxyapatite and fluorapatite *(4)*.

Solid solutions are important in radiochemistry. Radium is present in uranium ore, but in such small amounts that it cannot be easily precipitated from solution. To overcome this disadvantage, barium ions are added to the solution in addition to sulfate. The radium will substitute for the barium in the barium sulfate precipitate. In this case the barium is acting as the carrier for the radium *(5)*.

From a synthetic standpoint, substitutional solid solutions might be expected to form whenever the exchangeable atoms or ions undergo similar chemical reactions and are both present in the reaction medium. Of course, the relative quantities of exchangeable atoms or ions present in the medium used for synthesis may or may not be preserved in the resulting solid. General routes to preparation of substitutional solid solutions include comelting, coprecipitation, codeposition from gas and solution phases, and codecomposition of volatile precursor molecules (chemical vapor deposition, CVD). (Chapter 10 gives a further description of solid-state synthetic techniques.) If the reactivities of the exchangeable species in the solid solution are similar, parallel reaction paths for these atoms or ions will generally be found in decomposition reactions of the solid solutions. Examples are given in the exercises.

Laboratory. Students can grow solid solutions derived from colorless crystals of alum [$KAl(SO_4)_2 \cdot 12H_2O$] and purple chrome alum [$KCr(SO_4)_2 \cdot 12H_2O$]. As these compounds form a complete solid solution, the color of the [$KCr_xAl_{1-x}(SO_4)_2 \cdot 12H_2O$] crystals can be tuned by varying the composition. The experiment is written so that the students can design their own experiments to explore the effect of reaction conditions on crystal growth (*see* Experiment 3).

Variable Stoichiometry

As a result of the influence of Dalton's Law of Multiple Proportions, most contemporary chemists have viewed materials as having fixed compositions. During the 18th century, however, Berthollet held the opposite view from Dalton: Berthollet proposed that materials could have variable compositions, depending on the conditions of formation. Many such systems have been discovered in modern times, and the terms “berthollide” or “nonstoichiometric” are sometimes used to describe compounds that exhibit variable stoichiometry (*6–8*).

Compounds with variable stoichiometry are solids in which the stoichiometry can vary from a simple integral relationship, typically over a range of composition, but the basic crystal structure does not vary over the same range. The two most common ways in which variable stoichiometry arises are from interstitial atoms, which are atoms inserted into the void spaces in a structure, or from vacancies of atoms in the structure. Variable stoichiometry is most common in compounds of the *d*-, *f*-, and *p*-block metals containing soft (polarizable) anions such as S^{2-} ions. It is also prevalent in many transition metal oxides, where the valence of the transition metal can readily change to maintain charge neutrality. Compounds containing hard anions such as fluorides, chlorides, sulfates, and nitrates rarely have variable stoichiometry. Table 3.2 lists some common materials with variable stoichiometry.

Table 3.2. Materials with Variable Stoichiometry

Compounds	Range of x	
Hydrides		
TiH_x	1.0–2.0	
ZrH_x	1.5–1.6	
HfH_x	1.7–1.8	
NbH_x	0.64–1.0	
GdH_x	fluorite[a] type, 1.8–2.3	hexagonal[a], 2.85–3.0
ErH_x	fluorite type, 1.95–2.31	hexagonal, 2.82–3.0
LuH_x	fluorite type, 1.85–2.23	hexagonal, 1.74–3.0
Oxides		
TiO_x	rock salt[a] type, 0.7–1.25	rutile type[a], 1.9–2.0
VO_x	rock salt type, 0.9–1.20	rutile type, 1.8–2.0
NbO_x	rock salt type, 0.9–1.04	
Fe_xO	rock salt type, 0.88–0.95	
UO_{2+x}	0–0.25	
Sulfides		
ZrS_x	0.9–1.0	
YS_x	0.9–1.0	
Cu_xS	1.77–2.0	

[a] Fluorite, hexagonal, rock salt, and rutile are different structure types. *See* Chapter 5.

SOURCE: Adapted from reference 9.

Transition metal hydrides are classic examples of compounds with variable stoichiometry. These compounds are best thought of as metals with variable amounts of hydrogen inserted in the void spaces of the metal crystal. For example, palladium is a transition metal that forms a metal hydride; a maximum of 0.8 hydrogen atoms per palladium atom can be inserted in the octahedral holes (Chapter 5) of the fcc palladium crystal. In many cases, the formation of metal hydrides is readily reversible. For example, hydrogen may be removed from many metal hydrides by raising the temperature. The reversible formation and decomposition of transition metal hydrides has been an area of active research, as these compounds can be used as hydrogen storage materials.

Similarly, materials of variable composition that contain lithium have been of interest in the development of new solid-state battery materials. As Ti^{4+} ions are reduced to Ti^{3+}, lithium ions can be reversibly inserted into the octahedral holes (Chapter 5) found between two sulfide layers in TiS_2 to yield Li_xTiS_2 ($0 \le x \le 1$). This material is a promising candidate for use in lightweight solid-state lithium batteries.

In many compounds of variable stoichiometry, a change in composition has a dramatic effect on material properties. For example, the sodium tungsten bronzes, Na_xWO_3 ($0 \le x \le 1$), show a wide variety of color over the range of composition (*see* Experiment 8). Even a seemingly immeasurable variation in stoichiometry can cause a material to be highly colored. For example, trapping an electron at a halide vacancy in an alkali halide crystal ($MX_{1-\partial}$, where ∂ is 10^{-3} to 10^{-6} or less) leads to the intense color of the so-called F-center (Chapter 6). Variable stoichiometry can also have a large effect on the electrical properties of a material. Variations in the oxygen stoichiometry in the high-temperature superconductors play a critical role in determining whether a material is superconducting or not. For example, $YBa_2Cu_3O_{6.9}$ is a superconductor with a high T_c (onset temperature of superconductivity), whereas when more of the oxygen atoms are removed, as in $YBa_2Cu_3O_{6.1}$, superconductivity is destroyed.

Finally, if stoichiometrically equivalent numbers of normally occupied metal and nonmetal sites are vacant (e.g., when one Ca^{2+} and two F^- sites are empty in CaF_2), the compound will appear to be stoichiometric (the metal–nonmetal ratio will be a simple whole-number ratio) even though it is not a perfect structure. Careful measurements of the density of a single crystal, however, can reveal such missing atoms. A classic example is titanium monoxide, TiO. At a titanium:oxygen ratio of 1:1, as many as 15% of each of the ideal cation and anion sites may be vacant.

A Caveat for Classroom Use

In discussing material from this chapter, it is important to differentiate substances that have tunable compositions from those that do not. Certainly the composition of a molecule like water is not tunable. Thus, when determining empirical formulas for molecules, only integers should appear in the formula. Fractional numbers of atoms arise logically, as shown, for solids that are clearly identified as having tunable stoichiometry.

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Additional Reading

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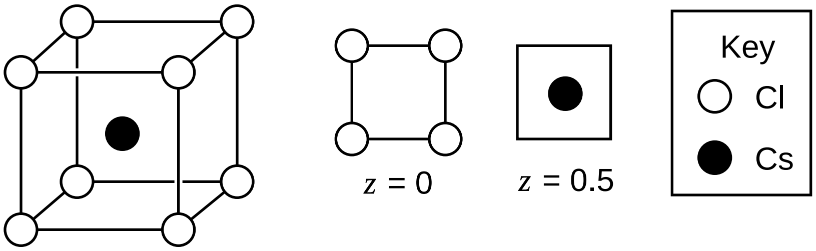
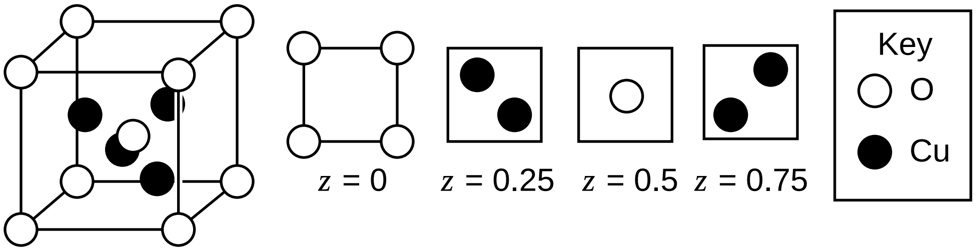
Exercises

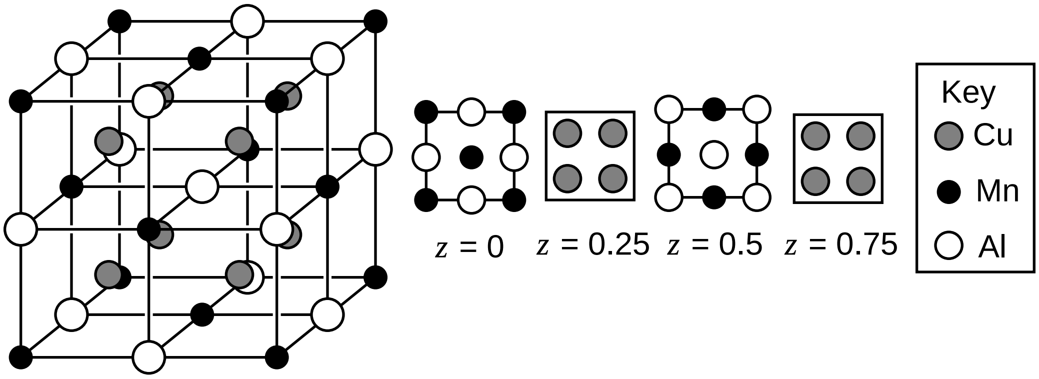
1. The unit cell pictures in this problem can be used for questions regarding unit cell occupancy or stoichiometry. For example, verify the stoichiometry for each of the structures. Information about some of the materials is also included.
   a. *Cesium chloride.* (Other compounds that crystallize with the CsCl structure: CsCl, CsBr, CsI, TlCl, TlBr, TlI, and many intermetallic compounds such as AgCd, AgZn, AlFe, AuZn, CoFe, HgMg, and NiTi.).



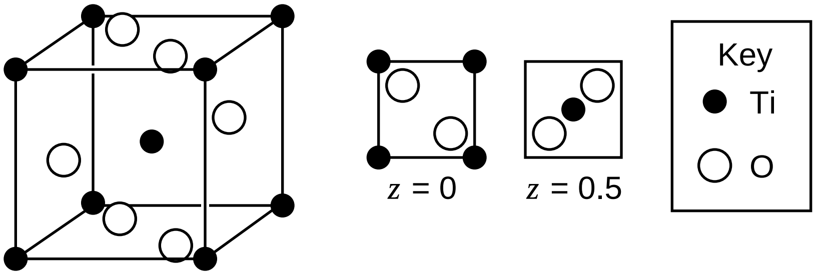
   b. *Cuprite* (Cu_2O). This compound is a p-type semiconductor and was used in the construction of the first photocells. Ag_2O and Pb_2O have the same structure.



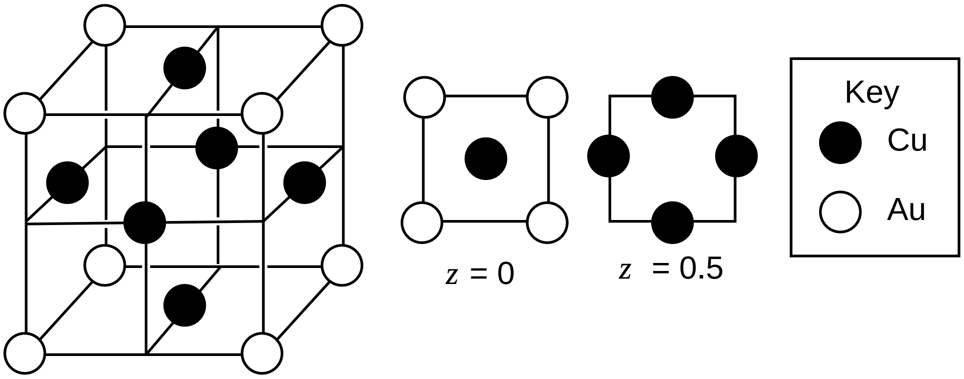
c. Cu_2AlMn



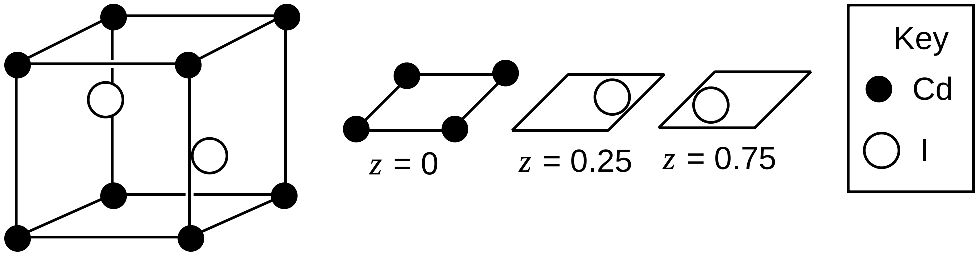
d. *Rutile* (TiO_2). This compound is the main pigment in white paint. Other compounds with this structure include the difluorides of Co, Fe, Mg, Mn, Ni, Pd, and Zn; and GeO_2, IrO_2, RuO_2, and SnO_2.



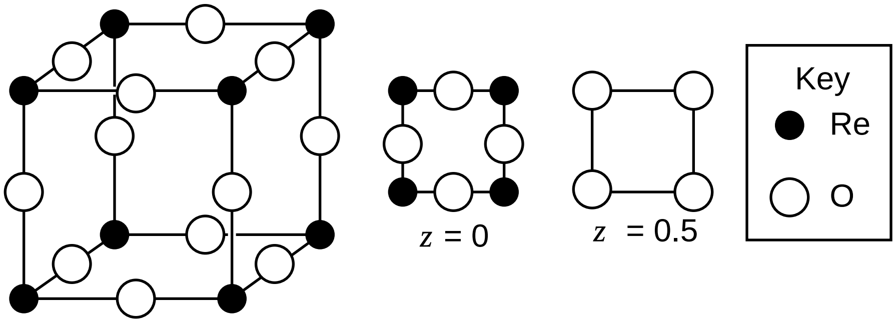
e. Cu_3Au



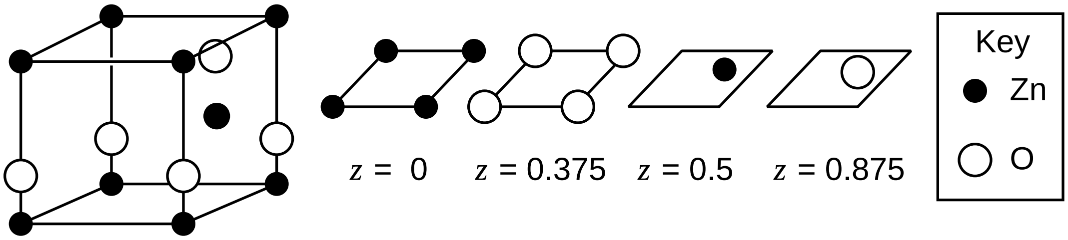
f. *Cadmium iodide* (CdI_2).



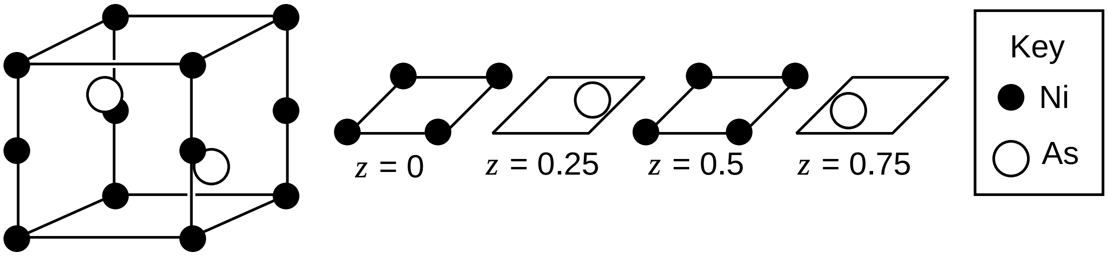
g. *ReO_3*. Other compounds with this structure include MoF_3 and NbF_3.



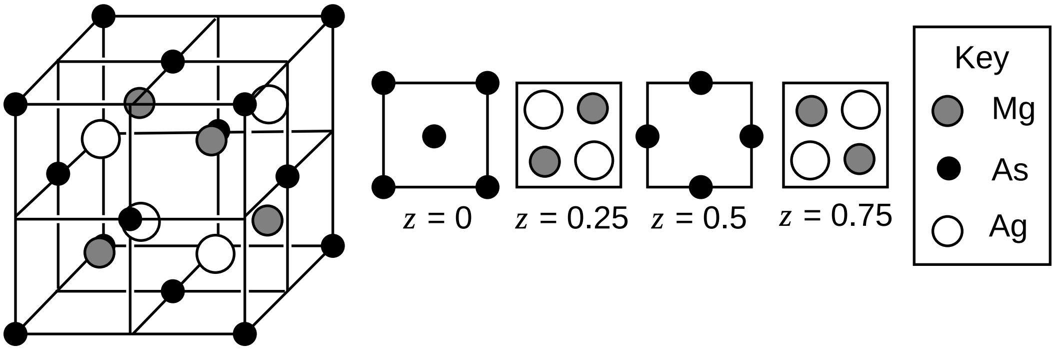
h. *ZnO* is a semiconductor. It is used in the production of rubber to shorten vulcanization times, as a paint pigment, and as an agent to improve the chemical durability of glasses. This structure is also adopted by AlN and BeO.



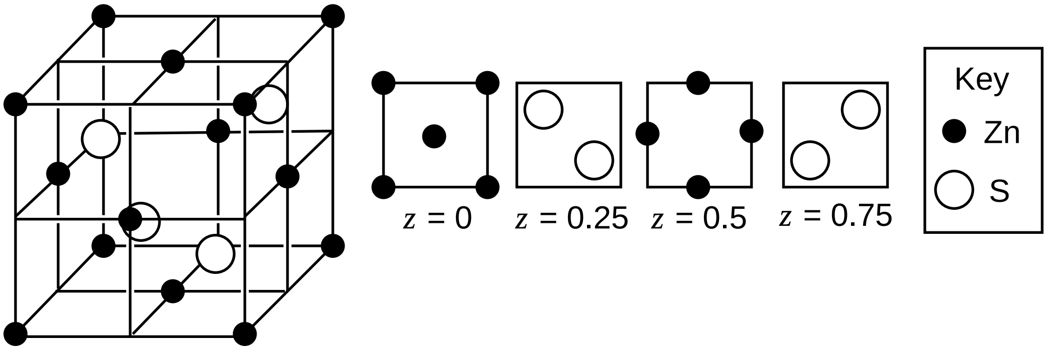
i. *Nickel arsenide* (NiAs).



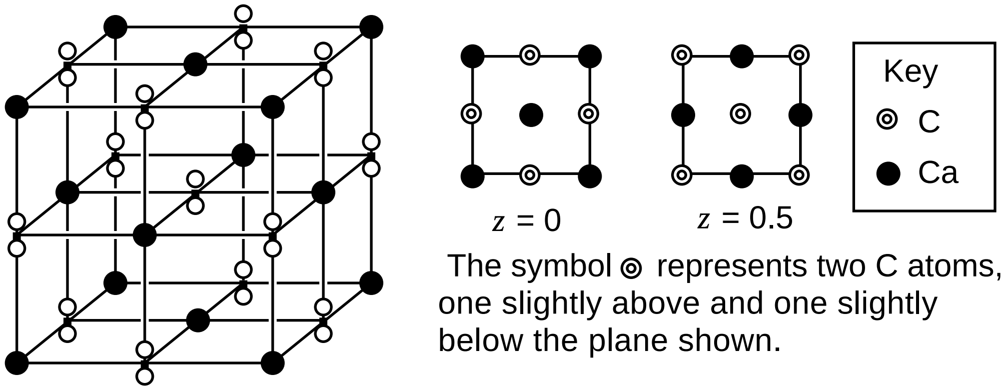
j. *MgAgAs*



k. *Zinc blende* (ZnS). This mineral is the main source of the element zinc. Many of the important semiconductors have this structure (namely GaP, GaAs, GaSb, InP, and InSb). These semiconductors have also been used as infrared detectors, photoresistors, photocells, and transistors. Fluorescent lamps make use of the highly luminescent ZnS and CdS that are doped with Cu^{2+} and Mn^{2+}, for example. Other compounds that crystallize with the ZnS structure are ZnS, ZnSe, BeS, BeSe, BeTe, HgS, HgSe, HgTe AlP, GaP, InP, SiC, AgI, CuBr, and CuCl.



l. *Calcium carbide* (CaC_2). This compound has an extremely high melting point (2300 °C) and reacts with water to liberate acetylene. BaC_2, MgC_2, SrC_2, and UC_2 adopt this structure, as do the peroxides BaO_2, CaO_2, and SrO_2.



The symbol ⊚ represents two C atoms, one slightly above and one slightly below the plane shown.

2. What is the formula of the compound that crystallizes in a cubic unit cell with the following (a–e)?

What is the percent composition of the compound that crystallizes in a cubic unit cell with (a–e)?

What mass of ions is required to prepare 5.00 g of the compound that crystallizes in a cubic unit cell with (a–e)?

a. a rubidium ion on each of the corners of the unit cell and a bromide ion in the center of the unit cell? (Other compounds that crystallize with the CsCl structure: CsCl, CsBr, CsI, TlCl, TlBr, TlI, and many intermetallic compounds such as AgCd, AgZn, AuZn, and HgMg.)

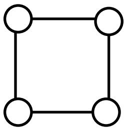
b. nickel ions at each of the corners and the middle of each face and oxide ions in the middle of the edges and the center of the unit cell? (Other compounds that crystallize with the NaCl structure: AgCl, LiF, LiCl, LiBr, LiI, NaF, NaBr, NaI, KCl, KBr, KI, NaH, KH, RbH, MgO, CaO, SrO, CoO, NiO, CaS, CaSe, CaTe, MnS, MnSe, SnSe, SnTe, TiC, VC, ScN, TiN, and VN.)

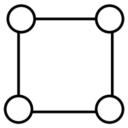
c. sulfide ions at each of the corners and the middle of each face and four cadmium ions within the unit cell? (Other compounds that crystallize with the zinc blende structure: ZnS, ZnSe, BeS, BeSe, BeTe, CdS, CdSe, HgS, HgSe, HgTe AlP, GaP, InP, SiC, AgI, CuBr, and CuCl.)

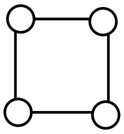
d. a titanium ion at each of the corners of the unit cell, oxide ions in the middle of each edge, and a strontium ion in the center of the cell? (Other compounds that crystallize with the idealized perovskite structure: $BaTiO_3$, $CsCaF_3$, $CsCdBr_3$, and $CaVO_3$.

e. a rhenium ion at each of the corners of the unit cell and oxide ions in the middle of each edge?

3. For all of the simple cubic (sc), body-centered cubic (bcc), and face-centered cubic (fcc) structures, at least a square array of spheres would be seen when looking down upon a unit cell cube face, as illustrated here using circles for the atoms in the three structures. For the sc structure, no additional atoms would be added, because all atoms in layers beneath the first layer lie directly under the atoms shown, and there are no additional atoms in the unit cell. Sketch the additional atoms that would have to be added to the bcc and fcc pictures to make them accurate representations of what you would see looking down on the structure from above.


sc


bcc


fcc

4. ___A___ crystallizes in a cubic unit cell with an edge length of ___B___ and with a(n) ___A___ atom on each of the corners of the unit cell and in the center of the unit cell. Using this information calculate the density of ___A___.

A = barium B = 5.025 Å

A = lithium B = 3.509 Å

A = molybdenum B = 3.147 Å

A = tantalum B = 3.306 Å

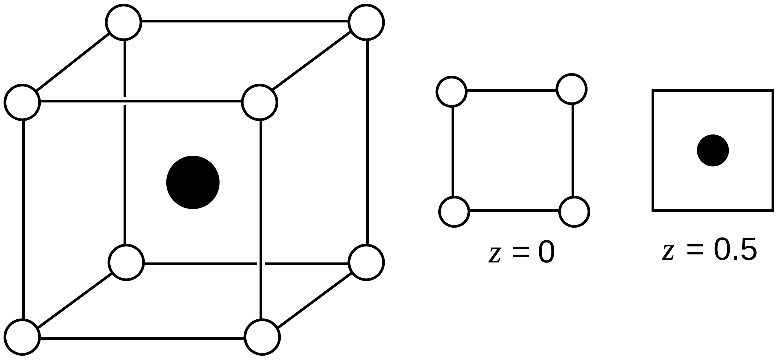
A = vanadium B = 3.024 Å

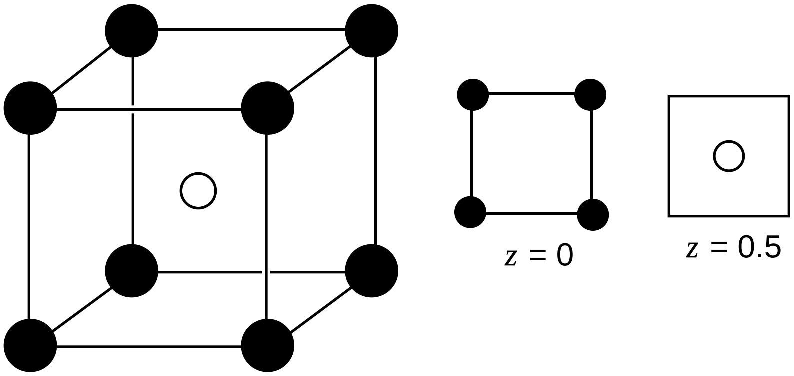
A = tungsten B = 3.165 Å

5. Aluminum crystallizes in a cubic unit cell with an edge length of 4.050 Å and with an aluminum atom on each of the corners of the unit cell and in the center of each of the faces. Using this information calculate the density of aluminum.

6. Given the unit cell length of a cubic compound, its density, and the contents of the unit cell and their atomic weights, determine Avogadro's number. For example, determine the value of Avogadro's number from the atomic weights of calcium and fluorine and the following information. The unit cell length of CaF_2 is 5.46295 Å. The density of CaF_2 is 3.1805 g/cm^3. CaF_2 crystallizes with calcium ions at each of the corners and the middle of each edge of the unit cell and with eight fluoride ions within the unit cell.

7. In this chapter it was stated that more than one unit cell can be chosen for a structure. If they represent the same structure, however, the unit cells must have the same types of atoms (with the same stoichiometric relationships between them) and the same coordination geometry around each type of atom. The following are two possible representations of CsCl. Do they represent the same CsCl structure?





8. What is the maximum and minimum percent of Ga in the Ga(P, As) solid-solution system?

Other Solid Solutions

K (Cl, Br)

Biotite $[K(Mg,Fe^{II})_3(OH,F)_2(Si_3AlO_{10})]$

Ga(P, As)

Sphalerite is tunable from ZnS to $Zn_{0.68}Fe_{0.32}S$

$Y_{3-x}Gd_xFe_5O_{12}$

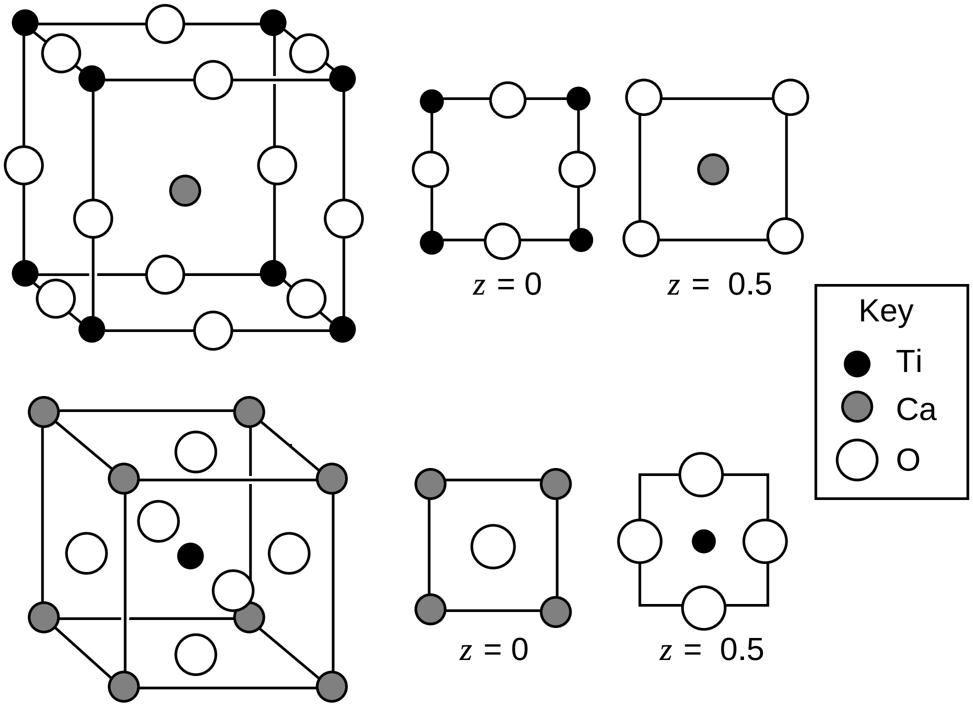
bcc: V_xMo_{1-x}, W_xTa_{1-x}, W_xNb_{1-x}

hcp: Zn_xRe_{1-x}, Zn_xRu_{1-x}, Ru_xRe_{1-x}, Ru_xOs_{1-x}, Os_xRe_{1-x}

(hcp is hexagonal close-packed, see Chapter 5.)

fcc: Rh_xPt_{1-x}, Pd_xAu_{1-x}, Pd_xAg_{1-x}

9. The following are two representations that have been used for the perovskite structure. By the criteria given in problem 7, do they represent identical structures?



10. How many grams of AgBr can be made from 1.00 g of $KCl_{0.30}Br_{0.70}$?

11. The iron oxides can exhibit variable stoichiometry. A compound of iron and oxygen forms a cubic unit cell of edge length 4.29×10^{-8} cm. The crystalline compound has a density of 5.66 g/cm^3. Calculate:
 a. the mass of one unit cell
 b. the average number of ions of iron and oxygen in a unit cell if the atomic ratio of iron to oxygen is 0.932:1.000
 c. The percentage of occupied sites of each type of ion if FeO crystallizes in the NaCl structure. (Hint: NaCl contains four ions of each type in the unit cell.)

12. Titanium oxides are known to exhibit variable stoichiometry. A titanium oxide (TiO_x) is analyzed and found to be 70.90% Ti by mass. What is the value of x in the formula for the compound?

13. What mass of ___A___ must be processed to isolate ___B___ of ___C___?

A = $Cd_{0.010}Zn_{0.99}S$	B = 1.000 metric ton (1000 kg)	C = Cd
A = $UO_{2.10}$	B = 1.000 metric ton (1000 kg)	C = U
A = $Cu_{1.79}O$	B = 1.00 g	C = Cu

14. Calculate weight percentages of the elements in the following solid solutions:

% Cd, % S, % Se in $CdS_{0.29}Se_{0.71}$

% Na, % W, % O in $Na_{0.24}WO_3$

15. Determine the values of x and y in $Ga_{0.46}Al_xP_{0.37}As_y$.

16. What mass of sodium fluoride, the active ingredient in some fluoride toothpastes, is required to convert 1.00 g of $Ca_5(PO_4)_3OH$ to $Ca_5(PO_4)_3(OH)_xF_{1-x}$? (Choose a value for *x* between 0 and 1.)

$$Ca_5(PO_4)_3OH + (1-x)NaF \rightarrow Ca_5(PO_4)_3(OH)_xF_{1-x} + (1-x)NaOH$$

17. What is the total mass of oxide formed when 0.5356 g of Si_xGe_{1-x} is converted into a mixture of SiO_2 and GeO_2? (Choose a value for *x* between 0 and 1.)

18. Some of the calcium dihydrogen phosphate used in fertilizers is prepared from the reaction of $Ca_5(PO_4)_3(OH)_xF_{1-x}$ with sulfuric acid. The HF produced in the reaction is recovered and used in the production of other compounds.

$$2\ Ca_5(PO_4)_3(OH)_xF_{1-x} + 7\ H_2SO_4 \rightarrow$$

$$3\ Ca(H_2PO_4)_2 + 7\ CaSO_4 + 2x\ H_2O + (2-2x)HF$$

What mass of HF is produced by the reaction of 1.000 metric tons of $Ca_5(PO_4)_3(OH)_xF_{1-x}$? (Choose a value for *x* between 0 and 1.)

19. What mass of cadmium chloride is formed when 0.5356 g of CdS_xSe_{1-x} is converted into $CdCl_2$? (Choose a value for *x* between 0 and 1.)

$$CdS_xSe_{1-x} + 2\ HCl \rightarrow CdCl_2 + x\ H_2S(g) + (1-x)H_2Se$$

20. What volume of dry H_2S at STP can be formed when 0.5356 g of CdS_xSe_{1-x} is converted into $CdCl_2$? (Choose a value for *x* between 0 and 1.)

$$CdS_xSe_{1-x} + 2\ HCl \rightarrow CdCl_2 + x\ H_2S(g) + (1-x)H_2Se$$

21. Which contains more hydrogen, by mass, in one cubic centimeter, lithium hydride or liquid hydrogen? Liquid hydrogen has a density of 0.070 g/cm^3. Lithium hydride is a solid that crystallizes with a cubic unit cell (a = 4.085 A) with lithium ions at each of the corners and the middle of each face and hydride ions in the middle of the edges and the center of the unit cell.

22. When the chlorides of rubidium and potassium are mixed and heated to about 800 °C, the following reaction will occur:

$$KCl + RbCl \rightarrow 2K_{0.5}Rb_{0.5}Cl$$

How many grams of each starting material should be mixed in order to prepare 10.0 g of the final product?

23. Classify the following substances as discrete molecules, alloys, or salts.
   a. TiO_2
   b. C_5H_{12}
   c. NaK
   d. ClF_3
   e. $SrBr_2$

24. Which of the following combinations of atoms do you expect to yield a discrete molecule and which should produce an extended solid?
   a. Ba and O
   b. N and O
   c. Cu and Ni
   d. Na and F

25. The table that follows lists the crystal structure and atomic radius of several metallic elements. Select pairs of atoms that are likeliest to form a complete family of substitutional solid solutions using the indicated structures and justify your answer.

Element	Structure	Atomic radius, Å
Cu	fcc	1.28
Mg	hcp	1.60
Mo	bcc	1.36
Ni	fcc	1.25
V	bcc	1.31

26. In the pattern, sketch and label unit cells that
a. contain one P and one Q in a single unit cell
b. contain two Ps and two Qs in a single unit cell.

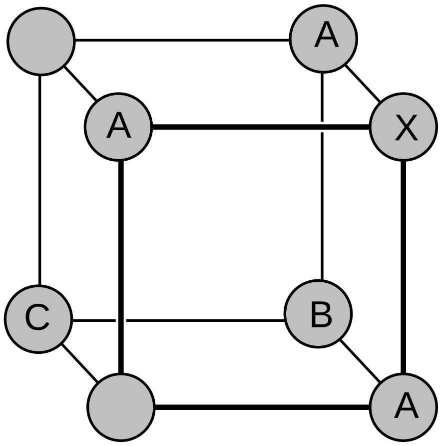
P Q P Q P Q P Q P Q P

Q P Q P Q P Q P Q P Q

P Q P Q P Q P Q P Q P

Q P Q P Q P Q P Q P Q

27. The following is a simple cubic (sc) unit cell. In the sc structure, a given sphere, labeled X, has six nearest neighbors, three of which are shown and labeled A. The next nearest neighbor spheres to X are across the diagonal of a face of the cube (a face diagonal). One such sphere is shown and labeled B.
a. How many such spheres are there at this same distance from sphere X?
b. The next nearest neighbor to sphere X is labeled C and lies across the so-called body diagonal of the cube. How many such spheres are there at this same distance from sphere X?



28. In the body-centered cubic structure, the sphere in the center of the cube has eight nearest neighbors, which lie at the corners of the cube. The next nearest neighbor spheres to the sphere in the center of the cube are at the centers of adjacent cubic unit cells. How many such spheres are there?

29. Which of the following combinations of atoms is most likely to form a salt (an ionic compound)?
    a. Ba, Ne
    b. Cs, Cl
    c. S, N
    d. Ti, Hf

30. Because of the similar size and chemistry of As and P and the fact that GaAs and GaP have the same kind of crystal structure, it is possible to form solid solutions of tunable stoichiometry with the composition of $GaAs_{1-x}P_x$, where x takes on any value between 0 and 1, that is, $0 \le x \le 1$. What is the formula weight in grams per mole for such a solid when $x = 0.25$?

31. The formula weight in grams per mole for the substitutional solid solution $CdS_{0.10}Se_{0.90}$ is which of the following?
    a. 144
    b. 149
    c. 187
    d. 191

32. Is a solid solution like $Cu_{0.5}Ni_{0.5}$ distinguishable from a 1:1 equimolar mixture of Cu and Ni by elemental analysis? How might a magnet distinguish them?