

## PACKING OF SPHERES

Atoms may be regarded as spheres for some purposes. When so regarded, the arrangement of the atoms that make up the crystal structure of a mineral may be approximated by the packing of spheres.

Atoms have, by definition, a neutral electrical charge. When electrons are added to a neutral atom, it becomes a negatively charged ion, called an anion. An atom from which electrons are removed becomes a positively charged ion, called a cation. The size of the atom is determined by the size of the electron cloud surrounding the nucleus. Since atoms have more electrons than a neutral atom, while cations have fewer electrons, it follows that an anion will be larger than an atom, and an atom will be larger than a cation of the same element. Indeed it is generally true that anions are larger than cations.

Over three thousand five hundred minerals are known. The crystal structure of most of these minerals has been determined. Most minerals are composed of ions or atoms of two or more elements. A few are composed of atoms of a single element. Certain structure types for the latter case will be examined in Part B of the exercise. The structures of the former are quite varied, and often difficult to visualize. However, it is true that many crystal structures are composed of smaller units linked together. In Part A of this exercise, some of these units will be examined.

### Part A - Examination of mineral structural units

When two or more atoms or ions are linked together in a structure, it is observed that certain basic geometrical patterns occur frequently. These units may be two or three-dimensional. The structure of the units is observed to be dependent on the relative size of the ions involved. Other factors, such as electrical charge, may also play a role but will be neglected at this stage. To categorize the relative size of ions, the radius ratio is used. This is almost always the cation size divided by the anion size. The radius ratio ranges between 0 and 1. Different configurations are observed for different radius ratios. The configuration may be categorized by the number of large ions (again, usually anions) surrounding a single small ion (usually the cation). Since this ratio is always in the form N:1 (where N is an integer) the coordination number (or CN) is expressed as a Roman numeral.

At this point the following table (Table 1) of radius ratio ranges, observed CN, and geometrical configurations, will be presented without further explanation. The reasons for the observed configurations are explained in the text and will be discussed in lecture. Normally only one of two coordination numbers are possible for a given anion-cation pair. Thus the ranges given below usually allow the configuration of a given pair to be predicted if the radii are known.

**TABLE 1**

<u>Radius Ratio</u>	<u>CN</u>	<u>Configuration</u>
0.000-0.155	II	Linear
0.155-0.225	III	Trigonal Planar
0.225-0.414	IV	Tetrahedral
0.414-0.732	IV	Square planar
0.414-0.732	VI	Octahedral
0.732-1.000	VIII	Cubic

**LAB EXERCISE A**

Styrofoam spheres of various radii, rulers, and toothpicks will be supplied. Measure the different spheres. Calculate the radius ratio for different pairs of spheres. From the above chart, determine what type of configuration is favored. Using toothpicks and the selected spheres build this configuration. Examine the model you build.

Note two things.

1. Does the cation touch each anion?
2. Do the anions touch their nearest neighbors?

Build at least one model for each configuration.

Next build models which represent non-stable (i.e., configurations which do not have the radius ratio listed) configurations. Note the same information as for the stable models.

The CD-ROM which accompanies the textbook has an excellent set of diagrams for the various configurations under the "Coordination of Ions" section.

**Write-up**

For your write-up, prepare a table listing the sizes of spheres used, the calculated radius ratio, the configuration built, and the answers to the two questions above. Attempt to determine what ratio (for each configuration) allows the answer to both of the above questions to be "yes." Tables should be neat, and logically organized. **This will be one of the criteria used in grading the laboratory report.**

**PART B - SOME STRUCTURES OF SINGLE ELEMENT SUBSTANCES**

Some minerals, like gold, silver, and copper, are composed of atoms of only one element. These atoms are often found in structures known as closest-packed structures. In these structures, spheres of equal radii are packed as closely as possible. This may be done in two or three dimensions. In nature, only three dimensional structures normally exist. It is useful to examine the two dimensional structure first, however.

**In two dimensions**, spheres of equal radii pack into a network of interlocking hexagons. These may be represented by circles on a flat surface (pennies, etc.). Any circle will be surrounded by six other circles (nearest neighbors). Between the circles are holes, called **VOIDS**. Since each void is surrounded by three circles, we may assign  $\frac{1}{3}$  of each void to a circle. Each circle is surrounded by six voids. Therefore, there are twice as many voids as circles ( $\frac{1}{3} \times 6 = 2$ ). This type of packing may also be imagined to consist of trigonal arrays of circles grouped together. The voids in the two-dimensional case are known as intra-layer voids.

**In three dimensions**, spheres also pack together. There are voids between layers (called inter-layer voids). There are two distinct types of inter-layer void, with different coordination numbers. (To determine the coordination number of a void, imagine placing a small sphere, like a pea or marble, at the center of the void and determine its coordination number).

### LAB EXERCISE B

For the first part of the exercise arrange circles (or spheres) of the same radii into the above arrangement. Verify that each of the above statements is true. *Based on your conclusion from Part A, what is the largest circle (sphere) that would fit in an intra-layer void without pushing the larger spheres apart?* (Express your answer as a radius ratio, relative to the radius of the larger circle.)

Build a three-dimensional structure by adding a second layer of spheres. Do this by placing spheres over voids in the first layer. (If you place a sphere over a sphere, the resulting structure is close-packed, not closest-packed.) Carefully observe the resulting structure. Note the two different types of inter-layer void. *What are the coordination numbers of the two types of void? What type of coordination polyhedra do the spheres form around each void?* Voids are usually named for the coordination polyhedron that surrounds them (i.e., a cubic void).

Continue building the model by adding a third layer. If you place the third layer so that it exactly overlaps the bottom layer (which may be called the A layer) you achieve a sequence ABA. If this pattern is continued (ABABABAB...) the resulting type of packing is known as **hexagonal closest packing (HCP)**. The other possibility is to arrange the third layer so that it does not overlap either A or B, thus giving ABC. If the ABC arrangement is continued (ABCABCABC...) the structure has **cubic closest packing (CCP)**. Again carefully examine the HCP and CCP structures. *What type of inter-layer voids are present between the second and third layers? By analogy with the two-dimensions case, calculate the ratio of voids to spheres for each type of void, for both HCP and CCP.*

Metals often crystallize in either HCP or CCP. Many other structures, especially of the silicates, may be derived from HCP or CCP. *To complete the assignment, draw a top plan of both HCP and CCP.* Use red to represent the A layer, blue for the B layer, and green for the C layer. See Frye page 29 (on reserve in the library) if you need additional help.

The CD-ROM which accompanies the textbook has animations of both HCP and CCP structures under the "Closest Packing" section.

## Write-up

For the write-up of section B, answer each of the questions in *italics* above. Metals often crystallize in either HCP or CCP. Many other structures, especially of the silicates, may be derived from HCP or CCP. To complete the assignment, draw a top plan of both HCP and CCP. Use **red** to represent the A layer, **blue** for the B layer, and **green** for the C layer and prepare the top plan. See Frye page 29 (on reserve in the library) if you need additional help. Computer drawings may be used if you choose, provided you do the drawings yourself.

The write-up is due at the beginning of the next lab section, or as decided by the GTA.

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