# Experiment 24

# MOLECULAR MODELS AND CRYSTALLINE STRUCTURES

## Objective

The purpose of this experiment is to use handcraft candy beads and sticky tack to construct molecular models and crystal structures in order to understand their delicate three-dimensional structures.

## Lab techniques

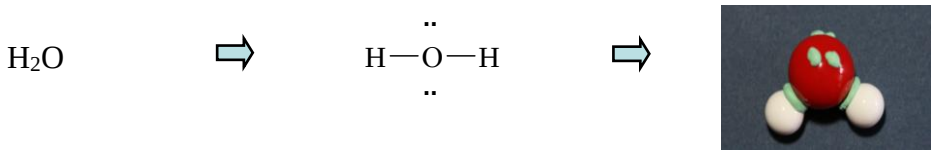
- Constructing models of molecules and crystalline structures.

## Principle

### I. Molecular shape

Shape and size of a molecule, together with strength and polarity of its bonds, largely determine the properties of that molecule. Due to the presence of dipole moment, a polar molecule shows greater intermolecular forces and hence affects its vapor pressure, boiling point, enthalpy of vaporization, and solubility etc. The polarity of a molecule is determined not only by the bond polarity but also the geometry of the molecule. For example, carbon dioxide, $CO_2$, is a linear and nonpolar molecule; whereas water, $H_2O$, is a bent and polar molecule.

Lewis structure shows the number and types of bonds between atoms in a molecule. However, it does not indicate the shapes of molecules. Incorporate with the Valence Shell Electron Pair Repulsion (VSEPR) theory, the molecular shape and polarity of a molecule can be determined. VSEPR model is based on the understanding that electron pairs are negatively charged and repel one another. The best arrangement of a given number of electron pairs is the one that minimizes the repulsions among them. For example, the central carbon atom of methane ($CH_4$) is $sp^3$ hybridized, which uses four valence electrons to form four covalent bonds with the valence electrons of four hydrogen atoms. Thus, there are four electron pairs surrounding the carbon atom and arranged in a tetrahedral shape with a bond angle of 109.5$^o$. In this experiment, candy beads used in handicrafts will represent atoms; sticky tack is applied as chemical bonds to construct the molecular model. With a three-dimensional model in hands, one can understand the relationship between spatial arrangement and polarity of a molecule better. The flowchart of the experiment is shown in Fig. 24-1.




**Count the total number of valence electrons**, i.e. 8 valence electrons in water molecule.

**Draw Lewis structure and determine the geometry of electron pairs**, i.e. tetrahedral for water molecule.

**Determine the molecular geometry and polarity,** i.e. bent and polar for water molecule.

Figure 24-1 Flowchart for predicting molecular shape

## II. Crystalline structure

In a crystalline solid, the atoms, ions, or molecules are arranged orderly in space. These solids usually have flat surfaces, or faces, that make definite angles with one another. A crystalline solid can be represented by a three-dimensional array of points called a crystal lattice. Each point in the lattice is called a lattice point. There are 14 different lattices that describe all the known crystalline solids. Take the cubic system as an example. It includes simple cubic, body-centered cubic and face-centered cubic. Because of the different arrangement of atoms, they show various coordination numbers, number of atoms in a unit cell, and packing efficiency. These may affect the melting point, density, and malleability of the substance.

In a crystalline structure, the arrangement of lattice points in a single layer is shown in Fig. 24-2. In Fig. 24-2 (A), it is an open arrangement; each sphere is in contact with four neighboring spheres and has a coordination number of 4. In Fig. 24-2 (B), it is a closest packing arrangement; each sphere is surrounded by six spheres in the layer and shows the most efficient arrangement.

(A) (B)

Figure 24-2 Two arrangements for packing spheres in two dimensions. (A) an open packing; (B) a closest packing.

Fig. 24-3 portrays an example of a multilayered, closest-packing order. A second layer of spheres can be placed in the indentation on top of the first layer. A third layer can then be added above the second with the spheres sitting in the indentation of the second layer. However, there are two types of indentation for the third layer, and result in different structures. If the spheres of the third layer are placed in line with those of the first layer, given the layer sequence of ABAB (Fig. 24-3(B)), it is a hexagonal closest packing (hcp). On the other hand, the spheres of

the third layer may not sit above the spheres of the first layer, and the layer sequence is ABC as shown in Fig. 24-3 (C). The structure is known as cubic closest packing (ccp) or face-centered cubic.

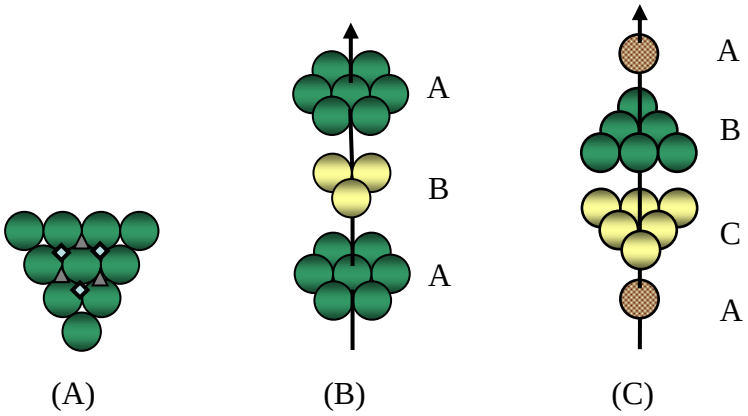



Figure 24-3 (A) Closest packing of a single layer of spheres; (B) the hexagonal closest packing; (C) the cubic closest packing.

The crystal structure of an ionic compound depends to a great extent on the relative sizes of the two types of ions present. In general, the larger ions (usually the anions, the radius is represented by $r_-$) arrange themselves in the closest packing arrangement with the smaller ions (usually the cations, the radius is represented by $r_+$) fit into a tetrahedral hole, octahedral hole, or cubic hole according to the ratio of the cation and anion radii, $r_+/r_-$. This kind of arrangement maximizes the attractive force between cations and anions and minimizes the corresponding repulsive force at the same time. For example, in the crystal structure of NaCl, the chloride ions arrange themselves in a face-centered cubic structure and the sodium ions occupy the octahedral holes. In this experiment, the candy beads will be used to represent the spheres of the lattice point within the crystalline structure. You need to construct the cubic and closest packing crystal structures to observe their spatial arrangements.

## Apparatus

Molecular model set (1 box, including candy beads of various colors and sticky tack), colored paper (can be self-prepared), digital camera (self-prepared), and USB (self-prepared).

## Procedure

### I. Molecular shape

1. Check the number of candy beads and sticky tack inside the molecular model set. Restore the lost ones if necessary.

Figure 24-4 Molecular model set

Black beads: representing C atoms, 14 pcs
White beads: representing H atoms, 16 pcs
Red beads: representing O atoms, 6 pcs
Blue beads: representing N atoms, 6 pcs
Green beads: representing Cl atoms, 6 pcs
Others: 8 pcs
A few pieces of sticky tack.

2. Draw the Lewis structure of the molecules or ions listed in Table 24-1. Determine their molecular structures, bond angles, and hybridization of the central atoms according to the VSEPR theory.
3. Use beads and sticky tack in the molecular model set to construct the molecular model in correct bond angles. Record the molecular model with a digital camera and determine the polarity of the molecule.
   Note: Take the photograph in a suitable position to show the molecular shape. The background is suggested to be backed with a plain-colored paper to obtain a higher resolution.

**II. Crystalline structure**

4. Cubic system
   Use beads with the same size as spheres of lattice points and construct the simple cubic, body-centered cubic, and face-centered cubic crystal structures according to Table 24-2. Record the crystal models with a digital camera. Observe the corresponding packing efficiency, spatial arrangement, and coordination number; calculate the number of atoms in a single unit cell.
5. The closest packing
   According to Table 24-2 and with reference to Fig. 24-3, construct the crystalline structures of hexagonal closest packing and cubic closest packing, and record them with a digital camera. At the same time, rotate the cubic closest packing model to show its face-centered cubic structure.
6. Ionic solids
   Refer to Table 24-2, construct and observe the tetrahedral hole, octahedral hole, and cubic hole of the crystal models.

## References

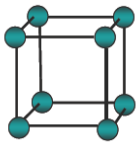
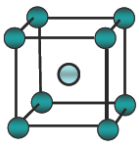
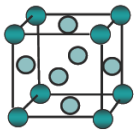
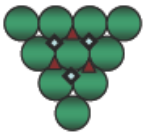
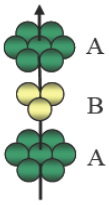
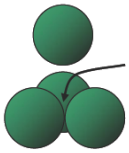
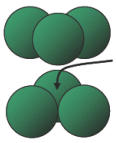
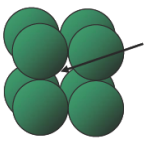
1. She, J.-L; Chen, H.-J. Cheap and Colorful Modeling-sets for Molecular Shapes and Crystal Structures, paper presented at *20th Biennial Conference on Chemical Education (BCCE)*, July 27-31, 2008, Indiana, U.S.A.

2. Irgolic, K.; Peck, L.; O'Connor, R.; Glenn, P. *Fundamentals of Chemistry in the Laboratory*; 2nd ed., Burgess Publishing Co.: Minnesoda, 1981; pp 97-108.
3. Brown, T. L.; LeMay, H. E. Jr.; Bursten, B. E. *Chemistry-The Central Science*; 10th ed., Pearson Education, Inc.: New Jersey, 2006; pp.345-359.

**Table 24-1 (Continue) Lewis structures and molecular shapes**

| Molecule | $KrF_2$ | $PF_6^-$ | $IF_5$ |
|---|---|---|---|
| Lewis structure | | | |
| Predicted shape and bond angle | | | |
| Hybridization of the central atom | | | |
| Constructed molecular model | | | |
| Molecule | $XeF_4$ | $CH_3CH_2CH_2CH_2OH$ | Other example |
| Lewis structure | | | |
| Predicted shape and bond angle | | | |
| Hybridization of the central atom | | | |
| Constructed molecular model | | | |

**Table 24-2 Crystalline structures**

| Cubic system | Simple cubic | Body-centered cubic | Face-centered cubic |
|---|---|---|---|
| Crystal lattice |  |  |  |
| Coordination number | | | |
| Atoms/unit cell | | | |
| Constructed crystal model | | | |
| Closest packing | Closest packing | Hexagonal closest packing | Cubic closest packing |
| Crystalline arrangement |  |  |  |
| Constructed crystal model | | | |
| Ionic crystal | Tetrahedral hole e.g. ZnS | Octahedral hole e.g. NaCl | Cubic hole e.g. CsCl |
| Crystalline arrangement |  |  |  |
| Constructed crystal model | | | |