

UNIT 13

Modern Materials and the Solid State

Unit Overview

This unit explores advances in modern materials in the context of their underlying chemistry. Many common materials represent significant technological advances but are still based on basic chemical principles. Therefore, an understanding of chemistry is an excellent entry point not only to understand how a material behaves or a device works, but also to understand the ways in which cutting-edge advances are made.

Learning Objectives and Applicable Standards

Participants will be able to:

1. Differentiate between types of solid structures in terms of atomic interactions and order (or lack thereof) in the structure.
2. Recognize the conditions that influence phase changes in materials.
3. Identify different types of alloys in terms of their constituents and behavior.
4. Recognize and characterize the different allotropes of carbon.
5. Identify various naturally occurring and synthetically created polymers.

Key Concepts and People

1. **Modern Materials:** The chemistry of matter in the solid state and the applications of solid materials are areas of some of the most cutting-edge research in chemistry and engineering.
2. **What Is a Solid?:** Both the identity of the elements and the arrangement of atoms in a solid affect the properties of the solid. At the most basic level, solids are classified as either amorphous or crystalline, depending on whether or not they exhibit long-range order at the atomic level.
3. **Ionic and Covalent-Network Solids:** Coulombic forces hold together ionic solids while covalent bonds hold together covalent solids.

4. **Molecular Solids:** Molecular solids, such as ice, are held together by intermolecular interactions of the molecules themselves. These interactions are weaker than the ionic or covalent interactions in ionic and covalent solids, and the physical characteristics of the solids reflect this.
5. **Metallic Solids:** Metals have readily accessible valence electrons, and in metallic solids the electrons are shared readily between atoms. Metals can be used in their pure form but can also combine to form alloys, whose properties are influenced by the identity and proportion of the components.
6. **Phase Changes in Solids:** Temperature and pressure influence the state of matter in which a material will be found. Phase diagrams summarize the behavior of materials under different temperature and pressure conditions.
7. **Natural and Synthetic Polymers:** Carbon is not only the basis of life but also the basis of polymer chemistry. Both naturally-occurring and synthetically-created polymers are tremendously important materials in modern life.
8. **Alloys:** Metals form alloys by combining in various proportions, and occasionally with trace amounts of non-metals.

Video

While chemical reactions in gases and liquids are essential to the understanding of chemistry, the chemistry of solid-state materials characterizes most of the interactions we have with matter on a daily basis. Chemists take advantage of the complexity of solids to engineer new materials, including nanoparticles, polymers, and advanced metal alloys. These new materials have many potential applications in sensors, advanced drug delivery systems, and space exploration. Today, modern materials are following a heritage—one that can be traced back to earlier civilizations—in which the properties of solids are manipulated to advance human needs.

VIDEO CONTENT

Host Science Introduction

Materials scientist and science writer Dr. Ainissa Ramírez, introduces the unique properties of solid-state materials through the example of a “memory metal,” an alloy that can be deformed at room temperature, but then returns to its original shape when heated. This segment emphasizes a central idea of the unit: The observable properties of bulk solid materials are the result of the interactions of their molecular components at the microscopic level.

Real World Example

“Atomic Arrangements”

Dr. Raquel Alonso Pérez, curator of the Mineralogical and Geological Museum at Harvard University, uses examples from the minerals in her collection to point out the different types

of bonding that hold solids together. Comparing the different forms of carbon - diamond and graphite - which differ greatly in their properties because of differences in their internal bonding arrangements, she reinforces that the external properties of solids result from these atomic and molecular structures.

Current Chemistry Research

“Carbon Nanotube Sensors”

Joseph Azzarelli’s research in the Swager group at MIT focuses on developing new sensors for agricultural, food, industrial, and environmental applications. He has found ways to use carbon nanotubes, yet another molecular form of carbon, as the heart of a sensor that can measure ethylene gas, a plant hormone that controls the ripening of fruit.

History of Chemistry

“Early Plastic”

In the 1800s, Leominster, Massachusetts became known as the “Comb City,” because factories there specialized in the manufacture of combs and other items made from natural materials, such as bone and horn. Paul Benoit, a curator at the Leominster Historical Society, describes how Leominster switched to man-made materials shortly after the turn of the 20th century. One of the first plastics was celluloid, a polymer that could be molded and cooled to make objects of many different shapes. Leominster made important contributions to the rise of today’s multi-billion dollar plastics industry.

Laboratory Demonstration

“Making Polymers”

One of the best-known plastics is nylon, which, like all polymers, is formed from linking together smaller molecules, or monomers, into large molecules. Harvard University Lecture Demonstrator Daniel Rosenberg shows how to react two monomers, diacid chloride and hexamethylenediamine, and come away with a long strand of nylon.

Current Chemistry Research

“Polymer Research in the Pharmaceutical Industry”

Dr. Trevor Castor, Chief Scientist at Aphios Corporation, is enveloping insulin inside biodegradable polymers. The polymer protects the insulin, a protein, from the harsh chemical environment in the digestive system. There, the encapsulated nanoparticles are so small that they are absorbed directly into the bloodstream. Once inside the blood, the polymer degrades, releasing the insulin. This technology has the potential to deliver insulin without injections, thereby improving quality of life for millions of people with diabetes.

Current Chemistry Research

“High Temperature Alloys”

Engineers at the Smithsonian Astrophysical Observatory are building components for a new spacecraft, one that will travel close enough to the Sun to take actual samples of the Sun’s corona. During the mission, the spacecraft will experience solar radiation that is 500 times more intense than it is on Earth, so the materials used must be able to withstand extremely high

temperatures. Smithsonian Astrophysicist Dr. Anthony Case and technology and product development manager Stephen McCrossan of Plansee USA, describe how alloys of molybdenum with tungsten and zirconium have the necessary characteristics.

Unit Text

Content Overview

The unit begins with a brief review of chemical bonding to introduce chemistry as the foundation for the performance of materials in the solid state. The development of solid materials, and the behavior of naturally occurring solid materials, depends not only on the chemistry but also the structure of the solid itself. Different types of solids exhibit different types of atomic interactions and different microscale geometry, and these both influence the behavior of the solids. At the very basic level, solids may be either amorphous or crystalline. Within those broad definitions, however, particularly for crystalline solids, a vast array of geometric arrangements and chemical interactions are possible.

Alloys such as bronze and steel are among the earliest examples of the engineering of solids, but the development of new alloys continues, and remains a significant contributor to industry. Carbon is not only the centerpiece of organic chemistry but also polymer chemistry, and is therefore another centerpiece of industrial and commercial applications. Both naturally occurring and synthetically created polymers are relevant to such applications. The production and the recycling of these products are major contributors to industry.

Sidebar Content

1. **The Chemistry of Steelmaking:** The chemical composition of steel dramatically affects its properties. Beginning in the mid-19th century with the Bessemer converter, production methods for steel have become significantly more controlled allowing for more variations on the composition of the alloy.
2. **Recycling Plastics:** Plastics can be recycled, but because the polymers that make them come in a wide range of chemical structures, different types must be processed differently.

Interactives

Historical Timeline of Chemistry

This interactive illustrates how different discoveries build upon, disprove, or reinforce previous theories. This not only reinforces basic chemistry concepts, but also emphasizes the nature of science. Scientists mentioned in this unit are listed on the timeline. It is interesting to note that even before the era of modern chemistry, advances in materials science helped shape civilization (e.g., Bronze Age, Iron Age).

Control a Haber-Bosch Ammonia Plant Interactive

Although the reaction in this interactive is not the manufacture of any of the materials discussed in the unit, the principles behind the successful operation of a chemical plant are similar to those for the successful manufacture of various modern materials. Please note that a lesson plan and student worksheet are available online with this interactive.

During the Session

Before Facilitating this Unit

Generally, we recommend watching the videos first before reading the written units. The sections of the video for this unit correlate very closely with the order of the topics in the text, and so the text may be brought in one segment at a time to address each topic in more detail. Encourage students to take the examples given in the text and video and think about as many other real-world examples as they can of the same sorts of materials. This unit can help bridge the gap between laboratory chemistry and real world applications, and provides opportunities for fun hands-on learning.

Tips and Suggestions

1. Materials science may be one of the easiest topics in which to emphasize the interdisciplinary nature of scientific research. Many of the principles described in this unit, however, are based on science beyond the scope of this course.
2. Understanding the chemistry of the components of a solid is a critical first step in understanding how the solid itself will behave.
3. Designing new materials is a challenge of chemistry (to know the properties of the raw materials), engineering (to determine the optimal combination of properties necessary to solve a particular problem), and occasionally physics (to understand on the microscopic level how the structure of a material will influence its function).

Starting the Session: Checking Prior Thinking

You might assign students a short writing assignment based on the following questions, and then spend some time discussing prior thinking. This will help elicit prior thinking and misconceptions.

1. Compare the geometry around a carbon atom with four single bonds; one double and two single bonds; one triple and one single bond; two double bonds. How do these shapes influence the structure of the molecule? How do you think they influence the behavior and appearance of a sample of the compound?
2. Suppose you have a sample of iron, a sample of rock salt, a sample of ice, and a sample of rubber. Which will melt the most easily? Which will break the most easily? Why?

Before Watching the Video

Students should be given the following questions to consider while watching:

1. How are pure metals different from ionic compounds? Do they look and behave the same?
2. Think about different types of plastic. Are they all equally rigid? Do they all qualify as being solid?
3. What is steel? Is it made up of one element or several?

Watch the Video

After Watching the Video

The various solids described in the video encompass all of the major types of bonding as well as many of the major classes of modern solid-state materials. Encourage students to draw connections between the current-research examples (plastics, alloys) with simpler, already-familiar examples (e.g., polyester, steel). Use these additional questions as follow-up, either as a group discussion or as short writing assignments.

1. In the video, you saw that different types of bonding can hold solids together in their most favorable structures, and that this type of bonding in turn influences the properties of the solid. Can you think of examples, besides the ones given, of different types of solids whose behavior reflects the kind of forces holding the solid together?
2. What sorts of forces hold samples of polymers together? What about carbon nanotubes? What about alloys? How are these different?
3. How are unit cells similar to molecular formulas? How are they different?

Group Learning Activities

“[Marshm]allotropes”

Objective

In this exercise, students use marshmallows and toothpicks to build models of the two main allotropes of carbon—diamond and graphite—in order to compare their structures. Students may also want to build a buckyball, a spherical allotrope of carbon with a molecular formula of C_{60} . You may wish to have each group responsible for the model of a single allotrope. If multiple groups build the same model, they may combine their models once they are built.

List of materials

- Marshmallows or other soft candies, 50 per group (at least 60 if building a buckyball)
- Toothpicks, 50 per group

- Pictures of the solid-state structures of graphite, diamond, and buckyball for reference (may be at the front of the room)

Procedure

1. Examine the structures of diamond, graphite, and a buckyball.
2. Using marshmallows as carbon atoms and toothpicks to bond between them, connect the marshmallows to mimic the structure of whichever allotrope you are building. For diamond, you may need to have one person hold the bond angles in place while others build up around the initial tetrahedra. For buckyballs, you may wish to build several hexagons and then connect them. For graphite, make several sheets so that the sheets can be laid on top of one another.
3. If multiple groups have made models of the same allotrope, combine the models once each group has exhausted their supply of materials.
4. Compare the models of the different allotropes for how easily they deform under pressure and under side-to-side shear.

Discussion

The following questions can help students reflect on this exercise. If possible, have students record their responses to the questions in a journal and spend some time discussing as a class.

1. Compare the macroscopic appearances of graphite and diamond. How do you think their atomic-level structures affect their observed macroscopic structure and properties?
2. Graphite is an excellent electrical conductor, while diamond is an insulator. What do you think is responsible for this? (Hint: what does it mean for something to conduct electricity?)

Hazards

There is no increased risk of harm to do this activity.

Disposal

Marshmallows and toothpicks may be disposed of in the trash.

Advances in Packing Peanuts

Adapted from Penn State's Materials Research Institute's "Packing Peanuts" activity.

Objective

Water-soluble packing peanuts made from cornstarch are now available as an alternative to the traditional Styrofoam. In this activity, students will compare the peanuts made from a natural polymer to those made from the synthetic polymers.

List of materials

- Styrofoam packing peanuts, 3-5 cups per group
- Cornstarch packing peanuts, 3-5 cups per group
- Large (~1 L) beakers or clear-sided boxes
- Eggs, 2 per group
- Meter stick, one per group
- Weight plates (or weights plus a watch glass to place directly onto the peanuts)

Procedure

1. Fill one beaker or box with Styrofoam packing peanuts, the other with cornstarch peanuts. Make sure that the two containers are filled as close to the same level as possible.
2. Place weight plates onto the top of the pile of Styrofoam peanuts until the peanuts are compressed by approximately 25% from their original height in the beaker. Make a note of how much weight was required to do this.
3. Repeat step 2 for the cornstarch peanuts, recording the weight required.
4. Remove the weights, and fill additional peanuts into the beakers (to equivalent heights) if they appear permanently compressed.
5. Drop an egg from 25 cm above the surface of the Styrofoam peanuts. Does it break?
6. Drop an egg from progressively higher above the Styrofoam peanuts. Note when the egg finally breaks (or when you run out of measurable height on the meter stick!).
7. Repeat steps 5 and 6 with an egg over the cornstarch peanuts.
8. Pour water into each beaker. Allow the beakers to stand for several minutes and note the appearance of the packing peanuts.

Discussion

The following questions can help students reflect on this exercise. If possible, have students record their responses to the questions in a journal and spend some time discussing as a class.

1. How are the two types of packing peanuts similar? How are they different?
2. Which of the two materials provided the best resistance to compression under loading of weight?
3. Which of the two materials provided the best protection for dropping an egg?
4. What are some of the advantages and disadvantages of these types of packing peanuts? When might you want to use one over the other?

Hazards

There is no increased risk of harm to do this activity.

Disposal

Cornstarch packing peanuts may be rinsed down the drain. Styrofoam peanuts may be washed and reused, or disposed of in the trash.

In-Class Chemical Demonstrations

Close-Packed Candy

Adapted from Penn State's Materials Science Research Institute's "Amorphous Solids" activity.

Objective

This demonstration will illustrate the two types of close-packing, hexagonal and cubic. The two structures have the same packing efficiencies, but differ in the pattern of the spheres after the first two layers. While the packing efficiency can be proven mathematically, comparing the numbers of spheres used to build four layers of each type of structure in the same size container, and then comparing the amount of sand, sugar, or water necessary just to fill the spaces between those spheres can also illustrate packing efficiency.

List of materials

- Spherical candies or marbles, 50 each of three different colors (or 50 each of one color and 150 each of two colors if demonstrating both hexagonal and cubic close-packing simultaneously)
- Clear box (two if demonstrating two packing structures simultaneously)
- Sand or sugar, enough to cover 4 layers of candy/marbles (depending on size of box and candies). If using marbles for crystal structures, use water to illustrate packing efficiency.
- Measuring cup

Procedure

1. Using one color of candy, fill a single layer on the bottom of the box. Gently shake the box to ensure that the layer is fully packed.
2. Using a second color of candy, build a second layer on top of the first in the interstitial sites. Ensure that the layer is fully packed.
3. For hexagonal close-packing, return to the first color of candy and build a third layer like the first two, with the spheres positioned in the interstitial sites directly above the spheres in the first layer. Build a fourth layer in the second color, with the spheres directly above the spheres in the second layer.
4. For cubic close-packing, build a third layer with the third color of candy, with the spheres

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in the interstitial sites offset from the first two layers. Build a fourth layer in the first color, with the spheres directly above the spheres in the first layer.

5. Have the students examine the differences between the two structures from both the side and the top, making note of the space between the spheres.
6. Pour sand, sugar, or water into the boxes and carefully spread around just enough to cover the layers and fill the gaps (do not shake the boxes). Once the space is completely filled, remove the spheres and measure the amount of sugar/sand/water used. This should be the same amount, or close to it, for the two structures.
7. Count the total number of spheres used to build each of the two models. These numbers should also be similar.

Discussion

The following questions can help students reflect on this exercise. If possible, have students record their responses to the questions in a journal and spend some time discussing as a class.

1. How do the two structures differ when viewed from the side? What do they have in common? Sketch what you see.
2. How do the two structures differ when viewed from the top? What do they have in common? Sketch what you see.
3. Sand and sugar were used to illustrate packing efficiency because they are significantly smaller particles than the candies/marbles used to build the structures. Could you have placed larger particles in between the spheres? Would this have given an accurate view of the amount of space between the spheres? Explain.
4. What role does packing efficiency play in the property of a given material?

Hazards

There is no increased risk of harm to do this activity.

Disposal

Marbles, sand, and any other inedible material may be reused. Candy and sugar may be disposed of in the trash.

Instant Polymers: Making Nylon, Making Rubber

Adapted from *Chemical Magic* by Leonard Augustine Ford.

Objective

This demonstration combines two classic demonstrations of rapid polymerization reactions, with two very different results. The reaction to generate nylon produces a filament that can be drawn out, while the coagulation to generate rubber produces a blob.

List of materials

- 250 mL beakers, 5
- Stirring rods, 2 (3 if spooling the nylon)
- Tweezers
- 10% acetic acid solution in water, ~50 mL
- Synthetic latex, ~50 mL
- 6 g sebacoyl chloride in 70 mL heptane (available individually from Aldrich or other chemical suppliers; prepare solution in advance of demo)
- 3 g 1,6-diaminohexane in 70 mL water (diamine available from Aldrich or other chemical suppliers; prepare solution in advance of demo)
- Methanol, ~200 mL

Procedure

1. Have the students observe the appearances of beakers filled with latex, acetic acid, sebacoyl chloride, and diaminohexane solutions.
2. Pour the latex solution into the acetic acid and stir vigorously with a stirring rod. The latex should form a ball.
3. Remove the ball from the beaker, squeeze out the liquid with your hands, and bounce the ball. Allow students to pass the ball around and inspect it.
4. Tilt the beaker containing the diaminohexane solution and carefully pour the solution of sebacoyl chloride down the lower wall to form two layers.
5. Dip a glass rod into the combined solutions at the interface of the layers, and carefully pull the film that forms at the interface. Pick this film up into the tweezers and pull the strand out from the beaker.
6. If desired, spool the resulting strand of nylon around two glass rods.
7. Wash the nylon with methanol to remove the acid generated in the reaction.

Discussion

These questions can help guide a discussion.

1. If the two solutions used to form the nylon had not been mixed together carefully, what do you think would have happened? (Hint: what happened with the other demo?)
2. The formation of the rubber is due to coagulation of the latex, while the formation of the nylon is due to a reaction between the two chemicals. Do you think that the rubber could have been formed into a filament the way the nylon was if the latex and acid solutions had been combined more carefully in the same the way the two solutions were for the nylon?

3. Look up the structures of sebacoyl chloride and 1,6-diaminohexane. If the reaction between these to produce nylon also produces HCl, how do you suppose the reaction proceeds? Draw a structure for the repeating unit of this polymer.

Hazards

It is good lab practice to review a chemical's Material Safety Data Sheet (MSDS) before working with any chemical. Follow instructions on the MSDS and encourage students to review them. Wear safety goggles, a lab coat, and gloves for both portions of this experiment. The experiments may be performed in a fume hood or on a desktop, but should be performed in a well-ventilated area if not in a hood. Methanol is toxic and flammable. Caution anyone who might have a latex allergy against handling the rubber ball. Latex will stain clothing permanently.

Disposal

Check local regulations for the safe disposal of methanol and any un-reacted organic acids and bases. An excess of acetic acid may be used to coagulate any residual latex. Any remaining nylon reagents may be stirred together to allow coagulating, and then rinsed with methanol and disposed of. The latex and nylon may be disposed in the trash.

Going Deeper (In-class Discussion or Reflection)

Instructors should allow up to 30 minutes for discussion at the end of the session, or students can use the time to reflect on one or more of these questions in journals.

1. Discuss how different types of polymer structures and processing techniques (amorphous vs. crystalline, crosslinked vs. not, etc.) influence the macroscopically observed properties of the polymers (pliability, conductivity, permeability, etc.).
2. Tin exists in two different crystal structures. Old organ pipes made of tin were discovered many years later to be off-key. Why did this happen?

References and Additional Resources

Ford, Leonard Augustine, and E. Winston Grundmeier. *Chemical Magic*. 2nd ed. New York: Dover Publications, 1993.

Penn State Materials Research Institute. Center for Nanoscale Science. "Packing Peanuts Activity." Accessed August 15, 2013, http://www.mrsec.psu.edu/education/nano-activities/polymers/packing_peanuts/packing_peanuts.pdf

Penn State Materials Research Institute. Center for Nanoscale Science. "Amorphous Solids." Accessed August 15, 2013, http://www.mrsec.psu.edu/education/nano-activities/liquid_metal/amorphous_solids/amorphous_solids.pdf

Penn State Materials Research Institute. Center for Nanoscale Science “Nano-Activities for Kids.” Accessed August 28, 2013. <http://www.mrsec.psu.edu/education/nano-activities/>

For Professional Development

In addition to watching the videos, reading the text, and going through the activities listed in the course guide, participants taking this course for professional development should read the following papers and answer the corresponding reflection questions. We recommend that participants answer these questions in a journal.

Further Reading and Reflection Questions

Hodgson, Steven C., Sephen W. Bigger, and Norman C. Billingham. “Studying Synthetic Polymers in the Undergraduate Chemistry Curriculum.” *Journal of Chemical Education*. 78:4 (2001). Accessed August 28, 2013. <http://ncsu.edu/project/chemistrydemos/Organic/PolymerLitReview.pdf>

1. Do you think it is important to expose students to polymers at the high school level? Why or why not?
2. The authors suggest that in introductory college level chemistry courses it is not always practical to devote a whole unit to polymers. Do you think this is true for the high school level? Why or why not?
3. To incorporate polymer chemistry into the already established curriculum, the authors suggest using polymer-related examples to teach general chemistry concepts. How might you incorporate polymers into your curriculum? What are some examples you could use?

Bodner, George M. “Why Lecture Demonstrations Are ‘Exocharmic’ for Both Students and Their Instructors.” *University Chemistry Education- Royal Society of Chemistry*. 5 (2001): 31-35. http://chemed.chem.purdue.edu/chemed/bodnergrouop/PDF_2008/71%20Demos%20UCEd.pdf

1. Do you agree with the author that demonstrations should contain “an element of the unexpected”? Why or why not?
2. Do you agree with the authors’ conclusions? Which ones in particular resonate with you? Which ones do you disagree with? Explain your reasoning.
3. What are some strategies you might use when conducting demonstrations to help bring about conceptual change for the learner?

Professional Development Assignments

1. After reading the papers above and reflecting on the questions presented, develop a lesson plan designed to teach material presented in this unit.
2. Using a group activity or classroom demonstration presented in this course guide, show how you would implement it into your classroom. Where would it fit into your curriculum or standards? Would you change the demonstration or activity in any way? How would you assess student learning?