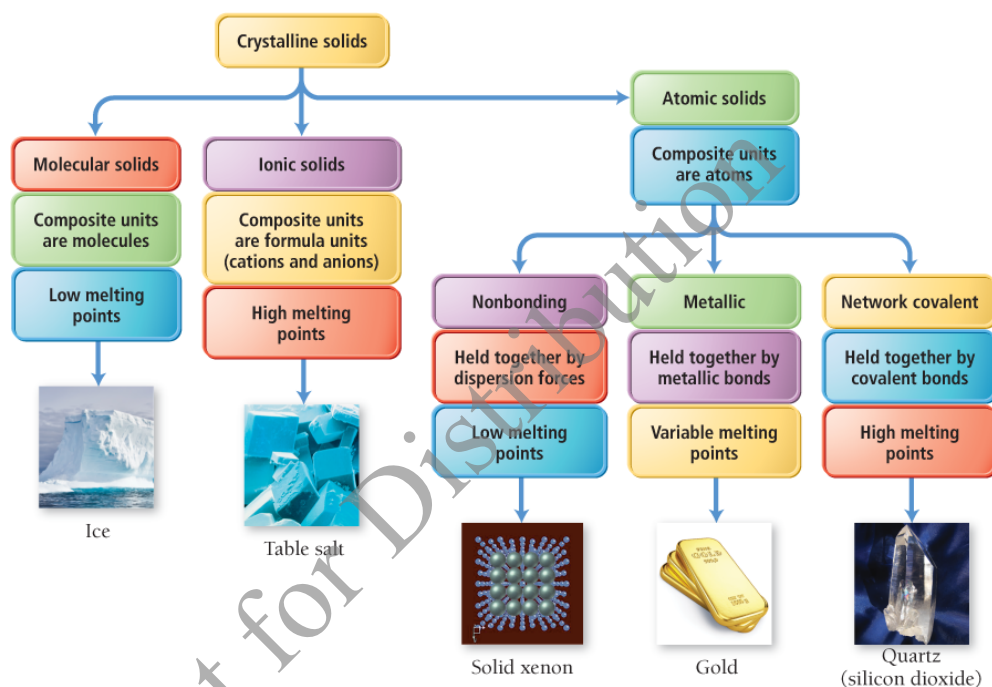


12.4: Crystalline Solids: The Fundamental Types

As we discussed in [Section 11.2](#), solids may be crystalline (comprising a well-ordered array of atoms or molecules) or amorphous (having no long-range order). We classify crystalline solids into three categories—molecular, ionic, and atomic—based on the individual units that compose the solid. Atomic solids can themselves be classified into three categories—nonbonding, metallic, and network covalent—depending on the types of interactions between atoms within the solid. [Figure 12.9](#) shows the different categories of crystalline solids.

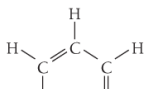
Figure 12.9 Types of Crystalline Solids



Molecular Solids

Molecular solids are solids whose composite units are *molecules*. The lattice sites in a crystalline molecular solid are therefore occupied by molecules. Ice (solid H_2O) and dry ice (solid CO_2) are examples of molecular solids. Molecular solids are held together by the kinds of intermolecular forces—dispersion forces, dipole–dipole forces, and hydrogen bonding—discussed in [Chapter 11](#).

Molecular solids as a whole tend to have low to moderately low melting points; however, their specific properties depend on the types of intermolecular forces present between the molecules as well as the structure of the molecule and the crystal structure of the solid. For example, benzene and toluene have similar molar masses and intermolecular forces (dispersion forces).

Compound	Structure	Molar Mass	Type of Intermolecular Force	Melting Point of Solid
Benzene (C_6H_6)		78.11 g/mol	Dispersion	5.5°C

Toluene		92.14 g/mol	Dispersion	-95.5 °C

However, the extra $-\text{CH}_3$ group on toluene prevents the molecules from packing as efficiently in the toluene crystal as they do in benzene. As a result, even though toluene has a higher molar mass than benzene, it has a much lower melting point.

Some molecular solids crystallize in more than one structure. The different structures are called **polymorphs**. The different structures can have different properties, including different melting points and solubilities. Polymorphism is important in pharmaceuticals because different forms of a drug can have different physiological activities. For example, ritonavir was among the first drugs found to be effective in treating HIV and AIDS. When ritonavir was first discovered and approved for use, only one crystal structure was known. However, soon after its widespread use, a polymorph was discovered. This polymorph was more stable, less water-soluble, and much less physiologically active. Even worse, small amounts of this polymorph in a sample could convert the active form into the inactive one. The drug manufacturer had to halt production of ritonavir until researchers solved the problem by switching from a capsule form to a refrigerated gelcap form and later to a stable tablet form.

Polymorphism can exist in any crystalline material, not just molecular solids.

Ionic Solids

The composite units of **ionic solids** are ions. Table salt (NaCl) and calcium fluoride (CaF_2) are examples of ionic solids. The forces holding ionic solids together are strong coulombic forces (or ionic bonds), and because these forces are much stronger than intermolecular forces, ionic solids tend to have much higher melting points than molecular solids. For example, sodium chloride melts at 801°C , while carbon disulfide (CS_2)—a molecular solid with a higher molar mass—melts at -110°C . We examine the structure of ionic solids in [Section 12.5](#).

Atomic Solids

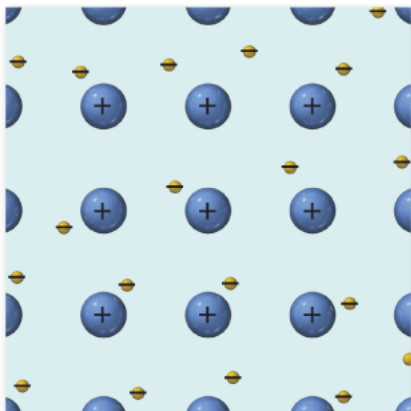
In **atomic solids** the composite units are individual atoms. Solid xenon (Xe), iron (Fe), and silicon dioxide (SiO_2) are examples of atomic solids. We classify atomic solids into three categories—*nonbonding atomic solids*, *metallic atomic solids*, and *network covalent atomic solids*—with each type held together by a different kind of force.

Nonbonding atomic solids are held together by relatively weak dispersion forces. In order to maximize these interactions, nonbonding atomic solids form closest-packed structures, maximizing their coordination numbers and minimizing the distance between composite units. Nonbonding atomic solids have very low melting points that increase uniformly with molar mass. The only nonbonding atomic solids are noble gases in their solid form. Argon, for example, has a melting point of -189°C , and xenon has a melting point of -112°C .

Metallic atomic solids, such as iron or gold, are held together by *metallic bonds*, which in the simplest model are represented by the interaction of metal cations with the sea of electrons that surrounds them. As we have already discussed, metals have a tendency to lose electrons, which means that they have relatively low ionization energies. When metal atoms bond together to form a solid, each metal atom donates one or more electrons to an **electron sea**. For example, we can think of sodium metal as an array of positively charged Na^+ ions immersed in a sea of negatively charged electrons (e^-), as shown in [Figure 12.10](#). Each sodium atom donates its one valence electron to the “sea” and becomes a sodium ion. The sodium cations are held together by their attraction to the sea of electrons.

Figure 12.10 The Electron Sea Model

In the electron sea model for metals, the metal cations exist in a “sea” of electrons.



Although the electron sea model we have just discussed is simple, it accounts for many of the properties of metals. For example, metals conduct electricity because—in contrast to ionic solids where electrons are localized on an ion—the electrons in a metal are free to move. The movement or flow of electrons in response to an electric potential (or voltage) is an electric current. Metals are also excellent conductors of heat, again because of the highly mobile electrons, which help to disperse thermal energy throughout the metal.

The electron sea model also accounts for the *malleability* of metals (their capacity to be pounded into sheets) and the *ductility* of metals (their capacity to be drawn into wires). Since there are no localized or specific “bonds” in a metal, we can deform it relatively easily by forcing the metal ions to slide past one another.

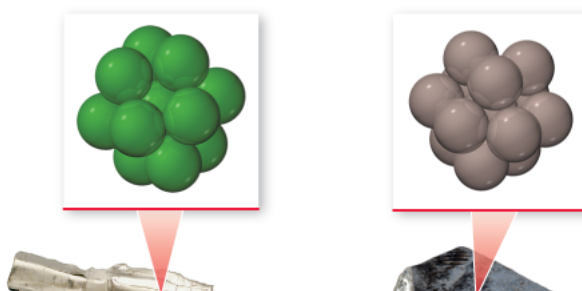


Copper can easily be drawn into fine strands like those used in household electrical cords.

Because metallic bonds are not directional, many metals tend to form closest-packed crystal structures. For example, nickel crystallizes in the cubic closest-packed structure, and zinc crystallizes in the hexagonal closest-packed structure (Figure 12.11). Metallic bonds have varying strengths. Some metals, such as mercury, have melting points below room temperature, whereas other metals, such as iron, have relatively high melting points (iron melts at 1538 °C).

Figure 12.11 Closest-Packed Crystal Structures in Metals

Nickel crystallizes in the cubic closest-packed structure. Zinc crystallizes in the hexagonal closest-packed structure.





Nickel (Ni)



Zinc (Zn)

Covalent bonds hold together **network covalent atomic solids**, such as diamond, graphite, and silicon dioxide. The crystal structures of these solids are more restricted by the geometrical constraints of the covalent bonds (which tend to be more directional than intermolecular forces, ionic bonds, or metallic bonds), so they *do not* tend to form closest-packed structures. Network covalent atomic solids have very high melting points because the crystalline solid is held together by covalent bonds. We examine some examples of this class of solids in [Section 12.6](#).

Example 12.5 Classifying Crystalline Solids

Classify each crystalline solid as molecular, ionic, or atomic.

- $\text{Au}(s)$
- $\text{CH}_3\text{CH}_2\text{OH}(s)$
- $\text{CaF}_2(s)$

SOLUTION

- Au is a metal and is therefore an atomic solid.
- Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) is a molecular compound. Solid ethanol is therefore a molecular solid.
- Calcium fluoride (CaF_2) is an ionic compound, so $\text{CaF}_2(s)$ is an ionic solid.

FOR PRACTICE 12.5 Which type of atomic solid is $\text{Au}(s)$?

Conceptual Connection 12.2 Crystalline Solid Types and Melting Points

Interactive

Not for Distribution