Chapter 12: The Solid State

12.1 Solids and their properties
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Chapter in Context

In the last chapter we focused on the non-bonding interactions between collections of atoms and molecules, IMFs, and on how these forces manifest themselves in the physical properties of liquids. In this chapter we continue this exploration with the addition of solids. Because solids have a lot of structural detail that is missing in liquids and gases, we will begin by looking at the structural features of some representative, although simple, solids. We will look briefly at bonding in solids, and conclude the chapter by tying the three states together in what is known as a phase diagram.

12.1 Solids and their properties

Solids can be pure substances or mixtures, crystalline or amorphous. A crystalline solid is one in which atoms are arranged in a regular way. There is long range order extending over the entire crystal, which can therefore be described as being composed of atomic/molecular-level building blocks that repeat. The atomic-level order in a crystalline solid is often reflected in the well-defined faces of the crystal, but many crystalline solids exist as fused polycrystalline masses in which the order is not readily apparent at the macroscopic level. Examples of pure substances that are crystalline solids at room temperature and pressure are iron metal, diamond, and table salt (NaCl) and sugar (C_{12}H_{22}O_{11}). In amorphous solids atoms are positioned in an irregular manor and the solids lack long range order. Many important solid materials are amorphous such as synthetic fibers, plastics, and glasses, but pure solid substances such as elemental phosphorus or sulfur may also exist in amorphous forms.

##Need a pretty photograph here and maybe change the examples above to match the picture.

Classification of Solids

The lack of a well-defined repeating structure means that amorphous materials are more difficult to describe systematically, and we will restrict our discussion here to crystalline solids. Like liquids, solids are condensed phases in which the constituent particles are in contact and the properties are determined by the nature of the interactions holding the particles together. Solids can be broadly classified, based on these interactions, as van der Waals, ionic, covalent or metallic.

Van der Waals (molecular) solids are those in which the particles are held together by the IMF’s discussed in the previous chapter. These forces are collectively known as Van der Waals forces: dipole-dipole including hydrogen bonding, dipole-induced dipole, and London dispersion forces. Van der Waals solids are typically molecular and it is important here to distinguish between the strengths of the intramolecular covalent bonds (200 to 600 kJ/mol) and the strengths of the intermolecular forces holding these molecules together in the solid (0.05 to 30 kJ/mol).
Ionic solids are composed of oppositely charged ions combined to produce a neutral solid. The forces holding the ions together are the coulomb forces between the oppositely charged ions. Since the charges, in this case, are whole charges rather than the small partial charges found in van der Waals solids, the attractive forces between ions in ionic solids are stronger than those between the molecules in van der Waals solids.

In covalent solids, the forces holding the solid together are covalent bonds. For example, in a diamond crystal each carbon atom is covalently bonded to its nearest neighbors, and the entire crystal can be viewed as a giant molecule. These solids are also called network-covalent or covalent network solids.

In metallic solids, positively charged spherical metal atom cores are held together by attractions to their valence electrons which are delocalized over the whole crystal. The details of the bonding in metals will be discussed later in the chapter.

### Summary of Crystalline Solids

<table>
<thead>
<tr>
<th>Interaction Type</th>
<th>Constituent Particles</th>
<th>Melting Point</th>
<th>Attractive Forces</th>
<th>Schematic Diagram</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Van derWaals</td>
<td>Molecules</td>
<td>Moderate to low</td>
<td>Dipole, H-bonds, Dispersion</td>
<td>![Schematic Diagram]</td>
<td>Iodine (I₂) Sucrose (C₁₂H₂₂O₁₁)</td>
</tr>
<tr>
<td>Ionic</td>
<td>Ions</td>
<td>High to very high</td>
<td>Ion-ion</td>
<td>![Schematic Diagram]</td>
<td>NaCl K₂SO₄</td>
</tr>
<tr>
<td>Covalent</td>
<td>Covalent Network</td>
<td>Very high</td>
<td>Covalent bonds</td>
<td>![Schematic Diagram]</td>
<td>Diamond (C) SiO₂</td>
</tr>
<tr>
<td>Metallic</td>
<td>Metal atoms</td>
<td>Variable</td>
<td>Metallic bonds</td>
<td>![Schematic Diagram]</td>
<td>Na W</td>
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</table>


<table>
<thead>
<tr>
<th>Type of Solid</th>
<th>Melting Point</th>
<th>Attractive Forces</th>
<th>Hardness</th>
<th>Conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular</td>
<td>Low</td>
<td>Van der Waals</td>
<td>Soft to Brittle</td>
<td>Nonconducting</td>
</tr>
<tr>
<td>Ionic</td>
<td>High to Very High</td>
<td>Ion-ion</td>
<td>Hard and Brittle</td>
<td>Nonconducting Solid, Conducting Liquid</td>
</tr>
<tr>
<td>Covalent Network</td>
<td>Very High</td>
<td>Covalent bonds</td>
<td>Very Hard</td>
<td>Usually Nonconducting</td>
</tr>
<tr>
<td>Metallic</td>
<td>Variable</td>
<td>Metallic bonds</td>
<td>Variable, Malleable</td>
<td>Conducting</td>
</tr>
</tbody>
</table>

**Crystalline Solids: The Unit Cell**

Crystalline solids have patterns that repeat. This is called translational symmetry because by translating an original object you come to an identical object. (Translate just means to slide the object without rotating it). In order to describe translational symmetry you don’t have to know what the objects are, just where they are located. In crystalline solids, the actual object that is being translated is represented by a point called a **lattice point**. The lattice point might represent a single atom, a single molecule, or a collection of atoms or molecules – whatever it represents repeats by translational symmetry. The collection of lattice points that describes the crystalline solid defines a crystal lattice. The lattice points can be used to draw boxes called unit cells, and another way of looking at the translational symmetry is to imagine using the unit cells as building blocks to construct the whole crystal.

In two dimensions, this is illustrated in the following figure, where the repeat unit shown in (a) is a single foot.
There are only 12 feet shown in the array, but imagine that the pattern repeats to cover a plane that contains Avogadro’s number of feet. In order to represent the translational symmetry, the lattice points must have identical environments in the pattern and therefore be in the same place relative to each foot. In (b), a lattice point is arbitrarily placed on each big toe. In (c), the lattice points are connected to form unit cells. Because each lattice point is shared by 4 cells and each cell has a lattice point in each of its 4 corners, there is one lattice point per unit cell (4 x ¼ = 1). There is one foot per lattice point and one lattice point per unit cell so there is one foot per unit cell, although to get a whole foot the pieces of the three feet that enter a single unit cell must be added. In (d), the lattice points show the translational symmetry without showing the object being translated. Notice that while the relative positions of the lattice points are uniquely determined by the underlying translational symmetry, there is more than one unit cell that can be drawn. A different choice of the unit cell is outlined in black in (d). Also, if you imagine sliding the lattice in (d) over the feet in (a), you can see that the lattice points could have been chosen in spaces between the feet, with one whole foot in each unit cell.

For actual crystals, we are interested in three dimensions. It turns out that nature doesn’t use many different kinds of translational symmetry, so that in three dimensions the translational symmetry in all crystalline solids can be described for the 7 existing crystal systems with just 14 patterns called Bravais lattices. With all of the complexity found in crystalline solids, this is pretty amazing. But remember that the objects represented by the lattice points can be very complex and can have internal symmetry.

The least symmetrical crystal system is triclinic: all cell edges unequal and all angles between the edges not equal to each other and not equal to 90°. The most symmetrical crystal system is cubic: all cell edges equal and all angles equal to 90°. The remaining five crystal systems run the gamut in between.
Since cubes serve as the unit cells in the systems that we will be examining, it is useful to visualize their features and what happens when identical cubes pack together to fill space. An isolated cube has 12 edges, 6 faces and 8 corners. When identical cubes are packed together, each face of a cube is shared by two cubes, each edge of a cube is shared by 4 cubes, and each corner of a cube is shared by 8 cubes. Also notice that six cube edges come together at each corner.

There are three possible Bravais lattices for the cubic system. These are shown in the following figure, where the spheres represent lattice points: simple or primitive cubic (P), body-centered cubic (BCC) and face-centered cubic (FCC). The difference between these is in the number of lattice points per unit cell.

In the simple cubic lattice, each of the eight corners of the unit cell contains a lattice point which is shared by the 8 unit cells that meet at each corner. Therefore, the 8 corner lattice points account for only 1 whole lattice point for each unit cell \((8 \times 1/8 = 1)\). In the body-centered cubic cell, in addition to the one lattice point from the corners, there is a lattice point in the center of the cube to give a total of two lattice points per unit cell. This means that whatever is represented by the lattice point at the corner of the cube is also found at its center. In a face-centered cubic cell, in addition to the lattice point associated with the corners, there is a lattice point in the center of each of the 6 faces. Since each face is shared by two cells, \(1/2\) of each face lattice point is assigned to each cell, and the six faces contribute 3 lattice points \((6 \times 1/2 = 3)\) per cell for a total of four lattice points per unit cell. In a face-centered cubic cell, whatever motif is associated with the lattice points at the corners of the unit cell also appears in the center of each face.
12.2 Atomic Solids

Metals

Because many metals crystallize in a cubic unit cell with only one atom per lattice point, some of the simplest crystal structures to visualize are those found for metals.

When there is one atom per lattice point, you can imagine that each atom lies with a lattice point at its center, and that the atom extends out from its center forming a sphere that makes contact with its nearest neighbors. The number of nearest neighbors is called the coordination number. The lattice points, and the contents of the unit cell when there is only one atom per lattice point, are compared in the following figure for the three types. In these cases, all of the atoms in the cell are identical and the different colors are only to make the geometry easier to visualize. Authors: The following is a Kotz 7e figure. Should we redo one with all the atoms the same color?

In a simple cubic arrangement, nearest neighbors make contact along the cell edges. Each atom has six nearest neighbors, because six cell edges come together in each corner. In the body-centered case the atom in the center makes contact with the 8 corner atoms, and contact is along the body diagonal. In a face-centered cell, contact is along the face diagonal. Although it is difficult to visualize here, in a face-centered cell each atom has 12 nearest neighbors. This will become easier to visualize when we consider close-packing below. Authors: Simplify? Do we care about coordination numbers?

To do calculations based on experimental data, it is often necessary to know the relationship between the edge length of the unit cell, $a$, and the radius of the atoms, $r$, that comprise it. Because the contact between atoms is different for each of the three types, the relationship between the edge length and the atom radius is also different for each.

In the simple cubic cell, where the atoms meet along the edge of the cell, the edge of each cell is twice the radius of the atom: $a = 2r$. 
In the face-centered cell, the contact is along the face diagonal. A face diagonal passes through the diameter of the atom in its face (a distance of $2r$) and halfway through each of two corner atoms for a distance of $r$ from each. The total distance along the face diagonal is therefore $4r$ and each edge has a length of $a$. From the Pythagorean theorem, $a^2 + a^2 = (\text{face diagonal})^2$ or face diagonal = $a\sqrt{2} = 4r$.

In the body-centered cell, the atoms meet along the body diagonal. The diagonal passes through the diameter of the atom in the center of the cell, but also passes halfway through each of the corner atoms. The contribution from each of the two corner atoms is $r$, and the contribution from the center atom is $2r$, so that the entire body diagonal has a length of $4r$. In this case the right triangle for the calculation is composed of the body diagonal ($4r$), an edge ($a$) and a face diagonal ($a\sqrt{2}$), outlined in red in the figure above, to give $a^2 + (a\sqrt{2})^2 = (4r)^2$ or $a\sqrt{3} = 4r$.

The results for all three are summarized in the following table and are valid for atomic substances that crystallize in cubic lattices with one atom per lattice point, where $a$ is the edge length of the unit cell and $r$ is the radius of the atom.

<table>
<thead>
<tr>
<th>Lattice</th>
<th>Atoms per cell</th>
<th>$r$ to a relationship</th>
<th>$r$ to a factor</th>
<th>Coordination number</th>
<th>% Volume Occupied</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple Cubic</td>
<td>1</td>
<td>$2r = a$</td>
<td>$r = 0.5a$</td>
<td>6</td>
<td>52.4</td>
</tr>
<tr>
<td>Body-centered Cubic</td>
<td>2</td>
<td>$4r = a\sqrt{3}$</td>
<td>$r = 0.43301a$</td>
<td>8</td>
<td>68.0</td>
</tr>
<tr>
<td>Face-centered Cubic</td>
<td>4</td>
<td>$4r = a\sqrt{2}$</td>
<td>$r = 0.35355a$</td>
<td>12</td>
<td>74.0</td>
</tr>
</tbody>
</table>

**EXAMPLE PROBLEM: Atomic Solids 1. Relationship between Edge Length and Atomic Radius**

Metallic uranium crystallizes in a body-centered cubic lattice, with one U atom per lattice point. How many atoms are there per unit cell? If the edge length of the unit cell is found to be 343 pm, what is the metallic radius of U in pm?
Solution: For a body-centered cubic lattice with one atom per lattice point, there are 2 atoms per unit cell. For this type of lattice the atoms are in contact along a body diagonal and \(4r = a\sqrt{2}\), where \(r\) is the metallic radius and \(a\) is the edge length of the cell.

Thus, \(r = 0.433a = 0.433 \times 343\) pm = 149 pm

EXAMPLE PROBLEM: Atomic Solids 2. Relationship between Density and Unit Cell Parameters.

The element silicon is found to crystallize in a face-centered cubic lattice, with an edge length of 541.7 pm. If the density of solid silicon is 2.348 g/cm\(^3\), how many Si atoms are there per unit cell?

Solution:

Step 1. Since the density is given in g/cm\(^3\), use the edge length to calculate the volume of the cell in cm\(^3\). Then use the density to calculate the mass in one unit cell.

For a cubic cell the volume is the edge length cubed. 1 pm = 10\(^{-10}\) m = 10\(^{-12}\) cm

\[V_{\text{cell}} = (541.7 \text{ pm})^3 = (541.7 \times 10^{-10} \text{ cm})^3 = 1.590 \times 10^{-22} \text{ cm}^3\]

\[M = D \times V\]

\[M_{\text{cell}} = 2.348 \text{ g/cm}^3 \times 1.590 \times 10^{-22} \text{ cm}^3 = 3.732 \times 10^{-22} \text{ g}\]

Step 2. Use the molar mass of silicon and Avogadro’s number to calculate the mass of 1 Si atom. Then divide the mass of the unit cell by the mass of 1 atom to get the number of atoms in the cell.

\[M_{\text{atom}} = \frac{28.09 \text{ g}}{\text{mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} = 4.665 \times 10^{-23} \text{ g/atom}\]

\[\text{number of atoms} = \frac{3.782 \times 10^{-22} \text{ g}}{\text{cell}} \times \frac{1 \text{ atom}}{4.665 \times 10^{-23} \text{ g}} = 8 \text{ atoms/cell}\]

Since you were told that the unit cell was face-centered cubic, are you surprised to see 8 atoms per cell? Silicon crystallizes with the diamond structure in which each atom is covalently bonded to 4 others to give a network covalent solid. It does have a face-centered cubic cell, but it has 2 atoms per lattice point for a total of 8 atoms per cell.

Active figure plus OWL homework.

X-ray Diffraction
Much of our knowledge of the structures of molecules and materials comes from the X-ray diffraction analysis of crystalline solids. In the single-crystal experiment, a beam of monochromatic X-rays strikes a small single crystal and the positions and the intensities of hundreds to thousands of diffracted beams are measured. Because it is the electrons in the atoms that scatter X-rays, the experiment gives information about the electron density in the crystal, which in turn shows how the atoms are arranged in the unit cell. An alternative experiment is neutron diffraction, where the neutron beam is scattered by the nuclei of the atoms. X-rays are more commonly used because they are easily generated in sealed tubes in the laboratory by bombarding a metal target with electrons, whereas the production of a neutron beam requires a nuclear reactor.

![Figure 12.XX X-ray photograph of a myoglobin crystal taken by the precession method. A spot appears wherever a diffracted beam hits the film. Darker spots correspond to more intense diffracted beams. The positions of the spots reflect the size and shape of the unit cell. The intensities of the spots reflect the arrangement of the atoms in the unit cell.]

The size and shape of the unit cell can be determined from the positions of the diffracted beams, while the intensities give information about what kinds of atoms are in the unit cell and where they are located. Because X-rays are electromagnetic radiation with wavelengths comparable to atomic dimensions, diffraction can be described in terms of the reflection of the X-ray beam off of sets of parallel planes in the crystal. These planes are drawn through lattice points and so reflect the periodicity of the scattering motifs. A diffracted beam is to be expected whenever the scattered radiation from the array of identical motifs is in phase. The condition for observing a reflection by diffraction from a crystal is known as Bragg’s Law and can be stated

\[ n\lambda = 2d \sin \theta \]

where \( \lambda \) is the wavelength of the X-radiation, \( n \) is an integer called the order of the reflection, \( d \) is the spacing between the set of planes for the reflection, and \( \theta \) is the angle that the incident X-ray beam
makes with the planes. A reflection with \( n=1 \) is called a first order reflection, \( n=2 \) a second order reflection, and so forth.

![Reflection Diagram](image)

\[
ab + bc = n\lambda = 2d \sin \theta
\]

Figure 12.xx Bragg’s Law: In order to have constructive interference, the difference in path length of the beam reflected from parallel planes, separated by a distance \( d \), must be an integral number of wavelengths, \( n\lambda \). The difference in path length is \( ab + cd \).

Because the planes are drawn through the lattice points, they reflect the size and shape of the unit cell. Therefore, the scattering angle from an appropriate set of planes can be used to determine the unit cell edge length, and this in turn can be used to determine the radius of an atom.

**EXAMPLE PROBLEM: Determining a d-spacing and a radius from a scattering angle.**

Silver metal crystallizes in a face-centered lattice with 1 atom per lattice point. Monochromated X-radiation from a copper target has a wavelength of 154 pm. If this radiation is used in a diffraction experiment with a silver crystal, a first order diffracted beam is observed at a theta value of 10.91°. What is the d-spacing between the planes that gave rise to this reflection? If this is the spacing between parallel planes that delimit the unit cell, what is the metallic radius of a silver atom?

**SOLUTION**

**Step 1.** Solve for \( d \) using the relationship \( n\lambda = 2d \sin \theta \), where \( n = 1 \), and \( \theta = 10.91^\circ \):

\[
d = \frac{n\lambda}{2 \sin \theta} = \frac{(1)(154 \text{ pm})}{2 \sin(10.91^\circ)} = 407 \text{ pm}
\]

**Step 2.** Determine the metallic radius of a silver atom.

The d-spacing corresponds to the edge length of the cubic cell and is 407 pm. Because the structure is cubic close-packed (face-centered cubic) the relationship between the edge length of the cell, \( a \), and the radius of the atom, \( r \), is \( 4r = a\sqrt{2} \).

\[
r = \frac{407\sqrt{2}}{4} = 144 \text{ pm}
\]
Close-packing of spheres and percent of occupied space

In a metal crystal, the metal atoms can be viewed as spheres that are packed together and one might expect that there would be many examples of metals that adopt each of the three structures described above. In fact, while many metals adopt the body-centered cubic structure (examples are barium, chromium, iron, lithium, manganese, molybdenum, tungsten and vanadium), and even more adopt the face-centered cubic structure (examples are aluminum, calcium, copper, gold, lead, nickel, silver and strontium), the simple cubic structure is rarely found for metals (polonius is a reported example). As a general rule, crystalline solids minimize their energies by packing atoms as closely together as possible, and this tendency is observed unless directional forces (such as covalent or hydrogen bonds) lower the energy enough to overcome it. The lack of metals found with the simple cubic structure suggests that this arrangement is not a good one for packing. To see if this is correct, let’s calculate the percent of the volume occupied in the three structures.

The volume of a cubic unit cell is easily calculated in terms of its edge length \( a \), and for each of the three types, the unit cell volume is simply \( a^3 \). The volume occupied by a spherical atom is easily calculated in terms of the radius \( r \) as \( \frac{4}{3} \pi r^3 \) and the number of atoms in each unit cell is known. The ratio of the volume occupied by atoms in the cell to the total volume of the cell can be calculated without knowing the value of either \( a \) or \( r \), because the ratio between them is known for each structural type. Putting this together gives the formula

\[
\text{% volume occupied} = n \times \frac{4}{3} \pi \left( \frac{a}{r} \right)^3 \times 100
\]

where \( n \) is the number of atoms per unit cell. Applying this to each structural type gives 52.4 %, 68.0 % and 74.0 % for simple cubic, body-centered cubic and face-centered cubic, respectively. The low percent of volume occupied for the simple cubic structure is consistent with the lack of metals that adopt this structure, while the most efficient packing arrangement is the face-centered cubic one. Is the face-centered cubic structure the most efficient packing arrangement possible?

It turns out that there are two ways to pack spheres the most efficiently, and that one of these corresponds to the face-centered cubic structure. As a result, the face-centered cubic structure is also called the cubic close-packed structure. The other way results in an hexagonal lattice and the structure is called the hexagonal close-packed structure. In both of these structures, the percent volume occupied is identical at 74.0 %.

When you pack spheres, there is always some space left open. It is useful to try to visualize the close-packing of spheres, because many ionic crystals consist of a lattice of nearly close-packed ions with smaller counter ions in the holes between them. Visualization of the packing is often done by stacking layers of spheres that are themselves packed as efficiently as possible.
The first layer of spheres has an arrangement where each sphere is surrounded by six spheres that form a hexagon. Wherever three spheres meet in a layer, a triangular depression is formed that could act as a seat for a sphere in the next layer, but these seats are so close together that adjacent ones can’t be occupied. In placing the second layer, whenever an atom occupies one of these seats a tetrahedral hole is formed in the center of the tetrahedral arrangement of the four atoms. At the same time, a set of octahedral holes is created with the vacant triangular seats at their centers. Here six atoms, three from each layer, come together. In an infinite array, there are two tetrahedral holes and one octahedral hole for each sphere.

The second layer is identical to the first one, but is shifted relative to it. Because the first and second layers are not directly over each other they are called A and B. When it comes to placing the third layer, there are two ways to do it, each one corresponding to one of the two possible close-packed structures. The third layer can be positioned so that the spheres are directly above the spheres in the first layer. This arrangement is called ABAB... and creates the hexagonal close-packed structure. Alternatively, the third layer can occupy the set of positions that are not directly above the spheres in the first layer. This arrangement is called ABCABC... and leads to the cubic close-packed structure. It’s a bit tricky to see that the ABC three layer stack is identical to the face-centered cubic lattice because the stacking direction is along the body diagonal of the cube. It is, however, easier to see here that the coordination number of the spheres in a close-packed structure is 12. Each sphere makes contact with 6 spheres in the same layer, and 3 spheres each in the layer above and the layer below, for a total of 12.

12.3 Some Simple Ionic Solids

In an ionic solid, both cations and anions are present, so that the previous structures composed of identical spheres cannot be used to describe them exactly. However, many ionic crystals can be visualized in terms of these structures. Often in ionic structures, one type of ion will occupy a set of
positions that corresponds to either the simple cubic structure or one of the close-packed structures, with the counter ions occupying positions defined by the holes in the lattice formed by the first ion. Since anions tend to be larger than cations, it is often easier to visualize that the anions form the basic framework and the cations sit in the holes, but this need not be the case. Regardless of how the ions pack into the unit cell, the ratios of the numbers of ions of each type must match the stoichiometry of the compound.

The CsCl Structure.

One of the simplest structural types for 1:1 salts, which is observed when the cation and the anion are close to the same size, is the cesium chloride structure. Cesium chloride crystallizes in a simple cubic unit cell with one cesium ion and one chloride ion, per lattice point. Since there is 1 lattice point per unit cell, there is one CsCl formula unit per unit cell. The cesium chloride unit cell is shown schematically in the following figure:

![CsCl Structure Diagram](image)

At first glance the cell looks body-centered, but it is not because the sphere at the center is not the same as the ones at the corners. The 8 red spheres at the corners each belong to 8 unit cells and therefore contribute only one red sphere to the unit cell (1/8 x 8 = 1). The cell also contains a whole purple sphere in its interior, so there is one red sphere and one purple sphere per unit cell. This gives a 1 to 1 ratio of red to purple, which is the correct ratio for CsCl. So which is the cesium ion and which is the chloride ion? The answer is it doesn’t matter. You can view the lattice as a simple cubic array of chloride ions with a cesium ion in the center of each unit cell, or as a simple cubic array of cesium ions with a chloride ion in the center of each unit cell. Alternatively, the structure has been described as interlocking simple cubic lattices of anions and cations.

When an ion lies in the center of a cube in which the counter ions occupy the corners, the ion in the center is said to be in a **cubic** hole. In the cesium chloride structure, both the cesium ion and the chloride ion have coordination numbers of 8. Some other compounds that adopt the cesium chloride structure are cesium bromide and thallium chloride.

**Octahedral and Tetrahedral Holes in the Cubic Close-packed Lattice.**

Before looking at more structures, it is useful to visualize the positions of the octahedral and tetrahedral holes in a cubic close-packed array of ions. In the diagrams below, the gray spheres show the positions of a cubic close-packed (face centered cubic) array of ions in the unit cell. The positions of the octahedral holes are shown in the cell on the left. There is an octahedral hole on each cell edge and in
the center of the cell. A cube has 12 edges, and each edge is shared by 4 cells, so there are 4 octahedral holes per unit cell, 3 from the edges \((1/4 \times 12 = 3)\) plus 1 in the center.

The positions of the tetrahedral holes are shown in the diagram to the right. There are 8 of these in a cubic arrangement in the interior of the cell. Points in the interior of the cell belong entirely to the unit cell, so there are 8 tetrahedral holes per unit cell.

The NaCl Structure.

The sodium chloride structure is another cubic structure commonly adopted by 1 to 1 salts. A model of the sodium chloride unit cell is shown to the left below, where the sodium ions are represented by white spheres and the chloride ions by gold spheres. The structure is face-centered cubic, with one sodium ion and one chloride ion per lattice point. Since there are 4 lattice points per unit cell this gives a total of 4 NaCl moieties per unit cell. You can come to the same conclusion by counting spheres in the unit cell. Notice that the gold-colored chloride ions have the same arrangement as in a face-centered metal with a cubic close-packed structure. Therefore there are a total of 4 chloride ions per cell (1 from the 8 corners plus 3 from the 6 faces). The sodium ions (white spheres) occupy the octahedral holes created by the chloride ions. This alone tells you there are 4 per cell. Or you can count: there is a sodium ion on each of the cell edges and one in the center of the cell, for a total of 4 sodium ions per unit cell. Notice that the ratio of \(\text{Na}^+\) to \(\text{Cl}^-\) is 4:4 or 1:1.
If the positions of the sodium ions and the chloride ions were interchanged, the same extended structure would result, and the sodium chloride structure is sometimes described as two interpenetrating face-centered cubic lattices. This can be seen by inspecting the extended structure to the right of the unit cell. Finally, both the cation and the anion have a coordination number of 6, as each is surrounded by an octahedron of counter-ions.

**The ZnS Structure.**

The ZnS (zinc blende) structure can be described as a cubic close-packed arrays of anions with cations in half of the tetrahedral holes. In the diagram below, sulfide ions are represented by gold spheres and zinc ions are represented by blue spheres. There are 4 zinc ions in the interior of the unit cell and 4 sulfide ions per unit cell, \((1/8 \times 8) + (1/2 \times 6)\), which gives the correct stoichiometry for a 1:1 salt. Each zinc ion makes contact with the 4 sulfide ions comprising the tetrahedral hole, and has a coordination number of 4.

**EXAMPLE PROBLEM: Determining a chemical formula from the unit cell contents.**

The unit cell of a compound of uranium and oxygen that crystallizes in a cubic unit cell is shown in the diagram below, where the gray spheres represent uranium ions and the red spheres represent oxide ions. What is the chemical formula of the compound? What is the coordination number of the uranium ions in the crystal?

**SOLUTION:** You may recognise that the lattice can be viewed as a cubic close-packed array of uranium ions with oxide ions in all of the tetrahedral holes. This gives 4 uranium ions and 8 oxide ions per unit cell, and a U:O ratio of 4:8. The chemical formula is therefore \(\text{UO}_2\).
Alternatively, the ions can simply be counted based on their positions in a cubic unit cell:
Uranium ions: corners = 8 x 1/8 = 1; faces = 6 x 1/2 = 3; total = 1 + 3 = 4.
Oxide ions: 8 in the interior of the cell = 8

To visualize the coordination number of the uranium ions, focus on the uranium ion on the top face of the cell. This ion has the four oxygen ions in the cell directly beneath it as nearest neighbors. But because of the translational symmetry, the uranium ion on the bottom face of the cell is identical to the one on the top face of the cell. This uranium ion is closest to the four oxygen ions directly above it in the cell. Therefore, in the extended structure, each uranium ion lies at the center of a cube of oxygen ions and has a coordination number of 8.

Nearest neighbors in simple ionic solids and the sizes of ions.

You have seen that different crystalline forms are observed for compounds that have the same stoichiometry. You might be wondering why this is the case. If ions are treated as hard spheres, to minimize energy we would expect that ions of opposite charge would be in contact and that there would be as many such interactions as possible. At the same time, ions of the same charge should repel one another, and would not be expected to be in close contact. Because a tetrahedral hole is smaller than an octahedral hole, which in turn is smaller than a cubic hole, relative size can dictate the type of vacancies that are filled in a lattice and this can dictate the type of lattice formed. Suppose a cation (red) is packed with anions (gray) as in the following diagrams. Let the square arrangements of 4 anions represent the four-atom plane in an octahedral hole, while the triangular arrangement of three represents three of the four anions comprising a tetrahedral hole.

![Diagram of nearest neighbors](image)

An unfavorable situation is depicted in the middle diagram. Here the cation (red) is in a hole formed by the anions (gray), but is too small to touch all of them simultaneously. A combination like this would not minimize energy, and the substance could better minimize its energy by having its cations in the smaller tetrahedral holes, where contact can be made with all of the anions. In the situation on the far right, a larger cation (green) placed in the octahedral hole drives the anions apart a bit and creates a favorable situation for ionic bonding. If a still larger cation was combined with the same anion, the cubic hole could become a better alternative than the octahedral hole, because a sufficiently larger cation could accommodate more anions and would permit 8 interactions per cation instead of 6. Thus for a given anion, a relatively small cation might result in a close-packed structure in which the cations occupied tetrahedral holes, a somewhat larger cation might favor occupation of the octahedral holes, while a still larger cation might result in a structure in which the cation occupies cubic holes.
Regardless of the packing arrangement, ions of opposite charge are assumed to be in contact, and the distance between their centers is taken to be the sum of their ionic radii. Many ionic radii have been obtained from the distances between ion centers obtained from crystallographic data. Since the distance gives a sum rather than an individual ionic radius, one of the values must be known in order to determine the other value. By looking at values from many different structures, sets of self-consistent experimental ionic radii can be determined.

**EXAMPLE PROBLEM: Density from unit cell data and ionic radii**

Magnesium sulfide crystallizes with the sodium chloride structure and is represented in the following model with $S^{2-}$ shown in green and $Mg^{2+}$ shown in red. If the radius of the $Mg^{2+}$ ion is 72 pm and the radius of the $S^{2-}$ ion is 184 pm, what is the density of crystalline MgS in g/cm$^3$?

**SOLUTION:** The mass of the unit cell can be calculated because there are four MgS formula units per unit cell and the molar mass is known. The volume of the unit cell can be calculated as its edge length cubed. Because the ions are in contact along an edge, the length of the edge is twice the sum of the ionic radii, which were given. The density is the ratio of the mass of the cell to the volume of the cell.

**Step 1.** Calculate the mass of the unit cell which contains 4 formula units of MgS (Molar mass = 56.37 g/mol).

\[
\frac{4 \text{ molecules}}{\text{cell}} \times \frac{56.37 \text{ g}}{\text{mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ molecules}} = 3.74 \times 10^{-22} \text{ g/cell}
\]

**Step 2.** Calculate the edge length of the unit cell, and from this its volume.

Edge length = 2(72.0 pm) + 2(184 pm) = 512 pm

\[
512 \text{ pm} \times \frac{10^{-12} \text{ m}}{\text{pm}} \times \frac{100 \text{ cm}}{\text{m}} = 5.12 \times 10^{-8} \text{ cm}
\]

\[
V_{\text{cell}} = (5.12 \times 10^{-8} \text{ cm})^3 = 1.34 \times 10^{-22} \text{ cm}^3
\]

**Step 3.** Calculate the density from the mass and the volume of the cell.

\[
D = \frac{3.74 \times 10^{-22} \text{ g}}{1.34 \times 10^{-22} \text{ cm}^3} = 2.79 \text{ g/cm}^3
\]
12.4 Other Types of Crystalline Solids.

It would be wrong to leave you with the impression that all ionic solids are simple, and that only ionic compounds form crystals with lattice points all-in-a-row. Let’s take a quick look at a few solids that are more complicated.

Ceramics are solid inorganic materials that are typically prepared by heating at elevated temperatures. In general, they are insulators, but in 1986 a lanthanum-barium-copper oxide ceramic was discovered to be a high-temperature superconductor. High temperature in this context was only 30K, but subsequent investigations have lead to temperatures above that of liquid nitrogen (77K) which is easily attained. These ceramics consist of layers of copper oxide spaced by layers containing other atoms. One such high-temperature superconductor is a yttrium-barium-copper oxide ceramic, with the unit cell shown in the following diagram. The spheres in the model on the right represent ionic radii.

The unit cell in this case is primitive orthorhombic (one lattice point per unit cell, all cell edges different lengths, all angles = 90°). You can see that, in this case, a single lattice point corresponds to a fairly complicated motif. Can you figure out the formula of the compound by looking at the unit cell? Hint: it’s sometimes called a 1-2-3 superconductor. Did you get it? The formula is YBa$_2$Cu$_3$O$_7$.

Zeolites are solid inorganic materials that have an aluminosilicate framework that results in a porous structure. They are network-covalent structures with additional materials housed in the pores. These substances can act as “molecular sieves” because their pore structures have molecular dimensions of variable sizes that can hold some molecules or ions, but not others. For example, zeolites are widely used for ion-exchange in water purification and softening, and in chemistry as drying agents.

Faujasite is a naturally occurring zeolite with a composition given by (Ca$_3$Na$_2$Mg)$_3$[Al$_7$Si$_{17}$O$_{48}$]·32 H$_2$O. It crystallizes in a face-centered cubic lattice, which means that it has 4 lattice points per unit cell, but it
has a complicated structure with a lot of symmetry. The unit cell of a synthetic calcium faujasite is shown in the following diagram, viewed down a body diagonal of the cube. A lot of atoms are super-imposed in the view shown, so don’t try to count them, but note the silicon-aluminum-oxygen covalent framework that extends throughout the crystal and the large cages and channels that are formed. This synthetic version has been dehydrated, and there are only calcium ions (green) present to maintain electrical neutrality.

**Organic** molecules don’t look much like they should form crystals, but they do (check out your sugar bowl sometime). Acetamide, CH$_3$CONH$_2$, is a small organic molecule that exists as a crystalline solid at room temperature. (Oddly enough it is considered to be a mineral). Models of its unit cell are shown below.
Acetamide has a unit cell with symmetry that is hard to visualize, so let’s not worry about that. Just focus on the facts that the crystal is made up of molecules that are packed together, and that the unit cell does repeat to fill space. There are no ions and no covalent networks so the molecules are held together in the crystal only by van der Waals forces. In addition to dispersion forces, there is extensive intermolecular hydrogen bonding between the hydrogen atoms of the NH\textsubscript{2} groups and the oxygen atoms of the CO groups. If you look closely at the space-filling model, you can see places where the H atoms of the NH\textsubscript{2} groups are cozying up to oxygen atoms. Acetamide melts at around 80°C and boils at 222°C. Compare this to N\textsubscript{2}N-dimethylacetamide, CH\textsubscript{3}CON(CH\textsubscript{3})\textsubscript{2}, which is a liquid at room temperature, boils at 165°C, and cannot form hydrogen bonds.

12.5 Bonding in Solids

Ionic Bonding: Lattice Energy

We have said that ionic solids are held together by the strong attractive forces between oppositely charged ions. Coulomb's law in this context can be written:

\[ E = a \frac{q_1 q_2}{r} \]

where \( a \) is a constant, \( q_1 \) and \( q_2 \) are the charges on the ions and \( r \) is the distance between their centers.

If the details of how the ions are packed together in the solid are known, it ought to be possible to use Coulomb's law to calculate the energy released when molar quantities of the isolated ions in the gas phase (zero interaction energy) come together to form a mole of crystalline solid. In such a calculation the strongest attractive forces would be between nearest neighbors of opposite charge, but it would be necessary to sum up all of the attractive and repulsive forces, including those operating at a distance. Summations like this are done, and give calculated values of the binding energy in crystals. These values can also be determined experimentally.

Let’s see if we can use some of the experimental results that you have already seen to get a more quantitative idea of what this means. The binding energy in a crystalline lattice is called the lattice energy and is given the symbol \( U \). It is the energy required to separate one mole of a crystalline ionic solid into its gaseous ions. Alternatively it can be defined as the energy released when one mole of a crystalline ionic solid forms from its gaseous ions. For example, for NaCl:

\[ \text{NaCl(s)} \rightarrow \text{Na}^+(g) + \text{Cl}^-(g) \quad U = \Delta H = \text{lattice energy (kJ/mol)} \]

Note that separating the ions is an endothermic process, while the reverse reaction is exothermic.

Recall Hess’s Law (Chapter 5) that says that if a process can be expressed as the sum of other processes, then \( \Delta H \) for the overall process is the sum of the \( \Delta H \)'s for the individual steps. The sum of the equations for the following 5 steps gives the equation for the lattice energy of sodium chloride.
(1) The vaporization (sublimation) of solid sodium metal

\[ \text{Na}(s) \rightarrow \text{Na}(g) \quad \Delta H_{\text{sublimation}}^o = 107 \text{ kJ} \]

(2) The first ionization energy of sodium: \( \text{(Chapter 7)} \)

\[ \text{Na}(g) \rightarrow \text{Na}^+(g) + e^- \quad \text{IE} = 496 \text{ kJ} \]

(3) The dissociation of \( \frac{1}{2} \) mol of \( \text{Cl}_2(g) \) – this is half of the Cl-Cl bond energy = 242 kJ/mol: \( \text{(Chapter 8)} \)

\[ \frac{1}{2} \text{Cl}_2(g) \rightarrow \text{Cl}(g) \quad \frac{1}{2} \text{BE} = 121 \text{ kJ} \]

(4) The electron affinity of chlorine: \( \text{(Chapter 7)} \)

\[ \text{Cl}(g) + e^- \rightarrow \text{Cl}^-(g) \quad \text{EA} = -349 \text{ kJ} \]

(5) The reverse of the enthalpy of formation of \( \text{NaCl}(s) \): \( \text{(Chapter 5)} \)

\[ \text{NaCl}(s) \rightarrow \text{Na}(s) + \frac{1}{2} \text{Cl}_2(g) \quad -\Delta H_f^o = -(-411 \text{ kJ}) = 411 \text{ kJ} \]

Taking the sum of (1) through (5) gives:

\[ \text{NaCl}(s) \rightarrow \text{Na}^+(g) + \text{Cl}^-(g) \quad U = 107 + 496 + 121 - 349 + 411 = 786 \text{ kJ} \]

So, the lattice energy of \( \text{NaCl}(s) \) is 786 kJ/mol. This process can also be described in terms of a cycle that is called a Born-Haber cycle. Authors: do we want a figure?

According to Coulombs law, the energy of interaction between ions of opposite charge increases with the magnitude of the charges and decreases with the distance between them. You can see these effects in the following table of lattice energies, where all of the compounds have the sodium chloride structure. Notice that for ions of the same charge, the magnitudes of the lattice energies decrease as the size of the ions \( \text{(Chapter 7)} \) increases, as this causes an increase in the distance between their centers. Also compare \( \text{MgO} \) with \( \text{NaF} \), where the ions have comparable sizes, but where the higher charge on the divalent ions leads to a much larger lattice energy.

<table>
<thead>
<tr>
<th>Compound</th>
<th>LiF</th>
<th>LiCl</th>
<th>LiBr</th>
<th>NaF</th>
<th>NaCl</th>
<th>NaBr</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>U (kJ/mol)</td>
<td>1037</td>
<td>852</td>
<td>815</td>
<td>926</td>
<td>786</td>
<td>752</td>
<td>3850</td>
</tr>
</tbody>
</table>
EXAMPLE PROBLEM: Calculating a lattice energy from thermodynamic data.

Calculate the lattice energy of KCl(s) using the following thermodynamic data (all data given is in kJ/mol). Would you expect this to be larger or smaller than the value for NaCl(s)?

<table>
<thead>
<tr>
<th>Substance</th>
<th>ΔH_{sublimation}</th>
<th>IE</th>
<th>BE</th>
<th>EA</th>
</tr>
</thead>
<tbody>
<tr>
<td>K(s)</td>
<td>+89.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K(g)</td>
<td></td>
<td>419</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl-Cl</td>
<td></td>
<td>242</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl(g)</td>
<td></td>
<td></td>
<td>−349</td>
<td></td>
</tr>
<tr>
<td>KCl(s)</td>
<td>ΔH_f = −437</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

SOLUTION

The lattice energy is ΔH for the reaction: KCl(s) → K⁺(g) + Cl⁻(g)

Use the data given to write five equations that will sum to give this reaction, and then sum their ΔH’s to get the ΔH value.

(1) K(s) → K(g)    \hspace{1cm} \Delta H_{\text{sublimation}} = 89.6 \text{ kJ}
(2) K(g) → K⁺(g) + e⁻ \hspace{1cm} \text{Ionization energy} = 419 \text{ kJ}
(3) \frac{1}{2} \text{Cl}_2(g) → Cl(g) \hspace{1cm} \frac{1}{2} \text{Bond energy} = 121 \text{ kJ}
(4) Cl(g) + e⁻ → Cl⁻(g) \hspace{1cm} \text{Electron affinity} = −349
(5) KCl(s) → K(s) + \frac{1}{2} \text{Cl}_2(g) \hspace{1cm} −\Delta H_f = −(−438 \text{ kJ}) = 437 \text{ kJ}

Sum (1) – (5):

KCl(s) → K⁺(g) + Cl⁻(g) \hspace{1cm} U = 89.6 + 419 + 121 −349 + 437 = 718 \text{ kJ}

The lattice energy of KCl is 718 kJ/mol. This value is smaller than that for NaCl (786 kJ/mol), as expected because of the larger size of K⁺ compared to Na⁺. Note that the standard heat of formation value for KCl(s) is for the formation of the salt from its elements, so that for the reverse equation the value has the opposite sign.

Do lattice energy OWL here if it is decided to keep this. Need to write.

Metallic Bonding: Band Theory

Most metals are solid crystalline materials that are malleable and ductile and good conductors of heat and electricity. In the simplest bonding model, the metal atom cores are imagined to be held together...
by delocalized valence electrons that account for the lack of directional preference in the bonding, and are free to move about the crystal to conduct electricity.

There is a more formal approach to the bonding in crystalline metallic solids that is similar to the molecular orbital theory that you saw in Chapter 9, except that the valence molecular orbitals in crystals involve all of the atoms in the crystal and so extend over the whole thing. In molecular orbital theory, when two identical orbitals from two identical atoms combine, two molecular orbitals, one of lower energy and one of higher energy, are produced. In a crystal that contains a mole of atoms, a mole of such orbitals will combine to produce a mole of molecular orbitals that extend over the crystal and are very closely spaced in energy, some of lower energy which confer stability and some of higher energy which do not. A group of such orbitals is called a band because the orbitals are nearly continuous in energy. The orbitals in the valence shells of the atoms combine to give a series of bands, some of which are separated by energy gaps.

In the isolated metal crystal, valence electrons occupy the lowest energy orbitals possible in what is called the valence band to account for bonding. The next lowest energy orbitals available act as the conduction band. In order for a material to be a conductor, electrons in the top of the valence band must be able to move into the conduction band when an electric field is applied. For this to happen, the difference in energy between the valence band and the conduction band must be sufficiently small. In a material that acts as a conductor, either the valence band and the conduction band are contiguous, or the valence band and the conduction band overlap, so there is no energy gap. Metals fall into this category and so are conductors.

In an intrinsic semiconductor, the valence band is full and the energy gap is small enough that if the solid is heated, thermal energy becomes sufficient to promote electrons from the valence band into the empty conduction band. Silicon is an example of a semiconductor. In an insulator, the valence band is full and the energy gap is so large that motion of electrons from it to the empty conduction band is prohibited. Diamond is an example of an insulator.

The conducting properties of a semiconductor can be improved by doping with another element. For example, in pure silicon the valence band is full and the conduction band is empty. If some of the silicon atoms are replaced by a group 5 atom such as arsenic, for each Si atom replaced an extra electron is introduced into the lattice. These electrons occupy levels just below the conduction band and are easily promoted into the conduction band, increasing the conductivity of the silicon when a potential difference is applied. Because the dopant introduces negative electrons, this is called an n-type semiconductor. However, if some of the silicon atoms are replaced by group 3 atoms such as gallium, there is one fewer electron in the valence band for each Si atom replaced. This creates positive holes
into which electrons can move when a potential difference is applied, again supporting a current. This is called a p-type semiconductor because it is the presence of positive holes that promotes the current.

Simulation – Metal Bonding: Band Theory

12.6 Phase Diagrams

Phase changes involving solids.

In a solid the particles are held in place relative to one another because they do not have enough energy to overcome the forces that hold them in place. As the temperature of the solid is increased, the average energy of the particles increases. When a temperature is reached where some of the surface particles have enough energy to move away from their neighbors, a dynamic equilibrium is established between the solid and the liquid. For as long as there is some solid present the addition of energy will not result in an increase in temperature, but will convert more solid to liquid. The stronger the attractive forces between the particles, the higher the temperature at which this will occur. A temperature at which a solid and a liquid are in equilibrium at a given pressure is called a melting point. Because solids and liquids are not very compressible and have comparable densities, the melting temperature of a solid does not change much with pressure. However, there is some pressure dependence, so that to specify a melting temperature precisely it is also necessary to specify the pressure. Because a crystal is composed of objects that repeat, the forces holding them together also repeat throughout the lattice. A pure crystalline solid is characterized by a sharp melting point, rather than the gradual softening seen in amorphous materials.

Because the melting point of a solid reflects the strength of the forces holding the particles in the solid together, in general, substances with relatively high melting points also have relatively high boiling points. However, the efficiency with which the particles in a solid pack together varies with their shape and with the geometric details of their interactions. This causes the variation of melting points with strength of attractive forces to be less regular than what is found for boiling points.

As you saw in Chapter 5, the conversion of a solid to a liquid is called melting or fusion and the energy required to effect the conversion is called the heat of fusion, \( \Delta H_{\text{fusion}} \). Fusion is always an endothermic process, because it always takes energy to overcome the forces holding the particles in a solid in place. The reverse process, freezing, is always exothermic. Some heats of fusion at the normal melting point and heats of vaporization at the normal boiling point are given in the following table.

**Table 12.XX Selected Heats of Fusion and Vaporization at the Temperature of the Normal Phase Transition.**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Heat of fusion (kJ/mol)</th>
<th>Melting Point °C</th>
<th>Heat of vaporization (kJ/mol)</th>
<th>Boiling Point °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>methane</td>
<td>0.94</td>
<td>-182.5</td>
<td>8.2</td>
<td>-161.6</td>
</tr>
<tr>
<td>ethane</td>
<td>2.86</td>
<td>-182.8</td>
<td>14.7</td>
<td>-88.6</td>
</tr>
<tr>
<td>propane</td>
<td>3.53</td>
<td>-187.6</td>
<td>19.0</td>
<td>-42.1</td>
</tr>
</tbody>
</table>
methanol  3.16   -97.0  35.3   64.7
ethanol  5.02   -114.3 38.6   78.4
1-propanol  5.20   -127  41.4   97.2
water    6.01   0.0   40.7  100.0
Na       2.60   97.82 97.42  881.4
NaBr     26.11  755   160.7 1390

Note that the heat of fusion is always smaller than the heat of vaporization for a given substance. This reflects the fact that the solid and liquid are both condensed phases in which the particles are fairly close together, while to go to the gas phase all of the attractive forces must be overcome.

Many solids are volatile enough to have appreciable vapor pressures, even at temperatures below their melting points. The direct conversion of a solid to a gas is called sublimation. Like fusion and vaporization, and for the same reasons, sublimation is an endothermic process. The reverse process, deposition, is therefore exothermic. The energy required to sublime a solid is called its heat of sublimation, ΔH\text{sublimation}. How do you think the magnitude of the heat of sublimation of a substance compares to its heat of vaporization? Since melting (s → ℓ) followed by vaporization (ℓ → g) results in the same overall change as sublimation (s → g), according to Hess’s law, the heat of sublimation should be equal to the sum of the heat of fusion and the heat of vaporization. Therefore the heat of sublimation should be the largest of the three.

\[ \Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}} \]
POSSIBLE EXAMPLE PROBLEM – Au: could use just (a) to keep it simple, or could give all values at 298K.

(a) Use the data in Table 12.XX to approximate the heat of sublimation for water. Why is this just an approximation?

(b) At 298 K, the standard heat of formation of H₂O(g) is -241.8 kJ/mol while the standard heat of formation of H₂O(ℓ) is -285.8 kJ/mol. Use this to calculate the heat of vaporization of water and compare your result to the value in table 12.XX.

SOLUTION

(a) ΔH_{sub} = ΔH_{fus} + ΔH_{vap} = 6.01 kJ/mol + 40.7 kJ/mol = 46.7 kJ/mol

For water, the heat of fusion is given at 0°C and the heat of vaporization is given at 100°C. Since ΔH does vary somewhat with temperature, the calculated value for ΔH_{sub} is only an approximation.

(b) H₂O(ℓ) → H₂O(g)  ΔH^* = -241.8 kJ/mol − (-285.8) kJ/mol = 44.0 kJ/mol

The value at 25°C is larger than the value at 100°C (40.7 kJ/mol). At the higher temperature, the molecules in the liquid have a higher average energy and are more gas-like (further apart and less short range order), so less energy should be needed for the conversion.

Could have some OWL here if we decide to do an example problem.

Phase Diagrams

A phase diagram summarizes the conditions at which phases are in equilibrium with each other or at which only a single phase is stable. For a one-component system, the phases are solid, liquid and gas, although some substances have more than one solid phase. The independent variables are temperature and pressure, and these are plotted on the x and y axes, respectively. The phase diagram for water, not to scale, is shown below.
Each point on the diagram represents a specific temperature and pressure. Areas on the diagram correspond to regions where only one phase is stable. Note that the gaseous phase is favored at lower pressures and higher temperatures (lower and to the right) while the solid phase is favored at higher pressures and lower temperatures (upper left). Also notice that the liquid phase occupies a region between the solid and the gaseous phases and is not stable below a certain pressure, regardless of the temperature.

Separating any two areas are lines where the two phases are in equilibrium. You have already seen part of the line TC. This is identical to the curve that shows how the vapor pressure varies with temperature. Since the boiling point is the temperature at which the vapor pressure equals the external pressure, this curve also shows how the boiling temperature varies with pressure. Analogous to this, the curve TA shows how the vapor pressure of the solid varies with temperature, while the line TB represents equilibrium between the solid and liquid phases and shows how the melting temperature varies with pressure. The normal melting point and the normal boiling point are the melting and boiling temperatures at a pressure of 1 atm, and are seen on the diagram where the line P = 1 atm intersects the solid-liquid and the liquid-vapor lines. For water the temperatures corresponding to 1 atm are the familiar 0°C and 100°C for melting and boiling, respectively.

It is instructive to relate the heating curves that were described in Chapter 5 to the line P = 1 atm on the phase diagram. Imagine starting with the solid at P = 1 atm and some temperature below 0°C. Also imagine that the sample is in a cylinder fitted with a frictionless piston that moves to adjust the volume so that the pressure on both sides of the piston is equal to 1 atm. As you heat the solid at constant pressure, its temperature increases until the solid-liquid equilibrium is reached. At this point, further heating causes the sample to melt at 0°C. Additional heating then increases the temperature of the liquid and moves you across the liquid region until the liquid-vapor line is reached and the sample
vaporizes at 100°C. Finally, additional heating raises the temperature of the gas and moves you into the region where the gas is the stable phase.

The liquid-vapor curve TC begins and ends in two points that you may not have seen before. Point T is called the **triple point**. This is the unique point on the diagram where all three phases meet and corresponds to the one temperature and pressure where all three phases are in equilibrium. On the high temperature end, the curve does not extend beyond point C, which is called the **critical point**. The temperature and pressure at this point are called the **critical temperature** and the **critical pressure**, respectively. Analogous to other points defining equilibrium between gas and liquid, the critical pressure is the pressure required to liquefy the gas at the critical temperature. Beyond the critical temperature it is not possible to liquefy the gas, regardless of the pressure. Some critical temperatures and pressures are given below:

<table>
<thead>
<tr>
<th>Substance (Formula)</th>
<th>Critical Temperature (°C)</th>
<th>Critical Pressure (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia, NH₃</td>
<td>132.5</td>
<td>111.5</td>
</tr>
<tr>
<td>Argon</td>
<td>-122.4</td>
<td>48.1</td>
</tr>
<tr>
<td>Bromine</td>
<td>310.8</td>
<td>102</td>
</tr>
<tr>
<td>Chlorine</td>
<td>143.8</td>
<td>76.0</td>
</tr>
<tr>
<td>Fluorine</td>
<td>-128.85</td>
<td>51.5</td>
</tr>
<tr>
<td>Helium</td>
<td>-267.96</td>
<td>2.24</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>-239.95</td>
<td>12.8</td>
</tr>
<tr>
<td>Krypton</td>
<td>-63.8</td>
<td>54.3</td>
</tr>
<tr>
<td>Methane, CH₄</td>
<td>-82.1</td>
<td>45.8</td>
</tr>
<tr>
<td>Neon</td>
<td>-228.75</td>
<td>27.2</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>-146.9</td>
<td>33.5</td>
</tr>
<tr>
<td>Oxygen</td>
<td>-118.6</td>
<td>49.8</td>
</tr>
<tr>
<td>Sulfur dioxide, SO₂</td>
<td>157.8</td>
<td>77.7</td>
</tr>
<tr>
<td>Water, H₂O</td>
<td>373.936</td>
<td>217.7</td>
</tr>
<tr>
<td>Xenon</td>
<td>16.6</td>
<td>57.6</td>
</tr>
</tbody>
</table>

Substances in which the intermolecular forces are relatively strong, such as the polar molecules ammonia, sulfur dioxide and water, have relatively high critical temperatures. Substances in which the intermolecular forces are weak, such as argon, hydrogen, nitrogen and oxygen have low critical temperatures. “Permanent” gases are gases whose critical temperatures are below room temperature, so they cannot be liquefied at room temperature, regardless of the pressure. If you’re thinking “wait a minute, I’ve seen liquid nitrogen” remember that it’s very cold!

At temperatures and pressures above the critical temperature and pressure, substances are known as **supercritical fluids**. Supercritical fluids can have properties that make them of practical importance. For example, supercritical carbon dioxide is used in one of the processes for decaffeinating coffee beans, replacing potentially carcinogenic solvents that were formally used. It is also used as a solvent for extracting compounds that are used as fragrances, permitting this to be done at temperatures that are low enough to avoid decomposition of the compounds.
Since the melting temperature is not very sensitive to pressure, the slope of the solid-liquid line on the phase diagram for water is greatly exaggerated. The negative slope for water is unusual and occurs because for water the density of the solid is less than the density of the liquid, due to the open structure of the hydrogen-bonded ice lattice. According to Le Chatelier if you increase the pressure on an equilibrium system it will respond to decrease the pressure. A pressure increase will cause the solid-liquid equilibrium to shift to favor the more dense phase because this will alleviate pressure by decreasing volume. For water, the liquid is the more dense phase, and raising the pressure causes the melting point to decrease (negative slope). This means that at a given temperature increasing the pressure enough will melt the solid. Notice that as you move to higher pressures, the liquid occupies more area on the phase diagram for water.

Contrast this to the behavior of carbon dioxide shown on the following phase diagram.

![Phase Diagram of Carbon Dioxide](image)

Carbon dioxide is a more typical substance in that the density of the solid is greater than the density of the liquid. Therefore, its melting point increases as the pressure increases, the solid-liquid line has a positive slope, and at higher pressures the solid occupies more area on the diagram. Carbon dioxide has an unusual feature in that it has neither a normal melting point nor a normal boiling point. This is because its triple point pressure is above 1 atm. Because the liquid does not exist as a stable phase below the triple point pressure of 5.19 atm, at 1 atm the solid sublimes to give the gas rather than melting. Since this happens at a temperature of -78°C, solid carbon dioxide is used for cooling and is called “dry ice” because it doesn’t melt.

**EXAMPLE PROBLEM: Phase Diagrams**

Answer the following questions based on the phase diagram for ammonia, NH₃, and on the following data: \( \Delta H_{\text{fusion}} = 331 \text{ J/g} \), \( \Delta H_{\text{vap}} = 1371 \text{ J/g} \), specific heat liquid = 4.75 J/g·K, specific heat gas = 0.037 J/g·K
(a) What is the normal melting point? The normal boiling point?
(b) At what temperature and pressure do the three phases coexist in equilibrium?
(c) Is ammonia a solid, a liquid or a gas at room temperature and pressure? If a gas, is it a permanent gas?
(d) Which is the more dense phase, the liquid or the solid?
(e) A 10.0 g sample of ammonia is heated at a constant pressure of 1 atm from a temperature of 200.0 K to a temperature of 400.0 K. How much energy in kJ is required?

SOLUTION:

(a) Normal refers to a pressure of 1 atm. The point on the liquid-solid line with a pressure of 1 atm has a temperature of 195.4 K. This is the normal melting point. The point on the liquid-vapor curve with a pressure of one atm occurs at a temperature of 239.8 K. This is the normal boiling point.

(b) Look for the one point that all three phases have in common (T). This is the triple point at 195.3 K and 0.059 atm.
(c) Take room temperature and pressure to be 298 K and 1 atm. This corresponds to the point indicated by the letter X on the diagram which is in the gaseous region. Ammonia is a gas at room temperature, but it is not a permanent gas. Because the temperature is below the critical temperature (405.5 K), it can be liquefied by increasing the pressure to about 11 atm at 298 K.

(d) The liquid-solid equilibrium line has a positive slope. Therefore, the solid is more dense than the liquid.

(e) This process is like the heating curves described in Chapter 5. The substance starts as a liquid at 1 atm and 200.0 K. The liquid is heated at constant pressure until its temperature reaches the normal boiling temperature of 239.8 K. Any attempt to heat the liquid further will cause liquid to vaporize at constant temperature. Note that as the liquid vaporizes, the volume must increase in order to maintain constant pressure. When all of the liquid has vaporized, further heating will raise the temperature of the gas to the final temperature of 400.0 K.

Energy required to raise the temperature of the liquid from 200 K to 239.8 K:
Q = (10.0 g)(4.75 J/g·K)(239.8 – 200.0) = 1891 J

Energy required to vaporize the liquid at 239.8 K
Q = (10.0 g)(1371 J/g) = 13710 J

Energy required to heat the gas from 239.8 K to 400.0 K
Q = (10.0 g)(0.037 J/g·K)(400.0 - 239.8) = 59.3 J

Total energy required = 1891 J + 13710 J + 59.3 J = 15660 J = 15.7 kJ

Phase Diagrams.