

## Chapter 38

## LIQUIDS AND SOLIDS

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We enter the final segment of our span of five Chapters regarding the phases and phase changes. We've completed a discussion of the factors which are responsible for the common phases, and now we discuss some aspects of the phases themselves. We have already completed gases: in Chapters 16 and 17, we had discussed the physical picture and the mathematical relationships of the gas phase. We've done preliminary descriptions for the liquid and solid phases and we will wrap up their characterization by adding a few more things here. As for mathematical relationships of the liquid and solid phase, these are far more tedious than the gas phase due to the complexity of quantifying the intermolecular forces which are present. Our emphasis here will therefore be descriptive.

We start with a few more properties of the liquid phase.

## 38.1 Liquids

Let's recall the general picture of the liquid phase from Chapter 34.



“ In a typical liquid phase, the particles are in loose contact and they are in motion. There is no fixed arrangement overall. In their motions, they constantly bump into each other, and it takes a while for any one particle to move around very far. Although overall movement is slow, they can occupy any location within the volume of the liquid. ”

Let's also bring back the entropy part from that Chapter.

“ The liquid phase has numerous options (fewer restrictions) because the particles are able to move a bit. There are options in terms of location and orientation. There are options in terms of motion; this involves speed and direction, along with vibration and rotation. The motions will be a bit limited due to the close contacts, but at least there are some. Overall, there is moderate entropy in the liquid phase. ”

We can refine this picture a bit at this time.

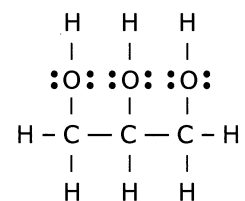
The particles are moving and they are in loose contact but there can also be preferred orientations relative to their neighbors. As we have seen, IFs can vary in strength and they can vary in their orientation preferences. The orientation preferences are highest for hydrogen bonding; neighboring molecules in such liquids will try to align in preferred directions relative to each other. Thus, at any given moment, some molecules may be well aligned with neighbors whereas other molecules may not be well aligned. All of the molecules are moving around slightly and the motions disrupt the orientations. This is the physical picture of liquids such as H<sub>2</sub>O: the molecules try to align with their neighbors and can do so for very brief periods before things have moved a bit; then they may be aligned with different neighbors. There is a problem with this preferred orientation business because it is restrictive and limits the options for direction; limiting options means limiting entropy. This will become an issue in some aspects in later Chapters. On the other hand, for liquids which lack strong hydrogen bonding, then the orientation preference is much weaker (if any). The options remain for many different directions and entropy remains more favorable.

This is sufficient for our molecular picture of what's happening in the liquid phase. Let me now introduce three properties of liquids: viscosity, surface tension and capillarity.

## • VISCOSITY

Our first property, viscosity, is the resistance to flow. A liquid which is slow to flow (slow to pour) is viscous. Commonly, we equate viscosity with "thickness". For example, we regard oils and syrups as thick which means they are of high viscosity.

In order to flow, the particles of the liquid must move past each other faster than their usual random motion would allow. Since neighbors attract each other due to IFs, then these attractions will resist that flow. These effects are more pronounced with hydrogen bonding and lots of it. Water is somewhat more viscous than most liquids but it is no match to the viscosity of compounds such as glycerol (C<sub>3</sub>H<sub>5</sub>(OH)<sub>3</sub>, at right). Glycerol has three O-H groups and is one thousand times more viscous than water. It's really syrupy stuff.

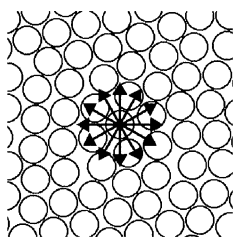


Oils are also very viscous but for different reasons. Petroleum oils are hydrocarbons, while food oils are compounds of C, H and O. (There are usually no O–H groups, so there is no hydrogen bonding in the food oils.) Molecules in these oils are typically very large, long and stringy, and this leads to extensive and strong dispersion interactions.

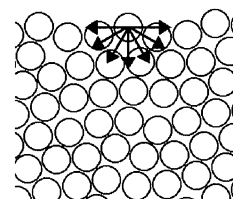
- SURFACE TENSION

Our second property is surface tension, which is actually a property of the surface of the liquid and not a property of the bulk of the liquid. For our purposes here, the surface of interest is the one which is open to air (or other gas phase) or open to a vacuum.

The surface of a liquid acts as if it is a weak, stretched skin. As such, the surface is regarded to have a tension which is therefore called surface tension. Since the surface acts as if it were stretched, it would like to contract to a smaller size. Thus, surface tension refers to the tendency of a liquid to reduce its surface area.



Surface tension arises due to IFs. Consider one molecule in the bulk of the liquid phase as shown at left. That molecule can sense attraction to surrounding molecules in all three dimensions. (Only two dimensions are drawn.) That attraction, on average over all motions, is equal in the three dimensions. Now consider a molecule at the surface of the liquid as shown at right. The molecule at the surface can sense attractions to the left and to the



right and it can sense attractions downward, but it has no attractions upward. The left/right attractions give a "skin effect"; this is why the surface behaves as if it is a weak skin which resists poke-through. The attraction downward is a net attraction inward; it is an attraction into the bulk of the liquid. Thus, surface molecules experience a net inward tug into the bulk and away from the surface. Overall, surface is disfavored relative to bulk, and a liquid will try to minimize its surface area.

For any given volume of a liquid, a sphere provides the minimum surface area for that volume. For this reason, a liquid volume will naturally prefer to be spherical; in other words, liquids prefer to be in spherical drops. Raindrops try to be spherical but they are distorted by friction as they fall through the air. If floating in air within a spacecraft beyond gravity, drops are spherical. In fact, one of the best ways to make perfect, spherical solids is in outer space. The material is melted and then dispersed into the desired particle size; while molten, the liquid forms perfect spheres due to surface tension and these are then allowed to cool to a solid.

Surface tension manifests itself in various other ways also. For example, beading is due to surface tension. Water will bead up on wax paper or on a waxed car or on a waxy leaf. The water is trying to form a sphere although gravity is flattening it out a bit. Water will also float things that would otherwise sink. For example, you can float a metal paper clip on water if you lay it down flat (and carefully) onto the water's surface. Of course, it will sink if it pokes too far through the surface.

Although surface tension is due to intermolecular forces, it is not straightforward to try to correlate the two. One big complication here is that molecules tend to arrange themselves differently at a surface than in the bulk. For example, for liquid water in contact with air, many molecules at the surface will extend one OH bond outwards into the air space, leaving those molecules short of their full hydrogen bonding capability. Nevertheless, water's surface tension is still high compared to many other molecular liquids. Notably, liquid metals have very high surface tension but it's not due to IFs. Metals use full chemical bonding (metallic network bonding) in their liquid phase; this is much stronger than IFs and this gives much stronger surface tension to metals when compared to molecular liquids. For example, mercury has an extreme tenacity to bead up on just about any nonmetallic surface. Even gold at its melting point of 1,064 °C is extremely beady.

- CAPILLARITY OR CAPILLARY ACTION

Our third property for liquids relates to a capillary tube. A capillary tube is any tube of very small bore. The term capillarity or capillary action derives from the entry of a liquid up into a capillary tube against the force of gravity. Capillarity depends on the liquid and also on the solid phase with which the liquid interacts. Thus, the physical phenomenon is not entirely a property of the liquid phase by itself. Nevertheless, capillary action depends on the surface tension of the liquid and this is one way of measuring surface tension.

Let me bring in two terms here: cohesion and adhesion. The adjectives are cohesive and adhesive. Cohesion is the attraction between particles in a single medium. For our discussion here, cohesion is the total IFs for the liquid by itself. Adhesion is the attraction between different media. Here, it applies to the interactions between the liquid and the solid. These attractions are also intermolecular forces. (The IFs responsible for adhesion include the IFs for mixtures but we haven't done all of those yet. We won't worry about that right now.)

For illustration purposes, let's consider water and glass. Water wets common glass because water has a strong adhesive interaction with that glass. This goes for clean glass. Dirty glass may not do this as well, and that includes glass with fingerprints.

If you have water in a clean glass container and if you look closely at the surface of the water where it meets the inside wall of the glass, you will see that the water curves up the wall a bit. If you do this in miniature by putting a glass capillary tube into a container of water, then the water will curve up the inside wall of the tube. (It curves up the outside wall also.) The curve upward on the inside wall will actually pull the water up into the tube. This is capillary action.

We'll take a closer look. Let's put a capillary tube into water, as shown at left as an overview. Water is attracted to glass due to adhesive forces, so the water tries to coat the glass by climbing up the walls. I show a preliminary, conceptual step of this at right, in a magnified view. There are two problems with climbing up walls. First, gravity always opposes things climbing up a wall. Second, the water inside the tube has now stretched its surface quite a bit and that is opposed by surface tension. In order to minimize its surface, the water's surface tension actually pulls the water up inside the tube, which I now show below left. This picture represents the final equilibrium condition: the water rises inside the tube due to adhesive forces and surface tension but this is balanced by the weight of the rising water which is pulled down by gravity. Ultimately, the height of the rise is a function of three things: the diameter of the tube, the density of the liquid and the liquid's surface tension. Since we can measure the height, diameter and density, then this provides a measure for surface tension. This is not just about water; other liquids can also be done in this manner.

This description assumes the tube material has a high adhesive attraction for the liquid. If the tube material has poor adhesive interaction with the liquid, then the liquid wants to avoid contact with the tube and you get an inverted result as shown at right. Water in a waxy tube does this. Mercury does this in a glass tube. This is still a surface tension effect but it's simply inverted to the case above.

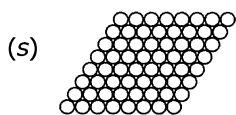
In addition to capillarity, these aspects tie into other phenomena related to wetting. I'll expand on this in Chapter 40 after we get more fully into mixtures.

This concludes our three properties for liquids and our discussion of the liquid phase itself. Let's proceed to solids.

### 38.2 Solids

Solids are better understood than liquids since the particles are in fixed positions. For molecular solids, this allows a better understanding of intermolecular forces since things aren't moving around all the time. Unfortunately, the treatment of IFs is still very complex so we will again focus only on the physical picture of the solid phase. We will also be including network compounds in our discussion here since most of those are also solids.

Here's the general picture from Chapter 34.



“ In a typical solid phase, the particles are in some fixed arrangement and they are locked in place. There is some wiggle room which allows the particles to rotate or to vibrate in that place, but they cannot move out of their fixed location. ”

And here's the entropy assessment also from that Chapter.

“ The solid phase does not have a lot of options. The particles are in fixed locations. They can vibrate in position and many can rotate in position to another orientation; these provide for some options but that's about it. Overall, there is little entropy. ”

The distinguishing feature of the solid phase is the part about the particles being locked in place. In general, there are two over-riding themes for locking particles into place: they can be arranged in an orderly fashion or they can be arranged with little or no order. The former are called crystalline solids and the latter are called amorphous solids.

In typical amorphous solids, there are huge molecules or huge ions which tend to be very long and tangled, unable to easily adopt an orderly arrangement. There are many different kinds of these, including various glasses and plastics. Due to the disorder, these do not have well-defined melting points; upon heating, they eventually soften to a melt. Some of these are even mixtures of large molecules, which complicates things. We will not consider these in further detail. Our emphasis here will instead be with the crystalline compounds.

Our discussion of crystalline solids will categorize these compounds in two different fashions: one will be by spatial arrangement and one will be by the chemical unit. We begin with the spatial arrangements.

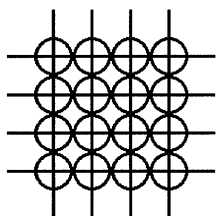
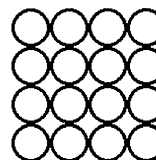
### 38.3 Classification of solids by lattice

The spatial arrangement in a solid is described by a lattice. We first encountered the term lattice back in Chapter 25 when we introduced lattice energy for ionic compounds.

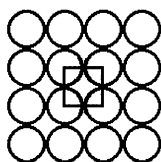
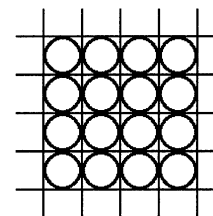
“ The word "lattice" refers to the arrangement of the chemical units within a crystal; this meaning is related to the normal dictionary use of "lattice", which refers to a pattern of things. When cations and anions come together to make a crystal, there are different patterns which they can adopt depending on cation/anion ratio, their sizes, etc. These patterns are the lattice. For a specific lattice, there will be some energy associated with that pattern. That energy is the "lattice energy" for that compound in that pattern. ”

These same aspects apply to all crystalline solids, not just ionics. Just remember that the lattice is the pattern or arrangement of the chemical components which are present. For molecular compounds, these will be the individual molecules; for networks, these will be the ions or atoms which are present.

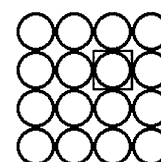
For any crystalline solid, we can identify a "unit cell" within the lattice. A unit cell is the simplest repeat pattern of the lattice. Let me elaborate on this description, but I'll start this with a two-dimensional example as shown at right. The circles represent whatever chemical component may be present in the sample.



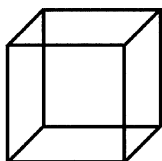
The lattice is the pattern of similar points. We can depict this in various ways by how we set up the lattice points. For example, we can consider the center of the circles to be the lattice points; these are shown connected by a grid at left. Alternatively we can choose the center of the space between the circles as our lattice points; these are shown connected by a grid at right. Both grids correctly represent the overall pattern.



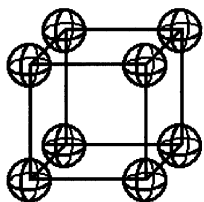
The unit cell is one block of our grid, as shown at left or at right for each grid above. Notice that the grid we choose is not required to enclose one single, full circle. The unit cell at left contains four quarters of different circles; as such, it contains one circle overall. The unit cell at right also contains one circle overall and it is a single circle. The two units cells left and right are equal. They are both squares of equal size



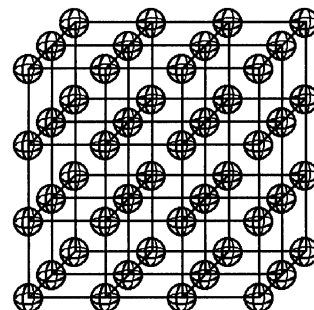
and they contain the same amount of chemical units. In each case, repeating the unit cell left/right and up/down will reproduce the full grids above.



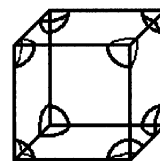
Now let's go to three dimensions. We now work with spheres to represent the chemical components. We will also work with cubic lattices, which means we will use 3D grids which are based on a cube and the unit cell is a cube. The cubic lattices are the easiest to visualize. A typical cube is shown at left.



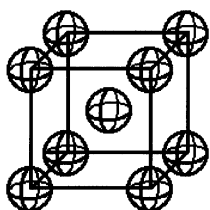
There are various ways of arranging chemical components based on a cube. The simplest is to locate them at the corners of the cube as shown at left. In fact, this is called the simple cubic lattice. Simple cubic is abbreviated sc, so we can say this is an sc lattice. A bigger part of such a lattice is shown at right, containing eighteen unit cells.



In the drawings here, the spheres are not touching. In a real solid, they will be touching but I drew them spaced apart for clarity. I will also tell you that the drawing above left is not a true unit cell because parts of the spheres are hanging outside the cube. The true unit cell is pictured at right; only one-eighth of each sphere is in this one cube, so I show one-eighth of a sphere at each of the eight corners. Since the unit cell has eight partial spheres of one-eighth each, then this works out to one full sphere per unit cell.

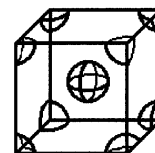


OK, that's simple cubic and that's as simple as they get. All cubic lattices begin with sc. We'll cover two further variations to this.

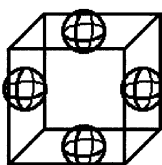


The first variation is to add a sphere in the center of the cube as shown at left. In this arrangement, the corner spheres actually touch the center sphere but they do not touch another corner; again, everything is drawn spread out for clarity. This lattice is called body-centered cubic (bcc), meaning that there is a sphere in the center of the body (cell). The picture at left is not the true unit cell because the corners are hanging out again. The true unit cell is shown at right. Each unit cell again has eight partial corner spheres of one-eighth

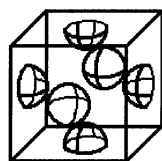
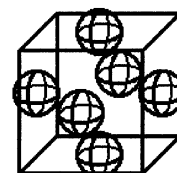
each, and now it also has a full sphere in the center; thus the total is two spheres per bcc unit cell.



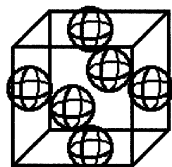
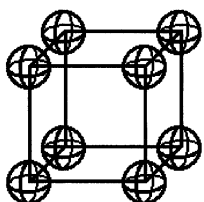
Starting again from simple cubic, the next variation is to add a sphere at the center of each face of the cube, in addition to the original corner positions. The center of a face is called a face center; this lattice is called face-centered cubic (fcc). This is a bit more complicated so I'll introduce this in steps.



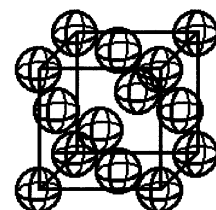
At left, we start with a preliminary drawing which shows a cube with a sphere in the center of only four faces. Each face cuts right through the middle of each sphere. Next, we add the face centers to the front face and to the back face as shown at right. Now we have one sphere at the center of each of all six faces.

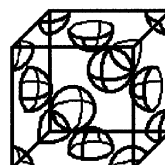
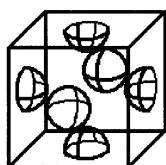
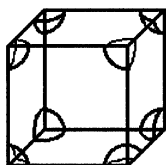


Only half of each sphere is in the cube; the other half is hanging out of the cube. At left, the halves of the spheres are shown which are inside the cube. Since each face-center sphere is only one-half in the cube, then each face center counts one half to the unit cell. There are six face centers and each sphere on face-center counts one-half; thus, the overall count is three spheres per unit cell for the face centers.



Now we bring in the cube corners (far left) and combine these with our face centers (near left). This gives us the final result: face-centered cubic, shown at right. This is really getting complicated, so let's look only at the parts inside the cube.





At far left, we have the one-eighth spheres at the corners. At near left, we have the face-center hemispheres. Put these together and you get the unit cell shown at right. Let's add up everything. The corners give one sphere and the face centers give three more spheres for a total of four spheres per unit cell.

This concludes our three cubic lattices: sc, bcc and fcc. Yes, these can get complicated, especially for fcc, but be able to break them down. They all have eight corner positions; in addition, bcc has one body center and fcc has six face centers. Keep in mind how the various positions count for the unit cell.

The eight corners are one-eighth each within one cube, for a total of one per unit cell.

The body center is contained wholly within the one cube, so it counts as one for the unit cell.

The six face centers are one-half each within one cube, for a total of three per unit cell.

For each type of lattice, we then have the following totals.

The sc lattice (corners only) has one sphere per unit cell.

The bcc lattice (corners and body center) has two spheres per unit cell.

The fcc lattice (corners and face centers) has four spheres per unit cell.

The importance of this count is that the spheres represent chemical components. We will see this shortly below. The count tells us how many chemical components there are per unit cell, and this is a characteristic of each type of lattice.

This completes the cubic lattices for our coverage here. There are various other lattices which can be derived from these based on distortions in lengths to give rectangular sides or distortions in angles away from the 90° angles of a cube. Beyond cubic, there are also hexagonal-based lattices. We're just dealing with the simplest cases here, so we're not going to bring in all of these. Just be aware that there are yet other lattices.

I'll point out some actual applications of our cubic systems in the next section when we talk about particular substances.

### 38.4 Classification of solids by chemical type

This is a different classification scheme and it has nothing to do with lattice. It is only based on the chemical type of compound (or elemental form). These break down into the following four categories.

1. Molecular compounds
2. Ionic network compounds
3. Metallic network compounds
4. Covalent network compounds

Be sure to recognize the key differences between these types. Molecular compounds only have intermolecular forces for holding the solid phase together. The network categories use their respective modes of chemical bonding: ionic, metallic or covalent. Some networks also use IFs in addition to chemical bonding, and we'll see a bit of this as we go.

#### • MOLECULAR COMPOUNDS

For these, the chemical components are the separate, individual molecules of the substance. We include in this category the elements of Group 18 which are present as individual atoms in their solid phase.

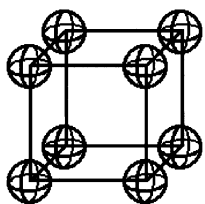
The Group 18 monatomics are indeed the simplest of this whole category. Dispersion is the only intermolecular force available for these. The simplest of the simplest is He. Helium has the weakest IFs of all substances. In fact, it cannot be frozen by cooling; it must be cooled and pressurized. Most of the Group 18 elements form fcc lattices; in our lattice pictures earlier, the spheres represent one single atom. For these elements, there are four atoms per unit cell according to the unit cell counting methods.

For molecular compounds, there is a massive range of different substances and these use the full range of intermolecular forces. In our lattice pictures above, each sphere represents one molecule, whatever its true shape may be. For example, O<sub>2</sub>(s) gives an fcc lattice; each diatomic molecule will lie at a sphere position in the prior drawings. Solid CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> also have fcc lattices and one molecule

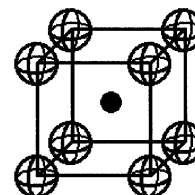
will lie at a sphere position in the drawings above. Each of these compounds has four molecules per unit cell. On the other hand, HCN has a bcc lattice with two molecules per unit cell.

#### • IONIC NETWORK COMPOUNDS

Ionic compounds have a network of cations and anions held by ionic bonding in three dimensions. The terminology for ionic lattices is different from the terminology of our other categories here. Commonly, the lattice type is based either on the cations or on the anions, but not on both. The other ion is then described as residing elsewhere in the unit cell. Let's see how this works.



We'll start with CsCl as an example. CsCl can be described as having chloride ions in a simple cubic lattice with a cation in the center of the unit cell. To illustrate this, we begin with the sc lattice at left with each sphere representing one  $\text{Cl}^-$  anion. We now locate one  $\text{Cs}^+$  cation in the center, to give the illustration at right. (I drew the cation completely black to distinguish it from the anions.) To many students, this looks like a bcc lattice since there's a  $\text{Cs}^+$  at the body center, but the practice is to base the lattice name on



identical chemical components. Thus, we name the lattice type according to the cations only or the anions only. In this example as described, the lattice is sc based on the anions.

There's another feature to introduce for dealing with ionic lattices. The unit cell must contain the same ratio of cations and anions as the ratio in the ionic formula. It doesn't have to be the same numbers, but it does have to be the same ratio. This is an important aspect for ionic lattices. We can apply this to CsCl as follows.

There are eight  $\text{Cl}^-$  corners, counting one-eighth each, for a total of one  $\text{Cl}^-$  per unit cell.

There is one  $\text{Cs}^+$  at the center contained wholly within the unit cell for a total of one  $\text{Cs}^+$  per unit cell.

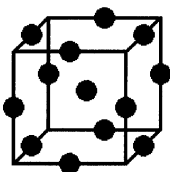
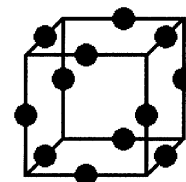
Thus and overall, our unit cell contains one  $\text{Cs}^+$  and one  $\text{Cl}^-$  and this 1:1 ratio is consistent with the 1:1 formula ratio.

The CsCl type of lattice is an easy one to start with but it is somewhat rare for ionics. Several other cesium salts and even some ammonium salts such as  $\text{NH}_4\text{Br}$  use this lattice type, but there aren't too many beyond those.

Let's do something very common: NaCl. This lattice type is called the rock salt lattice.

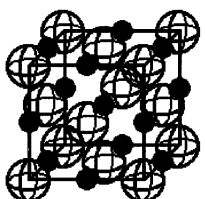
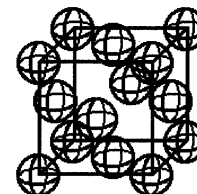
There are different ways of describing this lattice, but I'll just pick one to work with here. We can describe this as an fcc lattice of chloride ions with sodium cations at edge centers and at cube center.

OK, I just threw in a new position there, edge centers. It's just what it sounds like: the center of each edge of the cube. These are shown at right by themselves. There are twelve edges to a cube, so there are twelve edge centers. Only one fourth of each sphere is contained within the cube; thus, for counting purposes, each edge center counts one-fourth. Twelve edge centers at one-fourth each add up to a total count of three per unit cell.



The description says that  $\text{Na}^+$  ions are at each edge center and at the cube center. Let me add one cube center to the drawing, at left. This concludes the locations for our cations.

The  $\text{Cl}^-$  anions are at fcc lattice positions, as shown at right.



Now we put the cations and anions all together and we get a very crowded drawing as shown at left. But that figure shows whole spheres and most of them are hanging out again. Fortunately, you really don't need to draw these out every time in order to do a count. Let's just start the countdown and see how all of this works out.

Chloride ions (fcc unit cell)

The eight corners count one-eighth each:

The six face centers count one-half each:

Total:

one  $\text{Cl}^-$

three  $\text{Cl}^-$

four  $\text{Cl}^-$  per unit cell

Sodium ions

The twelve edge centers count one-fourth each:

The one at the cube center counts wholly:

Total:

three  $\text{Na}^+$

one  $\text{Na}^+$

four  $\text{Na}^+$  per unit cell

Notice that the count gives a 4:4 or 1:1 ratio of cations and anions which is consistent with the 1:1 formula ratio for NaCl.

This lattice type is very common for many ionics which have the 1:1 ratio of cation and anion. Other examples include the other halides of sodium, along with those for  $\text{Li}^+$  and  $\text{K}^+$ . Some oxides do this with 2+ cations, such as MgO, CaO, VO, MnO, etc. Even polyatomics can get in on this structure, although these may distort the cube a bit. For example,  $\text{CaC}_2$  and one form of  $\text{CaCO}_3$  adopt structures based on the rock salt lattice.

Things get more complicated with other ionic compounds, especially those with something other than a 1:1 cation:anion ratio. Furthermore, there are still other positions within a cube for locating the various cations or anions but we won't go into those. I will point out, however, that you can still do aspects of unit cell counting even if you can't always draw things out. Let's see an example.

$\text{CaF}_2$  forms an fcc lattice of calcium cations with the fluorides located elsewhere in the unit cell. How many fluoride ions are in each unit cell?

OK, we are only given the lattice positions for the  $\text{Ca}^{2+}$  ions. We don't know where the anions are, so we can't draw those out. We can still do the count, however, because we can relate the unit cell count to the formula ratio. Here's how that works. Since we know that the  $\text{Ca}^{2+}$  cations are in fcc positions, then there are four  $\text{Ca}^{2+}$  per unit cell. The formula tells us that the cation:anion ratio is 1:2, so there are twice as many anions in the unit cell. Thus, there must be eight  $\text{F}^-$  present per unit cell. That's your answer.

It's your turn.

.....  
**Example 1.**  $\text{Cu}_2\text{O}$  forms a bcc lattice of oxide ions. How many anions are present in the unit cell? How many cations are present in the unit cell?  
 .....

Do the count for the anions first, since the bcc lattice is based on those. Then, using that count and also the formula, find the number of cations.

Anions: \_\_\_\_\_ Cations: \_\_\_\_\_

This ends our discussion of the ionic networks.

#### • METALLIC NETWORK COMPOUNDS

For metals, we have a network of atoms which are bonded by metallic bonding. The atoms make up the lattice positions. We will focus on the elements here although this can also get into alloys and other compounds based on metal lattices.

Many metal elements adopt the cubic lattices of fcc and bcc. For example, the fcc metals include Ni, Cu, Ag, Au, Pb, etc. The bcc metals include all Group 1 metals, along with V, Cr, Mo, W, etc. Some, like iron and calcium, can go either way with both fcc and bcc forms, depending on conditions. Of all metals, there is one oddball that stands out: polonium. It's radioactive so it is not commonly encountered, but it is the only element (metal or otherwise) to form a simple cubic lattice.

The usual counting methods apply. Do a few.

.....  
**Example 2.** How many atoms are in one unit cell of gold? How many atoms are in one unit cell of chromium? How many atoms are in one unit cell of polonium?  
 .....



Au: \_\_\_\_\_ Cr: \_\_\_\_\_ Po: \_\_\_\_\_

That's all we need to note here. Let's go now to our final category.

• COVALENT NETWORK COMPOUNDS

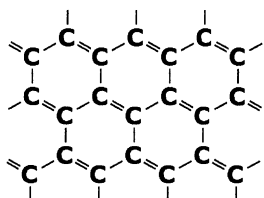
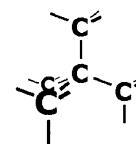
For these, we have atoms covalently bonded to other atoms throughout the network. Three-dimensional networks are common, although we will also bring in some 2D and 1D examples here also.

Many nonmetals and metalloids have elemental forms in this category. As mentioned since the end of Chapter 2, diamond and graphite are network forms of carbon. Diamond is a 3D network while graphite is a 2D network. Boron has several network allotropes (which are horrendously complicated). Sulfur and selenium have molecular allotropes and they also have a 1D network allotrope. Phosphorus has a molecular allotrope and a 2D network allotrope. As you can see, there is a lot of variety among the elements.

For the 3D networks, chemical bonding extends in all three dimensions throughout the network. For 2D networks, the chemical bonding gives sheets of atoms which may be only one or two atoms thick; these sheets stack on top of each other and are actually held there by IFs. For 1D networks, the chemical bonding gives chains of atoms; these chains align with other chains and are held by IFs. Thus, the other dimensions for 2D and 1D networks are held together by intermolecular forces.

Let me give more detail on some of these. I'll start by comparing the structures of diamond and of graphite. These two forms of the same element carry extremely different properties and, of course, extremely different value; all of this is due to the type of network bonding.

In diamond, all carbons are  $sp^3$  hybridized and tetrahedral shape. Each carbon is bonded to four other carbons, each of which is bonded to four carbons, etc. All bonds are single,  $\sigma$  bonds. A portion of this is drawn at right. This 3D network of CC bonds gives diamond its strength and tremendous hardness. This hardness finds tremendous use: diamond grit is widely used in cutting and drilling tools. In fact, most mined diamonds are not good enough for gems and these commonly end up in tools. Diamonds are also made industrially, primarily for tool applications.



In graphite, all carbons are  $sp^2$  hybridized and trigonal planar shape. Each carbon is bonded to three other carbons in its plane, each of which is bonded to three carbons in the same plane, etc. This sets up all the bonding in huge planes of atoms arranged in hexagons. (Some tile floors have hexagonal tiles; that's what a graphite layer looks like.) The hybrids provide CC  $\sigma$  bonds; the unused  $2p$  orbitals provide  $\pi$  bonds. The overall bond order for each CC bond is  $4/3$ . One resonance structure for a portion of a sheet is shown at right; many resonance structures are possible and this gives extreme delocalization across the sheet. In Chapter 33 with metallic bonding, we noted that extreme delocalization gives electrical conductivity. Graphite also conducts electricity and the Band Theory approach applies.

Because the bonding in graphite is within a sheet, this is a 2D network. When you stack up a bunch of different sheets on top of each other, you get the third dimension but it is now dispersion which holds the sheets together. Since dispersion is weaker than chemical bonding, the sheets are not held tightly together. This allows other molecules (especially air or other gases) to get in between the sheets, and this is typical for graphite in normal applications. This loosens the sheets even further relative to each other, allowing the sheets to slide readily across each other. This gives graphite its lubricating properties.

Let me bring in a 1D network elemental form. I'll show this with sulfur.

For sulfur in its 1D allotrope, the atoms are arranged in a long spiral chain. A portion of such a spiral by itself is drawn at right and the positions of sulfur atoms in such a spiral are drawn at left.



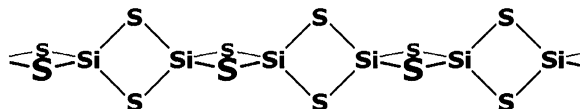
The sulfur atoms are bonded by single bonds (not shown in the diagram). Many such spiral chains run side-to-side, held together by dispersion.

So far, all of our covalent networks are elemental forms but there are also many compounds which are covalent networks. In the very beginning of Chapter 4, I mentioned boron nitride and silicon dioxide as network compounds. An illustration of the 2D network for boron nitride was given in the beginning of

Chapter 4. Go back and look; notice the hexagons. The combination of {B bonded to N} is isoelectronic to {C bonded to C}, so BN forms solids similar to carbon. A single 2D BN sheet is arranged just like a single sheet of graphite. There are distinct bonding differences, however, and all of the bonds in BN are more localized; hence, BN does not conduct electricity. Besides the 2D network, boron nitride also forms a 3D network which is just like the diamond network. For  $\text{SiO}_2$ , a variety of different networks are known, one of which is quartz. These have tremendous mineralogical importance due to the abundance of silica minerals on Earth. In all of these, Si is  $sp^3$  and tetrahedral shape; O is  $sp^3$  and bent shape. Each Si is bonded to four O and each O is bonded to two Si.

Silicon is actually very adept at networks. Another example is silicon carbide, SiC. This forms several different 3D networks, one of which is just like the diamond network. It is also very hard and it is used as an abrasive. Commercially, it goes by the name carborundum; you see it a lot in things like sandpaper.

I'll use silicon again to illustrate one example of a 1D network covalent compound:  $\text{SiS}_2$ . This forms very long chains of bonded Si and S atoms. Separate chains are then held together by intermolecular forces in the solid.



For our covalent networks here, I haven't given any specific lattices for the elements or compounds. That's because these are not so straightforward. For example, the diamond lattice derives from fcc but with four additional carbon atoms per unit cell, giving a grand total of eight. We'll leave it at that for our purposes here.

This wraps up our discussion of solids. With this we end our five Chapter sequence of the phases in general. Throughout these five Chapters, the primary emphasis has been on single substances by themselves. Beginning in the next Chapter, we start to mix things up.

## Problems

- True or false.
  - Water does not wet (does not make good contact with) wax paper because adhesion is much stronger than cohesion.
  - Compounds with stronger intermolecular forces tend to have higher viscosities.
  - Liquids desire to minimize their surface area and form spheres.
  - In a unit cell, each face-center particle counts one-fourth to that cell.
  - $\text{SiCl}_4$  forms an ionic network solid.
  - Diamond is a 3-dimensional covalent network solid in which all carbons are  $sp^3$  hybridized and all bonds are of  $\sigma$  type.
- Solid iron can form either a body-centered cubic lattice or a face-centered cubic lattice. How many iron atoms are in one unit cell of each type?
- Solid carbon dioxide forms a face-centered cubic lattice. How many molecules of carbon dioxide are in one unit cell?
- Potassium oxide forms a face-centered cubic lattice of oxide ions. How many anions are in one unit cell? How many cations are in one unit cell?
- What chemical type of solid is formed by each of the following substances?
 

a. silicon dioxide	b. hydrogen fluoride	c. argon
d. ammonium chloride	e. gold	f. sodium nitrate