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Solids and liquids

THESE are three different states of the matter: solid, liquid and gas. At this point, we have studied the properties of gases and liquid solutions. We have not encountered yet solids or pure liquids. This chapter fully deals with the properties of solids and liquids. Liquids have indeed very peculiar properties and this chapter will cover—among other—the vapor pressure. Liquids are not isolated; they are normally in contact with the atmosphere. The liquid molecules which are closer to the air can escape forming a vapor; this vapor exerts certain pressure. This vapor is what you feel, for example, when the weather is very humid. Finally, this chapter covers the idea of intermolecular forces. The molecules of an ideal gas are independent from each other. This means they do not see each other at all—they do not interact with each other. Differently, the molecules of liquids and solids interact with each other by means of stronger force that act between molecules—these are called intermolecular forces. The properties of this forces will help you understand why some liquids boil at higher temperature than others or some solids have higher melting point.

1.1 Intermolecular forces

The atoms of solids or liquids are connected by means of chemical bonds, forming molecules. Bonds are forces within molecules. These bonds can be ionic or covalent depending on the nature of the elements that form the compound. At the same time, the molecules of a liquid or solid compound interact with each other by means of intermolecular forces. The word intermolecular means between molecules. This section describes the three different types of intermolecular forces existing, its nature and intensity.


Dispersion forces All molecules are made of atoms and atoms contain electrons. The electrons of an atom are distributed homogeneously in the atom. This means that there are no negative or positive regions in an atom. On the other hand when two atoms get close together, the presence of each other alternates the electron distribution creating what is known as a temporary dipole. This temporary dipole results in dispersion forces. These forces exist in any chemical, as all chemicals contain atoms that can polarize temporarily. The larger the atomic number the stronger these forces, as in general the more electrons the stronger will be the temporary dipole.

Dipole-Dipole forces Dipole-dipole forces exist only in polar compounds, being the result of the permanent dipole moments existing in polar molecules. Examples of polar compounds are: HCl or H₂O. These forces are in general stronger than dispersion forces. Dipole moments result from differences in electronegativity of the atoms in a bond. Elements in the top right of the table (Cl, F) tend to be very electronegative



GOALS

- 1 Identify intermolecular forces
- 2 Identify different types of solids
- 3 Identify units cells
- 4 Calculate density of solids
- 5 Calculate vapor pressure

 **Discussion:** Do you know other states of the matter different than solid, liquid or gas?

and hence they tend to strongly attract the electrons on a chemical bonds. Differently, elements on the bottom left part of the table are electropositive and they tend to give away the electrons in the bond. In the periodic table, electronegativity increases going from left to right and top to bottom. As such, the molecule HCl would be polar as results from the combination of a electropositive atom (H) and an electronegative atom (Cl). Similarly, HF would be a polar molecule too. When comparing both, HF has a stronger dipole moment (as F is more electronegative than Cl) and hence would exhibit stronger dipole-dipole interactions.

Hydrogen bonds Hydrogen bonds are the strongest of all intermolecular forces and exist only in molecules containing very specific bonds; in particular they only exist in molecules containing H–F, H–N or H–O bonds. An example of molecule with hydrogen bonds is HF or NH₃.

Sample Problem 1

Indicate what types of intermolecular forces exist in the following molecules:

| | HCl | CH ₄ | H ₂ O | CH ₃ Cl |
|---------------|-----|-----------------|------------------|--------------------|
| Dispersion | | | | |
| Dipole-Dipole | | | | |
| H-bonds | | | | |

SOLUTION

All molecules can interact by means of dispersion forces. Differently, only polar molecules can interact by means of dipole-dipole forces. Finally, only molecules with a H–F, H–N or H–O bond can interact by means of hydrogen bonds. For these reason, from the table only HCl, H₂O and CH₃Cl has dipole forces, and only H₂O has hydrogen bonds.

| | HCl | CH ₄ | H ₂ O | CH ₃ Cl |
|---------------|-----|-----------------|------------------|--------------------|
| Dispersion | ✓ | ✓ | ✓ | ✓ |
| Dipole-Dipole | ✓ | ✗ | ✓ | ✓ |
| H-bonds | ✗ | ✗ | ✓ | ✗ |

STUDY CHECK

Indicate what types of intermolecular forces exist in the following molecules: NH₃, HF, and CH₃–CH₃.

Answer: all have dispersion, only NH₃, HF has dipole and only NH₃, HF has H-bonds.

Intermolecular forces of liquids and boiling Boiling a liquid requires energy. This energy is invested in separating the molecules from the liquid until they are spread apart. In order to separate the molecules of a liquid, we need to overcome intermolecular forces. Imagine boiling CH₄. We know the molecules of methane only interact among themselves by means of weak dispersion forces. Imagine now boiling water. Water is polar and water has O–H bonds, hence water molecules interact by means of dispersion, dipole-dipole and hydrogen bonds. The energy needed to separate the molecules of water will be larger than the energy required to separate the molecules of methane. The more intense the intermolecular forces, the higher the boiling point. Also, the more types of intermolecular forces present in a liquid the higher the boiling point. Finally, we can apply these ideas not only to liquids but also to solids.

Sample Problem 2

Compare the boiling point of these two molecules: HCl and H₂O.

SOLUTION

Let us build a table with the different types of intermolecular forces present in each liquid. The molecules of both liquids can interact by means of dispersion forces and also dipole-dipole forces, as both are polar molecules. Differently, only molecules with a H–F, H–N or H–O bond can interact by means of hydrogen bonds. For these reason, H₂O liquid contains hydrogen bonds.

| | HCl | H ₂ O |
|---------------|-----|------------------|
| Dispersion | ✓ | ✓ |
| Dipole-Dipole | ✓ | ✓ |
| H-bonds | ✗ | ✓ |

Hence, water will boil at a higher temperature.

STUDY CHECK

Compare the boiling point of these two molecules: CH₃F and CH₄.

Answer: BP(CH₃F) > BP(CH₄).

1.2 The solid state

What makes solids unique in comparison to liquids and gases? Their answer is their structure. There are two main different types of solids: crystalline solids and amorphous solids. Crystalline solids are made of atoms or molecules periodically, regularly, arranged in the three dimensions of the space. Examples of a crystalline solid are table salt or sugar. Amorphous solids have disordered structures. An example of an amorphous solid is window glass. This section will focus on the properties of crystalline solids as their periodicity makes their properties easier to study.

Crystalline lattice: the unit cell The structure of crystalline solids is periodic. The term does not refer to periodic in time, but in periodic in space. Hence, the structure of crystalline solids is the result of the repetition of a small piece of the structure in the space. The overall structure is called *crystalline lattice*. Here an example of a very simple two dimensional lattice. In this lattice, the central box is repeated infinitely in two directions of the space generating a lattice.

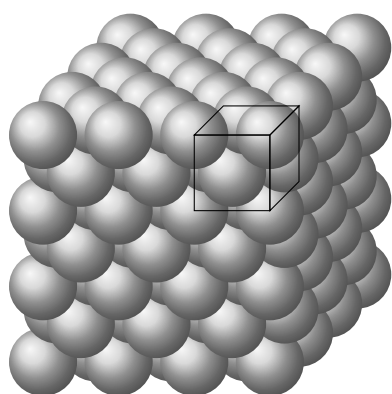


Figure 1.1 Unit cell of a solid of a crystalline solid. The whole structure of the solid results from the replication of a unit cell and just this unit cell is necessary to characterize the structure of the solid.

As the lattice is made of repetition, the smallest repeating unit is called the *unit cell*. Therefore, simply with the unit cell one can generate the whole crystal lattice by repeating the unit cell in the three dimensions. Therefore, it is unnecessary to study the crystalline whole lattice as the unit cell is enough to understand many properties of crystalline solids such as their density. In the following we will study in more detail the properties of crystalline solids and some of the most common unit cells.

Types of crystalline solids Examples of crystalline solids are: sugar and table salt. These two solids have very different constitutions. Table salt is made of ions: Na^+ and Cl^- . Sugar is made of molecules. We say NaCl is an ionic solid, whereas sugar is a *molecular solid*. Other examples of *ionic solids*: MgO , CaF_2 . Other examples of *molecular solids*: ice which is made of water molecules. A third type of crystalline solids are called *atomic solids*, as they are made of atoms. Think of metallic iron or graphite. Both are atomic solids made of atoms, Fe and C. Overall, molecular solids are made of molecules—often times covalent molecules—whereas ionic solids are made of ions and result from ionic compounds. Finally, atomic solids are made of atoms. In the following we will study more about a specific type of atomic solids: metallic solids. Metallic solids are indeed atomic solids made of metallic elements, such as for example gold ($\text{Au}_{(s)}$).

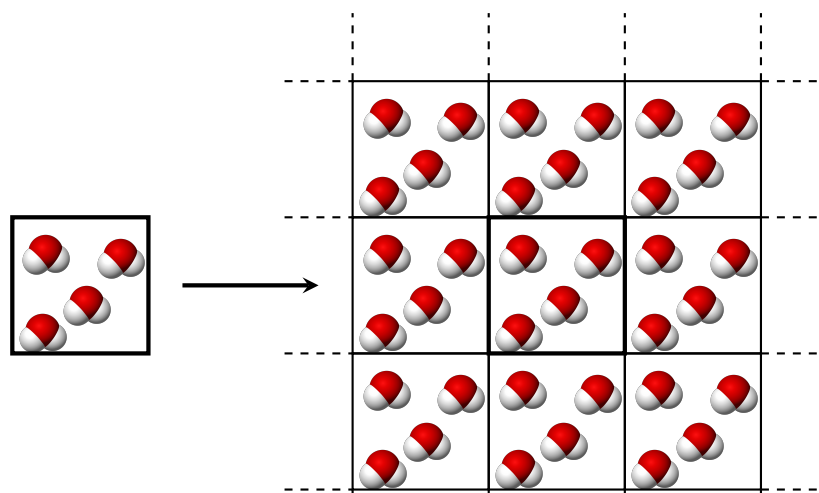


Figure 1.2 A periodic structure made of water molecules. The unit cell on the left contains four water molecules. The repetition of the unit cell, on the right, generates a two-dimensional structure.

Sample Problem 3

Classify the following solids as ionic, molecular or atomic: diamond, dry ice (CO_2), iron and CaF_2 .

| | diamond | CO_2 | Fe | CaF_2 |
|-----------|---------|---------------|----|----------------|
| Molecular | | | | |
| Ionic | | | | |
| Atomic | | | | |

SOLUTION

In general ionic solids correspond to ionic compounds and molecular solids correspond to covalent compounds. Therefore, dry ice should be a molecular solid and CaF_2 an ionic solid. Iron and dia-

mond are both made of atoms and hence they are atomic compounds.

| | diamond | CO ₂ | Fe | CaF ₂ |
|-----------|---------|-----------------|----|------------------|
| Molecular | X | ✓ | X | X |
| Ionic | X | X | X | ✓ |
| Atomic | ✓ | X | X | X |
| Metallic | X | X | ✓ | X |

STUDY CHECK

Classify the following solids as ionic, molecular or atomic: silver, graphite, CaCO₃ and NH₃(s).

Answer: metallic, atomic, ionic and molecular.

1.3 Metals and ionic solids

Among the different types of crystalline solids, metals and ionic solids are very important. This section will cover the structure of metallic solids like gold or iron and ionic solids like sodium chloride.

Closed packing of metals Metallic solids are the results of the packing of metal atoms the space. Picture a single layer of spheres all packed together. The most compact way to pack a layer of spheres is the situation in which one sphere is surrounded by six other spheres. This is called the closest packing. In this situation, each three spheres are connected by means of an indentation or dimple. Now the question is how do we pack a second layer on top of the first later. We can simply place the second layer just on top of the same positions of the first layer. This would lead to a simple cubic packing and this type of packing is not the most compact packing. The unit cell resulting from this packing is called *simple cubic*. We could also pack the second layer on the indentations of the second layer. As this second later would be located at different locations as the second layer, we call this second layer B and the first layer A. Now let us think about adding a third layer. There are two possible locations for this new layer; you can locate this third layer on top of the first layer layer—with this I mean on the same location as the first layer—this would lead to an ABAB packing, as the first layer is the same as the third layer. The unit cell resulting from this packing is called *hexagonal close cell*, (*hcp*). Differently, you can either locate the third layer on the indentations of the second layer leading to a ABC layer packing. In this packing the third layer is now now the same as the first layer. The unit cell resulting from this packing is called *face centered cubic*, (*fcc*).

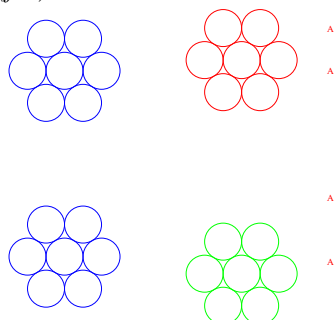


Figure 1.3 Different unit cells—such as sc, fcc or hcc—result from the different packing of metal layers. The simplest cubic structure results of placing two compact metal layer one on top of the other. When we place the second layer on the holes of the first layer we achieve a AB layer distribution and the resulting unit cell is called face centered unit cell. If we use a AB packing and now add a new layer on the holes of the second layer we obtain a ABC packing and the resulting unit cell is called hexagonal close cell.

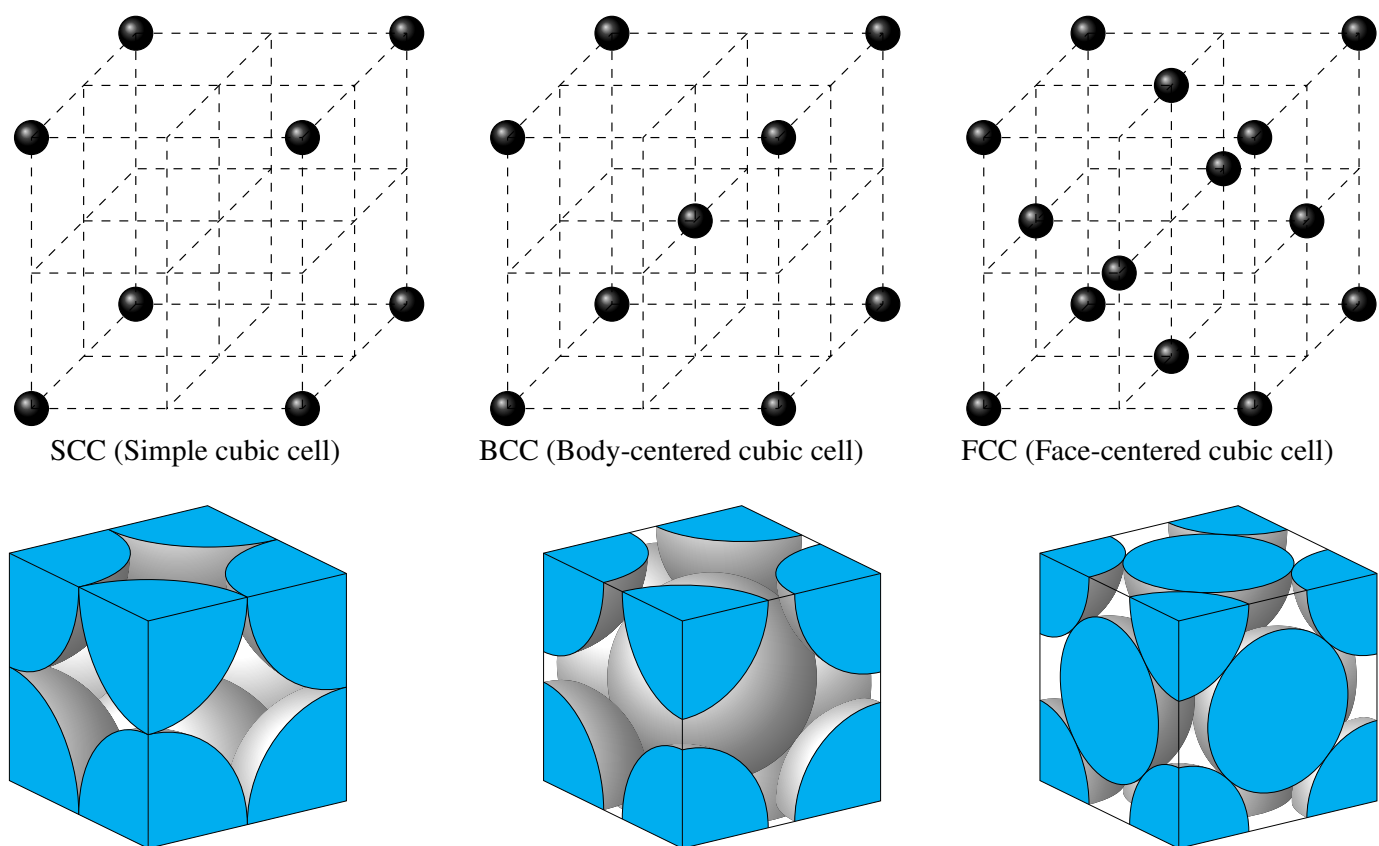
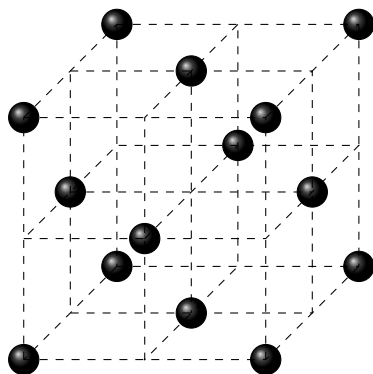


Figure 1.4 The different unit cells. Space-fill structures are shown on the bottom. The simple cubic unit cells have atoms in the corners of the cell. The body-centered cubic unit cell have atoms in the corners and one atom in the center. The face-centered unit cell has atoms in the corners and in the faces.

Atom sharing in unit cells Before we cover the different metallic units cells let us talk about atom sharing. Think about a cubit unit cell, that is a cube with one sphere (atom) in every corner of the cube. The whole lattice is produced by repeating the unit cell on the three dimensions. Hence, every corner of the cube is shared among other corders. This means, every corner-containing an atom-shares that atom with all units cells connected to that corner. Therefore, those atoms in the corner are not whole part of a single unit cell and they are shares. Every corner of a cube is shared among eight other cubes. Imagine pilling numerous boxes in layers. Every corner of each box is shared by three other boxes in the same plane and by four boxes on the plane on top—that is a total of eight boxes. They way you need to think of the different atoms in a single unit cell, is that they are shared depending on their location. As we discussed, corners of a cubic unit cell are shared by a total of 8 others unit cells. Atoms that belong to a face of a unit cell are shared by two unit cells. Atoms that are inside a unit cell fully belong to a single unit cell and they are not shared. Atoms that belong to a edge of the cube—an edge is the line that connects two vertexes of a cube—are shared by four units cells.

Sample Problem 4

The following structure is called face centered unit cell. This is a cubit unit cell with one atom in each corner of the cell and atoms also in the facets of the cell. Calculate the number of atoms in the unit cell:



SOLUTION

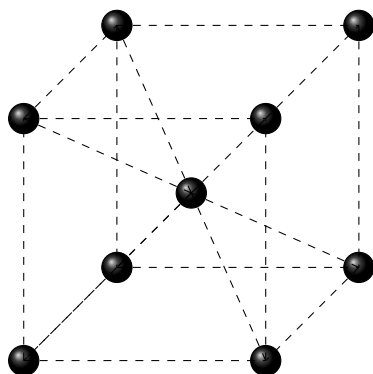
If you count the number of spheres in the drawing you might think the cell contains fourteen atoms. However, this is not true, as each sphere is shared by other unit cells. Remember each location of the unit cell counts as a fraction. If an atom is fully inside in the cell—not in the vertexes, neither in the faces or sides—the sharing factor is one. If an atom belongs to a vertex, the sharing factor is $\frac{1}{8}$. Atoms in a face has a sharing factor of $\frac{1}{2}$ and atoms in the edges have a sharing factor of $\frac{1}{4}$.

| Location | Sharing Factor, f | # atoms, N | $f \times N$ |
|----------|---------------------|--------------|--------------|
| Corner | $\frac{1}{8}$ | 8 | 1 |
| Faces | $\frac{1}{2}$ | 6 | 3 |

By multiplying the number of atoms in each location by the sharing factor and adding we obtain the total number of atoms in the cell. Overall, this unit cell has four atoms:

STUDY CHECK

The following structure is called simple body centered unit cell. This is a cubic unit cell with one atom in each corner of the cell and an atom also in the center of cell. Calculate the number of atoms in the unit cell:



Answer: 2.

Metal unit cells Here we will cover three different metal unit cells, all cubic cells. First, the simple cubic unit cell, with an atom each of the vertexes of the cell. This is the less compact unit cell with one atom per unit cell. Second, the body-centered unit cell is a cubic unit cell with atoms in the vertex of the cell and a single atom in the center of the cell. This cell has two atoms per unit cell. Third, the face-centered unit cell, with atoms in the vertex of the cell and also on the faces of the cell, on the sides of the cube.

This is the most compact unit cell, with four atoms per cell. In the following image you can manipulate a face-centered cubic cell.

150 *Cell parameter* Cubic unit cells have the shape of a cube and hence all side of the cube have the same length. This length is called cell parameter c . Unit cells with large cell parameter have more spacing between atoms. The opposite is true for cells with smaller cell parameter. The cell parameter of a unit cell is related to the atomic radius. Let us analyze the case of a face-centered unit cell. In each side of the cell, in each
155 face, we have four atoms in the vertexes and one in the center of the face. Of course these atoms do not belong only to this unit cell. However, if we symbolically cut the atoms in the face we can see the relation between the radius of the atom and the unit cell. The edges of the cell does not correspond to any cell parameter. However, the line that connect the bottom part with the opposite top part corresponds to a specific number of cell parameters, as the atoms are touching in this direction. In particular this distance is $4r$. Using Pythagoras theorem we have: $c^2 + c^2 = (4r)^2$. Therefore, $c = \sqrt{8}r$.

| Crystal structure | relation between c and r |
|-------------------|------------------------------|
| sc | $c = r$ |
| bcc | $c = \frac{4}{\sqrt{3}}r$ |
| fcc | $c = \sqrt{8}r$ |

Figure 1.5: Relationship between cell parameter c and atomic size r for different types of unit cells

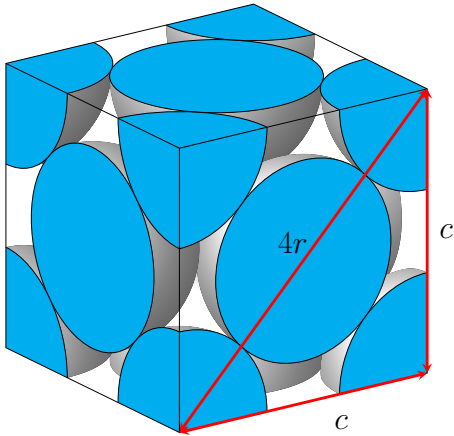
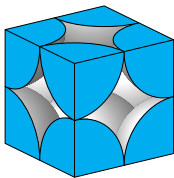


Figure 1.6 This is a space-filling representation of a fcc unit cell.

Sample Problem 5

For the following unit cell, calculate the relationship between the cell parameter and the atomic radius.

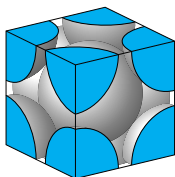


SOLUTION

For this unit cell, the atoms in the bottom part are touching. Hence, the cell parameter should be related to the atomic radius. In particular, two half atoms occupy the same distance as the cell parameter, so $c = r$.

STUDY CHECK

For the following unit cell, calculate the relationship between the cell parameter and the atomic radius.



Answer: $c = \frac{4}{\sqrt{3}}r$.

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Metal density Different metals have different density. The value for density will depend on the cell parameter but also on the compacity of the unit cell, the more compact the unit cell the more atoms per cell and hence the more density. The formula that relates density with cell parameter and atoms per cell is:

$$d = \frac{N \cdot AW}{c^3 \cdot 6.023 \times 10^{-7}} \quad \text{Metallic density formula}$$

where:

d is the density in $g \cdot ml^{-1}$

N is the number of atoms per unit cell

6.023×10^{-7} is related to the conversion between atoms and grams

AW is the atomic weight of the metal

c is the cell parameter in pm

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Sample Problem 6

Calculate density of iron ($AW = 55.845g \cdot mol^{-1}$) knowing this is a bcc metal with cell parameter is 286pm.

SOLUTION

We know that iron is a bcc metal and hence it has two atoms per unit cell. Also we know its atomic weight $AW = 55.845g \cdot mol^{-1}$ and the cell parameter $c = 286pm$. Using the metallic density formula:

$$d = \frac{2 \cdot 55.845}{286^3 \cdot 6.023 \times 10^{-7}} = \frac{111.69}{14.09} = 7.93g \cdot ml^{-1}$$

STUDY CHECK

Calculate density of gold ($AW=196.96g \cdot mol^{-1}$) knowing this is a fcc metal with cell parameter is 406pm.

Answer: $19.54g \cdot ml^{-1}$.

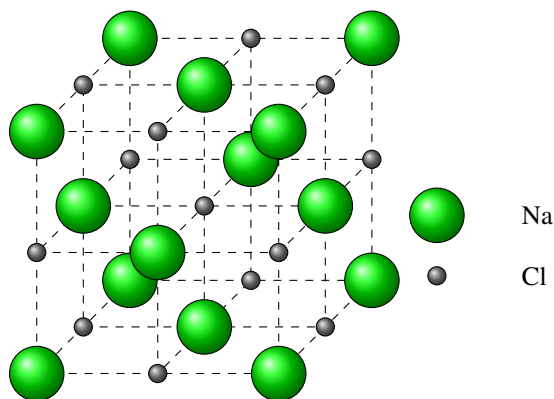
Ionic solids Ionic solids have high melting point and they are typically hard. They also do not conduct the electricity in solid form. An example of an ionic solid is NaCl. The structure of NaCl and many other ionic solids results from the superposition of two different compact lattices—this is the reason these are called binary solids as they are made of two units—and each lattice is superimposed. Normally, the largest ion (Na^+) forms a packed arrangement such as fcc or ccp, and the smallest ion (Cl^-) resides on

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the holes of the lattice. Here we will care about constructing the formula of the unit cell, such as NaCl by counting the atoms in the unit cell.

Sample Problem 7

Calculate the formula for the following unit cell



SOLUTION

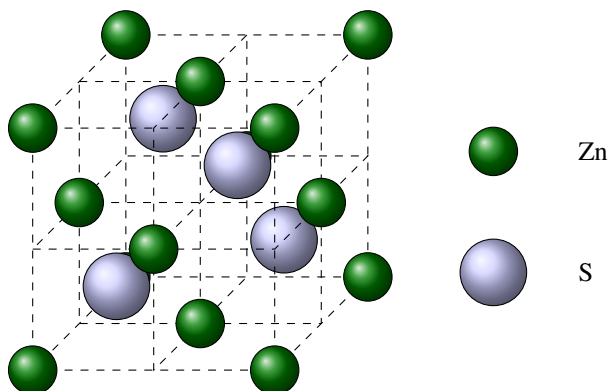
The unit cell contains Cl^- and Na^+ . Remember every location in the unit cell has different sharing factor. We will compute the number of atoms in each location and multiply by the sharing factor to calculate the number of Cl and Na in the cell:

| Location | Sharing Factor, f | # atoms, N | $f \times N$ |
|----------|---------------------|-----------------|--------------|
| Corner | $\frac{1}{8}$ | 8Na^+ | 1 |
| Faces | $\frac{1}{2}$ | 6Na^+ | 3 |
| sides | $\frac{1}{4}$ | 12Cl^- | 3 |
| Inside | 1 | 1Cl^- | 1 |

Overall, we have Na_4Cl_4 which corresponds with the formula NaCl.

STUDY CHECK

Calculate the formula for the following unit cell:



Answer: Zn_4S_4 .

1.4 Liquid state

This section will cover the liquid state. In particular the importance of the vapor pressure of a liquid and the role of the enthalpy of vaporization—remember enthalpy represents heat.

Vapor pressure of a liquid The molecules of a liquid that are in contact with the atmosphere are more likely to be able to escape into the gas phase forming what we call a vapor pressure. This effect is responsible for the humidity the air and the smell of liquid chemicals. Chemicals with high vapor pressure would vaporize readily and of they have a smell would be able to smell them readily also.

Enthalpy of vaporization, ΔH_{vap} The enthalpy of vaporization is the energy needed to vaporize a liquid. Think about the smell of a perfume you like. Now, think about the smell of water. Why a perfume smells and water does not. The enthalpy of vaporization of a perfume is small whereas ΔH_{vap} for water is larger ($41\text{ kJ} \cdot \text{mol}^{-1}$). This means it is easier for the perfume molecules to escape into the gas phase and hence produce a smell. Another example is acetone–nail polish remover. This chemical has a very distinctive smell. ΔH_{vap} for acetone is $31\text{ kJ} \cdot \text{mol}^{-1}$. If you compare this value with the value of water you can see acetone is more likely to have a smell. Mind that ΔH_{vap} values are normally positive. This corresponds to the fact that we have to give energy to the liquid in order to create a vapor, and hence the process is endothermic.

Sample Problem 8

Order the following compounds from high to low vapor pressure: C_6H_6 ($\Delta H_{vap}=31\text{ kJ} \cdot \text{mol}^{-1}$), $\text{C}_6\text{H}_5\text{OH}$ ($\Delta H_{vap}=39\text{ kJ} \cdot \text{mol}^{-1}$), H_2O ($\Delta H_{vap}=41\text{ kJ} \cdot \text{mol}^{-1}$)

SOLUTION

The larger ΔH_{vap} the harder it is to vaporize a liquid and hence the lower the vapor pressure of the liquid. If we compare the liquids in this example, water has the lowest vapor pressure, whereas cyclohexane (C_6H_6) has the highest vapor pressure.

STUDY CHECK

Order the following compounds from high to low vapor pressure (P_{vap}): NH_3 ($\Delta H_{vap}=23\text{ kJ} \cdot \text{mol}^{-1}$), CH_4 ($\Delta H_{vap}=8\text{ kJ} \cdot \text{mol}^{-1}$), C_4H_{10} ($\Delta H_{vap}=15\text{ kJ} \cdot \text{mol}^{-1}$)

Answer: $P_{vap}(\text{CH}_4) > P_{vap}(\text{C}_4\text{H}_{10}) > P_{vap}(\text{NH}_3)$.

Vapor pressure change with temperature This pressure strongly depends on temperature. That is the reason why summer days can also be humid days if you live near the seaside. The following formula gives the relation between vapor pressure and temperature. Mind that for every temperature we will have a vapor pressure value. In the formula you will to pairs of temperatures and hence two pairs of vapor pressures:

$$\ln\left(\frac{P_{vap,T_1}}{P_{vap,T_2}}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad \text{Clausius-Clapeyron relation}$$

where:

P_{vap,T_1} is the vapor pressure at temperature T_1 in Kelvin

ΔH_{vap} is the enthalpy of vaporization in $\text{J} \cdot \text{mol}^{-1}$

$R=8.314\text{ J/K/mol}$ is the constant of the gases in energy units

Sample Problem 9

The vapor pressure of water at 298K is 0.03 atm. Calculate the vapor pressure of water at 323K given $\Delta H_{vap} = 43.9 \text{ KJ} \cdot \text{mol}^{-1}$.

SOLUTION

In order to use the Clausius-Clapeyron relation we need two pairs of (T, P_{vap}) values. In this problem, we have the value of the vapor pressure at 298K, hence we have (298K, 0.03 atm) and they ask the pressure at 323K. Therefore the second pair is (323K, x atm), where X is the vapor pressure at 323K—what they are asking in the problem. We can call (298K, 0.03 atm) as (T_1, P_{vap,T_1}) and (323K, X atm) as (T_2, P_{vap,T_2}) . At this point we have $T_1 = 298\text{K}$ and $P_{vap,T_1} = 0.03\text{atm}$ and $T_2 = 323\text{K}$ and $P_{vap,T_2} = x$. We also have the enthalpy of vaporization. Minds that this value has to be given in $\text{J} \cdot \text{mol}^{-1}$ and hence, we will use $\Delta H_{vap} = 43.9 \times 10^3 \text{ J} \cdot \text{mol}^{-1}$. Now we can plug these values into the formula:

$$\ln\left(\frac{0.03}{x}\right) = \frac{43.9 \times 10^3}{8.314} \left(\frac{1}{323} - \frac{1}{298} \right)$$

Let us solve this step by step. First we solve the part on the right:

$$\ln\left(\frac{0.03}{x}\right) = -1.37$$

Now, in order to eliminate the logarithm we should use the exponential function in both sides:

$$\frac{0.03}{x} = e^{-1.37}$$

Calculating the exponential of -1.37 we have:

$$\frac{0.03}{x} = 0.25$$

That leads to a x value of 0.11 atm.

STUDY CHECK

Using the data below, calculate ΔH_{vap} for HNO_3 .

| T (K) | P_{vap} (mmHg) |
|-------|------------------|
| 10 | 26.6 |
| 20 | 47.9 |
| 30 | 81.3 |

Answer: 97.80 J/mol.

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1.5 Phase diagrams

Water can be found at different states: liquid, solid and gas. We know at room temperature—and atmospheric pressure—water is a liquid. However, what if we warm up a sample of water? When does it become vapor? And more importantly, what if the working pressure is not one atmosphere? Would water boil the same near the sea or on top of a mountain? The answer to all these questions can be found in the phase diagram of water. This section

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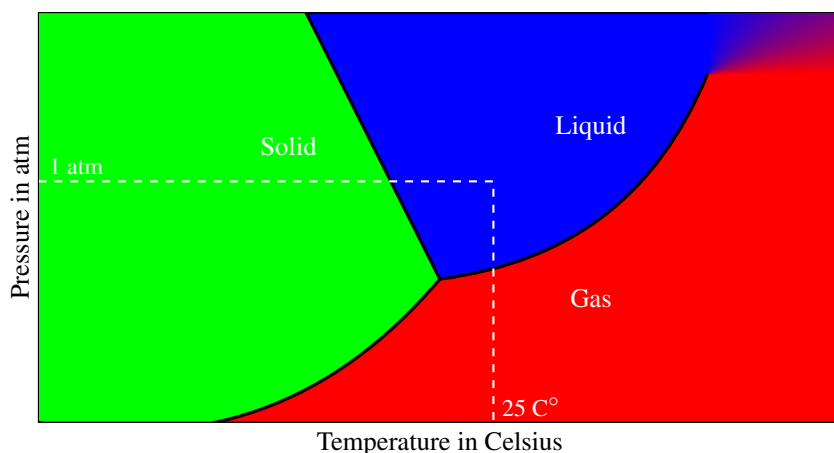


Figure 1.7: The phase diagram of water with pressure in the Y axis and temperature in the X axis. This diagram displays the different states of matter of water for different pressure and temperature conditions. The state of matter at any temperature and pressure conditions. You will learn how to read phase diagrams in order to predict

the state of matter at any temperature and pressure conditions. You will also learn how to identify critical and triple points. The coordinates of the triple point are 0.01°C and 0.006 atm . This means that at this low pressure and temperature conditions we have three phases in contact: water, ice and steam. The coordinates of the critical point are 374°C and 218 atm . A phase diagram is just a diagram with temperature in the X-axis and pressure in the Y-axis. It tells you whether you have gas, liquid or gas at a large range of pressure and temperature conditions. For example, the figure on the side of the page presents the phase diagram of water and the line indicates the phase present at (Temperature, Pressure) conditions of $(25^\circ\text{C}, 1\text{ atm})$. Obviously, this phase is liquid water. *Normal conditions* refer to pressure conditions of 1 atm . Hence, we say that the normal boiling point of water—this means at 1 atm —is 100°C . In the following we will analyze a set of experiments represented as vertical and horizontal lines in the diagram. Horizontal lines are cooling/heating experiments in which pressure is kept fixed and temperature changes. Vertical lines represent compression/decompression experiments in which pressure changes at constant temperature.

Heating experiments The figure on the side displays a set of cooling/heating experiments. In the first experiment, we start by having a solid that we heat up to obtain first a mixture between liquid and solid and then a pure liquid. In this experiment we just transitioned between solid into a liquid. Experiment 2 is different. We also start by having a solid. The difference is that this time we reach a point called *tripe point* in this point the three phase coexist at a single pressure and temperature. Therefore, in this experiment, we go from a solid into a mixture of solid, liquid and gas. After that we transition directly into a gas. Experiment number three is called sublimation. In this experiment we start by having a solid that transitions into a gas by means of a mixture of solid and gas.

Compression experiments The figure on the side also displays a set of compression/decompression experiments. The first experiment is a compression experiment in which we start from a gas and we end up having a liquid by means of a mixture of both. The second experiment start beyond the *critical point* and hence even if you compress the gas you will never reach a liquid state. The critical point is the point beyond which one cannot liquify a gas or gasify a liquid.

Important points in a phase diagram There are two important points in a phase diagram. One is the triple point in which three phases coexist. Another important point is the critical point belong which one cannot liquify or condense the chemical.

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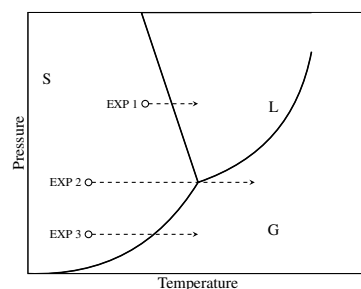


Figure 1.8: Some heating and compressing experiments.

250

Remember also the lines in a phase diagram represent phase transitions and hence two phases are present on these lines.

CHAPTER 1

INTERMOLECULAR FORCES

1.1 Indicate the strongest intermolecular force existing between the molecules of the following compounds:

(a) CH_3OH (b) H_2 (c) CCl_4

1.2 Indicate the strongest intermolecular force existing between the molecules of the following compounds:

(a) CH_4 (b) CCl_3H (c) HF (d) HCl

1.3 From the following pair of molecules, which molecule forms intermolecular H bonds? (a) HF or H_2 (b) NH_3 or CH_4

1.4 From the following pair of molecules, which molecule forms intermolecular H bonds? (a) $\text{CH}_3-\text{O}-\text{CH}_3$ or H_2O (b) HCl or HF

1.5 From the following pair of molecules, which molecule forms stronger dispersion forces? (a) Ar or He (b) H_2O or H_2S

1.6 From the following pair of molecules, which molecule forms stronger dispersion forces? (a) CH_3CH_3 or CH_4 (b) CH_4 or CH_3Cl

1.7 From the following pair of molecules, which molecule forms stronger dipole forces? (a) HCl or HBr (b) H_2O or H_2S

1.8 From the following pair of molecules, which molecule forms stronger dipole forces? (a) NH_3 or H_2O (b) HI or HBr

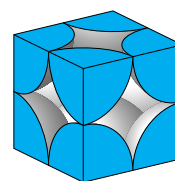
1.9 From the following pair of molecules, which molecule has higher boiling point? (a) CH_3CH_3 or CH_4 (b) CO_2 or H_2O

1.10 From the following pair of molecules, which molecule has higher boiling point? (a) HF or HCl (b) Ar or He

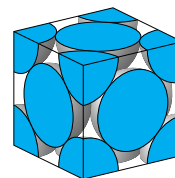
1.11 Indicate the number of atoms contained in the body-centered (bcc) cubic unit cell, for structures with the same type of atoms.

1.12 Indicate the number of atoms contained in the simple cubic (sc) unit cell, for structures with the same type of atoms?

1.13 The image displays the structure of Polonium. What is the number of atoms per unit cell for this metal?



1.14 The image displays the structure of Gold. What is the number of atoms per unit cell for this metal?

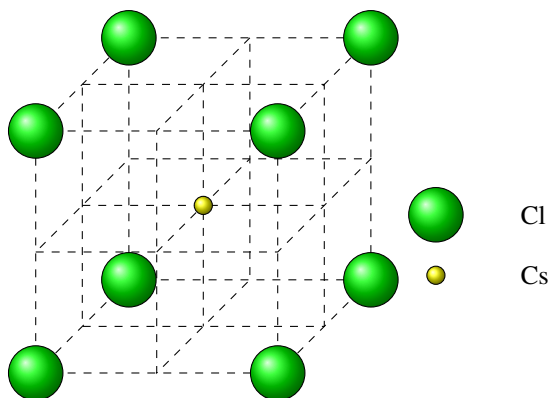


1.15 Identify the type of crystalline solid formed by the following compounds: (a) cesium chloride (b) tungsten

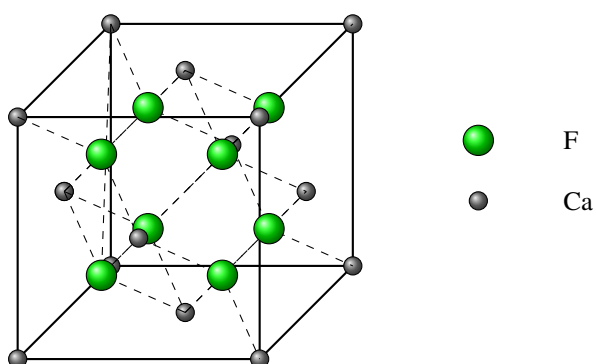
1.16 Identify the type of crystalline solid formed by the following compounds: (a) acetic acid (b) hydrogen sulfide

1.17 An element crystallizes in a face-centered cubic lattice and has a density of $1.5 \text{ g} \cdot \text{mL}^{-1}$ and a cell parameter of 452pm. Calculate the approximate mass of the element.

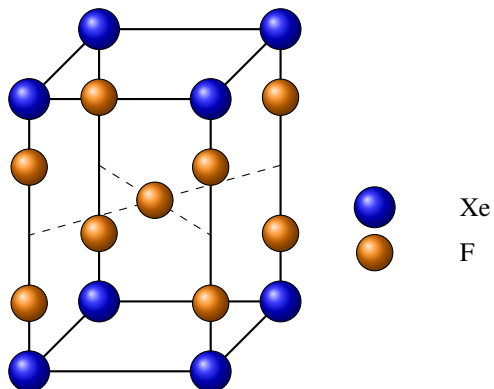
1.18 Calculate the formula for the following unit cell:



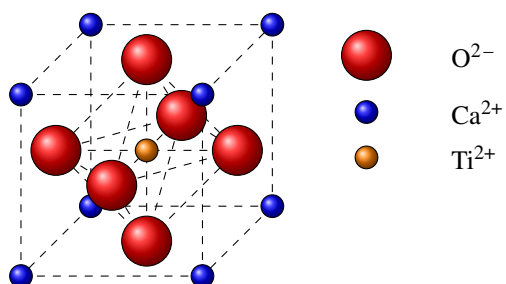
1.19 Calculate the formula for the following unit cell:



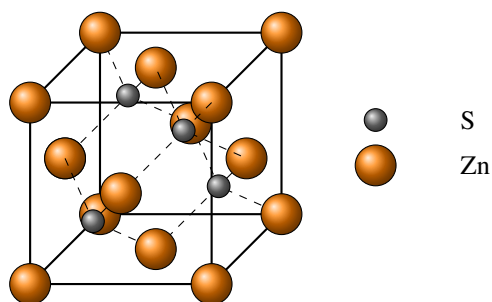
1.20 Calculate the formula for the following unit cell:



1.21 Calculate the formula for the following unit cell:



1.22 Calculate the formula for the following unit cell:



LIQUID STATE

1.23 A liquid has a enthalpy of vaporization of 30 kJ/mol and a boiling point of 122°C at 1.00 atm . Calculate its vapor pressure at 200°C .

1.24 What is the enthalpy of vaporization of a liquid that has a vapor pressure of 500 torr at 100°C and a boiling point of 90°C at 460 torr ?

Answers **1.1** (a) CH₃OH (hydrogen bonds) (b) H₂ (dispersion forces) (c) CCl₄ (dispersion forces) **1.3** (a) HF (b) NH₃ **1.5** (a) He (b) H₂S **1.7** (a) HCl (b) H₂O **1.9** (a) CH₃CH₃ (b) H₂O **1.11** 2 **1.13** 1 **1.15** (a) cesium chloride (ionic solid) (b) tungsten (atomic solid, metallic) **1.17** $20 \text{ g} \cdot \text{mol}^{-1}$