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Thermochemistry

ENERGY involves many aspects of our everyday life. Chemical reactions happening in our body consume or release energy as we walk, study, and even breath. We also use energy at home to warm food or turn on the lights, to drive our cars and go to work. The energy needed for our body to function comes from food. If we do not eat for a while, we run low of energy. Similarly, the burning of fossil fuels such as oil, propane, or gasoline provides enough energy to maintain our homes. Some reactions produce energy whereas others release energy. On the other hand, how do we measure the energy released or consumed in a reaction? Thermochemistry is the study of heat in chemical reactions. This chapter will answer this and other questions as it covers different aspects of thermochemistry that involves the interaction between chemistry and energy. You will learn about temperature, heat and how to quantitatively compute the energy exchanged during a chemical reaction.

1.1 Energy & temperature

When you are running, walking, dancing, or thinking, you are using energy to do work. In fact, energy is defined as the ability to do work. Suppose you are climbing a steep hill. Perhaps you become too tired to go on; you do not have sufficient energy to do any more work. Now suppose you sit down and have lunch. In a while you will have obtained energy from the food, and you will be able to do more work and complete the climb. Similarly, chemical energy is the energy stored in the structure of chemicals and it depends on the arrangement of molecules and the nature of these molecules.

Potential & Kinetic Energy: *heat* Energy can be classified as potential energy or kinetic energy. Kinetic energy is the energy of motion and any fast-moving object has kinetic energy. Think about a bullet coming out of a gun; as the bullet moves very fast it contains kinetic energy that can be released when it collides with a target. Potential energy is energy stored in objects located at a certain height. A boulder resting on top of a mountain has potential energy because of its location. If the boulder rolls down the mountain, the potential energy becomes kinetic energy. Water stored in a reservoir has potential energy. When the water goes over the dam, the potential energy is converted to kinetic energy. The potential energy resulting from the interaction of charged particles is called electrostatic energy. Heat refers to thermal energy, which is associated with the random motion of particles in a substance and therefore is related to kinetic energy. A frozen pizza feels cold because the particles in the pizza are moving slowly. As the pizza receives heat, the motion of the particles increase. Eventually the particles have enough energy to make the pizza hot and ready to be eaten. When a



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GOALS

- 1 Convert heat to temperature rise
- 2 Carry calorimetric calculations
- 3 Use the enthalpy table
- 4 Compute enthalpy changes
- 5 Apply Hess's Law to compute enthalpy

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Discussion: What do you think about renewable energy? List three benefits and three inconveniences of renewable sources of energy.

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substance receives heat it gets warmer and it raises its temperature, whereas if it loses heat it gets cooler and its temperature decreases.

Mechanical energy: work The sum of potential and kinetic energy is called mechanical energy. Mechanical energy refers to the ability to do work. Examples of work are a car engine moving or a balloon expanding its volume.

The law of conservation energy In this chapter we will analyze energy changes associated with chemical reactions. In order to do this, we need to define the system and its surroundings. The system will be the chemical reaction often happening in a beaker, whereas the surroundings would be the area surrounding the beaker. The system plus its surroundings is called the universe. The beaker may lose energy, and in that case energy will flow from the system to the surroundings. Similarly, the system may gain energy, flowing from the surroundings to the beaker. In a closed system, the energy is being conserved and when one type of energy disappears, a different type of energy will appear. As an example, if you drop an object from the top of a building, originally the object had potential energy that converts into kinetic energy as the object gains speed. This is called the law of conservation of energy.

Energy units Two different units of energy are often employed: calories (cal) and joules (J). Joule is the SI unit of energy equal to $\text{kg} \cdot \text{m}^2/\text{s}^2$. One can transform calories to joules and joules to calories using the following conversion factor:

$$1\text{cal} = 4.184\text{J} \quad \text{or} \quad \frac{1\text{cal}}{4.184\text{J}} \quad (1.1)$$

As a note, often you will read in food labels the caloric content of certain foods. In these labels, they use the unit Calorie, with capitalized C, that is not the same as a calorie. One Calorie represents a kilocalorie, and contains 1000calories.

Sample Problem 1

Convert the following energy values:

(a) 50000 cal to Kcal (b) 48000 J to cal

SOLUTION

We will use the conversion factor for kilo and the relationship between calorie and joule:

(a) $50000\text{cal} \times \frac{1\text{kcal}}{1000\text{cal}} = 50\text{kcal}$; (b) $48000\text{J} \times \frac{1\text{cal}}{4.184\text{J}} = 11472.2\text{cal}$.

◆ STUDY CHECK

Convert the following energy units:

(a) 200 cal to Kcal (b) 7000 J to cal

Answer: (a) 0.2Kcal; (b) 1673 cal.

Temperature Temperature indicates how hot or cold a substance is compared to another substance. Heat always flows from a substance with a higher temperature to a substance with a lower temperature until the temperatures of both are the same. When you drink hot coffee or touch a hot pan, heat flows to your mouth or hand, which is at a lower temperature. When you touch an ice cube, it feels cold because heat flows from your hand to the colder ice cube. Three units of temperature often employed are celsius ($^{\circ}\text{C}$, T_C), Fahrenheit ($^{\circ}\text{F}$, T_F) or Kelvin (K, T_K). If you need to convert temperature units from Fahrenheit to celsius or from celsius to Fahrenheit you need to

▼Flowers convert sunlight into chemical energy



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▼a bullet has kinetic energy



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▼water on a dam has potential energy



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▼thermal energy refers to heat



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Figure 1.1: Examples of different types of energy

use the formulas below:

$$T_F = 1.8T_C + 32$$

$$T_F = 1.8T_K - 459.4$$

$$T_K = T_C + 273$$

(1.2)

Sample Problem 2

Convert 25 °C to °F.

SOLUTION

- 1 Step one:** list of the given variables.

Analyze the Problem	Given	Asking
	$T_c = 25^\circ C$	T_F

- 2 Step two:** use the formula $T_F = 1.8T_C + 32$ to convert from °C to °F.

$$T_F = 1.8 T_c + 32$$

\nearrow
25°

- 3 Step three:** solve for $T_F = 1.8 \times 25 + 32 = 77^\circ F$.

◆ STUDY CHECK

Convert 200°C to K.

Answer: 473K.

Thermodynamics Thermochemistry is a subject of a broader field called thermodynamics, which studies the interconversion of energy (heat and other types) and mass. Thermodynamics study systems, like chemical reactions. The term system, refers to the part of the universe being study. Systems can be classified as: open, closed and isolated systems. An open system can exchange mass and energy with its surroundings, whereas a closed system can only exchange mass and not energy. Isolated systems cannot exchange neither mass nor energy with its surroundings. The state of a system is characterized by the values of its volume, pressure, temperature, energy and composition, so that if a system receives heat it will change its state. Energy, volume, pressure and temperature are called state functions—or state properties—, as these properties are determined by the state of the system, independently of the path used to reach that state. In another words, these properties are path-independent. For example, in a building, the floor location of a person would be a state function, as it would not matter the path the person took to reach that state. In contrast the amount of effort to make it to a specific floor will not be a state function, as it changes depending on the path used.

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1.2 The first law of thermodynamics. From energy to temperature

Materials can absorb heat and receive work. On one hand, think about a pizza in your oven, or a cup of milk in the microwaves. These substances receive heat from the oven or in form of microwaves and they become hot. Heat transforms in an increase of temperature. On the other hand, if you hammer a wall, the wall receives work from you and this work is translated to energy as the wall may break. Work and heat are both combined in a property called internal energy, E . Heat transform in a temperature change. Some substances like metals are able to increase its temperature very quickly with a small amount of heat received, whereas others need a larger amount of heat to rise up its temperature. Think about why you use oil to deep fried food? Why not using water? First of all, oil can rise its temperature very quickly and on top of that it does not boil easily.

Work Think about what happens at a car's engine. In an engine, chemical energy is converted in movement and with this movement, a car is able to carry work. Work (W) is force (F) applied over a distance (Δh):

$$W = F \cdot \Delta h = (P \cdot A) \cdot \Delta h$$

For the case of a gas confined in a cylindrical container, force is related to pressure times area (A). Therefore, if the pressure is constant as $A \cdot \Delta h$ equals to volume (V), we have that

$$W = -P \cdot \Delta V \quad (1.3)$$

where:

100 W represent work

P is the pressure

ΔV is the change of volume calculated as $V_{final} - V_{initial}$

The minus sign is just a convention, as in chemistry the work done by the surroundings to a system is considered positive, as the system gains work (energy). Therefore, when 105 ΔV is negative because the system receives work, the value of W has to be positive. In another words, the sign convention for work is:

$W > 0$ the system receives work and $W < 0$ the system gives away work

As a final note, the type of work that involves change in volume at constant pressure is normally called PV work.

Sample Problem 3

Calculate the work (in $L \cdot atm$) involved in the expansion of a gas from 10L to 20L at constant external pressure of 2atm. Convert the value in joules using $1J=101.3L \cdot atm$.

SOLUTION

We will use Equation 1.3 that related work with pressure and volume change:

$$W = -P \cdot \Delta V = -2atm \cdot (20 - 10)L = -20L \cdot atm$$

If we convert this value into J:

$$-20L \cdot atm \times \frac{1J}{101.3L \cdot atm} = -0.2J$$

As the value is negative, it means that the system gives away work.

❖ STUDY CHECK

Calculate the work (in $\text{L} \cdot \text{atm}$) involved in the compression of a gas from 10L to 5L at constant external pressure of 5atm. Convert the value in joules using $1\text{J}=101.3\text{L} \cdot \text{atm}$.

Answer: $25\text{L} \cdot \text{atm}, 0.24\text{J}$.

Heat capacity The heat capacity c of a material is defined as:

$$c = \frac{\text{heat adsorbed}}{\text{temperature increase}} \quad (1.4)$$

The heat capacity is a characteristic property of each material that indicates the energy required to rise its temperature and can be expressed in $\text{cal}/^\circ\text{C}$ or $\text{J}/^\circ\text{C}$ units. As this property depends on the amount of matter, often times the heat capacity is expressed per mass as the specific heat capacity (c_e) or mole unit as the molar heat capacity c_m . For example, the specific heat of water is $1\text{cal/g}^\circ\text{C}$ that is the same as $4.184\text{J/g}^\circ\text{C}$. That means that we need to give 1 calorie in order to warm up one gram of water 1°C . Similarly, the specific heat of aluminum, a metal, is $0.2\text{cal/g}^\circ\text{C}$ or $0.89\text{J/g}^\circ\text{C}$; that means the energy needed to rise the temperature of an aluminum gram is 0.2 calories of 0.89 J . Mind the difference between these two values: we need to give 1 cal in order to increase the temperature of a gram of water in 1°C , whereas we need to give 0.2 cal in order to increase the temperature of a gram of aluminum in 1°C . Why are these two numbers so different? The answer is because water and aluminum are different materials. Normally metals warp up very easily, that is, they need less heat to increase their temperature, whereas liquids need more heat to increase their temperature. That is why pans and cooking pots tend to be metallic. Mind the specific heat if water is a well known value that you need to be familiar with:

$$c_e^{\text{H}_2\text{O}} = 4.184\text{J/g}^\circ\text{C} \quad \text{or} \quad c_e^{\text{H}_2\text{O}} = 1\text{cal/g}^\circ\text{C} \quad (1.5)$$

Table 1.1 Values of specific heat for different materials

Material	Specific heat ($\text{J/g}^\circ\text{C}$)	Material	Specific heat ($\text{J/g}^\circ\text{C}$)
$\text{H}_2\text{O(l)}$	4.184	Fe(s)	0.444
ethyl alcohol _(l)	2.460	Au(s)	0.129
vegetable oil _(l)	1.790	Cu(s)	0.385
$\text{NH}_3\text{(l)}$	4.700	$\text{H}_2\text{O(s)}$	2.010
Dry Air _(g)	1.0035	$\text{CO}_2\text{(g)}$	0.839

Heat When a material receives heat, that heat normally becomes temperature as the temperature of the material increases. For example, if you warm milk in a microwave, the milk's temperature increases from room temperature (25°C) to a higher temperature. How to estimate the temperature increase given the heat received? Or how to estimate the heat needed to increase the temperature of an object? We can use the following formula:

$$Q = m \cdot c_e \cdot (T_f - T_i) \quad (1.6)$$

where:

Q is the amount of heat received, either in cal or J.

m is the mass of material in grams

c_e is the specific heat of the material (in $\text{cal/g}^\circ\text{C}$ or $\text{J/g}^\circ\text{C}$)

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$T_f - T_i = \Delta T$, is the temperature change from the initial to the final temperature

A system can receive or give away heat and this is indicated by the sign of Q . The sign convention for heat is:

$Q > 0$ the system receives heat and $Q < 0$ the system gives away heat

Sample Problem 4

How many calories are absorbed by a 45.2g piece of aluminum ($c_e = 0.214 \frac{\text{cal}}{\text{g}^\circ\text{C}}$) if its temperature rises from 25°C to 50°C .

SOLUTION

- 1 Step one: list of the given variables.

Analyze the Problem	Given	Asking
	$c_e = 0.214 \frac{\text{cal}}{\text{g}^\circ\text{C}}$ $m = 45.2\text{g}$ $T_{\text{initial}} = 25^\circ\text{C}$ $T_{\text{final}} = 50^\circ\text{C}$	Q

- 2 Step two: use the formula $Q = m \cdot c_e \cdot (T_{\text{final}} - T_{\text{initial}})$ to temperature increase to heat absorbed:

$$Q = m \cdot c_e \cdot (T_{\text{final}} - T_{\text{initial}})$$

The diagram shows the formula $Q = m \cdot c_e \cdot (T_{\text{final}} - T_{\text{initial}})$. Arrows point from the values in the problem statement to each term in the equation: a blue arrow from 25°C to T_{final} , a red arrow from 45.2g to m , and another red arrow from $0.214 \frac{\text{cal}}{\text{g}^\circ\text{C}}$ to c_e .

- 3 Step three: solve $Q = 45.2 \cdot 0.214 \cdot (50 - 25) = 241.82\text{cal}$.

❖ STUDY CHECK

How many calories are absorbed by 100g of Gold ($c_e = 0.0308 \frac{\text{cal}}{\text{g}^\circ\text{C}}$) if its temperature rises from 25°C to 100°C .

Answer: $Q = 231\text{cal}$.

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First law of thermodynamics: the internal energy The combination of work (W) and heat (Q) is called internal energy (ΔE):

$$\Delta E = Q + W \quad (1.7)$$

The first law of thermodynamics—the law of conservation of energy—states that the energy of the universe is constant.

Sample Problem 5

When a hot balloon inflates and deflates in order to change its height. It receives 10^3J of heat and its volume increases from $3.0 \times 10^5\text{L}$ to $3.5 \times 10^5\text{L}$ at fixed external pressure of 1atm . Calculate the internal energy of the hot balloon, using $1\text{J}=101.3\text{L} \cdot \text{atm}$.

SOLUTION

We will use Equation 1.3 that related work with pressure and volume change. As the resulting unit of work will be $\text{L} \cdot \text{atm}$, we will directly convert the value into J :

$$W = -P \cdot \Delta V = -1\text{atm} \cdot (3.5 \times 10^5 - 3.0 \times 10^5)\text{L} \times \frac{1\text{J}}{101.3\text{L} \cdot \text{atm}} = -493.6\text{J}$$

Now we will add the value of heat (10^3J) to the value of work to calculate the internal energy:

$$\Delta E = Q + W = 10^3 + (-493.6) = 1493.6\text{J}$$

Overall, the hot balloon receives more heat than the work it gives away and hence the resulting internal energy is positive—the system gains energy.

❖ STUDY CHECK

When a hot balloon deflates, it receives 10^7J of work from the external atmosphere and its temperature change from 90°C to 25°C . Given that the air initially contained in the balloon has a mass of $3 \times 10^5\text{g}$ and a specific heat of $1\text{J/g}^\circ\text{C}$ Calculate the internal energy of the hot balloon.

Answer: $-9.5 \times 10^6\text{J}$.

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1.3 Calorimetry

A calorimeter is a tool used to measure the exchange of heat happening in chemical reactions and calorimetry is the science that measures heat exchange by using calorimeters. There are two types of calorimeters, very fancy and expensive ones called constant-volume calorimeters and more affordable ones, in the form of a coffee cup, called constant-pressure calorimeters. This section will show you how to carry calorimetric calculations.

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The calorimeter A calorimeter is device used to measure the energy exchanged in a chemical reaction—we call this molar heat of reaction, ΔQ_r . In essence, a calorimeter is a closed system that does not let the heat come through its walls. By measuring the temperature change inside the calorimeter we can compute the energy exchange in a chemical reaction happening inside the calorimeter. If the temperature inside a calorimeter increases, this means that the reaction releases energy. In the contrary, if the temperature inside a calorimeter decreases, this means that the reaction consumes energy. There are two different types of calorimeters: constant-pressure and constant-volume calorimeters. As a note, ΔQ_r is called molar heat of reaction as it represents energy per mole, with units of kJ/mol .

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Exothermic and endothermic reactions Some reactions release heat and are called exothermic. Others absorb heat and are called endothermic. Think for example the combustion of the gas in a cooking stove, it produces heat and hence the

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chemical reaction happening is exothermic. Differently, if you cook bread, it needs heat to rise. Similarly, if you melt an ice cube you need to give energy to the cube so that it becomes water. These are examples of endothermic reactions. Endothermic reactions have positive ΔQ_r whereas exothermic reactions have negative ΔQ_r .

Constant-pressure calorimeter A constant-pressure calorimeter is the simplest of all calorimeters and is called constant-pressure as the pressure inside the calorimeter is constant and equal to the atmospheric pressure. A constant-pressure calorimeter is just a double coffee cup covered with a lid. Inside this cup a chemical reaction occurs in a liquid phase. If the reaction produces any gases as the cup is just covered with a lid, the pressure will always be equal to the atmospheric pressure as the gas can escape through the lid. The formula used in calorimetry with a constant-pressure calorimeter has only two terms. Let us use a reaction that produced heat as an example. Inside a constant-pressure calorimeter, you introduced two reagents, and a reaction happens producing heat. The heat exchanged from the reaction (first term) changes the temperature of the liquid inside the calorimeter (second term). At the same time, we assume that the walls of the calorimeter do not absorb heat. The formula used in calorimetry with a constant-pressure calorimeter is the following:

$$0 = n \cdot \Delta Q_r + \Delta Q_{water} \quad \text{constant pressure}$$

where:

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$n \cdot \Delta Q_r$ is the heat exchanged due to a chemical reaction

ΔQ_{water} is the heat received or released by water

The water contribution is given by the heat formula given above. After we plug the formula of the heat into the formula above we arrive to the constant-pressure calorimetry formula:

$$0 = n \cdot \Delta Q_r + V \cdot d \cdot c_e^{\text{sol}} \cdot (T_f - T_i) \quad \text{constant pressure}$$

where:

ΔQ_r is the heat exchanged due to a chemical reaction in J/mol

n is the number of moles of the limiting reagent

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V is the volume of water in mL contained in the calorimeter

d is the density of the solution in g/mL

c_e^{sol} is the specific heat of the solution: tend to be similar to water, $4.184\text{J/g}^\circ\text{C}$

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$T_f - T_i = \Delta T$, is the temperature change from the initial to the final temperature

Sample Problem 6

We mix 5mL of NaOH 0.5M with 5mL of HCl 0.5M both at 25°C in a constant-pressure calorimeter. The final temperature inside the calorimeter is 27°C . Calculate the heat of reaction if the solution density is 1g/mL and the specific heat of the solution is $4.184\text{J}/^\circ\text{C}$.

SOLUTION

Analyze the Problem	Given	Asking
	$n = 5 \times 10^{-3} L$ $0.5M = 2.5 \times 10^{-3}$ moles $V = 10mL$ $d = 1g/mL$ $T_f = 27^\circ C$ $T_i = 25^\circ C$ $c_e^{\text{H}_2\text{O}} =$ $4.184\text{J/g}^\circ\text{C}$	ΔQ_r

We have all data needed to solve the calorimetry formula. We have the moles of the limiting reagent, the overall volume of the mixture, the density of the mixture, the temperature change and the specific heat of the solution. Plugging all values into the calorimetry formula we have:

$$0 = n \cdot \Delta Q_r + V \cdot d \cdot c_e^{\text{sol}} \cdot (T_f - T_i)$$

$$0 = 2.5 \times 10^{-3} \text{mol} \cdot \Delta Q_r + 10g \cdot 4.184\text{J/g}^\circ\text{C} \cdot (27^\circ\text{C} - 25^\circ\text{C})$$

Solving for ΔQ_r we obtain -33472J/mol that is the same as -33.5KJ/mol . As the value is negative, it means that the reaction produced energy and hence is exothermic.

◆ STUDY CHECK

We mix 2.5mL of NaOH 0.5M with 2.5mL of HCl 0.5M both at 25°C in a constant-pressure calorimeter. The heat of reaction is -40KJ/mol . Calculate the final temperature inside the calorimeter, if the solution density is 1g/mL and the specific heat of the solution is $4.184\text{J/g}^\circ\text{C}$.

Answer: 27.39°C .

Constant-volume calorimeter A constant-volume calorimeter—also known as a bomb calorimeter—is a more complex and costly calorimeter in which normally gas phase reactions occur. This type of calorimeters are rigid and even if gas is produced the volume of the container will not change—that is why is called a constant-volume calorimeter. Constant-volume calorimeters are used to calculate the energy value of food—and for example calculate the calories in a bag of chips.

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The formula to carry calorimetric calculations with a constant-volume calorimeter has three terms: the first term represents the energy exchanged due to the reaction, the second term represents the energy exchanged by water in the calorimeter, and the last term represents the heat exchanged by the walls of the calorimeter. The formula used in a constant-volume calorimeter is the following:

$$0 = n \cdot \Delta Q_r + \Delta Q_{\text{water}} + \Delta Q_{\text{walls}}$$

where:

$n \cdot \Delta Q_r$ is the heat exchanged due to a chemical reaction

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ΔQ_{water} is the heat received or released by water

ΔQ_{walls} is the heat absorbed by the walls

$$0 = n \cdot \Delta Q_r + m \cdot c_e^{\text{H}_2\text{O}} \cdot (T_f - T_i) + c^{\text{cal}} \cdot (T_f - T_i)$$
Constant-volume

where:

ΔQ_r is the heat exchanged due to a chemical reaction in J/mol

200 n is the number of moles reacted inside the calorimeter

m is the mass of water contained in the calorimeter

$c_e^{\text{H}_2\text{O}}$ is the specific heat absorbed of water: $4.184\text{J/g}^\circ\text{C}$

c^{cal} is the heat capacity of the calorimeter also known as calorimeter factor

205 $T_f - T_i = \Delta T$, is the temperature change from the initial to the final temperature

Sample Problem 7

A 3 mol-sample of a chemical is burned in a constant-volume calorimeter with 10g of water and a heat capacity of $10\text{KJ}/^\circ\text{C}$. Calculate the heat of reaction knowing that the initial temperature of the water inside the calorimeter is 25°C and the final 40°C .

SOLUTION

	Given	Asking
Analyze the Problem	$n = 3\text{mol}$ $m = 10\text{g}$ $T_f = 40^\circ\text{C}$ $T_i = 25^\circ\text{C}$ $c^{\text{cal}} = 10^4\text{J}/^\circ\text{C}$ $c_e^{\text{H}_2\text{O}} = 4.184\text{J/g}^\circ\text{C}$	ΔQ_r

We have all data needed to solve the calorimetry formula. We have the moles of chemical inside the calorimeter, the heat capacity of the calorimeter, the initial and final temperature of water, and the amount of water. Mind that the specific heat of water is always given and you need to remember the value. Also and more importantly mind that the units of the heat capacity of the calorimeter are $\text{KJ}/^\circ\text{C}$, whereas the units of the specific heat of water are $\text{J/g}^\circ\text{C}$ and hence, we need to convert KJ into J ; that is the reason we use $10000\text{J}/^\circ\text{C}$ as the heat capacity of the calorimeter. Plugging all values into the calorimetry formula we have:

$$0 = 3\text{mol} \cdot \Delta Q_r + 10\text{g} \cdot 4.184\text{J/g}^\circ\text{C} \cdot (40^\circ\text{C} - 25^\circ\text{C}) + 10000\text{J}/^\circ\text{C} \cdot (40^\circ\text{C} - 25^\circ\text{C})$$

Solving for ΔQ_r we obtain -50209J/mol that is the same as -50.209KJ/mol . As the value is negative, it means that the reaction produced energy and hence is exothermic.

❖ STUDY CHECK

A 2 mol-sample of a chemical reacts in a constant-volume calorimeter

with 20g of water and a heat capacity of $11\text{KJ}/^\circ\text{C}$. Calculate the heat of reaction knowing that the temperature of water inside the calorimeter rises 10°C .

Answer: -55KJ/mol .

▼A constant-volume calorimeter



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▼A constant-pressure calorimeter



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Figure 1.2: Different types of calorimeters. A constant-volume calorimeter is also called a bomb calorimeter. A constant-pressure calorimeter is also called a coffee-cup calorimeter.

1.4 Enthalpy

In the last section we have seen that when a chemical reaction proceeds it exchanges energy with the surroundings. This energy can be measured in many different conditions. When it is measured at constant pressure—these are regular conditions in chemistry, think about a reaction happening at a beaker—this energy change has a different name: it is called enthalpy and is represented with the symbol ΔH_f° . In this section we will cover the different types of enthalpies depending on the type of reaction—formation or reaction—and we will find out how to compute the enthalpy change for a reaction using tables of standard enthalpies given at the end of the chapter.

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What is enthalpy? You want to think about enthalpy as heat. There are different ways to measure the heat exchanged in a system—as constant-pressure heat or constant-volume heat. Enthalpy, is the constant-pressure heat. It is important in chemistry, as many chemical reactions happen at constant pressure, that is, in open containers in contact with the atmosphere. Enthalpy, is indeed related to the internal energy

$$H = U + PV$$

Working at constant pressure we have

$$\Delta H = \Delta U + P\Delta V$$

as $\Delta U = Q - P\Delta V$ we have

$$\Delta H = Q_p$$

where Q_p means heat measured at constant pressure.

Table of standard enthalpies The values of enthalpies are tabulated at the end of the chapter. The term standard refers to standard pressure conditions (1 atm) and is indicated by a degree sign on the top right side (ΔH°). Let us see how to use this table. If you look for the standard enthalpy of C—an element—from the table you might find several values. The values of graphite carbon is $\Delta H_f^\circ = 0\text{KJ/mol}$. Differently, the values for diamond carbon is different than zero, being $\Delta H_f^\circ = 1.0\text{KJ/mol}$. Similarly, the value for gas carbon is not zero also, being $\Delta H_f^\circ = 716.67\text{KJ/mol}$. This is because the natural state of carbon is in the form of graphite. That is, the most common way in which we find carbon in nature is in the form of graphite and not diamond or gas. Let us find the standard enthalpy for molecular nitrogen, $\text{N}_2(\text{g})$ —another element. If you look into the table you will find a value of $\Delta H_f^\circ = 0\text{KJ/mol}$, again because the natural state of nitrogen is in the form of gas N_2 . How much is the standard enthalpy of gas hydrogen, H_2 ? If you look in the table, the value is also $\Delta H_f^\circ = 0\text{KJ/mol}$. The rule of thumb is: elements on its natural state have zero H_f° . Below we will explain more about the meaning of natural state. Now, look for the standard enthalpy of carbon monoxide gas, $\text{CO}(\text{g})$. The value should not be zero, as carbon dioxide is not an element and is made of two different types of atoms. Indeed, in the table we find $\Delta H_f^\circ(\text{CO}(\text{g})) = -110.5\text{KJ/mol}$.

Sample Problem 8

Using the enthalpy tables at the end of the chapter, locate the enthalpy values for: $\text{CaS}_{(\text{s})}$, $\text{AlCl}_3_{(\text{s})}$ and $\text{H}_2\text{O}_{(\text{l})}$.

SOLUTION

The enthalpy of calcium sulfide in solid state ($\text{CaS}_{(\text{s})}$) is -482.4KJ/mol . For the case of aluminum chloride in solid state too ($\text{AlCl}_3_{(\text{s})}$), the enthalpy is -705.63KJ/mol . Finally, the enthalpy of liquid water is -285.8KJ/mol .

❖ STUDY CHECK

Using the enthalpy tables at the end of the chapter, locate the enthalpy values for: $\text{I}_{2(\text{aq})}$, $\text{F}_{2(\text{g})}$ and $\text{C}_{\text{diamond}(\text{s})}$.

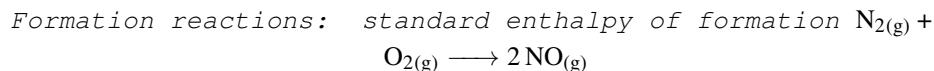
Answer: 23, 0, 1.9KJ/mol .

Natural state of an element The natural state of an element is the most stable state in which we find this element in nature. For example, you can find Aluminum as a solid, liquid or gas. However, its natural state is solid, as we find Al in nature as a solid. That is the reason why $\Delta H_f^\circ(\text{Al}_{(\text{g})}) = 314\text{KJ/mol}$, whereas $\Delta H_f^\circ(\text{Al}_{(\text{s})}) = 0\text{KJ/mol}$. In general, for metals, its natural state is solid. For non-metallic elements, such as hydrogen, oxygen, nitrogen, fluorine, chlorine, its natural state is in the form of a diatomic gas molecule. For example, $\Delta H_f^\circ(\text{H}_{2(\text{g})}) = 0\text{KJ/mol}$, $\Delta H_f^\circ(\text{N}_{2(\text{g})}) = 0\text{KJ/mol}$ or $\Delta H_f^\circ(\text{O}_{2(\text{g})}) = 0\text{KJ/mol}$. For the case of carbon, its natural state is graphite, $\Delta H_f^\circ(\text{C}_{\text{graphite}(\text{s})}) = 0\text{KJ/mol}$. Molecules such as H_2O or NO have standard enthalpy different than zero. Mind that molecules are not elements, and hence are made of different elements.

Table 1.2 Standard states for different elements. For all $\Delta H_f^\circ = 0\text{KJ/mol}$

Element	Standard state	Element	Standard state
Hydrogen	$\text{H}_2(\text{g})$	Oxygen	$\text{O}_2(\text{g})$
Nitrogen	$\text{N}_2(\text{g})$	Chlorine	$\text{Cl}_2(\text{g})$
Iron	$\text{Fe}(\text{s})$	Aluminium	$\text{Al}(\text{s})$
Carbon	$\text{C}_{\text{graphite}}(\text{s})$	Phosphorus	$\text{P}_4(\text{s})$
Fluorine	$\text{F}_2(\text{g})$	Bromine	$\text{Br}(\text{l})$
Mercury	$\text{Hg}(\text{l})$	Sulfur	$\text{S}_8(\text{s})$
Iodine	$\text{I}_2(\text{s})$	Silicon	$\text{Si}(\text{s})$

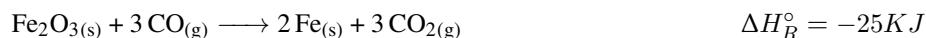
The formation reaction starts with natural-state elements (e.g. H_2 , N_2 , etc.) to form a 250 chemical. For example, the formation reaction of NO is given by:



On the products side we have the chemical formed (NO) whereas on the reactant side we have the elements that make NO on its natural state (H_2 and N_2) The enthalpy associated with this reaction is called standard enthalpy of formation $\Delta H_f^\circ(\text{NO}(\text{g}))$. This value is often listed on the right of the reaction:



ΔH_R° and ΔH_f° Consider the following two reactions:



The first example represents a formation reaction and thus the enthalpy is labeled as ΔH_f° . In contrast, the second reaction is not a formation reaction. This is because the reactants are not elements on its natural state: $\text{CO}(\text{g})$ and $\text{Fe}_2\text{O}_3(\text{s})$ has enthalpies different than zero. For this reason, the second enthalpy is labeled as ΔH_R° , and is called standard enthalpy of reaction. 265

Standard enthalpy change for a reaction In order to calculate the standard enthalpy for a reaction you need to use the following formula:

$$\boxed{\Delta H_R^\circ = \Delta H_{\text{products}}^\circ - \Delta H_{\text{reactants}}^\circ} \quad \text{Enthalpy change}$$

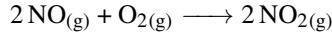
where:

ΔH_R° is the standard enthalpy change of the reaction

$\Delta H_{\text{products}}^\circ$ is the standard enthalpy of all products

$\Delta H_{\text{reactants}}^\circ$ is the standard enthalpy of all reactants 270

Now, imagine we need to calculate the change of standard enthalpy for the following reaction:



We need to locate three enthalpies from the table: $\Delta H_f^\circ(\text{NO}(\text{g}))$, $\Delta H_f^\circ(\text{O}_2(\text{g}))$, $\Delta H_f^\circ(\text{NO}_2(\text{g}))$. If you locate these values in the table you will see $\Delta H_f^\circ(\text{O}_2(\text{g})) = 0\text{KJ/mol}$, whereas $\Delta H_f^\circ(\text{NO}(\text{g})) = 90.29\text{KJ/mol}$ and $\Delta H_f^\circ(\text{NO}_2(\text{g})) = 33.2\text{KJ/mol}$.

Using the formula for ΔH_R° we have:

$$\Delta H_R^\circ = \Delta H_{products}^\circ - \Delta H_{reactants}^\circ =$$

$$= [2 \cdot \Delta H_f^\circ(\text{NO}_{2(g)})] - [2 \cdot \Delta H_f^\circ(\text{NO}_{(g)}) + \Delta H_f^\circ(\text{O}_{2(g)})] = \\ = [2 \cdot 33.2] - [2 \cdot 90.29 + 0] = -114\text{KJ}$$

This reaction is exothermic and releases heat.

Sample Problem 9

Using the enthalpy table, calculate ΔH_R° for the following reactions:

- (a) $4 \text{H}_{2(g)} + \text{O}_{2(g)} \longrightarrow 2 \text{H}_{2\text{O(l)}}$
- (b) $3 \text{H}_{2(g)} + \text{N}_{2(g)} \longrightarrow 2 \text{NH}_{3(g)}$
- (c) $2 \text{Al}_{(s)} + 3 \text{Cl}_{2(g)} \longrightarrow 2 \text{AlCl}_{3(s)}$

SOLUTION

In order to answer all questions, we need a set of ΔH_f° values: $\Delta H_f^\circ(\text{H}_{2(g)})$, $\Delta H_f^\circ(\text{O}_{2(g)})$, $\Delta H_f^\circ(\text{N}_{2(g)})$, $\Delta H_f^\circ(\text{Al}_{(s)})$ are all zero, whereas $\Delta H_f^\circ(\text{H}_{2\text{O(l)}}) = -285.8\text{KJ/mol}$, $\Delta H_f^\circ(\text{NH}_{3(g)}) = -45.0\text{KJ/mol}$ and $\Delta H_f^\circ(\text{AlCl}_{3(s)}) = -705.63\text{KJ/mol}$. For the first example, we have:

$$\Delta H_R^\circ = [2 \cdot \Delta H_f^\circ(\text{H}_{2\text{O(l)}})] - [4 \cdot \Delta H_f^\circ(\text{H}_{2(l)}) + \Delta H_f^\circ(\text{O}_{2(g)})] \\ = [2 \cdot -285.8] - [4 \cdot 0 + 0] = -572\text{KJ}$$

For the second example:

$$\Delta H_R^\circ = [2 \cdot \Delta H_f^\circ(\text{NH}_{3(g)})] - [2 \cdot \Delta H_f^\circ(\text{Al}_{(s)}) + 3 \cdot \Delta H_f^\circ(\text{Cl}_{2(g)})] \\ = [2 \cdot -45] - [2 \cdot 0 + 3 \cdot 0] = -90\text{KJ}$$

Finally, for the last reaction:

$$\Delta H_R^\circ = [2 \cdot \Delta H_f^\circ(\text{AlCl}_{3(s)})] - [3 \cdot \Delta H_f^\circ(\text{H}_{2(g)}) + \Delta H_f^\circ(\text{N}_{2(g)})] \\ = [2 \cdot -705.63] - [3 \cdot 0 + 0] = -1411\text{KJ}$$

◆ STUDY CHECK

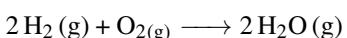
Using the enthalpy table, calculate ΔH_R° for the following reaction:



Answer: -25KJ .

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Heat-Mole conversions Remember that a chemical reaction can be translated into a series of conversion factors that relate the moles of reactants with the products or with other reactants. At the same time, a chemical reaction involving heat can be converted into a series of conversion factors that related energy and the moles of reactants and products. For the exothermic reaction:



$\Delta H = -572\text{KJ}$.

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the moles of hydrogen are related to heat as:

$$\frac{2 \text{ moles of H}_2}{-572 \text{ KJ}} \text{ or } \frac{-572 \text{ KJ}}{2 \text{ moles of H}_2}$$

Similarly, we can relate energy with moles of O₂ or moles of water:

$$\frac{1 \text{ moles of O}_2}{-572 \text{ KJ}} \text{ or } \frac{-572 \text{ KJ}}{1 \text{ moles of O}_2} \quad \frac{2 \text{ moles of H}_2\text{O}}{-572 \text{ KJ}} \text{ or } \frac{-572 \text{ KJ}}{2 \text{ moles of H}_2\text{O}}$$

We will use these relationships to convert moles of reactant or products into heat.

Sample Problem 10

Hydrogen reacts with nitrogen to produce ammonia (NH₃) according to the following reaction



Calculate: (a) the enthalpy of reaction; (b) indicate whether the reaction is endo or exothermic; (c) calculate the heat exchanged when produced 5 moles of ammonia.

SOLUTION

(a) the heat of reaction is -92KJ, and (b) the reaction is exothermic as the heat appears as a product. This means the reaction produces heat. (c) We will use the conversion factor that relates ammonia with heat and will set up the moles of ammonia on the bottom of the conversion factor so that the units will cancel and energy will remain

$$5 \cancel{\text{ moles of NH}_3} \times \frac{-92 \text{ KJ}}{2 \cancel{\text{ moles of NH}_3}} = -230 \text{ KJ,}$$

that is: 5 moles of ammonia produce -230KJ. The fact that this value is negative means that heat will be released.

◆ STUDY CHECK

Calculate the number of hydrogen moles needed to generate -200KJ.

Answer: 6.5 moles.

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1.5 Hess's Law: Manipulating reaction enthalpies

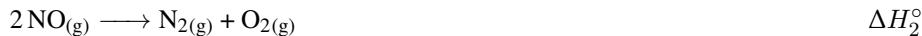
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In the previous section we relied on a table of standard enthalpies of formation in order to compute enthalpy changes in general reaction. This enthalpy change ΔH_R° is related to the heat exchanged in the reaction. In this section we will not use the tables of enthalpy anymore. Imagine you do not have access to this table. And we will find alternative ways to predict ΔH_f° given a series of reactions with known enthalpies. In short you will have to identify the enthalpies that are zero—the enthalpies corresponding to an element on its natural state—and set up an equation that helps you find out the missing enthalpy.

Reverting reactions Imagine they give you the following reaction:



²⁹⁵ and you need to calculate the enthalpy change for this other reaction:



If you compare both reaction you will see the second reaction equals to the first reaction but reverted. If you revert a reaction, the enthalpy change changes sign. Therefore, $\Delta H_2^\circ = 114 \text{KJ}$.

³⁰⁰ *Timing reactions by a number* Imagine they give you the following reaction:

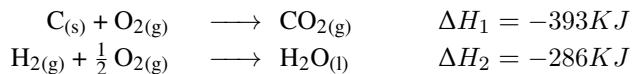


and you need to calculate the enthalpy change for this other reaction:



³⁰⁵ If you compare both reaction you will see the second reaction equals to the first reaction timed by two. If you time a reaction by two, the enthalpy change should also be timed by two. Therefore, $\Delta H_2^\circ = 2 \cdot -114 = -228 \text{KJ}$.

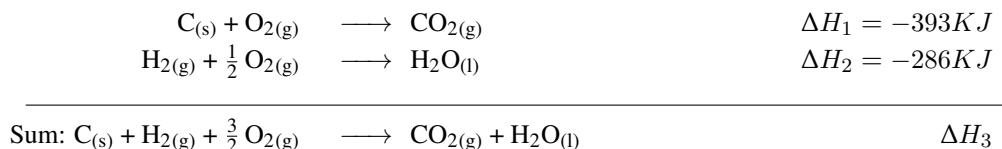
Combining reactions Imagine they give you the following two reactions:



and ask the enthalpy change for the following reaction:



If you look closely to the last reaction, you will see it results from adding the first two reactions, so that:



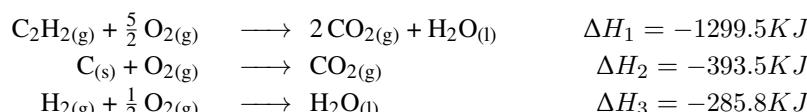
³¹⁵ Therefore, $\Delta H_3 = \Delta H_1 + \Delta H_2 = -679 \text{KJ}$. When adding two chemical reactions the resulting enthalpy is the result of adding the enthalpy of both reactions.

Sample Problem 11

Calculate the enthalpy for this reaction:



Given the following thermochemical equations:



SOLUTION

In order to get the enthalpy for reaction (4) we will have to combine reactions

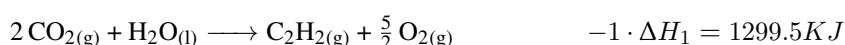
(1), (2) and (3), by adding, subtracting, or multiplying by a number so that the results adds up to reaction (4). A trick to do this is compare molecule by molecule in reaction (4) and see in which reaction we can find the same one. For example, reaction (4) contains $2C_{(s)}$ in the reactant side. $C_{(s)}$ can also be found in (2) also as reactant. However, in (2) $C_{(s)}$ is not timed by 2. There we will use two times reaction (2):



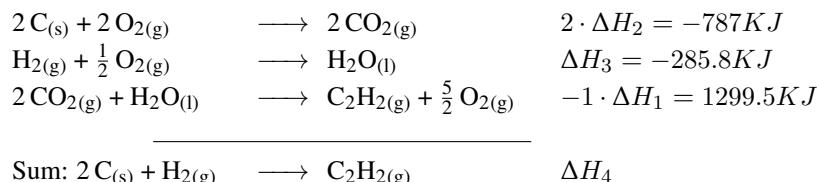
Reaction (4) also contains $H_{2(g)}$, which can be found in (3). There we will use (3) as it is:



Reaction (4) also contains $C_2H_{2(g)}$ as a product. We can find the same chemical in (1) but as a reactant. There we will have to invert (1):



If we add the three previous reactions, we have:

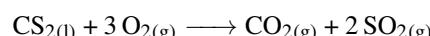


Therefore in the enthalpy for the reaction (4) will be:

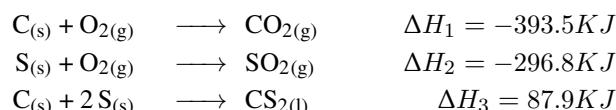
$$\Delta H_4^\circ = 2 \cdot \Delta H_2 + \Delta H_3 - 1 \cdot \Delta H_1 = 226.7 KJ$$

STUDY CHECK

Calculate the enthalpy for this reaction:



Given the following thermochemical equations:



Answer: $-1075 KJ$.

Table 1.3 Standard enthalpy table at 1atm and 298K in KJ/mol.

Substance	ΔH_f°	Substance	ΔH_f°	Substance	ΔH_f°
Aluminum					
$\text{Al}_{(s)}$	0	$\text{AlCl}_{3(s)}$	-705.63	$\text{Al}_2\text{O}_{3(s)}$	-1675.5
$\text{Al(OH)}_{3(s)}$	-1277	$\text{Al}_2(\text{SO}_4)_{3(s)}$	-3440	$\text{NH}_{3(aq)}$	-80.8
$\text{NH}_{3(g)}$	-46.1	$\text{NH}_4\text{NO}_{3(s)}$	-365.6	$\text{Al}_{(g)}$	314
Barium					
$\text{BaCl}_{2(s)}$	-858.6	$\text{BaCO}_{3(s)}$	-1213	$\text{Ba(OH)}_{2(s)}$	-944.7
$\text{BaO}_{(s)}$	-548.1	$\text{BaSO}_{4(s)}$	-1473.2	$\text{BaSO}_{4(s)}$	-1473.2
Boron					
$\text{BCl}_{3(s)}$	-402.96				
Bromine					
$\text{Br}_{2(l)}$	0	$\text{Br}_{-(aq)}$	-121	$\text{Br}_{(g)}$	111.884
$\text{Br}_{2(g)}$	30.91	$\text{BrF}_{3(g)}$	-255.60	$\text{HBr}_{(g)}$	-36.29
Cadmium					
$\text{Cd}_{(s)}$	0	$\text{CdO}_{(s)}$	-258	$\text{Cd(OH)}_{2(s)}$	-561
$\text{CdS}_{(s)}$	-162	$\text{CdSO}_{4(s)}$	-935		
Calcium					
$\text{Ca}_{(s)}$	0	$\text{Ca}_{(g)}$	178.2	$\text{Ca}_{(g)}^{2+}$	1925.90
$\text{CaC}_{2(s)}$	-59.8	$\text{CaCO}_{3(s)}$	-1206.9	$\text{CaCl}_{2(s)}$	-795.8
$\text{CaCl}_{2(aq)}$	-877.3	$\text{Ca}_3(\text{PO}_4)_{2(s)}$	-4132	$\text{CaF}_{2(s)}$	-1219.6
$\text{CaH}_{2(s)}$	-186.2	$\text{Ca(OH)}_{2(s)}$	-986.09	$\text{Ca(OH)}_{2(aq)}$	-1002.82
$\text{CaO}_{(s)}$	-635.09	$\text{CaSO}_{4(s)}$	-1434.52	$\text{CaS}_{(s)}$	-482.4
$\text{CaSiO}_{3(s)}$	-1630				
Caesium					
$\text{Cs}_{(s)}$	0	$\text{Cs}_{(g)}$	76.50	$\text{Cs}_{(l)}$	2.09
$\text{Cs}_{(g)}^+$	457.964	$\text{CsCl}_{(s)}$	-443.04		
Carbon					
$\text{C}_{\text{graphite}(s)}$	0	$\text{C}_{\text{diamond}(s)}$	1.9	$\text{C}_{(g)}$	716.67
$\text{CO}_2(g)$	-393.509	$\text{CS}_{2(l)}$	89.41	$\text{CS}_{2(g)}$	116.7
$\text{CO}_{(g)}$	-110.525	$\text{COCl}_{2(g)}$	-218.8	$\text{CO}_2(aq)$	-419.26
$\text{HCO}_3^{-}(aq)$	-689.93	$\text{CO}_3^{2-}(aq)$	-675.23		
Chlorine					
$\text{Cl}_{(g)}$	121.7	$\text{Cl}_{-(aq)}$	-167.2	$\text{Cl}_2(g)$	0
Chromium					
$\text{Cr}_{(s)}$	0				
Copper					
$\text{Cu}_{(s)}$	0	$\text{CuO}_{(s)}$	-155.2	$\text{CuSO}_{4(aq)}$	-769.98
Fluorine					
$\text{F}_{2(g)}$	0				
Hydrogen					
$\text{H}_{(g)}$	218	$\text{H}_{2(g)}$	0	$\text{H}_2\text{O}_{(g)}$	-241.818
$\text{H}_2\text{O}_{(l)}$	-285.8	$\text{H}_{(aq)}^+$	0	$\text{OH}_{(aq)}^-$	-230
H_2O_2	-187.8	$\text{H}_3\text{PO}_{4(l)}$	-1288	$\text{HCN}_{(g)}$	130.5
$\text{HBr}_{(l)}$	-36.3	$\text{HCl}_{(g)}$	-92.30	$\text{HCl}_{(aq)}$	-167.2
$\text{HF}_{(g)}$	-273.3	$\text{HI}_{(g)}$	26.5		
Iodine					
$\text{I}_{2(s)}$	0	$\text{I}_{2(g)}$	62.438	$\text{I}_{2(aq)}$	23
$\text{I}_{(aq)}^-$	-55				

(cont.) Standard enthalpy table at 1atm and 298K.

Substance	ΔH_f°	Substance	ΔH_f°	Substance	ΔH_f°
Iron					
Fe _(s)	0	Fe ₃ C _(s)	5.4	FeCO _{3(s)}	-750.6
FeCl _{3(s)}	-399.4	FeO _(s)	-272	Fe ₃ O _{4(s)}	-1118.4
Fe ₂ O _{3(s)}	-824.2	FeSO _{4(s)}	-929	Fe ₂ (SO ₄) _{3(s)}	-2583
FeS _(s)	-102	FeS _{2(s)}	-178		
Lead					
Pb _(s)	0	PbO _{2(s)}	-277	PbS _(s)	-100
PbSO _{4(s)}	-920	Pb(NO ₃) _{2(s)}	-452	PbO _(s)	-276.6
Magnesium					
Mg _(s)	0	Mg ²⁺ _(aq)	-466.85	MgCO _{3(s)}	-1095.7
MgO _(s)	-601.6	MgSO _{4(s)}	-1278.2	MgCl _{2(s)}	-641.8
Manganese					
Mn _(s)	0	MnO _(s)	-384.9	MnO _{2(s)}	-519.7
Mn ₂ O _{3(s)}	-971	Mn ₃ O _{4(s)}	-1387	MnO _{4-(aq)}	-543
Mercury					
HgO _(s)	-90.83	HgS _(s)	-58.2		
Nitrogen					
N _{2(g)}	0	NH _{3(aq)}	-80.8	NH _{3(g)}	-45.90
NH ₄ Cl	-314.55	NO _{2(g)}	33.2	N ₂ O _(g)	82.05
NO _(g)	90.29	N ₂ O _{4(g)}	9.16	N ₂ O _{5(s)}	-43.1
Oxygen					
O _(g)	249	O _{2(g)}	0	O _{3(g)}	143
Phosphorus					
P _{4(s)}	0	P _{red(s)}	-17.4	P _{black(s)}	-39.3
PCl _{3(l)}	-319.7	PCl _{3(g)}	-278	PCl _{5(s)}	-440
PCl _{5(g)}	-321	P ₂ O _{5(s)}	-1505.5		
Potassium					
KBr _(s)	-392.2	K ₂ CO _{3(s)}	-1150	KClO _{3(s)}	-391.4
KCl _(s)	-436.68	KF _(s)	-562.6	K ₂ O _(s)	-363
KClO _{4(s)}	-430.12				
Silicon					
Si _(g)	368.2	SiC _(s)	-74.4	SiCl _{4(l)}	-640.1
SiO _{2(s)}	-910.86				
Silver					
AgBr _(s)	-99.5	AgCl _(s)	-127.01	AgI _(s)	-62.4
Ag ₂ O _(s)	-31.1	Ag ₂ S _(s)	-31.8		
Sodium					
Na _(s)	0	Na _(g)	+107.5	NaHCO _{3(s)}	-950.8
Na ₂ CO _{3(s)}	-1130.77	NaCl _(aq)	-407.27	NaCl _(s)	-411.12
NaF _(s)	-569.0	NaOH _(aq)	-469.15	NaOH _(s)	-425.93
Na ₂ O _(s)	-414.2				
Sulfur					
S ₈ monoclinic _(s)	0.3	S ₈ rhombic _(s)	0	H ₂ S _(g)	-20.63
SO _{2(g)}	-296.84	SO _{3(g)}	-395.7	H ₂ SO _{4(l)}	-814
Titanium					
Ti _(s)	0	Ti _(g)	468	TiCl _{4(g)}	-763.2
TiCl _{4(l)}	-804.2	TiO _{2(s)}	-944.7		
Zinc					
Zn _(g)	130.7	ZnCl _{2(s)}	-415.1	ZnO _(s)	-348.0

CHAPTER 1

ENERGY AND TEMPERATURE

1.1 Answer the following questions: (a) What is the name of the energy associated with the motion of particles in a substance? (b) What is the name of the energy stored in the chemical bonds of a carbohydrate molecule? (c) What is the name of the energy stored in height?

1.2 Carry the following conversions: (a) 650J into calories (b) 3.25 kcal into joules (c) 41°F into celsius

1.3 Carry the following conversions: (a) 20°C to F (b) 300K to °C

THE FIRST LAW OF THERMODYNAMICS

1.4 A sample of gas expands from 3 to 4 L at constant pressure. Using $1L \cdot atm = 101.3J$, calculate the work done in J under the following conditions: (a) The gas expands against the vacuum. (b) The gas expands against a constant pressure of 5atm

1.5 A 50g piece of aluminum ($c_e = 0.214 \frac{cal}{g^\circ C}$) initially at 25°C absorbs 100cal. Calculate the final temperature of the aluminum piece.

1.6 A sample of gas expands carrying work on the surroundings of 120J and absorbing 150J of heat from the surroundings. Calculate the change of the internal energy of the system in J.

1.7 A 200g piece of iron ($c_e = 0.1 \frac{cal}{g^\circ C}$) initially at 15°C absorbs 1000cal. Calculate the final temperature of the metal piece.

1.8 How many calories are required to raise the temperature of a 35 g sample of iron from 25°C to 35°C? Iron has a specific heat of $0.108 \frac{cal}{g^\circ C}$.

1.9 What is the final temperature of a 35 g sample of iron at 25°C after receiving 50cal? Iron has a specific heat of $0.108 \frac{cal}{g^\circ C}$.

1.10 What is the initial temperature of a 50 g sample of aluminum that after receiving 50cal reaches a temperature

of 50°C? Al has a specific heat of $0.2 \frac{cal}{g^\circ C}$.

1.11 What is the specific heat of a metal if a 100 g sample at 25°C warms up until 50°C after receiving 100cal?

CALORIMETRY

1.12 A 3 moles sample of C(s) is burned in a constant-volume calorimeter containing 40g of water. The temperature inside the calorimeter increases from 25.0°C to 25.89 °C. The calorimeter constant is $9.90 \frac{kJ}{^\circ C}$. Calculate the molar heat of the reaction.

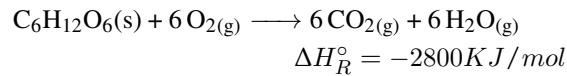
1.13 A 10 grams sample of fructose (MW=180g/mol) is burned in a constant-volume calorimeter containing 50g of water. The temperature inside the calorimeter increases 7°C . The calorimeter constant is $10.8 \frac{kJ}{^\circ C}$. Calculate the molar heat of the reaction.

1.14 When a 0.09-g sample of trinitrotoluene (TNT, MW=213g/mol), is burned in a bomb calorimeter, the temperature increases from 23.5 °C to 27.1°C. The heat capacity of the calorimeter is $400 \frac{J}{^\circ C}$, and it contains 100 mL of water. Calculate the molar heat of the reaction. Remember that the density of water is 1g/mL.

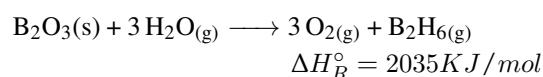
1.15 We mix 50mL of 2M HCl with 100mL of 1.5M NaOH in a coffee-cup calorimeter. Both solutions are initially at 20°C. Calculate the final temperature of the solution in the calorimeter considering that the specific heat of the mixture is $4.184 \frac{J}{g^\circ C}$ and the density of the solution is 1g/mL. The molar heat of the reaction is -56kJ/mol.

ENTHALPY

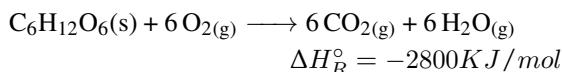
1.16 Identify the following reaction as endothermic or exothermic.



1.17 Identify the following reaction as endothermic or exothermic.



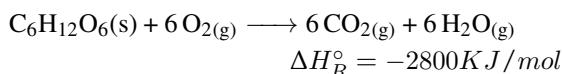
1.18 For the following reaction:



Fill the conversion factor:

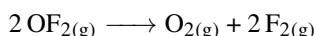
$$\frac{\text{moles of O}_2}{-2800 \text{ KJ}}$$

1.19 In the following combustion reaction:



glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) burns to produce carbon dioxide and water. Calculate the heat involved in the combustion of 3 moles of glucose.

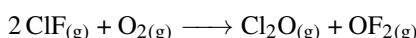
1.20 Calculate the enthalpy of reaction for:



given:

$$\Delta H_f^\circ(\text{OF}_{2(\text{g})}) = 24.5 \text{ KJ}$$

1.21 Calculate the enthalpy of reaction for:



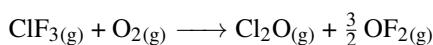
given:

$$\Delta H_f^\circ(\text{ClF}_{(\text{g})}) = -56 \text{ KJ}$$

$$\Delta H_f^\circ(\text{Cl}_2\text{O}_{(\text{g})}) = 88 \text{ KJ}$$

$$\Delta H_f^\circ(\text{OF}_{2(\text{g})}) = 25 \text{ KJ}$$

1.22 Calculate the enthalpy of reaction for:



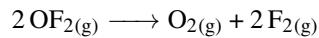
given:

$$\Delta H_f^\circ(\text{ClF}_{3(\text{g})}) = -156 \text{ KJ}$$

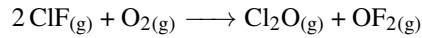
$$\Delta H_f^\circ(\text{Cl}_2\text{O}_{(\text{g})}) = 88 \text{ KJ}$$

$$\Delta H_f^\circ(\text{OF}_{2(\text{g})}) = 25 \text{ KJ}$$

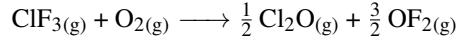
1.23 Using the following reactions:



$$\Delta H_1 = -49 \text{ KJ}$$

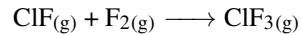


$$\Delta H_2 = 225 \text{ KJ}$$

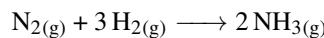


$$\Delta H_3 = 324 \text{ KJ}$$

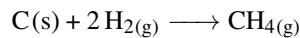
Determine the enthalpy change for:



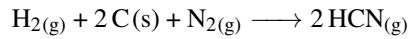
1.24 Using the following reactions:



$$\Delta H_1 = -92 \text{ KJ}$$



$$\Delta H_2 = -75 \text{ KJ}$$

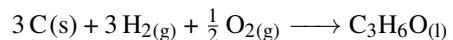


$$\Delta H_3 = 270 \text{ KJ}$$

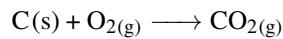
Determine the enthalpy change for:



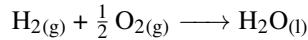
1.25 Using the following reactions:



$$\Delta H_1 = -285 \text{ KJ}$$

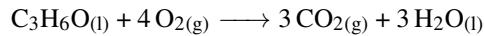


$$\Delta H_2 = -394 \text{ KJ}$$

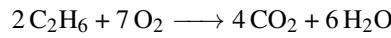


$$\Delta H_3 = -286 \text{ KJ}$$

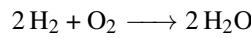
Determine the enthalpy change for:



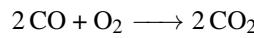
1.26 Using the following reactions:



$$\Delta H_1 = -3120 \text{ KJ}$$

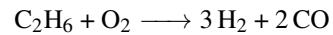


$$\Delta H_2 = -479 \text{ KJ}$$



$$\Delta H_3 = -566 \text{ KJ}$$

Determine the enthalpy change for:



Answers 1.1 (a) kinetic energy (b) chemical energy (c) potential energy **1.3** (a) $68^{\circ}F$ (b) $27^{\circ}C$ **1.5** $34.34^{\circ}C$
1.7 $T_{Final} = 65^{\circ}C$ **1.9** $38^{\circ}C$ **1.11** $0.04\text{cal/g}^{\circ}\text{C}$ **1.13** -1387KJ/mol **1.15** $29^{\circ}C$ **1.17** endothermic **1.19** 8400KJ
1.21 225KJ **1.23** -187KJ **1.25** -1755KJ

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Solids and liquids

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HERE 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 these forces will help you understand why some liquids boil at higher temperature than others or some solids have higher melting point.

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GOALS

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

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

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2.1 Intermolecular forces

Atoms in liquid or solid compound are connected by means of chemical bonds, and bonds are forces within molecules. These bonds can be ionic or covalent depending on the nature of the elements that form the molecule. 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 existing types of intermolecular forces as well as its nature and intensity.

Intermolecular forces and intramolecular interactions

Molecules are made of atoms which connect by means of *intramolecular* interactions such as covalent or ionic bonds. Differently, molecules interact with each other by means of *intermolecular* interactions. The prefix *inter* means "occurring between", whereas the prefix *intra* means "occurring within". Intermolecular forces are responsible for the melting and boiling point of a chemical. On one hand, the stronger the forces the higher the melting and boiling point. On the other hand, the more intermolecular interactions the higher the melting and boiling point. This is because in order to melt or boil a chemical we need to overcome the intermolecular forces that connect molecules in order to release them into a different state of matter. In the following we will describe the three main types of intermolecular forces (some books describe four types of intermolecular forces counting the ion-molecule interaction).

Dispersion forces All molecules are made of atoms which contain electrons. The

355 ▼Polymer molecules interact by means of dispersion

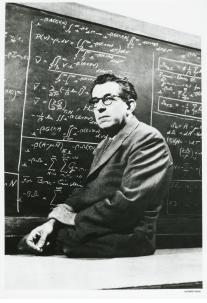


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electron density of an atom is distributed homogeneously without uneven charge distributions. As a consequence, atoms in general have no permanent dipole moment without negatively or positively charged regions. Still, when two atoms get close together, the presence of each other affects their electron density creating temporary dipole moments. We call this effect polarizability. This temporary dipoles are responsible for London dispersion forces, also called Van der Waals forces or simply dispersion forces.

360 ▼Fritz London a german physicist is responsible for the name of London forces



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360 ▼geckos stick because of the van der Waals force



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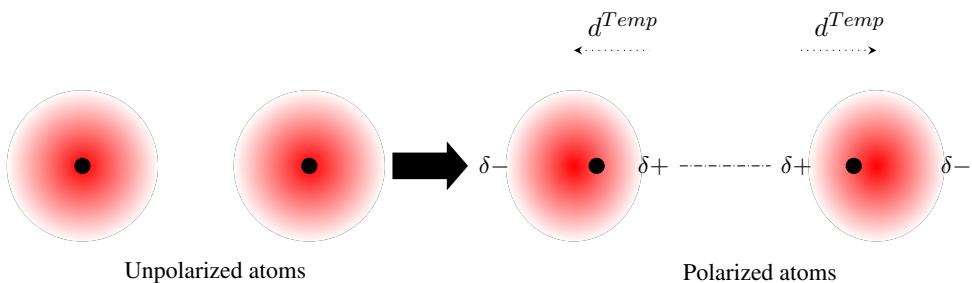


Figure 2.1 Dispersion forces result from instantaneous dipole moments resulting from the polarization of the electron density of atoms and molecules.

Dispersion forces exist in all chemicals, as all chemicals can be polarized. The larger the atomic number, or the molar weight of the compound, the stronger these forces. This is because in general the larger the atomic weight the more polarizable atoms are, and hence, they tend to generate stronger temporary dipoles, produced from charge polarization.

Table 2.1 Freezing and boiling point of the noble gases

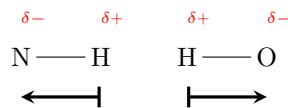
Gas	Atomic Weight (amu)	Melting Point (°C)	Boiling Point (°C)
He	2	–	4
Ne	10	25	27
Ar	18	84	87
Kr	36	116	121
Xe	54	162	167
Rn	6	202	211

370 The melting (or freezing) and boiling point of the noble gases are given in Table 2.1, where you can see how the larger the atomic mass of the gas the higher the melting—and boiling points. Mind that normally, the melting and freezing point of a substance are the same. Dispersion forces are common in chemicals made of hydrogen and carbon—we call these compounds hydrocarbons. The larger the size of the molecule the larger the effects of dispersion forces. For example:



380 *Dipole-Dipole forces* Atoms have different electronegativity that is, a different tendency to attract the electron density in a bond. In the periodic table, electronegativity increases going from left to right and top to bottom. Elements in the top right of the table (Cl, F) tend to be very electronegative 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. Dipole moments result from differences in electronegativity. When a electronegative atoms is

connected to a electropositive atom in a bond, the electronegativity difference creates permanent dipole moments and molecules with permanent dipole moment are called polar molecules. The dipole moment of a bond is a vector that points from the most electropositive atom to the most electronegative atom. For example for the O-H and N-H bonds,



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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. Dipole-dipole forces exist only in polar compounds, being the result of permanent dipole moments. This types of interactions are stronger than dispersion forces but weaker than normal interatomic covalent bonds. Molecules with dipole moment can attract each other by means of dipole forces, orienting themselves so that their positive side aligns with the negative side maximizing the electrostatic attraction. At the same type, dipole forces depend on the distance and at large distance are less effective.

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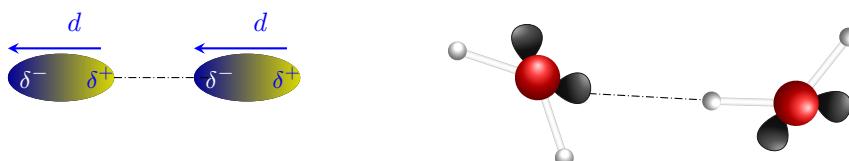


Figure 2.2 (Left) Dipole-dipole forces result from the interaction of permanent dipole moments existing in polar molecules. (Right) two water molecules interacting by means of hydrogen bonds

The dipole moment of a molecule is measured in Debye (D). For example, the dipole moment of HCl is 1.05D, whereas the dipole moment of HF is 1.82D. The stronger the dipole moment the stronger the dipole-dipole interactions. For example, when comparing C₃H₈ and CH₃OCH₃, the former has a almost null dipole moment, whereas the later has a dipole moment of 1.3D. The boiling point of C₃H₈ is -42°C whereas the boiling point of CH₃OCH₃ is -25°C. The table below list some dipole moments and boiling points showing the trend that the larger the dipole moment the higher (more positive) the boiling point.

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Table 2.2 Boiling (BP) point of a series of hydroacids

Compound	Dipole moment (Debyes)	Boiling Point (°C)
C ₃ H ₈	0.1	-42
CH ₃ OCH ₃	1.3	-25
CH ₃ Cl	2.0	-24
CH ₃ COH	2.7	-21
CH ₃ CN	3.9	-82

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 are HF or NH₃. Hydrogen bonds are a specific type dipole-dipole interactions responsible, among other, for some of

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the high boiling point of water. Due to the existence of hydrogen bonds water is liquid at room temperature (H_2O , BP=100°C), in comparison with similar molecules (H_2S , BP=-60°C). The anomalous character of oxygen, fluorine and nitrogen results from the fact that these are very electronegative elements with lone pairs of electrons—these are non-bonding pairs of electrons—that enable the creation of hydrogen bonds. In particular, oxygen has two lone pairs, nitrogen one and fluorine three. The combination of high electronegativity, the presence of lone pairs and the presence of hydrogen atoms, makes hydrogen bond possible.

Sample Problem 12

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

	HCl	CH_4	H_2O	CH_3Cl
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, H_2O and CH_3Cl has dipole forces, and only H_2O has hydrogen bonds.

	HCl	CH_4	H_2O	CH_3Cl
Dispersion	✓	✓	✓	✓
Dipole-	✓	✗	✓	✓
Dipole				
H-bonds	✗	✗	✓	✗

❖ STUDY CHECK

Indicate what types of intermolecular forces exist in the following molecules: NH_3 , HF, and CH_3-CH_3 .

Answer: all have dispersion, only NH_3 , HF has dipole and only NH_3 , 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 CH_4 . 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 13

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	✓	✓
D-D	✓	✓
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).

2.2 The solid state

What makes solids unique in comparison to liquids and gases? They answer is their structure. There are two main different types of solids: crystalline solids and amorphous solids.
 440 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.

⁴⁴⁵ *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
 450 infinitely in two directions of the space generating a lattice.

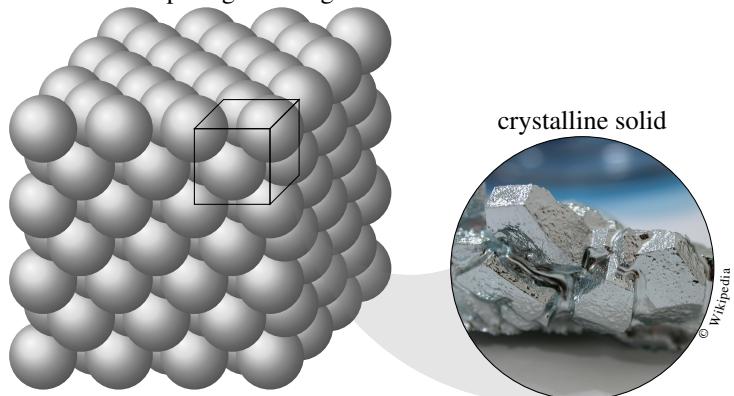


Figure 2.3 Unit cell of a solid of a crystalline solid. The whole structure of the solid results from the replication of a unit cell and just this unit cell is necessary to characterize the structure of the solid.

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
 455 repeating the unit cell in the tree 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:
 460 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, CaF₂. 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 or 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 ($\text{Au}_{(s)}$).
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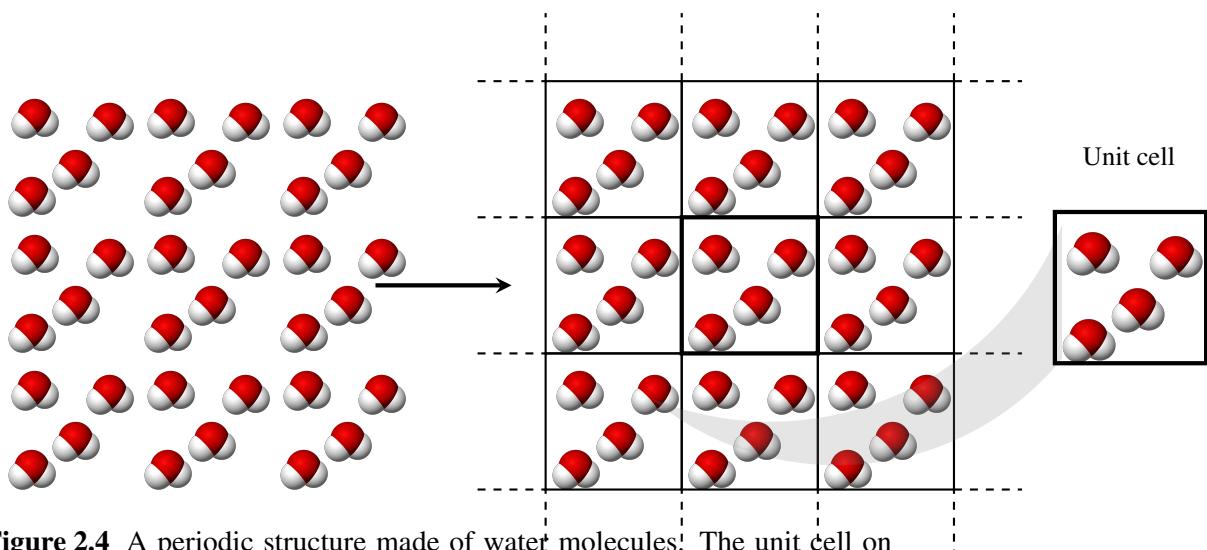


Figure 2.4 A periodic structure made of water molecules. The unit cell on the left contains four water molecules. The repetition of the unit cell, on the right, generates a two-dimensional structure.

Sample Problem 14

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

	diamond	CO_2	Fe	CaF_2
Molecular	✗	✓	✗	✗
Ionic	✗	✗	✗	✓
Atomic	✓	✗	✗	✗
Metallic	✗	✗	✓	✗

◆ STUDY CHECK

Classify the following solids as ionic, molecular or atomic: silver, graphite, CaCO_3 and $\text{NH}_3(s)$.

Answer: metallic, atomic, ionic and molecular.

2.3 Metals and ionic solids

Among the different types of crystalline solids, metals and ionic solids are very important.

⁴⁷⁵ This section will cover the structure of metallic solids like gold or iron and ionic solids like sodium chloride.

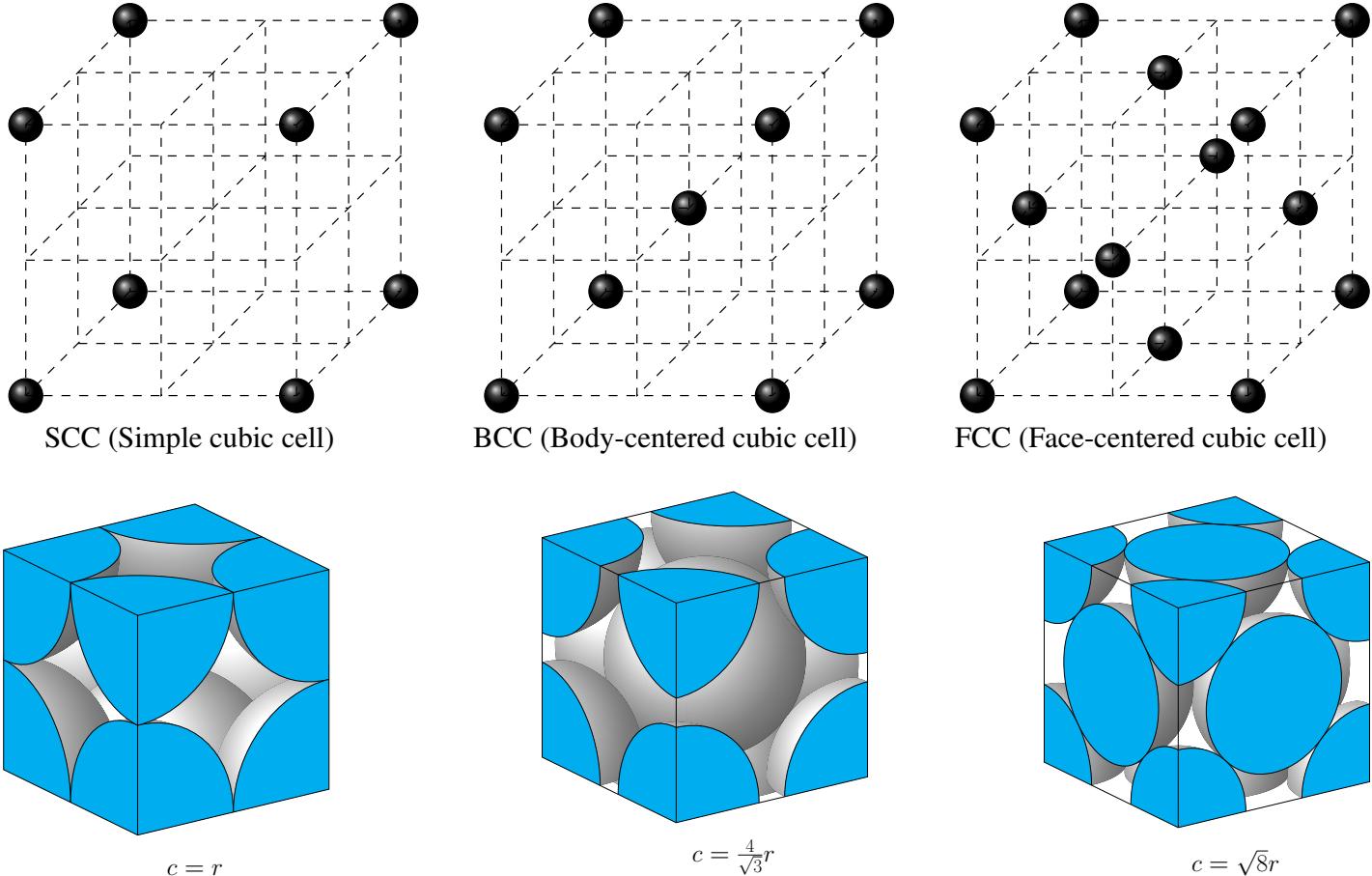


Figure 2.5 The different unit cells. Space-fill structures are shown on the bottom. The simple cubic unit cells have atoms in the corners of the cell. The body-centered cubic unit cell have atoms in the corners and one atom in the center. The face-centered unit cell has atoms in the corners and in the faces. The relationship between the cell parameter (c) and the atomic radius (r) is also given for each unit cell.

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)*. 495

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. 500

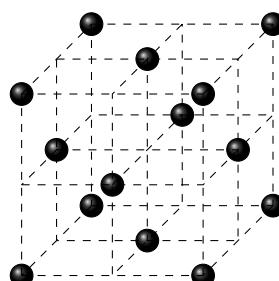
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Sample Problem 15

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

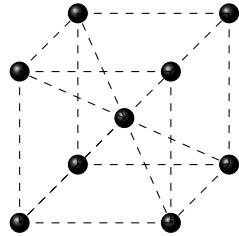
If you count the number of spheres in the drawing you might think the cell contains fourteen atoms. However, this is not true, as each sphere is shared by other unit cells. Remember each location of the unit cell counts as a fraction. If an atom is fully inside in the cell—not in the vertexes, neither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

Location	Sharing Factor, f	# atoms, N	$f \times N$
Corner	$1/8$	8	1
Faces	$1/2$	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.

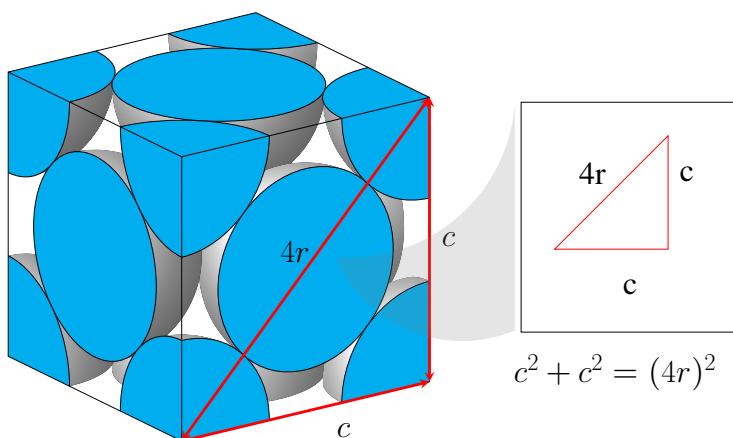
515 *Metal unit cells* Here we will cover three different metal unit cells, all cubic cells.

520 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.

525 *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 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, $c = \sqrt{8}r$.

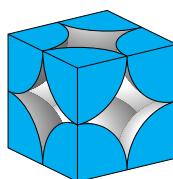
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Sample Problem 16

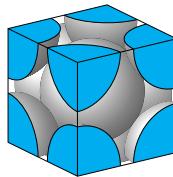
For the following unit cell, calculate the relationship between the cell parameter and the atomic radius.

**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.



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

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:

$$d = \frac{N \cdot AW}{c^3 \cdot 6.023 \times 10^{-7}}$$

Metallic density formula

where:

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

N is the number of atoms per unit cell

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

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AW is the atomic weight of the metal

c is the cell parameter in pm

Sample Problem 17

Calculate density of iron ($AW = 55.845 \text{ g} \cdot \text{mol}^{-1}$) 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 $AW = 55.845 \text{ g} \cdot \text{mol}^{-1}$ and the cell parameter

$c = 286\text{pm}$. Using the metallic density formula:

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

◆ STUDY CHECK

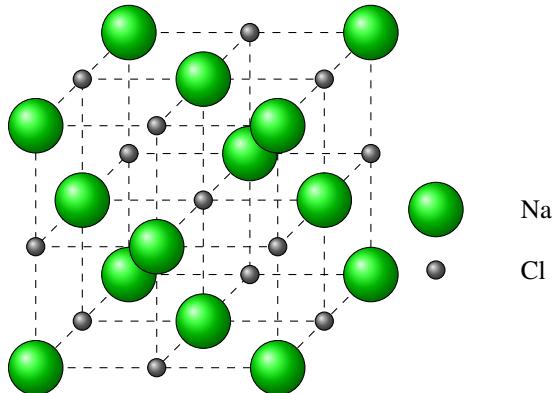
Calculate density of gold (AW=196.96 $\text{g} \cdot \text{mol}^{-1}$) knowing this is a fcc metal with cell parameter is 406pm.

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

⁵⁴⁵ *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 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 18

Calculate the formula for the following unit cell



SOLUTION

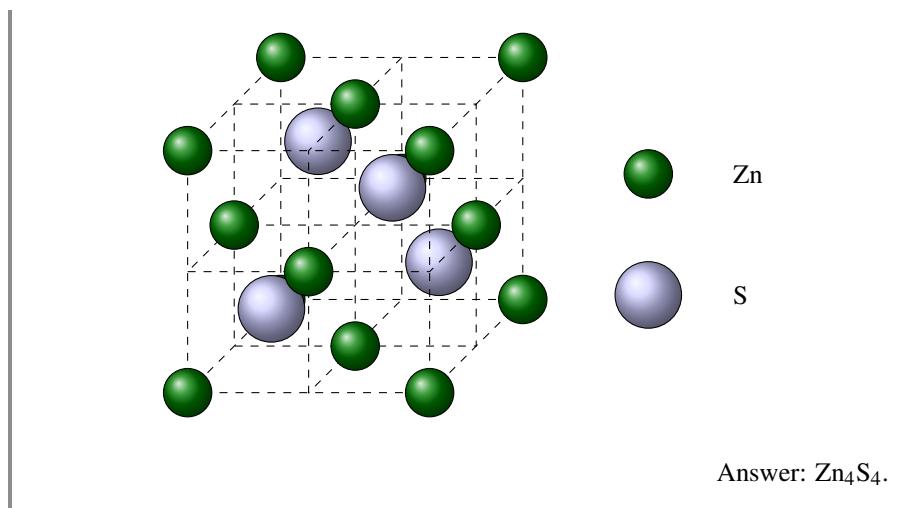
The unit cell contains Cl^- and Na^+ . Remember every location in the unit cell has different sharing factor. We will compute the number of atoms in each location and multiply by the sharing factor to calculate the number of Cl and Na in the cell:

Location	Sharing Factor, f	# atoms, N	$f \times N$
Corner	$1/8$	8Na^+	1
Faces	$1/2$	6Na^+	3
sides	$1/4$	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:



X-ray diffraction is

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X-ray diffraction: a method to measure cell parameters

X-ray diffraction is an experimental technique used to study the structure of solids and specifically to obtain cell parameters—the length of the unit cell that defines the structure of a crystal. X-rays, high-frequency radiation, scatter when they encounter a regular array of atoms in which the spacing is compatible with the x-ray wavelength. Diffraction results in two different types of wave interference: constructive and destructive. Constructive interference results in bright spots and destructive interference results in dark spots. Waves impacting atoms at a different lattice positions travel different distances. If the difference in distance equals to an integral number of wavelength there both rays will interfere constructively.

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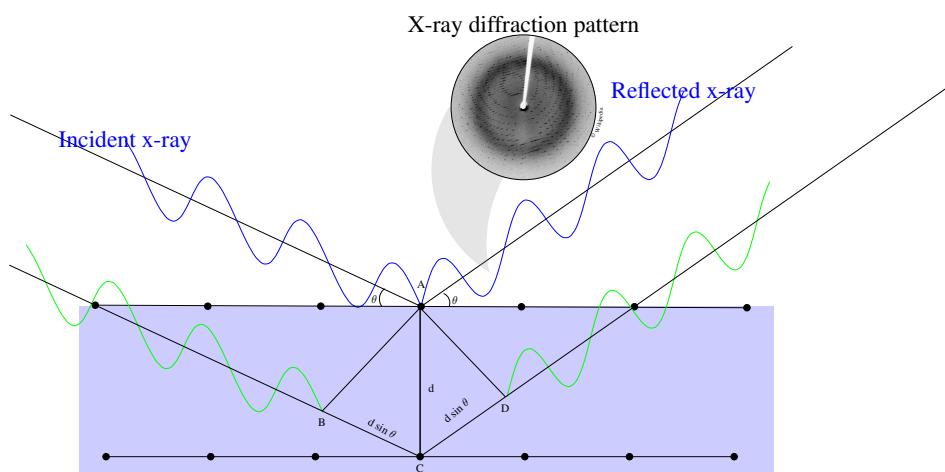


Figure 2.6 Reflection of x-rays in two different lattice points separated by a distance. The incident waves are in phase—maximums and minimums overlap—but the reflected waves are only in phase when the difference of distances traveled by both is an integral number of wavelengths. In the image $BC + CD = 2d\sin\theta$.

Bragg's equation relate the cell parameter (d) of a solid with the angle (θ) of the diffracted x-rays and its wavelength (λ). The number n is called the diffraction order and represents an integer values ($n=0, 1, 2, \dots$).

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$$n\lambda = 2ds\sin\theta \quad (2.1)$$

Sample Problem 19

We study the structure of a crystal using x-rays of 9nm, finding a first-order reflection at 20° . Calculate the distance between the planes responsible for this reflection.

SOLUTION

We should use Bragg's equation, using $\theta=20^\circ$, $\lambda=9\text{nm}$ and $n=1$. Solving for d we have:

$$1 \cdot 9 = 2dsin(20)$$

The calculated plane spacing is 26.3nm.

❖ STUDY CHECK

Two lattice planes separated by a distance of 4nm produce a first-order x-ray diffraction at 15° using radiation of wavelength of 3.2nm. Calculate the angle for the second-order diffraction.

Answer: 53°

2.4 Liquid state

This section will cover some of the properties of the liquid state. In particular the importance of the vapor pressure, the viscosity and the surface tension. All these properties are determined by the intermolecular forces that connect the molecules of a liquid.

Surface tension In a liquid there are two types of molecules, based on their location. Some molecules are located in the interior part of the liquid, far away from its surface. We call this the bulk of the liquid. Others are located at the surface of the liquid. The molecules at the bulk are pulled in all directions by the intermolecular forces so that overall there is no net pull in any direction. The molecules at the surface are pulled down and to the side by the surrounding molecules. However, they are not pulled up and hence they experience a new pull inward that causes the surface of the liquid to tighten up so that the surface minimizes its surface area. The surface tension of a liquid (γ_t) is a measure of the elastic force in the surface of the liquid. It is defined as the amount of energy needed to modify the surface of a liquid by unit of area, with units of milli Newton per meter, mN/m.

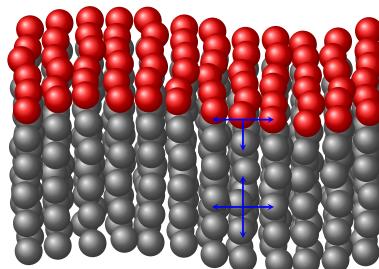


Figure 2.7 A representation of surface (red spheres) and bulk (blue spheres) liquid molecules as well as two types of meniscus: a concave and a convex meniscus, typical of water and mercury respectively. Surface molecules are pulled inwards creating the surface tension whereas bulk molecules are not.

Surface tension values depend on the temperature and the phases in contact and for example the surface tension of the water-air interface is different than the value for the water-mercury interface. The stronger the intermolecular forces, the higher the surface energy—it would take more energy to modify the surface of the liquid. For example, the surface tension of the C_6H_6 -air interface (29mN/m) is smaller than the surface tension of the H_2O -air interface (73mN/m). The surface tension is responsible for phenomena such as the beading of water on the plants leaves—water form beads or drops on the top of leaves—or the formation of the meniscus, a curved surface of a liquid in a narrow tube. Capillary results from the competitive effect of cohesive and adhesive forces. In the case of mercury, the cohesive forces are stronger than the adhesive and the meniscus created is convex. In the case of water the adhesive forces are stronger and the meniscus is concave.

▼A paper clip standing on water



© wikipedia

▼Water droplets



© www.piclist.com

▼Meniscus of water and mercury



© Flickr

▼A viscous liquid



© Flickr

▼Capillary for tubes of different diameters



© wikipedia

Table 2.3 Surface tension (γ_t) values for several interfaces at different temperatures.

Interface	γ_t (mN/m)	T	Interface	γ_t (mN/m)	T
H_2O -Air	73	20°C	H_2O -Hg	415	20°C
CH_3I -Air	67	20°C	H_2O -Air	73	22°C
C_6H_6 -Air	30	20°C	H_2O -Air	72	25°C
CH_3OH -Air	22	20°C	Hg-Air	486	20°C

▼ Rubbing alcohol has low heat of vaporization



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▼ Acetone has low heat of vaporization



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▼ Perfumes have low vaporization heat



© Wikipedia

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▼ Metals have high vaporization heat



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Viscosity Viscosity (η) is the measure of a fluid's resistance to flow. High viscosity liquids flow slowly and this effect results from the intermolecular forces. Liquids with strong intermolecular forces tends to present high viscosities. Viscosity, as well as surface tension, depends on temperature and high temperature reduce the viscosity. Molecular complexity also affect viscosity and long molecules made of carbon and hydrogen have higher viscosities than small molecules due to the fact that because of their size they present more intermolecular interactions. The units of viscosity are milli Pascal-second, mPa·s.

Table 2.4 Viscosities (η) for several substances at different temperatures.

Substance	η (mPa·s)	T	Substance	η (mPa·s)	T
Benzene	0.604	25°C	Honey	5000-20000	20°C
Water	1.0016	20°C	Pitch	2.3×10^{11}	10-30°C
Mercury	1.526	25°C			
Whole milk	2.12	20°C			
Olive oil	56.2	26°C			

Vapor pressure of a liquid The molecules of a liquid in contact with the atmosphere are more likely to escape into the gas phase forming what we call the vapor pressure of the liquid. When we put a liquid in a closed container, some of the liquid molecules would go into the gas. This process is called vaporization. Whereas molecules of the gas would also go back to the liquid phase. This process is called condensation. Therefore, vaporization and condensation compete until both processes occur at the same speed and the system reaches what we call as equilibrium. The vapor pressure at this state is called the equilibrium vapor pressure or simply the vapor pressure of the liquid. This effect is responsible for the humidity the air and the smell of liquid chemicals. Chemicals with high vapor pressure vaporize readily and if they have a smell, one would be able to smell them. Solids also have vapor pressure—solids also have a smell—as their molecules are also able to escape into a gas phase.

Table 2.5 Vapor pressure (P^{vap}) for several substances at different temperatures.

Substance	P^{vap} (mmHg)	T	Substance	P^{vap} (mmHg)	T
Tungsten	0.75	3203°C	Carbon dioxide	42753	20°C
Ethylene glycol	3.75	20°C	Nitrous oxide	42453	25°C
Water	17.5	20°C	Carbonyl sulfide	9412	25°C
Propanol	18.0	20°C	Propane	7584	27°C
Ethanol	43.7	20°C	Formaldehyde	3268	20°C
Acetaldehyde	740	20°C	Butane	1650	20°C

630 **Enthalpy of vaporization** The enthalpy of vaporization of a liquid (ΔH_{vap}) is the energy needed to vaporize a liquid. This energy is often called heat of vaporization or molar heat of vaporization. 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. In

general compounds with small heat of vaporization can vaporize easily. 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 (41kJ/mol). 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 31kJ/mol. If you compare this value with the value of water you can see acetone is more likely to have a smell.

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Table 2.6 Enthalpy of vaporization (ΔH_{vap}) for several substances and boiling points.

Substance	T	ΔH_{vap} (J/mol)	Substance	T	ΔH_{vap} (J/mol)
Acetone	56°C	31300	Water	100°C	40660
Aluminium	2519°C	294000	Phosphine	-88°C	14600
Ammonia	-33°C	23350	Propane	-42°C	15700
Butane	-1°C	21000	Methanol	64.7°C	35200
Ethanol	78 °C	38600	Isopropyl alcohol	83°C	44000
Hydrogen	-253°C	899.2	Iron	2862°C	340000

Vapor pressure change with temperature This vapor pressure strongly depends on temperature. That is the reason why summer days can also be humid days if you live near the seaside. In particular, this change depends on the value of the heat of vaporization. The reason for this, is because at higher temperature more molecules have enough kinetic energy to escape from the liquid into the gas phase. For chemicals with low heat of vaporization we can expect a more sharp change of the vapor pressure with temperature.

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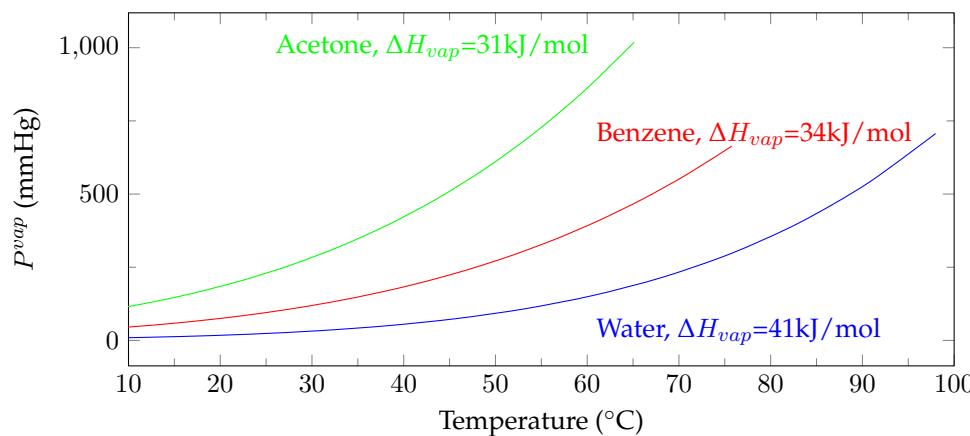


Figure 2.8 Vapor pressure change with temperature for three chemicals with different heat of vaporization.

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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:

$$\ln\left(\frac{P_{T_1}^{vap}}{P_{T_2}^{vap}}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Clausius-Clapeyron relation

660 where:

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

$P_{T_2}^{vap}$ is the vapor pressure at temperature T_2 in Kelvin

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

$R=8.314 J \cdot K^{-1} mol^{-1}$ is the constant of the gases in energy units

Sample Problem 20

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

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 (298K, x atm), where X is the vapor pressure at 298—what they are asking in the problem. We can call (298K, 0.03 atm) as $(T_1, P_{T_1}^{vap})$ and (298K, X atm) as $(T_2, P_{T_2}^{vap})$. At this point we have $T_1 = 298K$ and $P_{T_1}^{vap} = 0.03 atm$ and $T_2 = 323K$ and $P_{T_2}^{vap} = x$. We also have the enthalpy of vaporization. Mind that this value has to be given in $J \cdot mol^{-1}$ and hence, we will use $\Delta H_{vap} = 43.9 \times 10^3 J \cdot mol^{-1}$. 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 0.12 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.

2.5 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 will cover phase diagrams. 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.

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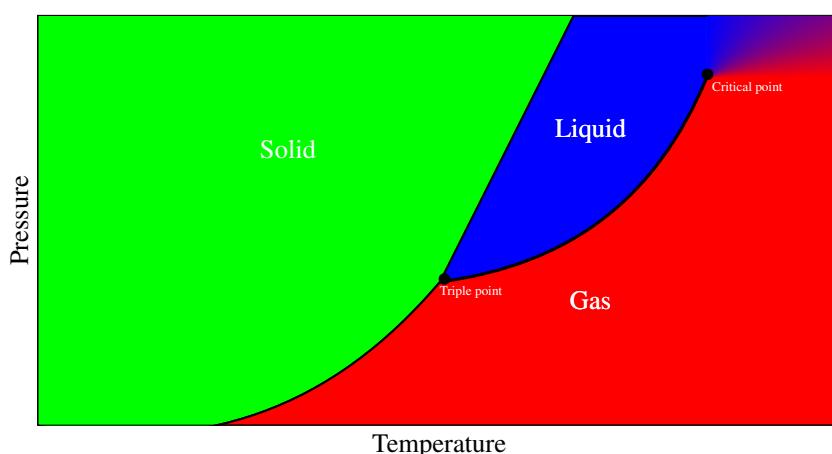


Figure 2.9 A typical phase diagram showing the different phases, the critical and the triple point. As the slope of the line that separates liquid and gas has an angle lower than 90° the solid phase has higher density than the liquid.

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Description of a phase diagram: important points A phase diagram is a representation of the different temperature and pressure conditions in which we can find the different states of matter of a substance. Normally, temperature is listed in the horizontal axis and pressure in the vertical axis. The different phase, liquid, solid and gas, are listed. At low temperature we tend to find solids and gases are common at high temperature. Similarly, at low pressures we tend to find gases and solids at high pressure. With pressure we refer to compressive pressure. The lines in a phase diagram represent equilibrium and the line separating solid and gas represents all the pressure and temperature conditions in which we can find a gas in equilibrium with a liquid. Similarly, the line separating liquid and solid represents all the pressure and temperature conditions in which we can find a liquid in equilibrium with a solid. With equilibrium, we mean that both phase are present and the process of phase transition proceeds at the same speed in both directions. There are two important points in a phase diagram: the critical point and the triple point. The triple point is the pressure and temperature conditions in which the three phases—solid, liquid and gas—coexist. Another important point is the critical point. Beyond this point one cannot liquefy (go from gas into a liquid) or condense (go from liquid into a gas) the substance. There is one more important feature one can extract from a phase diagram. Normally, but not always, solids are more dense than liquids. We can compare the density of the solid and the liquid by analyzing the slope of the line connecting both phase. If the slope is lower than 90° then the solid will be more dense than the liquid. If it is larger than 90° then

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the solid is less dense than the liquid. If the slope is 90° then both liquid and solid have the same density.

What are normal conditions? When we speak about normal conditions we refer to a pressure of 1 atm, which is the common atmospheric pressure. But remember that the atmospheric pressure depends on the height of the location where measured. And locations near the sea—at low height—tend to have higher pressure than locations near the mountains—at a larger height.

Phase transition terminology Each phase transition has a specific name. You may be familiar with some of the terms like freezing that involves the change from liquid to solid. Other names are listed below:

Liquid \longrightarrow Solid	Freezing
Liquid \longrightarrow Gas	Evaporation or vaporization
Solid \longrightarrow Liquid	Melting
Gas \longrightarrow Liquid	Condensation
Solid \longrightarrow Gas	Sublimation
Gas or Solid \longrightarrow Liquid	Liquefy

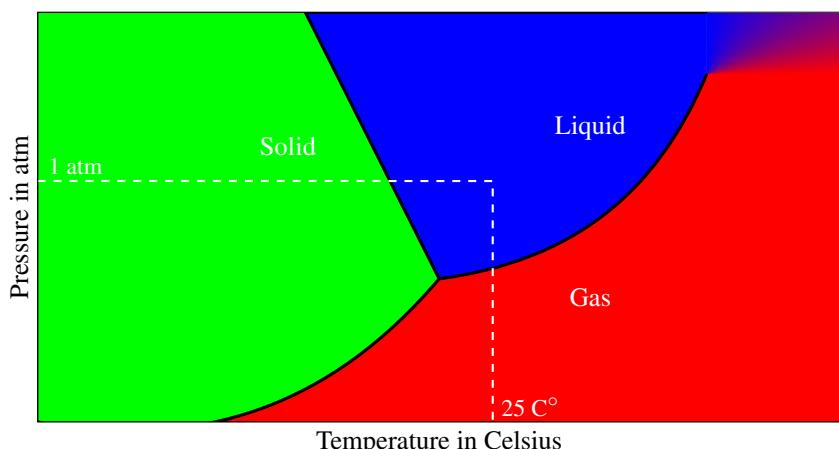


Figure 2.10 The phase diagram of water with pressure in the Y axis and temperature in the X axis. This diagram displays the different states of matter of water for different pressure and temperature conditions. The coordinates of the triple point are $(0.0098\text{ C}^\circ, 0.0060\text{ atm})$. This 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 $(374\text{ C}^\circ, 218\text{ atm})$. This means that for temperature beyond 374 C° it is not possible to liquefy steam.

Phase diagram of water 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 $(\text{Temperature}, \text{Pressure})$ conditions of $(25\text{ C}^\circ, 1\text{ atm})$. 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 and compression experiments We will analyze now some 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 *triple 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. We can also discuss some 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 starts 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 liquefy a gas or gasify a liquid.

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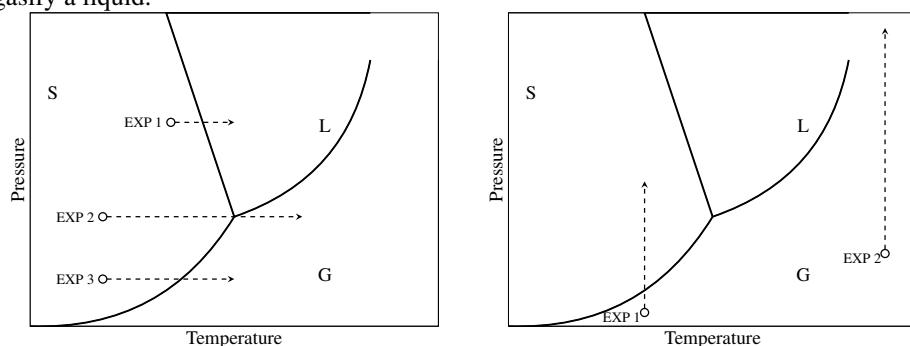


Figure 2.11 Heating experiments (left) and compression experiments (right).

Energy calculations involving phase transitions The enthalpy of vaporization of a substance gives you the amount of energy needed to vaporize an amount of substance. Similarly, the enthalpy of fusion tells you about the energy involved in the fusion process. Each phase—gas, liquid and vapor—has different specific heat. Using water as an example, imagine we need to calculate the energy involved in the heating of $m=18\text{ grams}$ ($n=1 \text{ mole}$) of water from 20°C to a 150°C . This energy results from three contributions: the energy needed to warm up liquid from 20°C to a 100°C (we can call this ΔT_1), the energy to boil 1 mole of water, and the energy to warm up 1 mole of gas water from 100°C to a 150°C (we can call this ΔT_2). The final calculation will be:

$$Q = m \cdot c_e^{\text{H}_2\text{O}(\ell)} \cdot \Delta T_1 + n \cdot \Delta H_{\text{vap}}^{\text{H}_2\text{O}} + m \cdot c_e^{\text{H}_2\text{O(g)}} \cdot \Delta T_2$$

Table 2.7 Properties of the different states of matter of water.

Property	Ice	Water	Steam
Density (g/mL)	0.93	1	0.6
$c_e (\text{J}\cdot\text{g}^{-1}\cdot{}^\circ\text{C}^{-1})$	2.18	4.184	1.99
ΔH_{fusion} (kJ/mol)	6.01		
ΔH_{vap} (kJ/mol)	44		

CHAPTER 2

INTERMOLECULAR FORCES

2.1 Indicate the strongest intermolecular force existing between the molecules of the following compounds:
 (a) CH₃OH (b) H₂ (c) CCl₄

2.2 Indicate the strongest intermolecular force existing between the molecules of the following compounds:
 (a) CH₄ (b) CCl₃H (c) HF (d) HCl

2.3 From the following pair of molecules, which molecule forms intermolecular H bonds? (a) HF or H₂
 (b) NH₃ or CH₄

2.4 From the following pair of molecules, which molecule forms intermolecular H bonds?
 (a) CH₃—O—CH₃ or H₂O (b) HCl or HF

2.5 From the following pair of molecules, which molecule forms stronger dispersion forces? (a) Ar or He (b) H₂O or H₂S

2.6 From the following pair of molecules, which molecule forms stronger dispersion forces? (a) CH₃CH₃ or CH₄ (b) CH₄ or CH₃Cl

2.7 From the following pair of molecules, which molecule forms stronger dipole forces? (a) HCl or HBr
 (b) H₂O or H₂S

2.8 From the following pair of molecules, which molecule forms stronger dipole forces? (a) NH₃ or H₂O
 (b) HI or HBr

2.9 From the following pair of molecules, which molecule has higher boiling point? (a) CH₃CH₃ or CH₄
 (b) CO₂ or H₂O

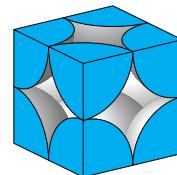
2.10 From the following pair of molecules, which molecule has higher boiling point? (a) HF or HCl (b) Ar or He

THE SOLID STATE

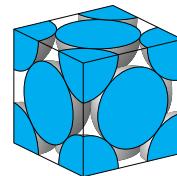
2.11 Indicate the number of atoms contained in the body-centered (bcc) cubic unit cell, for structures with the same type of atoms.

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

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



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

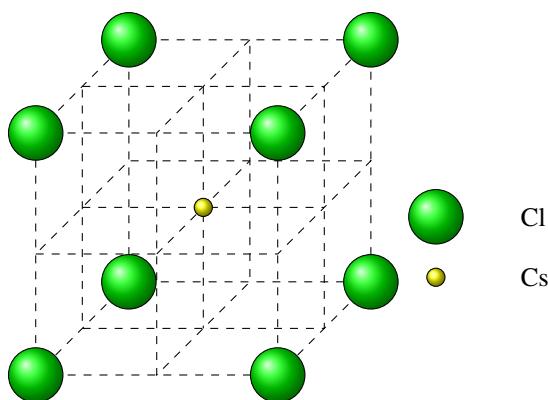


2.15 Identify the type of crystalline solid formed by the following compounds: (a) cesium chloride (b) tungsten

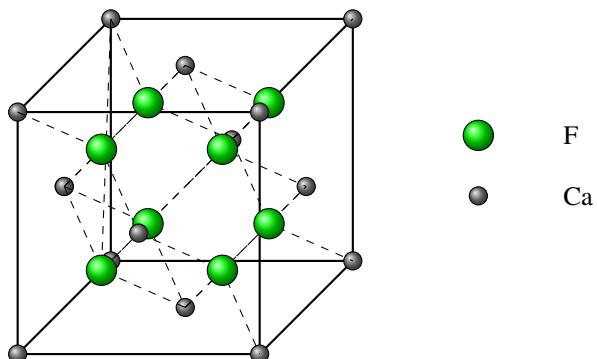
2.16 Identify the type of crystalline solid formed by the following compounds: (a) acetic acid (b) hydrogen sulfide

2.17 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.

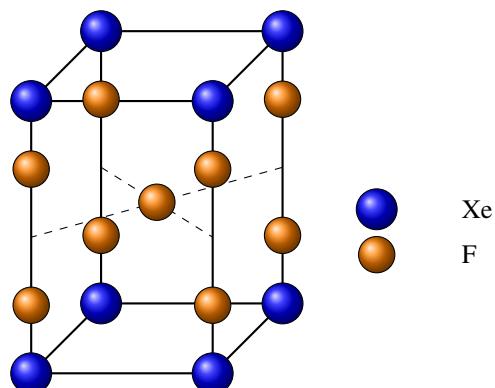
2.18 Calculate the formula for the following unit cell:



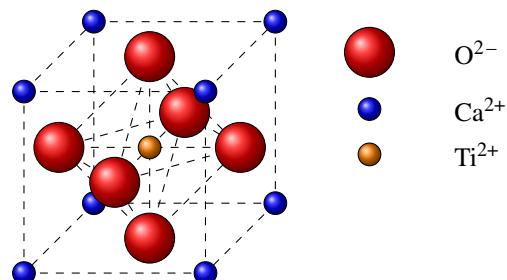
2.19 Calculate the formula for the following unit cell:



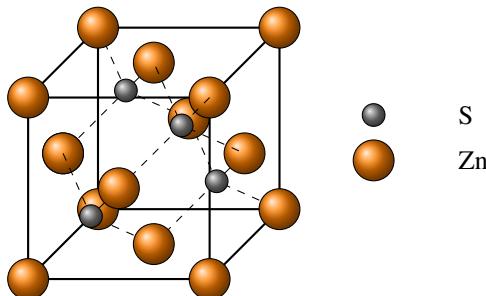
2.20 Calculate the formula for the following unit cell:



2.21 Calculate the formula for the following unit cell:

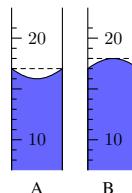


2.22 Calculate the formula for the following unit cell:

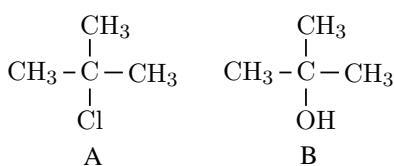


LIQUID STATE

2.23 Answer the following questions based on the image below: (a) Identify each meniscus as concave or convex
 (b) Which liquid has higher surface tension (c) Which liquid is more wettable (wets more)



2.24 Which of the following molecules present higher viscosity?



2.25 A liquid has an 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.

2.26 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?

2.27 The vapor pressure of a chemical at 32°C is 0.86 atm. Given that its heat of vaporization is 26 kJ/mol, calculate the vapor pressure at 50°C.

2.28 Calculate the heat of vaporization of a chemical that doubles its vapor pressure when the temperature increases from 10°C to 40°C.

2.29 For a chemical with heat of vaporization of 200kJ/mol, at what temperature will the vapor pressure be three times the value at 25°C?

2.30 Given that the vapor pressure at 33°C is 63mmHg for a chemical with molar heat of vaporization of 44kJ/mol, calculate the normal boiling point of this chemical—this is the boiling point at 760mmHg.

2.31 Order the following compounds from high to low vapor pressure (P^{vap}): NH₃ ($\Delta H_{vap}=23\text{ kJ/mol}$), CH₄ ($\Delta H_{vap}=8\text{ kJ/mol}$), C₄H₁₀ ($\Delta H_{vap}=15\text{ kJ/mol}$)

2.32 Order the following compounds from high to low vapor pressure: C₆H₆ ($\Delta H_{vap}=31\text{ kJ/mol}$), C₆H₅OH ($\Delta H_{vap}=39\text{ kJ/mol}$), H₂O ($\Delta H_{vap}=41\text{ kJ/mol}$)

Answers 2.1 (a) CH₃OH (hydrogen bonds) (b) H₂ (dispersion forces) (c) CCl₄ (dispersion forces) **2.3** (a) HF (b) NH₃ **2.5** (a) He (b) H₂S **2.7** (a) HCl (b) H₂O **2.9** (a) CH₃CH₃ (b) H₂O **2.11** 2 **2.13** 1 **2.15** (a) cesium chloride (ionic solid) (b) tungsten (atomic solid, metallic) **2.17** 20 g · mol⁻¹ **2.19** Cs₁Cl₁ **2.21** Cs₁Cl₁ **2.23** (a) a: concave; b: convex (b) b (c) a **2.25** 4.51atm **2.27** 1.52atm **2.29** 303°C