

Chapter 4

Big Idea #2: Bonding and Phases

Chemical and physical properties of materials can be explained by the structure and the arrangement of atoms, ions, or molecules and the forces between them.

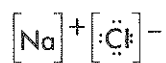
BONDS OVERVIEW

Atoms engage in chemical reactions in order to reach a more stable, lower-energy state. This requires the transfer or sharing of electrons, a process that is called **bonding**. Atoms of elements are usually at their most stable when they have eight electrons in their valence shells. As a result, atoms with too many or too few electrons in their valence shells will find one another and pass the electrons around until all the atoms in the molecule have stable outer shells. Sometimes an atom will give up electrons completely to another atom, forming an ionic bond. Sometimes atoms share electrons, forming covalent bonds.

IONIC BONDS

An ionic solid is held together by the electrostatic attractions between ions that are next to one another in a lattice structure. They often occur between metals and nonmetals. In an ionic bond, electrons are not shared. Instead, the cation gives up an electron (or electrons) to the anion.

The two ions in an ionic bond are held together by electrostatic forces. In the diagram below, a sodium atom has given up its single valence electron to a chlorine atom, which has seven valence electrons and uses the electron to complete its outer shell (with eight). The two atoms are then held together by the positive and negative charges on the ions.



The electrostatic attractions that hold together the ions in the NaCl lattice are very strong and any substance held together by ionic bonds will usually be a solid at room temperature and have very high melting and boiling points.

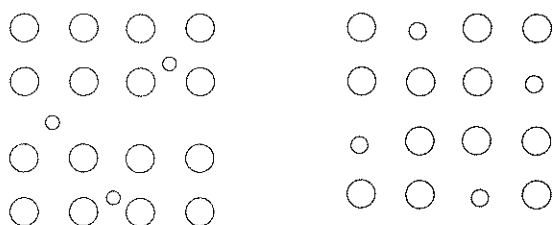
Two factors affect the melting points of ionic substances. The primary factor is the charge on the ions. According to Coulomb's law, a greater charge leads to a greater bond energy (often called lattice energy in ionic bonds), so a compound composed of ions with charges of +2 and -2 (such as MgO) will have a higher melting point than a compound composed of ions with charges of +1 and -1 (such as NaCl). If both compounds are made up of ions with equal charges, then the size of the ions must be considered. Smaller ions will have greater Coulombic attraction (remember, size is inversely proportional to bond energy), so a substance like LiF would have a greater melting point than KBr.

In an ionic solid, each electron is localized around a particular atom, so electrons do not move around the lattice; this makes ionic solids poor conductors of electricity. Ionic liquids, however, do conduct electricity because the ions themselves are free to move about in the liquid phase, although the electrons are still localized around particular atoms. Salts are held together by ionic bonds.

METALLIC BONDS

When examining metals, the sea of electrons model can be used. The positively-charged core of a metal, consisting of its nucleus and core electrons, is generally stationary, while the valence electrons on each atom do not belong to a specific atom and are very mobile. These mobile electrons explain why metals are such good conductors of electricity. The delocalized structure of a metal also explains why metals are both malleable and ductile, as deforming the metal does not change the environment immediately surrounding the metal cores.

Metals can also bond with each other to form alloys. This typically occurs when two metals are melted into their liquid phases, and are then poured together before cooling and creating the alloy. In an **interstitial alloy**, metal atoms with two vastly different radii combine. Steel is one such example—the much smaller carbon atoms occupy the interstices of the iron atoms. A **substitutional alloy** forms between atoms of similar radii. Brass is a good example, atoms of zinc are substituted for some copper atoms to create the alloy.



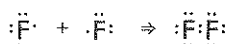
Interstitial
Alloy

Substitutional
Alloy

COVALENT BONDS

In a covalent bond, two atoms share electrons. Each atom counts the shared electrons as part of its valence shell. In this way, both atoms achieve complete outer shells.

In the diagram below, two fluorine atoms, each of which has seven valence electrons and needs one electron to complete its valence shell, form a covalent bond. Each atom donates an electron to the bond, which is considered to be part of the valence shell of both atoms.



The number of covalent bonds an atom can form is the same as the number of unpaired electrons in its valence shell.

Single bonds have one sigma (σ) bond and a bond order of one. The single bond has the longest bond length and the least bond energy.

The first covalent bond formed between two atoms is called a sigma (σ) bond. All single bonds are sigma bonds. If additional bonds between the two atoms are formed, they are called pi (π) bonds. The second bond in a double bond is a pi bond and the second and third bonds in a triple bond are also pi bonds. Double and triple bonds are stronger and shorter than single bonds, but they are not twice or triple the strength.

Summary of Multiple Bonds			
Bond type:	Single	Double	Triple
Bond designation:	One sigma (σ)	One sigma (σ) and one pi (π)	One sigma (σ) and two pi (π)
Bond order:	One	Two	Three
Bond length:	Longest	Intermediate	Shortest
Bond energy:	Least	Intermediate	Greatest

Network (Covalent) Bonds

In a network solid, atoms are held together in a lattice of covalent bonds. You can visualize a network solid as one big molecule. Network solids are very hard and have very high melting and boiling points.

The electrons in a network solid are localized in covalent bonds between particular atoms, so they are not free to move about the lattice. This makes network solids poor conductors of electricity.

The most commonly seen network solids are compounds of carbon (such as diamond or graphite) and silicon (SiO_2 —quartz). This is because both carbon and silicon have four valence electrons, meaning they are able to form a large number of covalent bonds.

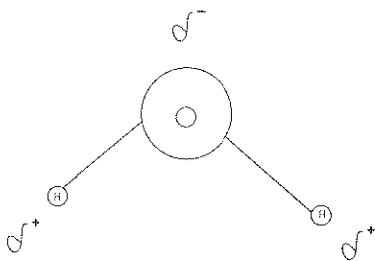
Silicon also serves as a semiconductor when it is doped with other elements. **Doping** is a process in which an impurity is added to an existing lattice. In a normal silicon lattice, each individual silicon atom is bonded to four other silicon atoms. When some silicon atoms are replaced with elements that have only three valence electrons (such as boron or aluminum), the neighboring silicon atoms will lack one bond apiece.

This missing bond (or “hole”) creates a positive charge in the lattice, and the hole attracts other electrons to it, increasing conductivity. Those electrons leave behind holes when they move, creating a chain reaction in which the conductivity of the silicon increases. This type of doping is called **p-doping** for the positively charged holes.

If an element with five valence electrons (such as phosphorus or arsenic) is used to add impurities to a silicon lattice, there is an extra valence electron that is free to move around the lattice, causing an overall negative charge that increases the conductivity of the silicon. This type of doping is called **n-doping** due to the free-moving negatively charged electrons.

Polarity

In the F_2 molecule shown on page 107, the two fluorine atoms share the electrons equally, but that's not usually the case in molecules. Usually, one of the atoms (the more electronegative one) will exert a stronger pull on the electrons in the bond—not enough to make the bond ionic, but enough to keep the electrons on one side of the molecule more than on the other side. This gives the molecule a dipole. That is, the side of the molecule where the electrons spend more time will be negative and the side of the molecule where the electrons spend less time will be positive.



In the water molecule above, oxygen has a higher electronegativity than hydrogen and thus will have the electrons closer to it more often. This gives the oxygen a negative dipole and each hydrogen a positive dipole.

Dipole Moment

The polarity of a molecule is measured by the dipole moment. The more polar the molecule is, the larger the dipole moment is. You will not need to calculate the strength of a dipole, but you should be familiar with the unit with which that strength is quantified. That unit is called the debye (D).

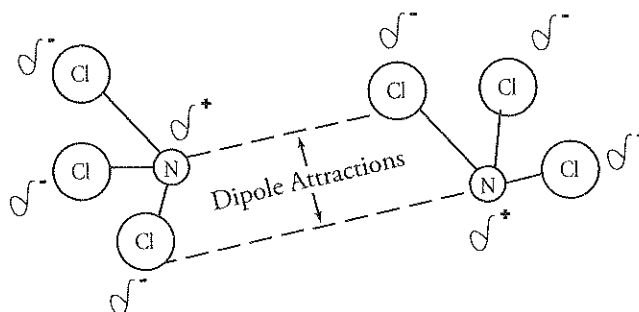
INTERMOLECULAR FORCES

Intermolecular forces (IMFs) are the forces that exist between molecules in a covalently bonded substance. These forces are what need to be broken apart in order for covalent substances to change phases. Note that when ionic substances change phase, bonds between the individual ions are actually broken. When covalent substances change phase, the bonds between the individual atoms remain in place, it is just the forces that hold the molecules to other molecules that break apart.

Dipole–Dipole Forces

Dipole–dipole forces occur between polar molecules: The positive end of one polar molecule is attracted to the negative end of another polar molecule.

Molecules with greater polarity will have greater dipole–dipole attraction, so molecules with larger dipole moments tend to have higher melting and boiling points. Dipole–dipole attractions are relatively weak, however, and these substances melt and boil at very low temperatures. Most substances held together by dipole–dipole attraction are gases or liquids at room temperature.

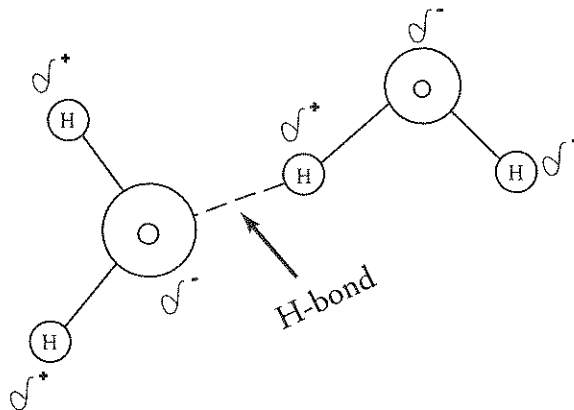


Hydrogen Bonds

Hydrogen bonds are a special type of dipole–dipole attraction. In a hydrogen bond, the positively charged hydrogen end of a molecule is attracted to the negatively charged end of another molecule containing an extremely electronegative element (fluorine, oxygen, or nitrogen—F, O, N).

Hydrogen bonds are much stronger than normal dipole–dipole forces because when a hydrogen atom gives up its lone electron to a bond, its positively charged nucleus is left virtually unshielded. Substances that have hydrogen bonds, such as water and ammonia, have higher melting and boiling points than substances that are held together only by other types of intermolecular forces.

Water is less dense as a solid than as a liquid because its hydrogen bonds force the molecules in ice to form a crystal structure, which keeps them farther apart than they are in the liquid form.



London Dispersion Forces

London dispersion forces occur between all molecules. These very weak attractions occur because of the random motions of electrons on atoms within molecules. At a given moment, a nonpolar molecule might have more electrons on one side than on the other, giving it an instantaneous polarity. For that fleeting instant, the molecule will act as a very weak dipole.

Since London dispersion forces depend on the random motions of electrons, molecules with more electrons will experience greater London dispersion forces. So among substances that experience only London dispersion forces, the one with more electrons will generally have higher melting and boiling points. London dispersion forces are even weaker than dipole–dipole forces, so substances that experience only London dispersion forces melt and boil at extremely low temperatures and tend to be gases at room temperature.

As molecules gain more electrons, the London dispersion forces between them start to become much more significant. Comparing the boiling point of a nonpolar substance with a large number of electrons vs. a polar substance with less electrons is difficult, and there is no simple rule to follow. For instance, water has hydrogen bonds and a boiling point of 100°C . Butane (C_4H_{10}) and octane (C_8H_{18}) are both completely nonpolar molecules, and while butane's boiling point is 34°C , octane's is 125°C . Even though octane has no permanent dipoles, it has so many electrons that its London dispersion forces are significant enough that they create greater intermolecular attractions than even the hydrogen bonds in water.

The role of London dispersion forces is often determined by comparing the molar mass of molecules. However, it is not the mass itself which affects the strength of the IMFs. Rather, it is simply that as mass (based on protons and neutrons) increases, so too do the number of electrons, as the molecule must remain electrically neutral.

Bond Strength

Ionic substances are generally solids at room temperature, and turning them into liquids (melting them), requires the bonds holding the lattice together to be broken. The amount of energy needed for that is based on the Coulombic attraction between the molecules.

Covalent substances, which are liquid at room temperature, will boil when the intermolecular forces between them are broken. For molecules with similar sizes, the following IMF ranking can help you determine the relative strength of the IMFs within the molecules.

- a. Hydrogen bonds
- b. Non-hydrogen bond permanent dipoles
- c. London dispersion forces (temporary dipoles)
 - i. Larger molecules are more polarizable and have stronger London dispersion forces because they have more electrons.

IMF Questions: Not So Impossible

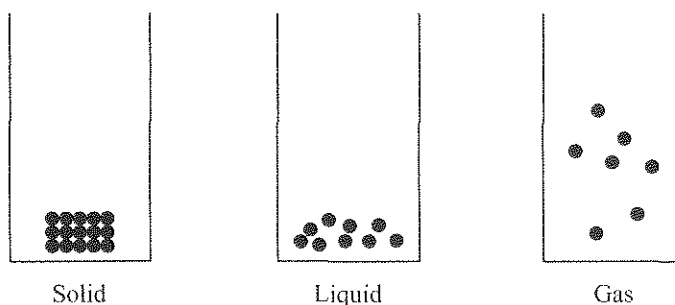
The AP Exam will most likely focus questions regarding IMFs on molecules with similar masses, as it is much easier to compare the strengths of their IMFs. However, understanding that London dispersion forces can have an impact on IMF-related trends when considering molecules with a large difference in their masses is worth keeping in mind.

The melting and boiling points of covalent substances are almost always lower than the melting and boiling point of ionic ones.

Metallic bonding, which often only involves one type of atom, tends to be very strong and thus metals (particularly the transition metals) tend to have high melting points. Network covalent bonding is the strongest type of bonding there is, and it is very difficult to cause substances that exhibit network covalent bonding to melt.

Bonding and Phases

The phase of a substance is directly related to the strength of its intermolecular forces. Solids have highly ordered structures where the atoms are packed tightly together, while gases have atoms spread so far apart that most of the volume is free space.



In other words, substances that exhibit weak intermolecular forces (such as London Dispersion forces) tend to be gases at room temperature. Nitrogen (N_2) is an example of this. Substances that exhibit strong intermolecular forces (such as hydrogen bonds) tend to be liquids at room temperature. A good example is water.

Ionic substances do not experience intermolecular forces. Instead, their phase is determined by the ionic bond holding the ions together in the lattice. Because ionic bonds are generally significantly stronger than intermolecular forces in covalent molecules, ionic substances are usually solid at room temperatures.

VAPOR PRESSURE

Beyond helping to determine the melting point and boiling point of covalent substances, the relative strength of the intermolecular forces in a substance can also predict several other properties of that substance. The most important of these is vapor pressure. Vapor pressure arises from the fact that the molecules inside a liquid are in constant motion. If those molecules hit the surface of the liquid with enough kinetic energy, they can escape the intermolecular forces holding them to the other molecules and transition into the gas phase.

This process is called vaporization. It is not to be confused with a liquid boiling. When a liquid boils, energy (in the form of heat) is added, increasing the kinetic energy of all of the molecules in the liquid until all of the intermolecular forces are broken. For vaporization to occur, no outside energy needs to be added. Note that there is a direct relationship between temperature and vapor pressure.

The higher the temperature of a liquid, the faster the molecules are moving and the more likely they are to break free of the other molecules. So, temperature and vapor pressure are directly proportional.

If two liquids are at the same temperature, the vapor pressure is dependent primarily on the strength of the intermolecular forces within that liquid. The stronger those intermolecular forces are, the less likely it is that molecules will be able to escape the liquid, and the lower the vapor pressure for that liquid will be.

LEWIS DOT STRUCTURES

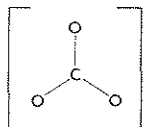
Drawing Lewis Dot Structures

At some point on the test, you'll be asked to draw the Lewis structure for a molecule or polyatomic ion. Here's how to do it.

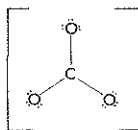
1. Count the valence electrons in the molecule or polyatomic ion; refer to page 74 for the periodic table.
2. If a polyatomic ion has a negative charge, add electrons equal to the charge of the total in (1). If a polyatomic ion has a positive charge, subtract electrons equal to the charge of the electrons from the total in (1).
3. Draw the skeletal structure of the molecule and place two electrons (or a single bond) between each pair of bonded atoms. If the molecule contains three or more atoms, the least electronegative atom will usually occupy the central position.
4. Add electrons to the surrounding atoms until each has a complete outer shell.
5. Add the remaining electrons to the central atom.
6. Look at the central atom.
 - (a) If the central atom has fewer than eight electrons, remove an electron pair from an outer atom and add another bond between that outer atom and the central atom. Do this until the central atom has a complete octet.
 - (b) If the central atom has a complete octet, you are finished.
 - (c) If the central atom has more than eight electrons, that's okay, too, as long as the total does not exceed twelve.

Let's find the Lewis dot structure for the CO_3^{2-} ion.

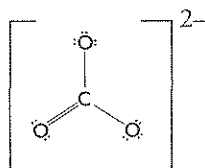
1. Carbon has 4 valence electrons; oxygen has 6.
 $4 + 6 + 6 + 6 = 22$
2. The ion has a charge of -2 , so add 2 electrons.
 $22 + 2 = 24$
3. Carbon is the central atom.



4. Add electrons to the oxygen atoms.

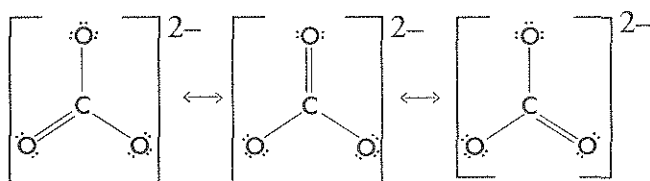


5. We've added all 24 electrons, so there's nothing left to put on the carbon atom.
6. (a) We need to give carbon a complete octet, so we take an electron pair away from one of the oxygens and make a double bond instead. Place a bracket around the model and add a charge of negative two.



Resonance Forms

When we put a double bond into the CO_3^{2-} ion, we place it on any one of the oxygen atoms, as shown below.



Don't Be Fooled By Appearances

Despite the conventional way the Lewis diagrams have been drawn, remember that the bonds of a compound that displays resonance are all identical. The only reason it looks like a mix of single and double bonds is because any attempt to illustrate a bond somewhere between these two strengths and lengths would be awkward.

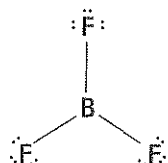
All three resonance forms are considered to exist simultaneously, and the strength and lengths of all three bonds are the same: somewhere between the strength and length of a single bond and a double bond.

To determine the relative length and strength of a bond in a resonance structure, a bond order calculation can be used. A single bond has a bond order of 1, and a double bond has an order of 2. When resonance occurs, pick one of the bonds in the resonance structure and add up the total bond order across the resonance forms, then divide that sum by the number of resonance forms.

For example, in the carbonate ion above, the top C–O bond would have a bond order of $\frac{1 + 2 + 1}{3}$, or 1.33. Bond order can be used to compare the length and strength of resonance bonds with pure bonds as well as other resonance bonds.

Incomplete Octets

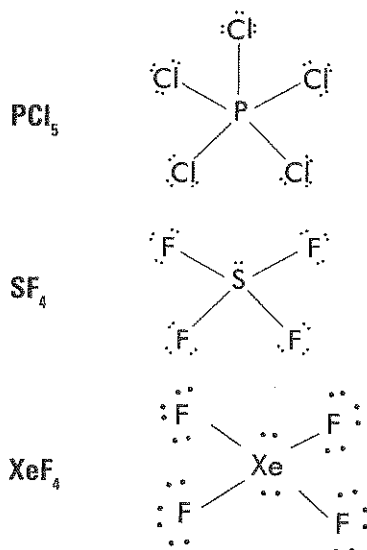
Some atoms are stable with less than eight electrons in their outer shell. Hydrogen only requires two electrons, as does helium (although helium never forms bonds). Boron is considered to be stable with six electrons, as in the BF_3 diagram below. All other atoms involved in covalent bonding require a minimum of eight electrons to be considered stable.



Expanded Octets

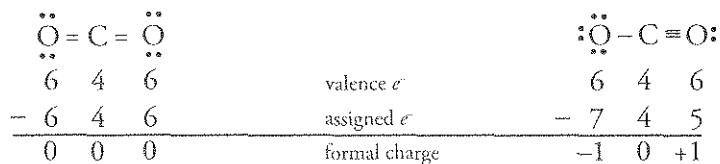
In molecules that have d subshells available, the central atom can have more than eight valence electrons, but never more than twelve. This means any atom of an element from $n = 3$ or greater can have expanded octets, but NEVER elements in $n = 2$ (C, N, O, etc.). Expanded octets also explains why some noble gases can actually form bonds; the extra electrons go into the empty d -orbital.

Here are some examples.



Formal Charge

Sometimes, there is more than one valid Lewis structure for a molecule. Take CO_2 ; it has two valid structures as shown below. To determine the more likely structure, formal charge is used. To calculate the formal charge on atoms in a molecule, take the number of valence electrons for that atom and subtract the number of assigned electrons in the Lewis structure. When counting assigned electrons, lone pairs count as two and bonds count as one.



The total formal charge for a neutral molecule should be zero, which it is on both diagrams. Additionally, the fewer number of atoms there are with an actual formal charge, the more likely the structure will be—so the left structure is the more likely one for CO_2 . For polyatomic ions, the sum of the formal charges on each atom should equal the overall charge on the ion.

Molecular Geometry

Electrons repel one another, so when atoms come together to form a molecule, the molecule will assume the shape that keeps its different electron pairs as far apart as possible. When we predict the geometries of molecules using this idea, we are using the **valence shell electron-pair repulsion (VSEPR) model**.

In a molecule with more than two atoms, the shape of the molecule is determined by the number of electron pairs on the central atom. The central atom forms **hybrid orbitals**, each of which has a standard shape. Variations on the standard shape occur depending on the number of bonding pairs and lone pairs of electrons on the central atom.

Here are some things you should remember when dealing with the VSEPR model.

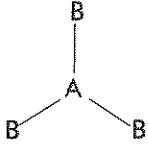
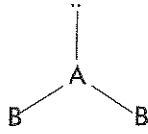
- Double and triple bonds are treated in the same way as single bonds in terms of predicting overall geometry for a molecule; however, multiple bonds have slightly more repulsive strength and will therefore occupy a little more space than single bonds.
- Lone electron pairs have a little more repulsive strength than bonding pairs, so molecules with lone pairs will have slightly reduced bond angles between terminal atoms.

The following pages show the different hybridizations and geometries that you might see on the test.

If the central atom has 2 electron pairs, then it has sp hybridization and its basic shape is linear.

<u>Number of lone pairs</u>	<u>Geometry</u>	<u>Examples</u>
0	B—A—B linear	BeCl ₂ CO ₂

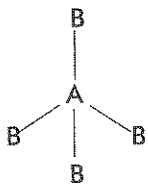
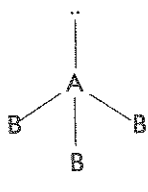
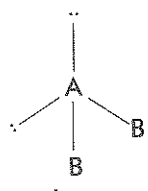
If the central atom has 3 electron pairs, then it has sp^2 hybridization and its basic shape is trigonal planar; its bond angles are about 120°.

<u>Number of lone pairs</u>	<u>Geometry</u>	<u>Examples</u>
0	 trigonal planar	BF ₃ SO ₃ NO ₃ ⁻ CO ₃ ²⁻
1	 bent	SO ₂

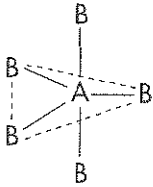
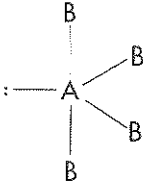
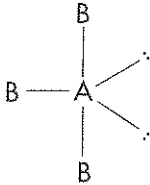
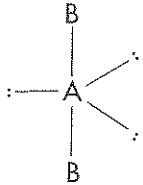
The angle between the terminal atoms in the bent shape is slightly less than 120° because of the extra lone pair repulsion.

If the central atom has 4 electron pairs, then it has sp^3 hybridization and its basic shape is **tetrahedral**; its bond angles are about 109.5° .

The angle between the terminal atoms in the trigonal pyramidal and bent shapes is slightly less than 109.5° because of the extra lone pair repulsion.

<u>Number of lone pairs</u>	<u>Geometry</u>	<u>Examples</u>
0	 <p>tetrahedral</p>	CH_4 NH_4^+ ClO_4^- SO_4^{2-} PO_4^{3-}
1	 <p>trigonal pyramidal</p>	NH_3 PCl_3 AsH_3 SO_3^{2-}
2	 <p>bent</p>	H_2O OF_2 NH_2^-

If the central atom has 5 electron pairs, its basic shape is **trigonal bipyramidal**.

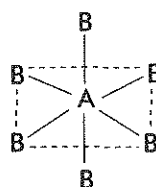
<u>Number of lone pairs</u>	<u>Geometry</u>	<u>Examples</u>
0	 <p>trigonal bipyramidal</p>	PCl_5 PF_5
1	 <p>folded square, seesaw, distorted tetrahedron</p>	SF_4 IF_4^+
2	 <p>T-shaped</p>	ClF_3 ICl_3
3	 <p>linear</p>	XeF_2 I_3^-

In trigonal bipyramidal shapes, place the lone pairs in axial position first. In octahedral shapes, place lone pairs in equatorial position first.

If the central atom has 6 electron pairs, its basic shape is octahedral.

<u>Number of lone pairs</u>	<u>Geometry</u>	<u>Examples</u>
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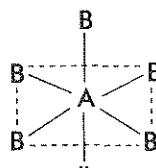
0



SF_6

octahedral

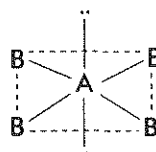
1



BrF_5
 IF_5

square pyramidal

2



XeF_4
 ICl_4^-

square planar

KINETIC MOLECULAR THEORY

For ideal gases, the following assumptions can be made:

- The kinetic energy of an ideal gas is directly proportional to its absolute temperature: The greater the temperature, the greater the average kinetic energy of the gas molecules.

The Average Kinetic Energy of a Single Gas Molecule

$$KE = \frac{1}{2}mv^2$$

m = mass of the molecule (kg)

v = speed of the molecule (meters/sec)

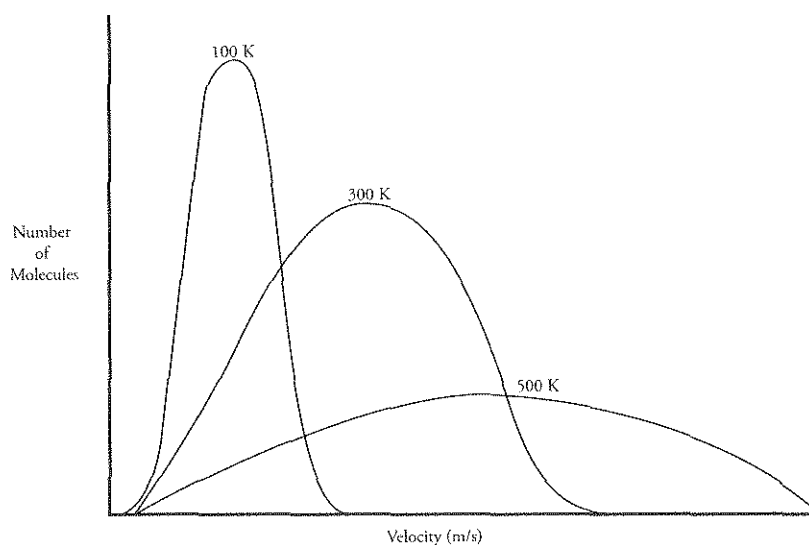
KE is measured in joules

- If several different gases are present in a sample at a given temperature, all the gases will have the same average kinetic energy. That is, the average kinetic energy of a gas depends only on the absolute temperature, not on the identity of the gas.
- The volume of an ideal gas particle is insignificant when compared with the volume in which the gas is contained.
- There are no forces of attraction between the gas molecules in an ideal gas.
- Gas molecules are in constant motion, colliding with one another and with the walls of their container without losing any energy.

MAXWELL-BOLTZMANN DIAGRAMS

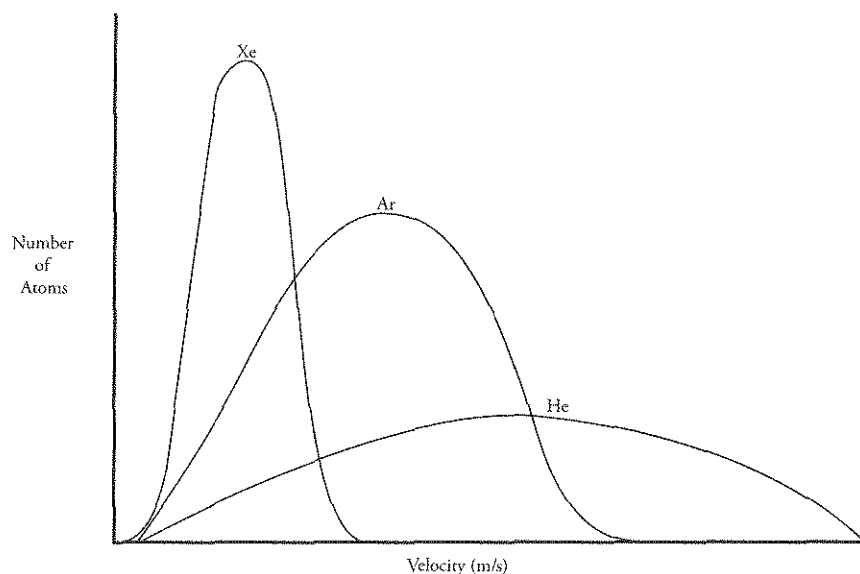
A Maxwell-Boltzmann diagram shows the range of velocities for molecules of a gas. Molecules at a given temperature are not all moving at the same velocity. When determining the temperature, we take the average velocity of all the molecules and use that in the relevant equation to calculate temperature. You do not need to know that equation (unless you are taking AP Physics!). All you need to know here is that temperature is directly proportional to kinetic energy.

The first type of Maxwell-Boltzmann diagram involves plotting the velocity distributions for the molecules of one particular gas at multiple temperatures. In the diagram on the next page, there are three curves representing a sample of nitrogen gas at 100 K, 300 K, and 500 K.



As you can see, the higher the temperature of the gas, the larger the range is for the velocities of the individual molecules. Gases at higher temperatures have greater kinetic energy (KE), and as all the molecules in this example have the same mass, the increased KE is due to the increased velocity of the gas molecules.

Maxwell-Boltzmann diagrams are also used to show a number of different gases at the same temperature. The diagram on the next page shows helium, argon, and xenon gas, all at 300 K:



In this case, all of the gases have the same amount of total kinetic energy because they have identical temperatures. However, not all of the atoms have the same mass. If the atoms have smaller masses, they must have greater velocities in order to have a kinetic energy identical to that of atoms with greater mass. Because helium atoms have the least mass, they have the highest average velocity. Xenon atoms, which have a much greater mass, have a correspondingly lower velocity.

EFFUSION

Effusion is the rate at which a gas will escape from a container through microscopic holes in the surface of the container. For instance, even though the rubber or latex that makes up a balloon may seem solid, after the balloon is filled with a gas, it will gradually shrink over time. This is due to the fact that there are tiny holes in the surface of the balloon, through which the even tinier gas molecules can escape.

The rate at which a gas effuses from a container is dependent on the speed of the gas particles. The faster the particles are moving, the more often they hit the sides of the container, and the more likely they are to hit a hole and escape. The rate of effusion thus increases with temperature, but also, if examining gases at the same temperature, the gas with the lower molar mass will effuse first.

It is likely you have experienced this; a balloon filled with helium will deflate more rapidly than one filled with air (which is composed primarily of nitrogen and oxygen) or one filled with carbon dioxide. There is a formula that quantifies the rate at which a gas will effuse, but that is beyond the scope of the exam. As long as you understand the basic principles behind effusion, you should be able to answer any questions on this topic that may come up.

THE IDEAL GAS EQUATION

You can use the ideal gas equation to calculate any of the four variables relating to the gas, provided that you already know the other three.

The Ideal Gas Equation

$$PV = nRT$$

P = the pressure of the gas (atm)

V = the volume of the gas (L)

n = the number of moles of gas

R = the gas constant, 0.0821 L·atm/mol·K

T = the absolute temperature of the gas (K)

You can also manipulate the ideal gas equation to figure out how changes in each of its variables affect the other variables. The following equation, often called the combined gas law, can only be used when the number of moles is held constant.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

P = the pressure of the gas (atm)

V = the volume of the gas (L)

T = the absolute temperature of the gas (K)

You should be comfortable with the following simple relationships:

- If the volume is constant: As pressure increases, temperature increases; as temperature increases, pressure increases.
- If the temperature is constant: As pressure increases, volume decreases; as volume increases, pressure decreases. That's Boyle's law.
- If the pressure is constant: As temperature increases, volume increases; as volume increases, temperature increases. That's Charles's law.

DALTON'S LAW

Dalton's law states that the total pressure of a mixture of gases is just the sum of all the partial pressures of the individual gases in the mixture.

Dalton's Law

$$P_{\text{total}} = P_a + P_b + P_c + \dots$$

You should also note that the partial pressure of a gas is directly proportional to the number of moles of that gas present in the mixture. So if 25 percent of the gas in a mixture is helium, then the partial pressure due to helium will be 25 percent of the total pressure.

Partial Pressure

$$P_a = (P_{\text{total}})(X_a)$$

$$X_a = \frac{\text{moles of gas A}}{\text{total moles of gas}}$$

DEVIATIONS FROM IDEAL BEHAVIOR

At low temperature and/or high pressure, gases behave in a less-than-ideal manner. That's because the assumptions made in kinetic molecular theory become invalid under conditions where gas molecules are packed too tightly together.

Two things happen when gas molecules are packed too tightly.

- *The volume of the gas molecules becomes significant.*
The ideal gas equation does not take the volume of gas molecules into account, so the actual volume of a gas under nonideal conditions will be larger than the volume predicted by the ideal gas equation.
- *Gas molecules attract one another and stick together.*
The ideal gas equation assumes that gas molecules never stick together. When a gas is packed tightly together, intermolecular forces become significant, causing some gas molecules to stick together. When gas molecules stick together, there are fewer particles bouncing around and creating pressure, so the real pressure in a nonideal situation will be smaller than the pressure predicted by the ideal gas equation.

DENSITY

You may be asked about the density of a gas. The density of a gas is measured in the same way as the density of a liquid or solid: in mass per unit of volume.

Density of a Gas

$$D = \frac{m}{V}$$

D = density

m = mass of gas, usually in grams

V = volume occupied by a gas, usually in liters

The density of any gas sample can also be determined by combining the density equation with the ideal gas law.

$$\text{If } D = \frac{m}{V}, \text{ then } V = \frac{m}{D}.$$

Substituting that into the ideal gas law:

$$\frac{Pm}{D} = nRT$$

A little rearrangement yields:

$$D = \frac{Pm}{nRT}$$

The term (m/n) describes mass per mole, which is how molar mass (MM) is measured. Thus:

$$D = \frac{P(\text{MM})}{RT}$$

If you are given the density of a gas and need to find the molar mass, this can also be rewritten as:

$$\text{MM} = \frac{DRT}{P}$$

SOLUTIONS

Molarity

Molarity (M) expresses the concentration of a solution in terms of volume. It is the most widely used unit of concentration, turning up in calculations involving equilibrium, acids and bases, and electrochemistry, among others.

When you see a chemical symbol in brackets on the test, that means they are talking about molarity. For instance, “[Na⁺]” is the same as “the molar concentration (molarity) of sodium ions.”

$$\text{Molarity } (M) = \frac{\text{moles of solute}}{\text{liters of solution}}$$

Mole Fraction

Mole fraction (X) gives the fraction of moles of a given substance (S) out of the total moles present in a sample.

$$\text{Mole Fraction } (X) = \frac{\text{moles of substance } S}{\text{total number of moles in solution}}$$

Solutes and Solvents

There is a basic rule for remembering which solutes will dissolve in which solvents.

Like dissolves like

That means that polar or ionic solutes (such as salt) will dissolve in polar solvents (such as water). That also means that nonpolar solutes (such as oils) are best dissolved in nonpolar solvents. When an ionic substance dissolves, it breaks up into ions. That's **dissociation**. Free ions in a solution are called electrolytes because they can conduct electricity.

The more ions that are present in an ionic compound, the greater the conductivity of that compound will be when those ions are dissociated. For instance, a solution of magnesium chloride will dissociate into three ions (one Mg²⁺ and two Cl⁻). A solution of sodium chloride will dissociate into just two ions (Na⁺ and Cl⁻). Thus, a solution of magnesium chloride will conduct electricity better than a solution of sodium chloride if both solutions have identical concentrations.

SOLUTION SEPARATION

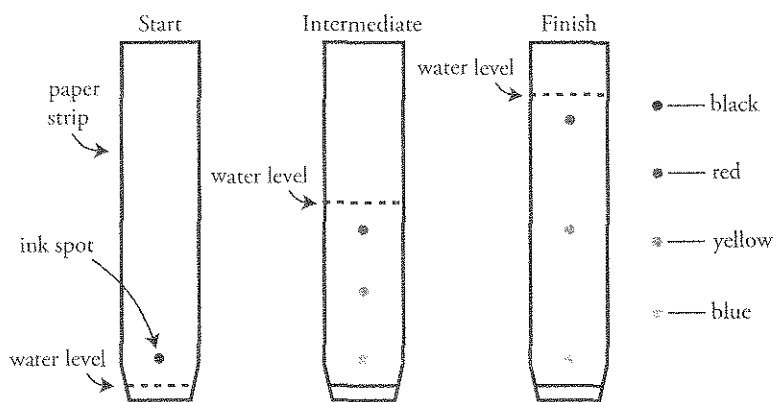
We can use intermolecular forces and the various Coulombic attractions that occur between ions and polar molecules in order to help separate various substances out from each other. There are several ways to do this.

Paper Chromatography

Chromatography is the separation of a mixture by passing it in solution through a medium in which the components of the solution move at different rates. There are several major types of chromatography. The first is paper chromatography, in which paper is the medium through which the solution passes.

Many chemical solutions, such as the ink found in most pens, are a mixture of a number of covalent substances. Each of these substances has its own polarity value, and thus has a different affinity depending on the solvent. One of the most common paper chromatography experiments involves the separation of pigments in black ink. Black ink is usually made up of substances of several different colors, which when combined create black.

In paper chromatography, a piece of filter paper is suspended above a solvent so that the very bottom of the paper is touching the solvent. The ink in question is dotted onto a line at the bottom of the filter paper that starts out just above the solvent level. As the solvent climbs the paper, the various substances inside the ink will be attracted to the polar water molecules. The more polar the substance is, the more it will be attracted to the water molecules, and the further it will travel. You might end up with something that looks like this:



Looking at that strip, you can conclude that the ink was made of three different substances. The one that traveled the farthest with the water (the red pigment) experienced the strongest attractions and was the most polar, whereas the one that didn't travel very far from the original starting line (the blue pigment) was the least polar. Paper chromatography is the most useful with colored substances, which is why ink is used in the above example. If there were components to the ink that had no visible color, you would not be able to see them on the filter paper, and that is one major limitation of paper chromatography.

The distance the ink travels along the paper is measured via the retention (or retardation) factor, also known as the R_f value. The R_f value is calculated as such:

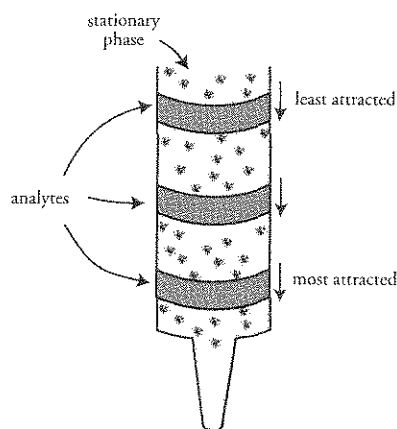
$$R_f = \frac{\text{Distance traveled by solute}}{\text{Distance traveled by solvent front}}$$

The stronger the attraction between the solute and the solvent front is, the larger the R_f value will be. In the diagram above, the red pigment would have the highest R_f value.

Water is not the only solvent that can be used in polar chromatography. There are many nonpolar solvents (such as cyclohexane) that can be used instead. In the case of a nonpolar solvent, the position of the various ink components in the above diagram would have been reversed—the most nonpolar substance would travel the furthest, and the most polar substance would travel the least.

Column Chromatography

Another type of chromatography is column chromatography. In this process, a column is packed with a stationary substance. Then, the solution to be separated (the analyte) is injected into the column, where it adheres to the stationary phase. After that, another solution (called the eluent) is injected into the column. As the eluent passes through the stationary phase, the analyte molecules will be attracted to it with varying degrees of strength depending on their polarity. The more attracted certain analyte molecules are to the eluent, the faster they will travel through (“elute”) and leave the column.



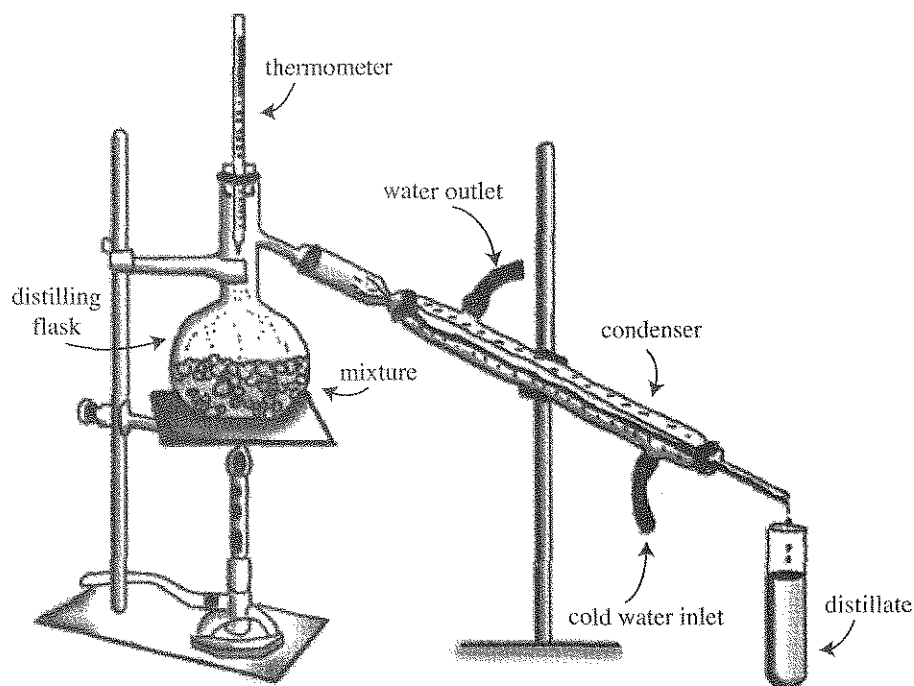
The speed at which the substances move through the column can be monitored, and if there is a sufficient polarity difference between the components they will leave the column at different times, allowing them to be separated. Generally, after collecting the eluted mixture, it can be analyzed for compositional analysis via a variety of methods.

In column chromatography, either liquids or gases can be used as the eluent, depending on the situation.

Distillation

A third method for separating solutions is distillation. Distillation takes advantage of the different boiling points of substances in order to separate them. For instance, if you have a mixture of water (BP: 100°C) and ethanol (BP: 78°C) and then heat that mixture to 85°C , the ethanol will boil but the water will not.

A condenser is a piece of glassware that consists of a smaller tube running through a larger tube. The larger tube has hose connections on it, allowing for water to be run through it. This effectively cools the inner tube and not the outer tube. At that point, the ethanol vapor, when run through the inner tube, will cool and condense back into a liquid form, which can be collected on the other side of the condenser.



A major advantage to distillation is that the solutions need not be colored at all to separate them. Keeping the flask at a constant temperature can be a challenge, which is why the temperature must be monitored closely to ensure that you are only boiling one component of the mixture at a time. The biggest disadvantage is that it cannot be used to separate a mixture that contains substances with unknown boiling points.

CHAPTER 4 QUESTIONS

Multiple-Choice Questions

1. Why does CaF_2 have a higher melting point than NH_3 ?
 - (A) CaF_2 is more massive and thus has stronger London dispersion forces.
 - (B) CaF_2 exhibits network covalent bonding, which is the strongest type of bonding.
 - (C) CaF_2 is smaller and exhibits greater Coulombic attractive forces.
 - (D) CaF_2 is an ionic substance and it requires a lot of energy to break up an ionic lattice.
2. Which of the following pairs of elements is most likely to create an interstitial alloy?
 - (A) Titanium and copper
 - (B) Aluminum and lead
 - (C) Silver and tin
 - (D) Magnesium and calcium
3. Why can a molecule with the structure of NBr_5 not exist?
 - (A) Nitrogen only has two energy levels and is thus unable to expand its octet.
 - (B) Bromine is much larger than nitrogen and cannot be a terminal atom in this molecule.
 - (C) It is impossible to complete the octets for all six atoms using only valence electrons.
 - (D) Nitrogen does not have a low enough electronegativity to be the central atom of this molecule.

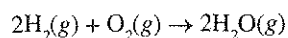
Use the following information to answer questions 4-7.

An evacuated rigid container is filled with exactly 2.00 g of hydrogen and 10.00 g of neon. The temperature of the gases is held at 0°C and the pressure inside the container is a constant 1.0 atm.

4. What is the mole fraction of neon in the container?
 - (A) 0.17
 - (B) 0.33
 - (C) 0.67
 - (D) 0.83
5. What is the volume of the container?
 - (A) 11.2 L
 - (B) 22.4 L
 - (C) 33.5 L
 - (D) 48.8 L
6. Which gas has the higher boiling point and why?
 - (A) Hydrogen, because it has a lower molar mass
 - (B) Neon, because it has more electrons
 - (C) Hydrogen, because it has a smaller size
 - (D) Neon, because it has more protons

7. Which gas particles have a higher RMS velocity and why?
- (A) Hydrogen, because it has a lower molar mass
 - (B) Neon, because it has a higher molar mass
 - (C) Hydrogen, because it has a larger atomic radius
 - (D) Neon, because it has a smaller atomic radius
8. Which of the following compounds would have the highest lattice energy?
- (A) LiF
 - (B) MgCl_2
 - (C) CaBr_2
 - (D) C_2H_6
9. A liquid whose molecules are held together by only which of the following forces would be expected to have the lowest boiling point?
- (A) Ionic bonds
 - (B) London dispersion forces
 - (C) Hydrogen bonds
 - (D) Metallic bonds
10. The six carbon atoms in a benzene molecule are shown in different resonance forms as three single bonds and three double bonds. If the length of a single carbon-carbon bond is 154 pm and the length of a double carbon-carbon bond is 133 pm, what length would be expected for the carbon-carbon bonds in benzene?
- (A) 126 pm
 - (B) 133 pm
 - (C) 140 pm
 - (D) 154 pm
11. Which of the following lists of species is in order of increasing boiling points?
- (A) H_2 , N_2 , NH_3
 - (B) N_2 , NH_3 , H_2
 - (C) NH_3 , H_2 , N_2
 - (D) NH_3 , N_2 , H_2
12. A mixture of gases contains 1.5 moles of oxygen, 3.0 moles of nitrogen, and 0.5 moles of water vapor. If the total pressure is 700 mmHg, what is the partial pressure of the nitrogen gas?
- (A) 210 mmHg
 - (B) 280 mmHg
 - (C) 350 mmHg
 - (D) 420 mmHg
13. A mixture of helium and neon gases has a total pressure of 1.2 atm. If the mixture contains twice as many moles of helium as neon, what is the partial pressure due to neon?
- (A) 0.2 atm
 - (B) 0.3 atm
 - (C) 0.4 atm
 - (D) 0.8 atm

14. Nitrogen gas was collected over water at 25°C. If the vapor pressure of water at 25°C is 23 mmHg, and the total pressure in the container is measured at 781 mmHg, what is the partial pressure of the nitrogen gas?
- (A) 46 mmHg
(B) 551 mmHg
(C) 735 mmHg
(D) 758 mmHg
15. A 22.0 gram sample of an unknown gas occupies 11.2 liters at standard temperature and pressure. Which of the following could be the identity of the gas?
- (A) CO₂
(B) SO₃
(C) O₂
(D) He
16. Which of the following expressions is equal to the density of helium gas at standard temperature and pressure?
- (A) $\frac{1}{22.4}$ g/L
(B) $\frac{2}{22.4}$ g/L
(C) $\frac{1}{4}$ g/L
(D) $\frac{4}{22.4}$ g/L
17. In an experiment 2 moles of H₂(g) and 1 mole of O₂(g) were completely reacted, according to the following equation in a sealed container of constant volume and temperature:



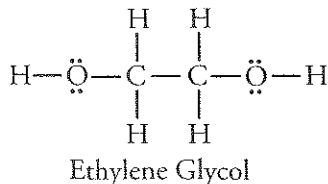
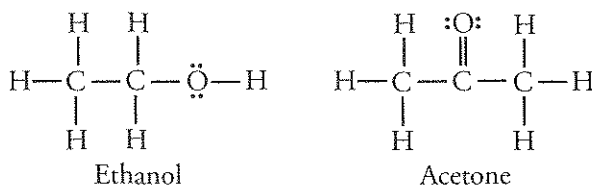
If the initial pressure in the container before the reaction is denoted as P_i , which of the following expressions gives the final pressure, assuming ideal gas behavior?

- (A) P_i
(B) $2P_i$
(C) $(3/2)P_i$
(D) $(2/3)P_i$
18. An ideal gas fills a balloon at a temperature of 27°C and 1 atm pressure. By what factor will the volume of the balloon change if the gas in the balloon is heated to 127°C at constant pressure?
- (A) $\frac{27}{127}$
(B) $\frac{3}{4}$
(C) $\frac{4}{3}$
(D) $\frac{2}{1}$

19. A gas sample with a mass of 10 grams occupies 5.0 liters and exerts a pressure of 2.0 atm at a temperature of 26°C. Which of the following expressions is equal to the molecular mass of the gas? The gas constant, R, is 0.08 (L·atm)/(mol·K).
- (A) $(0.08)(299)$ g/mol
 (B) $\frac{(299)(0.50)}{(2.0)(0.08)}$ g/mol
 (C) $\frac{299}{0.08}$ g/mol
 (D) $(2.0)(0.08)$ g/mol
20. A substance is dissolved in water, forming a 0.50-molar solution. If 4.0 liters of solution contains 240 grams of the substance, what is the molecular mass of the substance?
- (A) 60 g/mol
 (B) 120 g/mol
 (C) 240 g/mol
 (D) 480 g/mol
21. How many moles of Na_2SO_4 must be added to 500 milliliters of water to create a solution that has a 2-molar concentration of the Na^+ ion? (Assume the volume of the solution does not change).
- (A) 0.5 mol
 (B) 1 mol
 (C) 2 mol
 (D) 5 mol

Use the following Lewis diagrams to answer questions 22-24.

The following three substances are kept in identical containers 25°C. All three substances are in the liquid phase:

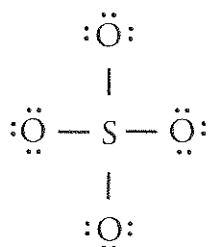


22. Which substance would have the highest boiling point?
- (A) Ethanol, because it is the most asymmetrical
 (B) Acetone, because of the double bond
 (C) Ethylene glycol, because it has the most hydrogen bonding
 (D) All three substances would have very similar boiling points because their molar masses are similar.

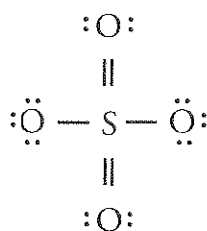
23. Which substance would have the highest vapor pressure?
- (A) Ethanol, because of the hybridization of its carbon atoms
 (B) Acetone, because it exhibits the weakest intermolecular forces
 (C) Ethylene glycol, because it has the most lone pairs assigned to individual atoms
 (D) All three substances would have similar vapor pressure because they have a similar number of electrons.
24. Which of the substances would be soluble in water?
- (A) Ethylene glycol only, because it has the longest bond lengths
 (B) Acetone only, because it is the most symmetrical
 (C) Ethanol and ethylene glycol only, because of their hydroxyl (–OH) groups
 (D) All three substances would be soluble in water due to their permanent dipoles.

Use the following information to answer questions 25-29.

There are several different potential different Lewis diagrams for the sulfate ion, two of which are below.



Structure A



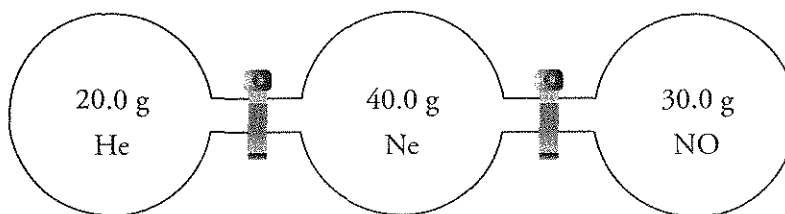
Structure B

25. What is the formal charge on the sulfur atom in the structure A?
- (A) –1
 (B) 0
 (C) +1
 (D) +2
26. What is the molecular geometry in the structure A?
- (A) Tetrahedral
 (B) Trigonal Planar
 (C) Trigonal Pyramidal
 (D) Octahedral
27. What is the S–O bond order in the structure B?
- (A) 1.0
 (B) 1.33
 (C) 1.5
 (D) 1.67
28. Which of the following statements regarding the structure B is true?
- (A) The double bonds must be located opposite of each other due to additional electron repulsion.
 (B) It is a more polar molecule than the molecule represented by structure A.
 (C) The bonds in the molecule are weaker than those in structure A.
 (D) All bonds in the molecule are identical to each other.

29. Which structure is more likely to correspond with the actual Lewis diagram for the sulfate ion?
- (A) Structure A; single bonds are more stable than double bonds
 - (B) Structure A; it has the most unshared pairs of electrons
 - (C) Structure B; there are more possible resonance structures
 - (D) Structure B; fewer atoms have formal charges

Use the following information to answer questions 30-32.

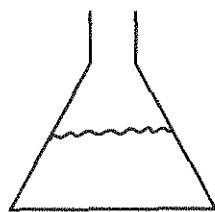
The diagram below shows three identical 1.0 L containers filled with the indicated amounts of gas. The stopcocks connecting the containers are originally closed and the gases are all at 25°C. Assume ideal behavior.



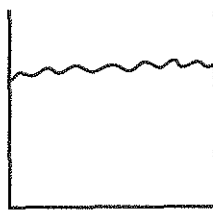
30. Which gas exerts the greatest pressure?
- (A) He
 - (B) Ne
 - (C) NO
 - (D) All gases exert the same amount of pressure.
31. Which gas has the strongest IMFs?
- (A) He
 - (B) Ne
 - (C) NO
 - (D) All gases have identical IMFs.
32. The stopcocks are opened. If the tubing connecting the containers has negligible volume, by what percentage will the pressure exerted by the neon gas decrease?
- (A) 25%
 - (B) 33%
 - (C) 50%
 - (D) 67%

Free-Response Questions

1. A 250 mL Erlenmeyer flask contains a mixture of two liquids: diethyl ether and ethylamine. The flask is attached to a distillation apparatus and heated until the mixture starts to boil.
 - (a) Why is it important to keep the flask at a constant temperature once the mixture starts to boil?
 - (b)
 - (i) Which liquid is the primary component of the distillate? Justify your answer in terms of IMFs.
 - (ii) The distillate is not a completely pure substance. Why?
 - (c) After the distillate is collected, half of it is transferred into a 250 mL beaker, as shown below. If both containers are left uncovered, which liquid (if either) will evaporate first? Why?



250 ml flask



250 ml beaker

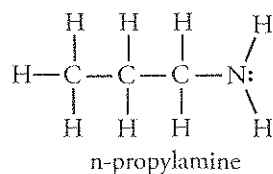
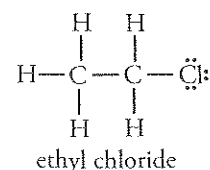
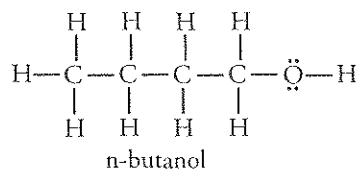
2. The carbonate ion CO_3^{2-} is formed when carbon dioxide, CO_2 , reacts with slightly basic cold water.
 - (a)
 - (i) Draw the Lewis electron dot structure for the carbonate ion. Include resonance forms if they apply.
 - (ii) Draw the Lewis electron dot structure for carbon dioxide.
 - (b) Describe the hybridization of carbon in the carbonate ion.
 - (c)
 - (i) Describe the relative lengths of the three C–O bonds in the carbonate ion.
 - (ii) Compare the average length of the C–O bonds in the carbonate ion to the average length of the C–O bonds in carbon dioxide.

3.

Substance	Boiling Point (°C)	Bond Length (Å)	Bond Strength (kcal/mol)
H ₂	-253°	0.75	104.2
N ₂	-196°	1.10	226.8
O ₂	-182°	1.21	118.9
Cl ₂	-34°	1.99	58.0

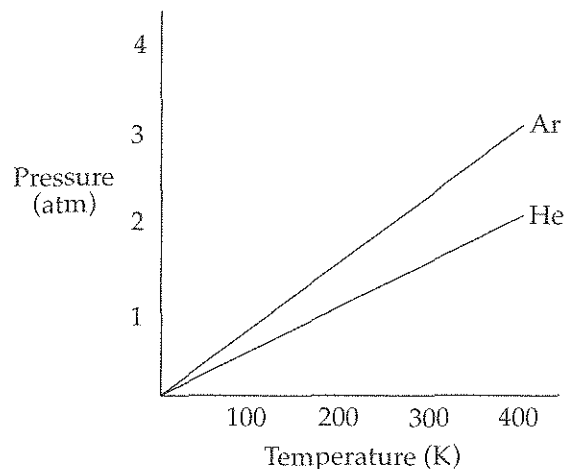
- (a) Explain the differences in the properties given in the table above for each of the following pairs.
- The bond strengths of N₂ and O₂
 - The bond lengths of H₂ and Cl₂
 - The boiling points of O₂ and Cl₂
- (b) Use the principles of molecular bonding to explain why H₂ and O₂ are gases at room temperature, while H₂O is a liquid at room temperature.

4. A student has a mixture containing three different organic substances. The Lewis diagrams of the substances are below:



- If the mixture was dabbed onto chromatography paper that was then placed into a nonpolar solvent, rank the R_f values for each component of the mixture from high to low after the solvent has saturated the paper. Justify your answer.
- If the mixture is poured into a chromatography column and then eluted with a very polar substance, which component of the mixture would leave the column first, and why?
- The mixture is heated until it begins to boil. Which substance would be the easiest to separate via distillation, and why?
 - After the substance begins boiling, it continues to be heated at the same rate. Compared to the rate at which it was changing prior to boiling, will the temperature increase faster, slower, or at the same rate? Explain.
- After the components of the mixture have been separated, they are returned to room temperature. Of the three substances, which would have the highest vapor pressure at room temperature? Justify your answer.
 - If the substances were heated (but not boiled), explain what would happen to their vapor pressures.

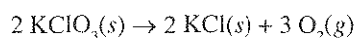
5.



The graph above shows the changes in pressure with changing temperature of gas samples of helium and argon confined in a closed 2-liter vessel.

- What is the total pressure of the two gases in the container at a temperature of 200 K?
- How many moles of helium are contained in the vessel?
- How many molecules of helium are contained in the vessel?
- Molecules of which gas will have a greater distribution of velocities at 200 K? Justify your answer.
- If the volume of the container were reduced to 1 liter at a constant temperature of 300 K, what would be the new pressure of the helium gas?

6.



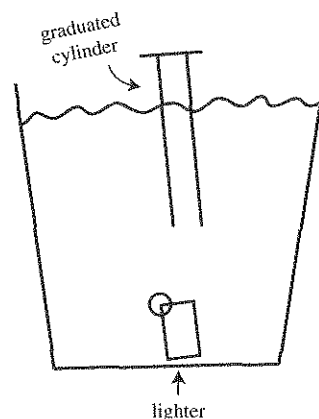
The reaction above took place, and 1.45 liters of oxygen gas were collected over water at a temperature of 29°C and a pressure of 755 millimeters of mercury. The vapor pressure of water at 29°C is 30.0 millimeters of mercury.

- What is the partial pressure of the oxygen gas collected?
- How many moles of oxygen gas were collected?
- What would be the dry volume of the oxygen gas at a pressure of 760 millimeters of mercury and a temperature of 273 K?
- What was the mass of the KClO_3 consumed in the reaction?

7. Equal molar quantities of two gases, O_2 and H_2O , are confined in a closed vessel at constant temperature.

- Which gas, if either, has the greater partial pressure?
- Which gas, if either, has the greater density?
- Which gas, if either, has the greater concentration?
- Which gas, if either, has the greater average kinetic energy?
- Which gas, if either, will show the greater deviation from ideal behavior?

8. A student performs an experiment in which a butane lighter is held underwater directly beneath a 100-mL graduated cylinder which has been filled with water as shown in the diagram below.



The switch on the lighter is pressed, and butane gas is released into the graduated cylinder. The student's data table for this lab is as follows:

Mass of lighter before gas release	20.432 g
Mass of lighter after gas release	20.296 g
Volume of gas collected	68.40 mL
Water Temperature	19.0°C
Atmospheric Pressure	745 mmHg

- (a) Given that the vapor pressure of water at 19.0°C is 16.5 mmHg, determine the partial pressure of the butane gas collected in atmospheres.
- (b) Calculate the molar mass of butane gas from the experimental data given.
- (c) If the formula of butane is C_4H_{10} , determine the percent error for the student's results.
- (d) The following are common potential error sources that occur during this lab. Explain whether or not each error could have been responsible for the error in the student's results.
- The lighter was not sufficiently dried before massing it after the gas was released.
 - The gas in the lighter was not held underwater long enough to sufficiently cool it to the same temperature of the water and was actually at a higher temperature than the water.
 - Not all of the butane gas released was collected in the graduated cylinder.

CHAPTER 4 ANSWERS AND EXPLANATIONS

Multiple-Choice

- D Calcium is a metal, and fluorine is a nonmetal. Their electronegativities differ sufficiently for them to create an ionic bond, which is stronger than all other bond types except for network covalent bonding (which NH_3 does not exhibit).
- B Interstitial alloys form when atoms of greatly different sizes combine. The aluminum atoms would have a chance to fit between the comparatively larger lead atoms.
- A Only atoms with at least three energy levels ($n = 3$ and above) have empty d -orbitals that additional electrons can fit into, thus expanding their octet.
- B Moles of $\text{H}_2 = \frac{2.00 \text{ g}}{2.00 \text{ g/mol}} = 1.00 \text{ mol}$ (remember, hydrogen is a diatomic)
Moles of $\text{Ne} = \frac{10.00 \text{ g}}{20.0 \text{ g/mol}} = 0.500 \text{ mol}$
Total moles = 1.50 moles. $X_{\text{Ne}} = \frac{\text{moles Ne}}{\text{total moles}} = \frac{0.500}{1.500} = 0.33$
- C At STP, 1 mol of gas takes up 22.4 L of space: $(1.5)(22.4) = 33.5 \text{ L}$.
- B Both gases only have London dispersion forces. The more electrons a gas has, the more polarizable it is and the stronger the intermolecular forces are.
- A The gas molecules have the same amount of kinetic energy due to their temperature being the same. Via $KE = \frac{1}{2}mv^2$, if KE is the same, then the molecule with less mass must correspondingly have a higher velocity.
- B First, C_2H_6 is not an ionic substance and thus has no lattice energy. Next, LiF is composed of ions with charges $+1$ and -1 , and will not be as strong as the two compounds which have ions with charges of $+2$ and -1 . Finally, MgCl_2 is smaller than CaBr_2 , meaning it will have a higher lattice energy, as (according to Coulomb's law) atomic radius is inversely proportional with bond energy.

9. **B** A liquid with a low boiling point must be held together by weak intermolecular forces, of which London dispersion forces are the weakest kind.
10. **C** Resonance is used to describe a situation that lies between single and double bonds, so the bond length would also be expected to be in between that of single and double bonds. The best answer here is 140 pm, (C).

11. **A** H_2 experiences only London dispersion forces and has the lowest boiling point.

N_2 also experiences only London dispersion forces, but it is larger than H_2 and has more electrons, so it has stronger interactions with other molecules.

NH_3 is polar and undergoes hydrogen bonding, so it has the strongest intermolecular interactions and the highest boiling point.

12. **D** From Dalton's law, the partial pressure of a gas depends on the number of moles of the gas that are present.

The total number of moles of gas present is

$$1.5 + 3.0 + 0.5 = 5.0 \text{ total moles}$$

If there are 3 moles of nitrogen, then $\frac{3}{5}$ of the pressure must be due to nitrogen.

$$\left(\frac{3}{5}\right)(700 \text{ mmHg}) = 420 \text{ mmHg}$$

13. **C** From Dalton's law, the partial pressure of a gas depends on the number of moles of the gas that are present. If the mixture has twice as many moles of helium as neon, then the mixture must be $\frac{1}{3}$ neon. So $\frac{1}{3}$ of the pressure must be due to neon.

$$\left(\frac{1}{3}\right)(1.2 \text{ atm}) = 0.4 \text{ atm.}$$

14. **D** From Dalton's law, the partial pressures of nitrogen and water vapor must add up to the total pressure in the container. The partial pressure of water vapor in a closed container will be equal to the vapor pressure of water, so the partial pressure of nitrogen is:

$$781 \text{ mmHg} - 23 \text{ mmHg} = 758 \text{ mmHg}$$

15. A Use the following relationship:

$$\text{Moles} = \frac{\text{liters}}{22.4 \text{ L/mol}}$$

$$\text{Moles of unknown gas} = \frac{11.2 \text{ L}}{22.4 \text{ L/mol}} = 0.500 \text{ moles}$$

$$\text{MW} = \frac{\text{grams}}{\text{mole}}$$

$$\text{MW of unknown gas} = \frac{22.0 \text{ g}}{0.500 \text{ mole}} = 44.0 \text{ grams/mole}$$

That's the molecular weight of CO_2 .

16. D Density is measured in grams per liter. One mole of helium gas has a mass of 4 grams and occupies a volume of 22.4 liters at STP, so the density of helium gas at STP is $\frac{4}{22.4}$ g/L.
17. D There are initially 3.0 moles of gas in the container. If they react completely, 2.0 moles of gas are produced. 2.0 moles of gas will exert exactly $\frac{2}{3}$ as much pressure as three moles of gas.
18. C From the ideal gas laws, for a gas sample at constant pressure:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Solving for V_2 we get $V_2 = V_1 \frac{T_2}{T_1}$.

So V_1 is multiplied by a factor of $\frac{T_2}{T_1}$.

Remember to convert Celsius to Kelvin, $\frac{127^\circ\text{C} + 273}{27^\circ\text{C} + 273} = \frac{400 \text{ K}}{300 \text{ K}} = \frac{4}{3}$

19. A $\text{MM} = \frac{DRT}{P}$. The density of this gas is $\frac{10.0 \text{ g}}{5.0 \text{ L}}$, or $\frac{2.0 \text{ g}}{\text{L}}$.
Plugging that in yields $\text{MM} = \frac{(2.0)(0.08)(299)}{(2.0)}$. The value of 2.0 cancels out, leaving the answer $(0.08)(299)$.

20. **B** First find the number of moles.

$$\text{Moles} = (\text{molarity})(\text{volume})$$

$$\text{Moles of substance} = (0.50 \text{ M})(4.0 \text{ L}) = 2 \text{ moles}$$

$$\text{Moles} = \frac{\text{grams}}{\text{MW}}$$

$$\text{So MW} = \frac{240 \text{ g}}{2 \text{ mol}} = 120 \text{ g/mol.}$$

21. **A** Let's find out how many moles of Na^+ we have to add.

$$\text{Moles} = (\text{molarity})(\text{volume})$$

$$\text{Moles of } \text{Na}^+ = (2 \text{ M})(0.5 \text{ L}) = 1 \text{ mole}$$

Because we get 2 moles of Na^+ ions for every mole of Na_2SO_4 we add, we need to add only 0.5 moles of Na_2SO_4 .

22. **C** Hydrogen bonds are the strongest types of intermolecular forces when dealing with molecules of a similar size. Ethylene glycol has twice as many hydrogen bonds as ethanol (acetone has none), and so it would have the highest boiling point.
23. **B** Vapor pressure arises from molecules breaking free from the intermolecular forces holding them together. Acetone, which has no hydrogen bonding, thus has the weakest intermolecular forces of the three and thus would have the highest vapor pressure.
24. **D** Water is very polar, and using the concept of "like dissolves like," any substance with polar molecules would be soluble in water. As all three molecules are polar, all three liquids would be soluble in water.
25. **D** Valence electrons – assigned electrons = formal charge: $6 - 4 = +2$.
26. **A** Four charge clouds and no lone pairs means tetrahedral geometry.
27. **C** Six total bonds divided by four locations gives a bond order of 1.5.
28. **D** In any molecule displaying resonance, all bonds are identical.

29. **D** The formal charge tables for each diagram are below (note: for structure B, the double-bonded oxygens are the first two, and the single bonded are the last two)

Structure A					Structure B				
S	O	O	O	O	S	O	O	O	O
6	6	6	6	6	6	6	6	6	6
4	7	7	7	7	6	6	6	7	7
+2	-1	-1	-1	-1	0	0	0	-1	-1
Formal charge					Formal charge				

The total formal charge on each potential structure is -2 , which is correct as that is the charge on a sulfate ion. However, the right-hand structure has fewer atoms with formal charges, making it the more likely structure.

30. **A** Pressure is directly dependent on the number of moles. In their respective containers, there are 5 moles of He, 2 moles of Ne, and 1 mole of NO. As there are the most moles of He, the He must exert the greatest pressure.
31. **D** One of the precepts of kinetic molecular theory is that gas molecules exert no forces on each other, thus, in all containers there are no IMFs present.
32. **D** $P_1V_1 = P_2V_2$

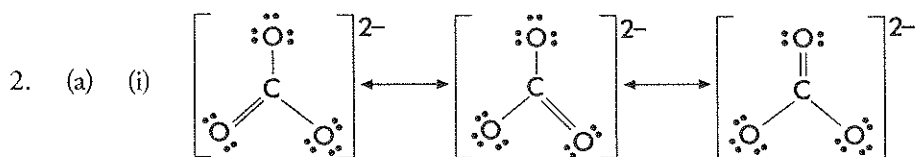
$$P_1(1.0 \text{ L}) = P_2(3.0 \text{ L})$$

$$P_2/P_1 = 1.0/3.0$$

Thus, the pressure of the neon gas is 33% of what it was originally, meaning a decrease of 67%. Note that the same calculation could be used for any of the gases; each gas is expanding to take up three times as much space as it has originally, and thus exerts one-third as much pressure.

Free-Response

- If the temperature were to be increased, it may go higher than the boiling point of both substances, not just the one with the lower boiling point. This would create a very impure distillate.
 - The diethyl ether would be in the distillate. Ethylamine contains hydrogen bonding, which is the strongest type of IMF, while diethyl ether does not.
 - Even below the boiling point of ethylamine, some of the ethylamine will spontaneously convert into a gas. The molecules within both liquids are constantly moving, and even if the ethylamine does not boil, some of its molecules will evaporate, convert into a gas, and then be condensed, becoming part of the distillate.
 - The liquid in the beaker will evaporate first. Evaporation occurs when molecules in the liquid phase have sufficient kinetic energy to break free of the IMFs within the liquid. In order to break free, the molecules must first hit the surface of the liquid. The surface area of the liquid in the beaker is greater than the surface area of the liquid in the test tube, thus, the molecules in the beaker are more likely to hit the surface and evaporate.



- The central carbon atom forms three sigma bonds with oxygen atoms and has no free electron pairs, so its hybridization must be sp^2 .
- All three bonds will be the same length because when a molecule exhibits resonance, all the bonds are identical to each other, being somewhere in character between single bonds and double bonds.

- (ii) The C–O bonds in the carbonate ion have resonance forms between single and double bonds, while the C=O bonds in carbon dioxide are both double bonds.

The bonds in the carbonate ion will be shorter than single bonds and longer than double bonds, so the carbonate bonds will be longer than the carbon dioxide bonds.

3. (a) (i) The bond strength of N_2 is larger than the bond strength of O_2 because N_2 molecules have triple bonds and O_2 molecules have double bonds. Triple bonds are stronger and shorter than double bonds.
- (ii) The bond length of H_2 is smaller than the bond length of Cl_2 because hydrogen is a smaller atom than chlorine, allowing the hydrogen nuclei to be closer together.
- (iii) Liquid oxygen and liquid chlorine are both nonpolar substances that experience only London dispersion forces of attraction. These forces are greater for Cl_2 because it has more electrons (which makes it more polarizable), so Cl_2 has a higher boiling point than O_2 .

- (b) H_2 and O_2 are both nonpolar molecules that experience only London dispersion forces, which are too weak to form the bonds required for a substance to be liquid at room temperature.

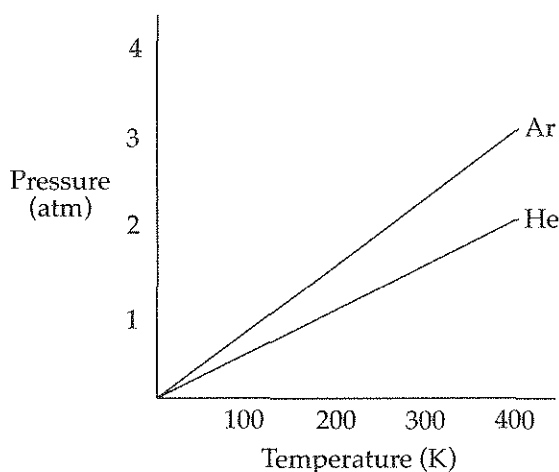
H_2O is a polar substance whose molecules form hydrogen bonds with each other. Hydrogen bonds are strong enough to form the bonds required in a liquid at room temperature.

4. (a) All three components are polar, but ethyl chloride has no hydrogen bonding and thus has the weakest dipoles, meaning it would travel the furthest and have the highest R_f value.

Between n-butanol and n-propylamine, both have H-bonds but the butanol has more electrons, meaning its London dispersion forces are stronger. It thus has the highest polarity and would have the smallest R_f value. So: ethyl chloride > n-propylamine > n-butanol.

- (b) n-butanol is the most polar and would be most attracted to a polar eluent, and thus would leave the column first.

- (c) (i) Ethyl chloride has the weakest overall IMFs, and thus would have the lowest boiling point and be the easiest to separate out.
- (ii) Prior to boiling, molecules in all three substances were speeding up as heat was added. The increased velocity caused the temperature increase. Once the ethyl chloride starts boiling, though, the heat that would ordinarily be causing the molecules to speed up is instead breaking the IMFs. While the molecules of both the n-butanol and n-propylamine would still be experiencing a velocity increase, those of the ethyl chloride would not. Thus, the overall rate of the temperature change would be less than it was prior to the ethyl chloride starting to boil.
- (d) (i) The substance with the weakest IMFs would allow the largest number of molecules to escape the liquid phase and turn into a gas, which is the cause of vapor pressure. As such, the ethyl chloride should have the highest vapor pressure of the three substances.
- (ii) As temperature increases, so does the molecular velocity. The faster the molecules are going, the more energy they have, and the more likely they are to be able to overcome the IMFs and escape the liquid phase. For all substances, as temperature increases, so does vapor pressure.



5. (a) Read the graph, and add the two pressures.

$$P_{\text{Total}} = P_{\text{He}} + P_{\text{Ar}}$$

$$P_{\text{Total}} = (1 \text{ atm}) + (1.5 \text{ atm}) = 2.5 \text{ atm}$$

- (b) Read the pressure (1 atm) at 200 K, and use the ideal gas equation.

$$n = \frac{PV}{RT} = \frac{(1.0 \text{ atm})(2.0 \text{ L})}{(0.082 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(200 \text{ K})} = 0.12 \text{ moles}$$

- (c) Use the definition of a mole.

$$\text{Molecules} = (\text{moles})(6.02 \times 10^{23})$$

$$\text{Molecules (atoms) of helium} = (0.12)(6.02 \times 10^{23}) = 7.2 \times 10^{22}$$

- (d) As both gases are at the same temperature and thus have the same kinetic energy, the molecules of helium will have a higher average velocity because they have less mass. The higher the average velocity of a gas is, the wider the distribution curve is for the velocities of the individual gas molecules.

- (e) Use the following relationship:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Since T is a constant, the equation becomes:

$$P_1 V_1 = P_2 V_2$$

$$(1.5 \text{ atm})(2.0 \text{ L}) = P_2(1.0 \text{ L})$$

$$P_2 = 3.0 \text{ atm}$$

6. (a) Use Dalton's law.

$$P_{\text{Total}} = P_{\text{Oxygen}} + P_{\text{Water}}$$

$$(755 \text{ mmHg}) = (P_{\text{Oxygen}}) + (30.0 \text{ mmHg})$$

$$P_{\text{Oxygen}} = 725 \text{ mmHg}$$

- (b) Use the ideal gas law. Don't forget to convert to the proper units.

$$n = \frac{PV}{RT} = \frac{\left(\frac{725}{760} \text{ atm}\right)(1.45 \text{ L})}{(0.082 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(302 \text{ K})} = 0.056 \text{ moles}$$

- (c) At STP, moles of gas and volume are directly related.

$$\text{Volume} = (\text{moles})(22.4 \text{ L/mol})$$

$$\text{Volume of O}_2 = (0.056 \text{ mol})(22.4 \text{ L/mol}) = 1.25 \text{ L}$$

- (d) We know that 0.056 moles of O_2 were produced in the reaction.

From the balanced equation, we know that for every 3 moles of O_2 produced, 2 moles of $KClO_3$ are consumed. So there are $\frac{2}{3}$ as many moles of $KClO_3$ as O_2 .

$$\text{Moles of } KClO_3 = \left(\frac{2}{3}\right)(\text{moles of } O_2)$$

$$\text{Moles of } KClO_3 = \left(\frac{2}{3}\right)(0.056 \text{ mol}) = 0.037 \text{ moles}$$

$$\text{Grams} = (\text{moles})(\text{MW})$$

$$\text{Grams of } KClO_3 = (0.037 \text{ mol})(122 \text{ g/mol}) = 4.51 \text{ g}$$

7. (a) The partial pressures depend on the number of moles of gas present. Because the number of moles of the two gases are the same, the partial pressures are the same.
- (b) O_2 has the greater density. Density is mass per unit volume. Both gases have the same number of moles in the same volume, but oxygen has heavier molecules, so it has greater density.
- (c) Concentration is moles per volume. Both gases have the same number of moles in the same volume, so their concentrations are the same.
- (d) According to kinetic-molecular theory, the average kinetic energy of a gas depends only on the temperature. Both gases are at the same temperature, so they have the same average kinetic energy.
- (e) H_2O will deviate most from ideal behavior. Ideal behavior for gas molecules assumes that there will be no intermolecular interactions.

H_2O is polar, and O_2 is not. H_2O undergoes hydrogen bonding, while O_2 does not. So H_2O has stronger intermolecular interactions, which will cause it to deviate more from ideal behavior.

8. (a) $745 \text{ mmHg} - 16.5 \text{ mmHg} = 729 \text{ mmHg}$
 $\frac{729 \text{ mmHg}}{760 \text{ mmHg}} = 0.959 \text{ atm}$
- (b) To determine the mass of the butane, subtract the mass of the lighter after the butane was released from the mass of the lighter before the butane was released.

$$20.432 \text{ g} - 20.296 \text{ g} = 0.136 \text{ g}$$

To determine the moles of butane, use the ideal gas law, making any necessary conversions first.

$$PV = nRT$$

$$(0.959 \text{ atm})(0.06840 \text{ L}) = n(0.0821 \text{ atm}\cdot\text{L/mol}\cdot\text{K})(292 \text{ K})$$

$$n = 2.74 \times 10^{-3} \text{ mol}$$

Molar mass is defined as grams per mole, so

$$0.136 \text{ g}/2.74 \times 10^{-3} \text{ mol} = 49.6 \text{ g/mol}$$

(c) Actual molar mass of butane:

$$(12.00 \text{ g/mol} \times 4) + (1.01 \text{ g/mol} \times 10) = 58.08 \text{ g/mol}$$

Percent error is:

$$\frac{|\text{Actual value} - \text{experimental value}|}{\text{Actual value}} \times 100\%$$

So:

$$\frac{|58.08 - 49.6|}{58.08} \times 100\% = 14.5\% \text{ error}$$

- (d) (i) If the lighter is not sufficiently dried, then the mass of the butane calculated will be artificially low. That means the numerator in the molar mass calculation will be too low, which would lead to an experimental molar mass that is too low. This is consistent with the student's error.
- (ii) If the temperature of the butane is higher than the water temperature, the calculated moles of butane will be artificially high. This means the denominator in the molar mass calculation will be too high, which would lead to an experimental molar mass that is too low. This is consistent with the student's error.
- (iii) If some butane gas escaped without going into the graduated cylinder, the volume of butane gas collected will be artificially low. That will make the calculation for moles of butane too low, which in turns means the denominator of the molar mass calculation will be too low. This would lead to an experimental molar mass that is too high. This is NOT consistent with the student's error.

