

7. The difference in phases (gas, liquid, or solid) is affected by the strength of the intermolecular attractions, the speed of the molecules, and the pressure at which they are kept. The strength of the intermolecular attractions are affected by the type of bonding within the molecule, the shape and symmetry of the molecule, and the size of the molecule. All of these factors contribute to how the electron clouds are distributed throughout the molecule and how tightly these clouds are pulled toward and controlled by positive nuclei within the molecule. Molecules with asymmetrical distributions of its electron clouds such that one end of the molecule has a relatively high electron density compared to the other will have strong intermolecular attractions with its neighbors with similar electron cloud distributions. This is because the end of the molecule that has a relatively high electron cloud density will have a net partial negative charge, while the other end will have a net partial positive charge so the positive end of one molecule will be attracted to the negative end of the other molecule. Even molecules with overall symmetrical distributions of its electron clouds can have temporary shifts in the electron cloud distributions. How significant this temporary shift can become depends on the how strongly the electron clouds are pulled toward and controlled by the nuclei within the molecule; with the more significant shifts coming from the more weakly held electron clouds. The stronger the intermolecular attractions, the more likely a substance is to form the intermolecular bonds that are present in a liquid or a solid at a given temperature. Further, the faster a molecule is moving, the less likely the intermolecular bonds will form because the intermolecular attractions are not sufficient to "hold" or bond two molecules due to the high speed of the molecules. Lastly, the higher the pressure, the more likely a substance is to form a liquid or a solid because of the close proximity of gas molecules at high pressure. This is general theory that will help with parts (a) and (b) below.

(a) Both substances,  $F_2$  and  $I_2$ , are at the same pressure (1 atm), so this factor does not favor the formation of a liquid or a solid by either substance more so than the other. Both of these molecules are at the same temperature, they have the same kinetic energy. This does not mean they have the same average speed. Since  $KE = \frac{1}{2}mv^2$ , a molecule with less mass will be moving faster, on average, than one with more mass at a given temperature. From the periodic table, the average mass of the  $F_2$  molecule can be determined to be 38.00 u, while the  $I_2$  molecule has an average mass of 253.82 u. Since the  $I_2$  molecule is significantly more massive than the  $F_2$  molecule, iodine is more likely to be a solid at  $25^\circ C$  for the reasons stated above. Both of these substances are diatomic gases. Thus, the molecules of both substances are symmetrical with purely covalent bonds joining the two identical atoms in each type of molecule. However, the fluorine atom has valence electrons in the second energy level, which is much closer to the nucleus than iodine which has its valence electrons in the fifth energy level. Since the valence electrons (which are the ones that "bond" the two atoms together in the molecule) are further from the nucleus in the iodine, the electron clouds are less tightly held. In addition, there is a greater shielding effect of the electrons in energy levels below the valence electrons in iodine because there are more electron-filled energy levels. Both of these factors contribute to the iodine molecule having less tightly held electron clouds than fluorine, so more shifting of the electron clouds, and, Therefore, stronger intermolecular attractions (for the reasons discussed above). Combining the slower speed of the iodine molecules at  $25^\circ C$  and the less tightly held electron clouds,  $I_2$  has stronger intermolecular attractions than  $F_2$ , and, thus, iodine is a solid at  $25^\circ C$  while fluorine is a gas.

7. (continued)

- (b) Both Na and Cs are metals from column IA in the periodic table, so both have only one valence electron giving both a low first ionization energy which means they both lose this valence electron relatively easily (compared to other atoms). When both Na and Cs lose an electron they both form a +1 ion, but the positive charge from the nucleus of Na has a bigger effect on neighboring ions because it only has two energy levels of electrons below its valence electron to shield the positive charge of its nucleus from its neighbors, while Cs has five energy levels. This shielding effect is magnified by the fact that the fourth and fifth energy levels of Cs hold 32 electrons because of additional *d* orbital electrons that are not present in the first two energy levels that hold only 2 *s* orbital electrons in the first energy level and 8 *s* and *p* orbital electrons in the second energy level. The  $\text{Na}^{+1}$  ion only has these first two energy levels, so it can be said that the  $\text{Na}^{+1}$  ion has a much larger charge density than the  $\text{Cs}^{+}$  ion. Both F and Cl are halogen nonmetals from column VIIA in the periodic table, so they both have seven valence electrons giving both high electron affinities when they form a -1 ion. However, fluorine has a higher electron affinity than chlorine because its valence electrons are in the second energy level with shielding coming only from the two electrons in the first energy level; whereas chlorine has its valence electrons in the third energy level with shielding from the first and second energy levels. (As stated above the second energy level has 8 electrons.) This gives the  $\text{F}^{-}$  ion a greater charge density than the  $\text{Cl}^{-}$  ion. This means that both the positive and negative charge densities in the NaF compound are greater than in CsCl. This makes a greater attractive force between the ions in NaF than those in CsCl. This stronger bonding in NaF means the molecules require a higher temperature (melting point) to break these bonds to go from solid to liquid than CsCl. At higher temperatures, molecules move faster (temperature is defined as a measure of the average kinetic energy of molecules). The stronger NaF bonds can remain intact better than CsCl when each substance's constituent ions move at higher speeds. Thus, NaCl will have a higher melting point ( $993^{\circ}\text{C}$ ) than CsCl ( $645^{\circ}\text{C}$ ).
- (c) The central I<sup>-</sup> ion in the  $\text{ICl}_4^{-}$  ion has 8 valence electrons so when bonding with Cl its bonding orbitals are  $d^2sp^3$  which are at the corners of an octagon. The 8 valence electrons in the  $d^2sp^3$  create two lone pairs that will go at opposite corners of the octagon to minimize repulsions from these negatively charged lone pairs. Therefore, the four chlorine atoms that bond will go at the remaining corners of the octagon and form a square planar molecule. The central B<sup>-</sup> ion in the  $\text{BF}_4^{-}$  ion has 4 valence electrons so when bonding with Cl its bonding orbitals are  $sp^3$  which are at the corners of a tetrahedron. None of these orbitals will contain lone pairs so the  $\text{BF}_4^{-}$  ion will have a tetrahedral shape.

7. (continued)

(d) The process of dissolving is solvent (water) molecules, through intermolecular attractions, particularly hydrogen bonding, pulling solute (ammonia or phosphine) molecules away from each other. These two molecules have, essentially, identical structures, each with the central atom (N from  $\text{NH}_3$  and P from  $\text{PH}_3$ ) from column VA in the periodic table. Therefore, the central atom from each has five valence electrons that will occupy  $sp^3$  bonding orbitals with one lone pair of electrons and three bonded pairs with the H atoms to form a trigonal pyramidal molecule. This molecule is polar with the side of the molecule containing the lone pair of electrons having the partial negative charge, while the side with the three hydrogens having the partial positive charge. The only structural difference between these two molecules is that the central atom of ammonia, N, has valence electrons in the second energy level, while that of phosphine, P, has valence electrons in the third energy level. This gives the N atom a greater electronegativity than P, so the electron clouds from the bonded H atoms in the molecule will be pulled greater towards N in ammonia than they will towards P in phosphine. This gives the ammonia molecule more charge separation than the phosphine, thus, making it more polar. As a result, stronger hydrogen bonds will form (both between the H of  $\text{H}_2\text{O}$  with the N of  $\text{NH}_3$  and between the H of  $\text{NH}_3$  and the O of  $\text{H}_2\text{O}$ ) when ammonia dissolves in water than when phosphine dissolves in water. (The hydrogen bonds that will form when phosphine dissolves in water are between the H of  $\text{H}_2\text{O}$  and P of  $\text{PH}_3$  and H of  $\text{PH}_3$  and O of  $\text{H}_2\text{O}$ ). This stronger hydrogen bonding will allow water pull the ammonia molecules away from each other (which is the process of dissolving) better than water can pull the molecules of phosphine away from each other. Therefore, ammonia is very soluble in water, whereas phosphine is only moderately soluble.

08. (a)  $4 + 6 = 10$  valence electrons     $4 + 2(6) = 16$  valence electrons

$$\frac{10}{2} = 5 \text{ pairs of electrons} \quad \frac{16}{2} = 8 \text{ pairs of electrons}$$



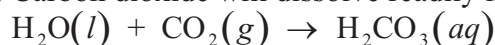
carbon monoxide



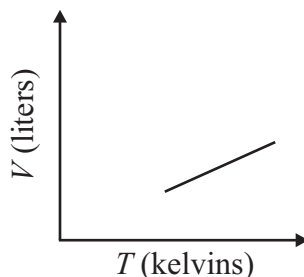
carbon dioxide

(b) linear

(c) Carbon dioxide will dissolve readily in water to form a solution with a pH below 7.



(d)



(e) (i) Temperature is a measure of the average kinetic energy of the molecules in a system. Since both of these containers are at the same temperature, have the same average kinetic energy. Therefore, the average kinetic energy of the  $\text{CO}_2(g)$  molecules is equal to the average kinetic energy of the  $\text{CO}(g)$  molecules.

(ii) Average kinetic energy is calculated using the relationship  $\text{KE}_{\text{ave}} = \frac{1}{2} m \overline{v^2}$ , where  $\text{KE}_{\text{ave}}$  is the average kinetic energy,  $m$  is the mass of the molecule, and  $\overline{v^2}$  is the average of the squares of the speed of the molecules. These two gases are at the same temperature so they have the same average kinetic energy. However, since  $\text{KE}_{\text{ave}} = \frac{1}{2} m \overline{v^2}$ , a molecule with less mass will have a greater root-mean-square speed than one with more mass at a given temperature ( $25^\circ\text{C}$  in this case). From the atomic mass values of the periodic table, the average molecular mass of a  $\text{CO}(g)$  molecule is 28.011 u, whereas, the average molecular mass of a  $\text{CO}_2(g)$  molecule is 44.011 u. Since a  $\text{CO}(g)$  molecule is less massive than a  $\text{CO}_2(g)$  molecule, root-mean-square speed of the  $\text{CO}_2(g)$  molecules is less than the root-mean-square speed of the  $\text{CO}(g)$  molecules.

(iii) The ideal gas law,  $PV = nRT$ , relates pressure, volume, number of moles (thus, number of molecules) present, and absolute temperature. The two gases have equal volumes and equal temperatures. Since the  $\text{CO}$  gas is at double the pressure of the  $\text{CO}_2$  gas, the  $\text{CO}$  gas will double the number of moles (thus number of molecules) of the  $\text{CO}_2$  gas. Therefore, the number of  $\text{CO}_2(g)$  molecules is less than the number of  $\text{CO}(g)$  molecules.

6. (a) Metal carbonates react with acids to form a metal salt, carbon dioxide, and water. Acid rain, which contains sulfuric acid, will react with the limestone (calcium carbonate) to produce calcium sulfate, carbon dioxide, and water according to the following reaction.



- (b) (i) Impurities (solutes) added to a solvent (water) will always elevate the boiling point of the pure solvent according to the equation  $\Delta T = K_b m_{\text{solute}}$  (where  $\Delta T$  is the increase in boiling point from the normal boiling point of the pure solvent,  $K_b$  is a constant that is a characteristic of the solvent, and  $m$  is the molality of the solute in solution)

- (ii) NaCl ionizes in water into two particles ( $\text{Na}^+$  and  $\text{Cl}^-$ ), whereas sugar ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) is nonionizing and so dissolves as one particle. The equation in 6. (b) (i) above is modified to  $\Delta T = iK_b m_{\text{solute}}$  (where  $i$  is the van't Hoff factor, defined as  $i = \frac{\text{moles of particles in solution}}{\text{moles of solute dissolved}}$ ).

The van't Hoff factor for sodium chloride is approximately 2 (not exactly 2 due to ion pairing), while the van't Hoff factor for sugar is one. Therefore, with equal concentrations of solute (0.10 M) the boiling point elevation for salt (NaCl) will be greater than that of sugar.

- (c) At low temperatures, the gas is moving so slowly that intermolecular attractions play a significant role. These attractive forces (which are relatively weak for methane since it is a nonpolar gas) are not significant at ordinary temperatures because the molecules are moving very fast compared to at low temperatures. At low temperatures, the molecules will be pulled closer together by these attractive forces and the volume of the gas will be less than expected by the ideal gas law equation ( $PV = nRT$ ) at a given temperature and pressure. A similar effect occurs when the gas is at high pressures because at these pressures, the molecules are pushed close together so the intermolecular attractive forces become significant resulting in smaller-than-expected volumes.
- (d) Water vapor molecules in the air is moving too fast for their intermolecular attractions to effect significant condensation. However, when they strike the surface of the cold glass of the beaker of ice bath, much of their kinetic energy is given to the cold glass (containing lower energy). This reduction in the kinetic energy of the water vapor molecules means that they are moving much slower than before the collision with the cold glass. The intermolecular attractions of the vapor molecules are strong enough to form intermolecular bonds and, thus, condense at these slower speeds.

6. (a) Be has four protons (positive charge) in the nucleus to attract its electrons while Li has only three. Since both atoms utilize the  $1s$  and  $2s$  orbitals only for its electrons in the ground state, but Be has a stronger nuclear pull for those electrons than Li, it will pull the electrons in tighter, thus, reducing the size of the electron cloud resulting in a smaller atomic radius than Li.
- (b.) K, with electron configuration of  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ , has only one valence electron, while Ca, with electron configuration of  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ , has two valence electrons. Therefore, it is relatively easy to remove one electron from each atom as in both atoms this electron would be removed from the  $4s$  orbital. To remove a second electron from potassium will be very difficult (very high ionization energy which is the energy required to remove an electron) because it would be removed from the  $3p$  orbital. An electron from the third energy level is much more difficult to remove than one from the fourth energy level because an electron in the third energy level is much closer to the nucleus and experiences a strong nuclear pull (and less shielding). Therefore, K would have a very high second ionization energy. Ca, on the other hand, would lose its second electron from the same  $4s$  orbital. Although it is always harder to remove the second electron from an atom than the first, its second ionization energy will be much lower than that of K.
- (c) The carbon-to-carbon bond in  $C_2H_4$  is a double bond consisting of a sigma bond from the overlap of a  $sp^2$  hybrid bonding orbital ( $120^\circ$  angles) from each carbon atom and a  $\pi$  bond formed from the overlap of an unhybridized  $p$  orbital from each carbon atom. The carbon-to-carbon bond in  $C_2H_6$  is a single bond consisting only of a sigma bond from the overlap of a  $sp^3$  hybrid bonding orbital ( $109^\circ$  angles) from each carbon atom. A double bond is stronger than a single bond (about twice as strong) and requires more energy to break it (about twice the energy). Therefore, the carbon-to-carbon bond energy in  $C_2H_4$  will be greater than carbon-to-carbon bond energy in  $C_2H_6$ .
- (d) Both  $Cl_2$  and  $Br_2$  are very nonpolar molecules whose only intermolecular attraction is due to dispersion interaction forces which are very weak. These dispersion interaction forces are caused by a temporary slight shift in the electron cloud of a molecule to one side causing that side of the molecule to have a partial negative charge and the side away from which it shifted to have a partial positive charge. This slight, temporary polarity in the molecule causes similar action in its neighboring molecules allowing weak intermolecular attractions of the opposite poles of charge. Not all dispersion interaction forces equal. The bigger the molecule, the less tightly held electron cloud is by the nucleus and more shifting of the electron cloud to one side of the molecule is allowed. Bigger molecules have less hold on their electron clouds because they have more electrons in more energy levels than smaller molecules. The more shifting of the electron cloud, the stronger the dispersion interaction forces. Since  $Br_2$  is the bigger than  $Cl_2$  it has stronger dispersion interaction forces. The stronger the intermolecular forces the higher the boiling point (the harder it is to boil so you must heat it to higher temperature to break these intermolecular bonds). Furthermore, at a given temperature, all molecules have the same kinetic energy, but this does not mean they are all moving at the same speed.  $KE = \frac{1}{2}mv^2$ , so if two molecules have the same KE, the more massive one will be moving at a slower speed at this temperature.  $Br_2$  is more massive than  $Cl_2$  and, therefore, it is moving slower at a given temperature. Boiling occurs when intermolecular bonds are broken. The faster a molecule is moving the easier it is to break these bonds.  $Br_2$  must be raised to higher temperature to move at the same speed as  $Cl_2$  at a lower temperature. For these two reasons (stronger intermolecular bonds and slower moving molecules at a given temperature)  $Br_2$  will have higher boiling point than  $Cl_2$ .

8. (a) Molecules are formed when atoms combine by mutual attraction for one or more pairs of electrons. In other words, two or more atoms share one or more pairs of electrons. This sharing of electrons between the atoms is not always equal sharing. One atom may have a stronger electrostatic pull for the electrons than its neighbor. This unequal sharing can result in a charge separation in the molecule where one end of the molecule is more positive (electrons pulled away from this end) while the other end is more negative (electrons pulled toward this end). Such a molecule is said to have a dipole (a positive pole and a negative pole) or is said to be polar. Intermolecular bonds are electrostatic forces of attraction **BETWEEN** molecules. These electrostatic forces are between the positive pole of one molecule and the negative pole of the other molecule. A substance will boil when these intermolecular bonds break. Temperature is a measure of the average kinetic energy of the molecules, thus, an indicator of how fast molecules are moving. As heat is added to a substance, the temperature increases indicating that the molecules are moving faster. When they move fast enough they are able to break the intermolecular bonds holding the molecules together so the molecules can escape each other and move independently of one another. This independent motion of the molecules is the gaseous (or vapor) phase. This is boiling and the temperature at which this occurs is called the boiling point.

Methane ( $\text{CH}_4$ ) is a molecule that has polar bonds but the shape of the molecule is very symmetrical so that these polar bonds all cancel one another's polarity in the molecule as a whole. Therefore, the molecule is nonpolar. Because of this, its intermolecular bonds are very weak. Therefore, it is able to break these bonds even when moving relatively slowly (low temperature) when compared to other substances. Thus it has a low boiling point.

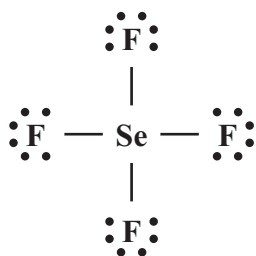
Ammonia ( $\text{NH}_3$ ) on the other hand is a very polar molecule because it has a "lone" pair of electrons which is a pair of electrons in the valence shell that was not formed by bonding with another atom. This lone pair is located on the nitrogen atom away from where the hydrogens are bonded to this nitrogen atom in the ammonia molecule. Furthermore, the nitrogen atom has a stronger pull for electrons than the hydrogen atoms to which it is bonded. This makes the hydrogen side of the molecule somewhat of a positive pole while the nitrogen side is a very negative pole due to its pull for hydrogen's electrons **AND** its lone pair. This makes the ammonia molecule very polar, thus, having very strong intermolecular bonds. Therefore the molecules must be moving very fast (relatively speaking) to break these bonds. Therefore, ammonia has a much higher boiling point than methane.

- (b) Both ethane and hexane are nonpolar substances because they are symmetrical. However, hexane is more polar (less nonpolar) because it is bigger and more massive. The bigger a molecule is the less tightly its electrons will be held in place allowing them to shift within the molecule and form temporary dipoles. Furthermore, temperature is a measure of average kinetic energy which means that at a given temperature, both molecules will have the same kinetic energy. This does not mean they will have the same speed. Since  $\text{KE} = \frac{1}{2}mv^2$ , a more massive molecule will move slower than a less massive molecule to have the same kinetic energy (same temperature).

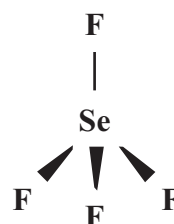
Since hexane is more polar than ethane and moves slower at a given temperature, it requires a higher temperature to boil. Therefore, hexane will still be a liquid at room temperature ( $25^\circ\text{C}$ ) while ethane will be a gas.

- (c) Silicon forms a network covalent bond which is a very strong bond. Chlorine is a very nonpolar substance. So it takes a lot more energy to break the bonds holding silicon atoms together than the intermolecular bonds between chlorine molecules. Therefore, silicon will have a much higher melting (and boiling) point than chlorine.
- (d) Lattice energy is the energy needed to pull apart the components of an ionic crystal. This energy is determined theoretically from Coulomb's law of electrostatic attraction between charged particles given by  $F = k \frac{q_1 q_2}{r^2}$ , where  $q_1$  and  $q_2$  is the charge on the positive and negative ions of the ionic crystal. Since  $\text{MgO}$  consists of +2 and -2 ions it will have approximately four times the lattice energy of sodium fluoride which has only +1 and -1 ions. Therefore,  $\text{MgO}$  will have a much higher melting point than  $\text{NaF}$ .

7. (a) All of the isotopes of selenium (atomic number 34) will have the same number of protons (34) and, therefore, electrons. However, different isotopes of selenium will have different numbers of neutrons, thus, have different masses.
- (b)  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^4$ . All electrons that are in energy levels lower than the valence (highest energy level) shell will be paired. There will be two unpaired electrons in the ground state of a selenium atom because there are three orbitals (positions in space) in the p subshell of the fourth energy level (valence shell). Each of these orbitals can hold two electrons. According to Hund's rule, a position in a subshell will not have paired electrons until each position in that subshell has one electron. Since the 4p orbital has four electrons, one will go in each of the three positions and the fourth one will create a pair in one of the positions. This leaves two positions with only one (unpaired) electron. Thus, there are only two unpaired electrons in a selenium atom in its ground state.
- (c) (i) Ionization energy is the energy required to remove an electron from an atom. Since bromine (atomic number 35) has one more proton in its nucleus, it will have a stronger force of attraction between the positive nucleus and the negative valence electrons. Therefore, it will be harder, and require more energy, to remove a valence electron from bromine than selenium. Therefore, selenium will have a lower first ionization energy than bromine. Note: This force of attraction is given by Coulomb's law,  $F = k \frac{q_1 q_2}{r^2}$ , where F is the force of attraction (or repulsion between the two charged objects), k is Coulomb's constant,  $q_1$  is the charge on one object (such as the nucleus),  $q_2$  is the charge on a second object (such as a valence electron), and r is the distance between the two charged objects.
- (ii) Tellurium has the same number of valence electrons as selenium. However, the valence electrons of tellurium are significantly further from the pull of the nucleus than are the valence electrons of selenium because the valence electrons in a tellurium atom in its ground state are in the fifth energy level while the valence electrons in a selenium atom in its ground state are in the fourth energy level. According to Coulomb's law, the further apart the two charged objects the weaker the force of attraction (or repulsion) between them. Since the valence electrons in a tellurium atom (in the ground state) are farther from the nucleus than the valence electrons in a selenium atom (in the ground state), the tellurium atom's valence electrons will be less tightly held and therefore easier to remove.
- (d) The total number of valence electrons in  $\text{SeF}_4$  is  $4 + 4(7) = 32$ , and there are four Se-F bonds. Each bond requires two of the valence electrons, so that is a total of eight of the 32 valence electrons used for bonding. Each of the four fluorine atoms will require six more electrons to fill its orbitals, so  $4(6) = 24$  electrons which are all the remaining valence electrons. Therefore the Lewis structure can be shown on the left while the molecular structure is shown on the right below. Since there are four pairs of electrons around the central atom, these pairs will arrange at the corners of a tetrahedron ( $109.5^\circ$ ).



Lewis Structure



Molecular Structure