Homework #2  
Chapter 16  
Liquid and Solids

7. Vapor Pressure: The pressure exerted by the vapor of a liquid when the vapor and the liquid are in dynamic equilibrium. The vapor pressure reflects the fact that within a system there is a distribution of energies that molecules can have, therefore, some molecules will have enough energy to overcome the intermolecular forces and enter into the gas phase. All liquids have some vapor pressure. The stronger the intermolecular forces the smaller the vapor pressure. All solids also have a vapor pressure. This is why if you leave ice in the freezer for a long time it “disappears.” The vapor pressure of solids is less than the vapor pressure of liquids. As the temperature increases the molecules have more energy, therefore, more molecules can escape into the gas phase (vapor pressure increases). When the vapor pressure is equal to the atmospheric pressure the solution boils.

9. a) Surface Tension  
   As the intermolecular forces increase (↑), surface tension increases (↑).

   b) Viscosity  
   As the intermolecular forces increase (↑), the viscosity increases (↑).

   c) Melting Point  
   As the intermolecular forces increase (↑), the melting point increases (↑).

   d) Boiling Point  
   As the intermolecular forces increase (↑), the boiling point increases (↑).

   e) Vapor Pressure  
   As the intermolecular forces increase (↑), the vapor pressure decreases (↓).

11. Intermolecular Forces: The forces of attraction/repulsion between molecules. Intramolecular Forces: The forces of attraction/repulsion within a molecule. Intramolecular forces are stronger than the intermolecular forces. Types of intermolecular forces:
   Dipole-Dipole Forces: The interaction between two electric dipoles in different molecules.
   Hydrogen Bonding: The attraction between a hydrogen atom (that is bonded to an O, N, or F atom) and an O, N, or F atom in a neighboring molecule.
   London Dispersion Forces: The force of attraction that arises from the interaction between instantaneous electric dipoles on neighboring molecules.

In order for Hydrogen bonding to occur there must be a hydrogen atom that is bonded to an O, N, or F atom. Since O, N, and F are extremely electronegative they cause the electron on hydrogen to spend most of the time around the O, N, or F. This generates a partial positive charge on the hydrogen atom and a partial negative charge on the O, N, or F atom. The partial positive charge on the H atom is attracted to a partial negative charge on the O, N, or F atom in an adjacent molecule.
In order for dipole-dipole forces to be present, a molecule must be polar. The partial positive end of one molecule is attracted to the partial negative end of another molecule. Hydrogen Bonding is just an extreme case of dipole-dipole forces. In both cases a dipole must be present. The magnitude of the dipole is usually larger for hydrogen bonding than pure dipole-dipole forces.

Electrons do not have to be evenly distributed around a molecule. Occasionally an instantaneous dipole moment is set-up within a nonpolar molecule. London forces are the attractions between the instantaneous dipole moments. London forces are similar to dipole-dipole forces in that they both results from attraction between positive and negative charges. London forces are weaker than dipole-dipole forces because there is no permanent dipole moment.

12. Listed in order of decreasing strength
   Metallic bonding, covalent network, ionic: Found in systems that form crystals or macromolecules. (Strongest)
   Hydrogen-Bonding: H-bonding is the strongest intermolecular force; it only occurs when a hydrogen atom is bonded to an O, N, or F atom.
   Dipole-Dipole: Occurs in polar molecules
   London Dispersion: Occurs in all molecules (Weakest)

   There is overlap between the strengths. Look at the table in problem 20 – benzene (which only has London dispersion forces) has a higher boiling point than acetone (which has dipole-dipole and London dispersion forces). Therefore, the London dispersion forces must be greater than the dipole-dipole forces in this case.

13. $\Delta H_{\text{fus}}$ is the energy needed for water to go from a solid to a liquid and $\Delta H_{\text{vap}}$ is the energy needed for water to go from a liquid to a gas. When water goes from a solid to a liquid the molecules are still very close to each other, therefore, very few of the hydrogen bonding forces will have to be overcome. When water goes from a liquid to a gas, the molecules must spread out; therefore, most of the hydrogen bonding forces will have to be overcome. This results in $\Delta H_{\text{vap}}$ being larger than $\Delta H_{\text{fus}}$.

15. a) London Dispersion  b) Dipole-Dipole
    c) H-Bonding  d) Ionic
    e) London Dispersion  f) Dipole-Dipole
    g) Ionic  h) Ionic
    i) London Dispersion although C-F bonds are polar, polymers are so large that London dispersion forces are the predominant intermolecular force.
    j) London Dispersion  k) Dipole-Dipole
    l) H-Bonding  m) Dipole-Dipole
    n) London Dispersion
16. a) OCS will have stronger intermolecular forces because it is a polar molecule therefore, it will have dipole-dipole forces between molecule. While CO$_2$ is a nonpolar molecule therefore, there are only London dispersion forces between molecules.

b) Both SeO$_2$ and SiO$_2$ are bent molecules making both of them polar which results in them having the following intermolecular forces: dipole-dipole forces and London forces. SeO$_2$ will have stronger intermolecular forces because it is a larger molecule than SO$_2$ and the larger the molecule the less energy it takes to generate instantaneous dipole moments.

c) H$_2$NCH$_2$CH$_2$NH$_2$ will have stronger intermolecular forces than CH$_3$CH$_2$CH$_2$NH$_2$ because H$_2$NCH$_2$CH$_2$NH$_2$ has the ability to form double the hydrogen bond with neighboring molecules than CH$_3$CH$_2$CH$_2$NH$_2$.

d) H$_2$CO will have stronger intermolecular forces than CH$_3$CH$_3$.

H$_2$CO is a polar molecule and will have both dipole-dipole forces and London dispersion forces while CH$_3$CH$_3$ is a non-polar molecule and will only have London dispersions forces.

e) CH$_3$OH will have stronger intermolecular forces than H$_2$CO.

Hydrogen-bonding can occur between neighboring molecules in CH$_3$OH, whereas the strongest intermolecular force in H$_2$CO is dipole-dipole forces.

17. a) Highest boiling point, greatest intermolecular forces.

- HBr: dipole-dipole and London dispersion (greatest boiling point)
- Kr: London dispersion
- Cl$_2$: London dispersion

b) Highest freezing point, greatest intermolecular forces.

- H$_2$O: H-bonding, dipole-dipole, and London dispersion
- NaCl: Ionic (highest freezing point)
- HF: H-bonding, dipole-dipole, and London dispersion

c) Lowest vapor pressure, highest intermolecular forces

- Cl$_2$: London dispersion
- Br$_2$: London dispersion
- I$_2$: London dispersion (lowest vapor pressure)

Note: The smaller the molecule the smaller the London dispersion forces.

d) Lowest freezing point, smallest intermolecular forces

- N$_2$: London dispersion (lowest freezing point)
- CO: dipole-dipole, and London dispersion
- CO$_2$: London dispersion

Note: The smaller the molecule the smaller the London dispersion forces.

e) Lowest boiling point, smallest intermolecular forces

- CH$_4$: London dispersion (lowest boiling point)
- CH$_3$CH$_3$: London dispersion
- CH$_3$CH$_2$CH$_3$: London dispersion

Note: The smaller the molecule the smaller the London dispersion forces.
f) Highest boiling point, largest intermolecular forces
   - HF: H-bonding, dipole-dipole, and London dispersion (highest boiling point)
   - HCl: dipole-dipole, and London dispersion
   - HBr: dipole-dipole, and London dispersion

19. a) The more spread out the molecule is the easier it is to align instantaneous dipole moments. Therefore n-pentane (larger intermolecular forces) has a higher boiling point than neopentane.
   b) HF is capable of H-bonding while HCl is not, therefore, HF has a higher boiling point than HCl.
   c) LiCl is an ionic compound, which is ionic bonds which are stronger than any type of intermolecular forces. Therefore, LiCl has a higher boiling point than HCl.
   d) The larger the molecule the larger the London forces, therefore, n-hexane has a larger boiling point than n-pentane.

20. Benzene | Naphthalene | Carbon tetrachloride

All of the molecule are nonpolar therefore, the only intermolecular force that they have is London dispersion forces. The larger the molecule the larger the London dispersion forces. In addition, benzene/naphthalene are flat molecules make them able to get closer to other benzene/naphthalene molecules which increases the strength of the London dispersion forces.
Therefore in order of decreasing intermolecular forces
   Naphthalene > benzene > carbon tetrachloride
Naphthalene would be expected to have the greatest boiling point, melting point, and $\Delta H_{\text{vap}}$ and carbon tetrachloride would be expected to have the smallest boiling point, melting point, and $\Delta H_{\text{vap}}$. 
Benzoic acid and acetic acid are polar and have COOH groups which results in dipole-dipole and H-bonding intermolecular forces. Acetone is polar but it unable to H-bond to itself therefore will have weaker intermolecular forces than the other two. Benzoic acid will have greater London forces than acetic acid because of the benzene group on benzoic acid having more atoms and being flatter than the methyl (CH₃) group on acetic acid.

Therefore, in order of decreasing intermolecular forces

- benzoic acid > acetic acid > acetone

Benzoic acid would be expected to have the greatest boiling point, melting point, and ΔH_{vap} and acetone would have the smallest boiling point, melting point, and ΔH_{vap}.

If we look at all six molecules we might guess that the order of decreasing intermolecular forces is:

- benzoic acid > acetic acid > acetone > naphthalene > benzene > carbon tetrachloride

However, the data shows the acetone and naphthalene are out of place from what we might expect. This is a result of two factors. Acetone is a small molecule, therefore, although it does have dipole-dipole forces and London dispersion forces the London dispersion forces are small due to the size making it seem out of order. Naphthalene only has London dispersion forces but since it is a large flat molecule; the London dispersion forces are large making it have a higher boiling point than acetic acid (which is small) even though acetic acid is able to H-bond.

21. The only intermolecular forces that Ar has are London dispersion forces. Argon is a small atom, therefore, the atom/molecule that has the boiling point closest to argon must be small and only have London dispersion forces.

- Cl₂ London dispersion
- HCl dipole-dipole, and London dispersion
- F₂ London dispersion
- NaF Ionic
- HF H-bonding, dipole-dipole, and London dispersion

F₂ is smaller than Cl₂, therefore, it is closer in size to argon causing F₂ to have the closest boiling point to argon.
23. CH₃CH₂OH  H-bonding, dipole-dipole, and London dispersion
   CH₃CH₂CH₃  London dispersion
   CH₃COCH₃  dipole-dipole, and London dispersion
In order of increasing intermolecular forces:
   CH₃CH₂CH₃ < CH₃COCH₃ < CH₃CH₂OH
The greater the intermolecular forces the higher the boiling point.
As the intermolecular forces increase the boiling point increases.
In order of increasing boiling point:
   CH₃CH₂CH₃ < CH₃OCH₃ < CH₃CH₂OH

27. a) Surface Tension: The tendency of molecules at the surface of a liquid to be pulled inward, resulting in a smooth surface. (The greater the intermolecular forces the greater the surface tension.)
   b) Viscosity: The resistance of a fluid (a gas or liquid) to flow: the higher the viscosity, the slower the flow. (The greater the intermolecular force the greater the viscosity.)
   c) Melting Point: The temperature at which a solid turns into a liquid as long as constant heat is supplied. (The greater the intermolecular forces the greater the melting point.)
   d) Boiling Point: The temperature at which a liquid turns into a gas as long as constant heat is supplied. (The greater the intermolecular forces the greater the boiling point.)
   e) Vapor Pressure: The pressure exerted by the vapor of a liquid (or a solid) when the vapor and the liquid (or solid) are in dynamic equilibrium. (The greater the intermolecular forces the lower the vapor pressure.)

29. Water is a polar molecule and wax is a nonpolar molecule. The water molecules have the lowest energy when surrounded by other polar molecules. If the water beads, then more water molecules can be surround by the polar water molecules instead of by the nonpolar wax molecules. Therefore, the overall energy for water to bead is less than if the water lied flat on the wax surface. In addition, because water can H-bond it results in additional stability for water molecules to be surrounded by other water molecules.

33. a) Crystalline solids form ordered arrays and amorphous solids do not.
   b) Ionic solids are formed from a metal and a nonmetal held together by ionic bonds (a positive ion attracted to a negative ion) and molecular solids are formed from two nonmetals covalently bonded to form molecules. Molecules held together by forces: intermolecular hydrogen-bonding, dipole-dipole, and/or London forces.
   c) In covalent network solids, the atoms form a covalent network through the entire system (one large molecule all held together by sharing electrons) and in molecular solids the molecules are discrete and held together by intermolecular forces.
d) In covalent network solids, the electrons are localized (insulators and semiconductors) and in metallic solids, the electrons are delocalized (metals).

40. **Molecular Solids**: Are formed from covalent molecules that have relatively weak forces between the molecules.

**Covalent Networks**: Are commonly formed by boron, carbon, and silicon atoms and molecules. Instead of forming individual molecules, covalent networks have covalent bonds through the extent of the solid.

**Atomic Solids**: Solid formed by only 1 type of atom. Note: If the elements form a diatomic molecule, an atomic solid will not be formed and instead a molecular solid will form.

**Ionic Solids**: Needs both a metal and a nonmetal to form.

**Metallic Solids**: Contain only metal elements.

<table>
<thead>
<tr>
<th>a) Molecular</th>
<th>b) Covalent network</th>
<th>c) Atomic/Covalent network</th>
</tr>
</thead>
<tbody>
<tr>
<td>d) Molecular</td>
<td>e) Atomic/metallic</td>
<td>f) Molecular</td>
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<tr>
<td>g) Ionic</td>
<td>h) Molecular</td>
<td>i) Ionic</td>
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<td>j) Atomic/Metallic</td>
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<td>o) Molecular</td>
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<td>p) Ionic</td>
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</tbody>
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43. \[ n\lambda = 2ds\sin\theta \]

\[(1)(1.54 \text{ Å}) = 2ds\sin(14.22^\circ) \]
\[d = 3.13 \text{ Å} \]

45. **Cubic closed pack systems (face centered cubic)** - Fig 16.15 - have 4 atoms per unit cell

Calculate the mass of the Ca atoms

\[ 4 \text{ Ca atoms} \left( \frac{1 \text{ mol Ca}}{6.022 \times 10^{23} \text{ Ca atoms}} \right) \left( \frac{40.08 \text{ g Ca}}{1 \text{ mol Ca}} \right) = 2.66 \times 10^{-22} \text{ g} \]

Calculate the volume of the unit cell

The atoms in the face of the unit cell touch. Therefore, the length of one of the sides of the unit cell can be calculated using the Pythagorean Theorem.

\[ h^2 = s_1^2 + s_2^2 \]
\[(4r)^2 = 2l^2 \]
\[ (4(197 \times 10^{-10} \text{ cm}))^2 = 2l^2 \]
\[ l = 5.57 \times 10^{-8} \text{ cm} \]
Faced centered cubic crystals have 4 atoms per unit cell.

If we calculate the volume of the unit cell we will be able to calculate the mass of the 4 atoms.

Calculate the volume of the unit cell

\[ d = \frac{m}{V} \]

\[ 10.5 \text{ g/cm}^3 = \frac{m}{(4.09 \times 10^{-8} \text{ cm})^3} \]

\[ m = 7.18 \times 10^{-22} \text{ g} \]

Calculate the mass of 1 atom

\[ \frac{m}{4} = \frac{7.18 \times 10^{-22} \text{ g}}{4} = 1.80 \times 10^{-22} \text{ g} \]

Calculate molar mass

\[ mN_a = (1.80 \times 10^{-22} \text{ g}) \left( 6.022 \times 10^{23} \frac{1}{\text{mol}} \right) = 108 \text{ g/mol} \]

Therefore, X is silver.

78. a) Ti (at center) 1 atom = 1

Ca (at the corners of the cell) (8 atoms) \( \frac{1}{8} = 1 \)

O (at the sides of the cell) (6 atoms) \( \frac{1}{2} = 3 \)

\[ \text{CaTiO}_3 \]

b) The titanium atoms are at the corners of the unit cell and the oxygen atoms are centered on each side of the unit cell.

Ti (8 atoms) \( \frac{1}{8} = 1 \)

Ca 1 atom = 1

O (12 atoms) \( \frac{1}{4} = 3 \)

\[ \text{CaTiO}_3 \]

c) 6 oxygen atoms are surrounding each titanium atom in both cases.

81. A volatile liquid vaporizes easily. Volatile liquids have large vapor pressures. The intermolecular forces are small in volatile liquids.
86. The question wants us to find the boiling point, which is the temperature when the vapor pressure equals the external pressure.

\[ \ln \left( \frac{P_{\text{vap}_1}}{P_{\text{vap}_2}} \right) = \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \]

At sea level water boils at 100°C. Therefore, at 100°C the vapor pressure is 760. Torr.

\[ \ln \left( \frac{760 \text{ Torr}}{520 \text{ Torr}} \right) = \frac{40,700 \text{ J/mol}}{8.3145 \text{ J/molK}} \left( \frac{1}{T_2} - \frac{1}{373K} \right) \]

\[ T_2 = 363K = 90°C \]

The highest temperature that liquid water can be at is the boiling temperature. Therefore, the question is asking what the pressure would have to be to raise the boiling temperature of water to 350°C.

\[ \ln \left( \frac{760 \text{ Torr}}{P_{\text{vap}_2}} \right) = \frac{40,700 \text{ J/mol}}{8.3145 \text{ J/molK}} \left( \frac{1}{623K} - \frac{1}{373K} \right) \]

\[ P_{\text{vap}_2} = 147,000 \text{ torr} \]

87. The question wants you to find the normal boiling point (which is the boiling point at 1 atm). At the boiling point the vapor pressure equals the external pressure. Before you can calculate the normal boiling point you must determine \( \Delta H_{\text{vap}} \).

\[ \ln \left( \frac{P_{\text{vap}_1}}{P_{\text{vap}_2}} \right) = \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \]

\[ \ln \left( \frac{213 \text{ Torr}}{836 \text{ Torr}} \right) = \frac{\Delta H_{\text{vap}}}{8.3145 \text{ J/molK}} \left( \frac{1}{353K} - \frac{1}{313K} \right) \]

\[ \Delta H_{\text{vap}} = 31,400 \text{ J/mol} \]

Find the normal boiling point

\[ \ln \left( \frac{213 \text{ Torr}}{760 \text{ Torr}} \right) = \frac{31,400 \text{ J/mol}}{8.3145 \text{ J/molK}} \left( \frac{1}{T_2} - \frac{1}{313K} \right) \]

\[ T_2 = 350K = 77°C \]
\[ \ln(P_{\text{vap}}) = -\frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T} \right) + C \]

You can plug in the pressure in any units that you want but the temperature must be in Kelvin.

\[-\frac{\Delta H_{\text{vap}}}{R} = -\text{slope}\]

\[ \text{Li} \]

\[-\frac{\Delta H_{\text{vap}}}{8.3145 \text{ J/mol}\cdot K} = -19,043 K \]

\[ \Delta H_{\text{vap}} = 158,000 \text{ kJ/mol} \]

\[ \text{Mg} \]

\[-\frac{\Delta H_{\text{vap}}}{8.3145 \text{ J/mol}\cdot K} = -16,695 K \]

\[ \Delta H_{\text{vap}} = 139,000 \text{ kJ/mol} \]

Alternative way of solving the problem without a graph:

\[ \ln(P_{\text{vap}}) = -\frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T} \right) + C \]

\[ \text{slope} = -\frac{\Delta H_{\text{vap}}}{R} = \frac{\text{rise}}{\text{run}} \]

Use the first and last points

\[ \text{Li} \]

\[ \text{slope} = -\frac{\Delta H_{\text{vap}}}{8.3145} = \frac{\text{run}}{\text{run}} \]

\[ \Delta H_{\text{vap}} = 159,000 \frac{\text{J}}{\text{mol}} = 159 \frac{\text{kJ}}{\text{mol}} \]
\[ \text{Mg} \]

\[
slope = -\frac{\Delta H_{\text{vap}}}{R} = \frac{\text{rise}}{\text{run}} = \frac{\Delta H_{\text{vap}}}{8.3145 \frac{J}{mol \cdot K}} = \frac{\ln(760 \text{ mmHg}) - \ln(1 \text{ mmHg})}{1383K - 893K} = -16.718K
\]

\[ \Delta H_{\text{vap}} = 139,000 \frac{J}{mol} = 139 \frac{kJ}{mol} \]

The bonding is stronger in Li than in Mg because you have to raise the temperature of the Li higher than that of Mg to get to the same vapor pressure.

91.

Since \( \Delta H_{\text{vap}} \) is 4 times larger than \( \Delta H_{\text{fus}} \), line 4 should be 4 times longer than line 2.

\[ q = nC\Delta T \]

therefore, \( \Delta T = \frac{1}{nC} \) \( q \) making the slope of the line inversely proportional to the heat capacity. Since the solid had the largest heat capacity it should have the smallest (least steep slope). The gas has the smallest heat capacity, therefore, it should have the largest (most steep slope).

96. \( q_{\text{ice}} = -q_{\text{water}} \)

\[ q_{\text{ice}}(\text{ice}(\text{ice} \rightarrow 0.0°C) + q_{\text{water ice}} + q_{\text{water ice}}(0.0°C \rightarrow T_f) = -q_{\text{water}}(80.0°C \rightarrow T_f) \]

\[ m_{\text{ice}}C_{\text{ice}}\Delta T(\text{ice}(\text{ice} \rightarrow 0.0°C) + n_{\text{ice}}\Delta H_{\text{fus}} + m_{\text{ice}}C_{\text{water}}\Delta T(0.0°C \rightarrow T_f) \]

\[ = -m_{\text{water}}C_{\text{water}}\Delta T(80.0°C \rightarrow T_f) \]

\[ (20.0 \text{ g}) \left(2.08 \frac{J}{g°C} \right)(0.0°C - 0.0°C) + (20.0 \text{ g}) \left(1 \text{ mol H}_2\text{O} \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \right)(6.010 \frac{J}{mol}) \]

\[ + (20.0 \text{ g}) \left(4.18 \frac{J}{g°C} \right)\left(T_f - 0.0°C\right) \]

\[ = -(100.0 \text{ g}) \left(4.18 \frac{J}{g°C} \right)\left(T_f - 80.0°C\right) \]

\[ 7,090 J + 83.6 \frac{J}{°C} T_f = -418\frac{J}{°C} T_f + 33,200 J \]

\[ T_f = 52.0°C \]
The triple point is E
The normal boiling point is where the dotted line (showing 1 atm) meets the liquid/gas solid line between regions B and C. To get the temperature for the normal boiling point read the temperature off the x axis.
The normal freezing point is where the dotted line (showing 1 atm) meets the solid/liquid solid line between regions A and B. To get the temperature for the normal freezing point read the temperature off the x axis.
The critical point is G
The solid is denser than the liquid. This can be determined by looking at the slope of the line between the solid and the liquid. If you increase the pressure, at a constant temperature, the slope of the line will result in more of the denser substance forming. In this case more solid forms, therefore, the solid is denser than the liquid.

126. NaCl ionic
MgCl$_2$ ionic
AlCl$_3$ ionic
SiCl$_4$ (tetrahedral) London dispersion
PCl$_3$ (trigonal pyramidal) dipole-dipole, and London dispersion
SCl$_2$ (bent) dipole-dipole, and London dispersion
Cl$_2$ London dispersion

The general trend is that all of the ionic complexes have much higher melting points than the covalent complexes. AlCl$_3$ melting point is less than NaCl or MgCl$_2$ because it is the least ionic (the difference in electronegativity between Al and Cl is the smallest of the three ionic compounds) of the three.

NaF ionic
MgF$_2$ ionic
AlF$_3$ ionic
SiF$_4$ (tetrahedral) London dispersion
PF$_5$ (trigonal bipyramidal) London dispersion
SF$_6$ (octahedral) London dispersion
F$_2$ London dispersion

The general trend is that all of the ionic complexes have much higher melting points than the covalent complexes. Of the covalent complexes, F$_2$ is nonpolar and has nonpolar bonds. In addition, it is very small, therefore has a significantly lower melting point than the other complexes.