Bonding and the Determination of Melting Points and Boiling Points

Melting Point/Freezing Point:
The temperature at which a liquid becomes a solid and a solid becomes a liquid. 0°C is the freezing point of water at atmospheric pressure, 1538 °C is the melting point of iron. Above these temperatures, the material is a liquid, below, it is a solid.

Boiling Point/Condensation Point:
The temperature at which a liquid becomes a gas and a gas becomes a liquid. 100°C is the boiling point of water at atmospheric pressure; 2750 °C is the boiling point of iron. Above these temperatures, the material is a gas, below, it is a liquid.

Solid:
In the solid phase, the bonds holding the material together are strong enough that movement of the individual molecules is prevented. A solid may be a glass (amorphous) or a crystal (ordered), but it always a solid.

Liquid:
In the liquid phase, the bonds holding the material together are constantly breaking and reforming. The material is disordered (there are exceptions to this rule, liquid crystals for example, but for our purposes we will focus on a disordered liquid)

Gas:
In the gas phase there are no longer any bonds holding the molecules together. The thermal energy available is enough to break any bonds that may form.

Figure 1: Solid, liquid and gas

1 http://martine.people.cofc.edu/111LectWeek1_files/image008.jpg
Table 1 Summary of Bonding Forces

<table>
<thead>
<tr>
<th>Intermolecular (between molecules*)</th>
<th>London Dispersion aka Instantaneous Dipole-Induced Dipole.</th>
<th>non polar molecule and a non polar molecule</th>
<th>Cl₂ and Cl₂ or Ar and Ar or C₆H₆ and C₆H₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dipole-Induced Dipole.</td>
<td>polar molecule and non polar molecule</td>
<td>HCl and Cl₂</td>
<td></td>
</tr>
<tr>
<td>Dipole- Dipole.</td>
<td>polar molecule and polar molecule</td>
<td>HCl and HCl</td>
<td></td>
</tr>
<tr>
<td>Hydrogen Bonding</td>
<td>N-H, F-H, O-H</td>
<td>H₂O and H₂O</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Intramolecular (within the molecule)</th>
<th>Covalent</th>
<th>two elements with electronegativity difference of &lt;0.4</th>
<th>C and C, C and H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polar Covalent</td>
<td>two elements with electronegativity difference of 0.4-1.6</td>
<td>HCl, H₂O, HF</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Intra/Intermolecular (within and between the molecules)</th>
<th>Metallic</th>
<th>metals</th>
<th>Na, Al, Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic</td>
<td>metal and non metal (electronegativity difference of &gt;1.6-2.0)</td>
<td>NaCl, MgO</td>
<td></td>
</tr>
</tbody>
</table>

| Network Covalent                                      | two elements with electronegativity difference of 0-1.6 | diamond, BN, graphite |

*Please note that throughout this paper, a molecule describes a discrete unit, so Cl₂ and Ar are both considered molecules, despite Ar being only a single atom.

**London Dispersion aka Instantaneous Dipole-Induced Dipole aka Induced Dipole-Induced Dipole.**

The strength of a London Dispersion bond is directly proportional to the polarisability and therefore the size of the molecule. Therefore, the melting point (and boiling point) increases.

He < Ne < Ar < Kr < Xe

F₂ < Cl₂ < Br₂ < I₂

There is a covalent bond between the halogen atoms. This bond does NOT break as the material goes through the various phase transitions. The bonding responsible for the
solid/liquid/gas transformation (ie the bonds that are breaking and reforming) is the London Dispersion aka Instantaneous Dipole-Induced Dipole.

\[ \text{CH}_4 < \text{C}_2\text{H}_6 < \text{C}_3\text{H}_8 < \text{C}_4\text{H}_{10} < \text{C}_5\text{H}_{12} < \text{C}_6\text{H}_{14} \]

Aside from elements, this can also be applied to more complex molecules. For example linear hydrocarbons also show an increase in melting point and boiling point with molecular weight (size).

![Diagram](image)

Figure 2: The formation of an instantaneous dipole is shown, which can then induce a dipole in a neighbouring molecule. This induction of a dipole will continue among all other atoms. This is the weakest of the intramolecular forces, but in a large and polarisable molecule can result in a solid at room temperature (I$_2$).

**Dipole- Dipole.**

In this case, the polarity of the polar covalent bond must be considered. This will determine the strength of dipole-dipole interaction, but note that the polar covalent bond itself does NOT break. The strength of a Dipole- Dipole bond is directly proportional to the strength of the dipole and therefore the electronegativity difference of the elements.
However, melting point is also affected by molecular weight, so even though from dipole-dipole interactions alone (and hydrogen bonding for the HF) one would expect the melting points to follow the trend of HF > HCl > HBr > HI, the trend is actually HF > HCl < HBr < HI, due to the increasing molecular weight of the halogens.

**Hydrogen Bonding**

Hydrogen bonding is a special type of dipole-dipole bonding that occurs when you have H bonded to O, N, F. The large difference in electronegativity and small size of the hydrogen creates a strongly polarised bond intramolecular and results in a much stronger intermolecular bond than would be otherwise predicted.

![Figure 3: Hydrogen bonding in water. The polar covalent intramolecular bond between O and H results in a very strong dipole. The attraction between these dipoles (dotted lines in figure) is the hydrogen bonding.](http://course1.winona.edu/sberg/ILLUST/H-bond2.gif)
Figure 4: The change in boiling point with the hydrides of group 14 (C-Sn) group 15 (N-Sb), group 16 (O-Te) and group 17 (F-I). Note that H$_2$O has a higher boiling point than HF, even though the HF bond is more polar. This is due to the fact that H$_2$O can form two hydrogen bonds off of every molecule.

**Ionic Bonding**

For the purposes of comparing melting points (ie, when not explicitly asked to calculate them), one only needs to consider the simplified version in which the main factors affecting an electrostatic interaction are set up. This is $(+Z)(-Z)/r$, so the absolute magnitude of the positive ion $(+Z)$, the absolute magnitude of the negative ion $(-Z)$ and the distance between them $(r)$.

For rough comparisons, it easy to see that difference is charge is going to be more important than the difference in radius. Radii between the positive and negative ion generally vary by a factor of ca 50%, if they are in close periods, while going from 1+/1$-$ interaction to a 2+/2$-$ interaction is a factor of 4 and a 3+/3$-$ interaction is a factor of 9. Therefore, one would consider the radii only if the charges were the same.

**Example One:** Radii is slightly complicated, but charge and radii give the same trend and charge significantly trumps radii

eg: NaCl vs MgS

radii: The radius is similar. Mg$^{2+}$ (72 pm) is smaller than Na$^+$ (102 pm) and S$^{2-}$ (184 pm) is larger than Cl$^-$ (181 pm) Therefore NaCl is $(102+181)/2 = 142$ pm and MgS is

http://www.goiit.com/templates/default/images/chapters/chem_bond/fig.20.gif
(72+184)/2=128 pm and the radius is smaller for the MgS. It is NOT required to calculate this value unless a question explicitly requests it. The values are here to give demonstrate that the values are similar and the difference is of a lesser magnitude than the charge.

charge: NaCl 1*1=1 versus MgS 2*2=4

MgS would have the stronger bond (higher charge and smaller radius) and therefore the higher melting point

NaCl 801 °C MgS >2000 °C

Example Two: Charge and radii give opposite trend and charge significantly trumps radii
e.g: LiF vs MgS
radii: Mg$^{2+}$ (72 pm) is smaller than Li$^+$ (76 pm) and S$^{2-}$ (184 pm) is larger than F$^-$ (133 pm) Therefore LiF is (76+133)/2 = 105 pm and MgS is (72+184)/2=128 pm and the radius is smaller for the LiF by 20%.

charge: LiF 1*1=1 versus MgS 2*2=4

MgS would have the stronger bond (Four times (400%) the strength of LiF from charge and only 20% weaker than LiF from the radius) and therefore the higher melting point

LiF 845 °C MgS >2000 °C

Example Three: Charge is the same and therefore radii must be considered

NaCl vs KCl
radii K$^+$ > Na$^+$
charge 1*1=1 versus 1*1=1

NaCl would have the stronger bond and therefore the higher melting point

NaCl 801 °C KCl 770 °C

It should be noted that these rules are simplified and do not always hold true (LiCl has a lower melting point than NaCl for example) in the real world.

The full equation of ionic bonding for calculations was given in lecture and is:

$$E = -\frac{N_A M z^+ z^- e^2}{4\pi\varepsilon_0 r_0} \left(1 - \frac{1}{n}\right),$$

This calculates the full lattice energy for the crystal and takes into account factors such as crystal geometry and lattice structure.

Metallic Bonding

Metallic bonding is always intra/intermolecular, meaning it is a bulk bonding and the bonds between the individuals atoms are the bonds that are broken upon melting or boiling. Metallic bonding is present in all metals. The bond strength is determined by three factors:

1) **Number of electrons in the bond.** This can be determined from the ion that the metal would form, so for Na (Na$^+$), it is 1 electron, for Mg(Mg$^{2+}$), it is 2 electrons and Ti(Ti$^{3+}$), is 3 electrons. The more electrons in the bond, the stronger the bond.
2) **Size of the atom.** The bond is between the positive nucleus and the electrons in the bond, so the larger the atom, the weaker the bond. This is essentially an electrostatic interaction.

3) **Degree of ionicity.** This is how much the electron is actually given up to the bond. When discussing metallic bonding, it is often assumed that electrons is freely given up and is not bound to any specific atom. This is not entirely true. Cs essentially gives up its entire electron, but the other elements do not. This can be determined from the ionisation energy. The higher the ionisation energy, the less sharing of the electrons and the weaker the bond is. This factor does not affect the trends in bond strength for the alkali and alkaline earth metals as factors 1 and 2 are more significant, but it does start to affect the bond strength for the transition metals, resulting in W having the highest melting point of any metal. Transition metals also have magnetism because they do not share the electrons and therefore they retain their spin.

![Metallic bonding in an alkali metal](image1)

**Figure 5:** Metallic bonding in an alkali metal (1 electron per ion)

![Crystal structure of solid metals](image2)

**Figure 6:** Some crystal structure of solid metals. All metals are crystalline, as opposed to amorphous.
Network Covalent Bonding

In network covalent bonding, there are standard covalent (or polar covalent bonds, but the extend through the bulk of the material and therefore are responsible for determining the melting points. In this case the covalent bonds are inter/intramolecular bonds. A good example of network covalent bonding is diamond.

Figure 7: Diamond is a three dimensional array of sp³ hybridised carbon atoms that form a covalent network.

Exceptions and Other Considerations for Future Thought

It is worth mentioning that there a notable exceptions to the categories of bonding described above. Some compounds do not melt or boil. Instead they decompose. Generally, this means that the covalent bonds within the molecule break (or rearrange) before the intermolecular forces holding the molecules together break.

Graphite is interesting structure in that it combines both network covalent bonding along the 2 dimensional planes and also Van der Vaals bonding between the planes. Polymers are similar with a combination of linear network covalent bonding along the length of the polymer and then some sort of intermolecular bonding between the chains. The type of bonding determined by the substituents on the polymer. For example, DNA has hydrogen bonding and proteins have many different types of bonding that will eventually determine a complex 3 dimensional structure.
Figure 8: Graphite combines both network covalent bonding along the 2 dimensional planes (also electronically conducting) and also Van der Vaals bonding between the planes.

Figure 9: DNA has covalent (and polar covalent) bonding along the backbone and the two chains are held together by hydrogen bonding.
Example Questions

For these pairs of elements or compounds, choose the one likely to have a higher melting point. Briefly justify your answers and *name the specific bonding force* responsible for each.

(a) Ne He

(b) KCl MgO

(c) H-F H-Cl

(d) Na Rb
(a) Ne  He  Ne-. Both elements are non polar so the force responsible for the melting point is LDF. The most important factor in determining the strength of LDF is polarisability and that is directly proportional to size. As Ne is n=2 and He is n=1, Ne is larger than He and therefore has a higher polarisability and therefore the LDF are stronger and therefore the melting point is higher.

(b) KCl  MgO  MgO- The bonding is ionic (the electronegativity difference between K and Cl and Mg and O confirms this). Size wise, there is not a significant difference. K+/Cl- is a 1+/1- interaction and Mg2+/O2- is a 2+/2- interaction so the bond strength is therefore 4 times higher than the KCl. This is more significant than the minor differences in size or electronegativity.

(c) H-F  H-Cl  H-F- The bonding in HF is hydrogen bonding and the bonding in HCl in dipole dipole. Therefore, despite the higher molecular weight of HCl, the HF has the higher melting point.

(d) Na  Rb  Na- the bonding in both cases is metallic. Both have an oxidation state of one, but the Na is smaller than the Rb and therefore the metallic bond is stronger. (The difference in ionization energy is not significant enough to make a difference)