Chapter 8 – Chemical Forces

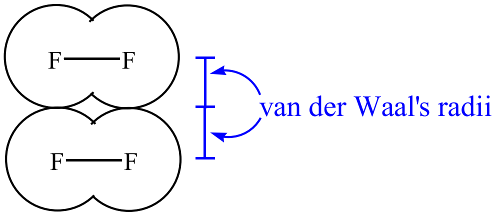
Understanding the relative melting/boiling points of two substances requires an understanding of the forces acting between molecules of those substances. These intermolecular forces are important for many additional reasons. For example, solubility and vapor pressure are governed by intermolecular forces. The same factors that give rise to intermolecular forces (e.g. bond polarity) can also have a profound impact on chemical reactivity.

Chemical Forces

Internuclear Distances and Atomic Radii

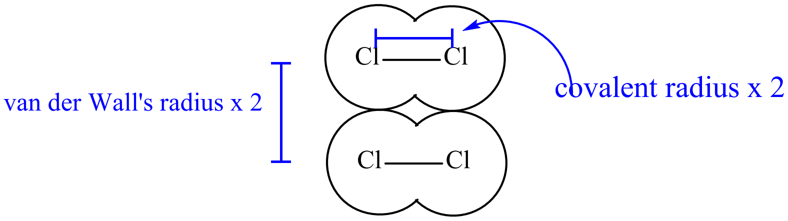
There are four general methods of discussing interatomic distances: van der Waal's, ionic, covalent, and metallic radii. We will discuss the first three in this section. Each has a unique perspective of the nature of the interaction between interacting atoms/ions.

Van der Waal's Radii - half the distance between two nuclei of the same element in the solid state not chemically bonded together (e.g. solid noble gases). In general, the distance of separation between adjacent atoms (not bound together) in the solid state should be the sum of their van der Waal's radii.



Ionic Radii – Ionic radii were discussed in Chapter 4 and you should go back and review that now. One further thing is worth mentioning here. Evidence that bonding really exists and is attractive can be seen in ionic radii. For all simple ionic compounds, the ions attain noble gas configurations (e.g. in NaCl the Na^+ ion is isoelectronic to neon and the Cl^- ion is isoelectronic to argon). For the sodium chloride example just given, van der Waal's radii would predict (Table 8.1, p. 292) a distance of separation of 3.50 Å, while the actual distance is 2.81 Å (*vs*. 2.85 Å predicted by adding ionic radii). This shortening (*ca*. 20%) is evidence for a strong attractive force.

Covalent Radii - half of the distance between two nuclei of the same element singly bonded together. A similar argument for covalent bonding to be net attractive can be made as was done for ionic bonding. For all homonuclear diatomic molecules, the atoms are separated by less than predicted by doubling the van der Waal's radius. For example, chlorine atoms in Cl_2 lie 1.99 Å apart, while van der Waal's radii predict a separation of *ca*. 3.60 Å (a 45% shortening). Read through the bottom of p. 294 (actually ending on the first line of p. 295), but don't worry about the details of how the covalent radii can be estimated.



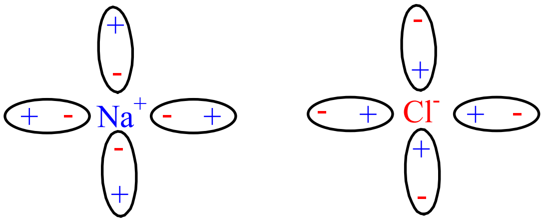
Types of Chemical Forces

Covalent Bonding and Ionic Bonding

Read these sections on your own. They are largely a review of Chapters 5 and 6 and, for that matter, a chapter in your freshman book. One thing that is worth reiterating is that, on average, ionic bonds and covalent bonds are equally strong. It is the nature of the attraction that differs, not the magnitude.

Ion-Dipole Forces

This is the strongest of the non-bonded interactions. It typically occurs when ionic compounds are dissolved in polar solvents. This is usually a salt dissolved in water, but can include organic salts dissolved in polar organic compounds (e.g. $[Et_4N]Br$ in acetone). The negative end of the dipole will be attracted to positive ions and vice-versa. Thus, the polar molecules will align themselves with the

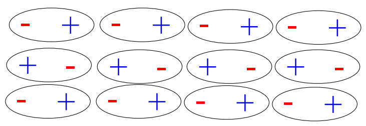


ions to which they are attracted.

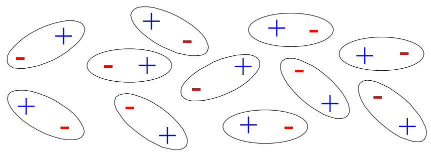
The magnitude of the interaction depends on the ionic charge and the size of the dipole. The size of the interaction is given by $E = -\frac{|Z|\mu e}{4\pi\varepsilon_0 r^2}$ where μ = dipole moment and r = distance of separation between the ion and the molecular (center of the) dipole. Note that ion-dipole forces vary as $1/r^2$ ($E \propto \frac{1}{r^2}$) whereas ion-ion forces vary as 1/r ($E \propto \frac{1}{r}$). Thus, they act over much shorter distances than do ionic bonds.

Dipole-dipole Interactions

Dipoles tend to align with oppositely charged ends directed at each other. These are the next strongest intermolecular force.



solid

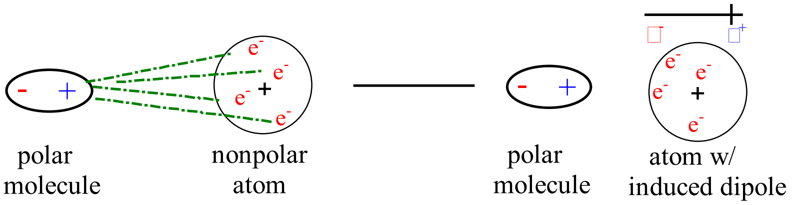


liquid

The first graphic would most accurately portray a solid. In room temperature liquids there is plenty of energy to disrupt these forces; so while the molecules will attempt to align, significant disorder will exist in the liquid phase and frequently the ends of the dipoles with like charges will approach one another. The force of attraction is given by: $E = \frac{-2\mu_1\mu_2}{4\pi\varepsilon_0 r^3}$. Thus, this force starts out weaker than ion-dipole (μ_2 is smaller than Z in the numerator) and weakens even more rapidly as distance increases. Dipole-dipole interactions occur in polar molecular compounds (e.g. acetone and dichloromethane).

Induced Dipole Interactions

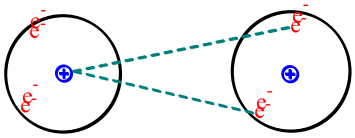
Induced dipole interactions occur when nonpolar molecules are mixed with ions or polar molecules (e.g. dissolving benzene in acetone). The easiest way to think about this interaction is to imagine the nonpolar molecule as a sphere whose electron cloud is distorted by a nearby charge. The electrons on the nonpolar molecule are attracted to the positive end of the dipole (see figure below) and repelled by the negative end of the dipole. The interaction lasts as long as the polar molecule is in close proximity to the nonpolar molecule.



The energy of attraction for an ion to nonpolar molecules is given by: $E = -\frac{Z^2 \alpha e^2}{2r^4}$ and for a polar molecule to a nonpolar molecule by: $E = -\frac{\mu^2 a}{r^6}$ where α is the tendency of the electron cloud on the nonpolar molecules to be distorted. In both cases the forces are quite weak and operate over very short distances. Of the two, the latter interaction is more common (e.g. solvent mixtures).

Instantaneous Dipole-Induced Dipole Interactions

These are sometimes called London dispersion forces and are the forces that act between nonpolar molecules and allow them to be liquefied. London dispersion forces occur when a momentary imbalance in the electron density on an atom or molecule causes a dipole to be established for an instant. The attraction then occurs just like in a dipole-induced dipole interaction. This dipole may then induce a dipole in a neighboring molecule and this can propagate for some distance. It is simplest to show with a small molecule, but as we'll see in the next paragraph, it becomes more significant as molecules become larger. The energy of attraction is $E = -\frac{2\mu\mu}{r^6}$. They operate over the shortest distance of all forces and are usually the weakest.



The strength of the interaction also depends on the polarizability of the nonpolar molecule. Other things being roughly equal, the polarizability of a molecule increases with size; that is, it is easier to distort a large electron cloud than a small one because the electrons in the former are held less tightly. Thus, in large nonpolar molecules (e.g. paraffin) London dispersion forces can become substantial. In general chemistry, you were probably told that London dispersion forces increase with molecular weight. <u>This is not really true</u>. It is true that larger masses will frequently affect physical properties in the same way as do intermolecular forces, but not for the same reason. London dispersion forces are affected by molecular volume, much less so by molecular mass. One example of this is the boiling points of hydrogen isotopes.

	Mass (g/mol)	Boiling point
H_2	2	20 K
D_2	4	23 K
T_2	6	25 K

As you can see, a 3-fold increase in mass results in only a 5 degree (25%) increase in boiling point. Similarly, for the series of compounds:

Compound	Melting point	Boiling point
CH_4	-182 ºC	-164 ºC
CF_4	-150 ºC	-130 ºC
CCl_4	-23 ºC	76 ºC

CF_4 which is only slightly larger than CH_4, but is 5.5 times heavier, has melting and boiling points very similar to methane but far different from CCl_4 which is only 1.75 times heavier than CF_4.

<u>Repulsive Forces</u>

These are the forces that keep two molecules from collapsing to a point. They are nuclear-nuclear and core electron repulsions. The repulsive energy is given by $E = k/r^n$ (n = 12 frequently).

Hydrogen Bonding

This is a special bonding case that lies somewhere between dipole-dipole interactions and covalent bonding. It occurs when a hydrogen atom is bound to some very electronegative, small atom (F, O, N), although it does extend in significantly weakened fashion to a couple of second row elements (Cl and S). For this situation, the hydrogen atom may create a very strong interaction with a neighboring very electronegative, small atom. Physical evidence for hydrogen bonding comes from X-ray crystallography. You would expect that one element-to-H bond would be of standard length, while the other would roughly equal the sum of their van der Waal's radii (i.e. a standard nonbonded interaction). In molecules where hydrogen bonding occurs, the latter bond will be considerably shorter than expected. In some extreme cases where the hydrogen atom binds to two atoms of the same element, the bonds may be of equal lengths. Hydrogen bonds in nonionic situations can have energies on the order of 50 kJ/mol (compare to the C-H single bond = 400 kJ/mol). One way they are manifested is in higher melting points (e.g. H_2O = 0 ºC, H_2S = -85 ºC, H_2Se = -60 ºC, H_2Te = -49 ºC).

Hydrates and Clathrates

We'll briefly discuss one aspect of this section. Beginning (i.e. first year) students are frequently confused by the existence of hydrates. The compounds are usually written as $M_xX_y{\bullet}zH_2O$ and little to no information is provided about what role the water molecules play in its composition. Towards the end of general chemistry one learns about coordination compounds and that explains the role of much of the water molecules in these compounds, but not all. As you learned earlier, simple crystal lattice packing patterns involve packing anions in a closest packed array and filling in the tetrahedral and octahedral holes with cations (p. 8 & 9 of Chapter 4 notes). If the cations aren't small enough for the holes, the lattice has to expand to accommodate them and this may create gaps in the lattice. Solvent molecules (in this case water) can fill in the empty space and these molecules are lattice solvates (or hydrates for the case of water). Unlike coordinated water molecules, these do not bind in any way to the lattice host molecules, the water simply occupies holes in the structure.

Effects of Chemical Forces

Melting and Boiling Points

The forces we have just discussed are responsible for many of the bulk properties of a material. How strongly molecules are held together may be inferred from their melting points and boiling points. Molecular substances tend to have low melting and boiling points. Note that both rise as the molecules get larger. This is predicted by the description of London dispersion forces. Also, larger molecules with polar bonds may have higher than expected mp/bp.

High symmetry also raises melting points because more stable lattices are generated. E.g., neopentane (CMe_4) melts at -16 ºC *vs*. -130 ºC for *n*-pentane. Other things being equal, more symmetrical molecules will have higher melting points because they pack more efficiently meaning they have higher lattice energies. For this reason, the effect on boiling points is typically much smaller.

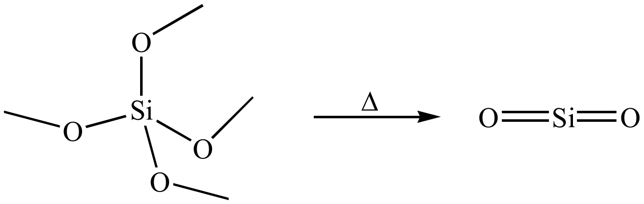
High symmetry helps to explain a curious feature in chemistry, sublimation. That a material should go from solid to liquid to gas as the temperature increases is intuitive. That it skips directly from the solid phase to gas phase surprises most people, and not without good reason. We think of a solid as a collection of molecules locked into fixed positions, largely unable to move except for bond vibrations. The addition of heat causes molecules to wiggle in place until they break out of their lattice slot and begin to slide past one another. This is melting. Eventually, enough energy is added that intermolecular forces are completely overcome and the molecule breaks into the gas phase.

So why does sublimation occur? High symmetry allows more efficient packing that, in turn, raises melting points (greater lattice energy) relative to similar, less symmetrical substances. Also, highly symmetrical molecules will generally have a much greater ability to rotate in the solid phase without disturbing their neighbors than will low symmetry molecules. Thus, molecules are able to effectively store thermal energy by spinning in place until they can break directly into the gas phase. Consider CO_2, which is linear and highly symmetrical ($D_{\infty h}$). Unlike less symmetrical molecules of comparable size (e.g. H_2O), thermal energy can cause CO_2 to rotate around its C_∞ axis without disrupting the lattice. Even at high rates of rotation, the lattice remains reasonably undisturbed until individual CO_2 molecules go directly into the gas phase.

As was discussed briefly earlier in the notes, fluoro- compounds have unusually low mp/bps because the electron clouds on fluorine are difficult to polarize.

	mp
SiF_4	-90°
PF_5	-83°
SF_6	-50°

In general, melting and boiling points will increase as the strengths of the intermolecular forces increase. The highest temperatures are required for ionic and covalent network lattices. A word of caution here: A common misconception is that if a molecule possesses covalent bonds, it will have a high melting point. This is <u>not</u> true if the bonds are internal to the molecule. That is, hexane has a low melting point because the only attraction to an adjacent hexane molecule is caused by London dispersion forces. In contrast, diamond has a very high melting point because there is a lattice in which each C atom is connected to four other C atoms. To melt it, these C-C bonds must be broken. Quartz has a structure as shown in the figure below (each oxygen atom is bound to two silicon atoms). On melting, the giant lattice is broken into smaller sublattices, each containing many of the units shown in the figure. For this reason, the melting point exceeds 1700 ºC (ultimately when the quartz "boils," SiO_2 forms). The high temperature is required because strong Si-O σ-bonds are replaced by weak Si=O π-bonds and that requires a great deal of energy.



Ionic compounds exhibit a wide range of melting points. We already talked about this when discussing Fajan's rules in Chapter 4 (page 131). As cations become more polarizing (smaller/more positive) and anions become more polarizable (larger/more negative) melting points and boiling points decrease. This is because strong lattices have uniform charge distribution. As ions are polarized, bonding becomes directional. That is, some interactions strengthen while others weaken. These weakened interactions are easier to disrupt or melt. Remember the localized, asymmetric charge distribution caused by polarization is an instantaneous disruption that has only a fleeting existence. Look at Table 8.6 and 8.7 on pp 309-310. See how halide salt melting points and boiling points decrease as anions gets larger. Silver compounds are lower than potassium because silver is comparably good at polarizing anions. The sodium values are anomalously high showing that other factors are present. Table 8.7 shows cation effects.

Solubility

You have likely heard the familiar adage "like dissolves like." We will now examine why this is true. The simpler case is the dissolving of nonpolar substrates in nonpolar solvents. In both cases London dispersion forces operate, so the interactions are likely to be small for each and about equal in magnitude. Therefore, $\Delta H_{mix} \approx 0$. Thus, the mixing of nonpolar solvents is entropy driven ($T\Delta S \approx -1\frac{1}{2}$ kJ/mol). This term is fairly small, but is enough to allow mixing to occur.

Why don't nonpolar and very polar substances mix? Let's assume London dispersion forces in each are comparable. The dipole-dipole interaction in the polar molecule will be much stronger than the London dispersion forces. Thus, the energy released from a polar-polar interaction will be much more negative (favorable) than the nonpolar-polar induced dipole interaction. Therefore, more energy is released by having the polar molecules aggregate and exclude the nonpolar molecules (into a second layer) than by allowing complete mixing.

What about dissolving salts in a polar liquid? From the previous two examples, either solvent-salt interactions will be equal in energy to solvent-solvent and ion-ion interactions and dissolution will be entropy driven or the ion-solvent interactions will be stronger than the solvent-solvent/ion-ion interactions and the process will be enthalpy driven. As it happens, entropy is usually not a major factor in determining if a salt dissolves.

For a salt to dissolve, solvation energy must be more negative (favorable) than lattice energy. This can happen because each ion will be solvated by several solvent molecules. Although ion-dipole forces are weaker than ion-ion forces, they are stronger than the dipole-dipole forces in the solvent. Each ion is solvated by several solvent molecules and this may override the strength of the lattice. For salts with highly charged anions or cations, the lattice energy will increase more rapidly than solvation energy which is why salts with highly charged ions frequently have lower solubilities.

In rare cases, the lattice energy is ever so slightly more stable than the solvation energy. In these cases, dissolution is entropy driven and the salts form cold solutions when they dissolve.

Finally, salts composed of ions of very different sizes tend to have much higher solubilities than those of similar sizes. Ions of similar sizes pack more efficiently and minimize anion-anion repulsions. This generates more stable crystals (higher lattice energies) and correspondingly lower solubilities.

August 18, 2025