Chapter 5 – Which Sections for the Exam?

Chapter 5: You need to know all of sections 1-8. We are skipping sections 9-16. Realize that in the future, you might take the MCAT and have to know some things from sections 9-16. We will all live in hopes that there are very few such questions on the MCAT.

Carry over from previous chapters

In order to understand the discussion about dipoles and partial charges, you MUST know what those are and what polarity is. Chapter 3 introduced this concept. You should also still know your periodic table trends – especially size and electronegativity.

Why molecules stick

If molecules had no sticking power, all substances would be gases. There would be no condensed phases of solid or liquid. Well thank goodness there ARE forces of attraction (the sticky) *between* molecules. These forces are called intermolecular forces. They are also known as Van der Waal's forces. These are the forces that we are most concerned with in chapter 5. These are also the forces that govern various physical properties such as boiling point, melting point, heat of fusion, heat of vaporization, surface tension, viscosity, etc… I'll come back to this after I remind you of the forces of attraction that we have all ready covered quite extensively.

Intramolecular forces are the forces of attraction *within* molecules and are simply the bonds that hold the atoms together to make the molecule in the first place. Realize that intermolecular forces are much much less than intramolecular forces. At least 10 times less and possibly 1000 times less depending on what you are comparing. Looking back to chapter 2 you can see how strong an intramolecular force (covalent bonding) really is. Check out Table 2.3 on page 75 to see numerous bond dissociation energies. Those are the amounts of energy that would be required to pull those bonds apart. The lowest value on that table is 157 kJ/mol and goes up to 837 kJ/mol. Also on page 75 is Table 2.2 which has a carbon-oxygen triple bond at 1062 kJ/mol. Realize that is just a sampling of all the possible covalent bond strengths, but you need to have an idea of where all those strength are on the energy scale – I'd ballpark figure these at around 400 kJ/mol. Now let's get back to the main topic here.

Intermolecular forces: All intermolecular forces are governed by charges attracting or repulsing one another. Heck, pretty much everything chemically speaking can be traced back to this fundamental interaction of charges. Bearing that in mind, it is still not just a simple case of positive attracts negative. We want to *quantify* the amount of attraction/repulsion so that we can better understand and predict the properties that are a result of these intermolecular interactions.

Ion-Ion interaction: I really hate putting this down as a true inter*molecular* force. It is certainly a great force – just as strong and as powerful as the intramolecular forces of covalent bonds. Ion-ion interaction IS the reason we have ionic compounds. All ionic compounds are solids because of this great big pull that cations have on anions (and vice versa). Ion-ion interaction is what gives us the large values for the crystal lattice energy of salts (i.e. ionic compounds). The potential energy (E_P) of this interaction is

$$E_P \propto \frac{z_1 z_2}{r}$$

Where z_1 and z_2 are the charges on the two ions and r is the distance between them. It's worth noting that when oppositely charged ions are involved (positive/negative), the potential energy is lowered (negative values). Positive (higher) potential results when like charges come together. Also, when highly charged ions come together (like +3 and -2) you can get lattice energies well over 10,000 kJ/mol.

Ion-dipole interaction: You got half of the strong interaction of ion-ion but you've lost the other half to a mere dipole. Dipoles truly deserve the word *partial* in partial charge. Only a little bit of charge is there - a little positive (δ^+) and a little negative (δ^-). Although there is variability in the amounts of these charges (think electronegativity scale), they are still piddly little compared to full-blown charge found in cations and anions. The potential energy will be less negative now:

$$E_P \propto -\frac{|z|\mu}{r^2}$$

Where μ is the dipole strength. These forces are not influential until the distance is considerably small – note the $1/r^2$ dependence.

Dipole-dipole interaction: We now knock down the strength of the interaction even more. Dipole-dipole interaction is

$$E_P \propto -\frac{\mu_1 \mu_2}{r^3}$$

Where μ is the dipole strength. Now the distance dependence is $1/r^3$. And this is only if the molecules are relatively stationary like in a liquid or solid. In a gas the dipole-dipole interaction is reduced further due to fast rotation of the molecule. This effectively "blurs" the partial charges to even smaller values and the resulting potential energy interaction is

$$E_P \propto -\frac{\mu_1^2 \mu_2^2}{r^6}$$

This leads to extremely small forces of attraction. So small that for gases, they can essentially be ignored – which is what you do in the kinetic molecular theory of ideal gases, where you assume that only kinetic energy is the major player in terms of the energy of the gas.

London (Dispersion) Forces: Sometimes the word "dispersion" is not there, and sometimes the word "London" is not there. Sometimes the term Van der Waal's Forces are (mistakingly) used to describe only these particular forces. The fact is that London forces are present in ALL molecules. The roll they play (whether major or minor) is what we must consider. These forces are the major force for all non-polar molecules. All substances CAN be liquefied and therefore they ALL have some degree of attractive forces within them. The potential energy for London forces is

$$E_P \propto -\frac{\alpha_1 \alpha_2}{r^6}$$

Where α is the polarizability of the molecules. We first encountered polarizability in section 2.14 in your book. That discussion was limited to atoms and ions. You must expand that rationale to molecules. The larger the molecule, the more polarizable and therefore, the greater the London forces. Another attractive force like this one is the dipole-induced dipole. This is the result when a non-polar (no permanent dipole) molecule can be induced to have a dipole. It doesn't matter if it is induced by a real (permanent) dipole from a polar molecule or whether by a momentary dipole from a non-polar molecule. Once set-up, the partial charges in the dipoles do cause attractions. These attractions are reinforced, the bigger the molecule happens to be.

H-bonding: When a H atom is covalently bonded to a N, O, or F atom, a very polar bond is formed. So polar is the bond that the H atom is almost stripped completely of its electrons. To the outside world (just outside that molecule mind you) that H atom looks almost like a bare proton. It carries a very large partial positive charge – more so than any other partial positive that you might encounter. This H will then act like a magnet for the lone pairs of electrons on its neighboring molecules. In particular, it goes after the lone pairs on the other H-bonded N's , O's , and F's. The interaction is strong enough to get it the name H-bonding. Bear in mind that the interaction is NOT a covalent bond, but it is about 10% of the strength of a covalent bond and that is why it gets that name.

Get that Intermolecular Feeling...

Now that we've got all those different types of interactions down lets look at Table 5.1 (p 162) and get a feel for the actual amounts of energy involved. Look at it and realize that those are approximate values. At the end of this review sheet is a figure that I created which has more of a range for each type of interaction. Take a look at my figure and try to get a good mental picture of all these interactions and their relative values. Are you feeling it? I knew you could.

I must remind you that although dispersion forces are the weakest of all the forces, that is just per single interaction. Real molecules have real shapes, volumes, and sizes. Those little interactions can certainly add up to a substantial amount of force. It is for this reason that most substances are solids once you get a big enough molecule. The dispersion forces are quite impressive in great numbers.

Put it all together now.

You now know the forces that hold substances together. You also know the relative strengths of those forces. So now you should be able to predict some relative outcomes of physical properties DUE to those forces.

So read the book and your notes (and any other reference you want) and KNOW how the following properties are affected by intermolecular forces.

viscosity   surface tension   capillary action

meniscus (covex or concave?)

We also discussed in class
vapor pressure   heat of fusion

heat of vaporization

Think about what the property does when forces get bigger and smaller. How does temperature affect these forces? BTW, nobody should miss how temperature affects these forces. You DO know right? The hotter you get something, the more likely you are to evaporate or melt it, right? The end result of constant heating is to vaporize everything into gas state – which happens to be the state where ALL these forces of attraction are so RELATIVELY weak that they can be ignored. The thermal motion brought on by heat will eventually overcome any "sticking power" that is present. More heat, less stick, less stick, less likely to be a solid or liquid and MORE likely to become a gas. See, that wasn't too hard was it. Hopefully this makes perfectly logical sense to you. And the truer that previous sentence becomes, the better your understanding will be of the material.

Adhesive vs Cohesive Forces

Adhesive forces are the forces of attraction between a liquid and a surface (think water-to-glass). **Cohesive forces** are the forces of attraction between a liquid and itself (think water-to-water). Both of these forces are actually rooted in the same intermolecular forces that we have already discussed. When the adhesive forces are greater than the cohesive forces, a liquid will tend to try and wet the surface. The liquid will MAXIMIZE attractive forces by maximizing the contact with the surface (see NOTE below). This is what happens with water on glass. The water tends to "crawl up" the side of a glass wall and maximize contact.

If you have a LARGE glass container, you hardly notice the water that has crawled up the wall. Overall, the water does look pretty flat. However, if you force the surface area of the water to be smaller and smaller by shrinking the diameter of the glass container, you will start to SEE this crawling up AND the surface will start to look concave. This new spherical shape on the surface is called a meniscus. The fact that there is a meniscus has everything to do with surface tension also. If you have no surface tension (or close to none), you will have no meniscus.

concave   **convex**
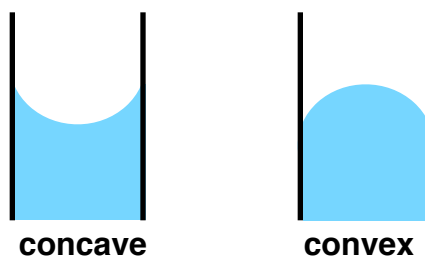
Standard Read the Book Part

Once again I'm asking you to READ. Yes, read your book. You must read over and over to get things straight. Read everything in context. If our book is not getting through to you, go to the chemistry library and read another one.

Standard Disclaimer: Any mistakes on this review sheet are NOT intentional. You should crosscheck all stated information. You should double check your book too (see errata).

NOTE: Anytime we MAXIMIZE attractive forces we are in effect MINIMIZING the potential energy of the substance. So this is yet another way that matter tends to find its way into lower energy states. We will discover in Chapter 7 that it is really the 2nd Law of Thermodynamics which governs all spontaneous processes. Entropy is the ultimate factor when nature picks a course of action. For 95% of what we study, lowering the potential energy of a system will readily increase the entropy of the universe. I didn't say always! – there's that other 5%, remember?

Intermolecular Forces
(forces *between* molecules)

Intramolecular Forces
(forces *within* molecules)

WEAK   MODERATE   STRONG   VERY STRONG

0   2   5   10   20   100   400   1000 *

←dispersion→   ← H-bonding→   ─── ion-ion ───

← dipole-dipole →← ion-dipole →   ─── covalent bonds ───

ZERO attraction is only possible with IDEAL GASES.   * units are in kJ/mol of interactions