Dr. McCord **Spring 2010**

CHAPTER 5
Exam 3 Review Topics

Chapter 5 – Which Sections for the Exam?

Chapter 5: All sections except sections 5.11 and 5.12 were covered. Section 12 is an interesting section on atmospheric chemistry but we will not cover it. Also sections 6-9 have lots of technical proofs that will NOT be on the exam. Let me point you to the KEY parts of those sections. Note the 2 boxed formulas, one for kinetic energy and the other for rms particle velocity. Also, LOOK at the plot of a Maxwell-Boltzmann distribution and how the curve shifts with temperature (Figure 5.16). Know your definitions of effusion and diffusion plus the boxed equations relating velocity (rate) and mass and temperature (all of this is ON this review sheet too).

Fundamentals

Know how to calculate molar mass. Know your nomenclature (still). Be able to calculate amounts of reactants or products when given amounts of reactant or products – this is called stoichiometry – KNOW IT. See chapters 1-3 Know how to determine the limiting reactant and how much product it leads to. Be able to incorporate percent yield into a problem if necessary. All that is new is moles to P or V instead of grams.

How to measure pressure

Know the basics of how a manometer works and how a barometer works. Know how to calculate the pressure due to a standing column of liquid:

$$P = dgh \qquad \text{or} \qquad P = \rho gh$$

d and ρ (rho) are density. Watch your units here. Pressure will be in Pascals if you use kg/m^3 for density, and m for height. If the column is mercury, just get the height in mm and you've now got torr.

Gas Laws

Know the NAMES and the law associated with each name (scientist).

Boyle's Law: Pressure is inversely proportional to volume (assuming constant temperature and amount of gas, moles). Any units will work here.

$$P \propto 1/V \qquad P_1V_1 = P_2V_2 = \text{constant}$$

Charles' Law: Volume is directly proportional to *absolute* temperature (assuming constant pressure and amount of gas, moles). Any units for volume but remember, T must be Kelvin.

$$V \propto T \qquad \frac{V_1}{T_1} = \frac{V_2}{T_2} = \text{constant}$$

Avogadro's Law: Volume is directly proportional to amount of gas in moles. (assuming constant temperature and pressure).

$$V \propto n \qquad \frac{V_1}{n_1} = \frac{V_2}{n_2} = \text{constant}$$

Combined Gas Law: Most books and people refer to this as Boyle's Law + Charles' Law which is

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad \text{(assuming constant } n\text{)}$$

However, our book throw's in Avogadro's Law also giving:

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2} = \text{constant}$$

which is fine, except that this is really just the

Ideal Gas Law in disguise. The constant that is defined by this version of the combined gas law is the Universal Gas constant, R. So by definition:

$$R = \frac{PV}{nT} \quad \text{which rearranges to give}$$

$$PV = nRT$$

which is the **Ideal Gas Law** we all know and love. When you use the ideal gas law be sure and use the right units on P, V, n, and T. You have no choice on n and T, they must be in moles and Kelvin. Now you've got choices for units on P and V and THAT's why we've got different values (OK, mostly different) of R listed in the book. Here are my favorites (feel free to find one as your favorite):

$R = 0.08206 \ \frac{\text{L·atm}}{\text{mol·K}}$ the old trusty L·atm one

$R = 8.314 \ \frac{\text{kPa·L}}{\text{mol·K}}$ or $\frac{\text{Pa}\cdot\text{m}^3}{\text{mol}\cdot\text{K}}$ the SI unit one

$R = 62.36 \ \frac{\text{L·torr}}{\text{mol·K}}$ you gotta like torr

You might notice that these all just differ by the unit factors for pressure conversions. Like

$$0.08206 \times 760 = 62.36$$

See, it's not so bad. But I know what you're thinking. Do I (state your name) need to memorize all those values of R? Why not? Drop that value of R into your next conversation and watch your popularity skyrocket. Oh well, I will still print those values on the cover sheet to the exam for you to refer to while your brain is slowly melting during the exam.

Kinetic Molecular Theory of Gases

I need to put this on this review sheet - I haven't yet though. So READ section 5.6 - especially that green boxed listing of bulleted points. If I get around to updating this review sheet you'll see KMT here.

STP vs SATP

A standard is whatever you chose as standard. Sometimes we chose different standards – and yes, I think that defeats the point in the first place but there you go. Know the difference in STP and SATP:

STP: 0˚C and 1 atm (old school, most of our problems)

SATP: 25˚C and 1 bar (new school, newer problems although some still have atm as the pressure unit)

Realize that you WILL need to convert ˚C into Kelvin. Also, due to the confusing nature of these standards, I WILL put the definitions on the front of the exam.

Let's MIX it up a bit

All those laws are great and work really well for most gases at reasonable pressures and temperatures. You can even apply those laws to mixtures of gases and just treat the whole mix as one big family of gas - that is you COUNT ALL the moles regardless of the type. When you do this you are calculating TOTAL pressure due to ALL the gases present. After you do that, I'm still going to want to know what the pressure is for each individual gas. The pressure exerted by say helium in a mixture of helium, neon, and xenon is the partial pressure of helium, P_{He}. Now the big lesson (and name!),

Dalton's Law of Partial Pressures: The total pressure of a system is equal to the sum of all the partial pressures within the system. Mathematically:

$$P_{\mathrm{total}} = P_{\mathrm{A}} + P_{\mathrm{B}} + P_{\mathrm{C}} + \ldots$$

Now also realize that each of those partial pressures will have it's own version of the ideal gas law. What I mean is that $P_{\mathrm{A}}V = n_{\mathrm{A}}RT$. See, I'm only counting moles of A in this equation and I therefore get out P_{A}. One of the other neat results of this law is that the partial pressure's ratio to the total pressure exactly matches its mole fraction. Uh-oh, what's a mole fraction? The number of moles of A divided by the total moles of gas in the mixture. Mole fraction of A is given by the symbol x_{A} (OK, so it's χ_{A} in the book – much too greek for me). So by definition:

$$x_{\mathrm{A}} = \frac{\text{mol A}}{\text{mol A} + \text{mol B} + \text{mol C} + \ldots}$$

and you can set that equal to the pressure ratios:

$$x_{\mathrm{A}} = \frac{P_{\mathrm{A}}}{P_{\mathrm{total}}} \quad \text{and therefore} \quad P_{\mathrm{A}} = x_{\mathrm{A}} P_{\mathrm{total}}$$

So you can use pressures to get mole fractions OR use mole fractions to get pressures. Cool.

The confusion on effusion

Effusion of a gas is when a gas slips through a very small hole (or holes) from a high pressure to a low pressure. This IS what is going on when your once large and buoyant helium balloon (fun) is now much smaller and is now riding around on the floor (not as fun). Helium effuses through the pores of the latex balloon. How fast does the helium effuse? Graham knows.

Graham's Law of Effusion: At constant temperature, the rate of effusion of a gas is inversely proportional to the square root of its molar mass.

$$\text{rate of effusion} \propto 1/\sqrt{M}$$

and so if you compare two gases at the same temperature you'll get

$$\frac{\text{rate of effusion of A}}{\text{rate of effusion of B}} = \sqrt{\frac{M_{\mathrm{B}}}{M_{\mathrm{A}}}}$$

The same exact relation works for average speed also.

Temperature has the same square root dependence, but it is directly proportional to the rate of effusion or speed. For a given molar mass at two differents temperatures:

$$\frac{\text{rate of effusion (or speed) at } T_2}{\text{rate of effusion (or speed) at } T_1} = \sqrt{\frac{T_2}{T_1}}$$

You can now combine the two affects of mass and temperature and get

$$\text{rate of effusion (or speed)} \propto \sqrt{\frac{T}{M}}$$

This can be set to an equality with a little work. YOU, however do not need to worry about that work and just look at the final equation:

$$v_{\mathrm{rms}} = \left(\frac{3RT}{M}\right)^{1/2}$$

Where v_{rms} is the root mean square speed.

You don't know how it feels – to be me

Ah yes, Tom Petty sang it so well and he never realized just how much all the real gases love that song. How DOES it feel to be real? Well for starters, you've got a real volume yourOWNself. Real gas molecules DO have real diameters and take up space – ideal gases do NOT have a real diameter – they are just a point in space. Speaking of point, Tom Petty says in the same song, "let's get to the point…" See he was talking about ideal gases right? Actually, now that I think about it, and sing the rest of that chorus… he's talking about a whole other gas. But WAIT! Yes, he IS talking about real gases now that I think about it! Another line, "… think of me what you will, I've got a little space to fill". SEE? That's what gases do – fill space. I digress.

A great way to show non-ideality is too calculate a gases actual (real) molar volume, V_{m}, and compare it to the molar volume of an ideal gas, $V_{\text{m}}^{\text{ideal}}$. When compared as a ratio, you get the **compression factor, *Z***.

$Z = \dfrac{V_{\text{real}}}{V_{\text{ideal}}}$ which also equals $\dfrac{PV_{\text{real}}}{nRT}$ which

is plotted vs pressure in your book in Figure 5.22. You book doesn't call it Z but that is what it is. An ideal gas will have Z = 1 under ALL conditions. Real gases have real forces at play. A value of $Z < 1$ corresponds to attractive forces being dominant. A value of $Z > 1$ corresponds to repulsive forces being dominant. Note that as zero pressure is approached, all real gases take on ideal behavior (Z = 1). Real gases aren't that far off the line at 1 atm either, which is why the ideal gas law works so well most of the time.

How to improve on an already IDEAL equation?

It is possible to come up with an equation that attempts to include the effects of attractions and repulsions between the gas particles. It does not predict the exact behavior of a real gas, but it comes closer. The main problem is that you must PICK the real gas you want the "law" to work for. All gases are NOT the same in the real world of gases, especially at high pressures and low temperatures – that is where the ideal gas law is at it's worst.

The van der Waals equation:

$$\left(P + a\frac{n^2}{V^2}\right)(V - nb) = nRT$$

Now we've got a fixed up equation that has added two new paramaters. One to deal with attractions (a),and one to deal with replusions (b). These are the van der Waals parameters and they are NOT temperature dependent – yea! You DO need to look up the values for a and b for every gas you want to work with though. The parameter a is an "adjustment" for attractive forces between molecules. The bigger a is, the smaller the pressure will be. The parameter b is like a volume correction term – it is roughly the volume of a mole of condensed gas. It essentially accounts for the repulsions between the gas particles.

Life's a Gas – now you know more about it.

Yes, read your book. Try some of those problems in the back of the chapter. You'll feel so GOOD about yourself.

Chapter 16 – Which Sections for the Exam?

Chapter 16: You need to know only the first part of the chapter on intermolecular forces - this is sections 1 and 2. We are not covering all the crystal structure material which are sections 3-9. We also covered bits of section 10. In particular, we covered the concept of vapor pressure and how intermolecular forces affect it. Plus, some of the section on changes of state. Refer to your notes. You should note that the material for sections 1 and 2 was covered more thoroughly in class (and on this review sheet).

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. 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 15. These are also the forces that govern various physical properties such as boiling point, melting point, 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. On average, intermolecular forces are 100 times less depending on what you are comparing. Looking back to Chapter 13 you can see how strong an intramolecular force (covalent bonding) really is. Check out Table 13.6 on page 608 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 149 kJ/mol and goes up to 1072 kJ/mol for a carbon-oxygen triple bond. Realize that is just a sampling of all the possible covalent bond strengths, but you need to have an idea of where all those strengths are on the energy scale and what their average is. Let's put the average 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.

What's in a name?
When its Van der Waals, its a lot.

Intermolecular Forces have historically also been called Van der Waal forces which is really the correct interpretation - meaning it covers all the forces between molecules. However, be warned, many books (and questions) equate Van der Waal forces with ONLY dispersion forces. Check out Wikipedia for Van der Waals forces - you'll see there under the definition section that the term can be meant one way or another. Best to know the authors intent as they say. Unfortunately our history is steeped in tradition and the term on *Quest* usually refers to just dispersion forces. We'll try to stick with this concept on the exam. In other classes (biology, etc...) you might have to adjust your thinking on this term.

Quantifying Molecular Interaction

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 (actually can be stronger). However, cations and anions combine to make *ionic* compounds or salts which are technically NOT molecules so the whole "molecular" term doesn't really fit. None-the-less, 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. The potential energy (E_P) of this interaction is

$$E_\mathrm{P} \propto \frac{q_1 q_2}{r}$$

Where q_1 and q_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) due to the attractive forces. Positive potentials results when like charges come together (repulsions). Also, when highly charged ions come together (like +3 and -2) you can get lattice energies well over 10,000 kJ/mol.

Dipole-dipole interaction: We now knock down the strength of the positive/negative interaction by a considerable amount. Now we use partial positive and partial negative as our "sticking points". 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. This interaction in equation form is shown as

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

Where μ is the dipole strength. Notice that the distance dependence is $1/r^3$. From distance alone this puts the force at about 1% of ion-ion attraction. Most "regular" dipole-dipole potential energies have averages around 4 to 5 kJ/mol of interactions. I say "regular" because I must contrast this to H-bonding which is just a stronger version of the same thing. Also remember that these dipoles are *permanent* dipoles and are at the heart of polar substances.

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 an actual covalent bond, but it is about 10% of the strength of a covalent bond and that is why it gets that name. If a typical H-bond dipole is double a "regular" dipole, then you can see how the result from the equation above would be about 4 times the E_P value. For this reason, the average H-bond interaction has a potential energy of around 20 kJ/mol of interactions. Water is up around 36 kJ/mol. Note that H-bonding doesn't have a different equation than dipole-dipole. They are both the same equation - it's just that the dipoles are considerably bigger for H-bond type substances.

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, polar AND non-polar. The roll they play (whether major or minor) is what we must consider. These forces are the ONLY 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 dispersion forces is

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

Where α is the polarizability of the molecules. The polarizability quantifies the tendency of a collection of charges (like the electrons in a molecule) to become distorted by an applied electric field (like a nearby charge or dipole). The larger the molecule, the more polarizable and therefore, the greater the London forces. For atomic systems, the higher the atomic number the larger the polarizability and thus the London force. This is because the more electrons there are the more they start to populate the larger atomic orbitals. The further out an electron is from the nucleus the easier it can be influenced and moved by another source. Once the charge is shifted you get a *temporary* dipole - there one minute, gone the next (or should I say femtosecond?).

Once you have the temporary dipole, you can have in participate in a 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 temporary 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.

Now if we only look at that the $1/r^6$ part of that equation we can certainly see why dispersion forces are the smallest of all intermolecular forces. At the same distances, a dispersion interaction can be 1000 to 10000 times less than ion-ion interactions. That is so small, that if there is no appreciable polarizability (α), then the substance is most likely a gas at normal temperatures (case in point : all the noble gases). So by taking into account distance (r) and typical α's we find the typical molecule to have about 2 kJ/mol for this interaction - certainly the smallest of our three intermolecular forces. But hey! That 2 kJ/mol average is a "loaded" average for a "typical" molecule. What exactly IS a typical molecule? That's a loaded question if ever there was one. Let's try this in a different way, read on...

Relatively small molecules are going to have very small amounts of dispersion forces present. As a matter of fact, very small molecules will almost always be gases because of this. Water is one of those rare small molecules that has enough "pull" to become a liquid at room temperature thanks to H-bonding between the molecules. As molecules get larger (careful, larger in size doesn't always mean mass - remember your trends), polarizability increases and dispersion forces start playing a larger role in the cohesiveness (see cohesive forces later in this review) of a substance. Two molecules could have the same mass and make-up (isomers) and the one with the largest surface area will have the largest dispersion forces. Increasing surface area will increase the number of electrons available for polarization and therefore increase the forces in between.

Ion-dipole interaction: You got half of the strong interaction of ion-ion but you've lost the other half to a mere dipole. The equation you get is a combination of the ion-ion one and the dipole-dipole one.

$$E_{\mathrm{P}} \propto -\frac{|q|\mu}{r^2}$$

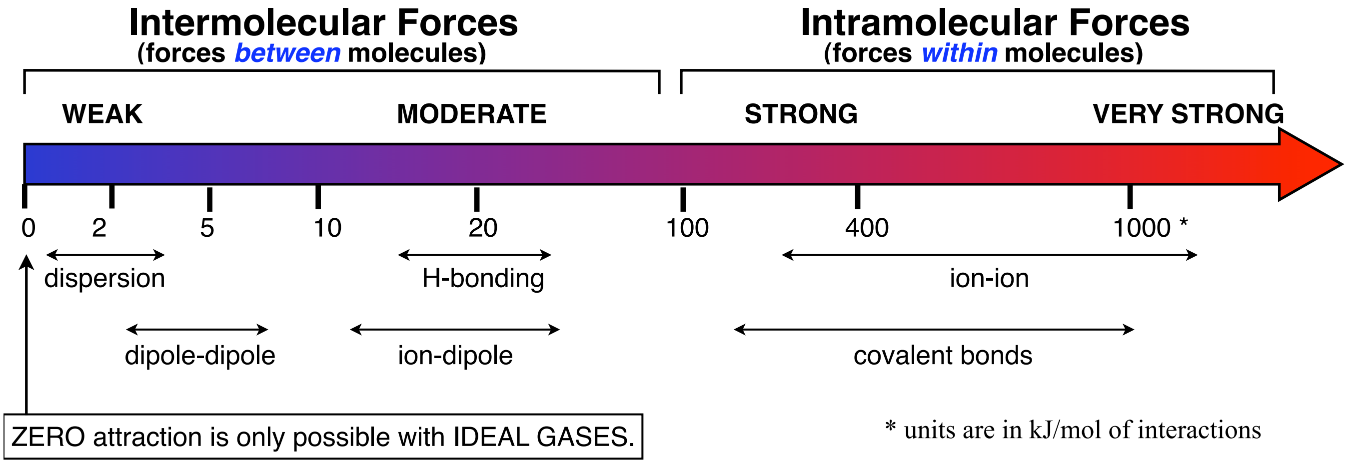
Where q is the charge on the ion (+ or – doesn't matter) and μ is the dipole strength. Note the $1/r^2$ dependence - this pulls this force up into the same league as H-bonding and a little extra (depends on the ion). It's a little misleading also in that you must have both ions and dipoles for this to exist. You get it 2 ways: (1) Dissolve a salt into water and you've got ions swimming amidst dipoles. (2) Or you can have a salt (ions) that "pulls" some polar molecule (dipole, probably water) into its crystal lattice. This is precisely what happens with "hydrate" salts. If you have an ion with a high charge density (charge/size), it will greatly attract water molecules via this interaction. So much so that the salt will form with water molecules in the salt. Sodium carbonate has a Na^+ ion which is small enough to pull in a water - actually 10 waters. The new formula is $Na_2CO_3 \cdot 10H_2O$. That is sodium carbonate decahydrate. The waters of hydration are shown separately from the salt but attached via the dot. Realize that dot is just an attachment and NOT a multiplication. $CuSO_4 \cdot 5H_2O$ is another example of a hydrated salt. These waters are strongly attached and can only be driven off via high temperatures (much more than 100°C). Remember, the higher the charge, the more likely this will happen - most +2 and +3 cations will pull in waters. Li^+ and Na^+ are the only +1 cations that are small enough to still pull in the water, all the other group 1A cations do not form hydrates.

Get that Intermolecular Feeling...

Now that we've got all those different types of interactions down lets look at the figure at the end of this review sheet and get a feel for the actual amounts of energy involved. Look at it and realize that those are approximate values. 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.

Do realize in the following diagram that dispersion forces are capable of much more when the molecule (or atom) containing them increases in size. Polarizability will increase considerably with a molecule's surface area (size). One should always access what the conditions are as to which force is the governing force and what its magnitude is.



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?) **melting point**

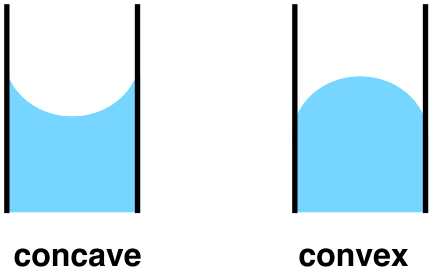
vapor pressure **boiling point**

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.



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. Of course, only read the sections that we are covering. 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 the next section of the course 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?