Chapter 37 INTERMOLECULAR FORCES

We've completed three Chapters on the balance of entropy versus intermolecular forces, working with the general notion of the IFs taken as a whole. Now we want to look at these IFs separately in more detail.

37.1 Three IFs

There are numerous types of IFs and different substances can use different combinations of these. We will consider three primary types for single substances; when we reach mixtures in Chapter 39, we will add two more which can operate between different substances in solution. As we go here, keep in mind that intermolecular forces are the forces operating between molecules. They are not chemical bonds.

Chemical bonds hold atoms together within molecules and networks. The energies of chemical bonds are typically hundreds-to-thousands of kJ/mol (Chapter 25).

Intermolecular forces operate between molecules. Each single interaction is typically much weaker than a chemical bond. On the other hand, one molecule may be interacting with many neighboring molecules, so the importance lies in the collective sum of all interactions with all surrounding molecules. These energies range from several kJ/mol to several dozens of kJ/mol total over all interactions (although some can go higher).

These distinctions are important. Only in mixtures will we find an IF whose collective sum has enough energy to approach chemical bond energies, but we won't get to that until Chapter 39.

OK, here are the three IFs which we are covering for the primary interactions between separate molecules of a single compound.

1. Dipole-dipole 2. Hydrogen bonding 3. Dispersion

Of the three, dispersion is by far the most important because it applies to everything; usually it is the strongest IF for a particular substance. For small molecules which have hydrogen bonding, however, hydrogen bonding is usually the strongest. Dipole-dipole is very common and it can be substantial but hydrogen bonding and/or dispersion are usually stronger for any given compound. We'll look more at the relative strengths of IFs later in this Chapter.

We will discuss these three IFs in the order of preliminary background coverage. You already have the most background for dipole-dipole, so that will be our first for discussion. Then we will do hydrogen bonding, some of which also ties into some aspects from previous coverage. Finally, we do dispersion. Dispersion is different.

By the way, there are yet other IFs but our interest here is in the primary general players. Besides, some of those get a bit weird, such as quadrupoles and octapoles which are cousins to dipoles. I'm just not covering that part of the family.

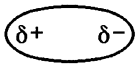
37.2 Dipole-dipole

The dipole-dipole intermolecular force is the result of a molecular dipole of one molecule interacting with the molecular dipole of another molecule. As we saw in Chapter 29, a molecular dipole is the result of molecular polarity. Back then, I told you how important molecular polarity was.

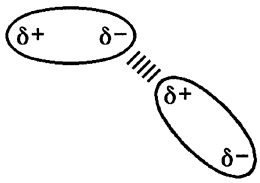
> “ Molecular polarity is an IMMENSELY important property and it has major impact in many areas in chemistry. It is important for you to be able to assess whether a molecule is polar or not. ”

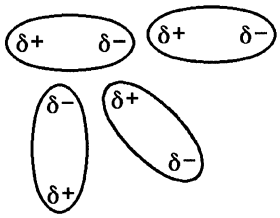
We are going to see a major application of molecular polarity at this time. If you didn't quite get that stuff back in Chapter 29, then go back to it now. It's in Section 29.5.

Before we proceed, I must add a technicality. There are different kinds of dipoles and we will see two others later. To distinguish these different types of dipoles, specific adjectives can be applied. For molecular polarity, the molecule's dipole is specifically called a "permanent dipole" because it is permanently present as a result of the molecule's identity (which includes shape). This is the most common application for the term dipole and, for this reason, if you don't see an adjective, then it's usually the permanent dipole. That applies for our present usage: dipole-dipole is the interaction of permanent dipoles on adjacent molecules.



I'll illustrate this interaction with a generic polar molecule which has some charge distribution (dipole) as shown at left. Now let's place it into proximity with another molecule of its own kind, such as shown at right. The opposite, partial charges of the dipoles are attracted to each other and the molecules will tend to align in directions which enhance this attraction. With more molecules in the same vicinity, there will be an overall preference to align the various neighbors such that the opposite ends of their dipoles are interacting, as shown at left. It may not be perfect alignment for everyone but, overall, this provides mutual attraction. In the solid phase, the molecules are commonly locked in a specific orientation and this can enhance the dipole-dipole interaction. In liquids, the molecules are constantly moving and bumping and turning; nevertheless, they will still have some preferred orientation relative to each other and they still engage in dipole-dipole attraction.





The dipole-dipole intermolecular force is available to all polar molecules. Furthermore, it will be stronger for more polar molecules than for less polar molecules. In order for you to predict whether a substance has dipole-dipole interaction, then all you must do is ask yourself if the molecule is polar. If the molecule is nonpolar, then it does not have a permanent dipole and it cannot do this intermolecular force. If the molecule is polar, then it has a permanent dipole and it can do dipole-dipole attraction. Let's take the examples from Section 29.5 and spell this out for those cases.

H_2O, CH_3F, ClF_5, ClF_3 and SF_4 are polar and have a dipole. Each of the pure compounds experiences dipole-dipole attraction in their liquid and solid phases.

BeH_2, BH_3, $SiCl_4$, XeF_2 and $AsCl_5$ are nonpolar and therefore do not have a dipole. These lack dipole-dipole attraction.

Water has been our principal example of polarity. Its polarity was first introduced way back in Chapter 10. It was part of the weirdness of water.

> ❝ Thus, water is polar. Now, that's an understatement. Most compounds are polar, but what sets water aside is that it is very polar. Water as a liquid is much more polar than most other liquids. Although other intermolecular forces add to water's weirdness (as will be seen in Chapter 37), this strong polarity is the important property for our purposes presently. This polarity enables water to dissolve and to dissociate a vast assortment of ionic and covalent solutes, a feat which very few other liquids can even approach at ordinary conditions. ❞

We can now say that water has a strong dipole-dipole interaction. But, as also noted in the quote, there's another IF which adds to water's weirdness. We see that one next.

37.3 Hydrogen bonding

Hydrogen bonding is the attraction which occurs between a hydrogen atom in a very polar covalent bond and a nearby orbital which is available for interaction. Lone pair orbitals are the best for this interaction, so we will limit to those for our coverage here.

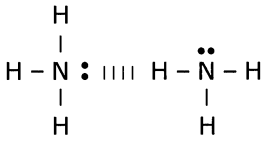
Let's look at this more closely. Consider a molecule which has a very electronegative atom, designated A, and that this atom A is bonded to a hydrogen atom. Consider also that the molecule has one or more lone pair orbitals, either on atom A or on some other atom B. Now, since A has a very high EN, the A–H bond is very polar and the H has a large positive partial charge, δ+. This positive partial charge is located on the very small hydrogen atom, so this is very concentrated for a partial charge. This partial charge can interact strongly with the electrons of a lone pair orbital from a nearby atom (B), whether that atom is in the same molecule or in a neighboring molecule. This gives a charge attraction between the H and atom B. This results in an attraction between the two molecules overall. This attraction is called hydrogen bonding. In this context, we say that B is the acceptor of the hydrogen bond and AH (or just A) is the donor of the hydrogen bond.

For the best hydrogen bonding, you want the most polarity in the A–H bond; thus, A must be one of the most electronegative atoms. You also want the lone pair orbital on acceptor B to be small and focused in a particular direction. This will allow hydrogen's δ+ to sense a high concentration of negative electron charge. In order to have a small lone pair orbital, you need B to be a small atom. Furthermore, in order for the lone pair orbital to be focused in a particular direction, the orbital should be a *p* atomic

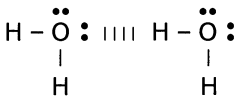
orbital or a hybrid orbital. Lone pairs in *s* orbitals do not do this well because the *s* orbitals are spherical and lack directionality.

When you combine the condition for high electronegativity and the small size, you get the following grand result: the best atoms for A and B in hydrogen bonding are N, O or F. Based on strength alone, we will limit to these cases within our primary coverage here. Let's illustrate a few of these; we can use simple Lewis structures to show this interaction without getting bogged down in shape information.

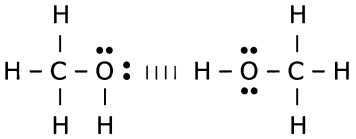
The pre-eminent example for N is NH_3:



The pre-eminent example for O is H_2O:



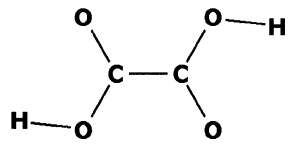
The pre-eminent example for F is HF:



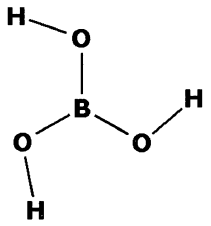
Fluorine is limited to HF. N and O, however, can do hydrogen bonding throughout many of their compounds. As another example, this is shown for methanol, CH_3OH, at left.

In the N and O examples shown here, the lone pair is in sp^3 hybrid orbitals; for HF, the lone pair originates in a 2*p* atomic orbital. Hydrogen bonding will also work well with *sp* or sp^2 lone pairs.

I want to make two points for clarification at this time. First, keep in mind that "hydrogen bonding" is an intermolecular force and it does not involve full chemical bonding. Although the word "bonding" is in the term, this is still an IF and it is not a full chemical bond. Second, do not confuse aspects regarding hydrogen bonding with aspects of dipole-dipole. I mention this because some students get parts of the two IFs mixed up. These are separate and independent intermolecular forces. Dipole-dipole depends on molecular polarity; hydrogen bonding does not depen
d on molecular polarity but it does depend on bond polarity. Dipole-dipole interaction requires a polar molecule; hydrogen bonding can be present for polar or for nonpolar molecules.



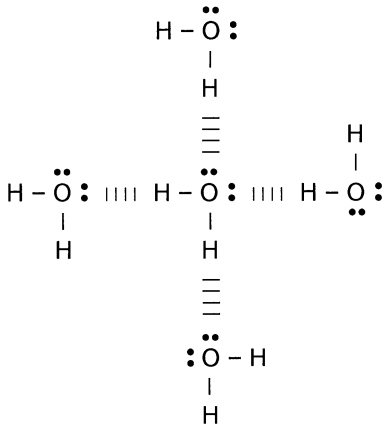
For example, oxalic acid ($H_2C_2O_4$) and boric acid (H_3BO_3) are nonpolar in the solid phase but they still have very strong hydrogen bonding with their neighbors. (I show their shapes, not their Lewis structures, left and right. Each compound is completely planar. They each have four central atoms so they're tricky to evaluate for molecular polarity, but they are both nonpolar.) Remember these distinctions so that you do not mix up these two intermolecular forces.



Hydrogen bonding is an incredibly important interaction. If present in a small molecule such as any of those above, then hydrogen bonding is the strongest IF. Even in big molecules, it can have a major contribution. Biology uses hydrogen bonding extensively. All of your proteins use hydrogen bonding to contribute to their overall form. Your genes contain DNA molecules which are partly held together by hydrogen bonding. And all of biology ultimately depends on that weird substance which we call water. Let's talk a bit more about water.

In water, we have the ultimate hydrogen bonding. For its size, it is the most efficient in utilizing hydrogen bonding. There are two hydrogens bonded to each oxygen and each oxygen has two lone pairs. Each O can donate both of its H's into hydrogen bonding to adjacent molecules and that same O can

accept two hydrogen bonds from other molecules. I show this for the central water molecule at right. Look at that molecule in the middle. All hydrogens and all lone pairs can be fully used in the grand sum of all hydrogen bonding interactions. Counting its own two covalent O–H bonds and the two hydrogen bonds which it accepts, the O is tetrahedral. This is water at its best. This is water at its finest. The two compounds which are closest to water in size and in hydrogen bonding are NH_3 and HF, but neither of these can use all hydrogens and all lone pairs all at once. Water is the ultimate.



The impact of hydrogen bonding on the properties of water is enormous. I alluded to this in the last Chapter when I talked about water's weird freezing curve with the backwards lean in the phase diagram.

> ❝ As we'll see in Chapter 37, the total intermolecular forces in water are incredibly strong for such a small molecule. In the solid phase, where IFs are the strongest anyway, this imposes a specific positioning of the water molecules in interconnected, zigzag rings. It turns out that these rings are not the most compact arrangement. As the solid melts, the H_2O molecules in the liquid are no longer restricted to interconnected rings; on average, the molecules can get a bit closer together so the liquid is initially more compact. Being more compact (more dense), the liquid is favored by higher pressure; as a result, less thermal energy (lower mp) is needed to melt at higher *P*. ❞

In ice, water molecules arrange themselves in zigzag rings because this allows them to fully utilize all hydrogens and all lone pairs in hydrogen bonding. When ice melts, molecules in the liquid are now in motion relative to each other and this causes some problems for holding on to all of the hydrogen bonding. Some of the hydrogen bonds between some neighbors are interrupted; this is a very fast process, however, and some neighbors are losing hydrogen bonds while others are re-forming them. On average, there is only a slight decrease in hydrogen bonding when solid ice melts to liquid water. Nevertheless, this partly disrupts the zigzag rings in ice and this allows the individual molecules to get a bit closer in the liquid, on average. Thus, water shrinks a bit upon melting. Conversely, water expands on freezing. You may be familiar with that if you ever placed water in a glass container in the freezer: as it freezes, the water expands and shatters the glass container. That's hydrogen bonding at work. Collectively, that's how strong those hydrogen bonds are.

With hydrogen bonding, we complete a significant part of the Grand Puzzle as it relates to water. Water is weird because the liquid has a very special combination of high polarity along with strong and extensive hydrogen bonding. This makes water so different from so many other compounds. No other compound of similar size and mass as water is a solid up to 0 °C and a liquid up to 100 °C at one atm. Even many larger and heavier molecules cannot match those properties. Water is special, all because of intermolecular forces. This is what makes water so abundant as a liquid at Earth surface conditions. And the story doesn't end with this much. There are even more ramifications to this, to be seen in Chapter 40.

For now, we close on hydrogen bonding and we turn to our third IF.

37.4 Dispersion

This one is a bit different and it needs more background information.

Dispersion is based on temporary dipoles. These are very different from the permanent dipoles of dipole-dipole interaction. Permanent dipoles are always present in polar molecules. Temporary dipoles can exist in any molecule, even nonpolar ones, and their presence depends on the circumstances. When the circumstances change, the temporary dipole changes and can cease to exist. That's why they're called "temporary". When present at some point in time, the temporary dipole can add to or subtract from a permanent dipole.

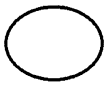
Dispersion involves two kinds of temporary dipoles: an induced dipole and an instantaneous dipole. Let me first talk about an induced dipole.

In this usage, the verb "induce" has the same as the dictionary meaning: it means to cause. Thus, to induce a dipole means to cause a dipole to occur. This can happen between neighboring chemical

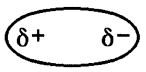
units: one can induce (cause) a dipole in a neighbor next to it. The resulting dipole is called an "induced dipole" and it exists only for as long as the neighbor is causing it. If that neighbor moves away, then the induced dipole ceases to exist.

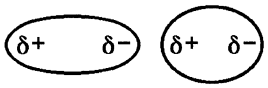
Induced dipoles arise due to the nature of orbitals. Recall that orbitals are three-dimensional field regions holding electrons and they are not hard objects. Since they are not hard objects, they can be distorted by a nearby source of charge. These nearby sources of charge can be an ion charge or a partial charge. The resulting distortion in a molecule's orbital can lead to an imbalance of charge which is a dipole of its own. This dipole, however, is only temporary and it only lasts as long as the nearby source of charge is present.

Let me show you how an induced dipole can arise in a molecule. I'll pick a nonpolar molecule as our target subject here, which I'll illustrate as shown at right. Since nonpolar, it has a fully even distribution of charge throughout, on average.



If we bring a source of charge into this molecule's proximity, then that charge source will cause a distortion in the orbitals and this will form a dipole. A negative charge source repels the electrons in the orbital(s) of our target molecule; a positive charge source attracts the electrons in the orbital(s) of our molecule. I'll show this using a polar molecule, as depicted at left, as our source of nearby charge. The polar molecule has a permanent dipole and it has partial charges. When the polar molecule and our target nonpolar molecule come into proximity, the polar molecule causes (induces) a distortion in our target molecule, giving an imbalance in charge and hence a dipole. This is illustrated at right. That dipole only exists for as long as the polar molecule is close at hand. Once the polar molecule moves away, the target molecule goes back to nonpolar with a fully even distribution of charge, on average.





There are two factors which strongly influence the ability of a molecule to undergo an induced dipole and therefore these two factors will affect the strength of the dispersion interaction. The first factor is polarizability. To explain this, let me introduce a new term: polarize. As a verb, to "polarize" means to make polar, or to cause a change in charge distribution. In our usage here, it is similar in meaning to inducing a dipole. Thus, we can say that one molecule can induce a dipole in another molecule or we can say that one molecule can polarize another molecule. This process is called polarization. The ability to undergo polarization is called polarizability. Polarizability is the ability or the tendency to become polarized; in other words, it is the ability or tendency to undergo a change (distortion) in charge distribution. Greater polarizability will give stronger dispersion.

When describing a molecule's polarizability, it is common to refer to the softness or hardness of the molecule or of its atoms. Soft atoms have orbitals which distort more readily; they are more polarizable and they are able to provide stronger dispersion. Hard atoms have orbitals which are more difficult to distort; these atoms are less polarizable and will give weaker dispersion. A big factor for soft vs. hard atoms is the size of the orbitals. We saw in Section 23.3 that the size of orbitals determines the size of atoms, and this gives a Periodic Trend. Atoms lower in the Periodic Table and/or to the left in a Row are larger and have larger orbitals. Larger orbitals extend further from the nucleus and their electrons are less tightly held; this makes the orbitals easier to distort. This brings us to the following overall results.

Atoms lower and/or to the left in the Periodic Table have larger orbitals. These atoms are more polarizable (softer). Molecules which contain softer atoms will be more polarizable and they will have stronger dispersion forces.

Atoms higher and/or to the right in the Periodic Table have smaller orbitals. These atoms are less polarizable (harder). Molecules which contain harder atoms will be less polarizable and they will have weaker dispersion forces.

The effects of orbital size are huge. H and He, in the First Period with only 1*s*, have lousy polarizability. Atoms in the Second Period have low polarizability, especially the small atoms more to the right in the Period. By the time you get to the Third Period, however, things have softened up quite a bit and they get much softer in the later Periods. This trend is evidenced by the monatomics of Group 18, for which the strength of dispersion increases downward, He < Ne < Ar < Kr < Xe < Rn. In polyatomics, it only takes one soft atom to have a big effect. For example, dispersion strengths run CH_3F < CH_3Cl < CH_3Br < CH_3I. Iodine is very soft and is outstanding for dispersion; this dominates the intermolecular forces of its compounds.

Caution! The terms soft and hard are relative only. No atom is hard in the rock-like sense. The orbitals are still field regions in 3D space, and some distort more or less readily than others.

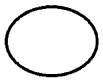
In addition to hard/soft properties of atoms, there is a second factor which influences the strength of dispersion and that deals with the surface area of the molecule. Molecules with a larger surface area can interact with more neighbors and are more able to be induced to undergo charge distortion; thus, these will be capable of stronger dispersion.

There are several ways for different molecules to have more surface area. The most direct way is to have more atoms. For example, C_2H_6 has stronger dispersion forces than CH_4. Another way to get more surface area is to have bigger atoms in the molecule; bigger atoms are softer, however, and that tends to be the major factor. A final way to get more surface area is to have long, stringy molecules. This may not be as obvious, but consider a piece of cooked spaghetti. Stretched out, the full surface of the strand is exposed. If you roll it up into a ball, it has its least exposed surface area overall because parts of the strand are covered by other parts of the strand; some of the strand lies buried within the overall outer surface. For molecules with the same number of atoms, long and stringy molecules have more surface area than molecules which are balled up. Long and stringy molecules will have stronger dispersion in comparison.

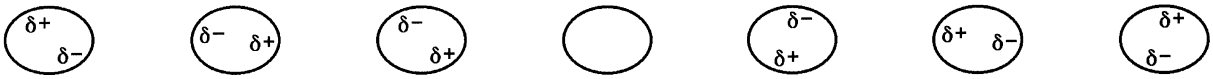
Alright, we're finally done with the induced dipole part of the background for dispersion. Dispersion also has an instantaneous dipole part, and that's the part that does the inducing. Let's do that part now.

An instantaneous dipole is a temporary dipole which arises from momentary changes in charge distribution within a molecule and <u>which originates in the molecule itself</u>. The last phrase is important, since it distinguishes this type of dipole from the induced dipole.

Variations in charge distribution within molecules occur at all times, regardless of polar or nonpolar. I will illustrate this using a nonpolar molecule again. Here is our generic nonpolar molecule from above. Since it's nonpolar, there is no permanent dipole.



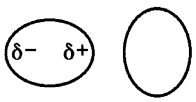
There's a technicality to this permanent dipole business which I must now introduce. We didn't cover this back in Chapter 29 but we need to bring it into the picture now. Permanent dipoles reflect an average over time. Although that's on average, at any split-second in time, that may not be the case. Orbitals experience fleetingly fast fluctuations in charge distribution, even on their own. Thus, at some extremely short instant in time, our nonpolar molecule may have a very temporary charge imbalance. This would only last for an extremely short instant, and in some other instant the charge imbalance would be reversed or nonexistent or different in some other way.



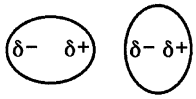
The fluctuations are incredibly fast; even within a billionth of a second, the charge distribution balances out and the molecule is nonpolar on average. Those temporary dipoles which originate from orbital fluctuations and which only last for an instant are called <u>instant</u>aneous dipoles.

That finishes our background information. Now we put instantaneous dipole together with induced dipole and we get dispersion. To illustrate, start with two adjacent nonpolar molecules, as shown at right.

Although nonpolar on average, they are subject to instantaneous dipoles. Let's say, at some specific instant in time, the left molecule has an instantaneous dipole as shown.



This can then induce a dipole in its neighbor, giving rise to an attraction. This particular attraction will only last an instant, but in the next instant there will be another attraction from a different fluctuation. The grand sum of all of these interactions over time is dispersion.



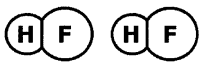
OK, that's it for dispersion. Remember that it arises from an instantaneous dipole and an induced dipole. Remember that it is stronger for softer atoms (which are lower and/or more to the left in the Periodic Table).

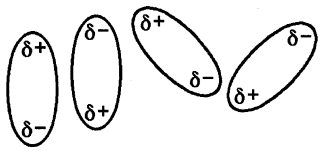
This wraps up our three IFs for now. Again, these IFs are available for single compounds by themselves. We will add more IFs to the pictures when we do mixtures in Chapter 39.

37.5 Orientation effects

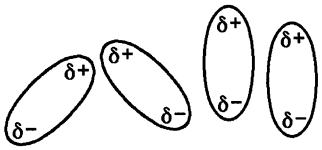
We'll look at some applications in a moment, but I first need to bring up a point which has very important consequences later. That point deals with the effect of orientation of adjacent molecules on the strength of intermolecular forces.

Of our three IFs, hydrogen bonding is the most dependent on the correct orientation of adjacent molecules. This is because H is small to begin with, and it needs to be near a lone pair with a particular direction. Let's use HF as an example. The orientation of the two molecules shown at left allows for a very strong hydrogen bonding interaction. Although I drew them in a line, the alignment doesn't have to be perfectly straight; in fact, adjacent HF molecules prefer to be at an angle to each other because this places the hydrogen of one molecule close to the lone pair of a fluorine of the other molecule. Compare this to the situation at right. That orientation is no good because the hydrogen of one molecule is nowhere close to the fluorine lone pairs on the other molecule. That orientation cannot have any hydrogen bonding. Overall, the strongest hydrogen bonding interactions have the most restrictive orientation requirement. These restrictions limit the options which are possible with respect to orientation. Hydrogen bonding is the pickiest of the three IFs for direction.





Dipole-dipole also has an orientation dependence, but the demands are looser than for hydrogen bonding. There are more options in the way the neighbors can align, such as shown at left. The dipoles can be reasonably close without a rigorous restriction to align one atom with one lone pair somewhere, as in the case of hydrogen bonding. Besides, dipole-dipole is weaker than hydrogen bonding so it can't afford to be too restrictive. On the other hand, aligning the same dipole ends as shown at right is no good. Except for those conditions, there are much fewer restrictions imposed for orientation in a dipole-dipole interaction when compared to hydrogen bonding.



Dispersion has the fewest restrictions on orientation. These are instantaneous dipoles arising in any direction and they can induce a dipole in any direction. There are lots of options for orientation.

Orientation effects differ for liquid and solid phases. In liquid phase, the molecules are in motion so they can constantly change direction and re-align with different neighbors. In solid phase, the molecules are locked in place and the orientations are usually fixed. The solid phase benefits from the fixed orientations and the IFs are stronger.

That's all I need to note for now. Why is this even mentioned? Did you catch the "options" versus the "restrictions" for orientation? I'm setting you up for the effects of entropy later. This is important for pure compounds, especially water. This will become hugely important when we deal with aqueous mixtures, especially in Chapter 40. Hydrogen bonding is vastly important but very restrictive in the aqueous world. Every cell in your body depends upon this. You'll see this later.

37.6 What IF?

Having completed our discussion of the IFs, it is now time to put the discussion to work. There are several ways of applying these things and there are different kinds of questions to consider. First, you can be asked which of the three primary IFs are operating for a particular substance. Here's what you need to consider in order to answer that.

- In order for dipole-dipole to be operating, the molecule must be polar. Thus, you must evaluate whether the molecule is polar or nonpolar.
- In order for hydrogen bonding to be operating, there must be an N–H or O–H or F–H bond. Look for one or more of those. If present, they will also have lone pairs. You may want to draw out a Lewis structure.
- Dispersion is the easiest: everything has dispersion.

Second, you can be asked which is the strongest IF for a particular substance. For our comparisons of the relative strengths of the IFs, we will only be making general estimates. Measurements or calculations

of individual IF strengths is not a simple task and we will not work with numbers. We will just work with generalities and we will avoid any close calls. Here is our general rating system for comparing the three intermolecular forces with respect to which one is strongest in a particular substance.

In most substances, dispersion is the strongest IF.
If present, the strength of hydrogen bonding will exceed the strength of dispersion in small molecules. Hydrogen bonding can also exceed dispersion in bigger molecules if there are multiple N–H or O–H bonds. (Water itself has multiple interactions.)
Dipole-dipole is rarely the strongest IF in any substance. Dispersion is almost always stronger than dipole-dipole except in a very few, very small, very polar molecules such as H_2O. In most of those very few cases, however, hydrogen bonding is also present and that is the strongest IF.

Thus, the strongest IF for our purposes will be dispersion or hydrogen bonding. If you are asked for the strongest IF for a particular compound, then just look at those two. Beyond that, we can list, but we won't rank, the others.

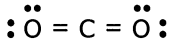
Let's start on some examples.

For each of the following, identify which IFs are operating and then predict which is strongest.

▸ CO_2

Is dispersion operating?
Yes. Always.

Is dipole-dipole operating?
You need to know if the molecule is polar. To do that, you need the shape. The Lewis structure is at right. If you do VSEPR, you get linear shape. By any of the methods of Chapter 29, you can determine that it is nonpolar. Nonpolar means no permanent dipole. Therefore, there is no dipole-dipole interaction.



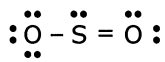
Is hydrogen bonding operating?
No, there are no hydrogens.

We conclude overall that CO_2 only has dispersion working for it.

▸ SO_2

Is dispersion operating?
Yes. Always.

Is dipole-dipole operating?
Same routine as above. Is it polar? First, what's the shape? One Lewis structure is shown at right; there is resonance but we don't need that for shape. VSEPR will tell you the shape is bent. From this you can determine that the molecule is polar. That means SO_2 has a permanent dipole and that means it has dipole-dipole interaction.



Is hydrogen bonding operating?
No hydrogens.

Overall we see that SO_2 has dispersion and dipole-dipole working for it. OK, which is stronger? That will be dispersion.

▸ H_2O

Is dispersion operating?
Yes. Always.

Is dipole-dipole operating?
Yes, as previously noted.

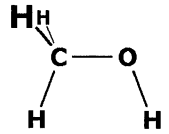
Is hydrogen bonding operating?
You bet, as previously noted. In fact, each and every molecule can donate two hydrogen bonds and can accept two hydrogen bonds. Outstanding.

Beyond any shadow of any doubt, hydrogen bonding is the strongest IF; then dipole-dipole, and then dispersion. Dispersion for water is actually poor. Water is one of the very few compounds where dipole-dipole interaction is stronger than dispersion.

▸ CH_3OH

Is dispersion operating?
Yes. Always.

Is dipole-dipole operating?
Is it polar? First, what's the shape? I gave the Lewis structure earlier in this Chapter when I mentioned this compound for hydrogen bonding. We have two central atoms, C and O. VSEPR will tell you that the C is tetrahedral and the O is bent, as shown at right. Given that O is the most electronegative atom here and all bonds to it are polar bonds, then this will be a polar molecule overall. Since this is polar, then dipole-dipole will be operating.



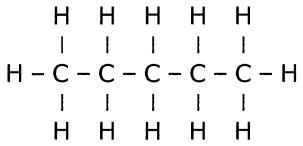
Is hydrogen bonding operating?
Yes, as noted in the prior Lewis structures. There is an O–H bond and O has lone pairs.

Overall, methanol has dispersion, dipole-dipole and hydrogen bonding. Hydrogen bonding is the strongest.

▸ C_5H_{12} (pentane)

Is dispersion operating?
Yes. Always.

Is dipole-dipole operating?
Is it polar? Well, what's the shape? The Lewis structure is at right. You have five central atoms and VSEPR will tell you that each is tetrahedral. That makes it real tough to evaluate molecular polarity, so I am going to introduce at this time a clue for compounds of this type.



Pentane belongs to a family of compounds called hydrocarbons which are compounds composed of carbon and hydrogen only. These are extremely numerous and extremely common. For example, in addition to pentane, hydrocarbons include the compounds methane, propane and naphthalene; hydrocarbons also include various mixtures such as paint thinner, some components in gasoline, etc. In general, hydrocarbons have a variety of shapes and this can get complicated for the evaluation of molecular polarity. There is one characteristic, however, which helps this evaluation: CH bonds are only weakly polar so there's not a lot of bond polarity available. Many of the molecules (such as methane and naphthalene) adopt shapes which cancel out the weak bond polarities. Others are typically weakly polar and simply not significant. (There are exceptions such as molecules with triple/single bond order combinations, but we won't worry about those here.) To avoid this tedium, I will give a guideline for our use: unless told otherwise, assume hydrocarbons are nonpolar for practical purposes. As a consequence of that, we assume that dipole-dipole interaction is not significant. That includes pentane for the present example

OK, that was a long answer to that question. Now the final IF.

Is hydrogen bonding operating?
No. There are no N–H, O–H or F–H bonds.

Our final answer on pentane is that dispersion is the only significant interaction.

By the way, as we get into molecules with more than one central atom, things can get more complicated with respect to judging molecular polarity. As for methanol above, cases with only two central atoms can usually be figured out by inspection. For hydrocarbons, we'll use the guideline as given regardless of how many central atoms. For other cases with multiple central atoms, I'll just tell you polar or not; I did this earlier in the Chapter for oxalic acid and boric acid.

OK, your turn.

. . . . . .

Example. Which IFs are operating for each of the following compounds? For clues, each line is one IF. After you write out all IFs, circle the one IF which is strongest for that compound.

$SiCl_4$ _____

SF_4 _____ _____

NH_3 _____ _____ _____

. . . . . .

If you want to, draw out Lewis structures here.

Now let's do things a little differently. Let's compare different compounds and ask the question of which one has the greater total strength of intermolecular forces. Remember: it is the total IFs which help to determine the phase of a compound at a given set of conditions. That was all part of the battle and the balance of IFs versus entropy as introduced in Chapter 34. Thus, the phase itself serves as a general indicator of the total strength of IFs. We can also use phase change, as done in Chapter 35 for liquid/gas equilibria. Here's the summary I gave right at the end of that Chapter.

Weak IFs	Strong IFs
lower ΔH°_{vap}	higher ΔH°_{vap}
higher concentration in (g)	lower concentration in (g)
higher EVP	lower EVP
lower bp	higher bp

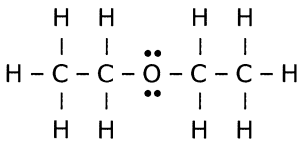
Liquid/gas equilibria are the best for these comparisons. As noted in Chapter 36, there are more complications with solid phase although some overall generalities do remain.

Let's return to our comparisons in Chapter 35 regarding diethyl ether, methanol and water. Here's what I said back then.

> " We haven't gotten to the specific details of intermolecular forces yet so, for now, I'll just tell you the final result of such a comparison for these three compounds: diethyl ether has the weakest IFs, methanol is in the middle, and water has the strongest IFs.
>
> | | diethyl ether, $C_2H_5OC_2H_5$ | methanol, CH_3OH | water, H_2O |
> |---|---|---|---|
> | IFs: | weakest | middle | strongest |
>
> Later you will see how to judge the comparative strengths of IFs for different compounds. "

Later is now. We've examined the intermolecular forces for methanol and water above. Let's look now at diethyl ether.

The Lewis structure is at right. First, there's dispersion, as always. Second, I will tell you that the molecule is polar, so there's dipole-dipole. Third, there is no hydrogen bonding. Overall, dispersion is the strongest IF for this compound.



Now, let's compare the three compounds and see how they stack up to each other.

Dispersion

Based on the number and types of atoms, the dispersion strengths run $C_2H_5OC_2H_5 > CH_3OH > H_2O$.

Dipole-dipole

This comparison is tough to do for these compounds, so I will just tell you that the dipole-dipole strengths run $C_2H_5OC_2H_5 < CH_3OH < H_2O$.

Hydrogen bonding

No question here: H_2O wins overwhelmingly, then CH_3OH. $C_2H_5OC_2H_5$ has none.

Now, total them up. Overall, it's the hydrogen bonding that stands out in the totals. Because of this, H_2O is the easy winner, followed by CH_3OH. $C_2H_5OC_2H_5$ does not have hydrogen bonding; it's last in the totals although it does have the best dispersion. This comparison results in the ranking of physical properties as presented in Chapter 35.

	diethyl ether, $C_2H_5OC_2H_5$	methanol, CH_3OH	water, H_2O
ΔH°_{vap} (25 °C):	27.4 kJ	37.8 kJ	44.0 kJ
EVP (25 °C):	536 Torr	127 Torr	23.8 Torr
normal bp:	35 °C	65 °C	100. °C

Notice the impact of IFs on these properties! Again, IFs provide for liquid and solid phases for molecular compounds.

Let's do another comparison. We'll compare the total intermolecular forces for HF, HCl, HBr and HI. They're all diatomics so these are somewhat easy cases.

Dispersion

They all have one H but a different halogen atom, so we need to focus on the halogen atoms. This is a straightforward soft/hard comparison. The polarizability of the molecules runs HI > HBr > HCl > HF and the dispersion strengths will follow that same trend. The effect will be large because the halogen atoms are from different Periods.

Dipole-dipole

They're all polar and the polarities run HI < HBr < HCl < HF. The strength of the dipole-dipole interaction will follow the same trend.

Hydrogen bonding

No competition: HF wins. None of the others comes close.

Overall, for these small molecules, hydrogen bonding will dominate the outcome: HF is best for total IFs. After that, dispersion is the most important factor so the runners-up are HI > HBr > HCl. This comparison based on IFs reflects the trend in the boiling points: HCl is lowest at 188 K, then HBr at 206 K, then HI at 238 K and finally HF at 293 K.

Now, let's change things a bit. Consider the compounds CH_3F, H_2NOH and PCl_3. At room temperature and one atm, one of the compounds is a solid, one is a liquid and one is a gas. Which is which?

In order to do this, you must understand the relationship of the phases to the total IFs. Solids have the strongest IFs, so the solid in this example will have the strongest IFs of the three. Gases have the weakest (if any) IFs, so the gas in this example will have the weakest IFs of the three. The liquid in this example will be intermediate. Thus, the question is asking you to rank the total IFs.

You may want to sketch out some Lewis structures. Here's some space. CH_3F and PCl_3 are easy cases with one central atom; H_2NOH has two central atoms. If you want to check your Lewis structure for H_2NOH, it was Example 8 at the end of Chapter 26. Try it first, but go back and look if needed.

Let's start in on the comparisons.

Dispersion

The winner here is easily PCl_3 with four atoms from the Third Period. The other two are much weaker; each has three hydrogens and two atoms from the Second Period, so we can't rank those any further.

Dipole-dipole

You can work these out and you should be able to see that all are polar. Ranking these, however, is more difficult. The molecules themselves are not too complex: all have 4 - 5 atoms each; the shapes of their atoms are tetrahedral, trigonal pyramidal and bent. The C–F bond in CH_3F is the most polar of all bonds in the three compounds, and it is true that CH_3F is the most polar molecule

here. Beyond that, however, nothing really stands out in comparing H_2NOH and PCl_3, so we'll leave it there.

Hydrogen bonding
We have a clear winner here: H_2NOH. In fact, it has several N–H and O–H bonds and this provides for multiple hydrogen bonding interactions. The others do not have hydrogen bonding.

Putting it all together, H_2NOH will have the strongest total IFs due to hydrogen bonding; it is the solid. PCl_3 comes in second due to dispersion and it is indeed the liquid. CH_3F is the gas; dipole-dipole and dispersion are just not real strong here and there's just not a lot going for it.

With this we close on our illustrations here. This also ends our discussion of the intermolecular forces for now. I've spent quite a bit of time on them because they are so important. They affect many physical properties even beyond what we've seen so far. They will come into play again when we begin mixtures in Chapter 39.

Problems

1. True or false.
   a. P is softer than As.
   b. SiH_4 cannot do hydrogen bonding.
   c. CH_4 has stronger dispersion than C_2H_6.
   d. Sulfur trioxide has a permanent dipole.
   e. Nonpolar molecules cannot have an induced dipole.
   f. Phosphorus tribromide has a higher EVP than sulfur dichloride (at the same temperature).

2. True or false.
   a. An argon atom cannot undergo an instantaneous dipole.
   b. For hydrogen bonding, the best orbitals for lone pairs are *s*-orbitals.
   c. Selenium is less polarizable than sulfur.
   d. The dipole-dipole interaction for BF_3 is greater than the dipole-dipole interaction for PF_3.
   e. Orientation effects are greater for hydrogen bonding than for dispersion.
   f. In general, stronger dispersion will result in a lower normal boiling point.

3. Which intermolecular forces are operating for each of the following compounds?
   a. HCCH b. BCl_3 c. Cl_2SO d. AsH_3

4. Which intermolecular forces are operating for each of the following compounds? If more than one is operating, which is the strongest?
   a. H_2S b. $SiCl_4$ c. NH_3 d. XeF_4

5. Consider the compounds below.
   HF H_2S PBr_3 SF_2 H_3CNH_2
   a. Which compound(s) have hydrogen bonding?
   b. Which compound(s) have dipole-dipole?
   c. Which one compound has the weakest dispersion?
   d. Which one compound has the strongest dispersion?

6. Consider HBr, Br_2 and HCl. Based on intermolecular forces, rank these from lowest to highest (normal) boiling point.

7. Consider the following compounds.

   SO_2 H_2CBr_2 C_2H_6 (H_3CCH_3) H_3CSH P_2H_4 (H_2PPH_2)

   a. Which one has the highest normal boiling point?

   b. Which one has the lowest ΔH°_{vap}?

   c. Which one has the highest EVP (at same T)?

8. Of the following compounds, only one is a liquid at standard conditions; the others are gases. Which one is the liquid?

   H_2S OF_2 CF_4 SiH_4 $SiCl_4$

9. Three of the following compounds are gases at 25 °C and 1 atm. Which three are the gases?

   HCl PH_3 CI_4 CH_4 S_2Cl_2 (ClSSCl) H_2O_2 (HOOH)