

Chapter 10

AQUEOUS SOLUTIONS AND REACTIONS: Background

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At this time, we will start into coverage of several specific types of reactions. We already discussed one category, combustion reactions, in Chapter 6. There are vast numbers of reactions, and chemists categorize these in different ways. Different instructors cover different categories of reactions; I may not cover all of those and your instructor may add some. For now, I am going to cover aqueous chemistry. This Chapter begins a sequence of six Chapters dealing with different kinds of reactions in aqueous solution. We will devote additional Chapters down the road to even more aspects on this broad topic. Why such an emphasis on aqueous? It's because of the absolute, sheer, total importance. We live in a water world. There is no escaping this. That is how Nature developed the planet and that is how Nature developed your cells. The importance of aqueous chemistry to you cannot be overstated. Your cells do aqueous reactions. Your environment does aqueous reactions. You yourself were conceived in an aqueous broth, a vestige of the species origin. These things are part of your world. Whether you know it or not.

Of the many kinds of reactions which are common in water, we will cover four types for now. These are in the following Chapters. We can't start them yet. We must first develop the picture of the water world a bit more in order to understand what is going on.

10.1 Water basics

We grow up in a world surrounded by water as a normal experience of human life. We drink water. We drink aqueous beverages. We eat many foods which are predominantly water. Our own bodies are predominantly water. To us, water is a normal everyday liquid. But there is an irony here: the simple fact is that WATER IS NOT NORMAL AT ALL in the chemical and physical sense. Water, in fact, is the exception and not the rule for liquids in general. Water is weird. Its properties are strange. Compared to all other compounds which are close to water in size or mass, only water is a liquid at normal Earth conditions. All the others are gases. Why is one compound a gas and another compound is a liquid under similar conditions? This is a very interesting question, but we're not ready for the details yet. I'll tell you this much now: there is an inherent drive in all of Nature to favor the gas phase out of all three common phases (gas, liquid, solid). This applies to everything. That drive is part of "entropy" but entropy is bigger than this and I'm not going there right now. Simply for now, if a compound is NOT a gas, then something else is going on. In network compounds, this something else is chemical bonds and these bonds keep the atoms closely connected to one another. In molecular compounds, this something else is called "intermolecular forces". Intermolecular forces are the ways by which molecules interact with each other in their immediate surroundings. This can lead to molecules actually clinging to each other; this is how a liquid phase and a solid phase overcome Nature's preference for gas phase. This is all we need for now. We will get into more details regarding entropy and intermolecular forces, and the balance between the two, beginning in Chapter 34.

Notice that I said water is a liquid at normal Earth conditions. If the Earth were much hotter and/or if the amount of water on the planet was very small, then all the water would be in the gas phase. Or if the Earth was much colder, then the water would be mostly ice. Under either set of conditions, there would be no rivers, no oceans, etc. to help shape the planet. No water liquid for life as we know it. These more extreme conditions do apply to other planets, moons and other celestial bodies. I don't just mean our Solar System. Think for a moment. There are hundreds of billions of stars in our own Milky Way galaxy. Billions of those are estimated to have rocky planets. Some of those planets will have conditions for liquid phase water and possibly for life of an Earthen type. Many will not have liquid phase water, but then they might have life based on other compounds and not of an Earthen type. Even the word "life" will have to be redefined in order to accommodate these. Sound strange? Many strange things wait to be discovered. There's a whole universe out there! Curiously, you don't even have to leave Earth to discover new organisms, and much of our own planet remains underexplored. There are assuredly many living creatures waiting to be discovered in the ocean depths and cave depths of Earth.

You are able to be here because Earth has suitable conditions for liquid phase water. Importantly, water is liquid phase under these conditions because it has strange and unusual properties. There is one thing that water can do better than just about any other solvent at these conditions: it can dissolve many ionic compounds. Water can also dissolve many covalent compounds, too, but so can many other solvents. Why is this important? The ability to dissolve ionics opens up entirely different worlds of chemistry. On the one hand, water can dissolve many ionics, but not all. The oceans contain massive

amounts of dissolved compounds, mostly simple ionics. On the other hand, rocks are also primarily ionic compounds and these don't dissolve readily in water. Much of this is important for shaping Earth. It's also important for shaping biology. The chemistry of life is inextricably associated with the ability of water to dissolve some ionics but not others. Like the sea, your blood is a soup of dissolved ions. Yet, your bones and teeth are also ionic compounds, although these don't dissolve.

There are actually two phenomena which are critically important to the total aqueous picture. The two phenomena are solubility and dissociation. Solubility is the more general of the two: you can have solubility without dissociation, but you cannot have dissociation without solubility. Both of these can apply to solutes which are ionic compounds and to solutes which are covalent compounds. So don't think that we're leaving out covalents. These are still very important to the total picture. And don't think that solubility and dissociation are easy to do, because they are not. This is where water's weirdness really comes to light: the ability to dissolve and to dissociate many different kinds of compounds.

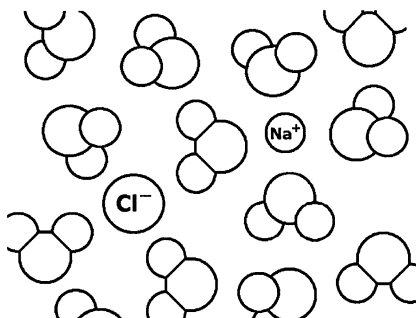
For our present purposes, solubility refers to whether a compound does or does not dissolve to a significant extent. The underlined part is very important to understanding solubility, and I will explain this further in the next Chapter. For now, I give two simple examples.

You know sodium chloride, NaCl, as the primary component of table salt. You know this dissolves very well in water. We say that sodium chloride is "soluble".

You may not know barium sulfate, BaSO₄, from experience, but we did use it in the last Chapter as the product of an aqueous reaction and we said at the time that it was not soluble and it formed a white powder. We can now state that barium sulfate does not dissolve to a significant extent and we therefore consider it "insoluble".

Actually, some of you may know BaSO₄ from experience. I mentioned in Chapter 2 that some barium compounds are used for taking GI (gastro-intestinal) X-rays. Barium sulfate is the so-called "barium swallow". They slurry it in water, add some flavoring and who knows what else, and tell you to drink it. It goes into your digestive tract and it blocks X-rays (it's "radiopaque"), and this provides the image of that part of your digestive plumbing.

The second phenomenon to consider is dissociation. Dissociation is a general term in chemistry and it refers to the break-up of one chemical unit into two or more others. Our concern here is ionic dissociation: the process of separating a solute into individual ions in solution. I'll illustrate this with sodium chloride again. Remember that sodium chloride is an ionic network compound with ionic bonds



between sodium cations and chloride anions, extending over three dimensions. When it dissolves in water, you get separated Na⁺ cations surrounded by water molecules, and you get separated Cl⁻ anions surrounded by water molecules. I've drawn a bit of this at left, where the unlabelled molecules are H₂O. (In reality, there can be hundreds or thousands more H₂O molecules than there are ions. Also, things are in closer contact than what I've drawn. I mention these points but I'm keeping the picture simple here.) The reason that you get separated ions is that the water molecules aren't just innocently surrounding the ions: they're actually interacting with the ions. Before I describe this further, I want to introduce some terms.

In general, for any solute of any kind dissolving in any solvent of any kind, the solvent molecules surround the solute and interact with it in some manner. This process is called "solvation". We say the solute particles are "solvated". Solvation and solvated are general terms for any solvent. In the specific case with water as the solvent, the term "hydration" means the same as solvation. We say that the solute particles in water are "hydrated".

Historically, some of the early studies of ions involved electricity. This related to the fact that water solutions with ionic solutes can conduct electricity, whereas pure water does not significantly conduct electricity. One term that arose from this historical connection is still in use: "electrolyte". Compounds which dissolved in water and allowed the solution to conduct electricity (e.g., table salt, NaCl) were called electrolytes. Compounds which dissolved in water and did not give rise to significant conductivity (e.g., table sugar, C₁₂H₂₂O₁₁) were called "nonelectrolytes". Many people equate electricity with some electrons flowing through a metal conductor but, in an ionic solution, it's the ions doing the electricity, not electrons. Electricity is really about charge flow, not just electron flow. Since ions have charges, too, then you can conduct electricity by letting ions move around: cations go one way and anions go the other way. That's

electricity. That's how your nerves send electrical signals: it's how you breathe, it's how you eat, it's how your heart beats, it's how you move. Electricity by ion flow, not by electron flow. These things are part of you. Whether you know it or not.

Since it's really ions that allow the solution to conduct electricity, an electrolyte is ANY compound which dissolves in water to give ions. A nonelectrolyte is any compound which dissolves in water but does not give ions. Watch the wording! Many ionic compounds are good electrolytes, but so also are many covalent compounds. Yes, some covalent compounds can dissolve in water and can form ions, although they have no ions themselves when pure. It's the water that causes this. This is part of the weirdness of water and it's part of what makes water so special.

OK, you need to be aware of where we're at so you can see where we're going. I've just set the scene for some of the most important aspects of water: dissolving and dissociating a variety of ionic and covalent compounds. Let me recap this.

- ▶ Water can dissolve some ionic compounds and separate them into individual ions.
Dissociation is not a simple task. In order to separate the ions, water must overcome the strong ionic bonding between the cations and anions within the ionic network.
- ▶ Water can dissolve some covalent compounds; water can separate some (not all) of these to form ions.
Again, dissociation is not a simple task. Remember that a covalent compound has no ions to begin with. It only has covalent bonds. In order for dissociation to happen, water must break a covalent bond in the solute molecule.

In both cases, water breaks up chemical bonding (ionic or covalent) in order to form the separated ions. SO HOW CAN THIS HAPPEN? Breaking up is hard to do. Chemical bonds are very strong and we would not normally consider water to react so strongly with something. Well, like I said above, WATER IS WEIRD. And irrefragably so.

10.2 Why is water weird?

Water's weirdness stems from the interactions between the water molecules and the solute particles. In all honesty, these interactions also occur with some other solvents, but what makes water different is that the interactions are so strong. These interactions are part of intermolecular forces which I mentioned early in the Chapter. We don't need everything about those right now and we can't do them all right now anyway. So I will limit to the essentials. Although other aspects do contribute, we are going to focus only on "polarity" for now.

A bit of background first. Before doing water, I'm going to do a simpler example with just a diatomic molecule. I'll do hydrogen fluoride, HF, since we did it in Chapter 3 as our first example of a covalently bonded molecule. We need to talk about covalent bonds again.



In Chapter 3, we described covalent bonds as the sharing of electrons by two or more atoms. For hydrogen fluoride, we said there were two electrons shared between the H and the F. Now I will expand on that simple picture. Yes, a covalent bond involves shared electrons, but the fact is that the sharing is usually not 50-50. In HF, the sharing is very uneven with F taking more of the share; that leaves H short in the share. So it's not 50-50. What is the share? The actual numerical distribution doesn't matter at this point. It only matters that the share is not even. MOST COVALENT BONDS DO NOT INVOLVE AN EVEN SHARE. This has serious consequences.

Remember that electrons carry negative charges. If the bond electrons are not evenly distributed over the bond then the charges overall are not evenly distributed either. For hydrogen fluoride, the end of the molecule towards F has more than 50-50 of the bond share. This makes the F end a bit negative overall. The end of the molecule towards H has less than 50-50 of the bond share. This makes the H end a bit positive overall, because now there's not enough electron charge to offset the hydrogen's nuclear charge.

This uneven distribution of charge is called "polarity". The adjective is "polar". These terms can be applied to a covalent bond or, in general, to an entire molecule. We say that HF has a polar covalent bond. The two ends of the bond carry unbalanced charge. The actual value of the charge is not important for our purposes, but typically the charges due to a bond polarity are some fraction of ± 1 . We call these "partial charges" because they are not a full charge. WARNING! Don't confuse these with ion charges: those are completely different. Remember the distinctions.

Ion charges are due to different numbers of electrons and protons in a specific chemical unit. The values of the charges are always a \pm whole number.

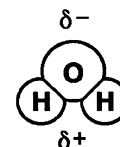
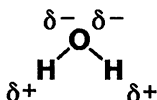
Partial charges are due to uneven electron distribution in a bond or over a whole molecule. These are typically some fraction of ± 1 per bond.

Ion charges are symbolized by 1+, 2+, 1-, 2-, etc. Partial charges are a fractional charge and are symbolized using a lowercase Greek delta, δ . The actual amount of the partial charge can often be measured or calculated, but that is not important for us right now. For HF, we symbolize the partial charge of the H end as $\delta+$ and the partial charge of the F end as $\delta-$, as shown on the left. There're other symbols based on arrows; we adopt the traditional one here, which is an arrow with a positive tail. The positive tail lies at the $\delta+$ end and the arrow points to the $\delta-$ end, as shown on the right. The two pictures are equal; you can use $\delta+/\delta-$ symbols or you can use the arrow to represent the same thing. I'll refer back to these illustrations in a later Chapter, so you need to flag them: write "HF flag" in the margin.



As I mentioned, polarity can refer to a covalent bond or to the whole molecule. We can say that hydrogen fluoride has a polar covalent bond and we can say that hydrogen fluoride is a polar molecule. I'm only using HF as an easy introduction to polarity. Now, let's get back to water.

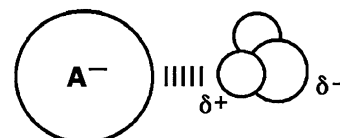
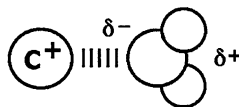
Each H_2O molecule has two covalent bonds and both of them are polar. The electrons in each bond are not shared 50-50. The oxygen end of each bond has more than an even share; each hydrogen has less than an even share. (If you're wondering, you'll see in Chapter 25 how to know which atom gets the bigger share of electrons. For now, I'm just telling you.) The polarity for each bond in water is shown on the left. The two individual bond polarities add to give the molecule an overall polarity, shown on the right with the atoms drawn as circles. The grand result is that each and every molecule of water has an uneven charge distribution. The bottom side of the molecule with the two H's is partial positive and the top side of the molecule with the O is partial negative. Flag this part also for later referral: write " H_2O flag" in the margin.



Thus, water is polar. But 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.

This is what I needed to introduce. Now we shall see how all of this falls into place.

Opposite charges always attract each other. Those charges can be whole ion charges or they can be the fractional, partial charges of polar things. The net result is that a water molecule's partial charges will attract ions. The $\delta-$ portion of the water molecules will attract cations. The $\delta+$ portion of the water molecule will attract anions. The illustration on the left shows the O side of one water molecule interacting with a generic cation (labeled C^+ for cation, not to be taken for carbon). On the right, the illustration shows the $\delta+$ on one H interacting with a generic anion (labeled A^-). A string of parallel lines (|||||) is



often used to emphasize an interaction and I've included it in the illustrations here. (They're not always required and I won't always use them unless I want to for emphasis.) Notice how the ion charges and the partial charges are interacting, either with the polarity of the molecule overall or with the polarity of one bonded atom. These interactions are an essential feature of the hydration of ions.

The attractions between a polar molecule and an ion can be good but they're not always great. Some are better than others, but that depends on which ions are involved. For example, a water molecule is more attracted to a 3+ cation than to a 1+ cation. Even so, the attractions are often not as strong as full chemical bonds. However, they work very well for water for two reasons. First, because water's polarity is stronger than the polarity of most other liquids, each of these attractions is stronger in water than in most other solvents. Second, it's not just one water molecule which is interacting, it's a bunch. Each dissolved ion is surrounded by a bunch of water molecules, all piling around, often in layers, trying to get in on the charge attraction. There could be 10, 15, or more water molecules attracted to each and every ion. Although one interaction is not so great, the grand sum of all interactions can be great.

Now remember why we're here. In the recap at the end of the last Section, I said water can dissolve and dissociate some ionic compounds and some covalent compounds. And then I posed a question.

In both cases, water overcomes chemical bonding (ionic or covalent) in order to form the separated ions. SO HOW CAN THIS HAPPEN?

The answer lies in the very strong polarity of water. It's a bunch of water molecules piling around each and every ion, attracted by charge. All together, the attractions can be strong enough to overcome chemical bonds in some cases. This is what makes dissociation possible in some cases. This applies for both ionic compounds and covalent compounds in some cases. But only in some cases, and not in others. Why only in some cases?

It's really a question of balance.

10.3 Balance

This is the first good taste of the importance of balance which I mentioned in Chapter 1.

“ What we are dealing with in many cases is the balance of opposing processes. Different forces working against each other. Nature's tug-of-war. ”

We shall see how this applies to solubility and to dissociation. The explanations for ionic and for covalents will differ, so I will break these into separate parts.

• THE IONIC PART

In the recap earlier, I summarized the following.

Water can dissolve some ionic compounds and separate them into individual ions.

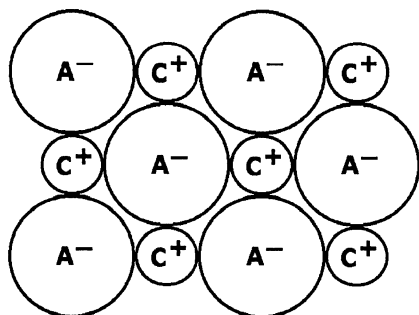
Dissociation is not a simple task. In order to separate the ions, water must overcome the strong ionic bonding between the cations and anions within the ionic network.

Let me put it another way. It costs energy to overcome the ionic bonding in the solid compound. Something must pay that cost, or the compound will not dissolve and dissociate. The payment can come from several sources, and that's where the strength of water's polarity comes into play. Another contribution can arise from entropy, but entropy can work for or against dissolving and dissociating. The entropy part is more complicated, and we're just not doing that right now. We'll come back to this point beginning in Chapter 39. For now, let's just deal with the energy issues.

With respect to energies, the question of solubility and of dissociation for an ionic compound in water boils down to two opposing factors.

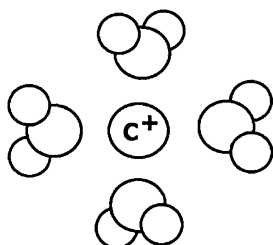
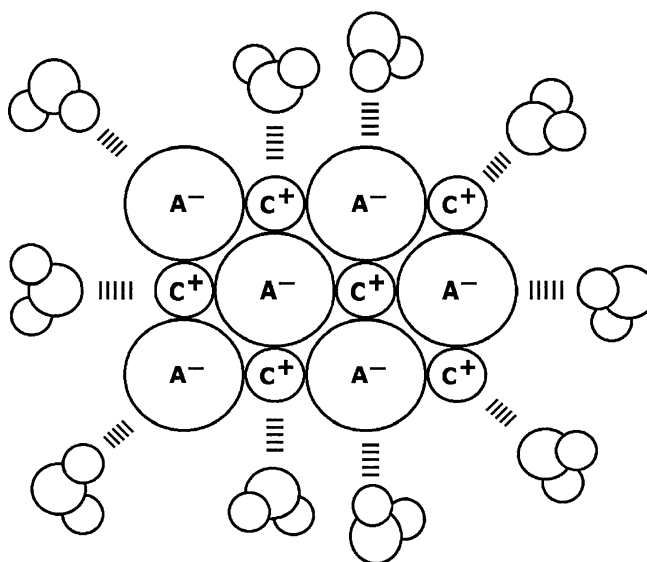
- ▶ 1. The strength of the ionic bonding between all the cations and all the anions in the ionic network compound.
Those ionic bonds are holding the solid together. You must break those ionic bonds, so this is the price which must be paid for solubility and for dissociation.
- ▶ 2. The strength of the attractions between water molecules and the individual cations and anions.
This is the hydration part which pays toward the total expense of solubility and dissociation.

THESE TWO STRENGTHS ARE IN OPPOSITION TO EACH OTHER. The first favors the ionic compound staying together as a solid and NOT dissolving. The second favors dissolving and dissociating.

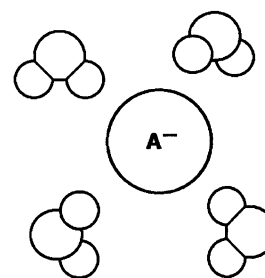


Let's look at a generic, ionic compound composed of a three-dimensional network of cations (C^+) and anions (A^-). (For simplicity, I'm only drawing two dimensions.)

Now let's see what happens when it's thrown into a bucket of water. Within the solid, ionic bonds hold the cations and anions in place. Meanwhile, water molecules interact with the ions of the solid, trying to pull the ions apart.



If possible, this leads to dissolving (solubility) and to dissociation into separated, hydrated cations (left) and anions (right). I just drew each of these with four water molecules, but remember that there's a bunch of waters involved and they're can be layers of them crawling all over the ions in three dimensions.



Notice that I said if possible. Whether it actually happens will be determined by the opposing strengths above and the relative costs. We can cite two possible outcomes.

- ▶ A. If the hydration interactions are strong enough and if all of these together can pay a sufficient price, then ionic bonding can be overcome and the compound will be soluble. The compound will dissolve to a significant extent.
- ▶ B. If the hydration interactions are not strong enough and they cannot pay a sufficient price, then they will NOT overcome the ionic bonding and the compound will be insoluble. The compound will NOT dissolve to a significant extent.

There it is, folks, in a nutshell. Again, it's a matter of the balance of opposing factors. And although we will bring in entropy and other factors further down the road, at this point of the journey still early in the Grand Puzzle, we can see how balance will play such an important part.

Now let me tell you about that annoying phrase which I keep underlining, "to a significant extent". There are no numbers which define one compound as soluble and another as insoluble. There is a wide range to solubilities and the soluble/insoluble distinction is a relative comparison, based on practical significance. Technically, even an "insoluble" compound gives tiny traces of ions in solution. This can be measured. For example, our "insoluble" example, BaSO_4 , dissolves a tiny bit: 0.00024 g of barium sulfate will dissolve in 100 mL H_2O . This is NOT a significant extent. A compound we call "soluble" will dissolve in an amount which is generally thousands to hundreds-of-thousands times greater than this. So, what you must understand is that "insoluble" does NOT mean "not soluble". Instead, "insoluble" means insignificantly soluble although often measurable. Here's a picture to keep in mind. A teaspoon of a soluble compound will dissolve in less than a gallon of water. A teaspoon of an insoluble compound will not dissolve in a gallon of water and not in 10 gallons of water, although it might dissolve in the Pacific Ocean. Get the picture? Here's another illustration. When you drink water, you might use a glass cup. I think we can agree that it's safe to consider glass as an insoluble compound. But even glass has a measurable solubility! Have you ever bought distilled water in the store? It comes in plastic bottles.

They can't store it in glass for long periods of time because some ions from the glass will dissolve in the water. You might never notice it by sight or by taste but even glass dissolves, although in extremely tiny amounts. Glass is insoluble: it's insignificantly soluble although it can be measured.

OK, this ends the ionic part.

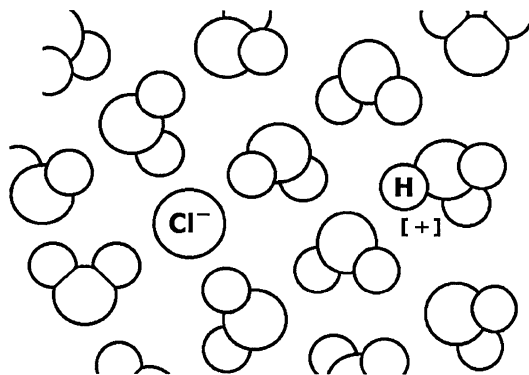
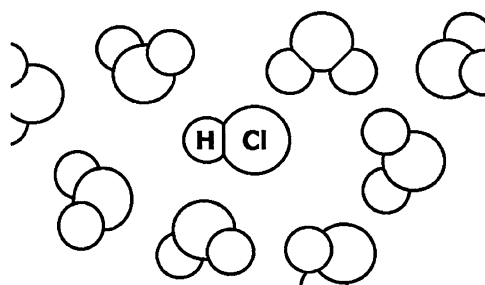
- THE COVALENT PART

Water can dissolve many covalent compounds, but only molecular ones. Unlike the case for ionic networks which can be soluble or insoluble, all covalent networks are insoluble. Of the covalent, molecular compounds which can dissolve, some of these can dissociate to ions, but most don't. Most covalent solutes are just neutral molecules in solution. Why do some covalent compounds dissolve while others don't? For the cases which do not dissociate, then the hydration interaction for ions as described above is not available. Something else must pay toward dissolving. Other kinds of interactions then come into importance, but we're not going to go into all of them right now. One big factor, however, is the solute compound's own polarity. If the solute compound by itself is fairly polar, then its own δ^+/δ^- partial charges can interact with the partial charges of the water molecules; this can favor solubility. Sugars and alcohols are polar molecules, and this is one of the reasons (along with other reasons) why so many dissolve so well in water. If soluble, then we must also consider why some solutes dissociate to ions while others stay intact as neutral molecules. In the case of sugars and alcohols and many other solutes, only neutral molecules are present in solution: they dissolve but they do not dissociate. Each of the molecules is surrounded by water molecules which are interacting through polarity. There are no ions. These compounds are nonelectrolytes, as mentioned earlier.

What we need to distinguish and to focus on now are those covalents which do dissociate to ions in aqueous solution. One of the best covalent compounds for doing this is hydrogen chloride, HCl. We talked about this compound in earlier Chapters. By itself, hydrogen chloride is a binary, covalent compound; it's a gas at normal conditions. It has one covalent bond which is very polar. It is similar to hydrogen fluoride which we also talked about earlier. In HCl, the bond share is again very uneven; the chlorine end has more than a 50-50 share while the hydrogen end is less than 50-50.



The gas dissolves extremely well in water...



...but instead of simple hydration, the water molecules actually pull apart the HCl covalent bond to give a Cl^- ion and one or more polyatomic ions containing the H^+ part (which I'll get to in a moment below).

To be honest, this is a very dramatic case of dissociation of a covalent compound and most things just won't do this. Let's go back to what I had said in the earlier recap for covalents.

Water can dissolve some covalent compounds; water can separate some (not all) of these to form ions.

Again, dissociation is not a simple task. Remember that a covalent compound has no ions to begin with. It only has covalent bonds. In order for dissociation to happen, water must break a covalent bond in the solute molecule.

There is some parallel between the dissociation of covalents and the dissociation of ionics. Both types result in hydrated ions, both involve opposing strengths and both involve balance, but they start out at different places: covalent bonds versus ionic bonds. I gave the two opposing strengths for ionic dissociation above. The two factors for the dissociation of a covalent bond are the following.

- ▶ 1. The strength of the covalent bond between the two atoms in the solute molecule.
You must break this bond, so this strength is the price which must be paid for dissociation.
- ▶ 2. The strength of the attractions between water molecules and the individual cations and anions which are formed.

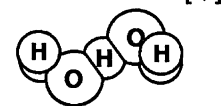
This is the part which pays toward the expense of dissolving and dissociation.

Again, THESE TWO STRENGTHS ARE IN OPPOSITION TO EACH OTHER. The first favors keeping the covalent bond together and NOT dissociating. The second favors dissociating.

Dissociation is primarily limited to a very small fraction of covalent compounds in general. By far, most cases of this small fraction have a hydrogen atom in a very polar covalent bond. Why does hydrogen matter? There are two reasons, one involving the cost of breaking the covalent bond and one involving the payback from the hydration of ions.

I'll do the cost aspect first. I can't go into a lot of details here, but I can explain a bit of it as follows. Our examples of polar covalent bonds involving hydrogen showed the H end of the bond to have the $\delta+$ partial charge. The extent of this polarity is very important: in general, a bond with high polarity is more prone to dissociation to ions. For example, covalent bonds between O and H are much more polar than covalent bonds between C and H. As such, OH bonds are much more prone to dissociate in water than are CH bonds. (Watch the wording. I said much more prone to dissociate, not guaranteed to dissociate. Other factors are also involved. Some may dissociate but others may not.) Thus and overall, bonds to H which are more-and-more polar and which carry a bigger-and-bigger $\delta+$ partial charge on H will cost less to dissociate to a full $1+$ ion charge. However, it still costs.

The other side of the balance sheet is the interaction of the H^+ ion with water molecules. In reality, this greatly exceeds simple hydration. Instead of monatomic H^+ ions, there are actually two polyatomic ions produced. One of these is H_3O^+ (at left) which gets its own name of "hydronium ion". The second cation is $H_5O_2^+$ (at right). These are the bare-bones, fundamental chemical units which are present in an aqueous solution of " H^+ ". These H_3O^+ and $H_5O_2^+$ cations are then hydrated, and those hydrations tend to be very strong. There's more to this story, and I will come back to this in Chapter 54; for now, suffice it to say that the total strength of the many interactions allows water to break apart very polar covalent bonds involving H, at least in some cases.



As you can see, there is no such thing as monatomic H^+ in water. Although it is often written $H^+(aq)$, it's ALWAYS present as polyatomic units involving H_3O^+ and $H_5O_2^+$. In fact, monatomic H^+ ions do not exist in any solution whatsoever. As noted in Chapter 4, monatomic H^+ ions do not even exist in any compound. H^+ is always covalently bonded to something in a solution or in a compound.

(Notice that I am saying in solution or in a compound. As noted previously, the H^+ ion does exist by itself in space, but I'm talking normal conditions right now.)

Let me make a note about terminology. The H^+ ion would have no electrons at all; it's just a nucleus. By far, most hydrogen atoms are the 1H isotope, which has no neutrons. Thus, if it were to exist by itself, then H^+ would simply be a proton. Although it does not exist by itself in solution or in any compound, H^+ is commonly referred to as "proton". When a compound transfers H^+ to a water molecule, then we say that the compound "protonates" the water molecule. We can also reverse the focus and say the water molecule is "protonated". In the present usage, the HCl molecules protonate water molecules to give H_3O^+ and $H_5O_2^+$; the term "protonated water" refers to these polyatomics, H_3O^+ and $H_5O_2^+$.

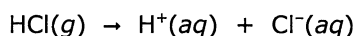
I should point out to you at this time that there are variations in the manner by which $H^+(aq)$ is presented. Some texts and some instructors write this as $H_3O^+(aq)$. The reason for this is to emphasize that $H^+(aq)$ doesn't really exist by itself in water. Unfortunately, H_3O^+ by itself is not entirely correct either. Writing $H^+(aq)$ is OK, since the phase designation is understood to incorporate the interactions of that phase. In other words, writing $H^+(aq)$ is understood to include H_3O^+ and $H_5O_2^+$, and it serves as a general symbol for protonated water. Some instructors may require their students to specifically write H^+ as H_3O^+ all the time. That's fine. In fact, the different representations have advantages in different

situations. I'll mostly write it as the H^+ way, but sometimes I'll write it as H_3O^+ . Check with your instructor to see if s/he wants it written a certain way.

OK, let's wrap things up for covalent solutes overall. Here's where we're at: the dissociation of covalent bonds in water is primarily limited to solutes which have very polar ($\delta+$) bonds to a hydrogen. The reasons for this are twofold.

- ▶ Bonds which are very polar are more easily broken by water.
- ▶ The total strengths involved in forming H_3O^+ and $H_5O_2^+$, along with their hydration interactions, can cover much of the cost of breaking the covalent bond in the solute molecule.

By the way, anytime a covalent molecule dissociates according to the above, you get " H^+ " and you get an anion. The anion is also hydrated but it lies within the usual range of hydration strengths. It's the H^+ part that is so special. These covalent compounds are acids, which are an extremely important class of compounds in aqueous solution. In fact, an aqueous solution of HCl is not called aqueous hydrogen chloride; it's called hydrochloric acid. We can use a balanced equation to depict hydrogen chloride gas dissolving and dissociating in water.



We'll talk much more about acids in the next Chapter.

10.4 Technical aside

Having spent much of this Chapter describing solubility and dissociation, I'm going to throw in a technicality here. Keep in mind that we are still in the early stages of the Grand Puzzle and I am still presenting pieces here and there which will be tied together later.

When some compounds dissolve, they can dissociate as we saw above. Sometimes, however, they don't dissociate completely. This will depend on the compound itself and on its concentration in solution. We will see more of this for covalent solutes in Chapter 11. This can also happen for ionic solutes, and this is the technicality which I wish to describe right now.

As an example, consider the dissolving of iron(III) chloride. In aqueous solution, $FeCl_3$ dissociates and you get some $Fe^{3+}(aq)$ and $Cl^-(aq)$, but you also get some polyatomic ions such as $FeCl_2^+(aq)$. This is a technicality which I simply want to mention; it's way too much detail to handle right now. In a dilute solution, many of the most common ionic compounds do indeed dissociate and they dissociate to a majority extent. Furthermore, many ionic solutes will react as if they were fully dissociated. So, at this stage of the game, it remains a satisfactory and useful approximation to assume full dissociation in general for ionic solutes. That's what we'll do. We will consider some of these technicalities much later, in Chapter 59.

This is enough for now, for where we are at, in the Grand Puzzle.

Problems

1. True or false.
 - a. Water molecules have an uneven distribution of charge overall.
 - b. In a solution of $KBr(aq)$, individual ions of K^+ and of Br^- interact with solvent water molecules.
 - c. All substances which dissolve in water are electrolytes.
 - d. When sugar dissolves in water, nearly all of the sugar molecules dissociate.
 - e. Cations in water are attracted to the $\delta+$ side of water molecules.
 - f. An aqueous solution of 0.01 M calcium chloride contains 0.01 M $Ca^{2+}(aq)$ and 0.01 M $Cl^-(aq)$.
 - g. Water can pull H^+ off some covalent molecules.
2. In an aqueous solution of an acid, what are the formulas of the two (fundamental) cations that are present?