Chapter 54   ACID-BASE EQUILIBRIA, Part 1

As our attention now turns specifically to aqueous equilibria, it is useful to recall the vast impact of aqueous reactions in general. Opener to Chapter 10:

❝ 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. ❞

Much of your aqueous self and your aqueous world are equilibrium processes, although many may not necessarily be at equilibrium. We will be touching on equilibrium aspects in this and the following six Chapters.

We begin with acid-base equilibria, which have involved some of the best understood systems for many years. Before beginning, it's time to refresh and to update some of the relevant aspects going back to Chapters 10 - 12.

54.1 Refresh

We open with early definitions from Section 11.4.

❝ For now, our working definitions for acids and bases depend on how compounds behave when they dissolve in water:

An acid is any compound which dissolves in water and forms H^+ (protonated water).
A base is any compound which dissolves in water and forms OH^-. ❞

We continue with these simple definitions for now but we will expand upon them as we go. Now return to the meaning behind $H^+(aq)$. Section 10.3:

❝ 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, <u>monatomic H^+ ions do not exist in any solution whatsoever</u>. As noted in Chapter 4, <u>monatomic H^+ ions do not even exist in any compound</u>. H^+ is always covalently bonded to something in a solution or in a compound...
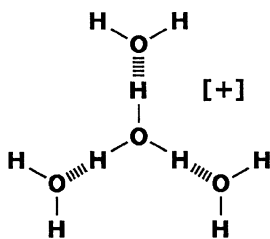
Let me make a note about terminology. The H^+ ion would have no electrons at all; it's just a nucleus. By far, most hydrogen atoms are the ^1H isotope, which has no neutrons. Thus, if it were to exist by itself, then H^+ would simply be a proton. Although it does not exist by itself in solution or in 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
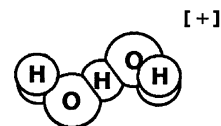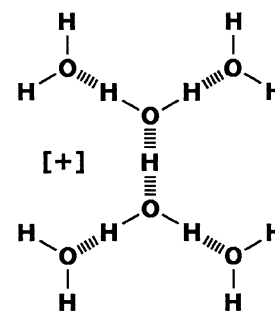
to emphasize that $H^+(aq)$ doesn't really exist by itself in water. Unfortunately, H_3O^+ by itself is not entirely correct either. Writing $H^+(aq)$ is OK, since the phase designation is understood to incorporate the interactions of that phase. In other words, writing $H^+(aq)$ is understood to include 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. **"**

UPDATE, HERE AND NOW: As noted back then, H_3O^+ and $H_5O_2^+$ are the fundamental ions behind the notation $H^+(aq)$. And I said at the time that I would come back to this story. We can now add a few more points about these. Each ion is hydrated strongly with surrounding water molecules by way of ion-dipole interaction as well as hydrogen bonding. Notably, hydrogen bonding between either of these ions and a water molecule is much stronger than hydrogen bonding between two molecules of H_2O as present in water alone. Due to the strength of the interactions, H_3O^+ is sometimes written as $H_9O_4^+$, depicted at left, and $H_5O_2^+$ is sometimes written as $H_{13}O_6^+$, as shown at right. (For simplicity, both structures are drawn flat, but all oxygens are trigonal pyramidal, counting the hydrogen bond.) There are yet other variations, and all of this highlights more of the importance of hydrogen bonding in aqueous systems. But we won't n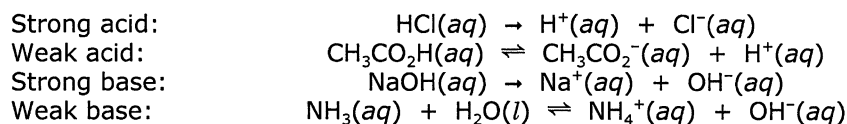eed this level of detail as we continue, and we can stick with our fundamental formulas of H_3O^+ and $H_5O_2^+$, if needed (although they won't usually be needed). I can also add at this time that these two ions are in equilibrium with each other

$$H_3O^+(aq) + H_2O(l) \rightleftharpoons H_5O_2^+(aq)$$
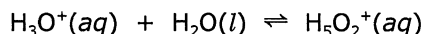
and the kinetics are extremely fast for this interchange.

As you can see by all of this, there's actually quite a bit going on in solutions of "$H^+(aq)$". As noted and quoted above from Chapter 10, I will continue to primarily use the simple designation H^+ although some cases will be easier using H_3O^+. Just remember that even $H_3O^+(aq)$ will always have $H_5O_2^+(aq)$ in solution with it.

Let's now return to the notion of strong vs. weak acids and bases. Here are common examples.

Strong acid: $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$
Weak acid: $CH_3CO_2H(aq) \rightleftharpoons CH_3CO_2^-(aq) + H^+(aq)$
Strong base: $NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$
Weak base: $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

Note that the double half-arrows convey the sense of opposing processes and an equilibrium system, which is characteristic of weaks. Single full-arrows convey the lack of a significant opposing process and the lack of an equilibrium, which is characteristic of strongs. These examples were among our first foray into the notion of equilibrium back in Section 12.4.

" A lot of reactions involve equilibria but many others do not, at least not to a significant extent. An excellent example of this difference is provided by the strong and weak acids and bases. In a nutshell and for practical purposes, <u>weaks involve equilibria and strongs do not</u>. THIS IS THE KEY DIFFERENCE BETWEEN STRONG AND WEAK CASES OF ACIDS AND BASES. **"**

We then expanded on this for each case.

" Acetic acid dissociates, but not a lot.

$$CH_3CO_2H(aq) \rightarrow H^+(aq) + CH_3CO_2^-(aq)$$
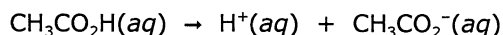
The reason is that the backwards reaction also occurs: acetate can react with H^+ to re-form the acid.

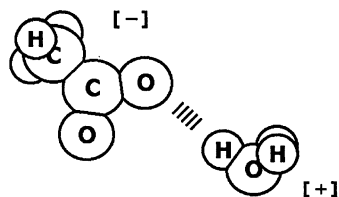$$H^+(aq) + CH_3CO_2^-(aq) \rightarrow CH_3CO_2H(aq)$$
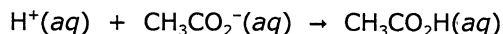
Both processes occur at the same time. Some molecules dissociate to ions and some ions recombine to form neutral molecules. This is an equilibrium. We can represent this as

$$CH_3CO_2H(aq) \rightleftharpoons H^+(aq) + CH_3CO_2^-(aq)$$
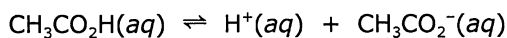
Why is this an equilibrium and a strong acid such as hydrochloric acid is not? We have to go back to the whole story. Remember, H^+ doesn't just form by itself. CH_3CO_2H doesn't just willingly break one of its bonds. NO ACID MOLECULE IN WATER WILL EVER BREAK ITS OWN BOND BY ITSELF. Something has to <u>pull</u> off the H^+, and it's really the H_2O molecules that do this. This is better seen in the H_3O^+ version of the equation.

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$
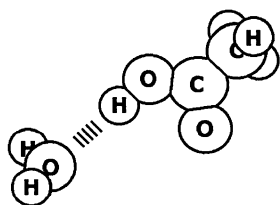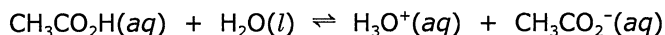
I've illustrated this notion of pulling in the diagram on the left. Water is trying to pull H^+ off the molecule of acetic acid. If it wins, you get acetate and H_3O^+ (and also $H_5O_2^+$ as in any case of protonated water). Some waters do win, but acetate does not surrender willingly: it pulls back! I show this on the right. These are opposing processes. They are in competition... 🙿

UPDATE, HERE AND NOW: We now recognize this interaction to start on the left as hydrogen bonding. Water uses a lone pair as hydrogen bond acceptor while acetic acid is the donor. In essence, the hydrogen bonding represents a pull by water on the H of acetic acid. If the water actually pulls off such a heist of a hydrogen, then you have dissociation. But water is not very successful at this overall, and the equilibrium lies far to the left. We now also know that equilibrium connects to $\Delta G°$ which is itself composed of $\Delta H°$ and $\Delta S°$. For this process, the enthalpy term is very small ($\Delta H° = -0.25$ kJ) suggesting that the pull in either direction is fairly equal. On the other hand, the dissociation is substantially opposed by entropy ($\Delta S° = -92.1$ J/K). Why is $\Delta S°$ so negative? This is a very notable point as we head into many aspects of ionic dissociation in aqueous solution. We can tie this to the very strong orientation effects of ion-dipole IFs which negatively impact entropy. In general, the dissociation of a neutral molecule into ions in aqueous solution is opposed by entropy. Finally, we now also know that $\Delta G°$ gives us K which is then a quantitative measure of the equilibrium position. We have worked quite a bit with this equilibrium in several Chapters since Chapter 46, and K had been given (in Chapter 52) as 1.8×10^{-5}.

Flash back again to Chapter 12.

🙾 Now we compare this to a strong acid. How do strongs behave differently? I'll show this with hydrochloric acid. Water yanks on the neutral HCl molecule (shown at left), and breaks the bond to form H_3O^+ and Cl^- (shown at right). Now here comes the important part: chloride does NOT pull back. Chloride is fairly content just being its old, hydrated self in water. It doesn't really care about fighting over some H^+. That means there is no opposing process. There is no competition. THERE IS NO EQUILIBRIUM. We can represent this by using the standard single-full-arrow in the chemical equation.

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

OR

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$ 🙿
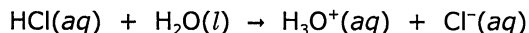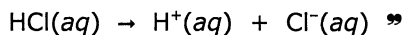
UPDATE, HERE AND NOW: Although this may start off as hydrogen bonding, this just goes all the way to dissociation. Chloride is not putting up much resistance and there is no significant equilibrium.

Return to Chapter 12.

🙾 These aspects are critically important. Let me summarize the key differences between strong and weak acids.

- When a strong acid dissolves in water, water pulls H^+ off the acid molecule, leaving behind an anion. The anion does not pull back on H^+ to a significant extent. There is no significant equilibrium.
- When a weak acid dissolves in water, water pulls H^+ off the acid molecule, leaving behind an anion. The anion, however, pulls back on H^+ and these two processes are in competition. This makes up an equilibrium.
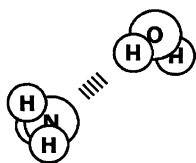
The notion of competition is also important in distinguishing weak bases and strong bases. When ammonia dissolves in water, some ammonia molecules pull apart some water molecules to give NH_4^+ and OH^-. Now it's the hydroxide which competes, pulling back on the H^+ in the ammonium cation. There's your competition. There's your equilibrium:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$ **"**
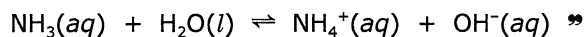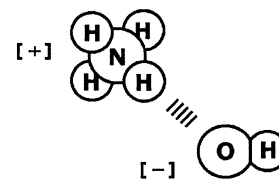
UPDATE, HERE AND NOW: You can see this starting off as hydrogen bonding again on the left between the neutral molecules. Ammonia uses a lone pair as hydrogen bond acceptor, while water is now the donor. With enough pull, a molecule of ammonia can dissociate a water molecule. But ammonia is not very successful at this, and the equilibrium again lies well to the left. This one is slightly endothermic and again opposed by entropy. You can calculate $\Delta H°$, $\Delta S°$ and $\Delta G°$ using values from Appendix A.

Resume.

" On the other hand, when sodium hydroxide dissolves in water, you get full dissociation into separate $Na^+(aq)$ and $OH^-(aq)$ ions. No competition. No equilibrium. That makes it a strong base.

$$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$$
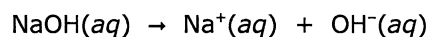
Thus, the distinction between strong and weak bases has a parallel to the acids. Let's summarize this.

• Weak bases are characterized by an equilibrium competition between opposing processes.
• Strong bases lack an opposing process; there is no significant competition and there is no equilibrium.

Equilibria are incredibly important. There's a lot more to this stuff, and we'll come back to this in more detail in later Chapters. **"**

UPDATE, HERE AND NOW: We have indeed been seeing the importance of equilibria and we continue to develop this picture. But let me bring in a technical point here.

I have repeatedly referred to strongs as having no "significant" competition or no "significant" equilibrium or no "significant" whatever. Strong acids and bases are overwhelmingly dissociated at typical, dilute concentrations. This is the working definition, in practice, of a strong acid or base. Thus, a strong is nearly 100% dissociated at dilute conditions (such as 0.001 mol per L, for example), although technically it may only be 99% or so. The remainder which is not dissociated is not considered "significant". In stark contrast, weak acids and bases typically give much less dissociation even at dilute conditions. There is a very extensive range for these, commonly running from 0.1% dissociation up to 10% or 20% at dilute conditions. There are some which might be 60% or 80% dissociated, and there are borderline cases which approach the strongs. Thus, there is a range of these things. Technically, there is no exact, numerical cutoff between strong and weak but, on yet another practical basis, most weak acids which are typically encountered are well outside the range of strongs. Thus, for our practical purposes, our working definition of a strong remains one which is overwhelmingly dissociated at dilute conditions while a weak will have much less dissociation.

This would be a good time to bring back the strong vs. weak lists from Section 11.3.

" STRONG VERSUS WEAK ACIDS. There are six strong acids that are commonly encountered in chemistry and these can simply be memorized as strong. These six are the following.

Hydrochloric acid, HCl   Hydrobromic acid, HBr   Hydroiodic acid, HI
Nitric acid, HNO_3 Perchloric acid, $HClO_4$ Sulfuric acid, H_2SO_4

Although there are other strong acids, they are not nearly as common. Most other acids are weak and you can assume this unless told otherwise.

STRONG VERSUS WEAK BASES. By far, the most common strong bases are the soluble metal hydroxides. Less common, but still strong, are the soluble metal oxides. For weak bases, ammonia is by far the most common and it should be memorized as such. There are still many others, but they are not as common at this stage of the game.

Let me add a comment about the strong bases. To be a strong base, the compound must dissociate completely to produce OH⁻. If the compound is not soluble, then it cannot dissolve (to a significant extent) and therefore it cannot dissociate (to a significant extent). This eliminates most ionic hydroxides and oxides from being strong bases, since most are not soluble. On a practical basis, the soluble cases mostly involve the ionic hydroxides and oxides of Group 1 and Group 2, except for Be and Mg. **"**

We will continue for now with this list, but we will be modifying it as we go.

This ends the old stuff.

54.2 Autoionization

In the illustrations above, water acts to pull on H^+ from an acid but the H^+ of water is pulled upon by a base. Thus, water goes both ways, and it can even go both ways with other water molecules. Water molecules can pull on each other and compete for H^+ from each other.
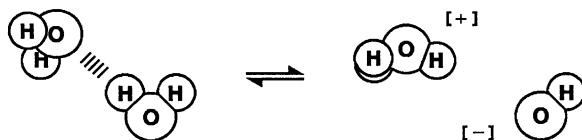

On the left, water molecules do their usual hydrogen bonding thing. Again, the hydrogen bonding acts somewhat as a pull by one water molecule operating on its neighbor. If the pull is sufficient, you get some ionization as given on the right side of the equation. Those ions could recombine to form neutral water molecules or they can become separated from each other and stay as such until they run into another opposite somewhere else. You have opposing processes overall, and an equilibrium.

This particular equilibrium is called autoionization. Auto- is used in the normal dictionary sense meaning self-; in other words, this is self-ionization. Autoionization is the ionization of a single compound of and by itself, among its own molecules. Water is not at all unique for this; many compounds undergo autoionization and there are a range of K values for these. But our focus here is on water.

We can write a balanced equation for autoionization based on the above illustration.

$$2\ H_2O(l)\ \rightleftharpoons\ H_3O^+(aq)\ +\ OH^-(aq)$$
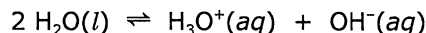
or we can write this in simplified format as

$$H_2O(l)\ \rightleftharpoons\ H^+(aq)\ +\ OH^-(aq)$$
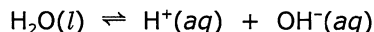
and these two equations mean the same thing. We can write K expressions for either format

$$K\ =\ [H_3O^+]\,[OH^-] \qquad OR \qquad K\ =\ [H^+]\,[OH^-]$$

and these also mean the same thing. I will work primarily with the $[H^+]$ version. Notice that H_2O does not appear in the K's, as is usual for a liquid. Technically, the thermodynamic properties of a solvent in a solution can be different from the properties of the pure liquid by itself. Nevertheless, the properties are the same for a solvent in a sufficiently dilute solution. We will follow this throughout; thus, the activity of $H_2O(l)$ will remain unity in our coverage, even when it is the solvent.

Water's autoionization equilibrium constant is specifically labeled K_w. Thus, we can write

$$K_w\ =\ [H^+]\,[OH^-]$$

and its value has been measured over a range of temperatures. Here are some.

T	10. °C	20. °C	25 °C	30. °C	40. °C
K_w	2.9×10^{-15}	6.8×10^{-15}	1.0×10^{-14}	1.5×10^{-14}	2.9×10^{-14}

Only two sigfigs are shown although more are known. We will be getting into calculations which are not always exact, so we will usually work with K values to only two sigfigs for aqueous equilibria. What do I mean by "not always exact"? It's a real vs. ideal problem again. Ionic solutes are very prone to deviations from ideality, much moreso than neutral solutes. Because of this, the calculations can be off unless the ion concentrations are very dilute. We'll just use two sigfigs in K's as a general practice for aqueous solutions involving ions.

The thermodynamic parameters of water's autoionization at 25 °C are the following.

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$
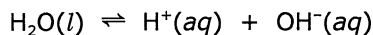
$$\Delta H° = 55.84 \text{ kJ} \qquad \Delta S° = -80.70 \text{ J/K} \qquad \Delta G° = 79.90 \text{ kJ}$$

This process is opposed by both enthalpy and entropy. Since it is endothermic, K_w increases as temperature increases, as seen in the above list. K_w is still a very small number at all temperatures, so there's really not much of an equilibrium here. To illustrate, at 25 °C, this amounts to 1.8 $H^+(aq)$ ions and 1.8 $OH^-(aq)$ ions per billion water molecules.

We will be working at 25 °C unless told otherwise, so

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

and, since autoionization gives 1:1 H^+ and OH^-, then $[H^+] = [OH^-]$ and we have

$$[H^+] = [OH^-] = 1.0 \times 10^{-7} \text{ M}$$

in pure water. This equality of $[H^+]$ and $[OH^-]$ may or may not be true in solutions with other compounds present. Regardless, every aqueous solution will have some $[H^+]$ and some $[OH^-]$, and one is calculable from the other given the K_w relationship. This brings us to the characterization of aqueous solutions as neutral, acidic or basic according to the following.

neutral solution	$[H^+] = [OH^-] = 1.0 \times 10^{-7} \text{ M}$
acidic solution	$[H^+] > [OH^-]$ $[H^+] > 1.0 \times 10^{-7} \text{ M}$ $[OH^-] < 1.0 \times 10^{-7} \text{ M}$
basic solution	$[H^+] < [OH^-]$ $[H^+] < 1.0 \times 10^{-7} \text{ M}$ $[OH^-] > 1.0 \times 10^{-7} \text{ M}$

Although the numbers can be minute amounts, they are definitely measurable and they are critically important in many applications. For example, all living organisms depend on the correct concentrations of these ions, typically in the 10^{-6} to 10^{-8} range. There are biological applications outside this range but these are usually injurious or destructive, such as for attack, defense or digestion.

Given the tremendous importance of these numbers in their many applications, and given that the concentrations can be very small, a logarithmic system was developed for dealing with these more easily.

54.3 p

A 'p' function is a negative logarithm, where the log is the common type, base 10. Taking the 'p' of anything means taking the negative log of that item. For a solute, this means taking the negative log of its activity, a; for other things, it's just the negative log of whatever.

$$pH = -\log a(H^+)$$
$$pOH = -\log a(OH^-)$$
$$pK = -\log K$$

This is not just a chemistry term. For example, if you're studying a fish kill in a lake, you may want to measure the pO_2.

$$pO_2 = -\log a(O_2(aq))$$

Ever since we introduced activity in Chapter 46, we assumed ideal behavior and we set the activity of an aqueous solute to be its unitless molar concentration. As such, pH and pOH become the following.

$$pH = -\log [H^+]$$
$$pOH = -\log [OH^-]$$
For each, [ ] is understood to be a number of M's but is unitless.

As noted in the last section, however, ionic solutes are very prone to deviations from ideality, and the extent of their nonideal behavior increases with their concentration. For very dilute solutions, these equations do work well. For example, for 1.0×10^{-4} mole HCl dissolved in 1.00 L solution, the pH will be 4.00 or very close, as calculated. As concentration increases, however, even still low in the 10^{-2} to 10^{-1} M range, the deviations can become significant and these calculations become less reliable. Some of this will still be contained within the fundamental meaning of sigfigs; in other words, we understand there is

some uncertainty in the final sigfig of some value. On the other hand, some deviations will exceed the usual levels of uncertainty. These deviations will also be more significant when some other ionic solute is present, such as 1 M NaCl. Again, ionics are the primary culprits; neutral solutes follow ideal behavior much better. For example, regarding the pO_2 example above, the activity of $O_2(aq)$ and the concentration of $O_2(aq)$ will be the same at the real concentrations which are encountered.

Why are ionics such deviants?

We made preliminary mention of this in Section 43.1. Interactions between two ions are much stronger than between two neutrals, or even between one ion and one neutral. An ion charge is a higher charge than a partial charge of a permanent or temporary dipole, and this explains why ion-dipole interaction is a much stronger interaction than the other intermolecular forces. The full ion charges also allow for other interactions beyond what we've covered. For example, they can also allow for aggregations of ions in solution; we will consider more of that aspect later in Chapter 59. Thermodynamic activities take into account all such interactions, but these become very tedious to calculate in ionic solutions. It remains correct that, at very low concentrations, the extra interactions are not significant and concentrations will equal the activities. At higher concentrations, however, the concentrations will differ more from activities and that gives more deviations from ideality. Despite the technicalities here, we will stay with the equation pH = $-\log$ [H$^+$] for simplicity, and likewise for pOH = $-\log$ [OH$^-$], knowing that they are best for dilute solutions and only approximate for otherwise. There are better (and more complicated) equations for pH calculations which address the activities better but we won't go into those. In real applications, if you want to prepare a solution with a certain pH, then it is common to do the calculations as to be shown here and to prepare the solution accordingly. Then you measure the real pH. The real pH may differ in the second decimal or it may even differ in the first decimal if the total concentrations of all ions are high enough. You then adjust the pH as necessary to get it where you want. That's life in the real world.

The calculation of pH from [H$^+$] is the negative log; going backwards, the calculation of [H$^+$] is the antilog of negative pH. For example:

$$\text{if } [H^+] = 3.2 \times 10^{-3} \qquad \text{then pH} = -\log(3.2 \times 10^{-3}) = 2.49$$
$$\text{if pH} = 2.49 \qquad \text{then } [H^+] = 10^{-2.49} = 3.2 \times 10^{-3}$$

Likewise for pOH and [OH$^-$].

$$\text{if } [OH^-] = 2.7 \times 10^{-4} \qquad \text{then pOH} = -\log(2.7 \times 10^{-4}) = 3.57$$
$$\text{if pOH} = 3.57 \qquad \text{then } [OH^-] = 10^{-3.57} = 2.7 \times 10^{-4}$$

Keep in mind that concentrations are still in M although the activities are unitless.

Let me make a point about sigfigs.

Although we had simply treated sigfigs for natural logarithms according to the standard multiplication/division practice, we now consider a separate treatment for common logs. Here's how this works, using the first pH example above.

$$pH = -\log(3.2 \times 10^{-3})$$

Chop up the log.

$$pH = -\log(3.2 \times 10^{-3}) = -[\log(3.2) + \log(10^{-3})]$$

Within the original value of 3.2×10^{-3}, the 3.2 has two sigfigs. The 10^{-3} is exact; it simply gives the decimal place in the value 0.0032. Thus, the sigfig information in the original value is within the 3.2 part. When you take the log of that, you cut it to the same number of sigfigs.

3.2 has two sigfigs. Its log is 0.51, rounded to two sigfigs.
10^{-3} is exact. Its log is $-3.000...$ which is also exact. Since exact, it does not affect a round-off decision.

$$pH = -[\log(3.2) + \log(10^{-3})] = -[0.51 + (-3.000...)]$$

This now follows the usual addition/subtraction process for sigfigs.

$$pH = -[0.51 + (-3.000...)] = 2.49$$

The answer is limited to two decimal places due to the 0.51 value. Thus, after taking a log, the number of decimal places to keep will equal the number of sigfigs in the original number. For going backwards, when taking an antilog (10^{-x}), the number of decimal places in x will determine the number of sigfigs in

the final number. Thus, as seen for $10^{-3.57}$ upstairs, there were two decimal places in the exponent and that means two sigfigs in the final value, 2.7×10^{-4}.

Although this is the sigfig practice for logs and antilogs in general, we will impose one more rule for logs involving pH and pOH, due to possible nonideal behavior. So that we don't get too carried away, we will limit calculated pH and pOH values to two decimals max, even if the sigfigs say we could have more. There's no reason to show a third decimal by these calculations, even if the sigfigs would allow it.

Now let's return to K_w

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

and take the negative log

$$-\log K_w = -\log [H^+] - \log [OH^-] = -\log(1.0 \times 10^{-14})$$

to get p's

$$pK_w = pH + pOH = 14.00$$

and this is a very useful relationship. Know it. This provides a very convenient way of interconverting between pH and pOH. Thus, for example, given pH = 2.49, we can find pOH from

$$pOH = 14.00 - 2.49 = 11.51$$

and vice versa. While we're at it, since pure water has $[H^+] = [OH^-] = 1.0 \times 10^{-7}$ M, then pH = 7.00 and pOH = 7.00. Know these also.

With these relationships, we can add pH and pOH to the characterizations of neutral, acidic and basic solutions.

neutral solution	$[H^+] = [OH^-] = 1.0 \times 10^{-7}$ M	pH = 7.00 pOH = 7.00
acidic solution	$[H^+] > [OH^-]$ $[H^+] > 1.0 \times 10^{-7}$ M $[OH^-] < 1.0 \times 10^{-7}$ M	pH < 7.00 pOH > 7.00
basic solution	$[H^+] < [OH^-]$ $[H^+] < 1.0 \times 10^{-7}$ M $[OH^-] > 1.0 \times 10^{-7}$ M	pH > 7.00 pOH < 7.00

Diagrammatically, the various parameters are as follows.

The scale does continue left and right, so there are negative pH's and negative pOH's, but this is enough for the scale drawing here.

Some of these connections can seem confusing at first. For example, the acidity of a solution is associated with $[H^+]$ or with pH but in opposite directions: as acidity increases, $[H^+]$ increases but pH decreases. The opposite directions are a result of the inverse relationships which are involved. We can summarize these as follows.

  ▸ The product $[H^+] \times [OH^-]$ is a constant (K_w), so $[H^+]$ and $[OH^-]$ are inversely related. As one goes up, the other goes down.
  ▸ A negative log is an inverse relationship. As $[H^+]$ goes up, pH goes down. As $[OH^-]$ goes up, pOH goes down.

▸ pH and pOH have a constant sum (14.00). As one goes up, the other goes down.

Thus, as [H$^+$] goes up ↑ or down ↓, we have the following relationships.

$$[H^+] \uparrow \;\rightarrow\rightarrow\rightarrow\; [OH^-] \downarrow \qquad\qquad\qquad [H^+] \downarrow \;\rightarrow\rightarrow\rightarrow\; [OH^-] \uparrow$$

$$\downarrow \qquad\qquad\qquad \downarrow \qquad\qquad \text{OR} \qquad\qquad \downarrow \qquad\qquad\qquad \downarrow$$

$$\downarrow \qquad\qquad\qquad \downarrow \qquad\qquad\qquad\qquad\qquad \downarrow \qquad\qquad\qquad \downarrow$$

$$pH \downarrow \;\rightarrow\rightarrow\rightarrow\; pOH \uparrow \qquad\qquad\qquad pH \uparrow \;\rightarrow\rightarrow\rightarrow\; pOH \downarrow$$

Keep in mind the inverse relationships.

pH is one of the most common indicators of acidity levels used in all sorts of applications, not just the laboratory. Industrial processes often take pH into account. Acid rain and its effects on waterways are typically measured by pH. Closer to home, even the fish in an aquarium need to have a certain pH range for the tank water or they die. Soil is another important application of pH. Many plants prefer soils in the pH range near 6.0 - 7.0, whereas other plants demand more acidic soils. If your azaleas are just not doing too well, check the soil pH. You can measure pH by a variety of means. The most accurate methods involve electronic pH meters. Less expensive and very handy methods use dyes which give a color which is specific for a particular pH; these dyes are commonly available as solutions or they are impregnated into papers which are then used as test strips. These things are part of your world, at least in pet stores and garden centers.

Let's consider a couple of simple pH, pOH calculations.

What is the pH of a solution of 0.00128 mol nitric acid dissolved in 700. mL total volume?

To do this, you must first note that HNO$_3$ is a strong acid, so it is fully dissociated.

$$HNO_3(aq) \rightarrow H^+(aq) + NO_3^-(aq)$$
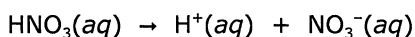
The original 0.00128 mol HNO$_3$ forms 0.00128 mol H$^+$ and 0.00128 mol NO$_3^-$. We want [H$^+$]

$$[H^+] = \frac{0.00128 \text{ mol}}{0.700 \text{ L}} = 0.00183 \text{ M}$$

which goes into pH (as an activity).

$$pH = -\log [H^+] = -\log(0.00183) = 2.74$$

(Although our log rule for sigfigs would allow three decimal places in the answer, this answer shows our limitation to two decimals for these calculations of pH and pOH.) The pH is less than 7, as expected for an acidic solution.

Next: what are the pH and pOH of a 2.80 L solution prepared using 0.465 g potassium hydroxide?

KOH is a strong base. All KOH is dissociated to K$^+$ and OH$^-$.

$$KOH(aq) \rightarrow K^+(aq) + OH^-(aq)$$
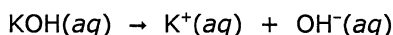
We need [OH$^-$].

$$[OH^-] = \frac{0.465 \text{ g}/(56.11 \text{ g/mol})}{2.80 \text{ L}} = 0.00296 \text{ M}$$

That goes to pOH.

$$pOH = -\log [OH^-] = -\log(0.00296) = 2.53$$

We can get pH from that.

$$pH = 14.00 - 2.53 = 11.47$$

Done. pOH is less than 7 while pH is greater than 7, as expected for a basic solution.

The calculation of pH and pOH is straightforward for strong acids and bases. Weaks won't be so easy, as you will see in the next two Chapters.

54.4 Give/take and conjugate

According to our working definitions going back to Chapter 11, an acid is anything which dissolves in water and forms or increases $[H^+]$ and a base is anything which dissolves in water and forms or increases $[OH^-]$. We can place this in a pH/pOH perspective.

An acid is any compound which decreases pH (or increases pOH).
A base is any compound which increases pH (or decreases pOH).

Furthermore, since H^+ and OH^- react with each other by the reverse of autoionization

$$H^+(aq) + OH^-(aq) \rightleftharpoons H_2O(l)$$
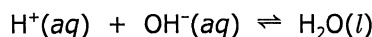
then these ions cancel or neutralize each other. This reverse equilibrium has $K = 1/K_w = 1.0 \times 10^{14}$, which is large. This is the basis of neutralization reactions, going back to Section 12.2. This reaction provides additional interpretation of acids and bases.

An acid is any compound which reacts with a base (or with OH^-).
A base is any compound which reacts with an acid (or with H^+).

Overall, acid-base reactions in water involve the transfer of H^+ or of OH^- from one chemical unit to another (which could include coming from a water molecule). As such, acid-base reactions can be regarded as proton transfer or hydroxide transfer reactions. An acid is the chemical unit which loses H^+ or gains OH^-, and a base is the chemical unit which takes the H^+ or loses OH^-. Returning to the term "protonated" as used previously, we extend the term and now define the verbs protonate and deprotonate as follows. To protonate something is to give or lose H^+ to that something. To deprotonate something is to take H^+ away from that something. Thus, many acids and bases are givers and takers, respectively, of H^+. We can depict this in terms of the transfer of H^+ between a generic acid HA and a generic base B.

$$\begin{array}{ccccccc}
\text{giver} & & \text{taker} & & & & \\
A\text{–}H & + & B & \rightleftharpoons & A^- & + & H\text{–}B^+ \\
\text{acid} & & \text{base} & & & &
\end{array}$$
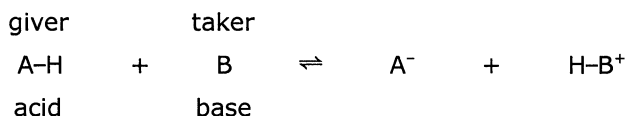
We can summarize this as follows.

An acid gives (loses) H^+ to a base.   OR   An acid protonates a base.
A base takes H^+ from an acid.   OR   A base deprotonates an acid.

Historically, the terms "proton donor" and "proton acceptor" have been used for many acids and bases. These terms are a bit too gentle and potentially misleading. No acid willingly breaks its bond and "donates" H^+. The H^+ must be ripped off. Likewise, the base is not simply "accepting" H^+; it is ripping off the H^+.

Some acids, however, do not give (lose) H^+; instead, they operate by taking OH^-. Boric acid, H_3BO_3 or $B(OH)_3$, is an example.

$$B(OH)_3(aq) + H_2O(l) \rightleftharpoons B(OH)_4^-(aq) + H^+(aq)$$
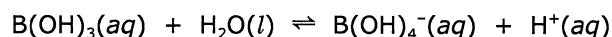
Thus, boric acid takes OH^- away from H_2O, leaving behind H^+. Of course, it doesn't just leave H^+ behind: another molecule of H_2O is pulling it off.

$$B(OH)_3(aq) + 2\,H_2O(l) \rightleftharpoons B(OH)_4^-(aq) + H_3O^+(aq)$$
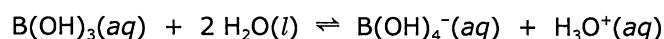
Another example is SO_3 which reacts immediately (and very vigorously) with water to form the strong acid, H_2SO_4, which is fully dissociated.

$$SO_3(aq) + H_2O(l) \rightarrow HSO_4^-(aq) + H^+(aq)$$
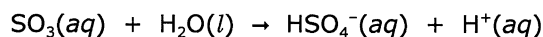
Other acids, such as SO_2, can also be depicted as taking OH^- from water.

$$SO_2(aq) + H_2O(l) \rightleftharpoons HSO_3^-(aq) + H^+(aq)$$
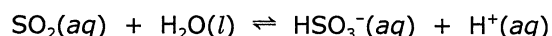
The cases of SO_2 and (with some parallel) CO_2, will be further examined in the next Chapter.

We now have a variety of ways of interpreting aqueous acids and bases, and these ways tend to complement each other. The different ways offer somewhat different perspectives, and one may work better than another for a particular application.

Some chemical units can act as an acid or as a base and it depends on the circumstances. One of the most common ions which can do this is bicarbonate. HCO_3^- can rip H^+ off some acid (including from protonated water itself)

$$HCO_3^-(aq) \ + \ H^+(aq) \ \rightleftharpoons \ H_2CO_3(aq)$$
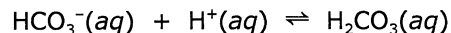
and in this context, bicarbonate is a base. On the other hand, HCO_3^- can also undergo its own acid dissociation

$$HCO_3^-(aq) \ \rightleftharpoons \ CO_3^{2-}(aq) \ + \ H^+(aq)$$
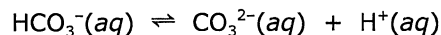
in which case it is having H^+ pulled off by water. In this context, bicarbonate is an acid. Substances which can go either way and which can act as an acid or as a base are called amphoteric. Ampho- relates to amphi-, meaning both. Thus, HCO_3^- is amphoteric. HCO_3^- is the hydrogen anion of the weak acid H_2CO_3 and it was the first hydrogen anion introduced way back in Section 4.2. Go back and read that portion of Section 4.2 if you're rusty; we will be using the term quite a bit. For now, we can make the following generality.

All hydrogen anions derived from weak acids are amphoteric.

Know this, and remember that it's only for hydrogen anions from <u>weak</u> acids. Hydrogen anions from strong acids are not amphoteric. The most common example of this is HSO_4^-. We'll come back to this point later in the next Chapter. Flag this paragraph.

By the way, here's an updated, alternate way for describing a hydrogen anion: a hydrogen anion is an anion which results from protonating a 2– or more negative anion. HCO_3^- results from protonating CO_3^{2-}, as seen by the reverse of the last equation above; thus, HCO_3^- is a hydrogen anion. This is just another way of looking at the term.

Hydrogen anions are not the only things which are amphoteric. Water itself can actually go both ways. When $HCl(g)$ dissolves in water, it is H_2O which does the rip off,

$$HCl(aq) \ + \ H_2O(l) \ \rightarrow \ H_3O^+(aq) \ + \ Cl^-(aq)$$
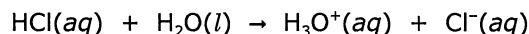
so water is the base in this context. When $NH_3(g)$ dissolves in water, H_2O is the loser of H^+,

$$NH_3(aq) \ + \ H_2O(l) \ \rightleftharpoons \ NH_4^+(aq) \ + \ OH^-(aq)$$
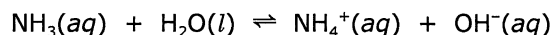
so water is the acid in this context. Thus, water is amphoteric. A related term is amphiprotic which means the same thing but this term applies for a solvent instead of for solutes. Thus, water is an amphiprotic solvent. As a solute in some other solvent, however, water would be called amphoteric. We don't need this distinction, so we'll just use amphoteric for general usage.

Now, more terminology of a different type.

The term "conjugate" relates acid/base chemical units which differ by a transferable H^+. The conjugate acid has the H^+ but the conjugate base does not. A conjugate acid is formed by protonating the base; a conjugate base is formed by deprotonating the acid. Let's illustrate the terminology with a few examples. Consider CH_3CO_2H.

$$CH_3CO_2H(aq) \ \rightleftharpoons \ CH_3CO_2^-(aq) \ + \ H^+(aq)$$
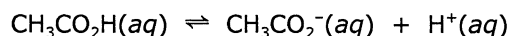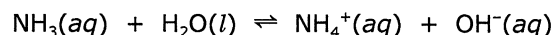
The forward direction is the deprotonation of the acid to give $CH_3CO_2^-$, which is the conjugate base. The reverse direction is the protonation of $CH_3CO_2^-$ to give CH_3CO_2H, which is the conjugate acid. CH_3CO_2H and $CH_3CO_2^-$ differ by H^+ and these together constitute a conjugate pair; each is the conjugate of the other. This also applies when an acetate salt, such as $NaCH_3CO_2$, is dissolved in water.

$$CH_3CO_2^-(aq) \ + \ H_2O(l) \ \rightleftharpoons \ CH_3CO_2H(aq) \ + \ OH^-(aq)$$
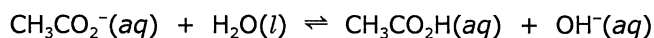
Again, acetate is the conjugate base and acetic acid is the conjugate acid.

Now consider NH_3.

$$NH_3(aq) \ + \ H_2O(l) \ \rightleftharpoons \ NH_4^+(aq) \ + \ OH^-(aq)$$

In the forward direction, protonation of the base gives NH_4^+, which is the conjugate acid. In the reverse direction, the deprotonation of NH_4^+ gives NH_3 which is the conjugate base. Together, NH_3 and NH_4^+ are a conjugate pair; each is the conjugate of the other. This also applies when an ammonium salt, such as NH_4Cl, is dissolved in water.

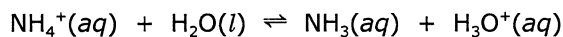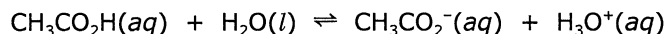$$NH_4^+(aq) \ \rightleftharpoons \ H^+(aq) \ + \ NH_3(aq)$$
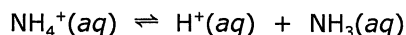
Ammonium is the conjugate acid and ammonia is the conjugate base.

Water and its conjugate ions also get in on this classification. Consider again the two base dissociations above using acetate and ammonia.

$$CH_3CO_2^-(aq) + H_2O(l) \rightleftharpoons CH_3CO_2H(aq) + OH^-(aq)$$

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$
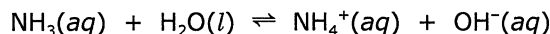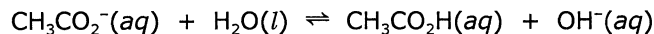
In both cases, H_2O is the conjugate acid and OH^- is the conjugate base. Now consider the two acid dissociations above using acetic acid and ammonium, with H_2O included in the equations for emphasis.

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons CH_3CO_2^-(aq) + H_3O^+(aq)$$

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

In these, H_2O is the conjugate base and H_3O^+ (or simply H^+) is the conjugate acid. Thus, H_2O has two possible conjugate relationships, and it depends on the reaction.

If H_2O is losing H^+, then H_2O is the acid and OH^- is the conjugate base.
If H_2O is taking H^+, then H_2O is the base and H_3O^+ is the conjugate acid.

H_2O has two conjugate relationships because it is amphoteric and it can go either way. This will be true for all amphoterics. Consider bicarbonate again. For its protonation, bicarbonate is the conjugate base while H_2CO_3 is the conjugate acid.

$$HCO_3^-(aq) + H^+(aq) \rightleftharpoons H_2CO_3(aq)$$
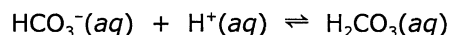
For its deprotonation, bicarbonate is the conjugate acid while CO_3^{2-} is the conjugate base.

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$$
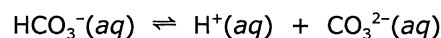
This conjugate terminology can be tricky until you get the hang of it. You may need to work with it a bit.

Note that conjugates are defined and connected by an H^+ in the chemical unit. These terms are also applied to strongs. For example, deprotonation of HCl gives Cl^- which is the conjugate base. Even though Cl^- is not significantly basic in water, it is still formed by deprotonation of HCl so it is still classified as the conjugate base of HCl.

OK, that's enough terminology for a while.

Problems

1. True or false.

    a. Hydrobromic acid is a strong acid.

    b. Chloride has no significant pull on H^+ of H_3O^+.

    c. Water can completely dissociate HF.

    d. In pure water, $[OH^-] = 1.0 \times 10^{-14}$ M.

    e. The protonation of a base gives a conjugate acid.

2. True or false.

    a. Acetate has no significant pull on H^+ of H_3O^+.

    b. Oxalic acid is a weak acid.

    c. In basic solution, pOH > pH.

    d. A solution of pH 3 is more acidic than a solution of pH 4.

    e. NO_2^- is the conjugate base of nitric acid.

3. True or false.

    a. When ammonia dissolves in water, every molecule of ammonia becomes protonated.

    b. Autoionization of water is exergonic at standard conditions at 25 °C.

    c. As $[OH^-]$ increases, pH increases.

    d. As pOH increases, $[H^+]$ decreases.

    e. $H_2PO_4^-$ and HPO_4^{2-} are a conjugate pair.

4. True or false.

    a. Upon dissolving in water, hydrogen iodide will protonate water.

    b. Water molecules can pull on each other and break an O–H bond (at least to some extent).

    c. A solution of pH 6 is more basic than a solution of pOH 6.

    d. Water can protonate a base and it can deprotonate an acid.

    e. Bisulfate is the conjugate acid of sulfate.

5. Use $\Delta H°$ and $\Delta S°$ for autoionization to calculate $\Delta G°$ at body temperature, 37 °C. What is K_w at this temperature? What is the pH of pure water at body temperature?

6. a. Give the formula of the product of the deprotonation of hydrofluoric acid.

    b. Give the formula of the conjugate acid of bromide ion.

    c. Give the formula of the conjugate base of phosphoric acid.

7. a. Give the formula of the product of the deprotonation of chlorous acid.

    b. Give the formula of the conjugate acid of cyanide.

    c. Give the formula of the conjugate base of ammonium ion.

8. Which of the following is/are amphoteric?

    sulfide   water   chloride   hydrogen oxalate ion   dihydrogen arsenate ion

9. A solution contains 0.00835 mol nitric acid in 2.50 L.

    a. What is the $[H^+]$ in the solution?

    b. What is the pH of the solution?

    c. What is the pOH of the solution?

10. A solution contains 5.10×10^{-4} mol KOH in 600.0 mL.

    a. What is the $[OH^-]$ in the solution?

    b. What is the pOH of the solution?

    c. What is the pH of the solution?

11. A solution contains 0.756 g perchloric acid in 800. mL of solution. What is the pH?

12. A solution contains 0.360 g sodium hydroxide in 5.00 L. What is the pH?

13. You need to prepare 2.50 L of a KOH solution with pH = 11.18. How many grams of KOH are needed?

14. Pure hydrogen chloride is a gas. How many liters of HCl(g) at 541 Torr and 25 °C are needed to prepare 14.0 L of aqueous solution with pH = 4.10?