Introduction to acid-base chemistry

A Chem1 Reference Text
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Contents

The concepts of an acid, a base, and a salt are ancient ones that modern chemical science has adopted and refined. Our treatment of the subject at this stage will be mainly qualitative, emphasizing the definitions and fundamental ideas associated with acids and bases. The quantitative treatment of acid-base equilibrium systems is treated in another unit.

1 Acids

The term *acid* was first used in the seventeenth century; it comes from the Latin root *ac-*, meaning "sharp", as in *acetum*, vinegar. Acids have long been recognized as a distinctive class of compounds whose aqueous solutions exhibit the following properties:

- A characteristic sour taste;
- ability to change the color of litmus[1] from blue to red;
- react with certain metals to produce gaseous H_2;
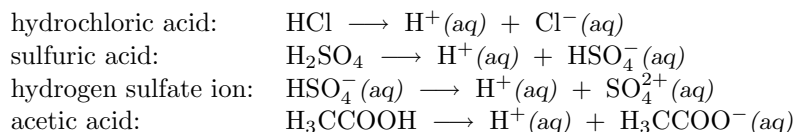- react with *bases* to form a salt and water.

The first chemical definition of an acid turned out to be wrong: in 1787, Antoine Lavoisier, as part of his masterful classification of substances, identified the known acids as a separate group of the "complex substances" (compounds). Their special nature, he postulated, derived from the presence of some common element that embodies the "acidity" principle, which he named *oxygén*, derived from the Greek for "acid former". Lavoisier had assigned this name to the new gaseous element that Joseph Priestly had discovered a few years earlier as the essential substance that supports combustion. Many combustion products (oxides) do give acidic solutions, and oxygen is in fact present in most acids, so Lavoisier's mistake is understandable.

In 1811 Humphrey Davy showed that muriatic (hydrochloric) acid (which Lavoisier had regarded as an element) does not contain oxygen, but this merely convinced some that chlorine was not an element but an oxygen-containing compound. Although a dozen oxygen-free acids had been discovered by 1830, it was not until about 1840 that the hydrogen theory of acids became generally accepted. By this time, the misnomer *oxygen* was too well established a name to be changed.[2]

1.1 Acids and the hydrogen ion

The key to understanding acids (as well as bases and salts) had to await Michael Faraday's mid-nineteenth century discovery that solutions of salts (known as *electrolytes*) conduct electricity. This implies the existence of charged particles that can migrate under the influence of an electric field. Faraday named these particles *ions* ("wanderers"). Later studies on electrolytic solutions suggested that the properties we associate with acids are due to the presence of an excess of *hydrogen ions* in the solution.

By 1890 the Swedish chemist Svante Arrhenius (1859-1927) was able to formulate the first useful theory of acids: an acidic substance is one whose molecular unit contains at least one hydrogen atom that can dissociate, or ionize, when dissolved in water, producing a hydrated hydrogen ion and an anion:

hydrochloric acid:	$HCl \longrightarrow H^+(aq) + Cl^-(aq)$
sulfuric acid:	$H_2SO_4 \longrightarrow H^+(aq) + HSO_4^-(aq)$
hydrogen sulfate ion:	$HSO_4^-(aq) \longrightarrow H^+(aq) + SO_4^{2+}(aq)$
acetic acid:	$H_3CCOOH \longrightarrow H^+(aq) + H_3CCOO^-(aq)$

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[1] Litmus is a dye found in certain lichens. The name is of Scandinavian origin, e.g. *lit* (color) + *mosi* (moss) in Icelandic.
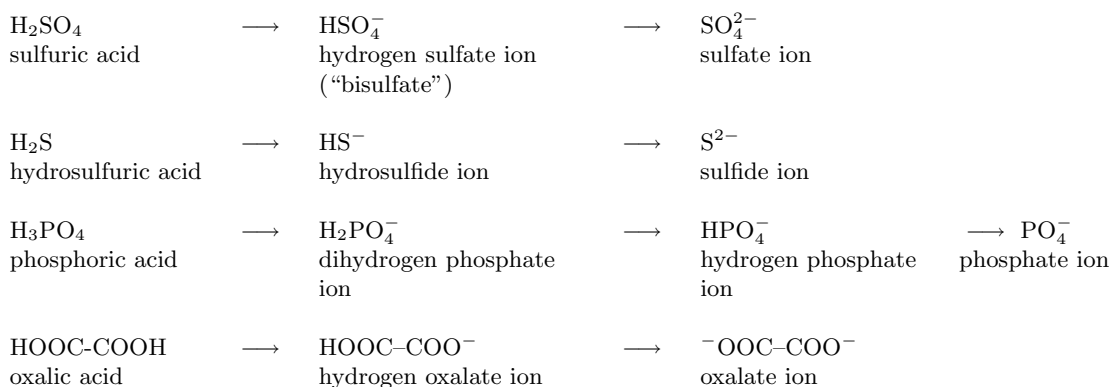
[2] It would clearly have been better if the name *hydrogen*, which means "water former", had been assigned to O, which describes this element as much as it does *hydro*gen. The *oxy-* prefix comes from the Greek word $o\xi\upsilon\varsigma$, "sour".

Strictly speaking, an "Arrhenius acid" must contain hydrogen. However, there are substances that do not themselves contain hydrogen, but still yield hydrogen ions when dissolved in water; the hydrogen ions come from the water itself, by reaction with the substance. A more useful operational definition of an acid is therefore the following:

> *An acid is a substance that yields an excess of hydrogen ions when dissolved in water.*

There are three important points to understand about hydrogen in acids:

- Although all Arrhenius acids contain hydrogen, not all hydrogen atoms in a substance are capable of dissociating; thus the –CH$_3$ hydrogens of acetic acid are "non-acidic". An important part of knowing chemistry is being able to predict which hydrogen atoms in a substance will be able to dissociate.

- Those hydrogens that do dissociate can do so to different degrees. The *strong* acids such as HCl and HNO$_3$ are effectively 100% dissociated in solution. Most organic acids, such as acetic acid, are *weak*; only a small fraction of the acid is dissociated in most solutions. HF and HCN are examples of weak inorganic acids.

- Acids that possess more than one dissociable hydrogen atom are known as *polyprotic* acids; H$_2$SO$_4$ and H$_3$PO$_4$ are well-known examples. Intermediate forms such as HPO$_4^{2-}$, being capable of both accepting and losing protons, are called *ampholytes*.

|				
H$_2$SO$_4$ sulfuric acid	$\longrightarrow$	HSO$_4^-$ hydrogen sulfate ion ("bisulfate")	$\longrightarrow$	SO$_4^{2-}$ sulfate ion
H$_2$S hydrosulfuric acid	$\longrightarrow$	HS$^-$ hydrosulfide ion	$\longrightarrow$	S^{2-} sulfide ion
H$_3$PO$_4$ phosphoric acid	$\longrightarrow$	H$_2$PO$_4^-$ dihydrogen phosphate ion	$\longrightarrow$	HPO$_4^-$ hydrogen phosphate ion $\longrightarrow$ PO$_4^-$ phosphate ion
HOOC-COOH oxalic acid	$\longrightarrow$	HOOC–COO$^-$ hydrogen oxalate ion	$\longrightarrow$	$^-$OOC–COO$^-$ oxalate ion

2   Bases

The name *base* has long been associated with a class of compounds whose aqueous solutions are characterized by:

- a bitter taste;

- a "soapy" feeling when applied to the skin;

- ability to restore the original blue color of litmus that has been turned red by acids;

- ability to react with acids to form salts. The word "alkali" is synonymous with base. It is of Arabic origin, but the root word comes from the same Latin *kalium* (potash) that is the origin of the symbol for potassium; wood ashes have been the traditional source of the strong base KOH since ancient times.

Just as an acid is a substance that liberates hydrogen ions into solution, a base yields hydroxide ions when dissolved in water:

$$NaOH(s) \longrightarrow Na^+(aq) + OH^-(aq)$$
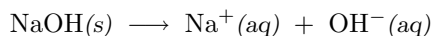
Sodium hydroxide is an Arrhenius base because it contains hydroxide ions. However, other substances which do not contain hydroxide ions can nevertheless produce them by reaction with water, and are therefore classified as bases. Two classes of such substances are the metal *oxides* and the hydrogen compounds of certain *nonmetals*:

$$Na_2O + H_2O \longrightarrow 2\,NaOH \longrightarrow 2\,Na^+(aq) + 2\,OH^-(aq)$$
$$NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$$
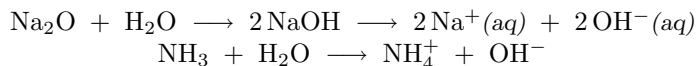
3 Neutralization

Acids and bases react with one another to yield two products: water, and an ionic compound known as a *salt*. This kind of reaction is called a *neutralization* reaction.

$$Na^+ + OH^- + H^+ + Cl^- \longrightarrow H_2O + Na^+ + Cl^-$$
$$K^+ + OH^+ + H^+ + NO_3^- \longrightarrow H_2O + K^+ + NO_3^-$$
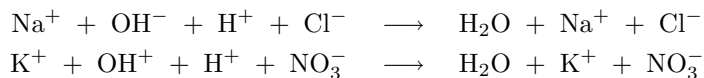
These reactions are both exothermic; although they involve different acids and bases, it has been determined experimentally that they all liberate the same amount of heat (57.7 kJ) per mole of H^+ neutralized. This implies that all neutralization reactions are really the one net reaction

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O \tag{1}$$

The "salt" that is produced in a neutralization reaction consists simply of the anion and cation that were already present. The salt can be recovered as a solid by evaporating the water.

4 Dissociation of water

The ability of acids to react with bases depends on the tendency of hydrogen ions to combine with hydroxide ions to form water. This tendency is very great, so the reaction in Eq 1 is practically *complete*. No reaction, however, is really 100 percent complete; at *equilibrium* (when there is no further net change in amounts of substances) there will be at least a minute concentration of the reactants in the solution. Another way of expressing this is to say that any reaction is at least slightly *reversible*.

This means that in pure water, the reaction

$$H_2O \longrightarrow H^+(aq) + OH^-(aq)$$
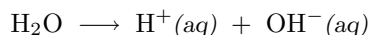
will proceed to a very slight extent. Experimental evidence confirms this: the most highly purified water that chemists have been able to prepare will still conduct electricity very slightly. From this electrical conductivity it can be calculated that the equilibrium concentration of both the H^+ ion and OH^- ions is almost exactly 1.00×10^7 at $25\,°C$. This amounts to one H_2O molecule in about 50 million being dissociated.

The degree of dissociation of water is so small that you might wonder why it is even mentioned here. The reason it is important arises from the need to use the concentrations for H^+ and OH^- in pure water to define the *equilibrium constant*

$$[H^+][OH^-] = 10^{-7} \times 10^{-7} = K_w = 10^{-14}$$

in which the square brackets [] refer to the concentrations of the substances they enclose.

The details of equilibrium constants and their calculation are treated in a later chapter. For the moment, it is only necessary that you know the following rule:

The product of the hydrogen ion and hydroxide ion concentrations in any aqueous solution will always be 1.00×10^{14} at $25\,°C$.

In other words,

$$[H^+][OH^-] = 1.00 \times 10^{-14} \tag{2}$$

This expression is known as the *ion product* of water, and it applies to *all aqueous solutions*, not just to pure water. The consequences of this are far-reaching, because it implies that if the concentration of H^+ is large, that of OH^- will be small, and *vice versa*. This means that H^+ ions are present in *all* aqueous solutions, not just acidic ones. This leads to the following important definitions, which you must memorize:

$$
\begin{array}{lll}
\text{acidic solution:} & [H^+] > [OH^-] & \\
\text{alkaline solution:} & [H^+] < [OH^-] & \\
\text{neutral solution:} & [H^+] = [OH^-] & (= 1.00 \times 10^{-7}\,M \text{ at } 25\,°C)
\end{array}
$$

5 The pH scale

The possible values of $[H^+]$ and $[OH^-]$ in an aqueous solution can span many orders of magnitude, ranging from about $10^{1.3}$ to $10^{-15.3}$. It is therefore convenient to represent them on a more compressed logarithmic scale. By convention, we use the *pH* scale[3] to denote hydrogen ion concentrations:

$$pH = -\log_{10}[H^+]$$

or conversely,

$$[H^+] = 10^{-pH}$$

We can also define

$$pOH = -\log_{10}[OH^-]$$

and

$$pK_w = -\log K_w$$

From Eq 2 it follows that

$$pH + pOH = pK_w \quad (= 14.0 \text{ in pure water at } 25\,°C) \tag{3}$$

In a neutral solution at $25\,°C$, the pH will be 7.0; a higher pH corresponds to an alkaline solution, a lower pH to an acidic solution. In a solution with $[H^+] = 1\,M$, the pH would be 0; in a $0.00010\,M$ solution of H^+, it would be 4.0. Similarly, a $0.00010\,M$ solution of NaOH would have a pOH of 4.0, and thus a pH of 10.0. It is very important that you thoroughly understand the pH scale, and be able to convert between $[H^+]$ or $[OH^-]$ and pH in both directions.

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[3]This notation was devised by the Swedish chemist Sørensen in 1909. The "p" as used in pH, pK, etc. stands for the German word *Potenz* which means "power" in the sense of an exponent.
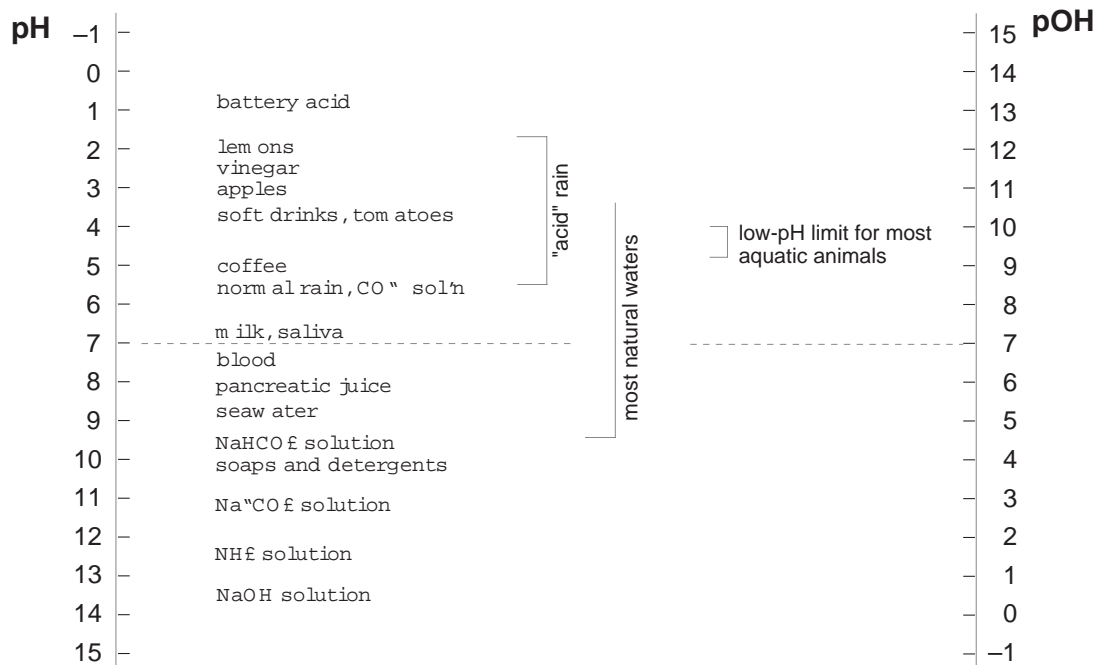
Figure 1: The pH scale

As is explained in more detail on page 9, hydrogen ions do not have an independent existence in water, so what we write as "$[H^+]$" is really a more complicated species. Furthermore, if the total concentration of ions of all kinds in the solution exceeds about $0.001\,M$, a significant fraction of them will be associated into neutral pairs such as $H^+{\cdot}Cl^-$, for example, and thus reducing the concentration of "free" ions to smaller value which we will call the *effective* concentration. It is the effective concentration of H^+ that determines the degree of acidic character of a solution, and this is what methods for determining the pH actually measure. For this reason pH is now defined in terms of the effective H^+ concentration. You need not be concerned with the details of this at the moment, but it is something you should know about later on in connection with acid-base equilibrium calculations.

6   Titration

Since acids and bases readily react with each other, it is experimentally quite easy to find the amount of acid in a solution by determining how many moles of base are required to neutralize it. This operation is called *titration*, and you should already be familiar with it from your work in the Laboratory.

We can titrate an acid with a base, or a base with an acid. The substance whose concentration we are determining is the substance being titrated; the substance we are adding in measured amounts is the *titrant*. The idea is to add titrant until the solution has been exactly neutralized; at this point, the number of moles of titrant added tells us the concentration of base (or acid) in the solution being titrated.

Problem Example 1

36.00 ml of a solution of HCl was titrated with $0.44\,M$ KOH. The volume of KOH solution required to neutralize the acid solution was 27.00 ml. What was the concentration of the HCl?
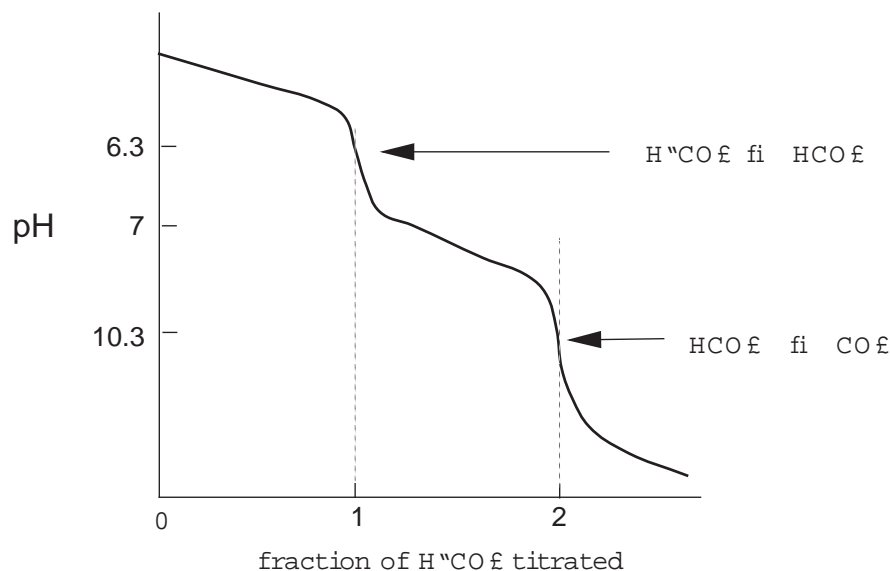
Figure 2: Titration curve for Na_2CO_3 with HCl

Solution: The number of moles of titrant added was

$$(.027 \text{ L})(.44 \text{ mol L}^{-1}) = .0119 \text{ mol}$$

This is also the number of moles of HCl; its concentration is therefore
$(.0119 \text{ mol}) \div (.036 \text{ L}) = 0.33 \, M$.

6.1   Titration curves

The course of a titration can be followed by plotting the pH of the solution as a function of the quantity of titrant added. Fig. **??** shows two such curves, one for a strong acid (HCl) and the other for a weak acid, acetic acid, denoted by HAc. Looking first at the HCl curve, notice how the pH changes very slightly until the acid is almost neutralized. At that point, shown in the magnified view at the top of the Figure, just one additional drop of NaOH solution will cause the pH to jump to a very high value– almost as high as that of the pure NaOH solution.

Compare the curve for HCl with that of HAc. For a weak acid, the pH jump near the neutralization point is less steep. Notice also that the pH of the solution at the neutralization point is greater than 7. These two characteristics of the titration curve for a weak acid are very important for you to know.

If the acid or base is polyprotic, there will be a jump in pH for each proton that is titrated. Fig. 2 shows (on the right) the titration of a solution of sodium carbonate with HCl. Both solutions have identical concentrations. The CO_3^{2-} ion is a base, so the pH of the solution starts out quite high. As protons are added they convert CO_3^{2-} into HCO_3^- and eventually to carbonic acid, H_2CO_3.

Notice how the vertical parts of the titration curve correspond to volumes of HCl that are equal to the initial volume of CO_3^{2-} solution (i.e., equal numbers of moles, since the concentrations of the two solutions are equal), and also to *twice* this volume. This second equivalence point reflects the fact that two moles of HCl are required to neutralize one mole of carbonate ion:

$$2\,H^+ \;+\; CO_3^{2-} \;\longrightarrow\; H_2CO_3$$
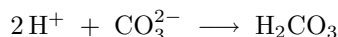
6.2   Finding the equivalence point: indicators

When enough base has been added to react completely with the hydrogens of a monoprotic acid, the *equivalence point* has been reached. If a strong acid and strong base are titrated, the pH of the solution will be 7.0 at the equivalence point. However, if the acid is a weak one, the pH will be greater than 7; the "neutralized" solution will not be "neutral" in terms of pH. For a polyprotic acid, there will be an equivalence point for each titratable hydrogen in the acid; these typically occur at pH values that are 4-5 units apart.

The key to a successful titration is knowing when the equivalance point has been reached. The easiest way of finding the equivalence point is to use an *indicator* dye; this is a substance whose color is sensitive to the pH. One such indicator that is commonly encountered in the laboratory is phenolphthalein; it is colorless in acidic solution, but turns intensely red when the solution becomes alkaline. If an acid is to be titrated, you add a few drops of phenolphthalein to the solution before beginning the titration. As the titrant is added, a local red color appears, but quickly dissipates as the solution is shaken or stirred. Gradually, as the equivalence point is approached, the color dissipates more slowly; the trick is to stop the addition of base after a single drop results in a permanently pink solution.

Different indicators change color at different pH values. Since the pH of the equivalance point varies with the strength of the acid being titrated, one tries to fit the indicator to the particular acid. One can titrate polyprotic acids by using a suitable combination of several indicators.

7   The proton donor-acceptor concept of acids and bases

Arrhenius viewed acids and bases as substances which produce hydrogen ions or hydroxide ions on dissociation. As useful a concept as this has been, it did not do a very good job of explaining why NH_3, which contains no OH^- ions, is a base and not an acid, why a solution of $FeCl_3$ is acidic, or why a solution of Na_2S is alkaline.

The more general working definition of acids and bases we have been using is due to Franklin, who in 1905 developed a theory in which the solvent plays a central role. According to this view, an acid is a solute that gives rise to a cation characteristic of the solvent, and a base is a solute that yields a dissolved ion which is also characteristic of the solvent.

If the solvent is water, these two ions are always H^+*(aq)* and OH^-*(aq)*, but in the case of liquid ammonia, which is also a good solvent, the corresponding ions would be NH_4^+ and NH_2^-. That the solvent does play some special role is implied by the self-ionization reactions

$$H_2O \longrightarrow H^+(aq) + OH^-(aq)$$

and

$$2\,NH_3 \longrightarrow NH_2^- + NH_4^+$$
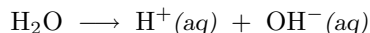
Franklin thus generalized the acid-base concept somewhat, and extended it to non-aqueous solvents.

It was not until 1923, however, that the Danish chemist J.N. Brønsted proposed a theory that is both simpler and more general:[4]

> An acid is a *proton donor*; a base is a *proton acceptor*.

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[4]In the same year the English chemist T.M. Lowry published a paper setting forth some similar ideas without producing a definition; in a later paper Lowry himself points out that Brønsted deserves the major credit, but the concept is still widely known as the Brønsted-Lowry theory.

| substance	acid	conjugate base
hydrochloric acid	HCl	Cl^-
acetic acid	CH_3CH_2COOH	$CH_3CH_2COO^-$
nitric acid	HNO_3	NO_3^-
potassium dihydrogen phosphate	$H_2PO_4^-$	HPO_4^-
sodium hydrogen sulfate	HSO_4^-	SO_4^{2-}
sodium sulfide	HS^-	S^-
ammonium chloride	NH_4^+	NH_3
iron(III) chloride	$Fe(H_2O)_6^{3+}$	$Fe(H_2O)_5OH^{2+}$
water	H_2O	OH^-
hydronium ion	H_3O^+	H_2O

Table 1: Some common congugate acid-base pairs

These definitions carry a very important implication: a substance cannot act as an acid without the presence of a base to accept the proton, and *vice versa.*

A reaction of an acid with a base is thus a *proton exchange* reaction; if the acid is denoted by AH and the base by B, then we can write a generalized acid-base reaction as

$$AH \ + \ B \ \longrightarrow \ A^- \ + \ BH^+$$
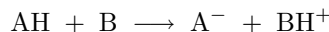
But the product BH^+ is now capable of losing its newly-acquired proton to another acceptor, and is therefore potentially another acid:

$$acid_1 \ + \ base_2 \ \longrightarrow \ base_1 \ + \ acid_2$$
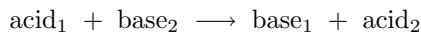
In this schematic reaction, $base_1$ is *conjugate* to $acid_1$, and $acid_2$ is conjugate to $base_2$. The term *conjugate* means "connected with", the implication being that any species and its conjugate species are related by the gain or loss of one proton. Table 1 shows the conjugate pairs of a number of typical acid-base systems.

Amphiprotic species   Many substances can both donate and accept protons: examples are $H_2PO_4^-$, HCO_3^-, NH_3, and H_2O. Such substances are said to be *amphiprotic*; the dissolved species themselves are called *ampholytes*.

Acid-base reactions   Within the Arrhenius concept, neutralization of H^+ by OH^- is the only type of acid-base reaction that can occur. The Brønsted concept broadens our view, encompassing a wide variety of reactions whose common feature is the transfer of a proton from a donor to an acceptor (Table 2).

7.1   The hydronium ion

The Arrhenius view of an acid is a substance that dissociates in water to produce a hydrogen ion. There is a serious problem with this, however: the hydrogen ion is no more than a proton, a bare nucleus. Although it carries only a single unit of positive charge, this charge is concentrated into a volume of space that is only about a hundred-millionth as large as the volume occupied by the smallest atom. Owing to its extremely small size, the proton will be attracted to any part of a nearby atom or molecule in which there is an exess of negative charge. Such places exist on any atom that possesses non-bonding

reaction	$acid_1$	$base_2$	$acid_2$	$base_1$
1) ionization of H_2O	H_2O	H_2O	H_3O^+	OH^-
2) ionization of HCN	HCN	H_2O	H_3O^+	CN^-
3) ionization of NH_3	NH_3	H_2O	NH_4^+	OH^-
4) hydrolysis of NH_4Cl	NH_4^+	H_2O	H_3O^+	NH_3
5) hydrolysis of $CH_3COO^-Na^+$	H_2O	CH_3COO^-	CH_3COOH	OH^-
6) neutralization of HCl by NaOH	H_3O^+	OH^-	H_2O	H_2O
7) neutralization of NH_3 by acetic acid	CH_3COOH	NH_3	NH_4^+	CH_3COO^-
8) dissolution of BiOCl by HCl	$2H_3O^+$	BiOCl	$Bi(H_2O)^{3+}$	$2H_2O$ + Cl^-
9) decomposition of $Ag(NH_3)_2^+$ by HNO_3	$2H_3O^+$	$Ag(NH_3)_3^+$	$2NH_4^+$	$3H_2O$ + Ag^+
10) displacement of HCN by CH_3COOH	CH_3COOH	CN^-	HCN	CH_3COO^-
11) displacement of NH_3 by $Ca(OH)_2$	NH_4^+	OH^-	H_2O	NH_3

Table 2: Examples of proton donor-acceptor reactions

electrons, and here that protons attach themselves to the acceptor atom by forming a shared-electron (coordinate) bond with the lone pair. The stronger the bond, the more tightly the proton is held to the acceptor, and the weaker is the acid. Thus the species $:F^-$, $:NH_3$ and $H_2O:$ are all bases. Since the latter of these is the majority species in all aqueous solutions, it follows that *the hydrogen ion cannot exist as an independent particle* in such solutions.

Although other kinds of dissolved ions have water molecules bound to them more or less tightly, the interaction between H^+ and H_2O is so strong that writing "H^+*(aq)*" hardly does it justice. Instead, we consider the combination H_3O^+ to be the species that defines an acidic solution. This is known as the *hydronium* ion.

According to the Brønsted concept, an acid HA is a substance that is able to transfer a proton to a water water molecule, yielding H_3O^+ and leaving the anion A^- as the conjugate base:

$$HA + H_2O \longrightarrow A^- + H_3O^+ \tag{4}$$
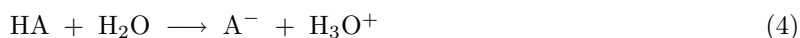
Notice that the because the water molecule accepts a proton, H_2O is acting as a *base* here. Thus what Arrhenius would have regarded as the simple dissociation of HA is now regarded as a reaction of an acid with a base in its own right. Although Eq 4 is certainly closer to describing what actually happens than $HA \longrightarrow H^+ + A^-$, this last equation is so much easier to write that chemists still use it to represent acid-base reactions in contexts in which the proton donor-acceptor mechanism does not need to be emphasized. Thus we still talk about "hydrogen ions" and use the formula "H^+" in writing chemical equations as long as you remember that they are not to be taken literally in the context of aqueous solutions.

> Interestingly, experiments indicate that the proton does not stick to a single H_2O molecule, but changes partners many times per second. This molecular promiscuity, a consequence of the uniquely small size and mass the proton, allows it to move through the solution by rapidly hopping from one H_2O molecule to the next, creating a new H_3O^+ ion as it goes. The overall effect is the same as if the H_3O^+ ion itself were moving. Similarly, a hydroxide ion, which can be considered to be a "proton hole" in the water, serves as a landing point for a proton from another H_2O molecule, so that the OH^- ion hops about in the same way.
> Because hydronium- and hydroxide ions can "move without actually moving" and thus without having to plow their way through the solution by shoving aside water molecules as do other ions, solutions which are acidic or alkaline have extraordinarily high *electrical conductivities*.
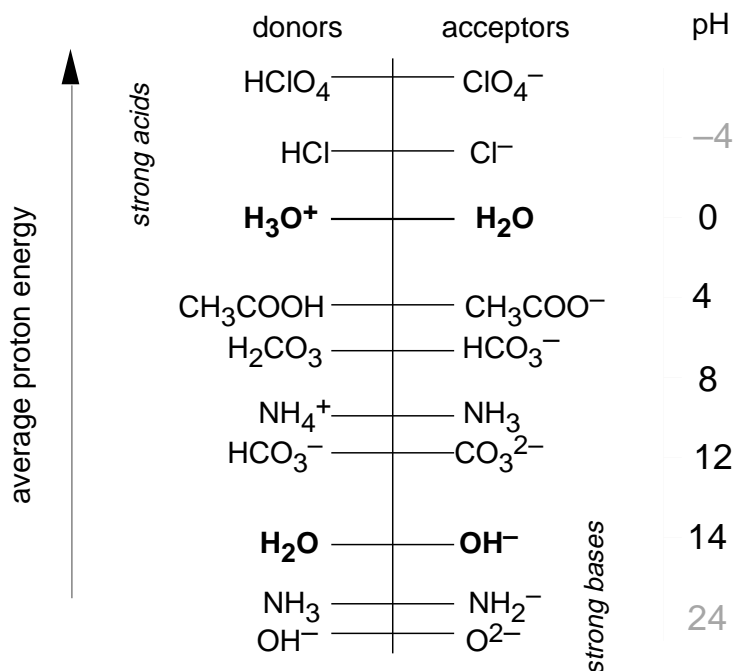
Figure 3: Relative strengths of acids and bases on the "proton ladder"

7.2   Acid strengths and the role of water

Acid-base reactions are essentially competitions of two acceptors (bases) for a proton. Thus when we say that HCl acts as a strong acid in water, we mean that H_2O is a much stronger base than is Cl^-. Similarly, HCN is a weak acid in water because the proton is is able to share the lone pair electrons of the cyanide ion :CN^- more effectively than it can with H_2O:. Thus the reaction

$$HCN \; + \; H_2O \; \rightleftharpoons \; H_3O^+ + CN^-$$
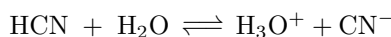
proceeds to only a very small extent.

But what do we really mean by acid "strength"? Coordination of the proton with an electron pair brings more electrons closer to more nuclei; as with all bond formation, this is accompanied by a fall in the potential energy. If we assume that the proton will tend to "fall" (energetically speaking) to its lowest possible state, then a simple diagram as in Fig. 3 can help us understand this concept. Several hypothetical acid-base pairs are shown here, joined by horizontal lines. You can think of this diagram as a "proton ladder"; the higher the acid-base pair on the diagram, the greater will be the tendency of the proton to fall from the acid at that level to a base at a lower level. If two or more bases are present in the solution, the protons will fall into the lowest-lying (stronger) base before reacting with the higher one. The tendency for a given proton transfer reaction to occur is governed by the vertical distance (energy) that the proton can fall in that particular reaction.

Notice that H_2O is shown in two places on this diagram. Near the top it is the conjugate *base* of H_3O^+, while near the bottom it is an *acid* whose conjugate base is OH^-. HCl acts as a strong acid in water because protons can fall from HCl to H_2O, producing H_3O^+. This fall is so favorable energetically that we say HCl is a "strong" acid; a 1 M solution of HCl is really a 1 M solution of H_3O^+.

Contrast the case of HCl with that of HCN. The HCN/CN^- pair lies below the H_2O/H_3O^+ line. If HCN is to donate a proton to water, in input of energy is needed to boost the proton up to the level of

H_2O, resulting in the formation of H_3O^+ and CN^-. This means that the reaction

$$HCN \ + \ H_2O \ \longrightarrow \ H_3O^+ \ + \ CN^-$$
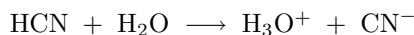
is energetically unfavorable. The reaction would not occur at all except for the small amount of thermally-induced collisions that occasionally gives one molecule enough energy to bridge the gap. As a result, only a tiny proportion of the HCl molecules in water will react; we say that hydrocyanic acid is a very weak acid.

Although HCN is a weak acid in pure water, it can be titrated with NaOH solution because the hydroxide ion (near the bottom of the diagram) is a low-energy (strong) base. This is in fact the reason we use a strong base such as NaOH as a titrating agent; even a relatively "weak" acid will react completely with a base as strong as OH^-.

The dual entry of H_2O in Fig. 3 reflects the fact that water plays more than the passive role of a solvent in acid-base chemistry. Water is in fact a direct participant in any proton transfer reaction that takes place in aqueous solution, and its conjugate acid H_3O^+ and base OH^- are respectively the strongest acid and the strongest base that can exist in aqueous solution.

The leveling effect. To understand this last statement, consider the acids HCl or HNO_3, both of which are certainly stronger acids than H_3O^+ according to their locations on the ladder. But being above H_3O^+, they are also above its conjugate base H_2O, so both acids will lose their protons to H_2O, yielding a solution in which the only remaining acid (proton donor) is H_3O^+. Similarly, the amide ion NH_2^- is a stronger base than OH^-. But this means that when $NaNH_2$ is dissolved in water, the NH_2^- will suck the protons out of an equivalent number of H_2O molecules, leaving OH^- as the strongest remaining base in the solution:

$$NH_2^- \ + \ H_2O \ \longrightarrow \ NH_3 \ + \ 2\,OH^-$$
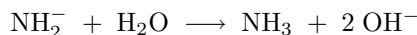
This principle, which says that all acids stronger than H_3O^+ or bases stronger than OH^- appear to be *equally strong* (that is, totally dissociated) in aqueous solution, is known as the *leveling effect*. Another way of expressing the same idea is that the difference between degrees of dissociation of 99%, 99.9%, and 99.99% is rarely significant.

The acid dissociation constant and the pK_a In order to express the strength of an acid quantitatively, we write the equilibrium constant for the reaction in Eq 4:

$$K_a = \frac{[H^+][A^-]}{[HA]} \tag{5}$$

in which the bracketed terms represent the equilibrium concentrations of the various species. It will be apparent that the more complete the dissociation of HA, the greater will be the value of K_a. An acid is considered to be "strong" if K_a is unity or greater.

For the same reasons that it is convenient to express hydrogen ion concentrations on the logarithmic pH scale, it is common practice to express acid strengths as $pK_a \equiv -\log K_a$. Strong acids have pK_as of zero or less, while those of weak acids are positive.

7.3   Autoprotolysis

Neutral molecules that are amphiprotic and that can exist as liquids are able to undergo *autoprotolysis*: what Arrhenius would have called "self-ionization". The most important autoprotolysis reaction for us is that of water

$$2\,H_2O \ \longrightarrow \ H_3O^+ \ + \ OH^-$$
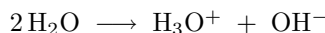
name	acid	base	K_a
perchloric acid	$HClO_4$	ClO_4^-	(> 100)
hydriodic acid	HI	I^-	(> 100)
hydrobromic acid	HBr	Br^-	(> 100)
sulfuric acid	H_2SO_4	HSO_4^-	(> 100)
hydrochloric acid	HCl	Cl^-	(> 100)
nitric acid	HNO_3	NO_3^-	(> 100)
hydronium ion	H_3O^+	H_2O	1
oxalic acid	HOOC–COOH	HOOC–COO$^-$	.056
sulfurous acid	H_2SO_3	HSO_3^-	.017
hydrogen sulfate ion	HSO_4^-	SO_4^{2+}	.012
chlorous acid	$HClO_2$	ClO_2^-	.011
phosphoric acid	H_3PO_4	$H_2PO_4^-$	.0071
iron(III) ion	$Fe(H_2O)_6^{3+}$	$FeOH(H_2O)_5^{2+}$	.0068
hydrofluoric acid	HF	F^-	6.8E-4
carbonic acid	H_2CO_3	HCO_3^-	1.7E-4
oxalate ion	HOOC–COO$^-$	$C_2O_4^{2-}$	1.7E-4
acetic acid	CH_3COOH	CH_3COO^-	1.8E-5
aluminum(III)	$Al(H_2O)_6^{3+}$	$AlOH(H_2O)_5^{2+}$	1.1E-5
hydrosulfuric acid	H_2S	HS^-	8.9E-8
dihydrogen phosphate ion	$H_2PO_4^-$	HPO_4^{2-}	6.3E-8
hydrogen sulfite ion	HSO_3^-	SO_3^{2-}	6.2E-8
hypochlorous acid	HClO	ClO^-	6.0E-8
copper(II) ion	$Cu(H_2O)_4^{2+}$	$CuOH(H_2O)_3^+$	1.0E-8
ammonium ion	NH_4^+	NH_3	5.9E-10
hydrocyanic acid	HCN	CN^-	4.8E-10
zinc(II) ion	$Zn(H_2O)_6^{2+}$	$ZnOH(H_2O)_5^+$	1.5E-10
hydrogen carbonate ion	HCO_3^-	CO_3^{2+}	4.8E-11
hydrogen peroxide	H_2O_2	HO_2^-	2.6E-12
monohydrogen phosphate ion	HPO_4^{2-}	PO_4^{3-}	4.4E-13
hydrosulfide ion	HS^-	S^{2-}	1.3E-13
water	H_3O^+	OH^-	1.0E-14

Table 3: Strengths and conjugate bases of some common acids

in which one H_2O is acting as the acid and the other is the base.

In the context of Fig. 3 it is easy to see why this reaction proceeds only to a small extent: for H_2O to act as an acid in in pure water, its proton must be elevated from the H_2O/OH^- level near the bottom of the diagram up to H_3O^+/H_2Onear the top. This energy gap is so great that the product of the ion concentrations is only about 10^{-14}.

Non-aqueous acid-base systems   Water plays a crucial role in the acid-base chemistry of aqueous solutions, but in the absence of water it is possible to have other families of acids and bases in which different solvents play a role analogous to that of water. Perhaps the most common of these is the liquid ammonia system[5]. Like water, NH_3 is amphiprotic and can engage in autoprotolysis:

$$2\,NH_3 \longrightarrow NH_2^- + NH_4^-$$

In liquid ammonia, all acids stronger than the ammonium ion are "strong" (totally dissociated) acids, and the amide ion is the strongest base.

solvent	formula	conj. acid	conj. base	$K_{\text{autoprot.}}$
ammonia	NH_3	NH_4^+	NH_2^-	10^{-33}
methanol	CH_3OH	$CH_3OH_2^+$	CH_3O^-	$10^{-16.7}$
formic acid	$HCOOH$	$HC(OH)_2^+$	$HCOO^-$	10^{-6}
sulfuric acid	$SO(OH)_3$	$S(OH)_4^+$	$SO_2(OH)_2^-$	$10^{-3.8}$

Similarly, pure liquid sulfuric acid has a very small tendency to accept a proton:

$$SO(OH)_3 + H^+ \longrightarrow S(OH)_4^+$$
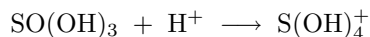
In this respect H_2SO_4 is a much weaker base than water, so whereas strong acids such as HCl and HNO_3 are 100 percent dissociated in water and therefore appear to be equally strong in that solvent, they are only partially ionized in liquid sulfuric acid, in which HCl is 100 times stronger than HNO_3.

8   Types of acids and bases

You will already have noticed that not every compound that contains hydrogen atoms is acidic; NH_3, for example, is a base. Similarly, some compounds containing the group -OH are basic, but others are acidic. An important part of understanding chemistry is being able to recognize what substances will exhibit acidic and basic properties in aqueous solution. Fortunately, most of the common acids and bases fall into a small number of fairly well-defined groups, so this is not particularly difficult.

8.1   Hydrides as acids and bases

Strictly speaking, the term *hydride* refers to ionic compounds of the most electropositive metals; these contain the hydride ion, H^-. However, the term is often used in its more general sense to refer to any binary compound XH_n in which X stands for any element.

The hydride ion is a very strong proton acceptor:

$$H^- + H^+ \longrightarrow H_2$$

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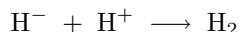
[5]Ammonia is a gas under ordinary conditions, but it can be condensed to a liquid by cooling to $-33\,^{\circ}C$ at 1 atm pressure. Liquid ammonia is a good solvent for many ionic and polar substances, and is sometimes used for applications in which water would be unsuitable because of its reaction with the solute.

CH$_4$	10^{-46}	NH$_3$	10^{-35}	H$_2$O	10^{-16}	HF	10^{-3}
		PH$_3$	10^{-27}	H$_2$S	10^{-7}	HCl	10^7
				H$_2$Se	10^{-4}	HBr	10^9
				H$_2$Te	10^{-3}	HI	10^{10}

Table 4: Approximate acid strengths for some binary hydrogen compounds

Because it is even a stronger base than H$_2$O, the H$^-$ ion cannot exist in aqueous solution because it abstracts protons from water:

$$H^- + H_2O \longrightarrow H_2(g) + OH^-(aq)$$
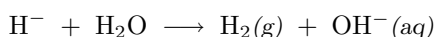
Thus the *ionic hydrides* are basic in character; compounds such as NaH and CaH$_2$ react with water to liberate hydrogen gas and produce an alkaline solution.

The *covalent hydrides* tend to be acidic, but sometimes only very slightly so. Some, like H$_2$O and NH$_3$, display basic properties as well; in ammonia, the basic property dominates.

In general, the acidity of the non-metallic hydrides increases with the atomic number of the element to which it is connected. Thus as the element M moves from left to right across the periodic table or down within a group, the acids MH become stronger (Table 4).

Attempts to explain these trends in terms of a single parameter such as the electronegativity of M tend not to be very useful. The problem is that acid strengths depend on a number of factors such as the strength of the M-H bond and the energy released when the resultant ions become hydrated in solution. It is easier at this stage just to learn the rule.

Ammonia

We usually think of NH$_3$ as a base rather than an acid; like H$_2$O, it is amphoteric, but in aqueous solution, the basic properties dominate. Ammonia is a weak base; only a small fraction of the NH$_3$ molecules in water will accept protons:

$$NH_3 + H_2O \longrightarrow NH_4^+(aq) + OH^-(aq) \tag{6}$$
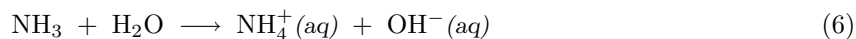
An aqueous solution of NH$_3$ is sometimes called "ammonium hydroxide". This misnomer reflects the need, in pre-Brønsted times, to postulate the existence of a substance NH$_4$OH that could dissociate according to Arrhenius' theory to yield the products of Eq 6. The state of ammonia in water is best described as NH$_3$(aq); there is no physical evidence for the existence of ammonium hydroxide, NH$_4$OH, but the name seems to remain forever etched on reagent bottles in the chemical laboratory.

When ammonia acts as an acid, it forms the *amide ion* NH$_2^-$.

$$NH_3 \longrightarrow NH_2^- + H^+ \tag{7}$$

Ammonia is a weak acid, so its conjugate base is a strong proton acceptor. It is in fact a stronger base than OH$^-$, and so it, like the H$^-$ ion, cannot exist in aqueous solution:

$$NH_2^- + H_2O \longrightarrow NH_3(aq) + OH^-(aq) \tag{8}$$
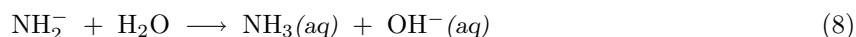
If solid sodium amide, NaNH$_2$, is added to water, the result will be an alkaline solution smelling strongly of ammonia. Thus the acidic nature of ammonia can only manifest itself in a solvent other than water.

8.2   Hydroxy compounds as acids and bases

Compounds containing the group –OH constitute the largest category of acids, especially if the organic acids (discussed separately farther on) are included. M–OH compounds also include many of the most common bases.

Whether a compound of the general type M–O–H will act as an acid or a base depends in the final analysis on the relative strengths of the M–O and the O–H bonds. If the M–O bond is weaker, then the –OH part will tend to retain its individuality and will act as a hydroxide ion. If the O–H bond is weaker, the MO– part of the molecule will remain intact and the substance will be acidic.

8.3   Metal–OH compounds

In general, if M is a metallic element, the compound MOH will be basic. The case of the highly electropositive elements of Groups 1 and 2 is somewhat special in that their solid MOH compounds exist as interpenetrating lattices of metal cations and OH$^-$ ions, so those that can dissolve readily in water form strongly alkaline solutions; KOH and NaOH are well known examples of strong bases. From the Brønsted standpoint, these different "bases" are really just different sources for the single strong base OH$^-$.

As one moves into Group 2 of the periodic table the M-OH compounds become less soluble; thus a saturated solution of $Ca(OH)_2$ is only weakly alkaline. Hydroxides of the metallic elements of the p-block and of the transition metals are so insoluble that their solutions are not alkaline at all. Nevertheless these solids dissolve readily in acidic solutions to yield a salt plus water, so they are formally bases.

8.4   –OH compounds of the nonmetals

The acidic character of these compounds, known collectively as *oxyacids*, is attributed to the displacement of negative charge from the hydroxylic oxygen atom by the electronegative central atom. The net effect is to make the oxygen slightly more positive, thus easing the departure of the hydrogen as H$^+$.

The presence of other electron-attracting groups on the central atom has a marked effect on the strength of an oxyacid. Of special importance is the doubly-bonded oxygen atom. With the exception of the halogen halides, all of the common strong acids contain one or more of these oxygens, as in sulfuric acid $SO_2(OH)$, nitric acid $NO_2(OH)$ and phosphoric acid $PO(OH)_3$. In general the strengths of these acids depends more on the number of oxygens than on any other factor, so periodic trends are not so important. Chlorine happens to be the only halogen for which all four oxyacids are known, and the K_a values for this series show how powerfully the Cl–O oxygen atoms affect the acid strength.

ClOH	ClO(OH)	ClO$_2$(OH)	ClO$_3$(OH)
hypochlorous acid	chlorous acid	chloric acid	perchloric acid
$10^{-7.2}$	.011	10	$\approx 10^{10}$

8.5   Organic acids

The *carboxyl* group –CO(OH) is the characteristic functional group of the organic acids. The acidity of the carboxylic hydrogen atom is due almost entirely to electron-withdrawal by the non-hydroxylic oxygen atom; if it were not present, we would have an alcohol –COH whose acidity is smaller even than that of H_2O.

This partial electron withdrawal from one atom can affect not only a neighboring atom, but that atom's neighbor as well. Thus the strength of a carboxylic acid will be affected by the bonding environment of the carbon atom to which it is connected. This propagation of partial electron withdrawal through several adjacent atoms is known as the *inductive effect*) and is extremely important in organic chemistry. A very

good example of the inductive effect produced by chlorine (another highly electronegative atom) is seen by comparing the strengths of acetic acid and of the successively more highly substituted chloroacetic acids:

CH_3–COOH	$ClCH_2$–COOH	Cl_2CH–COOH	Cl_3–COOH
acetic acid	monochloroacetic acid	dichloroacetic acid	trichloroacetic acid
1.8×10^{-5}	.0014	.055	.63

Phenols The acidic character of the carboxyl group is really a consequence of the enhanced acidity of the –OH group as influenced by the second oxygen atom that makes up the –COOH group. The benzene ring has a similar although weaker electron-withdrawing effect, so hydroxyl groups that are attached to benzene rings also act as acids. The most well known example of such an acid is phenol, C_6H_5OH[6]. Compared to carboxylic acids, phenolic acids are quite very weak:

CH_3–COOH	C_6H_5–COOH	C_6H_5OH
acetic acid	benzoic acid	phenol
1.8×10^{-5}	6.3×10^{-5}	1.1×10^{-10}

8.6 Amines and organic bases

We have already discussed organic acids, so perhaps a word about organic bases would be in order. The –OH group, when bonded to carbon, is acidic rather than basic, so alcohols are not the analogs of the inorganic hydroxy compounds. The amines, consisting of the $-NH_2$ group bonded to a carbon atom, are the most common class of organic bases. Amines give weakly alkaline solutions in water:

$$CH_3NH_2 \ + \ H_2O \ \longrightarrow \ CH_3NH_3^+ \ + \ OH^- (aq) \tag{9}$$
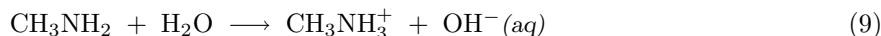
Amines are end products of the bacterial degradation of nitrogenous organic substances such as proteins. They tend to have rather unpleasant "rotten fish" odors. This is no coincidence, since seafood contains especially large amounts of nitrogen-containing compounds which begin to break down very quickly. Methylamine, CH_3NH_2, being a gas at room temperature, is especially apt to make itself known to us. Addition of lemon juice or some other acidic substance to fish will convert the methylamine to the methylaminium ion $CH_3NH_3^+$. Because ions are not volatile they have no odor.

8.7 Oxides as acids and bases

The division between acidic and basic oxygen compounds largely parallels that between the –OH compounds. The oxygen compounds of the highly electropositive metals of Groups 1-2 actually contain the oxide ion O^{2-}. This ion is another case of a proton acceptor that is stronger than OH^-, and thus cannot exist in aqueous solution. Ionic oxides therefore tend to give strongly alkaline solutions:

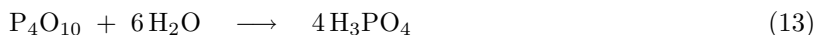$$O_2^- \ + \ H_2O \ \longrightarrow \ 2OH^- (aq) \tag{10}$$

In some cases, such as that of MgO, the solid is so insoluble that little change in pH is noticed when it is placed in water. CaO, however, which is known as *quicklime*, is sufficiently soluble to form a strongly alkaline solution with the evolution of considerable heat; the result is the slightly-soluble *slaked lime*, $Ca(OH)_2$.

   Oxygen compounds of the transition metals are generally insoluble solids having rather complex extended structures. Although some will dissolve in acids, they display no acidic properties in water.

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[6]Phenol, also known as carbolic acid, is used as a disinfectant. An aqueous solution containing phenol is sold under the trade name Lysol.

8.8   Acid anhydrides

The binary oxygen compounds of the non-metallic elements tend to produce acidic solutions when they are added to water. Compounds such as SO_3, CO_2, and P_4O_6 are sometimes referred to as the acid *anhydrides* ("acids without water").
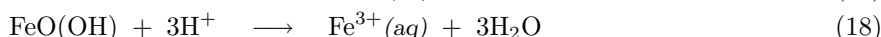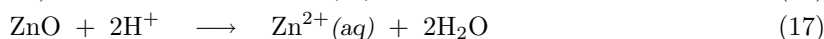
$$CO_2 + H_2O \longrightarrow H_2CO_3 \tag{11}$$

$$SO_3 + H_2O \longrightarrow H_2SO_4 \tag{12}$$

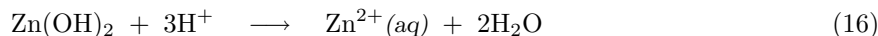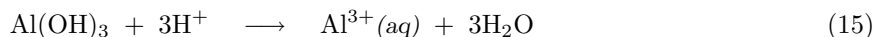$$P_4O_{10} + 6\,H_2O \longrightarrow 4\,H_3PO_4 \tag{13}$$

In some cases, the reaction involves more than simply incorporating the elements of water. Thus nitrogen dioxide, used in the commercial preparation of nitric acid, is not an anhydride in the strict sense:

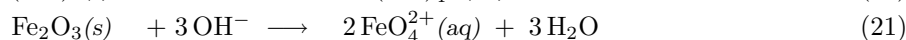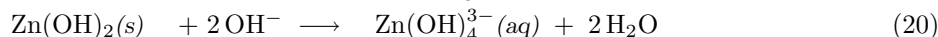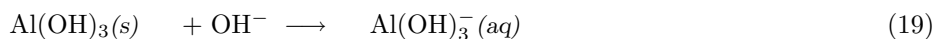$$3\,NO_2 + H_2O \longrightarrow 2\,HNO_3 + NO \tag{14}$$

8.9   Amphoteric oxides and hydroxides

The oxides and hydroxides of the metals of Group 3 and higher tend to be only weakly basic, and most display an amphoteric nature. Most of these compounds are so slightly soluble in water that their acidic or basic character is only obvious in their reactions with strong acids or bases.

In general, these compounds tend to be more basic than acidic; thus the oxides and hydroxides of aluminum, iron, and zinc all dissolve in strong acid:

$$Al(OH)_3 + 3H^+ \longrightarrow Al^{3+}(aq) + 3H_2O \tag{15}$$

$$Zn(OH)_2 + 3H^+ \longrightarrow Zn^{2+}(aq) + 2H_2O \tag{16}$$

$$ZnO + 2H^+ \longrightarrow Zn^{2+}(aq) + 2H_2O \tag{17}$$

$$FeO(OH) + 3H^+ \longrightarrow Fe^{3+}(aq) + 3H_2O \tag{18}$$

However, in concentrated hydroxide solutions, these substances form anionic species which are the conjugate bases of the oxide or hydroxide:

$$Al(OH)_3\text{(s)} + OH^- \longrightarrow Al(OH)_3^-\text{(aq)} \tag{19}$$

$$Zn(OH)_2\text{(s)} + 2\,OH^- \longrightarrow Zn(OH)_4^{3-}\text{(aq)} + 2\,H_2O \tag{20}$$

$$Fe_2O_3\text{(s)} + 3\,OH^- \longrightarrow 2\,FeO_4^{2+}\text{(aq)} + 3\,H_2O \tag{21}$$

These are called the *aluminate*, *zincate*, and *ferrate* ions. Other products, in which only some of the –OH groups of the parent hydroxides are deprotonated, are also formed, so there are actually whole series of these oxyanions for most metals.

8.10   Salts

A solution of NaCl in pure water will be perfectly neutral because Cl^-, being the conjugate base of an exceedingly strong acid, is itself a negligibly weak proton acceptor. However, if we dissolve some NaF or sodium acetate $CH_3COO^-\,Na^+$ in water, the solution will be definitely alkaline. HF and CH_3COOH are weak acids, so their conjugate bases F^-(aq) and CH_3COO^-(aq) will be reasonably good proton acceptors– strong enough, anyway, to act as weak bases in water:

$$F^-\text{(aq)} + H_2O \longrightarrow HF\text{(aq)} + OH^- \tag{22}$$

$$CH_3COO^- + H_2O \longrightarrow CH_3COOH + OH^- \tag{23}$$
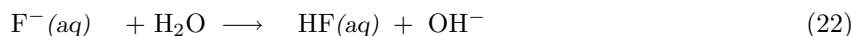
Thus the rule (which you are expected to know): *an aqueous solution of a salt of a weak acid will be alkaline.* This phenomenon is sometimes called *hydrolysis* ("water splitting")– again, a reminder of times before the concept of proton transfer acid-base reactions had become accepted.

If a salt contains the ammonium ion as its cation, then hydrolysis will produce an acidic solution if there are no weak-acid anions to override the effect. Thus a solution of ammonium sulfate will be acidic:

$$NH_4(aq) + H_2O \longrightarrow NH_3(aq) + H_3O^+(aq) \tag{24}$$
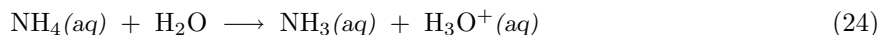
8.11   Metal cations

Iron(III) chloride is an an orange solid which dissolves in water to give a distinctly acidic solution. How can this be? Neither the Cl^- nor the Fe^{3+} ions contain protons, so how can they donate protons to H_2O to give a solution of H_3O^+?
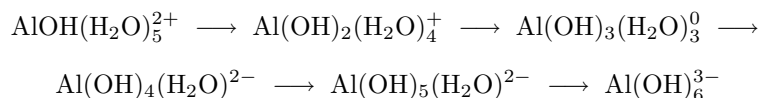
The answer is that the protons come from the water molecules in the primary hydration shell of the metal cation. These are the water molecules, usually about six in number, that are closest and most tightly bound to the cation by ion-dipole attraction. If the charge on the cation is +2 or greater, the electric field strength at the edge of the hydration shell will be great enough to promote the loss of a hydrogen ion from one of the water molecules:

$$Fe(H_2O)_6^{3+} + H_2O \longrightarrow Fe(H_2O)_5(OH)^{2+} + H_3O^+ \tag{25}$$
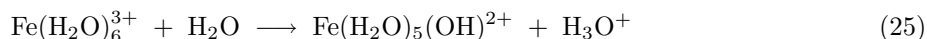
As a consequence of this reaction, a solution of $FeCl_3$ is a stronger acid than an equimolar solution of acetic acid. A solution of $FeCl_2$, however, will be a much weaker acid; the +2 charge is considerably less effective in easing the loss of the proton. In general, the smaller and more highly charged the cation, the more acidic will it be; the acidity of the alkali metals and of ions like $Ag^+(aq)$ is negligible.

ion	In^{3+}	Bi^{3+}	Fe^{3+}	Sn^{2+}	Fe^{2+}	Cu^{2+}	Mg^{2+}
acid constant	0.6	.01	.007	1E–4	5E–9	5E–9	1.6E–13

It should be possible for a hydrated cation to lose more than one proton. For example, an $Al(H_2O)_6^{3+}$ ion should form, successively, the following species:

$$AlOH(H_2O)_5^{2+} \longrightarrow Al(OH)_2(H_2O)_4^+ \longrightarrow Al(OH)_3(H_2O)_3^0 \longrightarrow$$

$$Al(OH)_4(H_2O)^{2-} \longrightarrow Al(OH)_5(H_2O)^{2-} \longrightarrow Al(OH)_6^{3-}$$

However, removal of protons becomes progressively more difficult as the charge decreases from a high positive value to a negative one; the last three species have not been detected in solution. In dilute solutions of aluminum chloride the principal species are Al^{3+} and $AlOH^{2+}$ (i.e., $Al(H_2O)_6^{3+}$ and $AlOH(H_2O)_5^{2+}$).

In more concentrated solutions the situation is complicated by reactions in which two or more hydroxy-cations polymerize into multi-center complexes. For example, the two aluminum species mentioned above exist largely as $Al_4(OH)_{10}^{2+}$ and $Al_6(OH)_{15}^{3+}$ in concentrated aluminum ion solutions. Similarly, in solutions of bismuth salts the principal ions are Bi^{3+}, $BiOH^{2+}$, and $Bi_6(OH)_{12}^{6+}$; there is no evidence for $Bi(OH)_2^+$.

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