

Chapter 12

Acid-Base Chemistry

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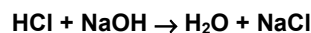
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12.0 INTRODUCTION

The terms "acid" and "base" have been used for several centuries. Acids were characterized by their sour taste and their corrosive nature, while bases were substances that were slippery, had a bitter taste, and reacted with acids. However, these simple definitions had to be refined as the chemical properties of acids and bases became better understood. The first chemical definition of acids and bases was that of Svante Arrhenius.* An Arrhenius acid is a substance that produces H^{1+} ions when dissolved in water, while an Arrhenius base produces OH^{1-} ions. In this theory, an acid *ionizes* in water much as an ionic substance, and the equilibrium constant for the ionization is often referred to as the **acid ionization constant**. For example, dissolving HCl in water is represented as follows in Arrhenius acid-base theory:



The reaction of an acid with a base is called **neutralization**, and the products are water and a **salt**. The cation of a salt is derived from the base, and the anion comes from the acid. The following reaction is the neutralization of HCl with NaOH to produce the salt NaCl:



Arrhenius acid-base theory is very limited because its definitions are restricted to behavior in water. Consequently, broader definitions for these very important classes of compounds were developed. In this chapter, we examine the Lewis and the Brønsted-Lowry (or simply Brønsted) theories of acid-base chemistry. We begin our discussion of acids and bases with the more general Lewis definition and then use the more restricted Brønsted definition in a discussion of acid-base reactions in water.

THE OBJECTIVES OF CHAPTER 12 ARE TO:

- define acids and bases;
- show examples of Lewis and Brønsted acid-base reactions;
- explain how acids are named;

* Arrhenius acids and bases were first introduced in Section 10.5 where we used them as another class of electrolytes.

- discuss the factors dictating the extent of proton transfer in acid-base reactions;
- explain the factors dictating the relative strengths of acids;
- define K_a and show how the equilibrium constants of acid-base reactions are related to the K_a values of the acids involved in the equilibrium;
- explain the acid-base chart and how it is used to predict the extent of proton transfer in acid-base reactions; and
- define pH and pK_a .

12.1 LEWIS ACIDS AND BASES

A **Lewis base** contains a lone pair, a **Lewis acid** contains an empty orbital that can overlap with the lone pair, and a **Lewis acid-base reaction** is the formation of a coordinate covalent bond (bonds in which both bonding electrons are supplied by the same atom) between a Lewis acid and a Lewis base. A Lewis base is readily identified by the presence of a lone pair (Figure 12.1a). Bases are strengthened by negative charge. Lewis acids (Figure 12.1b) are often more difficult to identify. The following should help:

- A Lewis acid must be able to accommodate an additional electron region (the new bond), so, if it obeys the octet rule, a Lewis acidic atom must have less than four regions.
- Attack by a lone pair is facilitated by positive charge, so Lewis acidity is strengthened by positive charge.

The bond between two atoms is covalent only when the interacting orbitals have similar energies because large energy separations favor ionic bonds. Thus, the formation of a coordinate covalent bond in a Lewis acid-base reaction is facilitated when the energy of the empty orbital of the Lewis acid is close to that of the lone pair of the Lewis base. The energies of lone pairs are typically lower than those of empty orbitals, so the strongest interactions occur when the energy of the lone pair is high for a lone pair and the energy of the empty orbital is low for an empty orbital. For example, consider the cases of Na^{1+} and Ag^{1+} as shown in Figure 12.2. The energy of the empty orbital of Ag^{1+} is much lower than that of Na^{1+} ; *i.e.*, the energy of the empty orbital of Ag^{1+} is low for an empty orbital. Thus, the empty orbital on Ag^{1+} is sufficiently close to that of the lone pair on the Br^{1-} ion that the Ag-Br bond is covalent. However, the energy of the empty orbital on Na^{1+} is so high that the Na-Br bond is ionic. Thus, Ag^{1+} is a Lewis acid, but Na^{1+} is not. In general, H^{1+} and cations of metals with high effective nuclear charge (metals such as Ag and Pb that lie low and to the right of the periodic table) have empty orbitals that are relatively low in energy, so they are good Lewis acids, but cations of metals with low effective nuclear charges (such as those in Groups 1A and 2A) are very high in energy, so their bonds with

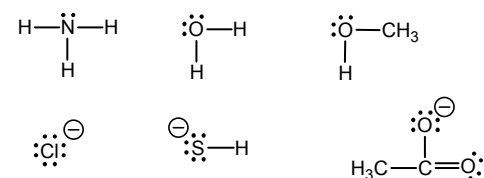


Figure 12.1a Some Lewis Bases

Atoms with lone pairs are Lewis basic. Negative charge strengthens their basicity.

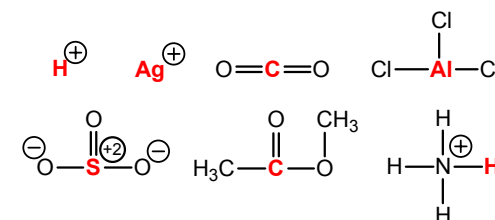


Figure 12.1b Some Lewis Acids

Atoms (highlighted in red) with fewer than four electron regions are Lewis acidic. Positive charge strengthens their acidity.

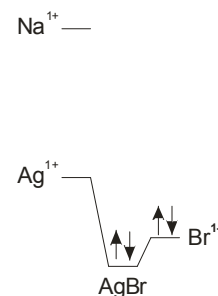


Figure 12.2 Metal ions with low-energy empty orbitals are Lewis acidic.

The empty orbital on Ag is relatively low in energy, so it forms a covalent bond with the lone pair on Br^{1-} ion. The empty orbital on Na^{1+} is very high in energy, so its bonds to anions are ionic. Therefore, Ag^{1+} is Lewis acidic, but Na^{1+} is not.

anionic substances are ionic, and they are not Lewis acidic. We conclude that

Strong Lewis acids have low-energy empty orbitals, and strong Lewis bases have high-energy lone pairs.

Oxidizing agents and Lewis acids are both characterized by empty valence orbitals that are low in energy, while reducing agents and Lewis bases both have high-energy electrons. Consequently, many Lewis acids are also oxidants and many Lewis bases are also reductants. Indeed, oxidants and Lewis acids are often defined as electron acceptors, and reductants and Lewis bases as electron donors. The obvious question becomes, “What determines whether electrons are transferred or shared when a lone pair comes into contact with an empty orbital?” As has been the case so often in our study of chemistry, the answer lies in their relative energies: electrons do whatever is most efficient at increasing their electrical potential in order to lower their energy. If the energy of the empty orbital is lower than that of the lone pair, the electrons simply transfer from the reductant to the more positive electrical potential on the oxidant in a redox reaction. However, if the empty orbital is at higher energy, the electrons lower their energy by forming a covalent bond between an acid and a base, which increases their electrical potential by exposing them to part of the nuclear charge on the acid. The example of H^{1+} , which is both an oxidant and an acid, is considered in Figure 12.3. If H^{1+} encounters a zinc atom, it behaves as an oxidant and accepts the higher energy electrons from the reductant zinc. However, electrons will not flow from a Br^{1-} ion to the higher energy orbital on H^{1+} , so the lone pair on Br^{1-} ion lowers its energy by forming an H-Br covalent bond. Br^{1-} is a base in the presence of H^{1+} , but it is a reductant in the presence of something like Cl_2 that has an empty orbital at lower energy ($2Br^{1-} + Cl_2 \rightarrow Br_2 + 2Cl^{1-}$).

Curved arrows are used to indicate the direction of electron pair attack in Lewis acid-base reactions.

- A curved arrow from a lone pair on one atom to another atom indicates that the lone pair becomes a covalent bond between the atoms.
- A curved arrow from a bond to an atom indicates that the bonding electrons become a lone pair on the atom.

Figure 12.4 demonstrates the use of curved arrows in Lewis acid-base reactions involving metals. The acidic nature of Ag^{1+} ions is demonstrated in Figures 12.4a and b, where the lone pair of the base (Cl^{1-} ion or NH_3 molecule) attacks the acid (Ag^{1+}) to produce a covalent bond. The curved arrow in each case points from the lone pair on the base to the silver ion and implies that the lone pair becomes a covalent bond between the acid and the

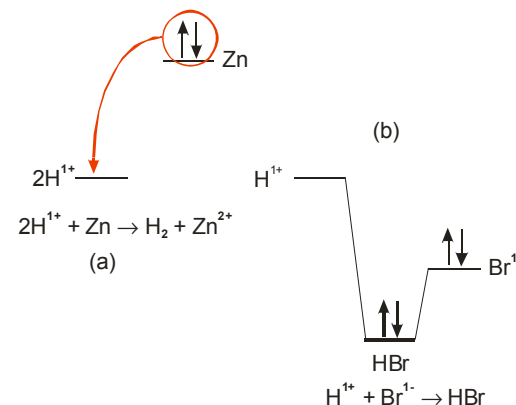


Figure 12.3 H^{1+} as oxidant and acid

a) H^{1+} is an oxidizing agent in the presence of Zn because the electrons on Zn are higher in energy; i.e., the electrons transfer. b) H^{1+} is an acid in the presence of Br^{1-} because the lone pair on Br^{1-} is lower in energy; i.e., the electrons are shared.

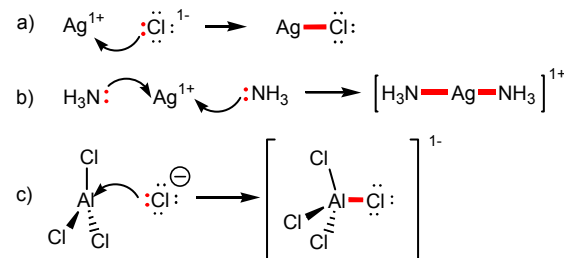


Figure 12.4 Metal ions as Lewis acids.

- a) precipitation of $AgCl$
 b) formation of $Ag(NH_3)_2^{1+}$
 c) formation of $AlCl_4^{1-}$
 The red lone pairs become the red bonds.

base. The aluminum atom of AlCl_3 has only six valence electrons and three electron regions surrounding it, so AlCl_3 is a strong Lewis acid. The Lewis acid-base reaction of AlCl_3 with Cl^- ion is shown in Figure 12.4c. The curved arrow shows that the lone pair on the base is converted into an Al-Cl bond. The increase in the number of electron regions results in geometry and hybridization changes as the number of electron regions surrounding the Al atom goes from three (trigonal planar, sp^2) to four (tetrahedral, sp^3).

Now consider the three-step reaction of SO_3 and H_2O to form H_2SO_4 , the reaction that is the primary cause of acid rain. The oxygen atom of the water molecule contains two lone pairs, so water is a Lewis base, while the sulfur atom in SO_3 has only three electron regions, which makes SO_3 Lewis acidic. As shown in Figure 12.5a, a lone pair on the oxygen atom in water is shared with the sulfur atom to form a new S-O σ bond. Simultaneously, the electrons in the S=O π bond are converted into a lone pair on the oxygen (curved arrow from the bond to the atom), and the hybridization of the sulfur atom goes from sp^2 to sp^3 (from trigonal planar to tetrahedral). The resulting structure places positive formal charge on the oxygen atom, which is eliminated by transferring a proton (shown in red in Figure 12.4b) from that oxygen atom to one that carries negative formal charge. The proton transfer is accomplished with two acid-base reactions with the solvent. In the first, a proton (red) is transferred from the oxygen atom with positive formal charge to a solvent molecule (water). In the second, a proton (blue) is transferred from the solvent to an oxygen atom with negative formal charge. Although Figure 12.5b shows only one water molecule, it is more likely that *two* are involved: one to remove the proton from the oxygen with positive charge and another to donate a proton to a lone pair on one of the other oxygen atoms.

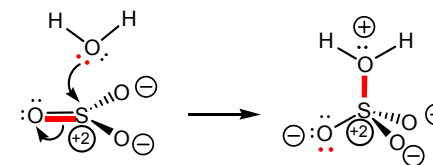


Figure 12.5a $\text{SO}_3 + \text{H}_2\text{O}$, Step 1

Red lone pair on water becomes S-O bond, and π electron pair in S=O bond becomes red lone pair on O. Lone pairs on two oxygen atoms have been omitted.

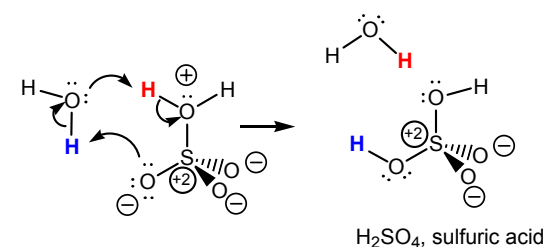
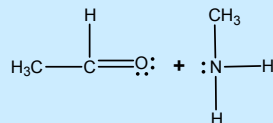


Figure 12.5b $\text{SO}_3 + \text{H}_2\text{O}$, Step 2

Water assists in a proton transfer to reduce formal charge.

Example 12.1

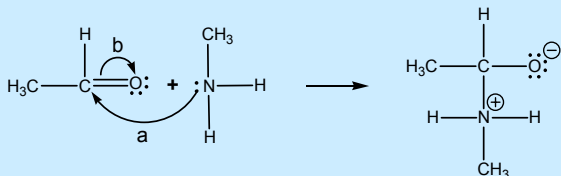
Use curved arrows to show the mechanism* of the Lewis acid-base reaction between the following and draw the Lewis structure of the product.



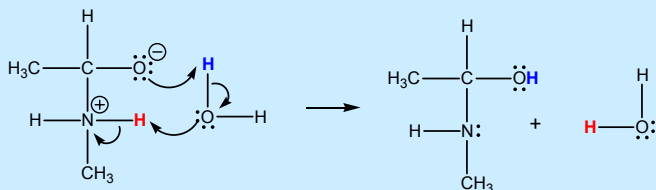
We first identify the Lewis acidic and basic sites. The nitrogen atom and the carbon atoms in the CH_3 groups each have four electron regions, so they are not Lewis acidic. H atoms in C-H bonds are not acidic, nor are they acidic in N-H bonds unless the nitrogen has a positive formal charge as in NH_4^{1+} . That leaves the carbon and oxygen atoms in the C=O

* Recall from Chapter 9 that a reaction mechanism shows the individual steps required to convert the reactants to products. In Lewis acid-base reactions, each step is represented with curved arrows that show the movement of electrons to form either bonding pairs or lone pairs.

bond. The bond is polar with the negative end on oxygen and the positive end on carbon. The partial positive charge and only three electron regions make the carbon atom Lewis acidic. The lone pair on the nitrogen atom makes it Lewis basic. The attack is from the lone pair on N to the C atom in the C=O bond. The lone pair on the N atom is used to form a C-N bond (Arrow a below). The two additional electrons in the C-N bond would put 10 electrons around the C atom, so the π electrons in the C=O bond are converted into a lone pair on the oxygen atom (Arrow b).



The positive formal charge on the N atom makes the H atoms attached to it acidic, so the formal charge is eliminated by a solvent-assisted proton transfer similar to that shown in the reaction of SO_3 and water. The proton shown in red below is transferred from N to a water molecule as the N-H bonding pair is converted to a lone pair on N. Another proton (blue) is transferred from a water molecule to the O atom with negative formal charge. The resulting product has no formal charge.



The above reaction is an example of organic chemistry, which is introduced in the following chapter. Organic chemistry has many Lewis acid-base reactions with mechanisms that are almost identical to the one shown here; the only difference is the identity of the acid and the base.

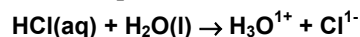
To summarize, a Lewis acid-base reaction results in the formation of a coordinate covalent bond between an acid and a base. The bonding pair comes from the lone pair of the base. The acid must have an empty orbital that can overlap with the filled orbital on the base to form the bond. If the very broad classification of Lewis is used to define acid-base reactions, then *a very large number of chemical reactions can be classified as either acid-base or redox reactions. In one, a base **shares** its electrons with an acid; in the other, a reductant **transfers** its electrons to an oxidant.**

* There are many similarities in the treatment of redox and acid-base chemistry that will be indicated in the margin as we proceed through this chapter.

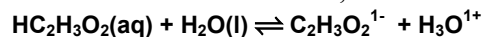
12.2 BRØNSTED ACIDS

Brønsted acids are proton donors, and **Brønsted bases** are proton acceptors. The Brønsted definition is a special case of the Lewis definition. In both, a base contains a lone pair that it shares with the acid in a covalent bond. All Lewis bases are Brønsted bases, and all Brønsted bases are Lewis bases. However, a Lewis acid is *any* species that can share the lone pair, while the species that shares the lone pair *must* be a proton in the Brønsted definition. A Brønsted acid is the species that contains the proton. A **Brønsted acid-base** reaction is a proton transfer from the acid to the base.[†]

In Chapter 10, we classified acids that are strong electrolytes as strong acids. **Strong acids** dissociate 100% in water. The dissociation of an acid in water is viewed as ionization in Arrhenius theory, but acids are not ionic compounds, and the term “ionization” is misleading. Brønsted theory views the dissociation of an acid in water as a proton transfer between the acid and water, which is a Brønsted base. The chemical equation for the proton transfer between hydrochloric acid, a strong acid, and water is*



The single arrow indicates that the above reaction is extensive and there are essentially no HCl molecules in the equilibrium mixture. Most acids are not strong electrolytes, but they do produce some ions in solution. These weak electrolytes are classified as **weak acids**. Consider the reaction of acetic acid, a weak acid, and water.



Acetic acid is a weak acid as only about 1% of the molecules react to produce acetate ions. HClO is an even weaker acid as less than 0.1% of HClO molecules transfer their protons to water to form of ClO^{1-} . Thus, the reaction of a weak acid and water is not extensive, which is represented by double arrows in the chemical equation.

In order for HX to be acidic, the H-X bond must break to produce H^{1+} and X^{1-} ions, but that can happen only if it is a polar bond. Thus, *a hydrogen atom must be covalently bound to a highly electronegative atom to be acidic*. There are a great number of compounds with hydrogen atoms covalently bound to atoms that are not very electronegative, but these compounds are not Brønsted acids. The most common examples are organic compounds because the C-H bond is not polar (C and H have very similar electronegativities). For example, the C-H bonds in CH_4 do not produce H^{1+} when they break, so CH_4 cannot be a Brønsted acid. The H-Cl bond is very polar, so breaking the H-Cl bond does produce H^{1+} ions, which makes HCl a Brønsted acid.

† Redox reactions involve the transfer of the basic unit of negative charge (the electron), while Brønsted acid-base reactions involve the transfer of the basic unit of positive charge (the proton).

* As in Chapter 11, it is assumed that all ions are in aqueous solution, so the (aq) is omitted for clarity.

Acidic protons are often written first in the formula to indicate that they are acidic. For example, the hydrogen atoms in HCN and HSO_4^{1-} are acidic, while those in NH_3 and CH_4 are not. An important exception to this rule is NH_4^{1+} , which contains one acidic proton. $\text{HC}_2\text{H}_3\text{O}_2$ (acetic acid) contains one acidic hydrogen, written first in the formula, and three hydrogen atoms that are not acidic (Figure 12.6). However, *placing the acidic proton first in the formula can be misleading because it often places the proton next to an atom to which it is not bound*. For example, the acidic proton in $\text{HC}_2\text{H}_3\text{O}_2$ is bound to an oxygen atom not a carbon atom. Consequently, acetic acid is often written as CH_3COOH , which indicates an O-H bond and better represents the true structure of the acid. Similarly, H_2SO_4 contains two O-H bonds but no S-H bonds (Figure 12.4b).

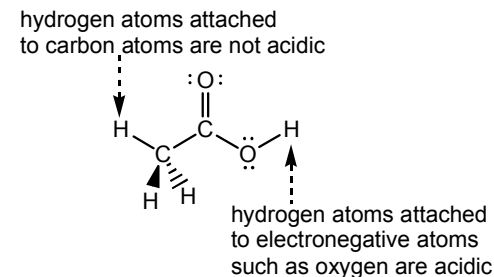
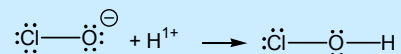


Figure 12.6 Only protons bound to highly electronegative atoms are acidic.

Example 12.2

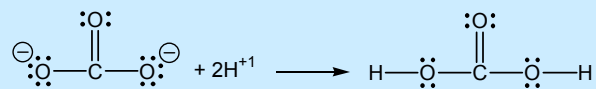
a) Draw the Lewis structure of HClO.

The Lewis structure of the ClO^{1-} ion shows that the negative charge is centered on the O atom, so the acidic proton is bound to it.



b) Draw the Lewis structure of H_2CO_3 .

The Lewis structure of the CO_3^{2-} ion places the negative formal charge on two of the oxygen atoms, so the acidic protons must be bound to them.



Although the chemical formulas frequently place the acidic proton next to the central atom of an oxoanion (chlorine and carbon above), the acidic proton is always attached to one of the oxygen atoms.

NAMING ACIDS

The manner in which an acid is named depends on whether it is a binary acid (an acid that contains only two elements, such as HCl and H_2S) or a polyatomic acid (an acid that contains more than two elements, such as HClO or H_3PO_4).

Binary Acids

Binary acids are derived from gases. The gases are named using the rules outlined in Section 5.3. For example, HCl(g) is hydrogen chloride, and HF(g) is hydrogen fluoride.

When they are dissolved in water, the names are changed in the following manner:

- 1) replace “hydrogen” with “hydro”,
- 2) change the *-ide* ending to *-ic* and
- 3) add the word “acid”.

Some examples are given in Table 12.1.

Acids Derived from Polyatomic Anions

Acids derived from polyatomic ions are **oxoacids**, *i.e.*, they are protonated oxoanions. The *acidic proton is always attached to an oxygen atom*. They are named as follows:

- 1) change the *-ate* ending of the polyatomic ion to *-ic* * or
- 2) change the *-ite* ending of the polyatomic ion to *-ous** and
- 3) add the word “acid”.

In summary, an *elementate* ion becomes an *elementic* acid, and an *elementite* ion becomes an *elementous* acid. If the acid is also an ion, its name is unchanged. For example, the HPO_4^{2-} and $\text{H}_2\text{PO}_4^{1-}$ ions are the monohydrogen phosphate ion and dihydrogen phosphate ion[†], respectively. Some examples of oxoacids are given in Table 12.2.

Example 12.3

a) Name the acid H_2CO_3 .

The CO_3^{2-} ion is the carbonate ion (Table 4.1), so the acid is carbonic acid.

b) Name the acid HCO_3^{1-} .

Acids that are ions are named as the ion, so HCO_3^{1-} is the hydrogen carbonate ion or the bicarbonate ion.

c) What is the formula of selenous acid?

The *-ous* ending tells us that the acid is derived from a polyatomic ion with an *-ite* ending; *i.e.*, the acid is derived from the selenite ion. Selenium is a Group 6A nonmetal, so its chemical properties are expected to be similar to those of sulfur. The sulfite ion is SO_3^{2-} , so selenite is SeO_3^{2-} and selenous acid is H_2SeO_3 . It contains two O-H bonds.

d) What is the formula of hydroselenic acid?

The name starts with hydro, so this is a binary acid of H and Se. Se is in Group 6A, so it is expected to form a -2 anion, which requires two protons. Hydroselenic acid is H_2Se .

Table 12.1 Examples of binary acid names

Formula	Name	Formula	Name
HBr(g)	hydrogen bromide	HBr(aq)	hydrobromic acid
HCl(g)	hydrogen chloride	HCl(aq)	hydrochloric acid
HCN(g)	hydrogen cyanide	HCN(aq)	hydrocyanic acid ^a
HF(g)	hydrogen fluoride	HF(aq)	hydrofluoric acid
HI(g)	hydrogen iodide	HI(aq)	hydroiodic acid

^a HCN is not a binary compound, but HCN is a gas and the name of the CN^{1-} ion (cyanide ion) ends in *-ide*, so, HCN(aq) is named in the same manner as the binary acids.

* If the non-oxygen atom is sulfur, replace *-ate* with *-uric* and *-ite* with *-urous*. If it is phosphorus, replace *-ate* with *-oric* and *-ite* with *-orous*.

[†] In an older, but still common, method, ions with acidic protons are named by using the prefix ‘bi’ instead of the word ‘hydrogen’. Thus, HSO_4^{1-} is either hydrogen sulfate or bisulfate.

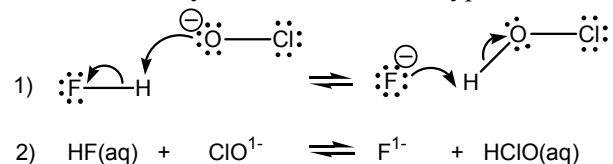
Table 12.2 Names of some oxoanions and their oxoacids

Ion Formula	Ion Name	Oxoacid Formula	Oxoacid Name
ClO^{1-}	hypochlorite ion	HClO^a	hypochlorous acid
ClO_2^{1-}	chlorite ion	HClO_2	chlorous acid
BrO_3^{1-}	bromate ion	HBrO_3	bromic acid
IO_4^{1-}	periodate ion	HIO_4	periodic acid
NO_3^{1-}	nitrate ion	HNO_3	nitric acid
NO_2^{1-}	nitrite ion	HNO_2	nitrous acid
PO_4^{3-}	phosphate ion	H_3PO_4	phosphoric acid
SO_4^{2-}	sulfate ion	H_2SO_4	sulfuric acid
SO_3^{2-}	sulfite ion	H_2SO_3	sulfurous acid

^a The proton in HClO is attached to the O not the Cl (Example 12.1), so it is often written as HOCl. However, the O is never written first in HClO_2 , HClO_3 , or HClO_4 , so we use HClO for the formula to be consistent with the other members of this group of acids.

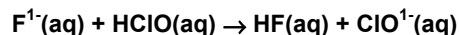
12.3 BRØNSTED ACID-BASE REACTIONS

The reaction between hydrofluoric acid and hypochlorite ion can be written in two ways



The top representation shows the Lewis formalism that uses curved arrows to show the direction of electron pair attack, *which is opposite to the direction of proton transfer*. The bottom representation is the way the reaction is typically written in the Brønsted formalism. We use both formalisms when writing acid-base reactions in this chapter.

In the reaction between HF and ClO^{1-} , a proton transfers from HF, the acid, to ClO^{1-} , the base. The curved arrows show that the H-F bonding pair remains on the fluorine atom as a lone pair, while a lone pair on the oxygen atom is converted to an H-O bonding pair. The resulting fluoride ion has a lone pair that it can use to bond to an acid, so it is a base. Thus, proton donation has converted the acid HF into the base F^{1-} . Proton transfer also converts the base (ClO^{1-}) ion into an acid (HClO), so the products of the acid-base reaction are also an acid and a base, which can also undergo an acid-base reaction to produce the original reactants in the back-reaction.



When the rates of the forward and reverse reactions are equal, the reaction reaches a dynamic equilibrium in which both reactions continue at the same rate with no net change in the equilibrium concentrations. Consequently, acid-base reactions are often written with double arrows to indicate the competing reactions.

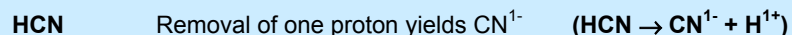
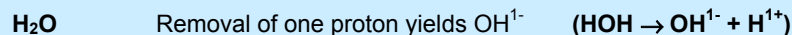
The acid in a Brønsted acid-base reaction loses a single proton to become a base, while the base accepts a single proton to become an acid. An acid and a base that differ by a *single proton* are conjugate to one another and form a **conjugate acid-base pair**.* F^{1-} ion is the **conjugate base** of HF, and HClO is the **conjugate acid** of ClO^{1-} . We conclude the following:

The products of a Brønsted acid-base reaction are the conjugate base of the reacting acid and the conjugate acid of the reacting base. In other words, all Brønsted acid-base reactions consist of two conjugate acid-base pairs and nothing else.

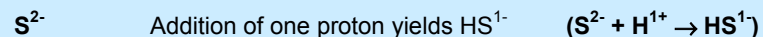
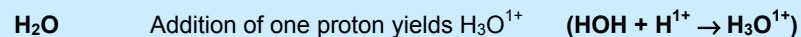
* In redox reactions, electron transfer converts an oxidant into a reductant and the reductant into an oxidant. The reductant and the oxidant that it becomes are called a redox couple. Redox reactions consist of two redox couples just as acid-base reactions consist of two conjugate acid-base pairs.

Example 12.4

a) Write the conjugate base of each of the following acids:



b) Write the conjugate acid of each of the following bases:

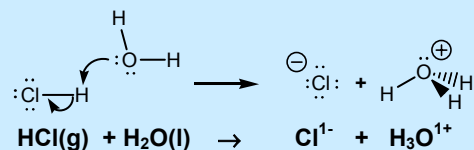


Note that H_2O was used as an example of both an acid and a base in Example 12.4. Substances that can function as either an acid or a base are said to be **amphiprotic**. $\text{H}_2\text{PO}_4^{1-}$ is another amphiprotic substance in Example 12.4.

Example 12.5

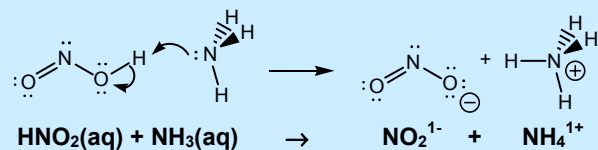
Draw Lewis structures of the reactants and products of the following reactions. Indicate the mechanism with curved arrows and include all nonzero formal charges.

a) Hydrogen chloride gas is dissolved in water.



The two conjugate acid-base pairs are (HCl , Cl^{1-}) and (H_2O , H_3O^{1+}).

b) Nitrous acid is added to a solution of ammonia.



The two conjugate acid-base pairs are (HNO_2 , NO_2^{1-}) and (NH_3 , NH_4^{1+}).

12.4 EXTENT OF PROTON TRANSFER

All acid-base reactions reach a dynamic equilibrium because the forward and reverse reactions do not stop at equilibrium. The position of the equilibrium is referred to as the **extent of proton transfer**: *if the concentration of at least one reactant in an acid-base reaction is much smaller than any of the product concentrations, then the reaction is an extensive proton transfer*. Consider the following generic* acid-base equilibrium:



If $K \gg 1$, the equilibrium concentration of at least one reactant (term in the denominator) is very small,[†] which means that the forward proton transfer is more extensive than the reverse. If $K \sim 1$, the concentrations of reactants and products are similar and the extents of proton transfer of the forward and reverse reactions are similar. If $K \ll 1$, the concentrations of at least one product (term in the numerator) is very small, so little proton transfer takes place because the reverse reaction is the more extensive proton transfer.

Recall from Section 9.11 that extensive reactions are frequently written with single arrows to emphasize that the back reaction can be neglected when calculating the amount of product that is formed. The value of K at which the reverse reaction can be ignored in an acid-base reaction varies with the reactant concentrations, but, for purposes of discussion, we will arbitrarily assume that the reaction can be written with a single arrow when $K \geq 10^3$.[§] However, extensive reactions do reach equilibrium and can be written with double arrows; the single arrow simply indicates that essentially all of at least one of the reactants disappears during the reaction. In this text, double arrows will always be used for reactions in which $K < 10^3$ to emphasize the importance of the back reaction in determining the equilibrium concentrations. For example, consider the following aqueous reaction:



K is greater than 10^3 , so the denominator of the equilibrium constant must be very small; *i.e.*, $[\text{HF}]$ and/or $[\text{ClO}^{1-}]$ are/is nearly zero at equilibrium. Thus, the proton transfer from HF to ClO^{1-} is extensive, and the reaction *could have been* written with a single arrow.

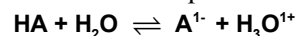
* 'HA' and 'HB' are used to indicate generic acids, and 'A¹⁻' and 'B¹⁻' are used to denote their conjugate bases.

† Concentrations of acids and bases are normally less than 1 M, so the terms in the numerator cannot make K a very large number. Instead, a large value of K is obtained because at least one of the terms in the denominator is very small.

§ A value of K greater than 10^3 implies that over 95% of at least one reactant is consumed with normal concentrations.

12.5 ACID AND BASE STRENGTHS

The strength of an acid is determined by the ease with which it donates its proton. It is easier to remove a proton from a stronger acid than from a weaker acid. Since the H-A bond must be broken in order for HA to donate a proton, the strength of the bond is an important factor in dictating the strength of an acid. In general, *a strong H-A bond implies a weak acid*. For example consider the following reaction of a generic acid with water:



~4% of the acid molecules react when the acid is HF, but ~100% react when the acid is HCl. Thus, HCl donates its proton to water much more extensively than does HF, which means that HCl is a much stronger acid. The difference in acid strengths can be attributed to differences in bond energies: $D_{\text{H-F}} = 565 \text{ kJ/mol}$ and $D_{\text{H-Cl}} = 431 \text{ kJ/mol}$. H-Cl is the stronger acid because it has the weaker bond.

However, bond energies alone do not account for the relative strengths of all acids. For example, the C-H bond energy is ~413 kJ/mol, which is even weaker than the H-Cl bond, but hydrogen atoms attached to carbon are not acidic. The reason bond energies alone do not completely explain acid strengths is shown in Figure 12.7. The bond energy is the energy required to break the bond to form neutral atoms and, as shown in Figure 12.7a, this requires that each atom retains one of the bonding electrons. The acid strength, however, is a measure of how easily the bond is broken to form ions, and as shown in Figure 12.7b, this requires that one atom retains both bonding electrons, while the other atom retains none. The latter process is favored by large electronegativity differences between the two bound atoms (that is, by polar bonds). This is why our definition of a Brønsted acid indicates that the acidic proton must be covalently bound to an electronegative atom. Consequently, *the strength of an acid also increases with the electronegativity of the atom to which the proton is attached*. HCl is a strong acid because the HCl bond is very polar, while CH₄ is not acidic because the C-H bond is not polar. HF is a much weaker acid than HCl, even though the HF bond is much more polar, so the bond strength is the more important consideration in this case.

A large number of acids are oxoacids, but their acid strengths vary considerably even though the acidic proton is always attached to an oxygen atom. To understand the variation in their strengths, we need only examine the factors that govern the O-H bond energy. We will represent an oxoacid as XO_nH, where X is an atom that may have other atoms attached to it (often other oxygen atoms). The strength of the O-H bond depends

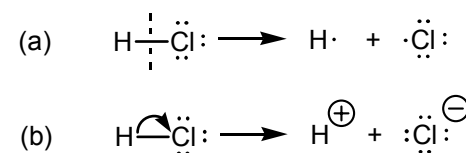


Figure 12.7 Two ways to break an HCl bond

(a) Each atom retains one of the bonding electrons. This is the type of bond breakage to which the bond energies apply. (b) The more electronegative atom retains both electrons. This is the type of bond breakage that accompanies an acid-base reaction.

upon the electron density in the bond, which, in turn, depends upon the electron withdrawing ability of X: *the more electron density X draws from the O-H bond, the weaker the bond becomes, and the stronger the acid becomes.* The following two factors dictate the electron withdrawing abilities of X:

1. **Oxidation state:** The ability of X to withdraw electrons from the O-H bond increases with its oxidation state, so the strength of an oxoacid increases with the oxidation state of X. For example, HNO_3 is a stronger acid than HNO_2 because the oxidation state of the nitrogen atom is greater in HNO_3 (+5) than in HNO_2 (+3).
2. **Electronegativity:** The amount of electron density withdrawn from the O-H bond increases with the electronegativity of X, as does the acid strength of the oxoacid. HClO_2 is a stronger acid than HBrO_2 because chlorine is more electronegative than bromine.

A strong acid is one that has a weakly bound hydrogen, but a strong base is one that forms a strong bond with hydrogen. Consequently, strong acids have weak conjugate bases, and weak acids have strong conjugate bases. In other words, *the strength of a base varies inversely with the strength of its conjugate acid.* For example, the fact that HClO_2 is a stronger acid than HBrO_2 means that BrO_2^{1-} is a stronger base than ClO_2^{1-} . This is because Br is less electronegative than Cl, so less electron density is withdrawn from the oxygen atom in BrO_2^{1-} . The increased electron density lowers the electrical potential at the oxygen atom, which raises the energy of its lone pairs and makes BrO_2^{1-} a stronger base.

If a proton transfer is extensive, then the forward reaction is more extensive than the reverse reaction, which means that the reacting acid gives up its proton more easily than the produced acid. We conclude that *an acid-base reaction is extensive when the reacting acid is stronger than the produced acid*,* which has the following implications:

$K \gg 1$: Reacting acid is stronger than produced acid, and proton transfer is extensive.

$K \sim 1$: Reacting and produced acids have comparable strengths.

$K \ll 1$: Reacting acid is weaker than produced acid, so little reaction takes place.

* The equilibrium concentrations of the weaker acid and base are always greater than the equilibrium concentrations of the stronger acid and base because the stronger acid and base react more extensively to produce the weaker acid and base.

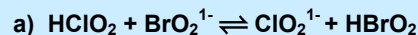
Example 12.6

$K = 10^5$ for $\text{HC}_2\text{H}_3\text{O}_2 + \text{NH}_3 \rightleftharpoons \text{NH}_4^{1+} + \text{C}_2\text{H}_3\text{O}_2^{1-}$. Which is the stronger acid, $\text{HC}_2\text{H}_3\text{O}_2$ or NH_4^{1+} ? Which is the stronger base, NH_3 or $\text{C}_2\text{H}_3\text{O}_2^{1-}$?

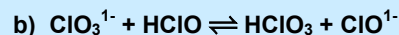
$K \gg 1$, so the reacting acid is stronger than the produced acid and the reacting base is stronger than the produced base. We conclude that acetic acid is a stronger acid than ammonium ion and ammonia is a stronger base than acetate ion.

Example 12.7

Predict whether $K > 1$ or $K < 1$ for the following acid-base reactions:



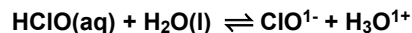
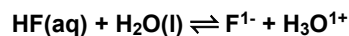
Chlorine is more electronegative than bromine, so HClO_2 is a stronger acid than HBrO_2 . Thus, $K > 1$ because the produced acid is weaker than the reacting acid.



The oxidation state of the chlorine is +5 in HClO_3 and +1 in HClO , so HClO_3 is the stronger acid. Thus, $K < 1$ because the produced acid is stronger than the reacting acid.

12.6 THE ACID DISSOCIATION CONSTANT, K_a

In order to predict the extent of an acid-base reaction, we need know only the *relative* strengths of the reacting and produced acids. This is done by measuring how extensively each acid reacts with a reference base. The reference base is water, and the extent of the reaction is given by the value of the equilibrium constant for the reaction.* Consider the examples of HF and HClO with water.



The equilibrium constant for the reaction of an acid with *water*, is called the **acid dissociation** or **acid ionization constant** and given the symbol K_a . Water is the solvent, and in the dilute solutions common to most acid-base reactions, its concentration is essentially the same as in the pure liquid. In addition, its concentration is essentially unchanged by the reaction. Consequently, it is treated as a pure liquid, as indicated by '(l)' in the chemical equation. Pure liquids enter the equilibrium constant expression as 1 (unity), which is not shown. Therefore, the K_a expressions for HF and HClO are

$$K_a(\text{HF}) = \frac{[\text{F}^{1-}][\text{H}_3\text{O}^{1+}]}{[\text{HF}]} = 7.2 \times 10^{-4} \quad \& \quad K_a(\text{HClO}) = \frac{[\text{ClO}^{1-}][\text{H}_3\text{O}^{1+}]}{[\text{HClO}]} = 3.5 \times 10^{-8}$$

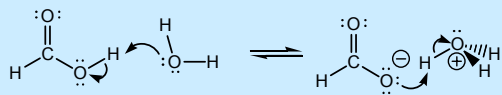
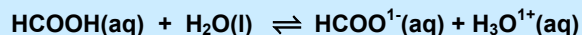
$K_a(\text{HF}) \ll 1$, so $[\text{F}^{1-}][\text{H}_3\text{O}^{1+}] \ll [\text{HF}]$ at equilibrium. Consequently, only a small fraction of the acid reacts with water, which means that HF is a weak acid. Furthermore, $K_a(\text{HClO}) < K_a(\text{HF})$, so HClO is a weaker acid than HF.

* Relative reducing or oxidizing strengths were measured by referencing the half-reaction to a reference half-reaction (the SHE). The extent of that reaction was given by the value of \mathcal{E}^0 for the cell, which is a measure of the equilibrium constant of a redox reaction.

Example 12.8

The K_a of formic acid (HCOOH) is 1.8×10^{-4} . Write the chemical equation (Brønsted and Lewis) and the mathematical expression to which this number applies.

The K_a of formic acid is the equilibrium constant for the reaction of formic acid with water.



The equilibrium constant expression for the reaction is

$$K_a = \frac{[\text{HCOO}^{1-}][\text{H}_3\text{O}^{1+}]}{[\text{HCOOH}]} = 1.8 \times 10^{-4}$$

Example 12.9

Buffers are solutions of weak acids and their conjugate bases. Buffered solutions function to maintain the pH of a solution because the addition of an acid is neutralized by the weak base and the addition of a base is neutralized by the weak acid. What is the hydronium ion concentration in a buffered solution that is 0.10 M in HClO ($K_a = 3.5 \times 10^{-8}$) and 0.15 M in ClO^{1-} ion?

We are given K_a , [HClO], and $[\text{ClO}^{1-}]$, so we substitute the known values into the K_a expression and solve for the hydronium ion concentration.

$$K_a = 3.5 \times 10^{-8} = \frac{[\text{ClO}^{1-}][\text{H}_3\text{O}^{1+}]}{[\text{HClO}]} = \frac{(0.15)[\text{H}_3\text{O}^{1+}]}{0.10} = 1.5[\text{H}_3\text{O}^{1+}]$$

$$[\text{H}_3\text{O}^{1+}] = \frac{3.5 \times 10^{-8}}{1.5} = 2.3 \times 10^{-8} \text{ M}$$

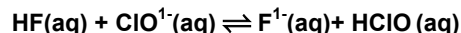
Thus far we have used only the relative strengths of the reacting and produced acids to determine if a reaction is extensive, but the K_a values of the reacting and produced acids can be used to determine the value of the equilibrium constant for the reaction.

$$K = \frac{K_a \text{ reacting acid}}{K_a \text{ produced acid}} \quad \text{Eq. 12.1}$$

The equilibrium constant for an acid-base reaction equals the K_a of the reacting acid divided by the K_a of the produced acid. If the reacting acid is stronger than the produced acid, then $K_a(\text{reacting}) > K_a(\text{produced})$, in which case, $K > 1$ and the reaction is extensive.

Combining Equation 12.1 and our rule that Brønsted acid-base reactions for which K

$> 10^3$ are extensive and can be written with single arrows, we can state that a reaction can be written with a single arrow when the K_a of the reacting acid is at least 10^3 times greater than that of the produced acid. As an example of the application of Equation 12.1, consider the following reaction:



HF ($K_a = 7.2 \times 10^{-4}$) is the reacting acid and HClO ($K_a = 3.5 \times 10^{-8}$) is the produced acid. $K_a(\text{HF}) > K_a(\text{HClO})$, so the reacting acid is stronger than the produced acid. We conclude that the equilibrium constant for the reaction between HF and ClO^{1-} is large, and the proton transfer is extensive. The value of the equilibrium constant can be determined with Equation 12.1 as follows:

$$K = \frac{K_a(\text{HF})}{K_a(\text{HClO})} = \frac{7.2 \times 10^{-4}}{3.5 \times 10^{-8}} = 2.1 \times 10^4$$

$K > 10^3$, so the reaction is extensive and could be written with a single arrow. That the above is indeed the equilibrium constant for the reaction can be verified by dividing the K_a expressions

$$K = K_a(\text{HF}) \times \frac{1}{K_a(\text{HClO})} = \frac{[\text{H}_3\text{O}^{1+}][\text{F}^{1-}]}{[\text{HF}]} \times \frac{[\text{HClO}]}{[\text{H}_3\text{O}^{1+}][\text{ClO}^{1-}]} = \frac{[\text{F}^{1-}][\text{HClO}]}{[\text{HF}][\text{ClO}^{1-}]}$$

The expression is indeed the equilibrium constant expression for the reaction.

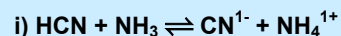
Example 12.10

K_a values: $\text{HCN} = 4.0 \times 10^{-10}$; $\text{HNO}_2 = 4.0 \times 10^{-4}$; $\text{HF} = 7.2 \times 10^{-4}$; $\text{NH}_4^{1+} = 5.6 \times 10^{-10}$.

a) **What is the strongest acid? Which has the strongest conjugate base?**

The acid with the largest K_a is HF, so it is the strongest acid. The acid with the smallest K_a is HCN, so it is the weakest acid. Conjugate base strengths are opposite the acid strengths, so F^{1-} ion would be the weakest base and CN^{1-} ion the strongest base.

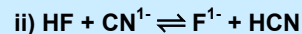
b) **Indicate whether each of the following aqueous reactions is extensive and could be represented with a single arrow.**



We can use the K_a values to see that NH_4^{1+} ion, the produced acid, is a stronger acid than HCN, the reacting acid, so the reaction is not extensive. Using Equation 12.1 we obtain

$$K = \frac{K_a(\text{HCN})}{K_a(\text{NH}_4^{1+})} = \frac{4.0 \times 10^{-10}}{5.6 \times 10^{-10}} = 0.71$$

The reaction is not extensive, but the value of $K \sim 1$, so the equilibrium concentration of HCN will be only slightly higher than that of CN^{1-} .



$K_a(\text{HF}) \gg K_a(\text{HCN})$, so this reaction is extensive. Applying Equation 12.1, we obtain

$$K = \frac{K_a(\text{HF})}{K_a(\text{HCN})} = \frac{7.2 \times 10^{-4}}{4.0 \times 10^{-10}} = 1.8 \times 10^6$$

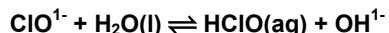
$K \gg 10^3$, so essentially all of one reactant will be consumed and the chemical equation could be written with a single arrow.

c) Which acid base reaction would be most extensive?

The most extensive reaction is between the strongest acid (HF) and the strongest base (CN^{1-}), which is Reaction ii in Part b.

12.7 AQUEOUS SOLUTIONS OF WEAK BASES

Water is also an acid, so it can react with weak bases to produce hydroxide ion and the conjugate acid of the weak base. Consider the reaction of hypochlorite ion with water:



The reaction involves the breaking of an O-H bond of water, which is called **hydrolysis**, so these reactions are also hydrolysis reactions. Most weak bases are found as salts, so salts such as KClO, NaF, KCN, and LiNO_2 all form basic solutions in water because their reaction with water produces hydroxide ion.

12.8 THE ACID-BASE TABLE

The acid-base table shown in Table 12.3 (next page) lists several acids and their K_a values in descending order. Thus, stronger acids are at the top of the table, and stronger bases are at the bottom of the table. The K_a 's of the acids are given in the center column.

Stronger acids are located above weaker acids, so proton transfer is extensive when the reacting acid is above (stronger than) the produced acid. Stated somewhat differently, *the reaction between an acid and a base is extensive when the acid is above the base on the acid-base table* (Figure 12.8). Protons transfer spontaneously 'downhill' in our acid-base table just as electrons transferred spontaneously 'downhill' in our table of standard reduction potentials. Compare Figures 11.3 and 12.8 to see the similarities of the two reaction types.

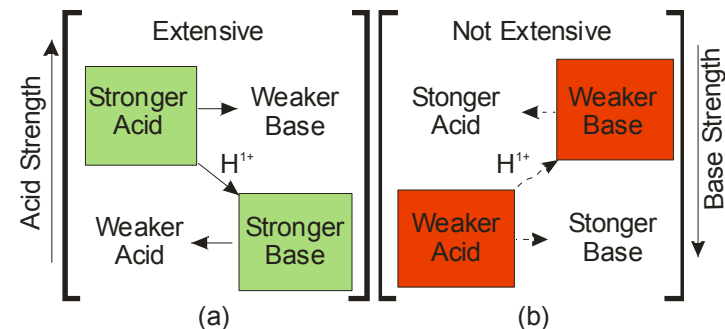


Figure 12.8. Reactivity from the relative position of reactants and products on an acid-base table

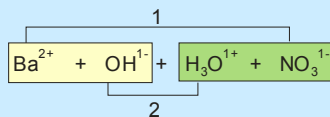
(a) The reaction of a stronger acid and base to produce a weaker acid and base is extensive. (b) The reaction of a weaker acid and base to produce a stronger acid and base is not extensive. The diagonal arrow represents the direction of the proton transfer and the horizontal arrows point toward the products of the reaction. The proton transfer is extensive when it is 'downhill' from the strong acid to the strong base, but only little reaction occurs when it is 'uphill' from the weak acid to the weak base.

Any acid (HA) that is above H_3O^{1+} in Table 12.3 is a strong acid ($K_a \gg 1$) and reacts extensively with water to produce H_3O^{1+} and its conjugate base (A^{1-}), which is why solutions of strong acids are strong electrolytes. Just as a solution of sodium chloride is represented as $\text{Na}^{1+} + \text{Cl}^{1-}$, hydrochloric acid is represented as $\text{H}_3\text{O}^{1+} + \text{Cl}^{1-}$. Hydrofluoric acid is a weak acid ($K_a \ll 1$) and a weak electrolyte (only about 4% of the molecules in a 0.1 M solution of HF are in the form of H_3O^{1+} and F^{1-} ions), so it is written as HF, *not* as $\text{H}_3\text{O}^{1+} + \text{F}^{1-}$ because HF represents the predominant species in an aqueous solution. *A solution of a strong acid is represented by the hydronium ion and its conjugate base, but a solution of a weak acid is written as the unreacted (undissociated) acid.* Note that in each case, the solution is represented by the principle species present; that is, the one(s) present with the greatest concentration(s).

Example 12.11

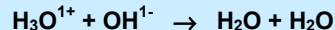
Write net equations for the following reactions. Determine the value of the equilibrium constant. Use a single arrow for reactions in which $K \geq 10^3$.

a) Solutions of barium hydroxide and nitric acid are mixed.



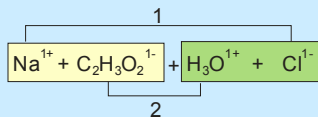
Nitric acid is a strong acid, so it must be written as $\text{H}_3\text{O}^{1+} + \text{NO}_3^{1-}$.

- All nitrates are soluble (Solubility Rule 2), so Ba^{2+} and NO_3^{1-} do not react; they are spectator ions.
- H_3O^{1+} is the strongest acid that can exist in water (all of the acids above H_3O^{1+} react with water to produce H_3O^{1+}), and OH^{1-} is the strongest base in water (any base below OH^{1-} reacts with water to produce OH^{1-}). Consequently, they react extensively.



The preceding chemical equation is the general equation for the reaction of any strong acid and any strong base. H_3O^{1+} is the reacting acid and H_2O is the produced acid, so $K = (1.0)/(1.0 \times 10^{-14}) = 1.0 \times 10^{14}$, which is so large that the reaction is usually written with a single arrow rather than double, equilibrium arrows; but it is still an equilibrium process.

b) Solutions of sodium acetate and hydrochloric acid are mixed.



Hydrochloric acid is a strong acid, so it is written as $\text{H}_3\text{O}^{1+} + \text{Cl}^{1-}$.

Table 12.3 An Acid-Base Table

Acid	K_a	Base
HClO_4	$\gg 1$	ClO_4^{1-}
HX	$\gg 1$	X^{1-} (X=I, Br, Cl)
H_2SO_4	$\gg 1$	HSO_4^{1-}
HNO_3	$\gg 1$	NO_3^{1-}
H_3O^{1+}	1.0	H_2O
H_2SO_3	1.5×10^{-2}	HSO_3^{1-}
HSO_4^{1-}	1.2×10^{-2}	SO_4^{2-}
H_3PO_4	7.5×10^{-3}	$\text{H}_2\text{PO}_4^{1-}$
HF	7.2×10^{-4}	F^{1-}
HNO_2	4.0×10^{-4}	NO_2^{1-}
$\text{HC}_2\text{H}_3\text{O}_2$	1.8×10^{-5}	$\text{C}_2\text{H}_3\text{O}_2^{1-}$
H_2CO_3	4.3×10^{-7}	HCO_3^{1-}
HSO_3^{1-}	1.0×10^{-7}	SO_3^{2-}
H_2S	1.0×10^{-7}	HS^{1-}
$\text{H}_2\text{PO}_4^{1-}$	6.2×10^{-8}	HPO_4^{2-}
HClO	3.5×10^{-8}	ClO^{1-}
NH_4^{1+}	5.6×10^{-10}	NH_3
HCN	4.0×10^{-10}	CN^{1-}
HCO_3^{1-}	4.7×10^{-11}	CO_3^{2-}
HPO_4^{2-}	4.8×10^{-13}	PO_4^{3-}
HS^{1-}	1.3×10^{-13}	S^{2-}
H_2O	1.0×10^{-14}	OH^{1-}
NH_3	$\ll 10^{-14}$	NH_2^{1-}
OH^{1-}	$\ll 10^{-14}$	O^{2-}

Stronger Acids

Weaker Bases

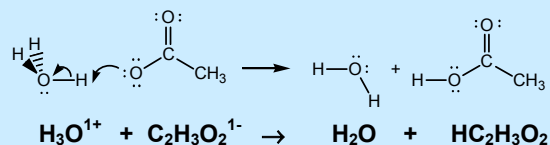
Weaker Acids

Stronger Bases

Acids and bases that lie between the lines drawn above water as a base and below water as an acid exist in aqueous solution, *i.e.*, they are weak acids and bases. Those above or below the lines react extensively with water to produce either H_3O^{1+} or OH^{1-} ; *i.e.*, they are strong acids and bases.

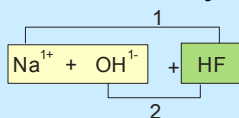
The arrows on the sides indicate the result of extensive proton transfer: stronger acids are converted into weaker acids and stronger bases are converted into weaker bases.

1. Sodium chloride is soluble (Solubility Rule 1), so Na^{1+} and Cl^{1-} are spectator ions.
2. Acetate ion is a weak base, but it is well below H_3O^{1+} on the acid-base chart. Consequently, an extensive proton transfer reaction occurs.



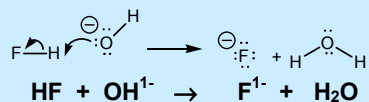
This reaction is representative of a strong acid reacting with a weak base. These types of reactions are extensive and are, therefore, usually written with single arrows. For the above reaction, $K = (1.0)/(1.8 \times 10^{-5}) = 5.6 \times 10^4$.

c) Solutions of sodium hydroxide and hydrofluoric acid are mixed.



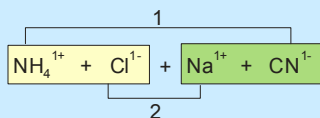
HF is a weak acid and must be written in the molecular form.

1. NaF is soluble (Solubility Rule 1), so Na^{1+} is a spectator ion.
2. HF is a weak acid, but OH^{1-} is a strong base, located well below the weak acid, so an extensive reaction is predicted.

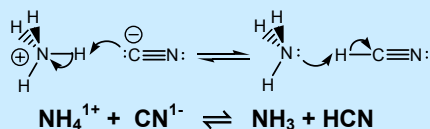


This is a reaction between a weak acid and a strong base. Reactions of weak acids with hydroxide ion are extensive because hydroxide ion is a very strong base. Consequently, they are typically written with a single arrow. $K = (7.2 \times 10^{-4})/(1.0 \times 10^{-14}) = 7.2 \times 10^{10}$.

d) Solutions of ammonium chloride and sodium cyanide are mixed.

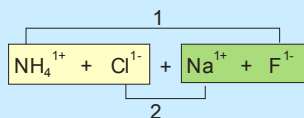


1. NH_4CN is soluble (Solubility Rule 1), but NH_4^{1+} is also a weak acid and CN^{1-} is a weak base. Checking the acid-base table, we see that NH_4^{1+} and CN^{1-} are close to one another, so we expect the equilibrium constant to be close to 1.
2. NaCl is soluble, so Na^{1+} and Cl^{1-} are spectator ions.

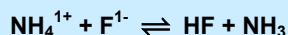


This is an example of a reaction of a weak acid and a weak base. Double arrows are used because the reacting acid (NH_4^{1+}) and the produced acid (HCN) are of comparable strengths, so the reverse reaction is important in determining the amount of product. For this reaction, $K = (5.6 \times 10^{-10}) / (4.0 \times 10^{-10}) = 1.4$, so $[\text{NH}_3][\text{HCN}] \sim [\text{NH}_4^{1+}][\text{CN}^{1-}]$ at equilibrium.

e) **Solutions of ammonium chloride and sodium fluoride are mixed.**



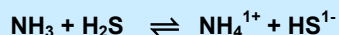
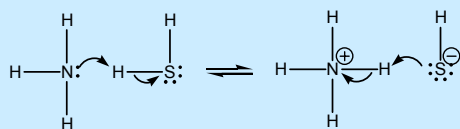
1. No precipitate is predicted, but there is a weak acid/weak base reaction. The reacting acid (NH_4^{1+}) is much weaker than the produced acid (HF), so very little reaction is expected. $K = (5.6 \times 10^{-10}) / (7.2 \times 10^{-4}) = 7.8 \times 10^{-7}$. Consequently, the concentrations of NH_4^{1+} and F^{1-} ions do not change appreciably during the reaction. The reverse reaction dominates, so double arrows are used.



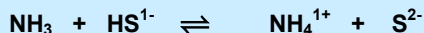
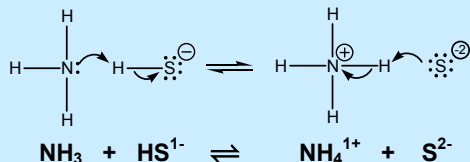
2. NaCl is soluble, so Na^{1+} and Cl^{1-} are spectator ions.

f) **Hydrogen sulfide is added to an excess of aqueous NH_3 .**

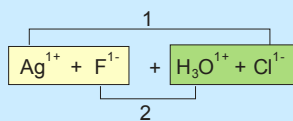
This is a weak acid/weak base reaction. H_2S is a diprotic acid (having two protons); but, in Brønsted acid-base reactions, the protons are removed one at a time. H_2S is a stronger acid than NH_4^{1+} , but the equilibrium constant ($K = (1.0 \times 10^{-7}) / (5.6 \times 10^{-10}) = 1.8 \times 10^2$) is not greater than 10^3 , so double arrows are used.



HS^{1-} is amphiprotic because it is not only the conjugate base of H_2S , but it is also the conjugate acid of the S^{2-} ion. However, a check of the acid-base table indicates that HS^{1-} is such a weak acid that it does not react extensively with the remaining (excess) NH_3 ($K = (1.3 \times 10^{-13}) / (5.6 \times 10^{-10}) = 2.3 \times 10^{-4}$). HS^{1-} is the predominant sulfur-containing species.

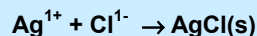


g) Solutions of silver fluoride and hydrochloric acid are mixed.

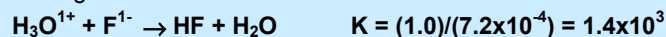


Hydrochloric acid is a strong acid and must be written as $\text{H}_3\text{O}^{1+} + \text{Cl}^{1-}$.

1. Silver chloride is insoluble, so it precipitates from the solution (Solubility Rule 3).



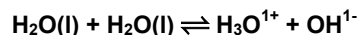
2. This is a strong acid-weak base reaction.



Both reactions are extensive.

12.9 pH AND pK_a

Water is both an acid and a base and can react with itself.



Water is a pure liquid and enters the equilibrium constant as unity. The equilibrium constant for this reaction is called the **ion product constant for water** and given the symbol K_w

$$K_w = [\text{H}_3\text{O}^{1+}] [\text{OH}^{1-}] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C} \quad \text{Eq. 12.2}$$

In pure water, the hydronium and hydroxide ion concentrations are the same because they are produced in a 1:1 ratio from water. Consequently, in pure water at 25°C ,

$$[\text{H}_3\text{O}^{1+}] = [\text{OH}^{1-}] = \sqrt{K_w} = 1.0 \times 10^{-7} \text{ M} \quad \text{Eq. 12.3}$$

Solutions for which Equation 12.3 is valid are called **neutral**; solutions in which $[\text{H}_3\text{O}^{1+}] > [\text{OH}^{1-}]$ are called **acidic**; and solutions in which $[\text{H}_3\text{O}^{1+}] < [\text{OH}^{1-}]$ are called **basic** or **alkaline**.

The hydronium ion concentration is an important characteristic of the solution, but it is normally a small number. To avoid the use of exponentials in discussions of hydronium ion concentrations, we define the **pH** as

$$\text{pH} = -\log[\text{H}_3\text{O}^{1+}] \quad \text{Eq. 12.4}$$

The exponent of $[\text{H}_3\text{O}^{1+}]$ is usually negative, so the sign of $\log[\text{H}_3\text{O}^{1+}]$ is usually negative.

The negative sign in Equation 12.4 assures that the pH is *usually* positive. Because of the negative sign, a high pH implies a low hydronium ion concentration, and a low pH implies a high hydronium ion concentration. However, Equation 12.2 shows solutions with low hydronium ion concentrations have high hydroxide ion concentrations, so a high pH also implies a high hydroxide ion concentration and a low pH implies a low hydroxide ion concentration. A neutral solution is one in which $[\text{H}_3\text{O}^{1+}] = [\text{OH}^{1-}] = 1.0 \times 10^{-7} \text{ M}$, so the pH of a neutral solution is determined to be $\text{pH} = -\log(1.0 \times 10^{-7}) = 7.0$. The hydronium ion is greater in an acidic solution, so the pH of an acidic solution is less than 7.0. The hydroxide ion concentration is less in a basic solution, so the pH of a basic solution is greater than 7.0. These conclusions are summarized in Table 12.4.

Rearranging Equation 12.2, we obtain the hydronium ion concentration in an aqueous solution as a function of the hydroxide ion concentration,

$$[\text{H}_3\text{O}^{1+}] = \frac{K_w}{[\text{OH}^{1-}]} = \frac{1.0 \times 10^{-14}}{[\text{OH}^{1-}]} \quad \text{Eq. 12.5}$$

K_a values are frequently used as a measure of an acid's ability to donate a proton, but the large exponential associated with many of the values is awkward. Consequently, a scale similar to the pH scale for $[\text{H}_3\text{O}^{1+}]$ has been defined for acids:

$$\text{p}K_a = -\log K_a \quad \text{Eq. 12.6}$$

A high $\text{p}K_a$ indicates a weak acid. For example, the fact that the $\text{p}K_a$ of acetic acid (4.74) is less than the $\text{p}K_a$ of HCN (9.21) means that acetic acid is a stronger acid.

Example 12.12

a) What is the pH of a solution in which $[\text{H}_3\text{O}^{1+}] = 1.3 \times 10^{-5} \text{ M}$? What is $[\text{OH}^{1-}]$?

$$\text{pH} = -\log [\text{H}_3\text{O}^{1+}] = -\log (1.3 \times 10^{-5}) = -(-4.89) = 4.89$$

$\text{pH} < 7$, so this is an *acidic* solution.

Solving Equation 12.2 for $[\text{OH}^{1-}]$, we obtain

$$[\text{OH}^{1-}] = \frac{1.0 \times 10^{-14}}{[\text{H}_3\text{O}^{1+}]} = \frac{1.0 \times 10^{-14}}{1.3 \times 10^{-5}} = 7.7 \times 10^{-10} \text{ M}$$

b) What is the pH of a 0.10 M HCl solution?

Hydrochloric acid is a strong acid, so all of the HCl is converted into hydronium and chloride ions. Thus, $[\text{H}_3\text{O}^{1+}] = 0.10 \text{ M}$ (the concentration of the acid), which means that the pH of the solution is $-\log(0.10) = 1.00$.

Table 12.4 Solution type versus pH

Solution pH	solution type
above 7	basic
equal to 7	neutral
below 7	acidic

- c) The pH of a 0.10 M solution of HBrO is 4.82, and the pH of a 0.10 M solution of HClO is 4.27. Which is the stronger acid?

Both acids have the same concentration, so the one with the greater hydronium ion concentration is the stronger acid. The acid with the lower pH has the greater hydronium ion concentration, so HClO is the stronger acid. This is expected because chlorine is more electronegative than bromine. An appreciation of how weak these acids are can be gained by comparing their pH to that of the 0.10 M HCl solution discussed in Part b above. The pH of the 0.10 M strong acid solution is 1.0, while the pH of these acid solutions is greater than 4.0. A difference of over 3 pH units means that the concentration of the hydronium ion in a 0.10 M strong acid solution is over 1,000 (10^3) times greater than in these two weak acid solutions.

- d) What is the pH of a 0.022 M Ba(OH)₂ solution?

First, determine the hydroxide ion concentration from the concentration of Ba(OH)₂ and the fact that there are two moles of hydroxide ion in each mole of Ba(OH)₂.

$$[\text{OH}^{1-}] = \frac{0.022 \text{ mol Ba(OH)}_2}{\text{L of solution}} \times \frac{2 \text{ mol OH}^{1-}}{\text{mol Ba(OH)}_2} = 0.044 \text{ M}$$

We use Equation 12.5 to obtain the hydronium ion concentration

$$[\text{H}_3\text{O}^{1+}] = \frac{1.0 \times 10^{-14}}{0.044} = 2.3 \times 10^{-13} \text{ M}$$

and Equation 12.4 to determine the pH.

$$\text{pH} = -\log [\text{H}_3\text{O}^{1+}] = -\log(2.3 \times 10^{-13}) = 12.64$$

Example 12.13

The pK_a of phenol is 10.0 while the pK_a of the hydrogen sulfite (bisulfite) ion is 7.0. Which acid is the stronger acid?

The strength of an acid increases as its pK_a decreases, so the bisulfite ion is the stronger acid because it has the lower pK_a.

Example 12.14

Indicate the solution with the greater hydronium ion concentration in each pair.

- a) 0.10 M HNO₂ or 0.15 M HNO₂?

The acids are identical, so the only difference is concentration. The more concentrated acid (0.15 M HNO₂) has the greater hydronium ion concentration.

b) 0.10 M KF or 0.15 M KF?

Both are solutions of the same weak base, so the hydroxide ion concentration and pH increase with the concentration of the base. Thus, the less concentrated base (0.10 M KF) has the lower OH^{1-} concentration and the greater H_3O^{1+} concentration.

c) 0.05 M benzoic acid ($\text{pK}_a = 4.19$) or 0.05 M lactic acid ($\text{pK}_a = 3.85$)?

Lactic acid has the lower pK_a , so it is the stronger acid and has the greater H_3O^{1+} concentration.

d) a solution with pH = 3 or one with a pH = 5?

The solution with the lower pH (pH = 3 solution) has the higher H_3O^{1+} ion concentration.

e) 0.1 M $\text{Ba}(\text{OH})_2$ or 0.15 M KOH?

Both are strong base solutions. $[\text{OH}^{1-}] = 2(0.10) = 0.20$ M in the $\text{Ba}(\text{OH})_2$ solution, but it is only 0.15 M the KOH solution. The 0.15 M KOH has the lower hydroxide ion concentration, so it has the greater hydronium ion concentration.

12.10 CHAPTER SUMMARY AND OBJECTIVES

A Lewis base is a substance with an electron pair that can be used to form a covalent bond. A Lewis acid is a substance with an empty orbital that can overlap with the electron pair on the base to form a bond. The Lewis definition is the most general acid-base definition. A Brønsted acid is a proton donor, and a Brønsted base is a proton acceptor. All Brønsted bases are Lewis bases and *vice versa*. The *proton is a Lewis acid* because it will readily accept a pair of electrons to share in a covalent bond, but the *proton defines all Brønsted acids*.

As the strength of the H-A bond increases the strength of HA as an acid decreases and the strength of its conjugate base, A^{1-} , increases. Many acids contain the unit H-O-X. For these oxoacids, the acid strength increases as the electronegativity and/or the oxidation state of X increases. The relative strength of an acid is measured by its acid dissociation constant, K_a , which is the equilibrium constant for the reaction of the acid with water. If $K_a \gg 1$, the acid is a strong acid; if $K_a \ll 1$, the acid is a weak acid. The equilibrium of a Brønsted acid-base reaction is equal to the K_a of the reacting acid divided by the K_a of the produced acid.

The products of a Brønsted acid-base reaction are the conjugate base of the reacting acid and the conjugate acid of the reacting base. The reaction is extensive when the produced acid and base are weaker than the reacting acid and base, which is quantified by

the expression $K = K_a(\text{reacting})/K_a(\text{produced})$.

The pH of a solution is often used instead of the hydronium ion concentration to avoid the awkwardness of using large, negative exponentials. The pH is defined as $-\log[\text{H}_3\text{O}^{1+}]$. Solutions with $\text{pH} = 7$ are said to be neutral, while solutions with $\text{pH} > 7$ are basic and those with $\text{pH} < 7$ are acidic. Exponentials can also be avoided when referring to the K_a of the acid by using $\text{p}K_a$, which is defined as $-\log K_a$. A high $\text{p}K_a$ implies a weak acid.

After studying the material presented in this chapter, you should be able to:

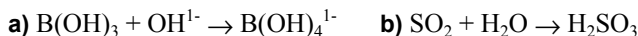
1. define acids and bases using both the Lewis and Brønsted definitions (Sections 12.1 and 12.2);
2. identify the acid and the base in a reaction (Sections 12.1 and 12.2);
3. explain how acids are named (Section 12.2);
4. discuss the factors dictating the extent of proton transfer in an acid-base reaction (Sections 12.3 and 12.4);
5. explain the factors dictating the relative strengths of acids (Section 12.5);
6. define K_a (Sections 12.6);
7. use the acid-base table to write acid-base reactions and to predict the extent of proton transfer (Section 12.7);
8. determine the equilibrium constant for an acid-base reaction from the K_a values of the reacting and produced acids (Section 12.7);
9. define pH and determine the pH of a solution from the hydronium ion concentration (Section 12.8);
10. determine the hydronium ion concentration in a solution given the hydroxide ion concentration and *vice versa* (Section 12.8); and
11. define $\text{p}K_a$ and determine the $\text{p}K_a$ of an acid from its K_a (Section 12.8).

12.11 EXERCISES

- Distinguish between an Arrhenius, a Brønsted, and a Lewis acid.
- Define a Lewis acid and a Lewis base.
- What is a salt?
- What is a conjugate acid-base pair?
- Use curved arrows to show the mechanisms of the following Lewis acid-base reactions. Identify the Lewis acid and the Lewis base. What is the hybridization of the boron before and after reaction (a)? What is the hybridization of the carbons before and after reaction b? Note that reaction (b) is a two-step reaction like that shown in Figure 12.4.

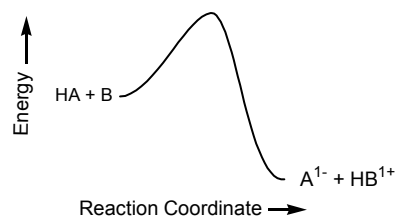


- Use curved arrows to show the mechanisms of the following Lewis acid-base reactions. Identify the Lewis acid and the Lewis base. What is the hybridization of the boron before and after reaction (a)? What is the hybridization of the sulfurs before and after reaction b? Note that reaction (b) is a two-step reaction like that shown in Figure 12.4.



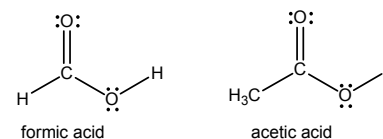
- The potential energy diagram below is for following the acid-base reaction:
 $\text{HA(aq)} + \text{B(aq)} \rightarrow \text{A}^{1-}(\text{aq}) + \text{HB}^{1+}(\text{aq})$

- Which is the stronger acid?
- Which is the stronger base?
- What is the magnitude of the equilibrium constant for the reaction ($K > 1$ or $K < 1$)?
- Draw a probable transition state (Section 9.7).



- What is the conjugate acid of each of the following?
 a) F^{1-} b) OH^{1-} c) HSO_3^{1-} d) S^{2-}
- What is the conjugate base of each of the following?
 a) HClO b) NH_4^{1+} c) H_3PO_4 d) HSO_3^{1-}
- CH_3 and CH_2 groups are said to be *electron donating* groups because they place electron density on the atoms to which they are attached. Which is a stronger base CH_3NH_2 or NH_3 ? Explain.

- Which is the stronger acid, formic acid or acetic acid? Which acid has the greater $\text{p}K_a$? Explain your answers. Refer to Exercise 10 for information about CH_3 groups.



- Which is the stronger base, NH_3 or NF_3 ? Explain.
- List the following compounds in order of increasing acidity. (Recall that from Exercise 10 that CH_3 groups are electron donating.)
 H-O-H H-O-Cl H-O-CH_3 H-O-I
- Indicate the stronger acid in each of the following pairs and explain your choice:
 - H_3AsO_4 or H_3AsO_3
 - H_2SeO_4 or H_2SO_4
 - CH_4 or NH_3 (see Table 9.1 on page 176)
- Indicate the stronger acid in each of the following pairs and explain your choice:
 - H_2SeO_3 or HSeO_3^{1-}
 - HIO_4 or HIO_2
 - CH_3COOH or CF_3COOH
- Use curved arrows and Lewis structures to indicate the mechanisms of the following acid-base reactions:
 - $\text{HClO}_2 + \text{H}_2\text{O}$ b) $\text{PO}_4^{3-} + \text{HCN}$ c) $\text{HC}_2\text{H}_3\text{O}_2 + \text{OH}^{1-}$
- Use curved arrows and Lewis structures to indicate the mechanisms of the following acid-base reactions.
 - $\text{HF} + \text{S}^{2-}$ b) $\text{NH}_3 + \text{HNO}_2$ c) $\text{H}_2\text{SO}_3 + \text{C}_2\text{H}_3\text{O}_2^{1-}$
- Equal amounts of benzoic acid and sodium acetate are mixed. At equilibrium, the concentration of the benzoate ion is just slightly greater than that of the acetate ion. What can be concluded about the relative acid strengths of acetic acid and benzoic acid?
- Consider the reaction, $\text{HBrO} + \text{CN}^{1-} \rightleftharpoons \text{BrO}^{1-} + \text{HCN}$ $K = 5$
 - Which is the weaker of the two acids in the above reaction?
 - Which is the weaker of the two bases in the above reaction?
 - Given that $K = 0.08$ for $\text{HBrO} + \text{ClO}^{1-} \rightleftharpoons \text{BrO}^{1-} + \text{HClO}$ predict where on the acid-base table should HBrO be placed, above HClO , between HClO and HCN , or below HCN ?

20. Consider the following reaction: $\text{H}_2\text{C}_2\text{O}_4 + \text{F}^{1-} \rightleftharpoons \text{HC}_2\text{O}_4^{1-} + \text{HF}$ $K \sim 100$

- a) Which of the two bases is stronger?
- b) Which of the two acids is stronger?
- c) What is the approximate value of K_a for $\text{H}_2\text{C}_2\text{O}_4$?

21. The K_a of nitrous acid (HNO_2) is 4.0×10^{-4} .

- a) Write the reaction to which this equilibrium constant applies.
- b) Express the K_a of nitrous acid in terms of concentrations.

For Exercises 22 and 23, use Equation 12.1 and Table 12.3 to determine the value of the equilibrium constant and write the equilibrium constant expression for each reaction.

22. a) $\text{H}_2\text{CO}_3 + \text{SO}_4^{2-} \rightleftharpoons \text{HCO}_3^{1-} + \text{HSO}_4^{1-}$

b) $\text{H}_2\text{S} + \text{NH}_3 \rightleftharpoons \text{HS}^{1-} + \text{NH}_4^{1+}$

c) $\text{S}^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HS}^{1-} + \text{OH}^{1-}$

23. a) $\text{NO}_2^{1-} + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_2 + \text{OH}^{1-}$

b) $\text{HSO}_3^{1-} + \text{HCO}_3^{1-} \rightleftharpoons \text{SO}_3^{2-} + \text{H}_2\text{CO}_3$

c) $\text{H}_3\text{PO}_4 + \text{OH}^{1-} \rightleftharpoons \text{H}_2\text{PO}_4^{1-} + \text{H}_2\text{O}$

For Exercises 24 and 25, write net equations for the acid-base reactions that occur when the given aqueous solutions are mixed. Determine the value of the equilibrium constant. Use single arrows for extensive reactions ($K > 1000$) but double arrows otherwise.

24. a) $\text{HNO}_2 + \text{NaOH}$ b) $\text{NH}_4\text{Cl} + \text{Na}_2\text{SO}_3$

c) $\text{NaClO} + \text{NaH}_2\text{PO}_4$ d) $\text{HBr} + \text{NH}_3$

e) $\text{HF} + \text{NaCN}$ f) $\text{H}_3\text{PO}_4 + \text{NaC}_2\text{H}_3\text{O}_2$

g) $\text{HClO}_4 + \text{NaH}_2\text{PO}_4$

25. a) $\text{NaC}_2\text{H}_3\text{O}_2 + \text{HCN}$ b) $\text{KOH} + \text{HI}$

c) $\text{H}_2\text{S} + \text{K}_2\text{HPO}_4$ d) $\text{NaOH} + \text{HClO}$

e) $\text{NaNO}_2 + \text{H}_2\text{CO}_3$ f) $\text{NH}_4\text{Cl} + \text{KOH}$

g) $\text{HNO}_3 + \text{KF}$

26. Indicate whether each of the following is a strong electrolyte, a weak electrolyte, or a nonelectrolyte:

- a) HF b) NaF c) HCl d) CH_3Cl

27. Indicate whether each of the following is a strong electrolyte, a weak electrolyte, or a nonelectrolyte:

- a) NH_3 b) C_6H_6 c) HClO d) NH_4Cl

28. What is meant by a neutral solution?

29. Which of the following compounds could be used to lower the pH of a solution?

- a) K_2S b) NH_4Cl c) KCl d) KHSO_4 e) HF

30. Indicate whether each of the following solutions is acidic, basic, or neutral:

- a) 0.1 M KNO_2
- b) a solution with a pH of 3
- c) a solution in which $[\text{OH}^{1-}] = 10^{-4}$ M
- e) a solution in which $[\text{OH}^{1-}] = 10^{-8}$ M

31. Indicate whether each of the following solutions is acidic, basic, or neutral:

- a) 0.10 M CH_3COOH
- b) 0.10 M NaCN
- c) 0.10 M KBr
- d) a solution in which $[\text{H}_3\text{O}^{1+}] = 10^{-5}$ M

32. Indicate which solution in each pair has the lower pH:

- a) 0.1 M HClO_2 or 0.2 M HClO_2
- b) 0.1 M K_3PO_4 or 0.2 M K_3PO_4
- c) 0.1 M $\text{HC}_2\text{H}_3\text{O}_2$ or 0.1 M HNO_2
- d) 0.1 M NaOH or water

33. Calculate the pH of each of the following strong acid solutions:

- a) 0.0032 M HCl b) 0.016 M HCl c) 1.5 M HNO_3

34. Calculate the pH of each of the following strong acid solutions:

- a) 0.80 M HCl
- b) 2.1×10^{-5} M HClO_4
- c) 2.1×10^{-3} M HCl

35. Calculate the pH of the following basic solutions:

- a) 0.0032 M NaOH
- b) 0.016 M KOH
- c) 0.040 M $\text{Ba}(\text{OH})_2$

36. Write the expression for K_a for each of the following acids and the chemical equation to which it applies.

- a) NH_4^{1+} b) H_3PO_4 c) HSO_3^{1-} d) CH_3COOH

37. Determine the pK_a of each of the following weak acids:
a) HF b) HClO c) HS^{1-}
38. Determine the pK_a of each of the following weak acids:
a) $H_2PO_4^{1-}$ b) H_2O c) H_2S
39. The pK_a of acid HA is greater than that of acid HB.
a) Which is the stronger acid?
b) Which is the stronger base, B^{1-} or A^{1-} ?
40. The pK_a of acid HA is greater than that of acid HB.
a) Which has the higher pH, 0.1 M HA or 0.1 M HB?
b) Which has the higher pH, 0.1 M KA or 0.1 M KB?
41. What is the K_a of an acid with a pK_a of 4.87?
42. Formic acid ($HCOOH$) is a weak acid. Write the K_a reaction and determine the value of K_a if $[HCOOH] = 0.10$ M and $[HCOO^{1-}] = [H_3O^{1+}] = 0.0042$ M. Above which acid in Table 12.3 would formic acid be placed?
43. Phenol (C_6H_5OH) is a weak acid with $K_a = 1.0 \times 10^{-10}$.
a) Write the reaction to which this number applies.
b) What is the pK_a of phenol?
c) What is the concentration of phenol in a solution in which $[C_6H_5O^{1-}] = 3.2 \times 10^{-6}$ M and $pH = 6.00$?
44. Determine the hydronium ion concentration in a solution in which the concentrations of acetic acid and acetate ion are equal. What is the pH of this solution? The K_a of acetic acid is 1.8×10^{-5} .