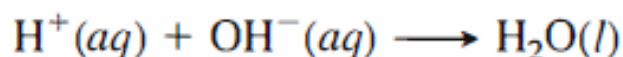# CHAPTER EIGHTEEN

Acid-Base Equilibria

18.1 ACIDS AND BASES IN WATER

o Most laboratory work with acids and bases involves water, which is a product in all reactions between strong acids and strong bases:

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

the net ionic equation of this reaction shows, water is the product:

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

Furthermore, whenever an acid dissociates in water, solvent molecules participate in the reaction:

$$HA(g \text{ or } l) + H_2O(l) \longrightarrow A^-(aq) + H_3O^+(aq)$$

H_3O^+: **hydronium ion**

Because the proton is so small, its charge density is very high, so its attraction to water is especially strong.

Figure 18.1 The hydrated proton.
The charge of the H^+ ion is highly concentrated because the ion is so small. In aqueous solution, it forms a covalent bond to a water molecule, yielding an H_3O^+ ion that associates tightly with other H_2O molecules. Here, the $H_7O_3^+$ ion is shown.
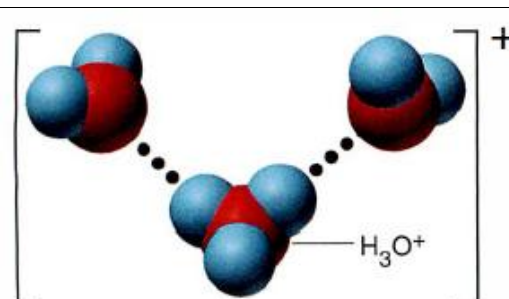
Release of H$^+$ or OH$^-$ and the Arrhenius Acid-Base Definition

The earliest and simplest definition of acids and bases:

➢ An acid is a substance that has H in its formula and dissociates in water to yield H$_3$O$^+$.

➢ A base is a substance that has OH in its formula and dissociates in water to yield OH$^-$.

Examples of Arrhenius acids: HCl, HNO$_3$, and HCN,

Examples of Arrhenius bases: NaOH, KOH, and Ba(OH)$_2$.

When an acid and a base react, they undergo **neutralization**.

No matter which strong acid and base react, and no matter which salt forms, **ΔH^o$_{rxn}$ is about -56 kJ** per mole of water formed, because the actual reaction is always the same- a hydrogen ion and a hydroxide ion form water:

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l) \qquad \Delta H^{\circ}_{rxn} = -55.9 \text{ kJ}$$
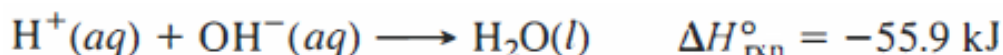
Variation in Acid Strength: The Acid-Dissociation Constant (K$_a$)

Acids and bases differ greatly in their strength in water. We generally classify them as either strong or weak

➢ Strong acids dissociate completely into ions in water (Figure 18.2):

$$HA(g \text{ or } l) + H_2O(l) \longrightarrow H_3O^+(aq) + A^-(aq)$$

Because the reaction is essentially complete (at equilibrium, Q$_c$ = K$_c$ >> 1) , it is not very useful to express it as an equilibrium process.

➢ Weak acids dissociate very slightly into ions in water (Figure 18.3):

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

At equilibrium, the great majority of HA molecules are undissociated. Thus, [H$_3$O$^+$] << [HA]$_{init}$. In other words, [HA]$_{eq}$ $\cong$ [HA]$_{init}$, so the value of K$_c$ is very small.

Hydrocyanic acid is an example of a weak acid:

$$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$$

$$Q_c = \frac{[H_3O^+][CN^-]}{[HCN][H_2O]} \quad \text{(at equilibrium, } Q_c = K_c \ll 1)$$

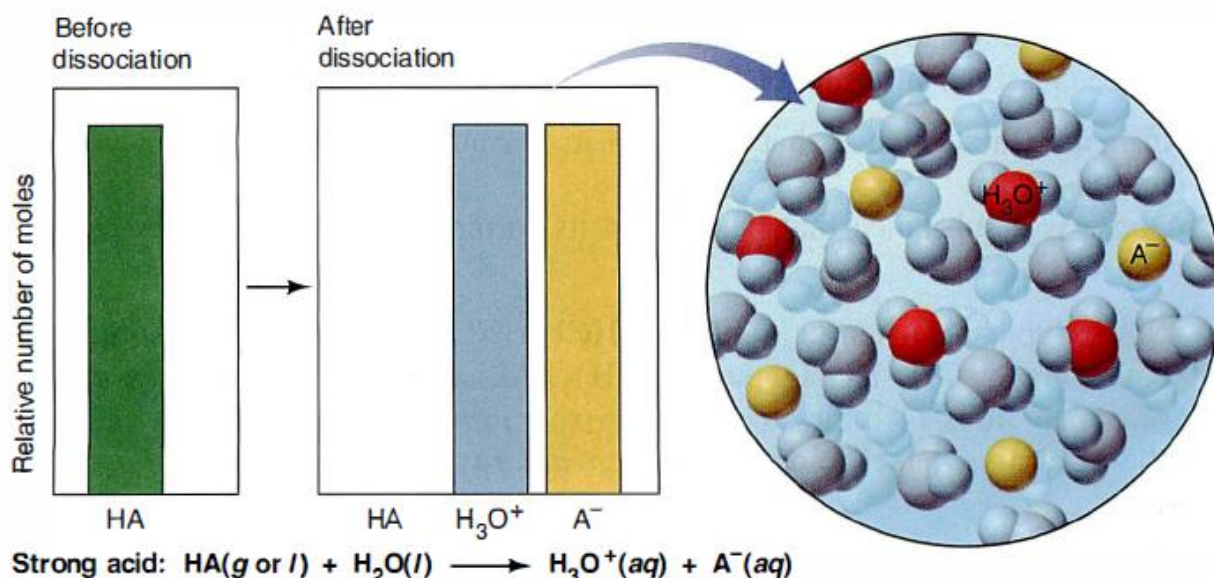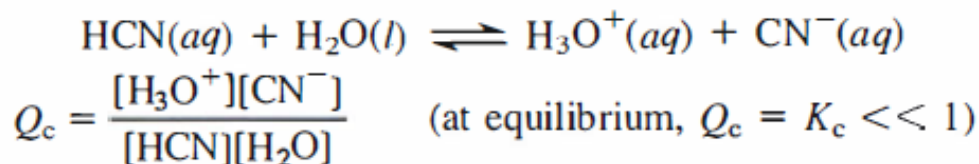Strong acid: HA(g or l) + H₂O(l) ⟶ H₃O⁺(aq) + A⁻(aq)

Figure 18.2 The extent of dissociation for strong acids. The bar graphs show the relative numbers of moles of species before (*left*) and after (*right*) acid dissociation occurs. When a strong acid dissolves in water, it dissociates completely, yielding H₃O⁺(aq) and A⁻(aq) ions; virtually no HA molecules are present.

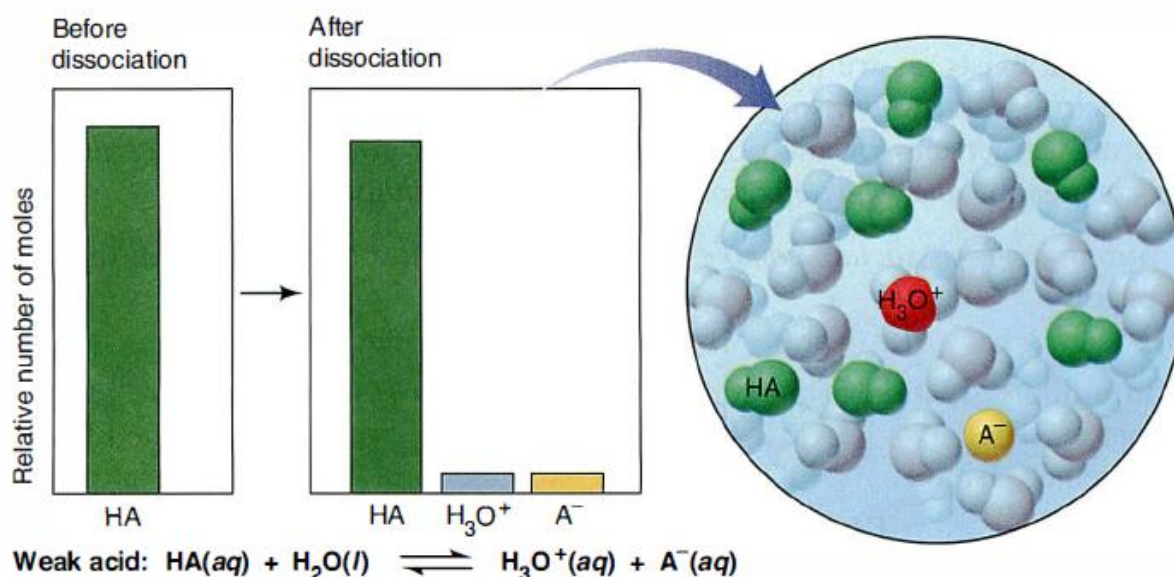Weak acid: HA(aq) + H₂O(l) ⇌ H₃O⁺(aq) + A⁻(aq)

Figure 18.3 The extent of dissociation for weak acids. In contrast to a strong acid in water (see Figure 18.2), a weak acid dissociates very little, remaining mostly as intact acid molecules and, thus, yielding relatively few H₃O⁺(aq) and A⁻(aq) ions.

The Meaning of K_a

The equilibrium expression for the dissociation of a general weak acid, HA, in water is:

$$K_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

The acid-dissociation constant (or acid-ionization constant), Ka:

$$K_c[H_2O] = K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Like any equilibrium constant, K_a is a number whose magnitude is temperature dependent and tells how far to the right the reaction has proceeded to reach equilibrium.

Listed below are some benchmark K_a values for typical weak acids;

- For a weak acid with a relatively high K_a ($\sim 10^{-2}$), a 1 M solution has $\sim 10\%$ of the HA molecules dissociated. The K_a of chlorous acid ($HClO_2$) is 1.1×10^{-2}, and 1 M $HClO_2$ is 10.% dissociated.
- For a weak acid with a moderate K_a ($\sim 10^{-5}$), a 1 M solution has $\sim 0.3\%$ of the HA molecules dissociated. The K_a of acetic acid (CH_3COOH) is 1.8×10^{-5}, and 1 M CH_3COOH is 0.42% dissociated.
- For a weak acid with a relatively low K_a ($\sim 10^{-10}$), a 1 M solution has $\sim 0.001\%$ of the HA molecules dissociated. The K_a of HCN is 6.2×10^{-10}, and 1 M HCN is 0.0025% dissociated.

A list of K_a values for some common acids appears in Appendix C.

Classifying the Relative Strengths of Acids and Bases

You can often classify acids and bases qualitatively as strong or weak just from their formulas:

➢ **Strong acids**. Two types of strong acids, with examples that you should memorize, are

1. The hydrohalic acids HCl, HBr, and HI

2. Oxoacids in which the number of O atoms exceeds the number of ionizable protons by two or more, such as HNO_3, H_2SO_4, and $HClO_4$; for example, in H_2SO_4, 4 O's - 2 H's = 2.

➢ **Weak acids**. There are many more weak acids than strong ones. Four types, with examples, are;

1. The hydrohalic acid HF

2. Acids in which H is not bonded to O or to a halogen, such as HCN and H_2S

3. Oxoacids in which the number of O atoms equals or exceeds by one the number of ionizable protons, such as HClO, HNO_2, and H_3PO_4

4. Carboxylic acids (general formula RCOOH , with the ionizable proton shown in red), such as CH_3COOH and C_6H_5COOH

➢ **Strong bases**. Water-soluble compounds containing O^{2-} or OH^- ions are strong bases. The cations are usually those of the most active metals:

1. M_2O or MOH, where M = Group I A(1) metal (Li, Na, K, Rb , Cs)

2. MO or $M(OH)_2$, where M = Group 2A(2) metal (Ca, Sr, Ba)

[MgO and $Mg(OH)_2$ are only slightly soluble in water, but the soluble portion dissociates completely.]

➢ **Weak bases**. Many compounds with an electron-rich nitrogen atom are weak bases (none are Arrhenius bases). The common structural feature is an N atom with a lone electron pair:

1. Ammonia (NH_3)

2. Amines (general formula RNH_2, R_2NH, or R_3N), such as $CH_3CH_2NH_2$, $(CH_3)_2NH$, and $(C_3H_7)_3N$.

SAMPLE PROBLEM 18.1 Classifying Acid and Base Strength from the Chemical Formula

Problem Classify each of the following compounds as a strong acid, weak acid, strong base, or weak base:
(a) H_2SeO_4 (b) $(CH_3)_2CHCOOH$
(c) KOH   (d) $(CH_3)_2CHNH_2$

Plan We examine the formula and classify each acid or base, using the text descriptions. Particular points to note for acids are the numbers of O atoms relative to H atoms and the presence of the —COOH group. For bases, note the nature of the cation or the presence of an N atom that has a lone pair.

Solution (a) Strong acid: H_2SeO_4 is an oxoacid in which the number of O atoms exceeds the number of ionizable protons by two.

(b) Weak acid: $(CH_3)_2CHCOOH$ is a carboxylic acid, as indicated by the —COOH group.

(c) Strong base: KOH is one of the Group 1A(1) hydroxides.

(d) Weak base: $(CH_3)_2CHNH_2$ has a lone pair on the N and is an amine.

FOLLOW-UP PROBLEM 18.1 Which member of each pair is the stronger acid or base?
(a) HClO or $HClO_3$
(b) HCl or CH_3COOH
(c) NaOH or CH_3NH_2

18.2 AUTOIONIZATION OF WATER AND THE pH SCALE

Water itself dissociates into ions very slightly in an equilibrium process known as **autoionization** (or **self-ionization**):

$H_2O(l)$ + $H_2O(l)$ $\rightleftharpoons$ $H_3O^+(aq)$ + $OH^-(aq)$
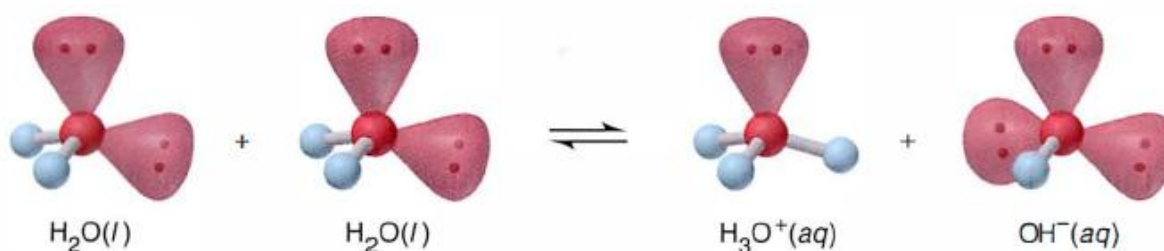
The Equilibrium Nature of Autoionization: The Ion-Product Constant for Water (K_w)

Like any equilibrium process, the autoionization of water is described quantitatively by an equilibrium constant:

$$K_c = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

Because the concentration of H_2O is essentially constant, the term can be rewritten to obtain a new equilibrium constant, **the ion-product constant for water**, K_w:

$$K_c[H_2O]^2 = K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ (at 25°C)}$$

$$[H_3O^+] = [OH^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7} \, M \text{ (at 25°C)}$$

Pure water has a concentration of about 55.5M (1000 g.L^{-1}/18.02 g.mol^{-1}). Thus only 1 in 555 million water molecules dissociates reversibly into ions !

Autoionization of water has two major consequences for aqueous acid-base chemistry:

1. A change in [H_3O^+] causes an inverse change in [OH$^-$], and vice versa:

   Higher [H_3O^+] ===> lower [OH$^-$] and Higher [OH$^-$] ===> lower [H_3O^+]

2. Both ions are present in all aqueous systems.

   In an acidic solution   [H_3O^+] > [OH$^-$]

   In a neutral solution   [H_3O^+] = [OH$^-$]

   In a basic solution   [H_3O^+] < [OH$^-$]

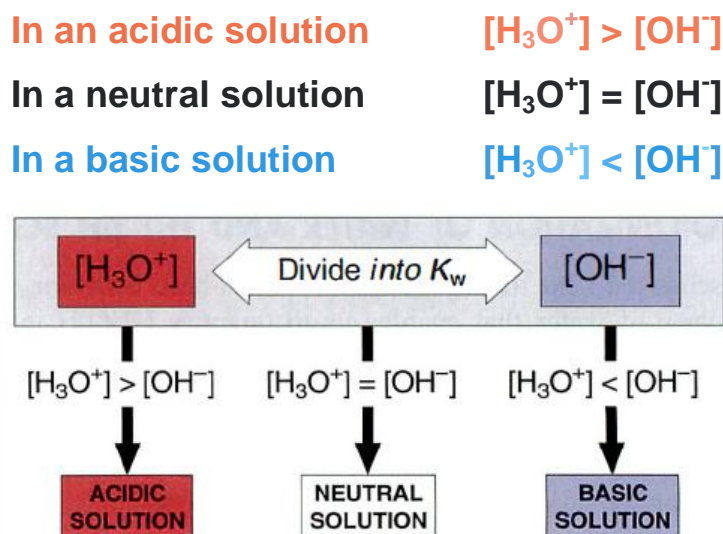**Figure 18.4** The relationship between [H_3O^+] and [OH$^-$] and the relative acidity of solutions.

SAMPLE PROBLEM 18.2 Calculating $[H_3O^+]$ and $[OH^-]$ in Aqueous Solution

Problem A research chemist adds a measured amount of HCl gas to pure water at 25°C and obtains a solution with $[H_3O^+] = 3.0\times10^{-4}$ M. Calculate $[OH^-]$. Is the solution neutral, acidic, or basic?

Plan We use the known value of K_w at 25°C (1.0×10^{-14}) and the given $[H_3O^+]$ (3.0×10^{-4} M) to solve for $[OH^-]$. Then, we compare $[H_3O^+]$ with $[OH^-]$ to determine whether the solution is acidic, basic, or neutral (see Figure 18.4).

Solution Calculating $[OH^-]$:

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0\times10^{-14}}{3.0\times10^{-4}}$$

$$= 3.3\times10^{-11}\ M$$

Because $[H_3O^+] > [OH^-]$, the solution is acidic.

Check It makes sense that adding an acid to water results in an acidic solution. Moreover, because $[H_3O^+]$ is greater than 10^{-7} M, $[OH^-]$ must be less than 10^{-7} M to give a constant K_w.

FOLLOW-UP PROBLEM 18.2 Calculate $[H_3O^+]$ in a solution that is at 25°C and has $[OH^-] = 6.7\times10^{-2}$ M. Is the solution neutral, acidic, or basic?

Expressing the Hydronium Ion Concentration: The pH Scale

In aqueous solutions, $[H_3O^+]$ can vary from about 10 M to 10^{-15} M. The pH is defined as:

$$pH = -\log [H_3O^+]$$

pH of a neutral solution	$= 7.00$
pH of an acidic solution	< 7.00
pH of a basic solution	> 7.00

$$[H_3O^+] = 10^{-pH}$$

Hydroxide ion concentration can be expressed as pOH:

$$pOH = -\log [OH^-]$$

Equilibrium constants can be expressed as pK:

$$pK = -\log K$$

The Relations Among pH, pOH, and pK$_w$

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ (at 25°C)}$$

$$-\log K_w = (-\log [H_3O^+]) + (-\log [OH^-]) = -\log (1.0 \times 10^{-14})$$

$$pK_w = pH + pOH = 14.00 \quad \text{(at 25°C)}$$

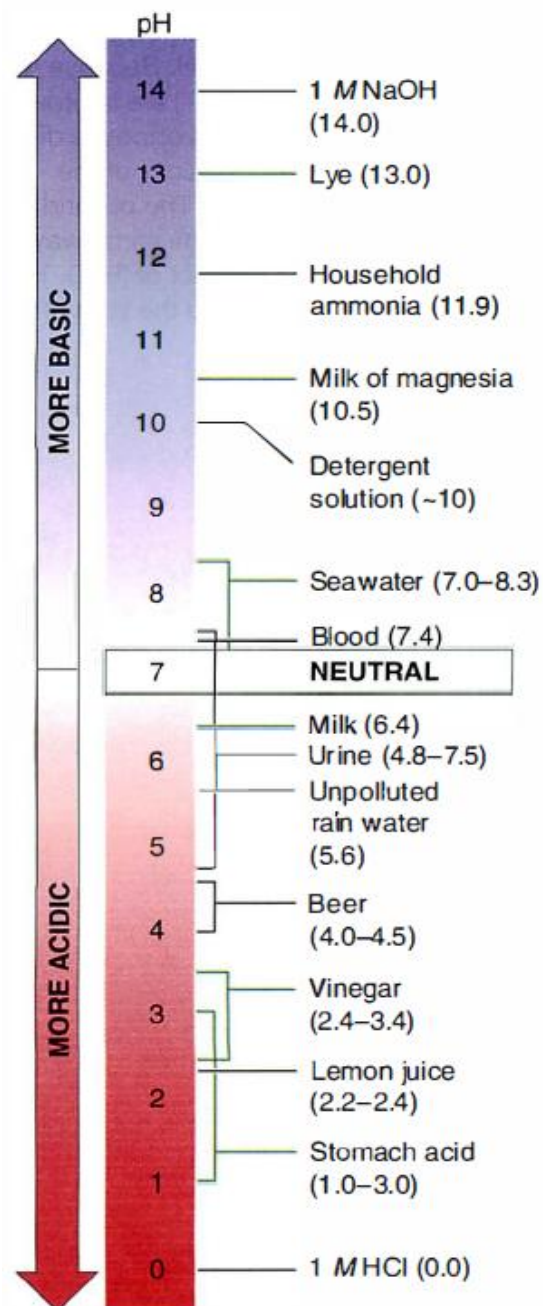|	[H$_3$O$^+$]	pH	[OH$^-$]	pOH
	1.0 x 10^{-15}	15.00	1.0 x 10^1	−1.00
	1.0 x 10^{-14}	14.00	1.0 x 10^0	0.00
	1.0 x 10^{-13}	13.00	1.0 x 10^{-1}	1.00
BASIC	1.0 x 10^{-12}	12.00	1.0 x 10^{-2}	2.00
	1.0 x 10^{-11}	11.00	1.0 x 10^{-3}	3.00
	1.0 x 10^{-10}	10.00	1.0 x 10^{-4}	4.00
	1.0 x 10^{-9}	9.00	1.0 x 10^{-5}	5.00
	1.0 x 10^{-8}	8.00	1.0 x 10^{-6}	6.00
NEUTRAL	1.0 x 10^{-7}	7.00	1.0 x 10^{-7}	7.00
	1.0 x 10^{-6}	6.00	1.0 x 10^{-8}	8.00
	1.0 x 10^{-5}	5.00	1.0 x 10^{-9}	9.00
	1.0 x 10^{-4}	4.00	1.0 x 10^{-10}	10.00
	1.0 x 10^{-3}	3.00	1.0 x 10^{-11}	11.00
ACIDIC	1.0 x 10^{-2}	2.00	1.0 x 10^{-12}	12.00
	1.0 x 10^{-1}	1.00	1.0 x 10^{-13}	13.00
	1.0 x 10^0	0.00	1.0 x 10^{-14}	14.00
	1.0 x 10^1	−1.00	1.0 x 10^{-15}	15.00

Figure 18.6 The relations among [H$_3$O$^+$], pH, [OH$^-$], and pOH.

Figure 18.5 The pH values of some familiar aqueous solutions.

pH scale values:
- 1 M NaOH (14.0)
- Lye (13.0)
- Household ammonia (11.9)
- Milk of magnesia (10.5)
- Detergent solution (~10)
- Seawater (7.0–8.3)
- Blood (7.4)
- NEUTRAL (7)
- Milk (6.4)
- Urine (4.8–7.5)
- Unpolluted rain water (5.6)
- Beer (4.0–4.5)
- Vinegar (2.4–3.4)
- Lemon juice (2.2–2.4)
- Stomach acid (1.0–3.0)
- 1 M HCl (0.0)

Table 18.1 The Relationship Between K$_a$ and pK$_a$		
Acid Name (Formula)	K$_a$ at 25°C	pK$_a$
Hydrogen sulfate ion (HSO$_4^-$)	1.0×10^{-2}	1.99
Nitrous acid (HNO$_2$)	7.1×10^{-4}	3.15
Acetic acid (CH$_3$COOH)	1.8×10^{-5}	4.74
Hypobromous acid (HBrO)	2.3×10^{-9}	8.64
Phenol (C$_6$H$_5$OH)	1.0×10^{-10}	10.00

SAMPLE PROBLEM 18.3 Calculating $[H_3O^+]$, pH, $[OH^-]$, and pOH

Problem In an art restoration project, a conservator prepares copper-plate etching solutions by diluting concentrated HNO_3 to 2.0 M, 0.30 M, and 0.0063 M HNO_3. Calculate $[H_3O^+]$, pH, $[OH^-]$, and pOH of the three solutions at 25°C.

Plan We know from its formula that HNO_3 is a strong acid, so it dissociates completely; thus, $[H_3O^+] = [HNO_3]_{init}$. We use the given concentrations and the value of K_w at 25°C (1.0×10^{-14}) to find $[H_3O^+]$ and $[OH^-]$ and then use them to calculate pH and pOH.

Solution Calculating the values for 2.0 M HNO_3:

$$[H_3O^+] = 2.0\ M$$

$$pH = -\log [H_3O^+] = -\log 2.0 = -0.30$$

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0\times10^{-14}}{2.0} = 5.0\times10^{-15}\ M$$

$$pOH = -\log (5.0\times10^{-15}) = 14.30$$

Calculating the values for 0.30 M HNO_3:

$$[H_3O^+] = 0.30\ M$$

$$pH = -\log [H_3O^+] = -\log 0.30 = 0.52$$

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0\times10^{-14}}{0.30} = 3.3\times10^{-14}\ M$$

$$pOH = -\log (3.3\times10^{-14}) = 13.48$$

Calculating the values for 0.0063 M HNO_3:

$$[H_3O^+] = 6.3\times10^{-3}\ M$$

$$pH = -\log [H_3O^+] = -\log (6.3\times10^{-3}) = 2.20$$

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0\times10^{-14}}{6.3\times10^{-3}} = 1.6\times10^{-12}\ M$$

$$pOH = -\log (1.6\times10^{-12}) = 11.80$$

Check As the solution becomes more dilute, $[H_3O^+]$ decreases, so pH increases, as we expect. An $[H_3O^+]$ greater than 1.0 M, as in 2.0 M HNO_3, gives a positive log, so it results in a negative pH. The arithmetic seems correct because pH + pOH = 14.00 in each case.

Comment On most calculators, finding the pH requires several keystrokes. For example, to find the pH of 6.3×10^{-3} M HNO_3 solution, you enter: 6.3, EXP, 3, +/−, log, +/−.

FOLLOW-UP PROBLEM 18.3 A solution of NaOH has a pH of 9.52. What is its pOH, $[H_3O^+]$, and $[OH^-]$ at 25°C?
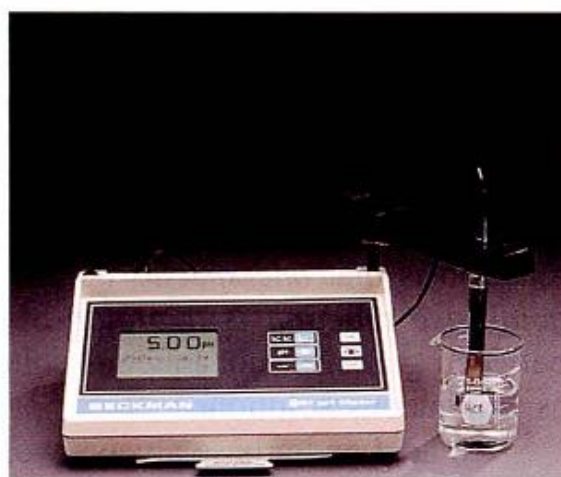
Measuring pH

In the laboratory, pH values are usually obtained with **an acid-base indicator** or, more precisely, with an instrument called a **pH meter**.

Acid-base indicators are organic molecules whose colors depend on the acidity or basicity of the solution in which they are dissolved.

The pH meter measures $[H_3O^+]$ and transforms it into displayed pH units.

A   **B**

Figure 18.7 Methods for measuring the pH of an aqueous solution. A, A few drops of the solution are placed on a strip of pH paper, and the color is compared with the color chart. B, The electrodes of a pH meter immersed in the test solution measure $[H_3O^+]$.

18.3 PROTON TRANSFER AND THE BRONSTED-LOWRY ACID-BASE DEFINITION

A major shortcoming of the Arrhenius acid-base definition: many substances that yield OH^- ions when they dissolve in water do not contain OH in their formulas. Examples; ammonia, amines, and many salts of weak acids, such as NaF.

Another limitation; water has to be the solvent for acid-base reactions.

According to the Bronsted-Lowry acid-base definition;

> ➤ **An acid is a proton donor**, any species that donates an H^+ ion.
>
> HNO_3 and $H_2PO_4^-$ are two of many examples. All Arrhenius acids are Bronsted-Lowry acids.
>
> ➤ **A base is a proton acceptor**, any species that accepts an H^+ ion. A base must contain a lone pair of electrons to bind the H^+ ion;
>
> a few examples are NH_3, CO_3^- , and F^-, as well as OH^- itself.

From this perspective, acid-base reactions can occur **between gases**, in **nonaqueous solutions**, and in **heterogeneous mixtures**, as well as in **aqueous solutions**. Consider two typical acidic and basic solutions:

1. Acid donates a proton to water (Figure 18.8A). HCl (the acid) donates the H^+, and H_2O (the base) accepts it:
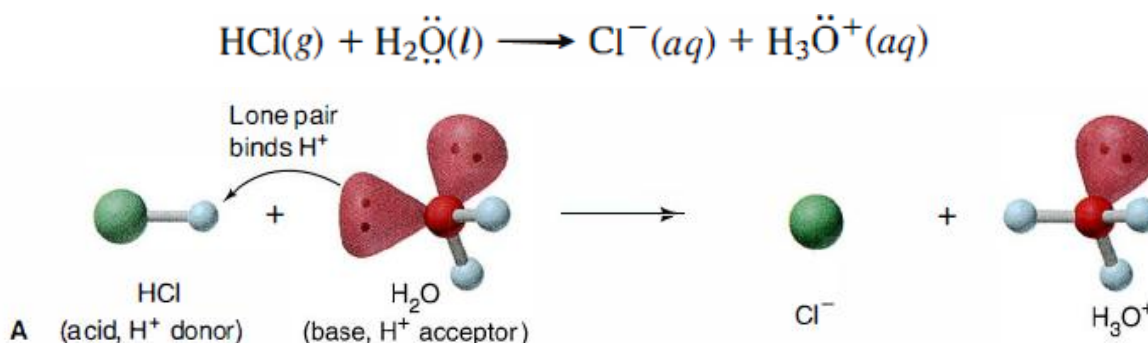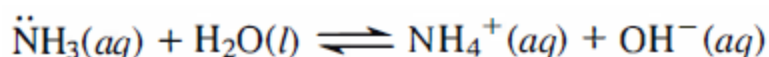
$$HCl(g) + H_2\ddot{O}(l) \longrightarrow Cl^-(aq) + H_3\ddot{O}^+(aq)$$

Fig. 18.8 A

2. Base accepts a proton from water (Figure 18.8B).

$$\ddot{N}H_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

H_2O (the acid) has donated the H^+, and NH_3 (the base) has accepted it.
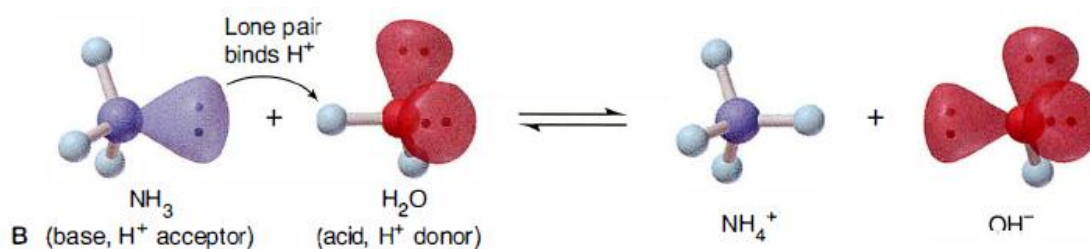
Fig. 18.8 B

The Conjugate Acid-Base Pair

Let's examine the reaction between hydrogen sulfide and ammonia:

$$H_2S + NH_3 \rightleftharpoons HS^- + NH_4^+$$

➤ H_2S and HS⁻ are a **conjugate acid-base pair**: HS⁻ is the conjugate base of the acid H_2S

➤ NH_3 and NH_4^+ form a **conjugate acid-base pair**: NH_4^+ is the conjugate acid of the base NH_3.

Every acid has a conjugate base, and every base has a conjugate acid. Note that, for any conjugate acid-base pair,

• The conjugate base has one *fewer* H and one *more* minus charge than the acid.

• The conjugate acid has one *more* H and one *fewer* minus charge than the base.

$$acid_1 + base_2 \rightleftharpoons base_1 + acid_2$$

Table 18.2 **The Conjugate Pairs in Some Acid-Base Reactions**

	Acid	+	Base	$\rightleftharpoons$	Base	+	Acid
Reaction 1	HF	+	H_2O	$\rightleftharpoons$	F^-	+	H_3O^+
Reaction 2	HCOOH	+	CN^-	$\rightleftharpoons$	$HCOO^-$	+	HCN
Reaction 3	NH_4^+	+	CO_3^{2-}	$\rightleftharpoons$	NH_3	+	HCO_3^-
Reaction 4	$H_2PO_4^-$	+	OH^-	$\rightleftharpoons$	HPO_4^{2-}	+	H_2O
Reaction 5	H_2SO_4	+	$N_2H_5^+$	$\rightleftharpoons$	HSO_4^-	+	$N_2H_6^{2+}$
Reaction 6	HPO_4^{2-}	+	SO_3^{2-}	$\rightleftharpoons$	PO_4^{3-}	+	HSO_3^-

Notice that:

• Acids and bases can be neutral, cationic, or anionic.

• The same species can be an acid or a base, depending on the other species reacting. Water behaves this way in reactions 1 and 4, and HPO_4^{2-} does so in reactions 4 and 6.

SAMPLE PROBLEM 18.4 Identifying Conjugate Acid-Base Pairs

Problem The following reactions are important environmental processes. Identify the conjugate acid-base pairs.

(a) $H_2PO_4^-(aq) + CO_3^{2-}(aq) \rightleftharpoons HCO_3^-(aq) + HPO_4^{2-}(aq)$

(b) $H_2O(l) + SO_3^{2-}(aq) \rightleftharpoons OH^-(aq) + HSO_3^-(aq)$

Plan To find the conjugate pairs, we find the species that donated an H^+ (acid) and the species that accepted it (base). The acid (or base) on the left becomes its conjugate base (or conjugate acid) on the right. Remember, the conjugate acid has one more H and one fewer minus charge than its conjugate base.

Solution (a) $H_2PO_4^-$ has one more H^+ than HPO_4^{2-}; CO_3^{2-} has one fewer H^+ than HCO_3^-. Therefore, $H_2PO_4^-$ and HCO_3^- are the acids, and HPO_4^{2-} and CO_3^{2-} are the bases. The conjugate acid-base pairs are $H_2PO_4^-/HPO_4^{2-}$ and HCO_3^-/CO_3^{2-}.

(b) H_2O has one more H^+ than OH^-; SO_3^{2-} has one fewer H^+ than HSO_3^-. The acids are H_2O and HSO_3^-; the bases are OH^- and SO_3^{2-}. The conjugate acid-base pairs are H_2O/OH^- and HSO_3^-/SO_3^{2-}.

FOLLOW-UP PROBLEM 18.4 Identify the conjugate acid-base pairs:

(a) $CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$

(b) $H_2O(l) + F^-(aq) \rightleftharpoons OH^-(aq) + HF(aq)$

Relative Acid-Base Strength and the Net Direction of Reaction

If the stronger acid and base are written on the left, the net direction is to the right, so $K_c > 1$.

$$HNO_3 \ + \ H_2O \ \longrightarrow \ NO_3^- \ + \ H_3O^+$$

stronger acid + stronger base ⟶ weaker base + weaker acid

On the other hand, with weak acids such as HF, the F⁻ wins because it is a stronger base than H_2O:

$$HF \ + \ H_2O \ \rightleftharpoons \ F^- \ + \ H_3O^+$$

weaker acid + weaker base ⟵ stronger base + stronger acid

We can rank conjugate pairs in terms of the ability of the acid to transfer its proton (Figure 18.9). Note, especially, that *a weaker acid has a stronger conjugate base*.
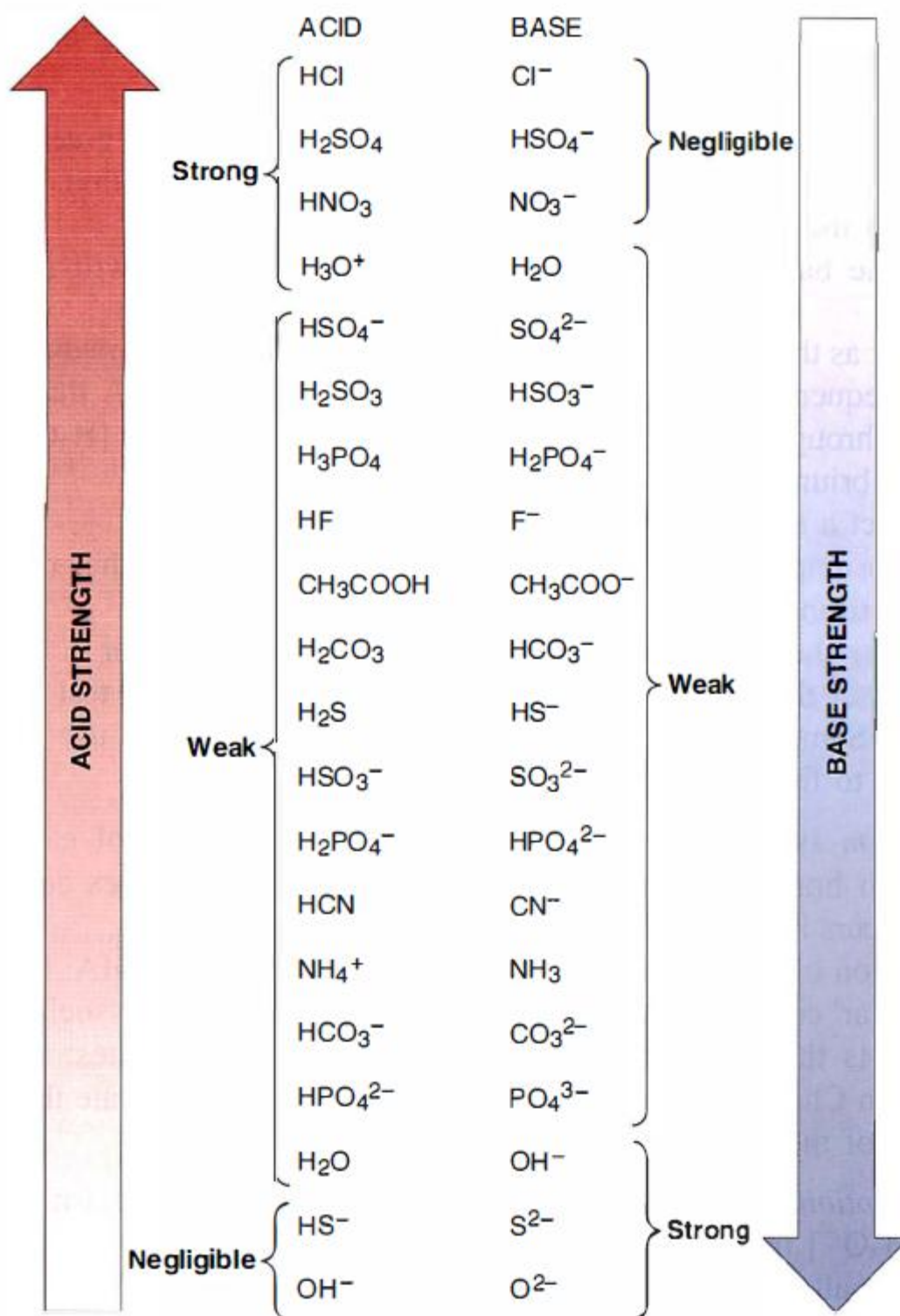
14

ACID	BASE	
Strong		
HCl	Cl⁻	
H_2SO_4	HSO_4^-	**Negligible**
HNO_3	NO_3^-	
H_3O^+	H_2O	
Weak		
HSO_4^-	SO_4^{2-}	
H_2SO_3	HSO_3^-	
H_3PO_4	$H_2PO_4^-$	
HF	F^-	
CH_3COOH	CH_3COO^-	
H_2CO_3	HCO_3^-	**Weak**
H_2S	HS^-	
HSO_3^-	SO_3^{2-}	
$H_2PO_4^-$	HPO_4^{2-}	
HCN	CN^-	
NH_4^+	NH_3	
HCO_3^-	CO_3^{2-}	
HPO_4^{2-}	PO_4^{3-}	
H_2O	OH^-	
Negligible		
HS^-	S^{2-}	**Strong**
OH^-	O^{2-}	

ACID STRENGTH (increasing upward) *BASE STRENGTH* (increasing downward)

Figure 18.9 Strengths of conjugate acid-base pairs. The stronger the acid is, the weaker its conjugate base. The strongest acid appears at top left and the strongest base at bottom right. When an acid reacts with a base farther down the list, the reaction proceeds to the right ($K_c > 1$).

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SAMPLE PROBLEM 18.5 Predicting the Net Direction of an Acid-Base Reaction

Problem Predict the net direction and whether K_c is greater or less than 1 for the following reaction (assume equal initial concentrations of all species):

$$H_2PO_4^-(aq) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + HPO_4^{2-}(aq)$$

Plan We first identify the conjugate acid-base pairs. To predict the direction, we consult Figure 18.9 to see which acid and base are stronger. The stronger acid and base form the weaker acid and base, so the reaction proceeds in that net direction. If the reaction *as written* proceeds to the right, then [products] is higher than [reactants], and $K_c > 1$.

Solution The conjugate pairs are $H_2PO_4^-/HPO_4^{2-}$ and NH_4^+/NH_3. $H_2PO_4^-$ is higher on the list of acids, so it is stronger than NH_4^+; and NH_3 is lower on the list of bases, so it is stronger than HPO_4^{2-}. Therefore,

$$H_2PO_4^-(aq) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + HPO_4^{2-}(aq)$$

stronger acid + stronger base ⟶ weaker acid + weaker base
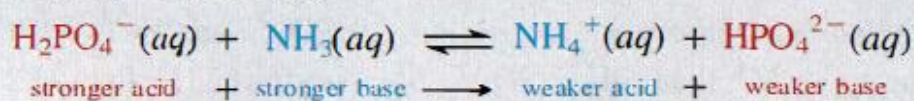
The net direction is to the right, so $K_c > 1$.

FOLLOW-UP PROBLEM 18.5 Predict the net direction and whether K_c is greater or less than 1 for the following reaction:

$$H_2O(l) + HS^-(aq) \rightleftharpoons OH^-(aq) + H_2S(aq)$$

18.4 SOLVING PROBLEMS INVOLVING WEAK-ACID EQUILIBRIA

In general, there are two types of equilibrium problems involving weak acids and their conjugate bases:

> 1. Given equilibrium concentrations, find K_a.
>
> 2. Given K_a and some concentration information, find the other equilibrium concentrations.

We make two assumptions to simplify the arithmetic:

1. The $[H_3O^+]$ from the autoionization of water is negligible.

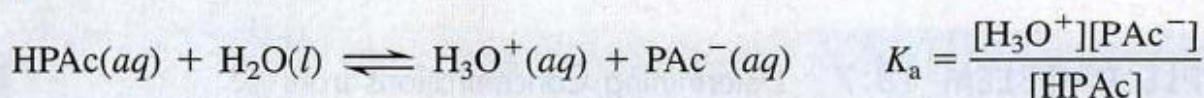$$[H_3O^+] = [H_3O^+]_{from\ HA} + [H_3O^+]_{from\ H_2O} \approx [H_3O^+]_{from\ HA}$$

2. A weak acid has a small Ka. Therefore, it dissociates to such a small extent that we can neglect the change in its concentration to find its equi librium concentration:

$$[HA] = [HA]_{init} - [HA]_{dissoc} \approx [HA]_{init}$$

Finding K_a Given Concentrations

SAMPLE PROBLEM 18.6 Finding K_a of a Weak Acid from pH of Its Solution

Problem Phenylacetic acid ($C_6H_5CH_2COOH$, simplified here to HPAc) builds up in the blood of persons with phenylketonuria, an inherited disorder that, if untreated, causes mental retardation and death. A study of the acid shows that the pH of 0.12 M HPAc is 2.62. What is the K_a of phenylacetic acid?

Plan We are given [HPAc]$_{init}$ (0.12 M) and the pH (2.62) and must find K_a. We first write the equation for HPAc dissociation and the expression for K_a to see which values we need to find:

$$HPAc(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PAc^-(aq) \qquad K_a = \frac{[H_3O^+][PAc^-]}{[HPAc]}$$

- To find $[H_3O^+]$: We know the pH, so we can find $[H_3O^+]$. Because a pH of 2.62 is more than four pH units (10^4-fold) *lower* than the pH of pure water itself (pH = 7.0), we can assume that $[H_3O^+]_{from\ HPAc} >> [H_3O^+]_{from\ H_2O}$. Therefore, $[H_3O^+]_{from\ HPAc} + [H_3O^+]_{from\ H_2O} \approx [H_3O^+]_{from\ HPAc} \approx [H_3O^+]$.
- To find $[PAc^-]$: Because each HPAc that dissociates forms one H_3O^+ and one PAc^-, $[H_3O^+] \approx [PAc^-]$.
- To find $[HPAc]$: We know [HPAc]$_{init}$. Because HPAc is a weak acid, we assume that very little dissociates, so $[HPAc]_{init} - [HPAc]_{dissoc} = [HPAc] \approx [HPAc]_{init}$.

We set up a reaction table, make the assumptions, substitute the equilibrium values, solve for K_a, and then check the assumptions.

Solution Calculating $[H_3O^+]$:

$$[H_3O^+] = 10^{-pH} = 10^{-2.62} = 2.4 \times 10^{-3}\ M$$

Setting up the reaction table, with $x = [HPAc]_{dissoc} = [H_3O^+]_{from\ HPAc} = [PAc^-] \approx [H_3O^+]$:

Concentration (M)	HPAc(aq)	+	H₂O(l)	⇌	H₃O⁺(aq)	+	PAc⁻(aq)
Initial	0.12		—		1×10^{-7}		0
Change	$-x$		—		$+x$		$+x$
Equilibrium	$0.12 - x$		—		$x + (<1 \times 10^{-7})$		x

Making the assumptions:
1. The calculated $[H_3O^+]$ ($2.4 \times 10^{-3}\ M$) >> $[H_3O^+]_{from\ H_2O}$ ($<1 \times 10^{-7}\ M$), so we assume that $[H_3O^+] \approx [H_3O^+]_{from\ HPAc} = x$ (the change in [HPAc])
2. HPAc is a weak acid, so we assume that $[HPAc] = 0.12\ M - x \approx 0.12\ M$.
Solving for the equilibrium concentrations:

$$x \approx [H_3O^+] = [PAc^-] = 2.4\times10^{-3}\ M$$

$$[HPAc] = 0.12\ M - x = 0.12\ M - (2.4\times10^{-3}\ M) \approx 0.12\ M \text{ (to 2 sf)}$$

Substituting these values into K_a:

$$K_a = \frac{[H_3O^+][PAc^-]}{[HPAc]} \approx \frac{(2.4\times10^{-3})(2.4\times10^{-3})}{0.12} = 4.8\times10^{-5}$$

Checking the assumptions by finding the percent error in concentration:

1. For $[H_3O^+]_{\text{from } H_2O}$: $\dfrac{1\times10^{-7}\ M}{2.4\times10^{-3}\ M} \times 100 = 4\times10^{-3}\%$ (<5%; assumption is justified).

2. For $[HPAc]_{\text{dissoc}}$: $\dfrac{2.4\times10^{-3}\ M}{0.12\ M} \times 100 = 2.0\%$ (<5%; assumption is justified). We had already shown above that, to two significant figures, the concentration had not changed, so this check was not really necessary.

Check The $[H_3O^+]$ makes sense: pH 2.62 should give $[H_3O^+]$ between 10^{-2} and $10^{-3}\ M$. The K_a calculation also seems in the correct range: $(10^{-3})^2/10^{-1} = 10^{-5}$, and this value seems reasonable for a weak acid.

Comment $[H_3O^+]_{\text{from } H_2O}$ is so small relative to $[H_3O^+]_{\text{from } HA}$ that, from here on, we will disregard it and enter it as zero in reaction tables.

FOLLOW-UP PROBLEM 18.6 The conjugate acid of ammonia is NH_4^+, a weak acid. If a 0.2 M NH_4Cl solution has a pH of 5.0, what is the K_a of NH_4^+?

Finding Concentrations Given K_a

SAMPLE PROBLEM 18.7 Determining Concentrations from K_a and Initial [HA]

Problem Propanoic acid (CH_3CH_2COOH, which we simplify as HPr) is a carboxylic acid whose salts are used to retard mold growth in foods. What is the $[H_3O^+]$ of 0.10 M HPr ($K_a = 1.3\times10^{-5}$)?

Plan We know the initial concentration (0.10 M) and K_a (1.3×10^{-5}) of HPr, and we need to find $[H_3O^+]$. First, we write the balanced equation and the expression for K_a:

$$HPr(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Pr^-(aq) \qquad K_a = \frac{[H_3O^+][Pr^-]}{[HPr]} = 1.3\times10^{-5}$$
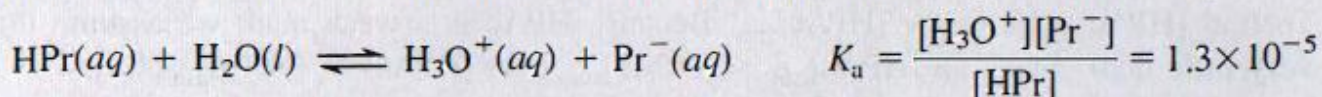
We know $[HPr]_{\text{init}}$ but not [HPr]. If we let $x = [HPr]_{\text{dissoc}}$, x is also $[H_3O^+]_{\text{from HPr}}$ and $[Pr^-]$ because each HPr that dissociates yields one H_3O^+ and one Pr^-. With this information, we can set up a reaction table. In solving for x, we assume that, because HPr has a small K_a, it dissociates very little; therefore, $[HPr]_{\text{init}} - x = [HPr] \approx [HPr]_{\text{init}}$. After we find x, we check the assumption.

Solution Setting up a reaction table, with $x = [HPr]_{\text{dissoc}} = [H_3O^+]_{\text{from HPr}} = [Pr^-] = [H_3O^+]$:

Concentration (M)	HPr(aq)	+	H₂O(l)	⇌	H₃O⁺(aq)	+	Pr⁻(aq)
Initial	0.10		—		0		0
Change	−x		—		+x		+x
Equilibrium	0.10 − x		—		x		x

Making the assumption: K_a is small, so x is small compared with $[HPr]_{init}$; therefore, $0.10\,M - x \approx 0.10\,M$. Substituting into the K_a expression and solving for x:

$$K_a = \frac{[H_3O^+][Pr^-]}{[HPr]} = 1.3 \times 10^{-5} \approx \frac{(x)(x)}{0.10}$$

$$x \approx \sqrt{(0.10)(1.3 \times 10^{-5})} = \boxed{1.1 \times 10^{-3}\,M = [H_3O^+]}$$

Checking the assumption:

For $[HPr]_{dissoc}$: $\dfrac{1.1 \times 10^{-3}\,M}{0.10\,M} \times 100 = 1.1\%$ (<5%; assumption is justified).

Check The $[H_3O^+]$ seems reasonable for a dilute solution of a weak acid with a moderate K_a. By reversing the calculation, we can check the math: $(1.1 \times 10^{-3})^2/0.10 = 1.2 \times 10^{-5}$, which is within rounding of the given K_a.

Comment In these problems, we assume that the concentration of HA that dissociates ($[HA]_{dissoc} = x$) can be neglected because K_a is relatively small. However, this is true only if $[HA]_{init}$ is relatively large. Here's a benchmark to see if the assumption is justified:

- If $\dfrac{[HA]_{init}}{K_a} > 400$, the assumption is justified: neglecting x introduces an error < 5%.

- If $\dfrac{[HA]_{init}}{K_a} < 400$, the assumption is *not* justified; neglecting x introduces an error > 5%, so we solve a quadratic equation to find x.

The latter situation occurs in the follow-up problem.

FOLLOW-UP PROBLEM 18.7 Cyanic acid (HOCN) is an extremely acrid, unstable substance. What is the $[H_3O^+]$ and pH of 0.10 M HOCN ($K_a = 3.5 \times 10^{-4}$)?

The Effect of Concentration on the Extent of Acid Dissociation

Suppose the initial concentration of HPr in the above sample problem is one-tenth as much, 0.010M rather than 0. 10M. After filling in the reaction table and making the same assumptions, we find that

$$x = [HPr]_{dissoc} = 3.6 \times 10^{-4}\,M$$

Now, let's compare the percentages of HPr molecules dissociated at the two different initial acid concentrations, using the relationship;

$$\text{Percent HA dissociated} = \frac{[HA]_{dissoc}}{[HA]_{init}} \times 100$$

Case 1: $[HPr]_{init} = 0.10\ M$

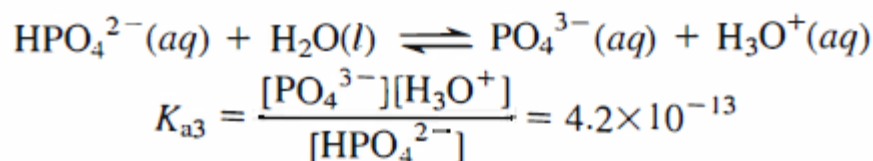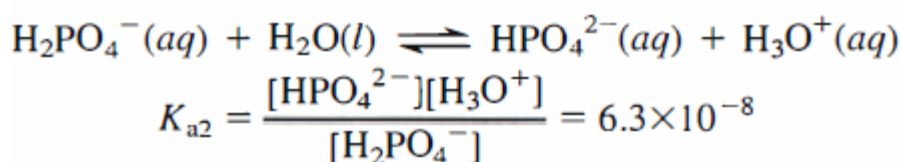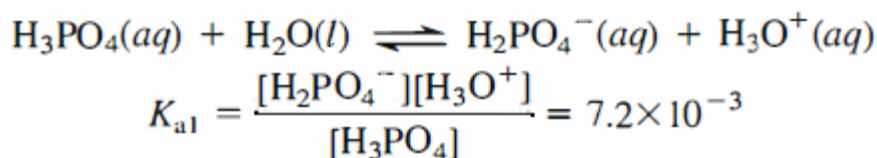$$\text{Percent dissociated} = \frac{1.1 \times 10^{-3}\ M}{1.0 \times 10^{-1}\ M} \times 100 = 1.1\%$$

Case 2: $[HPr]_{init} = 0.010\ M$

$$\text{Percent dissociated} = \frac{3.6 \times 10^{-4}\ M}{1.0 \times 10^{-2}\ M} \times 100 = 3.6\%$$

As the initial acid concentration decreases, the percent dissociation of the acid increases.

The Behavior of Polyprotic Acids

Acids with *more than one ionizable proton* are **polyprotic acids**. In a solution of a polyprotic acid, one proton at a time dissociates from the acid molecule, and each dissociation step has a different K_a. For example, phosphoric acid is a triprotic acid (three ionizable protons), so it has three Ka values:

$$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + H_3O^+(aq)$$
$$K_{a1} = \frac{[H_2PO_4^-][H_3O^+]}{[H_3PO_4]} = 7.2 \times 10^{-3}$$

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq)$$
$$K_{a2} = \frac{[HPO_4^{2-}][H_3O^+]}{[H_2PO_4^-]} = 6.3 \times 10^{-8}$$

$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons PO_4^{3-}(aq) + H_3O^+(aq)$$
$$K_{a3} = \frac{[PO_4^{3-}][H_3O^+]}{[HPO_4^{2-}]} = 4.2 \times 10^{-13}$$

As you can see from the relative K_a values, H_3PO_4 is a much stronger acid than H_2PO4^-, which is much stronger than HPO_4^{2-}. (Appendix C lists several polyprotic

acids and their multiple Ka values.)

$$K_{a1} > K_{a2} > K_{a3}$$

Successive acid-dissociation constants typically differ by several orders of magnitude. This fact greatly simplifies pH calculations involving polyprotic acids because *we can usually neglect the H_3O^+ coming from the subsequent dissociations*.

18.5 WEAK BASES AND THEIR RELATION TO WEAK ACIDS

When a base (B) dissolves, it accepts a proton from H_2O, which acts as an acid, leaving behind an OH^- ion:

$$B(aq) + H_2O(aq) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

$$K_c = \frac{[BH^+][OH^-]}{[B][H_2O]}$$

we incorporate $[H_2O]$ in the value of K_c and obtain the **base-dissociation constant** (or **base-ionization constant**), K_b:

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

In aqueous solution, the two large classes of weak bases are:

    (1) ammonia and the amines and

    (2) the anions of weak acids.

Molecules as Weak Bases: Ammonia and the Amines

Ammonia is the simplest nitrogen-containing compound that acts as a weak base in water:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad K_b = 1.76\times10^{-5} \text{ (at 25°C)}$$
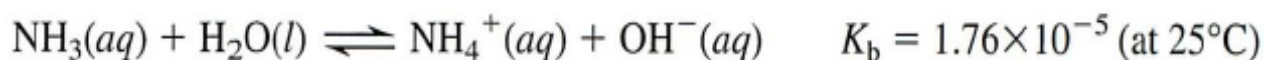
In a 1.0 M NH_3 solution, for example, $[OH^-] = [NH_4^+] = 4.2 \times 10^{-3}$ M, so about 99.58% of the NH_3 is not ionized.

A list of several bases with their K_b values appears in Appendix C.

If one or more of the H atoms in NH_3 is replaced by an organic group (designated as R), an **amine** results: **RNH_2, R_2NH, or R_3N**.

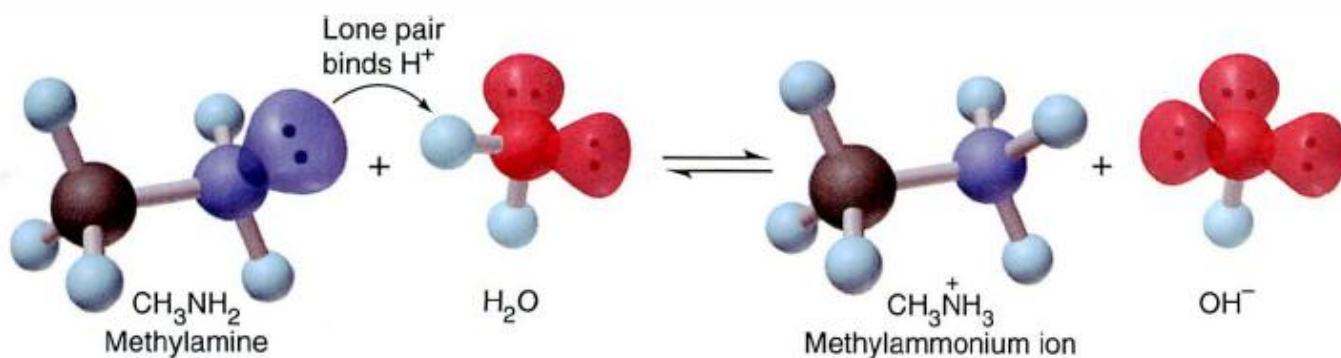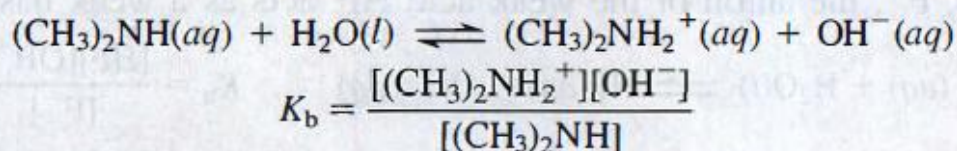Figure 18.10 depicts this process for methylamine, the simplest amine.

Figure 18.10 Abstraction of a proton from water by methylamine. The amines are organic derivatives of ammonia. Methylamine, the simplest amine, acts as a base in water by accepting a proton, thereby increasing $[OH^-]$.

SAMPLE PROBLEM 18.8   Determining pH from K_b and Initial [B]

Problem Dimethylamine, $(CH_3)_2NH$ (see margin), a key intermediate in detergent manu-facture, has a K_b of 5.9×10^{-4}. What is the pH of 1.5 M $(CH_3)_2NH$?

Plan We know the initial concentration (1.5 M) and K_b (5.9×10^{-4}) of $(CH_3)_2NH$ and have to find the pH. The amine reacts with water to form OH^-, so we have to find $[OH^-]$ and then calculate $[H_3O^+]$ and pH. The balanced equation and K_b expression are

$$(CH_3)_2NH(aq) + H_2O(l) \rightleftharpoons (CH_3)_2NH_2^+(aq) + OH^-(aq)$$

$$K_b = \frac{[(CH_3)_2NH_2^+][OH^-]}{[(CH_3)_2NH]}$$

Because $K_b \gg K_w$, the $[OH^-]$ from the autoionization of water is negligible, and we disregard it. Therefore,

$$[OH^-]_{from\ base} = [(CH_3)_2NH_2^+] = [OH^-]$$

Because K_b is small, we assume that the amount of amine reacting is small, so

$$[(CH_3)_2NH]_{init} - [(CH_3)_2NH]_{reacting} = [(CH_3)_2NH] \approx [(CH_3)_2NH]_{init}$$

We proceed as usual, setting up a reaction table, making the assumption, and solving for x. Then we check the assumption and convert $[OH^-]$ to $[H_3O^+]$ using K_w; finally, we calculate pH.

Solution Setting up the reaction table, with

$$x = [(CH_3)_2NH]_{reacting} = [(CH_3)_2NH_2^+] = [OH^-]$$

Concentration (M)	$(CH_3)_2NH(aq)$	$+$	$H_2O(l)$	$\rightleftharpoons$	$(CH_3)_2NH_2^+(aq)$	$+$	$OH^-(aq)$
Initial	1.5		—		0		0
Change	$-x$		—		$+x$		$+x$
Equilibrium	$1.5 - x$		—		x		x

Making the assumption:
K_b is small, so $[(CH_3)_2NH]_{init} \approx [(CH_3)_2NH]$; thus, $1.5\ M - x \approx 1.5\ M$.
Substituting into the K_b expression and solving for x:

$$K_b = \frac{[(CH_3)_2NH_2^+][OH^-]}{[(CH_3)_2NH]}$$

$$= 5.9\times10^{-4} \approx \frac{x^2}{1.5}$$

$$x = [OH^-] \approx 3.0\times10^{-2}\ M$$

Checking the assumption:

$$\frac{3.0\times10^{-2}\ M}{1.5\ M} \times 100 = 2.0\%\ (<5\%;\ \text{assumption is justified})$$

Note that the Comment in Sample Problem 18.7 applies to weak bases as well:

$$\frac{[B]_{init}}{K_b} = \frac{1.5}{5.9\times10^{-4}} = 2.5\times10^3 > 400$$

Calculating pH:

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0\times10^{-14}}{3.0\times10^{-2}} = 3.3\times10^{-13}\ M$$

$$pH = -\log(3.3\times10^{-13})$$

$$= 12.48$$

Check The value of x seems reasonable: $\sqrt{(\sim6\times10^{-4})(1.5)} = \sqrt{9\times10^{-4}} = 3\times10^{-2}$. Because $(CH_3)_2NH$ is a weak base, the pH should be several pH units greater than 7.

FOLLOW-UP PROBLEM 18.8 Pyridine (C_5H_5N, see margin) plays a major role in organic syntheses as a solvent and base. It has a pK_b of 8.77. What is the pH of 0.10 M pyridine?

Anions of Weak Acids as Weak Bases

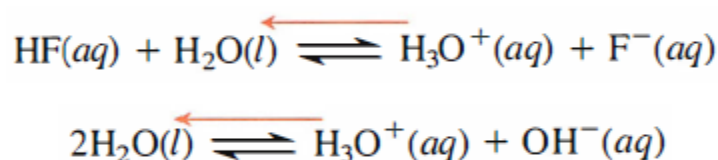The other large group of Bronsted-Lowry bases consists of anions of weak acids:

$$A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq) \qquad K_b = \frac{[HA][OH^-]}{[A^-]}$$
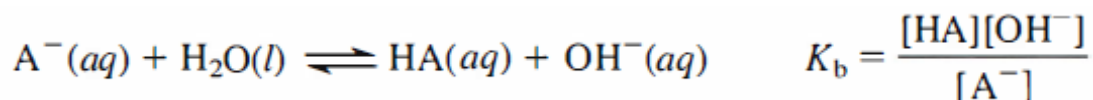
For example, F⁻, the anion of the weak acid HF, acts as a weak base:

$$F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq) \qquad K_b = \frac{[HF][OH^-]}{[F^-]}$$
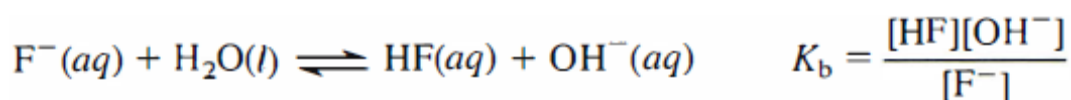
Why is a solution of HA acidic and a solution of A⁻ basic?

1. The acidity of HA(aq).

$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$$

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

Of all the species present; HF, H_2O, H_3O^+, F⁻, and OH⁻, the two that can influence the acidity of the solution are H_3O^+ , predominantly from HF, and OH⁻ from water. **The solution is acidic because [H$_3$O$^+$]$_{from\ HF}$ >> [OH⁻]$_{from\ H2O}$.**

2. The basicity of A⁻(aq).

Consider the species present in 1 M NaF. The salt dissociates completely to yield a stoichiometric concentration of F⁻. The Na⁺ ion behaves as a spectator, and some F⁻ reacts as a weak base to produce very small amounts of HF and OH⁻:

$$F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq)$$

the species present are the same as above. The two species that affect the acidity are OH⁻, predominantly from the F⁻ reaction with water, and H_3O^+ from water. In this case, **[OH⁻]$_{from\ F⁻}$ >> [H$_3$O$^+$] $_{from\ H2O}$, so the solution is basic**.

To summarize:

✓ In an HA solution, [HA] >> [A⁻] and [H$_3$O$^+$]$_{from\ HA}$ >> [OH⁻]$_{from\ H2O}$, so the solution is acidic.

✓ In an A⁻ solution, [A⁻] >> [HA] and [OH-]$_{from A-}$ >> [H$_3$O$^+$]$_{from H2O}$, so the

solution is basic.

The Relation Between K$_a$ and K$_b$ of a Conjugate Acid-Base Pair

An important relationship exists between the K$_a$ of HA and the K$_b$ of A⁻:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$
$$A^- + H_2O \rightleftharpoons HA + OH^-$$
$$\overline{2H_2O \rightleftharpoons H_3O^+ + OH^-}$$
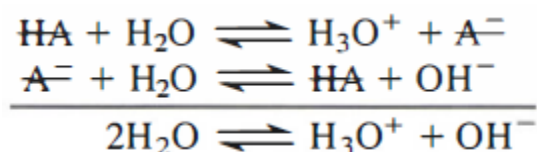
The sum of the two dissociation reactions is the auto ionization of water.

$$\frac{[H_3O^+][A^-]}{[HA]} \times \frac{[HA][OH^-]}{[A^-]} = [H_3O^+][OH^-]$$

$$K_a \quad \times \quad K_b \quad = \quad K_w$$

To find the K$_b$ value for F⁻ , for instance, we look up the K$_a$ value for HF and relate

it to K$_w$:

$$K_b \text{ of } F^- = \frac{K_w}{K_a \text{ of HF}} = \frac{1.0 \times 10^{-14}}{6.8 \times 10^{-4}} = 1.5 \times 10^{-11}$$

SAMPLE PROBLEM 18.9 Determining the pH of a Solution of A⁻

Problem Sodium acetate (CH$_3$COONa, or NaAc for this problem) has applications in photographic development and textile dyeing. What is the pH of 0.25 M NaAc? K_a of acetic acid (HAc) is 1.8×10^{-5}.

Plan From the formula (NaAc) and the fact that all sodium salts are water soluble, we know that the initial concentration of acetate ion, Ac⁻, is 0.25 M. We also know the K_a of the parent acid, HAc (1.8×10^{-5}). We have to find the pH of the solution of Ac⁻, which acts as a base in water:

$$Ac^-(aq) + H_2O(l) \rightleftharpoons HAc(aq) + OH^-(aq) \qquad K_b = \frac{[HAc][OH^-]}{[Ac^-]}$$
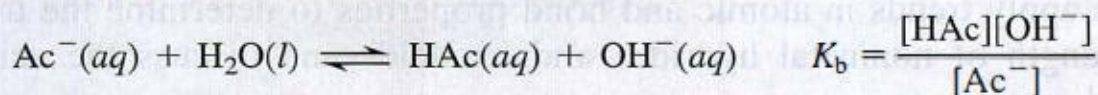
If we calculate [OH⁻], we can find [H$_3$O$^+$] and convert it to pH. To solve for [OH⁻], we need the K_b of Ac⁻, which we obtain from the K_a of HAc and K_w. All sodium salts are soluble, so we know that [Ac⁻] = 0.25 M. Our usual assumption is that [Ac⁻]$_{init}$ ≈ [Ac⁻].

Solution Setting up the reaction table, with $x = [Ac^-]_{reacting} = [HAc] = [OH^-]$:

Concentration (M)	$Ac^-(aq)$	$+$	$H_2O(l)$	$\rightleftharpoons$	$HAc(aq)$	$+$	$OH^-(aq)$
Initial	0.25		—		0		0
Change	$-x$		—		$+x$		$+x$
Equilibrium	$0.25 - x$		—		x		x

Solving for K_b:

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Making the assumption: Because K_b is small, $0.25\ M - x \approx 0.25\ M$.

Substituting into the expression for K_b and solving for x:

$$K_b = \frac{[HAc][OH^-]}{[Ac^-]} = 5.6 \times 10^{-10} \approx \frac{x^2}{0.25} \qquad x = [OH^-] \approx 1.2 \times 10^{-5}\ M$$

Checking the assumption:

$$\frac{1.2 \times 10^{-5}\ M}{0.25\ M} \times 100 = 4.8 \times 10^{-3}\% \ (<5\%;\ \text{assumption is justified})$$

Note that
$$\frac{0.25}{5.6 \times 10^{-10}} = 4.5 \times 10^8 > 400$$

Solving for pH:

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.2 \times 10^{-5}} = 8.3 \times 10^{-10}\ M$$

$$pH = -\log(8.3 \times 10^{-10}) = \boxed{9.08}$$

Check The K_b calculation seems reasonable: $\sim 10 \times 10^{-15}/2 \times 10^{-5} = 5 \times 10^{-10}$. Because Ac^- is a weak base, $[OH^-] > [H_3O^+]$; thus, pH > 7, which makes sense.

FOLLOW-UP PROBLEM 18.9 Sodium hypochlorite (NaClO) is the active ingredient in household laundry bleach. What is the pH of 0.20 M NaClO?

18.6 MOLECULAR PROPERTIES AND ACID STRENGTH

The strength of an acid depends on its ability to donate a proton, which depends in turn on the strength of the bond to the acidic proton.

Trends in Acid Strength of Nonmetal Hydrides

Two factors determine how easily a proton is released from a nonmetal hydride:
the **electronegativity of the central nonmetal** (**E**) and the **strength of the E-H
bond**. Figure 18.11 displays two periodic trends:

1. Across a period, nonmetal hydride acid strength increases.

As E becomes more electronegative, electron density around H is withdrawn,
and the E- H bond becomes more polar. As a result, H^+ is released more
easily to a surrounding water molecule.

Thus, HCl is a stronger acid than H_2S because Cl is more electronegative (EN =
3.0) than S (EN = 2.5).

2. **Down a group, nonmetal hydride acid strength increases.**

As E becomes larger, the E-H bond becomes longer and weaker, so H^+
comes off more easily. Thus, in Group 6A(l6) , for example,

$$H_2O < H_2S < H_2Se < H_2Te$$
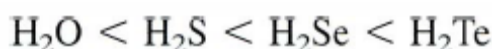
**Figure 18.11 The effect of atomic and
molecular properties on nonmetal
hydride acidity.** As the electronegativity
of the nonmetal (E) bonded to the ioniz-
able proton increases (*left to right*), the
acidity increases. As the length of the
E—H bond increases (*top to bottom*), the
bond strength decreases, so the acidity
increases. (In water, HCl, HBr, and HI are
equally strong.)

Electronegativity increases,
acidity increases →

	6A(16)	7A(17)
	H_2O	HF
	H_2S	HCl
	H_2Se	HBr
	H_2Te	HI

Bond strength decreases,
acidity increases ↓

Trends in Acid Strength of Oxoacids

Two factors determine the acid strength of oxoacids: the electronegativity of the central nonmetal (E) and the number of O atoms.

1. **For oxoacids with the same number of oxygens around E, acid strength increases with the electronegativity of E**.

$$HOCl > HOBr > HOI$$

K_a of $HOCl = 2.9 \times 10^{-8}$ K_a of $HOBr = 2.3 \times 10^{-9}$ K_a of $HOI = 2.3 \times 10^{-11}$

2. **For oxoacids with different numbers of oxygens around a given E, acid strength increases with number of O atoms**.

$$HOCl < HOClO < HOClO_2 < HOClO_3$$

K_a of $HOCl$ (hypochlorous acid) $= 2.9 \times 10^{-8}$
K_a of $HOClO$ (chlorous acid) $= 1.12 \times 10^{-2}$
K_a of $HOClO_2$ (chloric acid) ≈ 1
K_a of $HOClO_3$ (perchloric acid) $= >10^7$
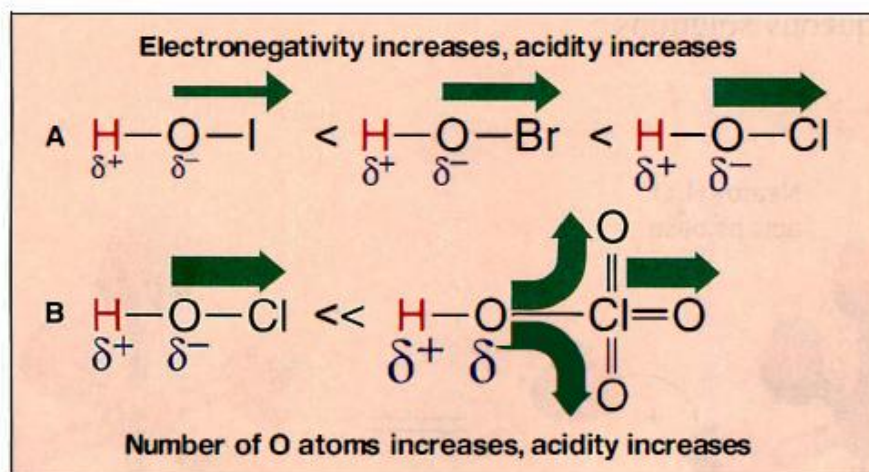
Figure 18.12 The relative strengths of oxoacids. A, Among these hypohalous acids, HOCl is the strongest and HOI the weakest. Because Cl is the most electronegative of the halogens shown here, it withdraws electron density (indicated by thickness of green arrow) from the O—H bond most effectively, making that bond most polar in HOCl (indicated by the relative sizes of the δ symbols). **B,** Among the chlorine oxoacids, the additional O atoms in HOClO₃ pull electron density from the O—H bond, making the bond much more polar than that in HOCl.

Acidity of Hydrated Metal Ions

Consider a general metal nitrate, $M(NO_3)_n$, as it dissolves in water;

$$M(NO_3)_n(s) + xH_2O(l) \longrightarrow M(H_2O)_x^{n+}(aq) + nNO_3^-(aq)$$
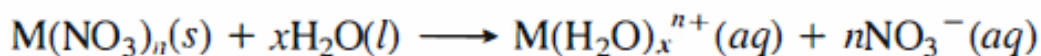
If the metal ion, M^{n+}, has a high charge density, it withdraws sufficient electron density from the O-H bonds of the bonded water molecules, so that a proton can be released ($M(H_2O)_x^{n+}$ acts as a typical Bronsted-Lowry acid):

$$M(H_2O)_x^{n+}(aq) + H_2O(l) \rightleftharpoons M(H_2O)_{x-1}OH^{(n-1)+}(aq) + H_3O^+(aq)$$
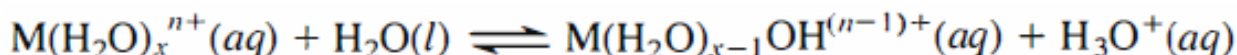
For example, when an aluminum salt, such as $Al(NO_3)_3$ dissolves in water, the following steps occur:

$$Al(NO_3)_3(s) + 6H_2O(l) \longrightarrow Al(H_2O)_6^{3+}(aq) + 3NO_3^-(aq)$$
$$\text{[dissolution and hydration]}$$

$$Al(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftharpoons Al(H_2O)_5OH^{2+}(aq) + H_3O^+(aq)$$
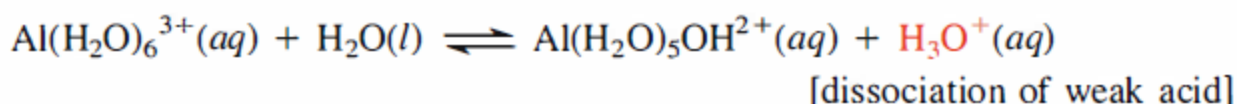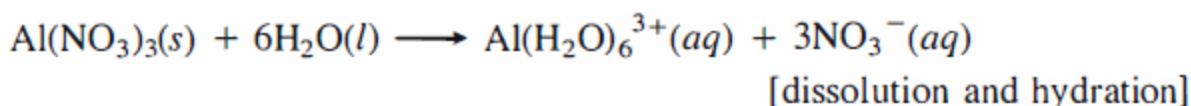$$\text{[dissociation of weak acid]}$$
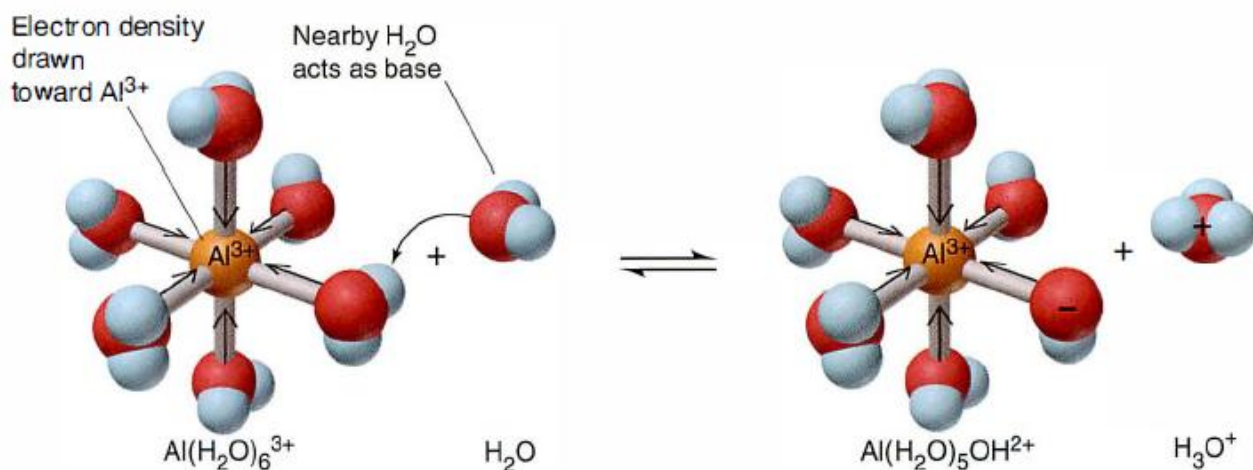
Figure 18.13 The acidic behavior of the hydrated Al^{3+} ion. When a metal ion enters water, it is hydrated as water molecules bond to it. If the ion is small and multiply charged, as is the Al^{3+} ion, it pulls sufficient electron density from the O-H bonds of the attached water molecules to make the bonds more polar, and an H^+ ion is transferred to a nearby water molecule.

18.7 ACID-BASE PROPERTIES OF SALT SOLUTIONS

Some types of salts, when dissolved in water, can affect the pH of the solution. You can predict the relative acidity of a salt solution from the relative ability of the cation and/or anion to react with water.
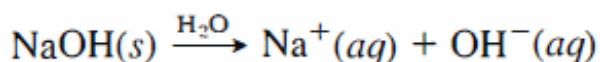
Salts That Yield Neutral Solutions

*A salt consisting of the **anion of a strong acid** and the **cation of a strong base** yields **a neutral solution** because the ions do not react with water.*

When a strong acid such as HNO_3 dissolves, complete dissociation takes place:

$$HNO_3(l) + H_2O(l) \longrightarrow NO_3^-(aq) + H_3O^+(aq)$$
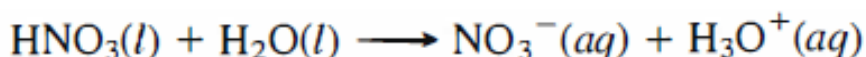
the *anion of a strong acid (NO_3^-) is a much weaker base than water*. Therefore, a strong acid anion is hydrated, but nothing further happens.

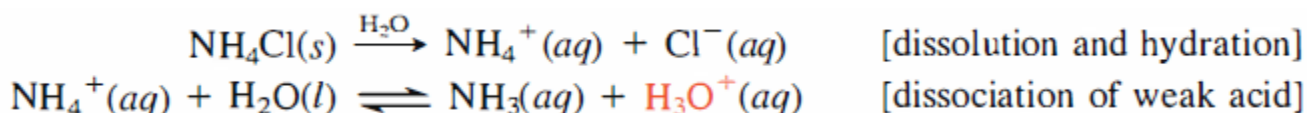Now consider the dissociation of a strong base, such as NaOH:

$$NaOH(s) \xrightarrow{H_2O} Na^+(aq) + OH^-(aq)$$

When *Na^+ enters water, it becomes hydrated but nothing further happens*. The cations of all strong bases behave this way.
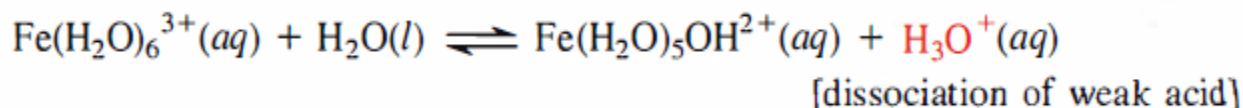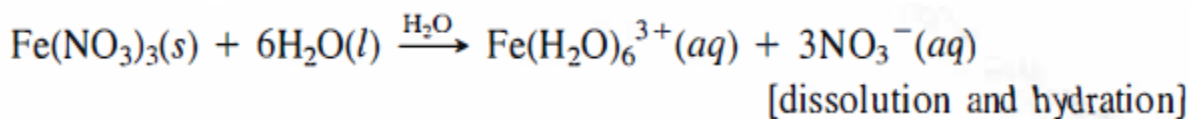
Salts That Yield Acidic Solutions

*A salt consisting of the **anion of a strong acid** and the **cation of a weak base** yields **an acidic solution** because the cation acts as a weak acid, and the anion does not react.*

➢ NH_4Cl produces an acidic solution because the NH_4^+ ion, the cation that forms from the weak base NH_3, is a weak acid, and the Cl^- ion, the anion of a strong acid, does not react.
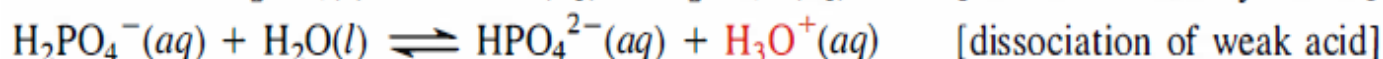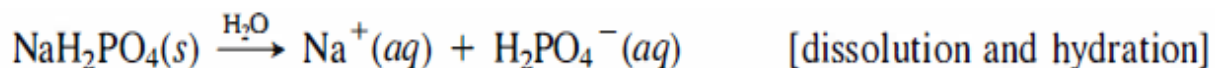
$$NH_4Cl(s) \xrightarrow{H_2O} NH_4^+(aq) + Cl^-(aq) \qquad \text{[dissolution and hydration]}$$
$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq) \qquad \text{[dissociation of weak acid]}$$

➢ Small, highly charged metal ions make up another group of cations that yield H_3O^+ in solution. For example, $Fe(NO_3)_3$ produces an acidic solution;

$$Fe(NO_3)_3(s) + 6H_2O(l) \xrightarrow{H_2O} Fe(H_2O)_6^{3+}(aq) + 3NO_3^-(aq)$$
[dissolution and hydration]

$$Fe(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftharpoons Fe(H_2O)_5OH^{2+}(aq) + H_3O^+(aq)$$
[dissociation of weak acid]

Fe^{3+} ion acts as a weak acid, whereas the NO_3^- ion does not react.

➢ Cations of strong bases and anions of polyprotic acids that still have one or more ionizable protons produce acidic solution.

For example, NaH_2PO_4 yields an acidic solution:

$$NaH_2PO_4(s) \xrightarrow{H_2O} Na^+(aq) + H_2PO_4^-(aq) \qquad \text{[dissolution and hydration]}$$
$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq) \qquad \text{[dissociation of weak acid]}$$

Salts That Yield Basic Solutions

*A salt consisting of the **anion of a weak acid** and the **cation of a strong base** yields a **basic solution** in water because the anion acts as a weak base, and the cation does not react.*

Sodium acetate, for example, yields a basic solution because the Na^+ ion does not react with water, and the CH_3COO^- ion, the anion of the weak acid CH_3COOH, acts as a weak base:
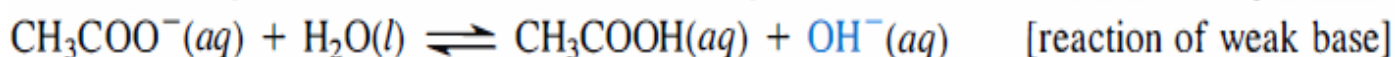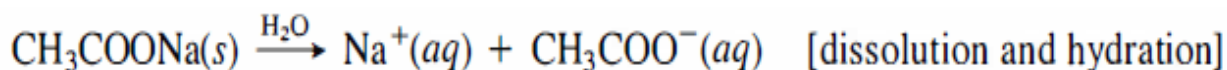
$$CH_3COONa(s) \xrightarrow{H_2O} Na^+(aq) + CH_3COO^-(aq) \quad \text{[dissolution and hydration]}$$
$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq) \quad \text{[reaction of weak base]}$$

Table 18.3 displays the acid-base behavior of the various types of salts in water.

Table 18.3 The Behavior of Salts in Water				
Salt Solution	Examples	pH	Nature of Ions	Ion That Reacts with Water
Neutral	$NaCl$, KBr, $Ba(NO_3)_2$	7.0	Cation of strong base Anion of strong acid	None
Acidic	NH_4Cl, NH_4NO_3, CH_3NH_3Br	<7.0	Cation of weak base Anion of strong acid	Cation
Acidic	$Al(NO_3)_3$, $CrCl_3$, $FeBr_3$	<7.0	Small, highly charged cation Anion of strong base	Cation
Acidic	NaH_2PO_4, $KHSO_4$, $NaHSO_3$	<7.0	Cation of strong base First anion of polyprotic acid	Anion
Basic	CH_3COONa, KF, Na_2CO_3	>7.0	Cation of strong base Anion of weak acid	Anion

SAMPLE PROBLEM 18.10 Predicting Relative Acidity of Salt Solutions

Problem Predict whether aqueous solutions of the following are acidic, basic, or neutral, and write an equation for the reaction of any ion with water:
(a) Potassium perchlorate, $KClO_4$ (b) Sodium benzoate, C_6H_5COONa
(c) Chromium trichloride, $CrCl_3$ (d) Sodium hydrogen sulfate, $NaHSO_4$

Plan We examine the formulas to determine the cations and anions. Depending on the nature of these ions, the solution will be neutral (strong-acid anion and strong-base cation), acidic (weak-base cation and strong-acid anion, highly charged metal cation, or first anion of a polyprotic acid), or basic (weak-acid anion and strong-base cation).

Solution (a) Neutral. The ions are K^+ and ClO_4^-. The K^+ ion is from the strong base KOH, and the ClO_4^- anion is from the strong acid $HClO_4$. Neither ion reacts with water.

(b) Basic. The ions are Na^+ and $C_6H_5COO^-$. Na^+ is the cation of the strong base $NaOH$ and does not react with water. The benzoate ion, $C_6H_5COO^-$, is from the weak acid benzoic acid, so it reacts with water to produce OH^- ion:

$$C_6H_5COO^-(aq) + H_2O(l) \rightleftharpoons C_6H_5COOH(aq) + OH^-(aq)$$

(c) Acidic. The ions are Cr^{3+} and Cl^-. Cl^- is the anion of the strong acid HCl, so it does not react with water. Cr^{3+} is a small metal ion with a high positive charge, so the hydrated ion, $Cr(H_2O)_6^{3+}$, reacts with water to produce H_3O^+:

$$Cr(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftharpoons Cr(H_2O)_5OH^{2+}(aq) + H_3O^+(aq)$$
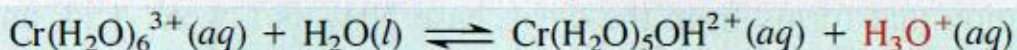
(d) Acidic. The ions are Na^+ and HSO_4^-. Na^+ is the cation of the strong base $NaOH$, so it does not react with water. HSO_4^- is the first anion of the diprotic acid H_2SO_4, and it reacts with water to produce H_3O^+:

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq)$$

FOLLOW-UP PROBLEM 18.10 Write equations to predict whether solutions of the following salts are acidic, basic, or neutral: (a) $KClO_2$; (b) $CH_3NH_3NO_3$; (c) CsI.

Salts of Weakly Acidic Cations and Weakly Basic Anions

The only salts left to consider are those consisting of a **cation that acts as a weak acid** and an **anion that acts as a weak base**. In these cases, both ions react with water, so the overall acidity of the solution depends on the relative acid strength (K_a) or base strength (K_b) of the separated ions.

For example, will an aqueous solution of ammonium cyanide, NH_4CN, be acidic or basic?

Ammonium ion is the conjugate acid of a weak base, so it acts as a weak acid:

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

Cyanide ion is the anion of the weak acid HCN and it acts as a weak base:

$$CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq)$$

We must compare the K_a of NH_4^+ with the K_b of CN^-

$$K_a \text{ of } NH_4^+ = \frac{K_w}{K_b \text{ of } NH_3} = \frac{1.0\times10^{-14}}{1.76\times10^{-5}} = 5.7\times10^{-10}$$

$$K_b \text{ of } CN^- = \frac{K_w}{K_a \text{ of } HCN} = \frac{1.0\times10^{-14}}{6.2\times10^{-10}} = 1.6\times10^{-5}$$
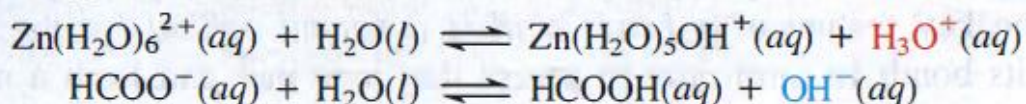
because K_b of CN^- > K_a of NH_4^+, the NH_4CN solution is basic.

SAMPLE PROBLEM 18.11 Predicting the Relative Acidity of a Salt Solution from K_a and K_b of the Ions

Problem Determine whether an aqueous solution of zinc formate, $Zn(HCOO)_2$, is acidic, basic, or neutral.

Plan The formula consists of the small, highly charged, and therefore weakly acidic, Zn^{2+} cation and the weakly basic $HCOO^-$ anion of the weak acid HCOOH. To determine the relative acidity of the solution, we write equations that show the reactions of the ions with water, and then find K_a of Zn^{2+} (from Appendix C) and calculate K_b of $HCOO^-$ (from K_a of HCOOH in Appendix C) to see which ion reacts to a greater extent.

Solution Writing the reactions with water:

$$Zn(H_2O)_6^{2+}(aq) + H_2O(l) \rightleftharpoons Zn(H_2O)_5OH^+(aq) + H_3O^+(aq)$$
$$HCOO^-(aq) + H_2O(l) \rightleftharpoons HCOOH(aq) + OH^-(aq)$$

Obtaining K_a and K_b of the ions: The K_a of $Zn(H_2O)_6^{2+}(aq)$ is 1×10^{-9}. We obtain K_a of HCOOH and solve for K_b of HCOO⁻:

$$K_b \text{ of HCOO}^- = \frac{K_w}{K_a \text{ of HCOOH}} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-4}} = 5.6 \times 10^{-11}$$

K_a of $Zn(H_2O)_6^{2+}$ > K_b of HCOO⁻, so the solution is acidic.

FOLLOW-UP PROBLEM 18.11 Determine whether solutions of the following salts are acidic, basic, or neutral: **(a)** $Cu(CH_3COO)_2$; **(b)** NH_4F.

18.8 ELECTRON-PAIR DONATION AND THE LEWIS ACID-BASE DEFINITION

The final acid-base concept we consider was developed by Gilbert N. Lewis.

The Lewis acid-base definition holds that

➢ A base is any species that donates an electron pair.

➢ An acid is any species that accepts an electron pair.

The Lewis definition, like the Bronsted-Lowry definition, requires that a base have an electron pair to donate, so it does not expand the classes of bases. However, it greatly expands the classes of acids.

Many species, such as CO_2 and Cu^{2+} , that do not contain H in their formula function as Lewis acids by accepting an electron pair in their reactions.

In the Lewis sense, the proton itself functions as an acid because it accepts the electron pair donated by a base.

$$B: + H^+ \rightleftharpoons B-H^+$$

Thus, all Bronsted-Lowry acids donate H^+ , a Lewis acid.

The product of any Lewis acid-base reaction is called an **adduct**, a single species that contains a new covalent bond:

$$A + :B \rightleftharpoons A-B \text{ (adduct)}$$
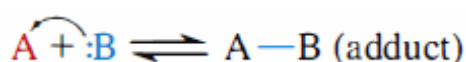
The key feature of a Lewis base is a **lone pair of electrons to donate**. The key feature of a Lewis acid is **a vacant orbital** (or the ability to rearrange its bonds to form one) **to accept** that lone pair and form a new bond.

Molecules as Lewis Acids

Many neutral molecules function as Lewis acids. In every case, the atom that accepts the electron pair is low in electron density because of either an electron deficiency or a polar multiple bond.

Lewis Acids with Electron-Deficient Atoms

The most important of these acids are covalent compounds of the Group 3A(13) elements **boron** and **aluminum**.

o For example, boron trifluoride accepts an electron pair from ammonia to form a covalent bond in a gaseous Lewis acid-base reaction:
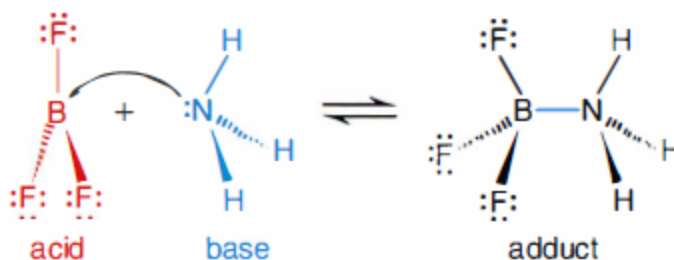

o Unexpected solubility behavior is sometimes due to adduct formation. Aluminum chloride, for instance, dissolves freely in relatively nonpolar diethyl ether because of a Lewis acid-base reaction;
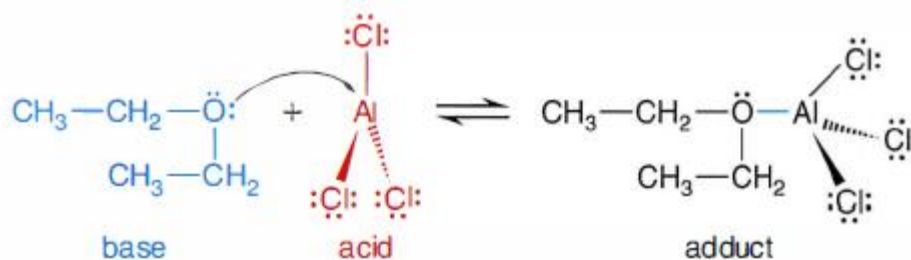
Lewis Acids with Polar Multiple Bonds

Molecules that contain **a polar double bond** also function as Lewis acids. As the electron pair on the Lewis base approaches the partially positive end of the double bond, one of the bonds breaks to form the new bond in the adduct.

- For example, consider the reaction that occurs when SO_2 dissolves in water;
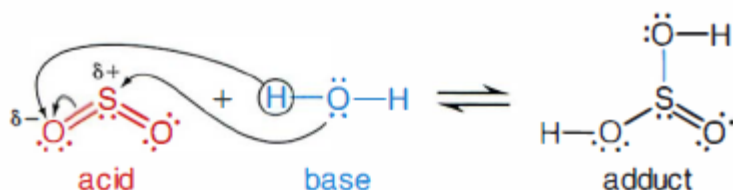

The resulting adduct is sulfurous acid.

- The formation of carbonates from a metal oxide and carbon dioxide is an analogous reaction that occurs in a nonaqueous heterogeneous system;
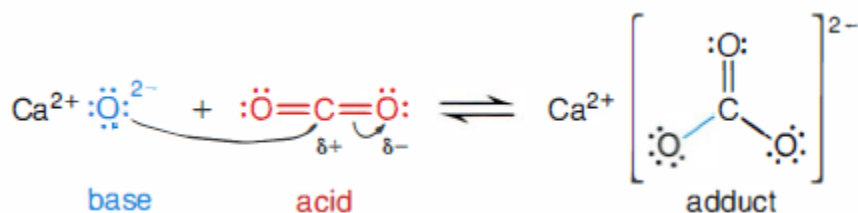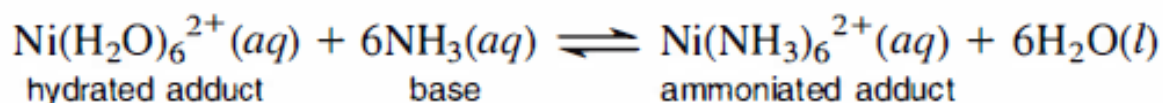

Metal Cations as Lewis Acids

Earlier we saw that certain hydrated metal ions act as Bronsted-Lowry acids. In the Lewis sense, the hydration process itself is an acid-base reaction, and any metal ion acts as a Lewis acid when it dissolves in water:
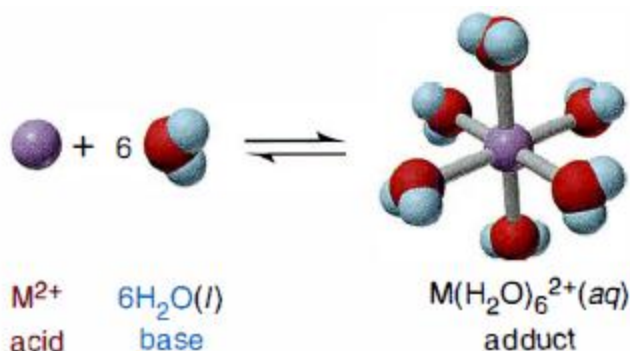
Ammonia is a stronger Lewis base than water because it displaces H_2O from a hydrated ion when aqueous NH_3 is added:

$$Ni(H_2O)_6^{2+}(aq) + 6NH_3(aq) \rightleftharpoons Ni(NH_3)_6^{2+}(aq) + 6H_2O(l)$$
$$\text{hydrated adduct} \qquad\qquad \text{base} \qquad\qquad \text{ammoniated adduct}$$

Many biomolecules are Lewis adducts with central metal ions. Most often, O and N atoms of organic groups, with their lone pairs, serve as the Lewis bases.

✓ Chlorophyll is a Lewis adduct of a Mg^{2+} ion and four N atoms in an organic ring system.

✓ Vitamin B12 has a similar structure with a central Co^{3+}, and so does heme, but with a central Fe^{2+}.

✓ Several other metal ions, such as Zn^{2+}, Mo^{2+}, and Cu^{2+}, are bound at the active sites of enzymes and function as Lewis acids in the enzymes' catalytic action.

SAMPLE PROBLEM 18.12 Identifying Lewis Acids and Bases

Problem Identify the Lewis acids and Lewis bases in the following reactions:
(a) $H^+ + OH^- \rightleftharpoons H_2O$
(b) $Cl^- + BCl_3 \rightleftharpoons BCl_4^-$
(c) $K^+ + 6H_2O \rightleftharpoons K(H_2O)_6^+$
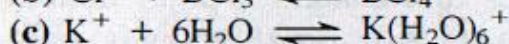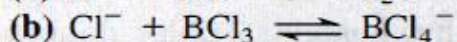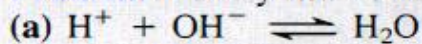
Plan We examine the formulas to see which species accepts the electron pair (Lewis acid) and which donates it (Lewis base) in forming the adduct.

Solution (a) The H^+ ion accepts an electron pair from the OH^- ion in forming a bond. H^+ is the acid and OH^- is the base.
(b) The Cl^- ion has four lone pairs and uses one to form a new bond to the central B. Therefore, BCl_3 is the acid and Cl^- is the base.
(c) The K^+ ion does not have any valence electrons to provide, so the bond is formed when electron pairs from O atoms of water enter empty orbitals on K^+. Thus, K^+ is the acid and H_2O is the base.

Check The Lewis acids (H^+, BCl_3, and K^+) each have an unfilled valence shell that can accept an electron pair from the Lewis bases (OH^-, Cl^-, and H_2O).

FOLLOW-UP PROBLEM 18.12 Identify the Lewis acids and Lewis bases in the following reactions:
(a) $OH^- + Al(OH)_3 \rightleftharpoons Al(OH)_4^-$
(b) $SO_3 + H_2O \rightleftharpoons H_2SO_4$
(c) $Co^{3+} + 6NH_3 \rightleftharpoons Co(NH_3)_6^{3+}$