Pearson

16.9: The Acid–Base Properties of Ions and Salts

Key Concept Video **The Acid-Base Properties of Ions and Salts**

We have already seen that some ions act as bases. For example, the bicarbonate ion acts as a base according to the following equation:

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$$

The bicarbonate ion, like any ion, does not exist by itself; to be charge neutral, it must pair with a counter ion (in this case a cation) to form an ionic compound, called a *salt*. For example, the sodium salt of bicarbonate is sodium bicarbonate. Like all soluble salts, sodium bicarbonate dissociates in solution to form a sodium cation and bicarbonate anion:

$$NaHCO_3(s) \rightarrow Na^+(aq) + HCO_3^-(aq)$$

The sodium ion has neither acidic nor basic properties (it does not ionize water), as we will see shortly. The bicarbonate ion, by contrast, acts as a weak base, ionizing water as just shown to form a basic solution. Consequently, the pH of a sodium bicarbonate solution is above 7 (the solution is basic).

In this section, we consider some of the acid–base properties of salts and the ions they contain. Some salts are pH-neutral when put into water, others are acidic, and still others are basic, depending on their constituent anions and cations. In general, anions tend to form either basic or neutral solutions, while cations tend to form either *acidic* or neutral solutions.

Anions as Weak Bases

We can think of any anion as the conjugate base of an acid. Consider the following anions and their corresponding acids:

This anion	is the conjugate base of	this acid
Cl^-		HCl
F^-		HF
NO_3^-		HNO_3
$C_2H_3O_2^-$		$HC_2H_3O_2$

In general, the anion A^- is the conjugate base of the acid HA. Since every anion can be regarded as the conjugate base of an acid, every anion itself can potentially act as a base. However, *not every anion does act as a base*—it depends on the strength of the corresponding acid. In general:

- An anion that is the conjugate base of a *weak acid* is itself a *weak base*.
- An anion that is the conjugate base of a *strong acid* is pH-*neutral* (forms solutions that are neither acidic nor basic).

For example, the Cl^- anion is the conjugate base of HCl, a strong acid. Therefore, the Cl^- anion is pH-neutral (neither acidic nor basic). The F^- anion, however, is the conjugate base of HF, a weak acid. Therefore, the F^- ion is itself a weak base and ionizes water according to the reaction:

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

We can understand why the conjugate base of a weak acid is basic by asking why an acid is weak to begin with. Hydrofluoric acid is a weak acid because, as we saw in Section 16.4, the HF bond is particularly strong. Therefore, the following reaction lies to the left:

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

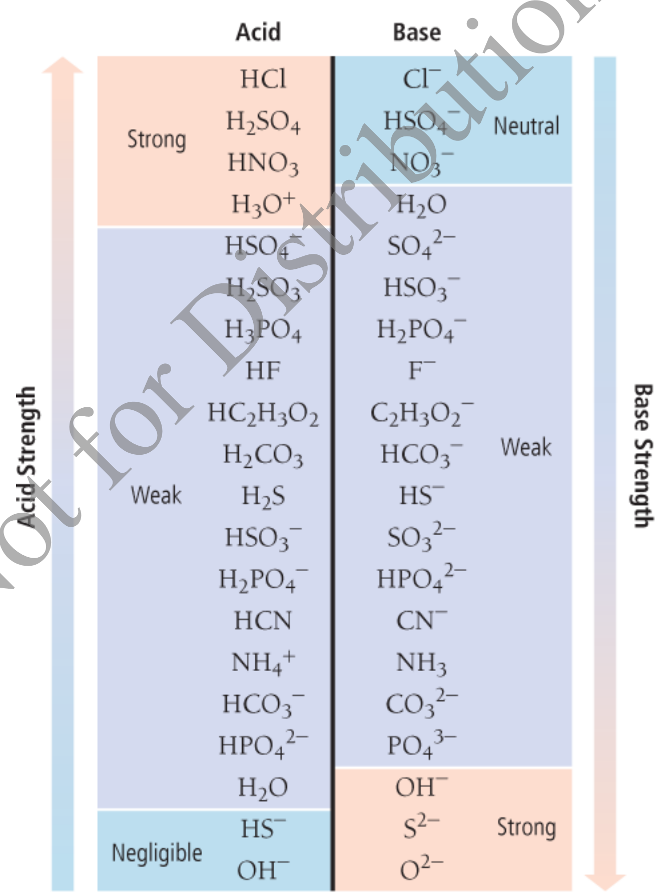
The strength of the HF bond causes the F^- ion to have significant affinity for H^+ ions. Consequently, when F^- is put into water, its affinity for H^+ ions allows it to remove H^+ ions from water molecules, thus acting as a weak base. In general, as shown in Figure 16.12, the weaker the acid, the stronger the conjugate base. In contrast, the conjugate base of a strong acid, such as Cl^-, does not act as a base because the HCl bond is weaker than the HF bond reaction; as a result, this reaction lies far to the right:

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

The Cl^- ion has a relatively lower affinity for H^+ ions. Consequently, when Cl^- is put into water, it does not remove H^+ ions from water molecules.

Figure 16.12 Strength of Conjugate Acid–Base Pairs

The stronger an acid, the weaker is its conjugate base.



Example 16.13 Determining Whether an Anion Is Basic or pH-Neutral

Classify each anion as a weak base or pH-neutral.

a. NO_3^-

b. NO_2^-

c. $C_2H_3O_2^-$

SOLUTION

a. From Table 16.3, you can see that NO_3^- is the conjugate base of a *strong* acid $(HNO_3)$and is therefore pH-neutral.

b. From Table 16.5 (or from its absence in Table 16.3), you know that NO_2^- is the conjugate base of a weak acid $(HNO_2)$and is therefore a weak base.

c. From Table 16.5 (or from its absence in Table 16.3), you know that $C_2H_3O_2^-$ is the conjugate base of a weak acid $(HC_2H_3O_2)$and is therefore a weak base.

FOR PRACTICE 16.13 Classify each anion as a weak base or pH-neutral.

a. CHO_2^-

b. ClO_4^-

We can determine the pH of a solution containing an anion that acts as a weak base in a manner similar to how we determine the pH of any weak base solution. However, we need to know K_b for the anion acting as a base, which we can readily determine from K_a of the corresponding acid. Recall from Section 16.5 the expression for K_a for a generic acid HA:

$$HA\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + A^-\,(aq)$$
$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Similarly, the expression for K_b for the conjugate base (A^-) is:

$$A^-\,(aq) + H_2O\,(l) \rightleftharpoons OH^-\,(aq) + HA\,(aq)$$
$$K_b = \frac{[OH^-][HA]}{[A^-]}$$

If we multiply the expressions for K_a and K_b we get K_w:

$$K_a \times K_b = \frac{[H_3O^+]\ \cancel{[A^-]}\ [OH^-]\ \cancel{[HA]}}{\cancel{[HA]}\qquad\qquad \cancel{[A]}} = [H_3O^+][OH^-] = K_w$$

Or simply,

$$K_a \times K_b = K_w$$

The product of K_a for an acid and K_b for its conjugate base is K_w $(1.0 \times 10^{-14}$ at $25\,°C.)$Consequently, we can find K_b for an anion acting as a base from the value of K_a for the corresponding conjugate acid.

For example, for acetic acid $(HC_2H_3O_2)$, $k_a = 1.8 \times 10^{-5}$. We calculate K_b for the conjugate base $(C_2H_3O_2^-)$by substituting into the equation:

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

Knowing K_b, we can find the pH of a solution containing an anion acting as a base, as demonstrated in Example 16.14.

Example 16.14 Finding the pH of a Solution Containing an Anion Acting as a

Base

Find the pH of a 0.100 M $NaCHO_2$solution. The salt completely dissociates into Na^+ $(aq)$and CHO_2^- (aq) and the Na^+ ion has no acid or base properties.

SOLUTION

1. Since the Na^+ ion does not have any acidic or basic properties, you can ignore it. Write the balanced equation for the ionization of water by the basic anion and use it as a guide to prepare an ICE table showing the given concentration of the weak base as its initial concentration.

$$CHO_2^-\,(aq) + H_2O\,(l) \rightleftharpoons HCHO_2\,(aq) + OH^-\,(aq)$$

	$[CHO_2^-]$	$[HCHO_2]$	$[OH^-]$
Initial	0.100	0.00	≈0.00
Change			
Equil			

2. Represent the change in the concentration of OH^- with the variable x. Define the changes in the concentrations of the other reactants and products in terms of x.

$$CHO_2^-\,(aq) + H_2O\,(l) \rightleftharpoons HCHO_2\,(aq) + OH^-\,(aq)$$

	$[CHO_2^-]$	$[HCHO_2]$	$[OH^-]$
Initial	0.100	0.00	≈0.00
Change	$-x$	$+x$	$+x$
Equil			

3. Sum each column to determine the equilibrium concentrations in terms of the initial concentrations and the variable x.

$$CHO_2^-\,(aq) + H_2O\,(l) \rightleftharpoons HCHO_2\,(aq) + OH^-\,(aq)$$

	$[CHO_2^-]$	$[HCHO_2]$	$[OH^-]$
Initial	0.100	0.00	≈0.00
Change	$-x$	$+x$	$+x$
Equil	$0.100 - x$	x	x

4. Find K_b from K_a (for the conjugate acid from Table 16.5).
Substitute the expressions for the equilibrium concentrations (from Step 3) into the expression for K_b.
In many cases, you can make the approximation that *x is small*.
Substitute the value of K_b into the K_b expression and solve for x.
Confirm that the *x is small* approximation is valid by calculating the ratio of x to the number it was subtracted from in the approximation. The ratio should be less than 0.05 (or 5%).

$$K_a \times K_b = K_w$$
$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-4}} = 5.6 \times 10^{-11}$$
$$K_b = \frac{[HCHO_2][OH^-]}{[CHO_2^-]}$$
$$= \frac{x^2}{0.100 - \cancel{x}} (x \text{ is small})$$
$$5.6 \times 10^{-11} = \frac{x^2}{0.100}$$
$$x = 2.4 \times 10^{-6}$$

$$\frac{2.4 \times 10^{-6}}{0.100} \times 100\% = 0.0024\%$$

Therefore the approximation is valid.

5. Determine the OH^- concentration from the calculated value of x.
Use the expression for K_w to find $[H_3O^+]$.
Substitute $[H_3O^+]$ into the pH equation to find pH.

$$\begin{aligned}
[OH^-] &= 2.4 \times 10^{-6} M \\
[H_3O^+][OH^-] &= K_w = 1.0 \times 10^{-14} \\
[H_3O^+](2.4 \times 10^{-6}) &= 1.0 \times 10^{-14} \\
[H_3O^+] &= 4.2 \times 10^{-9} M \\
pH &= -\log[H_3O^+] \\
&= -\log(4.2 \times 10^{-9}) = 8.38
\end{aligned}$$

FOR PRACTICE 16.14 Find the pH of a 0.250 M $NaC_2H_3O_2$ solution.

Interactive Worked Example 16.14 Finding the pH of a Solution Containing an Anion Acting as a Base

We can also express the relationship between K_a and K_b in terms of pK_a and pK_b. By taking the log of both sides of $K_a \times K_b = K_w$ we get:

$$\begin{aligned}
\log\ (K_a \times K_b) &= \log K_w \\
\log K_a + \log K_b &= \log K_w
\end{aligned}$$

Because $K_w = 10^{-14}$, we can rearrange the equation to get:

$$\log K_a + \log K_b = \log 10^{-14} = -14$$

Rearranging further:

$$-\log K_a - \log K_b = 14$$

Because $-\log K = pK$, we get:

$$pK_a + pK_b = 14$$

Cations as Weak Acids

In contrast to anions, which in some cases act as weak bases, cations can, in some cases, act as *weak acids*. We can generally divide cations into three categories: cations that are the counterions of strong bases; cations that are the conjugate acids of *weak* bases; and cations that are small, highly charged metals. We examine each individually.

Cations That Are the Counterions of Strong Bases

Strong bases such as NaOH or $Ca(OH)_2$ generally contain hydroxide ions and a counterion. In solution, a strong base completely dissociates to form OH^- (aq) and the solvated (in solution) counterion. Although these counterions interact with water molecules via ion–dipole forces, they do not ionize water and they do not contribute to the acidity or basicity of the solution. In *general, cations that are the counterions of strong bases are themselves pH-neutral* (they form solutions that are neither acidic nor basic). For example, Na^+, K^+, and Ca^{2+} are the counterions of the strong bases NaOH, KOH, and $Ca(OH)_2$ and are therefore themselves pH-neutral.

Cations That Are the Conjugate Acids of Weak Bases

A cation can be formed from any nonionic weak base by adding a proton (H^+) to its formula. The cation is the conjugate acid of the base. Consider the following cations and their corresponding weak bases:

This cation	is the conjugate acid of	this weak base
NH_4^+		NH_3
$C_2H_5NH_3^+$		$C_2H_5NH_2$
$CH_3NH_3^+$		CH_3NH_2

Any of these cations, with the general formula BH^+, acts as a weak acid according to the equation:

$$BH^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + B(aq)$$

In general, *a cation that is the conjugate acid of a weak base is a weak acid*.

We can calculate the pH of a solution containing the conjugate acid of a weak base just like that of any other weakly acidic solution. However, the value of K_a for the acid must be derived from K_b using the previously derived relationship: $K_a \times K_b = K_w$

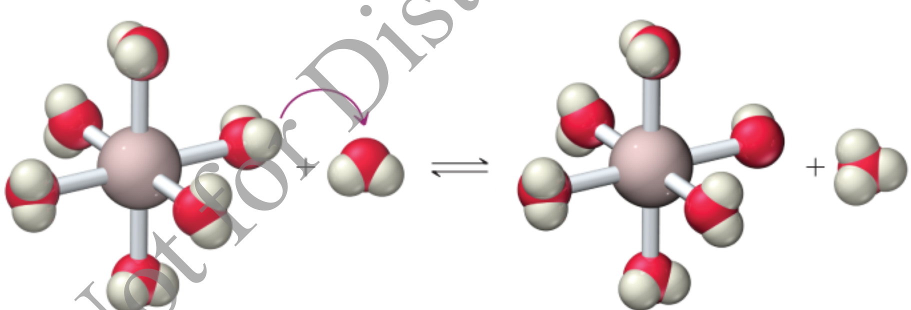
Cations That Are Small, Highly Charged Metals

Small, highly charged metal cations such as Al^{3+} and Fe^{3+} form weakly acidic solutions. For example, when Al^{3+} is dissolved in water, it becomes hydrated according to the equation:

$$Al^{3+}(aq) + 6\,H_2O(l) \rightarrow Al(H_2O)_6^{3+}(aq)$$

The hydrated form of the ion then acts as a Brønsted–Lowry acid:

$$Al(H_2O)_6{}^{3+}(aq) + H_2O(l) \rightleftharpoons Al(H_2O)_5(OH)^{2+}(aq) + H_3O^+(aq)$$



Neither the alkali metal cations nor the alkaline earth metal cations ionize water in this way, but the cations of many other metals do. The smaller and more highly charged the cation, the more acidic its behavior.

Example 16.15 Determining Whether a Cation Is Acidic or pH-Neutral

Classify each cation as a weak acid or pH-neutral.

a. $C_5H_5NH^+$
b. Ca^{2+}
c. Cr^{3+}

SOLUTION

a. The $C_5H_5NH^+$ cation is the conjugate acid of a weak base and is therefore a weak acid.

b. The Ca^{2+} cation is the counterion of a strong base and is therefore pH-neutral (neither acidic nor basic).

c. The Cr^{3+} cation is a small, highly charged metal cation and is therefore a weak acid.

FOR PRACTICE 16.15 Classify each cation as a weak acid or pH-neutral.

a. Li^{+}

b. $CH_3NH_3^{+}$

c. Fe^{3+}

Classifying Salt Solutions as Acidic, Basic, or Neutral

Since salts contain both a cation and an anion, they can form acidic, basic, or neutral solutions when dissolved in water. The pH of the solution depends on the specific cation and anion involved. We examine the four possibilities individually.

1. **Salts in which neither the cation nor the anion acts as an acid or a base form pH-neutral solutions.** A salt in which the cation is the counterion of a strong base and in which the anion is the conjugate base of a strong acid forms a *neutral* solution. Some salts in this category include:

$NaCl$ sodium chloride — $Ca(NO_3)_2$ calcium nitrate — KBr potassium bromide

Cations are pH-neutral. Anions are conjugate bases of strong acids.

2. **Salts in which the cation does not act as an acid and the anion acts as a base form basic solutions.** A salt in which the cation is the counterion of a strong base and in which the anion is the conjugate base of a *weak* acid forms a *basic* solution. Salts in this category include:

NaF sodium fluoride — $Ca(C_2H_3O_2)_2$ calcium acetate — KNO_2 potassium nitrite

Cations are pH-neutral. Anions are conjugate bases of weak acids.

3. **Salts in which the cation acts as an acid and the anion does not act as a base form acidic solutions.** A salt in which the cation is either the conjugate acid of a weak base or a small, highly charged metal ion and in which the anion is the conjugate base of a *strong* acid forms an *acidic* solution. Salts in this category include:

$FeCl_3$ iron(III) chloride — $Al(NO_3)_3$ aluminum nitrate — NH_4Br ammonium bromide

Cations are conjugate acids of weak bases or small, highly charged metal ions. Anions are conjugate bases of *strong* acids.

4. **Salts in which the cation acts as an acid and the anion acts as a base form solutions in which the pH depends on the relative strengths of the acid and the base.** A salt in which the cation is either the conjugate acid of a weak base or a small, highly charged metal ion and in which the anion is the conjugate base of a *weak* acid forms a solution in which the pH depends on the relative strengths of the acid and base. Salts in this category include:

FeF_3 iron(III) fluoride — $Al(C_2H_3O_2)_3$ aluminum acetate — NH_4NO_2 ammonium nitrite

Cations are conjugate acids of weak bases or small, highly charged metal ions.

Anions are conjugate bases of *weak* acids.

We can determine the overall pH of a solution containing one of these salts by comparing the K_a of the acid to the K_b of the base—the ion with the higher value of K dominates and determines whether the solution will be acidic or basic, as shown in part e of Example 16.16. Table 16.9 summarizes these possibilities.

Table 16.9 pH of Salt Solutions

		ANION	
		Conjugate base of strong acid	**Conjugate base c**
CATION	**Conjugate acid of weak base**	Acidic	Depends on relat
	Small, highly charged metal ion	Acidic	Depends on relat
	Counterion of strong base	Neutral	Basic

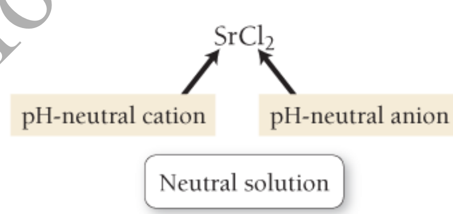
Example 16.16 Determining the Overall Acidity or Basicity of Salt Solutions

Determine if the solution formed by each salt is acidic, basic, or neutral.

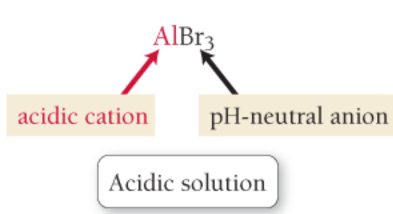
a. $SrCl_2$
b. $AlBr_3$
c. $CH_3NH_3NO_3$
d. $NaCHO_2$
e. NH_4F

SOLUTION

a. The Sr^{2+} cation is the counterion of a strong base $[Sr(OH)_2]$ and is pH-neutral. The Cl^- anion is the conjugate base of a strong acid (HCl) and is pH-neutral as well. The $SrCl_2$ solution is therefore pH-neutral (neither acidic nor basic).



b. The Al^{3+} cation is a small, highly charged metal ion (that is not an alkali metal or an alkaline earth metal) and is a weak acid. The Br^- anion is the conjugate base of a strong acid (HBr) and is pH-neutral. The $AlBr_3$ solution is therefore acidic.



c. The $CH_3NH_3^+$ ion is the conjugate acid of a weak base and is acidic. The (CH_3NH_2)anion is the conjugate base of a strong acid $(HNO_3)$and is pH-neutral. The $CH_3NH_3NO_3$solution is therefore acidic.

$CH_3NH_3NO_3$

acidic cation | pH-neutral anion

Acidic solution

d. The Na^+ cation is the counterion of a strong base and is pH-neutral. The CHO_2^- anion is the conjugate base of a weak acid and is basic. The $NaCHO_2$ solution is therefore basic.

$NaCHO_2$

pH-neutral cation | basic anion

Basic solution

e. The NH_4^+ ion is the conjugate acid of a weak base $(NH_3)$and is acidic. The F^- ion is the conjugate base of a weak acid and is basic. To determine the overall acidity or basicity of the solution, compare the values of K_a for the acidic cation and K_b for the basic anion. Obtain each value of K from the conjugate by using $K_a \times K_b = K_w$..

Since K_a is greater than K_b the solution is acidic.

NH_4F

acidic cation | basic anion

$$K_a(NH_4{}^+) = \frac{K_w}{K_b(NH_3)} = \frac{1.0 \times 10^{-14}}{1.76 \times 10^{-5}}$$
$$= 5.68 \times 10^{-10}$$
$$K_b(F^-) = \frac{K_w}{K_a(HF)} = \frac{1.0 \times 10^{-14}}{6.8 \times 10^{-4}}$$
$$= 1.5 \times 10^{-11}$$
$$K_a > K_b$$

Acidic solution

FOR PRACTICE 16.16 Determine if the solution formed by each salt is acidic, basic, or neutral.

a. $NaHCO_3$
b. $CH_3CH_2NH_3Cl$
c. KNO_3
d. $Fe(NO_3)_3$