

ACID-BASE EQUILIBRIA

TOPIC

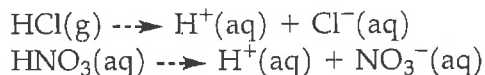
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A large portion of the AP exam is taken from the topic of acid-base equilibria treated in Chapters 16 and 17 of *Chemistry the Central Science*. It is important to be able to calculate quantitative parameters, especially pH, of solutions of strong and weak acids and bases. Writing and understanding chemical equations illustrating the Brønsted-Lowry definition of acids and bases and their relationships to the K_a and K_b expressions is important. It's also imperative to understand acid-base hydrolysis of salt solutions and how chemical structure affects acid-base behavior. Know how to recognize strong and weak acids and bases from their formulas and understand Lewis acids and bases.

Acids and Bases: A Brief Review

Section 16.1

The Arrhenius concept of acids and bases states that acids ionize in water solution to produce hydrogen ions. Acids are substances that increase the hydrogen ion, H^+ , concentration when dissolved in water. For example:



Bases are substances that increase the concentration of hydroxide ion, OH^- , when dissolved in water. A base dissociates to produce hydroxide ions in water. Notice in the examples below that sodium hydroxide is "monobasic" and barium hydroxide is "dibasic". The prefixes mono- and di- refer to the number of available hydroxides in each formula.



Section 16.5 Strong Acids and Bases

Strong acids and strong bases are strong electrolytes. Strong acids and strong bases ionize completely in dilute aqueous solution. There are seven common strong acids, and eight common strong bases. It is useful to memorize their names and formulas given in Table 16.1. Notice that the strong bases are the hydroxides of the Group 1 alkali metals, and the hydroxides of the heavier Group 2 alkaline earth metals. Strong acids and bases are generally, but not always, associated with the Arrhenius model for acids and bases.

Table 16.1. The names and formulas of strong acids and strong bases

Strong Acids		Strong Bases	
*sulfuric acid	H ₂ SO ₄	lithium hydroxide	LiOH
nitric acid	HNO ₃	sodium hydroxide	NaOH
perchloric acid	HClO ₄	potassium hydroxide	KOH
chloric acid	HClO ₃	rubidium hydroxide	RbOH
hydrochloric acid	HCl	cesium hydroxide	CsOH
hydrobromic acid	HBr	**calcium hydroxide	Ca(OH) ₂
hydroiodic acid	HI	**strontium hydroxide	Sr(OH) ₂
		**barium hydroxide	Ba(OH) ₂

*Sulfuric acid is a diprotic acid and only the first proton ionizes completely.

**Ca(OH)₂, Sr(OH)₂, and Ba(OH)₂ are dibasic and in each case, only the first hydroxide group dissociates completely.



Common misconception: The strong diprotic acid, sulfuric acid, H₂SO₄, does not dissociate completely. Therefore in an aqueous solution of sulfuric acid the concentration of the H⁺ ions are not double the concentration of the acid. The same is true of strong dibasic bases such as calcium hydroxide. In a solution of calcium hydroxide, Ca(OH)₂, the concentration of the OH⁻ ion is not double that of the calcium hydroxide.

Neutral ions, in general, are the aqueous anions of strong acids and the aqueous cations of strong bases. Table 16.2 lists the common cations and anions that are neutral in aqueous solution. In general, most all other anions are slightly basic and most all other cations are slightly acidic.

Table 16.2. Neutral ions are the aqueous anions of strong acids and the aqueous cations of strong bases

Neutral Aqueous Anions		Neutral Aqueous Cations	
nitrate	NO_3^-	lithium ion	Li^+
perchlorate	ClO_4^-	sodium ion	Na^+
chlorate	ClO_3^-	potassium ion	K^+
chloride	Cl^-	rubidium ion	Rb^+
bromide	Br^-	cesium ion	Cs^+
iodide	I^-	calcium ion	Ca^{2+}
* sulfate	SO_4^{2-}	strontium ion	Sr^{2+}
		barium ion	Ba^{2+}

* Sulfate ion, SO_4^{2-} , is weakly basic.

Your Turn 16.1

Explain why aqueous solutions of all of the following salts are neutral: NaCl , KNO_3 , LiClO_4 , BaBr_2 , CsI . Write your answer in the space provided.

Brønsted-Lowry Acids and Bases Section 16.2

The Brønsted-Lowry theory states:

Acids are proton (H^+) donors.

Bases are proton acceptors.

Consider the interaction of hydrogen chloride gas with water:



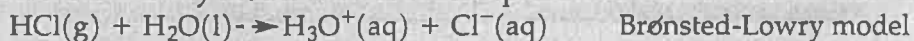
HCl is an acid because it donates a proton to water. H₂O is a base because it accepts a proton.

Hydronium ion, H₃O⁺(aq), is a hydrated proton. When water accepts a proton from an acid, the product is a hydronium ion.

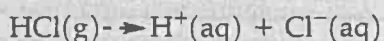
Notice that when water accepts a proton from HCl it becomes H₃O⁺. H₃O⁺(aq) is a hydrated proton called the hydronium ion.



Common misconception: Chemists use H⁺(aq) and H₃O⁺(aq) interchangeably to represent a hydrated proton, the ion responsible for the acidic properties of an aqueous solution. Both of the following equations are chemically equivalent. Notice how one emphasizes the Brønsted-Lowry model and the other represents the Arrhenius model.

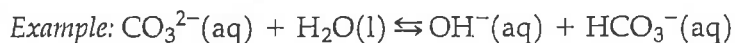


acid base



Arrhenius model

Sodium carbonate, Na₂CO₃, is a Brønsted-Lowry base because the carbonate ion accepts a proton from water. Water is an acid because it donates a proton to carbonate ion. Since the sodium ion is a neutral ion, we ignore it in the equation:



base acid

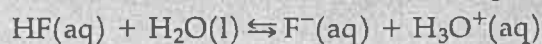
Conjugate acid-base pairs are two substances in aqueous solution whose formulas differ by an H⁺. The acid is the more positive species having the extra H. (See Table 16.3.)

Table 16.3. Examples of acid-base conjugate pairs

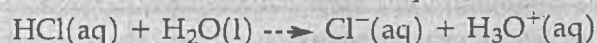
Acid	Base	Equations Involving Acid-Base Conjugate Pairs
NH ₄ ⁺ H ₂ O	NH ₃ OH ⁻	NH ₃ (g) + H ₂ O(l) ⇌ NH ₄ ⁺ (aq) + OH ⁻ (aq) base acid acid base
H ₂ SO ₃ H ₃ O ⁺	HSO ₃ ⁻ H ₂ O	H ₂ SO ₃ (aq) + H ₂ O(l) ⇌ HSO ₃ ⁻ (aq) + H ₃ O ⁺ (aq) acid base base acid

Acid-base reactions are reversible reactions. The reversible equations in Table 16.3 illustrate the focus of the Brønsted-Lowry model on the transfer of protons. In each reaction there are two sets of acid-base conjugate pairs.

Common misconception: HF is a weak acid so F^- is the conjugate base of HF. The reaction of HF with water is expressed as a reversible equilibrium:



However, HCl is a strong acid so Cl^- is not a conjugate base of HCl. The reaction of HCl with water is expressed as an irreversible reaction:



Because the HCl reaction is not reversible, Cl^- does not accept a proton, and is not a base. The same is true of all anions of strong monoprotic acids.



An **amphoteric** substance is one that can act either as an acid or a base. Notice in Table 16.3 that water acts as an acid when it transfers a proton to ammonia. It acts as a base when accepting a proton from sulfurous acid. Water is amphoteric because it can act as an acid or a base.

Weak Acids

Section 16.6

Weak acids are acidic substances that only partially ionize in aqueous solution. Weak acids are weak electrolytes. For example, hydrofluoric acid, acetic acid, and nitrous acid are all weak acids. (Each ionizes only partially to establish an equilibrium between the acid and its conjugate base.)

Table 16.4 shows the ionization of some weak acids in water. A more complete listing of the ionization constants of weak acids can be found in Appendix D, Table D-1 of *Chemistry the Central Science*.

Table 16.4. Ionization of some weak acids in water

Weak Acid	Conjugate Base	Equilibrium Expression, K_a	Value of K_a
$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$		$K_a = [H_3O^+][F^-]/[HF]$	6.8×10^{-4}
$HClO(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + ClO^-(aq)$		$K_a = [H_3O^+][ClO^-]/[HClO]$	3.0×10^{-8}
$HIO(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + IO^-(aq)$		$K_a = [H_3O^+][IO^-]/[HIO]$	2.3×10^{-11}
$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$		$K_{a1} = [H_3O^+][HCO_3^-]/[H_2CO_3]$	4.3×10^{-7}
$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$		$K_{a2} = [H_3O^+][CO_3^{2-}]/[HCO_3^-]$	5.6×10^{-11}

Section 16.7 Weak Bases

Weak bases are also weak electrolytes. Weak bases only partially ionize solution. Table 16.5 shows the ionization of some weak bases in water. A more complete listing of the ionization constants of weak bases can be found in Appendix D, Table D-2 of *Chemistry the Central Science*.

Table 16.5. Ionization of some weak bases in water

Weak Base	Conjugate Acid	Equilibrium Expression, K_b	Value
$\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{OH}^-(\text{aq}) + \text{NH}_4^+(\text{aq})$		$K_b = [\text{OH}^-][\text{NH}_4^+]/[\text{NH}_3]$	1.8×10^{-5}
$\text{C}_5\text{H}_5\text{N}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{OH}^-(\text{aq}) + \text{C}_5\text{H}_5\text{NH}^+(\text{aq})$		$K_b = [\text{OH}^-][\text{C}_5\text{H}_5\text{NH}^+]/[\text{C}_5\text{H}_5\text{N}]$	1.7×10^{-9}
$\text{HCO}_3^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{OH}^-(\text{aq}) + \text{H}_2\text{CO}_3(\text{aq})$		$K_b = [\text{OH}^-][\text{H}_2\text{CO}_3]/[\text{HCO}_3^-]$	2.3×10^{-8}
$\text{F}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{OH}^-(\text{aq}) + \text{HF}(\text{aq})$		$K_b = [\text{OH}^-][\text{HF}]/[\text{F}^-]$	1.5×10^{-11}

Weak bases tend to be neutral nitrogen compounds called amines, and anions other than the anions of strong acids. Amines have a pair of electrons that can attract protons. Anions have negative charges that can also attract protons.

The **acid ionization constant K_a** , is the equilibrium constant for the ionization of a weak acid in water.

The **base ionization constant K_b** , is the ionization constant for a weak base.



Common misconception: K_a and K_b are not new ideas. The respective subscripts "a" and "b" denote that K_a is a special case of K_c used to specify the ionization of a weak acid in water and that K_b is a special case for a weak base. Also, K_a and K_b are sometimes called the acid dissociation constant and the base dissociation constant, respectively.

The value of K_a or K_b indicates the relative extent to which a weak acid or weak base ionizes. For example, the larger the K_a , the greater the extent to which the acid ionizes. When comparing two weak acids, the one with the

larger K_a is said to be the "stronger" weak acid. It ionizes to a larger extent. Of the acids listed in Table 16.4, hydrofluoric acid, HF, has the largest K_a , so it ionizes to the greatest extent. HF is said to be the strongest of the weak acids listed. Similarly, of the bases listed in Table 16.5, ammonia, NH_3 , has the largest K_b so it is the strongest weak base of those listed.

Which acid listed in Table 16.4 is the weakest? Which base listed in Table 16.5 is the weakest base? On what do you base your answers? Write your answers in the space provided.

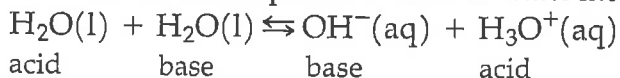
Your Turn 16.2

Carbonic acid, H_2CO_3 , is an example of a weak diprotic acid. Table 16.4 shows two ionization constants for carbonic acid. K_{a1} is the equilibrium constant for the ionization of the first proton. K_{a2} represents the equilibrium constant for the second proton ionization. For all polyprotic acids, the first proton to ionize is always the most readily ionized. The K_a value becomes successively smaller as successive protons are removed so $K_{a1} > K_{a2} > K_{a3}$.

The Autoionization of Water

Section 16.3

The **autoionization of water** is a reversible equilibrium where a water molecule transfers a proton to another water molecule.



Water is both a weak acid and a weak base. It is amphoteric. It has the ability to act as a proton donor (an acid) or a proton acceptor (a base).

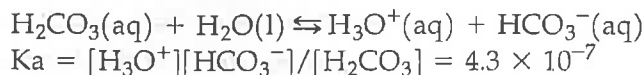
The **ion product constant** for water, K_w , is the equilibrium constant for the autoionization of water. K_w is a special case of K_c .

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

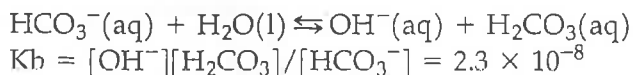
Section 16.8 **The Relationship Between K_a and K_b**

For any conjugate acid-base pair, $K_w = K_a \times K_b$.

Consider, for example, the reaction of carbonic acid with water:



Hydrogen carbonate ion, HCO_3^- , is the conjugate base of the weak acid, H_2CO_3 . Hydrogen carbonate reacts with water according to the following equation:



Common misconception: It is customary to tabulate only K_a or K_b for a conjugate pair because, using the relationship, one can be conveniently converted to the other. Typically only the equilibrium constants for non-ionic species appear in a table. For example, the K_b for ammonia, NH_3 , is reported in Appendix D of *Chemistry the Central Science*, but not the K_a for the conjugate acid ammonium ion, NH_4^+ . Similarly the K_a for acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, appears in Appendix D, but not the K_b for the conjugate base acetate ion, $\text{C}_2\text{H}_3\text{O}_2^-$. It is important to be able to recognize the conjugate of any given acid or base and to know how to calculate its corresponding K_a or K_b .

K_b for any conjugate base is the ratio of K_w to K_a of the acid:

$$K_b = K_w/K_a = ([\text{OH}^-][\text{H}_3\text{O}^+])/([\text{H}_3\text{O}^+][\text{HCO}_3^-]/[\text{H}_2\text{CO}_3])$$

$$= [\text{OH}^-][\text{H}_2\text{CO}_3]/[\text{HCO}_3^-]$$

$$K_b = K_w/K_a = 1.0 \times 10^{-14}/4.3 \times 10^{-7} = 2.3 \times 10^{-8}$$

Recall that water and protonated anions (HCO_3^- , HSO_3^- , H_2PO_4^- , etc.) tend to be amphoteric. That is, they can act as either acids or bases. To tell whether a protonated anion is acidic or basic in water we can do one of three things: Measure the pH of an aqueous solution containing the anion, use an acid-base indicator, or calculate and compare the K_a and K_b of the anion. If the K_a of the anion is larger than its corresponding K_b , the anion forms an aqueous solution that is acidic. If its K_b is larger, the solution is basic.

Table 16.6. The ionization of phosphoric acid

	Acid Ionization	Acid Ionization Constant
1	$\text{H}_3\text{PO}_4(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{H}_2\text{PO}_4^-(\text{aq})$	$K_{a1} = 7.5 \times 10^{-3}$
2	$\text{H}_2\text{PO}_4^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{HPO}_4^{2-}(\text{aq})$	$K_{a2} = 6.2 \times 10^{-8}$
3	$\text{HPO}_4^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{PO}_4^{3-}(\text{aq})$	$K_{a3} = 4.2 \times 10^{-13}$
	Base Ionization	Base Ionization Constant
4	$\text{H}_2\text{PO}_4^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{OH}^-(\text{aq}) + \text{H}_3\text{PO}_4(\text{aq})$	$K_b = K_w/K_{a1}$
5	$\text{HPO}_4^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{OH}^-(\text{aq}) + \text{H}_2\text{PO}_4^-(\text{aq})$	$K_b = K_w/K_{a2}$
6	$\text{PO}_4^{3-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{OH}^-(\text{aq}) + \text{HPO}_4^{2-}(\text{aq})$	$K_b = K_w/K_{a3}$

Consider the triprotic acid, phosphoric acid, H_3PO_4 . The sequential ionization of its three protons and the corresponding K_a 's are illustrated by the equations in Table 16.6. Notice that two species involved in the equations are amphoteric protonated anions, H_2PO_4^- and HPO_4^{2-} , and their reaction as bases are also illustrated in Table 16.6.

Example:

Is an aqueous solution of Na_2HPO_4 acidic or basic?

Solution:

Calculate the value of K_b for HPO_4^{2-} and compare it to the value of K_{a3} for HPO_4^{2-} . (Keep in mind that the aqueous sodium ion, $\text{Na}^+(\text{aq})$, is neutral.) The larger ionization constant will predict the acid-base characteristic of its aqueous solution.

For Equation 5,

$$K_b = K_w/K_{a2} = 1.0 \times 10^{-14}/6.2 \times 10^{-8} = 1.6 \times 10^{-7}$$

(We use K_{a2} to calculate the K_b for Equation 5 because Equation 5 includes the same conjugate pair as Equation 2.)

$$K_a = 4.2 \times 10^{-13} < K_b = 1.6 \times 10^{-7}$$

Because its K_b is larger than its K_a , HPO_4^{2-} forms a basic solution.

Lewis Acids and Bases

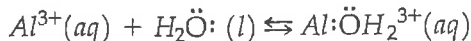
Section 16.11

A **Lewis acid** is an electron-pair acceptor.

A **Lewis base** is an electron-pair donor.

Example:

In the following equation, which species acts as a Lewis acid and which acts as a Lewis base? Explain:

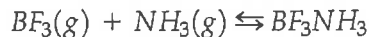
**Solution:**

In the example equation, the aluminum ion acts as a Lewis acid because it accepts a pair of electrons forming a covalent bond to oxygen. The water molecule acts as a Lewis base because it donates a pair of electrons.

Lewis acids commonly are highly charged metal cations in aqueous solutions. Their high charge allows them to attract a nonbonding pair of electrons belonging to one or more water molecules.

Your Turn 16.3

In the following equation, which species acts as a Lewis acid and which acts as a Lewis base? Explain:



Write your answer in the space provided.

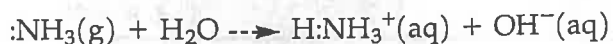
All three theories, Arrhenius, Brønsted-Lowry, and Lewis, are different ways of visualizing the same concept. The different classifications lead to different insights in understanding acid-base reactions.



Common misconception: Although aqueous calcium ion, Ca^{2+} , is the cation of a strong base and is generally considered to be neutral, it does show slightly acidic properties consistent with Lewis acid character and ion pairing.

The Arrhenius model focuses on what ions (H^+ for acids and OH^- for bases) are produced in solution. The Brønsted-Lowry model demonstrates acids and bases as proton transfer agents in chemical reactions. The Lewis concept emphasizes the pair of electrons that constitute bond-breaking and bond-making in an acid-base reaction.

Consider the reaction of ammonia with water:



Ammonia is clearly an Arrhenius base because it increases the hydroxide ions in solution. It is also a Brønsted-Lowry base because it accepts a proton.

Additionally it is a Lewis base because it donates a pair of electrons to make a new bond between nitrogen and hydrogen. Table 16.7 summarizes the major points of the three acid-base theories.

Table 16.7. Comparing acid-base models with definitions and examples

Model	Definition	Example Equation
Arrhenius acid Arrhenius base	Increases H^+ in solution Increases OH^- in solution	$\text{HCl}(\text{g}) \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ $\text{NaOH}(\text{s}) \rightarrow \text{Na}^+(\text{aq}) + \text{OH}^-(\text{aq})$
Brønsted acid Brønsted base	Proton donor Proton acceptor	$\text{HNO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{NO}_2^-(\text{aq})$ $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$
Lewis acid Lewis base	Electron pair acceptor Electron pair donor	$\text{Al}^{3+}(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{Al}:\text{OH}_2^{3+}(\text{aq})$ $\text{Ag}^+(\text{aq}) + :\text{NH}_3(\text{aq}) \rightleftharpoons \text{Ag}:\text{NH}_3^+(\text{aq})$

The pH Scale

Section 16.4

Molar concentrations of $\text{H}^+(\text{aq})$ are often expressed as pH, approximated for most solutions as the negative logarithm (base 10) of $[\text{H}^+]$.

$$\text{pH} = -\log[\text{H}^+] \quad \text{or} \quad \text{pH} = -\log[\text{H}_3\text{O}^+]$$

This mathematical model is accurate for pH's ranging from 2–12 and is often used as an approximation for pH's ranging from 0 to 14. Table 16.8 shows the relationships among $[\text{H}^+]$, $[\text{OH}^-]$, pH, and pOH for various solutions.

Table 16.9 shows the mathematical relationships involving pH. Notice that the equations in the left hand column of Table 16.9 are the logarithmic forms of the equations in the right hand column.

Table 16.8. The pH scale: Relationships of $[H^+]$, $[OH^-]$, pH, and pOH

$[H^+]$	pH	pOH	$[OH^-]$
1×10^{-14} 1×10^{-13}	14 13	0 1	1×10^{-0} 1×10^{-1}
1×10^{-12} 1×10^{-11}	12 11	2 3	1×10^{-2} 1×10^{-3}
1×10^{-10} 1×10^{-9}	10 9	4 5	1×10^{-4} 1×10^{-5}
1×10^{-8} 1×10^{-7}	8 7	6 7	1×10^{-6} 1×10^{-7}
1×10^{-6} 1×10^{-5}	6 5	8 9	1×10^{-8} 1×10^{-9}
1×10^{-4} 1×10^{-3}	4 3	10 11	1×10^{-10} 1×10^{-11}
1×10^{-2} 1×10^{-1}	2 1	12 13	1×10^{-12} 1×10^{-13}
1×10^{-0}	0	14	1×10^{-14}



Common misconception: It's common to see pH scales ranging from 0 to 14 as illustrated in Table 16.8. However, the assumption that $pH = -\log[H^+]$ is valid only for pH's ranging from about 2 through 12. At higher and lower pH's, which represent higher concentrations of acid or base, ion-ion pairing is common and $pH = -\log[H^+]$ is invalid.

Table 16.9. Mathematical relationships for interconverting $[H^+]$, $[OH^-]$, pH, and pOH

$pH = -\log[H^+]$	$[H^+] = 10^{-pH}$
$pOH = -\log[OH^-]$	$[OH^-] = 10^{-pOH}$
$pH + pOH = 14$	$[H^+][OH^-] = 1 \times 10^{-14}$

Table 16.10. Mathematical relationships for calculating $[H^+]$ and $[OH^-]$ in strong and weak acid and base solutions

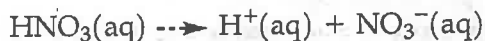
	Acid	Base
strong	$x = I$	$y = I$ (monobasic)
		$y = 2 \times I$ (dibasic)
weak	$K_a = x^2/I$ if $I > 100 K_a$	$K_b = y^2/I$ if $I > 100 K_b$
	$K_a \times K_b = K_w = 1 \times 10^{-14}$	

I = initial molar concentration of acid or base
 x = the moles per liter of acid that ionize
 y = the moles per liter of base that ionize

Calculations Involving Strong Acids and Strong Bases

Section 16.5

Strong acids ionize completely. Therefore no equilibrium is established because all of the initial concentration of the reactant acid is converted to products. For all strong acids the ICE tables are the same. For example, the ICE table for the ionization of 0.20 M nitric acid is:



<i>I</i>	0.20	0	0
<i>C</i>	-0.20	+0.20	+0.20
<i>E</i>	0	0.20	0.20

All of the strong acid ionizes so the initial concentration of the acid is the same as the final concentration of H^+ ion.

Example:

Calculate the $[H^+]$ and pH in a solution of 0.015M nitric acid, HNO_3 .

Solution:

$$[HNO_3] = [H^+] = 0.015 M$$

$$pH = -\log(0.015) = 1.82.$$

By similar reasoning, the $[OH^-]$ of a strong base solution is the same as the concentration of a monobasic strong base and double the concentration of a dibasic strong base.

$I = y$ for monobasic and

$I = 2y$ for dibasic where y = the moles per liter of base that ionizes.

Example:

Calculate the $[\text{OH}^-]$ and the pH in a 0.025 M KOH solution and the $[\text{OH}^-]$ and the pH in a 0.025 M $\text{Ba}(\text{OH})_2$ solution.

Solution:

For the KOH solution,

$$[\text{KOH}] = [\text{OH}^-] = 0.025 \text{ M}$$

$$p\text{OH} = -\log(0.025) = 1.60.$$

$$p\text{H} = 14 - p\text{OH} = 14 - 1.60 = 12.40.$$

For the solution of $\text{Ba}(\text{OH})_2$,

$$[\text{OH}^-] = 2 \times [\text{Ba}(\text{OH})_2] = 2 \times 0.025 \text{ M} = 0.050 \text{ M}$$

$$p\text{OH} = -\log(0.050) = 1.30.$$

$$p\text{H} = 14 - p\text{OH} = 14 - 1.30 = 12.70.$$

Section 16.6 Calculations Involving Weak Acids

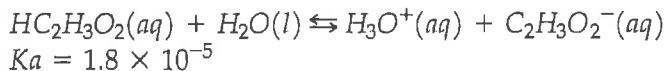
The ionization of a weak acid in water is a reversible equilibrium, and each weak acid ionization produces the same "ICE" table.

Example:

What is the pH of a 0.15 M solution of acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$?

Solution:

First set up an ICE table for the ionization of an initial concentration of acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$. Let x equal the number of moles per liter of weak acid that ionizes.



I	I	0	0
C	-x	+x	+x
E	I - x	x	x

$$K_a = [\text{H}_3\text{O}^+][\text{C}_2\text{H}_3\text{O}_2^-]/[\text{HC}_2\text{H}_3\text{O}_2] = (x)(x)/(I - x)$$

In general, if $I > 100 K_a$, then the assumption $I - x = I$ is a good approximation. Most weak acids do have a K_a that is less than 10^{-3} so I is usually $> 100 K_a$.

So the equation used for calculations involving the ionization of weak acids simplifies to:

$$K_a = x^2/I$$

where K_a is the ionization constant for the weak acid, x is the number of moles per liter of weak acid that ionize, and I is the initial molar concentration of weak acid.

$$K_a = x^2/I$$

$$1.8 \times 10^{-5} = x^2/0.15$$

$$x = [H^+] = 1.6 \times 10^{-3} M$$

$$pH = -\log [H^+] = -\log (1.6 \times 10^{-3}) = 2.78$$

Calculations for Weak Bases Section 16.7

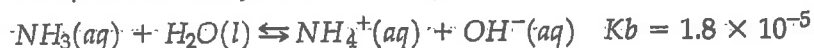
Like weak acids, weak bases all have the same ICE table. Even better, the ICE table for weak bases is the same as that for weak acids, except that base ionization produces hydroxide ion rather than hydrogen ion.

Example:

What is the pH of a 0.75 M solution of aqueous ammonia?

Solution:

Set up an ICE table for the reaction of ammonia with water.



I	0.75	0	0
C	-y	+y	+y
E	0.75 - y	y	y

For clarity, "y" is used instead of "x" to represent the number of moles per liter of base that ionize.

$$K_b = [OH^-][NH_4^+]/[NH_3] = (y)(y)/(I - y)$$

If $I > 100 K_b$ then y is very small compared to I , so the generic equation for calculations involving weak base ionizations is:

$$K_b = y^2/I$$

where K_b is the ionization constant for the weak base, y is the number of moles per liter of weak base that ionize and I is the initial molar concentration of weak base.

Common misconception: The most difficult part of performing calculations involving strong and weak acids and bases is recognizing the chemistry. Does the problem involve an acid or a base? Is the acid or base strong or weak? If you can first answer these questions based on the chemistry, then the calculations are relatively uncomplicated.



$$K_b = y^2/I$$

$$1.8 \times 10^{-5} = y^2/0.75$$

$$y = [\text{OH}^-] = 3.7 \times 10^{-3} \text{ M}$$

$$p\text{OH} = -\log [\text{OH}^-] = -\log (3.7 \times 10^{-3}) = 2.43$$

$$p\text{H} = 14 - p\text{OH} = 14 - 2.43 = 11.57$$

Your Turn 16.4

Classify the following as strong or weak acids or bases. Justify your answers. chloric acid, ammonium chloride, calcium hydroxide, ethyl amine, sodium cyanide. Write your answer in the space provided.

Once the identity of a strong or weak acid or base solution is established, the calculations fall into a predictable pattern.

Example:

Measurements show that the pH of a 0.10 M solution of acetic acid is 2.87. What is K_b for potassium acetate, $\text{KC}_2\text{H}_3\text{O}_2$?

Solution:

The question gives information regarding a solution of a weak acid but asks for the K_b of its conjugate weak base. First calculate K_a for the weak acid and then convert it to K_b for the conjugate base.

$$K_a = x^2/I$$

If the pH is 2.87, the $[\text{H}^+] = 10^{-2.87} = 1.3 \times 10^{-3} \text{ M}$.

$$[\text{H}^+] = [\text{C}_2\text{H}_3\text{O}_2^-] = x = 1.3 \times 10^{-3} \text{ M}$$

Substituting:

$$K_a = x^2/(0.10 - x)$$

$$K_a = (1.3 \times 10^{-3})(1.3 \times 10^{-3})/(0.10 - 1.3 \times 10^{-3} \text{ M})$$

$$K_a = 1.7 \times 10^{-5}$$

$$K_b = K_w/K_a = 1.0 \times 10^{-14}/1.7 \times 10^{-5} = 5.9 \times 10^{-10}$$

Acid-Base Properties of Salt Solutions

Section 16.9

Hydrolysis of salts refers to the reactions of salt ions with water. Recall that, except for the anions of strong acids, anions tend to be weak bases. Their negative charges tend to attract protons from water. Similarly, except for the cations of strong bases, cations are weakly acidic, either by attracting a pair of electrons from water, as with Lewis acids, or by donating an available proton to water.

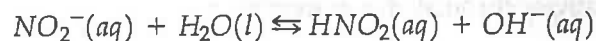
To classify a salt solution as acidic, basic, or neutral, disregard any neutral cations or anions listed in Table 16.2. If what is left is an anion, the salt is basic. If a cation remains, the salt is acidic. If both the cation and anion are listed in Table 16.2, the salt is neutral. If neither the cation nor anion are neutral, the acid or base character of the salt cannot be determined by examining its formula.

Example:

Classify the salt, sodium nitrite, NaNO_2 as acid, base, or neutral. Explain your reasoning. Write a chemical equation for its reaction with water.

Solution:

Sodium nitrite is a base. The sodium ion is a cation of a strong base so it is neutral. Nitrite is the conjugate base of the weak acid nitrous acid, HNO_2 . A solution of sodium nitrite in water will be basic because of the hydrolysis reaction of the nitrite ion with water. (We ignore the sodium ion because it is neutral.) The K_b of the nitrite ion can be calculated from the K_a of nitrous acid.



Example:

Classify an aqueous solution of methyl ammonium chloride, $\text{CH}_3\text{NH}_3\text{Cl}$, as acidic, basic, or neutral. Explain your reasoning. Write an equation to illustrate your answer.

Solution:

Methyl ammonium chloride is acidic because the chloride ion is neutral and the methyl ammonium ion is the conjugate weak acid of the base, methyl amine, CH_3NH_2 . The K_a of methyl ammonium ion can be calculated from the K_b of methyl amine.



Section 16.10

Acid-Base Behavior and Chemical Structure

Acidity of a substance is directly related to the strength of attraction for a pair of electrons to a central atom. In general, acidity increases with stronger attractions for electrons.

Three factors affect attraction for electrons:

1. Ionic charge. When comparing similar ions, the more positive ions are stronger acids. (The more negative ions are more strongly basic.) For example:

Relative acid strengths: $\text{Na}^+ < \text{Ca}^{2+} < \text{Cu}^{2+} < \text{Al}^{3+}$

Metal cations of higher charge act as Lewis acids in water. The higher the charge, the greater the attraction the ion has for electrons and the stronger is the acid. If the charges are equal, the smaller ion displays the stronger attraction for electrons.

Relative acid strengths: $\text{PO}_4^{3-} < \text{HPO}_4^{2-} < \text{H}_2\text{PO}_4^- < \text{H}_3\text{PO}_4$

Note that in this example, PO_4^{3-} is clearly a base because it has a negative charge, and H_3PO_4 is clearly an oxyacid. However, HPO_4^{2-} and H_2PO_4^- are recognized as amphoteric because they are protonated anions. The ionic charge generalization cannot predict whether a substance will be an acid (more acidic than water) or a base (less acidic than water) relative to water. It can predict only the acidity of substances relative to each other.

2. Oxidation number: When comparing similar formulas with the same central atom, the greater the oxidation number of the central atom, the stronger the acid. For example:

Relative strengths: $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$

Relative strengths: $\text{H}_2\text{SO}_3 < \text{H}_2\text{SO}_4$

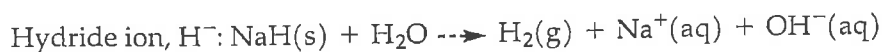
3. Electronegativity: When comparing similar formulas with different central atoms, in general, the greater the electronegativity of the central atom, the stronger the acid.

Relative strengths: $\text{H}_3\text{BO}_3 < \text{H}_2\text{CO}_3 < \text{H}_2\text{SO}_3 < \text{HNO}_3$

(Recall that the electronegativity of elements generally increases from the lower left to the upper right of the periodic table.)

Some Common Acid-Base Reactions

Besides the hydroxides of Groups 1 and 2, strong bases include hydrides, nitrides, and carbides:



Nitride ion, N^{3-} : $Mg_3N_2(s) + 6H_2O \rightarrow 2NH_3(g) + 3Mg^{2+}(aq) + 6OH^-(aq)$

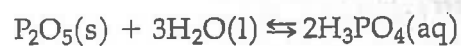
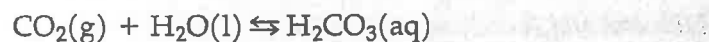
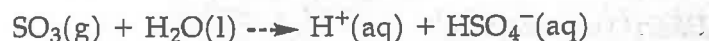
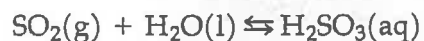
Carbide ion, C_2^{2-} : $Ca_2C_2(s) + 2H_2O \rightarrow C_2H_2(g) + Ca^{2+}(aq) + 2OH^-(aq)$

$C_2H_2(g)$ is ethyne (acetylene), $HC \equiv CH$.

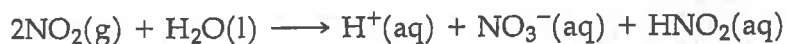
Strong bases also include oxides of Groups 1 and 2 such as Li_2O , MgO , and CaO . These "base anhydrides" react with water to give hydroxides:



Similarly, nonmetal oxides, called acid anhydrides, give solutions of acids in water.



Notice that the nonmetal tends to retain its oxidation number when going from the oxide to the acid. One notable exception is the reaction of nitrogen dioxide with water to form nitric acid and nitrous acid.



Notice that in all the equations, whenever a strong acid is formed, it is written in its ionized form to reflect its strong electrolytic character.

Multiple Choice Questions

1. According to the Lewis definition, an acid is a substance that
 - A) increases the hydrogen ion concentration in water.
 - B) can react with water to form H^+ ions.
 - C) can accept an electron pair to form a covalent bond.
 - D) can donate a proton to a base.
 - E) can react with water to form hydronium ions.
2. Which pair of chemical species is not a conjugate acid-base pair?
 - A) H_2CO_3 and CO_3^{2-}
 - B) OH^- and H_2O
 - C) HPO_4^{2-} and PO_4^{3-}
 - D) NH_3 and NH_4^+
 - E) CH_3NH_2 and CH_3NH^-
3. Which oxide when mixed in equal molar amounts with water forms a solution with the lowest pH?
 - A) CaO
 - B) CO_2
 - C) SO_2
 - D) SO_3
 - E) P_2O_5
4. When 0.2 moles of each of these salts are dissolved in one liter of water, what is the order of increasing pH (lowest pH first) of the resulting solutions?
 - A) $Na_2CO_3 < NaC_2H_3O_2 < NaCl < NH_4Cl$
 - B) $NaCl < Na_2CO_3 < NaC_2H_3O_2 < NH_4Cl$
 - C) $NH_4Cl < NaC_2H_3O_2 < NaCl < Na_2CO_3$
 - D) $NH_4Cl < NaCl < NaC_2H_3O_2 < Na_2CO_3$
 - E) $Na_2CO_3 < NaCl < NaC_2H_3O_2 < NH_4Cl$
5. Aqueous solutions of equal molar concentrations of these salts are listed in order of increasing pH.
 $NaBr < NaIO_3 < NaF < NaC_2H_3O_2 < Na_2SO_3$
Which acid is the weakest?

- A) HBr
B) HIO₃
C) HF
D) CH₃COOH
E) NaHSO₃
6. The net-ionic equation for the addition of 10.0 mL of 0.10 M sulfurous acid to 10.0 mL of 0.10 M aqueous sodium hydroxide is:
- A) $\text{H}_2\text{SO}_3 + 2\text{OH}^- \rightleftharpoons 2\text{H}_2\text{O} + \text{SO}_3^{2-}$
B) $\text{H}_2\text{SO}_4 + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} + \text{HSO}_4^-$
C) $\text{H}_2\text{SO}_3 + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} + \text{HSO}_3^-$
D) $\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O}$
E) $\text{HSO}_3^- + \text{NaOH} \rightarrow \text{NaSO}_3^- + \text{H}_2\text{O}$
7. Which is the acid anhydride of chlorous acid, HClO₂?
- A) Cl₂O
B) ClO
C) ClO₂
D) Cl₂O₃
E) Cl₂O₅
8. Equal molar aqueous solutions of the chloride salts of the following metals in their highest oxidation states were prepared and their respective pH's measured. Which is the correct order of pH?
- A) Sn < Al < Cu < Ca < K
B) K < Ca < Cu < Al < Sn
C) Al < Cu < Ca < Sn < K
D) Sn < Al < Ca < Cu < K
E) K < Cu < Ca < Al < Sn
9. The acid dissociation constants for the diprotic acid, malonic acid, H₂C₃H₂O₄, are $K_{a1} = 1.5 \times 10^{-3}$ and $K_{a2} = 2.0 \times 10^{-6}$.
What is K_b for HC₃H₂O₄⁻?
- A) $K_w \times K_{a1}$
B) $K_w \times K_{a2}$
C) K_w/K_{a1}

- D) K_w/K_{a_2}
- E) $K_{a_1} \times K_{a_2}$

10. What is the percent ionization of a 0.10 M solution of hydroazoic acid, HN_3 ? $K_a = 1.9 \times 10^{-5}$.
- A) 1.9×10^{-3}
 - B) 1.9
 - C) 0.19
 - D) 1.4
 - E) 0.14

Free Response Questions

1. Sulfurous acid, H_2SO_3 is a diprotic acid. $K_{a_1} = 1.7 \times 10^{-2}$.
 $K_{a_2} = 6.4 \times 10^{-8}$.
- a. Write an ionic equation for the aqueous ionization that corresponds to K_{a_1} .
Write an ionic equation for the aqueous ionization that corresponds to K_{a_2} .
Identify the conjugate acid-base pairs in each of your two equations.
 - b. Identify any amphoteric species, other than water, in your equations.
 - c. Assume the amphoteric species you identified in Part b is a base. Write an ionic equation for its aqueous ionization and calculate the corresponding K_b .
 - d. Is an aqueous solution of NaHSO_3 acidic or basic? Explain your reasoning.
 - e. Calculate the pH of a 0.50 M solution of Na_2SO_3 .
2. It is found that 0.30 M solutions of the three salts XCl_3 , YCl_2 , and ZCl have pH's of 5.5, 7.0, and 3.7, not necessarily in order. (X, Y, and Z are metal ions. Cl is the chloride ion.)
- a.
 - i. Explain how metal ions can act as acids in aqueous solution.
 - ii. Which pH goes with which salt? Explain.
 - iii. What is the approximate pH of a 0.010 M solution of ZOH ? Explain your reasoning.

- b. If a 0.5 M solution of copper(II) sulfate is added to a 1.0 M solution of sodium hydrogen carbonate, significant effervescence is observed. If the same copper(II) sulfate solution is added to a 1.0 M solution of sodium carbonate, little or no effervescence is observed. Explain these observations.

Additional Practice in Chemistry the Central Science

For more practice working acid-base equilibrium problems in preparation for the Advanced Placement examination, try these problems in Chapter 16 of Chemistry the Central Science:

Additional Exercises: 16.113, 16.114, 16.116, 16.117.

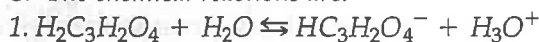
Integrated Exercises: 16.122, 16.124, 16.125, 16.128, 16.129, 16.130.

Multiple Choice Answers and Explanations

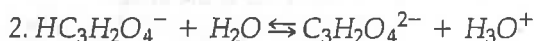
1. C. A Lewis acid is an electron pair acceptor. A Brønsted-Lowry acid is a proton donor. An Arrhenius acid increases $[H^+]$ when dissolved in water.
2. A. An acid-base conjugate pair consists of two chemical species that differ in formula by an H^+ . The species of the pair with the more positive charge (and hence the extra H) is the acid.
3. D. A lower pH implies a stronger acid. Nonmetal oxides tend to be acidic (acid anhydrides) while metal oxides tend to be basic (base anhydrides). When comparing oxides having different central atoms, the more electronegative atom forms the strongest acid. Sulfur is the most electronegative atom represented. When comparing oxides having the same central atom, the one with the greater number of oxygen atoms is more acidic.
4. D. A lower pH implies a stronger acid. In general, cations (except for the cations of strong bases), tend to be acidic and anions (except for the anions of strong acids) tend to be basic. The more positive the charge the more acidic the cation, and the more negative the charge the more basic the anion. Sodium ion is the neutral ion of the strong base, NaOH, and chloride is the neutral ion of the strong acid, HCl, so sodium chloride is neutral. Ammonium ion is slightly acidic, and acetate and carbonate ion are weak bases.

5. E. A higher pH implies a stronger base. The strongest base, Na_2SO_3 , has the weakest conjugate acid, NaHSO_3 . The sodium ions are neutral because Na^+ is the cation of the strong base, NaOH .
6. C. Sulfurous acid, H_2SO_3 , is a weak acid and should not be confused with sulfuric acid, H_2SO_4 , a strong acid. Sodium hydroxide is a strong electrolyte so the sodium ion is a spectator ion. Only one millimole each of the acid and base are present so only one of the two ionizable protons on sulfurous acid will react.
7. D. The oxidation number of chlorine in HClO_2 is +3. The acid anhydride of an acid is generally the nonmetal oxide with the same oxidation number of the nonmetal.
8. A. Charged metal cations in aqueous solutions are Lewis acids. The higher the charge of the metal cation, the more acidic the solution. When charges are equal, the smaller the cation, the more acidic the solution. The salts are: SnCl_4 , AlCl_3 , CuCl_2 , CaCl_2 , and KCl and their respective metal cations are: Sn^{4+} , Al^{3+} , Cu^{2+} , Ca^{2+} , and K^+ . Cu^{2+} is smaller than Ca^{2+} so Cu^{2+} is more acidic.

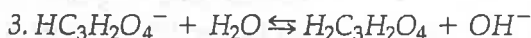
9. C. The chemical reactions are:



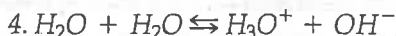
$$K_{a1} = [\text{HC}_3\text{H}_2\text{O}_4^-][\text{H}_3\text{O}^+]/[\text{H}_2\text{C}_3\text{H}_2\text{O}_4]$$



$$K_{a2} = [\text{C}_3\text{H}_2\text{O}_4^{2-}][\text{H}_3\text{O}^+]/[\text{HC}_3\text{H}_2\text{O}_4^-]$$



$$K_b = [\text{H}_2\text{C}_3\text{H}_2\text{O}_4][\text{OH}^-]/[\text{HC}_3\text{H}_2\text{O}_4^-]$$



$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

The correct equation is $K_b = K_w/K_{a1}$. Which K_a is the correct one to use in this case?

Substituting $K_b = K_w/K_{a1}$ we get the correct solution:

$$\frac{[\text{H}_2\text{C}_3\text{H}_2\text{O}_4][\text{OH}^-]}{[\text{HC}_3\text{H}_2\text{O}_4^-]} = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{([\text{HC}_3\text{H}_2\text{O}_4^-][\text{H}_2\text{C}_3\text{H}_2\text{O}_4])}$$

Alternatively: Reaction 3 includes the same conjugate pair as Reaction 1, so $K_b = K_w/K_{a1}$ is correct.

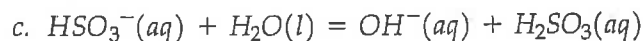
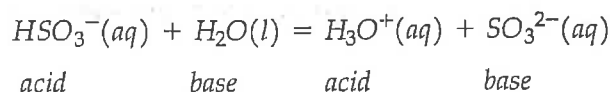
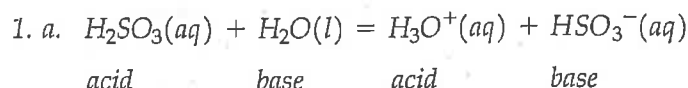
10. D. $K_a = x^2/I$ and % ionization = $(x/I)(100)$ where x is the moles per liter ionized and I is the initial concentration.

$$1.9 \times 10^{-5} = x^2/0.10$$

$$x = 1.4 \times 10^{-3}$$

$$\% \text{ ionization} = (1.4 \times 10^{-3}/0.10)(100) = 1.4$$

Answers to Free Response Questions



$$K_b = K_w/K_{a_1} = 1.0 \times 10^{-14}/1.7 \times 10^{-2} = 5.9 \times 10^{-13}$$

d. $\text{HSO}_3^-(\text{aq})$ forms an acidic solution because its K_a is much greater than its K_b .

$$K_{a_2} = 6.4 \times 10^{-8} > K_b = 5.9 \times 10^{-13}$$

e. $K_b = K_w/K_{a_2} = 1.00 \times 10^{-14}/6.4 \times 10^{-8} = 1.56 \times 10^{-7}$

$$K_b = y^2/I$$

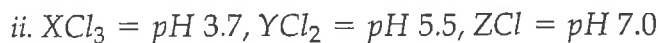
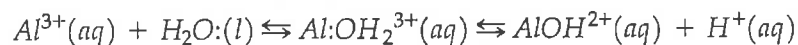
$$1.56 \times 10^{-7} = y^2/0.50$$

$$y = 2.8 \times 10^{-4} = [\text{OH}^-]$$

$$p\text{OH} = -\log [\text{OH}^-] = -\log 2.8 \times 10^{-4} = 3.55$$

$$p\text{H} = 14.00 - p\text{OH} = 14.00 - 3.55 = 10.45$$

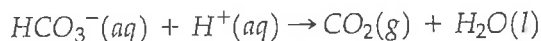
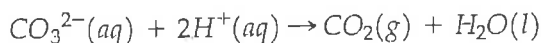
2. a. i. Highly charged metal cations are Lewis acids. They attract nonbonding pairs on water molecules. This attraction polarizes the H—O bond making it weaker causing $\text{H}^+(\text{aq})$ to enter the solution.



The higher the positive charge the more acidic the cation. Aqueous chloride ion, Cl^- , is neutral so does not affect the pH. X^{3+} is the most acidic ion and forms the solution with the lowest pH.

iii. $\text{pH} = 12.00$. Z^+ is a neutral ions because it forms a solution of pH 7.0 with chloride ion, also neutral. Therefore ZOH is a strong base.
 $p\text{OH} = -\log 0.01 = 2$. $\text{pH} = 14 - p\text{OH} = 14 - 2 = 12$.

- b. Both carbonate and hydrogen carbonate ions effervesce producing gaseous carbon dioxide in the presence of acids according to the following equations:



However, copper(II) ion is a weak Lewis acid which can provide only enough hydrogen ion to cause hydrogen carbonate to effervesce but not enough to cause carbonate ion to produce carbon dioxide. The stoichiometry requires each mole of carbonate ion to react with two moles of hydrogen ion.

Sulfate ion is nearly neutral and has no effect on the reaction.

Your Turn Answers

- 16.1. Aqueous solutions of the salts NaCl, KNO₃, LiClO₄, BaBr₂, and CsI are neutral because they contain neutral cations and neutral anions. The cations are all cations of strong bases, and the anions are all anions of strong acids.
- 16.2. Of the acids listed in table 16.4, HIO is the weakest because it has the smallest K_a value. In Table 16.5, fluoride ion is the weakest base listed because it has the smallest value of K_b.
- 16.3. BF₃ is a Lewis acid because it accepts a lone pair of electrons from the Lewis base, $\overset{\cdot\cdot}{\text{N}}\text{H}_3$. BF₃ has a non-octet Lewis structure where boron has only six electrons and readily accepts ammonia's non-bonding pair.
- 16.4. Chloric acid is listed in Table 16.1 as a strong acid.

Chloride is listed as a neutral ion in Table 16.2. Ammonium ion, NH₄⁺, is the conjugate acid of the weak base ammonia, NH₃.

Calcium hydroxide is listed in Table 16.1 as a dibasic strong base.

Ethyl amine is a neutral nitrogen compound and a weak base.

Cyanide ion, CN⁻, is the weak conjugate base of hydrocyanic acid, HCN. Sodium ion is listed in Table 16.2 as a neutral ion.