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Chapter 13
Acids and Bases

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Outline

1. Brønsted-Lowry acid-base model
2. The ion product of water
3. pH and pOH
4. Weak acids and their equilibrium constants
5. Weak bases and their equilibrium constants
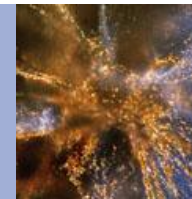6. Acid-base properties of salt solutions

Review from Chapter 4

- The Arrhenius definition of acid and base
    - Acids produce H^+ in water
    - Bases produce OH^- in water
    - H^+ from acids combines with OH^- from bases to produce water in a reaction called a neutralization

Brønsted-Lowry Acid-Base Model

- Brønsted-Lowry
  - Johannes Brønsted (1879-1947)
  - Thomas Lowry (1874-1936)
- Brønsted-Lowry model focuses on the **reaction that takes place between acid and base**, rather than on the independent nature of the acid or base, as the Arrhenius model does
  - Acids donate H^+ to bases
  - Bases accept H^+ from acids

The Nature of H$^+$

- The H$^+$ ion is the medium of exchange in a Brønsted-Lowry reaction
  - H$^+$ can also be called a proton
  - ***Acid-base reactions involve proton exchange***
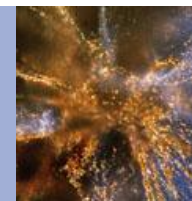
Conjugate Pairs

- The species that forms when a proton is removed from an acid is called the **conjugate base** of the acid
  - If the acid is HB, the conjugate base is B^-
- The only difference between the members of a conjugate acid-base pair is the position of the proton
- A species that can either accept or donate a proton is called amphiprotic
  - Consider water:
    - OH^- ß H_2O à H_3O^+

      Remove H^+ Add H^+

Examples of Conjugate Acid-Base Pairs

Conjugate Acid	Conjugate Base
HF	F^-
HSO_4^-	SO_4^{2-}
NH_4^+	NH_3

The Hydronium Ion

- Another way to write the H^+ ion is as H_3O^+
  - H_3O^+ is the hydronium ion
    - H^+ exists in water as hydronium ion, since H^+ itself would not be stable in water
  - Depending on the reason for writing the reaction, either H^+ or H_3O^+ can be used, and interchangeably
  - The only difference is the inclusion or exclusion of the H_2O molecule

Example 13.1

Example 13.1

(a) What is the conjugate base of HNO_2? The conjugate acid of F^-?

(b) The HCO_3^- ion, like the H_2O molecule, is amphiprotic. What is its conjugate base? Its conjugate acid?

Strategy To form a conjugate base, remove H^+; the effect is to lower the number of hydrogen atoms by one and lower the charge by one unit. Conversely, a conjugate acid is formed by adding H^+; this adds a H atom and increases the charge by one unit.
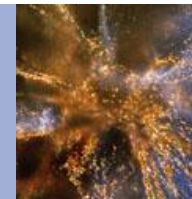
SOLUTION

(a) NO_2^-; HF   (b) CO_3^{2-}; H_2CO_3

The Ion Product of Water

- Water can react with itself in a reaction called **autoionization**

- Water can react with itself in an acid-base reaction:
  - $H_2O + H_2O \rightleftharpoons H_3O^+ \text{ (aq)} + OH^- \text{ (aq)}$

- An alternate way to write the reaction is:
  - $H_2O \rightleftharpoons H^+ \text{ (aq)} + OH^- \text{ (aq)}$
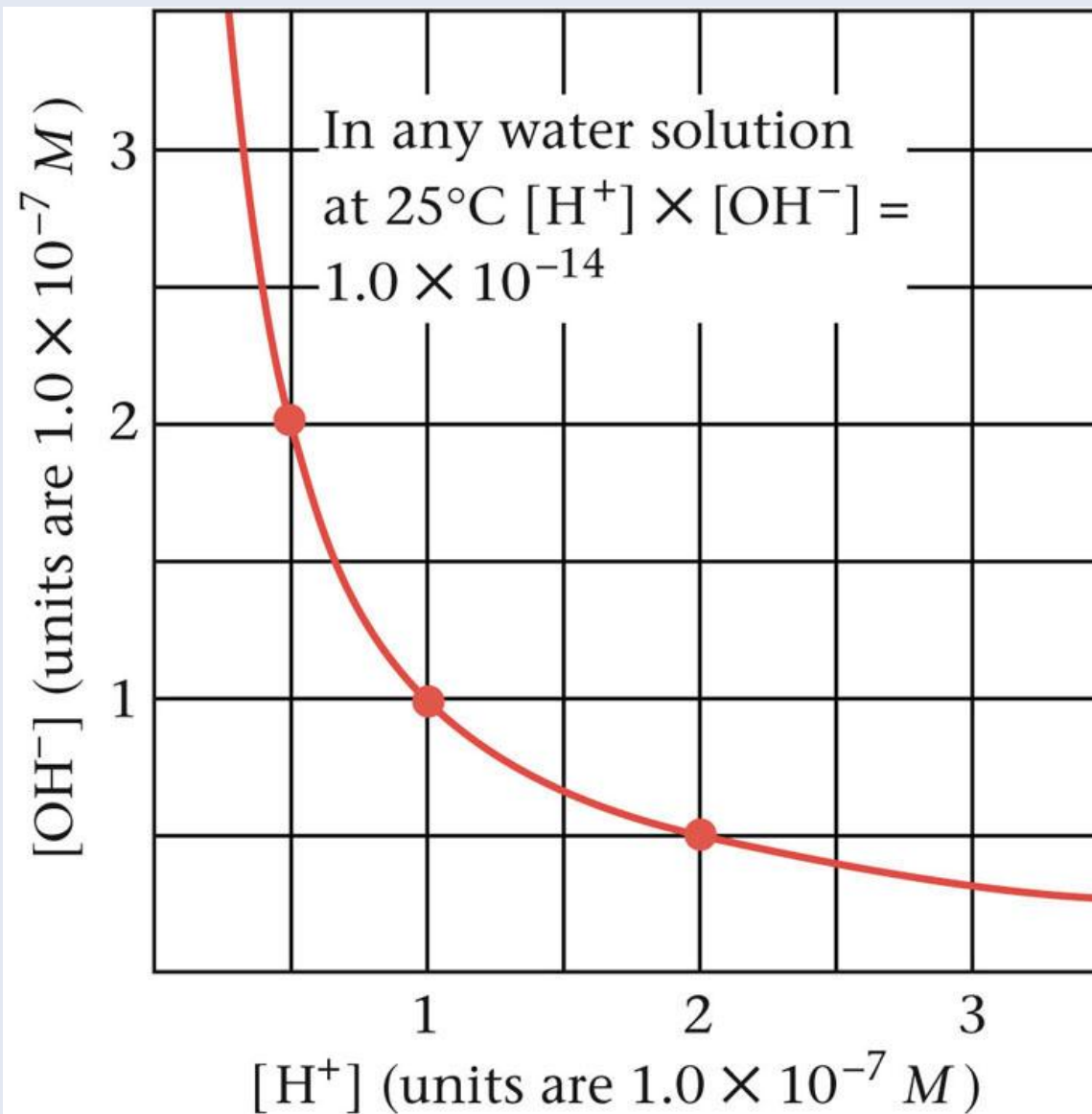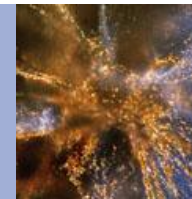
Equilibrium and the Auto-Ionization of Water

- $H_2O \rightleftharpoons H^+$ (aq) + OH^- (aq)
  - Recall that concentrations can be used to write equilibrium constant expressions
  - K for this reaction is $[H^+][OH^-]$
  - This K is called the **ion product constant of water, K_w**
    - $K_w = [H^+][OH^-]$
    - At 25 ° C, $K_w = 1.0 \times 10^{-14}$

Concentrations of H^+ and OH^- in pure water

- In pure water, $[H^+] = [OH^-] = 1.0 \times 10^{-14}$
  - $[H^+] = 1.0 \times 10^{-7}$
  - $[OH^-] = 1.0 \times 10^{-7}$
  - When the two concentrations are equal, the solution is said to be neutral
    - If $[H^+] > 1.0 \times 10^{-7}$, then $[OH^-] < 1.0 \times 10^{-7}$ and the solution is acidic
    - If $[OH^-] > 1.0 \times 10^{-7}$, then $[H^+] < 1.0 \times 10^{-7}$ and the solution is basic
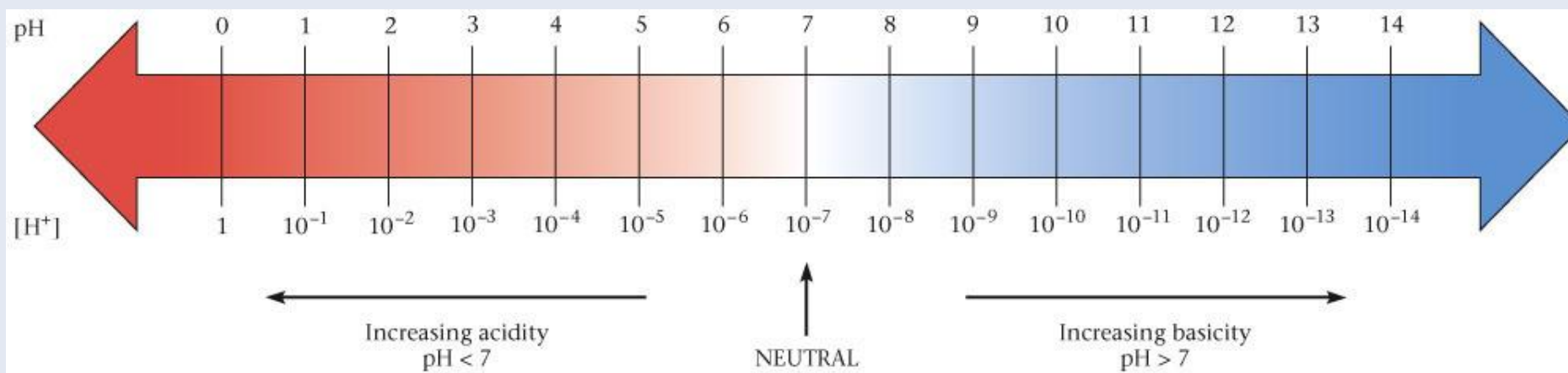
Figure 13.1

In any water solution at 25°C $[H^+] \times [OH^-] = 1.0 \times 10^{-14}$

y-axis: $[OH^-]$ (units are $1.0 \times 10^{-7}\ M$)
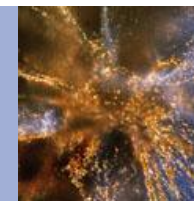
x-axis: $[H^+]$ (units are $1.0 \times 10^{-7}\ M$)
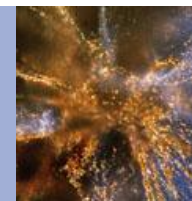
pH

- Defining equation for pH

$$pH = -\log[H^+]$$
$$[H^+] = anti\log(-pH) = 10^{-pH}$$

- The higher the pH, the less acidic the solution
- The lower the pH, the more acidic the solution

Figure 13.2

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pOH

- Defining equation for pH

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

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

- The higher the pOH, the more basic the solution
- The lower the pOH, the more acidic the solution

Relationship between pH and pOH

$$[H^+][OH^-] = 1.0 \, x10^{-14}$$

$$pH + pOH = 14$$

Example 13.2

Example 13.2

Example 13.2 **Graded**

Calculate, at 25°C

* (a) the $[H^+]$ and pH of a tap-water sample in which $[OH^-] = 2.0 \times 10^{-7}$.
** (b) the $[H^+]$ and $[OH^-]$ of human blood at pH 7.40.
*** (c) the pOH of a solution in which $[H^+] = 5.0[OH^-]$.

SOLUTION

(a) $[H^+] = \dfrac{1.0 \times 10^{-14}}{2.0 \times 10^{-7}} = 5.0 \times 10^{-8} \, M$

$pH = -\log_{10}(5.0 \times 10^{-8})$

You should find on your calculator that $\log_{10}(5.0 \times 10^{-8})$ is -7.30. Hence, $pH = 7.30$.

(b) Because the pH is 7.40, $[H^+] = 10^{-7.40}$. To find $[H^+]$, enter -7.40 on your calculator. Then either—

- punch the $\boxed{10^x}$ key, if you have one, or
- punch the $\boxed{INV}$ and then the $\boxed{LOG}$ key

Either way, you should find that $[H^+] = 4.0 \times 10^{-8} \, M$.
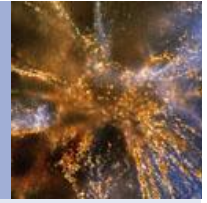Knowing $[H^+]$, the concentration of OH^- is calculated from Equation 13.1.

$$[OH^-] = \dfrac{1.0 \times 10^{-14}}{4.0 \times 10^{-8}} = 2.5 \times 10^{-7} \, M.$$

(c) Substitute into the K_W expression to find $[OH^-]$ and then convert to pOH.

$$5.0[OH^-] \times [OH^-] = 1.0 \times 10^{-14}$$

$$[OH^-]^2 = \dfrac{1.0 \times 10^{-14}}{5.0}; \qquad [OH^-] = 4.5 \times 10^{-8} \, M$$

$$pOH = -\log_{10}(4.5 \times 10^{-8}) = 7.35$$

pH and Blood

- From the previous example, it is seen that the [H$^+$] in blood is very small, about 4.0 X 10^{-8} M
  - Small changes in [H$^+$] can have dramatic physiological effects
    - Many biological reactions depend on [H$^+$]
    - An increase in [H$^+$] from 4.0 X 10^{-8} to 4.0 X 10^{-7} can increase the a reaction rate by a power of 10
  - Small increases in [H$^+$] can lead to *acidosis*; small decreases in [H$^+$] can lead to *alkalosis*
  - *Effective control of many physiological reactions depends on pH control*

pH of Strong Acids

- Recall from Chapter 4 that some acids are strong
  - HCl, HBr, HI, $HClO_4$, HNO_3, H_2SO_4
    - These completely ionize in water
    - $[H^+]$ is equal to the $[H^+]$ of the acid
  - A 0.10 M solution of HCl has $[H^+]$ = 0.10, so the pH of the solution is 1.0

Figure 13.3

$$H - Cl \quad + \quad H - O - H \quad \longrightarrow \quad \left[H - O - H \atop | \atop H \right]^{+} \quad + \quad Cl^{-}$$
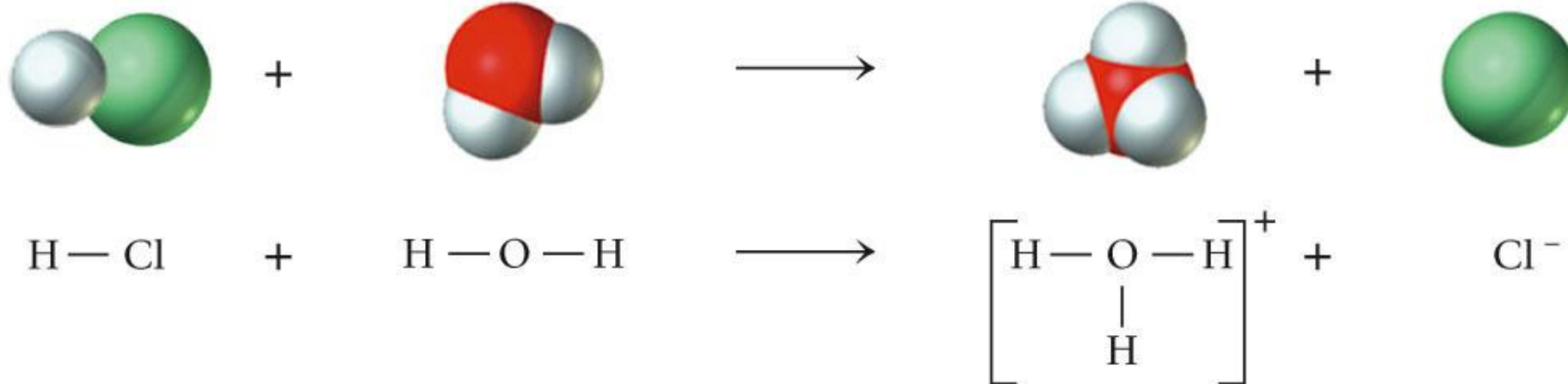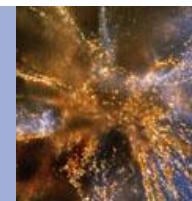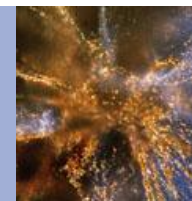
pH of Strong Bases

- Recall as well that some bases are strong:
  - LiOH, NaOH, KOH, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$
    - These bases ionize completely to OH^-
    - pOH is dependent on the concentration of the strong base
  - For an 0.10 M solution of NaOH,
    - $[Na^+] = [OH^-] = 0.10$
    - pOH = 1.0
    - pH = 13.0

Example 13.1

Example 13.1

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(b) The HCO_3^- ion, like the H_2O molecule, is amphiprotic. What is its conjugate base? Its conjugate acid?

Strategy To form a conjugate base, remove H^+; the effect is to lower the number of hydrogen atoms by one and lower the charge by one unit. Conversely, a conjugate acid is formed by adding H^+; this adds a H atom and increases the charge by one unit.

SOLUTION

(a) NO_2^-; HF (b) CO_3^{2-}; H_2CO_3
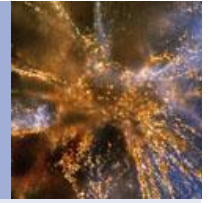
Measuring pH

- pH can be measured with a pH meter
  - Translates [H^+] into an electrical signal
  - Signal is shown on an analog or digital meter calibrated in pH units

Figure 13.4

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pH Indicators

- Universal indicator
  - Mixture of substances that change color depending on the concentration of H^+
  - Less accurate than pH meter
  - Depending on the indicator used, can display pH over a narrow or wide range of $[H^+]$
- Some plants can act as pH indicators
  - Color of some flowers in plants is dependent on the pH of the soil in which the plant is grown
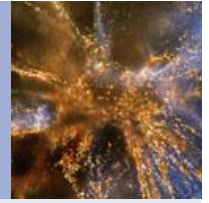
Figure 13.5

Figure 13.6
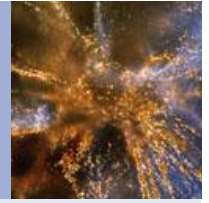
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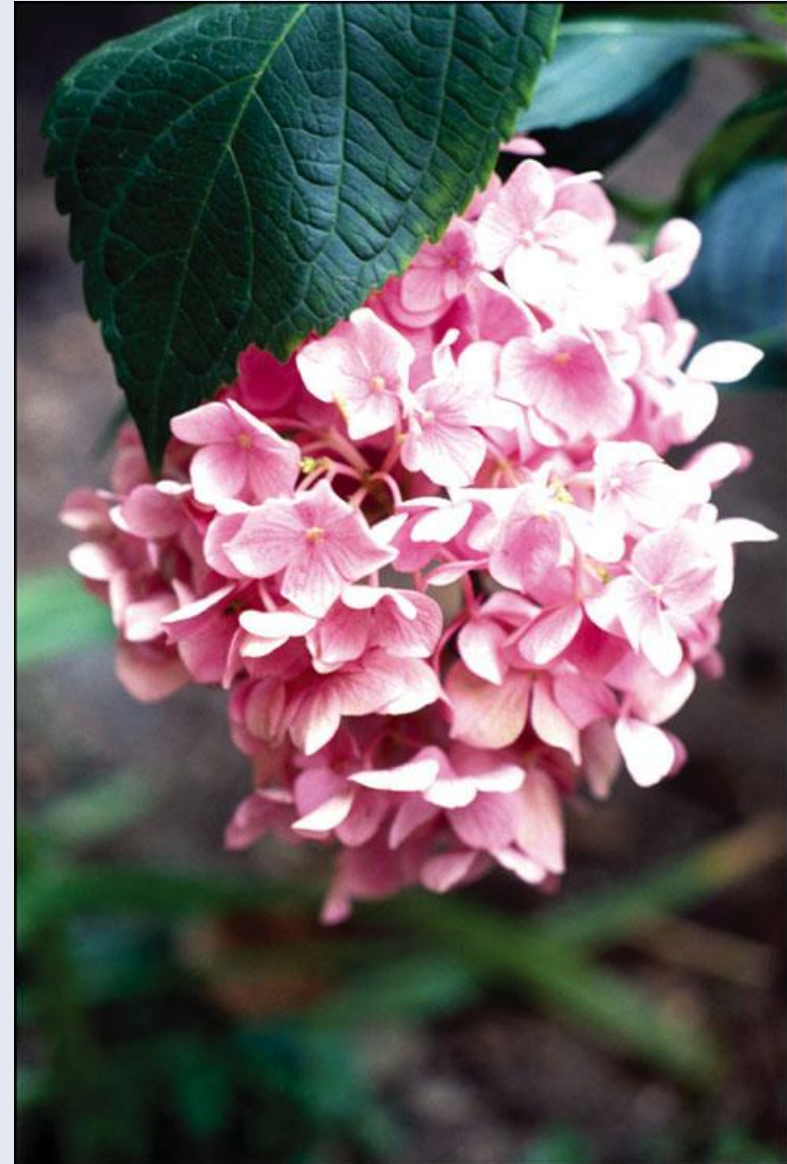
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Weak Acid Equilibrium Constants

- Weak acids ionize only partially
- Prototype reaction
  - HB (aq) + $H_2O \rightleftharpoons H_3O^+$ (aq) + B^- (aq)
- Two types of species that behave as weak acids
  1. Molecules with an ionizable hydrogen atom
     - HNO_2 (aq) + $H_2O \rightleftharpoons H_3O^+$ (aq) + NO_2^- (aq)
  2. Cations
     - NH_4^+ (aq) + $H_2O \rightleftharpoons H_3O^+$ (aq) + NH_3 (aq)

Metal Cations as Acids

- Many metal cations act as weak acids in water solution as well

    - $Zn(H_2O)_4^{2+}$ (aq) + $H_2O \rightleftharpoons H_3O^+$ (aq) $Zn(H_2O)_3(OH)^+$ (aq)

  - The bond that forms between the oxygen and the metal ion weakens the O-H bond

  - H^+ is more easily ionized as a result of the weakened bond

Equilibrium Constants for Weak Acids

- HB (aq) + H_2O ⇌ H_3O^+ (aq) + B^- (aq)
  - K_a is the acid equilibrium constant
  - Simplifying the above to HB (aq) ⇌ H^+ (aq) + B^- (aq)

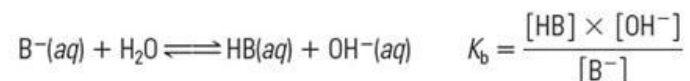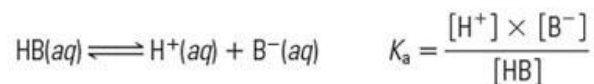$$K_a = \frac{[H^+][B^-]}{[HB]}$$

- K_a values are related to the weak acid strength
  - The smaller K_a is, the weaker the acid is

Table 13.2

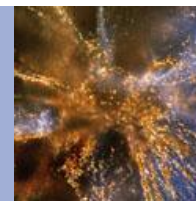**Table 13.2** Equilibrium Constants for Weak Acids and Their Conjugate Bases

	Acid	K_a	Base	K_b
Sulfurous acid	H_2SO_3	1.7×10^{-2}	HSO_3^-	5.9×10^{-13}
Hydrogen sulfate ion	HSO_4^-	1.0×10^{-2}	SO_4^{2-}	1.0×10^{-12}
Phosphoric acid	H_3PO_4	7.1×10^{-3}	$H_2PO_4^-$	1.4×10^{-12}
Hexaaquairon(III) ion	$Fe(H_2O)_6^{3+}$	6.7×10^{-3}	$Fe(H_2O)_5OH^{2+}$	1.5×10^{-12}
Hydrofluoric acid	HF	6.9×10^{-4}	F^-	1.4×10^{-11}
Nitrous acid	HNO_2	6.0×10^{-4}	NO_2^-	1.7×10^{-11}
Formic acid	$HCHO_2$	1.9×10^{-4}	CHO_2^-	5.3×10^{-11}
Lactic acid	$HC_3H_5O_3$	1.4×10^{-4}	$C_3H_5O_3^-$	7.1×10^{-11}
Benzoic acid	$HC_7H_5O_2$	6.6×10^{-5}	$C_7H_5O_2^-$	1.5×10^{-10}
Acetic acid	$HC_2H_3O_2$	1.8×10^{-5}	$C_2H_3O_2^-$	5.6×10^{-10}
Hexaaquaaluminum(III) ion	$Al(H_2O)_6^{3+}$	1.2×10^{-5}	$Al(H_2O)_5OH^{2+}$	8.3×10^{-10}
Carbonic acid	H_2CO_3	4.4×10^{-7}	HCO_3^-	2.3×10^{-8}
Dihydrogen phosphate ion	$H_2PO_4^-$	6.2×10^{-8}	HPO_4^{2-}	1.6×10^{-7}
Hydrogen sulfite ion	HSO_3^-	6.0×10^{-8}	SO_3^{2-}	1.7×10^{-7}
Hypochlorous acid	$HClO$	2.8×10^{-8}	ClO^-	3.6×10^{-7}
Hydrocyanic acid	HCN	5.8×10^{-10}	CN^-	1.7×10^{-5}
Ammonium ion	NH_4^+	5.6×10^{-10}	NH_3	1.8×10^{-5}
Tetraaquazinc(II) ion	$Zn(H_2O)_4^{2+}$	3.3×10^{-10}	$Zn(H_2O)_3OH^+$	3.0×10^{-5}
Hydrogen carbonate ion	HCO_3^-	4.7×10^{-11}	CO_3^{2-}	2.1×10^{-4}
Hydrogen phosphate ion	HPO_4^{2-}	4.5×10^{-13}	PO_4^{3-}	2.2×10^{-2}

$$HB(aq) \rightleftharpoons H^+(aq) + B^-(aq) \qquad K_a = \frac{[H^+] \times [B^-]}{[HB]}$$

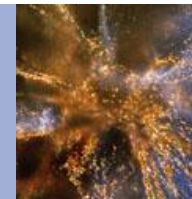$$B^-(aq) + H_2O \rightleftharpoons HB(aq) + OH^-(aq) \qquad K_b = \frac{[HB] \times [OH^-]}{[B^-]}$$

pK$_a$

- pK$_a$ = -logK$_a$
- The smaller pK$_a$ is, the stronger the acid
  - pK$_a$ follows the trend for pH

Example 13.4

Example 13.4

Example 13.4   Consider acetic acid, $HC_2H_3O_2$, and the hydrated zinc cation, $Zn(H_2O)_4^{2+}$.

(a) Write equations to show why these species are acidic.
(b) Which is the stronger acid?
(c) What is the pK_a of $Zn(H_2O)_4^{2+}$?

Strategy   In (a), note that in both cases a proton is transferred to a water molecule. The products are an H_3O^+ ion and the conjugate base of the weak acid. In (b) use Table 13.2 to find which weak acid has the larger K_a. In (c) use the equation

$$pK_a = -\log_{10}K_a$$

SOLUTION

(a) $HC_2H_3O_2(aq) + H_2O \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-(aq)$
$Zn(H_2O)_4^{2+}(aq) + H_2O \rightleftharpoons H_3O^+(aq) + Zn(H_2O)_3(OH)^+(aq)$

(b) $HC_2H_3O_2$ ($K_a = 1.8 \times 10^{-5}$) is stronger than $Zn(H_2O)_4^{2+}$ ($K_a = 3.3 \times 10^{-10}$).

(c) $pK_a = -\log_{10}(3.3 \times 10^{-10}) = 9.48$

Example 13.5

Example 13.5
Aspirin, a commonly used pain reliever, is a weak organic acid whose molecular formula may be written as $HC_9H_7O_4$. An aqueous solution of aspirin has total volume 350.0 mL and contains 1.26 g of aspirin. The pH of the solution is found to be 2.60. Calculate K_a for aspirin.

Strategy The approach used is very similar to that of Chapter 12, except that concentrations in moles per liter replace partial pressures. Note that you readily calculate:

- the original concentration of $HC_9H_7O_4$ (MM = 180.15 g/mol)

$$[HC_9H_7O_4]_o = \frac{1.26 \text{ g}}{0.3500 \text{ L}} \times \frac{1 \text{ mol}}{180.15 \text{ g}} = 0.0200 \ M$$

- the equilibrium concentration of H^+

$$[H^+]_{eq} = 10^{-2.60} = 2.5 \times 10^{-3} \ M$$

Your task is to calculate the acid equilibrium constant:

$$HC_9H_7O_4(aq) \rightleftharpoons H^+(aq) + C_9H_7O_4^-(aq) \qquad K_a = \frac{[H^+] \times [C_9H_7O_4^-]}{[HC_9H_7O_4]}$$
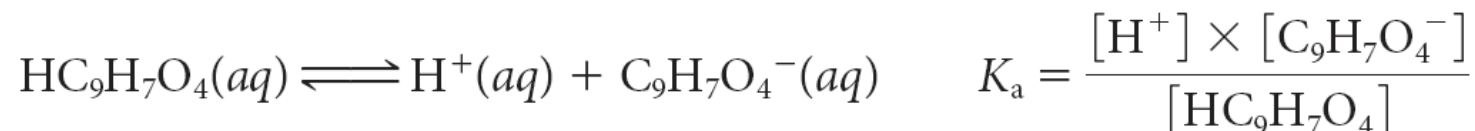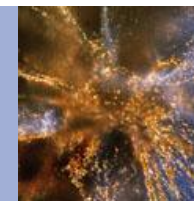
SOLUTION From the chemical equation for the ionization of the weak acid, it should be clear that *1 mol* of $C_9H_7O_4^-$ is *produced* and *1 mol* of $HC_9H_7O_4$ is *consumed* for every mole of H^+ produced. It follows that

$$\Delta[C_9H_7O_4^-] = \Delta[H^+] \qquad \Delta[HC_9H_7O_4] = -\Delta[H^+]$$

Originally, there is essentially no H^+ (ignoring the slight ionization of water). The same holds for the anion $C_9H_7O_4^-$; the only species present originally is the weak acid, $HC_9H_7O_4$, at a concentration of 0.0200 M.

Putting this information together in the form of a table,

	$HC_9H_7O_4(aq) \rightleftharpoons H^+(aq) + C_9H_7O_4^-(aq)$		
$[\ ]_0$	0.0200	0.0000	0.0000
$\Delta[\ ]$	−0.0025	+0.0025	+0.0025
$[\ ]_{eq}$	0.0175	0.0025	0.0025

(Numbers in color are those given or implied in the statement of the problem; the other numbers are deduced using the ionization equation printed above the table. The symbols $[\ ]_0$ and $[\ ]_{eq}$ refer to original and equilibrium concentrations, respectively.)

All the information needed to calculate K_a is now available,

$$K_a = \frac{(2.5 \times 10^{-3})^2}{0.0175} = 3.6 \times 10^{-4}$$

Reality Check Aspirin is a relatively *strong* weak acid; it would be located near the top of Table 13.2.

Percent Ionization

- The percent ionization of a weak acid is defined as

$$\%ionization = \frac{[H^+]_{equilibrium}}{[HB]_{initial}} \times 100\%$$

- For the calculation in example 13.5, the percent ionization is about 12 %
  - Note that the percent ionization depends on the molarity of the weak acid

Figure 13.8 - % Ionization and Concentration

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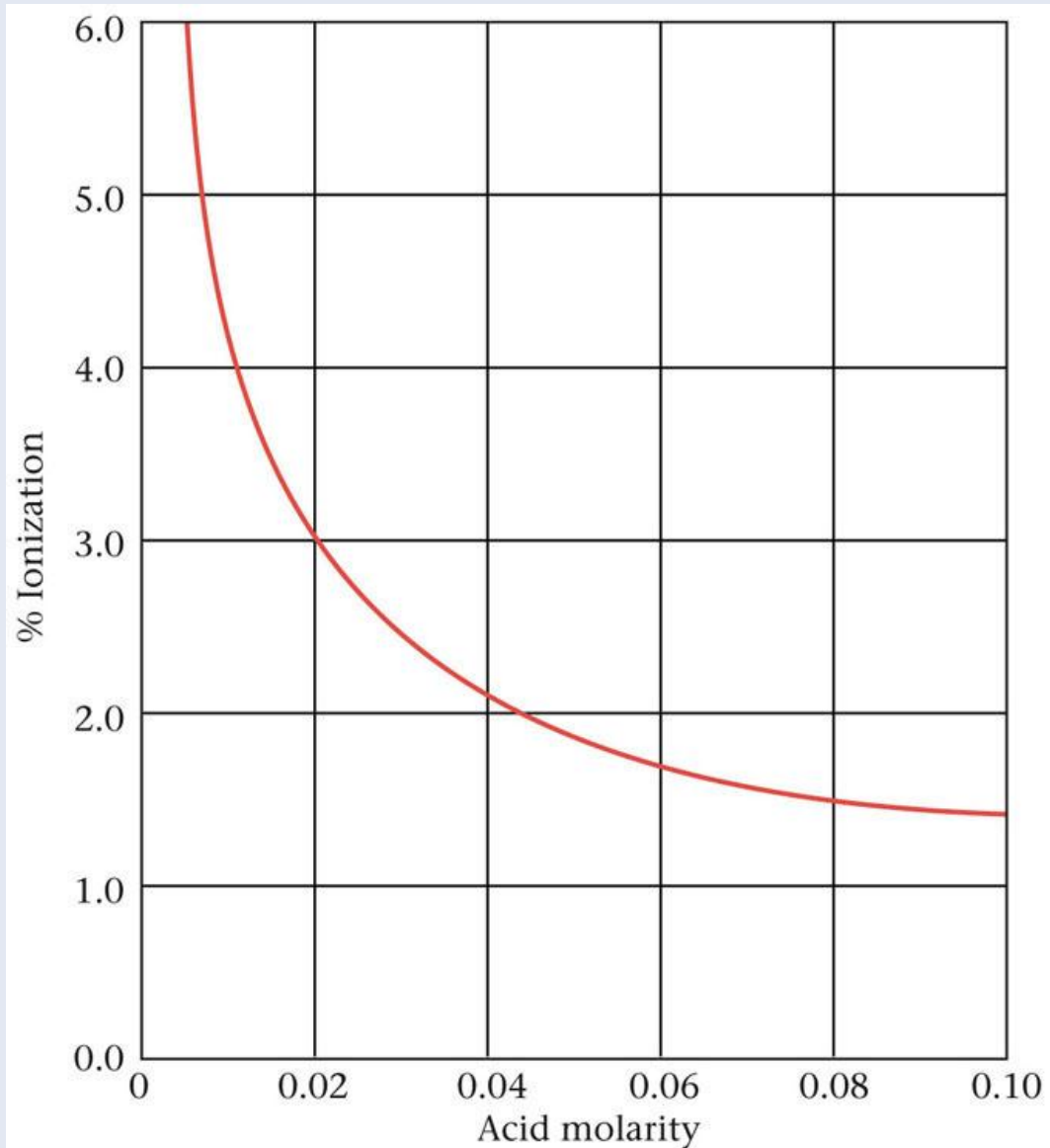
Example 13.6

Example 13.6

Example 13.6   Conceptual

In the box below, which has a volume of 0.50 L, the symbol ● represents 0.10 mol of a weak acid, HB. The symbol ● represents 0.10 mol of the conjugate base, B^-. Hydronium ions and water molecules are not shown. What is the percent ionization of the acid?
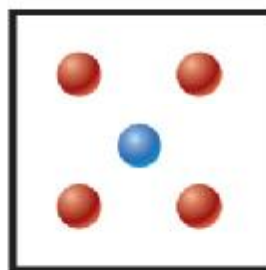
SOLUTION   There must, originally, have been five red circles. So,

$$\% \text{ ionization} = \tfrac{1}{5} \times 100 = 20\%$$

The other information given in the statement of the problem is irrelevant.

Calculating [H$^+$] in a Water Solution of a Weak Acid

- We can use the process for calculating equilibrium pressure for gaseous reactions that we looked at in Chapter 12 to calculate the equilibrium concentration of [H$^+$] for a weak acid

- The relationship between [HB], [H$^+$] and [B$^-$] is given in the equilibrium expression itself

Algebra Review – Quadratic Equations
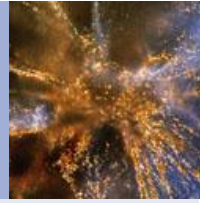
- Recall that for a quadratic equation in the form

$$ax^2 + bx + c = 0$$

- The roots are

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Example 13.7

Example 13.7 Nicotinic acid, $HC_6H_4O_2N$ ($K_a = 1.4 \times 10^{-5}$) is another name for niacin, an important member of the vitamin B group. Determine $[H^+]$ in a solution prepared by dissolving 3.0 g of nicotinic acid (MM = 123.11 g/mol), HNic, in enough water to form 245 mL of solution.

Strategy First, determine the molarity of the prepared solution:

$$\frac{3.0 \text{ g HNic}}{0.245 \text{ L}} \times \frac{1 \text{ mol}}{123.11 \text{ g}} = 0.10 \ M$$

Next, set up an equilibrium table similar to the one in the previous example. To accomplish that, note

- the original concentrations of HNic, H^+, and Nic^- are 0.10 M, 0.00 M, and 0.00 M, respectively, ignoring, tentatively at least, the H^+ ions from the ionization of water.
- the changes in concentration are related by the coefficients of the balanced equation, all of which are 1:

$$\Delta[\text{Nic}^-] = \Delta[\text{H}^+] \qquad \Delta[\text{HNic}] = -\Delta[\text{H}^+]$$

Letting $\Delta[H^+] = x$, it follows that $\Delta[\text{Nic}^-] = x$; $\Delta[\text{HNic}] = -x$. This information should enable you to express the equilibrium concentration of all species in terms of x. The rest is algebra; substitute into the expression for K_a and solve for $x = [H^+]$.

SOLUTION Setting up the table,

	$HNic(aq) \rightleftharpoons H^+(aq) + Nic^-(aq)$		
$[\ ]_0$	0.10	0.00	0.00
$\Delta[\ ]$	$-x$	$+x$	$+x$
$[\ ]_{eq}$	$0.10 - x$	x	x

Substituting into the expression for K_a,

$$K_a = \frac{(x)(x)}{0.10 - x} = 1.4 \times 10^{-5}$$

This is a quadratic equation. It could be rearranged to the form $ax^2 + bx + c = 0$ and solved for x, using the quadratic formula. Such a procedure is time-consuming and, in this case, unnecessary. Nicotinic acid is a weak acid, only slightly ionized in water. The equilibrium concentration of HNic, $0.10 - x$, is probably only very slightly less than its original concentration, 0.10 M. So let's make the approximation $0.10 - x \approx 0.10$. This simplifies the equation written above:

$$\frac{x^2}{\quad} = 1.4 \times 10^{-5}$$

Approximations Used in Calculations

- The value of K_a is usually known no more accurately than about $\pm 5\%$

- When solving for the unknowns used to work the equilibrium problem, for the expression

$$K_a = \frac{x^2}{a - x}$$

- Where a is the initial concentration of weak acid, you can neglect x in the denominator if doing so does not introduce an error of more than 5%, i.e.,

$$if \; \frac{x}{a} \leq 0.05, then$$

$$a - x \approx a$$

Approximations and Percent Ionization

- When

$$\frac{x}{a} = \frac{[H^+]_{eq}}{[HB]_o}$$

- Multiplying by 100% will give the percent ionization:

$$\frac{x}{a}\% = \frac{[H^+]_{eq}}{[HB]_o} \times 100\%$$

- If the percent ionization is 5% or less, you may make the approximation.

- If the percent ionization is greater than 5%, the quadratic formula or the successive approximation method is required

Example 13.8

Example 13.8

Example 13.8   Calculate $[H^+]$ in a 0.100 M solution of nitrous acid, HNO_2, for which $K_a = 6.0 \times 10^{-4}$.

Strategy   The setup is identical with that in Example 13.7. However, you will find, on solving for x, that $x > 0.050a$, so the approximation $a - x \approx a$ fails. The simplest way to proceed is to use the calculated value of x to obtain a better estimate of $[HNO_2]$, then solve again for $[H^+]$. An alternative is to use the quadratic formula. (This is a particularly shrewd choice if you have a calculator that can be programmed to solve quadratic equations.)

SOLUTION   Proceeding as in Example 13.7, you arrive at the equation

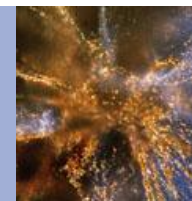$$K_a = \frac{x^2}{0.100 - x} = 6.0 \times 10^{-4}$$

Making the same approximation as before, $0.100 - x \approx 0.100$,

$$x^2 = 0.100 \times 6.0 \times 10^{-4} = 6.0 \times 10^{-5}$$

$$x = 7.7 \times 10^{-3} \approx [H^+]$$

To check the validity of the approximation, note that

Example 13.8, (Cont'd)

value of x just calculated, 0.0077, to find a more exact value for the concentration of HNO_2:

$$[HNO_2] = 0.100 - 0.0077 = 0.092\ M$$

Substituting in the expression for K_a,

$$K_a = \frac{x^2}{0.092} = 6.0 \times 10^{-4} \qquad x^2 = 5.5 \times 10^{-5}$$

$$x = 7.4 \times 10^{-3}\ M \approx [H^+]$$

This value is closer to the true $[H^+]$, because 0.092 M is a better approximation for $[HNO_2]$ than was 0.100 M. If you're still not satisfied, you can go one step further. Using 7.4×10^{-3} for x instead of 7.7×10^{-3}, you can recalculate $[HNO_2]$ and solve again for x. If you do, you will find that your answer does not change. In other words, you have gone about as far as you can go.

(2) *The quadratic formula.* This gives an exact solution for x but is more time-consuming. Rewrite the equation

$$\frac{x^2}{0.100 - x} = 6.0 \times 10^{-4}$$

in the form $ax^2 + bx + c = 0$. Doing this,

$$x^2 + (6.0 \times 10^{-4})x - (6.0 \times 10^{-5}) = 0$$

thus $a = 1$; $b = 6.0 \times 10^{-4}$; $c = -6.0 \times 10^{-5}$. Applying the quadratic formula,

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$= \frac{-6.0 \times 10^{-4} \pm \sqrt{(6.0 \times 10^{-4})^2 + (24.0 \times 10^{-5})}}{2}$$

If you carry out the arithmetic properly, you should get two answers for x:

$$x = 7.4 \times 10^{-3} \, M \qquad \text{and} \qquad -8.0 \times 10^{-3} \, M$$

The second answer is physically ridiculous; the concentration of H^+ cannot be a nega-tive quantity. The first answer is the same one obtained by the method of successive

Polyprotic Weak Acids

- Acids containing more than one ionizable hydrogen are called polyprotic
  - The anion formed in one step produces another H^+ in a successive ionization step
  - The equilibrium constant becomes smaller with each successive step

Triprotic Acid

- Phosphoric acid
  - H_3PO_4 (aq) $\rightleftharpoons$ H^+ (aq) + $H_2PO_4^-$ (aq) K_{a1}
  - $H_2PO_4^-$ (aq) $\rightleftharpoons$ H^+ (aq) + HPO_4^{2-} (aq) K_{a2}
  - HPO_4^{2-} (aq) $\rightleftharpoons$ H^+ (aq) + PO_4^{3-} (aq) K_{a3}
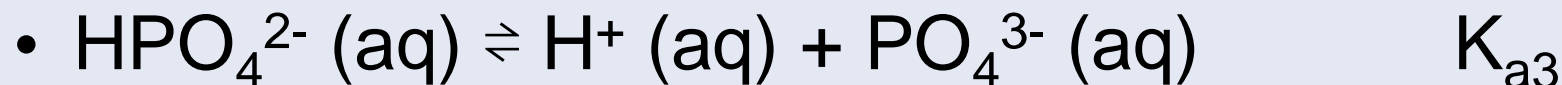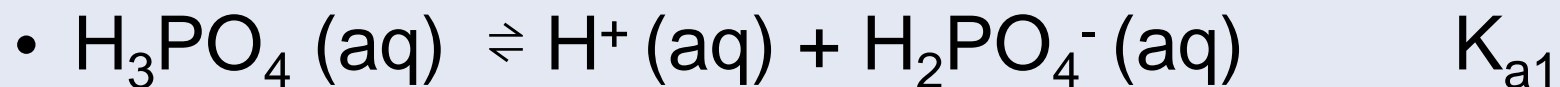
  - $K_{a1} > K_{a2} > K_{a3}$
  - With each successive step, *the acid becomes progressively weaker*

Table 13.3
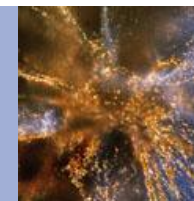
Table 13.3	Equilibrium Constants for Some Weak Polyprotic Acids at 25°C			
Acid	Formula	K_{a1}	K_{a2}	K_{a3}
Carbonic acid*	H_2CO_3	4.4×10^{-7}	4.7×10^{-11}	
Oxalic acid	$H_2C_2O_4$	5.9×10^{-2}	5.2×10^{-5}	
Phosphoric acid	H_3PO_4	7.1×10^{-3}	6.2×10^{-8}	4.5×10^{-13}
Sulfurous acid	H_2SO_3	1.7×10^{-2}	6.0×10^{-8}	

*Carbonic acid is a water solution of carbon dioxide:

$$CO_2(g) + H_2O \rightleftharpoons H_2CO_3(aq)$$
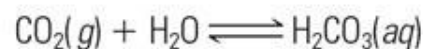
The ionization constants listed are calculated assuming that all the carbon dioxide that dissolves is in the form of H_2CO_3.

Example 13.9

Example 13.9　The distilled water you use in the laboratory is slightly acidic because of dissolved CO_2, which reacts to form carbonic acid, H_2CO_3. Calculate the pH of a 0.0010 M solution of H_2CO_3.

Strategy　In principle, there are two different sources of H^+ ions from H_2CO_3:

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \qquad K_{a1} = 4.4 \times 10^{-7}$$
$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq) \qquad K_{a2} = 4.7 \times 10^{-11}$$

In practice, essentially all the H^+ ions come from the first reaction, because K_{a1} is so much larger than K_{a2}. In other words, H_2CO_3 can be treated as if it were a weak monoprotic acid.

SOLUTION　For the first reaction, $H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$

$$K_{a1} = \frac{x^2}{0.0010 - x} = 4.4 \times 10^{-7} \qquad (x = [H^+] = [HCO_3^-])$$

Making the approximation $0.0010 - x \approx 0.0010$ and solving gives

$$x = (4.4 \times 10^{-10})^{1/2} = 2.1 \times 10^{-5}$$
$$pH = -\log_{10}(2.1 \times 10^{-5}) = 4.68$$

Note that the solution is indeed acidic, with a pH considerably less than 7. Notice that since

$$[H^+] = [HCO_3^-] \qquad \text{and} \qquad \frac{[H^+] \times [CO_3^{2-}]}{[HCO_3^-]} = K_{a2} = 4.7 \times 10^{-11}$$

it follows that $[CO_3^{2-}] = K_{a2} = 4.7 \times 10^{-11}$.

Weak Bases and their Equilibrium Constants

- Types of weak bases
  - Molecules
    - Ammonia, NH_3, and amines
    - NH_3 (aq) + H_2O ⇌ NH_4^+ (aq) + OH^- (aq)
  - Anions
    - Anions derived from weak acids are weak bases
    - I^- (aq) + H_2O ⇌ HI (aq) + OH^- (aq)

Example 13.10

Example 13.10 Write an equation to explain why each of the following produces a basic water solution.

(a) NO_2^- (b) Na_2CO_3 (c) $KHCO_3$

Strategy In each case, the anion reacts reversibly with a water molecule, picking up a proton from it. Two species are formed: the OH^- ion and the conjugate acid of the anion.

SOLUTION

(a) $NO_2^-(aq) + H_2O \rightleftharpoons HNO_2(aq) + OH^-(aq)$

(b) $CO_3^{2-}(aq) + H_2O \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$

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

Weak Base Equilibrium Constant

- NH_3 (aq) + H_2O ⇌ NH_4^+ (aq) + OH^- (aq)
  - The **base equilibrium constant, K_b** is

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

- For a generic weak base where
  - B (aq) + H_2O ⇌ HB^+ (aq) + OH^- (aq)

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

K_b by the Numbers

- As K_b becomes larger, base strength increases
- As with acids and K_a, we can define a pK_b:
  - $pK_b = -\log K_b$
  - As pK_b becomes smaller, base strength increases

Calculation of $[OH^-]$ in a Weak Base Solution

- The process of calculating the $[OH^-]$ in a weak base solution is the same as the process for calculating $[H^+]$ in a weak acid solution

Example 13.11

Example 13.11

Example 13.11   Graded

Consider sodium hypochlorite, NaOCl, the main component in household bleach. The hypochlorite ion, OCl^-, has $K_b = 3.6 \times 10^{-7}$. A solution is prepared by dissolving 12.0 g of NaOCl (MM = 74.45 g/mol) in enough water to make 835 mL of solution.

* *(a) What is the pH of the solution?
** (b) Household bleach is 5.25% NaOCl by mass. Assuming that its density is 1.00 g/mL, is household bleach more alkaline than the prepared solution?

Strategy

(a) The procedure is entirely analogous to that in Example 13.7. Take $[OH^-] = x$ and set up an equilibrium table, ignoring OH^- ions present in pure water. Solve for x, making the usual approximation. Then calculate pOH and finally the pH. You should obtain a pH greater than 7.

(b) Assume 100.0 g of solution, and determine [NaOCl], which is the same as $[OCl^-]$. Follow the strategy above for (a), and compare the two pH values obtained.

SOLUTION

(a) First, we obtain [NaOCl], which is equal to $[OCl^-]$:

$$[NaOCl] = \frac{12.0 \text{ g}}{0.835 \text{ L}} \times \frac{1 \text{ mol}}{74.45 \text{ g}} = 0.193 \ M$$

The equilibrium table is

	$OCl^-(aq) + H_2O \rightleftharpoons HOCl(aq) + OH^-(aq)$		
$[\ ]_0$	0.193	0.00	0.00
$\Delta[\ ]$	$-x$	$+x$	$+x$
$[\ ]_{eq}$	$0.193 - x$	x	x

Substituting into the equilibrium-constant expression, we find

$$K_b = \frac{x^2}{0.193 - x} = 3.6 \times 10^{-7}$$

Assuming $0.193 - x \approx 0.193$ and solving for x,

Since the % ionization,

$$\left(\frac{2.6 \times 10^{-4}}{0.193}\right) \times 100 = 0.14\% < 5.00\%,$$

the approximation is justified.

$$[OH^-] = 2.6 \times 10^{-4}$$

$$pOH = -\log_{10} 2.6 \times 10^{-4} = 3.59$$

$$pH = 14.00 - 3.59 = \boxed{10.41}$$

(b) If we assume 100.0 g of solution, then we can say that there are 5.25 g NaOCl in 100.0 mL of solution (since density is assumed to be 1.00 g/mL). Thus,
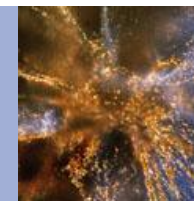
$$[NaOCl] = [OCl^-] = \frac{5.25 \text{ g}}{0.100 \text{ L}} \times \frac{1 \text{ mol}}{74.4 \text{ g}} = 0.706 \ M$$

Substituting into an equilibrium table (as in part (a)), we should get

$$K_b = \frac{x^2}{0.706 - x} = 3.6 \times 10^{-7}$$

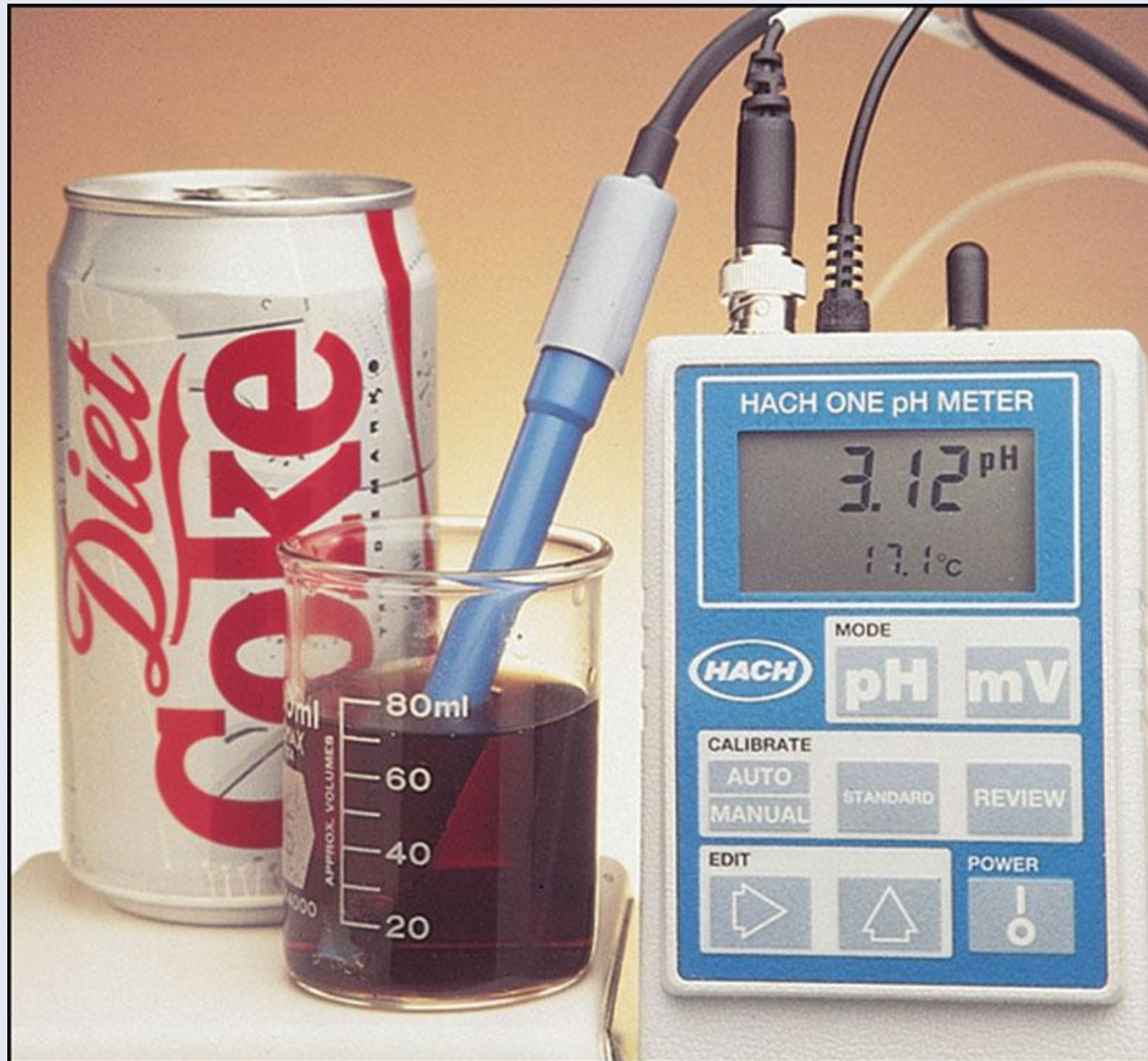Again assuming $0.706 - x \approx 0.706$ and solving for x, we obtain

Relation between K_a and K_b

- Consider the relation between a conjugate acid-base pair
    - $HB\ (aq) \rightleftharpoons H^+\ (aq) + B^-\ (aq)$ $\qquad K_I = K_a$ of HB
    - $B^-\ (aq) + H_2O \rightleftharpoons HB\ (aq) + OH^-\ (aq)$ $K_{II} = K_b$ of B^-
- These add to
    - $H_2O \rightleftharpoons H^+\ (aq) + OH^-\ (aq)$ $\qquad K_{III} = K_w$
- Since $K_I K_{II} = K_{III}$, $K_a K_b = K_w$
    - for a conjugate acid base pair only
    - In log form, $pK_a + pK_b = pK_w = 14$

Figure 13.4

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Notes on Acid-Base Strength

- K_a and K_b are inversely related
  - The larger K_a is, the smaller K_b is
- Features
  - Brønsted-Lowry acids
    - Strong acids
    - Weak acids
    - Acids weaker than water (conjugates of strong bases)
  - Brønsted-Lowry bases
    - Strong bases
    - Weak bases
    - Bases weaker than water (conjugates of strong acids)

Hydride ion

- Reaction of water with CaH_2
  - H^- is the conjugate base of H_2, a very weak acid
  - As a result, H^- is an extremely strong base

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Acid-Base Properties of Solutions of Salts

- A salt is an ionic solid containing a cation other than H^+ and an anion other than OH^-

- We can predict whether a salt will be acidic, basic or neutral by

  1. Deciding what effect the cation has on water

     - Is it acidic or is it neutral?

  2. Deciding what effect the anion has on water

     - Is it basic or is it neutral?

  3. Combining the two effects to decide the behavior of the salt in water

Cations

- Weak acid or spectator ion?
  - Most cations are acidic
    - These will change the pH by more than 0.5 pH units in a 0.1 M solution
  - Exceptions – these are spectators
    - Alkali metal cations
    - Heavier alkaline earth cations (Ca^{2+}, Sr^{2+}, Ba^{2+})

Anions

- Weak base or spectator ion?
  - Many anions are weak bases
    - These will change the pH by more than 0.5 pH units at 0.1 M
  - Exceptions – these are spectators
    - Anions of very strong acids: Cl^-, Br^-, I^-, NO_3^-, ClO_4^-

Sodium Chloride Solution
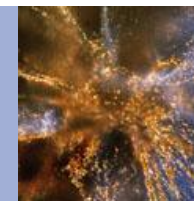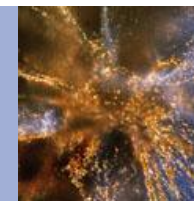

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Table 13.5

	Spectator		Basic		Acidic	
Anion	Cl^- Br^- I^-	NO_3^- ClO_4^-	$C_2H_3O_2^-$ F^- Many others	CO_3^{2-} PO_4^{3-}		
Cation	Li^+ Na^+ K^+	Ca^{2+} Sr^{2+} Ba^{2+}			NH_4^+ Mg^{2+} Transition metal ions	Al^{3+}

Table 13.5 Acid–Base Properties of Ions* in Water Solution

*For the acid-base properties of amphiprotic anions such as HCO_3^- or $H_2PO_4^-$, see the discussion at the end of this section.

Salts: Acidic, Basic or Neutral

- By comparing the K_a of an acidic cation with the K_b of a basic anion, the salt of both can be classified as acidic, basic or neutral

  - If $K_a > K_b$, the salt is acidic

    - NH_4F, $K_a = 5.6 \times 10^{-10}$; $K_b = 1.4 \times 10^{-11}$

  - If $K_b > K_a$, the salt is basic

    - NH_4ClO, $K_a = 5.6 \times 10^{-10}$; $K_b = 3.6 \times 10^{-7}$

Amphiprotic Anions

- HCO_3^-
  - $K_a = 4.7 \times 10^{-11}$
  - $K_b = 2.3 \times 10^{-8}$
- Because $K_b > K_a$, a solution of $NaHCO_3$ will be basic

Key Concepts

1. Classify a substance as a Brønsted-Lowry acid or base and write the net ionic equation to support the classification

2. Given $[H^+]$, $[OH^-]$, pH or pOH, calculate the three other quantities

3. Given the pH and original concentration of a weak acid, calculate K_a

4. Given the K_a and original concentration of a weak acid, calculate $[H^+]$

5. Given the K_b and original concentration of a weak base, calculate $[OH^-]$

6. Given K_a for a weak acid, calculate K_b for its conjugate base (or vice-versa).

7. Predict whether a salt will be acidic, basic or neutral.