

Chapter 16. Acid-Base Equilibria

Common Student Misconceptions

- Students often confuse a weak acid with a dilute acid.
- Students have problems with the numerical parts of this chapter. They should be strongly encouraged to do many problems on their own.
- Students often have difficulty using their calculators to take decimal logarithms and antilogarithms.
- Students confuse decimal (*log*) and natural (*ln*) logarithms.
- Students have a difficult time accepting that acids may be neutral as well as both positively and negatively charged species.
- Students tend to forget that $[\text{H}_3\text{O}^+][\text{OH}^-]$ is equal to 1.0×10^{-14} only at 25 °C.
- Students often wrestle with neutralization reactions producing solutions with pH different from 7.

Teaching Tips

- Determining pH of salts is often very conceptually and mathematically challenging. Solving and assigning many problems is needed to overcome these difficulties.
- Students should be made aware of the fact that terms such as *hydrogen ion*, *aqueous proton* – or simply *proton*, as well as *hydronium ion*, are often used interchangeably in the context of acid-base chemistry.
- Students should be reminded that water has both acidic and basic properties *depending* on what is mixed with it.
- Leveraging students' familiarity with Lewis Structures is useful in explaining relative strength of acids and reinforces ideas learned in Chapter 8.
- Remind students that, while strong acids and a vast majority of weak acids and weak bases are molecular substances, strong bases are ionic compounds.

Lecture Outline¹

16.1 Acids and Bases: A Brief Review^{2,3}

- Acids taste sour and cause certain dyes to change color.
- Bases taste bitter and feel soapy.
- Arrhenius concept of acids and bases:
 - An *acid* is a substance that, when dissolved in water, increases the concentration of H^+ ions.
 - Example: HCl is an acid.
 - An Arrhenius *base* is a substance that, when dissolved in water, increases the concentration of OH^- ions.
 - Example: NaOH is a base.
 - This definition is quite narrow in scope as it limits us to aqueous solutions.

16.2 Brønsted-Lowry Acids and Bases^{4,5}

- We can use a broader, more general definition for acids and bases that is based on the fact that acid-base reactions involve proton transfers.

¹ "Oxalic Acid" 3-D Model from Instructor's Resource CD/DVD

² "Acids and Bases" from Further Readings

³ "The Origin of the Term 'Base'" from Further Readings

⁴ "The Brønsted-Lowry Acid-Base Concept" from Further Readings

⁵ "Historical Development of the Hydrogen Ion Concept" from Further Readings

The H⁺ Ion in Water^{6,7}

- The H⁺(aq) ion is simply a proton (nucleus of a hydrogen atom without its valence electron).
- In water, clusters of hydrated H⁺(aq) ions form.
- The simplest cluster is H₃O⁺(aq).
 - We call this a **hydronium ion**.
 - Larger clusters are also possible (such as H₅O₂⁺ and H₉O₄⁺).
- Generally, we use H⁺(aq) and H₃O⁺(aq) interchangeably.

Proton-Transfer Reactions^{8,9,10,11}

- We will focus our attention on H⁺(aq).
- According to the Arrhenius definitions, an acid increases [H⁺] and a base increases [OH⁻].
- Another definition of acids and bases was proposed by Brønsted and Lowry.
- In the Brønsted-Lowry system, a **Brønsted-Lowry acid** is a species that donates H⁺ and a **Brønsted-Lowry base** is a species that accepts H⁺.
 - Therefore, a Brønsted-Lowry base does not need to contain OH⁻.
 - NH₃ is a Brønsted-Lowry base, but not an Arrhenius base.
- Consider NH₃(aq) + H₂O(l) ⇌ NH₄⁺(aq) + OH⁻(aq):
 - H₂O donates a proton to ammonia.
 - Therefore, water is acting as an acid.
 - NH₃ accepts a proton from water.
 - Therefore, ammonia is acting as a base.
 - An **amphiprotic** substance can behave either as an acid or as a base.
 - Thus, water is an example of an amphiprotic species.

Conjugate Acid-Base Pairs¹²

- Whatever is left of the acid after the proton is donated is called its conjugate base.
- Similarly, a conjugate acid is formed by adding a proton to the base.
- Consider HX(aq) + H₂O(l) ⇌ H₃O⁺(aq) + X⁻(aq):
 - HX and X⁻ differ only in the presence or absence of a proton.
 - They are said to be a **conjugate acid-base pair**.
 - X⁻ is called the **conjugate base**.
 - After HX (acid) loses its proton it is converted into X⁻ (base).
 - Therefore HX and X⁻ are a conjugate acid-base pair.
 - After H₂O (base) gains a proton it is converted into H₃O⁺ (acid).
 - H₃O⁺ is the **conjugate acid**.
 - Therefore, H₂O and H₃O⁺ are a conjugate acid-base pair.

Relative Strengths of Acids and Bases^{13,14}

- The stronger an acid is, the weaker its conjugate base will be.
- We can categorize acids and bases according to their behavior in water.
 1. *Strong acids* completely transfer their protons to water.

⁶ “Water” 3-D Model from Instructor’s Resource CD/DVD⁷ “Hydronium Ion” 3-D Model from Instructor’s Resource CD/DVD⁸ “Teaching Brønsted-Lowry Acid-Base Theory in a Direct Comprehensive Way” from Further Readings⁹ “Hydrogen Chloride” 3-D Model from Instructor’s Resource CD/DVD¹⁰ “Ammonia” 3-D Model from Instructor’s Resource CD/DVD¹¹ “Ammonium Ion” 3-D Model from Instructor’s Resource CD/DVD¹² Conjugate Acids and Bases” Activity from Instructor’s Resource CD/DVD¹³ Figure 16.3 from Transparency Pack¹⁴ “An Analogy for the Leveling Effect in Acid-Base Chemistry” from Further Readings

- No undissociated molecules remain in solution.
- Their conjugate bases have negligible tendencies to become protonated.
 - An example is HCl.
- 2. *Weak acids* only partially dissociate in aqueous solution.
 - They exist in solution as a mixture of molecules and component ions.
 - Their conjugate bases show a slight tendency to abstract protons from water.
 - These conjugate bases are weak bases.
 - Example: Acetic acid is a weak acid; acetate ion (conjugate base) is a weak base.
- 3. *Substances with negligible acidity* do not transfer a proton to water.
 - An example is CH₄.
 - The conjugate base of a substance with negligible acidity is a strong base.
- In every acid-base reaction, the position of the equilibrium favors the transfer of a proton from the stronger acid to the stronger base.
 - H⁺ is the strongest acid that can exist in equilibrium in aqueous solution.
 - OH⁻ is the strongest base that can exist in equilibrium in aqueous solution.
 - Hydronium ions and hydroxide ions are the strongest possible acid and base, respectively, that can exist in aqueous solution.
 - Stronger acids react with water to produce hydronium ions and stronger bases react with water to form hydroxide ions.
 - This effect is known as the *leveling effect* of water.

FORWARD REFERENCES

- Acid-base neutralization reaction will be discussed in detail in Chapter 17 (sections 17.1-17.3).
- Acid rain will be discussed in Chapter 18 (section 18.2).
- Inverse relationship between conjugate acids and bases will be mentioned in Chapter 20 (section 20.4).
- Acid-base properties in proton-transfer reactions involving OH⁻, H₂O, NH₃, etc. will be further discussed in Chapter 22 (section 22.1).

16.3 The Autoionization of Water^{15,16}

- In pure water the following equilibrium is established:

$$2\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq).$$
- This process is called the **autoionization** of water.

The Ion Product of Water¹⁷

- We can write an equilibrium constant expression for the autoionization of water.
- Because H₂O(l) is a pure liquid, we exclude it from the expression:

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

- **K_w** is called the **ion-product constant**.
 - At 25°C, the ion-product of water is:

$$1.0 \times 10^{-14} = K_w = [\text{H}_3\text{O}^+][\text{OH}^-].$$
- This applies to pure water as well as to aqueous solutions.
 - A solution is *neutral* if [OH⁻] = [H₃O⁺].
 - If the [H₃O⁺] > [OH⁻], the solution is *acidic*.
 - If the [H₃O⁺] < [OH⁻], the solution is *basic*.

¹⁵ “Acid and Base Dissociation Constants of Water and Its Associated Ions” from Further Readings

¹⁶ “Hydroxide Ion” 3-D Model from Instructor’s Resource CD/DVD

¹⁷ “K_w” Activity from Instructor’s Resource CD/DVD

FORWARD REFERENCES

- H₂O participating in acid-base reaction as a H⁺ donor or acceptor will be mentioned in Chapter 18 (section 18.3).

16.4 The pH Scale^{18,19,20,21,22,23,24,25,26,27}

- In most solutions, [H⁺] is quite small.
- We express the [H⁺] in terms of **pH**.

$$\text{pH} = -\log[\text{H}^+] = -\log[\text{H}_3\text{O}^+].$$
 - Note that this is a logarithmic scale.
 - Thus, a change in [H⁺] by a factor of 10 causes the pH to change by 1 unit.
- Most pH values fall between 0 and 14.
 - In neutral solutions at 25 °C, pH = 7.00.
 - In acidic solutions, [H⁺] > 1.0 × 10⁻⁷, so pH < 7.00.
 - As the pH decreases, the acidity of the solution *increases*.
 - In basic solutions, [H⁺] < 1.0 × 10⁻⁷, so pH > 7.00.
 - As the pH increases, the basicity of the solution increases (acidity *decreases*).

pOH and Other “p” Scales

- We can use a similar system to describe the [OH⁻].

$$\text{pOH} = -\log[\text{OH}^-].$$
- Recall that the value of K_w at 25 °C is 1.0 × 10⁻¹⁴.
 - Thus, we can describe a relationship between pH and pOH:

$$-\log[\text{H}^+] + (-\log[\text{OH}^-]) = \text{pH} + \text{pOH} = -\log K_w = 14.00.$$

Measuring pH^{28,29,30,31,32}

- The most accurate method to measure pH is to use a *pH meter*.
 - A pH meter consists of a pair of electrodes connected to a meter that measures small voltages.
 - A voltage that varies with pH is generated when the electrodes are placed in a solution.
 - This voltage is read by the meter, which is calibrated to display pH.
- Dyes that change color as pH changes are also useful.
 - They are called acid-base indicators.
 - Indicators are less precise than pH meters.
 - Many indicators do not have a sharp color change as a function of pH.
 - Most acid-base indicators can exist as either an acid or a base.
 - These two forms have different colors.

¹⁸ “One-Hundred Years of pH” from Further Readings¹⁹ “Do pH in Your Head” from Further Readings²⁰ “pH Estimation” Activity from Instructor’s Resource CD/DVD²¹ “Teaching the Truth about pH” from Further Readings²² “The pH Concept” from Further Readings²³ “Defining and Teaching pH” from Further Readings²⁴ “The Symbol for pH” from Further Readings²⁵ Figure 16.5 from Transparency Pack²⁶ “Acids and Bases” Activity from Instructor’s Resource CD/DVD²⁷ “Food is Usually Acidic, Cleaners Are Usually Basic” from Live Demonstrations²⁸ “Fruit Anthocyanins: Colorful Sensors of Molecular Milieu” from Further Readings²⁹ Figure 16.7 from Transparency Pack³⁰ “Colorful Acid-Base Indicators” from Live Demonstrations³¹ “Natural Indicators” Movie from Instructor’s Resource CD/DVD³² “Rainbow Colors with Mixed Acid-Base Indicators” from Live Demonstrations

- The relative concentration of the two different forms is sensitive to the pH of the solution.
- Thus, if we know the pH at which the indicator turns color, we can use this color change to determine whether a solution has a higher or lower pH than this value.
- Some natural products can be used as indicators. (Tea is colorless in acid and brown in base; red cabbage extract is another natural indicator.)

FORWARD REFERENCES

- Buffer capacity and pH range will be discussed in Chapter 17 (section 17.2).
- The effect of pH on solubility of poorly soluble salts and hydroxides will be discussed in Chapter 17 (section 17.5).
- H₂O as a proton donor and acceptor will be mentioned in Chapter 18 in the discussion of the role of the oceans (section 18.3).
- In Chapter 20 (section 20.6), measuring cell potentials will be used to determine pH.

16.5 Strong Acids and Bases

Strong Acids^{33,34,35}

- The most common strong acids are HCl, HBr, HI, HNO₃, HClO₃, HClO₄, and H₂SO₄.
- Strong acids are *strong electrolytes*.
 - All strong acids ionize completely in solution.
 - For example: nitric acid completely ionizes in water:

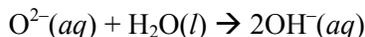
$$\text{HNO}_3(aq) + \text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{O}^+(aq) + \text{NO}_3^-(aq).$$
 - Since H⁺ and H₃O⁺ are used interchangeably, we write:

$$\text{HNO}_3(aq) \rightarrow \text{H}^+(aq) + \text{NO}_3^-(aq).$$
 - Note that we do not use equilibrium arrows for this equation because the reaction lies entirely to the right.
- In solutions the strong acid is usually the only significant source of H⁺.
 - Therefore, the pH of a solution of a monoprotic acid may usually be calculated directly from the initial molarity of the acid.
 - Caution: If the molarity of the acid is less than 10⁻⁶ M then the autoionization of water needs to be taken into account.

Strong Bases³⁶

- The most common strong bases are ionic hydroxides of the alkali metals or the heavier alkaline earth metals (e.g., NaOH, KOH, and Sr(OH)₂ are all strong bases).
- Strong bases are strong electrolytes and dissociate completely in solution.
 - For example:

$$\text{NaOH}(aq) \rightarrow \text{Na}^+(aq) + \text{OH}^-(aq)$$
- The pOH (and thus the pH) of a strong base may be calculated using the initial molarity of the base.
- Not all bases contain the OH⁻ ion.
 - Ionic metal oxides, for example, are basic.
 - They are thus able to abstract a proton from water and generate OH⁻.



FORWARD REFERENCES

- Adding strong acids and bases to buffers will be discussed in detail in Chapter 17 (section 17.2).

³³ “Colorful Effects of Hydrochloric Acid Dilution” from Live Demonstrations

³⁴ “Acid-Base Indicators Extracted from Plants” from Live Demonstrations

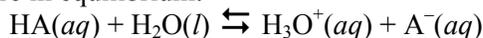
³⁵ “Introduction to Aqueous Acids” Animation from Instructor’s Resource CD/DVD

³⁶ “Disappearing Ink” from Live Demonstrations

- The use of strong acids and bases as titrants will be discussed in Chapter 17 (section 17.3).
- Basic oxides (also peroxides and superoxides) will be discussed in Chapter 22 (section 22. 5).

16.6 Weak Acids^{37,38,39,40,41,42,43}

- Weak acids are only partially ionized in aqueous solution.
 - There is a mixture of ions and un-ionized acid in solution.
 - Therefore, weak acids are in equilibrium:



or



- We can write an equilibrium constant expression for this dissociation:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \quad \text{or} \quad K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

- K_a is called the **acid-dissociation constant**.
- Note that the subscript “a” indicates that this is the equilibrium constant for the dissociation (ionization) of an acid.
- Note that $[\text{H}_2\text{O}]$ is omitted from the K_a expression. (H_2O is a pure liquid.)
- The larger the K_a , the stronger the acid.
 - K_a is larger since there are more ions present at equilibrium relative to un-ionized molecules.
 - If $K_a \gg 1$, then the acid is completely ionized and the acid is a strong acid.

Calculating K_a from pH

- In order to find the value of K_a , we need to know all of the equilibrium concentrations.
 - The pH gives the equilibrium concentration of H^+ .
 - Thus, to find K_a we use the pH to find the equilibrium concentration of H^+ and then use the stoichiometric coefficients of the balanced equation to help us determine the equilibrium concentration of the other species.
 - We then substitute these equilibrium concentrations into the equilibrium constant expression and solve for K_a .

Percent Ionization

- Another measure of acid strength is **percent ionization**.
 - For the reaction,



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

- Percent ionization relates the *equilibrium* H^+ concentration, $[\text{H}^+]_{\text{equilibrium}}$, to the *initial* HA concentration, $[\text{HA}]_{\text{initial}}$.

³⁷ “Pictorial Analogies XI: Concentrations and Acidity of Solutions” from Further Readings

³⁸ Table 16.2 from Transparency Pack

³⁹ “Weak vs. Strong Acids and Bases: The Football Analogy” from Further Readings

⁴⁰ “Equilibrium Constant” Activity from Instructor’s Resource CD/DVD

⁴¹ “Differences between Acid Strength and Concentration” from Live Demonstrations

⁴² “Formic Acid” 3-D Model from Instructor’s Resource CD/DVD

⁴³ “Methanol” 3-D Model from Instructor’s Resource CD/DVD

- The higher the percent ionization, the stronger the acid.
- However, we need to keep in mind that percent ionization of a weak acid decreases as the molarity of the solution increases.

Using K_a to Calculate pH

- Using K_a , we can calculate the concentration of H^+ (and hence the pH).
- Write the balanced chemical equation clearly showing the equilibrium.
- Write the equilibrium expression. Look up the value for K_a (in a table).
- Write down the initial and equilibrium concentrations for everything except pure water.
 - We usually assume that the equilibrium concentration of H^+ is x .
- Substitute into the equilibrium constant expression and solve.
 - Remember to convert x to pH if necessary.
- What do we do if we are faced with having to solve a quadratic equation in order to determine the value of x ?
 - Often this cannot be avoided.
 - However, if the K_a value is quite small, we find that we can make a simplifying assumption.
 - Assume that x is negligible compared with the initial concentration of the acid.
 - This will simplify the calculation.
 - It is always necessary to check the validity of any assumption.
 - Once we have the value of x , check to see how large it is compared with the initial concentration.
 - If x is $< 5\%$ of the initial concentration, the assumption is probably a good one.
 - If $x > 5\%$ of the initial concentration, then it may be best to solve the quadratic equation or use successive approximations.
 - Weak acids are only partially ionized.
 - Percent ionization is another method used to assess acid strength.

Polyprotic Acids⁴⁴

- **Polyprotic acids** have more than one ionizable proton.
- The protons are removed in successive steps.
 - Consider the weak acid, H_2SO_3 (sulfurous acid):

$$\begin{array}{l} H_2SO_3(aq) \rightleftharpoons H^+(aq) + HSO_3^-(aq) \quad K_{a1} = 1.7 \times 10^{-2} \\ HSO_3^-(aq) \rightleftharpoons H^+(aq) + SO_3^{2-}(aq) \quad K_{a2} = 6.4 \times 10^{-8} \end{array}$$
 - where K_{a1} is the dissociation constant for the first proton released, K_{a2} is for the second, etc..
- It is always easier to remove the first proton than the second proton in a polyprotic acid.
 - Therefore, $K_{a1} > K_{a2} > K_{a3}$, etc..
- The majority of the $H^+(aq)$ at equilibrium usually comes from the first ionization (i.e., the K_{a1} equilibrium).
 - If the successive K_a values differ by a factor of $\geq 10^3$, we can usually get a good approximation of the pH of a solution of a polyprotic acid by only considering the first ionization.

FORWARD REFERENCES

- The use of weak acids and bases as analytes in acid-base titrations will be discussed in Chapter 17 (section 17.3).
- Absorption of CO_2 by the oceans, and subsequent equilibria will be discussed in Chapter 18 (section 18.3).
- Weak acid (and base) ionization constants will be used in Chapter 19 to estimate ΔG° of ionization reactions.
- pH of electrolytes will be related to the cell potential in Chapter 20 (section 20.6).
- Weak acidic behavior of alcohols, incl. phenol, will be discussed in Chapter 24 (section 24.4).

⁴⁴ Table 16.3 from Transparency Pack

- The role of a triprotic H_3PO_4 in the formation of nucleic acids will be demonstrated in Chapter 24 (section 24.10).

16.7 Weak Bases^{45,46,47,48}

- Weak bases remove protons from substances.
- There is an equilibrium between the base and the resulting ions:

$$\text{weak base} + \text{H}_2\text{O}(l) \rightleftharpoons \text{conjugate acid} + \text{OH}^-(aq)$$

- Example:



- The **base-dissociation constant**, K_b , is defined as:

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

- The larger K_b , the stronger the base.

Types of Weak Bases

- Weak bases generally fall into one of two categories.
 - Neutral substances with a lone pair of electrons that can accept protons.
 - Most neutral weak bases contain nitrogen.
 - Amines** are related to ammonia and have one or more N–H bonds replaced with N–C bonds (e.g., CH_3NH_2 is methylamine).
 - Anions of weak acids are also weak bases.
 - Example: ClO^- is the conjugate base of HClO (weak acid):

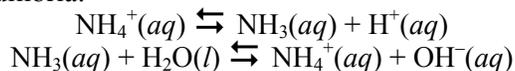
$$\text{ClO}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HClO}(aq) + \text{OH}^-(aq) \quad K_b = 3.33 \times 10^{-7}$$

FORWARD REFERENCES

- NH_3 as a weak base will be further mentioned in Chapter 22 (section 22.5).
- The fact that many organic compounds contain basic groups such as $-\text{NH}_2$, $-\text{NHR}$, and $-\text{NR}_2$ will be brought up in Chapter 24 (section 24.1).
- Amines, as weak bases, will be discussed in Chapter 24 (section 24.4).

16.8 Relationship Between K_a and K_b ⁴⁹

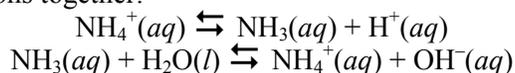
- We can quantify the relationship between the strength of an acid and the strength of its conjugate base.
- Consider the following equilibria:



- We can write equilibrium expressions for these reactions:

$$K_a = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]} \quad K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

- If we add these equations together:



⁴⁵ “Introduction to Aqueous Bases” Animation from Instructor’s Resource CD/DVD

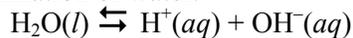
⁴⁶ Table 16.4 from Transparency Pack

⁴⁷ “Dimethylamine” 3-D Model from Instructor’s Resource CD/DVD

⁴⁸ “Hydroxylamine” 3-D Model from Instructor’s Resource CD/DVD

⁴⁹ Table 16.5 from Transparency Pack

- The net reaction is the autoionization of water.



- Recall that:

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

- We can use this information to write an expression that relates the values of K_a , K_b , and K_w for a conjugate acid-base pair.

$$K_a K_b = \left(\frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]} \right) \left(\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \right) = [\text{H}^+][\text{OH}^-] = K_w$$

- The product of the acid-dissociation constant for an acid (K_a) and the base-dissociation constant for its conjugate base (K_b) equals the ion-product constant for water (K_w):

$$K_a \times K_b = K_w$$

- Alternatively, we can express this as:

$$\text{p}K_a + \text{p}K_b = \text{p}K_w = 14.00 \text{ (at } 25^\circ\text{C)}$$

- Thus, the larger K_a (and the smaller $\text{p}K_a$), the smaller K_b (and the larger $\text{p}K_b$).
- The stronger the acid, the weaker its conjugate base and vice versa.

16.9 Acid-Base Properties of Salt Solutions⁵⁰

- Nearly all salts are strong electrolytes.
 - Therefore, salts in solution exist entirely of ions.
 - Acid-base properties of salts are a consequence of the reactions of their ions in solution.
- Many salt ions can react with water to form OH^- or H^+ .
 - This process is called **hydrolysis**.

An Anion's Ability to React with Water

- Consider an anion, X^- , as the conjugate base of an acid.
 - Anions from weak acids are basic.
 - They will cause an increase in pH.
 - Anions from strong acids are neutral.
 - They do not cause a change in pH.
 - Anions with ionizable protons (e.g., HSO_3^-) are amphiprotic.
 - How they behave in water is determined by the relative magnitudes of K_a and K_b for the ion:
 - If $K_a > K_b$, the anion tends to decrease the pH.
 - If $K_b > K_a$, the anion tends to increase the pH.

A Cation's Ability to React with Water^{51,52,53}

- Polyatomic cations that have one or more ionizable protons are conjugate acids of weak bases.
 - They tend to decrease pH.
- Many metal ions can cause a decrease in pH.
 - Metal cations of Group 1A and heavy alkaline earth metals are cations of strong bases and do not alter pH.
 - Metals with small, highly charged cations such as Fe^{3+} and Al^{3+} have K_a values comparable to values for familiar weak acids such as acetic acid.
 - The metal ions attract unshared electron pairs of water molecules and become hydrated.

⁵⁰ "Hydrolysis: Acidic and Basic Properties of Salts" from Live Demonstrations

⁵¹ "Hydrated Magnesium Cation" 3-D Model from Instructor's Resource CD/DVD

⁵² "Hydrated Aluminum Cation" 3-D Model from Instructor's Resource CD/DVD

⁵³ "Deprotonated Hydrated Aluminum Cation" 3-D Model from Instructor's Resource CD/DVD

- The larger the charge on the metal ion, the stronger the interaction between the ion and the oxygen of its hydrating water molecules.
- This weakens the O–H bonds in the water molecules and facilitates proton transfer from hydration water molecules to solvent water molecules.

Combined Effect of Cation and Anion in Solution

- The pH of a solution may be qualitatively predicted using the following guidelines:
 - Salts derived from a strong acid and a strong base are neutral.
 - Examples are NaCl and Ba(NO₃)₂.
 - Salts derived from a strong base and a weak acid are basic.
 - Examples are NaClO and Ba(C₂H₃O₂)₂.
 - Salts derived from a weak base (or a small cation with a charge of 2+ or greater) and a strong acid are acidic.
 - An example is NH₄NO₃ and AlCl₃.
 - Salts derived from a weak acid and a weak base can be either acidic or basic.
 - Equilibrium rules apply!
 - We need to compare K_a and K_b for hydrolysis of the anion and the cation.
 - For example, consider NH₄CN.
 - Both ions undergo significant hydrolysis.
 - Is the salt solution acidic or basic?
 - • The K_a of NH₄⁺ is smaller than the K_b of CN⁻, so the solution should be basic.

16.10 Acid-Base Behavior and Chemical Structure⁵⁴

Factors that Affect Acid Strength⁵⁵

- Consider H–X.
- For this substance to be an acid:
 - The H–X bond must be polar with H^{δ+} and X^{δ-}.
- In ionic hydrides, the bond polarity is reversed.
 - The H–X bond is polar with H^{δ-} and X^{δ+}.
 - In this case, the substance is a base.
- Other important factors in determining acid strength include:
 - The strength of the bond.
 - The H–X bond must be weak enough to be broken.
 - The stability of the conjugate base, X⁻.
 - The greater the stability of the conjugate base, the more acidic the molecule.

Binary Acids⁵⁶

- The H–X bond strength is important in determining relative acid strength in any *group* in the periodic table.
 - The H–X bond strength tends to decrease as the element X increases in size.
 - Acid strength increases down a group; base strength decreases down a group.
- H–X bond polarity is important in determining relative acid strength in any *period* of the periodic table.

⁵⁴ “Effect of Molecular Structure on the Strength of Organic Acids and Bases in Aqueous Solutions” from Live Demonstrations

⁵⁵ “Factors that Influence Relative Acid Strength in Water: A Simple Model” from Further Readings

⁵⁶ “The Correlation of Binary Acid Strengths with Molecular Properties in First-Year Chemistry” from Further Readings

- Acid strength increases and base strength decreases from left to right across a period as the electronegativity of X increases.
- For example, consider the molecules HF and CH₄.
 - HF is a weak acid because the bond energy is high.
 - The electronegativity difference between C and H is so small that the polarity of C–H bond is negligible, and CH₄ is neither an acid nor a base.

Oxyacids^{57,58,59,60}

- Many acids contain one or more O–H bonds.
 - Acids that contain OH groups (and often additional oxygen atoms) bound to the central atom are called **oxyacids**.
 - All oxyacids have the general structure Y–O–H.
- The strength of the acid depends on Y and the atoms attached to Y.
 - As the electronegativity of Y increases, so does the acidity of the substance.
 - The bond polarity increases and so does the stability of the conjugate base (usually an anion) increases.
- We can summarize how acid structure relates to the electronegativity of Y and the number of groups attached to Y:
 - For oxyacids with the same number of OH groups and the same number of oxygen atoms:
 - Acid strength increases with increasing electronegativity of the central atom, Y.
 - Example: HClO > HBrO > HIO
 - For oxyacids with the same central atom, Y:
 - Acid strength increases as the number of oxygen atoms attached to Y increases.
 - Example: HClO₄ > HClO₃ > HClO₂ > HClO

Carboxylic Acids

- There is a large class of acids that contain a –COOH group (a *carboxyl* group).
 - Acids that contain this group are called **carboxylic acids**.
 - Examples are acetic acid, benzoic acid, and formic acid.
- Why are these molecules acidic?
 - The additional oxygen atom on the carboxyl group increases the polarity of the O–H bond and stabilizes the conjugate base.
 - The conjugate base (*carboxylate anion*) exhibits resonance.
 - This gives it the ability to delocalize the negative charge over the carboxylate group, further increasing the stability of the conjugate base.
- The acid strength also increases as the number of electronegative groups in the acid increases.
 - For example, acetic acid is much weaker than trichloroacetic acid.

FORWARD REFERENCES

- Oxoacids and oxoanions containing halogens will be mentioned in Chapter 22 (section 22.4).
- Carboxylic acids will be discussed in Chapter 24 (section 24.4).
- Amphiprotic behavior of amino acids and zwitterions of amino acids will be discussed in Chapter 24 (section 24.7).
- The relative strength of acetic vs. pyruvic acids (with an additional carbonyl group) will be discussed in a sample integrative exercise in Chapter 24 (section 24.10).

⁵⁷ “The Relative Strength of Oxyacids and Its Application” from Further Readings

⁵⁸ Figure 16.18 from Transparency Pack

⁵⁹ “The Chemistry of Swimming Pool Maintenance” from Further Readings

⁶⁰ “Hypoiodous Acid” 3-D Model from Instructor’s Resource CD/DVD

16.11 Lewis Acids and Bases^{61,62,63}

- A Brønsted-Lowry acid is a proton donor.
- Focusing on electrons, a Brønsted-Lowry acid can be considered as an electron pair acceptor.
- Lewis proposed a new definition of acids and bases that emphasizes the shared electron pair.
 - A **Lewis acid** is an electron pair acceptor.
 - A **Lewis base** is an electron pair donor.
 - Note that Lewis acids and bases do not need to contain protons.
 - Therefore, the Lewis definition is the most general definition of acids and bases.
- What types of compounds can act as Lewis acids?
 - Lewis acids generally have an incomplete octet (e.g., BF_3).
 - Transition-metal ions are generally Lewis acids.
 - Lewis acids must have a vacant orbital (into which the electron pairs can be donated).
 - Compounds with multiple bonds can act as Lewis acids.
 - For example, consider the reaction:

$$\text{H}_2\text{O}(l) + \text{CO}_2(g) \rightarrow \text{H}_2\text{CO}_3(aq)$$
 - Water acts as the electron pair donor and carbon dioxide as the electron pair acceptor in this reaction.
 - Overall, the water (Lewis base) has donated a pair of electrons to the CO_2 (Lewis acid).
- The Lewis concept may be used to explain the acidic properties of many metal ions.
- Metal ions are positively charged and attract water molecules (via the lone pairs on the oxygen atom of water).
 - This interaction is called *hydration*.
- Hydrated metal ions act as acids.
 - For example:

$$\text{Fe}(\text{H}_2\text{O})_6^{3+}(aq) \rightleftharpoons \text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}(aq) + \text{H}^+(aq) \quad K_a = 2 \times 10^{-3}$$
- In general:
 - the higher the charge is, the stronger the $\text{M}-\text{OH}_2$ interaction.
 - the smaller the metal ion is, the more acidic the ion.
 - Thus, the pH increases as the size of the ion increases (e.g., Ca^{2+} vs. Zn^{2+}) and as the charge increases (e.g., Na^+ vs. Ca^{2+} and Zn^{2+} vs. Al^{3+}).

FORWARD REFERENCES

- Lewis bases and Crystal Field Theory will be discussed in Chapter 23 (section 23.6).

⁶¹ “The Research Style of Gilbert N. Lewis: Acids and Bases” from Further Readings

⁶² “Lewis Acid-Base Theory” Animation from Instructor’s Resource CD/DVD

⁶³ “Phosphorus Pentachloride” 3-D Model from Instructor’s Resource CD/DVD

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