

Section 14.1

Brønsted-Lowry Acids and Bases



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Learning Objectives



- Identify acids, bases, and conjugate acid-base pairs according to the Brønsted-Lowry definition
- Write equations for acid and base ionization reactions
- Use the ion-product constant for water to calculate hydronium and hydroxide ion concentrations
- Describe the acid-base behavior of amphiprotic substances

History of Acid/Base Theory



- In 1680, Robert Boyle reported traits of acid solutions
 - Ability to dissolve many substances
 - Change the colors of certain natural dyes
 - Lose these traits after coming in contact with alkali (base) solutions
- In the eighteenth century, it was recognized that acids
 - Have a sour taste
 - React with limestone to liberate a gaseous substance
 - Interact with alkalis to form neutral substances.

History of Acid/Base Theory



- In 1815, Humphry Davy contributed greatly to the development of the modern acid-base concept
 - Demonstrated that hydrogen is the essential constituent of acids.
- Joseph Louis Gay-Lussac concluded that acids are substances that can neutralize bases and that these two classes of substances can be defined only in terms of each other.
- In 1884, Svante Arrhenius defined an acid as a compound that dissolves in water to yield hydrogen cations and a base as a compound that dissolves in water to yield hydroxide anions.

Brønsted-Lowry Acids and Bases

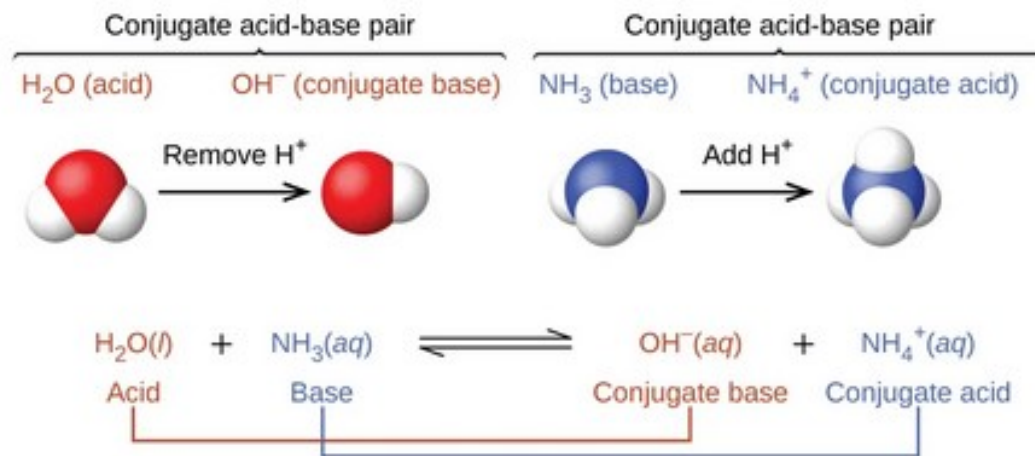


- In 1923, Johannes Brønsted and Thomas Lowry proposed a theory based on the transfer of hydrogen ions, H^+ (protons).
- A compound that donates a proton to another compound is called a **Brønsted-Lowry acid**.
- A compound that accepts a proton is called a **Brønsted-Lowry base**.
- An acid-base reaction is the transfer of a proton from a donor (acid) to an acceptor (base).

Conjugate Pairs



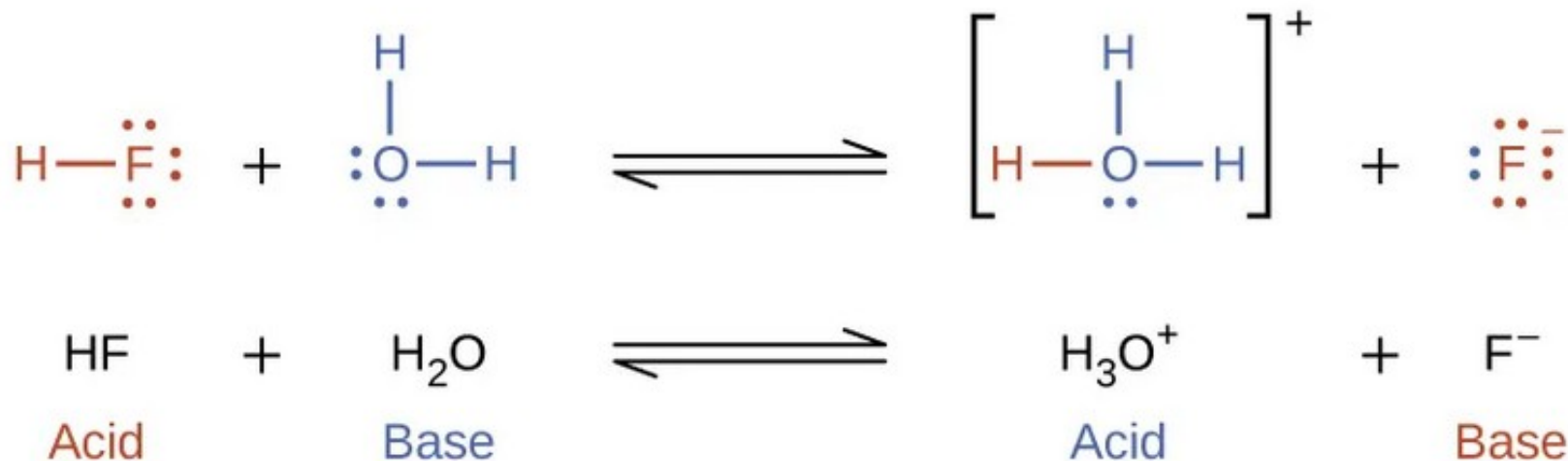
- When an acid donates H^+ , the species that remains is called the **conjugate base** of the acid
 - It reacts as a proton acceptor in the reverse reaction.
- When a base accepts H^+ , it is converted to its **conjugate acid**.



Acid Ionization



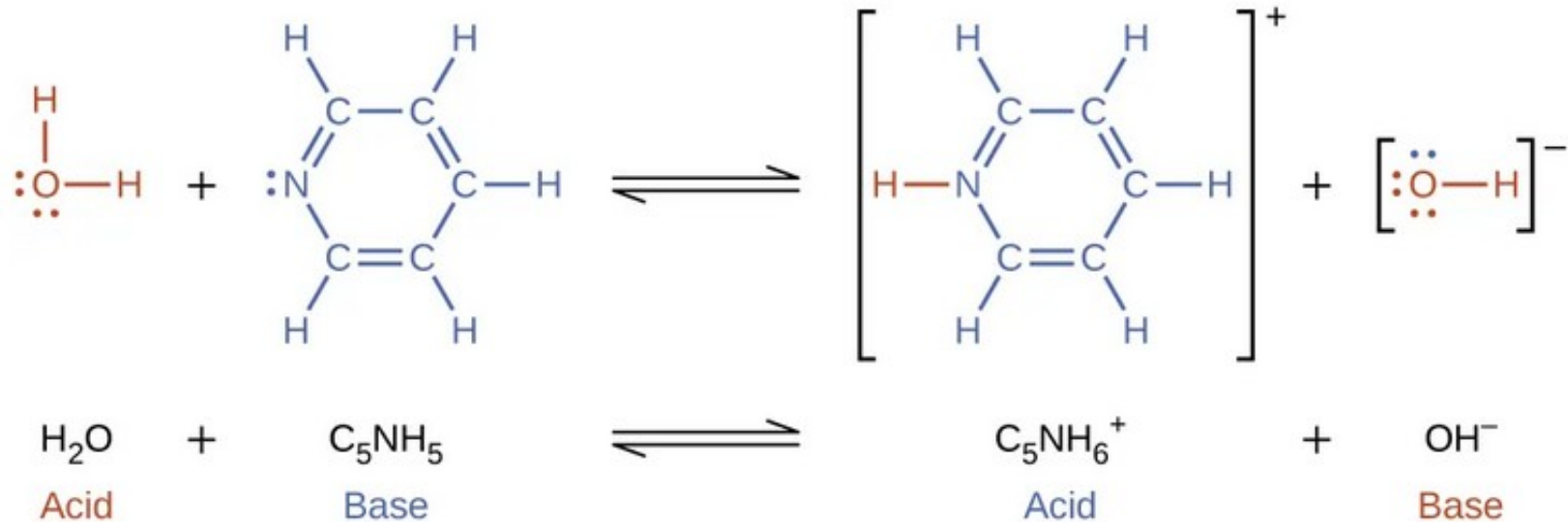
- The reaction between a Brønsted-Lowry acid and water is called **acid ionization**.



Base Ionization



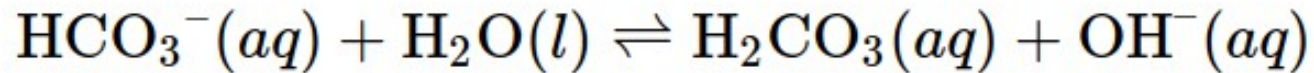
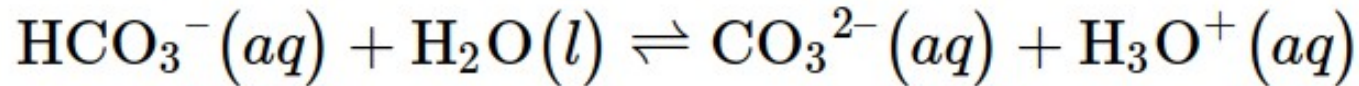
- **Base ionization** of a species occurs when it accepts protons from water molecules.



Amphoterism



- Species capable of either donating or accepting protons are called **amphiprotic**, or more generally, **amphoteric**.

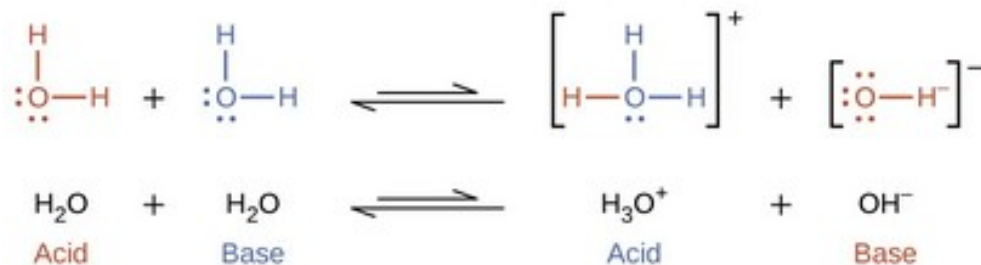


- When bicarbonate is added to water, both these equilibria are established simultaneously

Autoionization



- Molecules of an amphiprotic substance can react with one another to yield ions.

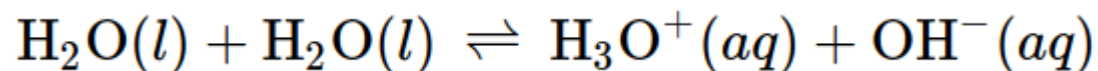


- This Process is called **autoionization**.
- The extent of the water autoionization process is reflected in the value of its equilibrium constant, the **ion-product constant for water, K_w** .

Autoionization of Water



- Pure water ionizes only slightly.
 - At 25 °C, K_w has a value of 1.0×10^{-14}
- The process is endothermic
 - The extent of ionization and the concentrations of hydronium ion and hydroxide ion increase with temperature.
 - At 100 °C, the value for K_w is about 5.6×10^{-1}



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

Section 14.2

pH and pOH



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Learning Objectives



- Explain the characterization of aqueous solutions as acidic, basic, or neutral
- Express hydronium and hydroxide ion concentrations on the pH and pOH scales
- Perform calculations relating pH and pOH



- The ion product of water shows that $[\text{H}^+]$ and $[\text{HO}^-]$ are inversely proportional.

$$[\text{H}^+] = \frac{K_w}{[\text{HO}^-]} \quad [\text{HO}^-] = \frac{K_w}{[\text{H}^+]}$$

- A solution is
 - **Neutral** if it contains equal concentrations of hydronium and hydroxide ions
 - **Acidic** if it contains a greater concentration of hydronium ions than hydroxide ions;
 - **Basic** if it contains a lesser concentration of hydronium ions than hydroxide ions.

pH



- A common means of expressing quantities that may span many orders of magnitude is to use a logarithmic scale.

$$\text{pX} = -\log X$$

- The pH of a solution is defined as

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

- Where $[\text{H}_3\text{O}^+]$ is the molar concentration of hydronium ion in the solution

pOH



- The hydroxide ion molarity may be expressed as a p-function, called pOH

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

- pOH is not as common a quantity as it is more difficult to measure and can be calculated from pH.

pH and pOH to $[H_3O^+]$ and $[HO^-]$



- We can rearrange the pH and pOH definitions to solve for $[H_3O^+]$ and $[HO^-]$

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

$$[OH^-] = 10^{-pOH}$$

Converting between pH and pOH



- The relationship between pH and pOH can be derived from the K_w expression:

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

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

$$\text{p}K_w = \text{pH} + \text{pOH}$$

- At 25 °C, the value of K_w is 1.0×10^{-14} so:

$$14.00 = \text{pH} + \text{pOH}$$

Neutral Solutions



- Neutral solutions have $[H^+] = [HO^-]$
 - At 25 °C

$$K_W = 1.00 \times 10^{-14} = (1.00 \times 10^{-7})(1.00 \times 10^{-7}) = [H^+][HO^-]$$

$$pH = -\log [H_3O^+] = -\log (1.0 \times 10^{-7}) = 7.00$$

$$pOH = -\log [OH^-] = -\log (1.0 \times 10^{-7}) = 7.00$$

Neutral Solutions



- Because K_w is dependent on temperature the pH and pOH of neutral solutions will also vary.

For example, at 80 °C

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (4.9 \times 10^{-7}) = 6.31$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (4.9 \times 10^{-7}) = 6.31$$

- This distinction can be important when studying certain processes, such as enzyme reactions in warm-blooded organisms at a temperature around 36–40 °C.

Common Examples



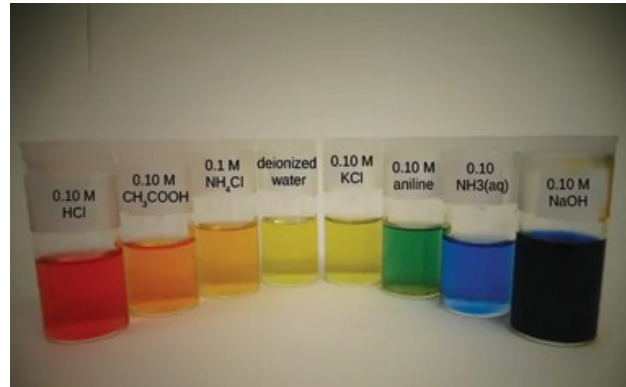
- Relationships between $[H_3O^+]$, $[OH^-]$, pH, and pOH for solutions classified as acidic, basic, and neutral

$[H_3O^+]$ (M)	$[OH^-]$ (M)	pH	pOH	Sample Solution
10^1	10^{-15}	-1	15	
10^0 or 1	10^{-14}	0	14	← 1 M HCl acidic
10^{-1}	10^{-13}	1	13	
10^{-2}	10^{-12}	2	12	← gastric juice ← lime juice
10^{-3}	10^{-11}	3	11	← 1 M CH_3CO_2H (vinegar) ← stomach acid
10^{-4}	10^{-10}	4	10	← wine ← orange juice
10^{-5}	10^{-9}	5	9	← coffee
10^{-6}	10^{-8}	6	8	← rain water
10^{-7}	10^{-7}	7	7	← pure water neutral
10^{-8}	10^{-6}	8	6	← blood ← ocean water ← baking soda
10^{-9}	10^{-5}	9	5	
10^{-10}	10^{-4}	10	4	
10^{-11}	10^{-3}	11	3	← Milk of Magnesia
10^{-12}	10^{-2}	12	2	← household ammonia, NH_3 ← bleach
10^{-13}	10^{-1}	13	1	
10^{-14}	10^0 or 1	14	0	← 1 M NaOH basic
10^{-15}	10^1	15	-1	

Measuring pH



- The acidity of a solution is typically assessed experimentally by measurement of its pH.
- The pOH of a solution is not usually measured, as it is easily calculated from an experimentally determined pH value.



Summary



Classification	Relative Ion Concentrations	pH at 25 °C
acidic	$[\text{H}_3\text{O}^+] > [\text{OH}^-]$	$\text{pH} < 7$
neutral	$[\text{H}_3\text{O}^+] = [\text{OH}^-]$	$\text{pH} = 7$
basic	$[\text{H}_3\text{O}^+] < [\text{OH}^-]$	$\text{pH} > 7$

Section 14.3

Relative Strengths of Acids and Bases



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Learning Objectives



- Assess the relative strengths of acids and bases according to their ionization constants
- Rationalize trends in acid–base strength in relation to molecular structure
- Carry out equilibrium calculations for weak acid–base systems

Acid-Base Strength



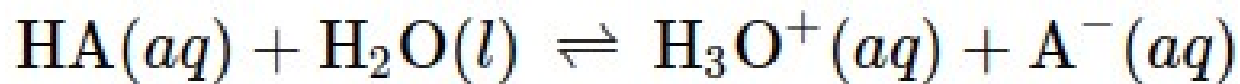
- The relative strength of an acid or base is the *extent to which it ionizes when dissolved in water*.
- A **strong** acid or base ionizes nearly completely.
- If little of the acid or base ionizes it is considered **weak**.
- There are many more weak acids and bases than strong ones.

6 Strong Acids		6 Strong Bases	
HClO ₄	perchloric acid	LiOH	lithium hydroxide
HCl	hydrochloric acid	NaOH	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	Ca(OH) ₂	calcium hydroxide
HNO ₃	nitric acid	Sr(OH) ₂	strontium hydroxide
H ₂ SO ₄	sulfuric acid	Ba(OH) ₂	barium hydroxide

Acid-Ionization Constant



- The relative strengths of acids may be quantified by measuring their equilibrium constants in aqueous solutions.
- The equilibrium constant for an acid is called the **acid-ionization constant, K_a** .
 - We do not include $[H_2O]$ in the equation.

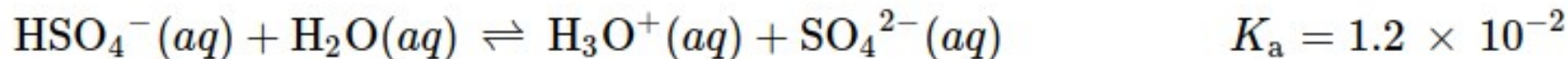
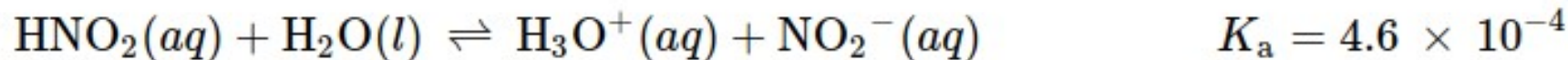
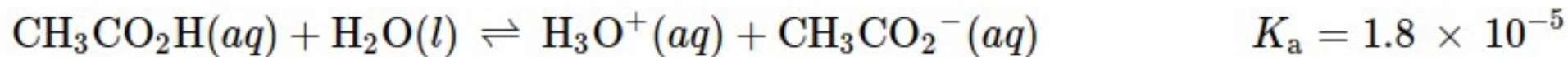


$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$



- The larger the K_a of an acid, the larger the concentration of H_3O^+ and A^- and the stronger the acid.
- K_a approaches ∞ when for strong acids.
- The K_a of weak acids is determined experimentally and tabulated.
 - The K_a for most weak acids is well known.
- A table of ionization constants for weak acids is provided in [Appendix H](#).

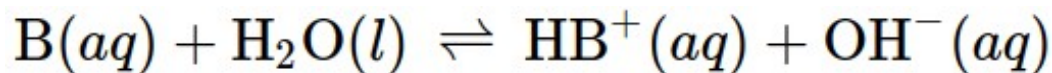
Relative Strength Example



Base-Ionization Constant



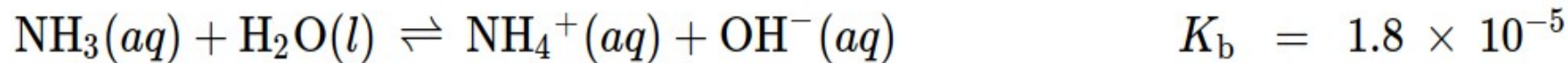
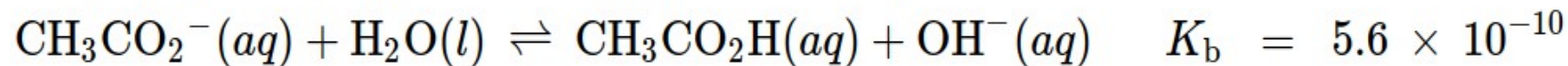
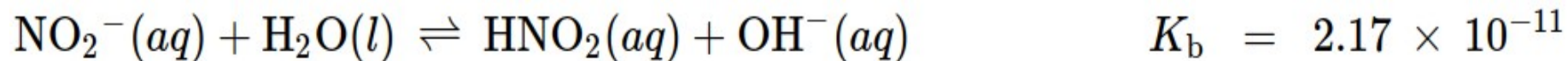
- Similar to acids, the relative strength of a base is described by the **base-ionization constant, K_b** .
- A stronger base has a larger ionization constant than does a weaker base.



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

- A table of ionization constants for weak bases appears in [Appendix I](#).

Relative Strength Example



Percent Ionization



- The **percent ionization** of a weak acid or base is defined in terms of the composition of an equilibrium mixture

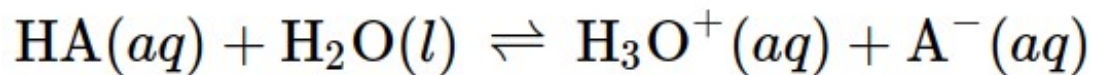
$$\% \text{ ionization} = \frac{[\text{H}_3\text{O}^+]_{eq}}{[\text{HA}]_0} \times 100 \% = \frac{[\text{HO}^-]_{eq}}{[\text{B}]_0} \times 100 \%$$

- Unlike K_a or K_b , the percent ionization of a weak acid or base varies with the initial concentration
 - Typically decreasing as concentration increases.

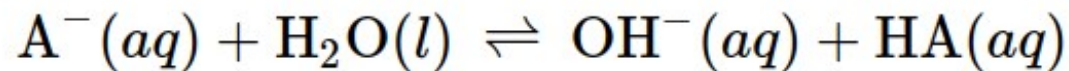
Conjugate Acid-Base Pairs



- For the conjugate acid-base pair HA / A^- , ionization equilibrium equations and ionization constant expressions are



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

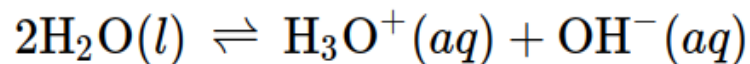
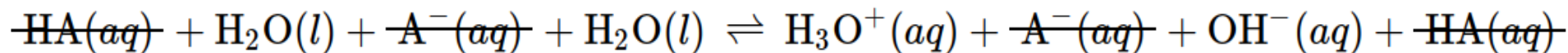


$$K_b = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$

Conjugate Acid-Base Pairs



- Adding these two chemical equations yields the equation for the autoionization for water.



$$K_a \times K_b = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \times \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = [\text{H}_3\text{O}^+][\text{OH}^-] = K_w$$

Conjugate Acid-Base Pairs



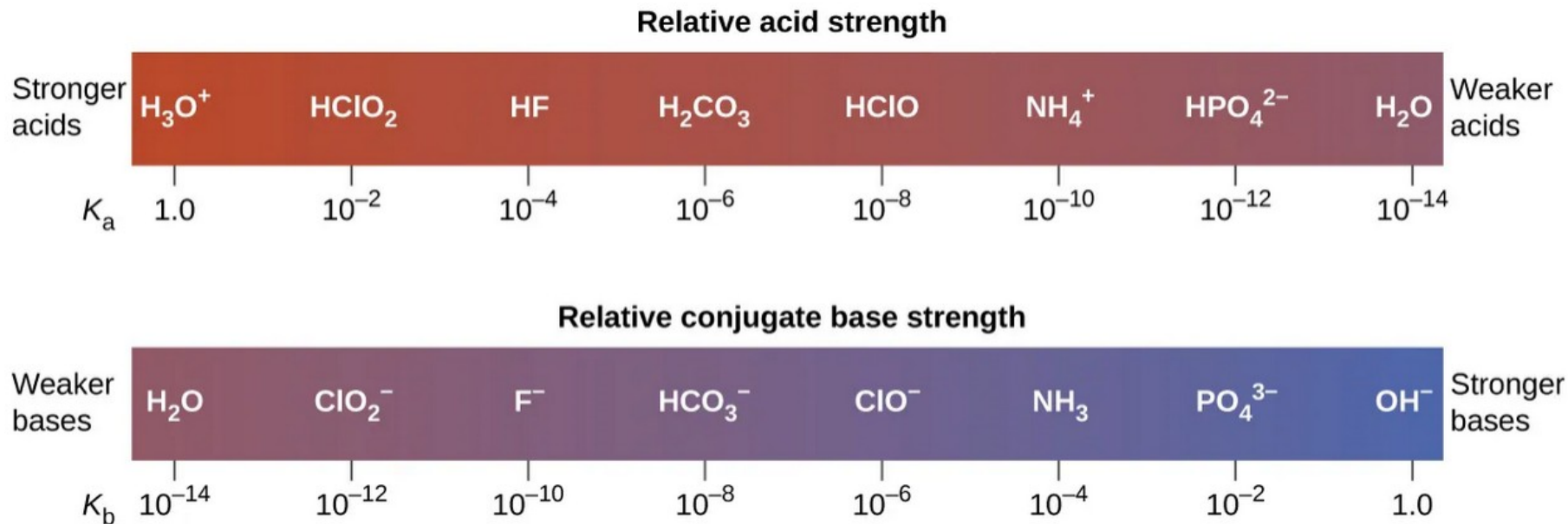
- We now have a means of converting between K_a and K_b for a conjugate acid/base pair.

$$K_a = \frac{K_w}{K_b} \qquad K_b = \frac{K_w}{K_a}$$

Conjugate-Pairs Strength



- The inverse proportional relation between K_a and K_b means the stronger the acid or base, the weaker its conjugate partner



Conjugate-Pairs Strength



- This figure shows strengths of conjugate acid-base pairs relative to the strength of water as the reference substance.

Acid			Base		
Increasing acid strength ↑	perchloric acid	HClO_4	Do not undergo acid ionization in water	ClO_4^-	perchlorate ion
	sulfuric acid	H_2SO_4		HSO_4^-	hydrogen sulfate ion
	hydrogen iodide	HI		I^-	iodide ion
	hydrogen bromide	HBr		Br^-	bromide ion
	hydrogen chloride	HCl		Cl^-	chloride ion
	nitric acid	HNO_3	Undergo complete acid ionization in water	NO_3^-	nitrate ion
	hydronium ion	H_3O^+		H_2O	water
	hydrogen sulfate ion	HSO_4^-		SO_4^{2-}	sulfate ion
	phosphoric acid	H_3PO_4		H_2PO_4^-	dihydrogen phosphate ion
	hydrogen fluoride	HF		F^-	fluoride ion
	nitrous acid	HNO_2		NO_2^-	nitrite ion
	acetic acid	$\text{CH}_3\text{CO}_2\text{H}$		CH_3CO_2^-	acetate ion
	carbonic acid	H_2CO_3		HCO_3^-	hydrogen carbonate ion
	hydrogen sulfide	H_2S		HS^-	hydrogen sulfide ion
	ammonium ion	NH_4^+		NH_3	ammonia
	hydrogen cyanide	HCN		CN^-	cyanide ion
	hydrogen carbonate ion	HCO_3^-		CO_3^{2-}	carbonate ion
	water	H_2O		OH^-	hydroxide ion
	hydrogen sulfide ion	HS^-	Undergo complete base ionization in water	S^{2-}	sulfide ion
	ethanol	$\text{C}_2\text{H}_5\text{OH}$		$\text{C}_2\text{H}_5\text{O}^-$	ethoxide ion
	ammonia	NH_3		NH_2^-	amide ion
	hydrogen	H_2		H^-	hydride ion
	methane	CH_4		CH_3^-	methide ion
			Increasing base strength ↓		

Leveling Effect



- Strong acids will ionize completely to produce H_3O^+ ions in water.
- H_3O^+ is therefore the strongest acid possible in water.
- This is the **leveling effect**. All acids stronger than H_3O^+ will ultimately be converted entirely to H_3O^+ .
- To measure the relative strength of strong acids we must use a less basic solvent.
- The same logic is applied to strong bases.

Effect of Molecular Structure on Acid-Base Strength



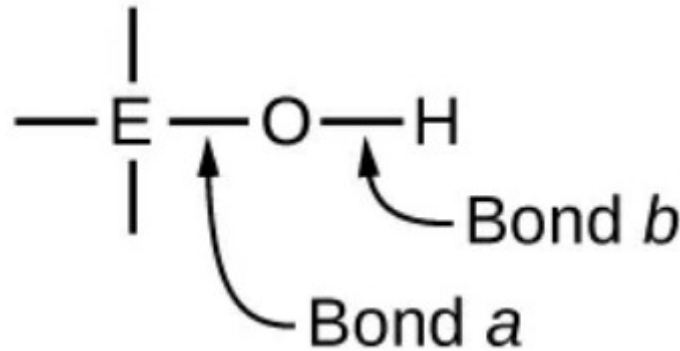
- The acid strength of binary compounds of hydrogen with nonmetals (A) increases as the H-A bond strength decreases down a group in the periodic table.

14	15	16	17	
6 CH₄ Neither acid nor base	7 NH₃ Weak base $K_b = 1.8 \times 10^{-5}$	8 H₂O Neutral	9 HF Weak acid $K_a = 6.8 \times 10^{-4}$	<div>Increasing acid strength</div> <div>Increasing base strength</div>
14 SiH₄ Neither acid nor base	15 PH₃ Very weak base $K_b = 4 \times 10^{-28}$	16 H₂S Weak acid $K_a = 9.5 \times 10^{-8}$	17 HCl Strong acid	
<div>Increasing acid strength</div> <div>Increasing base strength</div>				

Ternary Acids and Bases



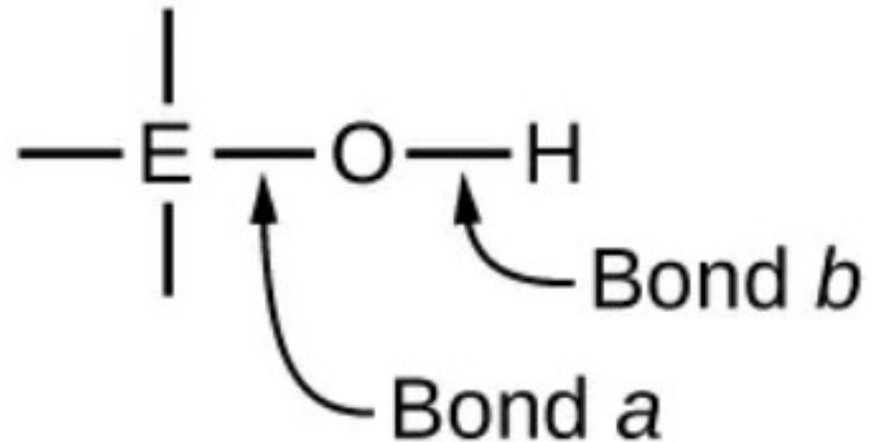
- Ternary compounds are composed of hydrogen, oxygen, and some third element (E)
- the central E atom is bonded to one or more O atoms, and at least one of the O atoms is also bonded to an H atom, $O_mE(OH)_n$.



Ternary Bases



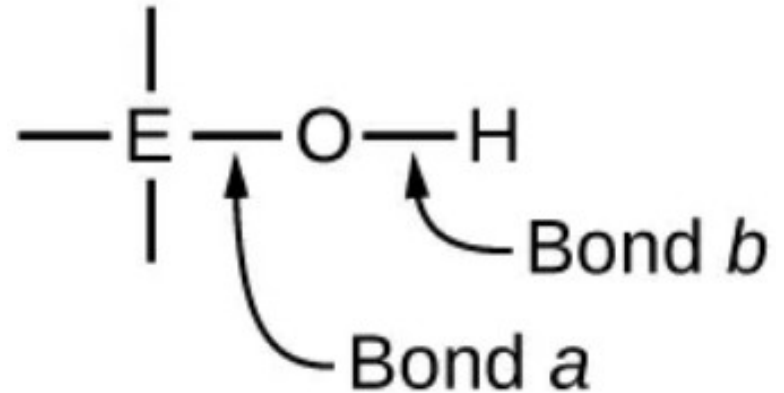
- If the central atom (E) has a low electronegativity the bond *a* is more readily broken than bond *b* between oxygen.
 - Hence bond *a* is ionic
 - Hydroxide ions are released to the solution
 - The compound is a base
 - Ex. $\text{Ca}(\text{OH})_2$ and KOH



Ternary Acids



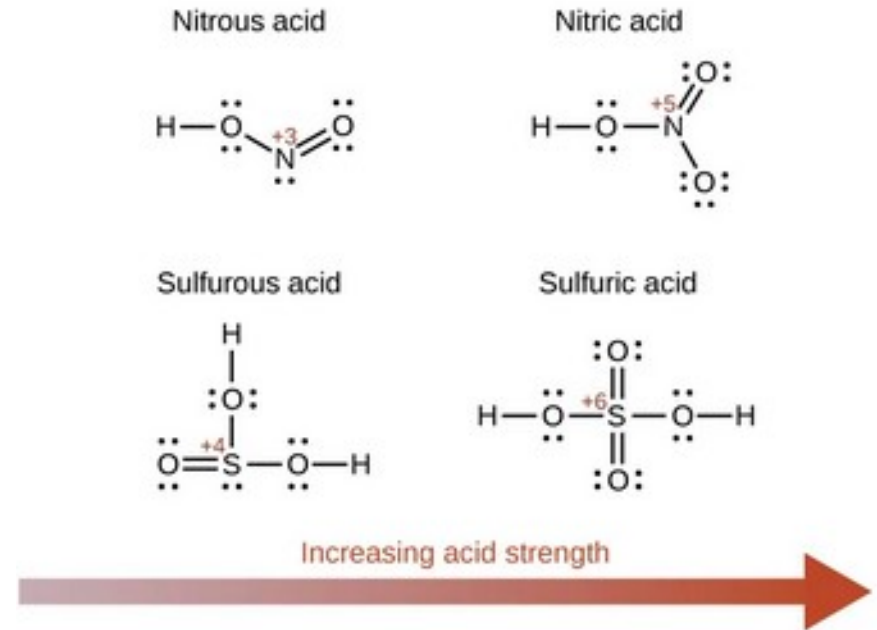
- If atom E has a relatively high electronegativity, bond *a* is strongly covalent.
 - Bond *b* is weakened because electrons are displaced toward E.
 - Bond **b** is polar and readily releases hydrogen ions to the solution
 - The compound behaves as an acid.



Oxyacids



- High electronegativities are characteristic of the more nonmetallic elements.
 - Nonmetallic elements form covalent compounds containing acidic -OH groups that are called oxyacids.
 - Increasing the oxidation number of the central atom E also increases the acidity of an oxyacid



Amphoteric Ternary Acids/Bases



- Hydroxy compounds of elements with intermediate electronegativities and relatively high oxidation numbers are usually amphoteric.
 - Ex. elements near the diagonal line separating the metals from the nonmetals in the periodic table
 - The hydroxy compounds act as acids when they react with strong bases and as bases when they react with strong acids.



Section 14.4

Hydrolysis of Salts



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Learning Objectives



- Predict whether a salt solution will be acidic, basic, or neutral
- Calculate the concentrations of the various species in a salt solution
- Describe the acid ionization of hydrated metal ions

Hydrolysis of Salts

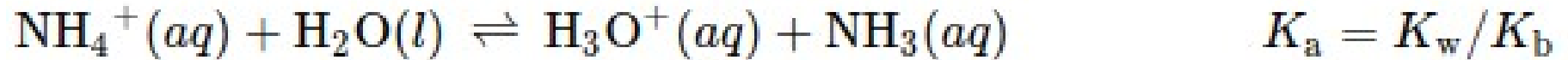


- Salts are ionic compounds composed of cations and anions
- They may be capable of undergoing an acid or base ionization reaction with water.
- Aqueous salt solutions may be acidic, basic, or neutral, depending on the relative acid-base strengths of the salt's constituent ions.

Salts with Acidic Ions



- Since ammonia is a weak base, K_b is measurable and $K_a > 0$
 - Ammonium ion is a weak acid



- HCl is a strong acid, K_a is immeasurably large and $K_b \approx 0$
 - Chloride ions don't undergo appreciable hydrolysis



Salts with Basic Ions



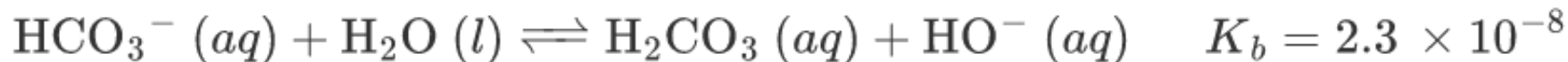
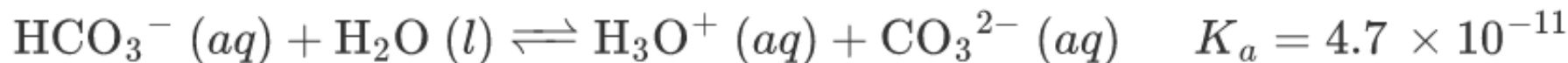
- The sodium ion does not undergo appreciable acid or base ionization and has no effect on the solution pH.
- Acetic acid is a weak acid, its K_a is measurable and $K_b > 0$
 - Acetate ion is a weak base



Salts with Acidic and Basic Ions



- Sodium does not hydrolyze to any appreciable extent.
- HCO_3^- can behave as both an acid and a base.

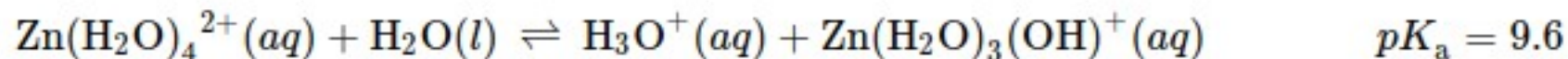
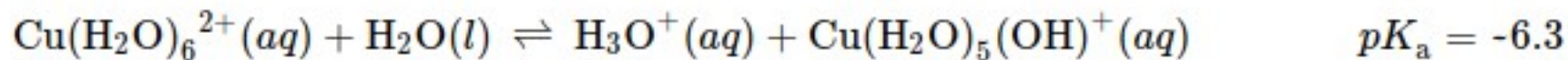
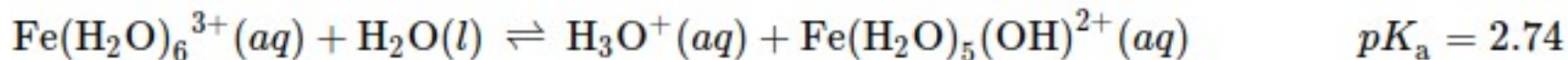


- Since $K_b \gg K_a$, the solution is basic

The Ionization of Hydrated Metal Ions



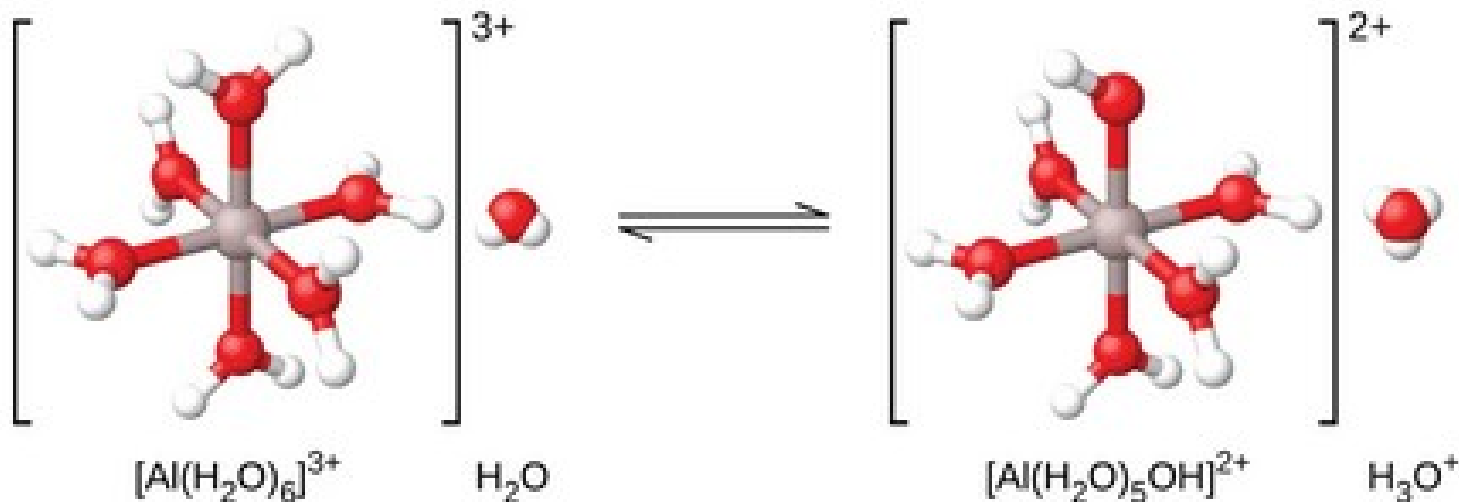
- Aside from group 1 and group 2 metals, most metal ions will undergo acid ionization to some extent when dissolved in water.
- The acid strength of these complex ions typically increases with increasing charge and decreasing size of the metal ions.



Covalently Bonded Water



- Hydrated metals covalently bonded to a fixed number of water molecules to yield a complex ion.



Step-Wise Proton Transfer



- Metal Hydrates will release protons in a step-wise fashion
 - This is an example of polyprotic acid



Section 14.5

Polyprotic Acids



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Learning Objectives

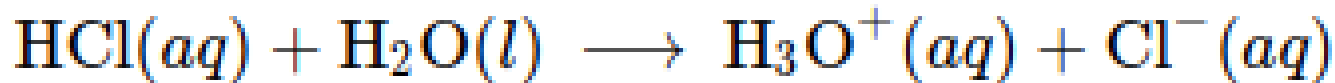


- Extend previously introduced equilibrium concepts to acids and bases that may donate or accept more than one proton

Monoprotic Acids



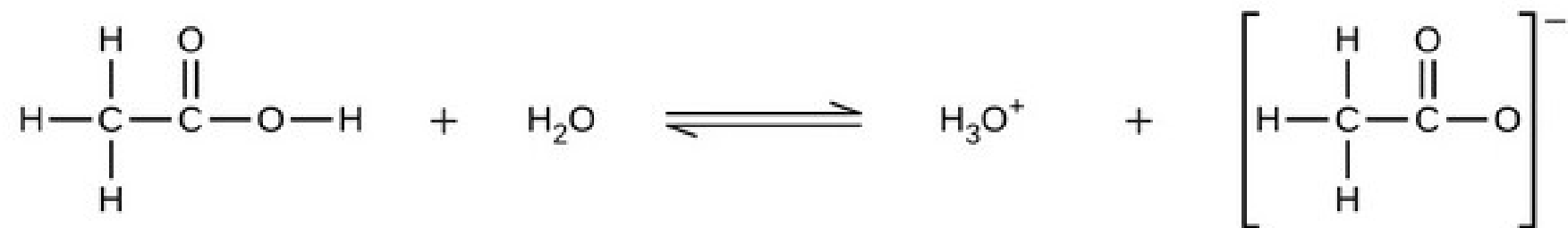
- Acids are classified by the number of protons per molecule that they can give up in a reaction.
- Acids that contain one ionizable hydrogen atom in each molecule are called **monoprotic acids**.



Multiple Hydrogens



- Not all of the hydrogens in an acid is acidic



Diprotic Acids



- **Diprotic acids** contain two ionizable hydrogen atoms per molecule
- Ionization of such acids occurs in two steps.
- The first ionization always takes place to a greater extent than the second ionization.

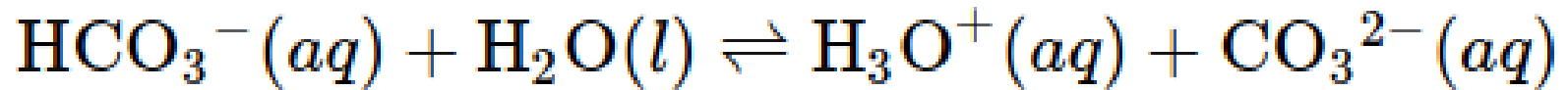
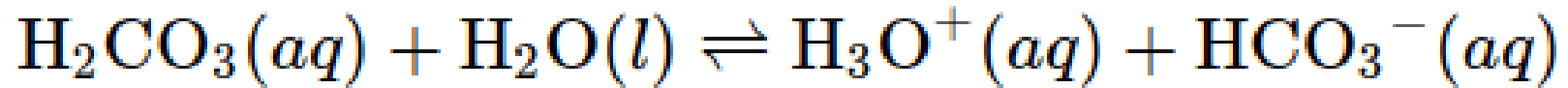
First ionization: $\text{H}_2\text{SO}_4(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{HSO}_4^-(aq)$

Second ionization: $\text{HSO}_4^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{SO}_4^{2-}(aq)$

$$K_{a1} = \text{more than } 10^2$$

$$K_{a2} = 1.2 \times 10^{-2}$$

Stepwise Ionization



$$K_{\text{H}_2\text{CO}_3} = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 4.3 \times 10^{-7}$$

$$K_{\text{HCO}_3^-} = \frac{[\text{H}_3\text{O}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 4.7 \times 10^{-11}$$

- $K_{\text{H}_2\text{CO}_3}$ is larger than $K_{\text{HCO}_3^-}$ by a factor of 10^4 , so H_2CO_3 is the dominant producer of hydronium ion in the solution.

Approximations



- If the first ionization constant of a weak diprotic acid is larger than the second by a factor of at least 20, it is appropriate to treat the first ionization separately and calculate concentrations resulting from it before calculating concentrations of species resulting from subsequent ionization.

Triprotic Acid



- A **triprotic acid** is an acid that has three ionizable H atoms.
- Like diprotic acid, each successive ionization reaction is less extensive than the former
- This is reflected in decreasing values for the stepwise acid ionization constants.
 - This is a general characteristic of polyprotic acids
 - Successive ionization constants often differ by a factor of about 10^5 to 10^6 .

Tripotric Acid Example



First ionization: $\text{H}_3\text{PO}_4(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{H}_2\text{PO}_4^-(aq)$

Second ionization: $\text{H}_2\text{PO}_4^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{HPO}_4^{2-}(aq)$

Third ionization: $\text{HPO}_4^{2-}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{PO}_4^{3-}(aq)$

$$K_{a1} = 7.5 \times 10^{-3}$$

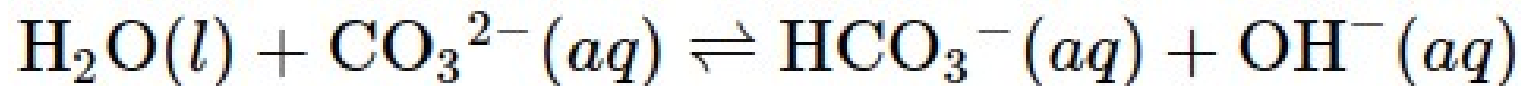
$$K_{a2} = 6.2 \times 10^{-8}$$

$$K_{a3} = 4.2 \times 10^{-13}$$

Polyprotic Bases



- All of the concepts we've learned for polyprotic acids can be applied to bases.
- The carbonate ion is an example of a **diprotic base**, it can accept two protons.



$$K_{b1} = 2.1 \times 10^{-4}$$

$$K_{b2} = 2.3 \times 10^{-8}$$

Section 14.6

Buffers



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Learning Objectives



- Describe the composition and function of acid–base buffers
- Calculate the pH of a buffer before and after the addition of added acid or base

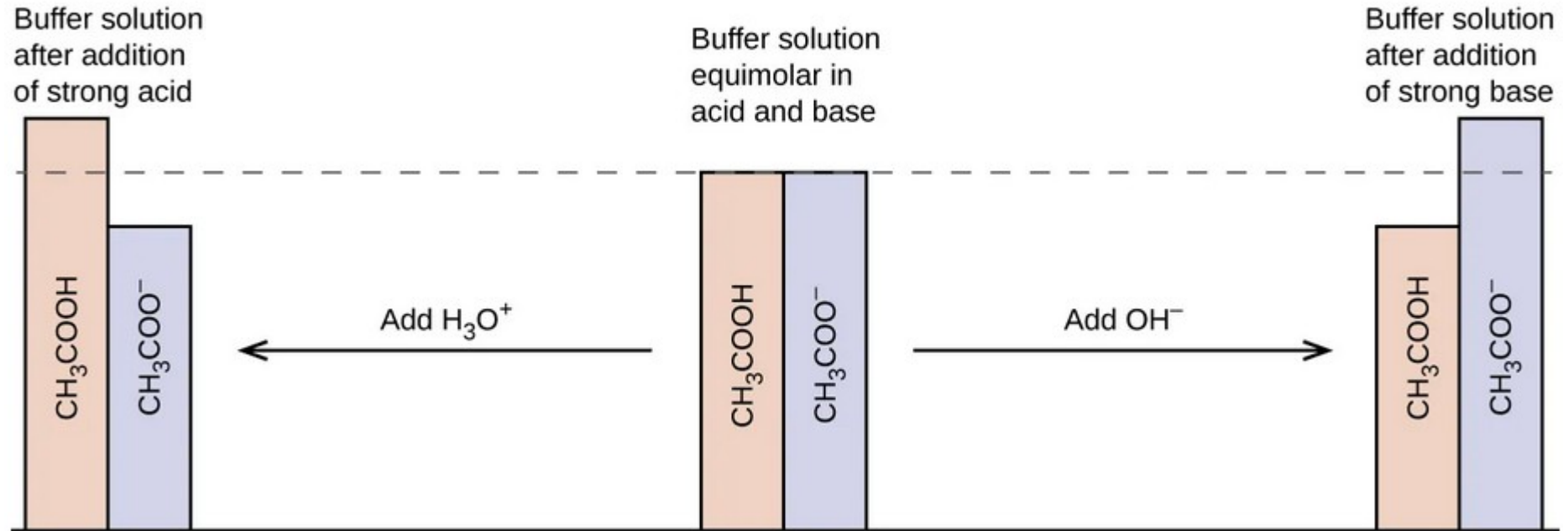
Buffers



- A solution containing a weak conjugate acid-base pair is called a buffer solution, or a buffer.
 - They are usually prepared from a weak acid or base and the salt of its conjugate pair.
- Buffer solutions resist a change in pH when small amounts of a strong acid or a strong base are added



How Buffers Work



Buffer Capacity



- Buffer solutions do not have an unlimited capacity to keep the pH relatively constant
 - The ability of a buffer solution to resist changes in pH relies on the presence of significant amounts of its weak acid-base pair.
 - When enough strong acid or base is added to lower the concentration of either member of the buffer pair, the buffering action within the solution is compromised.
- The **buffer capacity** is the amount of acid or base that can be added to a given volume of a buffer solution before the pH changes

Buffer Capacity



- Buffer capacity depends on the amounts of the weak acid and its conjugate base that are in a buffer mixture.
 - pH is determined by the ratio of conjugate pairs.



Selection of Suitable Buffer Mixtures

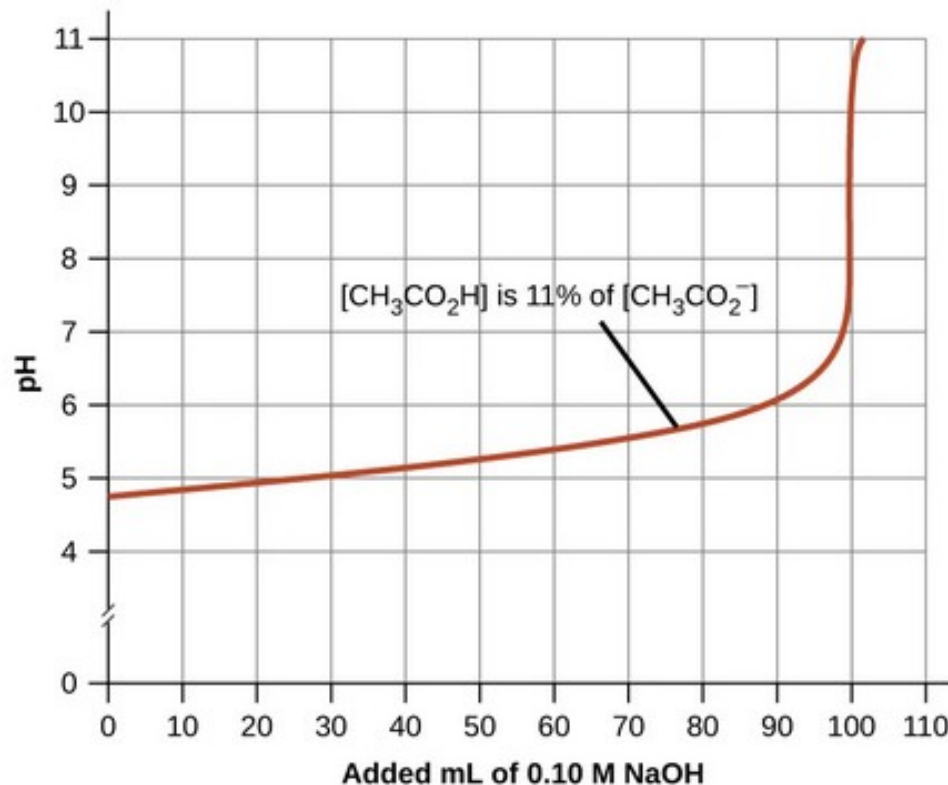


- A good buffer mixture should have about equal concentrations of both of its components.
 - This helps to avoid exhausting one of the components.
- Weak acids and their salts are better as buffers for pHs less than 7
- Weak bases and their salts are better as buffers for pHs greater than 7.

Selection of Suitable Buffer Mixtures



- A buffer solution has generally lost its usefulness when one component of the buffer pair is less than about 10% of the other.



The Henderson-Hasselbalch Equation



- The ionization-constant expression for a solution of a weak acid can be written as:

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

- Rearranging to solve for $[\text{H}_3\text{O}^+]$ yields:

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

The Henderson-Hasselbalch Equation



- Taking the negative logarithm of both sides of this equation gives

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

- Which can be written as

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

- It is important to note that the “x is small” assumption must be valid to use this equation.

Section 14.6

Buffers



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Learning Objectives

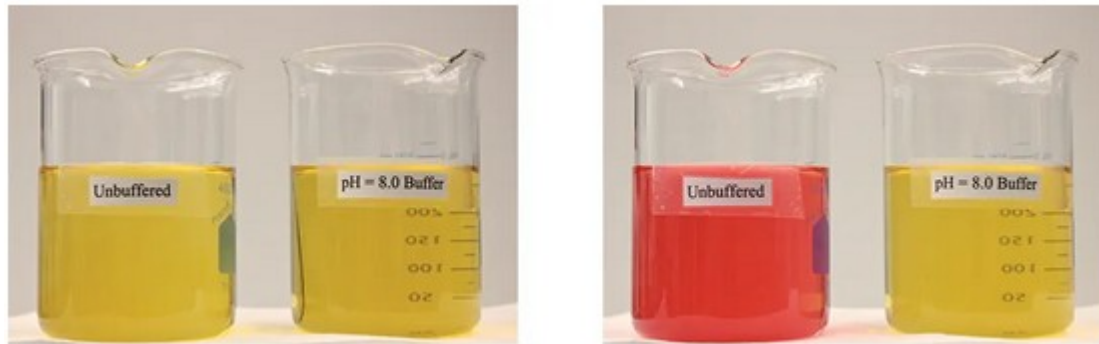


- Describe the composition and function of acid–base buffers
- Calculate the pH of a buffer before and after the addition of added acid or base

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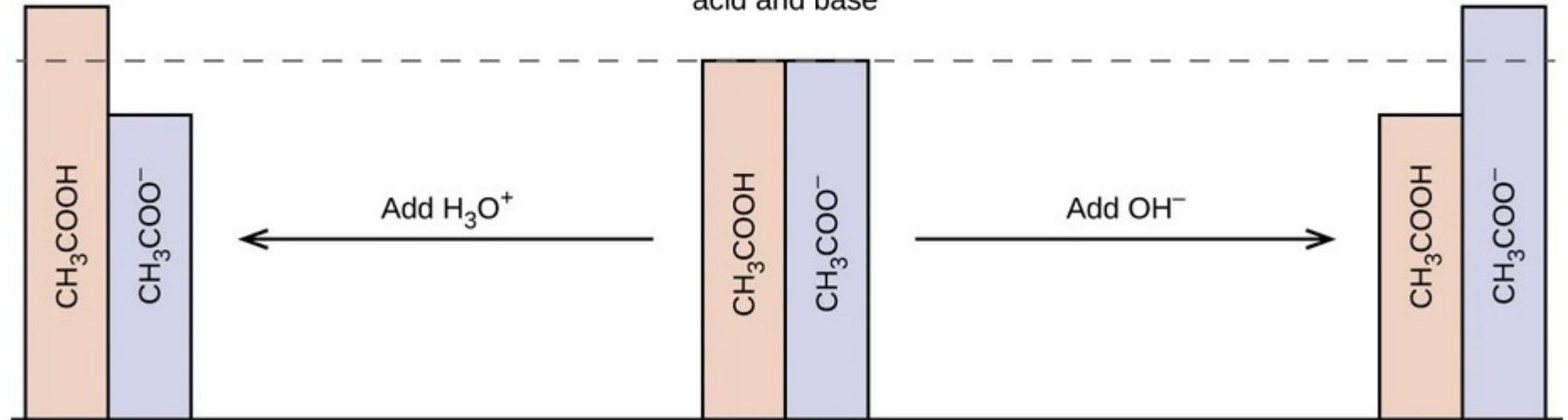
How Buffers Work



Buffer solution
after addition
of strong acid

Buffer solution
equimolar in
acid and base

Buffer solution
after addition
of strong base



Buffer Capacity



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Selection of Suitable Buffer Mixtures

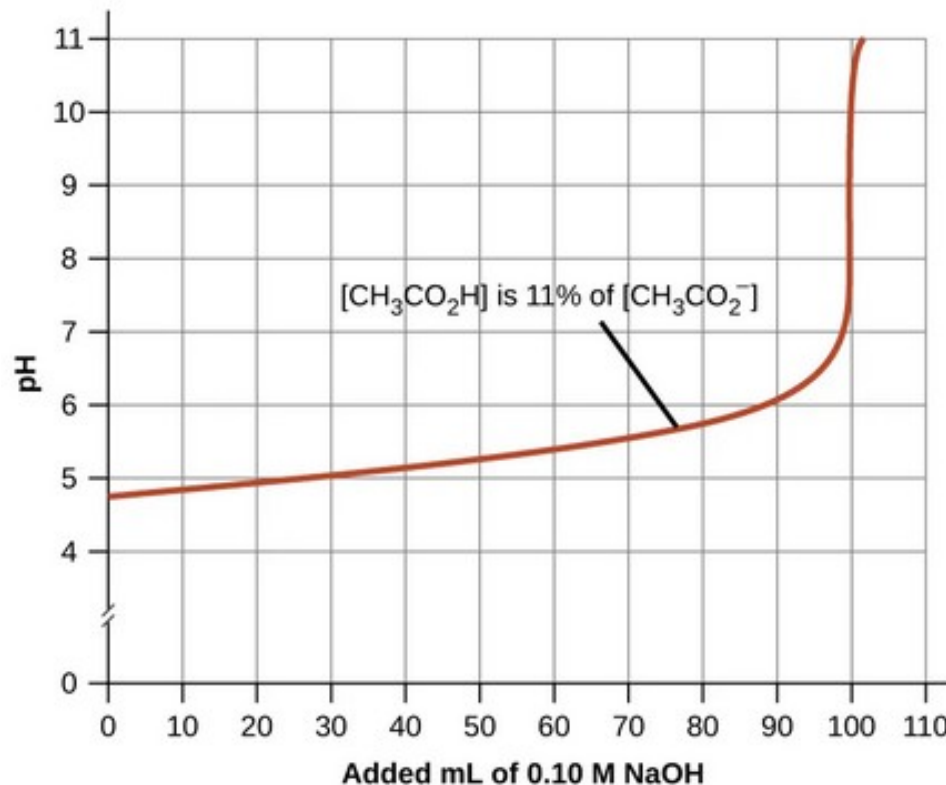


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$$[\text{H}_3\text{O}^+] = K_a \times \frac{[\text{HA}]}{[\text{A}^-]}$$

The Henderson-Hasselbalch Equation



- Taking the negative logarithm of both sides of this equation gives

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

- Which can be written as

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

- It is important to note that the “x is small” assumption must be valid to use this equation.

Section 14.7

Acid-Base Titration



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Learning Objectives



- Interpret titration curves for strong and weak acid-base systems
- Compute sample pH at important stages of a titration
- Explain the function of acid-base indicators

Titration Curves



- A titration curve is a plot of some solution property versus the amount of added titrant.
- For acid-base titrations, solution pH is a useful property to monitor because it varies predictably with the solution composition
- The shape of a titration curve is effected by the strength of the **titrand** (analyte) and **titrant**.

Titration Steps



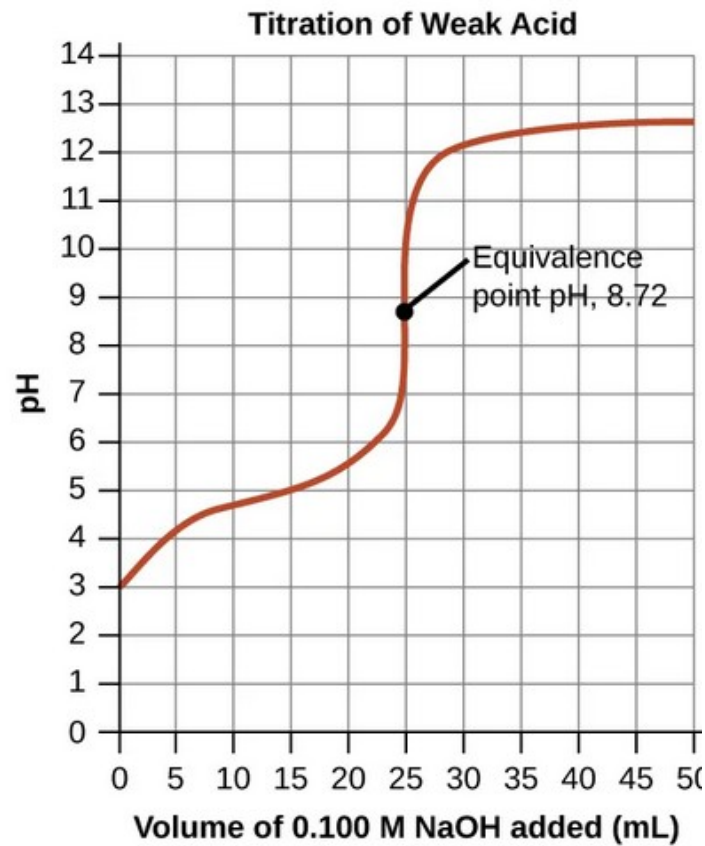
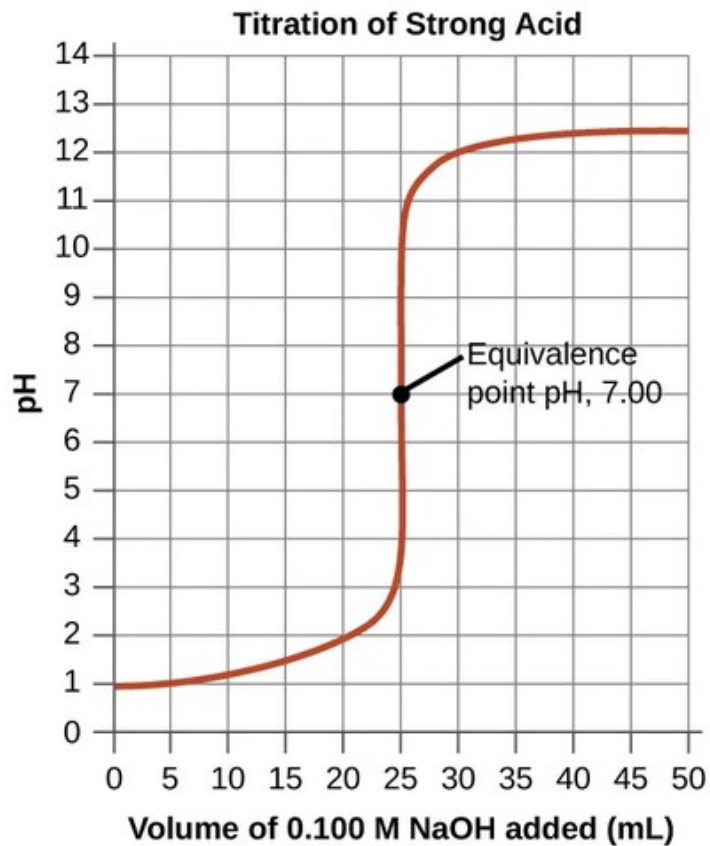
- 1) Initial state (added titrant volume = 0 mL): pH is determined by the acid being titrated
 - When concentrations are held equal, stronger acids will have a lower pH.
- 2) Pre-Equivalence Point: solution pH increases gradually and the acid is consumed by reaction with added titrant
 - composition includes unreacted acid, the reaction product and its conjugate base

Titration Steps



- 3) Equivalence Point: a drastic rise in pH is observed as the solution composition transitions from acidic to either neutral or basic
 - pH is determined by ionization constant of the conjugate base of the acid
- 4) Postequivalence Point: pH is determined by the amount of excess strong base titrant added

Picturing Titration



Acid-Base Indicators

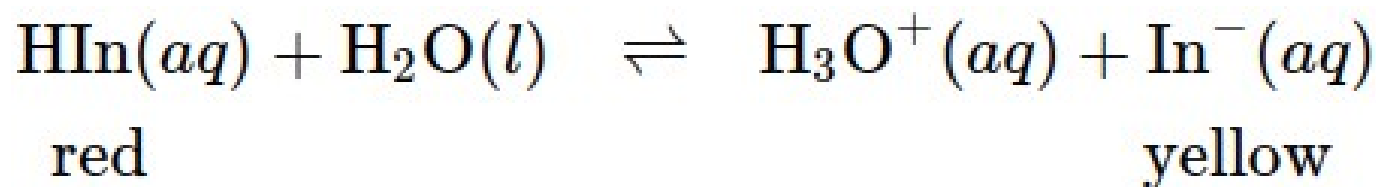


- Certain organic substances change color in dilute solution when the hydronium ion concentration reaches a particular value.
- These substances are called **acid-base indicators** and can be used to determine the pH of a solution.

Indicator Example



- The equilibrium in a solution of the acid-base indicator methyl orange can be represented by an equation in which we use HIn as a simple representation:

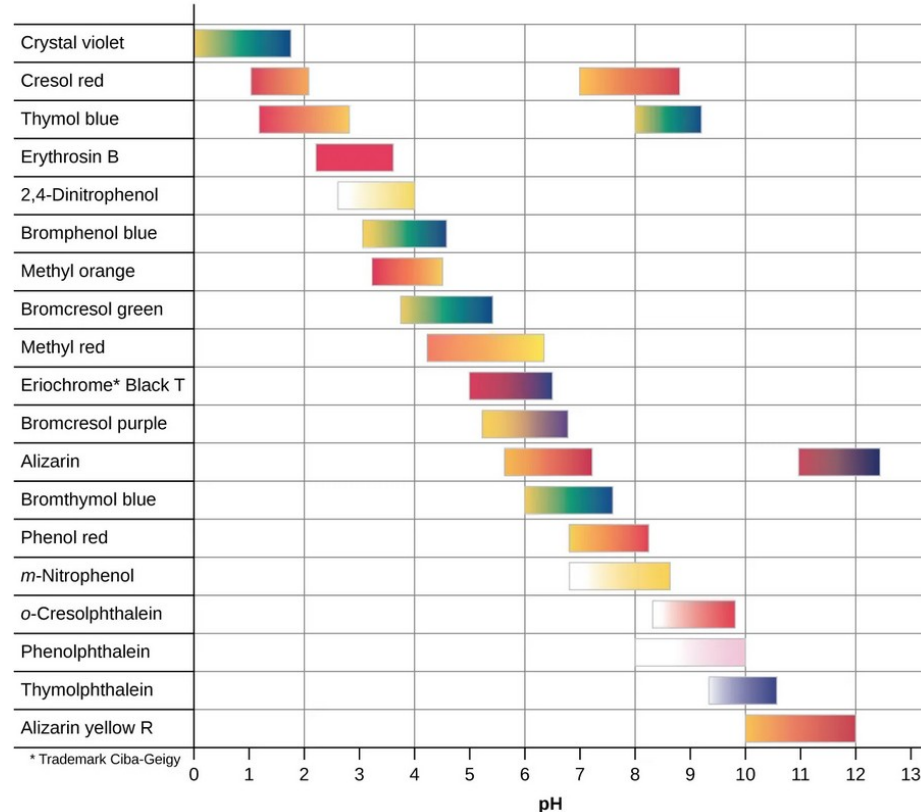


$$K_a = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]} = 4.0 \times 10^{-4} \quad \text{pH} = \text{p}K_a + \log \left(\frac{[\text{In}^-]}{[\text{HIn}]} \right)$$

Color Change Interval



- The **color change interval** (or pH interval) for an acid-base indicator is defined as the range of pH values over which a change in color is observed
- For most indicators this range is approximately $pK_a \pm 1$.



Selecting an Indicator



- An appropriate indicator should have a color change interval that encompasses the equivalence point.

