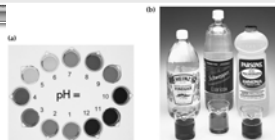


Chapter 14 - Aqueous Equilibria: Acids & Bases



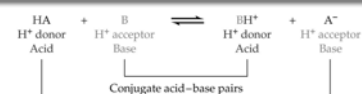
Acid-Base Concepts

- Acids and bases are all around us. They make up one of the most important (and practical) aspects of chemistry.
- What are some examples of each?
- What do you know about acids and bases?

Acid-Base Concepts

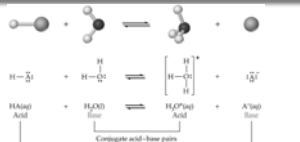
- CHM 151 taught Arrhenius theory
 - Acids produce hydrogen ions in water
 - $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$
 - Bases produce hydroxide ions in water
 - $MOH(aq) \rightleftharpoons M^+(aq) + OH^-(aq)$
- 152 used the Bronsted-Lowry theory
 - Acid: Substance that can donate H^+
 - Base: Substance that can accept H^+
 - Identify the acid and the base below:
 - $HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$

Acid-Base Pairs



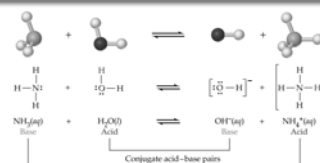
- Which substance donates H^+ ?
- Which substance accepts H^+ ?
- Conjugate acid-base pairs. Remember that most reactions proceed in both directions (there are only a few exceptions to this - namely strong acids and bases).

Acid-Base Pairs



- Write an equation for the dissociation of HCN in water. Identify the acid, the base, the conjugate acid, and the conjugate base.
- Worked Examples 14.1-2; Problems 14.1-3

Acid-Base Pairs



- Identify acid-base pairs in the reaction of HS⁻ with HF.

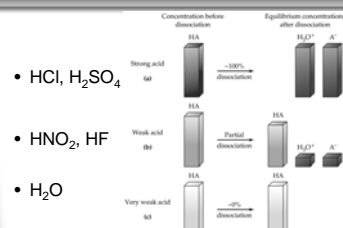
Strengths of Acids/Bases

- Competition for protons (H^+)
- $HS^-(aq) + HF(aq) \rightleftharpoons H_2S(aq) + F^-(aq)$
- Which acid is stronger?
- Which base is stronger?
- The proton is always transferred **from the stronger acid to the stronger base!**
- Stronger acid + stronger base \rightarrow weaker acid + weaker base

Strength of Acids

- Strong acids almost completely dissociate in water (strong electrolytes).
 - $HClO_4$, HCl , HBr , HI , HNO_3 , H_2SO_4
 - These have **weak** conjugate bases. Equilibrium lies very far to the right.
- Weak acids dissociate only a small percent (~5%) in water (weak electrolytes).
 - HF , CH_3COOH (aka CH_3CO_2H), HNO_2 , etc.
 - These have **strong** conjugate bases.

Strengths of Acids



- HCl , H_2SO_4
- HNO_2 , HF
- H_2O

Strength of Bases

- 8 Strong bases: NaOH, KOH, LiOH, RbOH, CsOH, Ca(OH)₂, Sr(OH)₂, Ba(OH)₂
- Don't react with water, just dissociate in it
- NH₃ compounds DO react with water
- NH₃ + H₂O ⇌ NH₄⁺ + OH⁻
- Draw the following in water: HNO₃, HF, NaOH, Ca(OH)₂, NH₃

Strength of Acids/Bases

TABLE 15.1 Relative Strengths of Conjugate Acid-Base Pairs

Stronger acid	Acid, HA	Base, A ⁻	Weaker base
↑	HClO ₄	ClO ₄ ⁻	↓
	HCl	Cl ⁻	
	HNO ₃	NO ₃ ⁻	
	H ₂ O	H ₂ O	
	H ₃ O ⁺	H ₂ O	
	H ₂ SO ₄	HSO ₄ ⁻	
	H ₂ SO ₃	HSO ₃ ⁻	
	H ₂ PO ₄	H ₂ PO ₄ ⁻	
	H ₂ PO ₃	H ₂ PO ₃ ⁻	
	H ₂ PO ₂	H ₂ PO ₂ ⁻	
↓	HF	F ⁻	↑
	CH ₃ COOH	CH ₃ COO ⁻	
	H ₂ CO ₃	HCO ₃ ⁻	
	H ₂ S	HS ⁻	
	NH ₄ ⁺	NH ₃	
	H ₂ CN ⁺	CN ⁻	
	HCO ₃ ⁺	CO ₃ ²⁻	
	H ₂ O	OH ⁻	
	NH ₃	NH ₂ ⁻	
	OH ⁺	OH ⁻	
H ₂	H ⁻		
Weaker acid	Very weak acids Negligible tendency to dissociate	Very weak bases Negligible tendency to be protonated in aqueous solution	Strong bases 100% protonated in aqueous solution

Strength of Acids/Bases

- Predict the products of the following reactions and then determine the direction in which they will shift. (Hint: determine which acid and base is stronger.)
- HF + NaOH
- Cl⁻ + NH₄⁺
- HClO₄ + NH₃
- Worked Example 14.3, Problems 14.4-5

Hydronium Ions

- HA (aq) ⇌ H⁺ (aq) + A⁻ (aq)
- Same as: HA + H₂O ⇌ H₃O⁺ + A⁻
- H⁺ is very reactive and will bond with O in H₂O to form H₃O⁺
- H⁺ and H₃O⁺ mean the same thing but H₃O⁺ is more accurate



H₃O⁺ — the hydronium ion, or hydrated H⁺

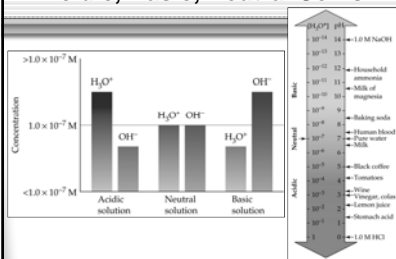
Dissociation of Water

- H₂O (l) + H₂O (l) ⇌ H₃O⁺ (aq) + OH⁻ (aq)
- Identify the acid-base pairs
- This is the dissociation of water, an amphoteric substance.
- Write an equilibrium expression for this equation.
- K_w is the ion-product constant for water.
- Calculate K_w if [H₃O⁺] = 1.0 × 10⁻⁷ M (experimentally determined for pure H₂O)

Dissociation of Water

- We can compare [H₃O⁺] and [OH⁻] for solutions to determine acidity or basicity.
- They're equal in neutral solutions.
- Which one is greater in acidic solutions?
- Basic solutions?
- [H₃O⁺] = 5.6 × 10⁻⁴ M. What is [OH⁻]? Is this solution acidic or basic?

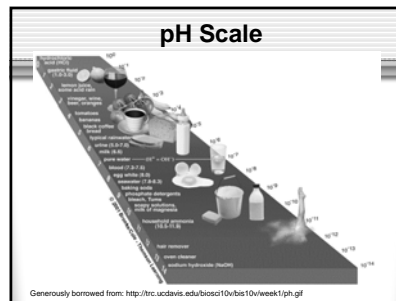
Acidic, Basic, Neutral Solns



pH Scale

- pH scale is logarithmic (like Richter scale for earthquakes).
- [H₃O⁺] = 1 × 10⁻² M has a pH of 2 but [H₃O⁺] = 1 × 10⁻¹² M has a pH of 12
- pH = -log [H₃O⁺] [H₃O⁺] = 10^{-pH}
- pOH = -log [OH⁻] [OH⁻] = 10^{-pOH}
- [H₃O⁺][OH⁻] = 1 × 10⁻¹⁴ = K_w
- pH + pOH = 14 (verify this)

pH Scale

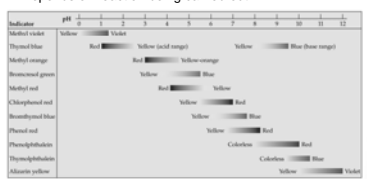


pH Sig Figs

- Calculate pH if $[H_3O^+] = 5.6 \times 10^{-4} M$.
- $pH = -\log(5.6 \times 10^{-4}) = 3.2518$
- Sig figs: the exponent (4) is exact, 5.6 determines how many decimal places
- $pH = 3.25$
- Find $[H_3O^+]$, pH, and pOH if $[OH^-] = 9.8 \times 10^{-9} M$
- Worked Examples 14.4 - 14.6, Problems 14.6 - 14.9

pH Indicators

- Different indicators change colors at different pH ranges. Depends on reaction being carried out.



Group Work

- Calculate $[H_3O^+]$, $[OH^-]$, pH, and pOH of a solution made by adding 2.250 g of LiOH to 250.0 mL of DI water.
- See sig fig rules, p. 552

pH of Strong Acids/Bases

- $HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$
- Calculate the concentration of acid if pH is measured to be 0.987.
- Calculate pH of 0.020 M $Sr(OH)_2$ soln.
- $Sr(OH)_2 \rightarrow Sr^{2+}(aq) + 2OH^-(aq)$
- Worked Examples 14.7-8 (except c); Problem 14.10

Equilibria of Weak Acids

- $HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$
 - Write equilibrium expression.
- % Ionization = $\frac{[H_3O^+]}{[HA]} \times 100\%$
- $pK_a = -\log K_a$
- As acid strength increases, indicate what will happen to the following (will they increase or decrease?):
 - $[H_3O^+]$
 - pH
 - % ionization
 - K_a
 - pK_a

pKa's of Weak Acids

- Table 14.2

Weak Acid Solutions

- Calculating equilibrium concentrations of weak acid solutions. (ICE tables!!!)
- Two possibilities:
 - Given $[HA]_{initial}$ and K_a , find all equilibrium concentrations and pH
 - Given $[HA]_{initial}$ and pH, find all equilibrium concentrations and K_a
- With small K values (very weak acids), we can assume that x will be small (easier math!).

Weak Acid Solutions

- Find the pH of a 0.50 M solution of HOCl (hypochlorous acid). $K_a = 3.5 \times 10^{-8}$
- ICE Table:

	HOCl	$H_2O \rightleftharpoons$	H_3O^+	OCl^-
Initial				
Equil.				
Change				

Weak Acid Solutions

- Test the approximation
- $x = 1.323 \times 10^{-4} M$
- $(x / [HA]) \times 100 < 5\%$
- $(1.3 \times 10^{-4} / 0.50) \times 100 = 0.026\%$
- Assumption checks out! Hooray, easy math!
- $x = [H_3O^+] = 1.3 \times 10^{-4} M$
- $pH = 3.89$
- What are pOH and $[OH^-]$?

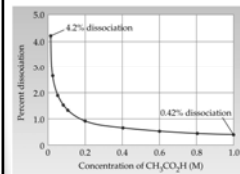
Weak Acid Solutions

- The pH of a formic acid solution is measured to be 2.58. Calculate the K_a and pK_a of this acid of a 0.0411 M solution.
- Worked Examples 14.9-10, Problems 14.12- 15

Percent Dissociation

- % dissociation is the same calculation as checking assumption of a small x.
 - $([H_3O^+]_{eq} / [HA]_i) \times 100\% < 5\%$
- Will the percent dissociated increase or decrease as an acid is diluted? Why?
- Calculate the percent dissociation from the previous problem.

Dilution and % Dissociation



- As we add water, more acid (or base) is dissociated. More dilute = more dissociation.

Group Work

- A 0.200 M solution of a weak acid is 9.4% dissociated. Using this information, calculate $[H_3O^+]_{eq}$, $[A^-]_{eq}$, $[HA]_{eq}$, and K_a .
- Ans: $[H_3O^+] = 0.019$ M, $[A^-] = 0.019$ M, $[HA] = 0.181$ M, and $K_a = 2.0 \times 10^{-3}$

Polyprotic Acids

- $H_2C_2O_4(aq) + H_2O(l) \rightleftharpoons HC_2O_4^-(aq) + H_3O^+(aq)$
 - $K_{a1} = [HC_2O_4^-][H_3O^+] / [H_2C_2O_4] = 5.9 \times 10^{-2}$
- $HC_2O_4^-(aq) + H_2O(l) \rightleftharpoons C_2O_4^{2-}(aq) + H_3O^+(aq)$
 - $K_{a2} = [C_2O_4^{2-}][H_3O^+] / [HC_2O_4^-] = 6.4 \times 10^{-5}$
- In general, $K_{a1} > K_{a2} > K_{a3} \dots$ Why?
- Find pH of a 0.15 M oxalic acid solution.
- ICE Table(s)

Polyprotic Acids

- $H_2C_2O_4(aq) + H_2O(l) \rightleftharpoons HC_2O_4^-(aq) + H_3O^+(aq)$
 - $K_{a1} = [HC_2O_4^-][H_3O^+] / [H_2C_2O_4] = 5.9 \times 10^{-2}$
- Assumption that x is small is no good (~63%). Use the quadratic!
 - $x^2 + 5.9 \times 10^{-2}x - 0.00885 = 0$
 - $x = 0.069$ M = $[HC_2O_4^-] = [H_3O^+]$
 - 0.15 M - x = $[H_2C_2O_4] = 0.081$ M

Polyprotic acids

- $HC_2O_4^-(aq) + H_2O(l) \rightleftharpoons C_2O_4^{2-}(aq) + H_3O^+(aq)$
 - $K_{a2} = [C_2O_4^{2-}][H_3O^+] / [HC_2O_4^-] = 6.4 \times 10^{-5}$
- $K_{a2} = (x)(0.069 + x) / (0.069 - x) = 6.4 \times 10^{-5}$
- Approx: $(x)(0.069) / (0.069) = 6.4 \times 10^{-5}$ (x is small enough for assumption!)
- $x = 6.4 \times 10^{-5}$ M
- $[HC_2O_4^-] = 0.069 - 6.4 \times 10^{-5} = 0.069$ M
- $[H_3O^+] = 0.069 + 6.4 \times 10^{-5} = 0.069$ M
- pH = 1.16
- $[H_2C_2O_4] = 0.081$ M, $[C_2O_4^{2-}] = 6.4 \times 10^{-5}$ M
- Worked Example 14.11-12, Problems 14.17-18

Weak Bases

- Same idea as acids, but use K_b instead
- $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
- $K_b = [NH_4^+][OH^-] / [NH_3]$
- Table 14.4: K_b Values for Weak Bases
- Why are amines (derivatives of NH_3) basic?
 - Lone e⁻ pair (δ^-) on N attracts H (δ^+) from water. N wins the competition and pulls H⁺ off of water.

Weak Bases

- Calculate the pH of a 0.50 M dimethylamine ((CH_3)₂NH) solution. $K_b = 5.4 \times 10^{-4}$
- $K_b = [(CH_3)_2NH_2^+][OH^-] / [(CH_3)_2NH]$
- ICE Table
- $K_b = x^2 / (0.50 - x) = 5.4 \times 10^{-4}$
- Check approximation!
 - $x = 0.01616$ M
 - $[(CH_3)_2NH_2^+] = [OH^-] = 0.016$ M
 - $[(CH_3)_2NH] = 0.50$ M - 0.016 = 0.48 M
- 2 ways to find pH

Weak Bases

- 1) $[\text{OH}^-] = 0.016 \text{ M}$
- $[\text{H}_3\text{O}^+] = K_w / [\text{OH}^-] = 1.0 \times 10^{-14} / 0.016 \text{ M}$
- $[\text{H}_3\text{O}^+] = 6.19 \times 10^{-13} \text{ M}$
- $\text{pH} = 12.21$
- 2) $[\text{OH}^-] = 0.016 \text{ M}$
- $\text{pOH} = 1.79$
- $\text{pH} = 14 - 1.79 = 12.21$
- MAGIC!!!
- Worked Example 14.13, Problems 14.19-20

Group Work

- Calculate the concentration of OH^- ions in a 0.075 M solution of hydrazine (N_2H_4), ($K_b = 8.9 \times 10^{-7}$). Calculate the pH of this solution.

Relation Between K_a and K_b

- Weak acid: $\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-$
 - $K_a = [\text{H}_3\text{O}^+][\text{A}^-] / [\text{HA}]$
- Weak base: $\text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^-$
 - $K_b = [\text{HA}][\text{OH}^-] / [\text{A}^-]$
- Multiply: $K_a \cdot K_b$
- $K_a \cdot K_b = [\text{H}^+][\text{OH}^-] = K_w$
- This is true only if the acid and base are **conjugate pairs!**

Relation Between K_a and K_b

- What is the K_b for hydrazine (N_2H_4) if K_a for N_2H_5^+ is 1.1×10^{-8} ? Also calculate $\text{p}K_a$ and $\text{p}K_b$.
- Worked Example 14.14, Problem 14.21

Acid-Base Properties of Salts

- Acid + Base \rightarrow Salt + Water
- Salts are ionic products of acid-base reaction
- Salts can be neutral, acidic, or basic depending on the strengths of the acid and base from which they're made.
- Anion in salt: comes from the acid
 - If acid is strong \rightarrow acidic or neutral solution (ex: NaCl)
- Cation in salt: comes from the base
 - If base is strong \rightarrow basic or neutral solution (ex: NaCl)

Properties of Salts

- Neutral Salts
 - $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$
 - Acid and base are strong; resulting salt is neutral.
 - There are only a few examples of this; what are they?
- Acidic Salts
 - $\text{NH}_3 + \text{HCl} \rightleftharpoons \text{NH}_4\text{Cl}$
 - Weak base + strong acid
 - Ammonium salts are acidic (cation comes from weak base so its conjugate acid is "strong")

Properties of Salts

- Basic Salts
 - Salts made from weak acids and strong bases give basic salts
 - Anion from weak acid; conjugate base is "strong"
 - Describe an example.
- Acidic cations and basic anions
 - $(\text{NH}_4)_2\text{CO}_3$: NH_4^+ is a weak acid; CO_3^{2-} is a weak base. Need more info to determine (have to compare K_a and K_b values).

Properties of Salts

- Many other salts also cause pH shifts when dissolved in water. These salts contain the conjugate acid (or base) of a weak base (or acid).
 - NH_4Cl : $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$
 - $\text{pH} < 7$
 - NaCH_3CO_2 : $\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^-$
 - $\text{pH} > 7$
- These reactions are called hydrolysis.

Group Work

- Classify the following as acid, base, or salt. For salts, classify them as acidic, basic, or neutral. For acidic or basic salts, write the reaction of hydrolysis.

KBr	LiCN
HCl	KOH
NaF	NaCH_3COO
NH_4Cl	RbI
NH_3	

Properties of Salts

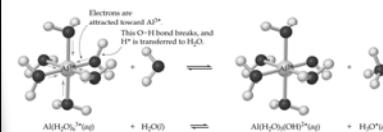
- Is KF an acidic, basic or neutral salt?
 - Write equations for this reaction in water.
 - Calculate pH of a 0.10 M KF solution. $K_a(\text{HF}) = 3.5 \times 10^{-4}$
- Is NH_4Cl acidic, basic, or neutral?
 - Write equations for this reaction in water.
 - Calculate pH of a 0.10 M NH_4Cl solution. $K_b(\text{NH}_3) = 1.8 \times 10^{-5}$

Properties of Salts

- Small, highly charged metals also make acidic salts; $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ($K_a = 1.4 \times 10^{-5}$)
- These are surrounded by waters in solution to give a hydrated cation.
- High charge on metal \rightarrow electrons on O are attracted to metal, easier to break O-H bond
- Calculate pH of a 0.20 M AlCl_3 solution.
 - $\text{Al}(\text{H}_2\text{O})_6^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}$
- Worked Example 14.15, Problem 14.22

Metal acids

- Al^{3+} as acid

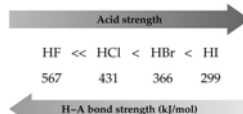


Percent Ionization

- Percent hydrolysis for acidic salts.
 - $[\text{H}_3\text{O}^+] / [\text{HA}] \times 100\%$
- Conjugate acid reacts with water to create H_3O^+
- Calculate pH and % hydrolysis of 1.1 M NH_4I solution.
 - $\text{NH}_4\text{I} \rightarrow \text{NH}_4^+ + \text{I}^-$
 - $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$
 - $K_a(\text{NH}_4^+) = K_w / K_b = 1.0 \times 10^{-14} / 1.8 \times 10^{-5}$

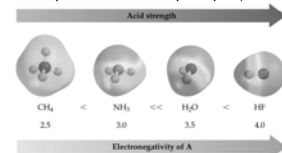
Acid Strength Factors

- Why is HF weak but HCl, HBr, and HI strong?
- Determined by bond strength and bond polarity.
- Strength: H-F is strongest in series (H and F are small and close together); other bonds are weaker and break easily in water (i.e., dissociate more)

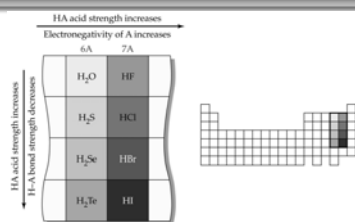


Acid Strength Factors

- In the same row (L-R), bond strengths are relatively similar, but electronegativity changes (bonds are more polar = easier to pull apart)



Acid Strength Factors



Lewis Acids and Bases

- Lewis: another definition of acids and bases
- Looks at electron transfer
- Brønsted-Lowry looks at H^+ transfer
- Acids are electron-pair acceptors, bases are electron-pair donors
 - $\text{H}^+ + \text{:NH}_3 \rightarrow \text{NH}_4^+$
 - Ammonia donates the electron pair to H^+ to make the bond; H^+ accepts the electron pair
- Worked Example 14.17, Problem 14.27

Lewis Acids and Bases

