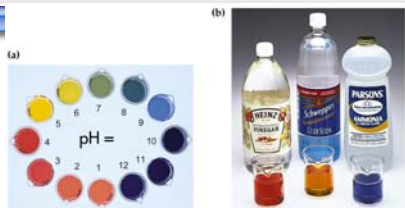


Chapter 14 - Aqueous Equilibria: Acids & Bases



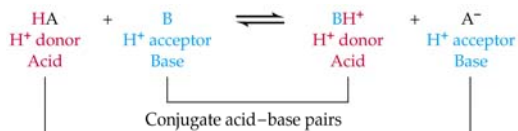
Acid-Base Concepts

- 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

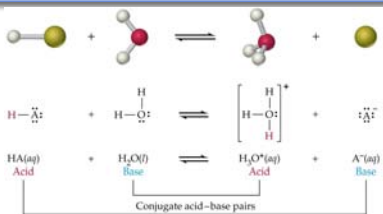
- CHM 151 taught Arrhenius theory
 - ♦ Acids produce hydrogen ions in water
 - $\text{HA (aq)} \rightleftharpoons \text{H}^+ \text{(aq)} + \text{A}^- \text{(aq)}$
 - ♦ Bases produce hydroxide ions in water
 - $\text{MOH (aq)} \rightleftharpoons \text{M}^+ \text{(aq)} + \text{OH}^- \text{(aq)}$
- Now Brønsted-Lowry theory
 - ♦ Acid: Substance that can donate H^+
 - ♦ Base: Substance that can accept H^+

Acid-Base Pairs



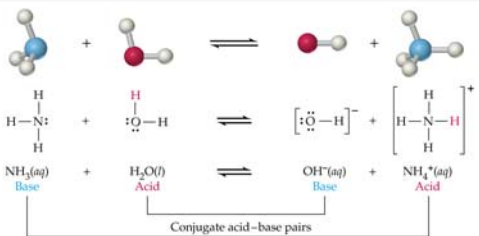
- Which substance donates H⁺?
- Which substance accepts H⁺?
- Conjugate acid-base pairs. Remember that reactions proceed in both directions.

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.

Acid-Base Pairs



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

Strengths of Acids/Bases

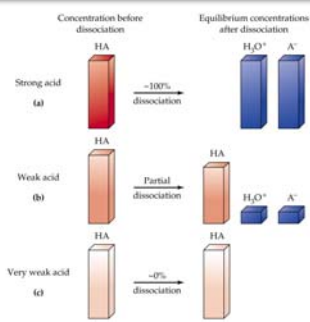
- Competition for protons (H^+)
- $HS^-(aq) + HF(aq) \rightleftharpoons H_2S(aq) + F^-(aq)$
- Which acid is stronger?
 - ♦ HF
- Which base is stronger?
 - ♦ HS^-
- The proton is always transferred to the stronger **base!**

Strength of Acids

- Strong acids almost completely dissociate in water.
 - ♦ $HClO_4$, HCl , HBr , HI , HNO_3 , H_2SO_4
 - ♦ These have weak conjugate bases. Equilibrium lies very far to the right.
- Weak acids (HF , CH_3COOH , HNO_2) have strong conjugate bases. Equilibrium lies to the left (most stay bonded, few dissociate).

Strength 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
 - ♦ $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$
- Example 14.3, Problem 14.4, Key Concept 14.4
- Draw the following in water: HNO₃, HF, NaOH, Ca(OH)₂, Fe(OH)₃

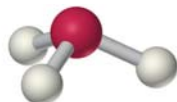
Strength of Acids/Bases

TABLE 15.1 Relative Strengths of Conjugate Acid-Base Pairs

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

Hydronium Ions

- $\text{HA (aq)} \rightleftharpoons \text{H}^+ \text{ (aq)} + \text{A}^- \text{ (aq)}$
- 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⁺

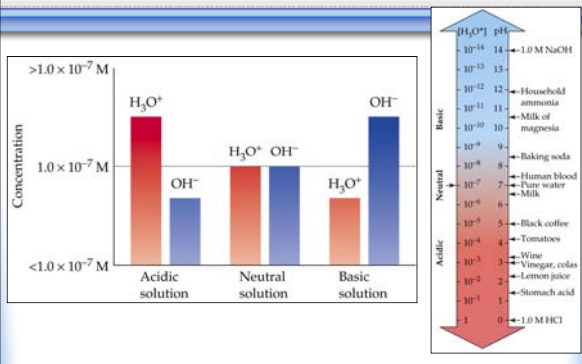
Dissociation of Water

- $\text{H}_2\text{O} (\text{l}) + \text{H}_2\text{O} (\text{l}) \rightleftharpoons \text{H}_3\text{O}^+ (\text{aq}) + \text{OH}^- (\text{aq})$
- Identify the acid-base pairs
- This is the dissociation of water, an amphoteric substance.
- Write an equilibrium expression for this eqn.
- K_w is ion-product constant for water.
- Calculate K_w if $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-7}$ (experimentally determined for pure H_2O)

Dissociation of Water

- We can compare $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ for solutions.
- They're equal in neutral solutions.
- Which is greater in acidic solutions?
- Basic solutions?
- $[\text{H}_3\text{O}^+] = 5.6 \times 10^{-4} \text{ M}$. What is $[\text{OH}^-]$?

Acidic, Basic, Neutral Solns



pH Scale

- Logarithmic scale (like Richter scale for earthquakes).
- $[\text{H}_3\text{O}^+] = 1 \times 10^{-2}$ has a pH of 2 but $[\text{H}_3\text{O}^+] = 1 \times 10^{-12}$ has a pH of 12
- $\text{pH} = -\log [\text{H}_3\text{O}^+]$ $[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$
- $\text{pOH} = -\log [\text{OH}^-]$ $[\text{OH}^-] = 10^{-\text{pOH}}$
- $[\text{H}_3\text{O}^+][\text{OH}^-] = 1 \times 10^{-14}$
- $\text{pH} + \text{pOH} = 14$ (verify this)

pH Sig Figs

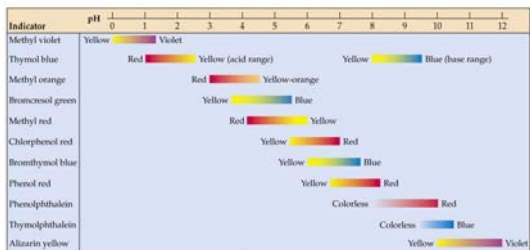
- $[\text{H}_3\text{O}^+] = 5.6 \times 10^{-4}$ M
- $\text{pH} = -\log (5.6 \times 10^{-4}) = 3.2518$
- Exponent is exact number, 5.6 determines how many decimals
- $\text{pH} = 3.25$
- Find $[\text{H}_3\text{O}^+]$, pH, and pOH if $[\text{OH}^-] = 9.8 \times 10^{-9}$ M
- Example 14.4 - 14.6, Problems 14.6 - 14.9

Group Quiz #7

- Calculate $[\text{H}_3\text{O}^+]$, $[\text{OH}^-]$, 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. 621
- Ans: $[\text{H}_3\text{O}^+] = 2.661 \times 10^{-14}$ M, $[\text{OH}^-] = 0.3758$ M, $\text{pH} = 13.5750$, $\text{pOH} = 0.4250$

pH Indicators

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



pH of Strong Acids/Bases

- $\text{HNO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$
- Calculate pH of 0.103 M HNO_3 solution.
 - pH = 0.987
- $\text{Sr}(\text{OH})_2 \rightleftharpoons \text{Sr}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$
- Calculate pH of 0.020 M $\text{Sr}(\text{OH})_2$ soln.
 - pH = 12.60
- Problems 14.10 and 14.11

Equilibria of Weak Acids

- $\text{HA}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{A}^-(\text{aq})$
 - Write equilibrium expression.
- $\text{p}K_a = -\log K_a$: stronger acid = lower $\text{p}K_a$
- % Ionization = $[\text{H}_3\text{O}^+] / [\text{HA}]_i \times 100\%$
- For a stronger acid, indicate if the following will be higher or lower:
 - $[\text{H}_3\text{O}^+]$
 - pH
 - % ionization
 - K_a
 - $\text{p}K_a$

Weak Acid Solutions

- Test the approximation
- $x = 1.323 \times 10^{-4} \text{ M}$
- $(x / [\text{HA}]_i) \times 100 < 5\%$
- $(1.3 \times 10^{-4} / 0.50) \times 100 = 0.026\%$
- Assumption checks out! Yeah, easy math!
- $x = [\text{H}_3\text{O}^+] = 1.3 \times 10^{-4} \text{ M}$
- $\text{pH} = 3.89$
- What are pOH and $[\text{OH}^-]$?
- Example 14.10, Problems 14.14, 14.15

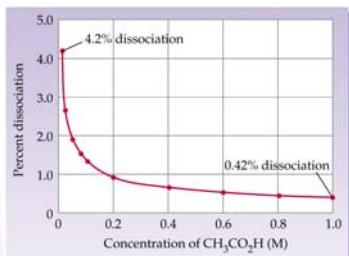
Example

- Find the K_a of a 1.25 M solution of nitrous acid. The pH of this solution is measured to be 1.62.

Percent Dissociation

- % dissociation is the same calculation as checking assumption of a small x .
 - ♦ $([\text{H}_3\text{O}^+]_{\text{eq}} / [\text{HA}]_i) \times 100\% < 5\%$
- 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, we can dissociate more. More dilute = more dissociation.

Practice

- A 0.200 M solution of a weak acid is 9.4 percent 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 $K_a = 2.0 \times 10^{-3}$

Individual Quiz #1

- The acid-dissociation constant for benzoic acid, $HC_7H_5O_2$, is 6.3×10^{-5} . Calculate the equilibrium concentrations of H_3O^+ , $C_7H_5O_2^-$, and $HC_7H_5O_2$ in the solution if the initial concentration of the acid is **0.50 M**.

Solutions

- 1) Find the K_a of a 1.25 M solution of nitrous acid. The pH of this solution is measured to be 1.62.
- 2) The acid-dissociation constant for benzoic acid, $\text{HC}_7\text{H}_5\text{O}_2$, is 6.3×10^{-5} . Calculate the equilibrium concentrations of H_3O^+ , $\text{C}_7\text{H}_5\text{O}_2^-$, and $\text{HC}_7\text{H}_5\text{O}_2$ in the solution if the initial concentration of the acid is 0.050 M.

Polyprotic Acids

- $\text{H}_2\text{C}_2\text{O}_4(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HC}_2\text{O}_4^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
 - ♦ $K_{a1} = [\text{HC}_2\text{O}_4^-][\text{H}_3\text{O}^+] / [\text{H}_2\text{C}_2\text{O}_4] = 5.9 \times 10^{-2}$
- $\text{HC}_2\text{O}_4^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{C}_2\text{O}_4^{2-}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
 - ♦ $K_{a2} = [\text{C}_2\text{O}_4^{2-}][\text{H}_3\text{O}^+] / [\text{HC}_2\text{O}_4^-] = 6.4 \times 10^{-5}$
- In general, $K_{a1} > K_{a2} > K_{a3} \dots$ Why?
- Find pH of a 0.15 M oxalic acid solution.
- ICE Table

Polyprotic Acids

- $\text{H}_2\text{C}_2\text{O}_4(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HC}_2\text{O}_4^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
 - ♦ $K_{a1} = [\text{HC}_2\text{O}_4^-][\text{H}_3\text{O}^+] / [\text{H}_2\text{C}_2\text{O}_4] = 5.9 \times 10^{-2}$
- Assumption that x is small is no good. Use the quadratic! (~63%)
- $x^2 + 5.9 \times 10^{-2}x - 0.00885 = 0$
- $x = 0.069 \text{ M} = [\text{HC}_2\text{O}_4^-] = [\text{H}_3\text{O}^+]$
- $0.15 \text{ M} - x = [\text{H}_2\text{C}_2\text{O}_4] = 0.081 \text{ M}$

Polyprotic acids

- $\text{HC}_2\text{O}_4^- (\text{aq}) + \text{H}_2\text{O} (\text{l}) \rightleftharpoons \text{C}_2\text{O}_4^{2-} (\text{aq}) + \text{H}_3\text{O}^+ (\text{aq})$
 - $K_{a2} = [\text{C}_2\text{O}_4^{2-}][\text{H}_3\text{O}^+] / [\text{HC}_2\text{O}_4^-] = 6.4 \times 10^{-5}$
- $K_{a2} = (x)(0.069 + x) / (0.069 - x) = 6.4 \times 10^{-5}$
- Approx: $(x)(0.069) / (0.069) = 6.4 \times 10^{-5}$ (x checks out!)
- $x = 6.4 \times 10^{-5} \text{ M}$
- $[\text{HC}_2\text{O}_4^-] = 0.069 - 6.4 \times 10^{-5} = 0.069 \text{ M}$
- $[\text{H}_3\text{O}^+] = 0.069 + 6.4 \times 10^{-5} = 0.069 \text{ M}$
- $\text{pH} = 1.16$
- $[\text{H}_2\text{C}_2\text{O}_4] = 0.081 \text{ M}$, $[\text{C}_2\text{O}_4^{2-}] = 6.4 \times 10^{-5} \text{ M}$
- Example 15.11, Problems 15.17, 15.18

Weak Bases

- Same idea as acids, but use K_b instead
- $\text{NH}_3 (\text{aq}) + \text{H}_2\text{O} (\text{l}) \rightleftharpoons \text{NH}_4^+ (\text{aq}) + \text{OH}^- (\text{aq})$
- $K_b = [\text{NH}_4^+][\text{OH}^-] / [\text{NH}_3]$
- 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 ($(\text{CH}_3)_2\text{NH}$) solution. $K_b = 5.4 \times 10^{-4}$
- $K_b = [(\text{CH}_3)_2\text{NH}_2^+][\text{OH}^-] / [(\text{CH}_3)_2\text{NH}]$
- ICE Table
- $K_b = x^2 / (0.50 - x) = 5.4 \times 10^{-4}$
- Check approximation!
- $x = 0.01616$: $[(\text{CH}_3)_2\text{NH}_2^+] = [\text{OH}^-] = 0.016 \text{ M}$
- $[(\text{CH}_3)_2\text{NH}] = 0.50 \text{ M} - 0.016 = 0.48 \text{ M}$
- 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!!!
- Example 14.12, Problems 14.19, 14.20

Group Quiz #8

- Calculate the molar 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: $K_a = [\text{H}^+][\text{A}^-] / [\text{HA}]$
- Weak base: $K_b = [\text{HA}][\text{OH}^-] / [\text{A}^-]$
- Multiply: $K_a * K_b$
- $K_a \cdot K_b = [\text{H}^+][\text{OH}^-] = K_w$
- True only if the acid and base are **conjugate pairs!**
- What is the K_b for hydrazine (N_2H_4) if K_a for N_2H_5^+ is 1.1×10^{-8} ?
- Example 14.13, Problem 14.21

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 strength of the acid or base from which they're made.
- Cation in salt: comes from the base
 - If base is strong \rightarrow basic or neutral solution (ex: NaCl)
- Anion in salt: comes from the acid
 - If acid is strong \rightarrow acidic or neutral solution (ex: NaCl)

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).
NH₄Cl: $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$
 - pH < 7
- NaCH₃CO₂: $\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^-$
 - pH > 7
- These reactions are called hydrolysis.

Properties of Salts

- Neutral Salts
 - NaOH + HCl \rightarrow NaCl + H₂O
 - Acid and base are strong, so resulting salt is neutral.
 - What is another example?
- Acidic Salts
 - HCl + NH₃ \rightleftharpoons NH₄Cl
 - Weak base + strong acid
 - Ammonium salts are acidic (cation from weak base, 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.
- Is KF an acidic, basic or neutral salt?
 - ♦ 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?
 - ♦ Calculate pH of a 0.10 M NH_4Cl solution. $K_b(\text{NH}_3) = 1.8 \times 10^{-5}$

Practice

- Classify the following salts as acidic, basic, or neutral. For acidic or basic salts, write the reaction of hydrolysis.
 - ♦ KBr
 - ♦ NaF
 - ♦ LiCN
 - ♦ NH_4Cl

Practice Answers

- Classify the following salts as acidic, basic, or neutral. For acidic or basic salts, write the reaction of hydrolysis.
 - ♦ KBr neutral
 - ♦ NaF basic: $\text{F}^- + \text{H}_2\text{O} \rightleftharpoons \text{HF} + \text{OH}^-$
 - ♦ LiCN basic: $\text{CN}^- + \text{H}_2\text{O} \rightleftharpoons \text{HCN} + \text{OH}^-$
 - ♦ NH_4Cl acidic: $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$

More Practice

- Classify the following salts as acidic, basic, or neutral. For acidic or basic salts, write the reaction of hydrolysis.
 - ♦ NaOCl
 - ♦ CsNO₃
 - ♦ CuCl
- Write the formula of an acidic salt
- Write the formula of a basic salt

Answers

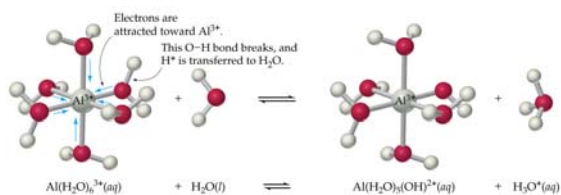
- ♦ NaOCl basic: $\text{OCl}^- + \text{H}_2\text{O} \rightleftharpoons \text{HOCl} + \text{OH}^-$
 - ♦ CsNO₃ neutral
 - ♦ Fe(NO₃)₃ acidic: $\text{Fe}^{3+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_3 + \text{H}_3\text{O}^+$
- Acidic: cation from a weak base, anion from a strong acid (ex: Co(NO₃)₃)
 - Basic: cation from a strong base, anion from a weak acid (ex: NaNO₂)

Properties of Salts

- Small, highly charged metals also make acidic salts; Al(H₂O)₆³⁺ (K_a = 1.4 × 10⁻⁵)
- These are surrounded by waters in solution to give a hydrated cation
- High charge on metal → electrons on O are attracted to metal, easier to break O-H bond
- Calculate pH of a 0.20 M AlCl₃ solution.
 - ♦ Al(H₂O)₆³⁺ + H₂O ⇌ H₃O⁺ + Al(H₂O)₅(OH)²⁺
- Example 14.14, Problem 14.22

Metal acids

- Al^{3+} as acid

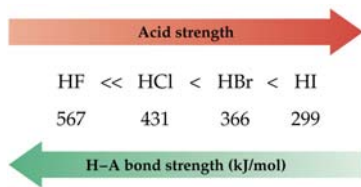


Percent Ionization

- 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 strength and polarity of H-X bond.
- H-F is strongest in series (H and F are small and close together); other bonds are weaker and break easily in water



Acid Strength Factors

- In the same row, bond strengths are relatively similar, but electronegativity changes are greater

CH_4 < NH_3 << H_2O < HF
 2.5 3.0 3.5 4.0

Acid Strength Factors

HA acid strength increases →
Electronegativity of A increases

	6A	7A
↑ HA acid strength increases / ↓ H-A bond strength decreases	H ₂ O	HF
	H ₂ S	HCl
	H ₂ Se	HBr
	H ₂ Te	HI

Lewis Acids and Bases

- Another way to define them
- 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
- Example 14.16, Problem 14.27

Lewis Acids and Bases

