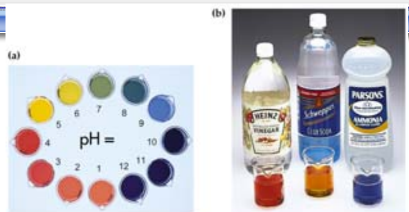
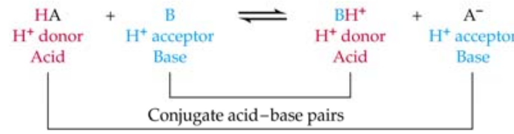
Chapter 14 - Aqueous Equilibria: Acids & Bases



Acid-Base Pairs

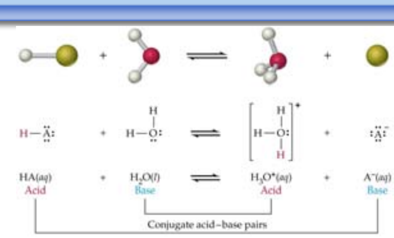


- Which substance donates H^+?
- Which substance accepts H^+?
- Conjugate acid-base pairs. Remember that reactions proceed in both directions.

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 Pairs

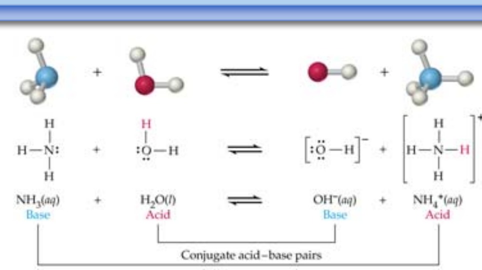


- Write an equation for the dissociation of HCN in water. Identify the acid, the base, the conjugate acid, and the conjugate base.

Acid-Base Concepts

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

Acid-Base Pairs



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

Strengths of Acids/Bases

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

Strength of 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
  - NH_3 compounds DO react with water
  - $NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$
- Example 14.3, Problem 14.4, Key Concept 14.4
- Draw the following in water: HNO_3, HF, NaOH, $Ca(OH)_2$, $Fe(OH)_3$

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).

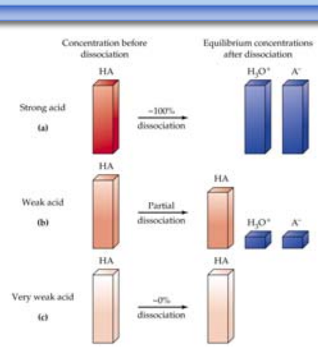
Strength of Acids/Bases

TABLE 15.1 Relative Strengths of Conjugate Acid–Base Pairs

	Acid, HA		Base, A^-		
Stronger acid	$HClO_4$ HCl H_2SO_4 HNO_3	Strong acids. 100% dissociated in aqueous solution.	ClO_4^- Cl^- HSO_4^- NO_3^-	Very weak bases. Negligible tendency to be protonated in aqueous solution.	Weaker base
	H_3O^+		H_2O		
	HSO_4^- H_3PO_4 HNO_2 HF CH_3CO_2H H_2CO_3 H_2S NH_4^+ HCN HCO_3^-	Weak acids. Exist in solution as a mixture of HA, A^-, and H_3O^+.	SO_4^{2-} $H_2PO_4^-$ NO_2^- F^- $CH_3CO_2^-$ HCO_3^- HS^- NH_3 CN^- CO_3^{2-}	Weak bases. Moderate tendency to be protonated in aqueous solution.	
	H_2O		OH^-		
Weaker acid	NH_3 OH^- H_2	Very weak acids Negligible tendency to dissociate.	NH_2^- O^{2-} H^-	Strong bases. 100% protonated in aqueous solution.	Stronger base

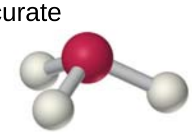
Strength of Acids

- HCl, H_2SO_4
- HNO_2, HF
- H_2O



Hydronium Ions

- HA (aq) $\leftrightarrows$ H^+ (aq) + A^- (aq)
- H^+ is very reactive and will bond with O in H_2O to form H_3O^+
- H^+ and H_3O^+ mean the same thing but H_3O^+ is more accurate



H_3O^+ — the hydronium ion, or hydrated H^+

Dissociation of Water

- H_2O (l) + H_2O (l) ⇆ H_3O^+ (aq) + OH^- (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 $[H_3O^+] = 1.0 \times 10^{-7}$ (experimentally determined for pure H_2O)

pH Scale

- Logarithmic scale (like Richter scale for earthquakes).
- $[H_3O^+] = 1 \times 10^{-2}$ has a pH of 2 but $[H_3O^+] = 1 \times 10^{-12}$ has a pH of 12
- pH = -log $[H_3O^+]$ $[H_3O^+] = 10^{-pH}$
- pOH = -log $[OH^-]$ $[OH^-] = 10^{-pOH}$
- $[H_3O^+][OH^-] = 1 \times 10^{-14}$
- pH + pOH = 14 (verify this)

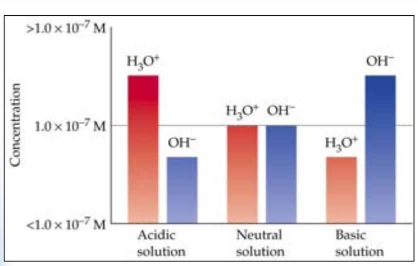
Dissociation of Water

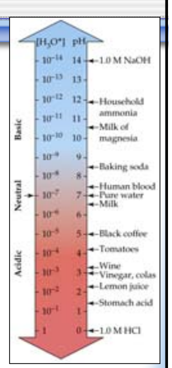
- We can compare $[H_3O^+]$ and $[OH^-]$ for solutions.
- They're equal in neutral solutions.
- Which one is greater in acidic solutions?
- Basic solutions?
- $[H_3O^+] = 5.6 \times 10^{-4}$ M. What is $[OH^-]$?

pH Sig Figs

- $[H_3O^+] = 5.6 \times 10^{-4}$ M
- pH = -log (5.6×10^{-4}) = 3.2518
- Exponent is exact number, 5.6 determines how many decimals
- pH = 3.25
- Find $[H_3O^+]$, pH, and pOH if $[OH^-] = 9.8 \times 10^{-9}$ M
- Example 14.4 - 14.6, Problems 14.6 - 14.9

Acidic, Basic, Neutral Solns



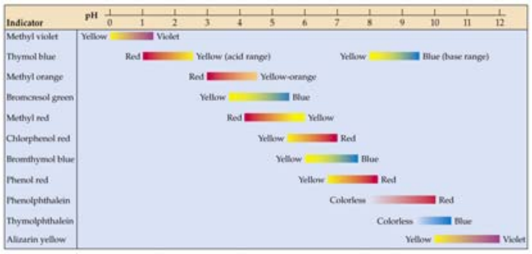


Group Quiz #7

- 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. 621
- Ans: $[H_3O^+] = 2.661 \times 10^{-14}$ M, $[OH^-] = 0.3758$ M, pH = 13.5750, pOH = 0.4250

pH Indicators

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



pKa's of Weak Acids

- Table 14.2

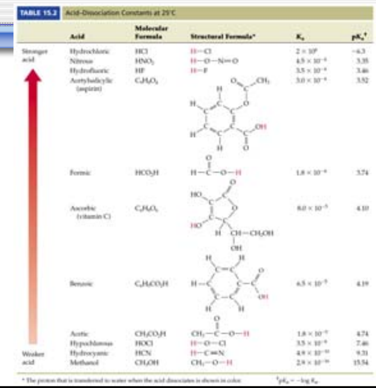


TABLE 15.2 Acid-Dissociation Constants at 25°C

	Acid	Molecular Formula	Structural Formula*	K_a	pK_a†
Stronger acid	Hydrochloric	HCl	H—Cl	2×10^{6}	−6.3
	Nitrous	HNO_2	H—O—N=O	4.5×10^{-4}	3.35
	Hydrofluoric	HF	H—F	3.5×10^{-4}	3.46
	Acetylsalicylic (aspirin)	$C_9H_8O_4$		3.0×10^{-4}	3.52
	Formic	HCO_2H	H—C(=O)—O—H	1.8×10^{-4}	3.74
	Ascorbic (vitamin C)	$C_6H_8O_6$		8.0×10^{-5}	4.10
	Benzoic	$C_6H_5CO_2H$		6.5×10^{-5}	4.19
	Acetic	CH_3CO_2H	CH₃—C(=O)—O—H	1.8×10^{-5}	4.74
	Hypochlorous	$HOCl$	H—O—Cl	3.5×10^{-8}	7.46
	Hydrocyanic	HCN	H—C≡N	4.9×10^{-10}	9.31
Weaker acid	Methanol	CH_3OH	CH₃—O—H	2.9×10^{-16}	15.54

* The proton that is transferred to water when the acid dissociates is shown in color. † $pK_a = -\log K_a$.

pH of Strong Acids/Bases

- $HNO_3(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + NO_3^-(aq)$
- Calculate pH of 0.103 M HNO_3 solution.
  - pH = 0.987
- $Sr(OH)_2 \leftrightarrows Sr^{2+}(aq) + 2OH^-(aq)$
- Calculate pH of 0.020 M $Sr(OH)_2$ soln.
  - pH = 12.60
- Problems 14.10 and 14.11

Weak Acid Solutions

- ICE tables
- Given $[HA]_i$ and K_a, find all equilibrium concentrations and pH
- Given $[HA]_i$ and pH, find all equilibrium concentrations and K_a
- With small K values, we can try assuming that *x* will be small to simplify math

Equilbria of Weak Acids

- $HA(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + A^-(aq)$
  - Write equilibrium expression.
- $pK_a = -\log K_a$: stronger acid = lower pK_a
- % Ionization = $[H_3O^+] / [HA]_i \times 100\%$
- For a stronger acid, indicate if the following will be higher or lower:
  - $[H_3O^+]$
  - pH
  - % ionization
  - K_a
  - pK_a

Weak Acid Solutions

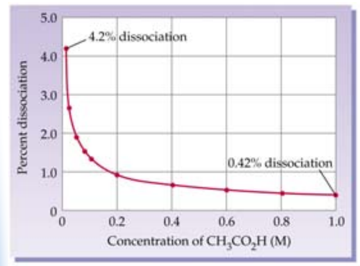
- Find the pH of a 0.50 M solution of HOCl (hypochlorous acid). $K_a = 3.5 \times 10^{-8}$
- ICE Table

	HOCl	⇆	H^+	OCl^-
Initial				
Equil.				
Change				

Weak Acid Solutions

- Test the approximation
- $x = 1.323 \times 10^{-4}$ M
- $(x / [HA]_i) \times 100 < 5\%$
- $(1.3 \times 10^{-4} / 0.50) \times 100 = 0.026\%$
- Assumption checks out! Yeah, easy math!
- $x = [H_3O^+] = 1.3 \times 10^{-4}$ M
- pH = 3.89
- What are pOH and $[OH^-]$?
- Example 14.10, Problems 14.14, 14.15

Dilution and % Dissociation



- As we add water, we can dissociate more. More dilute = more dissociation.

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.

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 $K_a = 2.0 \times 10^{-3}$

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.

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, $HC_7H_5O_2$, is 6.3 x 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 0.050 M.

Polyprotic acids

- $HC_2O_4^-(aq) + H_2O(l) \leftrightarrows C_2O_4^{2-}(aq) + H_3O^+(aq)$
  - $K_{a2} = [C_2O_4^{2-}][H_3O^+] / [HC_2O_4^-] = 6.4 \times 10^{-5}$
- $K_{a2} = (x)(0.069 + x) /(0.069 - x) = 6.4 \times 10^{-5}$
- Approx: $(x)(0.069) /(0.069) = 6.4 \times 10^{-5}$ (x checks out!)
- $x = 6.4 \times 10^{-5}$ 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
- Example 15.11, Problems 15.17, 15.18

Polyprotic Acids

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

Weak Bases

- Same idea as acids, but use K_b instead
- $NH_3(aq) + H_2O(l) \leftrightarrows NH_4^+(aq) + OH^-(aq)$
- $K_b = [NH_4^+][OH^-] / [NH_3]$
- 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.

Polyprotic Acids

- $H_2C_2O_4(aq) + H_2O(l) \leftrightarrows HC_2O_4^-(aq) + H_3O^+(aq)$
  - $K_{a1} = [HC_2O_4^-][H_3O^+] / [H_2C_2O_4] = 5.9 \times 10^{-2}$
- Assumption that x is small is no good. Use the quadratic! (~63%)
- $x^2 + 5.9\times10^{-2} x - 0.00885 = 0$
- $x = 0.069$ M $= [HC_2O_4^-] = [H_3O^+]$
- 0.15 M – x $= [H_2C_2O_4] = 0.081$ M

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: $[(CH_3)_2NH_2^+] = [OH^-] = 0.016$ M
- $[(CH_3)_2NH] = 0.50$ M – 0.016 = 0.48 M
- 2 ways to find pH

Weak Bases

- 1) $[OH^-] = 0.016$ M
- $[H_3O^+] = K_w / [OH^-] = 1.0 \times 10^{-14} / 0.016$ M
- $[H_3O^+] = 6.19 \times 10^{-13}$ M
- pH = 12.21
- 2) $[OH^-] = 0.016$ M
- pOH = 1.79
- 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: $K_a = [H^+][A^-] / [HA]$
- Weak base: $K_b = [HA][OH^-] / [A^-]$
- Multiply: $K_a * K_b$
- $K_a \cdot K_b = [H^+] [OH^-] = K_w$
- True only if the acid and base are **<u>conjugate pairs</u>**!
- 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 → 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 → basic or neutral solution (ex: NaCl)
- Anion in salt: comes from the acid
  - If acid is strong → 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).

  NH_4Cl: $NH_4^+ + H_2O \leftrightarrows NH_3 + H_3O^+$
  - pH < 7

  $NaCH_3CO_2$: $CH_3COO^- + H_2O \leftrightarrows CH_3COOH + OH^-$
  - pH > 7
- These reactions are called hydrolysis.

Properties of Salts

- Neutral Salts
  - $NaOH + HCl \rightarrow NaCl + H_2O$
  - Acid and base are strong, so resulting salt is neutral.
  - What is another example?
- Acidic Salts
  - $HCl + NH_3 \leftrightarrows NH_4Cl$
  - 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 (HF) = 3.5×10^{-4}
- Is NH_4Cl acidic, basic, or neutral?
  - Calculate pH of a 0.10 M NH_4Cl solution. K_b (NH_3) = 1.8×10^{-5}

More Pratice

- Classify the following salts as acidic, basic, or neutral. For acidic or basic salts, write the reaction of hydrolysis.
  - NaOCl
  - $CsNO_3$
  - CuCl
- Write the formula of an acidic salt
- Write the formula of a basic salt

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

Answers

- NaOCl — basic: $OCl^- + H_2O \leftrightarrows HOCl + OH^-$
- $CsNO_3$ — neutral
- $Fe(NO_3)_3$ — acidic: $Fe^{3+} + 3H_2O \leftrightarrows Fe(OH)_3 + H_3O^+$

- Acidic: cation from a weak base, anion from a strong acid (ex: $Co(NO_3)_3$)
- Basic: cation from a strong base, anion from a weak acid (ex: $NaNO_2$)

Practice Answers

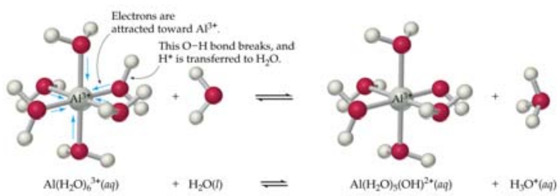
- Classify the following salts as acidic, basic, or neutral. For acidic or basic salts, write the reaction of hydrolysis.
  - KBr — neutral
  - NaF — basic: $F^- + H_2O \leftrightarrows HF + OH^-$
  - LiCN — basic: $CN^- + H_2O \leftrightarrows HCN + OH^-$
  - NH_4Cl — acidic: $NH_4^+ + H_2O \leftrightarrows NH_3 + H_3O^+$

Properties of Salts

- Small, highly charged metals also make acidic salts; $Al(H_2O)_6^{3+}$ ($K_a = 1.4 \times 10^{-5}$)
- These are surrounded by waters in solution to give a hydrated cation
- High charge on metal → electrons on O are attracted to metal, easier to break O-H bond
- Calculate pH of a 0.20 M $AlCl_3$ solution.
  - $Al(H_2O)_6^{3+} + H_2O \leftrightarrows H_3O^+ + Al(H_2O)_5(OH)^{2+}$
- Example 14.14, Problem 14.22

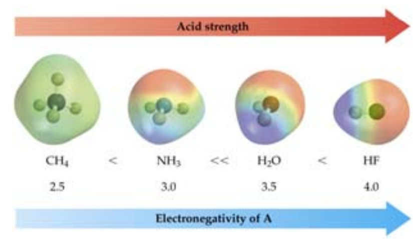
Metal acids

- Al^{3+} as acid



Acid Strength Factors

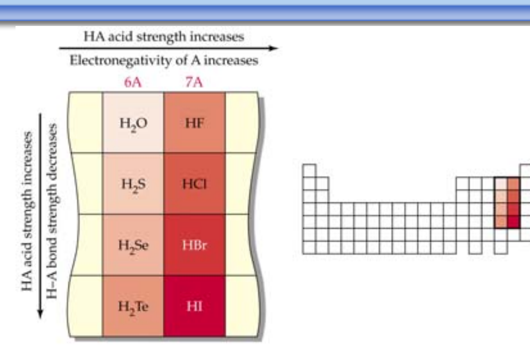
- In the same row, bond strengths are relatively similar, but electronegativity changes are greater



Percent Ionization

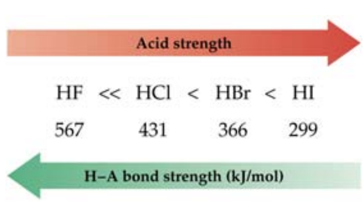
- Percent hydrolysis for acidic salts.
  - $[H_3O^+] / [HA]_i$ x 100%
- Conjugate acid reacts with water to create H_3O^+
- Calculate pH and % hydrolysis of 1.1 M NH_4I solution.
  - $NH_4I \rightarrow NH_4^+ + I^-$
  - $NH_4^+ + H_2O \leftrightarrows NH_3 + H_3O^+$
  - $K_a(NH_4^+) = K_w / K_b = 1.0 \times 10^{-14} / 1.8 \times 10^{-5}$

Acid Strength Factors



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



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
  - $H^+ + :NH_3 \rightarrow NH_4^+$
  - 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