CHAPTER 15. ACIDS AND BASES

General Properties of Acids & Bases:

Acids	Bases
taste sour	taste bitter
act corrosive	feel slippery
turn litmus paper red	turn litmus paper blue
examples: vinegar, lemon juice, gastric juice, soft drinks	examples: milk of magnesia, bleach, ammonia, detergents

15.1 Bronsted- Lowry Acids and Bases

Bronsted - Lowry Acid: substance that donates a proton.

Bronsted - Lowry Base: substance that accepts a proton.

During Bronsted reactions, one proton is transferred and a new acid and base are formed:

Reaction 1) $HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$

Acid Base Acid Base

Reaction 2) $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

Base Acid Acid Base

An acid and base that differ only in the presence/absence of 1 H^+ are called a conjugate acid/base pair.

conjugate base is formed by removing 1 H^+ from an acid.

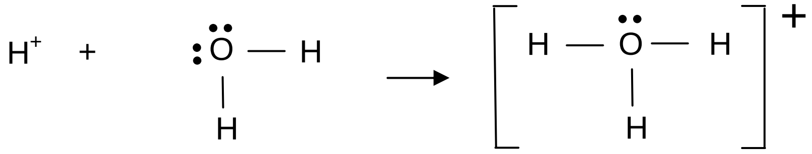
conjugate acid is formed by adding 1 H^+ to a base.

For Reaction 1: H_3O^+ is the conjugate acid of H_2O; $C_2H_3O_2^-$ is the conjugate base of $HC_2H_3O_2$.

Example. a) What is the conjugate acid of CO_3^{2-}?

b) What is the conjugate base of $H_2PO_4^-$?

Hydronium ion- H^+ is actually H_3O^+ in solution:



⇒ The H^+ ion is attracted to the electronegative O atom.

⇒ H^+ and H_3O^+ are used interchangeably in acid –base reactions and problems.

15.2 The Acid-Base Properties of Water

Water acts as an acid in reactions with bases, whereas it acts as a base for reactions involving acids. (Refer to Reactions 1 and 2 above.)

amphoteric: substance that can act as an acid or a base. (e.g. H_2O, HCO_3^-, $H_2PO_4^-$)

Water molecules can undergo a Bronsted proton transfer reaction:

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

Water ionizes to a very small extent ⇒ ~2 out of every billion water molecules are ionized.

⇒ The equilibrium constant for water ionization is called K_w.

$K_w = [H_3O^+][OH^-]$ or $K_w = [H^+][OH^-]$

$K_w = 1.0 \times 10^{-14}$ at 25 °C

⇒ Neutral: $[H^+] = [OH^-] = 1.0 \times 10^{-7}$ M
⇒ Acidic: $[H^+] > [OH^-]$
⇒ Basic: $[H^+] < [OH^-]$

Example. Calculate the $[OH^-]$ for a solution in which $[H^+] = 3.2\times10^{-4}$ M.

15.3 pH – A Measure of Acidity

pH is the –log of the H^+ concentration (in mol/L). The pH scale was proposed to give us more convenient numbers to work with.

Relationship Between pH and Acidity

pH < 7; $[H^+] > 1.0 \times 10^{-7}$ M	Acidic
pH = 7, $[H^+] = 1.0 \times 10^{-7}$ M	Neutral
pH > 7; $[H^+] < 1.0 \times 10^{-7}$ M	Basic

pH formulas and conversions

$pH = -\log [H^+]$ $[H^+] = 10^{-pH}$ (or $[H^+]$ = antilog (-pH))
$pOH = -\log [OH^-]$ $[OH^-] = 10^{-pOH}$ (or $[OH^-]$ = antilog(-pOH))
pH + pOH = 14 $[H^+][OH^-] = 1.0 \times 10^{-14}$

Significant Figures for ph Values - See Appendix 4

Numbers before the decimal are not counted as significant for a pH or pOH value.

E.g. If $[H^+] =$ **4.5**$\times10^{-3}$ M (2 significant figures); then pH = 2.**35** (2 numbers are given after the decimal point; the 2 before the decimal point is not considered significant – it's related to the exponent for the concentration term.)

Example. Complete the following table:

pH	$[H^+]$ M	$[OH^-]$ M	pOH
	1.0×10^{-9}		
		6.5×10^{-10}	
			2.30

15.4 Strength of Acids and Bases

Strong Acid: a substance that ionizes completely in water to form H_3O^+ ions (H^+ ions).

E.g. $HNO_{3}(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$

⇒ A one way arrow is used since this reaction is complete, all of the HNO_3 molecules break apart to form H_3O^+ and NO_3^- ions. (Thus, all of the reactants are converted to form products.)

Strong Acids: HCl, HBr, HI, HNO_3, H_2SO_4, $HClO_4$

Weak Acid: an acid that ionizes only to a small extent in water.

E.g. $HC_2H_3O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-(aq)$

⇒ A two-way arrow is used since this reaction is not complete but instead consists of an equilibrium mixture of $HC_2H_3O_2$, H_3O^+ and $C_2H_3O_2^-$.

⇒ Equilibrium lies to the left since most of the acid molecules have not ionized.

Strong Bases: a substance that ionizes completely in water to form OH^- ions.

E.g. $NaOH(s) \xrightarrow{H_2O} Na^+(aq) + OH^-(aq)$

⇒ The reaction goes to completion – all of the Na^+ and OH^- ions have dissociated from the solid lattice and no undissociated $NaOH(s)$ remains.

Strong Bases: Group 1A & 2A hydroxides (except Be)

Weak Bases: a base that ionizes only to a small extent in water.

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

⇒ Equilibrium lies to the left since most of the ammonia molecules have not accepted protons to form NH_4^+ and OH^- ions.

Relative Strengths of Conjugate Acid/Base Pairs - Table 15.2 (p 636)

1) A stronger acid loses its proton more readily than a weaker acid and a stronger base gains a proton more readily than a weaker base.
2) The stronger the acid, the weaker its conjugate base. Likewise, the stronger the base, the weaker its conjugate acid.

   Example. Compare the strength of the conjugate bases for HCl and $HC_2H_3O_2$.

3) Proton transfer reactions proceed from the stronger acid-base pair to the weaker acid-base pair. Thus, the equilibria lies on the side of the weaker acid-base pair.
4) H_3O^+ is the strongest acid present in aqueous solution; acids stronger than H_3O^+ completely ionize in water to form H_3O^+. OH^- is the strongest base present in aqueous solutions; bases stronger than OH^- react with water to form OH^-.

Example. Complete the following Bronsted reactions and predict the predominant direction of equilibrium.

1) $HF + S^{2-} \rightleftharpoons$

2) $NH_3 + HCO_3^- \rightleftharpoons$

Strong Acid Calculations

Since a strong acid is completely ionized: $[H^+] = [HA]$.

E.g. Calculate the pH for a 0.0013 M solution of HNO_3.

Strong Base Calculations

A strong base is completely ionized, so $[OH^-]$ is related to the concentration of the strong base by stoichiometry:

Group 1A: one mole of OH^- ions are formed for each mole of base ionized ⇒ $[OH^-] = [SB]$

Group 2A: two moles of OH^- ions are formed for each mole of base ionized ⇒ $[OH^-] = 2 \times [SB]$

Example. Calculate the pH for a 0.00175 M solution of $Ca(OH)_2$.

15.5 Weak Acids and Acid Ionization Constants

Hydrolysis Reaction for a Weak Acid (also called Acid Ionization or Acid Dissociation)

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq) \quad (\text{or } HA(aq) \rightleftharpoons H^+(aq) + A^-(aq))$$

Acid Ionization Constant: $K_a = \dfrac{[H_3O^+][A^-]}{[HA]}$ or $K_a = \dfrac{[H^+][A^-]}{[HA]}$

K_a Values are Listed in Table 15.3 (p 639)

⇒ Weak Acids: $K_a < 1$. The smaller the K_a value, the weaker the acid.

⇒ Strong Acids don't have K_a values ($K_a >> 1$ since complete ionization occurs).

Types of Weak Acids:

1) Neutral molecules that contain 1 or more ionizable H^+'s. A carboxylic acid is a type of weak acid that contains the $-CO_2H$ group. E.g. CH_3CO_2H
2) Cations that are conjugate acids of weak bases. E.g. NH_4^+
3) Anions derived from the ionization of polyprotic acids. E.g. HSO_4^-

Calculations for Weak Acids

1) Write the balanced hydrolysis reaction.
2) Construct the ICE table where $x = [H_3O^+]$: (Don't fill in values for $H_2O(l)$)
    ⇒ If given pH, $[H_3O^+]_{eq} = 10^{-pH}$
3) Write the K_a expression and substitute the equilibrium concentrations into the K_a expression.
4) Solve the K_a expression for the unknown variable.
    A. Use the Approximation Method to simplify the quadratic expression:
        - Assume x is small compared to the initial concentration of the acid: $[HA]_i - x \cong [HA]_i$
        - Check the approximation after you find x - the approximation is valid if $x \leq 5\% \, [HA]_i$ (this means that the acid is less than 5% ionized).
    B. If $x > 5\% \, [HA]_i$, the quadratic equation must be solved exactly.

Percent Ionization

$$\% \text{ Ionization} = \frac{x}{[HA]_i} \cdot 100\%$$

15.6 Weak Bases and Base Ionization Constants

Weak Base Ionization Rxn: $B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$

Base Equilibrium Constant: $K_b = \dfrac{[BH^+][OH^-]}{[B]}$

⇒ Weak bases: $K_b < 1$

⇒ K_b values are provided for some weak bases in Table 15.4.

Types of weak bases:

1) Neutral molecules that can accept a proton. Many weak bases contain N including NH_3 and a related class of compounds called amines. The lone pair of e-'s on the N acts as an electron pair donor, which is able to accept electrons.
2) Anions derived from weak acids. E.g. $C_2H_3O_2^-$, CO_3^{2-}

Calculations for weak bases: Follow the method used for weak acids except write the base hydrolysis reaction and the K_b expression.

⇒ $x = [OH^-]$ for K_b problems

15.7 The Relationship Between the Ionization Constants of Acids and Their Conjugate Bases

1. Acid hydrolysis: $HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$ $K_a =$

2. Conjugate base hydrolysis: $CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq)$ $K_b =$

3. Adding these reactions: $2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$ $K_w = [H_3O^+][OH^-]$

Thus, $\mathbf{K_a \times K_b = K_w = 1 \times 10^{-14}}$ and $\mathbf{pK_a + pK_b = 14}$

15.8 Diprotic and Polyprotic Acids

Polyprotic acids are acids that have two or more ionizable protons.

Table 15.5 lists the K_a values for some polyprotic acids.

Proton loss occurs sequentially in separate steps as shown below for H_2SO_3:

(1) $H_2SO_3(aq) \rightleftharpoons H^+(aq) + HSO_3^-(aq)$ $K_{a1} = 1.3 \times 10^{-2}$

(2) $HSO_3^-(aq) \rightleftharpoons H^+(aq) + SO_3^{2-}(aq)$ $K_{a2} = 6.3 \times 10^{-8}$

⇒ 1st H^+ is easiest to remove, so $K_{a1} > K_{a2.}$ (In step 1, the proton is lost from a neutral ion; whereas, in step 2, the proton is lost from a negatively charged ion.)

⇒ Acid strength decreases as protons are removed: $H_2SO_3 > HSO_3^-$

⇒ pH of a polyprotic acid solution primarily arises from $[H^+]$ formed in the 1st step.

15.9 Molecular Structure and the Strength of Acids

Strength of Binary Acids

1) Polarity of HX bond - Acids with more polar H-X bonds are stronger acids; Polarity↑ when X^- is more electronegative (the electrons are more attracted to X, so the acid is more likely to ionize into H^+ and X^- ions). Thus, HF is an acid but CH_4 is not.

2) Bond Strength - Acids with stronger H-X bonds are weaker acids; bond strength decreases as X becomes larger. Thus, HI > HBr > HCl > HF.

Generally, acid strength increases → a period and ↓ a group

Strength of Oxyacids: General Structure Z-O-H

1) Acid strength increases as electronegativity of Z increases. E.g. $HClO_3$ is stronger than $HBrO_3$
2) Acid strength increases as number of O's increases. E.g. $HClO_4$ is stronger than $HClO_3$

15.10 Acid-Base Properties of Salts

***Salt*:** Ionic compound formed during an acid-base neutralization reaction; for soluble ionic compounds, the cations and anions exist as moving ions in solution.

General Ion Categories

1) **Neutral ion**: no reaction occurs between the ion and water; the ion does not hydrolyze. Cations from strong bases and anions from strong acids are considered neutral. Cations: Group 1A & 2A (except Be) Anions: NO_3^-, Cl^-, Br^-, I^-, ClO_4^-, (except HSO_4^-)
2) **Acidic ion**: ion reacts with water to produce H^+ ions. Cations derived from weak bases and most metal ions (except Group 1A and 2A) are considered acidic. E.g. NH_4^+, Al^{3+}
3) **Basic ion**: ion reacts with water to produce OH^- ions. Most anions derived from weak acids are considered basic. E.g. $C_2H_3O_2^-$, ClO^-

Guidelines for Predicting pH of Salt Solutions

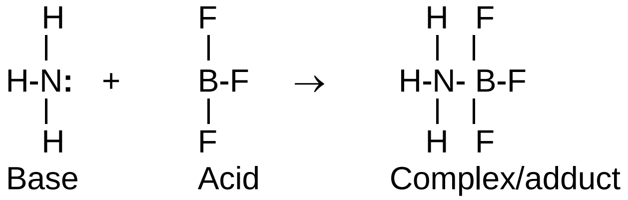
1) Neutral: cation is from a strong base and anion is from a strong acid. E.g. NaCl, $Ca(NO_3)_2$
2) Acidic: cation is conjugate acid of a weak base and anion is from a strong acid. E.g. NH_4Cl
3) Basic: cation is from a strong base and anion is conjugate base of a weak acid. E.g. $NaC_2H_3O_2$, BaC_2O_4
4) Salts containing an acidic cation and a basic anion may be acidic or basic. E.g. NH_4F Compare K_a & K_b values, larger value dictates the pH. (E.g. If $K_a > K_b$, the solution is acidic.)

15.12 Lewis Acids and Bases

Lewis Acid: substance that accepts an electron pair. E.g. BF_3, Al^{3+}

Lewis Base: substance that donates an electron pair. E.g. OH^-, H_2O, NH_3 and amines

Example Lewis Reaction:



$$H_3N\!: + BF_3 \rightarrow H_3N\text{-}BF_3$$

The hydration of a metal ion occurs by a Lewis acid-base reaction as shown below for Al^{3+}:

$$Al^{3+} + 6(H_2O) \rightarrow Al(H_2O)_6^{3+}$$

Note that the Lewis Acid-Base model is more general than the Bronsted or Arrhenius models. A Lewis acid does not have to contain an ionizable H^+ ion, so the Lewis model covers many reactions that do not involve proton transfer processes.