Chapter 14 Outline – Acids and Bases

The Nature of Acids and Bases
- Svante Arrhenius was the first to recognize the nature of acids and bases. He postulated that acids produce hydrogen ions(H^+) in solution and bases produce hydroxide ions(OH^-) in solution.
- Show Arrhenius example below:

- Arrhenius' theory did not apply to all bases.
- The **Brønsted-Lowry** model referred to an **acid** as **a proton(H^+) donor** and a **base** as a **proton acceptor**.
  o When HCl dissolves in water, each HCl molecule donates a proton to a water molecule and as such is considered a Brønsted-Lowry acid:
    - $HCl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$
    - H_3O^+ is the hydronium ion
  o A **conjugate acid –base** pair consists of two substances related to each other by donating and accepting of a single proton.
    - $HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$
      Acid   Base   Conjugate Conjugate
                             Acid   Base
    - **Think of reactions such as these as being a competition for the proton between the base and the conjugate base. In the above reaction, if water is the stronger base, the equilibrium will shift to the right. If A^- is a stronger base, the equilibrium position will be far to the left.**
    - Note: Both H_3O^+ and H^+ are commonly used to represent the hydrated proton.
    - When calculating the equilibrium constant for an acid, the symbol K_a is used. K_a is called the acid-dissociation constant.
- You should be able to write the dissociation for an acid. To do so, you remove a proton, H^+. See below.
- Example: Write the dissociation reaction for hydrochloric acid, HCl.
  $HCl(aq) \rightleftharpoons H^+(aq) + Cl^-(aq)$

- You try: a. Write the dissociation reaction for acetic acid, $HC_2H_3O_2$
         b. Write the dissociation reaction for the ammonium ion, NH_4^+.

Acid Strength
- The strength of an acid is defined by the equilibrium position of its dissociation reaction.
- **A strong acid dissociates completely** and its **equilibrium position lies far to the right**.
- **A strong acid yields a weak conjugate base. This conjugate base is a weaker base than water.**
- **A weak acid only partially dissociates** and its **equilibrium position lies far to the left**.
- **A weak acid yields a strong conjugate base. This conjugate base is a stronger base than water.**
- The common strong acids are: (MEMORIZE THESE!!!)
  o Hydrochloric acid $HCl \rightarrow H^+ + Cl^-$
  o Hydrobromic acid $HBr \rightarrow H^+ + Br^-$
  o Hydroiodic acid $HI \rightarrow H^+ + I^-$
  o Perchloric acid $HClO_4 \rightarrow H^+ + ClO_4^-$
  o Nitric acid $HNO_3 \rightarrow H^+ + NO_3^-$
  o Sulfuric acid $H_2SO_4 \rightarrow H^+ + HSO_4^-$
- Most acids are oxoacids, in which the acidic proton is attached to an oxygen atom.
- Organic acids contain the carboxyl group (-COOH).
- Organic acids are usually weak. Examples: acetic acid, CH_3COOH, and benzoic acid, C_6H_5COOH.

Systematic Name	Common Name	Formula
Methanoic Acid	Formic Acid	$HCOOH$
Ethanoic Acid	Acetic Acid	CH_3COOH
Propanoic Acid	Propanoic Acid	CH_3CH_2COOH
Butanoic Acid	Butyric Acid	$CH_3CH_2CH_2COOH$
Pentanoic Acid	Valeric Acid	$CH_3CH_2CH_2CH_2COOH$
Benzoic Acid	Benzoic Acid	C_6H_5COOH

- Draw organic acid structure below.

- **A substance is called amphoteric or amphiprotic if it can behave as an acid or a base**.
- Water is the most common amphoteric substance.
- Note the autoionization of water: $2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$
- K_w is used to represent the ion-product constant also known as the **dissociation constant for water**.
- $K_w = [H_3O^+][OH^-]$ or $[H^+][OH^-]$; Note: H_2O is not listed because it is a liquid.
- Experiments have shown that **at 25°C in pure water**: $[H^+] = [OH^-] = 1.0 \times 10^{-7} M$
- $K_w = (1.0 \times 10^{-7} M)(1.0 \times 10^{-7} M) = 1.0 \times 10^{-14} M$
- In a neutral solution: $[H^+] = [OH^-]$
- In an acid solution: $[H^+] > [OH^-]$
- In a basic solution: $[OH^-] > [H^+]$
- Example: Calculate the $[H^+]$ if the $[OH^-]$ is 1.0×10^{-5}.
  - Since $K_w = [H^+][OH^-] = 1.0 \times 10^{-14} M$
    $[H^+](1.0 \times 10^{-5}) = 1.0 \times 10^{-14} M$
    $[H^+] = 1.0 \times 10^{-9} M$
    Since, $[OH^-] > [H^+]$, this solution is basic.

- You try: Calculate the $[H^+]$ if the $[OH^-]$ is 1.0×10^{-11}.

- Try this: The K_w for water is found to be 1×10^{-13} at 60°C.
    $2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$
  Is this reaction endothermic or exothermic? Calculate $[H^+]$ and $[OH^-]$ at 60°C.

The pH Scale
- $pH = -\log[H^+]$
- $pOH = -\log[OH^-]$
- $pH + pOH = 14.00$
- The pH scale is a log scale; a pH of 3 is 10 times as acidic as a pH of 4 and 100 times as acidic as a pH of 5.
- Calculate the pH & pOH of a strong acid or strong base.

o **Example 1:** Calculate the pH & pOH of a 0.025 M HCl solution.
Since HCl is a **strong acid**, it dissociates completely. HCl $\rightarrow$ H$^+$ + Cl$^-$. Thus, [HCl] is equal to [H$^+$].
Thus, pH = -log[0.025]
pH = 1.6; pOH = 12.4
o **Example 2**: Calculate the pH & pOH of 0.0038 M NaOH solution.
NaOH is a **strong base**, so it dissociates completely. NaOH $\rightarrow$ Na$^+$ + OH$^-$ Thus [NaOH] is equal to [OH$^-$].
* Remember, when a base dissociates, hydroxide (OH$^-$) ion is produced, so you calculate the pOH first.
pOH = -log[0.0038]   **pOH = 2.4; pH = 11.6**

- Your turn: Calculate the pH & pOH of a 0.0045 M KOH solution.

- Try another. Calculate the pH and the pOH of a 3.0 M H$_2$SO$_4$ solution.

Calculating the pH of Weak Acid Solutions

Calculating pH Using Dissociation Constants:
Example: Calculate the pH of a 0.100 M benzoic acid solution.
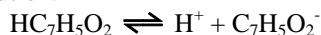
$$HC_7H_5O_2 \rightleftharpoons H^+ + C_7H_5O_2^-$$

$$K_a = \frac{[H^+]\,[C_7H_5O_2^-]}{[H\,C_7H_5O_2]}$$

$$\frac{6.4 \times 10^{-5}}{1} = \frac{[x][x]}{0.100}$$

$6.4 \times 10^{-6} = x^2$
x = 0.0025 therefore [H$^+$] = 0.0025

pH = -log[H$^+$]
pH = -log[0.0025]
pH = 2.6

You try: Calculate the pH of a 0.500 M formic acid solution.

Ionization Constants of Weak Acids		
Monoprotic Acid	Name	K_a
HIO$_3$	iodic acid	1.69×10^{-1}
HSO$_4^-$	bisulfate ion	1.2×10^{-2}
HClO$_2$	chlorous acid	1.2×10^{-2}
HC$_2$H$_2$ClO$_2$	monochloracetic acid	1.35×10^{-3}
HF	hydrofluoric acid	7.2×10^{-4}
HNO$_2$	nitrous acid	4.0×10^{-4}
HCHO$_2$	formic acid	1.8×10^{-4}
HC$_3$H$_5$O$_3$	lactic acid	1.38×10^{-4}
HC$_7$H$_5$O$_2$	benzoic acid	6.4×10^{-5}
HN$_3$	hydrazoic acid	1.8×10^{-5}
HC$_2$H$_3$O$_2$	acetic acid	1.8×10^{-5}
HC$_4$H$_7$O$_2$	butanoic acid	1.52×10^{-5}
HC$_3$H$_5$O$_2$	propanoic acid	1.34×10^{-5}
HClO	hypochlorous acid	3.5×10^{-8}
HBrO	hypobromous acid	2×10^{-9}
HCN	hydrocyanic acid	6.2×10^{-10}
H$_3$BO$_3$	boric acid	5.8×10^{-10}
NH$_4^+$	ammonium ion	5.6×10^{-10}
HC$_6$H$_5$O	phenol	1.6×10^{-10}
HIO	hypoiodous acid	2×10^{-11}
H$_2$O$_2$	hydrogen peroxide	1.8×10^{-12}

Calculating Dissociation Constants of a Weak Acid
Example: A 0.1000 M solution of acetic acid is only partially ionized. The $[H^+]$ in the solution is measured as 1.34 $\times 10^{-3}$M. What is the acid dissociation constant?

Concentrations	$[CH_3COOH]$	$[H^+]$	$[CH_3COO^-]$
Initial	0.1000	0	0
Change	0.1000-x	+x	+x
Equilibrium	0.0987	1.34×10^{-3}	1.34×10^{-3}

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

$$K_a = \frac{(1.34 \times 10^{-3})(1.34 \times 10^{-3})}{0.0987}$$

$$K_a = \mathbf{1.82 \times 10^{-5}}$$

You try: A 0.650 M solution of a weak acid is only partially ionized. The $[H^+]$ in the solution is measured as 3.56 $\times 10^{-5}$ M. What is the acid dissociation constant?

Calculating the pH of Weak Acid Mixtures
Calculate the pH of a solution that contains 1.00 M HCN and 5.00 M HNO_2. Also, calculate the concentration of cyanide ion (CN^-) in the solution at equilibrium.

Since the K_a of HCN (6.2×10^{-10}) is so much smaller than that of HNO_2 (4.0×10^{-4}), we should only consider HNO_2 when determining the pH.

$$K_a = \frac{[H^+][NO_2^-]}{[HNO_2]}$$

$$\frac{4.0 \times 10^{-4}}{1} = \frac{[x][x]}{5.00}$$

$0.0020 = x^2$

$x = 0.045$ therefore $[H^+] = 0.045$

pH = $-\log[H^+]$
pH = $-\log[0.045]$
pH = 1.35

To determine the $[CN^-]$, use the known value of [HCN], the K_a of HCN and the calculated value of $[H^+]$ from above.

$$K_a = \frac{[H^+][CN^-]}{[HCN]}$$

$$\frac{6.2 \times 10^{-10}}{1} = \frac{[0.045][CN^-]}{1.00}$$

$[CN^-] = 1.4 \times 10^{-8}$ M

You try: Calculate the pH of a solution that contains 3.00 M HF and 2.00 M HClO. Also, calculate the concentration of the hypochlorite ion (ClO^-) at equilibrium.

Calculating Percent Dissociation
- **Percent dissociation = [amount dissociated] x 100**
                          [initial concentration]
- **Percent dissociation increases as solutions are diluted.**

Example: Above it was calculated that a 5.00 M solution of HNO_2 dissociates to produce a $[H^+] = 0.045$ M. Calculate the percent dissociation.
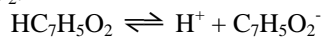
Percent dissociation = $\dfrac{0.045}{5.00}$ x 100

Percent dissociation = 0.90%

You try: Calculate the percent dissociation of a 2.45 M acetic acid solution.

Calculating K_a from Percent Dissociation

Example: In a 0.400 M aqueous solution, benzoic acid is 1.27% dissociated. Calculate the K_a of benzoic acid $HC_7H_5O_2$.

$$HC_7H_5O_2 \rightleftharpoons H^+ + C_7H_5O_2^-$$

Percent dissociation = $\dfrac{[amount\ dissociated]}{[initial\ concentration]}$ x 100

$1.27 = \dfrac{[amount\ dissociated]}{0.400}$ x 100

[amount dissociated] = $0.00508 = [H^+] = [C_7H_5O_2^-]$

$K_a = \dfrac{[H^+][C_7H_5O_2^-]}{[HC_7H_5O_2]}$

$K_a = \dfrac{[0.00508][0.00508]}{[0.400]}$

$K_a = 6.45 \times 10^{-5}$

You try: **AP Question 1 (2002B)**

$$HC_3H_5O_3\ (aq) \rightleftharpoons H^+(aq) + C_3H_5O_3^-(aq)$$
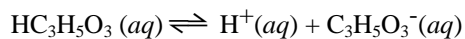
Lactic acid, $HC_3H_5O_3$, is a monoprotic acid that dissociates in aqueous solution, as represented by the equation above. Lactic acid is 1.66 percent dissociated in 0.50 M $HC_3H_5O_3$ (*aq*) at 298 K.

    a.   Write the expression for the acid-dissociation constant, K_a, for lactic acid and calculate its value.

    b.   Calculate the pH of 0.50 *M* $HC_3H_5O_3$.

    c.   Calculate the pH of a solution formed by dissolving 0.045 mole of solid sodium lactate, $NaC_3H_5O_3$ in 250. mL of 0.50 *M* $HC_3H_5O_3$. Assume that volume change is negligible.

    d.   A 100. mL sample of 0.10 *M* HCl is added to 100. mL of 0.50 *M* $HC_3H_5O_3$. Calculate the molar concentration of lactate ion, $C_3H_5O_3^-$ in the resulting solution.

Bases

- According to Arrhenius, a base is a substance that dissociates to produce hydroxide ions (OH^-).
    - $NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$
- The Brønsted-Lowry model calls bases proton acceptors. This theory explains why ammonia (NH_3) reacts with water to form a base. $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$
- **Strong bases dissociate completely.**
- **The strong bases are all the alkali hydroxides and calcium, barium & strontium hydroxide. Memorize these!**
- The alkaline-earth hydroxides are not very soluble and are used only when solubility is not important.
- $Ca(OH)_2$, also known as slaked lime, is widely used in industry. Slaked lime is used in scrubbing stack gases(see chapter 5) to remove sulfur dioxide from the exhaust of power plants and factories. It is also used in water treatment plants for softening hard water, which involves removing Ca^{2+} and Mg^{2+} ions that hamper the action of detergents.
- Slaked lime is produced when lime (CaO) is added to water. $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$
- Calculate the pH and pOH of a 0.100 M sodium hydroxide (NaOH) solution.

    $NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$
    NaOH is a strong base and therefore completely dissociates.
    $pOH = -log[OH^-]$
    $pOH = -log[0.100]$
    $pOH = 1$
    $pH + pOH = 14$
    $pH + 1 = 14$
    $pH = 13$

- Note: ammonia, (NH_3), and the related amines($R_xNH_{(3-x)}$) are all weak bases.
- Just like weak acids, weak bases also have a dissociation constant.
- A **base dissociation constant (K_b)** is *the ratio of the concentration of the dissociated form of a base to the undissociated form.* Scientists calculate a base's dissociation constant to determine how much of a base is in the ionic form.

- $B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$

    $K_b = \dfrac{[BH^+][OH^-]}{[B]}$

- **Example**: A 0.1000 M solution of weak base is only partially ionized. The [OH⁻] in the solution is measured as 1.34×10^{-3}M. What is the base dissociation constant?

Ionization Constants of Weak Bases		
Weak Base	**Name**	**K_b**
$(CH_3)_2NH$	dimethylamine	9.6×10^{-4}
CH_3NH_2	methylamine	4.4×10^{-4}
$CH_3CH_2NH_2$	ethylamine	5.6×10^{-4}
$(CH_3)_3N$	trimethylamine	7.4×10^{-5}
NH_3	ammonia	1.8×10^{-5}
N_2H_4	hyzadrine	9.6×10^{-7}
C_5H_5N	pyridine	1.7×10^{-9}
$C_6H_5NH_2$	aniline	3.8×10^{-10}

Concentrations	[B]	[BH⁺]	[OH⁻]
Initial	0.1000	0	0
Change	-x	+x	+x
Equilibrium	0.0987	1.34×10^{-3}	1.34×10^{-3}

$K_b = \dfrac{[BH^+][OH^-]}{[B]}$

$K_b = \dfrac{(1.34 \times 10^{-3})(1.34 \times 10^{-3})}{0.0987}$

$K_b = \mathbf{1.82 \times 10^{-5}}$

- **You try**: A 0.250 M solution of weak base is only partially ionized. The [OH⁻] in the solution is measured as 3.50×10^{-6}M. What is the base dissociation constant? What is the pH?

Calculating pH Using Dissociation Constants

Likewise, if you know the concentration of the base and the base dissociation constant, you can determine the pH.

Example: Calculate the pH of a 0.01 M ammonia solution.

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
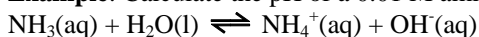
$$K_b = \frac{[NH_4^+]\,[OH^-]}{[NH_3]}$$

$$\frac{1.8 \times 10^{-5}}{1} = \frac{[x][x]}{0.01}$$

$1.8 \times 10^{-7} = x^2$

$x = 4.2 \times 10^{-4}$ therefore $[OH^-] = 4.2 \times 10^{-4}$

$pOH = -\log[OH^-]$
$pOH = -\log[4.2 \times 10^{-4}]$
pOH = 3.4
pH = 10.6

- You try: Calculate the pH of a 3.45 M aniline solution.

Polyprotic Acids

- Acids that can furnish more that one hydrogen are known as polyprotic acids.
- Many partially dissociated polyprotic acids are amphoteric (i.e. HSO_4^-, $H_2PO_4^-$, HPO_4^{2-}, etc.)
- Examples of polyprotic acids are sulfuric acid (H_2SO_4) and phosphoric acid (H_3PO_4).
- Sulfuric acid is a diprotic acid because it contains two ionizable hydrogen.
    - $H_2SO_4(aq) \rightleftharpoons H^+(aq) + HSO_4^-(aq)$
    - $HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)$
- Phosphoric acid is a triprotic acid because it contains three ionizable hydrogen.
    - $H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq)$
    - $H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq)$
    - $HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq)$
- For a typical polyprotic acid: $K_{a1} > K_{a2} > K_{a3}$

Ionization Constants of Polyprotic Acids				
Polyprotic Acid	Name	K_{a1}	K_{a2}	K_{a3}
H_2SO_4	sulfuric acid	large	1.2×10^{-2}	
H_2CrO_4	chromic acid	5.0	1.5×10^{-6}	
$H_2C_2O_4$	oxalic acid	6.5×10^{-2}	6.1×10^{-5}	
H_3PO_3	phosphorus acid	3×10^{-2}	1.6×10^{-7}	
H_2SO_3	sulfurous acid	1.5×10^{-2}	1.0×10^{-7}	
H_2SeO_3	selenous acid	4.5×10^{-3}	1.1×10^{-8}	
$H_2C_3H_2O_4$	malonic acid	1.4×10^{-3}	2.0×10^{-6}	
$H_2C_8H_4O_4$	phthalic acid	1.1×10^{-3}	3.9×10^{-6}	
$H_2C_4H_4O_6$	tartaric acid	9.2×10^{-4}	4.3×10^{-5}	
H_2CO_3	carbonic acid	4.5×10^{-7}	4.7×10^{-11}	
H_3PO_4	phosphoric acid	7.5×10^{-3}	6.2×10^{-8}	4.8×10^{-13}
H_3AsO_4	arsenic acid	5×10^{-3}	8×10^{-8}	6×10^{-10}
$H_3C_6H_5O_7$	citric acid	7.1×10^{-4}	1.7×10^{-5}	6.3×10^{-6}

- **For a typical polyprotic acid only the first dissociation is important in determining the pH.**
- Sulfuric acid is unique in being a strong acid in its first dissociation step and a weak acid in its second step. For concentrated solutions of sulfuric acid (1.0 M and higher), the large concentration of H^+ ions from the first step represses the second step. For a dilute solution of sulfuric acid, the second step does make a significant contribution, and the quadratic equation must be used to obtain the total H+ concentration.

Acid-Base Properties of Salts
- Salts are another name for ionic compounds.
- When salts dissolve in water they (usually) dissociate into ions. Under certain conditions, these ions can behave as acids or bases.

Strong Acid	Conjugate Base
HCl	Cl-
HBr	Br^-
HI	I^-
H_2SO_4	HSO_4^-
$HClO_4$	ClO_4^-
HNO_3	NO_3^-

Strong Base	Conjugate Acid
LiOH	Li^+
NaOH	Na^+
KOH	K^+
RbOH	Rb^+
CsOH	Cs^+
FrOH	Fr^+
$Ca(OH)_2$	Ca^{2+}
$Sr(OH)_2$	Sr^{2+}
$Ba(OH)_2$	Ba^{2+}

- Salts that consist of cations of strong bases and anions of strong acids have no effect on $[H^+]$ when dissolved in water.
  - $NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$ pH = 7
- Salts that consist of a conjugate acid of a weak base and the conjugate base of a strong acid produce acidic solutions.
  - $NH_4Cl(s) \rightarrow NH_4^+(aq) + Cl^-(aq)$ pH < 7
- Salts that consist of a conjugate acid of a strong base and the conjugate base of a weak acid produce basic solutions.
  - $NaC_2H_3O_2(s) \rightarrow Na^+(aq) + C_2H_3O_2^-(aq)$ pH > 7
- Salts that consist of a conjugate acid of a weak base and the conjugate base of a weak acid produce a solution with a pH that depends on the K_a & K_b values.
  - If $K_a > K_b$, the solution is acidic.
  - If $K_b > K_a$, the solution is basic. NH_4CN; $K_{a(NH4+)} = 5.6 \times 10^{-10}$, $K_{b(CN-)} = 1.6 \times 10^{-5}$
  - If $K_a = K_b$, the solution is neutral. $NH_4C_2H_3O_2$; $K_{a(NH4+)} = 5.6 \times 10^{-10}$, $K_{b(C2H3O2-)} = 5.6 \times 10^{-10}$

TABLE 14.6 Acid–Base Properties of Various Types of Salts

Type of Salt	Examples	Comment	pH of Solution
Cation is from strong base; anion is from strong acid	KCl, KNO_3, $NaCl$, $NaNO_3$	Neither acts as an acid or a base	Neutral
Cation is from strong base; anion is from weak acid	$NaC_2H_3O_2$, KCN, NaF	Anion acts as a base; cation has no effect on pH	Basic
Cation is conjugate acid of weak base; anion is from strong acid	NH_4Cl, NH_4NO_3	Cation acts as acid; anion has no effect on pH	Acidic
Cation is conjugate acid of weak base; anion is conjugate base of weak acid	$NH_4C_2H_3O_2$, NH_4CN	Cation acts as an acid; anion acts as a base	Acidic if $K_a > K_b$, basic if $K_b > K_a$, neutral if $K_a = K_b$
Cation is highly charged metal ion; anion is from strong acid	$Al(NO_3)_3$, $FeCl_3$	Hydrated cation acts as an acid; anion has no effect on pH	Acidic

- $K_w = K_a \times K_b$
- Calculating the pH of salts
    - Example: Calculate the pH of a 0.30 M NaF solution.

      NaF is made up of the conjugate acid(Na^+) of a strong base(NaOH) and the conjugate base(F^-) of a weak acid (HF). Thus, NaF will produce a basic solution. Find the K_a of the weak acid, HF. You can only reference the equilibrium concentration of the "weak" substance.

      The K_a of HF = 7.2×10^{-4}

      Since NaF will produce a basic solution, you need the K_b of the solution.

      $K_w = K_a \times K_b$

      $1.0 \times 10^{-14} = 7.2 \times 10^{-4} \times K_b$

      $1.4 \times 10^{-11} = K_b$

      $K_b = \dfrac{[BH^+][OH^-]}{[B]}$

      $1.4 \times 10^{-11} = x^2 / 0.30$

      $x = 2.0 \times 10^{-6} = [OH^-]$

      pOH = 5.69

      pH = 14.00 – 5.69 = 8.31

    - You try: Calculate the pH of a 0.60 M KCN solution.

    - Example: Calculate the pH of a 0.750 M NH_4Cl solution.

      NH_4Cl is made up of the conjugate base(Cl^-) of a strong acid(HCl) and the conjugate acid(NH_4) of a weak base (NH_3). Thus, NH_4Cl will produce an acidic solution. Find the K_b of the weak acid, NH_3. You can only reference the equilibrium concentration of the "weak" substance.

      The K_b of $NH_3 = 1.8 \times 10^{-5}$

      Since NH_4Cl will produce an acidic solution, you need the K_a of the solution.

      $K_w = K_a \times K_b$

      $1.0 \times 10^{-14} = K_a \times 1.8 \times 10^{-5}$

      $5.6 \times 10^{-10} = K_a$

      $K_a = \dfrac{[H^+][X^-]}{[HX]}$

      $5.6 \times 10^{-10} = x^2 / 0.750$

      $x = 2.05 \times 10^{-5} = [H^+]$

      pH = 4.69

    - You try: Calculate the pH of a 0.300 M NH_4NO_3 solution.

- **You try:** Identify the following salts as to whether they would make a solution acidic, basic or neutral and why:

      NaCl
      $KC_2H_3O_2$
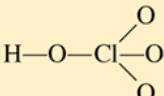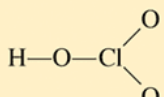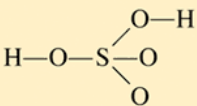 NH_4Cl
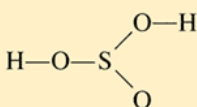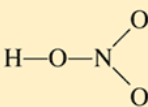 NH_4CN
      KOCl
      $NaNO_2$

The Effect of Structure on Acid-Base Properties

- Any molecule containing hydrogen is potentially an acid. However, many molecules that contain hydrogen exhibit no such acidic properties.
- Molecules containing C—H bonds do not produce acidic solutions because the C—H bond is strong and non-polar and thus no tendency to donate protons.
- Although the H—Cl bond in gaseous hydrogen chloride is stronger than a C—H bond, it is much more polar , and as a result it dissociates when dissolved in water.
- Two factors determine whether a H—X bond will be have as a Brønsted-Lowry base: the strength of the bond and the polarity of the bond.
- Fluorine has the highest electronegativity of the halogens and is the most polar of the H—halogen molecules. Based on this, it would be expected that HF would dissociate completely in water. But, HF is a weak acid instead of a strong acid like HCl, HBr and HI. This is because HF bond has an unusually strong bond when dissolved in water.
- Another important class of acids are the oxyacids(oxoacids). Note from the chart below that the strongest oxyacids in a series have the most oxygen atoms attached to the central atom. This is because oxygen's large electronegativity is able to attract electrons away from the central atom as well as the hydrogen. The net effect is to polarize and weaken the O—H bond.
-

TABLE 14.7
Bond Strengths and Acid Strengths for Hydrogen Halides

H—X Bond	Bond Strength (kJ/mol)	Acid Strength in Water
H—F	565	Weak
H—Cl	427	Strong
H—Br	363	Strong
H—I	295	Strong

TABLE 14.8   Several Series of Oxyacids and Their K_a Values

Oxyacid	Structure	K_a Value
$HClO_4$	H—O—Cl with three O	Large ($\sim 10^7$)
$HClO_3$	H—O—Cl with two O	~ 1
$HClO_2$	H—O—Cl—O	1.2×10^{-2}
$HClO$	H—O—Cl	3.5×10^{-8}
H_2SO_4	H—O—S with O—H and two O	Large
H_2SO_3	H—O—S with O—H and O	1.5×10^{-2}
HNO_3	H—O—N with two O	Large
HNO_2	H—O—N—O	4.0×10^{-4}

- For acids containing the H—O—X grouping, the greater the ability of X to draw electrons toward itself, the greater the acidity. Thus, the higher the electronegativity of X, the stronger the acid. The chart below shows this.

TABLE 14.9 Comparison of Electronegativity of X and K_a Value for a Series of Oxyacids

Acid	X	Electronegativity of X	K_a for Acid
HOCl	Cl	3.0	4×10^{-8}
HOBr	Br	2.8	2×10^{-9}
HOI	I	2.5	2×10^{-11}
$HOCH_3$	CH_3	2.3 (for carbon in CH_3)	$\sim 10^{-15}$

Acid-Base Properties of Oxides
- As observed above, compounds containing the H—O—X grouping act as acids. But, they can also act as bases if the hydroxide ion(-OH) is produced.
- If X has a high electronegativity, the O—X bond will be covalent and strong. When dissolved in water, the O—X bond remains intact. The O—H bond will break and release a proton (H^+). $HOCl \rightleftharpoons H^+ + OCl^-$ The O—Cl bond is covalent because there is small difference between the electronegativity of Cl and O. The O—H is weakened and the hydrogen ion breaks off.
- If X has a low electronegativity, the O—X bond will be ionic and subject to breaking apart in water. $NaOH \rightarrow Na^+ + OH-$ Sodium has a low electronegativity and so the Na—O bond is ionic and polar and it breaks apart in polar water.
- These principles help us to explain the acid-base behavior of oxides.
- Non-metal oxides react with water to form acids. $SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$
- Non-metal oxides are referred to as acidic oxides or acid anhydrides
- Metal oxides react with water to form bases. $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$
- Metal oxides are referred to as basic oxides or base anhydrides

Lewis Acid-Base Model
- A third theory of acids was proposed by Gilbert Lewis(1875-1946). He theory is more general that both Arrhenius and Brønsted-Lowry theories.
- **A Lewis acid is a substance that can accept a pair of electrons to form a covalent bond.**
- **A Lewis base is a substance that can donate a pair of electrons to form a covalent bond.**
- For example:
  $H^+ + OH^- \rightarrow H_2O$
  Lewis   Lewis
   acid   base
- You try: Identify the Lewis Acid and Lewis Base in the following
  $NH_3 + H^+ \rightarrow NH_4^+$

- The reason Lewis' Acid –Base Theory is necessary is because it explains reactions that Brønsted-Lowry and Arrhenius theories could not explain.
- The example every book in the entire world cites is:
  $BF_3 + NH_3 \rightarrow BF_3NH_3$
  I will demonstrate this on the board.
- Generally if you are asked to identify the Lewis acid and Lewis Base, the Lewis acid is usually a cation(+). The Lewis base is usually a neutral molecule.