Unit 6: ACIDS AND BASES

Chapter 16: Acids and Bases

16.1: Brønsted Acids and Bases

Physical and Chemical Properties of Acid and Base

| Acids | Bases | | | |
|---|--|--|--|--|
| Taste Sour (Citric Acids). | Taste Bitter. | | | |
| Burning Sensation (Stomach Acid). | Feels Slippery (Detergent, Degreaser). | | | |
| Corrosive with Metals (reacts to give off $H_{2(g)}$). | Alkaline in Nature (NaOH, Baking Soda). | | | |
| Red litmus remains Red; Blue litmus turns Red. | Red litmus turns Blue; Blue litmus remains Blue. | | | |
| Bromothymol Blue turns Yellow | Bromothymol Blue turns Blue. | | | |
| Phenolphthalein turns Colourless. | Phenolphthalein turns Pink. | | | |
| pH < 7 | pH > 7 | | | |
| pH Scale | _ | | | |
| 0 Acidic | 7 Basic 14 | | | |

Conceptual Definition: - an explanation that attempts to describe why things are the way they are.

<u>Arrhenius Concept</u>: - acids are H⁺ (proton) producers and bases are OH⁻ producers.

| Examples: | $\operatorname{HCl}_{(aq)} \to \operatorname{H}^{+}_{(aq)} + \operatorname{Cl}^{-}_{(aq)}$ | (HCl _(aq) is an Arrhenius Acid.) |
|-----------|--|---|
| | $\operatorname{NaOH}_{(aq)} \rightarrow \operatorname{Na}^{+}_{(aq)} + \operatorname{OH}^{-}_{(aq)}$ | (NaOH (aq) is an Arrhenius Base.) |

Brønsted-Lowry Model: - acids and bases <u>react with water</u> to **dissociate** where **acids are H⁺ (proton) donors** and **bases are H⁺ (proton) acceptors**.

- first proposed by Johannes Brønsted and Thomas Lowry.

<u>Hydronium Ion</u>: - an ion formed when an <u>acid "donated" H⁺ ion combined with a H₂O molecule</u> to form a <u>H₃O⁺ ion (hydronium ion)</u>.

- essentially has the same function as a H^+ ion, but H_3O^+ denotes that we are using the Brønsted-Lowry model.

Examples: HBr $_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Br^-_{(aq)}$ (HBr is a Brønsted-Lowry Acid – donated a proton) (H₂O is a Brønsted-Lowry Base – accepted a proton.)

 $NH_{3(aq)} + H_2O_{(l)} \Rightarrow NH_{4(aq)}^+ + OH_{(aq)}^-$ (H₂O is a Brønsted-Lowry Acid – donated a proton) (NH₃ is a Brønsted-Lowry Base – accepted a proton.)

- **Conjugate Base**: the product formed **after** the Acid donated a H⁺. (Acid \rightarrow Conjugate Base) - behaves like a base when the reaction is looking from reverse.
- **Conjugate Acid**: the product formed **after** the Base accepted a H⁺. (**Base** \rightarrow Conjugate Acid) - behaves like a acid when the reaction is looking from reverse.

Conjugate Acid-Base Pair: - the (acid/conjugate base) or (base/conjugate acid) pairs.



Conjugate Acid-Base Pairs: **B/HB⁺** and H₂O/OH⁻

<u>Acid Dissociation Constant</u> (K_a) : - the equilibrium constant of a Brønsted-Lowry Acid Dissociation.

Base Dissociation Constant (*K_b*): - the equilibrium constant of a Brønsted-Lowry Base Dissociation.

| Brønsted-Lowry Acid Dissociation | Brønsted-Lowry Base Dissociation |
|--|--|
| $\mathbf{HA}_{(aq)} + \mathbf{H}_{2}\mathbf{O}_{(l)} \rightleftharpoons \mathbf{H}_{3}\mathbf{O}^{+}_{(aq)} + \mathbf{A}^{-}_{(aq)}$ | $\mathbf{B}_{(aq)} + \mathbf{H}_2\mathbf{O}_{(l)} \rightleftharpoons \mathbf{HB}^+_{(aq)} + \mathbf{OH}^{(aq)}$ |
| $K_a = \frac{\left[H_3O^+\right]A^-}{\left[HA\right]}$ | $\boldsymbol{K}_{b} = \frac{\left[\boldsymbol{H}\boldsymbol{B}^{+}\boldsymbol{I}\boldsymbol{O}\boldsymbol{H}^{-}\right]}{\left[\boldsymbol{B}\right]}$ |

- **Example 1**: Write the Brønsted-Lowry dissociation reaction of the following. Identify the Brønsted-Lowry acid and base, along with the conjugate acid and base. Determine the conjugate acid-base pairs. State the equilibrium expression of the dissociation reaction.
- a. Acetic acid $(CH_3COOH_{(aq)})$ b. Cyanide Ion $(CN_{(aq)})$ $CH_3COOH_{(aq)} + H_2O_{(l)} \Rightarrow H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$ $CN^{-}_{(aq)} + H_2O_{(l)} \Rightarrow HCN_{(aq)} + OH^{-}_{(aq)}$ (Acid) (Base) (Conjugate (Conjugate (Base) (Acid) (Conjugate (Conjugate Acid) **Base**) Acid) **Conjugate Acid-Base Pairs: Conjugate Acid-Base Pairs:** CH₃COOH/CH₃COO⁻ and H₂O/H₃O⁺ **CN⁻/HCN and H₂O/OH⁻** $K_b = \frac{[\text{HCN}]\text{OH}^-]}{[\text{CN}^-]}$ $K_a = \frac{[H_3O^+]CH_3COO^-]}{[CH_3COOH]}$ **Assignment 16.1** pg. 568 #1 to 8

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Base)

16.2: The Acid-Base Properties of Water

<u>Autoionization of Water</u>: - the process where water dissociates into hydronium and hydroxide ions.

- water's dissociation constant is called <u>ion-product constant</u> ($K_w = 1.0 \times 10^{-14}$)
- when the solution is <u>neutral (pH = 7)</u>, $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7} \text{ mol/L}$



Example 1: At 25°C, $K_w = 1.0 \times 10^{-14}$.

a. Using the ICE box, show that $[H_3O^+] = [OH^-] = 1.0 \times 10^{-7}$ mol/L for a neutral solution. b. At 100°C, $K_w = 8.19 \times 10^{-13}$. What is the $[H_3O^+]$ and $[OH^-]$ for a neutral solution at 100°C?

a.

| | $H_2O_{(l)} \rightleftharpoons H_3O^+ [OH^-]$ | | | | | |
|-------------|---|--|----|------------|--|--|
| | | | | | | |
| Initial | | | 0 | 0 | | |
| Change | | | +x | + <i>x</i> | | |
| Equilibrium | x x | | | | | |

$$K_{w} = [H_{3}O^{+}][OH^{-}]$$

1.0 × 10⁻¹⁴ = (x)(x)
$$x^{2} = \sqrt{1.0 \times 10^{-14}}$$

$$x = 1.0 \times 10^{-7}$$

$$x = [H_{3}O^{+}] = [OH^{-}] = 1.0 \times 10^{-7} \text{ M}$$

b. At 100°C, using
$$K_w = 8.19 \times 10^{-13}$$

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

8.19 × 10⁻¹³ = (x)(x)
$$x^2 = \sqrt{8.19 \times 10^{-13}}$$

 $x = 2.86 \times 10^{-7}$

$$x = [H_3O^+] = [OH^-] = 2.86 \times 10^{-7} M$$

Example 2: Determine the $[H_3O^+]$ and/or $[OH^-]$ concentrations of the following solutions at 25°C.

a.
$$[OH^{-}] = 1.0 \times 10^{-4} \text{ mol/L}$$

 $K_w = [H_3O^{+}][OH^{-}]$
 $[H_3O^{+}] = \frac{K_w}{[OH^{-}]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-4}}$
 $[H_3O^{+}] = 1.0 \times 10^{-10} \text{ mol/L}$

b.
$$[H_3O^+] = 5.0 \times 10^{-5} \text{ M}$$

 $K_w = [H_3O^+][OH^-]$
 $[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{5.0 \times 10^{-5}}$
 $[OH^-] = 2.0 \times 10^{-10} \text{ M}$

16.3: pH - A Measure of Acidity

<u>**pH Scale**</u>: - a logarithmic scale to <u>measure the acidity (relative $[H_3O^+]$)</u> of a solution.

- the <u>lower the pH, the more acidic</u> (less basic) is the solution (more $[H_3O^+]$ and less $[OH^-]$).
- the higher the pH, the more basic (less acidic) is the solution (less $[H_3O^+]$ and more $[OH^-]$).
- <u>acidity is NOT the same as the acid strength</u>. Just because a solution has a low pH, it does not mean that it is a strong acid. (Highly Acidic ≠ Strong Acid)
- it is normally reported between 0 to 14 (with 7 as neutral), but it can be above 14 (very basic) or below 0 (very acidic).
- an <u>increase of 1 on a pH scale</u> means a <u>decrease of $[H_3O^+]$ by a factor of 10</u>; an increase of 2 on a pH scale means a decrease of $[H_3O^+]$ by a factor of 100.

pH Scale
$$[H_{3}O^{+}] > 1.0 \times 10^{-7} \text{ mol/L} \qquad [H_{3}O^{+}] < 1.0 \times 10^{-7} \text{ mol/L} \\ [OH^{-}] < 1.0 \times 10^{-7} \text{ mol/L} \qquad [OH^{-}] > 1.0 \times 10^{-7} \text{ mol/L} \\ 0 \qquad \text{Acidic} \qquad 7 \qquad \text{Basic} \qquad 14 \\ \text{Neutral} \end{cases}$$

Example: pH of Some Common Substances

| Substance | pН | Substance | pН | Substance | pН |
|--------------|------|------------|------|--|-------|
| 1 M of HCl | 0.00 | Milk | 6.30 | 1 M of Baking Soda (NaHCO ₃) | 9.68 |
| Stomach Acid | 2.00 | Rain Water | 6.70 | Ammonia as Household Cleaner | 12.00 |
| Lemon Juice | 2.50 | Pure Water | 7.00 | 1 M of NaOH | 14.00 |
| Vinegar | 3.00 | Blood | 7.50 | | |

<u>pOH Scale</u>: - a logarithmic scale to **<u>measure the basicity (relative [OH-])</u>** of a solution.

- the lower the pOH, the more basic (less acidic) is the solution (more [OH⁻] and less [H₃O⁺]).
- the higher the pOH, the less basic (more acidic) is the solution (less $[OH^-]$ and more $[H_3O^+]$).
- basicity is NOT the same as the base strength. Just because a solution has a low pOH, it does not mean that it is a strong base. (Highly Basic ≠ Strong Base)
- it is normally reported between 0 to 14 (with 7 as neutral), but it can be above 14 (very acidic) or below 0 (very basic).
- an <u>increase of 1 on a pOH scale</u> means a <u>decrease of [OH⁻] by a factor of 10</u>; an increase of 2 on a pOH scale means a decrease of [OH⁻] by a factor of 100.

pOH Scale
$$[OH^-] > 1.0 \times 10^{-7} \text{ mol/L}$$
 $[OH^-] < 1.0 \times 10^{-7} \text{ mol/L}$
 $[H_3O^+] < 1.0 \times 10^{-7} \text{ mol/L}$ $[H_3O^+] > 1.0 \times 10^{-7} \text{ mol/L}$
0 Basic N_{eutral} Acidic 14
 $pH \text{ and } pOH \text{ Scales}$
 $pH = -\log [H_3O^+]$ $pOH = -\log [OH^-]$
 $pH + pOH = 14.00$

Example 1: Calculate the pH and the pOH for the following solutions.

a. 0.0100 mol/L of HI (*aq*) (completely dissociates) b. 5.00×10^{-6} M of HClO_{4 (*aq*)} (completely dissociates)



Example 2: Calculate the $[H_3O^+]$ and the $[OH^-]$ for the following solutions.



16.4: Strength of Acids and Bases

Strong Acids: - acids that dissociate completely (100%) in water.

- when the acid dissociation constant (K_a) is much greater than 1. $(K_a >> 1)$
- the equilibrium position strongly favours the products.
- at equilibrium, the original acid concentration, $[HA]_{eq} \approx 0$; $[H_3O^+]_{eq} = [A^-]_{eq} = [HA]_0$.
- the conjugate base, A⁻, of a strong acid, HA is itself a weak base (cannot easily accept protons to do the reverse reaction).
- Note: Strong Acids DO NOT MEAN that they are VERY CORROSIVE. It is the $[H_3O^+]$ that defines acidity.



Examples: Strong Acids: HClO_{4 (aq)}, HI (aq), HBr (aq), HCl (aq), H₂SO_{4 (aq)} and HNO_{3 (aq)}

Example 2: Write the dissociation reaction of 0.250 M of HBr_(*aa*) and determine its $[H_3O^+]$.

(Strong Acid means $[HBr]_0 = [H_3O^+]$) $HBr_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Br_{(aq)}$ $[H_3O^+] = 0.250 M$ $[HBr]_0 = 0.250 M$

Weak Acids: - acids that dissociate LESS than 100% in water.

 $(K_a < 1)$

-the equilibrium position strongly favours the reactants.

-when the acid dissociation constant (K_a) is less than 1.

- -at equilibrium, the hydronium concentration is much less than the original acid concentration, $[HA]_{eq} > [H_3O^+]_{eq}$ or $[HA]_0 \approx [HA]_{eq}$.
- -the conjugate base, A⁻, of a weak acid is itself a stronger weak base (can easily accept protons to do the reverse reaction).
- Note: Weak Acids DO NOT MEAN that they are NOT CORROSIVE. It is the $[H_3O^+]$ that defines acidity. At a high enough concentration, a weak acid can be corrosive.

| | $HA_{(aq)}$ | + $H_2O_{(l)}$ | # | $\mathbf{H}_{3}\mathbf{O}^{+}_{(aq)}$ | + $A^{-}(aq)$ | |
|-------------|--------------|-------------------------------|---|---------------------------------------|------------------------|------|
| | (Weak Acid) | (Base) | | (Conjugate Acid) | (Conjugate Base-Strong | ger) |
| | [] | HA] | | [H ₃ O ⁺] | [A ⁻] | |
| Initial | x | | | 0 | 0 | |
| Change | — <i>y</i> | (where <i>y</i> << <i>x</i>) | | + <i>y</i> | + <i>y</i> | |
| Equilibrium | (<i>x</i> – | $y) \approx x$ | | у | y | |

Examples: Some Weak Acids: HOOCCOOH_(aq), H₂SO_{3 (aq)}, HSO₄⁻_(aq), H₃PO_{4 (aq)}, HNO_{2 (aq)}, H₃C₆H₅O_{7 (aq)}, HF (*aq*), HCOOH (*aq*), C₆H₈O₆ (*aq*), C₆H₅COOH (*aq*), CH₃COOH (*aq*), H₂CO₃ (*aq*), $H_2S_{(aq)}$, $HOCl_{(aq)}$, $HCN_{(aq)}$, $NH_4^+_{(aq)}$, and $H_3BO_{3(aq)}$

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Increasing Base Strength

| A _a and Kelative Strength of Some Common Acids and Bases at 25°C | | | | |
|---|--------------------------------------|--------------------------------|-----------------------------------|--|
| Acid Name | Acid Formula | Conjugate Base Formula | Ka | |
| perchloric acid | HClO _{4 (aq)} | $\text{ClO}_4^-(aq)$ | Very Large | |
| hydroiodic acid | $\mathrm{HI}_{(aq)}$ | $I^{-}_{(aq)}$ | Very Large | |
| hydrobromic acid | $\mathrm{HBr}_{(aq)}$ | $\mathrm{Br}^{-}_{(aq)}$ | Very Large | |
| hydrochloric acid | $HCl_{(aq)}$ | $\operatorname{Cl}^{-}_{(aq)}$ | Very Large | |
| sulfuric acid | $H_2SO_{4(aq)}$ | $HSO_4^-(aq)$ | Very Large | |
| nitric acid | $HNO_{3(aq)}$ | $NO_3(aq)$ | Very Large | |
| hydronium ion | $H_3O^+_{(aq)}$ | $H_2O_{(l)}$ | 1 | |
| oxalic acid | HOOCCOOH (aq) | $HOOCCOO^{-}_{(aq)}$ | 6.5×10^{-2} | |
| sulfurous acid | $H_2SO_{3(aq)}$ | HSO_3^- | 1.5×10^{-2} | |
| hydrogen sulfate ion | $HSO_4^{-}(aq)$ | $\mathrm{SO_4}^{2-}$ | 1.2×10^{-2} | |
| chlorous acid | $HClO_{2(aq)}$ | $\text{ClO}_2^{-}_{(aq)}$ | 1.2×10^{-2} | |
| phosphoric acid | $H_3PO_{4(aq)}$ | $H_2PO_4^{-}(aq)$ | 7.5×10^{-3} | |
| arsenic acid | $H_3AsO_{4(aq)}$ | $H_2AsO_4^{-}(aq)$ | 5×10^{-3} | |
| monochloracetic acid | $HC_2H_2ClO_2$ | $C_2H_2ClO_2^{-}(aq)$ | 1.35×10^{-3} | |
| citric acid | $H_3C_6H_5O_{7(aq)}$ | $H_2C_6H_5O_7^{-(aq)}$ | 8.4×10^{-4} | |
| hydrofluoric acid | $\mathrm{HF}_{(aq)}$ | $F^{-}_{(aa)}$ | 7.2×10^{-4} | |
| nitrous acid | $HNO_{2(aq)}$ | $NO_2^{(aq)}$ | 4.0×10^{-4} | |
| methanoic (formic) acid | HCOOH _(aq) | HCOO ⁻ (aa) | 1.8×10^{-4} | |
| lactic acid | $HC_{3}H_{5}O_{3(aq)}$ | $C_{3}H_{5}O_{3}^{-}(aa)$ | 1.38×10^{-4} | |
| ascorbic acid (vitamin C) | $H_2C_6H_6O_{6(aq)}$ | $HC_6H_6O_6^{-}(aa)$ | 7.9×10^{-5} | |
| benzoic acid | $C_6H_5COOH_{(aq)}$ | $C_6H_5COO^{-}(aa)$ | 6.4×10^{-5} | |
| hydrogen oxalate ion | HOOCCOO ⁻ _(aa) | $OOCCOO^{2-}_{(aa)}$ | 6.1×10^{-5} | |
| ethanoic (acetic) acid | $CH_3COOH_{(aq)}$ | $CH_3COO^{-}_{(aq)}$ | 1.8×10^{-5} | |
| dihydrogen citrate ion | $H_2C_6H_5O_7(aa)$ | $HC_{6}H_{5}O_{7}^{2-}(aa)$ | 1.8×10^{-5} | |
| hydrated aluminum (III) ion | $[Al(H_2O)_6]^{3+1}$ | $[AlOH(H_2O)_5]^{2+}$ | 1.4×10^{-5} | |
| propanoic acid | $C_2H_5COOH_{(aa)}$ | $C_{2}H_{5}COO^{-}(aa)$ | 1.3×10^{-5} | |
| hydrogen citrate ion | $HC_{6}H_{5}O_{7}^{2-}(aa)$ | $C_{6}H_{5}O_{7}^{3-}(aa)$ | 4.0×10^{-6} | |
| carbonic acid | $H_2CO_{3(aa)}$ | $HCO_3^{-}(aq)$ | 4.3×10^{-7} | |
| hydrosulfuric acid | $H_2S_{(aq)}$ | $HS^{-}_{(aa)}$ | 1.0×10^{-7} | |
| hydrogen sulfite ion | $HSO_3^{-}(aa)$ | $SO_3^{(2-)}$ | 1.0×10^{-7} | |
| dihydrogen arsenate ion | $H_2AsO_4(aa)$ | $HAsO_4^{2-}(aa)$ | 8×10^{-8} | |
| dihydrogen phosphate ion | $H_2PO_4^{-}(aq)$ | $HPO_4^{2-}(aq)$ | 6.2×10^{-8} | |
| hypochlorous acid | $HOCl_{(aa)}$ | $OCl^{-}(aq)$ | 3.5×10^{-8} | |
| hypobromous acid | $HOBr_{(aq)}$ | OBr(aq) | 2×10^{-9} | |
| hydrocyanic acid | $HCN_{(aa)}$ | $CN^{-}_{(aq)}$ | 6.2×10^{-10} | |
| hydrogen arsenate ion | $HAsO_4^{2-}(aa)$ | AsO_4^{3-} | 6×10^{-10} | |
| boric acid | $H_3BO_{3(aa)}$ | $H_2BO_3^{-}(aq)$ | 5.8×10^{-10} | |
| ammonium ion | $NH_4^+(aa)$ | $NH_{3}(aq)$ | 5.6×10^{-10} | |
| Phenol | $C_6H_5OH_{(aa)}$ | $C_6H_5O^{-}(aq)$ | 1.6×10^{-10} | |
| hydrogen carbonate ion | $HCO_3^{-}(aq)$ | $CO_3^{2-}(aq)$ | 5.6×10^{-11} | |
| hypoiodous acid | HOI _(aa) | $OI_{(ac)}$ | 2×10^{-11} | |
| hydrogen ascorbate ion | $HC_6H_6O_6^{-}(ac)$ | $C_{6}H_{6}O_{6}^{2-}(aa)$ | 1.6×10^{-12} | |
| hydrogen phosphate ion | HPO_4^{2-} | $PO_{4}^{3-}(aa)$ | 4.8×10^{-13} | |
| water (55.49 mol/L) | $H_2O_{(l)}$ | $OH^{-}(aq)$ | $1.0 \times 10^{-14} = K_{\odot}$ | |
| hydrogen sulfide ion | $HS^{-}(a)$ | S^{2-} | $\sim 10^{-19}$ | |

K_a and Relative Strength of Some Common Acids and Bases at 25°C

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Check out Strong and Weak Acids Animations at (http://www.sgc.peachnet.edu/users/larnold/WWW/courses/1212/rev1212.html)

Relative Strength of Acids and Conjugate Bases:

- 1. The stronger the acid (the bigger the value of K_a), the weaker its conjugate base.
- 2. The weaker the acid (the smaller the value of K_a), the stronger its conjugate base.

Example 2: Order the following acids from the strongest to the weakest. $HNO_{2(aq)}, H_2SO_{3(aq)}, HClO_{4(aq)}, HF_{(aq)}$

> According to the Acid and Bases Relative Strength Table on the previous page: HClO_{4 (aq)} >> H₂SO_{3 (aq)} > HF _(aq) > HNO_{2 (aq)} (K_a : very large >> 1.5 × 10⁻² > 7.2 × 10⁻⁴ > 4.0 × 10⁻⁴)

Example 3: Order the following conjugate base from the strongest to the weakest. $CN^{-}(aa)$, $SO_4^{2-}(aa)$, $Cl^{-}(aa)$, $CH_3COO^{-}(aa)$

> According to the Acids and Bases Relative Strength Table on the previous page: $\frac{\text{CN}_{(aq)} > \text{CH}_{3}\text{COO}_{(aq)} > \text{SO}_{4}^{2-}_{(aq)} >> \text{CI}_{(aq)}}{(K_{a}: 6.2 \times 10^{-10} < 1.8 \times 10^{-5} < 1.2 \times 10^{-2} << \text{Very Large})}$ $HCN_{(aq)} < CH_3COOH_{(aq)} < HSO_{4(aq)} << HCl_{(aq)}$

Monoprotic Acids: - acids that can donate a maximum of one proton.

Example 3: Write the dissociation reaction for the following monoprotic acids.

a. $HI_{(aa)}$

 $\operatorname{HI}_{(aq)} + \operatorname{H}_2\operatorname{O}_{(l)} \to \operatorname{H}_3\operatorname{O}^+_{(aq)} + \Gamma_{(aq)}$ Direct Arrow because HI (aq) is a Strong Acid (*K_a* is very large)

b. HCOOH_(aq)

 $\text{HCOOH}_{(aq)} + \text{H}_2\text{O}_{(l)} \Rightarrow \text{H}_3\text{O}^+_{(aq)} + \text{HCOO}^-_{(aq)}$ Double Arrow because HCOOH (aq) is a Weak Acid ($K_a = 1.8 \times 10^{-4} \ll 1$)

Diprotic Acids: - acids that can donate a maximum of two protons in stepwise dissociation.

$$H_{2}A_{(aq)} + H_{2}O_{(l)} \approx H_{3}O^{+}_{(aq)} + HA^{-}_{(aq)} K_{a1} = \frac{[H_{3}O^{+}]HA^{-}]}{[H_{2}A]}$$
(Original Diprotic Acid) (Base) (Conjugate Acid) (Conjugate Base)
$$HA^{-}_{(aq)} + H_{2}O_{(l)} \approx H_{3}O^{+}_{(aq)} + A^{2-}_{(aq)} K_{a2} = \frac{[H_{3}O^{+}]A^{2-}]}{[HA^{-}]}$$
(Conjugate Base of Original Diprotic Acid)

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Example 4: Write the stepwise dissociation reaction for the following diprotic acids.

a. $H_2SO_{4(aq)}$

b. HOOCCOOH (aq)

 $\mathrm{H}_{2}\mathrm{SO}_{4\,(aq)} + \mathrm{H}_{2}\mathrm{O}_{(l)} \rightarrow \mathrm{H}_{3}\mathrm{O}^{+}_{(aq)} + \mathrm{H}_{3}\mathrm{O}^{-}_{(aq)}$

Direct Arrow because $H_2SO_{4(aq)}$ is a Strong Acid (K_{a1} is very large)

 $HSO_4^{-}(aq) + H_2O_{(l)} \Rightarrow H_3O^{+}(aq) + SO_4^{2-}(aq)$

Double Arrow because $HSO_4^-(aq)$ is a Weak Acid ($K_{a2} = 1.2 \times 10^{-2} \ll 1$) HOOCCOOH $_{(aq)} + H_2O_{(l)} \approx H_3O^+_{(aq)} + HOOCCOO^-_{(aq)}$ HOOCCOO⁻ $_{(aq)} + H_2O_{(l)} \approx H_3O^+_{(aq)} + OOCCOO^{2-}_{(aq)}$ Double Arrow because both HOOCCOOH $_{(aq)}$ and HOOCCOO⁻ are Weak Acids (K_{a1} and $K_{a2} \ll 1$)

<u>Amphoteric Substances</u>: - chemical <u>species that can be an acid or a base</u>. - all <u>intermediate species of a diprotic acid</u> is an amphoteric substance.

Examples: Some Amphoteric Substances: HOOCCOO⁻_(aq), HSO₄⁻_(aq), HSO₃⁻_(aq), HCO₃⁻_(aq), HS⁻_(aq), HC₆H₆O₆⁻_(aq), and H₂O_(l)

Calculating the pH of Strong Acid Solutions

Major Species: - the predominant species of an acid or a base after dissociation.

- in acid and base dissociation, because they are aqueous, water $(H_2O_{(l)})$ is always listed as a major species.

<u>Major Species of a Strong Acid</u>: - as strong acid dissociates completely $(K_a > 1)$ in water, <u>the major</u> <u>species of all strong acids are H₃O⁺ and their conjugate bases</u>.

| $HA_{(aq)}$ | + | $H_2O_{(l)}$ | \longrightarrow H ₃ O ⁺ _(aq) | + $A^{-}_{(aq)}$ | |
|---------------|---|--------------|---|--------------------|-----|
| (Strong Acid) | | (Base) | (Conjugate Acid) | (Conjugate Base-We | ak) |

Example 5: List the major species $H_2SO_{4(aq)}$, and calculate its pH if it has a concentration of 1.00×10^{-5} M.

 $H_2SO_4_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + HSO_4^-_{(aq)}$ Since H_2SO_4 is a strong acid, the major species are: $H_3O^+_{(aq)}$, $HSO_4^-_{(aq)}$ and $H_2O_{(l)}$ (Even if H_2SO_4 is a **diprotic acid**, it <u>dissociates one proton at a time</u>. The conjugate base, HSO_4^- , is a weak acid. Weak acids dissociate differently than strong acids – next section.) $[H_3O^+] = [H_2SO_4]_0 = 1.00 \times 10^{-5} \text{ M}$ $pH = -\log [H_3O^+]$ $pH = -\log (1.00 \times 10^{-5})$ pH = 5.00

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Example 6: Determine the $[H_3O^+]$ and/or $[OH^-]$ concentrations of the following solutions at 25°C.

a. [HCl] = 0.350 mol/L HCl _(aq) + H₂O _(l) \rightarrow H₃O⁺ _(aq) + Cl⁻_(aq) (Strong Acid: [HCl]₀ = [H₃O⁺] = 0.350 M) $K_w = [H_3O^-][OH^-]$ [OH⁻] = $\frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{0.350}$ [OH⁻] = 2.86 × 10⁻¹⁴ mol/L b. [NaOH] = 0.0750 M NaOH _(aq) \rightarrow Na⁺ _(aq) + OH⁻_(aq) (Ionic Strong Base: [NaOH]₀ = [OH⁻] = 0.0750 M) $K_w = [H_3O^+][OH^-]$ [H₃O⁺] = $\frac{1.0 \times 10^{-14}}{0.0750}$ [H₃O⁺] = 1.33 × 10⁻¹³ mol/L

Oxoacids: - acids where the donating proton is attached to an oxygen atom.

- most acids are oxoacids because of the strong electronegativity of the oxygen atom, the hydrogen atom is more readily to leave as H⁺ ion.

Example: Sulfuric Acid (H₂SO_{4 (aq)}), successively donate protons to finally reach SO₄²⁻(aq)



Organic Acids: - acids of organic compounds, commonly known as carboxylic acids.

- alcohols can also be considered as organic acids, but they are really weak. This is because carboxylic acids have double-bonded oxygen for resonance to occur, whereas alcohols only contain single-bonded oxygen.

Example: Ethanoic (Acetic) Acid is compared to Phenol



16.5: Weak Acids and Acid Ionization Constants

<u>Major Species of a Weak Acid</u>: - since weak acid do not dissociate completely ($K_a < 1$) in water, <u>the</u> <u>major species of all weak acids are their original form and water</u>.

Procedure to calculate pH of Weak Acid Solutions:

- 1. List all the major species from all weak acids, <u>including water</u>.
- 2. Determine which species has the highest K_{a} . This is the <u>Strongest Acid (SA)</u> of the list.
- 3. Write the Brønsted-Lowry dissociation of this Strongest Acid.
- 4. Set up the ICE Box and the equilibrium expression.
- 5. If the <u>original weak acid concentration, $[HA]_0$, is much larger than K_a </u>, we can <u>approximate by</u> <u>assuming $[HA]_{eq} = ([HA]_0 x) \approx [HA]_0$ </u>. Thereby, simplifying the calculation. (A general rule of thumb: if $[HA]_0 \ge 1000 \times K_a$, we can use the approximation.)
- 6. Find the concentration of H_3O^+ .
- 7. <u>Verify</u> any <u>approximation</u> made by using the <u>5% rule</u>.

$$\left(\frac{\left[\mathrm{H}_{3}\mathrm{O}^{+}\right]}{\left[\mathrm{H}\mathrm{A}\right]_{0}}\times100\%\leq5\%\right)$$

Example 1: Determine the $[H_3O^+]$, and pH of 0.200 mol/L of HF $_{(aq)}$ ($K_a = 7.2 \times 10^{-4}$).

Major Species: $HF_{(aq)}$, $H_2O_{(l)}$ Strongest Acid: $HF(K_a = 7.2 \times 10^{-4})$ (K_a for H_2O is 1.0×10^{-14}) HF is a weak acid and undergoes Brønsted-Lowry Dissociation.



<u>**Percent Dissociation**</u>: - the amount of $[H_3O^+]$ dissociated from the original $[HA]_0$ expressed in percentage.

- strong acids will have % dissociation = 100%.
- weak acids will have % Dissociation < 100%



Example 2: Determine the $[H_3O^+]$ and pH of an acid mixture of 0.500 mol/L HOBr $_{(aq)}$ ($K_a = 2 \times 10^{-9}$) of 0.200 mol/L of CH₃COOH $_{(aq)}$ ($K_a = 1.8 \times 10^{-5}$). Calculate the % dissociation of this acid mixture.

Major Species: HOBr (aq), CH₃COOH (aq), H₂O (l)Strongest Acid: CH₃COOH ($K_a = 1.8 \times 10^{-5}$)(K_a for HOBr and H₂O are 2×10^{-9} and 1.0×10^{-14})CH₃COOH is a weak acid and undergoes Brønsted-Lowry Dissociation.CAN use Approximation:



Example 3: A 0.0500 mol/L of an unknown acid, HA, has a percent dissociation of 0.38%. What is the acid dissociation constant of this acid?

Major Species: $HA_{(aq)}$, $H_2O_{(l)}$ Strongest Acid: $HA(K_a = ?)$ (K_a for H_2O is 1.0×10^{-14} and has a 0.000 01 % dissociation) HA is a weak acid and undergoes Brønsted-Lowry Dissociation.

| $HA_{(aq)} + H_2O_{(l)} \Rightarrow H_3O^+_{(aq)} + A^{(aq)}$ | | | | | |
|--|-----------------------|--|------------------------|------------------------|--|
| | [HA] | | $[H_3O^+]$ | [A ⁻] | |
| Initial | 0.0500 M | | 0 | 0 | |
| Change | -1.9×10^{-4} | | $+1.9 \times 10^{-4}$ | 1.9×10^{-4} | |
| Equilibrium | 0.04981 M | | $1.9 \times 10^{-4} M$ | $1.9 \times 10^{-4} M$ | |
| $K_{a} = \frac{\left[\mathrm{H}_{3}\mathrm{O}^{+}\right]\!\left[\mathrm{A}^{-}\right]}{\left[\mathrm{H}\mathrm{A}\right]} = \frac{\left(1.9 \times 10^{-4}\right)\!\left(1.9 \times 10^{-4}\right)}{\left(0.04981\right)}$ | | | | | |

Attion. % Dissociation = $\frac{[H_3O^+]}{[HA]_0} \times 100\%$ $[H_3O^+] = (\%Dissociation)[HA]_0 / 100\%$ $[H_3O^+] = (0.38\%)(0.0500 \text{ M}) / 100\%$ $[H_3O^+] = 1.9 \times 10^{-4} \text{ M} = [A^-]$ $K_a = 7.2 \times 10^{-7}$

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Polyprotic Acids: - acids that can donate more than one protons.

- this includes all diprotic and <u>triprotic acids</u> (acids that can <u>donate three protons</u>).
- **polyprotic acids dissociate one proton at a time**. Each successive proton donation has its own K_a , which gets smaller until the last proton is donated. ($K_{a1} > K_{a2} > K_{a3} > ...$).
- the intermediates (conjugate bases of each dissociation except the last one) are themselves acids. Thus, <u>diprotic acid</u> can generate <u>one amphoteric species</u>, and <u>triprotic acid</u> can generate two amphoteric species.
- except for sulfuric acid (because K_{a1} is very large and K_{a2} is small), all polyprotic acids' [H₃O⁺] are calculated from their K_{a1} because successive proton donation from smaller subsequent K_a do not amount to any significant increase in the [H₃O⁺].

Examples: Some Polyprotic Acids:

- a. Diprotic Acids: H₂SO_{4 (*aq*)}, HOOCCOOH (*aq*), H₂SO_{3 (*aq*)}, H₂C₆H₆O_{6 (*aq*)}, H₂CO_{3 (*aq*)}, H₂S (*aq*) Diprotic Amphoteric Intermediates: HSO₄⁻(*aq*), HOOCCOO⁻(*aq*), HSO₃⁻(*aq*), HC₆H₆O₆⁻(*aq*), HCO₃⁻(*aq*), HS⁻(*aq*)
- b. Triprotic Acids: H₃PO_{4 (aq)}, H₃AsO_{4 (aq)}, H₃C₆H₅O_{7 (aq)}, H₃BO_{3 (aq)}

Triprotic Amphoteric Intermediates: $H_2PO_4^{-}(aq)$, $HPO_4^{2-}(aq)$, $H_2AsO_4^{-}(aq)$, $HAsO_4^{2-}(aq)$, $H_2C_6H_5O_7^{-}(aq)$, $HC_6H_5O_7^{2-}(aq)$, $H_2BO_3^{-}(aq)$, $HBO_3^{2-}(aq)$

Example 1: Determine the pH of 0.0500 M of sulfuric acid (H₂SO_{4 (*aq*)}) and the concentrations of HSO₄⁻(*aq*), and SO₄²⁻(*aq*). The acid dissociation constant is $K_{a2} = 1.2 \times 10^{-2}$.

$$H_2SO_4_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + HSO_4^-_{(aq)}$$

Since <u>H₂SO₄ is a strong acid</u>, the major species are: H₃O⁺_(aq), HSO₄⁻_(aq) and H₂O_(l).

 $[H_3O^+] = [H_2SO_4]_0 = 0.0500 \text{ M}$

pH = $-\log [H_3O^+]$ pH = $-\log (0.0500)$ pH = 1.30 (after K_{a1})

Next, we have to calculate $[HSO_4^{-}]$, $[SO_4^{2-}]$ and the final pH after the last proton donation.

Major Species: $HSO_4^-(aq)$, $H_2O_{(l)}$ Strongest Acid: $HSO_4^-(aq)$ ($K_{a2} = 1.2 \times 10^{-2}$)

HSO₄⁻ is a weak acid (Brønsted-Lowry Dissociation).

$$HSO_{4^{-}(aq)} + H_{2}O_{(l)} \approx H_{3}O^{+}(aq) + SO_{4^{-}(aq)}$$
CANNOT use Approximation:

$$\frac{|HSO_{4^{-}|} |H_{3}O^{+}| |SO_{4^{-}|} |H_{3}O^{+}| |SO_{4^{-}|} |KO_{4^{-}|} |HSO_{4^{-}|} |HSO_{4$$

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From the last two examples, we can see that sulfuric acid (H₂SO_{4 (aa)}) requires the calculation of $[H_3O^+]$ in both steps of the dissociation. Other polyprotic acids, such as $H_3C_6H_5O_7_{(aq)}$ only require the first dissociation step to calculate the $[H_3O^+]$.

<u>Assignment</u> 16.5 pg. 569–570 #37 to 52; pg. 571 #93

16.6 & 16.7: Weak Bases and Base Ionization Constants & The Relationship Between the Ionization and their Conjugate Bases

Strong Bases: - bases that dissociate completely (100%) in water.

- all alkali bases (Group IA cations with OH⁻) and some alkaline bases (Group IIA cations with OH⁻) are considered as strong bases because they are ionic compound that dissociates completely.

Examples: Strong Ionic Bases:

a. Alkali Bases: LiOH (aq), NaOH (aq), KOH (aq), RbOH (aq), and CsOH (aq) (gives off 1 mole of OH⁻ when 1 mole of alkali base is dissolved)

 $NaOH_{(aq)} \rightarrow Na^{+}_{(aq)} + OH^{-}_{(aq)}$

 $\operatorname{KOH}_{(aq)} \to \operatorname{K}^{+}_{(aq)} + \operatorname{OH}^{-}_{(aq)}$

b. Alkaline Bases: $Ca(OH)_{2(aq)}$, $Ba(OH)_{2(aq)}$, $Sr(OH)_{2(aq)}$ (gives off 2 moles of OH⁻ when 1 mole of alkaline base is dissolved)

 $Ba(OH)_{2(aq)} \rightarrow Ba^{2+}_{(aq)} + 2 OH^{-}_{(aq)} \qquad Sr(OH)_{2(aq)} \rightarrow Sr^{2+}_{(aq)} + 2 OH^{-}_{(aq)}$

Major Species of a Strong Base: - as alkali- and alkaline bases dissociate completely in water, the major species of all strong bases are OH⁻ and water.

> - special care must be taken with <u>alkaline bases</u> as they <u>generate 2</u> moles of OH⁻ per 1 mole of solid dissolved.

| $MOH_{(aq)}$ | \longrightarrow M ⁺ (aq) | + | $OH^{-}_{(aq)}$ |
|---------------|---------------------------------------|------------|----------------------------|
| (Strong Base) | (Spectator Metal Ca | tion) (Maj | or Species of Strong Base) |

Example 1: List the major species NaOH_(*aq*), and calculate its pH, pOH, $[H_3O^+]$ and $[OH^-]$ if it has a concentration of 1.00×10^{-4} M.



Example 2: List the major species $Sr(OH)_{2 (aq)}$, and calculate its pH, pOH, $[H_3O^+]$ and $[OH^-]$ if it has a concentration of 1.00×10^{-4} M.



Weak Bases: - bases that dissociate LESS than 100% in water.

- when the <u>base dissociation constant (K_b) is less than 1.</u> $(K_b < 1)$
- the equilibrium position strongly <u>favours the reactants</u>.
- at equilibrium, the hydroxide concentration is much less than the original base concentration, [OH]_{eq} < [B]_{eq} or [B]₀ ≈ [B]_{eq}.
- the <u>conjugate acid</u>, <u>HA</u>, of a weak base <u>is itself a stronger weak acid</u> (can easily donate protons to do the reverse reaction).

| | $\begin{array}{c} \mathbf{B}_{(aq)} + \mathbf{H}_2 \mathbf{O}_{(l)} \\ \text{(Weak Base)} & \text{(Acid)} \end{array}$ | = OH ⁻ _(aq) (Conjugate Base) | + HB ⁺ _(aq) (Conjugate Acid-Stronger) |
|-------------|--|---|--|
| | [B] | [OH ⁻] | [HB ⁺] |
| Initial | <i>x</i> | 0 | 0 |
| Change | $-y$ (where $y \ll x$) | + <i>y</i> | +y |
| Equilibrium | $(x-y) \approx x$ | у | у |

 $\boldsymbol{K}_{a} = \frac{\left[\boldsymbol{\mathrm{H}}_{3}\boldsymbol{\mathrm{O}}^{+}\right]\boldsymbol{\mathrm{B}}}{\left[\boldsymbol{\mathrm{H}}\boldsymbol{\mathrm{B}}^{+}\right]}$

Examples: Some Weak Bases: HOOCCOO⁻_(aq), HSO₃⁻_(aq), HSO₄⁻_(aq), H₂PO₄⁻_(aq), NO₂⁻_(aq), HCO₃⁻_(aq), H₂C₆H₅O₇⁻_(aq), F⁻_(aq), HCOO⁻_(aq), C₆H₇O₆⁻_(aq), C₆H₅COO⁻_(aq), CO₃²⁻_(aq), CH₃COO⁻_(aq), HS⁻_(aq), OCl⁻_(aq), CN⁻_(aq), NH₃ (_{aq)}, and NO₃⁻_(aq)

Base Dissociation Constant (K_b) : - the equilibrium constant of a dissociation of a weak base in water. - K_b of a weak base can be calculated from K_a of its conjugate acid and K_w .

$$\mathbf{B}_{(aq)} + \mathbf{H}_2 \mathbf{O}_{(l)} \rightleftharpoons \mathbf{OH}_{(aq)}^- + \mathbf{HB}_{(aq)}^+ \mathbf{K}_b = \frac{\mathbf{OH}_{(aq)}^- \mathbf{HB}_{(aq)}^+}{\mathbf{B}_{(aq)}^-}$$

(Weak Base) (Acid) (Conjugate Base) (Conjugate Acid)

$$\mathbf{HB}^{+}_{(aq)} + \mathbf{H}_{2}\mathbf{O}_{(l)} \rightleftharpoons \mathbf{H}_{3}\mathbf{O}^{+}_{(aq)} + \mathbf{B}_{(aq)}$$

(Weak Acid) (Base) (Conjugate Acid) (Conjugate Base)

 $K_a \times K_b = \frac{\left[\text{H}_3\text{O}^+\right]\text{B}}{\left[\text{HB}^+\right]} \times \frac{\left[\text{OH}^-\right]\text{HB}^+}{\left[\text{B}\right]} = \left[\text{H}_3\text{O}^+\right]\left[\text{OH}^-\right] = K_w$

Relationship between Conjugate Acid-Base Pair Dissociation Constants $K_w = K_a \times K_b$

<u>Major Species of a Weak Base</u>: - since weak acid do not dissociate completely $(K_b < 1)$ in water, <u>the</u> <u>major species of all weak bases are their original form and water</u>.

Procedure to calculate pH of Weak Base Solutions:

- 1. List all the major species from all weak bases, including water.
- 2. Calculate K_b from all weak bases using $K_w = K_a \times K_b$
- 3. Determine which species has the highest K_b . This is the <u>Strongest Base (SB)</u> of the list.
- 4. Write the Brønsted-Lowry dissociation of this Strongest Base
- 5. Set up the ICE Box and the equilibrium expression.
- 6. If the <u>original weak base concentration, $[B]_0$, is much larger than K_b </u>, we can <u>approximate by</u> <u>assuming $[B]_{eq} = ([B]_0 - x) \approx [B]_0$ </u>. Thereby, simplifying the calculation. (A general rule of thumb: if $[B]_0 \ge 1000 \times K_b$, we can use the approximation.)
- 7. Find the concentration of OH⁻.
- 8. <u>Verify</u> any <u>approximation</u> made by using the <u>5% rule</u>.

$$\left(\frac{\left[\text{OH}^{-}\right]}{\left[\text{B}\right]_{0}} \times 100\% \le 5\%\right)$$

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Example 3: Determine the [OH⁻], [H₃O⁺], pOH, pH and % dissociation of 0.200 mol/L of NaCN _(*aq*). $(K_a \text{ of HCN} = 6.2 \times 10^{-10}).$

NaCN dissociates completely in water:

 $NaCN_{(aq)} \rightarrow Na^{+}_{(aq)} + CN^{-}_{(aq)}$ (Weak Base)



<u>Assignment</u> 16.6 & 16.7 pg. 570 #53 to 58; pg. 571 #94

16.9: Acid-Base Properties of Salts

<u>Salts</u>: - ionic compounds that might dissociate in water.

- 1. <u>Neutral Salts</u>: when the <u>Cation comes from a Strong Base</u> and the <u>Anion is the Conjugate-Base of</u> <u>Strong Acid</u>.
 - no effect on pH; if dissolve in pure water, pH will remain at 7.

Examples: Some Neutral Salts:

- a. $\text{KNO}_{3(aq)}$ (K⁺ can be from a strong base $\text{KOH}_{(aq)}$; NO₃⁻ is the conjugate-base of a strong acid $\text{HNO}_{3(aq)}$)
- b. NaCl $_{(aq)}$ (Na⁺ can be from a strong base NaOH $_{(aq)}$; Cl⁻ is the conjugate-base a strong acid HCl $_{(aq)}$)
- 2. <u>Basic Salts</u>: when the <u>Cation comes from a Strong Base</u> and the <u>Anion is the Conjugate-Base of a</u> <u>Weak Acid</u>.
 - pH will increase; if dissolve in pure water, pH > 7 (Basic).

Examples: Some Basic Salts:

- a. NaCH₃COO (*aq*) (Na⁺ can be from a strong base NaOH (*aq*); CH₃COO⁻ is the conjugate-base of a weak acid CH₃COOH (*aq*))
- b. $KF_{(aq)}(K^+ \text{ can be from a strong base} KOH_{(aq)}; F^- \text{ is the conjugate base of a weak acid} HF_{(aq)})$

<u>Hydrolysis</u>: - the reaction of a base and a water to form a conjugate acid and OH⁻.

- it is basically the Brønsted-Lowry Dissociation of a weak base.

 $\mathbf{B}_{(aq)} + \mathbf{H}_2 \mathbf{O}_{(l)} \rightleftharpoons \mathbf{OH}^-_{(aq)} + \mathbf{HB}^+_{(aq)}$



(Weak Base) (Acid) (Conjugate Base) (Conjugate Acid)

Percent Hydrolysis: - the amount of [OH⁻] dissociated from the original [B]₀ expressed in percentage.

- strong bases will have % Hydrolysis = 100%.
- weak bases will have % Hydrolysis < 100%



3. <u>Acidic Salts</u>: - when the <u>Cation is the Conjugate-Acid of a Weak Base</u> and the <u>Anion is the</u> <u>Conjugate-Base of a Strong Acid</u>.

Example: $NH_4ClO_{4(aq)}$ is an acidic Salts: $(NH_4^+ \text{ is the conjugate-acid of a weak base - <math>NH_{3(aq)}$; $ClO_4^- \text{ is the conjugate-base of a strong acid - <math>HClO_{4(aq)}$)

Major Species: $NO_2^{-}(aq)$, $H_2O_{(l)}$

Example 1: Determine the pH and the percent hydrolysis of 0.235 M of sodium nitrite. The acid dissociation constant for nitrous acid is $K_a = 4.0 \times 10^{-4}$.

Sodium nitrite (NaNO₂) dissociates completely in H₂O: NaNO_{2 (s)} \rightarrow Na⁺_(aq) + NO_{2⁻(aq)} (Weak Base)

$$K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{4.0 \times 10^{-4}}$$
 $K_b = 2.5 \times 10^{-11}$

Strongest Base: NO_2^- ($K_b = 2.5 \times 10^{-11}$) (K_b for H₂O is $K_w = 1.0 \times 10^{-14}$) NO_2^- is a weak base and undergoes Brønsted-Lowry Dissociation.

 $NO_2^{-}(aq) + H_2O_{(l)} \Rightarrow HNO_2(aq) + OH^{-}(aq)$

| | | [HNO ₂] | [OH ⁻] |
|-------------|-------------|---------------------|----------------------------|
| Initial | 0.235 M | 0 | 0 |
| Change | - <i>x</i> | +x | + <i>x</i> |
| Equilibrium | (0.235 - x) | x | x |

$$K_{b} = \frac{[\text{HNO}_{2}][\text{OH}^{-}]}{[\text{NO}_{2}^{-}]} \quad 2.5 \times 10^{-11} = \frac{(x)(x)}{(0.235 - x)} \approx \frac{x^{2}}{(0.235)^{4}}$$
$$2.5 \times 10^{-11} (0.235) \approx x^{2}$$
$$5.875 \times 10^{-12} \approx x^{2}$$
$$x \approx \sqrt{5.875 \times 10^{-12}}$$

$$x = [OH^{-}] \approx 2.4 \times 10^{-6} M$$

 $pOH = -\log [OH^-]$ pH = 14 - pOH

CAN use Approximation:

$$\frac{\left[\text{NO}_{2}^{-}\right]_{0}}{K_{b}} = \frac{0.235 \text{ M}}{2.5 \times 10^{-11}} = 9.4 \times 10^{9} \ge 1000$$

Use 0.235 in the denominator, because $(0.235 - x) \approx 0.235$ [x is so small compared to 0.235 M]

$$pOH = -\log(2.4 \times 10^{-6}) \quad pH = 14 - (5.62)$$

$$pOH = 5.62 \quad pH = 8.38$$

$$h = 14 - (5.62) \quad pH = 8.38$$

$$h = 14 - (5.62) \quad pH = 8.38$$

$$h = 14 - (5.62) \quad pH = 8.38$$

$$h = 14 - (5.62) \quad pH = 8.38$$

$$h = 14 - (5.62) \quad pH = 8.38$$

$$h = 14 - (5.62) \quad pH = 8.38$$

As the small K_b suggests, the [OH⁻] is very small compared to $[NO_2^-]_0$. Therefore, % hydrolysis is also very small as a result.

0

Example 2: Determine the pH of 0.0750 M of ammonium nitrate. The base dissociation constant for NH_{3 (aq)} is $K_b = 1.8 \times 10^{-5}$.

Ammonium nitrate, NH₄NO₃, dissociates completely in water:

$$NH_4NO_{3(s)} \rightarrow NH_{4(aq)}^+ (Weak Acid) + NO_{3(aq)}^- \\ 0.0750 M \qquad 0.0750 M$$

Major Species: NH4⁺ (aq), H₂O (l)

$$K_a = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{1.8 \times 10^{-5}}$$
 $K_a = 5.556 \times 10^{-10}$

Strongest Acid: NH_4^+ ($K_a = 5.556 \times 10^{-10}$) (K_a for H₂O is $K_w = 1.0 \times 10^{-14}$) NH_4^+ is a weak acid and undergoes Brønsted-Lowry Dissociation.

| 1 | ${\rm NH_4}^+_{(aq)} + {\rm H_2O}_{(l)}$ | \Rightarrow H ₃ O ⁺ (<i>aq</i>) + | ► NH _{3 (aq)} | | CAN use Approximation. |
|---|---|---|---------------------------------|-----------------------------------|---|
| | $[\mathbf{NH_4}^+]$ | $[\mathrm{H}_{3}\mathrm{O}^{+}]$ | [NH ₃] | | CAN use Approximation: |
| Initial | 0.0750 M | 0 | 0 | | NH_4^+ 0.0750 M |
| Change | - <i>x</i> | +x | + <i>x</i> | | $\frac{1}{K_{\perp}} = \frac{1}{5.556 \times 10^{-10}}$ |
| Equilibrium | (0.075 - x) | x | x | | $a^{a} = 1.35 \times 10^{8} > 1000$ |
| $K_a = \frac{\left[\mathrm{H}_3\mathrm{O}^+\right]\mathrm{N}}{\left[\mathrm{N}\mathrm{H}_4^+\right]}$ | H ₃] 5.556 | $\times 10^{-10} = \frac{1}{(0.00000000000000000000000000000000000$ | $\frac{(x)(x)}{075-x)} \approx$ | $\approx \frac{x^2}{(0.075)}$ | Use 0.075 in the denominator, because $(0.075 - x) \approx 0.075$ [x is so small compared to 0.075 M] |
| | | 5.556×10^{-1} | ¹⁰ (0.075) <i>×</i> | $\approx x^2$ | |
| | | 4.16 | 57×10^{-11} | $\approx x^2$ | |
| | | | x | $\approx \sqrt{4.167 \times 1}$ | $\overline{0^{-11}}$ |
| | | x | $= [H_3O^+]$ | $\approx 6.455 \times 10^{\circ}$ | ⁻⁶ M |
| | | | pH = - log | $g[H_3O^+]$ | |
| | | | pH = -log | g (6.455 × 10 | |
| | | (| pH = 5.19 | | |
| Verify for | Using Approxim | ation: | | | |
| $\frac{\left[\mathrm{H_{3}O^{+}}\right]}{\left[\mathrm{NH_{4}^{+}}\right]_{0}} >$ | $<100\% = \frac{6.455 \times 0.075}{0.075}$ | $\frac{10^{-6} \text{ M}}{50 \text{ M}} \times 100$ |)% | | |
| | = 0.0086% | b≤5% Th | erefore, a | pproximatio | on would be appropriate. |

<u>Assignment</u> 16.9 pg. 570–571 #65, 68, 70 to 74

Chapter 17: Acid-Base Equilibria

17.2: The Buffer Solutions

| <u>Buffered Solution</u> : - a solution that <u>resists</u> - consists of a pair of <u>w</u> <u>base/conjugate acid</u> | a change in pH when a small amount of H_3O^+ or OH^- is added. eak acid/conjugate base common ion or a pair of weak common ion . |
|---|--|
| Acidic Buffered Solution: | $\mathbf{HA}_{(aq)} + \mathbf{H}_{2}\mathbf{O}_{(l)} \rightleftharpoons \mathbf{H}_{3}\mathbf{O}^{+}_{(aq)} + \mathbf{A}^{-}_{(aq)}$ |
| a. Small Amounts of H ₃ O ⁺ is Added: (<u>More</u> | $A^{-}_{(aq)} + H_3O^{+}_{(aq)} \rightarrow H_2O_{(l)} + HA_{(aq)}$ (H ⁺ - Strong Acid reacts <u>completely</u> with A ⁻) <u>e HA</u> – Weak Acid: <u>pH will only be lowered SLIGHTLY</u> !) |
| b. Small Amounts of OH [−] is Added: (<u>Mor</u> | $HA_{(aq)} + OH^{-}_{(aq)} \rightarrow H_2O_{(l)} + A^{-}_{(aq)}$ (OH ⁻ - Strong Base reacts <u>completely</u> with HA) <u>e A⁻</u> - Weak Base: <u>pH will only be raised SLIGHTLY</u> !) |
| Basic Buffered Solution: | $\mathbf{B}_{(aq)} + \mathbf{H}_2 \mathbf{O}_{(l)} \rightleftharpoons \mathbf{OH}^{(aq)} + \mathbf{HB}^+_{(aq)}$ |
| a. Small Amounts of H ₃ O ⁺ is Added: (<u>More</u> | $\begin{array}{l} \mathbf{B}_{(aq)} + \mathbf{H}_{3}\mathbf{O}^{+}_{(aq)} \rightarrow \mathbf{H}_{2}\mathbf{O}_{(l)} + \mathbf{HB}^{+}_{(aq)} \\ (\mathbf{H}^{+} - \text{Strong Acid reacts completely with B) \\ \underline{\mathbf{HB}^{+}} - \text{Weak Acid: pH will only be lowered SLIGHTLY!) \end{array}$ |
| b. Small Amounts of OH [−] is Added: (OH (<u>More</u> | $B_{(aq)} + H_2O_{(l)} \rightleftharpoons OH^{(aq)} + HB^+_{(aq)}$ |
| Example : $HCO_3^{-}(aq) / CO_3^{2-}$ is a buffer bec | ause HCO_3^- acts as an acid and CO_3^{2-} acts as a base whenever a |

small amount of strong base or acid is added to it. Thus, pH will remain somewhat constant.

 $\frac{\text{HCO}_3^{-}(aq) + \text{OH}^{-}(aq) \rightarrow \text{H}_2\text{O}_{(l)} + \text{CO}_3^{2-}(aq)}{\text{CO}_3^{2-}(aq) + \text{H}_3\text{O}^{+}(aq) \rightarrow \text{H}_2\text{O}_{(l)} + \text{HCO}_3^{-}(aq)}$ When small amounts of strong base is added: When small amounts of strong acid is added:

Example 1: Specify which of these systems can be classified as a buffer system.

| a. HNO ₃ / KNO ₃ | b. CH ₃ COOH / NaCH ₃ COO | c. H ₂ SO ₄ / NaHSO ₄ | d. NH ₃ / NH ₄ Cl |
|---|--|--|---|
| HNO ₃ is a strong acid. Hence, NO ₃ ⁻ is not a strong enough base to resist the change in pH. HNO ₃ / KNO ₃ is <u>NOT</u> a buffer system. | CH ₃ COOH is a <u>weak acid</u> . Therefore, CH ₃ COO ⁻ is a <u>strong enough weak base</u> to resist the change in pH. NaCH ₃ COO provides this base. CH ₃ COOH / CH ₃ COO ⁻ is a buffer system. | H_2SO_4 is a strong acid. Hence, HSO_4^- is not a strong enough base to resist the change in pH. H_2SO_4 / NaHSO ₄ is <u>NOT</u> a buffer | NH₃ is a <u>weak base</u> . Therefore, NH_4^+ is a <u>strong enough weak</u> <u>acid</u> to resist the change in pH. NH ₄ Cl provides this acid. NH₃ / NH₄Cl is a buffer system . |
| | | | |

Example 2: Calculate the pH of a 1.00 L buffered solution consisting of 0.500 M of methylamine

 $(K_b = 4.38 \times 10^{-4})$ with 0.450 M of CH₃NH₃Cl when:

- a. 0.0200 mol of KOH is added to it.
- b. $3.00 \text{ mL of } 0.750 \text{ M of HNO}_{3(aq)}$ is added to it.
- c. Contrast the pH's of the above two additions against the same additions to 1.00 L of water.

Methylamine (Base) Dissociation: $CH_2NH_2_{(aq)} + H_2O_{(l)} = CH_2NH_3^+_{(aq)} + OH_{(aq)}^-$ CH₃NH₃Cl: $CH_3NH_3Cl_{(aa)} \rightarrow CH_2NH_3^+(aa) + Cl_{(aa)}^-$ 0.450 M 0.450 M $\operatorname{CH}_{2}\operatorname{NH}_{2}(aq) + \operatorname{H}_{2}\operatorname{O}(l) \rightleftharpoons \operatorname{CH}_{2}\operatorname{NH}_{3}^{+}(aq) + \operatorname{OH}_{aq}^{-}(aq)$ **CAN use Approximation:** [CH₂NH₂] $[CH_2NH_3^+]$ $[OH^-]$ $\frac{\left[\text{CH}_{2}\text{NH}_{2}\right]_{0}}{K_{b}} = \frac{0.500 \text{ M}}{4.38 \times 10^{-4}}$ 0.500 M Initial 0.450 M 0 Change +x $+\mathbf{r}$ -xEquilibrium (0.5 - x)(0.45 + x)= 1142 > 1000 x $K_{b} = \frac{\left[\text{OH}^{-}\right]\left[\text{CH}_{2}\text{NH}_{3}^{+}\right]}{\left[\text{CH}_{2}\text{NH}_{2}\right]} \quad 4.38 \times 10^{-4} = \frac{(x)(0.45+x)}{(0.5-x)} \approx \frac{x(0.45)}{(0.5)}$ -Use 0.45 in the numerator, because $(0.45 + x) \approx 0.45$ [x is so $4.38 \times 10^{-4} \ \frac{(0.5)}{(0.45)} \approx x$ small compared to 0.45 M]. **Use 0.5 in the denominator**, because $(0.5 - x) \approx 0.5$ [x is so $x \approx 4.87 \times 10^{-4}$ small compared to 0.5 M]. Verify that we could use Approximation: $\frac{[OH^{-}]}{[CH_2NH_2]_0} \times 100\% = \frac{4.87 \times 10^{-4} \text{ M}}{0.500 \text{ M}} \times 100\%$ $pOH = -\log [OH^{-}]$ $pOH = -\log [OH^{-}]$ $pOH = -\log [OH^{-}]$ pH = 14 - pOHpH = 14 - 3.31 $pOH = -\log(4.87 \times 10^{-4})$ $= 0.0973\% \le 5\%$ Therefore, approximation would be appropriate. (pOH = 3.31)pH = 10.69**a.** 0.0200 mol of KOH is added to the buffered solution (Complete Rxn between OH⁻ & CH₂NH₃⁺). + $CH_2NH_3^+(aq)$ \rightarrow H₂O_(l) + CH₂NH₂(aq) $OH^{-}(aq)$ n of CH₂NH₃ n of CH₂NH₂ *n* of OH⁻ 0.0200 mol (Limiting) 0.450 mol 0.500 mol Before – 0.0200 mol + 0.0200 mol Change -0.0200 mol 0 0.430 mol 0.520 mol After Recalculate equilibrium concentrations using NEW $[CH_2NH_3^+]_0$ and $[CH_2NH_2]_0$ $\operatorname{CH}_{2}\operatorname{NH}_{2(aq)} + \operatorname{H}_{2}\operatorname{O}_{(l)} \rightleftharpoons \operatorname{CH}_{2}\operatorname{NH}_{3}^{+}_{(aq)} + \operatorname{OH}_{(aq)}^{-}$ **CAN use Approximation:** $[CH_2NH_2] \qquad [CH_2NH_3^+] \quad [OH^-]$ $\frac{\left[\text{CH}_{2}\text{NH}_{2}\right]_{0}}{K_{1}} = \frac{0.520 \text{ M}}{4.38 \times 10^{-4}} = 1187 \ge 1000$ Initial 0.520 M 0.430 M 0 Change +y(0.43 + y)Equilibrium (0.52 - v)Use 0.43 in the numerator, because (0.43 $K_{b} = \frac{\left[\text{OH}^{-1}\left[\text{CH}_{2}\text{NH}_{3}^{+}\right]}{\left[\text{CH}_{2}\text{NH}_{2}\right]} \quad 4.38 \times 10^{-4} \approx \frac{y(0.43)}{(0.52)}$ $4.38 \times 10^{-4} = \frac{(y)(0.43 + y)}{(0.52 - y)} \quad 4.38 \times 10^{-4} \frac{(0.52)}{(0.43)} \approx y$ $(+ y) \approx 0.43$ [y is so small compared to 0.43 M]. Use 0.52 in the denominator, because $(0.52 - y) \approx 0.52$ [y is so small compared to 0.52 M]. $v \approx 5.30 \times 10^{-10}$ $[OH^{-}] = 5.30 \times 10^{-4} \text{ mol/L}$ Verify that we could use Approximation: pH = 14 - pOH $\frac{[OH^{-}]}{[CH_2NH_2]_{0}} \times 100\% = \frac{5.30 \times 10^{-4} \text{ M}}{0.520 \text{ M}} \times 100\%$ $pOH = -\log [OH^-]$ pH = 14 - 3.28 $pOH = -\log(5.30 \times 10^{-4})$ pH = 10.72pOH = 3.28 $= 0.102\% \le 5\%$ (Appropriate Approximation) Page 215. Copyrighted by Gabriel Tang B.Ed., B.Sc.

First, we have to figure out the [OH⁻] and pH for the buffered solution system.

| b. 3.00 mL | of 0.750 M (0.0022: | 5 mol) | of HNO _{3 (} | _{aq)} is add | ed t | to the buffered solution | | |
|--|---|--------------------|-------------------------------------|--|----------|---|--------|--|
| (Comple | ete Reaction betwee H_2O^+ | n H ₃ O | ' & CH₂N ⊦ CH₂N | (\mathbf{H}_2) . | <u> </u> | $H_{2}O(0) + CH_{2}NH_{2}^{+}(\omega)$ | | |
| | $\frac{1130^{\circ}}{n \text{ of } \text{H}_2\text{O}^+}$ | | | | | $\frac{n \text{ of } CH_0 NH_0^+}{n \text{ of } CH_0 NH_0^+}$ | | |
| Before | 0.00225 mol (Limi | iting) | 0.500 | mol | | 0.450 mol | | |
| Change | - 0.00225 mol | , | - 0.0022 | 25 mol | | + 0.00225 mol | | |
| After | 0 | | 0.4977 | 5 mol | | 0.45225 mol | | |
| Recalculate | equilibrium concentr | rations | using NE | W [CH ₂] | NH | \mathbf{H}_{2} and $[CH_{2}NH_{3}^{+}]_{0}$ (neglect Δ volume) | | |
| CI | $H_2 NH_{2(aq)} + H_2 O_{(l)} =$ | ⇒ CH ₂ | $\mathrm{NH_3}^+_{(aq)}$ + | + OH [−] _(aq) | | CAN use Approximation: | | |
| | $[CH_2NH_2]$ | [CH | $[_2 \mathrm{NH_3}^+]$ | [OH ⁻] | | $[CH_2NH_2]_{0}$ 0.520 M | | |
| Initial | 0.49775 M | 0.45 | 5225 M | 0 | | $\frac{1}{K_{1}} = \frac{1187 \ge 100}{4.38 \times 10^{-4}} = 1187 \ge 100$ | 00 | |
| Change Equilibrium | -z | (0.45 | +z | +z | - 1 | Use 0.45225 in the numerator, because | e | |
| Equilibriui | $\begin{bmatrix} (0.49775 - z) \end{bmatrix}$ | (0.45 | (225 ± 2) | | | $(0.45225 + z) \approx 0.45225$ [z is so small | | |
| $K_b =$ | $\underbrace{[OH][CH_2NH_3]}_{[CH_2NH_3]}$ | 4.38 × | $10^{-4} \approx \frac{z(0)}{z(1)}$ | $\frac{0.45225}{10}$ | | compared to 0.45225 MJ. | | |
| | $[CH_2NH_2]$ | | (0 | .49775 | <u> </u> | -Use 0.49775 in the denominator, becau | use | |
| 4.38×10^{-4} | $=\frac{(y)(0.45225+z)}{(0.49775-z)}$ | 4.38 × | $10^{-4} \frac{(0.49)}{(0.49)}$ | 9775) 5225) ≈ : | z. | $(0.49775 - z) \approx 0.49775$ [z is so small compared to 0.49775 M]. | | |
| Verify that | we could use Appro | oximat | ion: | | | -4.82×10^{-4} mol// | | |
| [он-] | <i>4</i> 82 × 10 | $^{-4}$ M | | | | -4.82×10 III01/L $pH = 14 - pOH$ | ł | |
| | $\times 100\% = \frac{4.02 \times 10}{0.4977}$ | $\frac{1}{5}$ M | < 100% | | pO] | $DH = -\log [OH^{-}]$ $pH = 14 - 3.28$ | , , | |
| -0.00680/ | < 5% (Appropriat | | rovimatio | n) | pOł | $DH = -\log(4.82 \times 10^{-1})$ | | |
| - 0.090070 | | le App | IOXIIIatio | | pO] | OH = 3.32 $PH = 10.03$ | | |
| c. Contrast t | he pH's of the above | two ac | lditions ag | ainst the | sar | ame additions to 1.00 L of water. | | |
| i. 0.0200 | mol of KOH is adde | d to 1.0 | 00 L of wa | iter | | Adding the 0.0200 mol of KOH | | |
| pOH | = – log [OH ⁻] | pF | I = 14 - p | OH | | to buffered solution. | | |
| рОН | $= -\log(0.0200)$ | pF | I = 14 - 1 | .70 | | | | |
| рОН | = 1.70 | DI | I = 12.30 | S | | pH changes from 10.69 to 10.72 | | |
| | | Г | | | | | | |
| ii. $3.00 \text{ mL of } 0.750 \text{ M} (0.00225 \text{ mol}) \text{ of } \text{HNO}_{3(aq)} \text{ is added to } 1.00 \text{ L of water (neglect } \Delta \text{volume)}.$ | | | | | | | | |
| pH = | $-\log [H_3O^+]$ | | | | | Adding the 0.00225 mol of HNO ₃ | | |
| pH = | $-\log(0.00225)$ | | | | | to buffered solution. | | |
| DH = | 2.65 | | | | | pH changes from 10.69 to 10.68 | | |
| P | | | | | | pri changes i chi rolo, to roloo | | |
| | | | | | | | | |

<u>Assignment</u> 17.2 pg. 604 #1, 5 and 6

17.3: A Closer Look at Acid-Base Titrations

- <u>**pH Curve**</u>: a graph that shows the how the pH changes as the titration proceeds (as titrant is to the analyzed).
- <u>**Titration**</u>: a volumetric analysis that involves measuring the volume of known concentration solution to measure a given volume of an unknown concentration solution.

Titration Set-up



<u>Acid-Base Titration</u>: - volumetric analysis that assist in determining the unknown concentration in an acid and base neutralization.

Equivalent Point (Stoichiometric Point): - a point where the number of moles of H^+ is equivalent to the number of moles of OH^- . $(n_H^+ = n_{OH}^-)$

- **Endpoint**: a point where the indicator actually changes colour to indicate neutralization is completed.
- **Indicator**: a chemical that changes colour due to the pH of the solution (more in the next section).
- **Inflection**: the part of the curve where there is a sudden rise or drop in pH. - the midpoint of the inflection marks the equivalence point.





Strong Base (unknown concentration and known volume - analyte) titrated with Strong Acid (known concentration - titrant)



| • | A + 15.00 m | J of KOU odda | d: (Staighigmatria) | Doint) | | | | |
|----|--|--|--|---|--|--|--|--|
| C. | At 15.00 II | IL OI KOII (aq) aude | | | | | | |
| | Chamical | Spacios Prosont. | $\mathbf{H}_{\mathbf{O}}^{+} \mathbf{C}^{+} \mathbf{K}^{+}$ | | | | | |
| | Chemicai | species i resent. | | \mathbf{SR} \mathbf{R} | | | | |
| | | | L L | | | | | |
| | Net-Ionic | Equation: | $\mathrm{H}_{3}\mathrm{O}^{+}_{(aq)}$ | + $OH^{-}_{(aq)}$ | \rightarrow 2 H ₂ O (<i>l</i>) | | | |
| | | <i>n</i> of | H_3O^+ | | n of OH ⁻ | | | |
| | Before | (0.100 mol/L)(30.0 | 00 mL) = 3.00 mmol | (0.200 mol/L | L(15.00 mL) = 3.00 mmol | | | |
| | Change | - 3.0 | 0 mmol | | – 3.00 mmol | | | |
| | After | 0.00 | mmol | | 0.00 mmol | | | |
| | $[H_3O^+] = [$ | $OH^{-} = 1.00 \times 10^{-7}$ | mol/L | | | | | |
| | pH = -log | $[H_3O^+] = -\log(1.00)$ | 0×10^{-7}) | | pH = 7.00 | | | |
| d | A + 20.00 m | nL of KOH | d. (After Steichiom | tric Point) | | | | |
| u. | At 20.00 II | | | | | | | |
| | $\mathbf{S}\mathbf{A} \qquad \mathbf{A}$ | | | | | | | |
| | Chemical Species Present: H_3O' , CI , K' , OH , H_2O | | | | | | | |
| | Chemical | Species Present: | H_3O', Cl, K', B | ОН⁻, H ₂ О SB В | | | | |
| | Chemical | Species Present: | H_3O^+, Cl, K^+, B | OH ⁻ , H ₂ O SB B | | | | |
| | Net-Ionic | Species Present: Equation: | $H_{3}O^{+}, Cl, K^{+}, B$ $H_{3}O^{+}_{(aq)} = -$ | OH [−] , H ₂ O SB B + OH [−] _(aq) | \rightarrow 2 H ₂ O (<i>l</i>) | | | |
| | Net-Ionic | Species Present: Equation: <i>n</i> of | $H_{3}O^{+}, Cl, K^{+}, B$ $H_{3}O^{+}_{(aq)} = \frac{1}{2}H_{3}O^{+}$ | OH [−] , H ₂ O SB B + OH [−] _(aq) | $\rightarrow 2 \operatorname{H}_2 \operatorname{O}_{(l)}$ <i>n</i> of OH ⁻ | | | |
| | Net-Ionic Before | Equation: (0.100 mol/L)(30.0 | $H_{3}O^{+}, Cl, K^{+}, B$ $H_{3}O^{+}_{(aq)}$ $H_{3}O^{+}_{(aq)}$ $H_{3}O^{+}_{(aq)}$ | OH [−] , H ₂ O SB B + OH [−] _(aq) (0.200 mol/L | → $2 H_2O_{(l)}$ <i>n</i> of OH ⁻ .)(20.00 mL) = 4.00 mmol | | | |
| | Net-Ionic Before | Species Present: Equation: (0.100 mol/L)(30.0 (Limitin | $H_{3}O^{+}, Cl, K^{+}, B$ $H_{3}O^{+}_{(aq)}$ $H_{3}O^{+}$ $H_{3}O^{+}$ $H_{3}O^{+}$ $H_{3}O^{+}$ $H_{3}O^{+}$ $H_{3}O^{+}$ $H_{3}O^{+}$ $H_{3}O^{+}$ $H_{3}O^{+}$ $H_{3}O^{+}$ $H_{3}O^{+}_{(aq)}$ $H_{3}O^$ | OH^{-}, H_2O $SB B$ $+ OH^{-}_{(aq)}$ (0.200 mol/L) | $\rightarrow 2 \text{ H}_2 \text{O}_{(l)}$ $n \text{ of OH}^-$ $D(20.00 \text{ mL}) = 4.00 \text{ mmol}$ | | | |
| | Net-Ionic Before Change | Species Present: Equation: (0.100 mol/L)(30.0 (Limitin - 3.0 | $H_{3}O^{+}, Cl, K^{+}, H_{3}O^{+}(aq) = H_{3}O^{+}O^{+}O^{-}O^{-}O^{-}O^{-}O^{-}O^{-}O^{-}O^{-$ | OH [−] , H ₂ O SB B + OH [−] _(aq) (0.200 mol/L | → $2 H_2O_{(l)}$ <u><i>n</i> of OH⁻</u> D(20.00 mL) = 4.00 mmol - 3.00 mmol | | | |
| | Net-Ionic Before Change After | Species Present: Equation: (0.100 mol/L)(30.0 (Limitin) - 3.00 0.00 | H_3O^+, Cl, K^+, B $H_3O^+_{(aq)} - \frac{2}{2}H_3O^+$ 00 mL) = 3.00 mmol g Reagent) 0 mmol | OH [−] , H ₂ O SB B + OH [−] _(aq) (0.200 mol/L | $\rightarrow 2 H_2 O_{(l)}$ <i>n</i> of OH ⁻ .)(20.00 mL) = 4.00 mmol - 3.00 mmol 1.00 mmol | | | |
| | Net-Ionic Before Change After | Species Present: Equation: (0.100 mol/L)(30.0 (Limitin) - 3.00 0.00 | $H_{3}O^{+}, Cl, K^{+}, B$ $H_{3}O^{+}_{(aq)} - \frac{CH_{3}O^{+}}{C} = 3.00 \text{ mmol}$ $g \text{ Reagent} = 0 \text{ mmol}$ 1.00 mmol | OH [−] , H ₂ O SB B + OH [−] _(aq) (0.200 mol/L | $\rightarrow 2 H_2 O_{(l)}$ n of OH ⁻ .)(20.00 mL) = 4.00 mmol - 3.00 mmol 1.00 mmol | | | |
| | Net-Ionic Before Change After [OH ⁻] = - | Species Present: Equation: | $H_{3}O^{+}, Cl, K^{+}, B^{+}$ $H_{3}O^{+}_{(aq)}$ $H_{3}O^{+}_{(aq)}$ $H_{3}O^{+}_{(aq)}$ $H_{3}O^{+}_{(aq)}$ 0 mL = 3.00 mmol g Reagent 0 mmol 1.00 mmol 1.00 mmol | OH ⁻ , H ₂ O SB B + OH ⁻ _(aq) (0.200 mol/L = 0.0200 mol/L | $\rightarrow 2 H_2 O_{(l)}$ <u><i>n</i> of OH⁻</u> $D_{(l)}(20.00 \text{ mL}) = 4.00 \text{ mmol}$ - 3.00 mmol 1.00 mmol | | | |
| | Chemical Net-Ionic Before Change After $[OH^-] = -\frac{1}{1}$ | Species Present: Equation: $\frac{n \text{ of }}{(0.100 \text{ mol/L})(30.0 \text{ (Limitin)})}$ $(100 \text{ mol/L})(30.0 \text{ (Limitin)})$ $\frac{n_{\text{OH}^-}}{(0.000 \text{ mol/L})} = \frac{1}{(30.0 \text{ mol/L})}$ | $H_{3}O^{+}, Cl, K^{+}, B$ $H_{3}O^{+}_{(aq)} - \frac{1.00 \text{ mmol}}{1.00 \text{ mmol}}$ | OH [−] , H ₂ O SB B + OH [−] _(aq) (0.200 mol/L = 0.0200 mol/L | → $2 H_2O_{(l)}$ <u>n of OH⁻</u> J(20.00 mL) = 4.00 mmol - 3.00 mmol 1.00 mmol | | | |
| | Chemical Net-Ionic Before Change After $[OH^-] = -\frac{1}{1}$ $pOH = -\frac{1}{1}$ | Species Present: Equation: $ \frac{n \text{ of }}{(0.100 \text{ mol/L})(30.0 \text{ (Limitin)})(-3.0 \text{ (Limitin)})(-3.$ | $H_{3}O^{+}, Cl, K^{+}, B^{+}$ $H_{3}O^{+}_{(aq)} =$ | OH ⁻ , H ₂ O SB B + OH ⁻ _(aq) (0.200 mol/L = 0.0200 mol/L | → $2 H_2O_{(l)}$ <u><i>n</i> of OH⁻</u> .)(20.00 mL) = 4.00 mmol <u>- 3.00 mmol</u> 1.00 mmol | | | |
| | Chemical Net-Ionic Before Change After $[OH^-] = -$ POH = - pH = 14 | Species Present: Equation: $n 	ext{ of } (0.100 	ext{ mol/L})(30.0 	ext{(Limitin)})(30.0 	ext{(Limitin)})(3$ | $H_{3}O^{+}, Cl, K^{+}, B$ $H_{3}O^{+}(aq) = -\frac{1000}{2} H_{3}O^{+}(aq) =$ | OH [−] , H ₂ O SB B + OH [−] (<i>aq</i>) (0.200 mol/L | → $2 H_2O_{(l)}$ <u>n of OH⁻</u> J(20.00 mL) = 4.00 mmol <u>- 3.00 mmol</u> <u>1.00 mmol</u> <u>POH</u> = 1.70 <u>pH</u> = 12.30 | | | |
| | Chemical Net-Ionic Before Change After $[OH^-] = -\frac{1}{7}$ $pOH = -\frac{1}{7}$ pH = 14 (pH's results) | Species Present: Equation: $ \begin{array}{r} n \text{ of} \\ (0.100 \text{ mol/L})(30.0 \\ (Limitin) \\ -3.00 \\ \hline 0.00 \\ $ | H ₃ O ⁺ , Cl , K ⁺ , B H ₃ O ⁺ (aq) (aq) (H_3O^+) (aq) (H_3O^+) (aq) (aq) (H_3O^+) (aq) | OH ⁻ , H ₂ O SB B + OH ⁻ (<i>aq</i>) (0.200 mol/L = 0.0200 mol/L | $\rightarrow 2 \text{ H}_2 \text{O}_{(l)}$ $n \text{ of OH}^-$ $D(20.00 \text{ mL}) = 4.00 \text{ mmol}$ -3.00 mmol 1.00 mmol $pOH = 1.70$ $pH = 12.30$ Here | | | |

| pH of 30.0 mL of | 0.100 M HCl (aa) ti | itrated by 0.200 N | A of KOH (aa) |
|------------------|---------------------|--------------------|---------------|
| | (0,0) | | (***)/ |

| Volume of KOH added | pН | Volume of KOH added | pН | Volume of KOH | pН |
|---------------------|------|------------------------|-------|---------------|-------|
| | | | | added | |
| 0.00 mL | 1.00 | 14.60 mL | 2.75 | 15.40 mL | 11.25 |
| 5.00 mL | 1.24 | 14.80 mL | 3.05 | 15.60 mL | 11.42 |
| 10.00 mL | 1.60 | 14.90 mL | 3.35 | 15.80 mL | 11.54 |
| 11.00 mL | 1.71 | 14.95 mL | 3.65 | 16.00 mL | 11.64 |
| 12.00 mL | 1.85 | 14.99 mL | 4.35 | 20.00 mL | 12.30 |
| 13.00 mL | 2.03 | 15.00 mL (Equivalence) | 7.00 | 25.00 mL | 12.56 |
| 14.00 mL | 2.34 | 15.01 mL | 9.65 | 30.00 mL | 12.70 |
| 14.20 mL | 2.44 | 15.05 mL | 10.35 | 35.00 mL | 12.79 |
| 14.40 mL | 2.57 | 15.20 mL | 10.95 | | |



pH of 30.0 mL of 0.100 M HCl titrated by 0.200 M of KOH

2. <u>Titration Between Weak Acids and Strong Base</u>: - Equivalence Point always occur at pH > 7.







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| c. | At 15.00 mI | of KOH (<i>aq</i>) added: | (Stoichion | netric Poi | nt) | | | | |
|------------|--|---|---|---|-------------------------|-------------|------------------|----------------------------|--------------------------------|
| | Chemical S | pecies Present: | HCOOH, SA | K, OH SB | , H_2O A/B | | | | |
| | Not Ionic F | quation: HCO(| лн. т | | OH | | 、п | 0 + H | C00- |
| | | <i>n</i> of HCO | OH | , | of OH | | 7 11 | <u>n of HC</u> | OO^{-} |
| | Before | (0.100 mol/L)(3 | 0.00 mL) | (0.200 m | ol/L)(15 | 5.00 mL) | | 0 mm | ol |
| | | = 3.00 mm | nol | = (| 3.00 mm | nol | | | |
| | Change | - 3.00 m | mol | -3 | <u>8.00 mn</u> | nol | | +3.00 n | imol |
| | After | 0 mm | 01 | | <u>0 mm</u> | DI | | <u>3.00 n</u> | imol |
| | [HCOO ⁻] = | $\frac{n_{\rm HCOO^-}}{\rm Total Volume} = \frac{1}{(30)}$ | 3.00 m m).00 m L + 15 | $\frac{101}{5.00 \text{ mL}}$ = | = 0.0667 | 7 mol/L | | | |
| | At Stoichior | netric Point, after all | the OH ⁻ an | d HCOOF | I are use | ed up, the | resulti | ing solutior | ı follows |
| | the regular | weak base dissociation | on. | | | | Ann | rovimatio | n• |
| | | $HCOO^{-}_{(aq)} + H_2O_{(aq)}$ | o ⇒ HCOC | $\mathbf{H}_{(aq)} + \mathbf{O}$ | H ⁻ (aq) | СAN US | ר ארי ר | or oximation | 11. |
| | | [HCOO ⁻] | [HCO | OH] [(|)H ⁻] | HCOO | | 0.0667 M | [|
| | itial | 0.0667 M | | | 0 M | K_{b} | | 5.556×10 ⁻ | 11 |
| E | nalige | $\frac{-x}{(0.0667 - x)}$ | т. У | | r r | II 0.07 | = | 1.2×10^{9} | ≥ 1000 |
| | | (0.0007 - x) | | [| n lov-1 | Use 0.06 | 67 in (0.06) | the denom $(7 - r) \sim 0$ | inator, |
| K_b | $=\frac{K_{w}}{K}=\frac{1.0}{1.0}$ | $K_b = 5.55$ | $6 \times 10^{-11} = -10^{-11}$ | [HCOOH | OH- | is so sma | (U.UU all cor | $(07 - x) \approx 0.$ | 0.0667 MI. |
| | $K_a = 1.8$ | 3×10 | | ГНСОС |) | 2 | | | |
| | | 5.55 | $6 \times 10^{-11} = -10^{-11}$ | (x)(x) | ≈ — | x^2 | | | |
| | | | - | (0.0667 – | x) 0.0 | 0667 | | | |
| | [OH] = | $x = 1.92 \times 10^{\circ}$ mol | /L | | | pOH = – | log(1 | .92 × 10 °) | = 5.72 |
| | $\mathbf{pH} = 14 - \mathbf{p}$ | OH = 14 - 5.72 | | | | pH = 8.2 | 8 | | |
| d. | At 20.00 mI | of KOH _(aq) added: | (After Stoid | chiometri | c Point) | | | | |
| | Chemical S | pecies Present: | НСООН, | K ⁺ , OH ⁻ | , H ₂ O | | | | |
| | | | SA | SB | A/B | | | | |
| | Net-Ionic E | quation: HCOO | $OH_{(aq)}$ + | | OH ⁻ (a | (q) — | → H | $_{2}O_{(l)} + H$ | COO ⁻ (<i>aq</i>) |
| | | n of HCO | OH | n | of OH ⁻ | - | | | |
| | Before | (0.100 mol/L)(3 | 0.00 mL) | (0.200 m | ol/L)(20 | .00 mL) | | | |
| | Character | = 3.00 mmo | l (LR) | = 4 | .00 mm | ol | | | |
| | Change | - 3.00 mi | nol | - 3 | <u>.00 mm</u> .00 mm | | | | |
| | After all the | HCOOH is used up. | the resultin | g solution | has the | following | maio | r species. | |
| | Chemical S | pecies Present: | K ⁺ , OH⁻ , | H ₂ O | | U | 5 | 1 | |
| | | | SB | A/B | | | | | |
| | [OH ⁻] = — | | 1.00 m mol | = 0. | 0200 m | ol/L r | OH = | = -log(0.02 | (00) = 1.70 |
| | То | tal Volume (30.00 | mL + 20.00 |) m L) | | I | | -0(| |
| (n I) | pH = 14 - pOH = 14 - 1.70 $pH = 12.30$ | | | | | | | | |
| (pH nev | t s results fro | om similar Calculatio | ons with oth | er volume | s atter th | ie stoichio | metri | c point is li | sted on the |
| пол | · pu8·.) | | | | | | | | |

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| Volume of KOH added | pН | Volume of KOH added | pН | Volume of KOH added | pН |
|----------------------------------|------|------------------------|-------|---------------------|-------|
| 0.00 mL | 2.38 | 14.40 mL | 5.13 | 15.20 mL | 10.95 |
| 5.00 mL | 3.45 | 14.60 mL | 5.31 | 15.40 mL | 11.25 |
| 7.50 mL (Halfway to Equivalence) | 3.75 | 14.80 mL | 5.62 | 15.60 mL | 11.42 |
| 10.00 mL | 4.05 | 14.90 mL | 5.91 | 15.80 mL | 11.54 |
| 11.00 mL | 4.19 | 14.95 mL | 6.22 | 16.00 mL | 11.64 |
| 12.00 mL | 4.35 | 14.99 mL | 6.92 | 20.00 mL | 12.30 |
| 13.00 mL | 4.56 | 15.00 mL (Equivalence) | 8.28 | 25.00 mL | 12.56 |
| 14.00 mL | 4.89 | 15.01 mL | 9.65 | 30.00 mL | 12.70 |
| 14.20 mL | 5.00 | 15.05 mL | 10.35 | 35.00 mL | 12.79 |

pH of 30.0 mL of 0.100 M HCOOH (aq) titrated by 0.200 M of KOH (aq)





3. <u>Titration Between Weak Bases and Strong Acid</u>: - Equivalence Point always occur at pH < 7.

Weak Base (unknown concentration with known volume - analyte) titrated with



Example 3: Calculate the pH when 30.0 mL of 0.100 M of $CH_3NH_{2(aq)}$ ($K_b = 4.38 \times 10^{-4}$) is titrated with 0.200 mol/L of HCl_(aq) at:

- a. $0 \text{ mL of HCl}_{(aq)}$ added.
- c. 15.00 mL of $HCl_{(aq)}$ added.

- b. 7.50 mL of $HCl_{(aq)}$ added.
- d. 20.00 mL of HCl $_{(aq)}$ added.

a. At 0 mL of HCl_(aq) added, the pH will be calculated the weak base dissociation in the flask:

| • | CANNOT use Approximation: | | | | | | | |
|---|------------------------------------|----------------|--------------------|--|--|--|--|--|
| | [CH ₃ NH ₂] | $[CH_3NH_3^+]$ | [OH ⁻] | CHNH] 0 100 M | | | | |
| Initial | 0.100 M | 0 | 0 M | $\frac{1011_{3}101_{2}}{K} = \frac{0.100101}{4.29 \times 10^{-4}}$ | | | | |
| Change | - <i>x</i> | +x | + <i>x</i> | \mathbf{K}_{b} 4.38×10 | | | | |
| Equilibrium | (0.1 - x) | x | x | = 228.3 < 1000 | | | | |
| $K_{b} = \frac{\left[CH_{3}NH_{3}^{+}\right]OH^{-}\right]}{\left[CH_{3}NH_{2}\right]} \qquad 4.38 \times 10^{-4} = \frac{(x)(x)}{(0.1-x)} = \frac{x^{2}}{(0.1-x)} \qquad 501 \cup e(X^{2}/(0.1-X)) = -4.38$ | | | | | | | | |
| $pOH = -log [OH^-] = -log(0.00640) = 2.19$ | | | | | | | | |
| pH = 14 - pOH = 14 - 2.19 $pH = 11.81$ | | | | | | | | |

| b. At 7.50 mL of HCl _(aq) added: (Before Stoichiometric Point: at Halfway to Equivalence Point) | | | | | | | | | |
|---|--|---|--|--|--------------------|--------------------------------|--|--|--|
| Chemical Species Present: CH_3NH_3 , H_3O^+ , Cl^- , H_2O | | | | | | | | | |
| | | | SD | SA A/D | | | | | |
| | Net-Ionic E | quation: CH ₃ N | $\mathbf{H}_{2(aq)}$ + | - $H_3O^+_{(aq)}$ | | \rightarrow H ₂ C | $\mathbf{D}_{(l)} + \mathbf{CH}_3 \mathbf{NH}_3^+(aq)$ | | |
| | | n of CH ₃ N | \mathbf{H}_2 | $n \text{ of } \mathrm{H}_{3}\mathrm{O}^{+}$ | | i | <i>n</i> of CH ₃ NH ₃ ⁺ | | |
| | Before | (0.100 mol/L)(3) | 0.00 mL) | (0.200 mol/L)(7.5) | 0 mL) | | 0 mmol | | |
| | Change | = 3.00 mm | nol | = 1.50 mmol (1 | LR) | | + 1 50 mmol | | |
| | After | - 1.50 mm | 101 nol | - 1.50 MM0 | L | | + 1.50 mmol | | |
| | Alter | 1.50 III | | U IIIIIUI | | | 1.50 111101 | | |
| | ICH.NH.1- | $n_{ m CH_3NH_2}$ | 1.50 m n | -0.0400 | | ICH N | $\mathbf{H}^{+1} = [\mathbf{C}\mathbf{H}^{-1}]$ | | |
| | | Total Volume $\overline{(3)}$ | 0.00 mL + 7 | $\frac{1}{7.50 \text{ mL}} = 0.0400 \text{ I}$ | | СПЗІМ | $\mathbf{n}_3 = [\mathbf{C}\mathbf{n}_2\mathbf{N}\mathbf{n}_2]$ $\mathbf{n}\mathbf{H} \approx \mathbf{n}\mathbf{K}$ | | |
| | | $n_{_{CH}}$ NH $^+$ | 1 50 m | mol | | (Max] | Buffer Canacity) | | |
| | $[CH_3NH_3^+]$ | $=\frac{\text{Ch}_3\text{Nh}_3}{\text{Total Volume}}=\frac{1}{6}$ | $\frac{1.00 \text{ mL}}{30.00 \text{ mL}}$ + | $\frac{100}{-7.50 \text{ mL}} = 0.0400$ | mol/L | (1)101 | cupucity) | | |
| | After all the | H_2O^+ is used up the | resulting s | olution follows the | egular w | eak has | se dissociation | | |
| | | TH.NH. (1) + H.O (1) | → CH.NE | \mathbf{L}^+ \mathbf{L}^+ $\mathbf{O}\mathbf{H}^-$ | CAN | | a Annravimation. | | |
| | | $\frac{[CH_3NH_2]}{[CH_3NH_2]}$ | CH ₃ N | $\begin{array}{c c} \mathbf{H}_3 & (aq) \\ \mathbf{H}_3 & \mathbf{I} \\ \end{array} + \begin{array}{c} \mathbf{OH} & (aq) \\ \mathbf{OH}^- \\ \mathbf{I} \\ \end{array}$ | CAN | | e Approximation. | | |
| In | itial | 0.0400 M | 0 | 0.0400 M | [CH ₃] | NH_2_0 | $= \frac{0.0400 \mathrm{M}}{1000 \mathrm{M}}$ | | |
| C | hange | - <i>x</i> | +x | +x | K | X_b | 4.38×10^{-4} | | |
| E | quilibrium | (0.04 - x) | x | (0.04 + x) | | | = 91.3 < 1000 | | |
| K . : | _ CH ₃ NH ₃ | $\left[OH^{-} \right]$ (138 × | $10^{-4} = \frac{(x)}{(x)}$ | (0.04 + x) | 50 | lveQ | ((0.04+X)/ | | |
| Πb | [CH ₃ N | H ₂] | (0 | .04 - x) | , X | .04-/ .0,(0 | 3,0 <u>04</u> } | | |
| | | [OH ⁻] | = x = 4.29 | $\times 10^{-4}$ mol/L | | 4.287 | 2107932E-4 | | |
| | | pOH | [= -log [O | $H^{-}] = -\log(4.29 \times 1)$ | $0^{-4}) = 3.3$ | 37 | | | |
| | | p] | H = 14 - pC | OH = 14 - 3.37 | | | | | |
| (pH | I's results fro | om similar Calculatio | ns with oth | er volumes | | 6 | pH = 10.63 | | |
| bei | ore the stoic | nometric point is list | ed on the n | ext page.) | | | | | |
| c. | At 15.00 mI | of HCl _(aq) added: | (Stoichion | netric Point) | | | | | |
| | Chemical S | pecies Present: | CH ₃ NH ₂ , | H_3O^+ , CI^- , H_2O | | | | | |
| | | | SB | SA A/B | | | | | |
| | Net-Ionic E | quation: CH ₃ N | $H_{2(aq)}$ + | $ H_3O^+_{(aq)}$ | <u> </u> | \rightarrow H ₂ C | $D_{(l)} + CH_3 NH_3^+_{(aq)}$ | | |
| | | <i>n</i> of CH ₃ N | H_2 | $n \text{ of } \mathrm{H}_3\mathrm{O}^+$ | | i | <i>n</i> of CH ₃ NH ₃ ⁺ | | |
| | Before | (0.100 mol/L)(3) | 0.00 mL) | (0.200 mol/L)(15.0 | 00 mL) | | 0 mmol | | |
| | Change | = 3.00 mm | nol | = 3.00 mmo | | | 1 2 00 mm al | | |
| | After | - 5.00 mr | <u>101</u> | - 3.00 mmo | 1 | | + 5.00 mmol | | |
| | Altel | U IIIII | ,, | 0 1111101 | | | 5.00 1111101 | | |
| | $[CH_{3}NH_{3}^{+}] = \frac{n_{CH_{3}NH_{3}^{+}}}{2.00 \text{ mmol}} = 0.0667 \text{ mol/I}$ | | | | | | | | |
| | | Total Volume (3 | 30.00 mL + | 15.00 mL) | | | | | |
| | | | | | | | | | |

| At Stoich | hiometri | c Point, after all the | H_3O^+ ar | nd CH ₃ N | NH ₂ are use | ed up, the resulting solution follows the | | | |
|--|-----------------------------------|--|----------------------------------|----------------------------|---|---|--|--|--|
| regular w | сн | $(3NH_3^+(ag) + H_2O_{(1)})$ | ≠ CH ₃ N | $H_{2}(aa)$ | $+ H_3O^+(aa)$ | CAN use Approximation: | | | |
| | | [CH ₃ NH ₃ ⁺] | [CH | 3NH ₂ | $[\mathbf{H}_{3}\mathbf{O}^{+}]$ | $\left[CH_{3}NH_{3}^{+} \right]_{0} = 0.0667 M_{-}$ | | | |
| Initial | | 0.0667 M | | 0 | 0 M | $K_a = 2.28 \times 10^{-11}$ | | | |
| Change | | -x | | ⊦x | +x | $= 2.9 \times 10^9 > 1000$ | | | |
| Equilibri | ium | (0.0667 - x) | | x | x | Use 0.0667 in the denominator. | | | |
| K | 1.0×10 |)-14 | | CH NH | []H O+] | because $(0.0667 - x) \approx 0.03667$ [x | | | |
| $K_a = \frac{K_w}{K} =$ | $\frac{1.0\times10}{4.38\times1}$ | $\frac{K_{a}}{0^{-4}}$ $K_{a} = 2.28 \times 10^{-4}$ | $10^{-11} = \frac{\Gamma}{2}$ | | $\frac{12 \prod 130}{\text{NH}}$ | is so small compared to 0.0667 M]. | | | |
| $\mathbf{\Lambda}_{b}$ | 4.36×1 | 0 | | $\left[C \Pi_{3} \right]$ | | | | | |
| | | 2.28×10^{-10} | $0^{-11} = -$ | (x)(x) | $) \longrightarrow \approx -x$ | <u>x²</u> | | | |
| | | | | 0.0667 - | -x) 0.0 | 0667 | | | |
| $[\mathrm{H}_{3}\mathrm{O}^{+}] = x =$ | = 1.23 × | 10⁻⁶ mol/L pH | $(= -\log \theta)$ | $g[H_3O^+]$ | $= -\log(1.2)$ | 23×10^{-6}) pH = 5.91 | | | |
| d. At 20.00 | mL of | HCl _(aa) added: (Afte | er Stoich | niometr | ic Point) | | | | |
| Chemica | al Speci | es Present: Cl | H ₃ NH ₂ . | H_3O^+ . | CL. H ₂ O | | | | |
| | | | SB | SA | A/B | | | | |
| Not Ion: | . Terre | | | | $\mathbf{U} \mathbf{O}^{+}$ | | | | |
| Inet-Iom | ic Equa | $\frac{1011: CH_3NH_2}{n of CH_NH}$ | aq) ⁻ | | $\frac{\Pi_{3} \bigcup_{(aq)}}{n \text{ of } \mathbf{U}_{2}}$ | $ \overset{)}{\rightarrow} \Pi_2 \mathcal{O}_{(l)} + \mathcal{O} \Pi_3 \Pi_3 (aq) $ | | | |
| Pofor | 20 | $\frac{n \text{ of CH}_{3}\text{NI}}{(0.100 \text{ mol/L})(20.1)}$ | $\frac{12}{10}$ mL) | (0.200 | $\frac{n \text{ of } \Pi_3 \text{ of }}{(2000)}$ | $\frac{0}{100 \text{ mL}}$ | | | |
| Delui | e | (0.100 mol/L)(30.0) = 3.00 mmol (1) | (\mathbf{P}) | (0.200 | = 4.00 mm | nol | | | |
| Chan | σe | -3.00 mmo | JR) J | | -3.00 mm | nol | | | |
| After | 50 | 0 mmol | 1 | | <u> </u> | mol | | | |
| | de CU | | | 14: | 1.00 mm | | | | |
| After all | the CH | $_{3}NH_{2}$ is used up, the | resulting | g solutio | on has the | following major species. | | | |
| Cnemica | ai speci | es Present: CI | , H ₃ U , | , H_2O | | | | | |
| SA A/B | | | | | | | | | |
| $[H_3O^+] = \frac{n_{H_3O^+}}{1.00 \text{ mmol}} = \frac{1.00 \text{ mmol}}{1.00 \text{ mmol}} = 0.0200 \text{ mol/L}$ | | | | | | | | | |
| Total Volume $(30.00 \text{ mL} + 20.00 \text{ mL})$ | | | | | | | | | |
| pH = | -log [] | H_3O^+] = $-\log(0.0200)$ |)) | | | (pH = 1.70) | | | |
| (pH's results | s from s | imilar Calculations | with othe | er volun | nes after th | ne stoichiometric point is listed below) | | | |
| Uni s results | | curvaturion5 | | | and alter th | | | | |

pH of 30.0 mL of 0.100 M CH₃NH_{2 (ag)} titrated by 0.200 M of HCl_(ag)

| Volume of HCl added | pН | Volume of HCl added | pН | Volume of HCl added | pН |
|----------------------------------|-------|------------------------|------|---------------------|------|
| 0.00 mL | 11.81 | 14.40 mL | 9.26 | 15.20 mL | 3.05 |
| 5.00 mL | 10.92 | 14.60 mL | 9.08 | 15.40 mL | 2.75 |
| 7.50 mL (Halfway to Equivalence) | 10.63 | 14.80 mL | 8.77 | 15.60 mL | 2.58 |
| 10.00 mL | 10.33 | 14.90 mL | 8.47 | 15.80 mL | 2.46 |
| 11.00 mL | 10.20 | 14.95 mL | 8.16 | 16.00 mL | 2.36 |
| 12.00 mL | 10.03 | 14.99 mL | 7.46 | 20.00 mL | 1.70 |
| 13.00 mL | 9.82 | 15.00 mL (Equivalence) | 5.91 | 25.00 mL | 1.40 |
| 14.00 mL | 9.49 | 15.01 mL | 4.35 | 30.00 mL | 1.30 |
| 14.20 mL | 9.39 | 15.05 mL | 3.65 | 35.00 mL | 1.21 |

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Example 4: Calculate the concentration of 10.00 mL of Na₂S _(*aq*) is titrated with 0.0350 M of HBr _(*aq*) when the first and second equivalence points are at 13.34 mL and 27.88 mL respectively.

<u>For Acid-Base Stoichiometry, do NOT write the Net-Ionic Equation</u>. <u>Write the Molecular Equation</u> to do Stoichiometry. <u>We use the second equivalence point because Na₂S can accept two protons.</u>

| 2 HBr _(aq) + 27.88 mL 0.0350 mol/L | Na ₂ S _(aq) 10.0 mL ? mol/L | \rightarrow | $H_2S_{(aq)}$ | + | 2 NaBr (aq) |
|---|---|---------------|---------------|---|-------------|
| | 27.88 m L) = 0.97 | 758 mmo | l | | |

 $[Na_2S] = \frac{n}{V} = \frac{0.4879 \text{ mmol}}{10.0 \text{ mL}} = 0.04879 \text{ mol/L}$

 $[Na_2S] = 0.0488 \text{ mol/L}$

Neutralization Reactions Between Weak Acids and Weak Bases

- 1. The reaction is NOT one way, but in equilibrium.
- When writing out the equilibrium system, <u>list all major species first</u> (Do NOT Break up any Weak Acids and Weak Bases). Then, <u>reacts the Strongest Acid (SA donates a proton) and the Strongest Base (SB accepts a proton) from the list</u>.
- 3. Using the Table of the Relative Strengths of Acids, decide on which side of the equilibrium is the system favoured. (The equilibrium favours the side with the Weakest Acid (Lower K_a) because the stronger acid of the other side dissociates more.)



- **Example 5**: Write the net-ionic equation for the following neutralizations. Indicate the side of the equilibrium system that is favoured.
 - a. Acetic Acid reacts with Ammonia

SAAChemical Species Present: CH_3COOH, NH_3, H_2O
SBFavour ProductsNet-Ionic Equation: $CH_3COOH_{(aq)} + NH_3_{(aq)} \Rightarrow CH_3COO^-_{(aq)} + NH_4^+_{(aq)}$
(Stronger Acid)
 $K_a = 1.8 \times 10^{-5}$ Generation

b. Sodium Hydrogen Oxalate reacts with Calcium Sulfite



c. Sodium Hydrogen Carbonate reacts with Potassium Hydrogen Sulfite



Example 6: Four different weak acids are reacted with various conjugate bases, and the results are recorded as follow.

| $\mathrm{HW}_{(aq)} + \mathrm{X}_{(aq)}^{-} \rightleftharpoons \mathrm{HX}_{(aq)} + \mathrm{W}_{(aq)}^{-}$ | [products favoured] |
|--|----------------------|
| $\mathrm{HY}_{(aq)} + \mathrm{W}^{-}_{(aq)} \rightleftharpoons \mathrm{HW}_{(aq)} + \mathrm{Y}^{-}_{(aq)}$ | [products favoured] |
| $\mathrm{HZ}_{(aq)} + \mathrm{Y}^{-}_{(aq)} \rightleftharpoons \mathrm{HY}_{(aq)} + \mathrm{Z}^{-}_{(aq)}$ | [reactants favoured] |
| $\mathrm{HZ}_{(aq)} + \mathrm{X}^{-}_{(aq)} \rightleftharpoons \mathrm{HX}_{(aq)} + \mathrm{Z}^{-}_{(aq)}$ | [reactants favoured] |

List the acids in order of **increasing** strength.

First, we have to decide which acid is the weaker acid for each of these reactions.



17.4: Acid-Base Indicators

<u>Acid-Base Indicators</u>: - chemicals that change colours at a specific pH range.

- they are themselves organic acids. Since they are usually very big structurally, we usually use abbreviations to describe them in chemical equations.
- this is due to the acidic form of the indictor (HIn) has a different colour than its basic form (In⁻).

Example: Phenolphthalein (HPh (aq) /Ph⁻(aq)) changes colours from colourless to pink at a pH range of 8.0 to 10.0. At its mid-range (9.0 – average of 8.0 and 10.0), the colour would be light pink (colourless + pink).

 $\begin{array}{l} \mathbf{HPh}_{(aq)} + \mathrm{H}_{2}\mathrm{O}_{(l)} \rightleftharpoons \mathrm{H}_{3}\mathrm{O}^{+}_{(aq)} + \mathbf{Ph}^{-}_{(aq)} \\ (\mathrm{Colourless}) & (\mathrm{Pink}) \end{array} \qquad K_{a} = 1.0 \times 10^{-9} \qquad \mathrm{p}K_{a} = 9 \qquad \mathrm{Colour\ Change} = 9 \pm 1 \\ \end{array}$

At pH \leq 9, phenolphthalein is colourless.

At pH \ge 10, phenolphthalein is pink.

Example: Bromothymol Blue (HBb $_{(aq)}$ /Bb $^{-}_{(aq)}$) changes colours from yellow to blue at a pH range of 6.0 to 8.0. At its **mid-range (7.0 – average of 6.0 and 8.0**), the colour would be **green (yellow + blue)**.

 $\begin{array}{l} \textbf{HBb}_{(aq)} + \textbf{H}_2\textbf{O}_{(l)} \rightleftharpoons \textbf{H}_3\textbf{O}^+_{(aq)} + \textbf{Bb}^-_{(aq)} & K_a = 1.0 \times 10^{-7} & pK_a = 7 & \text{Colour Change} = 7 \pm 1 \\ \textbf{(Yellow)} & \textbf{(Blue)} & \end{array}$

At pH \leq 6, bromothymol blue is yellow.





At pH \ge 8, bromothymol blue is blue.

yellow yellow blue colourless



Example 1: A sample of rainwater is poured into five test tubes. A different indicator is added to each test tube. Four of the observations are recorded in the table below.

| methyl red | |
|-------------------|--|
| phenol red | |
| bromocresol green | |
| phenolphthalein | |
| bromothymol blue | |

Determine the pH of the rainwater and the predicted colour of the sample containing bromothymol blue.

First, we need to decide on the pH range that these indicators will change colors.

| Indicators | Colour Change | pH range | Colour Observed | Indicated pH | |
|-------------------|----------------------|-------------------|------------------------|--------------|--|
| methyl red | red to yellow | 4.8 to 6.0 | Yellow | pH > 6.0 | |
| phenol red | yellow to red | 6.6 to 8.0 | Yellow | pH < 6.6 | |
| bromocresol green | yellow to blue | 3.8 to 5.4 | Blue | pH > 5.4 | |
| phenolphthalein | colourless to pink | 8.2 to 10.0 | colourless | pH < 8.2 | |

From the indicated pH ranges, we can tell than the pH of the rain water is <u>between 6.0 to 6.6</u>. At such pH range, <u>bromothymol blue would appear green</u>. (The pH and colour range for bromothymol blue is 6.0 - 7.6; yellow to blue)

 Assignment

 17.4 pg. 604 #21 to 24

Extra Section: Environmental Issues Involving Acids and Bases

Acid Rain: - precipitation of water (rain) or (snow) that has a low pH (less than 5.0).

- natural rain is slightly acidic due to the small amount of CO_2 in the atmosphere.

$$\operatorname{CO}_{2(g)} + \operatorname{H}_2 O_{(l)} \rightarrow \operatorname{H}_2 \operatorname{CO}_{3(aq)}$$
 (Carbonic Acid – $K_a = 4.5 \times 10^{-7}$)

- however, the burning of fossil fuel by vehicles and industrial activities, and also emits other oxides such as $NO_{2(g)}$, $SO_{2(g)}$ and $SO_{3(aq)}$. These gaseous oxides (Lewis acids) combined with water in the atmosphere (Lewis base) to form various strong and weak acids. Thus, lowering the pH of rain and snow.

 $SO_{2 (g)} + H_2O_{(l)} \rightarrow H_2SO_{3 (aq)}$ (Sulfurous Acid - $K_a = 1.4 \times 10^{-2}$) $SO_{3 (g)} + H_2O_{(l)} \rightarrow H_2SO_{4 (aq)}$ (Sulfuric Acid - <u>Strong Acid</u>) $2 NO_{2 (g)} + H_2O_{(l)} \rightarrow HNO_{3 (aq)} + HNO_{2 (aq)}$ (Nitric Acid - <u>Strong Acid</u> and Nitrous Acid - $K_a = 4.5 \times 10^{-7}$)

Hydrogen ion concentration as pH from measurements made at the field laboratories, 1999



http://nadp.sws.uiuc.edu

(Above) Measurements of pH in the continental U.S in 1999. Note the most severely affected regions are concentrated in the East Coast as well as in the major cities.

Unit 6: Acids-Base



(Above) The Formation of Acid Rain.(Right) Measurements of pH in Eastern Canada and U.S in 1996. The lowest pHs are in the Great Lakes Region where most of the heavy industries are located.



Effects of Acid Rain:

- 1. <u>Marine Life (especially in-land lakes and rivers) is affected greatly</u>. Acid Rain lowers the pH that can destroy all life (plants and animals). Usually, acid lake and river appears to be crystal clear, with no sign of algae, plant and animal life.
- 2. <u>Vegetation (including forests) can be decimated</u>. Since the <u>soil acidity level are lowered</u>, further plant growth may not be possible and the surrounding <u>ecosystem is destroyed</u> as a result. Forests affected by acid rain appear to be charred with trees having no leaves and all branches are brittle.





(Left) an Acid Lake. Note the clear water with the absence of life. (Right) an Acid Forest. Note the lack of leaves, the brittle branches, and the charred looked of the tree trunks.

Honour Chemistry

- 3. In areas of where there is a sustain amount of humidity, acid rain can turn into <u>Acid Fog or Smog (SO₂ + H₂O) Combination of Smoke from Coal Burning and Fog</u>. <u>Humans may experience severe</u> respiratory problems as a result. The most notable case was in London, England and surrounding areas in December 1952 when smog was so serious that there were estimated 4700 deaths.
- 4. <u>Acid deposition</u> (acid rain depositing onto a solid metal or base that causes corrosion and neutralization) on city structures such as historical statues (usually made of limestone, CaCO₃) and buildings can cause expensive repairs and lost of priceless arts.



(Above) Smog in London during December, 1952.(Below) Smog over the Los Angeles skyline.(Right) Acid Depositions on Statues at the Schloss Sanssouci Palace in Berlin, Germany. Note the black "burn" deposits on the statutes.





Ways to Reduce Acid Rain:

- 1. <u>Burn Less Fossil Fuel</u>: drive more fuel efficient vehicles, develop alternate ways to generate electricity without combustion of fossil fuel, and reduce the amount of electricity used are all possible ways to cut down on gaseous oxides emissions.
- 2. <u>Enact Legislation to Regulate Emissions</u>: governments can pass legislation on industry to regulate the amount of gases that cause acid rain. Better filtering technology and frequent inspections of industrial facilities can hold companies accountable to these environmental laws.
- 3. <u>Adding Limestone</u> to acid lakes and rivers can raise the pH and reintroduce marine life that has been affected by acid rain.