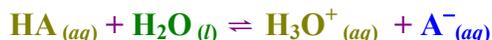
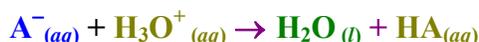


Chapter 17: Acid-Base Equilibria17.2: The Buffer Solutions

Buffered Solution: - a solution that **resists a change in pH** when a small amount of H_3O^+ or OH^- is added.
 - consists of a pair of **weak acid/conjugate base common ion** or a pair of **weak base/conjugate acid common ion**.

Acidic Buffered Solution:

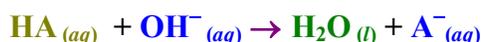
a. **Small Amounts of H_3O^+ is Added:**



(H^+ - Strong Acid reacts **completely** with A^-)

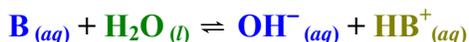
(**More HA – Weak Acid: pH will only be lowered SLIGHTLY!**)

b. **Small Amounts of OH^- is Added:**



(OH^- - Strong Base reacts **completely** with HA)

(**More A^- – Weak Base: pH will only be raised SLIGHTLY!**)

Basic Buffered Solution:

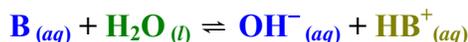
a. **Small Amounts of H_3O^+ is Added:**



(H^+ - Strong Acid reacts **completely** with B)

(**More HB^+ – Weak Acid: pH will only be lowered SLIGHTLY!**)

b. **Small Amounts of OH^- is Added:**



(OH^- - Strong Base increases $[\text{OH}^-]$; eq shifts left)

(**More B – Weak Base: pH will only be raised SLIGHTLY!**)

Example: $\text{HCO}_3^-_{(aq)} / \text{CO}_3^{2-}$ is a buffer because 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.

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

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

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

a. $\text{HNO}_3 / \text{KNO}_3$

HNO_3 is a strong acid. Hence, NO_3^- is not a strong enough base to resist the change in pH. **$\text{HNO}_3 / \text{KNO}_3$ is NOT a buffer system.**

b. $\text{CH}_3\text{COOH} / \text{NaCH}_3\text{COO}$

CH_3COOH is a weak acid. Therefore, CH_3COO^- is a **strong enough weak base** to resist the change in pH. NaCH_3COO provides this base. **$\text{CH}_3\text{COOH} / \text{CH}_3\text{COO}^-$ is a buffer system.**

c. $\text{H}_2\text{SO}_4 / \text{NaHSO}_4$

H_2SO_4 is a strong acid. Hence, HSO_4^- is not a strong enough base to resist the change in pH. **$\text{H}_2\text{SO}_4 / \text{NaHSO}_4$ is NOT a buffer**

d. $\text{NH}_3 / \text{NH}_4\text{Cl}$

NH_3 is a weak base. Therefore, NH_4^+ is a **strong enough weak acid** to resist the change in pH. NH_4Cl provides this acid. **$\text{NH}_3 / \text{NH}_4\text{Cl}$ is a buffer system.**

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

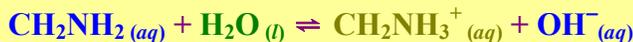
($K_b = 4.38 \times 10^{-4}$) with 0.450 M of $\text{CH}_3\text{NH}_3\text{Cl}$ when:

a. 0.0200 mol of KOH is added to it.

b. 3.00 mL of 0.750 M of $\text{HNO}_3_{(aq)}$ is added to it.

c. Contrast the pH's of the above two additions against the same additions to 1.00 L of water.

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



	$[CH_2NH_2]$	$[CH_2NH_3^+]$	$[OH^-]$
Initial	0.500 M	0.450 M	0
Change	-x	+x	+x
Equilibrium	(0.5 - x)	(0.45 + x)	x

CAN use Approximation:

$$\frac{[CH_2NH_2]_0}{K_b} = \frac{0.500 \text{ M}}{4.38 \times 10^{-4}} = 1142 \geq 1000$$

$$K_b = \frac{[OH^-][CH_2NH_3^+]}{[CH_2NH_2]} \quad 4.38 \times 10^{-4} = \frac{(x)(0.45 + x)}{(0.5 - x)} \approx \frac{x(0.45)}{(0.5)}$$

$$4.38 \times 10^{-4} \frac{(0.5)}{(0.45)} \approx x$$

$$x \approx 4.87 \times 10^{-4}$$

Use 0.45 in the numerator, because $(0.45 + x) \approx 0.45$ [x is so small compared to 0.45 M].
 Use 0.5 in the denominator, because $(0.5 - x) \approx 0.5$ [x is so small compared to 0.5 M].

Verify that we could use Approximation:

$$\frac{[OH^-]}{[CH_2NH_2]_0} \times 100\% = \frac{4.87 \times 10^{-4} \text{ M}}{0.500 \text{ M}} \times 100\% = 0.0973\% \leq 5\%$$

$[OH^-] = 4.87 \times 10^{-4} \text{ mol/L}$

pOH = -log [OH⁻]
 pOH = -log(4.87 × 10⁻⁴)

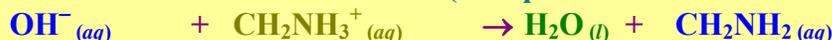
pH = 14 - pOH
 pH = 14 - 3.31

Therefore, approximation would be appropriate.

pOH = 3.31

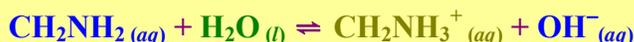
pH = 10.69

a. 0.0200 mol of KOH is added to the buffered solution (Complete Rxn between OH⁻ & CH₂NH₃⁺).



	n of OH ⁻	n of CH ₂ NH ₃ ⁺	n of CH ₂ NH ₂
Before	0.0200 mol (Limiting)	0.450 mol	0.500 mol
Change	-0.0200 mol	-0.0200 mol	+0.0200 mol
After	0	0.430 mol	0.520 mol

Recalculate equilibrium concentrations using NEW $[CH_2NH_3^+]_0$ and $[CH_2NH_2]_0$



	$[CH_2NH_2]$	$[CH_2NH_3^+]$	$[OH^-]$
Initial	0.520 M	0.430 M	0
Change	-y	+y	+y
Equilibrium	(0.52 - y)	(0.43 + y)	y

CAN use Approximation:

$$\frac{[CH_2NH_2]_0}{K_b} = \frac{0.520 \text{ M}}{4.38 \times 10^{-4}} = 1187 \geq 1000$$

$$K_b = \frac{[OH^-][CH_2NH_3^+]}{[CH_2NH_2]} \quad 4.38 \times 10^{-4} \approx \frac{y(0.43)}{(0.52)}$$

$$4.38 \times 10^{-4} = \frac{(y)(0.43 + y)}{(0.52 - y)} \quad 4.38 \times 10^{-4} \frac{(0.52)}{(0.43)} \approx y$$

$$y \approx 5.30 \times 10^{-4}$$

Use 0.43 in the numerator, because $(0.43 + y) \approx 0.43$ [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].

Verify that we could use Approximation:

$$\frac{[OH^-]}{[CH_2NH_2]_0} \times 100\% = \frac{5.30 \times 10^{-4} \text{ M}}{0.520 \text{ M}} \times 100\% = 0.102\% \leq 5\% \text{ (Appropriate Approximation)}$$

$[OH^-] = 5.30 \times 10^{-4} \text{ mol/L}$

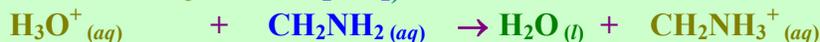
pOH = -log [OH⁻]
 pOH = -log(5.30 × 10⁻⁴)

pH = 14 - pOH
 pH = 14 - 3.28

pOH = 3.28

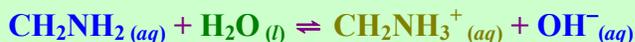
pH = 10.72

- b. 3.00 mL of 0.750 M (0.00225 mol) of $\text{HNO}_3(aq)$ is added to the buffered solution
(Complete Reaction between H_3O^+ & CH_2NH_2).



	n of H_3O^+	n of CH_2NH_2	n of CH_2NH_3^+
Before	0.00225 mol (Limiting)	0.500 mol	0.450 mol
Change	-0.00225 mol	-0.00225 mol	+0.00225 mol
After	0	0.49775 mol	0.45225 mol

Recalculate equilibrium concentrations using NEW $[\text{CH}_2\text{NH}_2]_0$ and $[\text{CH}_2\text{NH}_3^+]_0$ (neglect Δ volume)



CAN use Approximation:

$$\frac{[\text{CH}_2\text{NH}_2]_0}{K_b} = \frac{0.520 \text{ M}}{4.38 \times 10^{-4}} = 1187 \geq 1000$$

Use 0.45225 in the numerator, because $(0.45225 + z) \approx 0.45225$ [z is so small compared to 0.45225 M].

Use 0.49775 in the denominator, because $(0.49775 - z) \approx 0.49775$ [z is so small compared to 0.49775 M].

	$[\text{CH}_2\text{NH}_2]$	$[\text{CH}_2\text{NH}_3^+]$	$[\text{OH}^-]$
Initial	0.49775 M	0.45225 M	0
Change	-z	+z	+z
Equilibrium	$(0.49775 - z)$	$(0.45225 + z)$	z

$$K_b = \frac{[\text{OH}^-][\text{CH}_2\text{NH}_3^+]}{[\text{CH}_2\text{NH}_2]} \quad 4.38 \times 10^{-4} \approx \frac{z(0.45225)}{(0.49775)}$$

$$4.38 \times 10^{-4} = \frac{(y)(0.45225 + z)}{(0.49775 - z)} \quad 4.38 \times 10^{-4} \frac{(0.49775)}{(0.45225)} \approx z$$

Verify that we could use Approximation:

$$\frac{[\text{OH}^-]}{[\text{CH}_2\text{NH}_2]_0} \times 100\% = \frac{4.82 \times 10^{-4} \text{ M}}{0.49775 \text{ M}} \times 100\% = 0.0968\% \leq 5\% \text{ (Appropriate Approximation)}$$

$$[\text{OH}^-] = 4.82 \times 10^{-4} \text{ mol/L}$$

$$\text{pOH} = -\log [\text{OH}^-]$$

$$\text{pOH} = -\log(4.82 \times 10^{-4})$$

$$\text{pOH} = 3.32$$

$$\text{pH} = 14 - \text{pOH}$$

$$\text{pH} = 14 - 3.28$$

$$\text{pH} = 10.68$$

- c. Contrast the pH's of the above two additions against the same additions to 1.00 L of water.

- i. 0.0200 mol of KOH is added to 1.00 L of water

$$\text{pOH} = -\log [\text{OH}^-]$$

$$\text{pOH} = -\log(0.0200)$$

$$\text{pOH} = 1.70$$

$$\text{pH} = 14 - \text{pOH}$$

$$\text{pH} = 14 - 1.70$$

$$\text{pH} = 12.30$$

Adding the 0.0200 mol of KOH to buffered solution.

pH changes from 10.69 to 10.72

- ii. 3.00 mL of 0.750 M (0.00225 mol) of $\text{HNO}_3(aq)$ is added to 1.00 L of water (neglect Δ volume).

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log(0.00225)$$

$$\text{pH} = 2.65$$

Adding the 0.00225 mol of HNO_3 to buffered solution.

pH changes from 10.69 to 10.68

Assignment

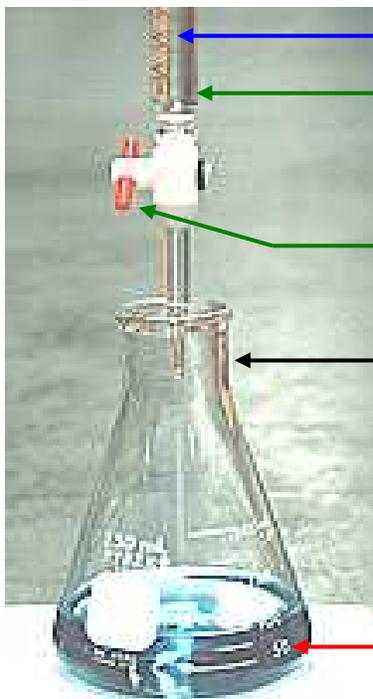
17.2 pg. 604 #1, 5 and 6

17.3: A Closer Look at Acid-Base Titrations

pH Curve: - a graph that shows the how the pH changes as the titration proceeds (as titrant is to the analyzed).

Titration: - 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



Titrant: - the solution of known concentration.

Buret: - a precise apparatus to deliver the titrant.
- the volume of the titrant added is read by subtracting the final volume and the initial volume.

Buret Valve: - can be adjusted to let one drop out at a time.

Erlenmeyer Flask: - a container commonly uses to hold the analyte. (Narrow mouth prevents splash and spillage.)

Analyte: - the solution of an unknown concentration.
- the exact volume is usually delivered by a pipet.

Acid-Base Titration: - 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.

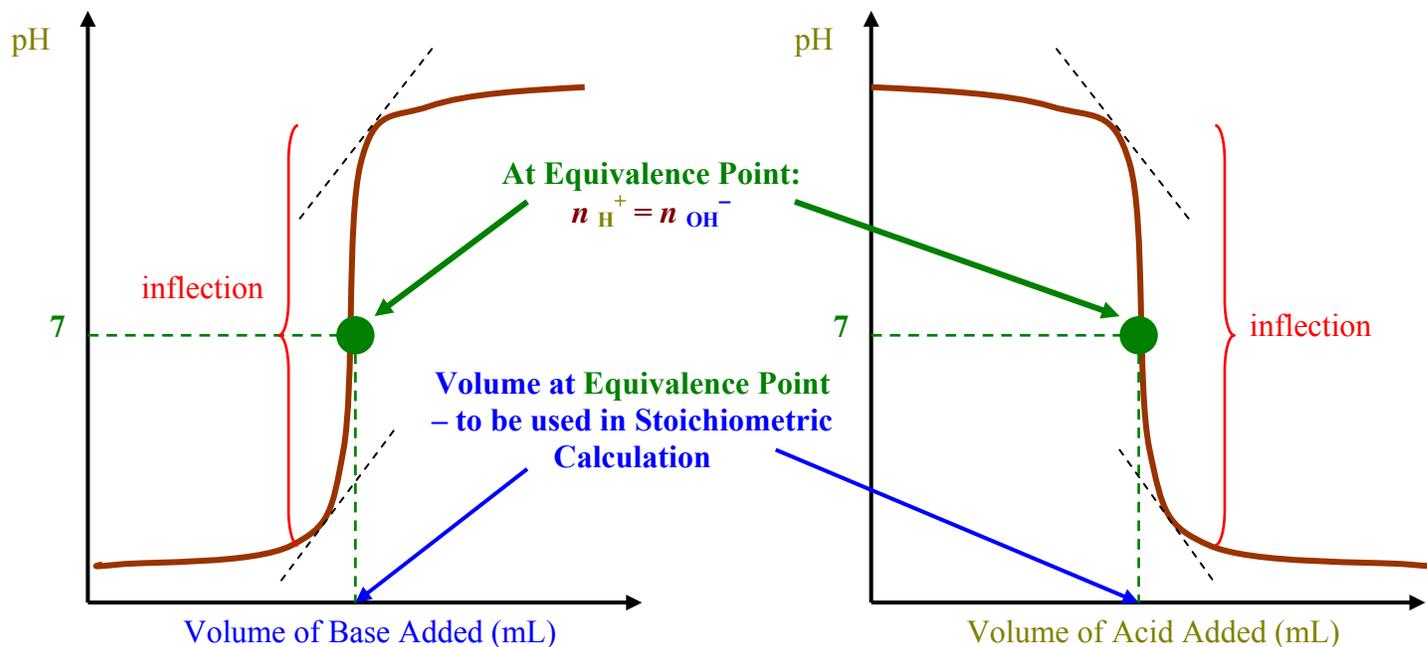
Indicator: - a chemical that changes colour due to the pH of the solution (more in the next section).

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.

1. Titration Between Strong Acids and Strong Base: - **Equivalence Point** always occur at **pH = 7**.

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

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



Example 1: Calculate the pH when 30.0 mL of 0.100 M of $\text{HCl}_{(aq)}$ is titrated with 0.200 M of $\text{KOH}_{(aq)}$ at:

- 0 mL of $\text{KOH}_{(aq)}$ added.
- 5.00 mL of $\text{KOH}_{(aq)}$ added.
- 15.00 mL of $\text{KOH}_{(aq)}$ added.
- 20.00 mL of $\text{KOH}_{(aq)}$ added.

a. At 0 mL of $\text{KOH}_{(aq)}$ added, the pH will be solely based on the $[\text{HCl}]$ in the flask:



$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log(0.100)$$

$$\text{pH} = 1.00$$

b. At 5.00 mL of $\text{KOH}_{(aq)}$ added: (Before Stoichiometric Point)



	n of H_3O^+	n of OH^-
Before Change	(0.100 mol/L)(30.00 mL) = 3.00 mmol	(0.200 mol/L)(5.00 mL) = 1.00 mmol (LR)
	- 1.00 mmol	- 1.00 mmol
After	2.00 mmol	0.00 mmol

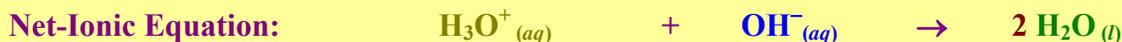
$$[\text{H}_3\text{O}^+] = \frac{n_{\text{H}_3\text{O}^+}}{\text{Total Volume}} = \frac{2.00 \text{ mmol}}{(30.00 \text{ mL} + 5.00 \text{ mL})} = 0.05714 \text{ mol/L}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log(0.05714)$$

$$\text{pH} = 1.24$$

(pH's results from similar Calculations with other volumes before the stoichiometric point is listed on the next page.)

c. At 15.00 mL of KOH_(aq) added: (Stoichiometric Point)



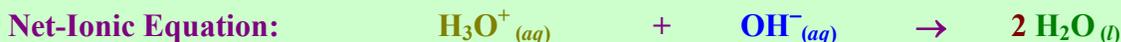
	n of H_3O^+	n of OH^-
Before	$(0.100 \text{ mol/L})(30.00 \text{ mL}) = 3.00 \text{ mmol}$	$(0.200 \text{ mol/L})(15.00 \text{ mL}) = 3.00 \text{ mmol}$
Change	$- 3.00 \text{ mmol}$	$- 3.00 \text{ mmol}$
After	0.00 mmol	0.00 mmol

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.00 \times 10^{-7} \text{ mol/L}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log(1.00 \times 10^{-7})$$

$$\text{pH} = 7.00$$

d. At 20.00 mL of KOH_(aq) added: (After Stoichiometric Point)



	n of H_3O^+	n of OH^-
Before	$(0.100 \text{ mol/L})(30.00 \text{ mL}) = 3.00 \text{ mmol}$ (Limiting Reagent)	$(0.200 \text{ mol/L})(20.00 \text{ mL}) = 4.00 \text{ mmol}$
Change	$- 3.00 \text{ mmol}$	$- 3.00 \text{ mmol}$
After	0.00 mmol	1.00 mmol

$$[\text{OH}^-] = \frac{n_{\text{OH}^-}}{\text{Total Volume}} = \frac{1.00 \text{ mmol}}{(30.00 \text{ mL} + 20.00 \text{ mL})} = 0.0200 \text{ mol/L}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log(0.0200)$$

$$\text{pOH} = 1.70$$

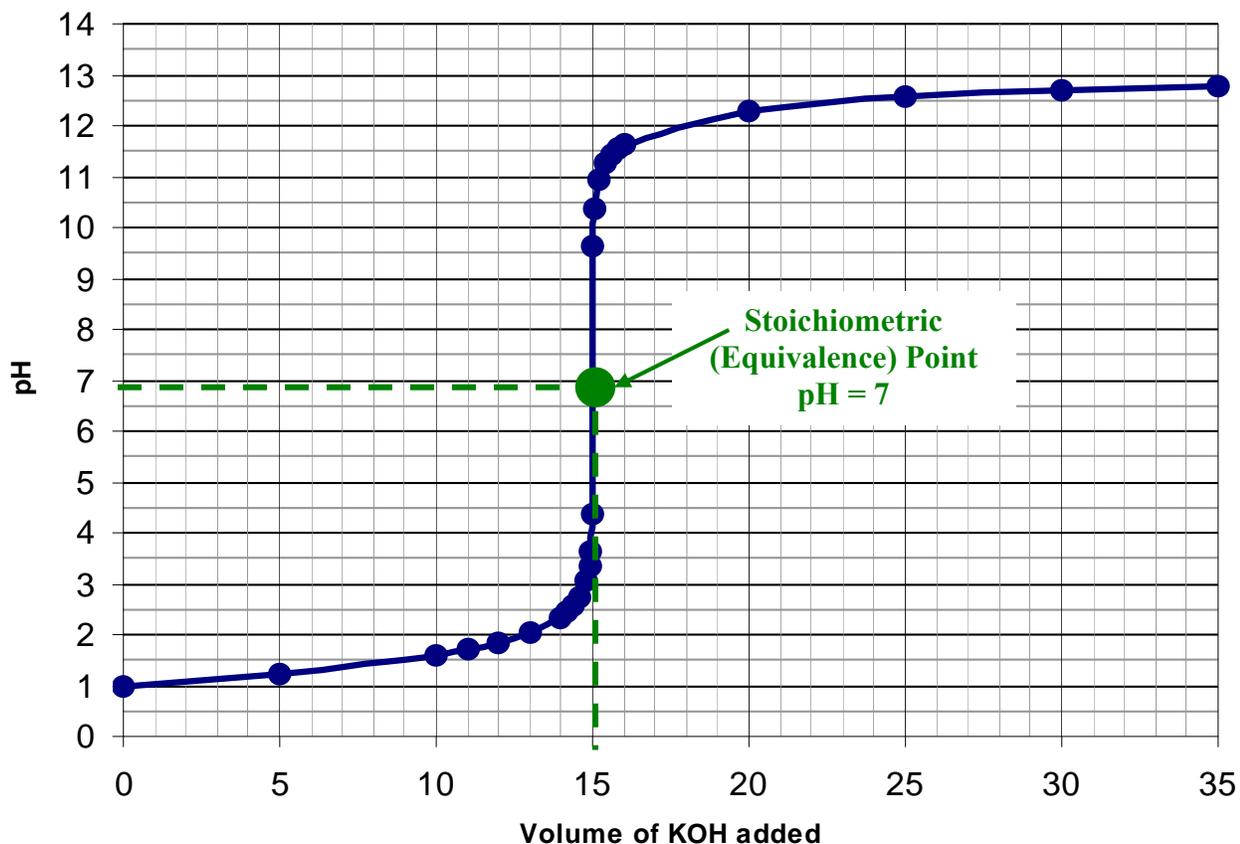
$$\text{pH} = 14 - \text{pOH}$$

$$\text{pH} = 12.30$$

(pH's results from similar Calculations with other volumes after the stoichiometric point is listed below.)

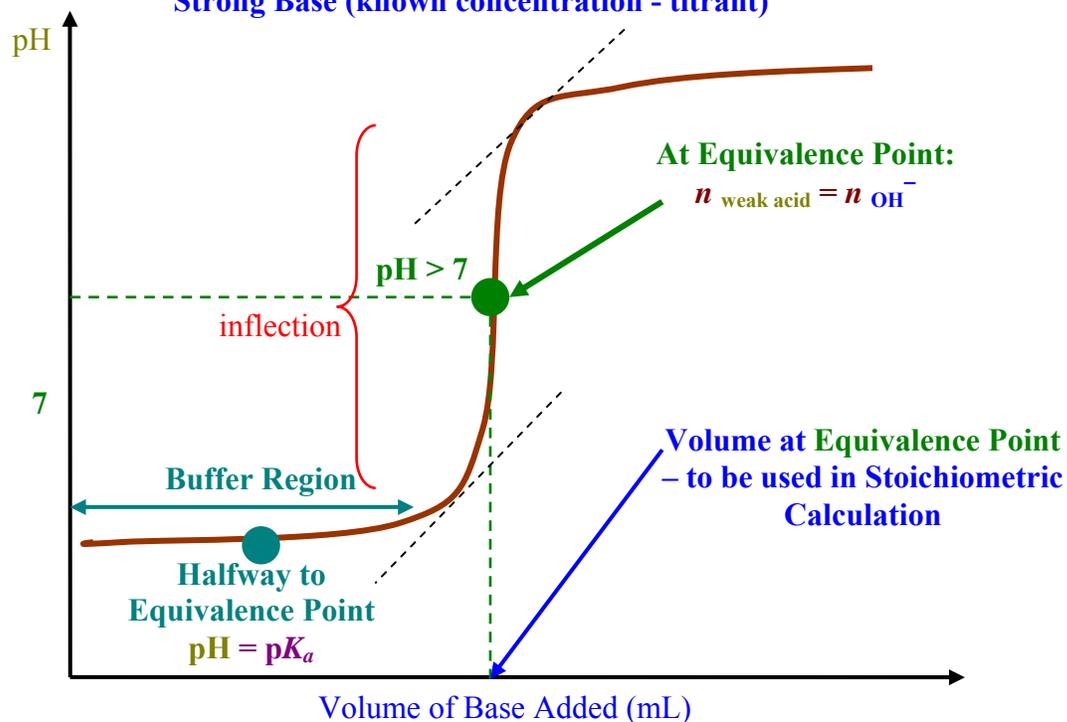
pH of 30.0 mL of 0.100 M HCl_(aq) titrated by 0.200 M of KOH_(aq)

Volume of KOH added	pH	Volume of KOH added	pH	Volume of KOH added	pH
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

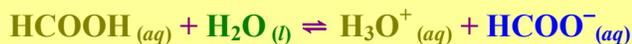
2. Titration Between Weak Acids and Strong Base: - Equivalence Point always occur at $\text{pH} > 7$.

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



- Example 2:** Calculate the pH when 30.0 mL of 0.100 M of $\text{HCOOH}_{(aq)}$ ($K_a = 1.8 \times 10^{-4}$) is titrated with 0.200 mol/L of $\text{KOH}_{(aq)}$ at:
- 0 mL of $\text{KOH}_{(aq)}$ added.
 - 7.50 mL of $\text{KOH}_{(aq)}$ added.
 - 15.00 mL of $\text{KOH}_{(aq)}$ added.
 - 20.00 mL of $\text{KOH}_{(aq)}$ added.

a. At 0 mL of $\text{KOH}_{(aq)}$ added, the pH will be calculated the weak acid dissociation in the flask:



	[HCOOH]	[H ₃ O ⁺]	[HCOO ⁻]
Initial	0.100 M	0	0 M
Change	-x	+x	+x
Equilibrium	(0.1 - x)	x	x

CANNOT use Approximation:

$$\frac{[\text{HCOOH}]_0}{K_a} = \frac{0.100 \text{ M}}{1.8 \times 10^{-4}} = 555.6 < 1000$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{HCOO}^-]}{[\text{HCOOH}]} \quad 1.8 \times 10^{-4} = \frac{(x)(x)}{(0.1-x)} = \frac{x^2}{(0.1-x)}$$

$$[\text{H}_3\text{O}^+] = x = 0.0042 \text{ mol/L}$$

```

solve(X^2/(.1-X)-
1.8E-4,X,0,(0.0.
1))
.0041535952
    
```

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log(0.042)$$

pH = 2.38

b. At 7.50 mL of $\text{KOH}_{(aq)}$ added: (Before Stoichiometric Point: at Halfway to Equivalence Point)

Chemical Species Present: HCOOH , K^+ , OH^- , H_2O
 SA SB A/B



	n of HCOOH	n of OH ⁻	n of HCOO ⁻
Before	(0.100 mol/L)(30.00 mL) = 3.00 mmol	(0.200 mol/L)(7.50 mL) = 1.50 mmol (LR)	0 mmol
Change	- 1.50 mmol	- 1.50 mmol	+ 1.50 mmol
After	1.50 mmol	0 mmol	1.50 mmol

$$[\text{HCOOH}] = \frac{n_{\text{HCOOH}}}{\text{Total Volume}} = \frac{1.50 \text{ mmol}}{(30.00 \text{ mL} + 7.50 \text{ mL})} = 0.0400 \text{ mol/L}$$

$$[\text{HCOO}^-] = \frac{n_{\text{HCOO}^-}}{\text{Total Volume}} = \frac{1.50 \text{ mmol}}{(30.00 \text{ mL} + 7.50 \text{ mL})} = 0.0400 \text{ mol/L}$$

$[\text{HCOOH}] = [\text{HCOO}^-]$
 $\text{pH} \approx \text{p}K_a$
 (Max Buffer Capacity)

After all the OH^- is used up, the resulting solution follows the regular weak acid dissociation.



	[HCOOH]	[H ₃ O ⁺]	[HCOO ⁻]
Initial	0.0400 M	0	0.0400 M
Change	-x	+x	+x
Equilibrium	(0.04 - x)	x	(0.04 + x)

CANNOT use Approximation:

$$\frac{[\text{HCOOH}]_0}{K_a} = \frac{0.0400 \text{ M}}{1.8 \times 10^{-4}} = 222.22 < 1000$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{HCOO}^-]}{[\text{HCOOH}]} \quad 1.8 \times 10^{-4} = \frac{(x)(0.04+x)}{(0.04-x)}$$

```

solve(X(0.04+X)/
(0.04-X)-1.8E-4,
X,0,(0.0.04))
1.784015157E-4
    
```

$$[\text{H}_3\text{O}^+] = x = 1.8 \times 10^{-4} \text{ mol/L} \quad \text{pH} = \text{p}K_a = -\log(1.8 \times 10^{-4})$$

(pH's results from similar Calculations with other volumes before the stoichiometric point is listed on page 306.)

pH = 3.75

c. At 15.00 mL of KOH_(aq) added: **(Stoichiometric Point)**

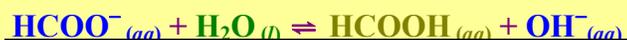
Chemical Species Present: HCOOH, K⁺, OH⁻, H₂O
SA SB A/B

Net-Ionic Equation: HCOOH_(aq) + OH⁻_(aq) → H₂O_(l) + HCOO⁻_(aq)

	n of HCOOH	n of OH ⁻	n of HCOO ⁻
Before	(0.100 mol/L)(30.00 mL) = 3.00 mmol	(0.200 mol/L)(15.00 mL) = 3.00 mmol	0 mmol
Change	- 3.00 mmol	- 3.00 mmol	+ 3.00 mmol
After	0 mmol	0 mmol	3.00 mmol

$$[\text{HCOO}^-] = \frac{n_{\text{HCOO}^-}}{\text{Total Volume}} = \frac{3.00 \text{ mmol}}{(30.00 \text{ mL} + 15.00 \text{ mL})} = 0.0667 \text{ mol/L}$$

At Stoichiometric Point, after all the OH⁻ and HCOOH are used up, the resulting solution follows the regular weak base dissociation.



	[HCOO ⁻]	[HCOOH]	[OH ⁻]
Initial	0.0667 M	0	0 M
Change	-x	+x	+x
Equilibrium	(0.0667 - x)	x	x

CAN use Approximation:

$$\frac{[\text{HCOO}^-]_0}{K_b} = \frac{0.0667 \text{ M}}{5.556 \times 10^{-11}} = 1.2 \times 10^9 \geq 1000$$

Use 0.0667 in the denominator, because (0.0667 - x) ≈ 0.03667 [x is so small compared to 0.0667 M].

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-4}} = 5.556 \times 10^{-11}$$

$$K_b = 5.556 \times 10^{-11} = \frac{[\text{HCOOH}][\text{OH}^-]}{[\text{HCOO}^-]}$$

$$5.556 \times 10^{-11} = \frac{(x)(x)}{(0.0667 - x)} \approx \frac{x^2}{0.0667}$$

$$[\text{OH}^-] = x = 1.92 \times 10^{-6} \text{ mol/L}$$

$$\text{pOH} = -\log(1.92 \times 10^{-6}) = 5.72$$

$$\text{pH} = 14 - \text{pOH} = 14 - 5.72$$

$$\text{pH} = 8.28$$

d. At 20.00 mL of KOH_(aq) added: **(After Stoichiometric Point)**

Chemical Species Present: HCOOH, K⁺, OH⁻, H₂O
SA SB A/B

Net-Ionic Equation: HCOOH_(aq) + OH⁻_(aq) → H₂O_(l) + HCOO⁻_(aq)

	n of HCOOH	n of OH ⁻
Before	(0.100 mol/L)(30.00 mL) = 3.00 mmol (LR)	(0.200 mol/L)(20.00 mL) = 4.00 mmol
Change	- 3.00 mmol	- 3.00 mmol
After	0 mmol	1.00 mmol

After all the HCOOH is used up, the resulting solution has the following major species.

Chemical Species Present: K⁺, OH⁻, H₂O
SB A/B

$$[\text{OH}^-] = \frac{n_{\text{OH}^-}}{\text{Total Volume}} = \frac{1.00 \text{ mmol}}{(30.00 \text{ mL} + 20.00 \text{ mL})} = 0.0200 \text{ mol/L} \quad \text{pOH} = -\log(0.0200) = 1.70$$

$$\text{pH} = 14 - \text{pOH} = 14 - 1.70$$

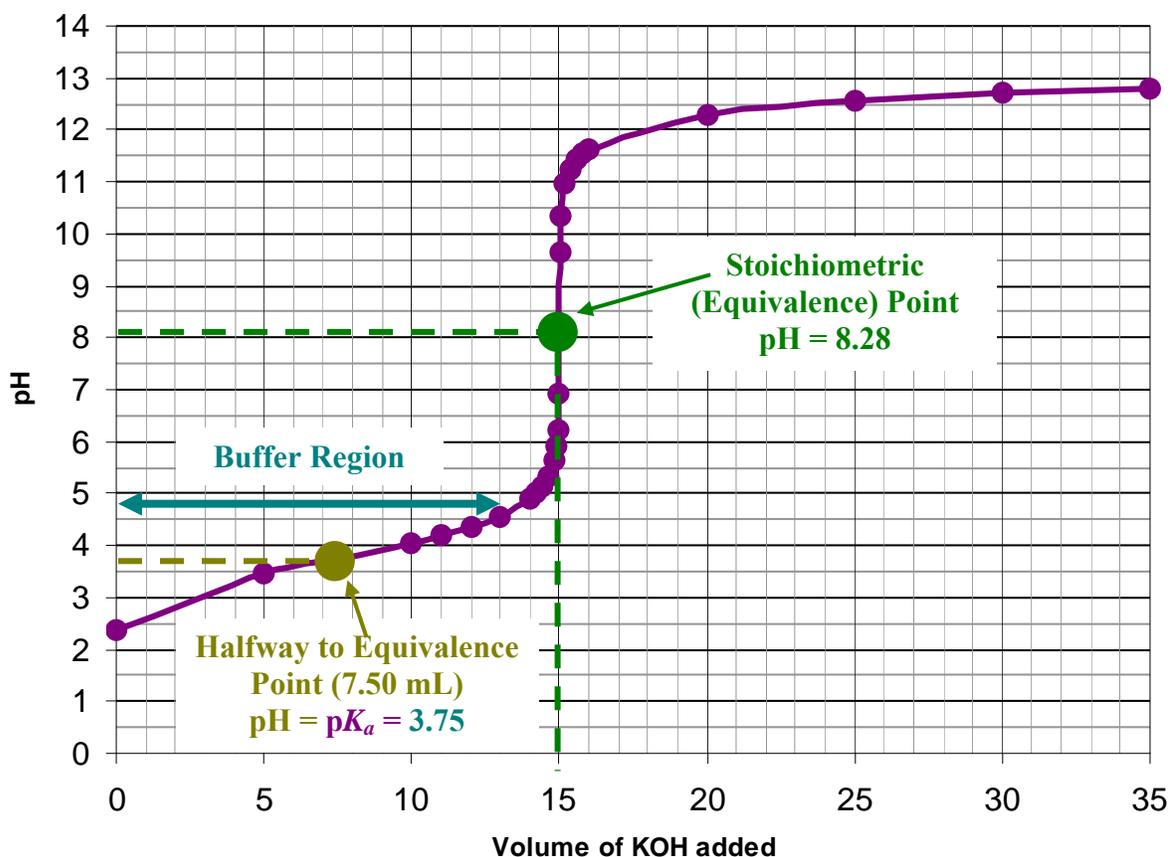
$$\text{pH} = 12.30$$

(pH's results from similar Calculations with other volumes after the stoichiometric point is listed on the next page.)

pH of 30.0 mL of 0.100 M HCOOH_(aq) titrated by 0.200 M of KOH_(aq)

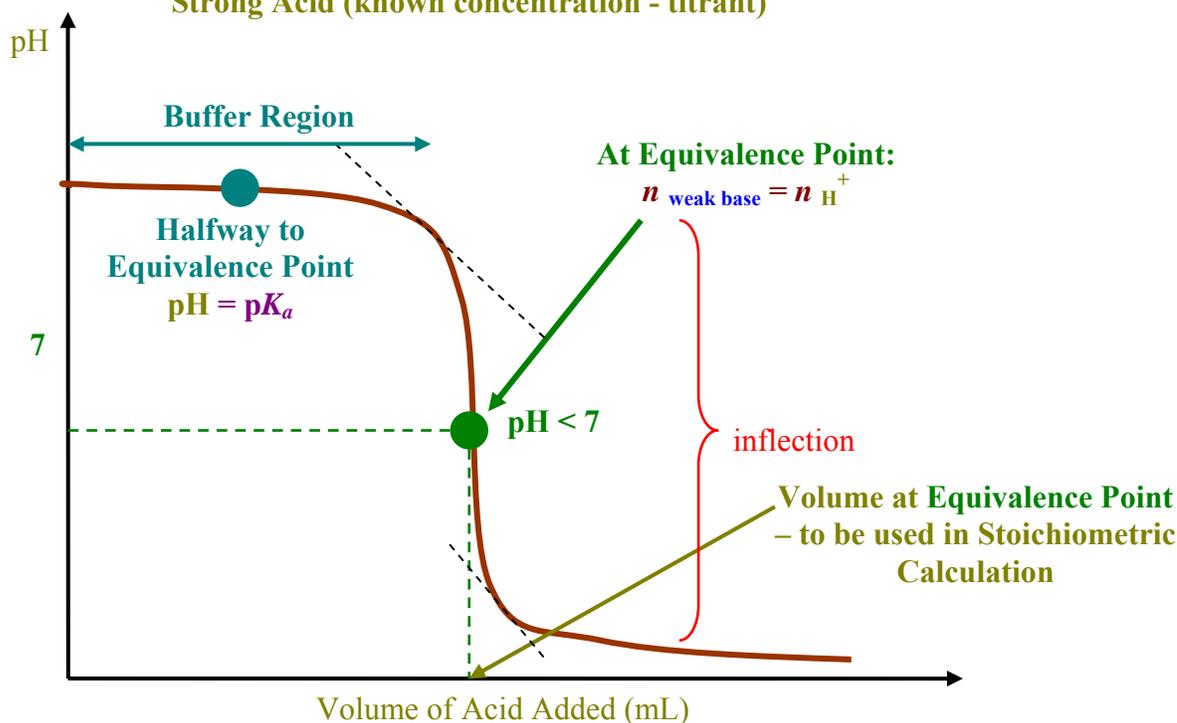
Volume of KOH added	pH	Volume of KOH added	pH	Volume of KOH added	pH
0.00 mL	2.38	14.40 mL	5.13	15.20 mL	10.95
5.00 mL	3.45	14.60 mL	5.31	15.40 mL	11.25
7.50 mL (Halfway to Equivalence)	3.75	14.80 mL	5.62	15.60 mL	11.42
10.00 mL	4.05	14.90 mL	5.91	15.80 mL	11.54
11.00 mL	4.19	14.95 mL	6.22	16.00 mL	11.64
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 titrated by 0.200 M of KOH



3. Titration Between Weak Bases and Strong Acid: - Equivalence Point always occur at $\text{pH} < 7$.

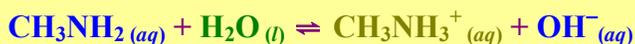
Weak Base (unknown concentration with known volume - analyte) titrated with Strong Acid (known concentration - titrant)



Example 3: Calculate the pH when 30.0 mL of 0.100 M of $\text{CH}_3\text{NH}_2(aq)$ ($K_b = 4.38 \times 10^{-4}$) is titrated with 0.200 mol/L of $\text{HCl}(aq)$ at:

- 0 mL of $\text{HCl}(aq)$ added.
- 7.50 mL of $\text{HCl}(aq)$ added.
- 15.00 mL of $\text{HCl}(aq)$ added.
- 20.00 mL of $\text{HCl}(aq)$ added.

a. At 0 mL of $\text{HCl}(aq)$ added, the pH will be calculated the weak base dissociation in the flask:



	$[\text{CH}_3\text{NH}_2]$	$[\text{CH}_3\text{NH}_3^+]$	$[\text{OH}^-]$
Initial	0.100 M	0	0 M
Change	-x	+x	+x
Equilibrium	(0.1 - x)	x	x

CANNOT use Approximation:

$$\frac{[\text{CH}_3\text{NH}_2]_0}{K_b} = \frac{0.100 \text{ M}}{4.38 \times 10^{-4}} = 228.3 < 1000$$

$$K_b = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]} \quad 4.38 \times 10^{-4} = \frac{(x)(x)}{(0.1-x)} = \frac{x^2}{(0.1-x)}$$

$$[\text{OH}^-] = x = 0.00640 \text{ mol/L}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log(0.00640) = 2.19$$

$$\text{pH} = 14 - \text{pOH} = 14 - 2.19$$

```
solve(X^2/(0.1-X)
-4.38E-4, X, 0, 0,
0.1)
.0064027793
```

$$\text{pH} = 11.81$$

At Stoichiometric Point, after all the H_3O^+ and CH_3NH_2 are used up, the resulting solution follows the regular weak acid dissociation.



	$[\text{CH}_3\text{NH}_3^+]$	$[\text{CH}_3\text{NH}_2]$	$[\text{H}_3\text{O}^+]$
Initial	0.0667 M	0	0 M
Change	-x	+x	+x
Equilibrium	(0.0667 - x)	x	x

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.38 \times 10^{-4}} \quad K_a = 2.28 \times 10^{-11} = \frac{[\text{CH}_3\text{NH}_2][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{NH}_3^+]}$$

$$2.28 \times 10^{-11} = \frac{(x)(x)}{(0.0667 - x)} \approx \frac{x^2}{0.0667}$$

$$[\text{H}_3\text{O}^+] = x = 1.23 \times 10^{-6} \text{ mol/L} \quad \text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.23 \times 10^{-6})$$

pH = 5.91

CAN use Approximation:

$$\frac{[\text{CH}_3\text{NH}_3^+]_0}{K_a} = \frac{0.0667 \text{ M}}{2.28 \times 10^{-11}} = 2.9 \times 10^9 \geq 1000$$

Use 0.0667 in the denominator, because $(0.0667 - x) \approx 0.03667$ [x is so small compared to 0.0667 M].

d. At 20.00 mL of $\text{HCl}_{(aq)}$ added: (After Stoichiometric Point)

Chemical Species Present: CH_3NH_2 , H_3O^+ , Cl^- , H_2O
 SB SA A/B

Net-Ionic Equation: $\text{CH}_3\text{NH}_2_{(aq)} + \text{H}_3\text{O}^+_{(aq)} \rightarrow \text{H}_2\text{O}_{(l)} + \text{CH}_3\text{NH}_3^+_{(aq)}$

	n of CH_3NH_2	n of H_3O^+
Before	(0.100 mol/L)(30.00 mL) = 3.00 mmol (LR)	(0.200 mol/L)(20.00 mL) = 4.00 mmol
Change	- 3.00 mmol	- 3.00 mmol
After	0 mmol	1.00 mmol

After all the CH_3NH_2 is used up, the resulting solution has the following major species.

Chemical Species Present: Cl^- , H_3O^+ , H_2O
 SA A/B

$$[\text{H}_3\text{O}^+] = \frac{n_{\text{H}_3\text{O}^+}}{\text{Total Volume}} = \frac{1.00 \text{ mmol}}{(30.00 \text{ mL} + 20.00 \text{ mL})} = 0.0200 \text{ mol/L}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(0.0200)$$

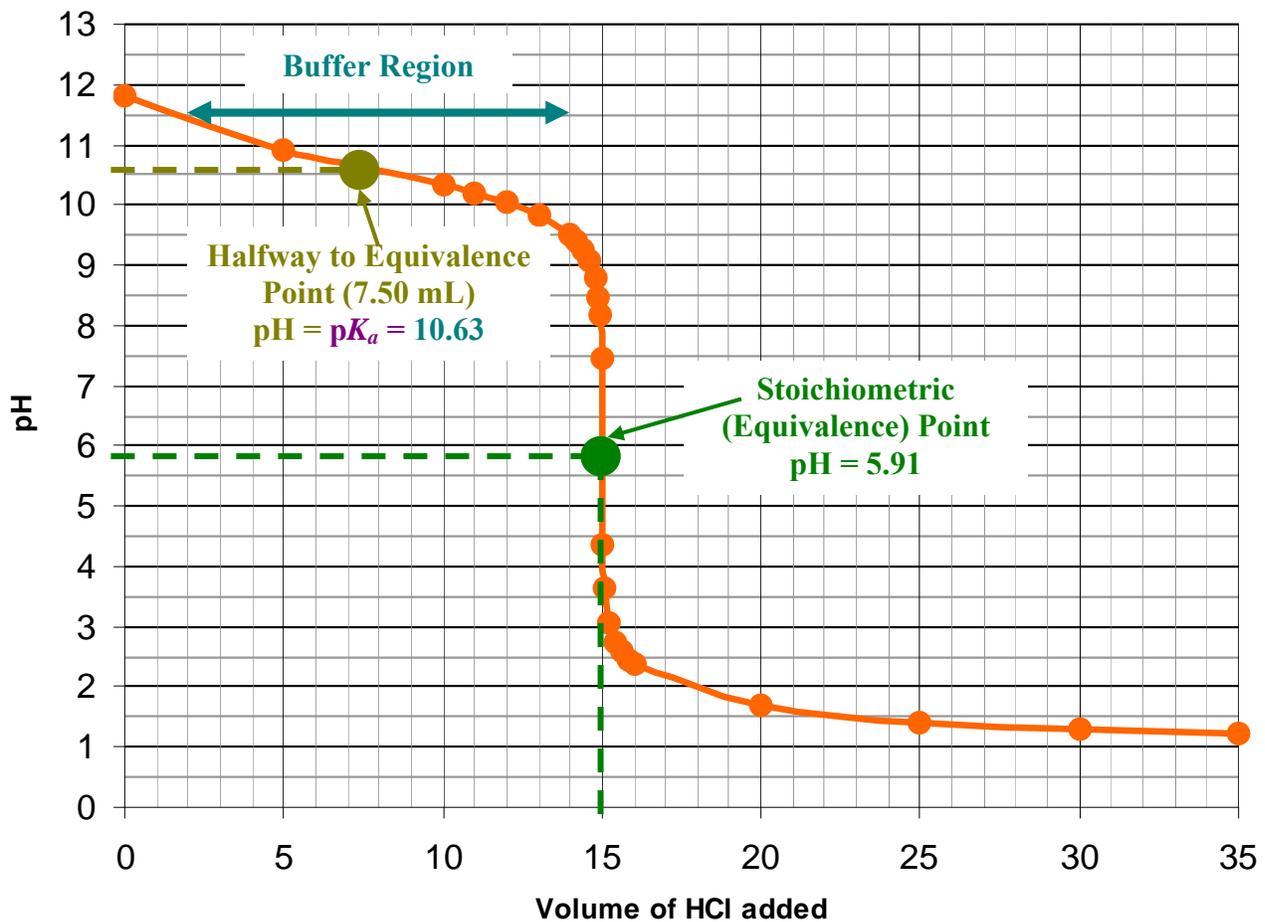
pH = 1.70

(pH's results from similar Calculations with other volumes after the stoichiometric point is listed below.)

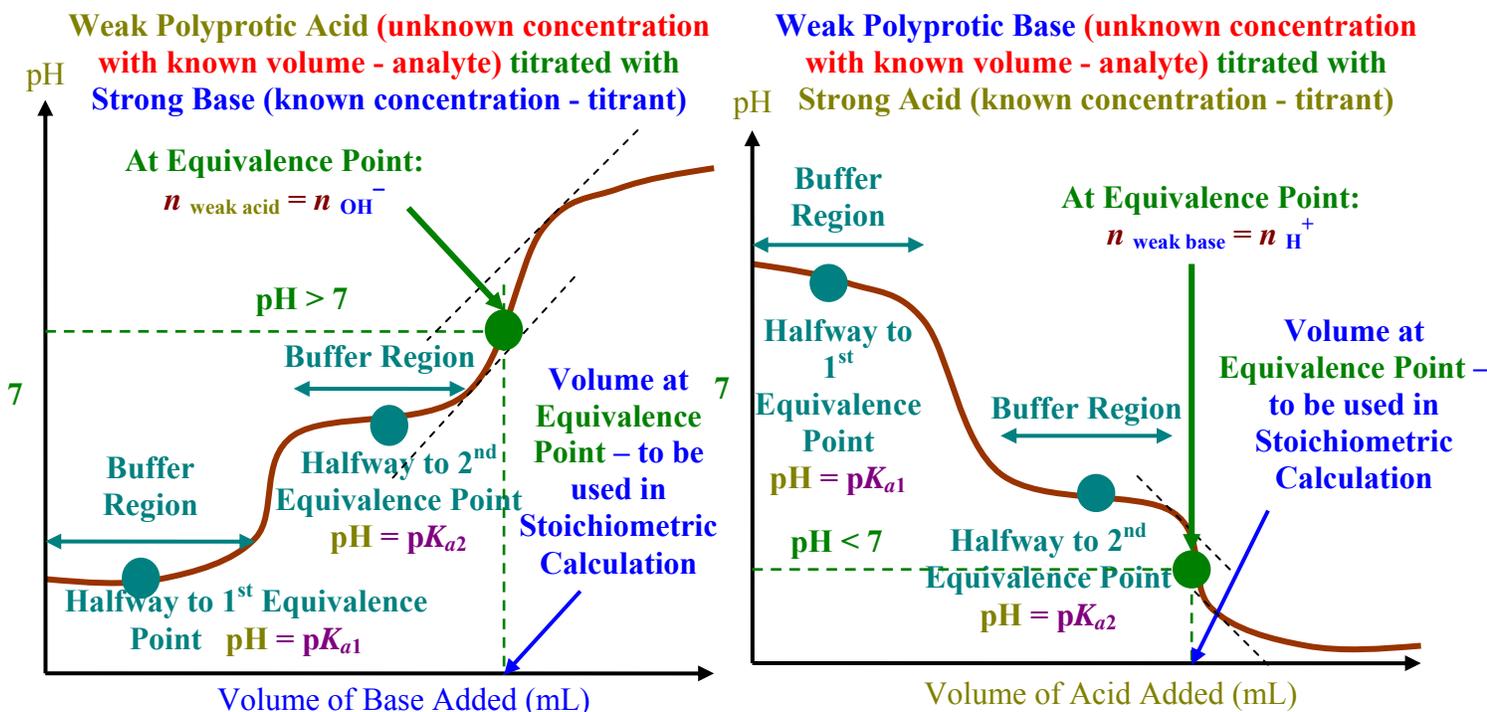
pH of 30.0 mL of 0.100 M $\text{CH}_3\text{NH}_2_{(aq)}$ titrated by 0.200 M of $\text{HCl}_{(aq)}$

Volume of HCl added	pH	Volume of HCl added	pH	Volume of HCl added	pH
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

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



4. **Titration Between Strong Acid/Bases and Polyprotic Acid/Base:** - there are multiple equivalence points.
 - the last equivalence point indicates the stoichiometric volume.



Example 4: Calculate the concentration of 10.00 mL of $\text{Na}_2\text{S}_{(aq)}$ is titrated with 0.0350 M of $\text{HBr}_{(aq)}$ when the first and second equivalence points are at 13.34 mL and 27.88 mL respectively.

For Acid-Base Stoichiometry, do NOT write the Net-Ionic Equation. Write the Molecular Equation to do Stoichiometry. We use the second equivalence point because Na_2S can accept two protons.



$$\textcircled{1} n_{\text{HBr}} = CV = (0.0350 \text{ mol/L})(27.88 \text{ mL}) = 0.9758 \text{ mmol}$$

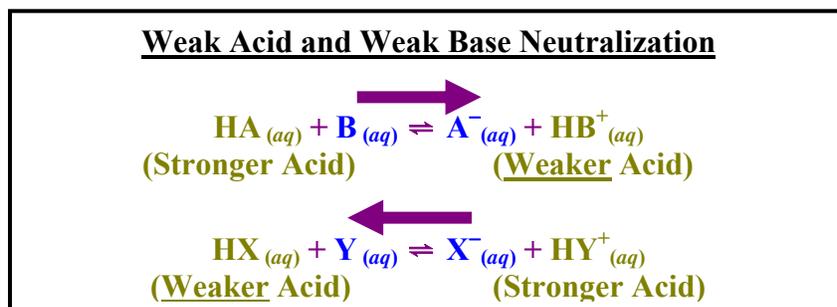
$$\textcircled{2} n_{\text{Na}_2\text{S}} = 0.9758 \text{ mmol HBr} \times \frac{1 \text{ mol Na}_2\text{S}}{2 \text{ mol HBr}} = 0.4879 \text{ mmol Na}_2\text{S}$$

$$\textcircled{3} [\text{Na}_2\text{S}] = \frac{n}{V} = \frac{0.4879 \text{ mmol}}{10.0 \text{ mL}} = 0.04879 \text{ mol/L}$$

$$[\text{Na}_2\text{S}] = 0.0488 \text{ mol/L}$$

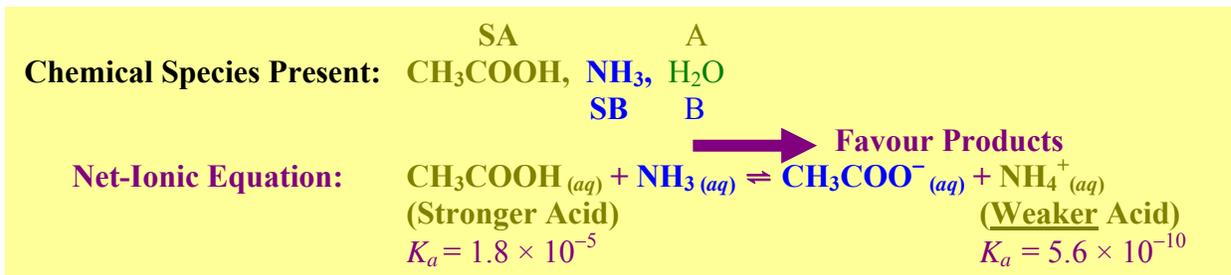
Neutralization Reactions Between Weak Acids and Weak Bases

- The reaction is NOT one way, but in equilibrium.
- When writing out the equilibrium system, **list all major species first (Do NOT Break up any Weak Acids and Weak Bases)**. Then, reacts the Strongest Acid (SA – donates a proton) and the Strongest Base (SB – accepts a proton) from the list.
- 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.)

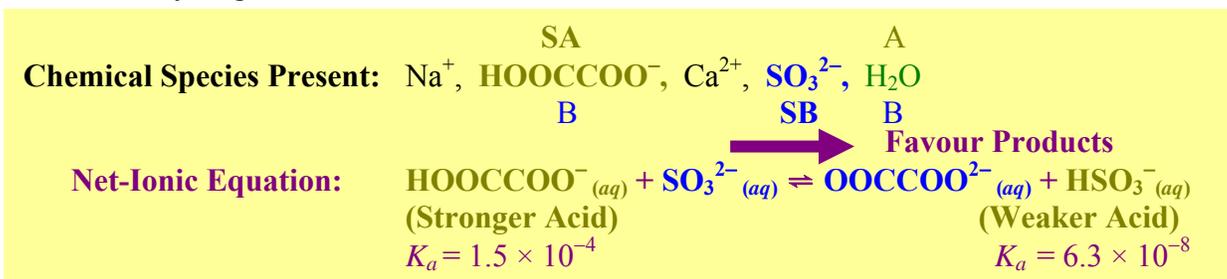


Example 5: Write the net-ionic equation for the following neutralizations. Indicate the side of the equilibrium system that is favoured.

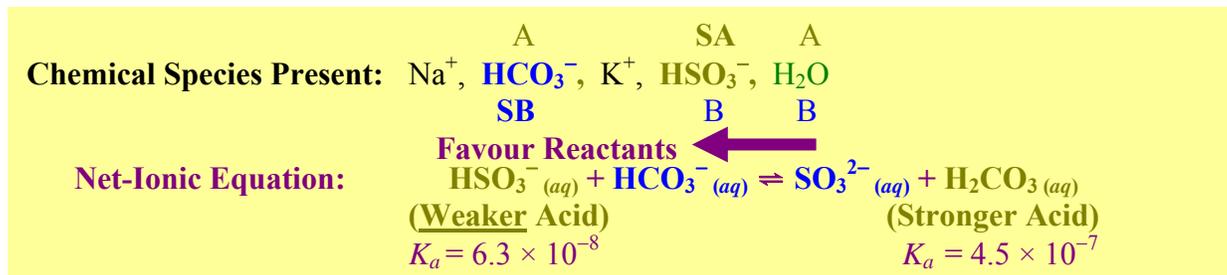
- a. Acetic Acid reacts with Ammonia



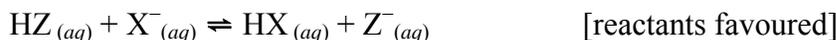
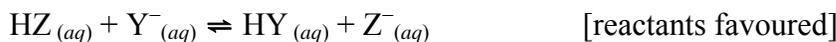
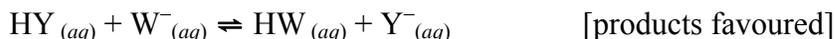
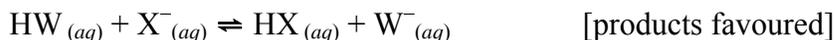
b. Sodium Hydrogen Oxalate reacts with Calcium Sulfite



c. Sodium Hydrogen Carbonate reacts with Potassium Hydrogen Sulfite

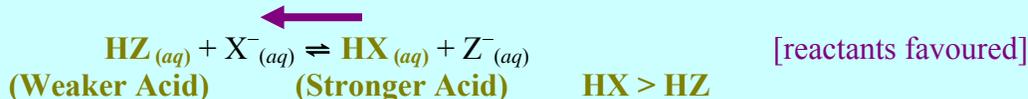
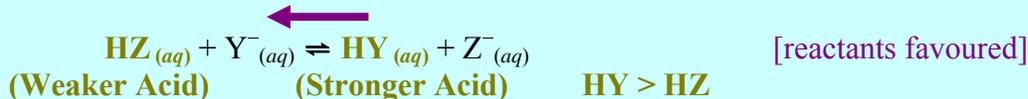
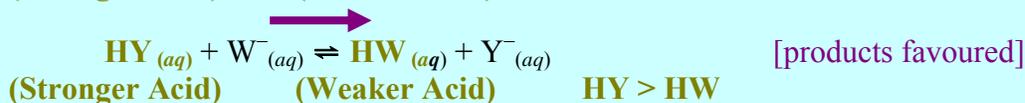
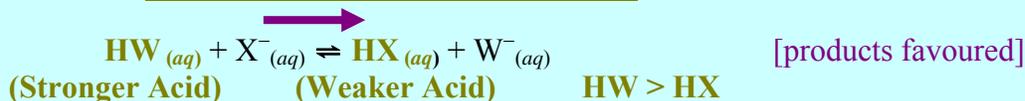


Example 6: Four different weak acids are reacted with various conjugate bases, and the results are recorded as follow.



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

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



Putting the inequalities together, we obtain in order of increasing acid strengths:



Assignment

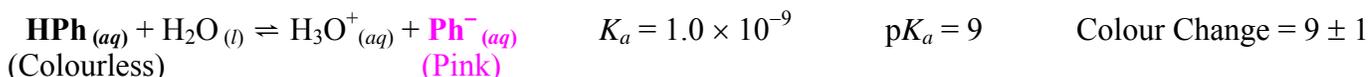
17.3 pg. 604 #17 to 20a

17.4: Acid-Base Indicators

Acid-Base Indicators: - 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 indicator (HIn) has a different colour than its basic form (In⁻).

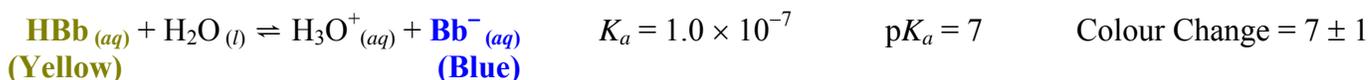
Example: Phenolphthalein (HPh_(aq)/Ph⁻_(aq)) changes colours from colourless to pink at a pH range of 8.0 to 10.0. At its **mid-range (9.0 – average of 8.0 and 10.0)**, the colour would be **light pink (colourless + pink)**.



At pH ≤ 9, phenolphthalein is colourless.

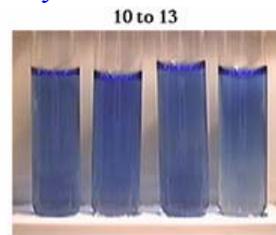
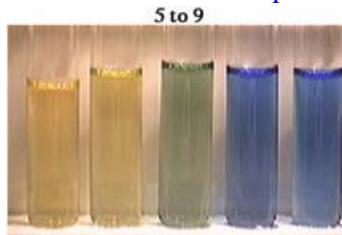
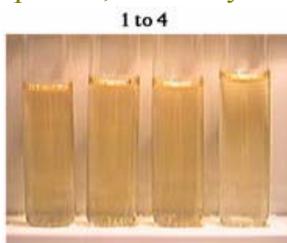
At pH ≥ 10, phenolphthalein is pink.

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)**.



At pH ≤ 6, bromothymol blue is yellow.

At pH ≥ 8, bromothymol blue is blue.



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	yellow
phenol red	yellow
bromocresol green	blue
phenolphthalein	colourless
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 that the pH of the rain water is **between 6.0 to 6.6**. At such pH range, **bromothymol blue would appear green**. (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

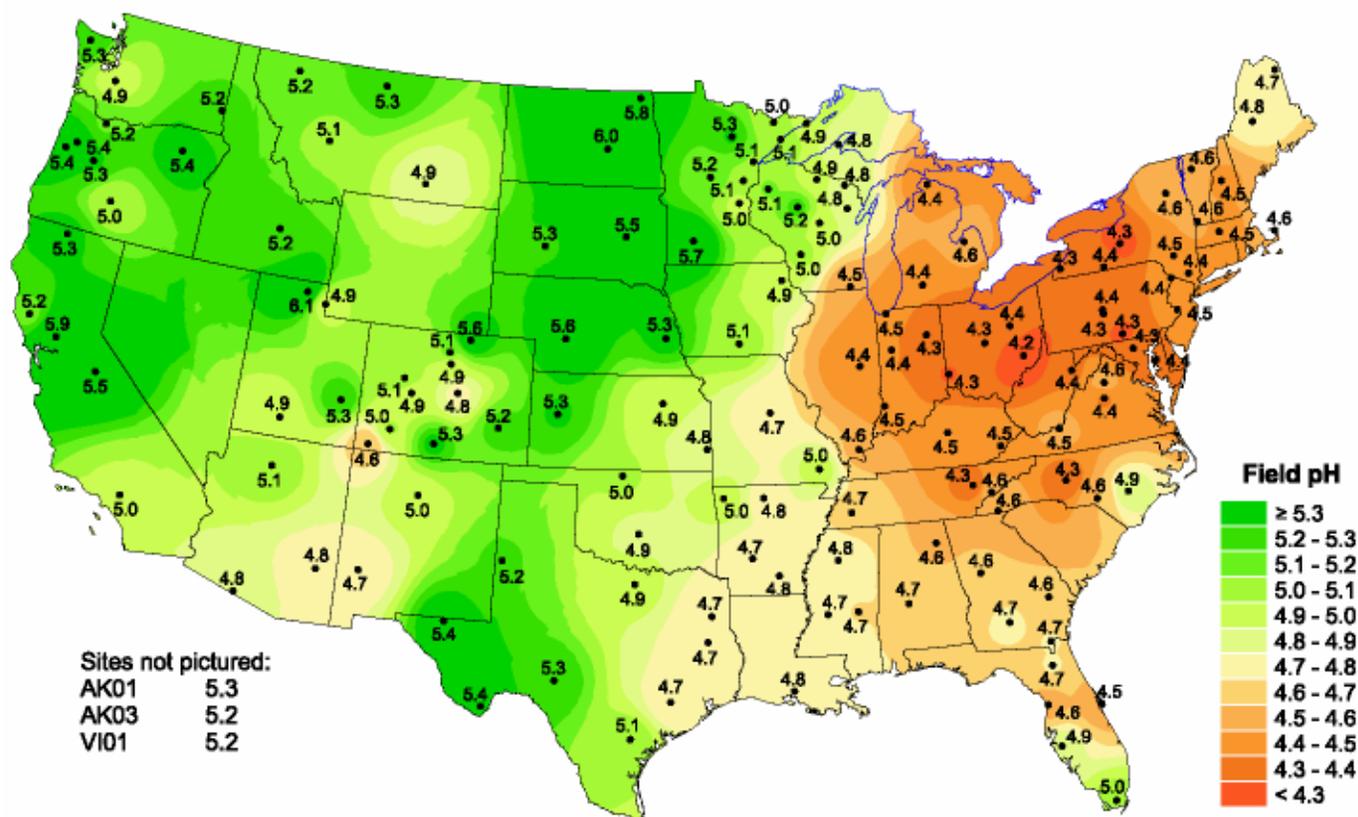
Acid Rain: - precipitation of water (rain) or (snow) that has a low pH (less than 5.0).
 - natural rain is slightly acidic due to the small amount of CO_2 in the atmosphere.



- however, the burning of fossil fuel by vehicles and industrial activities, and also emits other oxides such as $\text{NO}_2(g)$, $\text{SO}_2(g)$ and $\text{SO}_3(aq)$. 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.

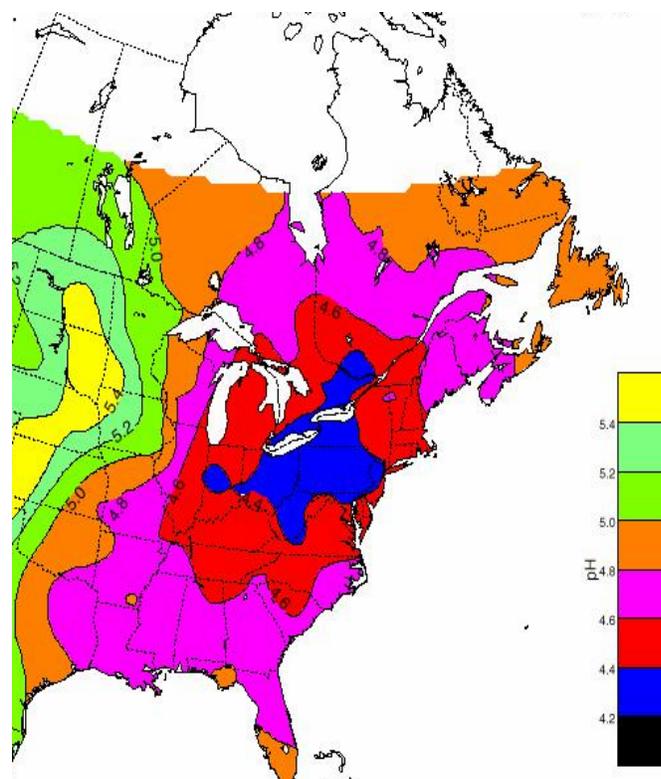
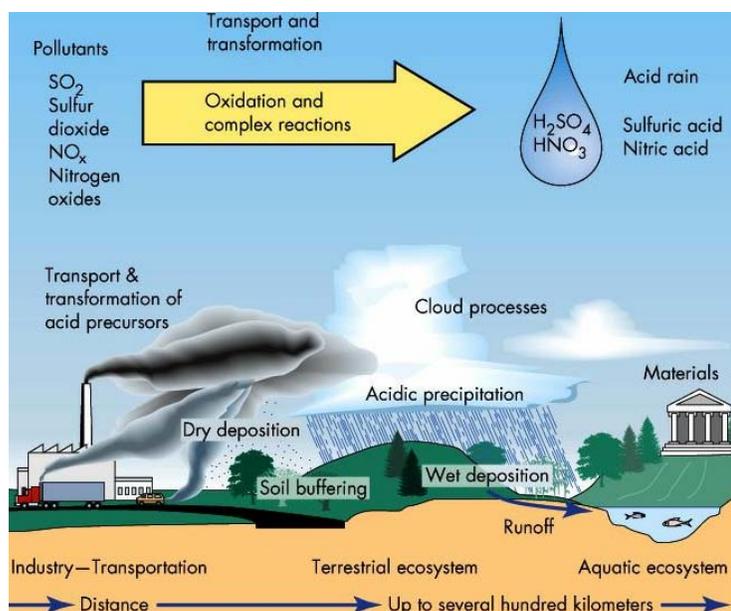


Hydrogen ion concentration as pH from measurements made at the field laboratories, 1999



National Atmospheric Deposition Program/National Trends Network
<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.



(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:

- Marine Life (especially in-land lakes and rivers) is affected greatly.** 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.
- Vegetation (including forests) can be decimated.** Since the soil acidity level are lowered, further plant growth may not be possible and the surrounding **ecosystem is destroyed** 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.

- In areas of where there is a sustain amount of humidity, acid rain can turn into **Acid Fog or Smog ($\text{SO}_2 + \text{H}_2\text{O}$) – Combination of Smoke from Coal Burning and Fog**. **Humans may experience severe 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.
- Acid deposition** (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, CaCO_3) 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 statues.



Ways to Reduce Acid Rain:

- Burn Less Fossil Fuel:** 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.
- Enact Legislation to Regulate Emissions:** 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.
- Adding Limestone** to acid lakes and rivers can raise the pH and reintroduce marine life that has been affected by acid rain.