

“A” students work
(without solutions manual)
~ 10 problems/night.

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Office Hours Th&F 2-3:30 pm

Module #17C:
Buffering and Titrations
Holding Proteins intact
By pH constant

FITCH Rules

General

- G1: Suzuki is Success
- G2: Slow me down
- G3: Scientific Knowledge is Referential
- G4: Watch out for Red Herrings
- G5: Chemists are Lazy

Chemistry

- C1: It's all about charge $E_{el} = k \left(\frac{q_1 q_2}{r_1 + r_2} \right)$
- C2: Everybody wants to “be like Mike”
- C3: Size Matters $E_{el} = k \left(\frac{q_1 q_2}{r_1 + r_2} \right)$
- C4: Still Waters Run Deep
- C5: Alpha Dogs eat first

What pH is best suited For the hydrogen bond?

(a) Front view

(b) Side view

$K_{a,Val,COOH} = 5.01 \times 10^{-3}$

$K_{a,Tyr,ROH} = 1.0 \times 10^{-10}$

Hemoglobin
Review Module 17B

Which pH (2, 7, 11) is most favorable for the formation of a hydrogen bond between Val and tyr in hemoglobin

$K_{a,Val,COOH} = 5.01 \times 10^{-3}$

$K_{a,Tyr,ROH} = 1.0 \times 10^{-10}$

$\% \text{ dissociated} = \frac{100[A_{aq}^-]}{[A_{aq}^-][H_3O_{aq}^+] + [A_{aq}^-]}$

pH	[H+]	KaCOOH 5.00E-03 %diss	Ka ROH 1.00E-10 %diss
2	1.00E-02	33.33333	1E-06
7	1.00E-07	99.998	0.09999
11	1.00E-11	100	90.90909

$\% \text{ dissociated} = \frac{100}{[H_3O_{aq}^+] + 1}$

$pH_2 = 10^{-2}$

$\% \text{ dissociatedCOOH} = \left[\frac{100}{[10^{-2}] + 5.01 \times 10^{-3}} \right] = 33.33$

How does the body maintain This pH?

Review Module 17B

<http://www.meddean.luc.edu/lumen/MedEd/MEDICINE/pulmonar/physio/pf4.htm>

How does the body maintain pH ~7?

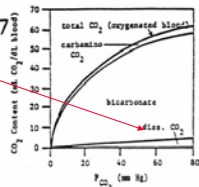
Remember it will have to constantly adjust to changes in pH
From an enormous number of chemical reactions!!!

Control is ultimately based on $CO_{2(g)}$

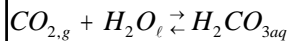
$$C_g = P_{CO_2} k_H \quad \text{Henry's law}$$

$k_H = 3.4 \times 10^{-2} \frac{\text{moles}}{L \cdot \text{atm}}$ **Respired (breathed) air $P_{CO_2} = 0.23 \text{ mm Hg}$**
Pressure increases through mechanics of lung
Aorta $P_{CO_2} = 41.8 \text{ mmHg}$

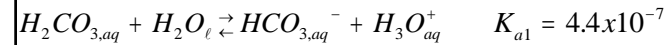
$$\left(42 \text{ mm}_{CO_2}\right) \left(\frac{1 \text{ atm}}{760 \text{ mm}}\right) \left(3.4 \times 10^{-2} \frac{M}{L \cdot \text{atm}}\right) = 1.87 \times 10^{-3} M_{27}$$



All dissolved CO_2 goes to carbonic acid



Carbonic acid is a weak acid
(anion is high charge density, **Oh Card me PleaSe!**)



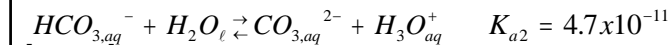
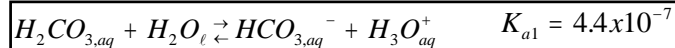
$$K_{a1} = \frac{[HCO_{3,eq}^{-}][H_3O_{aq,eq}^{+}]}{[H_2CO_{3,eq,init}]} = \frac{x(10^{-7} + x)}{([H_2CO_{3,eq,init}] - x)} \approx \frac{x^2}{([H_2CO_{3,eq,init}] - x)}$$

$$x = \sqrt{K_{a1}[H_2CO_{3,eq,init}]} = \sqrt{(4.4 \times 10^{-7})(1.87 \times 10^{-3})} = \sqrt{8.228 \times 10^{-10}} = 2.86 \times 10^{-5}$$

$$[H_3O_{aq,eq}^{+}] = x$$

$$p[H_3O_{aq,eq}^{+}] = -\log(2.86 \times 10^{-5}) = 4.54$$

This is too low!!! – we would not have the
Right amount of ionization on the protein



$$p[H_3O_{aq,eq}^{+}] = -\log(2.29 \times 10^{-5}) = 4.54$$

Will the pH get to the “right” value by the second acid
Dissociation reaction? Let’s make an “intelligent” guess

NO, would
Only slightly
Increase acidity

$$K_{a2} = \frac{[CO_{3,eq}^{2-}][H_3O_{aq,eq}^{+}]}{[HCO_{3,eq}^{-}]} = \frac{x(2.86 \times 10^{-5} + x)}{(2.86 \times 10^{-5} - x)} \quad K_{a2} \approx \frac{x(2.86 \times 10^{-5})}{(2.86 \times 10^{-5} - x)} \quad x = 4.7 \times 10^{-11}$$

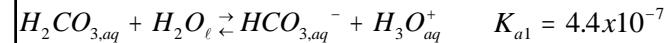
$$x^2 + (2.86 \times 10^{-5})x - 1.34 \times 10^{-15} = 0$$

$$(2.86 \times 10^{-5} - x)K_{a2} = x(2.86 \times 10^{-5} + x) \quad x = \frac{-2.86 \times 10^{-5} \pm \sqrt{(2.86 \times 10^{-5})^2 - 4(-1.34 \times 10^{-15})}}{2}$$

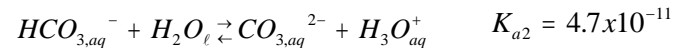
$$2.86 \times 10^{-5} K_{a2} - xK_{a2} = 2.86 \times 10^{-5} x + x^2 \quad x = \frac{-2.86 \times 10^{-5} \pm \sqrt{8.1796 \times 10^{-10} + 5.36 \times 10^{-15}}}{2}$$

$$x^2 + 2.86 \times 10^{-5} x - 2.86 \times 10^{-5} K_{a2} + xK_{a2} = 0 \quad x = \frac{-2.86 \times 10^{-5} \pm 2.8600093 \times 10^{-5}}{2}$$

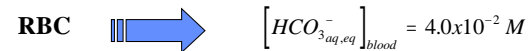
$$x^2 + (2.86 \times 10^{-5} + K_{a2})x - 2.86 \times 10^{-5} K_{a2} = 0 \quad x = \frac{9.37 \times 10^{-11}}{2} = 4.68 \times 10^{-11}$$

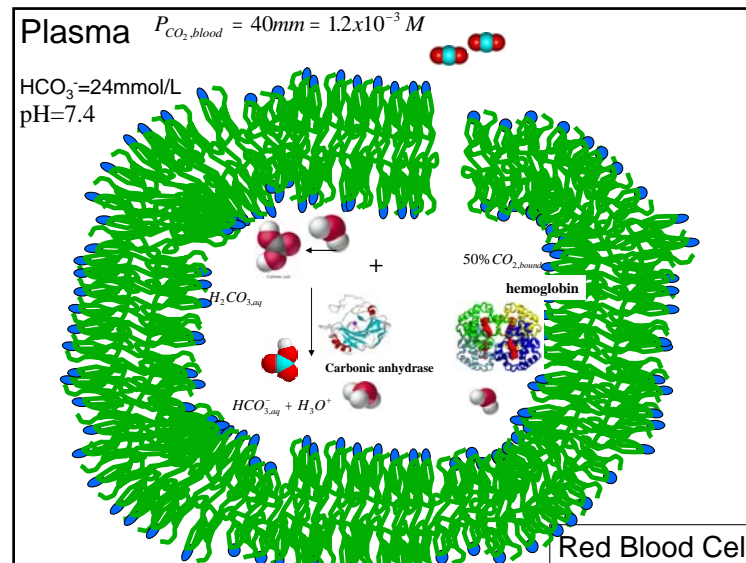
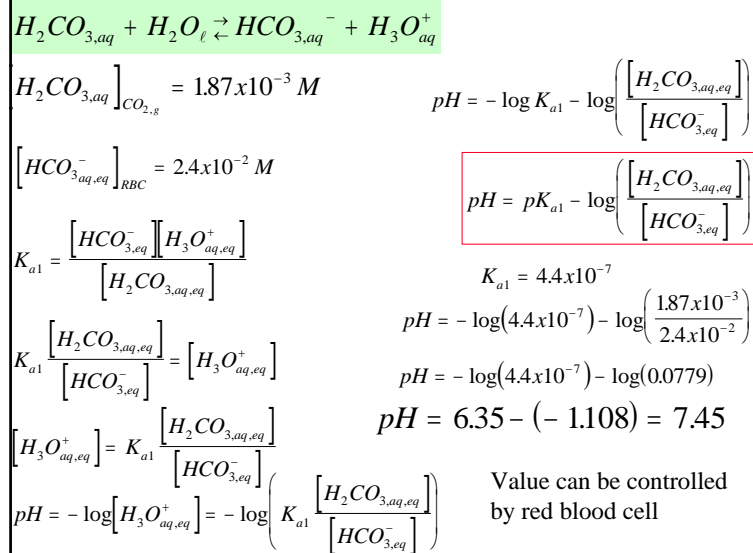


Will the pH get to the “right” value by the second acid
Dissociation reaction? $p[H_3O_{aq,eq}^{+}] = -\log(2.29 \times 10^{-5}) = 4.54$



To tweak blood pH to 7.4
red blood cells (RBC)
control $[HCO_3^{-}]$





That is the Context for Buffering

1. Must control concentration of both
 1. Conjugate acid
 2. Conjugate base
2. So what are the equations, etc. necessary to determining the buffering of a solution?

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 ~ 10 problems/night.

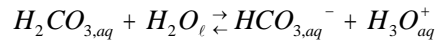
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Module #17C:
Buffering and Titrations
Henderson/Hasselbalch
Buffer Equation

The body controls the pH ($[H^+]$) concentration in blood by

1. controlling WA H_2CO_3 via $CO_{2,g}$
2. controlling WB HCO_3^- through activity of the red blood cells
3. The WA and WB are linked (conjugates) so that an equilibrium can be written between the two



4. All parameters are constant, leading to constant pH

$$pH = pK_{a1} - \log \left(\frac{[H_2CO_{3,aq,eq}]}{[HCO_{3,eq}^-]} \right)$$

5. This process is called **buffering**

A general equation can be written

$$pH = pK_a - \log \left(\frac{[HA_{,aq,eq}]}{[A_{,eq}^-]} \right)$$

$$pH = pK_a + \log \left(\frac{\left[\frac{mmoleA^-}{total mL} \right]}{\left[\frac{mmoleHA}{total mL} \right]} \right) \quad pH = pK_a - \log \left(\frac{[HA_{,aq,eq}]}{[A_{,eq}^-]} \right)$$

$$pH = pK_a + \log \left(\frac{mmoleA^- \left(\frac{1}{total mL} \right)}{mmoleHA \left(\frac{1}{total mL} \right)} \right) \quad pH = pK_a + \log \left(\frac{mmoleA^-}{mmoleHA} \right)$$

$$\frac{moles}{L} \times \frac{10^3 \text{ mmoles}}{moles} \times \frac{L}{10^3 \text{ mL}} = \frac{mmoles}{mL}$$

$$mL \times \frac{mmoles}{mL} = mmoles$$

$$mL \times M = mmoles$$

Henderson Hasselbach Equation

$$pH = pK_a - \log \left(\frac{[HA_{,aq,eq}]}{[A_{,eq}^-]} \right) \quad \text{OR} \quad pH = pK_a + \log \left(\frac{[A_{,eq}^-]}{[HA_{,aq,eq}]} \right)$$

$$pH = pK_a + \log \left(\frac{mmoleA^-}{mmoleHA} \right) \quad \text{if } \begin{array}{l} \text{Linked (conjugated)} \\ mmoleA^- = mmoleHA \end{array}$$

$$pH = pK_a + \log[1] = pK_a + 0$$

$$pH = pK_a$$

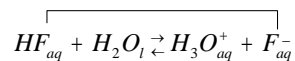
OJO this is NOT the "equivalence point"
 $mmole(titrant) = mmole(titrated)$



Fitch Rule G3: Science is Referential

Buffer Example 1 what is equilibrium pH of a solution of 1.0 M HF, and 1.0 M NaF? $K_a \text{ HF} = 7.2 \times 10^{-4}$

Do we have linked WA and WB both present?



$$pH = pK_a$$

Yes = buffer

$$pH = pK_a + \log \left[\frac{[A^-]}{[HA]} \right]$$

$$K_a = 7.2 \times 10^{-4}$$

$$pH = -\log(7.2 \times 10^{-4})$$

$$pH = pK_a + \log \left[\frac{[F^-]}{[HF]} \right]$$

$$pH = -\log(7.2 \times 10^{-4}) = 3.14$$

$$pH = pK_a + \log \left[\frac{1.0}{1.0} \right]$$

In preceding module 17B we calculated the pH of A solution of 1.0 M HF and found it to be

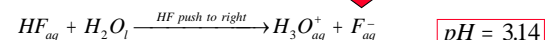
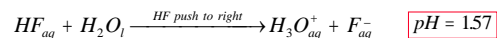
$$pH = pK_a + \log[1]$$

$$pH = 1.57$$

$$pH = pK_a + 0$$

What causes the difference?

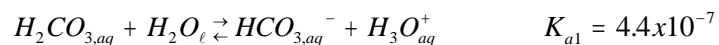
LeChatlier's Principle



Effect of added NaF is to reduce the ionization of HF

Buffer Example 2: What is the pH of 1.0 M H_2CO_3 in the presence of 1.0 M NaHCO_3

What is in solution? Are the chemical species linked by an equilibrium reaction?



Solution contains a weak acid in the presence of it's linked (conjugate) weak base

$$pH = pK_a + \log \left[\frac{[A^-]}{[HA]} \right]$$

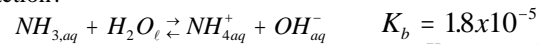
$$pH = 6.36 + \log(1)$$

$$pH = 6.36 + 0 = 6.36$$

$$pH = -\log(4.4 \times 10^{-7}) + \log \left[\frac{1M[\text{NaHCO}_3]}{1M[\text{H}_2\text{CO}_3]} \right]$$

Buffer Example 3: What is the pH of a solution containing 0.25 M NH_3 ($K_b = 1.8 \times 10^{-5}$) and 0.40 M NH_4Cl ?

What is in solution? Are the chemical species linked by an equilibrium reaction?



$$\text{or } \text{NH}_{4,aq}^+ + \text{H}_2\text{O}_l \rightleftharpoons \text{NH}_{3,aq} + \text{H}_3\text{O}_{aq}^+ \quad K_a = \frac{K_w}{K_b} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.556 \times 10^{-10}$$


Solution contains a weak acid in the presence of it's linked (conjugate) weak base

$$pH = pK_a + \log \left[\frac{[A^-]}{[HA]} \right]$$

$$pH = 9.25 + \log \left(\frac{0.25}{0.4} \right)$$

$$pH = -\log(5.55 \times 10^{-10}) + \log \left[\frac{0.25M[\text{NH}_{3,aq}]}{0.40M[\text{NH}_{4,aq}^+]} \right]$$

$$pH = 9.25 + (-0.204) = 9.05$$



I WANT YOU TO PRACTICE EVERY DAY!

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Module #17C: Buffering and Titrations
4 Kinds of Problems Reviewed

We now know how to do 4 types of problems

Limiting Reagent must involve SA or SB

$HCl_{aq} + NaOH \xrightarrow{\text{completely, Limiting reagent}} Cl^-_{aq} + H_2O_{aq} + Na^+_{aq}$
 $HA_{aq} + NaOH \xrightarrow{\text{completely, Limiting reagent}} A^-_{aq} + H_2O_{aq} + Na^+_{aq}$
 $Na^+_{aq} + A^-_{aq} + HCl \xrightarrow{\text{completely, Limiting Reagent}} HA_{aq} + Cl^-_{aq} + Na^+_{aq}$

Which reagent is completely consumed?
Which remains?

Equilibrium

WA $HA_{aq} + H_2O_{\ell} \rightleftharpoons A^-_{aq} + H_3O^+_{aq}$
 $K_a = \frac{[H_3O^+_{aq}][A^-_{aq}]}{[HA_{aq,eq}]} = \frac{x(x + 10^{-7})}{([HA_{aq,init}] - x)} \approx \frac{x^2}{[HA_{aq,init}]}$

WB $A^-_{aq} + H_2O_{\ell} \rightleftharpoons OH^-_{aq} + HA_{aq}$
 $K_b = \frac{[OH^-_{aq}][HA_{aq,eq}]}{[A^-_{aq,eq}]} = \frac{x(x + 10^{-7})}{([A^-_{aq,init}] - x)} \approx \frac{x^2}{[A^-_{aq,init}]}$

WA + conjugate (linked) WB $A^-_{aq} + H_2O_{\ell} \rightleftharpoons HA_{aq} + OH^-_{aq}$
 $pH = pK_a + \log \left[\frac{[A^-_{aq}]}{[HA_{aq}]} \right] \approx pK_a + \log \left[\frac{[A^-_{init}]}{[HA_{init}]} \right]$

To refresh your memory on Limiting Reagent Problems

Calculate the concentration of Na^+ , Cl^- , CH_3COO^- , and CH_3COOH in solution when 10.0 mL of 1.0 M HCl is added to 6.0 mL of 2.0 M NaAcetate acid ($NaCH_3COO$). Each solution is obtained from made from a stock solutions at 1 atm pressure

What do we know	What do we want	What is a red herring?
10.0 mL 1.0 M HCl	Conc.	
5.0 mL 2.0 M $NaCH_3COO$		
1 atm		

Classify the chemical substances added to solution:

- Strong Acid (**SA**) Protonated low q/r anion (No Clean Socks) HNO_3 , HCl , H_2SO_4
- Strong Base (**SB**) OH^- + low q/r Cation (Group 1 and 2) $NaOH$, KOH , $Ca(OH)_2$...
- Strong electrolyte (**SE**) Anion and Cation, low q/r $NaCl$, KNO_3 ...
- Weak Acid (**WA**) Protonated hi q/r anion (Oh Card me PleaSe) H_2CO_3 ...
- Weak Base (**WB**) Contains R group, anion hi q/r with cation low q/r Na_2CO_3
- Other or unknown (**OU**)

To refresh your memory on Limiting Reagent Problems

Calculate the concentration of Na^+ , Cl^- , CH_3COO^- and CH_3COOH in solution when 10.0 mL of 1.0 M HCl is added to 6.0 mL of 2.0 M NaAcetate acid ($NaCH_3COO$). Each solution is obtained from made from a stock solutions at 1 atm pressure

$(mL)M = mmoles$

SA/WB

Determine the Limiting Reagent

$Na^+_{aq} + A^-_{aq} + HCl \xrightarrow{\text{completely, Limiting Reagent}} HA_{aq} + Cl^-_{aq} + Na^+_{aq}$

HCl can produce

$(10.0 mL_{HCl}) \left(\frac{1.0 mole_{HCl}}{1 L_{HCl}} \right) \left(\frac{1 mole_{H^+}}{1 mole_{HCl}} \right) \left(\frac{1 mole_{CH_3COOH}}{1 mole_{H^+}} \right) = 10 mmoles_{CH_3COOH}$

WB can produce

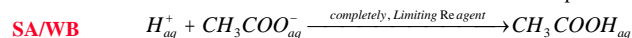
$H^+ + CH_3COO^-_{aq} \xrightarrow{\text{completely, Limiting Reagent}} CH_3COOH_{aq}$

$(6.0 mL_{NaCH_3COO}) \left(\frac{2.0 mole_{NaCH_3COO}}{1 L_{NaCH_3COO}} \right) \left(\frac{1 mole_{CH_3COO^-}}{1 mole_{NaCH_3COO}} \right) \left(\frac{1 mole_{CH_3COOH}}{1 mole_{CH_3COO^-}} \right) = 12 mmoles_{CH_3COOH}$

SA (HCl) is limiting reagent, completely consumed, 0mmoles
How much WB remains?
 WA formed is 10 mmoles

To refresh your memory on Limiting Reagent Problems

Calculate the concentration of Na^+ , Cl^- , CH_3COO^- , and CH_3COOH in solution when 10.0 mL of 1.0 M HCl is added to 6.0 mL of 2.0 M NaAcetate acid (NaCH_3COO). Each solution is obtained from made from a stock solutions at 1 atm pressure



SA (HCl) is limiting reagent, completely consumed, 0mmoles

WA formed is 10 mmoles

WB initial 12 mmoles; WB consumed:

$$(10.0\text{mL}_{\text{HCl}}) \left(\frac{1.0\text{mole}_{\text{HCl}}}{1\text{L}_{\text{HCl}}} \right) \left(\frac{1\text{mole}_{\text{H}^+}}{1\text{mole}_{\text{HCl}}} \right) \left(\frac{1\text{mole}_{\text{CH}_3\text{COOH}}}{1\text{mole}_{\text{H}^+}} \right) \left(\frac{1\text{mole}_{\text{CH}_3\text{COO}^-}}{1\text{mole}_{\text{CH}_3\text{COOH}}} \right) = 10\text{mmoles}_{\text{CH}_3\text{COO}^-}$$

Initial-consumed=12-10=2mmoles WB left

Concentrations after the limiting reagent reaction

$$[\text{CH}_3\text{COOH}] = \frac{10\text{mmoles}_{\text{CH}_3\text{COOH}}}{10.0\text{mL} + 6.0\text{mL}} = 0.625\text{M} \quad [\text{Na}^+] = \frac{(6\text{mL})2\text{M}}{10.0\text{mL} + 6.0\text{mL}} = 0.75\text{M}$$

$$[\text{CH}_3\text{COO}^-] = \frac{2.0\text{mmoles}_{\text{CH}_3\text{COO}^-}}{10.0\text{mL} + 6.0\text{mL}} = 0.125\text{M} \quad [\text{Cl}^-] = \frac{(10\text{mL})1.0\text{M}}{10.0\text{mL} + 6.0\text{mL}} = 0.625\text{M}$$

To refresh your memory on Limiting Reagent Problems

Concentrations

$$[\text{CH}_3\text{COOH}] = \frac{10\text{mmoles}_{\text{CH}_3\text{COOH}}}{10.0\text{mL} + 6.0\text{mL}} = 0.625\text{M} \quad [\text{Na}^+] = \frac{(6\text{mL})2\text{M}}{10.0\text{mL} + 6.0\text{mL}} = 0.75\text{M}$$

$$[\text{CH}_3\text{COO}^-] = \frac{2.0\text{mmoles}_{\text{CH}_3\text{COO}^-}}{10.0\text{mL} + 6.0\text{mL}} = 0.125\text{M} \quad [\text{Cl}^-] = \frac{(10\text{mL})1.0\text{M}}{10.0\text{mL} + 6.0\text{mL}} = 0.625\text{M}$$

In the preceding problem what kind of equilibrium problem remains?

You have 3 choices:

WA

WB

WB and its conjugate WA (or WA and its conjugate WB)

We have present a weak acid (WA) and it's linked (conjugate) weak base (WB)

$$\left. \begin{array}{l} [\text{CH}_3\text{COO}^-] = 0.125\text{M} \\ [\text{CH}_3\text{COOH}] = 0.625\text{M} \end{array} \right\} \text{Buffer equilibrium problem}$$



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Module #17C:
Buffering and Titrations
A feast of titrations

*Mama Alanah's
Dinner Feasts*



Choice of 3 Main
Dishes
SA plus SB
SA plus WB
SB plus WA

*Delightfully Refreshing and Pleasing to the Palate
Guaranteed to Feed your Brain*

Followed by 1 of 3 Crazy sides
WA
WB
WA and it's conjugate WB

Serving the North Shore since 1985!



We can combine Limiting reagent problems followed by an equilibrium problem to do a **titration**. Titrations allow us to determine the conc of an unknown

Titration involve 1 of 3 LR followed by 1 of 3 Eq

Limiting Reagent must involve SA or SB

$HCl_{aq} + NaOH \xrightarrow{\text{completely, Limiting reagent}} Cl^-_{aq} + H_2O_{aq} + Na^+_{aq}$ Which reagent is completely consumed?
 $HA_{aq} + NaOH \xrightarrow{\text{completely, Limiting reagent}} A^-_{aq} + H_2O_{aq} + Na^+_{aq}$ Which remains?
 $Na^+_{aq} + A^-_{aq} + HCl \xrightarrow{\text{completely, Limiting Reagent}} HA_{aq} + Cl^-_{aq} + Na^+_{aq}$

Equilibrium

WA $HA_{aq} + H_2O_l \rightleftharpoons A^-_{aq} + H_3O^+_{aq}$

$$K_a = \frac{[H_3O^+_{aq}][A^-_{aq}]}{[HA_{aq,eq}]} = \frac{x(x + 10^{-7})}{([HA_{aq,init}] - x)} \approx \frac{x^2}{[HA_{aq,init}]}$$

WB $A^-_{aq} + H_2O_l \rightleftharpoons OH^-_{aq} + HA_{aq}$

$$K_b = \frac{[OH^-_{aq}][HA_{aq,eq}]}{[A^-_{aq,eq}]} = \frac{x(x + 10^{-7})}{([A^-_{aq,init}] - x)} \approx \frac{x^2}{[A^-_{aq,init}]}$$

$x^2 + x(K + 10^{-7}) - K[Init] = 0$

WA + conjugate (linked) WB $HA_{aq} + H_2O_l \rightleftharpoons A^-_{aq} + H_3O^+_{aq}$ $pH = pK_a + \log \left[\frac{[A^-_{eq}]}{[HA_{eq}]} \right] \approx pK_a + \log \left[\frac{[A^-_{init}]}{[HA_{init}]} \right]$

Titrate 40 mL 0.20 **acetic acid** with 0.40 M NaOH (0, 5, 10, 19, 20, 21,25 mL); K_a acetic acid = 1.8×10^{-5}

Main Dish: Limiting Reagent Problem

$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$

$(0.20 M_{acetic\ acid})(40 mL_{acetic\ acid}) \left(\frac{1 mmole_{CH_3COO^-}}{1 mmole_{CH_3COOH}} \right) = 8 mmole_{CH_3COO^-}$
 $(0.40 M_{NaOH})(0 mL_{NaOH}) \left(\frac{1 mmole_{CH_3COO^-}}{1 mmole_{NaOH}} \right) = 0 mmole_{CH_3COO^-}$ **limiting**

Solution contains CH_3COOH
 Solution contains no NaOH
 Solution contains no CH_3COO^- **Side dish: WA**

$[H^+]_{aq} = x = 1.897 \times 10^{-3}$
 $pH = -\log(1.897 \times 10^{-3})$
 $pH = 2.72$

$K_a = 1.8 \times 10^{-5}$; try assumptions

$1.8 \times 10^{-5} \approx \frac{x^2}{0.20}$
 $\sqrt{(1.8 \times 10^{-5})(0.20)} \approx x = 1.897 \times 10^{-3}$

If you prefer – do an ICE chart

Equilibrium Calculation.

Rx 1	H_2O	H^+	OH^-
	55.5	10^{-7}	10^{-7}
Rx 2	CH_3CO_2H	H^+	$CH_3CO_2^-$
init	0.200	10^{-7}	0
change	-x	+x	+x
assume	$x \ll 0.2$	$x \gg 10^{-7}$	
equil	0.2	x	x

$Q = \frac{[CH_3CO_2^-]_{init}[H^+]_{init}}{[CH_3CO_2H]_{init}} = \frac{0(10^{-7})}{0.2} < K = 1.8 \times 10^{-5}$ **Because rx goes to right**
Sign of x is neg for reactants
 $1.8 \times 10^{-5} \approx \frac{x^2}{0.20}$
 $\sqrt{(1.8 \times 10^{-5})(0.20)} \approx x = 1.897 \times 10^{-3}$
 $pH = -\log(1.89 \times 10^{-3}) = 2.72$

Titrate 40 mL 0.20 **acetic acid** with 0.40 M NaOH 0, 5, 10, 19, 20, 21,25 mL; $K_a = 1.8 \times 10^{-5}$ check? yes.

Titrate 40 mL 0.20 **acetic acid** with 0.40 M NaOH (0, 5, 10, 19, 20, 21,25 mL); K_a acetic acid = 1.8×10^{-5}

Main Dish: Limiting Reagent Problem

$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$

$(0.40 M_{NaOH})(5 mL_{NaOH}) \left(\frac{1 mmole_{CH_3COO^-}}{1 mmole_{NaOH}} \right) = 2.0 mmole_{CH_3COO^-}$ **Limiting Reagent**
 $(0.20 M_{CH_3COOH})(40 mL_{CH_3COOH}) \left(\frac{1 mmole_{CH_3COO^-}}{1 mmole_{CH_3COOH}} \right) = 8.0 mmole_{CH_3COO^-}$

Solution contains 2.0 mmole CH_3COO^-

$[CH_3COO^-] = \frac{2.0 mmole_{CH_3COO^-}}{40 mL_{CH_3COOH} + 5 mL_{NaOH}} = 0.0444 M$

2.0 mmole CH_3COOH used to make 2 mmole CH_3COO^-

$[CH_3COOH] = \frac{8.0 mmole - 2.0 mmole}{40 mL_{CH_3COOH} + 5 mL_{NaOH}} = 0.1333 M$ **Side Dish: Buffer**

Titrate 40 mL 0.20 **acetic acid** with 0.40 M NaOH 0, 5, 10, 19, 20, 21, 25 mL; K_a acetic acid = 1.8×10^{-5}

mL	pH
0	2.72
5	4.27

$$\text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O}$$

$$[\text{CH}_3\text{COO}^-] = \frac{2.0 \text{ mmole}_{\text{CH}_3\text{COO}^-}}{40 \text{ mL}_{\text{CH}_3\text{COOH}} + 5 \text{ mL}_{\text{NaOH}}} = 0.0444 \text{ M}$$

$$[\text{CH}_3\text{COOH}] = \frac{8.0 \text{ mmole} - 2.0 \text{ mmole}}{40 \text{ mL}_{\text{CH}_3\text{COOH}} + 5 \text{ mL}_{\text{NaOH}}} = 0.1333 \text{ M}$$

Invoke Rule:
Chemists Are Lazy

$$\text{pH} = \text{p}K_a + \log \left[\frac{\frac{\text{mmolesA}^-}{\text{total mL}}}{\frac{\text{mmolesHA}}{\text{total mL}}} \right]$$

$$\text{pH} = \text{p}K_a + \log \left[\frac{0.0444}{0.1333} \right]$$

$$\text{pH} = 4.74 + (-0.522)$$

$$\text{pH} = 4.27$$

$$\text{pH} = 4.74 + \log \left[\frac{2}{6} \right] = 4.27$$

Titrate 40 mL 0.20 **acetic acid** with 0.40 M NaOH 0, 5, 10, 19, 20, 21, 25 mL; K_a acetic acid = 1.8×10^{-5}

mL	pH
0	2.72
5	4.27
10	4.74

Main Dish: Limiting Reagent Problem

$$\text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O}$$

(0.40 M_{NaOH}) (10 mL_{NaOH}) $\left(\frac{1 \text{ mole}_{\text{CH}_3\text{COO}^-}}{1 \text{ mole}_{\text{NaOH}}} \right) = 4.0 \text{ mmole}_{\text{CH}_3\text{COO}^-}$ Limiting Reagent

(0.20 M_{CH3COOH}) (40 mL_{CH3COOH}) $\left(\frac{1 \text{ mole}_{\text{CH}_3\text{COO}^-}}{1 \text{ mole}_{\text{CH}_3\text{COOH}}} \right) = 8.0 \text{ mmole}_{\text{CH}_3\text{COO}^-}$

Solution contains 4.0 mmole CH_3COO^-
 Solution contains 8.0 - 4.0 mmole CH_3COOH } **Side Dish: buffer**

$$\text{pH} = \text{p}K_a + \log \left[\frac{\text{mmolesA}^-}{\text{mmolesHA}} \right]$$

$$\text{pH} = 4.74 + \log \left[\frac{4}{8 - 4} \right] = 4.74 + \log 1 = 4.74$$

Titrate 40 mL 0.20 **acetic acid** with 0.40 M NaOH 0, 5, 10, 19, 20, 21, 25 mL; K_a acetic acid = 1.8×10^{-5}

mL	pH
0	2.72
5	4.27
10	4.74
19	6.02

Main Dish: Limiting Reagent Problem

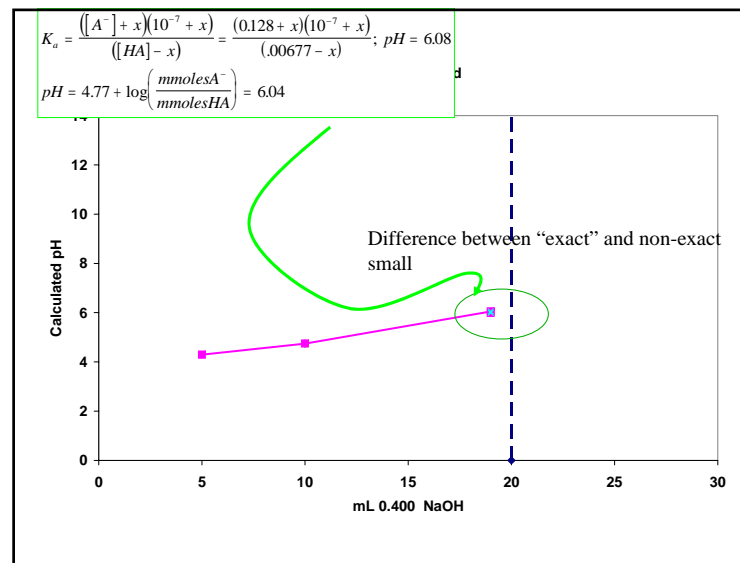
$$\text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O}$$

(0.40 M_{NaOH}) (19 mL_{NaOH}) $\left(\frac{1 \text{ mole}_{\text{CH}_3\text{COO}^-}}{1 \text{ mole}_{\text{NaOH}}} \right) = 7.6 \text{ mmole}_{\text{CH}_3\text{COO}^-}$ Limiting Reagent

(0.20 M_{CH3COOH}) (40 mL_{CH3COOH}) $\left(\frac{1 \text{ mole}_{\text{CH}_3\text{COO}^-}}{1 \text{ mole}_{\text{CH}_3\text{COOH}}} \right) = 8.0 \text{ mmole}_{\text{CH}_3\text{COO}^-}$

Solution contains 7.6 mmole CH_3COO^-
 8 CH_3COOH - 7.6 mmole OH = 0.4 mmole } **Side Dish: buffer**

$$\text{pH} = \text{p}K_a + \log \left[\frac{\text{mmolesA}^-}{\text{mmolesHA}} \right]$$

$$\text{pH} = 4.74 + \log \left[\frac{7.6}{8 - 7.6} \right] = 4.74 + \log \left(\frac{7.6}{0.4} \right) = 4.74 + 1.2787 = 6.02$$


Titrate 40 mL 0.20 **acetic acid** with 0.40 M NaOH 0, 5, 10, 19, 20, 21, 25 mL; K_a acetic acid = 1.8×10^{-5}

mL	pH
0	2.72
5	4.27
10	4.74
19	6.02

Main Dish: Limiting Reagent Problem

$$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$$

$$(0.40 M_{NaOH})(20 mL_{NaOH}) \left(\frac{1 \text{ mole}_{CH_3COO^-}}{1 \text{ mole}_{NaOH}} \right) = 8 \text{ mmole}_{CH_3COO^-}$$

$$(0.20 M_{CH_3COOH})(40 mL_{CH_3COOH}) \left(\frac{1 \text{ mole}_{CH_3COO^-}}{1 \text{ mole}_{CH_3COOH}} \right) = 8.0 \text{ mmole}_{CH_3COO^-}$$

Both Are Limiting Reagents **USED UP**

Solution contains 8 mmole CH_3COO^-

8 mmole CH_3COOH - 8 mmole OH^- = 0 mmole CH_3COOH

Side Dish: acetate = WB

$$CH_3COO^-_{aq} + H_2O_{\ell} \rightleftharpoons CH_3COOH_{aq} + OH^-_{aq}$$

Titrate 40 mL 0.20 **acetic acid** with 0.40 M NaOH 0, 5, 10, 19, 20, 21, 25 mL; K_a acetic acid = 1.8×10^{-5}

mL	pH
0	2.72
5	4.27
10	4.74
19	6.02
20	8.93

Solution contains 8 mmole CH_3COO^-

$$CH_3COO^-_{aq} + H_2O_{\ell} \rightleftharpoons CH_3COOH_{aq} + OH^-_{aq}$$

$$[CH_3COO^-] = \frac{8 \text{ mmole}}{40 \text{ mL} + 20 \text{ mL}} = 0.1333 \quad x \ll 0.1333?$$

$$x \gg 10^{-7} ???$$

$$K_b = \frac{[HA_{aq,eq}][OH^-_{aq}]}{[A^-_{aq,eq}]} = \frac{x(x + 10^{-7})}{([A^-_{aq,init}] - x)} \approx \frac{x^2}{[A^-_{aq,init}]}$$

$$K_b = \frac{K_w}{K_a} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.55 \times 10^{-10} \quad \sqrt{(5.55 \times 10^{-10})(0.1333)} \sim x = 8.59 \times 10^{-6}$$

K_b "small", assumps. Ok.

$$[OH^-] \sim x = 8.59 \times 10^{-6}$$

$$pH = 14 - (-\log(8.59 \times 10^{-6})) = 8.93$$

$$5.55 \times 10^{-10} \approx \frac{x^2}{0.1333}$$

If you prefer – do an ICE chart

Calculate equilibrium

	H_2O	H^+	OH^-
	55.5	10^{-7}	10^{-7}
init conc:	0.133	0	10^{-7}
change	-x	+x	+x
assume (not much reaction to right, K_b small)	$x \ll 0.133$		$x \gg 10^{-7}$
equil	0.133	x	x

$$Q = \frac{[CH_3CO_2H]_{init}[OH^-]_{init}}{[CH_3CO_2^-]_{init}} = \frac{0(10^{-7})}{0.2} \ll K \rightarrow$$

$$K_b = \frac{K_w}{K_a} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.55 \times 10^{-10}$$

K_b "small", assumps. Ok.

$$5.55 \times 10^{-10} = \frac{x^2}{0.133}$$

$$\sqrt{(5.55 \times 10^{-10})(0.133)} = x = 8.59 \times 10^{-6}$$

Sign of x for reactants is -

Titrate 40 mL 0.20 **acetic acid** with 0.40 M NaOH 0, 5, 10, 19, 20, 21, 25 mL **$pH = 14 - pOH = -\log(8.59 \times 10^{-6}) = 8.93$**

Titrate 40 mL 0.20 **acetic acid** with 0.40 M NaOH 0, 5, 10, 19, 20, 21, 25 mL; K_a acetic acid = 1.8×10^{-5}

mL	pH
0	2.72
5	4.27
10	4.74
19	6.02
20	8.93
21	11.82

Main Dish: Limiting Reagent Problem

$$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$$

$$(0.40 M_{NaOH})(21 mL_{NaOH}) \left(\frac{1 \text{ mole}_{CH_3COO^-}}{1 \text{ mole}_{NaOH}} \right) = 8.4 \text{ mmole}_{CH_3COO^-}$$

$$(0.20 M_{CH_3COOH})(40 mL_{CH_3COOH}) \left(\frac{1 \text{ mole}_{CH_3COO^-}}{1 \text{ mole}_{CH_3COOH}} \right) = 8.0 \text{ mmole}_{CH_3COO^-}$$

Limiting Reagent

Side dish: seconds of the main

Excess OH

$$[OH^-]_{excess} = \frac{8.4 - 8}{40 + 20 + 1} = 0.006557 \quad p[OH^-]_{excess} = -\log(0.006557)$$

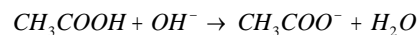
Or

$$p[OH^-]_{excess} = 2.18$$

$$[OH^-]_{excess} = \frac{(1 \text{ mL}_{excess})(0.40 M)}{40 + 20 + 1} = 0.006557 \quad pH = 14 - pOH = 14 - 2.18 = 11.82$$

Titrate 40 mL 0.20 acetic acid with 0.40 M NaOH 0, 5, 10, 19, 20, 21, 25 mL; K_a acetic acid = 1.8×10^{-5}

Main Dish: Limiting Reagent Problem



$$(0.40 \text{ M}_{\text{NaOH}})(25 \text{ mL}_{\text{NaOH}}) \left(\frac{1 \text{ mole}_{\text{CH}_3\text{COO}^-}}{1 \text{ mole}_{\text{NaOH}}} \right) = 10 \text{ mmole}_{\text{CH}_3\text{COO}^-}$$

$$(0.20 \text{ M}_{\text{CH}_3\text{COOH}})(40 \text{ mL}_{\text{CH}_3\text{COOH}}) \left(\frac{1 \text{ mole}_{\text{CH}_3\text{COO}^-}}{1 \text{ mole}_{\text{CH}_3\text{COOH}}} \right) = 8.0 \text{ mmole}_{\text{CH}_3\text{COO}^-} \quad \text{Limiting Reagent}$$

Side dish: seconds of the main
Excess OH

$$[\text{OH}^-]_{\text{excess}} = \frac{10 - 8}{40 + 20 + 5} = 0.030769 \quad p[\text{OH}^-]_{\text{excess}} = -\log(0.030769)$$

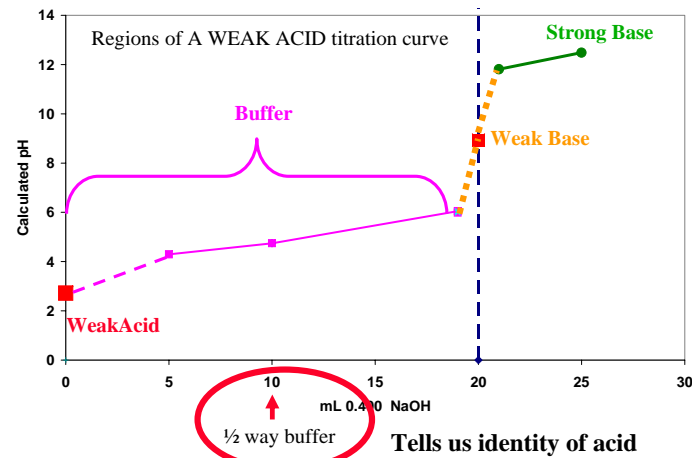
Or $p[\text{OH}^-]_{\text{excess}} = 1.511$

$$[\text{OH}^-]_{\text{excess}} = \frac{(5 \text{ mL}_{\text{excess}})(0.40 \text{ M})}{40 + 20 + 5} = 0.030769 \quad \text{pH} = 14 - p\text{OH} = 14 - 1.511 = 12.48$$

mL	pH
0	2.72
5	4.27
10	4.74
19	6.02
20	8.93
21	11.82
25	12.48

Defining some points on the Titration Curve

titration of acetic acid



1/2 way to the equivalence point



1/2 of HA is converted to A⁻

$$\frac{\text{mmoleHA}_{\text{initial}}}{2} = \text{mmoleHA}_{\text{remaining}} = \text{mmoleA}^-_{\text{formed}}$$

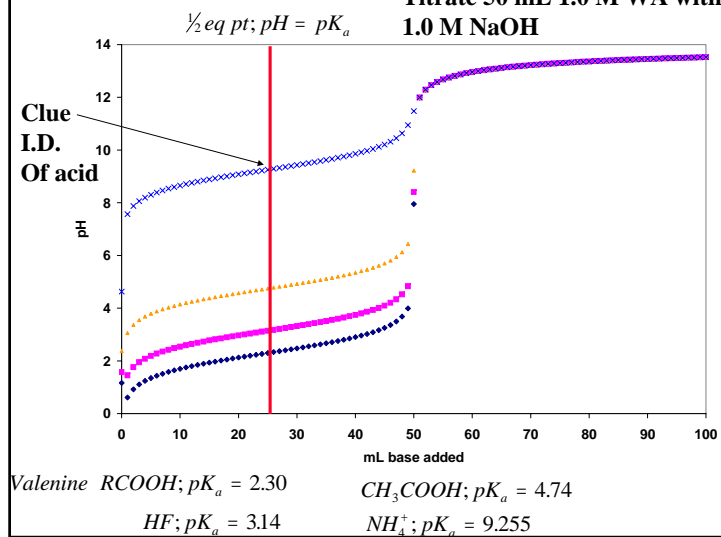
$$\text{pH} = \text{p}K_a + \log \left[\frac{\text{mmolesA}^-}{\text{mmolesHA}} \right]$$

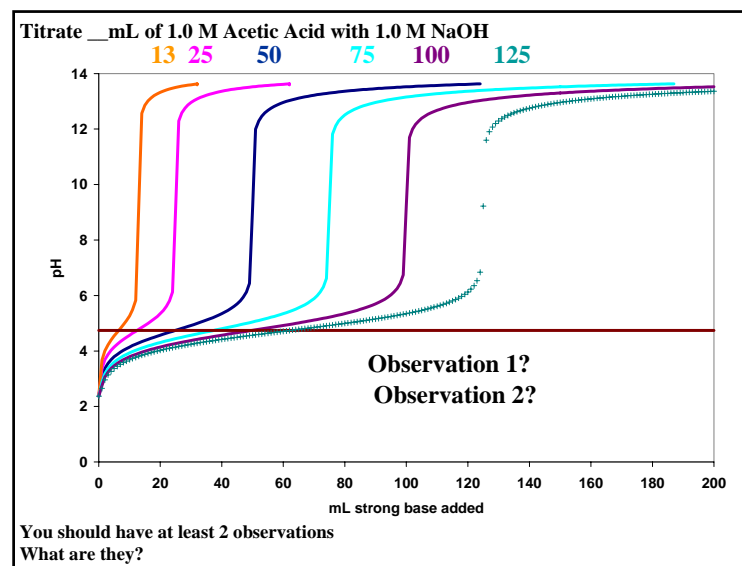
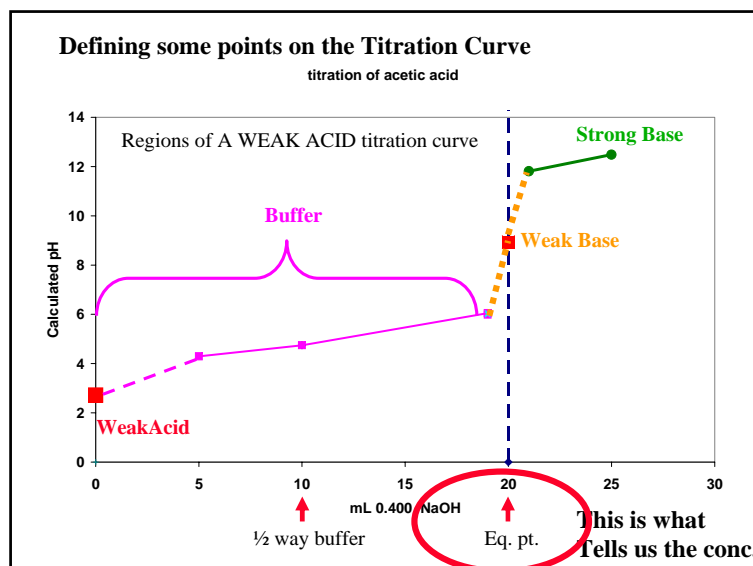
$$\text{pH} = \text{p}K_a + \log[1]$$

$$\text{pH} = \text{p}K_a$$

pK_a is a clue to the identity of the acid

Titrate 50 mL 1.0 M WA with 1.0 M NaOH





We found the equivalence point (large pH change) occurred when we added 20 mL of 0.40 M NaOH to 40 mL of an unknown conc of acetic acid. What was the original concentration of the acetic acid?

$$mmole(titrant) \Big|_{eq.pt} = mmole(titrated) \Big|_{eqpt}$$

or

$$(20mL)(0.40 M) = (40mL)x$$

$$x = \frac{(20mL)(0.40 M)}{40mL}$$

$$x = 0.20 M$$

$$(V)M = (V)M$$

$$(20)(0.40) = (40)M$$

$$M = \frac{(20)(0.40)}{40} = 0.2$$

Be sure to account for Multiple protons or hydroxides

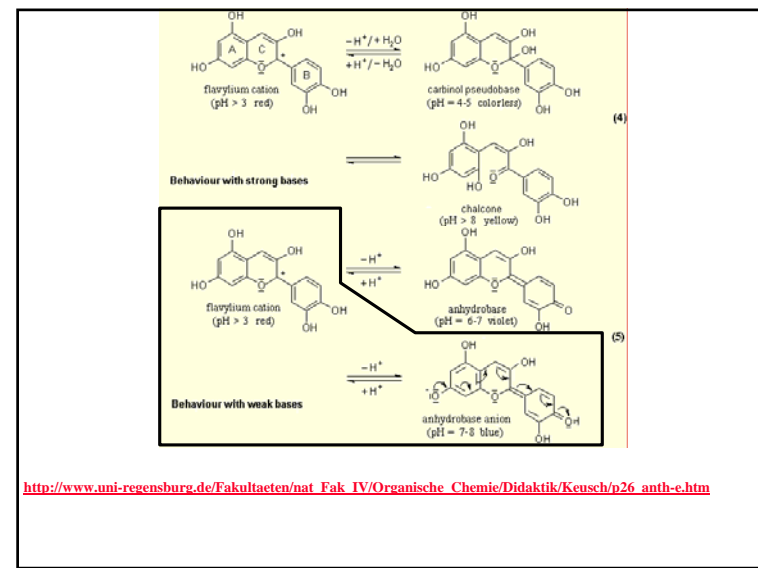
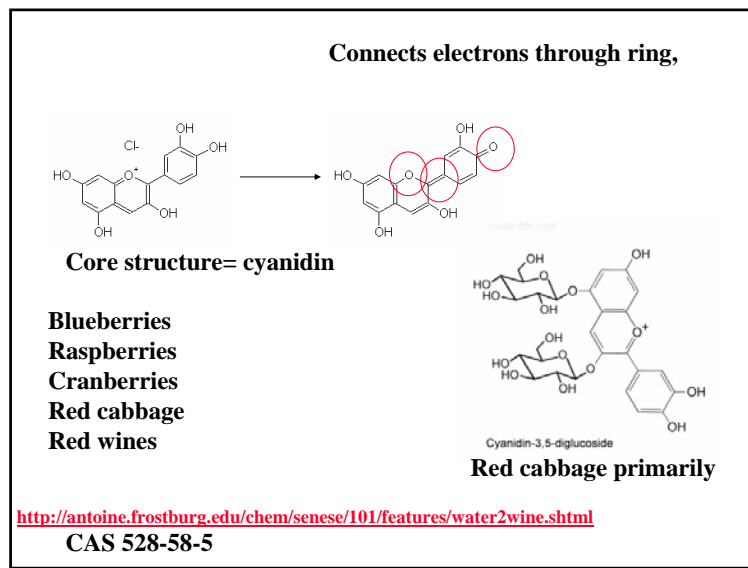
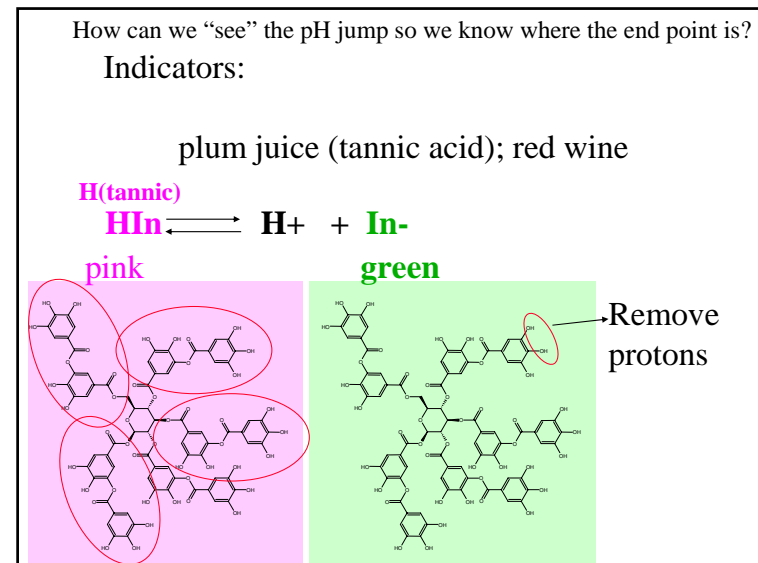
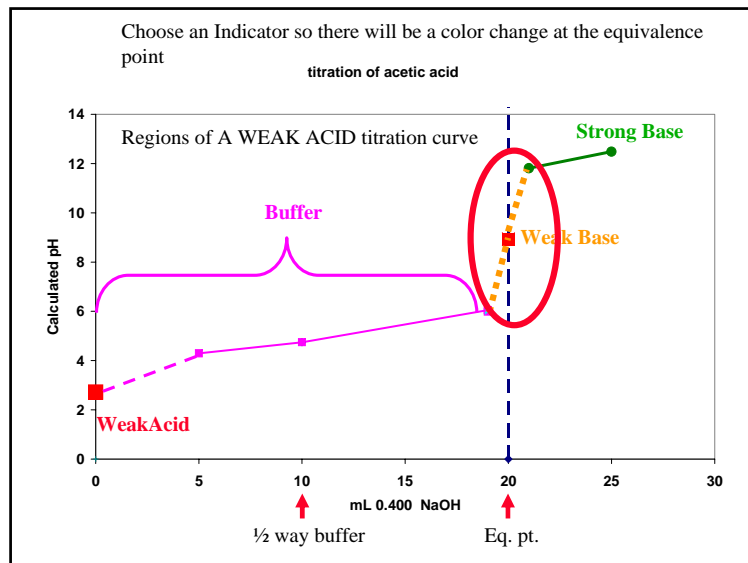
OJO, not $pH = pK_a$ $mmoleA^- = mmoleHA$

“A” students work (without solutions manual) ~ 10 problems/night.

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**Module #17C:
Buffering and Titrations
Indicators**



Hydrangea flower color based on available aluminum cation in the soil

Indicators:

plum juice (tannic acid) $K_a = \frac{[H^+][In^-]}{[HIn]}$

$HIn \rightleftharpoons H^+ + In^-$
 pink green

$\frac{K_a}{[H^+]} = \frac{[In^-]}{[HIn]}$

$\frac{K_a}{[H^+]} = \frac{\frac{\text{moles green}}{\text{total vol}}}{\frac{\text{moles pink}}{\text{total vol}}} = \frac{\text{moles green}}{\text{moles pink}}$

Observed color? When is it green vs pink?

Observed color? depends on mole ratio

Rule of thumb (10/1 or 1/10)

$\frac{K_a}{[H^+]} = \frac{10 \text{ moles green}}{\text{moles pink}} = \text{green}$ $\frac{K_a}{10} = [H^+]$

$pK_a - (-\log 10) = p[H^+]$ $pH_{\text{green}} = pK_a + 1$

$\frac{K_a}{[H^+]} = \frac{\text{moles green}}{10 \text{ moles pink}} = \text{pink}$ $10K_a = [H^+]$

$-\log 10 + pK_a = pH$ $pH_{\text{pink}} = pK_a - 1$

$\Delta pH_{\text{color change}} = pK_{a, \text{indicator}} \pm 1$

$\Delta pH = pK_a \pm 1$

Common Indicators (besides grape juice)

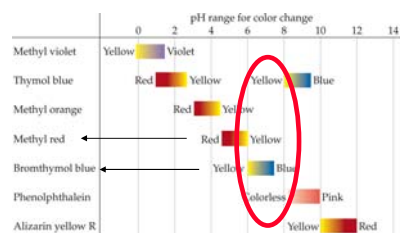
Name	$\Delta pH_{\text{color change}} = pK_a \pm 1$	pK_a
methyl violet	0-2	
thymol blue	1-3	
bromophenol blue	3-5	
methyl red	4.5-6.5	5
phenol red	6.5-8	
bromothymol blue	6-8	7.1
phenolphthalein	8-10	9
alizarin yellow R	10-12	

Change centered over pKa
 Color change over 2 pH units

Common Indicators (besides grape juice)

Name $\Delta\text{pH}_{\text{color change}} = \text{pK}_a \pm 1$ pK_a

methyl violet	0-2	Biggest pH change in our calculation was centered at pH 7
thymol blue	1-3	
bromophenol blue	3-5	
methyl red	4.5-6.5	
phenol red	6.5-8	
bromothymol blue	6-8	
phenolphthalein	8-10	9
alizarin yellow R	10-12	



Name $\Delta\text{pH}_{\text{color change}} = \text{pK}_a \pm 1$ pK_a

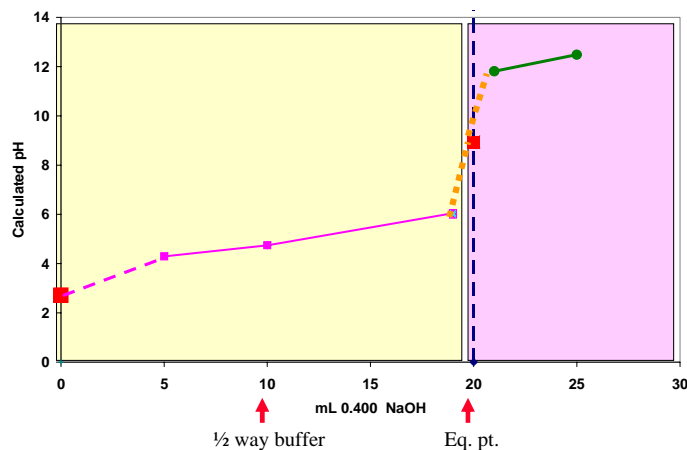
methyl violet	0-2	
thymol blue	1-3	
bromophenol blue	3-5	
methyl red	4.5-6.5	5
phenol red	6.5-8	
bromothymol blue	6-8	7.1
phenolphthalein	8-10	9
alizarin yellow R	10-12	

Titrate 40 mL 0.20 acetic acid with 0.40 M NaOH 0, 5, 10, 19, 20, 21, 25 mL

Can omit for BLB

Choose an Indicator so there will be a color change at the equivalence point

titration of acetic acid



“A” students work
(without solutions manual)
~ 10 problems/night.

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Module #17C:
Buffering and Titrations
Two more example titrations
WB/SA
SA/SB

A quick and dirty (WA/SB) titration curve.

mL added	problem	pH
0	WA	<pKa
1/2 to equivalence pt	buffer	pKa
equivalence pt	WB	
after equivalence pt	SB	>7

Can you predict how a WB/SA titration curve will work out?

Example Titration 2

titrate WB with SA

mL added	problem	pOH
0	WB	<pKb
1/2 to equivalence pt	buffer	pKb
equivalence pt	WA	
after equivalence pt	SA	<7

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

Example titrate 50 mL 0.1 M NH_3 0.2 M HCl

quick and dirty: 0 mL, 1/2 equivalence point, 1 mL before eq. pt., eq. pt., 1 mL after

0 mL HCl added; WB equilibrium chart

mL	pH
0	11.13

	$\text{NH}_3 + \text{H}_2\text{O}$	$\text{NH}_4^+ + \text{OH}^-$
init. conc.	0.1	0
change	-x	+x
assume? $K_b = 1.8 \times 10^{-5}$, not much reaction, yes	$0.1 > x$	$x > 10^{-7}$
equil.	0.1	x

$$Q = \frac{[\text{NH}_4^+]_{\text{init}} [\text{OH}^-]_{\text{init}}}{[\text{NH}_3]_{\text{init}}} = \frac{0(10^{-7})}{0.1} < K_b = 1.8 \times 10^{-5} \longrightarrow x = \sqrt{(1.8 \times 10^{-5})0.1}$$

$$K_b = 1.8 \times 10^{-5} = \frac{(x + 10^{-7})x}{0.1 - x} \approx \frac{x^2}{0.1} \quad x = 1.34 \times 10^{-3}$$

$$(1.8 \times 10^{-5})0.1 = x^2 \quad \text{pOH} = -\log(1.34 \times 10^{-3}) = 2.87$$

$$\text{pH} = 14 - \text{pOH} = 11.13$$

need to know eq. pt.

$$(50\text{mL})(0.1\text{M}\text{NH}_3) = x(0.2\text{M}\text{HCl})$$

$$x = 25\text{mL}_{\text{eq pt}}$$

$$\frac{1}{2} \text{ eq. pt.} = \frac{25\text{mL}}{2} = 12.5\text{mL}$$

$$K_{b,\text{NH}_3} = 1.8 \times 10^{-5}$$

$$\text{pH}_{1/2 \text{ eq. pt.}} = \text{pK}_a$$

$$\text{pK}_b = -\log(1.8 \times 10^{-5}) = 4.744$$

$$14 = \text{pK}_a + 4.744$$

$$K_w = K_a K_b; \quad K_a = \frac{K_w}{K_b}$$

$$\text{pK}_a = 9.25$$

OR

$$14 = \text{pK}_a + \text{pK}_b$$

$$\text{pH}_{1/2 \text{ eq. pt.}} = \text{pK}_a = 9.25$$

Example titrate 50 mL 0.1 M NH_3 0.2 M HCl; include 1 mL and 1 mL after eq.pt.

Eq pt = 25 mL; $pK_a=9.25$ (from preceding slide)
 1 mL before eq. pt = 24mL.; LR prob
 4.8 mmoles NH_4^+ } **Equilibrium prob?**
 0.2 mmoles NH_3
 Buffer

mL	pH
0	11.13
12.5	9.25
24	7.86

$(0.20 M_{HCl})(24mL_{HCl}) = 4.8mmoleH^+ added = 4.8mmolesHAformed$
 $(50mL)(0.10 M_{NH_3}) - 4.8mmoles = 0.2mmoles$
 $pK_a = 9.25$
 $pH = pK_a + \log\left(\frac{mmolesA^-}{mmolesHA}\right)$
 $pH = 9.25 + \log\left(\frac{0.2}{4.8}\right)$
 $pH = 9.25 - 1.38 = 7.86$

Example titrate 50 mL 0.1 M NH_3 , 0.2 M HCl; include 1 mL and 1 mL after eq.pt.

Eq. pt. Problem; WA

	NH_4^+	NH_3	H^+
init conc	.066	0	10^{-7}
change	-x	+x	+x
$K_a = 10^{-14}/(1.8 \times 10^{-5}) = 5.5 \times 10^{-10}$			
Assump?	$0.066 \gg x$		$x \sim 10^{-7}$
equil	0.066	x	$x + 10^{-7}$

$K_a = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.5 \times 10^{-10}$ $x = \frac{-10^{-7} \pm \sqrt{(10^{-7})^2 - 4(1)(-3.66 \times 10^{-11})}}{2(1)}$
 $5.5 \times 10^{-10} = \frac{x(10^{-7} + x)}{0.66 - x} \approx \frac{x(10^{-7} + x)}{0.66}$ $x = \frac{-10^{-7} \pm \sqrt{10^{-14} + 1.46 \times 10^{-10}}}{2}$
 $(5.5 \times 10^{-10})0.66 = 10^{-7}x + x^2$ $x = \frac{-10^{-7} \pm 1.21 \times 10^{-5}}{2}$
 $(3.66 \times 10^{-11}) = 10^{-7}x + x^2$
 $x^2 + 10^{-7}x - 3.66 \times 10^{-11} = 0$ $x = 6 \times 10^{-6}$ $pH = -\log(6 \times 10^{-6}) = 5.22$

Eq pt = 25 mL; $pK_a=9.25$ (from preceding slide)
 1 mL past eq. pt.; 26 mL; SA

mL	pH
0	11.13
12.5	9.25
24	7.86
25	5.22
26	2.5

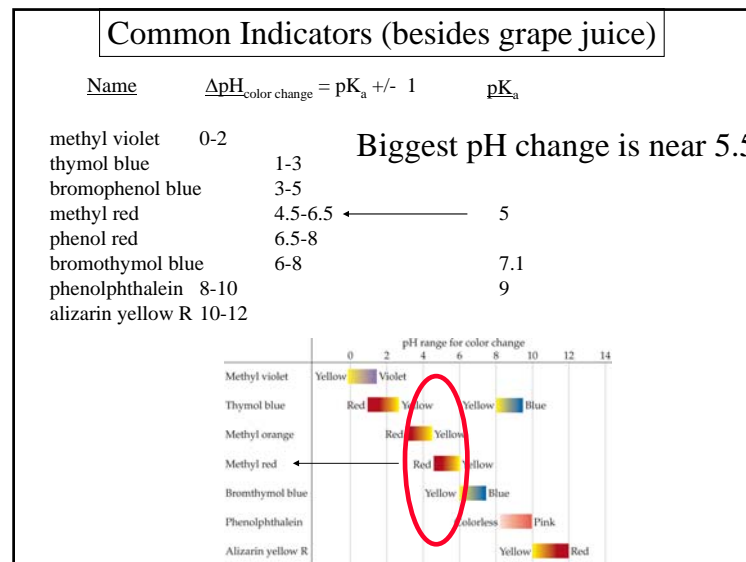
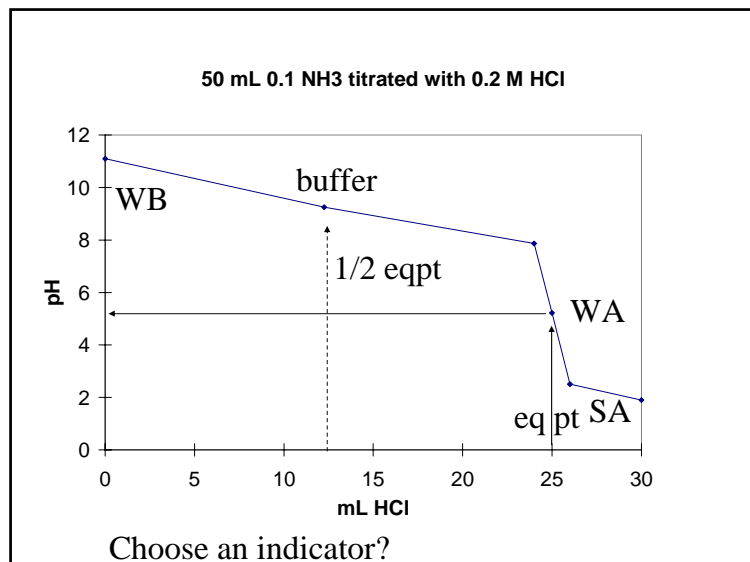
$\frac{(50mL)(0.1M_{NH_3/NH_4^+})}{50 + 25 + 1} = \frac{5mmole}{76mL} = [NH_4^+]$
 $\frac{(1mL_{excess})(0.2M_{HCl})}{50 + 25 + 1} = 2.63 \times 10^{-3} M = [H^+]$
 conc. SA = conc. $H^+ = 2.63 \times 10^{-3}$ **OR, limiting reagent**
 $pH = -\log(2.63 \times 10^{-3})$
 $pH = 2.5$
Limiting Reagent $(26mL_s)(0.2M_{HCl}) = 52mmoleNH_4^+$
 $(50mL_s)(0.1M_{HCl}) = 50mmoleNH_4^+$
 2mmole excess H^+
 $\frac{2mmole}{50 + 25 + 1} = 2.63 \times 10^{-3}$

Example titrate 50 mL 0.1 M NH_3 , 0.2 M HCl; include 1 mL and 1 mL after eq.pt.

5 mL past eq. pt.

mL	pH
0	11.13
12.5	9.25
24	7.86
25	5.22
30	1.9

$\frac{(5mL_{excess})(0.2M)}{50 + 25 + 5} = 1.25 \times 10^{-2} M = [H^+]$
 conc. SA = conc. $H^+ = 1.25 \times 10^{-2}$
 $pH = -\log(1.25 \times 10^{-2})$
 $pH = 1.9$



Example Titration 3: We have 25.0 mL of 0.200 M HNO₃. What will be the pH after we add 0, 20, 49, 50, 51, 75, 100 mL of 0.100 M NaOH

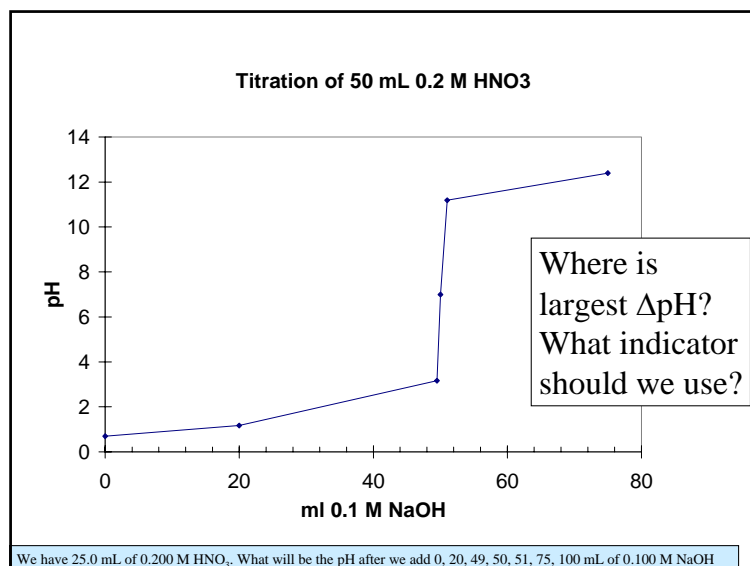
Main Course: SA/SB Side courses: more of same

Mmole HNO ₃ init <small>0.20M)(25mL)</small>	mL OH added	Mmoles OH added <small>(0.10M)(mL)</small>	Mmole H ⁺ excess	Mmole OH excess	Total Vol	[H ⁺] Or [OH ⁻]

Example Titration 3: We have 25.0 mL of 0.200 M HNO₃. What will be the pH after we add 0, 20, 49, 50, 51, 75, 100 mL of 0.100 M NaOH

Main Course: SA/SB Side courses: more of same

[H ⁺] Or [OH ⁻]			
5/25=0.2			pH=-log(0.2)=0.698
3/45=0.066			pH=-log(0.066)=1.17
0.1/74=0.00135			pH=-log(0.00135)=3.17
H ₂ O			pH=7
0.1/76=0.00136	pOH=-log(0.0013)=2.88	pH=14-pOH=11.12	
2.5/100=0.025	pOH=-log(0.025)=1.602	pH=14-pOH=12.398	
5/125=0.04	pOH=-log(0.04)=1.39	pH=14-pOH=12.61	

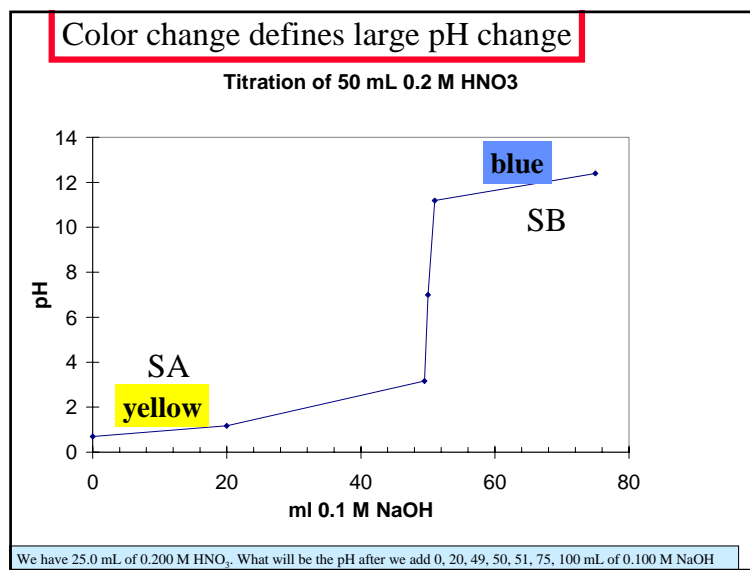


Common Indicators (besides grape juice)

Name	Δ pH _{color change} = pK _a +/- 1	pK _a
methyl violet	0-2	
thymol blue	1-3	
bromophenol blue	3-5	
methyl red	4.5-6.5	5
phenol red	6.5-8	7.1
bromothymol blue	6-8	7.1
phenolphthalein	8-10	9
alizarin yellow R	10-12	

Biggest pH change is near 7

pH range for color change



I WANT YOU
TO PRACTICE
EVERY DAY!

“A” students work
(without solutions manual)
~ 10 problems/night.

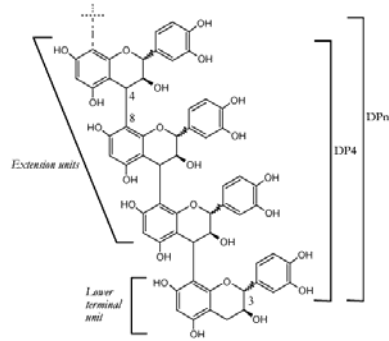
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508-3119
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Office Hours Th&F 2-3:30 pm

Module #17C:
Buffering and Titrations

END

Tannins – represent linked cyanidins



The general structure of a homologue procyanidin is 4→8 bonded, though there can be 4→6 branch points, and a gallic acid esterified at the 3 position.

Red wine - antioxidants

http://www.micro-ox.com/chem_tan.htm

Food Source	Anthocyanins	Glycoside form
apple	cyanidin	monoglycoside
blueberry	malvidin	monoglycoside
	petunidin	monoglycoside
	delphinidin	monoglycoside
cranberry	cyanidin	monoglycoside
	peonidin	monoglycoside
red cabbage	cyaniclin	diglycoside
strawberry	pelargonidin	monoglycoside
	cyanidin	monoglycoside