Chapter 15 Aqueous Equilibrium

Buffers and other phenomena

Review

- Recall when you hydrolyze a weak base the reaction looks like this:
- B + H_2O <== ==> BH + OH^-

base acid conj conj
acid base

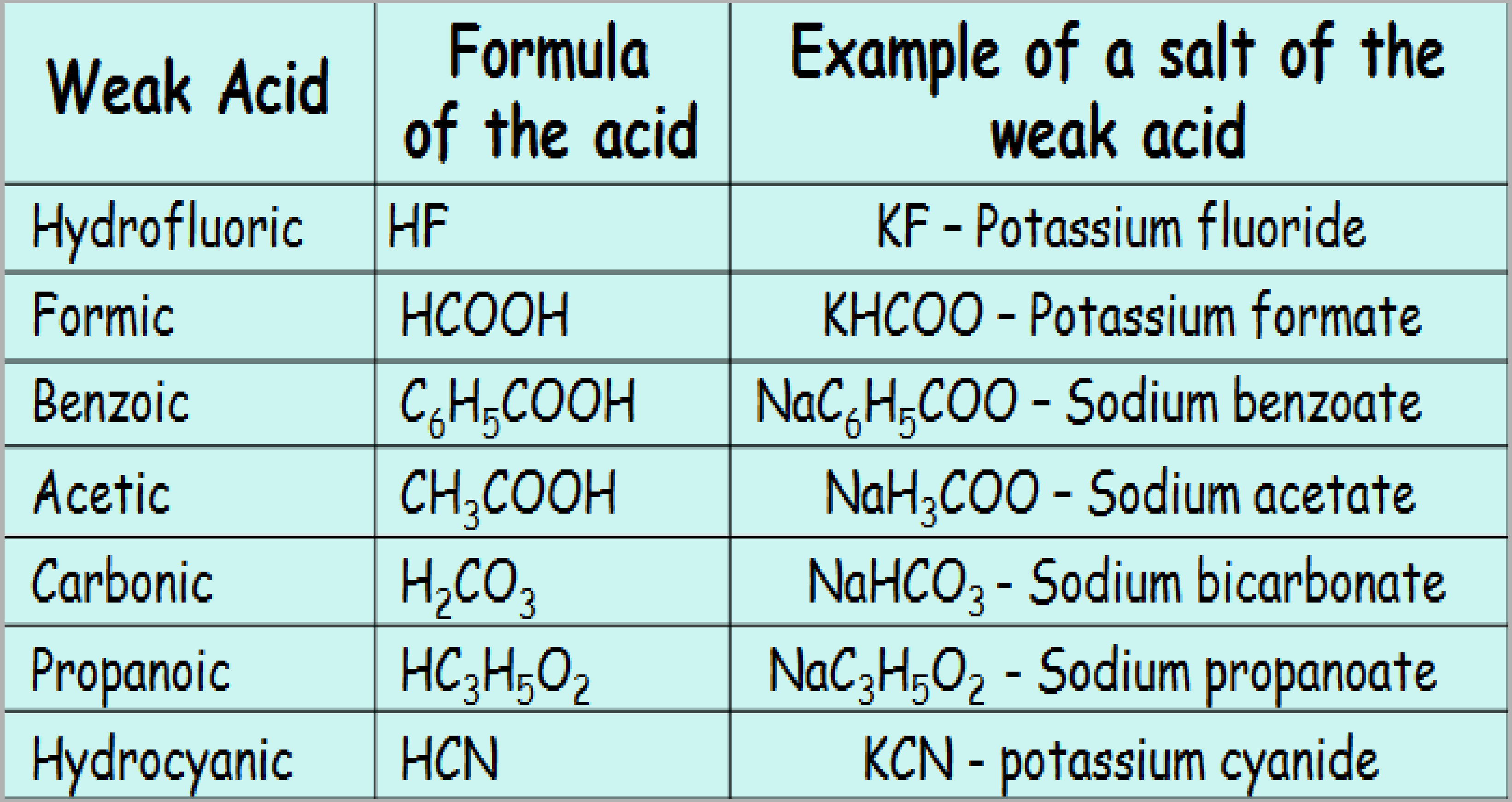
Buffered solutions

- Resist changes in pH when an acid or a base is added.
- Are made from
  - A weak acid and its salt
  - A weak base and its salt

Acid-Salt buffers

- Acid must be a weak acid. This means it has a reservoir of molecules from which a proton can be seperated if the need arises.
- The salt is made with the common anion of the acid (the acid’s conjugate base) and the cation of a strong base. Example $NaC_2H_3O_2$ can be thought of as resulting from NaOH + $HC_2H_3O_2$

Some examples of Acid/Salt pairs

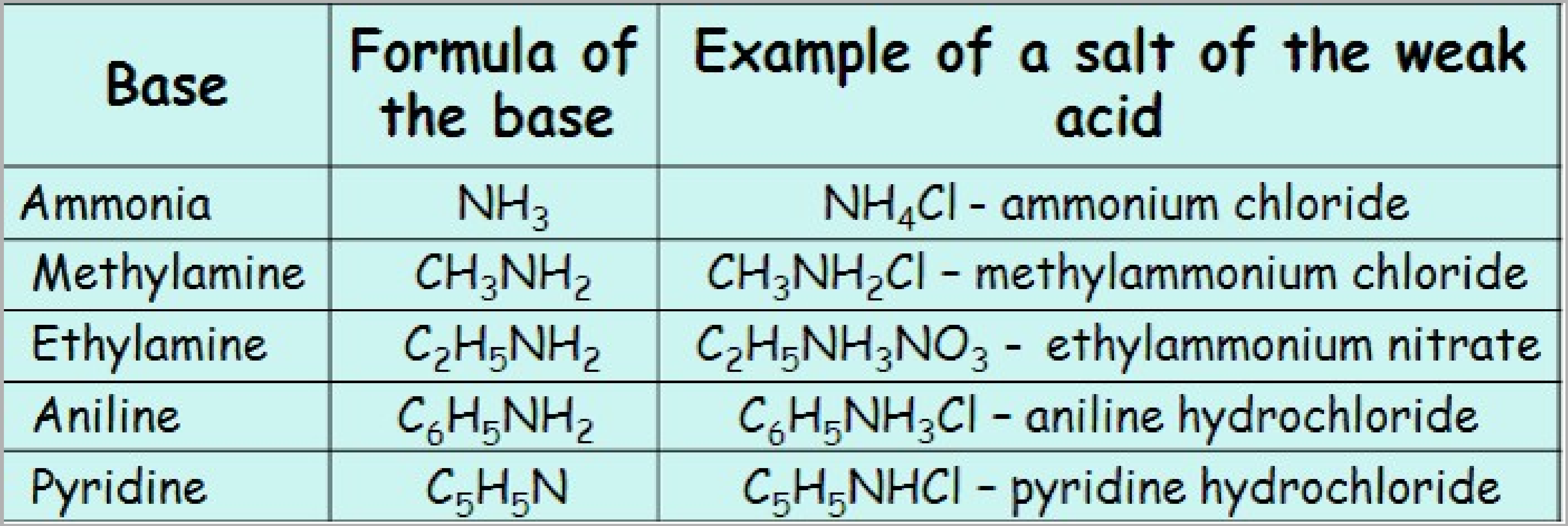


Weak Acid	Formula of the acid	Example of a salt of the weak acid
Hydrofluoric	HF	KF - Potassium fluoride
Formic	HCOOH	KHCOO - Potassium formate
Benzoic	C_6H_5COOH	NaC_6H_5COO - Sodium benzoate
Acetic	CH_3COOH	NaH_3COO - Sodium acetate
Carbonic	H_2CO_3	$NaHCO_3$ - Sodium bicarbonate
Propanoic	$HC_3H_5O_2$	$NaC_3H_5O_2$ - Sodium propanoate
Hydrocyanic	HCN	KCN - potassium cyanide

Base/Salt Buffers

- The salt in a base-salt buffer will include the cation of the base, and an anion the comes from a strong acid. Common anions would be chloride (HCl) and nitrate (HNO_3)

Base/salt pairs



Base	Formula of the base	Example of a salt of the weak acid
Ammonia	NH_3	NH_4Cl - ammonium chloride
Methylamine	CH_3NH_2	CH_3NH_2Cl – methylammonium chloride
Ethylamine	$C_2H_5NH_2$	$C_2H_5NH_3NO_3$ - ethylammonium nitrate
Aniline	$C_6H_5NH_2$	$C_6H_5NH_3Cl$ – aniline hydrochloride
Pyridine	C_5H_5N	C_5H_5NHCl – pyridine hydrochloride

Why do buffers work

- Consider an aqueous solution of HF:
  HF <====> H^{+} + F- according to LeChatelier’s principle, what would happen to the pH if we add NaF?
- HF <====> H^{+} + F-
- Na <====> Na+ + F-
- This would result in
- HF <====> $H^{+} + F^{-} + Na^{+}$ the common ion reverses the dissociation of HF and so more is molecular. pH goes up.

Base example of common ion

- $NH_3 + H_2O$ <=====> $NH_4^+ + OH^-$
- NH_4Cl (s) <=====> NH_4^+ + Cl^-
- <===
- Adding the common ion crowds the NH_4^+ this leads to less OH^- being formed in the first reaction. pH goes down.

Acid/Salt buffer example

- Calculate the pH of a buffer system containing 1.0 M HF (Ka = 7.2×10^{-4}) and 1.0 M NaF.
- $HF(aq) \Longleftrightarrow H^{+}(aq) + F^{-}(aq)$
- $Ka = \frac{[H+][F-]}{[HF]} = 7.2 \times 10^{-4}$

Example cont’d

	HF-	H+	F-
I	1.0	0	1.0
C	1.0 –x	x	1.0 +x
E			

Example continued

- $\underline{x(1.0 + x)} = 7.2 \times 10^{-4}$
- 1.0 - x
- simplifies (usually)
- $\underline{x(1.0)} = 7.2 \times 10^{-4}$
- 1.0
- $x = 7.2 \times 10^{-4}$
- pH = 3.14

Example cont’d

	HF-	H+	F-
I	1.0	0	1.0
C	1.0 –x	x	1.0 +x
E	1.0	7.2×10^{-4}	1.0

Couple of useful equations!!!

- When dealing with buffers, keep in mind
- $[H^+] = K_a \frac{[HA]}{[A^-]}$
- In buffer problems HA and A- are known as is Ka
- $pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) = pK_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)$

2nd Acid/Salt buffer

- Calculate the pH of a solution which contains 0.50 M acetic acid ($HC_2H_3O_2$ Ka = 1.8×10^{-5}) and 0.50 M sodium acetate.
- What are the possible ions in solution $HC_2H_3O_2$, Na^+, $C_2H_3O_2^-$, and H_20
- What reaction will control equilibrium
- $HC_2H_3O_2 <===> H^+ + C_2H_3O_2^-$

Example 2 cont’d

- Write the Ka expression
- $Ka = \frac{[H+]\,[C_2H_3O_2-]}{[HC_2H_3O_2]}$
- Set up and ice table and write an expression for the changes

ICE Table

	HAc-	H+	Ac-
I	0.50	0	0.50
C	0.50 –x	x	0.50 + x
E			

Substitute and Solve

- $1.8 \times 10^{-5} = \frac{(x)(0.50 + x)}{(0.50 - x)}$
- Since Ka is small then x should be small we can simplify this to:
- $1.8 \times 10^{-5} = \frac{(x)(0.50)}{(0.50)}$
- $1.8 \times 10^{-5} = x$ (x is less than 5%)
- pH = 4.74

pH change in a buffer problem

- Now take this buffer system and add 0.010 mol solid NaOH.
- What are the species present in water:
- $HC_2H_3O_2$, Na^+, $C_2H_3O_2^-$, OH^- ,and H_20
- OH- will cause $HC_2H_3O_2$ to lose H+ to neutralize OH-

pH change

- 1 do the stoichiometry of the problem, then worry about eqm.
- Reaction:
- $HC_2H_3O_2 + OH^- <===> C_2H_3O_2^- + H_2O$

ICE Table it

	HAc-	OH-	Ac-
I	1.0 L x .50 M = 0.50 mol	0.010 mol	1.0 L x .50 M = 0.50 mol
C	0.50 –0.010	- 0.010 mol	0.50 + 0.01 mol
E	0.49 mol	0.0 mol	0.51 mol

pH change cont’d

- Now substitute this into a Ka expression
- $1.8 \times 10^{-5} = \frac{[H+][C_2H_3O_2-]}{[HC_2H_3O_2]}$
- $1.8 \times 10^{-5} = \frac{(x)(0.51 + x)}{(0.49-x)}$
- Since Ka is small simplify to:
- $\frac{(x)(0.51)}{(0.49)} = 1.8 \times 10^{-5}$

pH change cont'd

- X = [H+] = 1.7×10^{-8}
- log 1.7×10^{-8} = 4.76
- the orginal solution had a pH of 4.74!
- pH hardly budged!!!!
- If we had added this much NaOH to pure water the pH would have ended at 12.00!!!
- Buffers really do work.

Got buffer?

pH of a buffer and pH change

- A buffered solution contains 0.25 of NH_3 (Kb = 1.8×10^{-5}) and 0.40 M NH_4Cl What is the pH of this solution
- Write the major species in solution

- Write a Kb expression.

pH of a buffer and pH change

	NH_3	NH4+	OH-
I	0.25	0.40	0
C	0.25–x	0.40 + x	+ x
E			

Substitute and solve the Kb

Substituting and solvation ;)

- $Kb = \underline{(0.40 + x)\ x}$
- $0.25-x$
- Since Kb is small
- $Kb = \underline{(0.40\ )\ x\ } = 1.8 \times 10^{-5}$
- 0.25
- $x = 1.1 \times 10^{-5}$

pH of a buffer and pH change

	NH_3	NH4+	OH-
I	0.25	0.40	0
C	0.25–x	0.40 + x	+ x
E	0.25	0.40	$1.1x10^{-5}$

So what is the pH?

- (-) log (1.1 x 10^{-5}) = 4.95 = pOH
- pH = 9.05

- pH without the common ion would’ve been 11.3 !!!

Ex. 2 pH of buffer solution

- What is the pH of a solution of 0.75M lactic acid ($HC_3H_5O_3$) and sodium lactate 0.25 M. Ka = 1.4×10^{-4}
- HLac, $Lac^- Na^+$ and H_2O major species
- $HC_3H_5O_3 \rightleftarrows H^+ + C_3H_5O_3^-$
- $Ka = \dfrac{[H^+][C_3H_5O_3^-]}{[HC_3H_5O_3]} = 1.4 \times 10^{-4}$

pH of a buffer

	HLac	H+	Lac-
I	0.75	0	0.25
C	0.75–x	+ x	0.25+ x
E			

Substitute and solve

- $$Ka = \frac{[H^+][C_3H_5O_3^-]}{[HC_3H_5O_3]} = 1.4 \times 10^{-4}$$
- $$Ka = \frac{(x)(0.25 + x)}{(0.75 - x)} = 1.4 \times 10^{-4}$$
- Since x is small
- $$Ka = \frac{(x)(0.25)}{(0.75)} = 1.4 \times 10^{-4}$$
- $[H+] = 4.2 \times 10^{-4}$ and pH = 3.38

Buffering capacity

- A weak solution of a buffer (low concentration) and a strong solution of a buffer (high concentration) will have the same pH (controlled by the dissassociation)
- The concentrated buffer will have much more buffer capacity. It will resist changing pH when more acid or base is added.

Further example

- Calculate the pH and pH change that results from bubbling 0.010 mol HCl gas through 1.0 L of 5.0 M HAc and 5.0 M NaAc
- Use short cut of Henderson-Hasselbalch eqn
- pH= pKa + log ([Ac-]/[HAc])
- pH= $-\log(1.8\text{x}10^{-5})$ + log (1)
- pH = 4.74 (before adding HCl)

Further example

- Major species: H+, Cl-, $C_2H_3O_2$-, Na+, H_2O,
- Strong conjugate base so the new H+ from the HCl will form molecular $HC_2H_3O_2$. Assume this reaction will go to completion, as long as there is $C_2H_3O_2$-
- Reaction of interest:
- $H^+ + C_2H_3O_2^-$ ==> $HC_2H_3O_2$

From HCl From eqm Can’t contribute to pH

Modified ICE table for stoich.

	H^+	$C_2H_3O_2^-$	$HC_2H_3O_2$
• Before	0.010 M	5.00 M	5.00 M
• After	0	4.99 M	5.01 M

- $\mathrm{pH} = \mathrm{pKa} + \log\left(\frac{[A^-]}{[HA]}\right)$
- pH = 4.74 + log (4.99/5.01) = 4.74 - 0.0017 or 4.74 So the buffer consumed all added H +

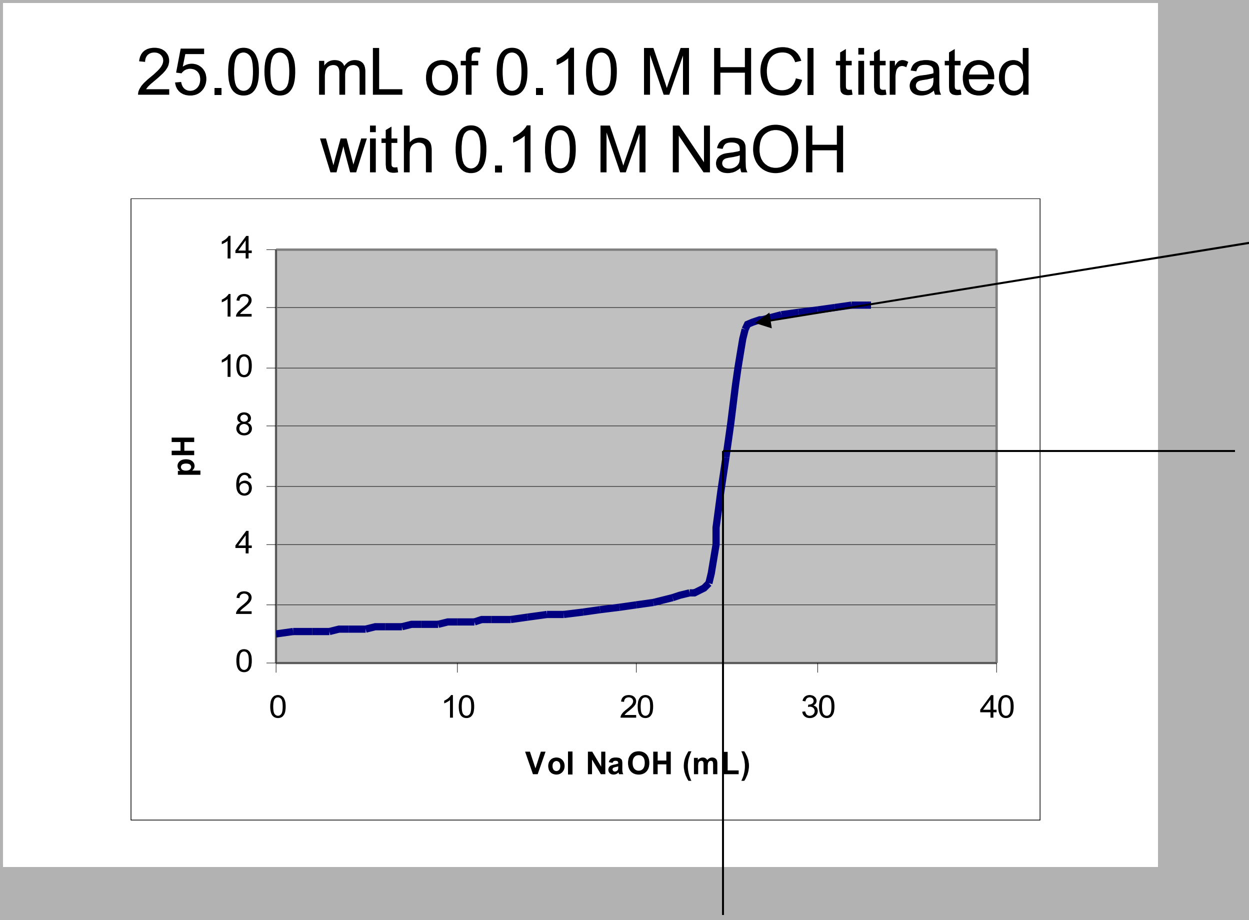
Selecting a buffer system

- Sometimes a chemist needs a buffer for a specific pH.
- **Buffers work best (highest buffer capacity when [A-] = [HA] or [A-]/[HA] = 1**
- so substitute this in the HH eqn
- pH = pKa + log([A-]/[HA]) but this is 1 so..
- **pH = pKa or as close as you can get**.

Titrations

- Titration is the stepwise addition of a known concentration of acid or base into an unknown until the unknown is just consumed. This is usually observed by the change of an indicator.

Strong Acid/Strong Base



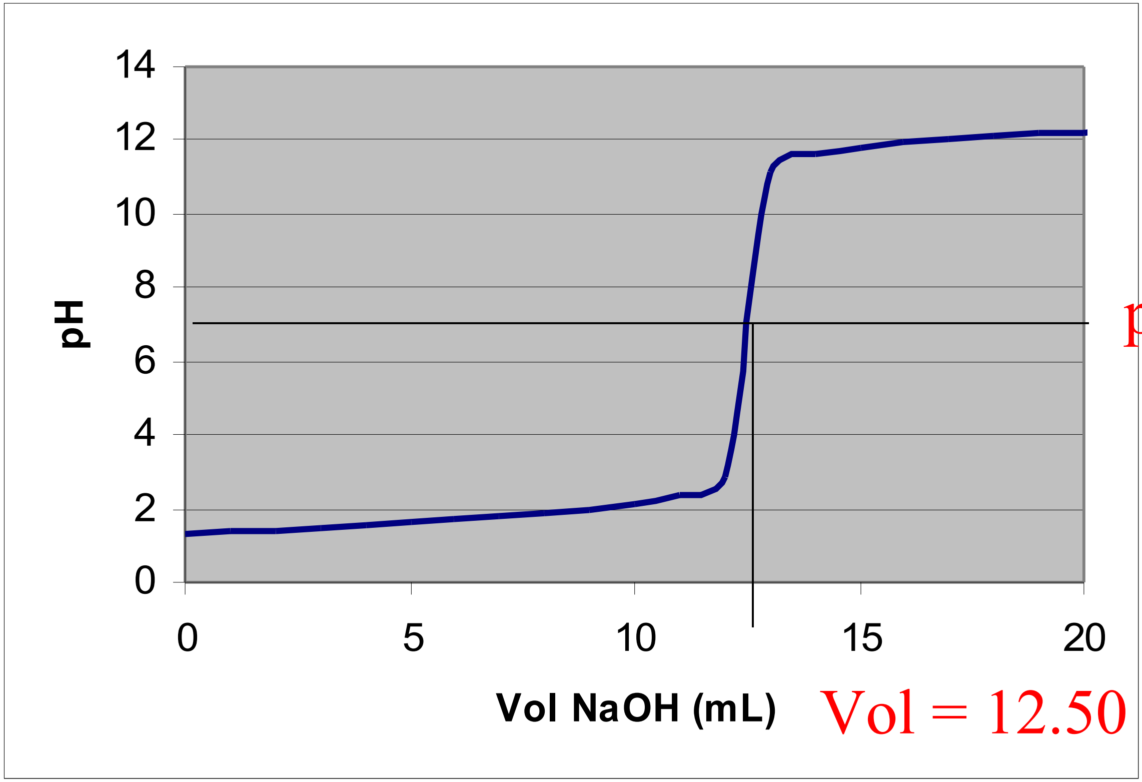
Sharp
curve
break

pH a EQ pt = 7

Equivalence point Na x Va = Nb x Vb

Reading Titration graphs

25.00 mL of ? M HCl titrated with 0.10 M NaOH



pH = 7

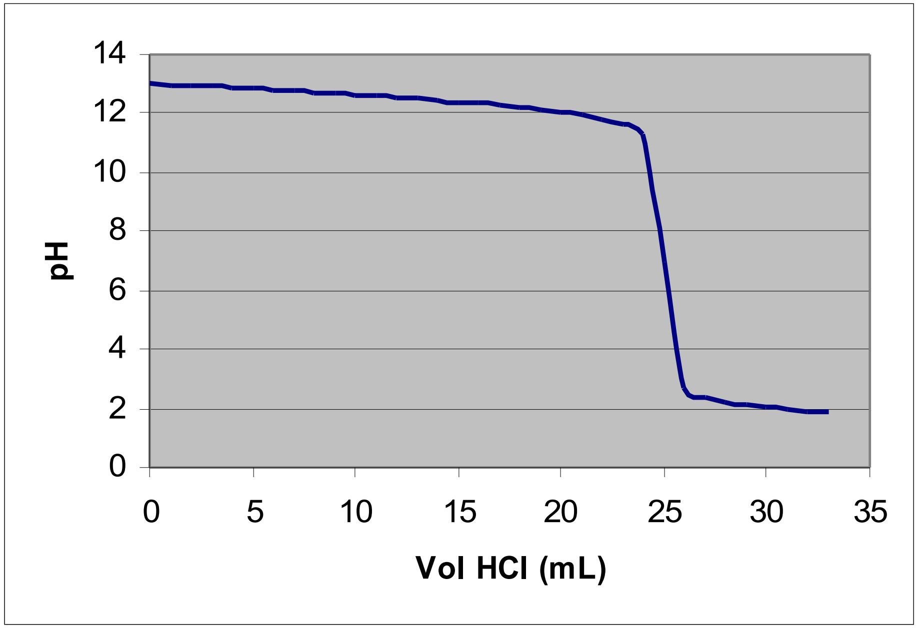
Vol = 12.50 mL

Reading Titration curves

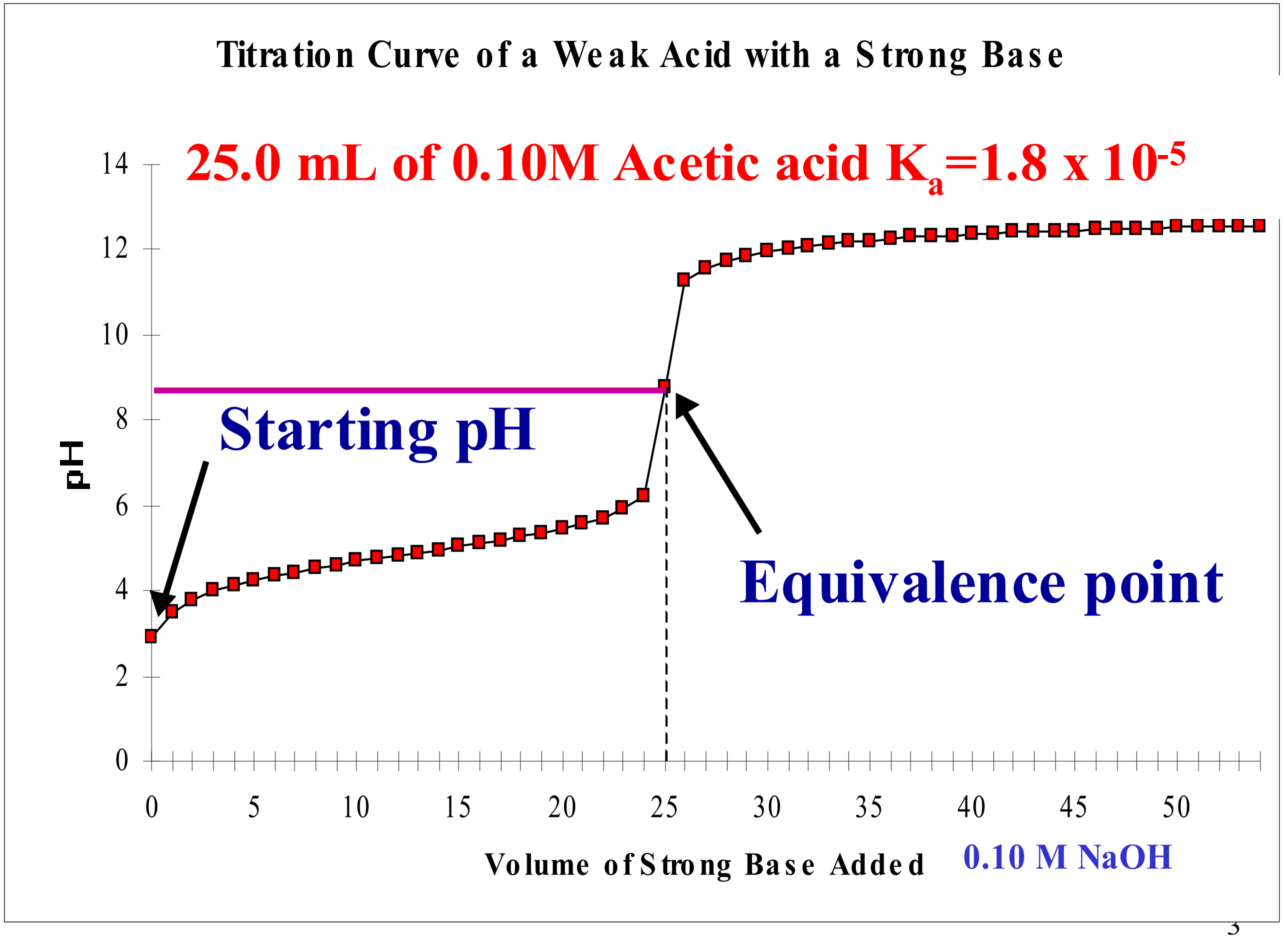
- 12.50 mL x 0.10 N = 25.00 mL x ? N HCl?
- 0.05 N HCl
- HCl = 1 eq/ mole so
- 0.05 M HCl is strength of unknown acid.

Strong Base titrated w acid.

25.00 mL of 0.10 M NaOH titrated with 0.10 M HCl



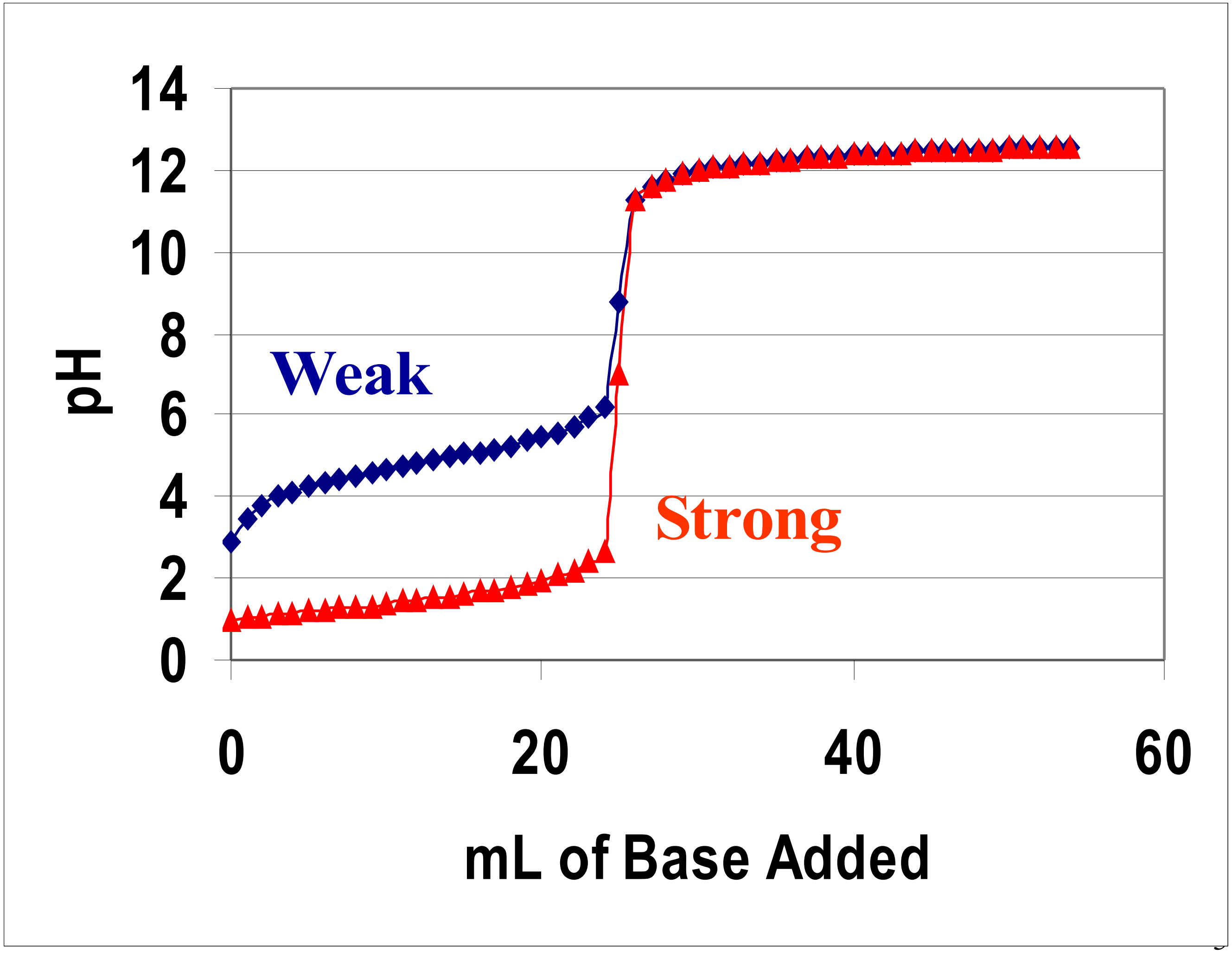
Titration of weak acid



Check for understanding

- Equivalence point is defined as
- $N_a \times V_a = N_b \times V_b$
- This is not typically pH=7 when dealing with weak acids!!!
- Why?

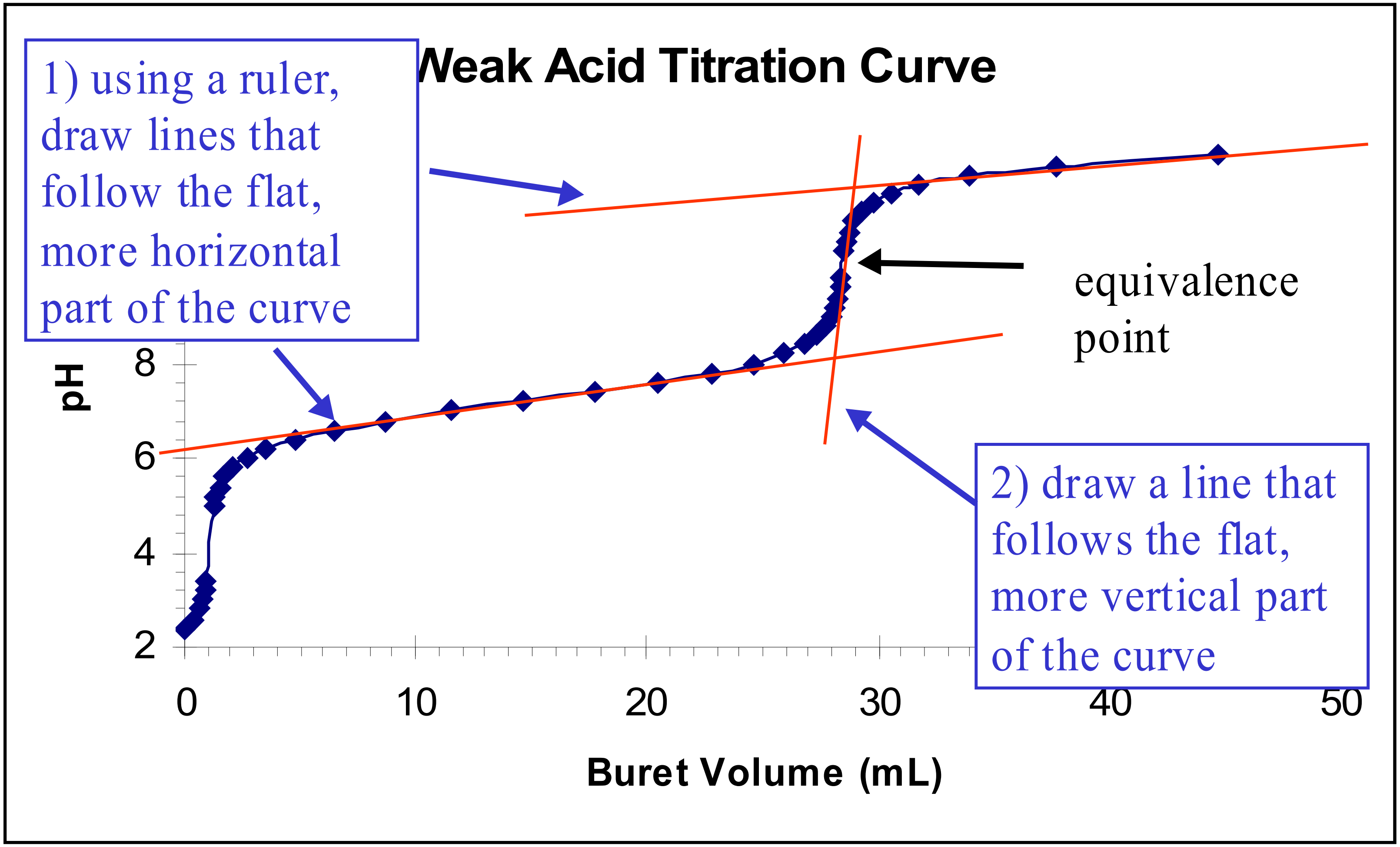
Comparison strong/ weak acid



Weak acids/Strong Acids

- The weaker the acid the lower the Ka
- The lower the Ka
- The shallower the titration curve is
- Higher initial pH
- The more sloped the equivalence break point transition is.

Find the Equivalence Point (Geometric method)

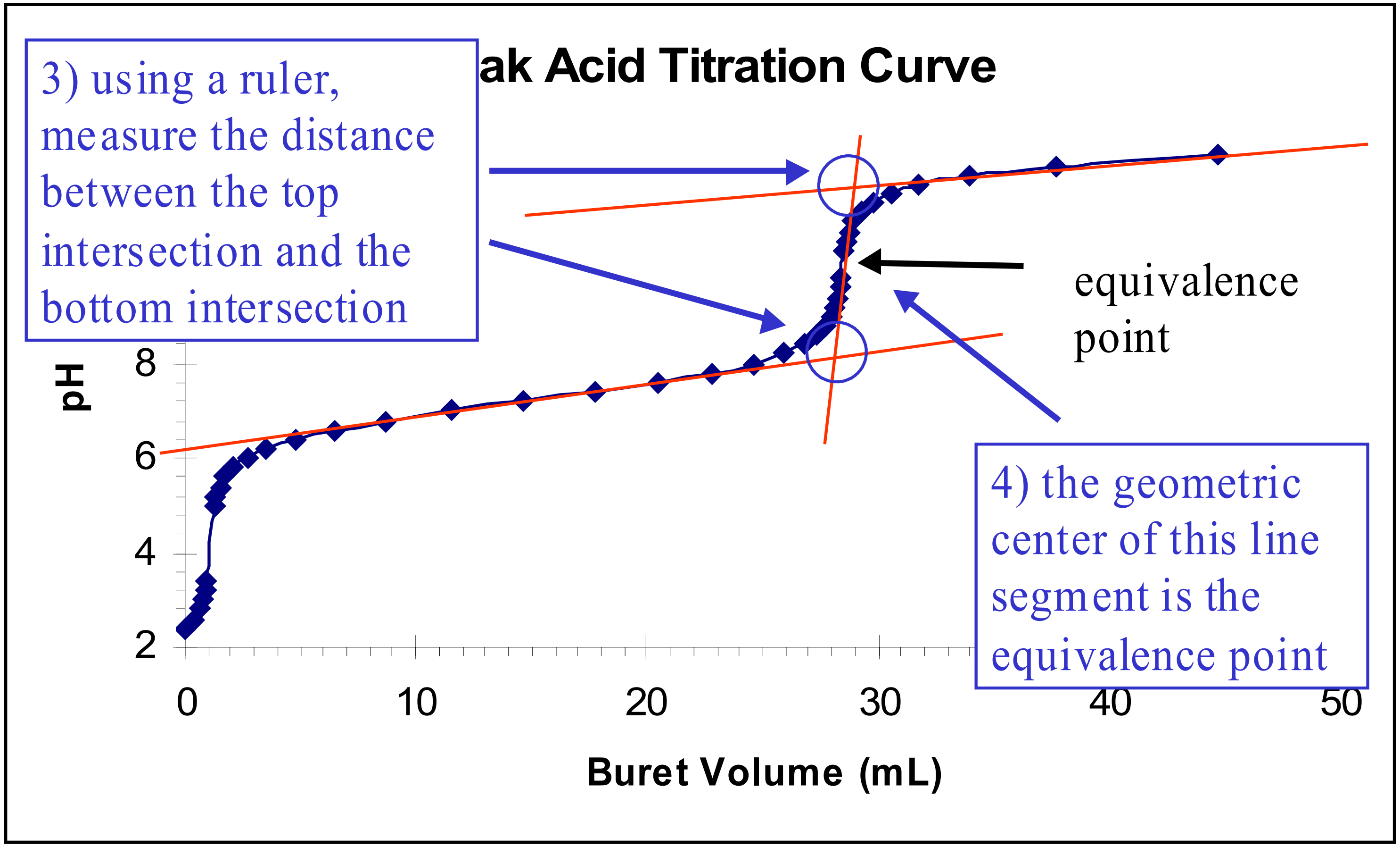


1) using a ruler, draw lines that follow the flat, more horizontal part of the curve

2) draw a line that follows the flat, more vertical part of the curve

equivalence point

Find the Equivalence Point (Geometric method)

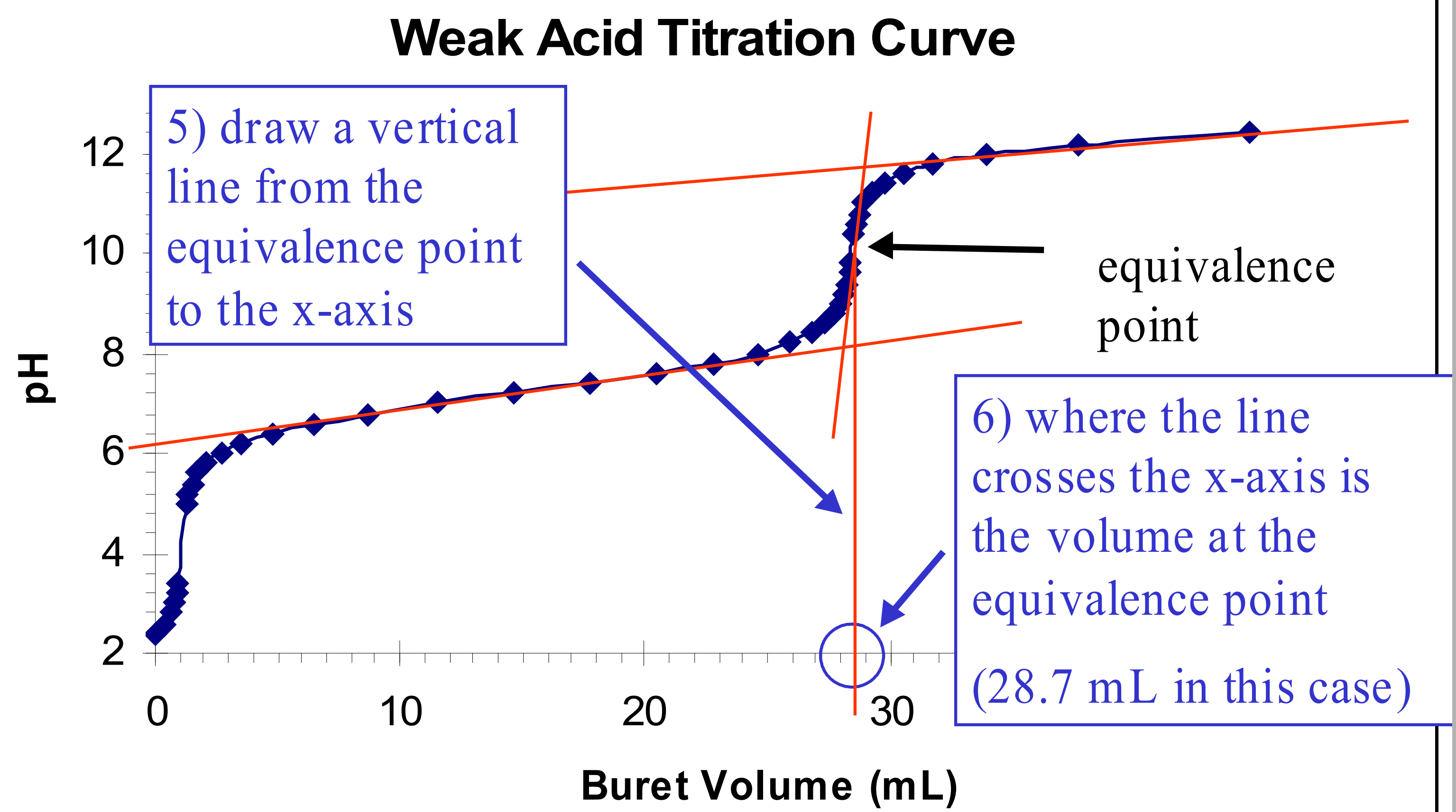


3) using a ruler, measure the distance between the top intersection and the bottom intersection

equivalence point

4) the geometric center of this line segment is the equivalence point

Find the Equivalence Point (Geometric method)



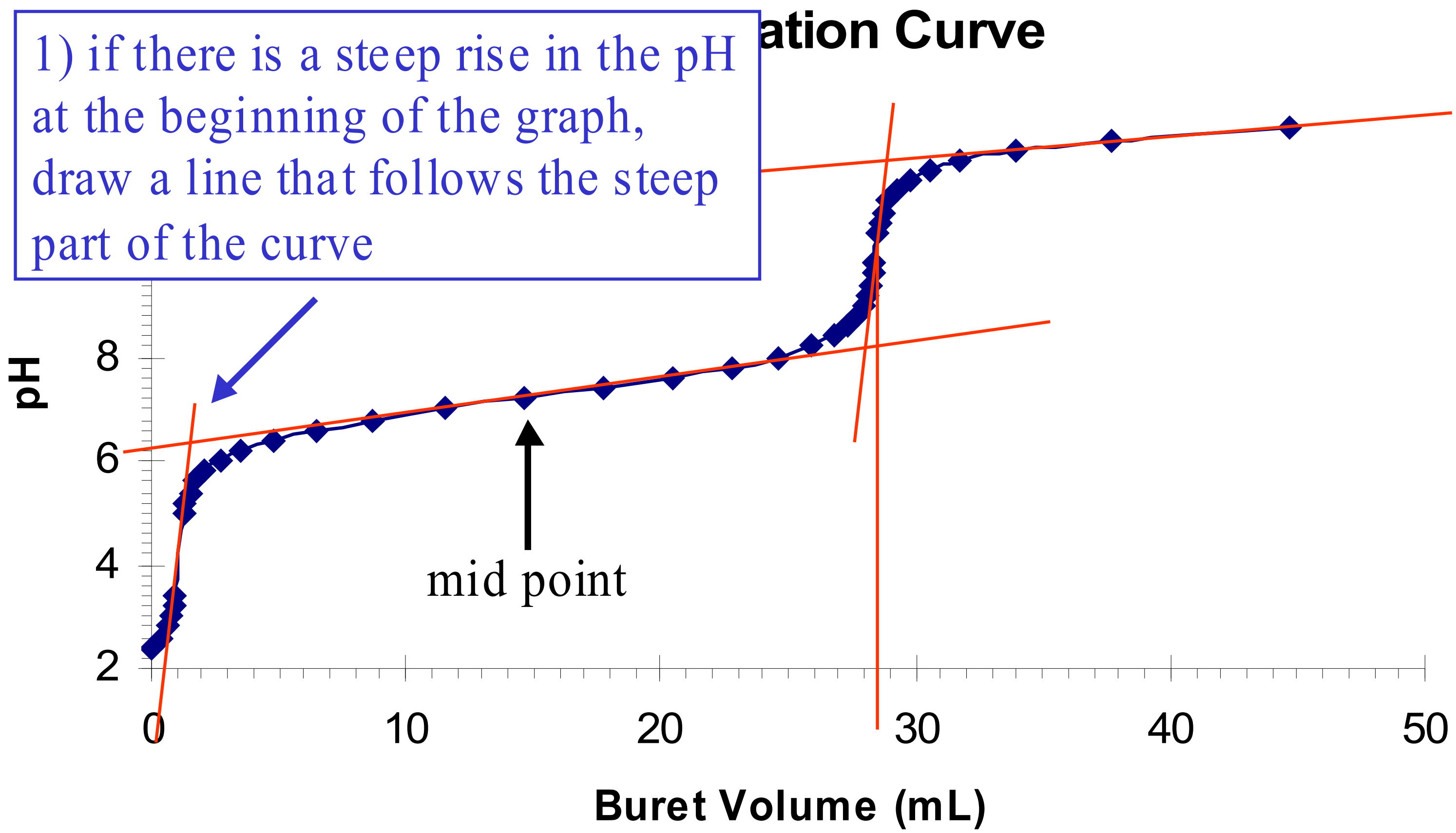
5) draw a vertical line from the equivalence point to the x-axis

equivalence point

6) where the line crosses the x-axis is the volume at the equivalence point

(28.7 mL in this case)

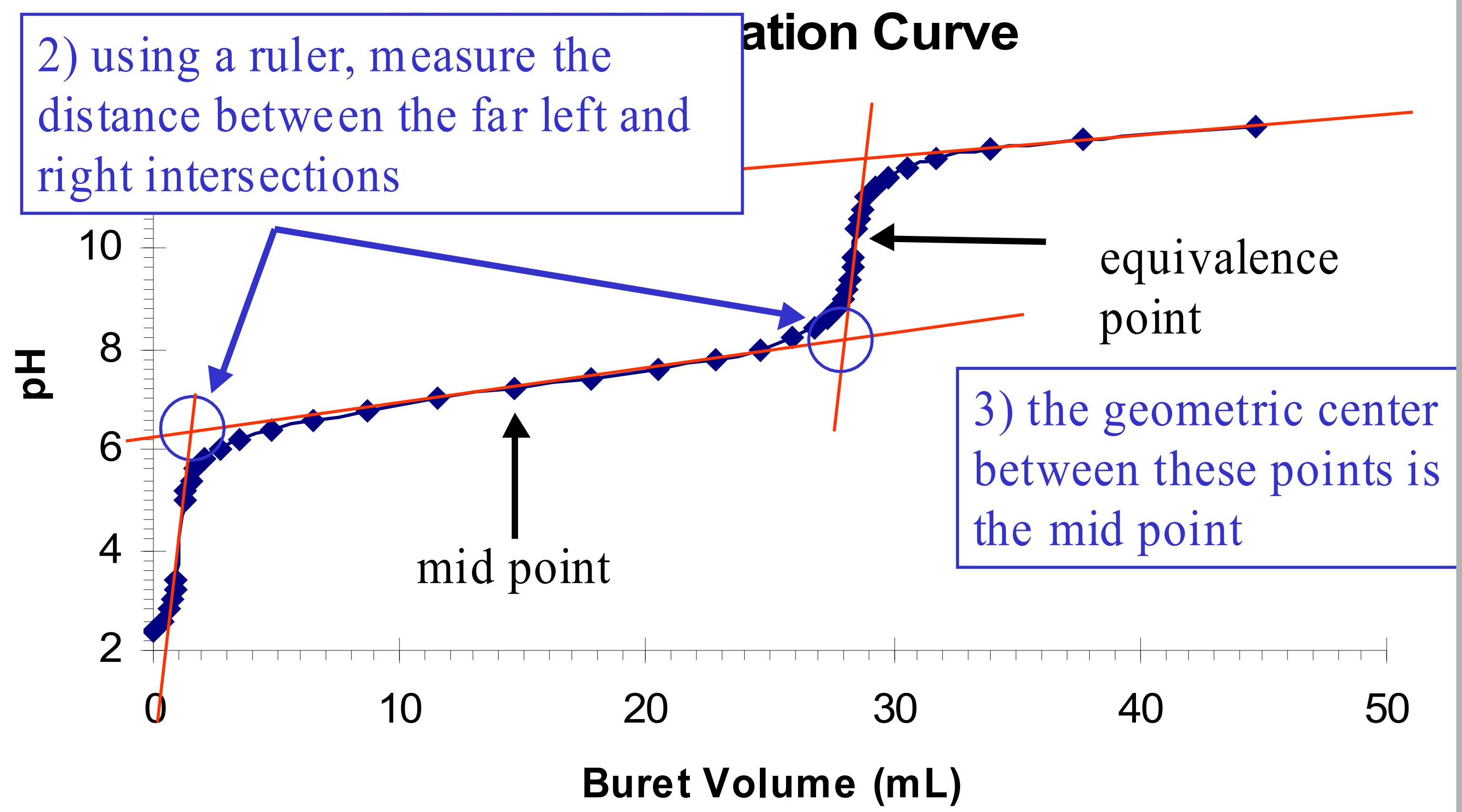
Find the Mid Point (Geometric method)



1) if there is a steep rise in the pH at the beginning of the graph, draw a line that follows the steep part of the curve

mid point

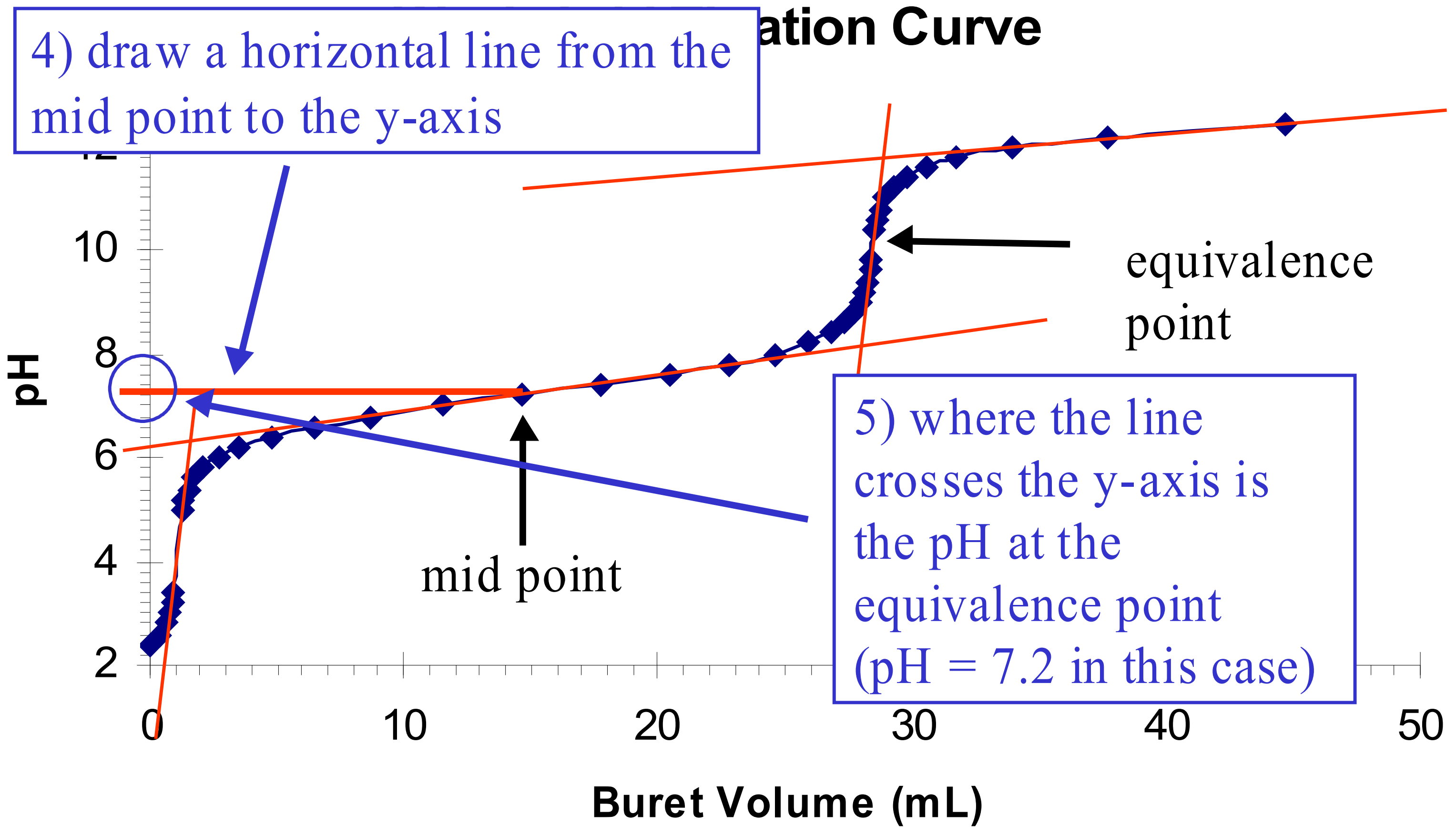
Find the Mid Point (Geometric method)



2) using a ruler, measure the distance between the far left and right intersections

3) the geometric center between these points is the mid point

Find the Mid Point (Geometric method)



4) draw a horizontal line from the mid point to the y-axis

equivalence point

mid point

5) where the line crosses the y-axis is the pH at the equivalence point (pH = 7.2 in this case)

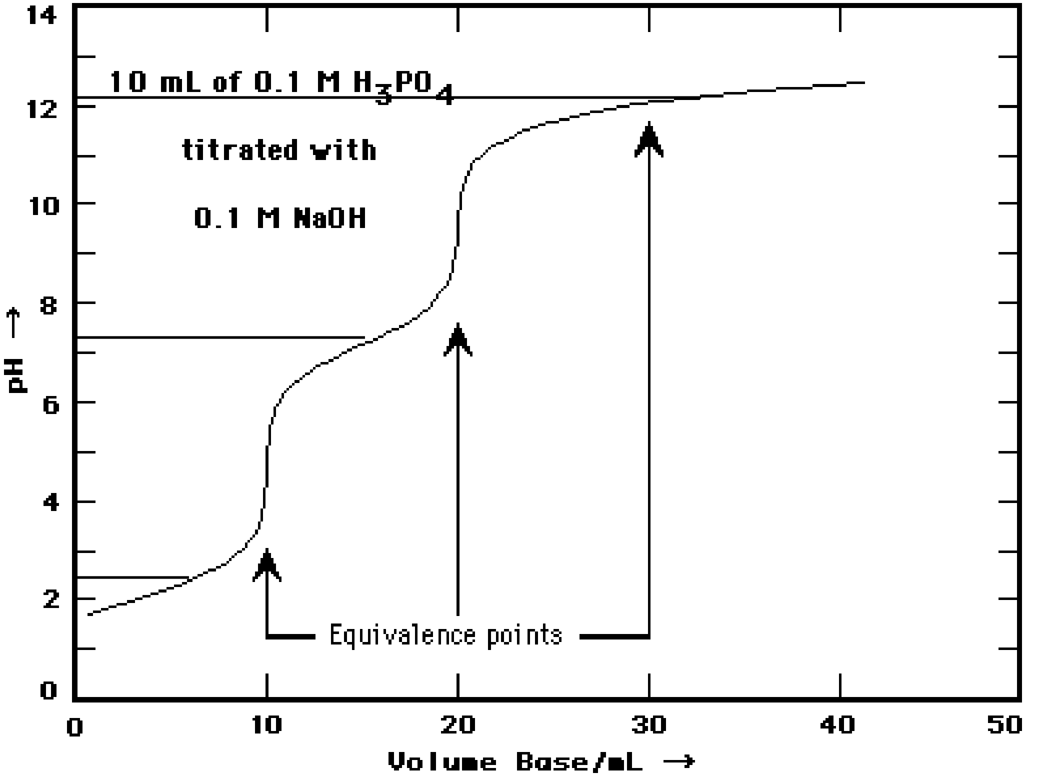
Finding Ka

- At mid-point, some thing miraculous happens

- $pH_{mid} = pKa$
- So time for antilog $10^{-pKa} = Ka$
- $10^{-7.2} =$ **6.31×10^{-8}**

What are the K_{a1}, K_{a2}, and K_{a3}

Titration curve of phosphoric acid,



How close did you get?

$H_3PO_{4(s)} + H_2O_{(l)}$ <==> $H_3O^+_{(aq)} + H_2PO_4^-{}_{(aq)}$ $K_{a1} = 7.5\times10^{-3}$

$H_2PO_4^-{}_{(aq)} + H_2O_{(l)}$ <==> $H_3O^+_{(aq)} + HPO_4^{2-}{}_{(aq)}$ $K_{a2} = 6.2\times10^{-8}$

$HPO_4^{2-}{}_{(aq)} + H_2O_{(l)}$ <==> $H_3O^+_{(aq)} + PO_4^{3-}{}_{(aq)}$ $K_{a3} = 2.14\times10^{-13}$