



How do you pick which acid to use in your buffer solution?

- pick an acid that has a  $pK_a$  as close as possible to the pH of the desired solution
- set up your solution so  $[A^-] = [HA]$   
 $pH = pK_a + \log 1$  but  $\log 1 = 0$   
so  $pH = pK_a$

### Titration (or pH Curve)

- adding a solution of known concentration (the titrant) until the substance being analyzed is used up
- you would add an acid to a base (or a base to an acid) until the “equivalence point” is reached.

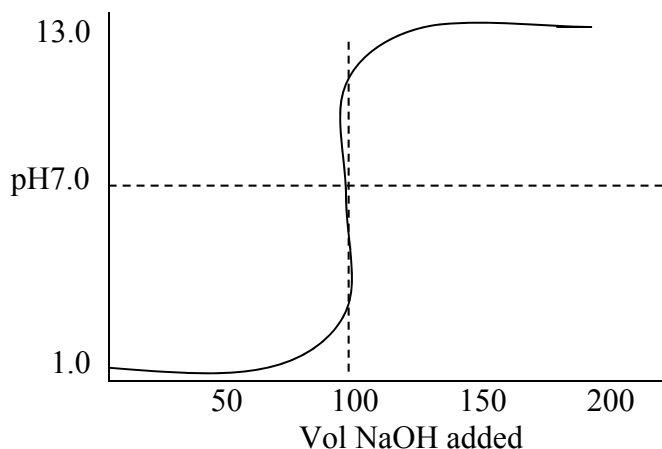
### Equivalence Point

- the point at which equal numbers of moles of  $H^+$  and  $OH^-$  have been added to a mixture
- an indicator changes color when the equivalence point is reached

### Titration (or pH) Curve

- a graph of pH (y-axis) vs volume of the titrant (x-axis)
- can be used to
  1. find the titration's equivalence point
  2. calculate the acids concentration
  3. for weak acids, determine the  $K_a$
- the shape of the graph depends on the strengths of the acid and base used

#### 1. Titrating a Strong Acid with a Strong Base



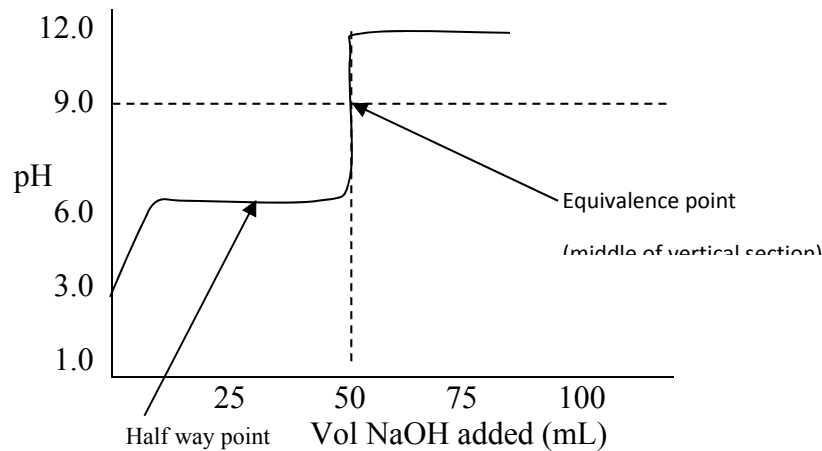
- as the base is first added the pH only changes a little because there is so much  $H^+$  (strong acid)

- the pH changes faster near the equivalence point because most of the  $H^+$  has been neutralized.
- for a strong acid – base titration, the pH at the equivalence point is 7.0

To find the [Acid]

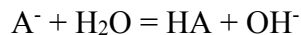
- at the equivalence point,  $\text{mol } OH^- = \text{mol } H^+$   
 so  $(\text{volume Base})(M_{\text{base}}) = \text{mol } OH^- = \text{mol } H^+$   
 therefore:  $M_{\text{acid}} = \text{mol } H^+ / \text{Vol Acid}$  (measured at the start of the titration)

2. Titrating a weak Acid with a strong Base



- pH increases rapidly at start (strong base)
- pH levels off near half way point (this point is half way to the equivalence point)
- pH levels off as a buffer solution is formed
  - $HA + OH^- \rightarrow A^- + H_2O$   
 at halfway point  $[HA] = [A^-]$   
 $HA = H^+ + A^-$  (buffer effect)

- at equivalence point, the  $pH > 7.0$  because of the reaction of the acids anion with  $H_2O$



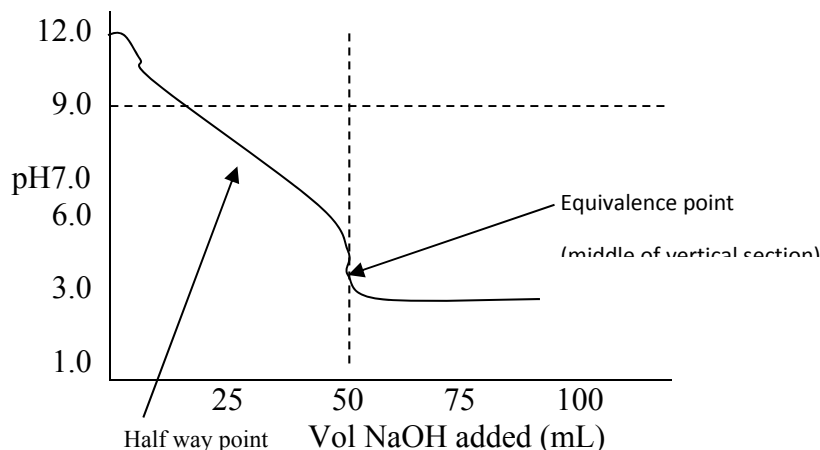
- the weaker the acid, the higher the pH at the equivalence point (It's conjugate base would be stronger)
- If the Molarity of the acid is known,  $K_a$  can be calculated at the halfway point
- at the halfway point, half of the HA has been converted to  $A^-$
- so  $\text{mol HA remaining} = \text{mol } A^-$  already formed or

$$[HA] = [A^-]$$

$$\text{since } K_a = [H^+] [A^-] / [HA]$$

$$K_a = [H^+] = \text{antilog } -pH \text{ (pH is known from the graph)}$$

3. Titrating a Weak Base ( $NH_3$ ) with a Strong Acid ( $HCl$ )



- curve levels off due to  $\text{NH}_3 / \text{NH}_4^+$  buffering
- $\text{pH} < 7$  at equivalence point because of the reaction  $\text{NH}_4^+ \rightarrow \text{NH}_3 + \text{H}^+$

### Acid – Base Indicators

- using an indicator is another way to identify the equivalence point in a titration
- the indicator changes color at the equivalence point (the “End Point”)
- indicators are actually weak acids whose conjugate base is a different color
  - ex. phenolphthalein  $\text{HIn} = \text{H}^+ + \text{In}^-$   
clear                      pink
- for titrating an acid with a base choose an indicator whose  $\text{pK}_a = \text{pH}$  at equivalence point +1  
or  $\text{pH} = \text{pK}_a - 1$
- for titrating a base with an acid choose  
or  $\text{pH} = \text{pK}_a + 1$

#### ex. Strong Acid with Strong Base

- at equivalence point,  $\text{pH} = 7.00$ 
  - $\text{pH} = \text{pK}_a - 1$
  - ∴  $\text{pK}_a = 8$  for indicator (fig. 15.8)
  - $K_a = 1 \times 10^{-8}$  (phenolphthalein)

#### ex. Weak Acid with Strong Base

- if at equivalence point,  $\text{pH} = 11.00$ 
  - $\text{pH} = \text{pK}_a - 1$
  - ∴  $\text{pK}_a = 12$  for indicator (fig. 15.8)
  - $K_a = 1 \times 10^{-12}$  (choose appropriate indicator from reference)

## Solubility Product Constant ( $K_{sp}$ )

- the equilibrium constant for a saturated solution of an ionic compound dissolved in  $H_2O$ 
  - ex.  $CaF_{2(s)} \rightleftharpoons Ca^{+2}_{(aq)} + 2F^{-}_{(aq)}$   
 $k_{sp} = [Ca^{+}][F^{-}]$
  - \*\* Solid  $CaF_2$  does not appear in the expression
- $k_{sp}$  values are given in table 14.4 and appendices in back of book

Ex. 15.12

The solubility of Copper I bromide is  $2.0 \times 10^{-4}$  M, at  $25^{\circ}C$ . What is the value of the  $k_{sp}$  for this salt?

15.12 (p.748) At 25°C, solubility of  $\text{Bi}_2\text{S}_3$  is  $1.0 \times 10^{-15} \text{M}$ .  $K_{\text{sp}}=?$

If you know a salt's  $K_{\text{sp}}$ , you can work the problem in the other direction and solve for the salt's solubility.

15.14 (p749) For  $\text{Cu}(\text{IO}_3)_2$ ,  $K_{\text{sp}}=1.4 \times 10^{-7}$   
Calculate its solubility at 25°C.

### Relative Solubilities

- if salts produce the same number of ions in solution, their  $K_{\text{sp}}$ 's can be used to compare solubilities.

Ex.  $\text{AgI } K_{\text{sp}}=1.6 \times 10^{-16}$   
 $\text{CuI } K_{\text{sp}}=5.0 \times 10^{-12}$

- since they each make 2 ions in solution.



$$[\text{M}^+]=[\text{X}^-]=Y$$

$$K_{\text{sp}}=[\text{M}^+][\text{X}^-]=(Y)(Y)=Y^2$$

$$Y=\text{solubility}=\sqrt{K_{\text{sp}}}$$

(therefore symbol-sorry couldn't find it on this computer)  $\text{CuI}$  is more soluble because its  $K_{\text{sp}}$  is larger

- if salts produce different numbers of ions in solution you would have to use the  $K_{\text{sp}}$  of each salt to actually calculate each salt's solubility
- you could then compare the solubilities directly

### Common Ion Effect

- a common ion is an ion that is found in 2 different solutes.

Ex.  $\text{CaF}_2 \setminus \text{F}^-$  is an ion "common" to both salts

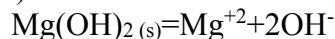
$\text{NaF} /$

- the presence of a common ion from one salt will decrease the solubility of a second salt

15.15 (p752) Calculate the solubility of  $\text{CaF}_2$  ( $K_{\text{sp}}=4 \times 10^{-11}$ ) in a solution that is 0.052M NaF.

- Any ion that causes a change in concentration of a dissolved ion will affect a salt's solubility

Ex.  $\text{Mg(OH)}_2$  is more soluble in Acid than in  $\text{H}_2\text{O}$



- In acid,  $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$   
from acid ^ ^from  $\text{Mg(OH)}_2$
- Removal of  $\text{OH}^-$  causes the equilibrium to shift to the right and more  $\text{Mg(OH)}_2$  will dissolve

- Another important example of this is the solubility of carbonates in acid

Ex.  $\text{Na}_2\text{CO}_3(s) = 2\text{Na}^+ + \text{CO}_3^{-2}$

- In acid:  $2\text{H}^+ + \text{CO}_3^{-2} \rightarrow \text{H}_2\text{CO}_3 \rightarrow \text{H}_2\text{O} + \text{CO}_2$
- As  $\text{CO}_3^{-2}$  is used up the equilibrium shifts to the right

- More  $\text{Na}_2\text{CO}_3$  dissolves so its solubility is increased

### Precipitation

- If solutions are mixed and the resulting ion product exceeds a salt's  $K_{sp}$ , that salt will precipitate out of the solution.

15.16 (p754) 750.0mL of  $4.0 \times 10^{-3}\text{M}$   $\text{Ce(NO}_3)_3$  are mixed with 300.0mL of  $2.0 \times 10^{-2}\text{M}$   $\text{KIO}_3$ .  
Will  $\text{Ce(IO}_3)_3$  precipitate? For  $\text{Ce(IO}_3)_3$ ,  $K_{sp} = 1.9 \times 10^{-16}$

### Complex Ions

- A metal ion surrounded by "ligands"

Ligand- a Lewis base (has a lone pair of electrons)

- Commonly  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{Cl}^-$ ,  $\text{CN}^-$ ,  $\text{OH}^-$ , &  $\text{SCN}^-$  (thiocyanate)

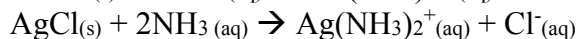
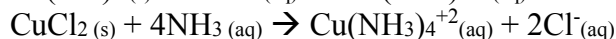
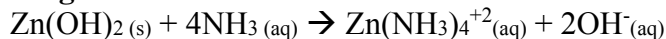
- The ligand forms a place where there can be attraction to a  $\text{H}_2\text{O}$  molecule
- This increases the solubility of the metal ion in the  $\text{H}_2\text{O}$
- The number of ligands attached to a metal ion is called the "coordination number"  
(commonly twice the ions charge)

Ex.  $(\text{Co(H}_2\text{O)}_6)^{+2}$        $\text{Ag(NH}_3)_2^{+1}$        $\text{Cu(NH}_3)_4^{+2}$

Ex.  $\text{AgCl}(s) + 2\text{NH}_3 = \text{Ag(NH}_3)_2^{+1} + \text{Cl}^-$

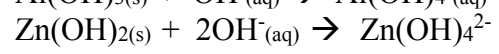
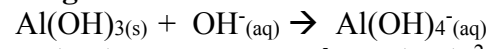
### Examples from AP Exams

#### $\text{NH}_3$ as a ligand:





**OH<sup>-</sup> as a ligand**



**CN<sup>-</sup> as a ligand**

