



How buffer works?

• Dilution:

 $pH = pK_a + log [A^-]/[HA]$

[A⁻] = mole of A/volume of solution (L)
[HA] = mole of HA/volume of solution (L)

 $pH = pK_a + log [mole of A^-/mole of HA]$

The pH of a buffer is nearly independent of volume.

 <u>Caution: if the buffer is diluted to very low</u> <u>concentration, when the dissociation of water has to be</u> <u>taken into consideration, [A] and [HA] will not be at</u> <u>the same as added</u>



How buffer works

Adding strong acid: the acid will react completely with the base, if K_a is small

buffer HA = 0.0296 mole; A⁻ = 0.1026 mole in a liter; adding 0.0120 mole of HCI; $K_a = 8.41 \times 10^{-9}$

	HA	⇒ H+ +	A-
initial	0.0296	0.0120	0.1026
end	0.0416		0.0906

Before acid is added: $pH = pK_a + log[A^-]/[HA] = 8.61$ After acid is added: pH = 8.41

• How about adding 0.0120 mole of HCI into 1 liter of water?



How buffer works?

 adding 0.0120 mole of HCl into 1 liter of water (pH = 7)

initial 0.0120 ---- ---end 0 0.0120 0.0120

H⁺

+

Cl

 $pH = -log [H^+] = -log 0.0120 = 1.92$

HCI

pH changes from 7 to 1.92 without buffer pH changes from 8.61 to 8.41 with buffer

How buffer works

- Adding strong base: base will completely react with weak acid. The treatment is similar to adding strong acid into buffer.
- As long as the weak acid or the conjugate base is not used up, the pH of buffer will not change much when adding strong base or acid



How to prepare buffer solution

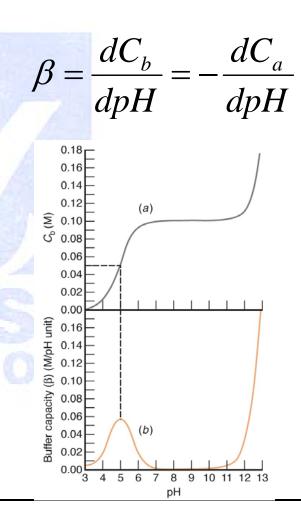
 Practically you don't mix acid and the conjugate base, but making a solution of weak acid (base), then use strong base (acid) to titrate the solution to the desire pH, the conjugate base (acid) forms insitu (real time, during titration)



Buffer capacity

 Buffer capacity is a measure of how well a solution resists changes in pH when strong acid or based is added.

 The maximum buffer capacity is when pH=pK_a. So a effective buffer should have a pH about pK_a±1.





Preparing diprotic buffer

• How many mL of 0.800 KOH should be added to 3.38 g oxalic acid (HOOCCOOH) to give pH 4.40? Reaction: $H_2Ox + OH^- \leftrightarrows HOx^- + H_2O$ $HOx^- + OH^- \leftrightarrows Ox^- + H_2O$ Equilibrium: $H_2Ox \leftrightarrows HOx^- + H^+$ $pK_{a1}=1.252$ $HOx^- \leftrightarrows Ox^- + H^+$ $pK_{a2}=4.266$

 $pH=pK_{a1}+log([HL^{-}]/[H_{2}L])$ $pH=pK_{a2}+log([L^{2-}]/[HL^{-}])$

What is the major species in pH 4.40 solution?



Preparing diprotic buffer

- Since $pH > pK_{a2}$, then Ox^{2-} is the major species in solution, so we can assume that the amount of H₂Ox can be ignored or almost all H₂Ox is reacted.
 - Step 1: $H_2Ox + OH^- \leftrightarrows HOx^- + H_2O$ to convert all (3.38 g or 0.0375 mol) H_2Ox to HOX⁻, 0.0375 mol or 46.92 mL of 0.800 M KOH is needed.
 - Step 2: Figure out how much HOx⁻ is converted to Ox^{2}

HOx⁻
$$\Rightarrow$$
 Ox²⁻ + H⁺ pK_{a2}=4.266
0.03754 0 ---

0.03754-x x 10^{4.4} $pH=pK_{a2}+log[Ox^{2-}]/[HOx^{-}]$

Initial

end

4.40 = 4.266+log [x/(0.03754-x)] ⇒ x=0.02164 mol or 27.05 ml of 0.800 M KOH



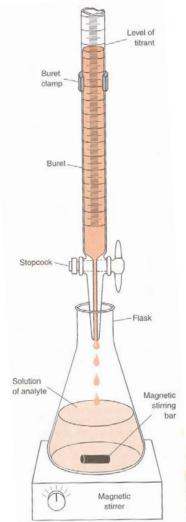
Acid-base Titration





Acid and Base Titration

- The goal is to determine the pH during the course of titration.
- The titration curve is the pH change against the amount titrant added.
- The end point is determined by the sudden change of pH



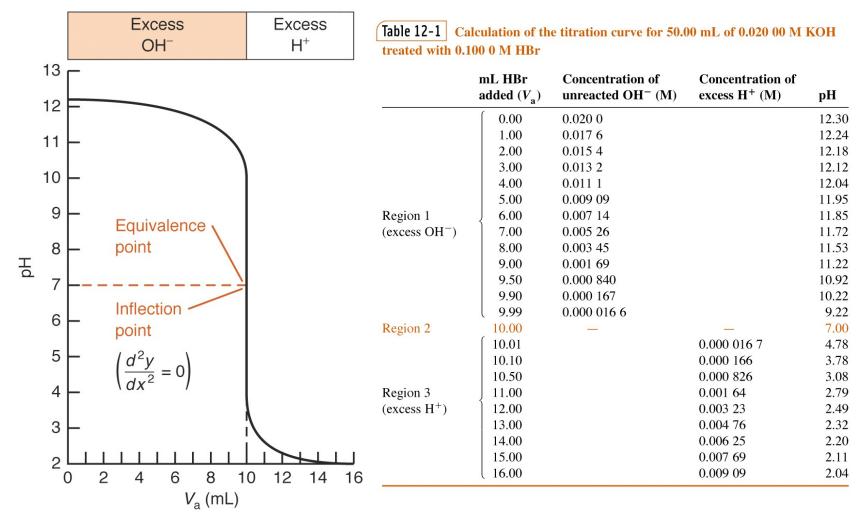


Titration of Strong Acid with Strong Base

- Titration reaction H⁺ + OH⁻ → H₂O the reaction is stoichiometric and complete – 1 mole of H⁺ reacts with 1 mole of OH⁻, forming 1 mole of water
- Example: Use 0.1000 M of HBr to titrate 50.00 mL of 0.0200 M of KOH. Mole of KOH: 0.05000 x 0.02000 = 0.001000 mole Need 0.001000 mole of HBr: V_{HBr}=0.001000/0.1000 = 0.01000 Liter or 10.00 mL



Titration curve for strong-strong





Before titration

Calculation of pH:

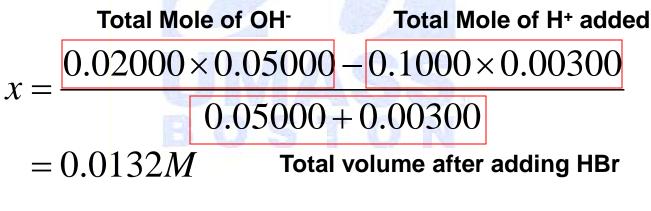
 $KOH \rightarrow K^+ + OH^-$ complete reaction

 $[H^+] = K_w/[OH^-] = 10^{-14}/0.02000 = 5.000 \times 10^{-13}$ pH = 12.30



Before the equivalence point

• For example 3.00 mL of HBr is added $H^+ + OH^- \rightarrow H_2O$ initial --- 0.02 -----end --- x -----



[H+] = Kw/[OH-]=7.58 x 10⁻¹³ M; pH = 12.12



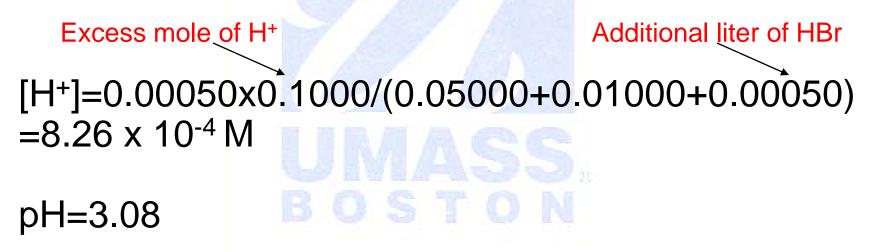
At Equivalence point

- OH⁻ ions react with Stoichiometric amount of H⁺. So H₂O is the only product (with KBr), the pH should be 7.
- The pH at the equivalence point equals to 7, only if the <u>titrant and analyte are both</u> <u>strong.</u>



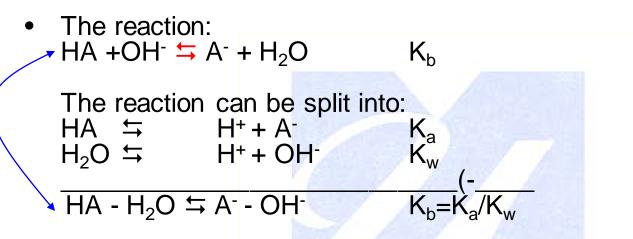
After the equivalence point

- Excess amount of strong acid (HBr) is added.
- Example: 10.50 mL of HBr is added; 10.00 reacts with KOH, 0.5 mL excess amount.





Titration of weak acid with strong base



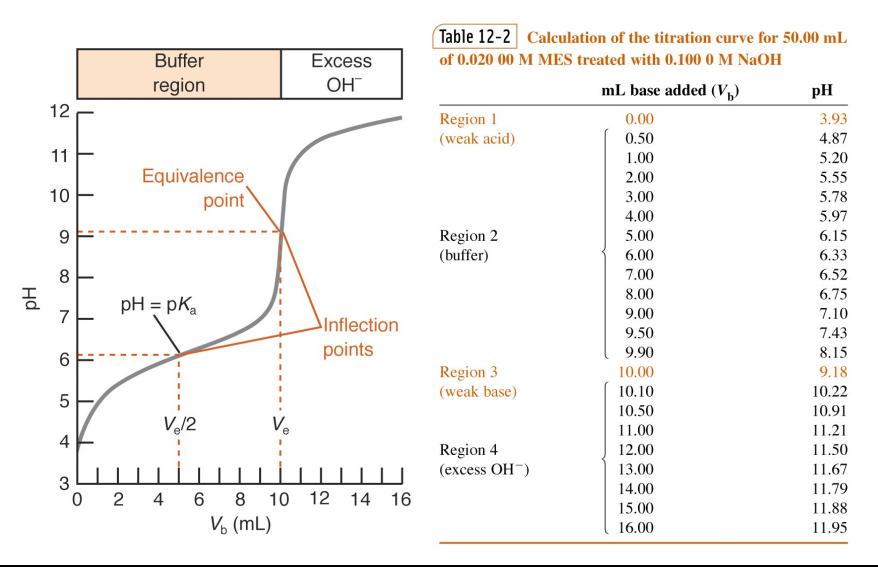
Example: use 0.1000 M NaOH to titrate 50.00 mL of 0.02000 M weak acid HA
 1 mole of NaoH reacts with 1 mole of HA, so at equivalence point:

 $V_{NaOH} \ge 0.1000$ (mmole of NaOH) = 50.00 ≥ 0.02000 (mmole of HA

V_{Naoh}=10.00 mL (same calculation as strong base/strong acid)



Titration curve





Before base is added

• Weak acid HA in water HA \leftrightarrows H⁺ + A⁻ $K_a=10^{-6.15}$ F-x x x

 $x^{2}/(0.02000-x)=10^{-6.15} \Rightarrow x=1.19x10^{-4}$ pH = 3.93



Before the equivalent

- Recall How the buffer is made.
- When NaOH is added, the reaction HA +OH⁻ + A⁻ + H₂O takes place, in the solution there are HA AND A⁻, we have a buffer here!!
- For example, 3.00 mL of NaOH is added mmole of NaOH added = 3.00x0.100=0.300
 0.300 mmole A⁻ formed mmole of HA left = 50.00x0.02000-0.300=0.7
 pH=pK_a+log([A⁻]/[HA])=6.15+log(0.3/0.7)=5.78
 Half way point: [A⁻] = [HA] ⇒ pH=pK_a

Concentration = mole/volume



At the equivalence point

• Stoichiometric amount NaOH reacts with HA, the solution can be treated as dissolving NaA into water.

 $A^- + H_2O \leftrightarrows HA + OH^- \qquad K_b = K_w/K_a$

F-x x x

F: the concentration of A⁻ - the product of the titration. 1 mole of HA produce 1 mole of NaA So, F=mole of NaA/total volume =mole of HA/total volume =(0.02000x0.05000)/(0.05000+0.01000)=0.0167M

 $x^{2}/(0.0167-x)=1.43x10^{-8} \Rightarrow x=1.54 \times 10^{-5} M$ *pH=9.18 pH ≠7!!!! Always above 7*



After the equivalence point

- The NaOH is much stronger base than A⁻, so the pH is determined by the OH⁻ added.
- Assume, 10.10 mL NaOH is added, 10 mL is used to react with HA, 0.1 mL extra.
 [OH⁻]=(0.00010x0.1000)/(50+10.10) =1.66x10⁻⁴M ⇒ pH = 10.22



Titration curve

• Two inflection point, equivalence point, the other is $V_b=1/2V_e$, while pH=pKa, having minimum slope because when pH=pKa, buffer capacity is at maximum.

