Acid and Base

Properties of Umass Boston

Dissociation of diprotic acid

- For the solution of H_2L^+

  $H_2L^+ \leftrightarrows HL + H^+$ $\quad K_{a1} = 4.69 \times 10^{-3}$

  $HL \leftrightarrows L^- + H^+$ $\quad K_{a2} = 1.79 \times 10^{-10}$

  Assumption:

  since $K_{a1} >> K_{a2}$

  so the dissociation of HL is insignificant comparing with the dissociation of H_2L^+, which can be treated as monoprotic acid.

- For the solution of L^-

  $L^- + H_2O \rightleftarrows HL + OH^-$ $\quad K_{b1} = K_w/K_{a2} = 5.48 \times 10^{-5}$

  $HL + H_2O \leftrightarrows H_2L^+ + OH^-$ $\quad K_{b2} = K_w/K_{a1} = 2.13 \times 10^{-12}$

Treatment of the intermediates

- Systematic treatment:

$HL \leftrightarrows H^+ + L^-$ K_{a2}

$HL + H_2O \leftrightarrows H_2L^+ + OH^-$ K_{b2}

Charge balance: $[H^+]+[H_2L^+]=[L^-]+[OH^-]$

$K_{a2} = [H^+][L^-]/[HL] \Rightarrow [L^-] = [HL]K_{a2}/[H^+]$

$K_{b2} = [H_2L^+][OH^-]/[HL] \Rightarrow [H_2L^+] = [HL]K_{b2}/[OH^-]$

$=[HL][H^+]K_{b2}/K_w$

$H_2L^+ \leftrightarrows HL + H^+$ K_{a1}

$K_{a1}K_{b2}=K_w \Rightarrow [H_2L^+]=[HL][H^+]/K_{a1}$

Approximations

$$[H^+] = \sqrt{\frac{K_{a1}K_{a2}[HL] + K_{a1}K_w}{K_{a1} + [HL]}}$$

- Since HL is week acid/base, the [HL]≈F (added) then

$$[H^+] = \sqrt{\frac{K_{a1}K_{a2}F + K_{a1}K_w}{K_{a1} + F}}$$

- Assume, $K_{a2}[HL] >> K_w$, then

$$[H^+] = \sqrt{\frac{K_{a1}K_{a2}F}{K_{a1} + F}}$$

- Assume, $F >> K_{a1}$

$$[H^+] = \sqrt{K_{a1}K_{a2}} \Rightarrow pH = 1/2(pK_{a1} + pK_{a2})$$

Polyprotic acids and bases

- Treatments of polyprotic acid and base are similar to that of diprotic acid and base

$H_3A \leftrightarrows H_2A^- + H^+$	K_{a1}
$H_2A^- \leftrightarrows HA^{2-} + H^+$	K_{a2}
$HA^{2-} \leftrightarrows A^{3-} + H^+$	K_{a3}
$A^{3-} + H_2O \leftrightarrows HA^{2-} + OH^-$	$K_{b1}=K_w/K_{a3}$
$HA^{2-} + H_2O \leftrightarrows H_2A^- + OH^-$	$K_{b2}=K_w/K_{a2}$
$H_2A^- + H_2O \leftrightarrows H_3A + OH^-$	$K_{b3}=K_w/K_{a1}$

- **Only deal with immediate neighbors**

Only deal with immediate neighbors

- H_3A is treated as monoprotic acid in H_3A solution, e.g. dissolving in water, $K_a=K_{a1}$

$H_3A \leftrightarrows H_2A^- + H^+$	K_{a1}
$H_2A^- \leftrightarrows HA^{2-} + H^+$	K_{a2}
$HA^{2-} \leftrightarrows A^{3-} + H^+$	K_{a3}

	H3A ⇆ H2A⁻ + H+		**K_{a1}**
begin	F	0	0
end	F-x	x	x

$$K \approx K_{a1} = \frac{x^2}{F - x}$$

Only deal with immediate neighbors

- H_2A^- and HA^{2-} are treated as the intermediate form for a diprotic acid.

$$H_3A \leftrightarrows H_2A^- + H^+ \qquad K_{a1}$$
$$H_2A^- \leftrightarrows HA^{2-} + H^+ \qquad K_{a2}$$
$$HA^{2-} \leftrightarrows A^{3-} + H^+ \qquad K_{a3}$$

- For H_2A^-

$$\underline{H_3A \leftrightarrows H_2A^- + H^+ \qquad K_{a1}}$$
$$\underline{H_2A^- \leftrightarrows HA^{2-} + H^+ \qquad K_{a2}}$$

$$[H^+] \approx \sqrt{\frac{K_{a1}K_{a2}F + K_1K_w}{K_1 + F}} \quad for \quad H_2A^-$$

- For HA^{2-}

$$\underline{H_2A^- \leftrightarrows HA^{2-} + H^+ \qquad K_{a2}}$$
$$\underline{HA^{2-} \leftrightarrows A^{3-} + H^+ \qquad K_{a3}}$$

$$[H^+] \approx \sqrt{\frac{K_{a2}K_{a3}F + K_{a2}K_w}{K_{a2} + F}} \quad for \quad HA^{2-}$$

Only deal with immediate neighbors

- A^{3-} is treated as monobasic, $K_b = K_{b1}$

$A^{3-} + H_2O \leftrightarrows HA^{2-} + OH^-$ $\quad K_{b1} = K_w/K_{a3}$

$HA^{2-} + H_2O \leftrightarrows H_2A^- + OH^-$ $\quad K_{b2} = K_w/K_{a2}$

$H_2A^- + H_2O \leftrightarrows H_3A + OH^-$ $\quad K_{b3} = K_w/K_{a1}$

	$A^{3-} + H_2O \leftrightarrows HA^{2-} + OH^-$			K_{b1}
begin	F	0	0	
end	F-x	x	x	

$$K \approx K_{b1} = \frac{x^2}{F - x}$$

Principal species – dominate type of species at certain pH

At the time $[H_3A]=[H_2A^-]= 1/2F$

	$H_3A \leftrightarrows H_2A^-$	+	$H+$	K_{a1}
begin	F	0	0	
end	0.5F	0.5F	x	

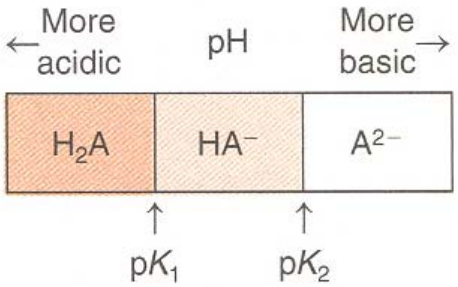
$$K \approx K_{a1} = \frac{[H^+]0.5F}{0.5F}$$

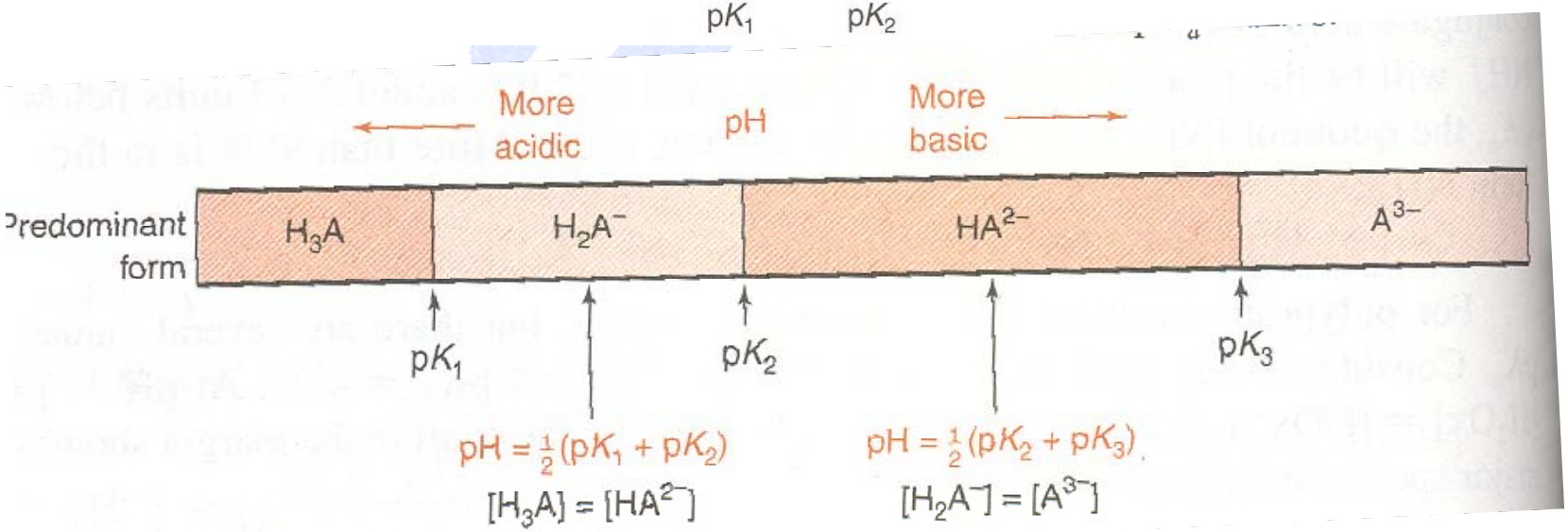
$$K = [H^+] \Rightarrow pH = pK$$

pH<pK ⇨ H_3A is the dominate species;
pH>pK⇨H_2A^- is the dominate species.

Principal species – dominate type of species at certain pH

pH	Major species
$pH < pK_1$	H_2A
$pK_1 < pH < pK_2$	HA^-
$pH > pK_2$	A^{2-}





Composition of solution

- General form of fraction for the polyprotic acid H_nA:

$$\alpha_{H_nA} = \frac{[H^+]^n}{D}$$

$$\alpha_{H_{n-1}A} = \frac{K_1[H^+]^{n-1}}{D}$$

$$\alpha_{H_{n-j}A} = \frac{K_1K_2\cdots K_j[H]^{n-1}}{D}$$

$$D = [H^+]^n + K_1[H^+]^{n-1} + K_1K_2[H^+]^{n-2} + \cdots\cdots + K_1K_2K_3\cdots\cdots K_n$$

Titration

Properties of Umass Boston

Titration

- Increments of reagent solution (titrant) are added to analyte until the reaction is completed
  - Titrant (know concentration)
  - Analyte (unknown)
  - End point: equivalence point – the quantity of added titrant is the exact amount necessary for stoichiometric reaction with the analyte

    Example: using known H_2SO_4 to titrate unknown KOH -
    $H_2SO_4 + 2\ KOH \rightarrow 2H_2O + K_2SO_4$
    at end point one mole of H_2SO_4 reacts with 2 mole of KOH

    .

Detection end point

- Detection of end point: indication – chemical, electrochemical, spectroscopic – means to mark change in a physical property of the solution

Example:

$HOOC\text{-}COOH + 2\ MnO_4^- + 6\ H^+ \rightarrow 10\ CO_2 + 2\ Mn^{2+} + H_2O$

(oxalic acid, analyte) (titrant, pink)

Terminology

- Titrant
- Analyte
- End point
- Indicator: compound with a physical property (color) that changes abruptly near the equivalence point.
- Titration error
- Blank titration
- Primary standard: pure and stable reagent (>99.9%) which can be accurately weighted to make titrant.
- Standardization: use primary standard solution to determine the non primary standard – standard solution.
- Direct titration: titrate the analyte until end point.
- Back titration: add excess amount of one standard solution and use the second standard solution to titrate the excess amount of the first standard solution – slow reaction with analyte or no clear indicator

Titration calculation

- the quantity of added titrant is the exact amount necessary for stoichiometric reaction with the analyte – ***relate the mole of titrate to the mole of analyte***

  Example: use 0.7344 M HCl to titrate 1.372 g of the mixture of Na_2CO_3 and $NaHCO_3$, 29.11 ml of HCl was consumed.

  $Na_2CO_3 + 2HCl \leftrightarrows 2\ NaCl + H_2O + CO_2\uparrow$

  $NaHCO_3 + HCl \leftrightarrows NaCl + H_2O + CO_2\uparrow$

  at the end point, all Na become NaCl

  1 mole Na_2CO_3 reacts with 2 mole HCl

  1 mole $NaHCO_3$ reacts with 1 mole HCl

  Total HCl consumed $0.7344 \times 29.11 \times 10^{-3} = 0.02138$ M

  Assume x gram of Na_2CO_3 in the mixture, then there is1.372-x gram of $NaHCO_3$

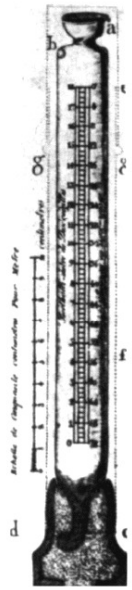
  Mole of Na_2CO_3: x/105.99(molecular weight)

  Mole of $NaHCO_3$: (1.372-x)/84.01

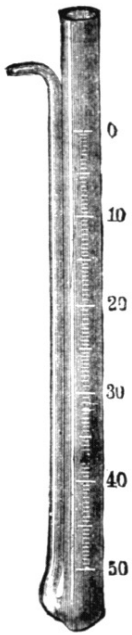
  thus: 2 x mole of Na_2CO_3 + mole of $NaHCO_3$ = mole of HCl

  $2 \times (x/105.99) + (1.372-x)/84.01 = 0.02138$

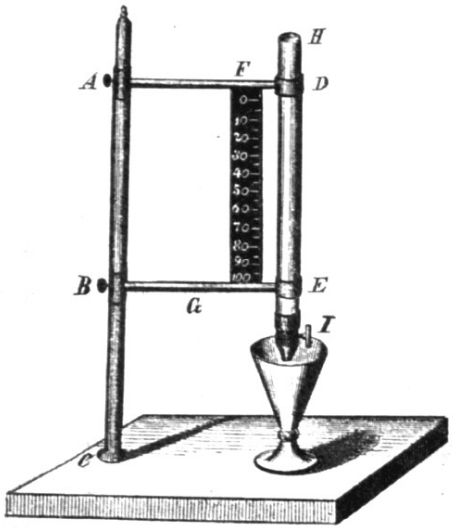
  $x = 0.724$ g ⇨ 0.724 g Na_2CO_3 and 1.372-0.724 = 0.648 g $NaHCO_3$



Descroizilles (1806)
Pour out liquid

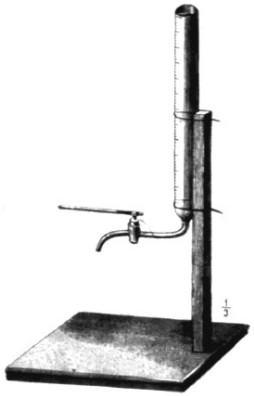


Gay-Lussac (1824)
Blow out liquid

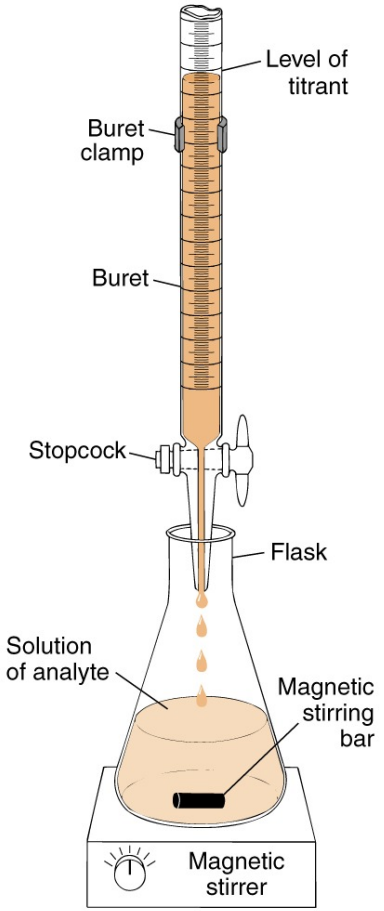


Henry (1846)
Copper stopcock

Mohr (1855)
Compression clip

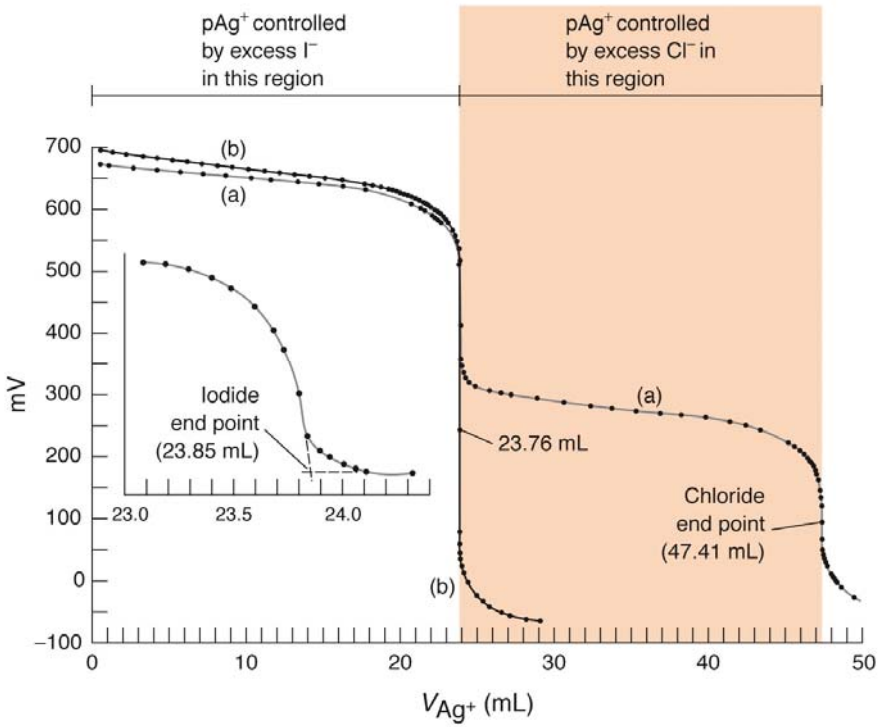


Mohr (1855)
Glass stopcock



Titration curve

- Change of the indication signal – the concentration of one reactant (potential, pH, optical absorption..) with the amount of titrant
  - Understand the chemistry during the titration
  - The influence of the conditions to the titration e.g. pH to the sharp end point.



Types of Titration

- Acid-base
- Redox (reduction – oxidation, electrochemical)
- Complex formation (EDTA)
- Precipitation

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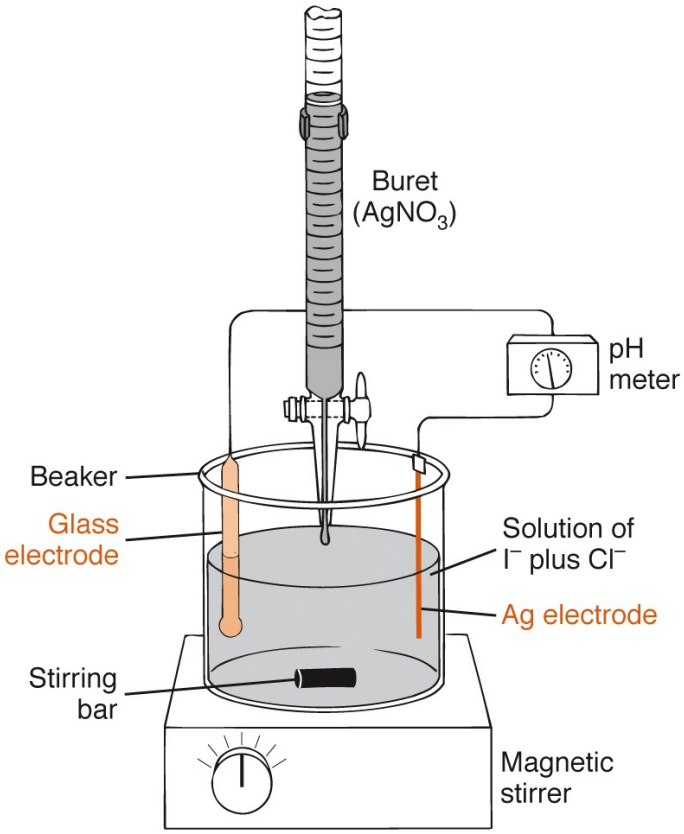
Precipitation Titration

- K_{sp} influence the sharpness of the end point and accuracy of precipitation titration, the larger K_{sp} the better.
- Ion selective electrodes are usually used to detect the change of one reactant



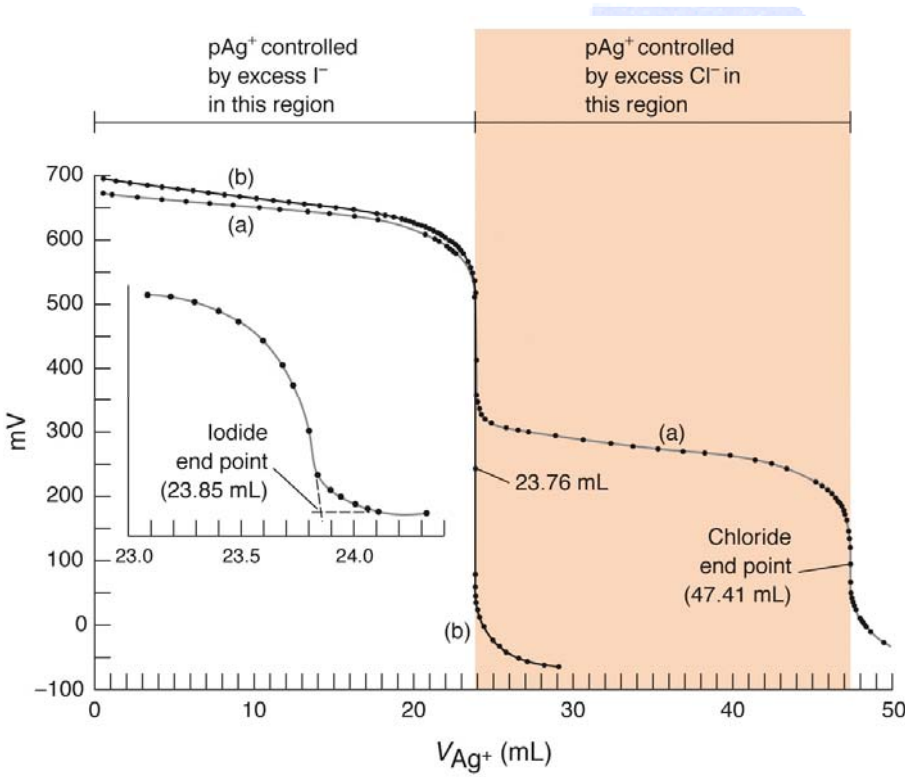
Example of Precipitation Titration

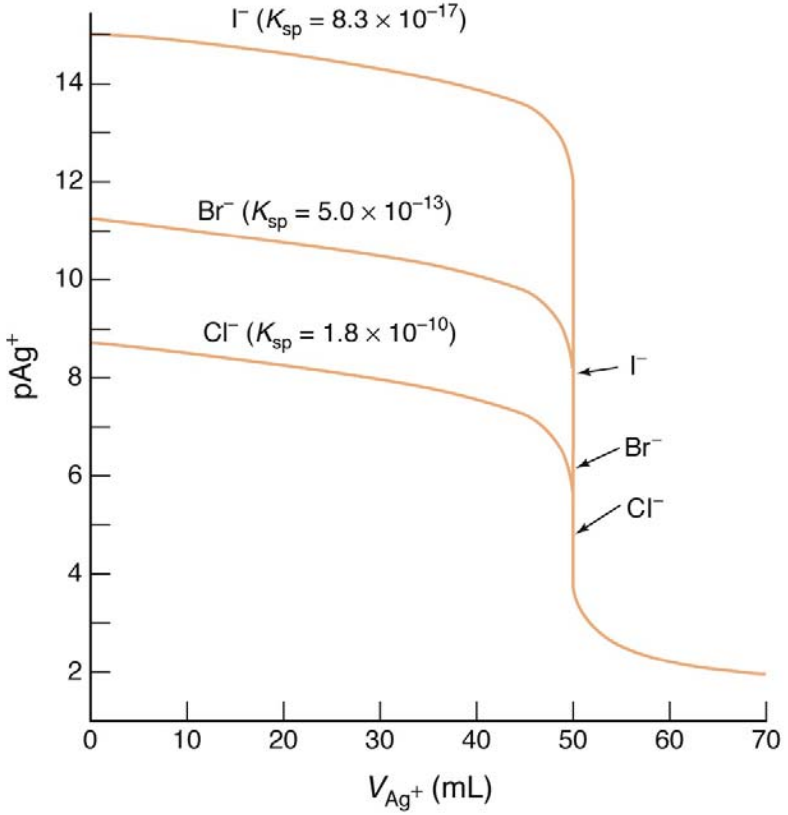
- Using $AgNO_3$ solution to titrate the solution containing KI and KCl
- Titration of a mixture, less soluble precipitate (larger K_{sp}) forms first.
- K_{sp1} has to be sufficiently different in order to separate the two different precipitates

Example of Precipitation Titration

- $Ag^+ + I^- \rightarrow AgI$
  $K_{SP}(AgI)=[Ag^+][I^-] \Rightarrow [Ag^+]=K_{sp}(AgI)/[I^-]$
  $[I^-]$ = initial concentration (unknown) – [Ag] added
- $Ag^+ + Cl^- \rightarrow AgCl$
  $K_{SP}(AgCl)=[Ag^+][Cl^-] \Rightarrow$
  $[Ag^+]=K_{sp}(AgI)/[Cl]$
  [Cl] = initial concentration (unknown) – [Ag] added-$[I^-]$
- Near the end point of I^-, co precipitation may happen

Titration Curve





Buffer

Properties of Umass Boston

Buffered Solution

- A buffered solution resists changes in pH when acids or bases are added or when dilution occurs.
- The buffer is made of the mixture of acid and its conjugate base.

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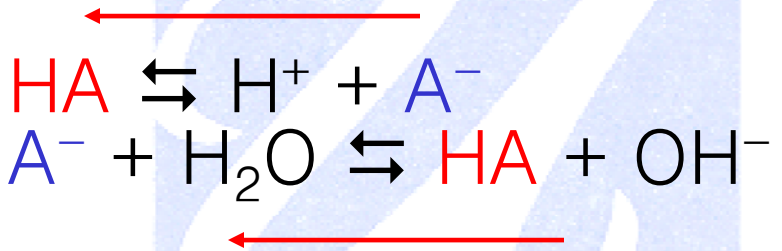
What happen if a weak acid is mixed with its conjugate base ?

- the moles of acid and conjugate base in the solution will remain close to the amounts added, because of Le Châtelier's principal.



- HA dissociates very little and adding A^- will make the equilibrium move to right side.
- A^- does not react with water much and adding HA will make the equilibrium move to right side

Henderson-Hasselbalch Equation

- The pH of the buffer - the central equation to treat buffer

$$HA \leftrightarrows H^+ + A^- \qquad K_a$$

$$K_a = [H^+][A^-]/[HA]$$

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

$$\boldsymbol{pH = pK_a + \log\{[A^-]/[HA]\}}$$

The same relation, different expression

- $A^- + H_2O \leftrightarrows HA + OH^-$ K_b

$K_b = [HA][OH^-]/[A^-]$

$\log K_b = \log [OH^-] + \log [HA]/[A^-]$

$[OH^-]=K_w/[H^+]$

$\log K_b = \log K_w - \log[H^+] + \log [HA]/[A^-]$

$-\log[H^+]=\log K_b - \log K_w - \log [HA]/[A^-]$

$pH = -\log K_w/K_b + \log [A^-]/[HA]$

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

Diprotic Buffers

- A buffer made from a diprotic (H_2L) or polyprotic (H_nL) acid

  $H_2L \leftrightarrows HL^- + H^+$ K_{a1}

  $HL^- \leftrightarrows L^{2-} + H^+$ K_{a2}

  Two Henderson-Hasselbalch equations, they are both true in the same solution

$$pH = pK_{a1} + \log([HL^-]/[H_2L])$$
$$pH = pK_{a2} + \log([L^{2-}]/[HL^-])$$

The pH change in buffer

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

Table 10-1 Effect of $[A^-]/[HA]$ on pH

$[A^-]/[HA]$	pH
100:1	$pK_a + 2$
10:1	$pK_a + 1$
1:1	pK_a
1:10	$pK_a - 1$
1:100	$pK_a - 2$