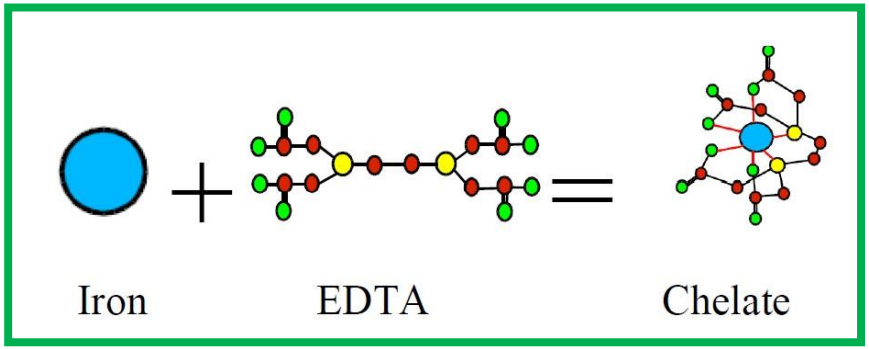
Types of reactions

- Acid-base: Transfer of a proton from acid to base

- Complexation: Formation of covalent bonds between a transition metal species and ligands



- Oxidation – reduction: Transfer of one or more electrons from the reducing agent to the oxidizing agent

$$MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O$$

violet color colorless manganous

- Precipitation (ionic salt): Electrostatic attraction of cations and anions to form an ionic lattice

Acid-base titrations

Revision of the basics:

- When acids (or bases) are added to water, they undergo ionisation.
  - $HA + H_2O \leftrightarrow A^- + H_3O^+$
- At equilibrium, an ionisation constant (K_a) may be defined:

$$K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

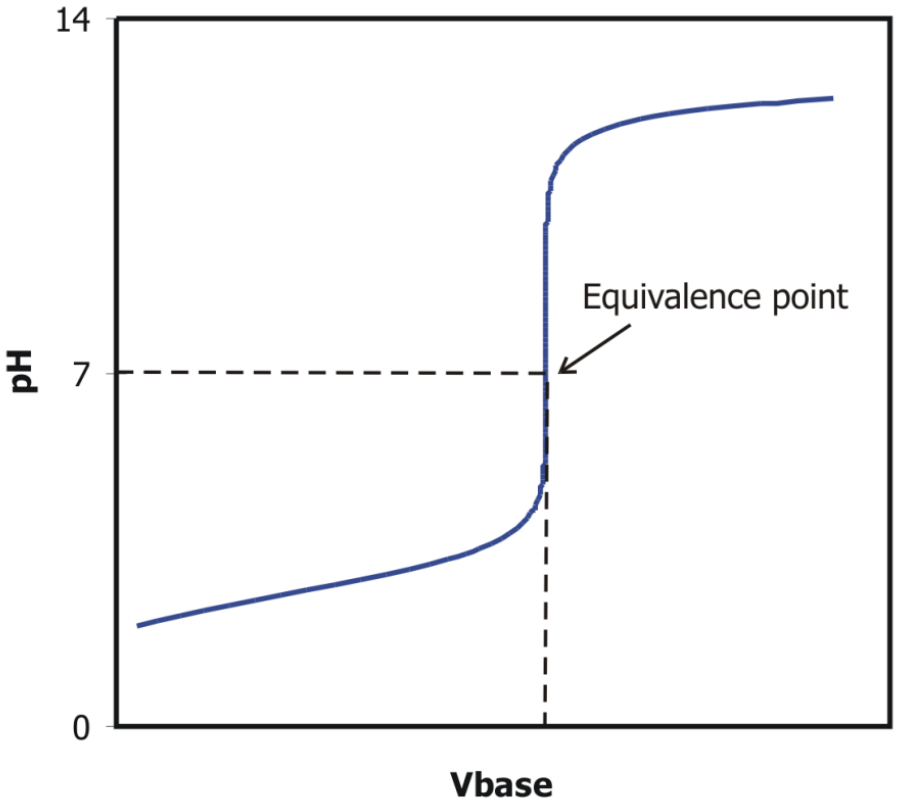
- K_a is a measure of the strength of an acid.
- pH = - log $[H^+]$

Titration of strong acids or bases

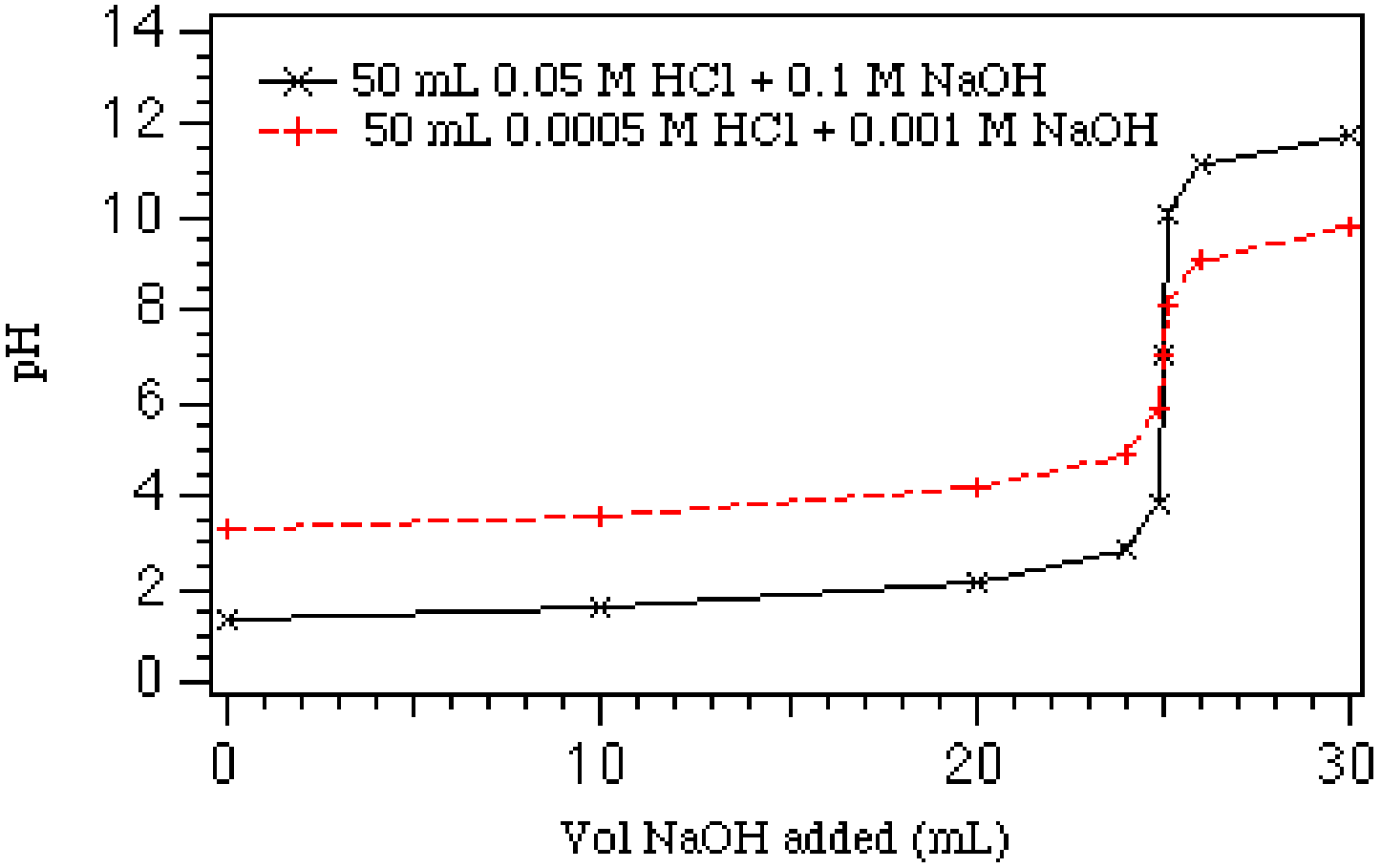
When a strong acid reacts with a strong base, both are completely ionised.

In the reaction between HCl and NaOH for example, complete neutralisation (equivalence point) is reached at a pH of 7.

The sharp change in pH near the equivalence point allows us to determine the completion of a reaction.



Effect of concentration on the magnitude of the endpoint break



Titration of weak acids and bases

- Less straightforward as they only ionise partially in water.
- Salts undergo hydrolysis - equivalence point will not be at pH 7.

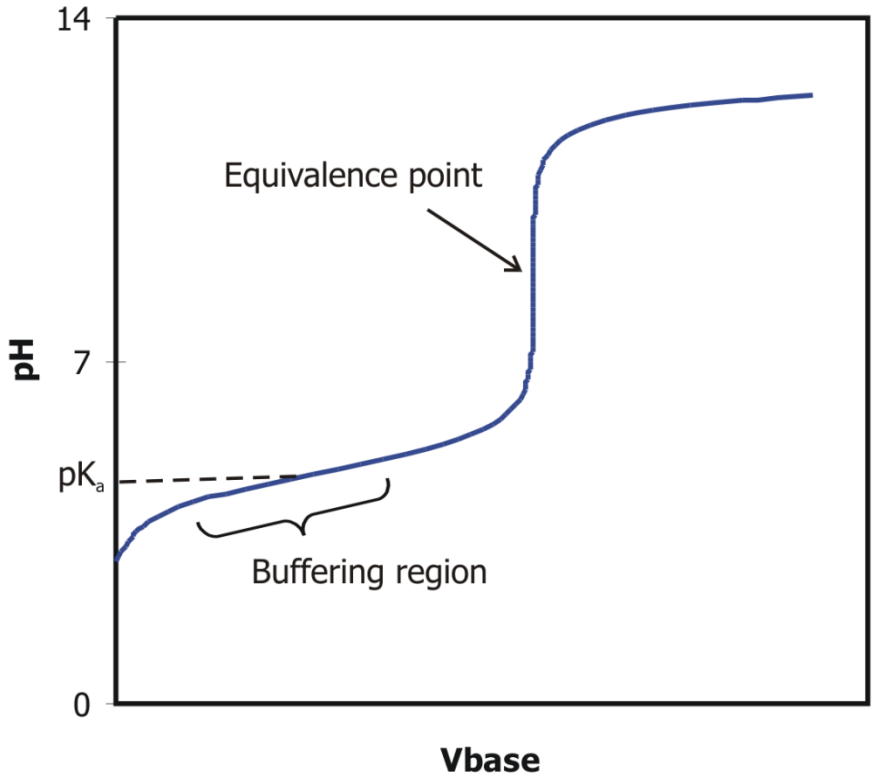
Example:

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

The CH_3COO^- ion produced acts as a base in water, producing the parent acid.

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

- Results in a 'lag' in reaching the equivalence point.
- Referred to as the buffering region - it takes a large amount of NaOH to produce a small change in pH.

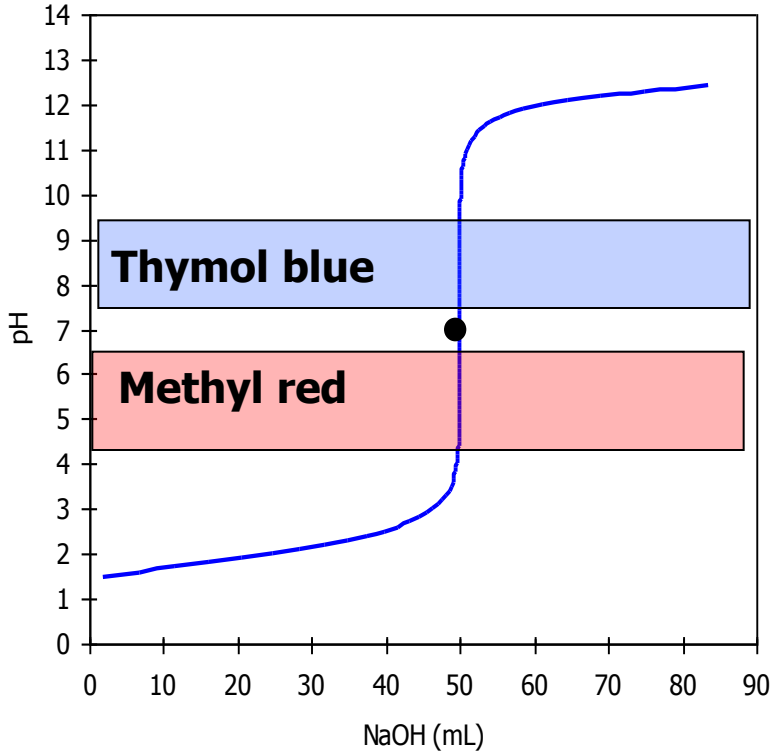


- Weak acid + strong base = basic salt (equivalence pH > 7)
- Strong acid + weak base = acidic salt (equivalence pH < 7)

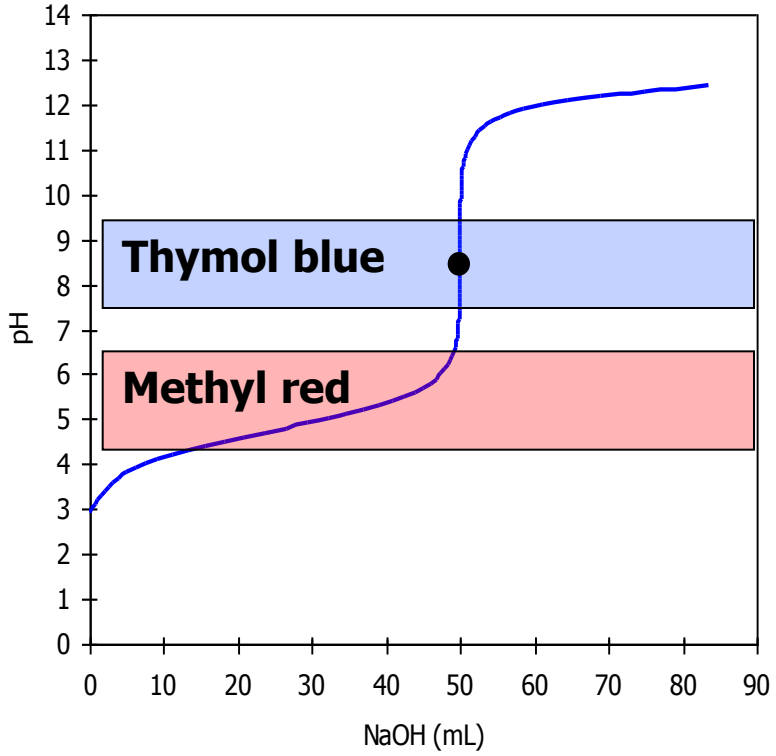
We can calculate pH using the Henderson-Hasselbalch equation:

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

Strong acid with a strong base



Weak acid with a strong base



Calculate the pH for the titration of 50.0 ml of 0.100 M HCl with 0.100 M NaOH after the addition of 0, 5 and 50 ml of base.

0.1 M *0.1 M, 50 mL*

- *At 5 mL:*

	HCl **50 mL, 0.1 M**	**NaOH** **0. 1 M**
Start		
react		
[H+]		

Find the pH at the following points in the titration of 30 mL of 0.05 M $HClO_4$ with 0.1 M KOH.

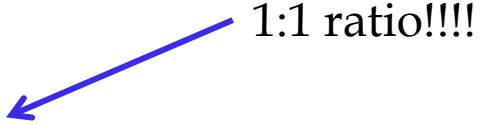
a) Before adding any KOH

b) When 10 mL of 0.1 M KOH is added

c) When 15 mL of 0.1 M KOH is added

d) When 20 mL of 0.1 M KOH is added

$$HClO_4 + 0.1\ M\ KOH \rightarrow KClO_4 + H_2O$$



$HClO_4$ + KOH → $KClO_4$ + H_2O

0.05 M, 30 mL 0.1 M, 10 mL

	$HClO_4$ 30 mL, 0.05 M	KOH 0. 1 M, 10
Start		
react		
final		

Calculate the pH for the titration between 50.0 ml of 0.100 M acetic acid and 0.100 M NaOH after the addition of 0, 10 and 50 ml of base (K_a for acetic acid = 1.75×10^{-5}).

$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

0.1 M, 50 mL 0.1 M, 10 mL (K_a for acetic acid = 1.75×10^{-5})

	CH_3COOH **50 mL, 0.1 M**	**NaOH** **0. 1 M, 10**
Start		
react		
Conc.		
final		

$$\underset{\text{0.1 M, 50 mL}}{CH_3COOH} + \underset{\text{0.1 M, 50 mL}}{NaOH} \rightarrow CH_3COONa + H_2O$$

- Some reminders:

$$K_b = \frac{K_w}{K_a} \longrightarrow 1.0 \times 10^{-14}$$

$$K_b = \frac{K_w}{K_a} = \frac{[HA][OH^-]}{[A\text{-}]}$$

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

0.1 M, 50 mL 0.1 M, 50 mL

- Acetic acid is a weak acid - salt hydrolyses in water. –OAc is treated as a base.

$$^{-}OAc + H_2O \rightarrow HOAc + OH^{-}$$

$$K_b = \frac{K_w}{K_a} = \frac{[HOAc][OH^-]}{[^-OAc]}$$

- All HOAc has been converted to ^{-}OAc - 5.00 mmol in 100 ml *i.e* 0.0500 M)

$$K_b = \frac{[OH^-][OH^-]}{[^-OAc]} \qquad 5.71 \times 10^{-10} = \frac{[OH^-][OH^-]}{0.0500}$$

$[OH^-]$ = 5.35×10^{-6} M
pOH = 5.27
pH = 8.73

Complexation reactions

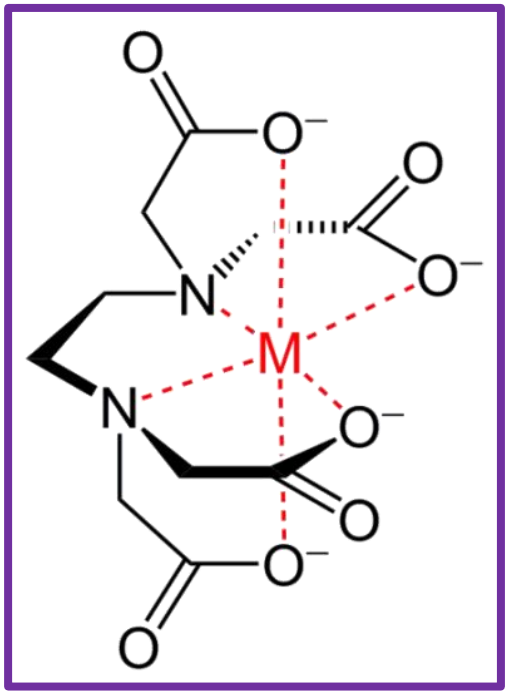
- Metal ions + electron-pair donors → coordination compounds or complexes
- No. of covalent bonds is the coordination number (2, 4, 6)
- The species can be []+, []- or []
- A ligand that has
  - 1 donor group = unidentate
  - 2 groups = bidenate…..
  - …tridentate, tetradentate…**hexadentate ….} → multidentate**

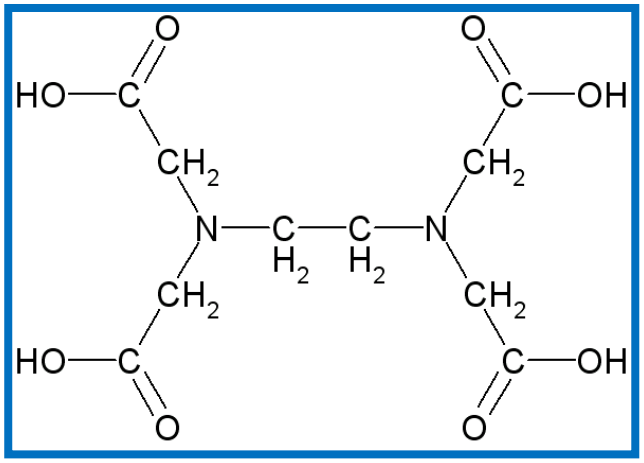
Complexometric titration

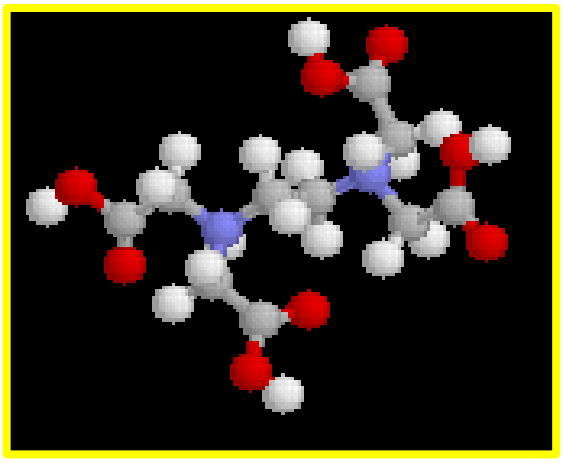
- Titration based on complex formation
- The metal ion reacts with a ligand to form a complex, and the equivalence point is determined by an indicator
- We can use complex reactions to quantify.
- Can form soluble complexes or precipitates
- Most commonly used ligands are multidentate ligands (chelating ligands)

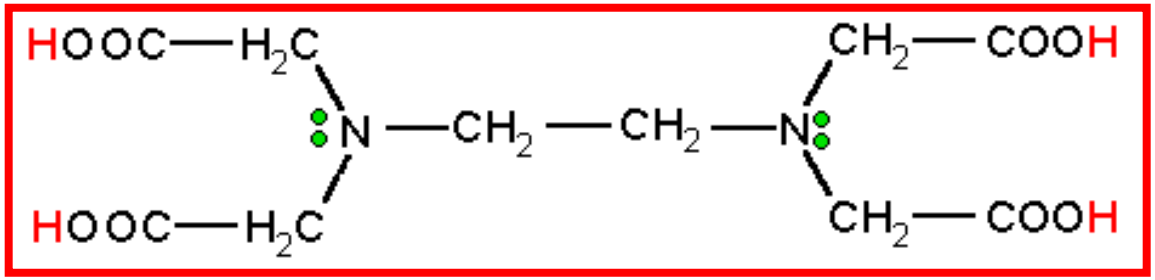
EDTA

- Ethylenediaminetetraacetic acid
- Forms 1:1 complexes with most metals
- Good primary standard
- Forms stable complexes









- Hexaprotic ligand (H_6Y^{2+})

pKa_1	0.0	
pKa_2	1.5	
pKa_3	2.00	
pKa_4	2.69	
pKa_5	6.13	
pKa_6	10.37	

- We can calculate the fraction of EDTA (α) in each form
- Free EDTA has the form Y^{4-}

Fractional composition

$$\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{[H_6Y^{2+}] + [H_5Y^{+}] + [H_4Y] + [H_3Y^{-}] + [H_2Y^{2-}] + [HY^{3-}] + [Y^{4-}]}$$

$$\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{[EDTA]}$$

pH	$\alpha_{Y^{4-}}$	pH	$\alpha_{Y^{4-}}$
0	1.3×10^{-23}	7	3.8×10^{-4}
1	1.4×10^{-18}	8	4.2×10^{-3}
2	2.6×10^{-14}	9	0.041
3	2.1×10^{-11}	10	0.30
4	3.0×10^{-9}	11	0.81
5	2.9×10^{-7}	12	0.98
6	1.8×10^{-5}	13, 14	1.00

Formation/Stability Constants

$$M^{n+} + Y^{4-} \leftrightarrow MY^{n-4} \qquad K_f = \frac{[MY^{n-4}]}{[M^{n+}][Y^{4-}]}$$

Ion	Log K_f	Ion	Log K_f
K^+	0.8	Zn^{2+}	16.50
Na^+	1.66	Pb^{2+}	18.04
Mg^{2+}	8.69	Ni^{2+}	18.62
Ca^{2+}	10.70	Cu^{2+}	18.80
Fe^{2+}	14.33	Fe^{3+}	25.1
Al^{3+}	16.13	Zr^{4+}	29.5

- Will a reaction occur or not?

Conditional Formation Constants

- When Y^{4-} is not predominant (at pH < 10.37)

- $K_f = \frac{[MY^{n-4}]}{[M^{n+}][Y^{4-}]}$ becomes $K_f = \frac{[MY^{n-4}]}{[M^{n+}]\alpha_{Y^{4-}}[EDTA]}$

- If the pH is fixed by a buffer, then

$$K'_f = K_f \times \alpha_{Y^{4-}} = \frac{[MY^{n-4}]}{[M^{n+}][EDTA]}$$

Conditional formation constant

EDTA titration curves

- We can quantify metals using EDTA as a titrant
- At any point in the titration we can calculate the value of pM (= -log[M^{n+}]).
- We can use this information to draw titration curves (like for acid-base curves!)
- We need information about the start of the titration, before equivalence point, at equivalence point and after equivalence point.

EDTA Titration Curves

- Titration reaction: $MY^{n-4} \leftrightarrows M^{n+} + EDTA$
- For large K'_f - reaction considered "complete" at each point in the titration.
- Titration curve:

Considering the titration of 50.0 ml of 0.0050 M Ca^{2+} solution with 0.0100 M EDTA at pH = 10

- After the **addition of 10.0 ml EDTA**, some Ca^{2+} will have reacted with the EDTA. To find the new [Ca^{2+}] :

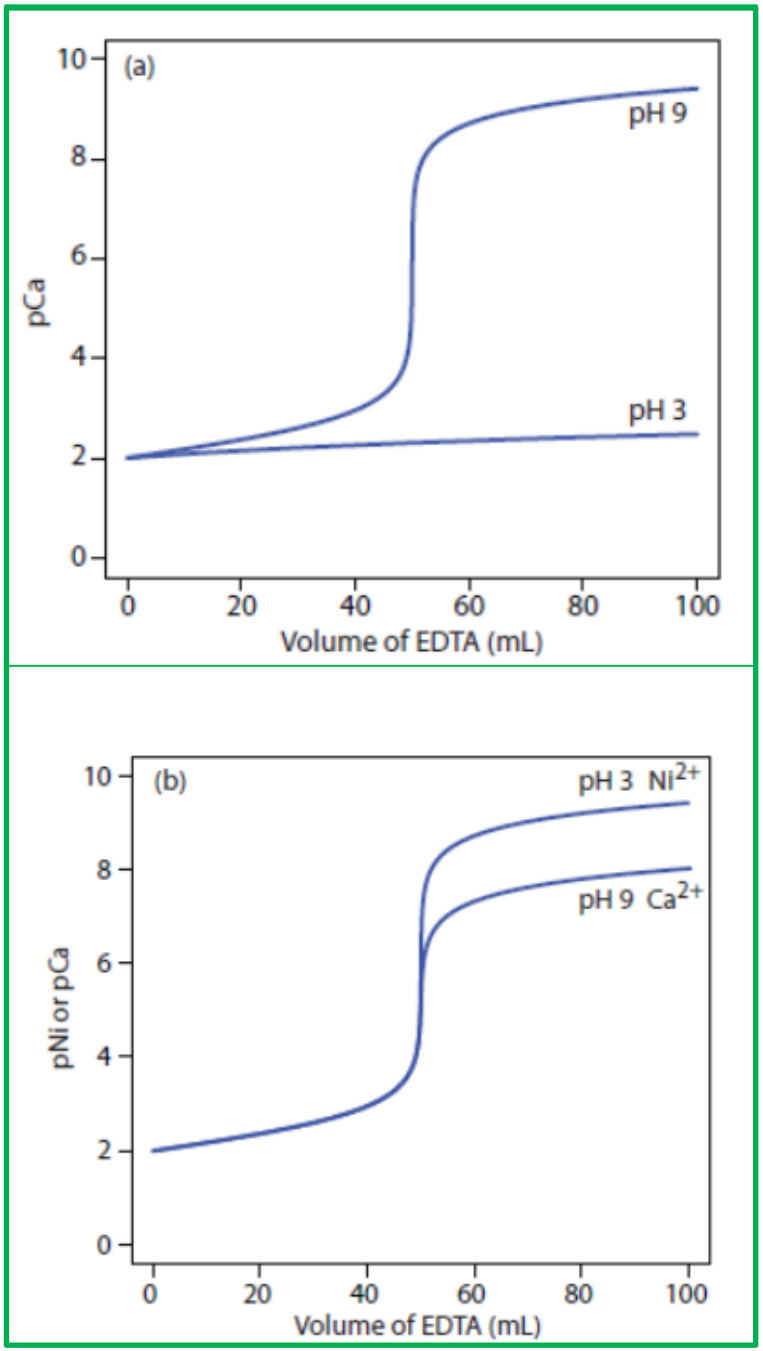
- After the equivalence point, all the Ca^{2+} has reacted and the only source of Ca^{2+} is again the dissociation of the CaY^{2-} complex.
- This time, we have excess EDTA in the solution.
- We must determine [EDTA] and [CaY^{2-}] from the stoichiometric quantities.
- Lets assume we add 50 mL after equivalence point…

EDTA and pH

- The metal –EDTA complex becomes less stable as pH decreases
- K_f decreases

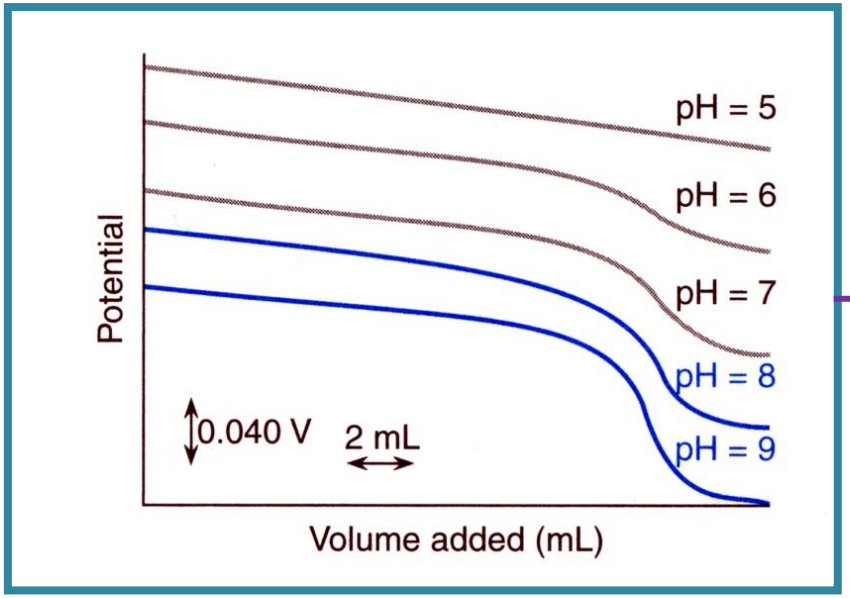
  $[Fe^{3+}] = 5.4x10^{-7}$ at pH 2.0

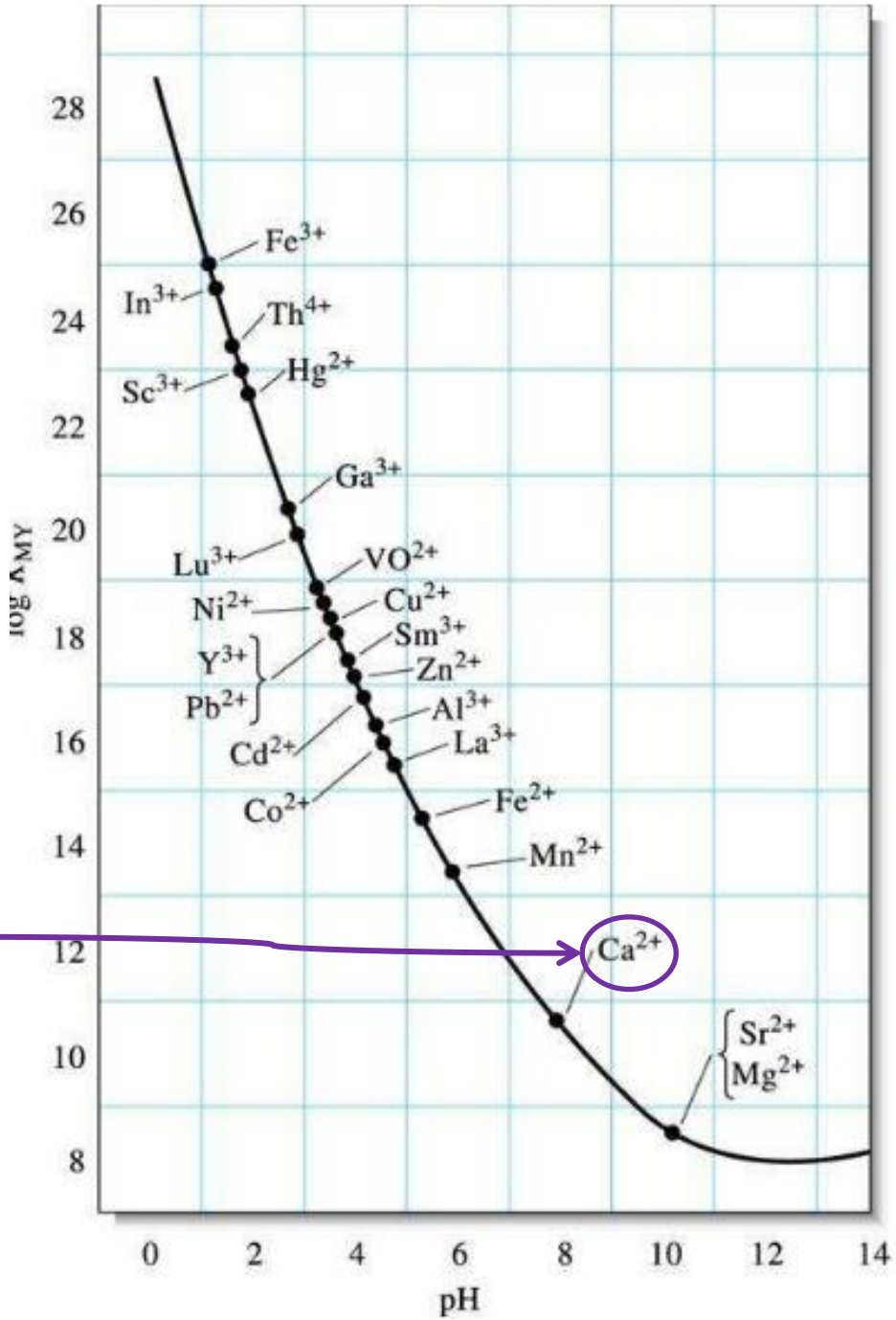
  $[Fe^{3+}] = 1.4x10^{-12}$ at pH 8.0
- In order to get a "complete" titration ($K_f \geq 10^6$), EDTA requires a certain minimum pH for the titration of each metal ion
- End point becomes less distinct as pH is lowered



Effect of pH

- Adjusting the pH - one type of metal ion (e.g. Fe^{3+}) can be titrated without interference from others (e.g. Ca^{2+})





Auxiliary Complexing agents

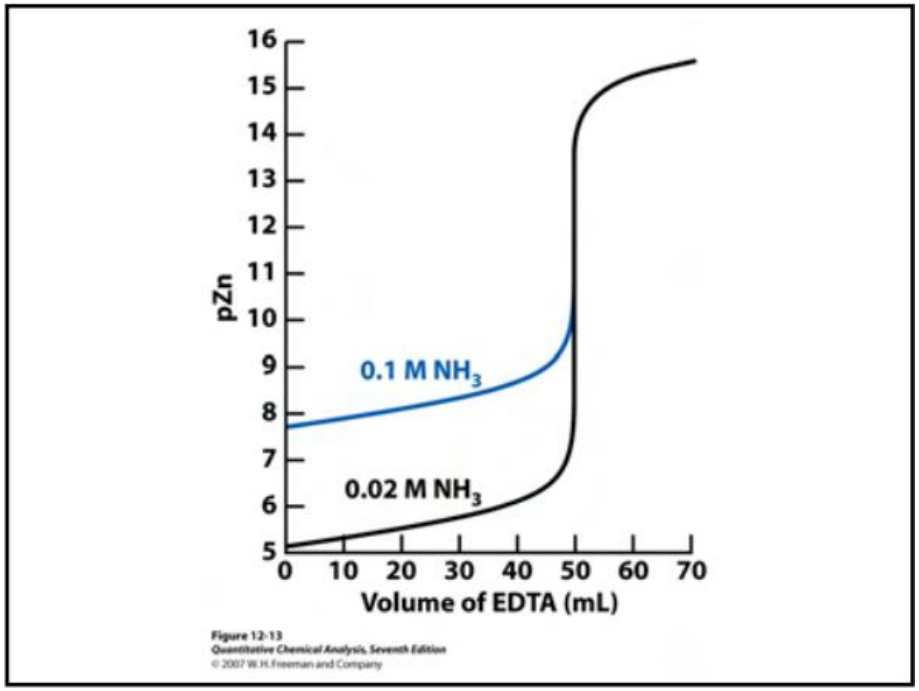
- Metal cations form complexes (M-hydroxides) at high pH.
- Problem for EDTA titrations which need to be at high pH!!
- We keep the cation in solution by using an auxiliary complexing agent
- They work as a buffer
- Must have a weaker K_f than metal-EDTA

Auxiliary complexing agent

- Titration of Cu^{2+} ($CuSO_4$) with EDTA
- Addition of ammonia buffer results in a dark blue solution
- Cu(II)-ammonia complex is formed
- Addition of EDTA displaces ammonia with corresponding color change

Auxiliary complexing agent

- Ammonia, tartrate, citrate, triethanolamine
- How does the concentration of NH_3 affect the titration?

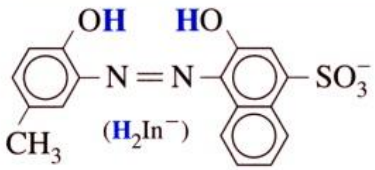
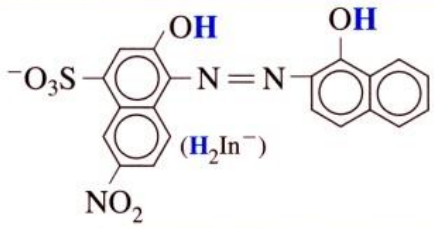
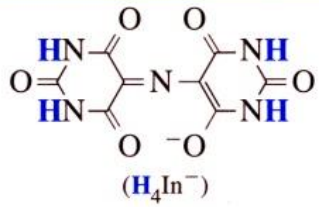
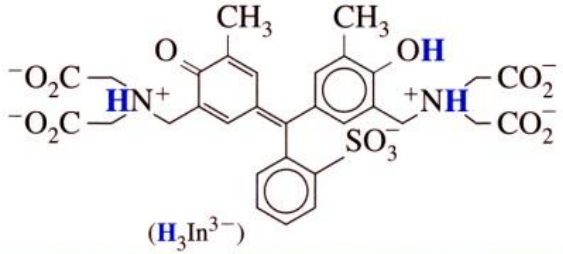
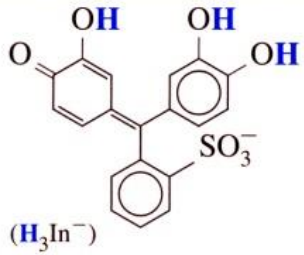


Metal-ion indicators

- EDTA does not have a specific indicator
- We first complex the indicator with the analyte to form a coloured complex.
- Then the indicator – metal analyte complex is titrated with EDTA
- EDTA displaces the indicator and forms a EDTA-metal analyte complex.
- A colour change in the solution indicates the displacement of the dye

- The end point of the titration is when the Mg-Indicator complex (red) is completely dissociated and the becomes Mg-EDTA and free Indicator (blue)
- $Mn^{2+} + In^{n-} \rightarrow M\text{-}In$ $M\text{-}In + EDTA \rightarrow M\text{-}EDTA + In$

Table 12-3 Common metal ion indicators

Name	Structure	pK_a	Color of free indicator	Color of metal ion complex
Calmagite		$pK_2 = 8.1$ $pK_3 = 12.4$	H_2In^- red HIn^{2-} blue In^{3-} orange	Wine red
Eriochrome black T		$pK_2 = 6.3$ $pK_3 = 11.6$	H_2In^- red HIn^{2-} blue In^{3-} orange	Wine red
Murexide		$pK_2 = 9.2$ $pK_3 = 10.9$	H_4In^- red-violet H_3In^{2-} violet H_2In^{3-} blue	Yellow (with Co^{2+}, Ni^{2+}, Cu^{2+}); red with Ca^{2+}
Xylenol orange		$pK_2 = 2.32$ $pK_3 = 2.85$ $pK_4 = 6.70$ $pK_5 = 10.47$ $pK_6 = 12.23$	H_5In^- yellow H_4In^{2-} yellow H_3In^{3-} yellow H_2In^{4-} violet HIn^{5-} violet In^{6-} violet	Red
Pyrocatechol violet		$pK_1 = 0.2$ $pK_2 = 7.8$ $pK_3 = 9.8$ $pK_4 = 11.7$	H_4In red H_3In^- yellow H_2In^{2-} violet HIn^{3-} red-purple	Blue

S.No.	Name of the Indicator	Colour change	pH range	Metals detected
1.	Mordant black II	Red to Blue	6-7	Ca, Ba, Mg, Zn, Cd, Mn, Pb, Hg
	Eriochrome blackT			
	Solochrome blackT			
2.	Murexide or Ammonium purpurate	Violet to Blue	12	Ca, Cu, Co
3.	Catechol-violet	Violet to Red	8-10	Mn, Mg, Fe, Co, Pb
4.	Methyl Blue	Blue to Yellow	4-5	Pb, Zn, Cd, Hg
	Thymol Blue	Blue to Grey	10-12	
5.	Alizarin	Red to Yellow	4.3	Pb, Zn, Co, Mg, Cu
6.	Sodium Alizarin sulphonate	Blue to Red	4	Al, Thorium
7.	Xylenol range	Lemon to Yellow	1-3	Bi, Thorium
			4-5	Pb, Zn
			5-6	Cd, Hg

EDTA titration techniques

- Direct (Analyte titrated with EDTA, may use aux agents)
- Back titration (Excess EDTA titrated with a metal ion)
- Displacement titration (Analyte that does not have an appropriate indicator displaces a metal-EDTA complex that undergoes colour change)
- Indirect titration

Titration selectivity

- We control pH to titrate different metal cations
- Not always easy *e.g.* analysing Al^{3+} if Mg^{2+} is present
- We can use a masking agent
- The masking agent will complex with the analyte leaving other cations to complex with EDTA
  - *e.g.* Fluoride reacts with Al^{3+}

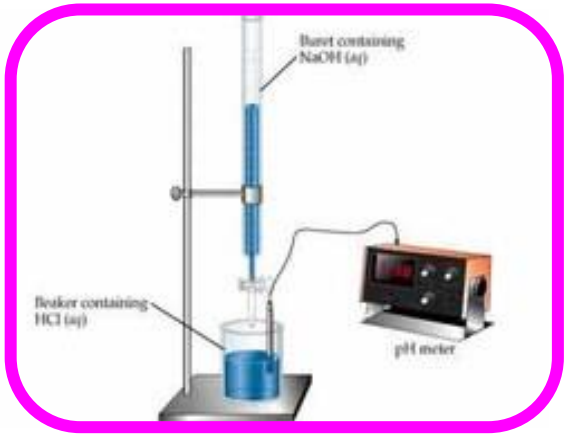
Masking and demasking example

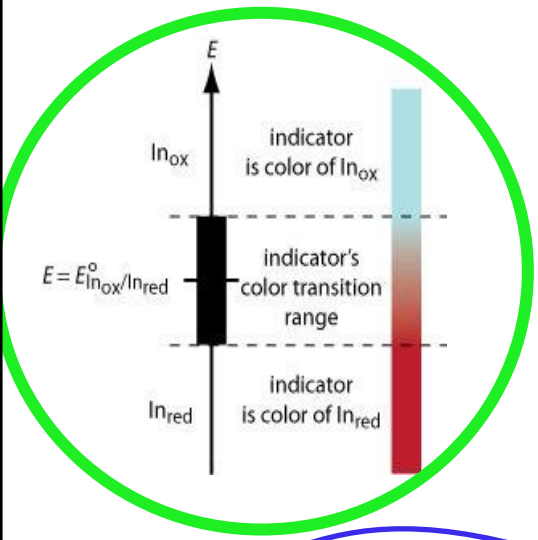
A solution containing Mg, Zn, and Cu can be titrated as follows:

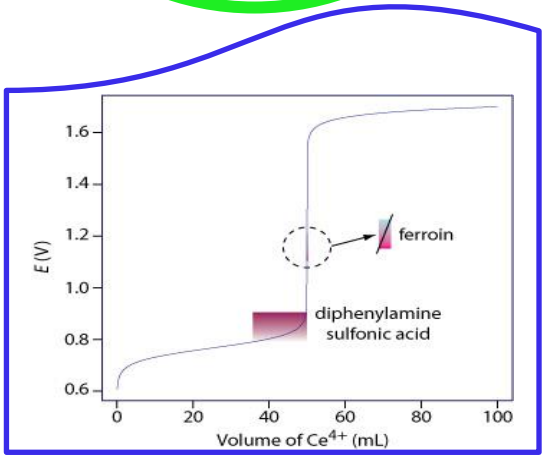
- Add excess of standard EDTA and back-titrate with standard Mg solution using solochrome black as indicator. This gives the sum of all the metals present.
- Treat an aliquot portion with excess of **KCN** and titrate as before. This gives Mg only.
- Add excess of **chloral hydrate** to the titrated solution in order to liberate the Zn from the cyanide complex, and titrate until the indicator turns blue. This gives the Zn only.
- The Cu content may then be found by difference

A 25.00 ml aliquot of a solution containing Cu^{2+} and Fe^{3+} was titrated with 16.06 ml of 0.05083 M EDTA. A second 25.00 ml aliquot of the Cu/Fe mixture was treated with NaF to form a stable iron-fluoride complex. This mixture was then titrated with 0.05083 M EDTA and the endpoint volume was found to be 5.43 ml. Calculate the molar concentrations of Cu^{2+} and Fe^{3+}.

1st titration: 25 mL aliquot, 16.06 mL of 0.05083 M EDTA
2nd titration: 25 mL aliquot, 5.43 mL of 0.05083 M EDTA



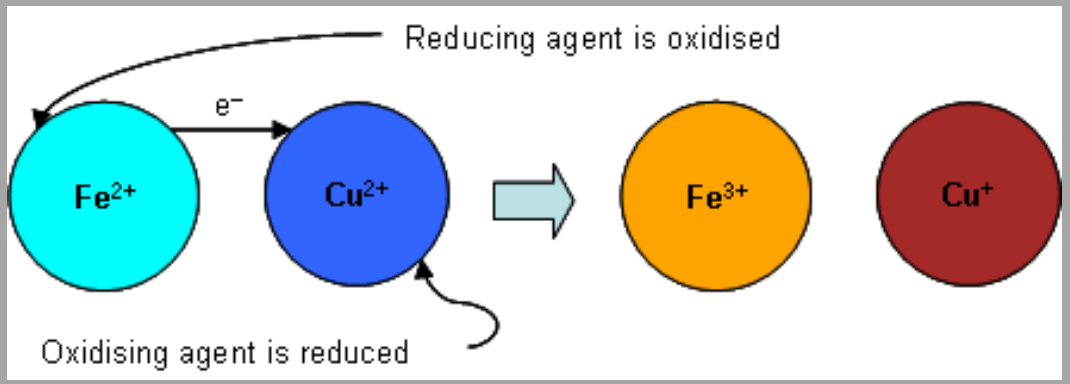




Redox titrations

Redox facts

Is the reaction redox?	If any atoms change oxidation number –YES!
What is oxidised?	↑ oxidation number (Fe^{2+})
What is reduced	↓ oxidation number (Cu^{2+})
Reducing agent	Substance with element oxidised (Fe^{2+})
Oxidising agent	Substance with element reduced (Cu^{2+})



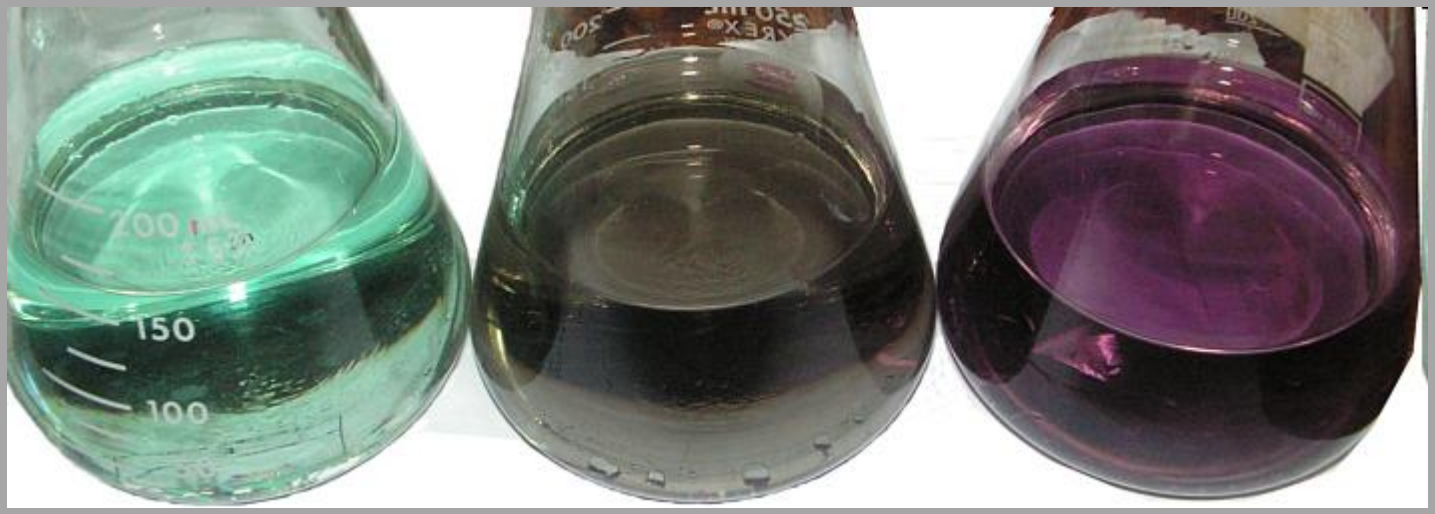
Redox titration

- Oxidation and reduction reaction between analyte and titrant
- We can deduce the shape of the redox titration curve using half reactions and their associated potentials.
- During the titration, the potential difference will change over time

Redox Indicators

- Redox indicators change colour based on the redox potential of the solution
- Respond to the appearance or disappearance of a reagent.
  - Starch as an indicator for excess iodine solution.
  - Thiocyanate as a detector of Fe^{3+}.

- *e.g.* 1,10-phenanthroline undergoes a change in colour when Fe(II) is oxidised. $Cr_2O_7^{2-} + 6\ Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6\ Fe^{3+} + 7H_2O$



- Starch is used as a redox indicator when triiodide (I_3^-) is present. Starch forms a very dark blue-black complex with triiodide which can be made by mixing iodine with iodide. The complex is not formed if only iodine or only iodide (I^-) is present.

Redox indicator range

- $E = \left(E^0 \pm \frac{0.05916}{n}\right)$ volts $(w.r.t$ SHE$)$

From a table

no. of electrons

- A redox titration is feasible if the difference is ≥ 0.2 V.
- The bigger the difference, the sharper the endpoint colour change

Iodometric Titrations

- The basic reaction in the determination of copper using the iodometric method is represented by the equation:

$$2Cu^{2+} + 4I^{-} \rightarrow 2CuI(s) + I_2$$

- The iodine is then titrated with thiosulphate solution (which has been standardised)

$$I_2 + 2\ S_2O_3^{2-} \rightarrow 2I^{-} + S_4O_6^{2-}$$

- The amount of iodine liberated in the reaction between iodide ion and an oxidizing agent is a measure of the quantity of oxidizing agent originally present in the solution.

- The amount of standard sodium thiosulfate solution required to titrate the liberated iodine is then equivalent to the amount of oxidizing agent.

- Iodometric methods can be used for the quantitative determination of strong oxidizing agents such as potassium dichromate, permanganate, hydrogen peroxide, cupric ion and oxygen.

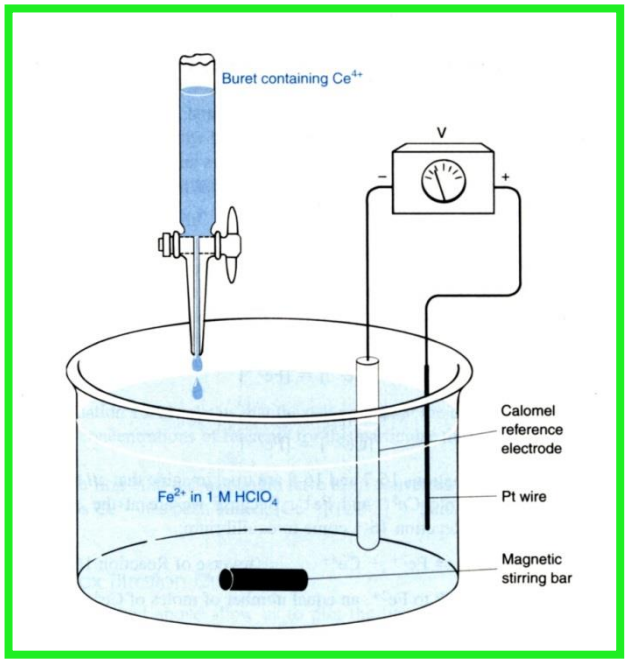
Example- Homework

- 0.3021 g of brass is dissolved in HCl and H_2SO_4. 4.0 g of KI was then added to the sample. This is titrated with 27.34 mL of a standard thiosulfate solution with a concentration of 0.1008 M. Calculate the %Cu in brass.

Redox titration curves

- Nernst Equation! : $$E = E^0 + \frac{RT}{nF} \ln \frac{[\text{Ox}]}{[\text{Red}]}$$

- Using Ce (titrant) and Fe: **$Fe^{2+} + Ce^{4+} \rightarrow Fe^{3+} + Ce^{3+}$**
- Calomel is the reference electrode (0.241 V)
- @the platinum electrode:
  - **$Fe^{3+} \rightarrow Fe^{2+} + e^-$** E^o = 0.767 V
  - **$Ce^{4+} + e^- \rightarrow Ce^{3+}$** E^o = 1.70 V



Before equivalence point

- Each aliquot of Ce^{4+} creates an equal number of moles of Ce^{3+} and Fe^{3+}
- Excess unreacted Fe^{2+} remains in solution
- Use iron half-reaction relative to calomel reference electrode

$$E = E_{+}(\textit{indicator electrode}) - E_{-}(\textit{reference electrode})$$

50mL of 0.05 M Fe^{2+} with 15mL, 25 mL and 26 mL 0.100 M Ce^{4+} . Calomel electrode is 0.241 V

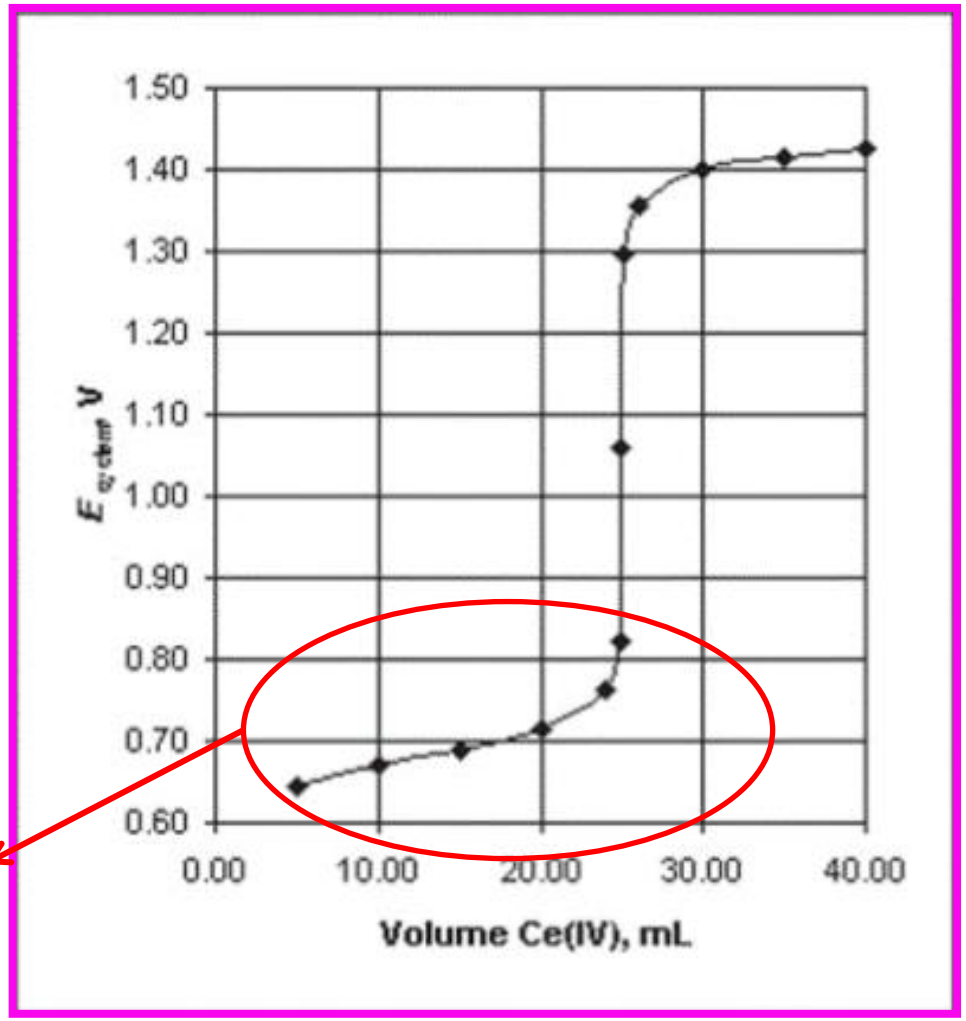
$Ce^{4+} + e^- \leftrightarrow Ce^{3+}$ $\quad E^0 = 1.70$ V

$Fe^{3+} + e^- \leftrightarrow Fe^{2+}$ $\quad E^0 = 0.767$ V

$Fe^{2+} + Ce^{4+} \leftrightarrow Ce^{3+} + Fe^{3+}$

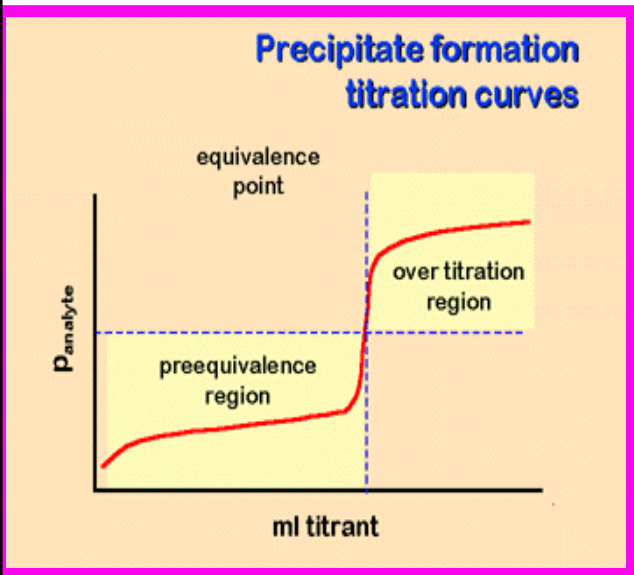
Titration curve

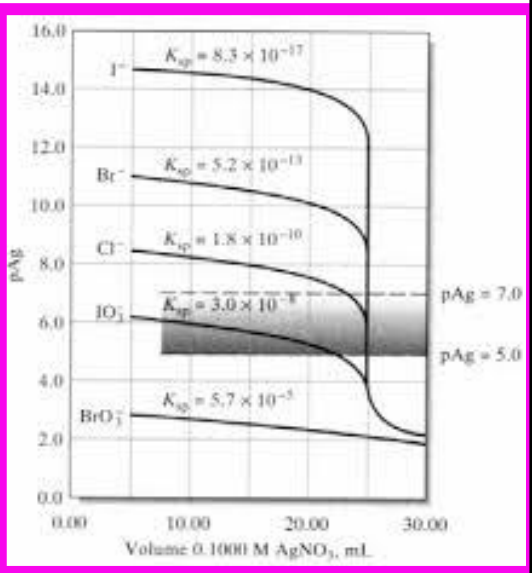
- 50.00 mL solution of 0.100 M Fe^{2+} with 0.100 M Ce^{4+} in 1 M H_2SO_4



$$E = 0.526 - 0.05916 \log\left(\frac{[Fe^{2+}]}{[Fe^{3+}]}\right)$$

Gravimetry & Precipitation Titrations





Precipitation reactions

- We can use precipitation in titration
- Most common to quantify chlorides, bromides, iodides, and thiocyanate using silver nitrate
- Technique is called **ARGENTOMETRIC TITRATION**
- The titrant reacts with the analyte → precipitate
- The first drop of titrant in excess will react with an indicator (color change)

Argentometric Titration - Mohr Method

- **C**hromate as an indicator.
- Chromate forms a precipitate with Ag^+
- Precipitate has a greater solubility than that of AgCl
- AgCl is formed first and after all Cl^- is consumed, the first drop of Ag^+ in excess will react with the chromate indicator giving a reddish precipitate.

$$Ag^+ + Cl^- \rightarrow AgCl \text{ (titration reaction)}$$

$$2\,Ag^+ + CrO_4^{2-} = \mathbf{Ag_2CrO_4} \text{ (endpoint reaction)}$$

Conditions for Mohr

- Neutral medium (~ pH 7)
- In alkaline solutions, silver will react with the hydroxide ions forming AgOH.
- In acidic solutions, chromate will be converted to dichromate.

Argentometric titration – Volhard Method

- Indirect method
- Fe^{3+} as an indicator.
- Excess amount of standard Ag^+ is added to the Cl^- solution:

$$Ag^+ + Cl^- \rightarrow AgCl + Ag^+$$

- The excess Ag^+ is then titrated with standard SCN^- :

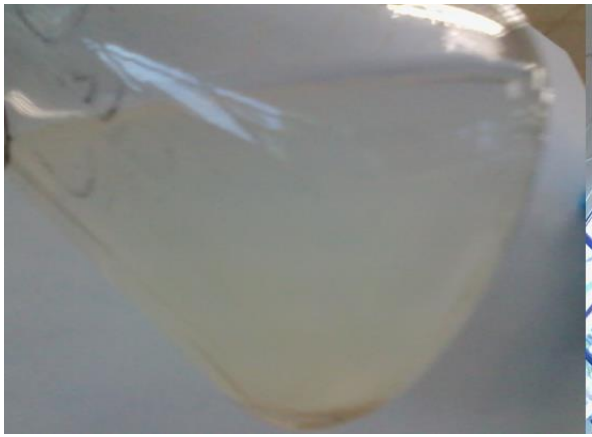
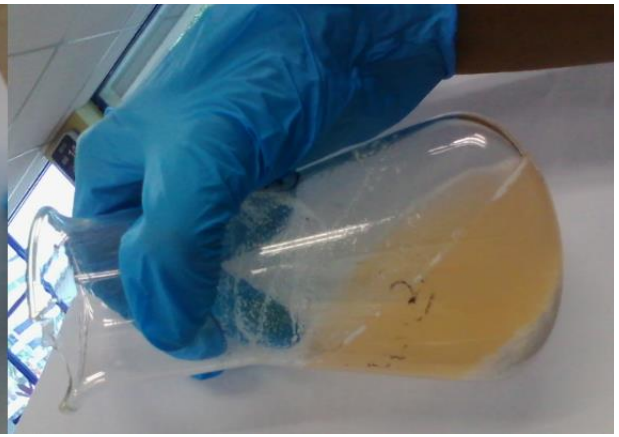
$$Ag^+ + SCN^- \rightarrow AgSCN$$

- The first excess of SCN results in a red color (endpoint)

$$Fe^{3+} + SCN^- = \mathbf{Fe(SCN)^{2+}}$$

Conditions for Volhard

- Acidic medium otherwise Fe indicator will react (precipitated Fe oxides)
- May need to filter the precipitate formed in the first reaction if it is more soluble than AgSCN.
- Can also add something to form a film around the precipitate *e.g.* nitrobenzene to prevent reaction

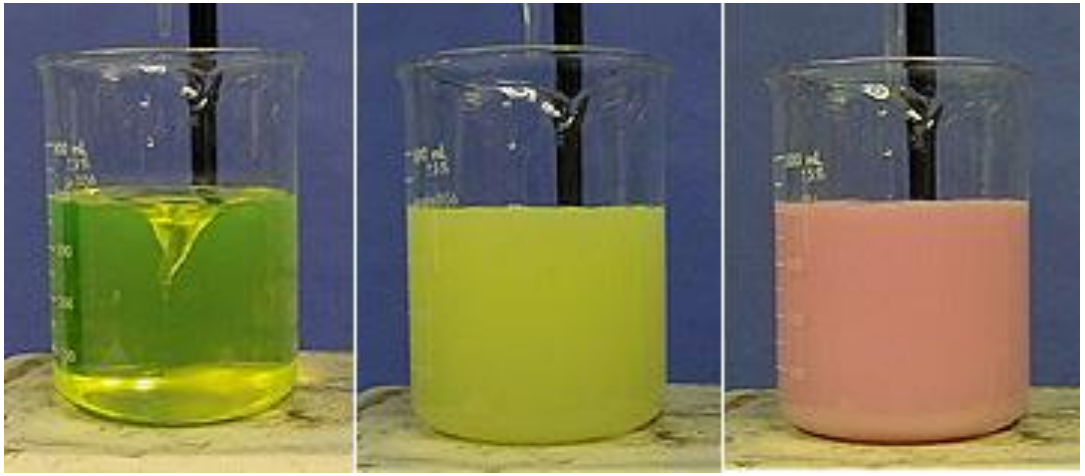
Argentometric titration - Fajans Method

- Adsorption indicator is used
- Silver to titrate Cl^-

$$Ag^+ + Cl^- \rightarrow AgCl \text{ (titration reaction)}$$

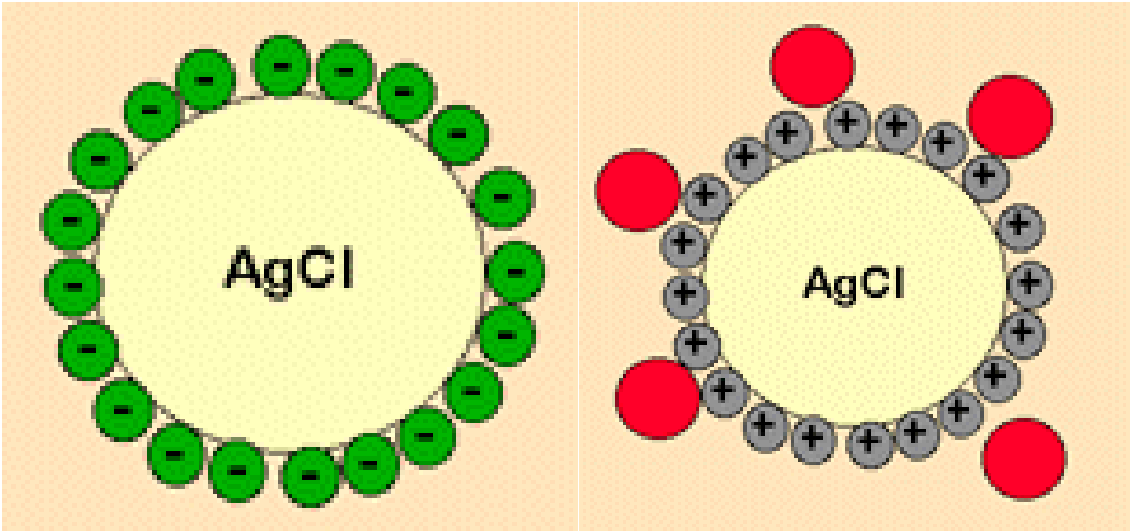
- Fluorescein adsorbs to the surface of colloidal AgCl.
- The first drop of excess $Ag^+ \rightarrow$ reddish color

$$Ag^+ + FI^- = AgF$$



Conditions for Fajans

- Fluorescein and its derivatives are weak acids,
- The pH of the solution should be slightly alkaline (keeps indicator in anion form)
- Should not be alkaline enough to convert Ag^+ into AgOH .



Mohr	Volhard	Fajan
Chromate	Fe	Fluorescein
Direct	Indirect	Direct
Neutral	Acidic	Slightly alkaline

Electrodes

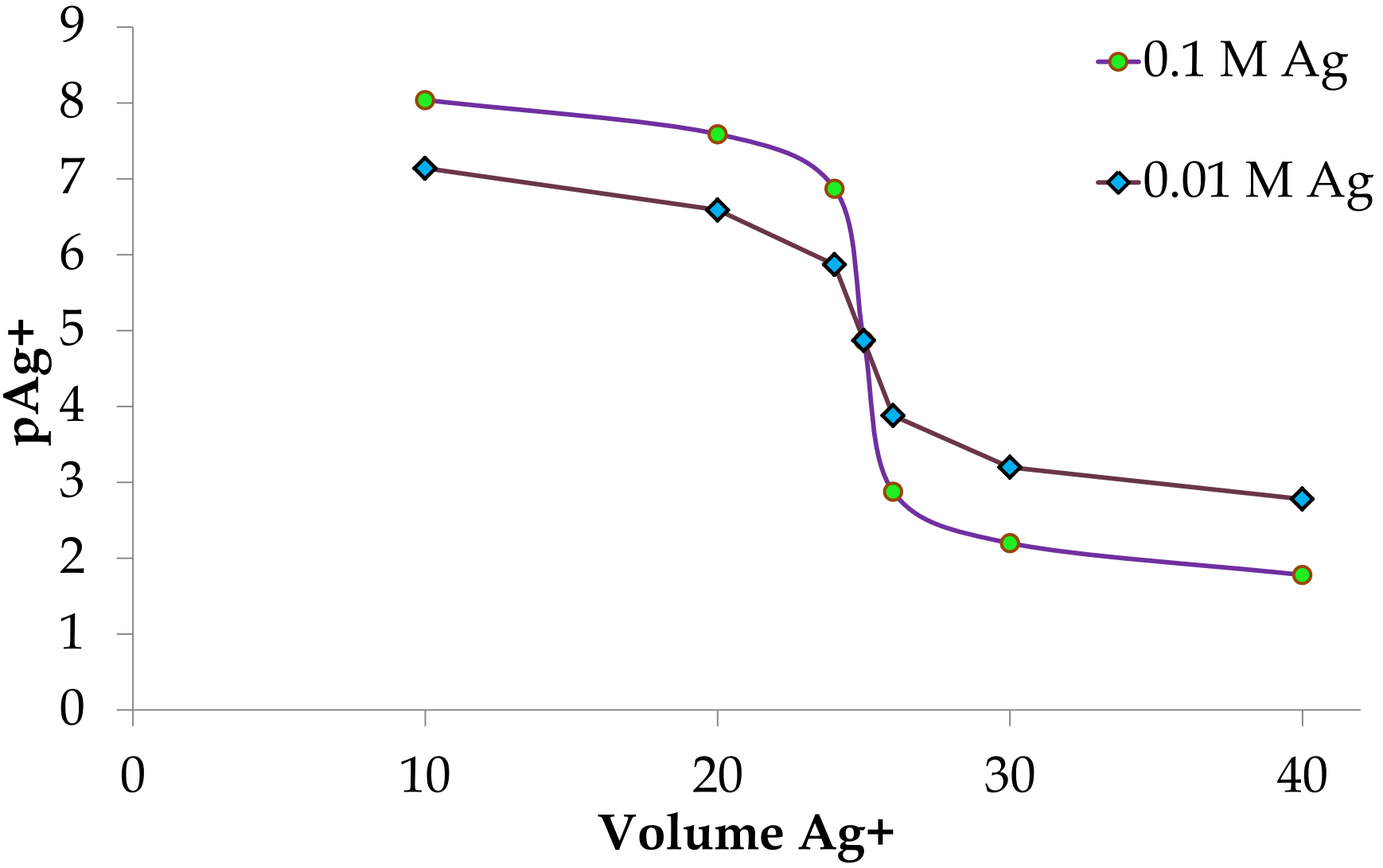
- Typically precipitation reaction are monitored by electrodes.
- We can use them to draw up precipitation curves to locate the equivalence point.
- Same as for acid-base titrations except we use the solubility product of the precipitate
- $K_{sp} = [A^+][B^-]$

Generate a titration curve for 50.00 mL of 0.0500 M NaCl with 0.1000 M $AgNO_3$

$$Ag^+ (aq) + Cl^- (aq) \Leftrightarrow AgCl(s),$$

$$K_{sp} = [Ag^+][Cl^-] = 1.82 \times 10^{-10}$$

Effect of concentration



Titrating a mixture

- Less soluble precipitates first
- Titration of 50.00 mL of a solution ($[I^-]$ = 0.0500M and $[Cl^-]$=0.0800 M) with 0.1000 M $AgNO_3$.
- K_{sp} (Cl^-) = 1.82 x 10^{-10} K_{sp} (I^-) = 8.3 x 10^{-17}
- We know that $K_{sp} = [Ag^+][Cl^-]$ and $K_{sp} = [Ag+][I^-]$

50.00 mL of ($[I^-]$ = 0.0500M and $[Cl^-]$ = 0.0800 M) solution with 0.1000 M $AgNO_3$

@25 mL:

- $n_{Cl^-} = 0.08\ M \times 0.05L = 0.004\ moles$
- $[Cl^-] = \frac{n}{v} = \frac{0.004\ mols}{0.05\ L + 0.025\ L} = 0.0533\ M$
- $[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.82 \times 10^{-10}}{0.0533\ M} = 3.41 \times 10^{-9}\ M \rightarrow pAg = 8.47$
- What about the I^-?
- $\frac{K_{sp}}{[Cl^-]} = \frac{K_{sp}}{[I^-]} \rightarrow \frac{[I^-]}{[Cl^-]} = \frac{K_{sp(I)}}{K_{sp(Cl)}} \rightarrow [I^-] = 2.43 \times 10^{-8}\ M$

50.00 mL of ($[I^-]$ = 0.0500M and $[Cl^-]$ = 0.0800 M) solution with 0.1000 M $AgNO_3$ @30 mL:

- $n_{Cl^-} = 0.08\ M \times 0.05L = 0.004$ moles
- $n_{Ag^+} = 0.100\ M \times 0.03L = 0.003$ moles
- $n_{I^-} = 0.05\ M \times 0.05L = 0.0025$ moles
- $[Cl^-] = \frac{n}{v} = \frac{0.004\ mols - (0.003 - 0.0025)\ mols}{0.05\ L + 0.03\ L} = 0.0438\ M$
- $[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.82 \times 10^{-10}}{0.0438\ M} = 4.16 \times 10^{-9}\ M \rightarrow pAg = 8.38$

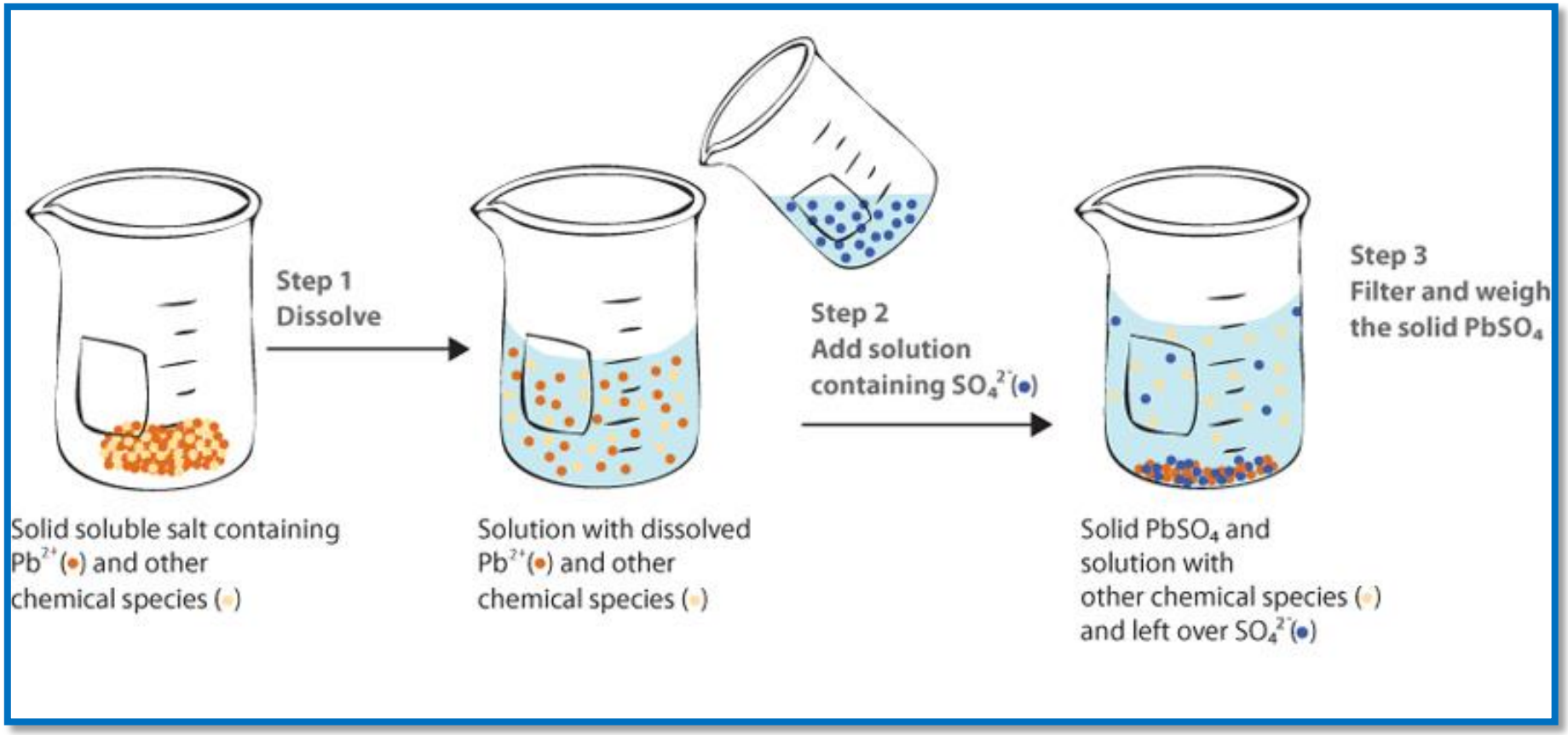
Gravimetric Analysis

- Analyte measured based on mass
- Analyte is precipitated out of solution in a chemical reaction
- Precipitate is washed of impurities
- Converting precipitate to a known composition
- Dried mass by difference weighed.

Steps for gravimetric analysis

- Preparation of the solution
- Precipitation
- Digestion
- Filtration
- Washing
- Drying or igniting
- Weighing
- Calculation

Example: Pb in water

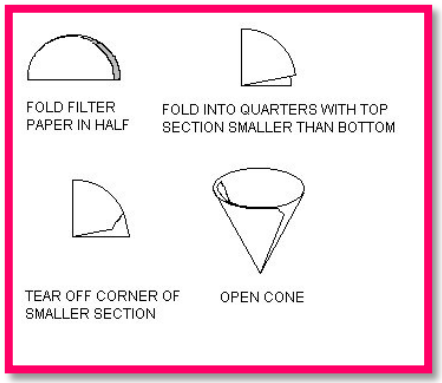


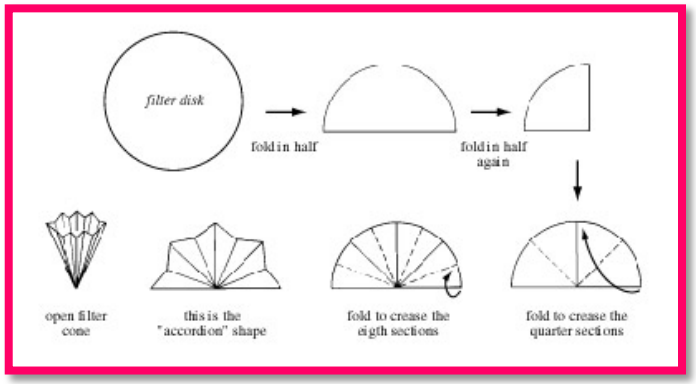
Details of each step

- The sample is dissolved, if it is not already insoluble.
- The solution may be treated to adjust the pH
  - To form the proper precipitate
  - To suppress the formation of other precipitates
- The precipitating reagent is added at a concentration that favors the formation of a "good" precipitate.
- This may require:
  - low concentration,
  - extensive heating (digestion)
  - control of the pH.
- Heating can help reduce the amount of coprecipitation.

- After the precipitate has formed and been allowed to "digest", the solution is carefully filtered.
- The filter is chosen to trap the precipitate

- However, they must be carefully cleaned to minimize contamination or carryover(cross-contamination).





- After the solution has been filtered - test to make sure that the analyte has been completely precipitated.
- Add a few drops of the precipitating reagent - if a precipitate is observed, the precipitation is incomplete.
- After filtration, the precipitate is heated so
  - The remaining moisture is removed (drying).
  - The precipitate is converted to a more chemically stable form. *e.g.* the Ca ion is precipitated with oxalate to produce calcium oxalate (CaC_2O_4); it can then be heated to convert to CaO.
  - The filter paper is removed – must use ash-less filter paper.
- Cool the precipitate in a desiccator.
- Weighed the product in the crucible (mass difference)
- Since the composition of the precipitate is known, it is simple to calculate the mass of analyte in the original sample

Criteria for using gravimetric analysis

- The precipitating agent should react specifically or at least selectively with the analyte.
- The precipitate must be easily transferred
- The precipitate must be of

–

- The precipitate must be easy to filtered *i.e.* large crystals

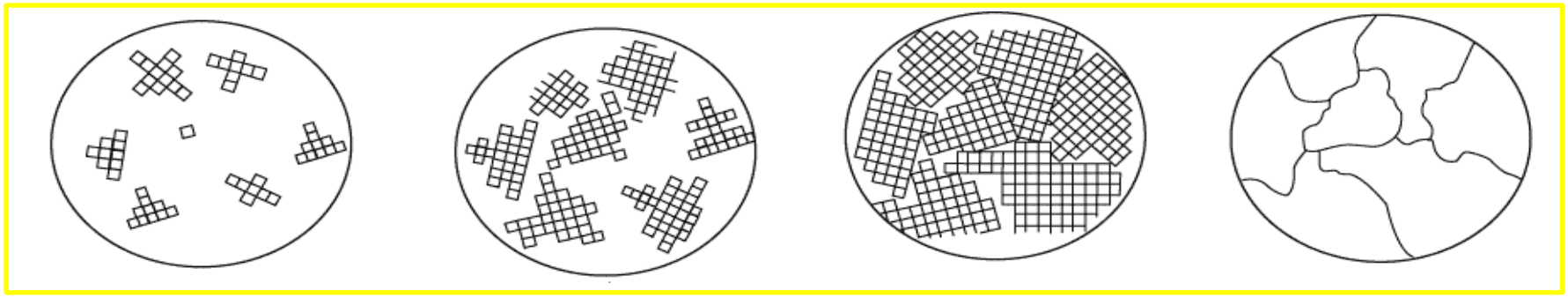
Filterability

- Want product to be large enough to collect on filter:
  - Best Case: Pure Crystals
  - Worst Case: Colloidal suspension: Difficult to filter due to small size, tend to stay in solution
- ***Whether crystals or colloids are obtained depends on conditions used in the precipitation***
- Particle size influenced by experimental variables as
  - precipitate solubility,
  - temperature,
  - reactant concentrations
  - rate at which reactants are mixed.

Precipitate formation

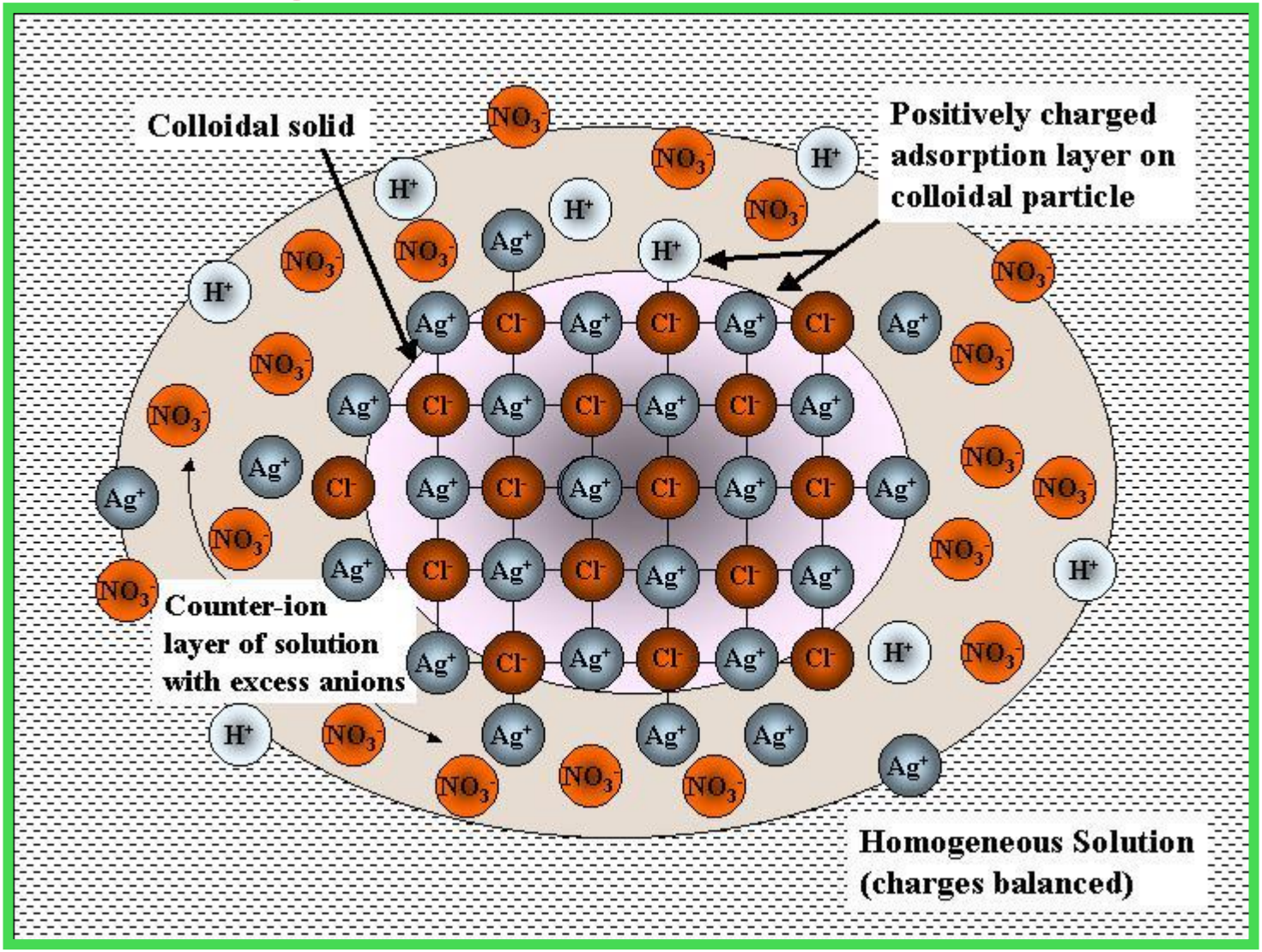
- Precipitates form by nucleation and particle growth.
- A few ions, atoms, or molecules come together to form a stable solid.
- Formed on the surface of suspended solid contaminants, *e.g.* dust particles.

Nucleation and particle growth



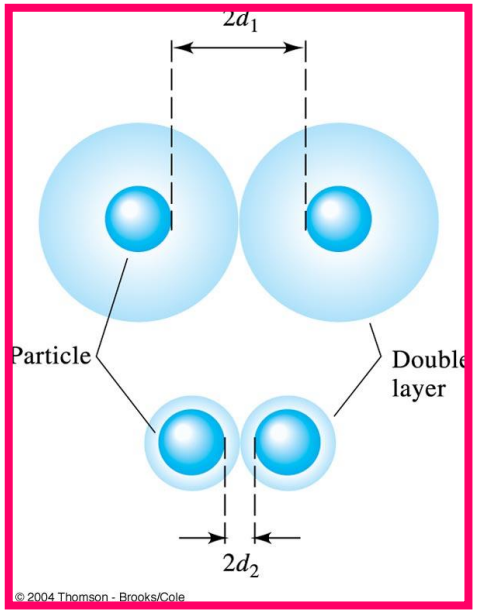
- Further precipitation involves a competition between additional nucleation and growth on existing nuclei (particle growth).
- If nucleation predominates, a precipitate containing a large number of small particles results
- If particle growth predominates, a smaller number of larger particles is produced. ☺

Coagulation of Colloids

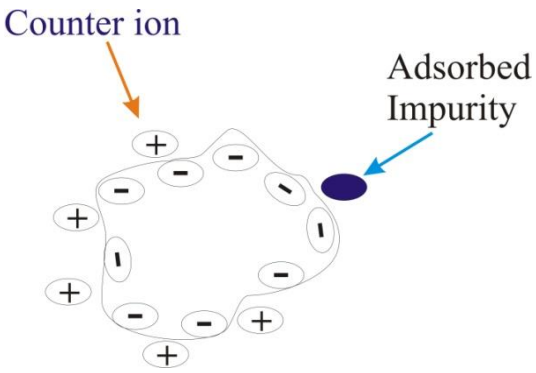


Colloidal precipitates

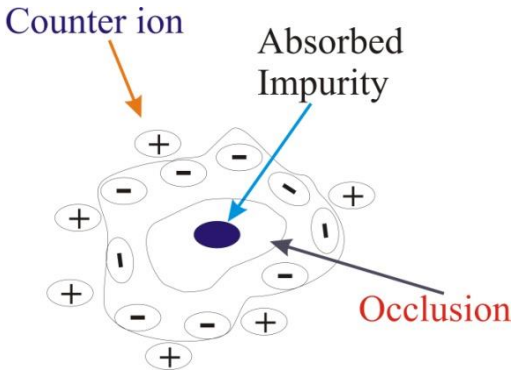
- Electric double layer prevents coagulation of indiviual particles.
- Heat decreases the thickness of the double layer.
- Increasing the electrolyte concentration (*i.e.* add more $AgNO_3$ for Cl precipitation) will also decrease this layer.
- ***Problem:*** Washing reverts coagulated colloid to original state - **PEPTISATION**



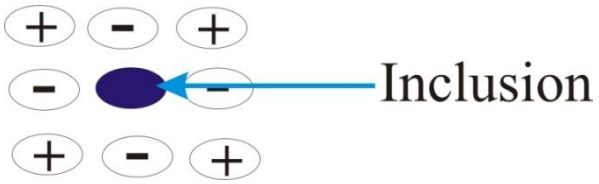
Crystal Impurities



Adsorbed to crystal surface

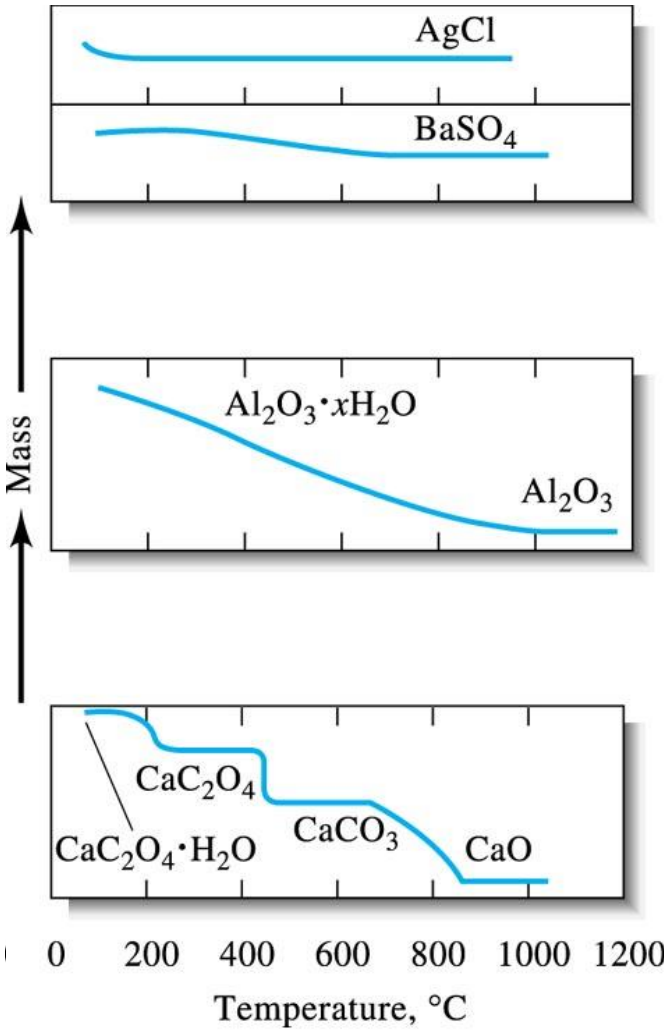


Absorbed or trapped within crystal pockets



Impurity placed in crystal instead of analyte

Filtering & Drying samples



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Weighing techniques

- Reproducible amounts of water – drying in an oven until constant mass
- Cannot touch crucible with fingers or dirty tongs – oil residue and dirt
- Cleaning off sides of crucible with a cloth – static charge
- Open container so no temperature/pressure issues

Gravimetric Example

A 2.00 g sample of limestone was dissolved in HCl and all the Ca in the sample was converted to $Ca^{2+}_{(aq)}$. Excess ammonium oxalate solution, $(NH_4)_2C_2O_{4(aq)}$, was added to the solution to precipitate the Ca ions as $CaC_2O_{4(s)}$. The precipitate was filtered, dried and weighed to a constant mass of 2.43 g. Determine the percentage by mass of calcium in the limestone sample.

Calculating using a gravimetric factor

$$GF = \frac{\text{f mass analyte}}{\text{f mass precipitate}} \times \frac{\text{mol analyte}}{\text{mol precipitate}} = \frac{\text{g analyte}}{\text{g precipitate}}$$

- Still need the equation
- Still uses stoichiometry

A barium halide exists as the hydrated salt $BaX_2.2H_2O$, where X is the halogen. A sample of the halide (0.2650 g) was dissolved in water (200 $cm^{3)}$ and excess sulfuric acid added. The precipitate formed (barium sulfate) was filtered, washed and dried. Precipitate weighed = 0.2533 g. Determine the identity of X.

25.00 mL of $Pb(NO_3)_2$ [MM = 331.2098 g mol^{-1}]solution with an unknown concentration reacts with excess aqueous Rb_3AsO_4. After filtering and drying, 0.0814 g of precipitate is found. What is the concentration of the lead(II) nitrate solution? $M(Pb_{3(}AsO_4)_2)$ = 692.2 g mol^{-1}