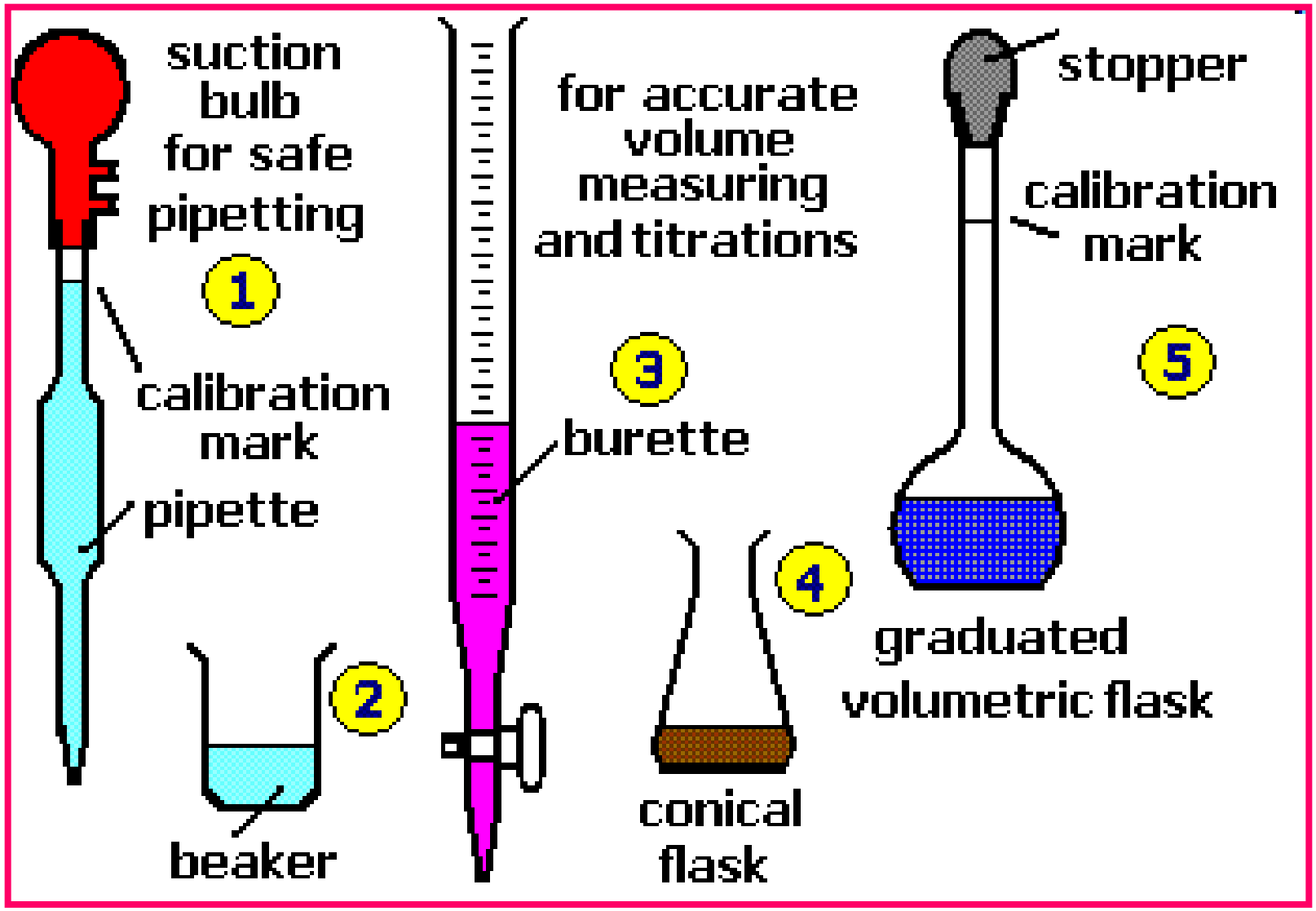
Volumetric (Titrimetric) Analysis

Volumetric analysis

- Chemical procedure used for determining the concentration of an unknown solution.
- A known volume of a solution of unknown concentration is reacted with a known volume of a solution of known concentration (standard).
- The standard solution is delivered from a burette so the volume delivered is known.
- We often use an indicator to show when the reaction is complete.
- This technique is known as titration

Volumetric Glassware



Equivalence point

- During the titration, the reaction is complete when all of the analyte has reacted stoichiometrically.
- This is called the **equivalence point**
- Equivalence point is a theoretical point.
- You already know how to calculate equivalence points from first year.

Titrations

What is the molarity of NaOH if 36.2 mL is required to react with 35.2 mL of 0.125 M HNO_3 according to the following reaction:

$$HNO_3 + NaOH \rightarrow NaNO_3 + H_2O$$

35.2 mL	**42.7 mL**
0.125 M	**? M**

n HNO_3 = 0.125 mol/L x 0.0352 L = 0.00440 mol

n NaOH = 0.00440 mol (mol ratio)

$$c = \frac{0.0044 \text{ mol}}{0.0427 \text{ L}} = 0.103 \text{ mol/L} \quad \text{or } 0.103 \text{ M}$$

Endpoint

- We cannot obtain equivalence point experimentally.
- We use an indicator (*e.g.* phenolphthalein) is often added to the reaction flask to produce a visual change in the solution at or near the equivalence point
- (appearance or disappearance of colour, solution turbidity).
- This point is called the **end point** of the titration.

Parameters for quantification

To ensure a successful and accurate analysis using titrations, there are some important points to consider:

- The titrant must be a standard (or be standardised)
- The reaction should proceed to a stable and well defined equivalence point.
- The equivalence point must be able to be detected using an indicator.
- The titrant and sample volume (or mass) must be accurately known.
- There should be no side reactions occurring.

Errors in titration

$$Error_{titration} = V_{endpoint} - V_{equivalence\ point}$$

- $V_{endpoint}$ is the actual volume required to reach the endpoint
- $V_{equivalence}$ point is the theoretical volume to reach equivalence point

Types of titrations

- Titrations can be divided into four categories, according to the type of reaction involved.

	Type of chemical to be analysed	Type of reagent used	Monitoring method
Acid/base	acid or base	alkali or acid	pH indicator or pH meter
Precipitation	ion that forms insoluble salts	compound containing the other ion needed to form the insoluble salt	conductivity
Redox	oxidising or reducing agent	suitable reducing or oxidising agent	natural colour change or redox indicator
Complexometric	metal ion that forms complexes	complexing agent	metal ion indicator

Standard Solutions

Standard solutions should:

- Be sufficiently stable over a period of time (there is no need to determine its concentration more than once).
- React rapidly with the analyte.
- React completely with the analyte, adequate endpoint.
- Selectively react with the analyte.

Standard solutions

A standard solution can be prepared in either of two ways:

- Direct method: the primary standard is accurately weighed and diluted to a known volume in a volumetric flask.
- Standardisation: the titrant to be standardised is used to titrate
  - A mass of primary standard
  - A weighed mass of secondary standard.
  - A measured volume of another solution.

Primary Standards

- Primary standards are highly purified compounds
- Can be accurately weighed
- serve as a reference material for titrimetric methods of analysis.
- The accuracy of quantification relies on the quality of these chemicals and how they are made into a standard solution.
- Examples are given in your notes.

Primary standards

A primary standard should have the following qualities:

- High purity (which can be confirmed).
- Stability towards air.
- No waters of crystallisation
- As high a molar mass as possible
- Readily available at modest cost.
- Reasonably soluble.

Secondary standards

- A secondary standard is a standard that is prepared in the laboratory.
- It is usually standardized against a primary standard.

You need to use a primary standard solution to accurately work out the concentration of the solution.

- *e.g.* Making a primary standard solution of Na_2CO_3 and then titrating that to find the accurate concentration of HCl will make the HCl solution secondary standard.

Titrations

The three types of volumetric titrations are:

- Direct titration
- Indirect titration
- Back titration

Direct Titration

- One step
- Direct reaction between titrant and analyte
- *e.g.* Acid-base titration
- All your titrations thus far

- A 25 mL aliquot of HCl was titrated with 0.115 M NaOH. The endpoint was reached after the addition of 18.3 mL NaOH. Calculate the concentration of the HCl.

$$\frac{?\ \text{mol HNO}_3}{1\ \text{L HNO}_3\ \text{soln}} = \frac{18.3\ \text{mL NaOH soln}}{25.00\ \text{mL HNO}_3\ \text{soln}}\left(\frac{10^3\ \text{mL}}{1\ \text{L}}\right)\left(\frac{0.115\ \text{mol NaOH}}{10^3\ \text{mL NaOH soln}}\right)\left(\frac{1\ \text{mol HNO}_3}{1\ \text{mol NaOH}}\right)$$

$$= \mathbf{0.0842\ M\ HNO_3}$$

Calculations with standardisation

- In a titrimetric determination, KHP, $C_8H_5KO_4$, (204.22 g mol^{-1}) reacts with NaOH according to the equation:

$$NaOH(aq) + KHC_8H_4O_4(aq) \text{ ---> } KNaC_8H_4O_4(aq) + H_2O(l)$$

- A 0.2878 g aliquot of pure KHP was titrated with a NaOH solution and the endpoint was found to be 12.94 mL. The NaOH solution was then used to determine the acetic acid content in vinegar. 100 mL of vinegar was titrated with the NaOH and the endpoint was 30.43 mL. Calculate the concentration of acetic acid in the sample.

Indirect Titration

- Two step process
- Analyte is replaced and the replacement titrated.
- Stoichiometric ratio between analyte and replacement.
- The titrant and analyte do not react with each other, but are related through the other substance.
- Example is the iodometric determination of Cu in brass.

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)

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

- 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

- 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.

Back Titration

- When the reaction between the analyte and the titrant is too slow
- When there is difficulty in determining the endpoint.
- The lack of a suitable indicator
- The formation of a precipitate
- Add an excess of titrant and titrate the excess.
- We determine the molar quantity of one of the initial reagents and not the analyte itself directly

Back Titration

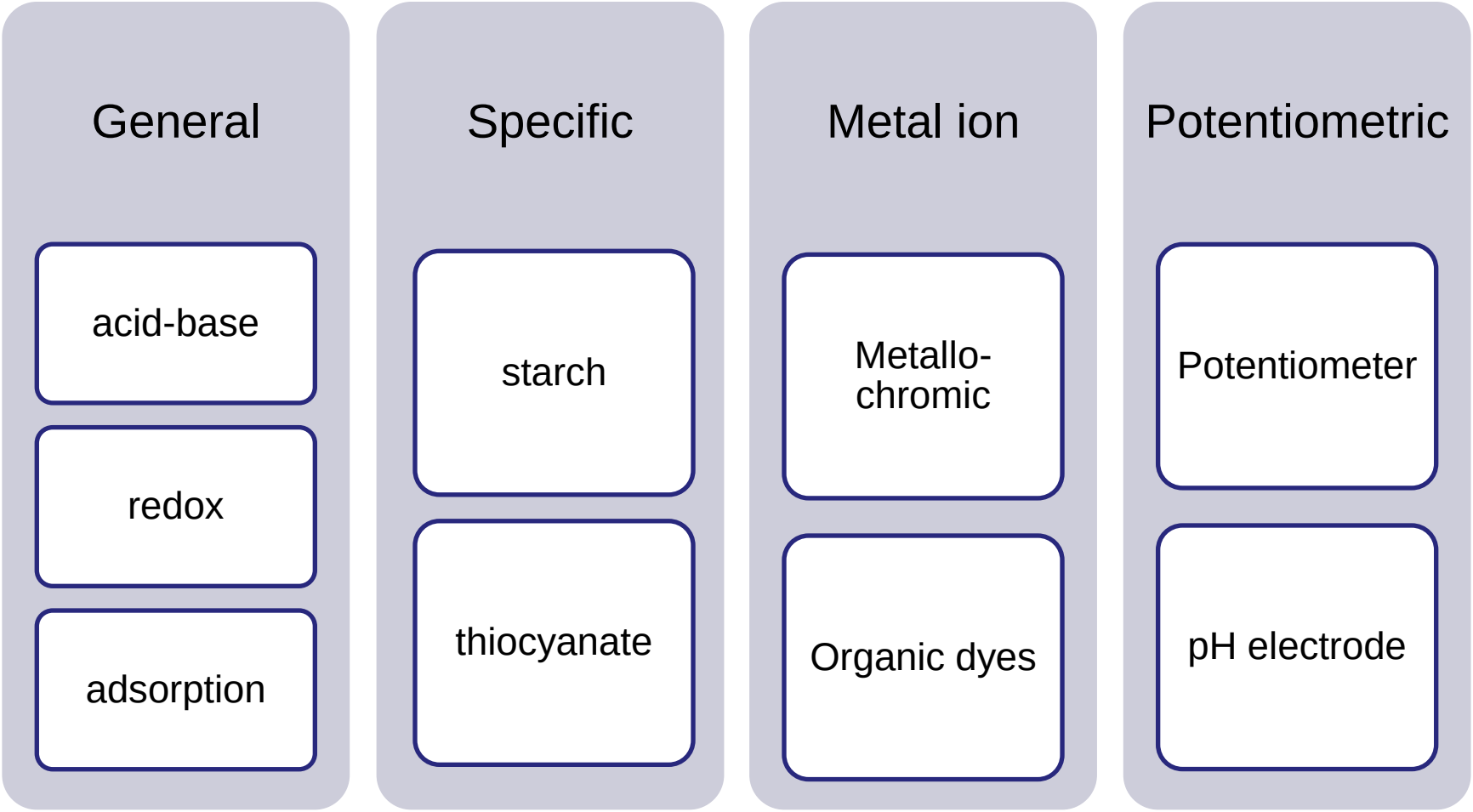
- Reagent (of known concentration) is added to the analyte in excess (known volume) – *Reaction 1*.
- The excess reagent is then titrated – *Reaction 2*.
- In a back titration, knowing initial amount of reagent added and amount that was left after the reaction (from titration) we can easily calculate how much reagent was used for the reaction with the analyte.

Example

- A 2.20 g piece of steel wool is dissolved in 20.0 mL of 1.00 M sulphuric acid, H_2SO_4. The excess sulphuric acid is determined by titration with a 0.500 M NaOH solution. 28.15 mL of sodium hydroxide is required to neutralise the acid. What was the percentage, by mass, of iron in the steel wool? The reaction between the Fe in steel wool and H_2SO_4 is given below.

$$Fe(s) + H_2SO_4(aq) \rightarrow FeSO_4(aq) + H_2(g)$$

Indicators


General
acid-base
redox
adsorption
Specific
starch
thiocyanate
Metal ion
Metallo-chromic
Organic dyes
Potentiometric
Potentiometer
pH electrode

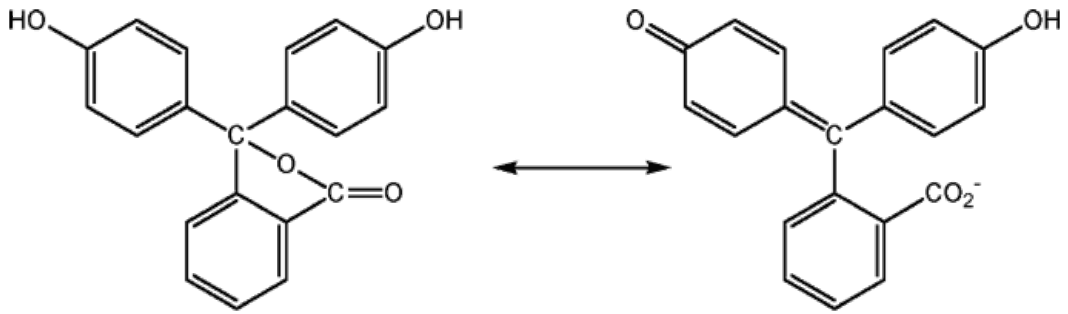
Indicators

- Signals the endpoint of a titration.
- Indicators are weak organic acids or bases that are different colours in their dissociated and un-dissociated states.
- Used in low concentrations so don't affect the equivalence point.
- Indicators detect the first excess of titrant.

General Indicators

- General indicators respond to changes in the titration environment
- *e.g.* a change in pH or a change in redox.
- The most commonly used general indicators are those used for acid-base titrations.

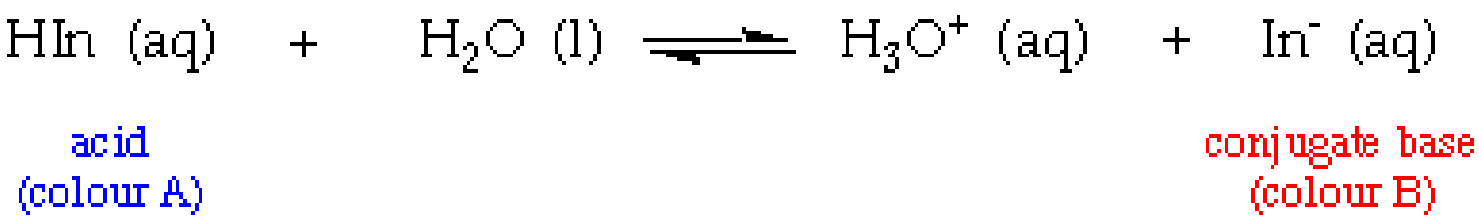
Phenolphthalein

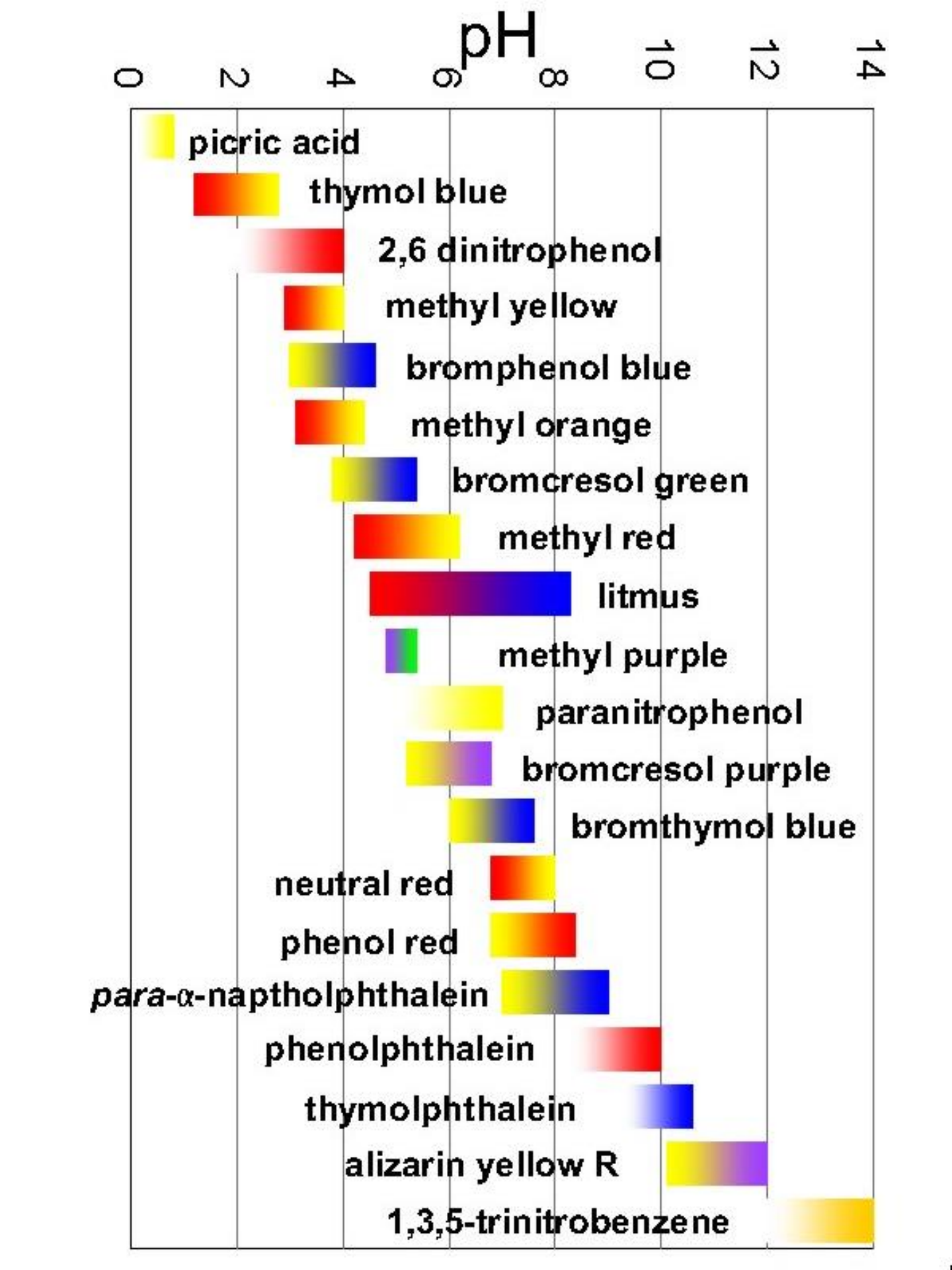


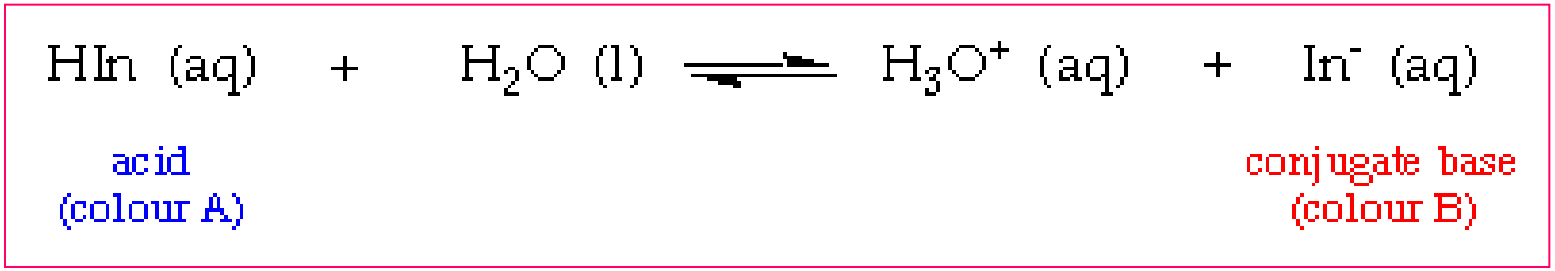
Colourless Pink

Acid-base indicators

- Organic molecules that are either weak acids or weak bases.
- The acid and its conjugate base are different in colour from each other.
- The colour change occurs at or near equivalence point.
- Indicators are often abbreviated HIn (acid) or In (base)

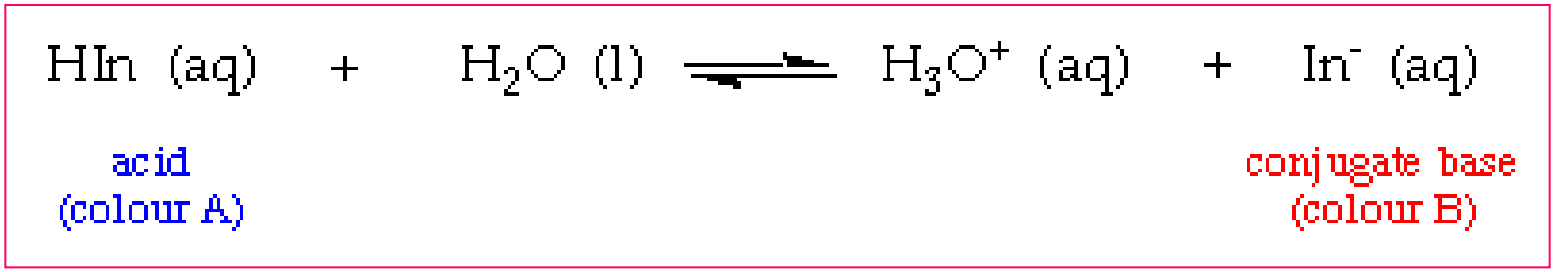



pH
0
2
4
6
8
10
12
14
picric acid
thymol blue
2,6 dinitrophenol
methyl yellow
bromphenol blue
methyl orange
bromcresol green
methyl red
litmus
methyl purple
paranitrophenol
bromcresol purple
bromthymol blue
neutral red
phenol red
para-α-naptholphthalein
phenolphthalein
thymolphthalein
alizarin yellow R
1,3,5-trinitrobenzene



- At low pH values the concentration of H_3O^+ is high and the equilibrium lies to the left. The equilibrium solution has the colour A.
- At high pH values, the concentration of H_3O^+ is low - the equilibrium position thus lies to the right and the equilibrium solution has colour B.
- the initial colour change that you see during the may not be an indication of the end point but rather of a particular pH

- To observe the colour change the ratio of the concentration between the acid and its conjugate base must be 10:1
- Therefore the general pH transition range for an indicator can be calculated so the most suitable indicator chosen for your titration.



$$pH = pK_a + \log \frac{[In^-]}{[HIn]}$$

Example:

- Methyl Red is a commonly used acid-base indicator.
- In acid-base titrations methyl red changes from red in an acidic medium to yellow in a basic medium
- The pKa for methyl red is 5.00, therefore the pH transition range is

$$pH = pKa \pm 1$$

pH range is between 4 and 6. (Actual is pH 4.2 – 6.3)

Redox Indicators

- Redox indicators change colour based on the redox potential of the solution
- *e.g.* 1,10-phenanthroline undergoes a change in colour when Fe(II) is oxidised.
- The table in your notes show some examples of redox indicators and the change in colour that occurs.

$$Cr_2O_7^{2-} + 6\ Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6\ Fe^{3+} + 7H_2O$$

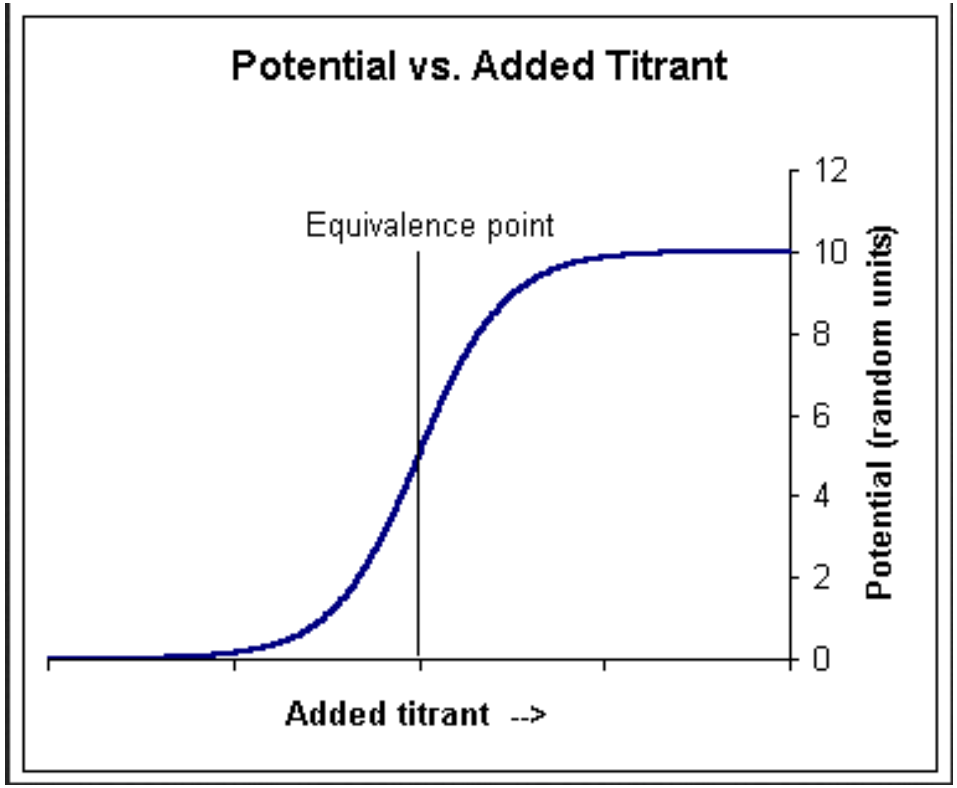
Specific Indicators

- Respond to the appearance or disappearance of a reagent.
  - Starch as an indicator for excess iodine solution.
  - Thiocyanate as a detector of Fe^{3+}.
  - Metal-ion indicators for complexometric titrations

- 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.

Potentiometric Indicators

- Change in voltage



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)