Introduction to titrimetry

Dr. Mai Ramadan

Definition

Titrimetry: analysis based upon measuring the amount of a reagent of a known concentration that is consumed by the analyte.

Volumetric titrimetry: a titrimetry in which the volume of a solution of a known concentration (Titrant) that is needed to react completely with the analyte is determined.

Standard solution (titrant): is a reagent of an accurately known concentration, that is used to carry out a volumetric analysis.

Definition

Primary standard: is a highly purified compound that serves as a reference material, can be weighed directly and used to ***standarize*** other solution.

It should have the following properties: high purity, stability to air, absence of hydrate water, soluble in the titration medium, has high formula weight, available at modest cost and reacts with standard solution stochiometrically

Requirements for titration

In order to perform a titration:

1) The reaction between unknown and standard should be stoichiometric. This means there should be a well defined and known reaction between the two.
2) The reaction should be rapid.
3) There should be no side reactions, and the reaction should be specific. If there are interfering substances, they must be removed.
4) There should be a marked change in some property of the solution when the reaction is complete. This may be a change in the color of the solution or in some electrical or other physical property of the solution. A color change is usually brought about by addition of an indicator whose color is dependent on the properties of the particular solution.
5) The reaction should be quantitative which means the reaction should proceed to completion.

Titration process

For Example:

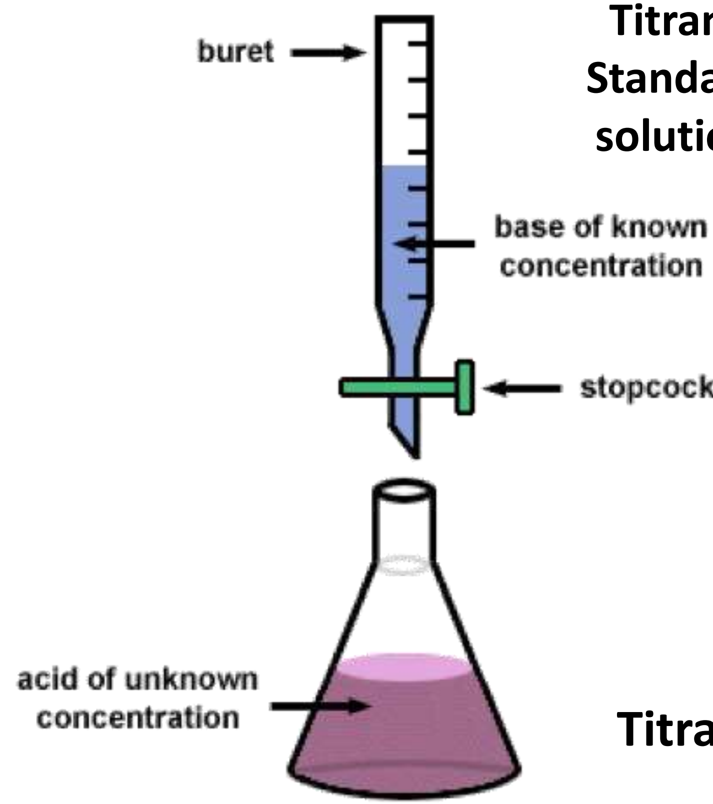
Titrate 50 ml 0.1 M HCl with 0.1 M NaOH Standard solution.

HCl + NaOH ⟶ NaCl + H2O

No. mol HCl = No. mol NaOH

Conc. (M) * V = Conc. (M) * V

Equivalence point Eq. P :50 ml NaOH



Titrant Standard solution

Titrand

Titration process

Equivalence point: is the point in a titration when the amount of added standard reagent exactly equal the amount of analyte. It is a theoretical point

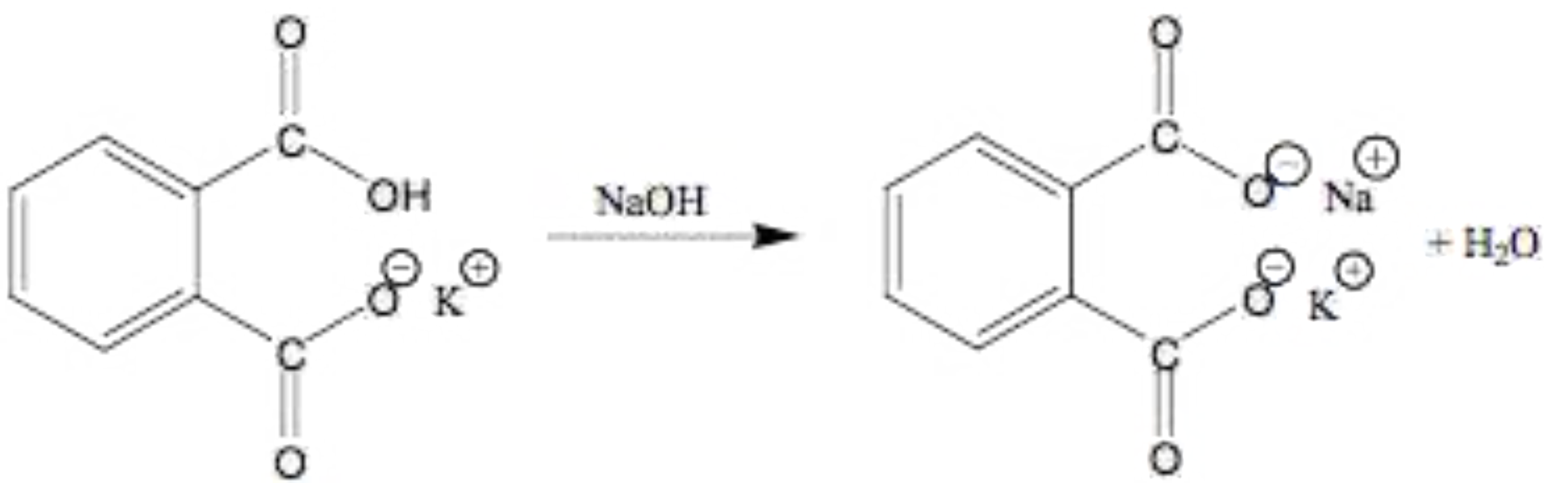
End point: is the point in a titration when physical change (like change of indicators, color) occurs. It is an experimental point.

The equivalence point and end point are not necessarily concurrent.

Standardization

Standardization:
is a process in which the concentration of a solution is determined by using the solution to titrate the a known amount of another reagent.

Standarization of 0.1 M NaOH by titrating a weighed amount of KHP (Potassium hydrogen phthalate).



Standardization

In the standardization of an unknown sodium hydroxide solution, 0.256g of KHP (MW = 204.22) react with exactly 22.62 ml of the unknown sodium hydroxide solution. What is the molarity of the unknown solution?

$$\text{No. Mol NaOH} = \frac{1 \text{ mol NaOH}}{1 \text{ mol KHP}} \times \text{No. mol KHP}$$

$$\text{No. mol NaOH} = \frac{1}{1} \times \frac{0.256\ (g)}{204.22\ (g/mol)} = 1.25*10^{-3}\ (mol)$$

$$\text{No. mol NaOH} = 1.25*10^{-3}\ (mol) = \text{Conc (M)} \times 22.62*10^{-3}\ (L)$$

Conc. NaOH (M) = 0.055 (M)

Concentration units

Molarity: is the number of moles of a reagent contained in one liter solution. It has as its unit the capital letter "M" and is read as "molar".

A solution labeled as 1.0 M NaOH, has the equivalent of 1.0 mole of NaoH dissolved in 1.0 liter of solution. **OR**
1.0 mmol NaOH dissolved in 1.0 mL of solution.

Notice that: the volume is liter of solution and not liter of water.

Concentration units

Normality (N) : is the number of equivalent of solute in one liter solution.

Molality (m): is defined as the number of moles of solute per kilogram of solvent. It has as its unit the lower case letter "m" and is read as "molal".

$$\%\ (v/v) = \frac{\text{volume of solute (ml)}}{\text{volume of solution (ml)}} * 100\%$$

$$\%\ (w/v) = \frac{\text{weight of solute (g)}}{\text{volume of solution (ml)}} * 100\%$$

Concentration units

Parts per million (ppm): is a unit of concentration often used when dealing with very small amounts of metal ions and other solutes in water, air or soil. (mg/L) or (mcg/ml)

$$\text{ppm} = \frac{\text{mg of solute}}{\text{L solution}}$$

A solution with a concentration of 1 ppm of Pb^{2+} is equal to 1 mg lead(II) ion per liter of water.

Units

Density and specific gravity:

Density: is the mass per unit volume (Kg/L) or (g/ml)

Specific gravity sp. gr : is the ratio of the mass of substance to the mass of an equal volume of water at 4 °C

Dilution

$$M_1V_1 = M_2V_2$$

M_1 = concentration of the first solution
V_1 = volume of the first solution
M_2 = concentration of the second solution
V_2 = volume of the second solution

Concentration and volume in the equation above can have any units as long as the units are the same for the two solutions

Examples

How to prepare 1.0 M, 1.0 L NaOH :

A 1.0 M NaOH solution would be made by measuring out the mass of 1.0 moles of NaOH which is 40.0 grams of NaOH.

The solid NaOH would be placed in a liter volumetric flask, and then distilled water would be added in small amounts with vigorous swirling of the flask to get the NaOH to dissolve.

Since the dissolving process for NaOH is quite exothermic, the flask should be lowered into cool water as the water is gradually added to the line on the flask.

Examples

What is the molar concentration of 37% (w/w) HCl (FW = 36.5 g/mol), has a specific gravity of 1.18 then describe the preparation of 1.0 L of 1.0 M HCl?

Density of HCl is 1.18 g solution $\longrightarrow$ 1 mL

So 100 g solution $\longrightarrow$ X mL

X = 84.75 mL

$$\text{Conc (M)} = \frac{\text{no mol HCl}}{\text{Vol solution (L)}} = \frac{37\text{ (g)}/ 36.5\text{ (g/mol)}}{84.75*10^{-3}\text{ (L)}} = 11.96\text{ M}$$

Examples

To prepare 1.0 L, 1.0 M HCl from 11.96 M original solution

$$M_1V_1 = M_2V_2$$

11.96 (M) * Vol (L) = 1.0 (M) * 1.0 (L)

Vol (L) = 0.08361 (L)

Transfer 83.61 mL or 98.66 g from the original solution into 1.0 Liter volumetric flask, and dilute with distilled water up to the mark on the flask.

Examples

If you have a primary standard Na_2CO_3 (FW = 105.99 g/mol) describe how should you prepare 500 ml of [Na+] 0.010 M?

$$Na_2CO_3 \longrightarrow 2\,Na^+ + CO_3^{-2}$$

$$[Na_2CO_3] = \frac{1}{2} \times [Na^+] = 0.005\ M$$

No. mol Na_2CO_3 = Conc.(M) * Vol (L) = 0.0025 (mol)

Wt Na_2CO_3 = no mol * MW = 0.265 (g)

Put accurately weighed Na_2CO_3 (0.265 g) in 500 mL volumetric flask, dissolve in water then complete the volume up to the mark on the flask.

Examples

A solution prepared by dissolving 0.1164 g of $(NH_4)_2Ce(NO_3)_6$ (FW = 548.3 g/mol) in 2.5 L of water. **Calculate the ppm of NH_4^+?**

$$(NH_4)_2Ce(NO_3)_6 \longrightarrow 2\ NH_4^+$$

$$\text{Conc (M)} = \frac{\text{No mol } (NH_4)_2Ce(NO_3)_6}{\text{Vol (L)}} = \frac{\dfrac{0.1164\ (g)}{548.3\ (g/mol)}}{2.5\ (L)}$$

$$= 8.492 * 10^{-5}\ (M)$$

$$[NH_4^+] = \frac{2}{1}\ X\ [(NH_4)_2Ce(NO_3)_6\ ] = 1.698 * 10^{-4}\ M$$

Examples

$$[NH_4^+] = 1.698*10^{-4}\ (M)$$

$$[NH_4^+] : 1.698*10^{-4}\ \text{mol}\ NH_4^+ \longrightarrow 1.0\ (L)$$

$$\text{ppm} = \frac{\text{Wt (mg)}}{\text{Vol (L)}}$$

$$NH_4^+ : 1.698*10^{-4}\ (\text{mol}) * 18\ (\text{g/mol}) * 10^3\ \text{mg} \longrightarrow 1.0\ L$$

$$NH_4^+ : 3.06\ (\text{mg/ L}) = 3.06\ (\text{ppm})$$

Examples

How could you prepare 250 ml , 0.5% NaCl from 3.5% (w/v) stock NaCl solution?

$$\mathbf{Conc._1 * V_1 = Conc._2 * V_2}$$

$$3.5\ \% \ * \ Vol_1\ (mL) = 0.5\ \% \ * \ 250\ (mL)$$

$$Vol_1 = 35.71\ (mL)$$

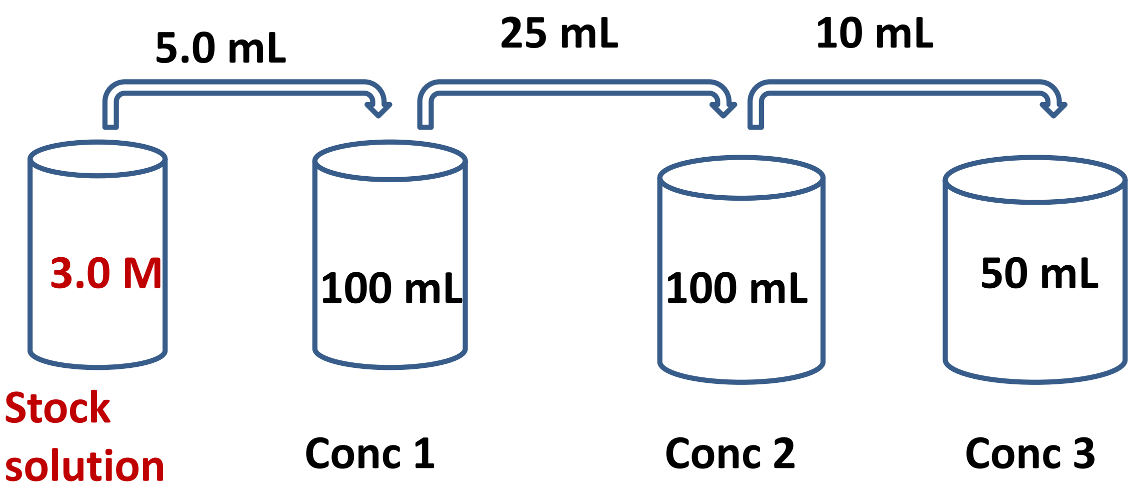
Transfer 35.71 mL from the stock solution using a pipette Into 250 mL volumetric flask then dilute with distilled water up to the mark on the flask.

Examples

HCL standard solution (3.0 M) was diluted as follows: 5.0 ml of the solution were transferred in 100 ml volumetric flask and diluted with des. Water. 25.0 ml of the resulting solution were diluted in 100 ml volumetric flask. Then 10.0 ml of last solution were diluted in 50 ml.

a) Calculate the molar and % (w/v) concentration of the end solution?

b) Calculate the dilution factor?



Examples

$Conc._1 * V_1$ (before dilution) = $Conc._2 * V_2$ (after dilution)

3.0 (M) X 5.0 (mL) =Conc 1 X 100 (mL)   Conc 1 = 0.15 (M)

0.15 (M) X 25 (mL)= Conc 2 X 100 (mL) Conc 2 = 0.0375 (M)

0.0375 (M)X 10 (mL)=Conc 3 X 50 (mL) Conc 3= 0.0075 (M)

The molar concentration of HCl end solution = 0.0075 (M)

Examples

HCl solution = 0.0075 (M)

0.0075 mol HCl ⟶ 1 L solution

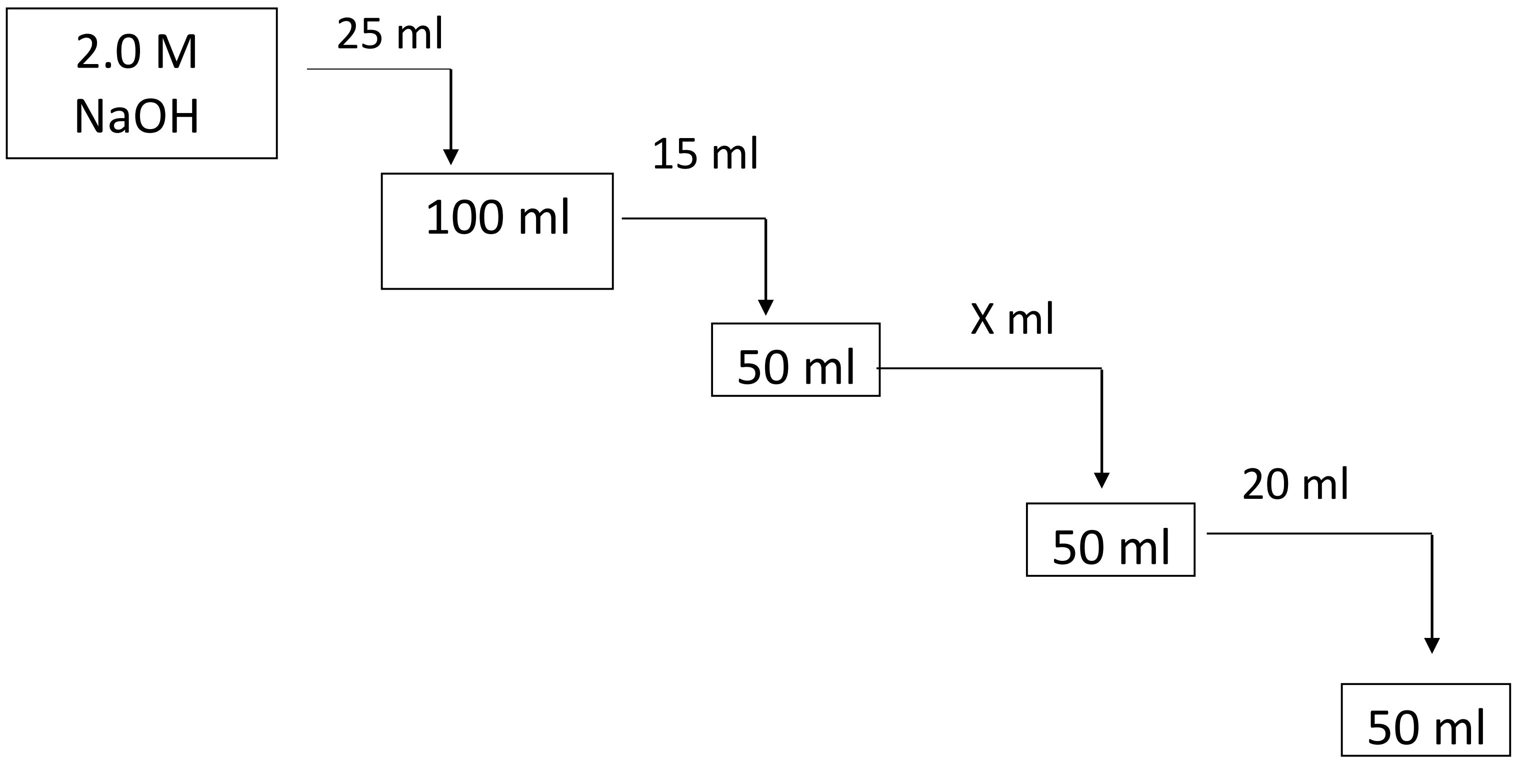
$$\% (w/v) = \frac{\text{Wt HCl (g)} * 100}{\text{Vol (mL)}} = \frac{0.0075 \text{ (mol)} * 36.5 \text{ (g/mol)}}{1000 \text{ (mL)}} \text{ X } 100 =$$

% w/v = 0.027%

$$\textbf{Dilution factor} = \frac{\text{Conc. Of stock solution}}{\text{Conc. Of end solution}} = \frac{3.0 \text{ (M)}}{0.0075 \text{ (M)}} = \textbf{400}$$

Examples

A 2.0 M NaOH (FW =40.00) **stock solution** was diluted as follows, 10.0 ml of the end solution has required 24.0 ml of 0.01 M HCl to be titrated. **Find out the molar concentration in each step (then express it as % w/v) and X ml?**



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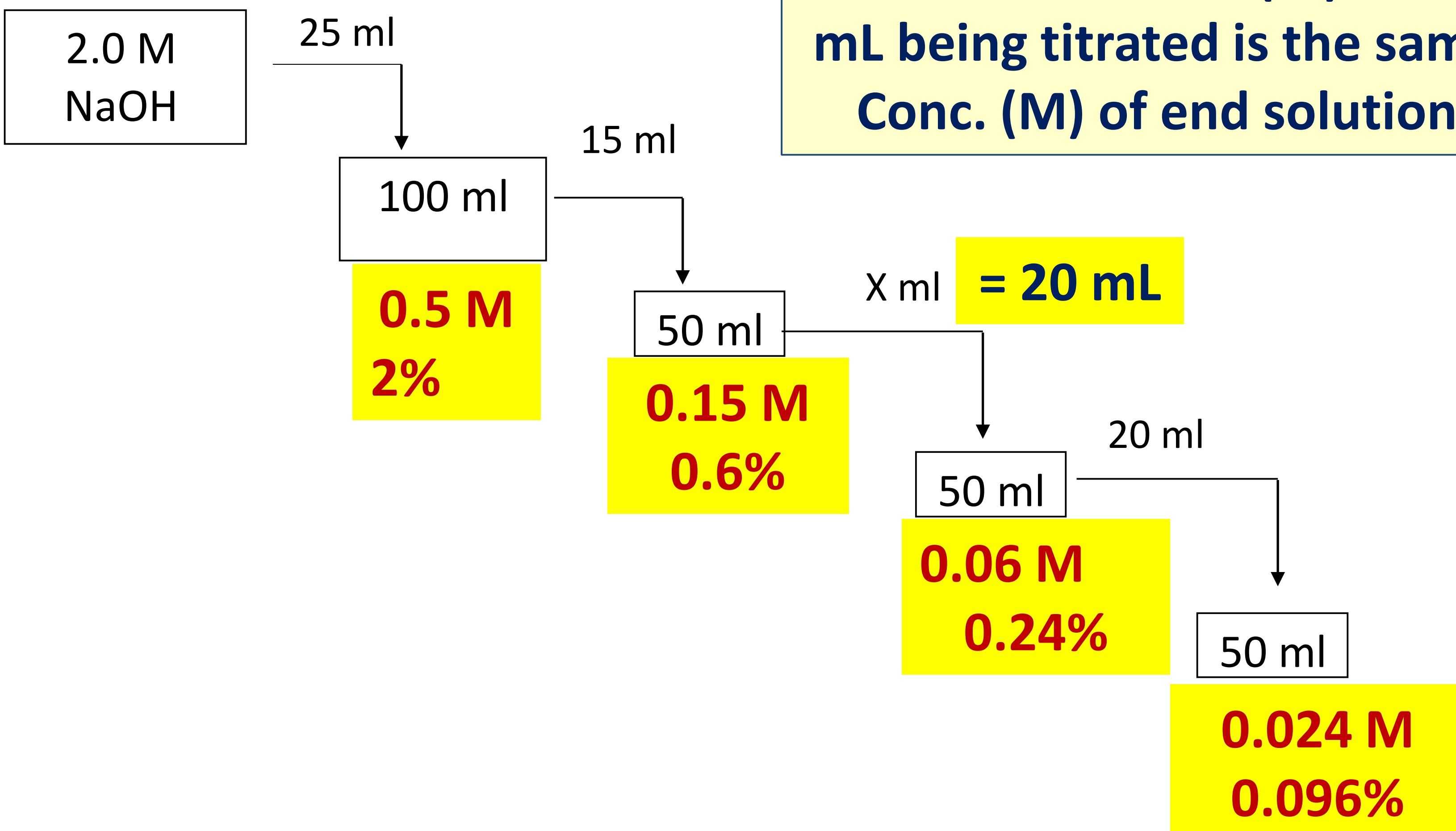
Remember Conc. (M) of 10 mL being titrated is the same Conc. (M) of end solution



Examples

A 50.0 ml of impure $CaCl_2 .2H_2O$ solution sample was treated with excess $AgNO_3$ solution. The resulting ppt. AgCl was filtered, washed and dried. It weighed 0.1873 g.
Calculate the % $CaCl_2 .2H_2O$ in solution then express the conc. of chloride and calcium ions in terms of ppm.

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(FW AgCl = 143.32, $CaCl_2 .2H_2O$= 146.99, Ca = 40.08, Cl = 35.453)

% $CaCl_2 .2H_2O$ (w/v) = 0.19%

[$CaCl_2 .2H_2O$] = 0.013 M, [Ca^{+2}] = 0.013 M, [Cl^{-}] =0.026 M
Conc. Ca^{+2} (ppm) = 521 ppm
Conc Cl^{-} (ppm) = 922 ppm

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Examples

How to prepare 1.0 M, 0.25 L NaOH :

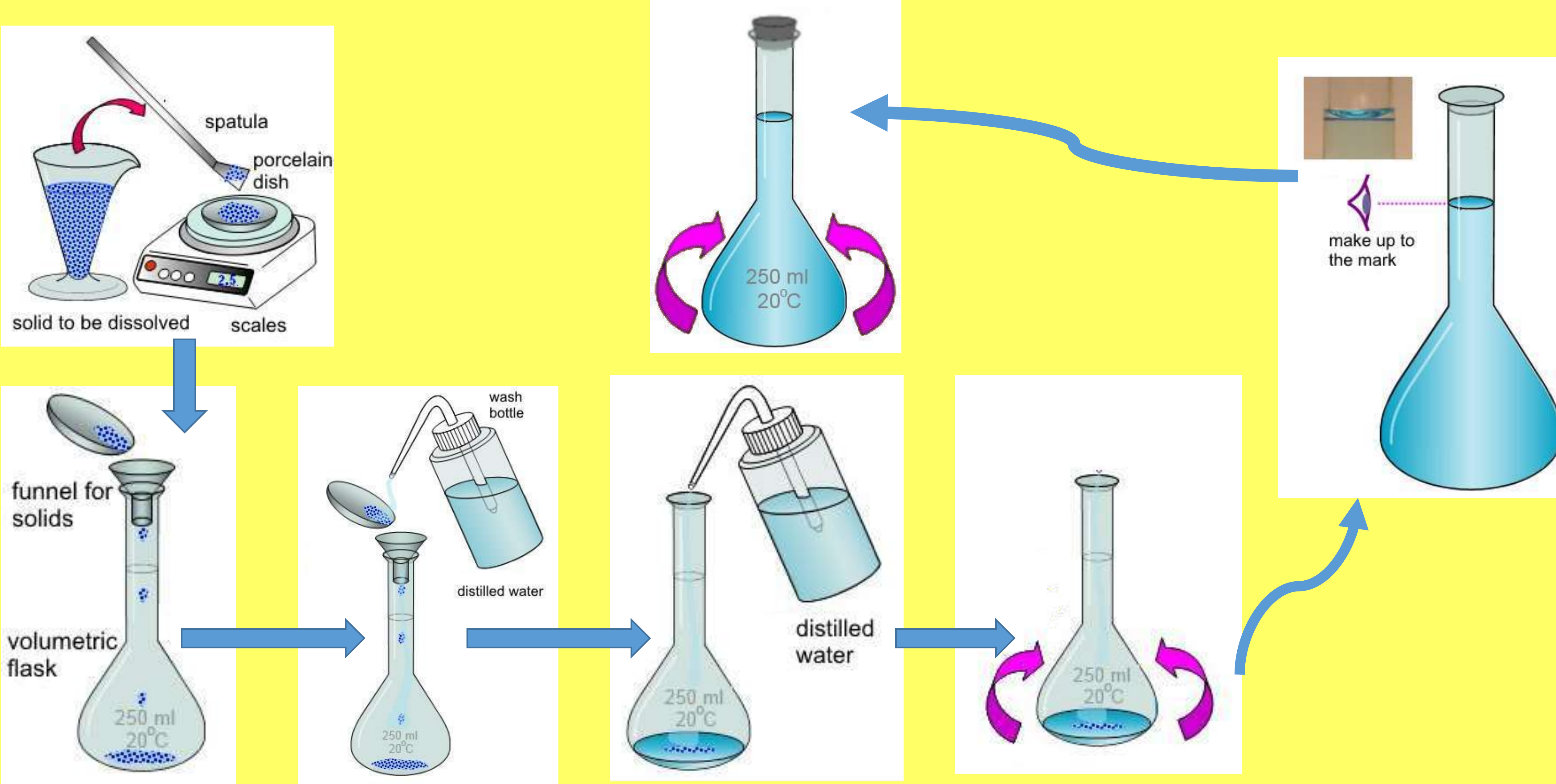
The no. of moles NaOH = Conc. (M) * Vol. (L)= 0.25 mole

Weight = no. moles * MW = 0.25 (mole)* 40 (g/mole) = 10 g

The solid NaOH would be placed in a 250 mL volumetric flask, and then distilled water would be added in small amounts with vigorous swirling of the flask to get the NaOH to dissolve.

Since the dissolving process for NaOH is quite exothermic, the flask should be lowered into cool water as the water is gradually added to the line on the flask thus the volume of solution is up to 250 mL.

How to prepare 1.0 M, 0.25 L NaOH



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Examples

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$$M_1V_1 = M_2V_2$$

11.96 (M) * Vol (L) = 1.0 (M) * 1.0 (L)

Vol (L) = 0.08361 (L)

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(a) A volume (V_s) containing the desired moles of solute (M_s) is measured from a stock solution of known concentration.

(b) The measured volume of stock solution is transferred to a second volumetric flask.

(c) The measured volume in the second flask is then diluted with solvent up to the volumetric mark [$(V_s)(M_s) = (V_d)(M_d)$].

Examples

If you have a primary standard Na_2CO_3 (FW = 105.99 g/mol) describe how should you prepare 500 ml of [Na+] 0.010 M?

$$Na_2CO_3 \longrightarrow 2\,Na^+ + CO_3^{-2}$$

$$[Na_2CO_3] = \frac{1}{2} \times [Na^+] = 0.005\ M$$

No. mol Na_2CO_3 = Conc.(M) * Vol (L) = 0.0025 (mol)

Wt Na_2CO_3 = no mol * MW = 0.265 (g)

Put accurately weighed Na_2CO_3 (0.265 g) in 500 mL volumetric flask, dissolve in water then complete the volume up to the mark on the flask.

Why

Continue

$$Na_2CO_3 \longrightarrow 2\,Na^+ + CO_3^{-2}$$

$$\textbf{No. mol } Na_2CO_3 = \frac{1 \text{ mol } Na_2CO_3}{2 \text{ mol } Na^+} \times \text{no. mol } Na^+$$

Divide both sides through volume of solution which is identical

$$\frac{\text{No. mol } Na_2CO_3}{\text{Volume}} = \frac{1 \text{ mol } Na_2CO_3}{2 \text{ mol } Na^+} \times \frac{\text{no. mol } Na^+}{\text{Volume}}$$

$$[Na_2CO_3] = \frac{1}{2} \times [Na^+]$$

Remember
This is true only for molarity

Examples

A solution prepared by dissolving 0.1164 g of $(NH_4)_2Ce(NO_3)_6$ (FW = 548.3 g/mol) in 2.5 L of water. **Calculate the ppm of NH_4^+?**

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Examples

$$[NH_4^+] = 1.698*10^{-4}\ (M)$$

$[NH_4^+]$: $1.698*10^{-4}$ mol NH_4^+ ⟶ 1.0 (L)

$$ppm = \frac{Wt\ (mg)}{Vol\ (L)}$$

NH_4^+ : $1.698*10^{-4}$ (mol) * 18 (g/mol) * 10^3 mg ⟶ 1.0 L

NH_4^+ : 3.06 (mg/ L) = **3.06 (ppm)**

Dilution process
&
Dilution factor

Examples

HCL standard solution (3.0 M) was diluted as follows: 5.0 ml of the solution were transferred in 100 ml volumetric flask and diluted with des. Water. 25.0 ml of the resulting solution were diluted in 100 ml volumetric flask. Then 10.0 ml of last solution were diluted in 50 ml.

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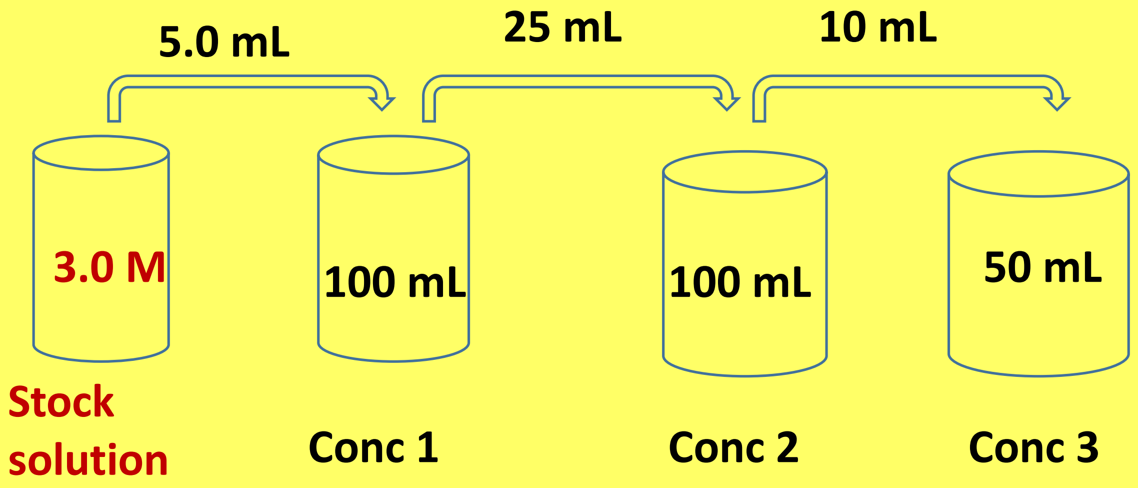

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Examples

How could you prepare 250 ml , 0.5% NaCl from 3.5% (w/v) stock NaCl solution?

$$\textbf{Conc.}_1 * V_1 = \textbf{Conc.}_2 * V_2$$

$$3.5\ \% * Vol_1\ (mL) = 0.5\ \% * 250\ (mL)$$

$$Vol_1 = 35.71\ (mL)$$

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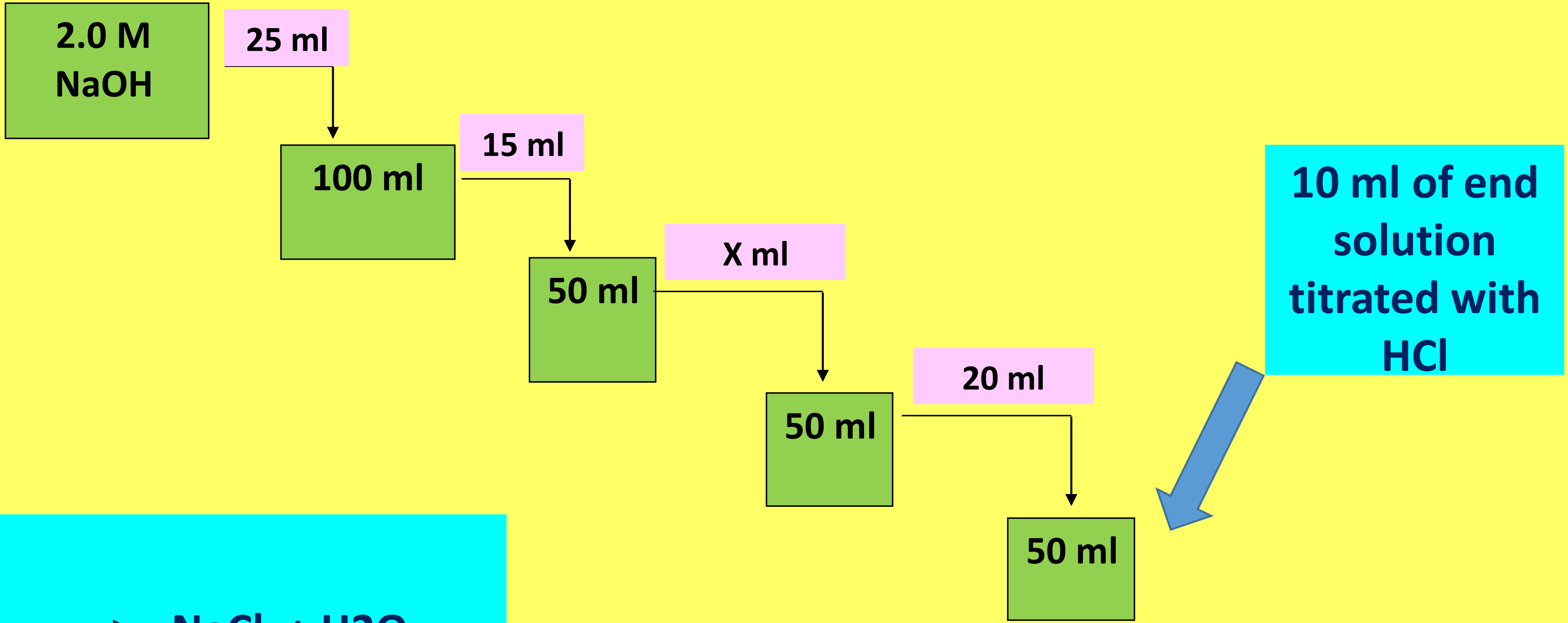

Titration:

HCl + NaOH → NaCl + H2O

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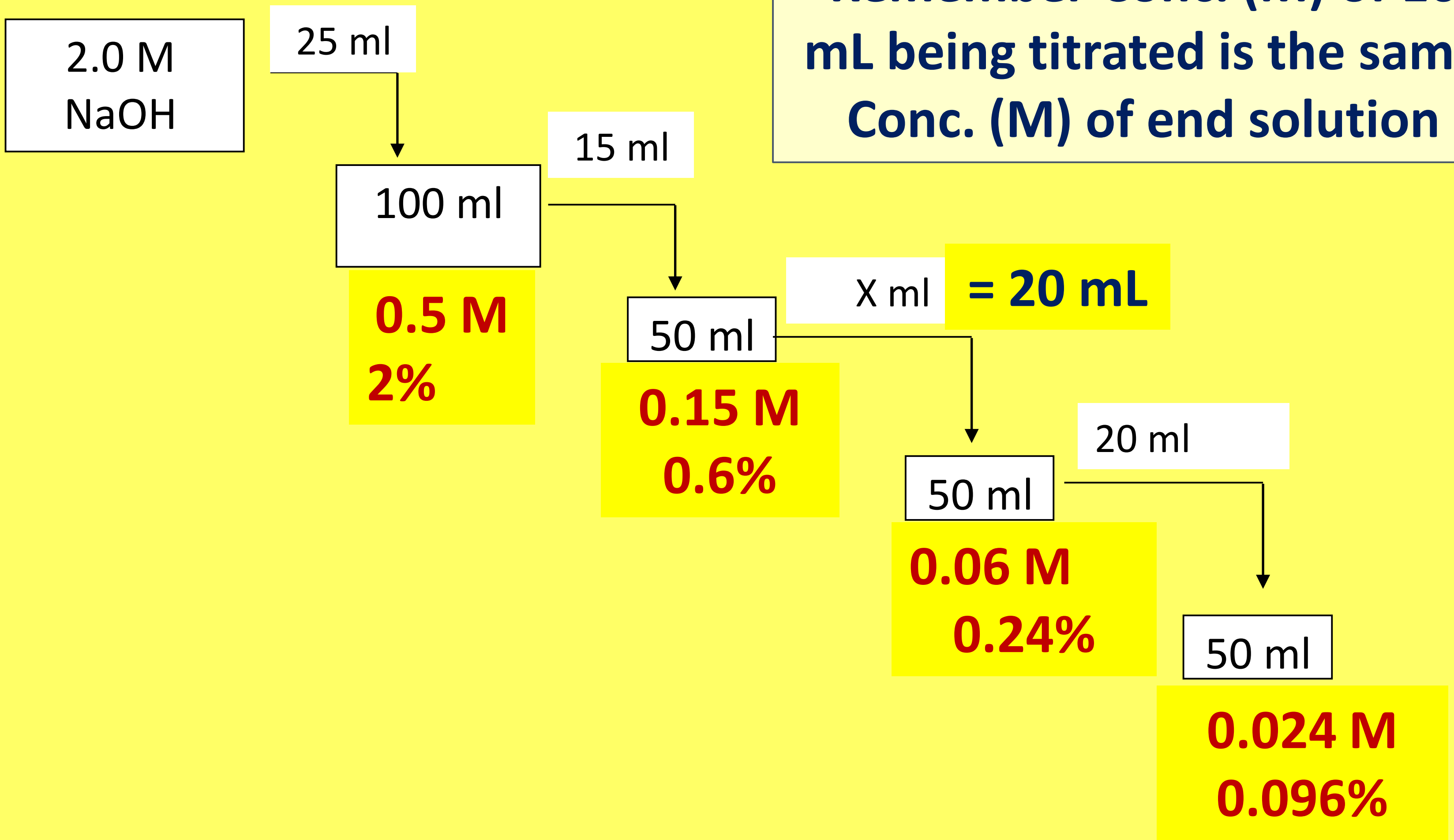

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