Volumetric Analysis:

Titrations are designed to work out the concentration of one substance by reacting it with a known substance, usually one made by the chemist from what is known as a primary standard.

A primary standard requires the following qualities:

1. Substance must have high purity
2. High molar Mass to decrease percentage error.
3. Must not change when exposed to air so not deliquescent or absorbs water
4. Must be soluble and have a known molecular formula

Titrations are usually done backwards.

Tips:

1. Do the basic steps for calculations – 1] Find moles. 2] Find or balance the reaction 3] do the stoichiometry and finally 4] Calculate the missing concentration.
2. Keep track of the volumes of the substances you are calculating the moles and concentrations off. Due to dilutions and titre samples being taken from the substances there are often 2-4 different volumes of some of the substances reacting and a common error is to miss one of these steps.
3. If confused even slightly quickly draw a basic diagram of what is happening and in what order.
4. Keep your work clear and well labelled. This will improve the amount of follow through marks you get if you make a mistake and reduce your chance of error.

Now try the following questions:

1. Ascorbic acid, $C_6H_8O_6$, is known as vitamin C. The vitamin C content in vitamin C tablets can be determined by adding a known excess volume of iodine solution to an aqueous solution of the vitamin C tablet. The remaining iodine can be titrated with sodium thiosulfate ($Na_2S_2O_3$).
   A researcher analysing the vitamin C in a particular brand of tablets carried out the following steps:
   a. A 250 mg (2.50×10^{-1} g) tablet was dissolved in 50.0 mL of water, and 100.0 mL of 0.0521 mol L^{-1} I_2 solution was added. This mixture was then made up to 250.0 mL with water in a volumetric flask.
   b. 20.0 mL aliquots of the resulting solution were titrated with 0.0493 mol L^{-1} sodium thiosulfate solution ($Na_2S_2O_3$)

   The following results were obtained:

Titration results	**Trials (mL)**			
	1	**2**	**3**	**4**
Final volume	15.27	15.92	14.28	15.67
Initial volume	0.47	1.96	0.50	1.75
Titre				

The relevant half-equations are:

$C_6H_8O_{6(aq)} \rightarrow C_6H_6O_{6(aq)} + 2H^+_{(aq)} + 2e^-$

$I_{2(aq)} + 2e^- \rightarrow 2I^-_{(aq)}$

$2S_2O_3{}^{2-}{}_{(aq)} \rightarrow S_4O_6{}^{2-}{}_{(aq)} + 2e^-$

a) Write and balance the equation for the reaction between iodine and thiosulfate ions

b) Write a balanced equation for the reaction between ascorbic acid (vitamin C) and iodine.

c) Calculate the mass of Vitamin C in the 250 mg tablet.

[0.164g]

d) Calculate the percentage by mass of vitamin C in the tablet.

[65.5%]

2. **[10 marks]** In order to analyse the iron content of a ferrochrome alloy, a solution of potassium permanganate was standardised and then titrated against the iron present in a sample of the alloy.

Standardisation Procedure

16.58g of hydrated ammonium iron (II) sulfate, $Fe(NH_4)_2(SO_4)_2.6H_20$, was dissolved in approximately 50 mL of distilled water and made up to 250.0 mL in a volumetric flask. 25.00 mL aliquots of this solution were acidified and titrated against potassium permanganate solution with a concentration of approximately 0.05 $molL^{-1}$. The following results were obtained:

Titration Result	**Trials (mL)**			
	1	**2**	**3**	**4**
Final volume	14.72	29.12	43.42	16.47
Initial volume	0.02	14.72	29.12	2.15
Titre				

Analysis of Alloy

5.900g of the iron alloy was dissolved in approximately 100mL of hot sulfuric acid, which dissolved the iron to form Fe^{2+} ions in solution. The resulting solution was filtered and made up to 250.0mL with distilled water. 20.00mL aliquots of this solution required an average titre of 13.40mL of the standardised potassium permanganate solution for complete reaction.

Calculate the percentage, by mass, of iron in the alloy.

3. **[20 marks]** Production of excess acid in the stomach leads to heartburn. This can be easily treated with antacids, which contain an active ingredient that neutralises the excess acid.

A commonly used antacid preparation is 'milk of magnesia', a suspension of the active ingredient $Mg(OH)_2$ in water. A suspension of $Al(OH)_3$ in water is also often used as an antacid.

A student set out to compare the effectiveness of a given quantity of two antacid preparations, one containing $Mg(OH)_2$ and the other $Al(OH)_3$, purchased from his local pharmacy. He titrated each of the preparations against a hydrochloric acid solution to determine how much of acid each could neutralise, and to determine the concentration of active ingredient in each of the preparations. He first standardised the hydrochloric acid solution available in the laboratory against a primary standard, and chose anhydrous sodium carbonate as the primary standard.

a) Did the student select an appropriate primary standard? Explain. [2]

The student prepared 1.00L of a 0.0248 $molL^{-1}Na_2CO_3$ solution. He titrated three 25.0mL aliquots of this solution against the HCl and found an average titre of 24.35mL.

b) Calculate the concentration of the standardised HCl solution. [4]

The student proceeded to compare his antacids for titration against the standardised HCl. He performed the following procedure for each of the antacids.

The antacid suspension was thoroughly shaken and 20.0g was weighed out and transferred to a 250.0mL volumetric flask, which was made up to the mark with deionised water and shaken vigorously. 10.0mL aliquots of this diluted suspension were transferred for titration, using an appropriate indicator, to conical flasks. The titration data for the $Al(OH)_3$ suspension are shown in the table blow.

Titration Result	**Volume HCl (mL)**			
	1	**2**	**3**	**4**
Final reading	23.20	44.96	22.12	42.18
Initial reading	0.58	22.98	0.20	20.26
Titre				

c) Complete the table and determine the average titre value for the HCl solution. [1]

Average titre:

d) The densities, in grams per millilitre, of the original antacid preparations are given blow.

Suspension	**Density (g mL^{-1})**
$Mg(OH)_2$	1.06
$Al(OH)_3$	1.12

i) Calculate the concentration, in mg per mL, of $Al(OH)_3$ in the original $Al(OH)_3$ suspension. [7]

ii) From his titration of the $Mg(OH)_2$ diluted suspension, the student found the mass of $Mg(OH)_2$ in the 250mL**diluted** suspension to be 1.13g. Determine the concentration of $Mg(OH)_2$ in the original **undiluted** suspension and express your answer in mg per mL. [2]

e) The directions for use on each of the antacid preparations suggest a standard adult dose of 10.0mL. Which of the preparations would be more effective (neutralise the most HCl) per standard dose? Show your working. [4]

4. **[15 marks]** The percentage of manganese in steel needs to be monitored carefully. To determine this, a 5.31g sample of steel was dissolved in concentrated acid and the manganese oxidised to permanganate ion, MnO_4^-. The volume of this solution was made up to 100.0mL in a volumetric flask.

The concentration of permanganate ion was determined by titration against a standard solution of oxalic acid. The oxalic acid solution was prepared by dissolving 2.42g of oxalic acid dehydrate ($H_2C_2O_4$.$2H_2O$) in a small volume of water, which was then made up to a final volume of 250.0mL in a volumetric flask.

A 20.00mL aliquot of the standard oxalic acid solution was transferred into a conical flask and acidified with some sulfuric acid. The permanganate solution was then titrated against this 20.00mL aliquot of oxalic acid solution. This was repeated three times. The results are shown in the table below.

	1	**2**	**3**	**4**
Final reading (mL)	9.54	17.59	25.57	33.64
Initial reading (mL)	0.97	9.54	17.59	25.57
Titre volume (mL)				

a) Write the balanced equation for the reaction between oxalic acid ($H_2C_2O_4$) and permanganate ion.[2]

b) Calculate the concentration of the standard oxalic acid solution. [3]

c) Determine the percentage of manganese in the original sample of steel. [8]

5. **[15 marks]** Citric acid is the active ingredient in some bathroom and kitchen cleaning solutions. A student determined the content of citric acid in a cleaner by titration with sodium hydroxide solution.

The sodium hydroxide solution first needed to be standardised. To do this, the student dissolved approximately 4g of sodium hydroxide pellets in water, to give an approximately 0.1 $molL^{-1}$ solution. This solution was standardised by titrating 20.00mL of the NaOH solution with a 0.105 $molL^{-1}$ standard hydrochloric acid solution. The average titration volume was 17.45mL.

a) Explain why sodium hydroxide is not suitable as a primary standard. [2]

b) Show that the concentration of the sodium hydroxide solution is 0.0916 $molL^{-1}$. Show sufficient workings to justify your answer. [3]

The student then weighed a 10.00mL aliquot of the cleaner and found it weighed 10.4g. This 10.00mL aliquot was next diluted to 100.0mL in a volumetric flask. Against the standardised sodium hydroxide solution, 20.00mL aliquots of the diluted cleaner were titrated. The table below shows the results of the titrations.

Titre	**1**	**2**	**3**	**4**
Final reading (mL)	25.30	23.55	22.40	22.25
Initial reading (mL)	3.50	2.70	1.50	1.30
Titre volume (mL)				

c) Calculate the average titre volume to be used in the calculation of the citric acid content. [2]

d) Given that citric acid ($C_6H_8O_7$) is a weak triprotic acid, determine the percentage composition by mass of citric acid in the cleaner. The molar mass of citric acid is 192.124 $gmol^{-1}$. [6]

e) Select a suitable indicator for this titration from the table below. Explain your choice. [2]

Indicator	**Colour change (low pH – high pH)**	**pH**
Methyl yellow	Red-yellow	2.4-4.0
Litmus	Red-blue	5.0-8.0
Bromothymol blue	Yellow-blue	6.0-7.6
Thymol blue	Yellow-blue	8.0-9.6

Volumetric Analysis Solutions:

1.
    a. $I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$
    b. $C_6H_8O_6 + I_2 \rightarrow C_6H_6O_6 + 2H^+ + 2I^-$
    c. $n(I_2) = cv = 0.0521 \times 0.1 = 0.00521$

       $n(I_2) = ½\ n(S_2O_3) = cv = 0.0493 \times \frac{13.89}{1000}$

       $= 6.846126667 \times 10^{-4}$ mol x ½

       $= 3.423063334 \times 10^{-4}$ mol

       $n(C_6H_8O_6) = n(I_2)$ reacted $= n(I_2)_{orig} - \frac{250}{20} n(I_2)_{20}$

       $= 9.301 \times 10^{-4}$ mol

       $m(C_6H_8O_6) = NM = 9.3117 \times 10^{-4} \times (6 \times 12.01 + 8 \times 1.008 + 6 \times 16) = 0.1638$ g.
    d. $\frac{0.164}{0.25} \times 100 = 65.6\%$
2. $n(MnO_4)_{14.34} = cv =$

   $n(Fe(NH_4)_2(SO_4)_2.6H_2O) = \frac{m}{M} = \frac{16.58}{392.17} = 0.0422775837$ mol

   $n(Fe\ldots)_{25} = 0.1 \times 0.043377\ldots = 0.00422775837$

   $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$

   $n(MnO_4^-)_{14.34} = \frac{1}{5} \times 0.004228 = 8.45551674 \times 10^{-4}$ mol

   $c(MnO_4^-) = \frac{n}{v} = \frac{8.455 \times 10^{-4}}{\frac{14.34}{1000}} = 0.05896455188$ mol L^{-1}

   $n(Fe^{2+})_{20} = \frac{5}{1} \times n(Fe)_{20} = \frac{250}{20} \times 0.00395 = 0.0493828122$ mol

   $m(Fe) = nm = 0.04938 \times 55.85 = 2.758$g

   $\%Fe = \frac{2.758}{5.9} \times 100 = 46\%$

3.

a. Soluble, high molar mass, pure, does not absorb water or decompose
b. $Na_2CO_3 + 2HCl \rightarrow H_2O + CO_2 + 2NaCl$
   $n(Na_2CO_3)_{25}$ = cv = 0.0248 x 0.025 = 0.00062 mL
   $n(HCl)_{24.35}$ = 2 x $n(Na_2CO_3)$ = 0.00124 mol
   [HCl] = $\frac{n}{v} = \frac{0.00124}{\frac{24.35}{1000}} = 5.098684211 \times 10^{-2}$ mol L^{-1}
c. 21.94 mL
d.
   i. $Al(OH)_3 + 3\ HCl \rightarrow AlCl_3 + 3H_2O$
      n(HCl) = cv = 5.092 x 10^{-2} x 0.02194 = 0.00118651316
      $n(Al(OH)_3)$ = $\frac{1}{3}$ n(HCl) = 0.000391 mol
      $m(Al(OH)_3)_{250}$ = 0.000391 x $\frac{250}{10} = 0.009352$
      $m(Al(OH)_3)$ = nm = 0.009322 x 78.004 = 0.72716
      $[\rho = \frac{m}{v}]$ = $\frac{20}{1.12} = 17.86$ mL
      $[Al(OH)_3]$ = $\frac{761.8}{17.86} = 40.72$ mg/mL
   ii. 1.13 $\rightarrow$ 1130 mg in 20g
      v = $\frac{2000}{1060} = 18.87$ mL
      $[Mg(OH)_2]$ = $\frac{1130}{18.87} = 59.88$ mg/mL
e. $m(Al(OH)_3)_{10}$ = 10 x 42.65 x 10^{-3} = 0.4265 g
   $n(Al(OH)_3)$ = $\frac{0.4265}{18.004} = 5.468 \times 10^{-3}$ mol
   3 x $n(Al(OH)_3)$ = n(HCl) = 3 x 5.468 x 10^{-3} = 0.01640 mol
   $Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O$
   $m(Mg(OH)_2)$ = 10 x 59.88mg = 0.5988g
   $n(Mg(OH)_2)$ = m/M = $\frac{0.5988}{58.326} = 0.01027$ mol
   n(HCl) = 2 x $n(Mg(OH)_2)$ = 2 x 0.01027 = 0.02054 mol
   $Mg(OH)_2$ neutralises more acid.

4.

a. $H_2C_2O_4 \rightarrow CO_2 + H_2O$
   $6H^+ + 2MnO_4^- + 5H_2C_2O_4 \rightarrow 2Mn^{2+} + 10CO_2 + 8\ H_2O$
b. $n(H_2C_2O_4)$ = m/M = $\frac{2.42}{125.008} = 0.0192$
   $[H_2C_2O_4]$ = n/v = $\frac{0.0192}{0.25} = 0.0768$ mol L^{-1}
c. $n(H_2C_2O_4)$ = cv = 0.768 x 0.02 = 0.001536
   $[MnO_4^-]$ = n/v = $\frac{0.006143}{0.008033} = 0.07647$ mol L^{-1}
   $n(MnO_4^-)_{100}$ = 0.1 x 0.007647 = 0.007647 mol
   n(Mn) = $n(MnO_4)$ = 0.007467 mol
   m(Mn) = nm = 0.007467 x 54.94 = 0.4201 g
   % = $\frac{0.4201}{5.31} = 7.911\%$

5.

a. Low molar mass, highly reactive so not pure, pellets absorb water, absorbs water from air (delicquescent), + CO_2 results in Na_2CO_3

b. NaOH + HCl → NaCl + H_2O

n(NaOH) = n(HCl)$_{17.45}$ = cv = 0.105 x $\frac{17.45}{1000} = 1.83225 \times 10^{-3}$ mol

[NaOH] = n/v = $\frac{1.83 \times 10^{-3}}{\frac{20}{1000}} = 9.16 \times 10^{-2}$ mol L^{-1}

c. $\frac{20.85+20.90+20.95}{3} = 20.90$ mL

d. n(NaOH) = cv = 0.0916 x $\frac{20.90}{1000} = 1.91444 \times 10^{-3}$ mol

n(citric acid) = 1/3 n(NaOH) = 1/3 x 1.91444 x 10^{-3} = 6.3615 x 10^{-4} mol

n(citric)$_{100}$ = $\frac{100}{20} \times 6.36 \times 10^{-4} = 3.19073 \times 10^{-3}$ mol

m(citric)$_{10(orig)}$ = nm = 3.19 x 10^{-3} x 192.184 = 0.6130 g

10 mL = 10.4 g

% = $\frac{0.6130}{10.4} \times 100 = 5.89\%$

e. Citric acid is weak and NaOH is strong, so basic side. Therefore, Thymol blue.

$C_6H_5O_7^{3-}$ + $3H_2O$ → $C_6H_8O_7$ + $3OH^-$