Acid-base

1. Draw a titration curve for the titration of 25.0 mL of 0.125 M NH_3 with 0.0625 M HCl.

2. the titration of 0.050 L of 0.10 M HCl (in flask) vs. 0.10 M NaOH (in buret)

3. You are given 90 mL of 0.6 M of the weak base NH_3 ($K_b = 1.8 \times 10^{-5)}$, and 1 M of the strong acid titrant HCl.
   - What is the pH before any acid is added?
   - What volume of acid (in mL) is needed to reach the equivalence (stoichiometric) point?
   - What volume of acid (in mL) is needed to reach the halfway point where pH = pK_a?
   - What is the pH after 50 mL of acid is added?
   - What is the pH at the equivalence (stoichiometric) point?
   - What is the pH after 60 mL of acid is added?

EDTA

1. Stability constants for the formation of some metal-EDTA complexes are listed:

Metal ion	K_f	Metal ion	K_f
Mg^{2+}	4.9×10^{8}	Cu^{2+}	6.3×10^{18}
Ni^{2+}	4.2×10^{18}	Zn^{2+}	3.2×10^{16}
Ba^{2+}	5.8×10^{7}	Mn^{2+}	6.2×10^{13}
Ca^{2+}	5.0×10^{10}	Pb^{2+}	1.1×10^{18}

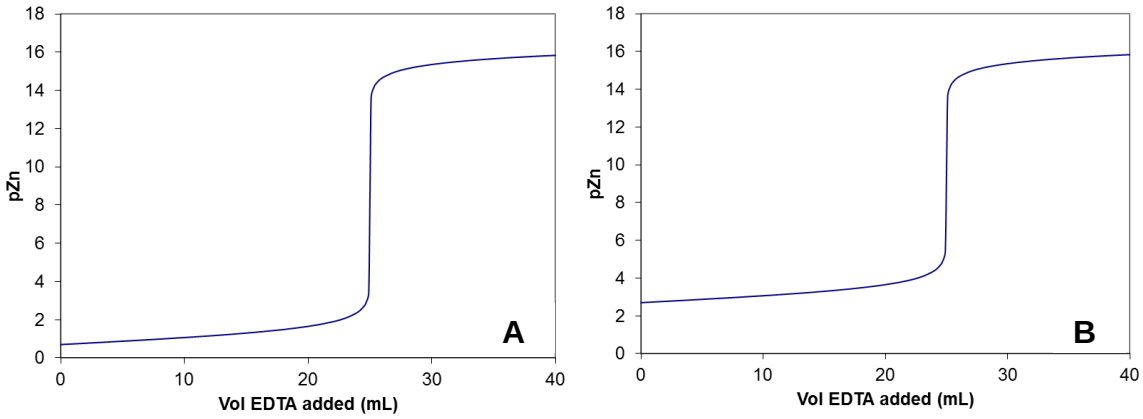
   a) What reaction will occur if a solution containing Mn^{2+} is added to a solution containing MgY^{2-}?
   b) What reaction will occur if a solution containing Mg^{2+} is added to a solution containing CuY^{2-}?

2. Calculate the concentration of free Pb^{2+} in a solution of 0.12 M PbY^{2-} at pH 4 and pH 8.

3. A standard solution of EDTA (0.200 M) is being used to titrate 50.00 mL of a 0.100 M Zn^{2+} solution (buffered at pH 8). Calculate the value of pZn after the addition of:

   a) 0 mL of EDTA solution.
   b) 10.00 mL of EDTA solution
   c) 20.00 mL of EDTA solution
   d) 25.00 mL of EDTA solution
   e) 40.00 mL of EDTA solution.
   f) Sketch a labelled titration curve.

4. If the following two curves were for the titration of 25.00 mL of Zn^{2+} solution with EDTA at pH 6. One of the curves is for the titration of 0.050 M Zn^{2+} with 0.050 M EDTA, the other is for 0.0005 M Zn^{2+} with 0.0005 M EDTA. Explain which graph is which.



5. Eriochrome Black T (EBT) is a good indicator for the titration of magnesium with EDTA. However, it is not so good for the titration of calcium. Given that the formation constants for the magnesium and calcium complexes with the indicator are $1x10^7$ and $2.5x10^5$ respectively;
   a) Briefly explain why EBT is not good for the titration of calcium,
   b) Would the use of EBT for the titration of calcium lead to a positive systematic error, a negative systematic error or a random error? Explain briefly.

6. A sample (0.5674 g) containing Cu and Fe was dissolved in water and diluted to 100 mL. A 25.00 mL aliquot of this solution was titrated with 32.12 mL of 0.0254 M EDTA. A second 25.00 mL aliquot mixture was treated with NaF to form a stable iron-fluoride complex. This mixture was then titrated with 0.0254 M EDTA and the endpoint volume was found to be 10.86 mL. Calculate the weight % of Cu and Fe in the sample.

7. A 25.00 mL aliquot of a solution containing Ca^{2+} and Mg^{2+} was buffered at pH 10 and titrated with 0.02432 M EDTA. The endpoint volume was 22.13 mL. The Mg^{2+} in a second 25.00 mL aliquot of the solution was precipitated by the addition of NaOH and the titrated with the 0.02432 M EDTA and the endpoint volume was found to be 17.14 mL. Calculate the molar concentrations of Ca^{2+} and Mg^{2+}.

Redox and Precipitation Titrations

1. The chloride concentration in tomato sauce was measured by the Mohr method. This involved titrating the chloride with silver. The titration process was as follows.

   Step 1: A mass of 0.1500 g NaCl was accurately weighed and dissolved in an amount of water. A few drops of indicator are added and the solution titrated with 34.38 mL silver nitrate solution. The concentration of $AgNO_3$ was then calculated.

   Step 2: A mass of 5.000 g of the tomato sauce sample was weighed and diluted to 50.00 mL. A 5.00 mL aliquot of this sample was then titrated with 22.64 mL of the $AgNO_3$ solution.
   The reaction equation for both titrations was:

   $$\mathbf{AgNO_3(aq) + Cl^-(aq) \rightarrow AgCl(s) + NO_3^-(aq)}$$

   a) What type of titration is the Mohr method?
   b) Identify the indicator that should be used and explain how it functions.
   c) Why is maintaining the neutral pH of the solution critical.
   d) Calculate the % mass Cl^- (w/w) in tomato sauce.
   e) Write down the similarities and differences with each of the different types of precipitation reactions.

2. 0.5342 g of a solid sample containing sodium iodide and sodium nitrate was dissolved in water and diluted to a final volume of 250.0 mL. A 25.00 mL aliquot of this solution was taken and treated with 25.00 mL of 0.0504 M $AgNO_3$ solution. The excess Ag^+ was then back-titrated with a standard (0.0498 M) NaSCN solution. The titration volume was 19.32 mL. Calculate the percentage of NaI in the solid mixture.

3. The chloride concentration in a solution was determined by gravimetric analysis. A 25.00 mL aliquot of the sample was pipetted into a beaker, some nitric acid was added and the mixture was diluted to about 100 mL with distilled water. Dilute silver nitrate was then added to precipitate silver chloride:

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

(The solubility product (K_{sp}) for silver chloride is 1.82×10^{-10})

A slight excess of $AgNO_3$ was added to make sure that all of the chloride had been precipitated. After all the $AgNO_3$ had been added, the final volume of solution was 120 mL and the *excess* Ag^+ concentration was 0.005 mol dm^{-3}. The mixture was heated almost to boiling for about 10 minutes. The beaker was covered and stored in the dark for at least one hour. The precipitate was then filtered, washed with very dilute nitric acid and dried; the mass of the precipitate was found to be 0.4258 g.

a) Use the mass of silver chloride formed to calculate the mass of chloride in the original sample solution.
b) What was the chloride concentration (g L^{-1}) in the original sample solution?
c) Why was the mixture “diluted to about 100 mL with distilled water”?
d) Why was the mixture “heated almost to boiling for about 10 minutes”?
e) Why was the beaker “covered and stored in the dark for at least one hour”?
f) Why was a solution of nitric acid used for washing the precipitate and not pure water?

Solubility Products in water at 25ºC

Substance	Formula	Ksp	Substance	Formula	Ksp
Silver bromide	AgBr	5.2×10^{-13}	Silver iodide	AgI	8.3×10^{-17}
Silver chloride	AgCl	1.82×10^{-10}	Silver thiocyanate	AgSCN	1.0×10^{-12}
Silver chromate	Ag_2CrO_4	1.1×10^{-12}			

4. In the titration of 25.00 mL of 0.100 M NaCl with 0.100 M $AgNO_3$: calculate pAg of the solution after the addition of:

   a) 10.00 mL of $AgNO_3$ solution
   b) 24.90 mL of $AgNO_3$ solution
   c) 25.00 mL of $AgNO_3$ solution
   d) 25.10 mL of $AgNO_3$ solution
   e) 30.00 mL of $AgNO_3$ solution

5. In the Mohr method for the determination of chloride by titration with silver ions, chromate is used as an indicator. When all the chloride has been used up, the silver ions then react with chromate to form the brick red silver chromate precipitate:

$$CrO_4^{2-}(aq) + 2Ag^+(aq) \rightarrow Ag_2CrO_4(s)$$

   Consider the titration of 25.00 mL of 0.0500 M Cl^- with 0.0500 M Ag^+, 1.0 mL of a 0.10 M solution of CrO_4^{2-} is added as indicator.

   a) What will be the silver ion concentration at the equivalence point?
   b) What will be the chromate ion concentration at the equivalence point?
   c) Will any Ag_2CrO_4 precipitate be formed at the equivalence point? Explain briefly.

6. A sample (1.4502 g) of a mixture of potassium dihydrogen phosphate (KH_2PO_4) and potassium chloride was dissolved in water and the phosphate was precipitated as magnesium ammonium phosphate hexahydrate $Mg(NH_4)PO_4.6H_2O$. The precipitate was filtered washed and heated strongly to convert the phosphate to magnesium pyrophosphate, $Mg_2P_2O_7$. The final mass of magnesium pyrophosphate was found to be 0.7852 g.

a) Calculate the percentage of potassium dihydrogen phosphate in the sample.
b) Why was the $Mg(NH_4)PO_4.6H_2O$ converted to $Mg_2P_2O_7$ before weighing? Would there have been any problems if the $Mg(NH_4)PO_4.6H_2O$ had been used as the weighing form?

7. The concentration of arsenic (as As_2O_3) in an insecticide is determined by precipitating the As as $MgNH_4AsO_4$ and after ignition, weighing the mass of $Mg_2As_2O_7$. Determine the %w/w As_2O_3 in a 3.254 g sample of insecticide if it yields 213 mg of $Mg_2As_2O_7$.