REDOX TITRATIONS

- Redox titrations can be used to find the amount of iron in a sample (or other reagents).
- In these titrations Fe^{2+} is oxidised to Fe^{3+} by an oxidising agent: $Fe^{2+} \rightarrow Fe^{3+} + e^-$
- The oxidising agent is usually acidified potassium manganate (VII) or potassium dichromate (VI):

  $MnO_4^- + 8\,H^+ + 5\,e^- \rightarrow Mn^{2+} + 4\,H_2O$ or $Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \rightarrow 2\,Cr^{3+} + 7\,H_2O$
- If the iron is not in the +2 oxidation state then
  - if it is the element Fe (0) then it reacted with sulphuric acid to oxidise it to Fe^{2+} ready for analysis
  - if it is Fe (+3) then it is reacted with Zn to reduce it to Fe^{2+} ready for analysis (the remaining zinc must be removed first to stop it reducing Fe^{3+} formed in the titration back to Fe^{2+}!)

Oxidising agent	**$KMnO_4$**	**$K_2Cr_2O_7$**
Half equation	$MnO_4^- + 8\,H^+ + 5\,e^- \rightarrow Mn^{2+} + 4\,H_2O$	$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \rightarrow 2\,Cr^{3+} + 7\,H_2O$
Overall equation with Fe^{2+}	$5\,Fe^{2+} + MnO_4^- + 8\,H^+ \rightarrow 5\,Fe^{3+} + Mn^{2+} + 4\,H_2O$	$6\,Fe^{2+} + Cr_2O_7^{2-} + 14\,H^+ \rightarrow 6\,Fe^{3+} + 2\,Cr^{3+} + 7\,H_2O$
Reacting ratio	$Fe^{2+} : MnO_4^- = 5:1$	$Fe^{2+} : Cr_2O_7^{2-} = 6:1$
Suitable acid	dilute H_2SO_4	dilute H_2SO_4, dilute HCl
Unsuitable acids (with reasons)	conc H_2SO_4 (oxidises some of the Fe^{2+}) conc HNO_3 (oxidises some of the Fe^{2+}) HCl (is oxidised by MnO_4^- to form Cl_2) ethanoic acid (weak acid so not enough H^+)	conc H_2SO_4 (oxidises some of the Fe^{2+}) conc HNO_3 (oxidises some of the Fe^{2+}) ethanoic acid (weak acid so not enough H^+)
Indicator	none – it is self indicating	barium diphenylaminesulphonate
Colour change at end point	colourless to first hint of pink	goes purple

Example calculation

Calculate the percentage of iron in a sample of steel wire if 1.51 g of the wire was dissolved in excess of dilute sulphuric acid and the solution made up to 250 cm^3 in a standard flask. 25.0 cm^3 of this solution was pipetted into a conical flask and needed 25.45 cm^3 of 0.02 mol dm^{-3} $KMnO_4$ for complete oxidation.

mol MnO_4^- = 0.02 x $^{25.45}/_{1000}$ = 0.000509

mol Fe^{2+} in 25 cm^3 = 5 x 0.000509 = 0.002545

mol Fe^{2+} in 250 cm^3 = 10 x 0.002545 = 0.02545

mass Fe = 55.8 x 0.02545 = 1.42 g

% Fe = $\frac{1.42}{1.51}$ x 100 = ***94.0%***

1) 24.3 cm^3 of 0.02 mol dm^{-3} $KMnO_4$ reacted with 20.0 cm^3 of an iron (II) solution. Calculate the molarity of the iron (II) ion.

2) 3.00 g of a lawn sand containing an iron (II) salt was shaken with dilute H_2SO_4. The resulting solution required 25.00 cm^3 of 0.0200 mol dm^{-3} potassium manganate (VII) to oxidise the Fe^{2+} ions in the solution to Fe^{3+} ions. Use this to calculate the percentage by mass of Fe^{2+} ions in this sample of lawn sand.

3) Calculate x in the formula $FeSO_4.xH_2O$ from the following data: 12.18 g of iron (II) sulphate crystals were made up to 500 cm^3 acidified with sulphuric acid. 25.0 cm^3 of this solution required 43.85 cm^3 of 0.01 mol dm^{-3} $KMnO_4$ for complete oxidation.

4) A tablet weighing 0.940 g was dissolved in dilute sulphuric acid made up to 250 cm^3 with water. 25.0 cm^3 of this solution was titrated with 0.00160 M $K_2Cr_2O_7$ requiring 32.5 cm^3 of the $K_2Cr_2O_7$. Calculate the percentage by mass of Fe^{2+} in the tablet.

5) Calculate the volume of 0.0200 mol dm^{-3} potassium manganate (VII) which just reacts with 0.142 g of iron (II) sulphate, in acid solution.

6) Ammonium iron (II) sulphate crystals have the following formula: $(NH_4)_2SO_4.FeSO_4.nH_2O$. In an experiment to find n, 8.492 g of the salt were dissolved and made up to 250 cm^3 solution with distilled water and dilute sulphuric acid. A 25.0 cm^3 portion of the solution was titrated against 0.0150 mol dm^{-3} $KMnO_4$, 22.5 cm^3 being required. Calculate n.

7) A piece of iron wire weighs 2.225 g. It is dissolved in acid, which oxidises it to Fe^{2+}, and made up to 250 cm3. A 25 cm^3 sample required 31.0 cm^3 of a 0.0185 mol dm^{-3} solution of potassium dichromate. Calculate the percentage of iron in the wire.

8) A 25.0 cm^3 aliquot of a solution containing Fe^{2+} and Fe^{3+} ions was acidified and titrated against 0.0200 M potassium manganate (VII) solution, requiring 15.0 cm^3. Zn reduces Fe^{3+} to Fe^{2+} and a second aliquot was reduced by zinc and after filtering off the excess zinc, was titrated with the same potassium manganate solution, requiring 19.0 cm^3. Calculate the concentrations of the Fe^{2+} and Fe^{3+} in the solution.

9) 13.2 g of iron (III) alum were dissolved in water and reduced to an iron(II) ion solution by zinc and dilute sulphuric acid. The mixture was filtered and the filtrate and washings made up to 500 cm^3 in a standard volumetric flask. 20.0 cm^3 of this solution required 26.5 cm^3 of 0.01 mol dm^{-3} $KMnO_4$ for oxidation. Calculate the percentage by mass of iron in iron alum.

10) A sample of solid ethanedioic acid ($H_2C_2O_4.2H_2O$) has been contaminated with potassium ethanedioate ($K_2C_2O_4.xH_2O$). A 1.780 g sample of this mixture was made up to a 250 cm^3 solution with distilled water. A 25 cm^3 sample was titrated against 0.100 mol dm^{-3} sodium hydroxide, requiring 17.35 cm^3. Another 25 cm^3 sample was acidified with sulphuric acid and titrated against 0.0200 mol dm^{-3} $KMnO_4$ solution, requiring 24.85 cm^3. Calculate x.

$$C_2O_4^{2-} \rightarrow 2\,CO_2 + 2\,e^-$$

11) A piece of rusted iron was analysed to find out how much of the iron had been oxidised to rust [hydrated iron(III) oxide]. A small sample of the iron was dissolved in excess dilute sulphuric acid to give 250 cm^3 of solution. The solution contains Fe^{2+} ions from the unrusted iron dissolving in the acid, and, Fe^{3+} ions from the rusted iron.

a) 25.0 cm^3 of this solution required 16.9 cm^3 of 0.020 mol dm^{-3} $KMnO_4$ for complete oxidation of the Fe^{2+} ions. Calculate the moles of Fe^{2+} ions in the sample titrated.

b) To a second 25.0 cm^3 of the rusted iron solution an oxidising agent was added to convert all the Fe^{2+} ions present to Fe^{3+} ions. The Fe^{3+} ions were titrated with a solution of $EDTA^{4-}$(aq) ions and 17.6 cm^3 of 0.10 mol dm^{-3} EDTA were required. Assuming 1 mole of EDTA reacts with 1 mole of Fe^{3+} ions, calculate the moles of Fe^{3+} ions in the sample.

c) From your calculations in (a) and (b) calculate the ratio of rusted iron to unrusted iron and hence the percentage of iron that had rusted.