Chem Factsheet

April 2003 Number 51

Redox Equilibria IV - Redox Titrations

Before working through this Factsheet you should:

- Understand and be confident with titration calculations and using $E^{\ominus}$ values (Factsheets No.23 and No. 45).

After working through this Factsheet you will:

- have met the specific reactions of potassium manganate (VII) and sodium thiosulphate/iodine (which are the quoted examples for redox titrations);
- be able to use the anti-clockwise rule and the 'balancing equations using electrons' method to write titration reactions from half-equations;
- have revised the method for calculations involving titrations.

1) Potassium manganate(VII) titrations

N.B. Used to be called 'potassium permanganate'.

Potassium manganate (VII) is usually found in laboratories as purple crystals which are then dissolved in water to form the solutions used in titrations.

The solution is a dark purple colour and is a **strong oxidising agent.** However, if it is not **acidified** (with dilute sulphuric acid) it produces a brown precipitate of MnO_2 which makes accurate titrations impossible (you cannot see the end-point).

> You must learn this half equation
> $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

Note the following points about the half-equation:

(a) MnO_4^- is the ion in $KMnO_4$, potassium manganate(VII), which is **purple**.
(b) In MnO_4^- the Mn has oxidation number = +7 (O = -2).
(c) $5e^-$ are involved – this will be the number when we are balancing half-equations to give the full equation.
(d) The Mn in MnO_4^- is REDUCED to Mn^{2+} (O.N. = +2) because it is the OXIDISING AGENT.

N.B. $Mn^{2+}(aq)$ is faintly pink in colour but at the concentrations used in the titrations the solution appears colourless.

In potassium manganate(VII) titrations there is **no indicator added** because the $KMnO_4$ acts as a **self-indicator**.

In the titration the purple $KMnO_4$ solution is in the burette and as it is added to the solution in the conical flask the purple colour is 'absorbed'. At the end-point **one drop** of $KMnO_4$ solutions produces a **pale pink colour** in the flask (a very slight excess of the $KMnO_4$ solution).

Standardising potassium manganate (VII) solution

A 'standardised solution' is one whose concentration (mol dm^{-3}) is known accurately by titrating it against an accurately made-up solution.

$KMnO_4(aq)$ is standardised by titrating it with **sodium ethanedioate, $Na_2C_2O_4$, solution.**

> You must learn this half equation
> $C_2O_4^{2-}(aq) \rightarrow 2CO_2(g) + 2e^-$

> ***Exam Hint: -*** *At A2 level you need to learn some of the specific half-equations relevant to redox titrations – THESE HAVE BEEN MARKED FOR YOU IN THIS FACTSHEET.*
>
> *However, it would be a mistake to try to learn **all** the titration equations – you need to use the METHOD for working out the full equation using:*
> *(a) $E^{\ominus}$ values and the anti-clockwise rule,*
> *(b) balancing equations using the 'electron method'.*

Before we look at this 'standardisation process' we need to remind ourselves of the **TITRATION CALCULATION METHOD:**

(1) The balanced chemical equation tells us the ratio of the species reacting together in the titration.
(2) The following equations are used:

$$\text{moles} = \frac{\text{volume (cm}^3)}{1000} \times \text{M(mol dm}^{-3})$$

$$\text{moles} = \frac{\text{grams}}{A_r/M_r} \qquad \%\ \text{purity} = \frac{\text{mass of pure} \times 100}{\text{mass of impure}}$$

Let's see the method being used in the following two examples:

Example 1

$25.0cm^3$ of sodium ethanedioate solution (concentration of 0.20 mol dm^{-3}) was warmed and titrated with potassium manganate (VII) solution. $19.60cm^3$ of the managate solution was required.

Calculate the concentration of the potassium managante (VII) solution.

Answer	**Explanation**
(a) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ (x2) $C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$ (×5) $2\ MnO_4^- + 16H^+ + 10e^- \rightarrow 2\ Mn^{2+} + 8H_2O$ $5\ C_2O_4^{2-} \rightarrow 10\ CO_2 + 10e^-$ --- $2MnO_4^- + 16H^+ + 5\ C_2O_4^{2-} \rightarrow 2Mn^{2-} + 10CO_2 + 8H_2O$	First find full equation
i.e. $2MnO_4^- \equiv 5C_2O_4^{2-}$	Use equation to find ratio of reactants
(b) Moles of $Na_2C_2O_4 = \frac{25}{1000} \times 0.20 = 0.005$	$\text{Moles} = \frac{cm^3}{1000} \times M$
(c) Moles of $KMnO_4 = 0.005 \times \frac{2}{5} = 0.002$	ratio is 2:5
(d) Concentration $= \frac{0.002 \times 1000}{19.60}$ $=$ **0.102 mol dm^{-3}**	$M = \frac{\text{moles} \times 1000}{cm^3}$

Example 2
A piece of iron weighs 0.368g. It is reacted with acid to dissolve it and then reduced to form Fe^{2+} ions. The resulting solution was titrated with potassium maganate(VII) solution. 38.60cm^3 of 0.02 potassium manganate (VII) solution were required.

What is the percentage purity of the iron?
($Fe^{2+} \rightarrow Fe^{3+} + e^-$)

Answer	**Explanation**
(a) $MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O$ $Fe^{2+} \rightarrow Fe^{3+} + e^-$ (×5) $MnO_4^- + 5Fe^{2+} + 58H^+ \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$	Finding the full equation by the 'balancing electrons' method.
$MnO_4^- \equiv 5Fe^{2+}$	Gives the **RATIO** of reactants.
(b) Moles of MnO_4^- = $\frac{38.6 \times 0.02}{1000}$ = 0.000772	Moles = $\frac{cm^3}{1000} \times$ M
(c) Moles Fe^{2+} = 0.000772 × 5 = 0.00386	ratio is 1:5
(d) Mass Fe^{2+} = 56 × 0.00386 = 0.216g	Mass = moles × A_r
(e) Percentage purity = $\frac{0.216 \times 100}{0.368}$ = 58.70%	M = $\frac{\text{moles} \times 1000}{cm^3}$

2. Sodium thiosulphate / iodine titrations
Sodium thiosulphate, $Na_2S_2O_3$, is a **REDUCING AGENT** and is used to titrate iodine, I_2.

You must learn this half equation
$2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$

The reacting ratio is $2S_2O_3^{2-} \equiv 1I_2$

In these titrations:
(a) I^- (aq) reacts with a particular chemical species and I_2 is produced,
(b) The amount of I_2 produced is found by titrating it with sodium thiosulphate,
(c) The amount of the original species can be found by the ratios of the two reactions.

When I_2(aq) is produced by a reaction it produces a **BROWN/ORANGE COLOUR** in the solution. As sodium thiosulphate is added from the burette the colour fades to a yellow colour and will eventually go colourless. However, it is impossible to see when a very pale yellow goes to colourless (the 'one drop' change at the end-point).

When the pale yellow stage is reached **STARCH SOLUTION** is added as an indicator – it produces a **DARK BLUE / PURPLE COLOUR**. At the end-point one drop of thiosulphate changes the blue colour to colourless.

Example 3
3.22g of iodine and 7g of potassium iodide are dissolved in distilled water and made up to 250cm^3. A 25.0cm^3 portion of this solution required 19.0cm^3 of sodium thiosulphate solution in a titration.

What is the concentration of the sodium thiosulphate solution?

Answer	**Explanation**
(a) Moles I_2 in 250 cm^3 = $\frac{3.22}{2 \times 127}$ = 0.0127	I = 127 moles = $\frac{\text{mass}}{M_r}$
(b) Moles I_2 in 25cm^3 = $\frac{0.0127}{10}$ = 0.00127	250 → 25
(c) $2S_2O_3^{2-} \equiv 1\ I_2$ Moles $S_2O_3^{2-}$ = 0.00127 × 2 = 0.00254	Ratio
(d) Concentration (m) = $\frac{0.00254}{19} \times 1000$ = 0.134 mol dm^{-3}	M = $\frac{\text{moles} \times 1000}{cm^3}$

Example 4
5.65g of a copper (II) salt is dissolved in water and made-up to 250cm^3. A 25.0cm^3 sample of solution is added to an excess of potassium iodide, KI. The iodine formed by the reaction required 21.0cm^3 of a 0.10 mol dm^{-3} solution of sodium thiosulphate for its reduction.

What is the percentage by mass of copper in the salt?

Answer	**Explanation**
(a) $2Cu^{2+} + 4I^- \rightarrow Cu_2I_2 + I_2$ so $2Cu^{2+} \equiv 1I_2$	Reacting ratio.
(b) $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$ so $2S_2O_3^{2-} \equiv 1I_2$	Reacting ratio
(c) $Cu^{2+} \equiv S_2O_3^{2-}$	Combing (a) + (b) to find thiosulphate to copper ratio.
(d) Moles $S_2O_3^{2-}$ = $\frac{21.0}{1000} \times 0.10$ = 0.002	Moles = $\frac{cm^3}{1000} \times$ M
(e) Moles Cu^{2+} in 25cm^3 = 0.002	Ratio from (c)
(f) Mass Cu^{2+} in 25cm^3 = 0.002 x 63.5 = 0.127g	Mass = moles × A_r A_r for Cu = 63.5 (ions have some mass as the element.)
(g) Mass of Cu^{2+} = 1.27g in original solution	25 → 250 (× 10)
(h) % Cu^{2+} = $\frac{1.27 \times 100}{5.65}$ = **22.48%**	

3. Other redox titrations
Although potassium manganate (VII) and sodium thiosulphate/iodine titrations are the ones quoted in A2 syllabuses they may not be the only ones you are questioned about.

For example, potassium dichromate (VI) solution is another oxidising agent used in redox titrations.

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

***Exam Hint: -** As long as the question gives you the relevant half-equations e.g. for $K_2Cr_2O_7$, it is exactly the same method as for potassium manganate (VII) – it is the **process** that matters i.e. balancing the equations using 'electrons' to find the reacting ratio then using the titration calculation equations.*

Note Factsheet 59 (Redox V: Answering questions on redox titrations) will go into more details of the calculations as well as practice questions.
From this Factsheet you should concentrate on:

1. learning the relevant half-equations;
2. understanding the processes in manganate (VII) and thiosulphate/iodine titrations;
3. familiarising yourself with the four examples of calculations given.

Questions

1. 25 cm^3 of sodium ethanedioate solution was warmed and titrated with potasium manganate(VII) solution. 17.20 cm^3 of potassium manganate(VII) solution of concentration 0.05 mol dm^{-3} were required.

   Calculate the concentration of the ethandioate solution.

2. 4.30 g of hydrogen peroxide solution was acidified, then titrated with potassium manganate(VII) solution of concentration 0.3 mol dm^{-3}. 21.80 cm^3 of potassium manganate(VII) solution were required.

   Calculate the percentage by mass of hydrogen peroxide in the solution. ($5O_2^- \rightarrow 5O_2 + 10e^-$)

3. A commercial medication contains potassium iodate. 1.20 g of the medication were dissolved in water and made up to 250 cm^3. A 25 cm^3 sample was added to an excess of potassium iodide, KI. The iodine formed by the reaction required 19.6 cm^3 of a 0.05 mol dm^{-3} solution of sodium thiosulphate for its reduction.

   What is the percentage by mass of potassium iodate in the medication? (K = 39, I = 127, O = 16)

   $IO_3^- + 6H^+ + 5e^- \rightarrow ½I_2 + 3H_2O$
   $I^- \rightarrow ½I_2 + e^-$

4. A student weighs out 8.02 g of an unknown iron(II) salt and dissolves it in distilled water. The solution is acidfied, then made up to 250 cm^3. 25 cm^3 of this solution were titrated with potassium dichromate solution. 16.8 cm^3 of the 0.4 mol dm^{-3} dichromate solution were required.

   Find the percentage by mass of iron in the unknown salt. (Fe = 56)
   $Fe^{2+} \rightarrow Fe^{3+} + e^-$
   $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

5. 25 cm^3 of liquid bleach, in which the active ingredient is NaClO, are made up to 250 cm^3 with distilled water. 25 cm^3 of this solution were added to an excess of potassium iodide. The iodine formed by this reaction required 20.30 cm^3 of a 0.02 mol dm^{-3} solution of sodium thiosulphate for its reduction.

   Find the concentration of ClO^- ions in the bleach.
   $2H^+ + ClO^- + 2e^- \rightarrow H_2O + Cl^-$

Answers

1. $2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$
   $2MnO_4^- : 5C_2O_4^{2-}$

   moles of MnO_4^- $= \frac{17.20}{1000} \times 0.05 = 0.00086$ moles

   moles of $C_2O_4^{2-}$ $= \frac{5}{2} \times 0.00086 = 0.00215$ moles

   concentration $= \frac{0.00215 \times 1000}{17.20} = 0.125$ moles

2. $2MnO_4^- + 16H^+ + 5O_2^- \rightarrow 2Mn^{2+} + 8H_2O + 5O_2$
   $2MnO_4^- : 5O_2^-$

   moles of MnO_4^- $= \frac{21.80}{1000} \times 0.3 = 0.00654$

   moles of O_2^- $= \frac{5}{2} \times 0.00654 = 0.01635$

   mass of $O_2 = 0.01635 \times (2 \times 1 + 2 \times 16) = 0.5559$ g
   percentage by mass = 12.9 %

3. $IO_3^- + 6H^+ + 5I^- \rightarrow 3I_2 + 3H_2O$
   $1IO_3^- : 3I_2$
   $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$
   $2S_2O_3^{2-} : 1I_2$

   So $6S_2O_3^{2-} : 3I_2$
   So $1IO_3^- : 6S_2O_3^{2-}$

   moles $S_2O_3^{2-}$ $= \frac{19.6}{1000} \times 0.05 = 0.00098$

   moles IO_3^- in 250 cm^3 $= \frac{1}{6} \times 0.00098 = 0.0001633$

   moles IO_3^- in 250 cm^3 = 0.001633
   mass of KIO_3 in 250 cm^3 = 0.001633 (39 + 127 + 3 × 16) = 0.3495 g
   so percentage by mass in medication = 29 %

4. $6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$
   $6Fe^{2+} : 1Cr_2O_7^{2-}$

   moles of $Cr_2O_7^{2-}$ $= \frac{16.8}{1000} \times 0.4 = 0.00672$
   moles of Fe^{2+} in 25 cm^3 = 6 × 0.00672 = 0.04032
   moles of Fe^{2+} in 250 cm^3 = 0.4032
   mass of Fe = 0.032 × 56 = 2.25792 g
   percentage of Fe = 28 %

5. $2I^- + 2H^+ + ClO^- \rightarrow I_2 + H_2O + Cl^-$
   $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

   $1ClO^- : 1I_2$ $1I_2 : 2S_2O_3^{2-}$

   So $1ClO^- : 2S_2O_3^{2-}$

   moles $2S_2O_3^{2-}$ $= \frac{20.30}{1000} \times 0.02 = 0.000406$

   moles ClO^- in 25 cm^3 $= \frac{0.000406}{2} = 0.000203$

   moles ClO^- in 250 cm^3 = 0.00203
   moles ClO^- in 25cm^3 bleach = 0.00203

   $[ClO^-] = 0.00203 \times \frac{1000}{25} = 0.0812$ mol dm^{-3}

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