

2. Redox experiments

Student Sheet

In this exercise, you perform simple redox reactions and, on the basis of your observations, deduce the relative oxidising abilities of a number of oxidising agents.

Learning outcomes

By the end of this exercise you will be able to:

- record colour changes accurately
- decide when to use a control experiment
- design tests to assess relative oxidising ability
- analyse a set of tabulated results and draw conclusions
- tabulate a set of conclusions
- write overall ionic equations from redox half equations
- deduce order of oxidising ability and the feasibility of reactions

The exercise

You will carry out a series of test-tube reactions to investigate the possible reactions between various oxidising agents and reducing agents. From your observations you will make deductions as to the relative oxidising strengths of a number of different species. Where your observations indicate that a reaction has occurred, you will write an ionic equation for this reaction by combining the appropriate redox half-equations.

Note 1 In order to justify your deduction that a reaction has occurred, it is necessary to **show** that an observable **change** has occurred. To do this, you **must quote** what you observed both **before and after** the reaction takes place. (See example below).

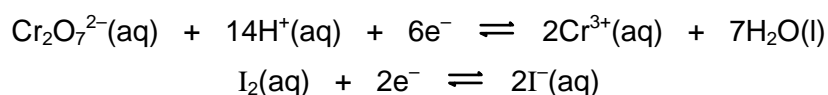
Note 2 When adding a coloured solution to a colourless solution, there will be a colour change to the colourless solution even if no reaction has occurred. This is because the colourless solution simply dilutes the coloured one. If the colour changes to a **different** or a **darker** colour, or the final mixture has **no colour** (the original colour having been bleached), a reaction has occurred.

To **prove** that a reaction has occurred, it is often necessary to perform a **control** experiment. To do this, you add the **same volume** of the coloured solution to **equal volumes** of pure water and your test sample. If the colour in your test sample is different to that in the control you can conclude that a reaction has occurred.

Background Information

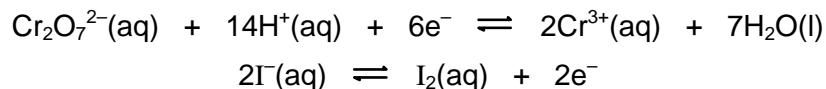
A stronger oxidising agent will oxidise the reduced form of a weaker oxidising agent and will itself be reduced.

Consider the two oxidising agents *acidified sodium dichromate(VI)* and *iodine*. As it is traditional to show half-equations as **reduction processes**, their **reduction** half-equations are shown below:

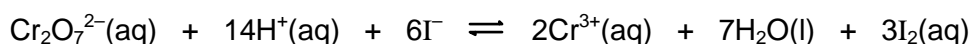


Appendix 2

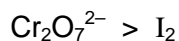
When an **orange solution** containing acidified dichromate ions is added to a **colourless solution** of iodide ions a **brown solution** is formed. When starch is added, the **brown solution** turns into a **blue-black solution**. This **change in colour** (orange to the darker colour – brown, or blue-black with starch) shows that iodine has been formed. Thus, iodide ions have been **oxidised** by the dichromate ions to iodine molecules while being **reduced** themselves to Cr^{3+} ions. The half-equations for these processes are:



The overall equation for the reaction is obtained by adding together the two half-equations. When you do this, you must ensure that **the electrons MUST cancel out**, so that the final equation **does not contain electrons**. So, we need to multiply the iodide/iodine half-equation by three (6:2 electron ratio) so that there are six electrons in each half-equation. Added together they give the overall equation:



Since the dichromate ions have oxidised the iodide ions to iodine, we can conclude that the order of oxidising strength is:














The reduction half-equations for the oxidising agents used in the tests which follow, are given below.

| reduction half-equations (in random order) | |
|--|---|
| $\text{I}_2(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{I}^-(\text{aq})$ | $\text{S}_4\text{O}_6^{2-} + 2\text{e}^- \rightleftharpoons 2\text{S}_2\text{O}_3^{2-}$ |
| $\text{Cl}_2(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-(\text{aq})$ | $\text{Br}_2(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{Br}^-(\text{aq})$ |
| $\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$ | $\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$ |
| $\text{ClO}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightleftharpoons \text{Cl}^-(\text{aq}) + 2\text{OH}^-(\text{aq})$ | |

Safety

There are potentially hazardous substances involved in this exercise. You **must** follow all health and safety instructions given to you by your teacher. Materials safety data sheets should be consulted so that the correct action can be taken in event of a spillage and/or accident.

| | |
|---|---|
|  | You must wear eye protection throughout this experiment |
|  | Iron(III) chloride, iron ammonium sulphate and potassium thiocyanate are harmful |
|  | Sodium chlorate and potassium manganate are oxidising |
|  | and harmful |
|  | Bromine is toxic |
|  | and corrosive |
|  | Hydrochloric acid and sulphuric acid are corrosive |
|  | Hexane is highly flammable |
|  | and harmful |
|  | Chlorine gas is toxic |
|  | Bromine, potassium manganate and hexane are dangerous for the environment . Your teacher will tell you how to dispose of these. |

Procedure

- Using a clean test-tube each time, carry out the tests given in the table on the next page, making sure each time that the contents of the test-tube are thoroughly mixed before making your observations.
- For each test, record your observations **clearly, concisely** and **precisely** in the table. Note where you used a control experiment.
- When you have completed tests 1 - 9 in the table, devise and perform other tests to compare the oxidising strength of the chlorate(I), $\text{ClO}^-(\text{aq})$, ion against iron(II), $\text{Fe}^{2+}(\text{aq})$, ions and against bromide, $\text{Br}^-(\text{aq})$, ions.
- Continue the table to record brief details of the tests you performed and the observations you made in part 3.

Analysis and evaluation

Complete the table by:

1. Writing an ionic equation for any reactions that have occurred. If you have concluded that 'no reaction' has occurred, clearly there will be no equation to write.
2. In the 'Deductions' column, state in words which reagent has oxidised which other reagent. For example, in the reaction of $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$ ions and $\text{I}^-(\text{aq})$ ions described above, you would write ' $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$ ions oxidise $\text{I}^-(\text{aq})$ '
3. Also in the deductions column, state which of the two oxidising agents present in the solution is the more powerful. For example, in the reaction of $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$ ions and $\text{I}^-(\text{aq})$ ions, you would write ' $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) > \text{I}^-(\text{aq})$ '
4. Arrange the oxidising agents you have used, include chlorate(I), in order of decreasing oxidising ability (strongest oxidising agent first).
5. Create a table to show, separately, the name, formula, reduction half-equation and Standard Electrode Potential, E^\ominus , value of each oxidising agent. Your table should show the oxidising agents you have used in order of decreasing oxidising ability (strongest oxidising agent first).
6. Obtain, from a data book, the E^\ominus value for each oxidising agent and add these data to your table.
7. Explain, in terms of their E^\ominus values, the order of the oxidising agents in your table.

The following questions concern Tests 3 & 4

- 1 Ask your teacher to check, and if necessary correct, your deductions for Tests 3 & 4.
- 2 Write cell descriptions for the redox system present in Test 3, where $\text{Fe}^{2+}(\text{aq})$ is mixed with $\text{Cl}_2(\text{aq})$, and the redox system present in Test 4, where $\text{Fe}^{2+}(\text{aq})$ is mixed with $\text{I}_2(\text{aq})$.
Hint: You should assume, in Test 3, that $2\text{Fe}^{2+}(\text{aq})$ is converted into $2\text{Fe}^{3+}(\text{aq})$, and that $\text{Cl}^-(\text{aq})$ is converted into $\text{Cl}_2(\text{aq})$.
 In Test 4, you should assume that $2\text{Fe}^{2+}(\text{aq})$ is converted into $2\text{Fe}^{3+}(\text{aq})$, and that $\text{I}^-(\text{aq})$ is converted into $\text{I}_2(\text{aq})$.
- 3 Use the E^\ominus values from your table to calculate the cell e.m.f, E^\ominus_{cell} , values for these two cells
- 4 On the basis of these E^\ominus_{cell} values, state and explain the feasibility of the cell reactions in Tests 3 and 4.

Appendix 2

| | Test | Observations | Ionic equation | Deduction |
|---|---|--------------|----------------|-----------|
| 1 | iron(III) + aqueous iodide Add about 8 drops of iron(III) solution to 1 cm ³ of aqueous iodide ions. Add a few drops of starch solution. | | | |
| 2 | iron(III) + aqueous bromide Add 2 cm ³ of aqueous bromide ions to 1 cm ³ of aqueous iron(III) ions. Add 1 cm ³ of hexane, cork, shake, and leave. | | | |
| 3 | iron(II) + aqueous chlorine Add 2 cm ³ of aqueous chlorine to 1 cm ³ of aqueous iron(II) ions. Observe any change, then add a few drops of potassium thiocyanate (KCNS) solution | | | |
| 4 | iron(II) + aqueous iodine Add about 4 drops of aqueous iodine to 1 cm ³ of aqueous iron(II) ions. Observe any change, then add a few drops of potassium thiocyanate (KCNS) solution | | | |
| 5 | iron(II) + acidified manganate(VII) Mix 1 cm ³ of aqueous MnO ₄ ⁻ ions with 1 cm ³ of dilute sulphuric acid. Add, dropwise, 3 cm ³ of iron(II) solution. Observe any change. Add a few drops of potassium thiocyanate (KCNS) solution. | | | |
| 6 | chlorine + bromide Add about 1 cm ³ of aqueous chlorine to 1 cm ³ of aqueous bromide ions. Add about 1 cm ³ of hexane, cork, shake and leave. | | | |

Appendix 2

| | | | | |
|---|--|--|--|--|
| 7 | bromine + iodide Add about 1 cm ³ of aqueous bromine to 1 cm ³ of aqueous iodide ions. Add about 1 cm ³ of hexane, cork, shake and leave. | | | |
| 8 | thiosulphate + iodine Add aqueous sodium thiosulphate, dropwise, to 1 cm ³ of aqueous iodine until any change is complete | | | |
| 9 | conc. HCl + manganate(VII) <i>Working in a fume cupboard</i> , add 8 drops of conc. HCl to 1 cm ³ of aqueous MnO ₄ ⁻ ions. Test any gas evolved with damp blue litmus paper | | | |

2. Redox experiments

Teachers' Notes

This exercise is very much 'hands-on' and, if the outcomes are clear and unambiguous, it provides considerable support in the development of a students' understanding of redox reactions, and of the use of standard electrode potentials in determining the feasibility of a proposed reaction.

Intended learning outcomes

Please see the Student Sheet

A suggested approach

Before your students undertake this exercise, they should have a reasonable basic understanding of redox reactions, standard electrode potentials, the calculation of cell e.m.f. values and the writing of cell descriptions. A brief review of these matters before they start the exercise will help to set the exercise in context.

The exercise makes use of simple test-tube reactions but, if sound results are to be obtained, each test must be performed with care and attention to detail.

Before starting the experiment, it is worth spending a little time reviewing the basic techniques of measuring and mixing. Students must not be allowed to mix the contents of a test-tube by inverting it while using a thumb as a bung! However, thorough mixing is essential if meaningful observations are to be made.

When students tackle the chlorate(I) investigation, it would be prudent to instruct them to show you their proposed tests before they perform them!

This exercise involves the use of potentially hazardous materials and so students should be closely supervised, unless they have considerable relevant practical experience.

Answer to questions

- The more positive the E^\ominus value, the more powerful the oxidising agent. The half-equation for the more positive species runs **forwards**, that for the less positive species runs **backwards**.
- Experiment 3 $\text{Pt} \mid \text{Fe}^{2+}(\text{aq}), \text{Fe}^{3+}(\text{aq}) \mid \mid \text{Cl}_2(\text{aq}), \text{Cl}^-(\text{aq}) \mid \text{Pt}$
Experiment 4 $\text{Pt} \mid \text{Fe}^{2+}(\text{aq}), \text{Fe}^{3+}(\text{aq}) \mid \mid \text{I}_2(\text{aq}), \text{I}^-(\text{aq}) \mid \text{Pt}$
- Experiment 3 $E^\ominus = +1.36 - (+0.77) = +0.59 \text{ V}$
Experiment 4 $E^\ominus = +0.54 - (+0.77) = -0.23 \text{ V}$
- Experiment 3 $E^\ominus = +\text{ve}$ reaction feasible as $\Delta G = -\text{ve}$
Experiment 4 $E^\ominus = -\text{ve}$ reaction not feasible as $\Delta G = +\text{ve}$

The chlorate(I) investigation

Typically, the tests used to determine the oxidising strength of the chlorate(I) ion relative to bromine and $\text{Fe}^{3+}(\text{aq})$ should be similar to:

Sodium chlorate(I) + bromide

| | |
|--------------|---|
| Test | add about 1 cm ³ of aqueous sodium chlorate(I) to 1 cm ³ of aqueous bromide ions. |
| Observations | <i>colourless solutions throughout</i> |
| Inferences | 'no reaction'; chlorate(I) does not oxidise $\text{Br}^-(\text{aq})$; $\text{Br}_2 > \text{ClO}^-$ |

Appendix 2

Iron(II) + sodium chlorate(I)

Test Add about 1 cm³ of aqueous sodium chlorate(I) to 1 cm³ of aqueous iron(II) ions
 Observations *colourless/pale green solution, turns brown*
 Inferences 'reaction'; 'chlorate(I) oxidises Fe²⁺(aq)'; ClO⁻ > Fe³⁺(aq)

Expected deduction

The oxidising strength of the chlorate(I) is **between** those of bromine and iron(II).

Order of oxidising strengths

| | | | | | | | |
|------------------------|-------------------------------|-----------------|-----------------|------------------|------------------|----------------|---|
| Oxidising agent | MnO ₄ ⁻ | Cl ₂ | Br ₂ | ClO ⁻ | Fe ³⁺ | I ₂ | S ₄ O ₆ ²⁻ |
| E° / V | 1.51 | 1.36 | 1.09 | 0.89 | 0.77 | 0.54 | 0.09 |

Technical information

Requirements per student/group

Apparatus

- Test-tubes and a test-tube rack
- Bungs/corks to fit test-tubes
- 10 cm³ measuring cylinder
- Dropping pipettes
- Access to an organic waste bottle labelled **Hexane (Flammable)**

Materials

Students will need access to the following:

- 0.5 mol dm⁻³ (approximate) aqueous iron(III) chloride labelled **Fe³⁺(aq)**
- 0.5 mol dm⁻³ (approximate) sodium thiosulphate labelled **S₂O₃²⁻(aq)**
- 0.1 mol dm⁻³ (approximate) aqueous potassium iodide labelled **I⁻(aq)**
- 10% aqueous sodium chlorate(I) labelled **sodium chlorate(I)(aq)**
- 0.1 mol dm⁻³ (approximate) aqueous iron(II) ammonium sulphate labelled **Fe²⁺(aq)**
- 0.1 mol dm⁻³ (approximate) aqueous potassium bromide labelled **Br⁻(aq)**
- 0.01 mol dm⁻³ (approximate) aqueous iodine made by dissolving 2.5 g iodine and 8 g of potassium iodide in water and making the solution up to 1 dm³ and labelled **I₂(aq)**
- 0.1 mol dm⁻³ (approximate) aqueous bromine solution labelled **Br₂(aq)**
- 0.02 mol dm⁻³ (approximate) aqueous potassium manganate(VII) labelled **MnO₄⁻(aq)**
- A solution made by diluting about 10 cm³ of 10% aqueous sodium chlorate(I) to 100 cm³ with water then adding 10 cm³ of dilute (2 mol dm⁻³) hydrochloric acid and labelled **Cl₂(aq)**
Alternatively, chlorine water may be prepared by bubbling chlorine gas through deionised water for several hours (**in a fume cupboard**)
- Dilute sulphuric acid labelled **Dilute sulphuric acid**
- 0.5 mol dm⁻³ (approximate) aqueous potassium thiocyanate labelled **KCNS(aq) (harmful)**
- Hexane
- 1% starch solution
- Access to concentrated hydrochloric acid
- Blue litmus paper

Notes

The concentrations suggested are approximate and it may well be that existing solutions of different concentrations will be adequate. Teachers are advised to try out the tests in advance of the assessment exercise and to make any necessary adjustments.

In **Test 9** a precipitate of manganese(IV) oxide may well be observed but the expected equation does not suggest its formation. If necessary, tell your students that the only equation needed in Test 9 is that obtained by combining the two half equations listed.

Safety

The main points are included on the Student Sheet but it is the teacher's responsibility to ensure that a full risk assessment is carried out prior to the practical session. As there are some hazards associated with the solutions used, safety issues should be stressed, and use of eye protection made **mandatory**. MSDS sheets should be consulted so that the correct action can be taken in event of a spillage and/or accident. Materials that are dangerous to the environment should be disposed of according to local regulations.

Appendix 2

| | test | observations | ionic equation | deductions |
|---|--|---|---|--|
| 1 | iron(III) + aqueous iodide Add about 8 drops of iron(III) solution to 1 cm ³ of aqueous iodide ions. Add a few drops of starch solution. | <ul style="list-style-type: none"> • <i>yellow/pale brown solution</i> • <i>added to colourless solution</i> • <i>forms darker brown solution</i> • <i>blue-black colour with starch</i> | $\text{Fe}^{3+}(\text{aq}) + 2\text{I}^{-}(\text{aq}) \rightleftharpoons 2\text{Fe}^{2+}(\text{aq}) + \text{I}_2(\text{aq})$ | <p>$\text{Fe}^{3+}(\text{aq})$ oxidises $\text{I}^{-}(\text{aq})$</p> <p>$\text{Fe}^{3+}(\text{aq}) > \text{I}_2(\text{aq})$</p> |
| 2 | iron(III) + aqueous bromide Add 2 cm ³ of aqueous bromide ions to 1 cm ³ of aqueous iron(III) ions. Add 1 cm ³ of hexane, cork, shake, and leave. | <ul style="list-style-type: none"> • <i>yellow/pale brown solution</i> • <i>added to colourless solution</i> • <i>no change</i> | No reaction | <p>$\text{Fe}^{3+}(\text{aq})$ does not oxidise $\text{Br}^{-}(\text{aq})$</p> <p>$\text{Fe}^{3+}(\text{aq})$ not $>$ $\text{Br}_2(\text{aq})$</p> |
| 3 | iron(II) + aqueous chlorine Add 2 cm ³ of aqueous chlorine to 1 cm ³ of aqueous iron(II) ions. Observe any change, then add a few drops of potassium thiocyanate (KCNS) solution | <ul style="list-style-type: none"> • <i>colourless/pale green solution</i> • <i>added to colourless solution</i> • <i>pale yellow/green solution formed</i> • <i>orange/red with KCNS</i> | $2\text{Fe}^{2+}(\text{aq}) + \text{Cl}_2(\text{aq}) \rightleftharpoons 2\text{Fe}^{3+}(\text{aq}) + 2\text{Cl}^{-}(\text{aq})$ | <p>$\text{Cl}_2(\text{aq})$ oxidises $\text{Fe}^{2+}(\text{aq})$</p> <p>$\text{Cl}_2(\text{aq}) > \text{Fe}^{2+}(\text{aq})$</p> |
| 4 | iron(II) + aqueous iodine Add about 4 drops of aqueous iodine to 1 cm ³ of aqueous iron(II) ions. Observe any change, then add a few drops of potassium thiocyanate (KCNS) solution | <ul style="list-style-type: none"> • <i>brown solution</i> • <i>added to colourless/pale green solution</i> • <i>no change (pale brown solution formed)</i> | No reaction | <p>$\text{Fe}^{3+}(\text{aq})$ does not oxidise $\text{Br}^{-}(\text{aq})$</p> <p>$\text{Fe}^{3+}(\text{aq})$ not $>$ $\text{Br}_2(\text{aq})$</p> |
| 5 | iron(II) + acidified manganate(VII) Mix 1 cm ³ of aqueous MnO_4^{-} ions with 1 cm ³ of dilute sulphuric acid. Add, dropwise, 3 cm ³ of iron(II) solution. Observe any change. Add a few drops of potassium thiocyanate (KCNS) solution. | <ul style="list-style-type: none"> • <i>colourless/pale green solution</i> • <i>added to purple solution</i> • <i>solution decolourised</i> • <i>orange/red with KCNS</i> | $\text{MnO}_4^{-}(\text{aq}) + 5\text{Fe}^{2+}(\text{aq}) + 8\text{H}^{+}(\text{aq}) \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 5\text{Fe}^{3+}(\text{aq}) + 4\text{H}_2\text{O}$ | <p>$\text{MnO}_4^{-}(\text{aq})$ oxidises $\text{Fe}^{2+}(\text{aq})$</p> <p>$\text{MnO}_4^{-}(\text{aq}) > \text{Fe}^{3+}(\text{aq})$</p> |

Appendix 2

| | | | | |
|---|---|--|---|--|
| 6 | <p>chlorine + bromide Add about 1 cm³ of aqueous chlorine to 1 cm³ of aqueous bromide ions. Add about 1 cm³ of hexane, cork, shake and leave.</p> | <ul style="list-style-type: none"> • colourless solution • turns yellow • hexane layer is darker yellow/brown | $\text{Cl}_2(\text{aq}) + 2\text{Br}^-(\text{aq}) \rightleftharpoons \text{I}_2(\text{aq}) + 2\text{Cl}^-(\text{aq})$ | <p>Cl₂(aq) oxidises Br⁻(aq) Cl₂(aq) > Br₂(aq)</p> |
| 7 | <p>bromine + iodide Add about 1 cm³ of aqueous bromine to 1 cm³ of aqueous iodide ions. Add about 1 cm³ of hexane, cork, shake and leave.</p> | <ul style="list-style-type: none"> • orange/red solution • added to colourless solution • turns darker yellow/brown • hexane layer is red/purple | $\text{Br}_2(\text{aq}) + 2\text{I}^-(\text{aq}) \rightleftharpoons 2\text{Br}^-(\text{aq}) + \text{I}_2(\text{aq})$ | <p>Br₂(aq) oxidises I⁻(aq) Br₂(aq) > I₂(aq)</p> |
| 8 | <p>thiosulphate + iodine Add aqueous sodium thiosulphate, dropwise, to 1 cm³ of aqueous iodine until any change is complete</p> | <ul style="list-style-type: none"> • colourless solution • added to brown solution • solution decolourised | $2\text{S}_2\text{O}_3^{2-}(\text{aq}) + \text{I}_2(\text{aq}) \rightleftharpoons \text{S}_4\text{O}_6^{2-}(\text{aq}) + 2\text{I}^-(\text{aq})$ | <p>I₂(aq) oxidises S₂O₃²⁻(aq) I₂(aq) > S₄O₆²⁻(aq)</p> |
| 9 | <p>conc. HCl + manganate(VII) <i>Working in a fume cupboard,</i> add 8 drops of conc. HCl to 1 cm³ of aqueous MnO₄⁻ ions. Test any gas formed with damp blue litmus paper</p> | <ul style="list-style-type: none"> • purple solution • brown colour (ignore reference to ppt) • litmus bleached | $2\text{MnO}_4^-(\text{aq}) + 16\text{H}^+(\text{aq}) + 10\text{Cl}^-(\text{aq}) \rightleftharpoons 2\text{Mn}^{2+}(\text{aq}) + 8\text{H}_2\text{O}(\text{l}) + 5\text{Cl}_2(\text{aq})$ | <p>MnO₄⁻(aq) oxidises Cl⁻(aq) MnO₄⁻(aq) > Cl₂(aq)</p> |