

## REDOX REACTIONS

### OXIDATION

Oxidation is

- i) increase in oxidation number.
- ii) loss of electrons = LEO.

### REDUCTION

Reduction is

- i) decrease in oxidation number.
- ii) gain of electrons = GER.

**NOTE:** If you are asked to explain oxidation/reduction reactions, you must explain it in terms of the loss and gain of electrons or change in oxidation number.

A method of following what happens to electrons in a reaction is to use oxidation numbers. The following rules are used to calculate oxidation numbers.

- Elements are zero (0). If it is not bonded to a different atom it is = 0.  
eg  $O_2$ , He, Al, P<sub>4</sub>, C are all zero.
  - Simple ions (non-radicals) have an oxidation number = charge on the ion.  
eg  $Na^+ = +1$ ,  $S^{2-} = -2$ ,  $Cr^{3+} = +3$
  - Hydrogen is +1 except when joined directly to metals (called metal \_\_\_\_\_).  
eg in HCl, CH<sub>4</sub>, NH<sub>4</sub>NO<sub>3</sub>, KOH hydrogen is +1 but in NaH it is -1
  - Oxygen is -2 except in peroxides (O<sub>2</sub><sup>2-</sup>).  
eg in H<sub>2</sub>O, CO<sub>2</sub>, CaO, SiO<sub>2</sub> oxygen is -2 but in H<sub>2</sub>O<sub>2</sub> it is -1.
  - Compounds and radical ions have their sum of oxidation numbers = total charge.
- eg  $SO_2 = S + 2O = 0$   
 $S + 2(-2) = 0$   
 $S = +4$
- eg  $S_2O_3^{2-} = 2S + 3O = -2$   
 $2S + 3(-2) = -2$   
 $2S = +4$   
 $S = +2$
- eg  $NaHSO_4 = Na^+ HSO_4^-$   
 $H + S + 4O = -1$   
 $+1 + S + 4(-2) = -1$   
 $S = +6$

Determine the Oxidation Numbers of the underlined element in the following chemicals.

- |                 |                   |
|-----------------|-------------------|
| 1. $H_2S$       | 11. $P_4O_{10}$   |
| 2. $Na_3P$      | 12. $SO_4^{2-}$   |
| 3. $Cr(OH)_4^-$ | 13. $Ba(MnO_4)_2$ |
| 4. $SO_2$       | 14. $H_3O^+$      |
| 5. $AlCl_3$     | 15. $HNO_3$       |
| 6. $CaCO_3$     | 16. $NH_3$        |
| 7. $NH_4^+$     | 17. $NaNO_2Br_3$  |

- |                  |                       |
|------------------|-----------------------|
| 8. $K_2FeO_4$    | 18. $K_3Fe(CN)_6$     |
| 9. $FeF_6^{3-}$  | 19. $Fe(H_2O)_6^{2+}$ |
| 10. $FeO_4^{3-}$ | 20. $Ba_2FeO_4$       |

Determine the oxidation state of the halogen in each of the following.

- |              |                  |
|--------------|------------------|
| 1. $FeCl_3$  | 5. $IO_3^-$      |
| 2. $NaOBr$   | 6. $Zn(ClO_4)_2$ |
| 3. $ClO_2^-$ | 7. $(IO)_2SO_4$  |
| 4. $SF_4$    | 8. $Ag_5IO_6$    |

Oxidation Numbers are used for?

1. Identifying oxidation/reduction (REDOX) reactions.

If there is a change in oxidation numbers, then it is a redox reaction.

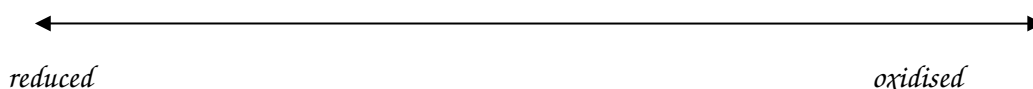
2. Identifying what has been oxidised and reduced.

If the oxidation number of an element **increases**, then that element has

been **oxidised**.

If the oxidation number of an element **decreases**, then that element has

been \_\_\_\_\_.



For each of the following equations, answer these questions.

- a) Is it a redox reaction?  
 b) What has been oxidised?  
 c) What has been reduced?

- 1)  $Zn + 4HNO_3 \rightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$
- 2)  $Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4$
- 3)  $CaCO_3 \rightarrow CaO + CO_2$
- 4)  $2Na + 2H_2O \rightarrow 2NaOH + H_2$
- 5)  $Fe + Cu^{2+} \rightarrow Cu + Fe^{2+}$
- 6)  $K_2CrO_4 + 2HCl \rightarrow K_2Cr_2O_7 + 2KCl + H_2O$
- 7)  $SO_2 + H_2O \rightarrow H_2SO_3$
- 8)  $2Cu(NO_3)_2 \rightarrow 2CuO + 4NO_2 + O_2$
- 9)  $Al_2(SO_4)_3 \rightarrow Al_2O_3 + 3SO_3$
- 10)  $TiCl_4 + 2H_2S \rightarrow TiS_2 + 4HCl$

### BALANCING REDOX REACTIONS

A redox reaction is - where electrons are transferred from one substance to another.

- a reaction in which there is a change in oxidation states.



Half equations LEO \_\_\_\_\_

GER \_\_\_\_\_

Redox equation \_\_\_\_\_

Why must the Ag half equation be multiplied by two? \_\_\_\_\_

\_\_\_\_\_

The steps used to balance redox reactions are as follows:

1. Identify what is being oxidised and reduced and their products.  
How? \_\_\_\_\_
2. Balance the atoms other than oxygen and hydrogen.
3. Balance the oxygen by adding water molecules.
4. Balance the hydrogen by adding hydrogen ions.
5. Balance the charge by adding electrons.
6. Make the number of electrons in each half equation the same.
7. Add the two half equations. Check,

**CHECK:** A balanced equation has the same number of atoms and an equal charge on each side. So check each equation for both.

**NOTE:** If one chemical is oxidised another must be reduced.  
Oxidation-reduction are always paired reactions.  
They always occur simultaneously, together, at the same time.

Write half equations for the following:

- 1)  $F_2 \rightarrow F$
- 2)  $H_2S \rightarrow S$
- 3)  $Cl \rightarrow Cl_2$
- 4)  $Sn^{2+} \rightarrow Sn^{4+}$
- 5)  $H_2O_2 \rightarrow O_2$
- 6)  $NO_2^- \rightarrow NO_3^-$
- 7)  $C_2O_4^{2-} \rightarrow CO_2$
- 8)  $MnO_4^- \rightarrow Mn^{2+}$
- 9)  $Fe^{3+} \rightarrow Fe^{2+}$
- 10)  $H^+ \rightarrow H_2$
- 11)  $MnO_4^{2-} \rightarrow MnO_4^-$
- 12)  $SO_4^{2-} \rightarrow S_2O_8^{2-}$
- 13)  $NO_3^- \rightarrow NO_2$
- 14)  $SO_3^{2-} \rightarrow SO_4^{2-}$
- 15)  $H_2O \rightarrow O_2$

Write half equations and add the half equations together for the following reactions:

- 16)  $NO_3^- + Cu \rightarrow Cu^{2+} + NO_2$
- 17)  $Co^{3+} + H_2O \rightarrow Co^{2+} + O_2$
- 18)  $Fe^{2+} + MnO_4^- \rightarrow Fe^{3+} + Mn^{2+}$
- 19)  $Cr_2O_7^{2-} + Zn \rightarrow Cr^{3+} + Zn^{2+}$
- 20)  $MnO_4^- + HCl \rightarrow Mn^{2+} + Cl_2$

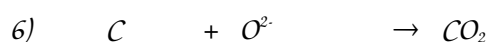
## OXIDISING AND REDUCING AGENTS

An oxidising agent takes electrons from another element and is reduced. The following chemicals are common oxidising agents. For each write the half equation showing the chemical as an oxidant.

- 1)  $O_2 \rightarrow$
- 2)  $Cl_2 \rightarrow$
- 3)  $MnO_4^- \rightarrow$
- 4)  $Cr_2O_7^{2-} \rightarrow$
- 5)  $H_2O_2 \rightarrow$
- 6)  $ClO^- \rightarrow$  (hypochlorite ion)
- 7)  $H^+ \rightarrow$
- 8)  $H_2SO_4 \rightarrow$  (conc sulfuric acid)
- 9)  $HNO_3 \rightarrow$  (conc nitric acid)

A reducing agent gives electrons to another element and is \_\_\_\_\_.

The following chemicals are common reducing agents. For each write the half equation showing the chemical as a reductant.



Oxidising agents ( ) and reducing agents ( ) are explained in terms of their relative ability to attract or lose electrons. Numerically this is put in order using the Standard Reduction Potential Table.

The elements at the top left are the best \_\_\_\_\_ agents.

The elements at the bottom right are the best \_\_\_\_\_ agents.

### IMPORTANT REDOX REACTIONS

#### 1) METAL DISPLACEMENT REACTIONS

The Standard Reduction Table shows the relative ease of reduction (the ability to \_\_\_\_\_ electrons). Metal ions near the bottom are \_\_\_\_\_ to reduce. That is they are **more stable as ions**. As you go up the Table metals ions are more likely to be reduced (gain electrons) to become metals. These metals are more stable in their metallic state than in their ionic state.

Which 3 metals prefer to be in their metallic state? \_\_\_\_\_

Which 3 metals prefer to be in their ionic state? \_\_\_\_\_

Would you expect a reaction to occur if zinc metal is added to a solution containing  $\text{Ag}^+$  ions? \_\_\_\_\_ Explain your answer. \_\_\_\_\_

Would you expect a reaction to occur if iron metal is added to a solution containing  $\text{Ca}^{2+}$  ions? \_\_\_\_\_ Explain your answer. \_\_\_\_\_

Complete the following table.

METAL	METAL ION	REACTION (yes/no)
magnesium	zinc ( $\text{Zn}^{2+}$ )	yes

zinc	silver ( )	
copper	nickel ( )	
aluminium	cobalt ( )	
silver	copper (II) ( )	
lead	sodium ( )	

### GENERAL EQUATION

\_\_\_\_\_ + \_\_\_\_\_ → \_\_\_\_\_ + \_\_\_\_\_

For this reaction to occur what relative position on the SRT must the metal and metal ion have?

### 2) HALOGEN DISPLACEMENT REACTIONS

Halogens (Group \_\_\_\_ ) can react with their ions (halogen ions are called \_\_\_\_\_).

Starting at the top of the Standard Reduction Table write down the order of appearance of the halogens. \_\_\_\_\_

Compare this to the periodic table. What is the similarity? \_\_\_\_\_

In terms of atomic structure, why is fluorine a stronger oxidising agent than iodine?

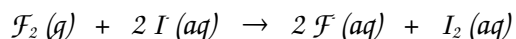
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\_\_\_\_\_  
\_\_\_\_\_

Complete the following table.

<i>HALOGEN</i>	<i>HALIDE</i>	<i>REACTION (yes/no)</i>
<i>fluorine</i>	<i>iodide (I)</i>	<i>yes</i>
<i>chlorine</i>	<i>fluoride ( )</i>	
<i>iodine</i>	<i>bromide ( )</i>	
<i>bromine</i>	<i>iodide ( )</i>	

For any reaction above write the balanced chemical equation.



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GENERAL EQUATION

\_\_\_\_\_ + \_\_\_\_\_ → \_\_\_\_\_ + \_\_\_\_\_

For this reaction to occur what relative position on the SRT must the halogen and halide have?

\_\_\_\_\_

### 3) DISPROPORTIONATION REACTIONS

Some chemicals will react with themselves and be oxidised and reduced. Look at pages 5 and 5, hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) can act as an oxidant or as a reductant. Copy the half equations and write the disproportionation reaction for hydrogen peroxide.

Half equations LEO \_\_\_\_\_

GER \_\_\_\_\_

Redox equation \_\_\_\_\_

This reaction occurs slowly without a catalyst. A beaker of hydrogen peroxide is left what will be in the beaker after a long period of time?

\_\_\_\_\_

Copper (I) in solution will readily disproportionate. Write the equations.

Half equations LEO \_\_\_\_\_

GER \_\_\_\_\_

Redox equation \_\_\_\_\_

#### 4) HYPOCHLORITE REACTION

Hypochlorite is common household source of chlorine. Chlorine is a strong oxidising agent and is used to kill bacteria and algae. What are 2 common uses of hypochlorite/chlorine?

Hypochlorite reacts with hydrogen ions to form hypochlorous acid (HOCl) which is the antibacterial agent and algicide. Write a balanced equation for the production of HOCl.

A number of unbalanced redox reactions are listed below. In each case:

- identify the oxidant and reductant;
- balance the equations.

- $\text{ClO}_3^- + \text{MnO}_4^- + \text{H}^+ \rightarrow \text{MnO}_2 + \text{ClO}_4^- + \text{H}_2\text{O}$
- $\text{Cr}_2\text{O}_7^{2-} + \text{H}^+ + \text{I}_2 \rightarrow \text{IO}_3^- + \text{Cr}^{3+} + \text{H}_2\text{O}$
- $\text{H}_2\text{SO}_3 + \text{MnO}_4^- \rightarrow \text{Mn}^{2+} + \text{H}_2\text{O} + \text{SO}_4^{2-} + \text{H}^+$
- $\text{NO}_3^- + \text{H}^+ + \text{S} + \text{H}_2\text{O} \rightarrow \text{NO} + \text{H}_2\text{SO}_3$
- $\text{MnO}_4^{2-} + \text{H}^+ \rightarrow \text{MnO}_4^- + \text{MnO}_2 + \text{H}_2\text{O}$
- $\text{PbO}_2 + \text{H}^+ + \text{Mn}^{2+} \rightarrow \text{MnO}_4^- + \text{Pb}^{2+} + \text{H}_2\text{O}$
- $\text{CuS} + \text{H}^+ + \text{NO}_3^- \rightarrow \text{Cu}^{2+} + \text{S} + \text{NO} + \text{H}_2\text{O}$
- $\text{I}_2 + \text{H}^+ + \text{NO}_3^- \rightarrow \text{IO}_3^- + \text{NO}_2 + \text{H}_2\text{O}$
- $\text{H}^+ + \text{Br}^- + \text{PbO}_2 \rightarrow \text{Pb} + \text{Br}_2 + \text{H}_2\text{O}$

Write ionic half equations and overall ionic equations for each of the following:

- Zinc metal decolourises copper (II) sulfate solution.
- Chlorine turns NaBr solution red.
- Magnesium dissolves in hydrochloric acid.
- $\text{MnO}_2$  solid reacts with concentrated hydrochloric acid, producing a greenish gas and a solution of  $\text{MnCl}_2$ .
- $\text{Na}_2\text{SO}_3$  decolourises a purple solution of acidified  $\text{KMnO}_4$ .
- $\text{SnCl}_2$  solution turns orange  $\text{K}_2\text{Cr}_2\text{O}_7$  solution green  $\text{Cr}^{3+}$  in acid solution.
- Metallic iron dissolves in dilute  $\text{H}_2\text{SO}_4$  yielding a colourless gas and a pale green solution of  $\text{FeSO}_4$ .
- Metallic magnesium reacts with silver nitrate solution.
- Chlorine reacts with  $\text{H}_2\text{S}$  solution, producing a pale yellow precipitate of sulfur.
- Bromine reacts with a solution of KI.
- A solution of KI reacts with an acidified solution of  $\text{KMnO}_4$ .

### REDOX TITRATIONS



What is a standard solution and what are 2 ways to get a standard solution?

To be used as a primary standard a chemical should be:

- a)
- b)
- c)

During the titration what is an equivalence point? How is this different from the endpoint?

1. 24.3 mL of  $0.02 \text{ mol L}^{-1} \text{KMnO}_4$  reacted with 20.0 mL of an iron(II) solution.
  - a) Write a balanced redox equation for the permanganate ion oxidising the iron(II) ion.
  - b) Calculate the molarity of the iron(II) ion.
  - c) How do recognise the end-point in this titration?
  - d) Calculate the percentage of iron in a sample of steel wire if 1.51 g of the wire was dissolved in excess of dilute sulfuric acid and the solution made up to 250 mL in a standard flask, 25.0 mL of this solution was pipetted into a conical flask and needed 25.45 mL of  $0.02 \text{ mol L}^{-1} \text{KMnO}_4$  for complete oxidation.
2. Given the following two half-reactions  
 $\text{S}_4\text{O}_6^{2-}(\text{aq}) + 2\text{e}^- \rightarrow 2 \text{S}_2\text{O}_3^{2-}(\text{aq})$  and  $\text{I}_2(\text{aq}) + 2\text{e}^- \rightarrow 2\text{I}^-(\text{aq})$ 
  - a) Write a balanced redox equation for the reaction of the thiosulfate ion  $\text{S}_2\text{O}_3^{2-}$  and iodine.
  - b) What mass of iodine reacts with 23.5 mL of  $0.012 \text{ mol L}^{-1}$  sodium thiosulfate solution.
  - c) 25 mL of a solution of iodine in potassium iodide solution required 26.5 mL of  $0.095 \text{ mol L}^{-1}$  sodium thiosulfate solution to titrate the iodine. What is the molarity of the iodine solution and the mass of iodine per L?
3. 2.83 g of a sample of haematite iron ore [iron (III) oxide,  $\text{Fe}_2\text{O}_3$ ] were dissolved in concentrated hydrochloric acid and the solution diluted to 250 mL. 25.00 mL of this solution was reduced with tin(II) chloride (which is oxidised to  $\text{Sn}^{4+}$  in the process) to form a solution of iron(II) ions. This solution required 26.4 mL of  $0.02 \text{ mol L}^{-1}$  potassium dichromate for oxidation.
  - a) Given the half-cell reactions  
 $\text{Sn}^{4+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sn}^{2+}(\text{aq})$   
 $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14 \text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow 2 \text{Cr}^{3+}(\text{aq}) + 7 \text{H}_2\text{O}(\text{l})$
  - b) Write a balanced redox equations for the reactions

- i) the reduction of iron(III) ions by tin(II) ions and
    - ii) the oxidation of iron(II) ions by the dichromate ion.
  - c) Calculate the percentage of iron(III) oxide in the ore.
4. An approximately  $0.02 \text{ mol L}^{-1}$  potassium permanganate solution was standardised against precisely  $0.1 \text{ mol L}^{-1}$  iron(II) ammonium sulfate solution.  $25.00 \text{ mL}$  of the solution of the iron(II) salt were oxidised by  $24.15 \text{ mL}$  of the permanganate solution. What is the molarity of the potassium permanganate solution?
  5.  $10.0 \text{ g}$  of iron(II) ammonium sulfate crystals were made up to  $250 \text{ mL}$  of acidified aqueous solution.  $25 \text{ mL}$  of this solution required  $21.25 \text{ mL}$  of  $0.02 \text{ mol L}^{-1}$  potassium dichromate for oxidation. Calculate  $x$  in the formula  $\text{FeSO}_4 \cdot (x\text{H}_2\text{SO}_4)_2 \cdot x\text{H}_2\text{O}$ .
  6. Given the half-reaction  $\text{C}_2\text{O}_4^{2-}(\text{aq}) \rightarrow 2 \text{CO}_2(\text{g}) + 2 \text{e}^-$ 
    - a) Write a balanced redox equation for permanganate ions oxidising the ethanedioate (oxalate) ion.
    - b)  $1.520 \text{ g}$  of ethanedioic acid crystals,  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , was made up to  $250 \text{ mL}$  of aqueous solution and  $25.0 \text{ mL}$  of this solution needed  $24.55 \text{ mL}$  of a potassium permanganate solution for oxidation. Calculate the molarity of the permanganate solution and its concentration in  $\text{g L}^{-1}$ .
  7. A standardisation of potassium permanganate solution yielded the following data:  $0.15 \text{ g}$  of potassium tetroxalate,  $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  needed  $23.2 \text{ mL}$  of the permanganate solution. What is the molarity of the permanganate solution? Use the equation and reasoning from Q6 to help you.
  8. Given the half-cell equation  $\text{O}_2(\text{g}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{H}_2\text{O}_2(\text{aq})$ 
    - a) Write a balanced redox ionic equation for the oxidation of hydrogen peroxide by potassium permanganate.
    - b)  $50 \text{ mL}$  of solution of hydrogen peroxide were diluted to  $1 \text{ L}$  with water.  $25.0 \text{ mL}$  of this solution, when acidified with dilute sulfuric acid, reacted with  $20.25 \text{ mL}$  of  $0.02 \text{ mol L}^{-1}$   $\text{KMnO}_4$ . What is the concentration of the original hydrogen peroxide solution in  $\text{mol L}^{-1}$ ?
  9.  $13.2 \text{ g}$  of iron(III) alum were dissolved in water and reduced to an iron(II) ion solution by zinc and dilute sulfuric acid. The mixture was filtered and the filtrate and washings made up to  $500 \text{ mL}$  in a standard volumetric flask.  $20.0 \text{ mL}$  of this solution required  $26.5 \text{ mL}$  of  $0.01 \text{ mol L}^{-1}$   $\text{KMnO}_4$  for oxidation. Calculate the percentage by mass of iron in iron alum.
  10. Calculate the concentration in  $\text{mol L}^{-1}$  and  $\text{g L}^{-1}$ , of a sodium ethanedioate ( $\text{Na}_2\text{C}_2\text{O}_4$ ) solution,  $5.00 \text{ mL}$  of which were oxidised in acid solution by  $24.5 \text{ mL}$  of a potassium permanganate solution containing  $0.05 \text{ mol L}^{-1}$ .

#### ANSWERS

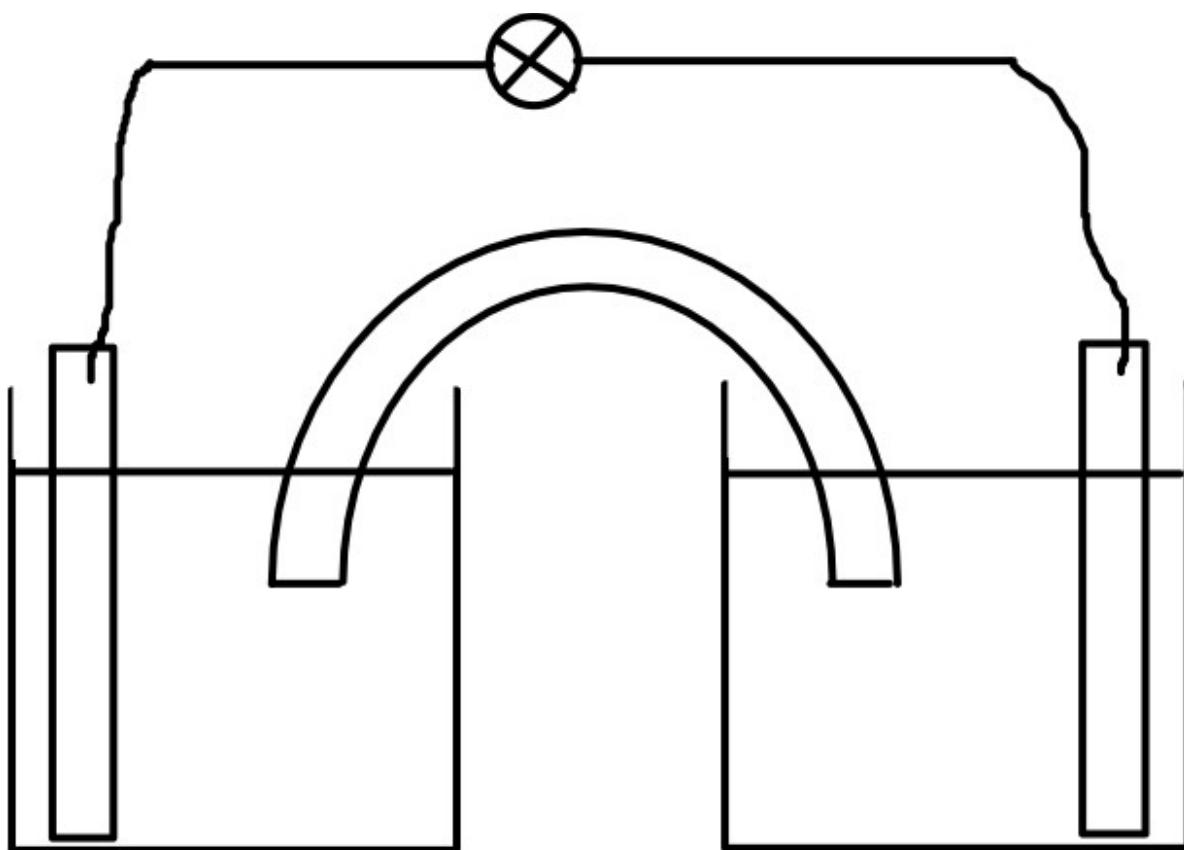
1.
  - a)  $\text{MnO}_4^-(\text{aq}) + 5 \text{Fe}^{2+}(\text{aq}) + 8 \text{H}^+(\text{aq}) \rightarrow \text{Mn}^{2+}(\text{aq}) + 5 \text{Fe}^{3+}(\text{aq}) + 4 \text{H}_2\text{O}(\text{l})$
  - b)  $n(\text{MnO}_4^-) = c \chi V = .02 \chi 0.0243 = 0.000486$   
 $n(\text{Fe}^{2+}) = 5 \chi 0.000486 = 0.00243$   
 $c = 0.122 \text{ mol L}^{-1}$
  - c) The purple solution does not turn colourless.
  - d)  $n(\text{MnO}_4^-) = c \chi V = .02 \chi 0.02545 = 0.000509$   
 $n(\text{Fe}^{2+}) = 5 \chi 0.000509 = 0.002545 \text{ moles in } 25 \text{ mL}$   
 $\text{In } 250 \text{ mL} = 250/25 \chi 0.002545 = 0.02545 \text{ moles}$   
 $m = n \chi M = 0.02545 \chi 55.85 = 1.42 \text{ g}$   
 $\% \text{ Fe} = 1.42/1.51 \chi 100 = 94.1 \%$
2.
  - a)  $2 \text{S}_2\text{O}_3^{2-}(\text{aq}) + \text{I}_2(\text{aq}) \rightarrow 2 \text{I}^-(\text{aq}) + \text{S}_4\text{O}_6^{2-}(\text{aq})$

- b)  $n(S_2O_3^{2-}) = 0.000282 \text{ mol}$   
 $n(I_2) = 0.000141 \text{ mol}$   
 $m(I_2) = 0.0358 \text{ g}$
- c)  $n(S_2O_3^{2-}) = 0.00252 \text{ mol}$   
 $n(I_2) = 0.00126 \text{ mol}$   
 $c(I_2) = 0.0503 \text{ mol L}^{-1} = 12.8 \text{ g L}^{-1}$
3. a) i)  $Sn^{2+} + 2 Fe^{3+} \rightarrow Sn^{4+} + 2 Fe^{2+}$   
 ii)  $Cr_2O_7^{2-}(aq) + 14 H^+(aq) + 6 Fe^{2+}(aq) \rightarrow 2 Cr^{3+}(aq) + 7 H_2O(l) + 6 Fe^{3+}$   
 b)  $n(Cr_2O_7^{2-}) = 0.000528$   
 $n(Fe^{2+}) = 0.00317 = 0.00158 \times 250/25 = 0.0158 \text{ mol of } Fe_2O_3 = 2.53 \text{ g}$   
 $\% = 89.3$
4.  $MnO_4^-(aq) + 5 Fe^{2+}(aq) + 8 H^+(aq) \rightarrow Mn^{2+}(aq) + 5 Fe^{3+}(aq) + 4 H_2O(l)$   
 $n(Fe^{2+}) = 0.0025$   
 $n(MnO_4^-) = 0.0005$   
 $c = 0.0207 \text{ mol L}^{-1}$
5.  $Cr_2O_7^{2-}(aq) + 14 H^+(aq) + 6 Fe^{2+}(aq) \rightarrow 2 Cr^{3+}(aq) + 7 H_2O(l) + 6 Fe^{3+}$   
 $n(Cr_2O_7^{2-}) = 0.000425 \text{ mol}$   
 $n(Fe^{2+}) = 0.00255 \times 10 = 0.0255 \text{ mol in } 250 \text{ mL}$   
 $M = 392.2 \text{ g} \cdot 283.9 = 108.3 / 18 = 6$
6.  $5 C_2O_4^{2-}(aq) + 2 MnO_4^-(aq) + 16 H^+(aq) \rightarrow 10 CO_2(g) + 2 Mn^{2+}(aq) + 8 H_2O$   
 $n(H_2C_2O_4 \cdot 2H_2O) = 0.01206 \text{ mol in } 250 \text{ mL} = 0.001206 \text{ mol in } 25 \text{ mL}$   
 $c(MnO_4^-) = 0.02 \text{ mol L}^{-1} = 3.04 \text{ g L}^{-1}$
7.  $5 (C_2O_4)_2^{4-}(aq) + 4 MnO_4^-(aq) + 32 H^+(aq) \rightarrow 20 CO_2(g) + 4 Mn^{2+}(aq) + 16 H_2O$   
 $n(KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O) = 0.00059 \text{ mol}$   
 $n(MnO_4^-) = 0.000472 \text{ mol}$   
 $c(MnO_4^-) = 0.0204 \text{ mol L}^{-1}$
8. a)  $2 MnO_4^-(aq) + 6 H^+(aq) + 5 H_2O_2 \rightarrow 2 Mn^{2+}(aq) + 8 H_2O + 5 O_2(g)$   
 b)  $n(MnO_4^-) = 0.000405 \text{ mol}$   
 $n(H_2O_2) = 0.00101 \text{ mol in } 25 \text{ mL}$   
 $c(H_2O_2) = 0.0405 \text{ mol L}^{-1} \text{ (diluted)}$   
 $c(H_2O_2) = 0.81 \text{ mol L}^{-1} \text{ (conc)}$
9.  $MnO_4^-(aq) + 5 Fe^{2+}(aq) + 8 H^+(aq) \rightarrow Mn^{2+}(aq) + 5 Fe^{3+}(aq) + 4 H_2O(l)$   
 $n(MnO_4^-) = 0.000265 \text{ mol}$   
 $n(Fe^{2+}) = 0.00133 \text{ mol in } 20 \text{ mL}$   
 $n(Fe^{2+}) = 0.0331 \text{ mol in } 500 \text{ mL} = n(Fe) \text{ in iron alum}$   
 $m(Fe) = 1.85 \text{ g} = 14.0 \%$
10.  $5 C_2O_4^{2-}(aq) + 2 MnO_4^-(aq) + 16 H^+(aq) \rightarrow 10 CO_2(g) + 2 Mn^{2+}(aq) + 8 H_2O$   
 $n(MnO_4^-) = 0.00123 \text{ mol}$   
 $n(C_2O_4^{2-}) = 0.00306 \text{ mol}$   
 $c(C_2O_4^{2-}) = 0.613 \text{ mol L}^{-1} = 82.1 \text{ g L}^{-1}$

## ELECTROCHEMICAL CELLS

Luigi Galvani was experimenting with animal parts and noticed frog legs on a copper hook jumped when they touched an iron rail. This experiment leads to the idea that 2 metals connected by a conducting solution can make electricity. Galvanic or electrochemical cells are designed so that half-equations occur in separate containers.

If a redox reaction is separated with oxidation occurring in one place and reduction in a different container then these reactions can be joined by an external wire to carry the electrons from the reduction cell to the oxidation cell. Draw an example of an electrochemical cell called the "Daniell Cell".



*Define the following words:*

1) *Electrolyte*

2) *Electrode*

3) *Anode*

4) *Cathode*

5) *Salt bridge*

6) *Anion*

7) Cation

8) External Circuit

The metal ion higher on the Standard Reduction Table will be reduced so the other metal will be oxidised.  
Which metal is higher? \_\_\_\_\_ Which metal is lower? \_\_\_\_\_

Answer the following:

- 1) If the metal higher is to be reduced then write the half equation showing the metal ion being reduced. This half of the cell has the voltage as written in the S.R.T.
- 2) If the lower metal is to be oxidised then write the half equation showing the metal being oxidised. Opposite direction to the S.R.T. This half of the cell has the voltage with the opposite sign to the one written in the S.R.T.
- 3) Add the half equation together and calculate the voltage of the cell.

	<u>EQUATIONS</u>	<u>EMF</u>
GERC	_____	_____ V
LEOA	_____	_____ V
REDOX	_____	_____ V

There is a method of abbreviating the electrochemical cell. For the Daniell Cell it is:  $\text{Zn}/\text{Zn}^{2+} // \text{Cu}^{2+}/\text{Cu}$ . Put the following words in the correct order: oxidising product, cathode, anode, oxidant.

---

Answer the questions (1, 2 & 3) as above for the following cells and write the abbreviation for each cell:

- a) Cu in  $\text{CuSO}_4$  joined to Ag in  $\text{AgNO}_3$  \*
- b) Mg in  $\text{MgSO}_4$  joined to Pb in  $\text{Pb}(\text{NO}_3)_2$
- c) Cu in  $\text{CuSO}_4$  joined to Pb in  $\text{Pb}(\text{NO}_3)_2$
- d) Ni in  $\text{NiSO}_4$  joined to Al in  $\text{AlCl}_3$  \*
- e) Sn in  $\text{SnSO}_4$  joined to Co in  $\text{CoCl}_2$

\* Doubling or tripling the half equation does NOT change the EMF.

#### PREDICTING REDOX REACTIONS

Will hydrogen gas react with chlorine gas? This question can be answered using the S. R. T. Write the half equations as they appear in the S. R. T. remembering to reverse the oxidation equation and EMF SIGN.

	<u>EQUATIONS</u>	<u>EMF</u>
GERC	_____	_____ V
LEOA	_____	_____ V
REDOX	_____	_____ V

If the final EMF is zero or negative then no reaction will occur.

If the final EMF is more than zero then a reaction can occur. It does not take into account the speed of reaction so some reactions with a positive EMF react very slowly. The larger the value the more likely the reaction is to be spontaneous, in other words, occur with no changes in conditions.

Would you expect the  $\text{H}_2/\text{Cl}_2$  reaction to be spontaneous? \_\_\_\_\_

Explain the following observations; this mixture is unreactive in the dark but explodes when put into strong light.

Can the following reactions occur? Calculate the EMF for the reactions and explain why/why not.

- Al metal with  $\text{Ag}^+$
- Cu metal with  $\text{F}_2$
- Cu metal with  $\text{Na}^+$
- Zinc ions with  $\text{H}_2$

### QUESTIONS

1. a) Illustrate the experimental arrangement by which the following half-cells could be coupled together to produce a cell EMF.

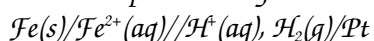
- $\text{Ag}^+$ , Ag and  $\text{Sn}^{2+}$ , Sn
- $\text{Cl}_2$ , Cl and  $\text{I}_2$ , I
- $\text{Fe}^{2+}$ , Fe and  $\text{Sn}^{4+}$ ,  $\text{Sn}^{2+}$

b) What are the standard EMF's of the above cells?

c) What are the standard states of the substances in the cells which would result in this standard EMF?

d) Which electrode is the anode and which is the cathode?

2. Consider the cell represented by



a) What is the anode in the cell?

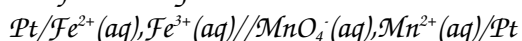
b) Write the anode half-equation.

c) What is the cathode?

d) Write the cathode half-equation.

e) Draw a diagram to show how you would construct this cell. List all of the reagents that you would use.

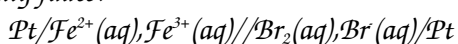
3. a) Using a labelled diagram, label the processes in the following cell which contribute to a flow of electricity.



b) For every 100 electrons that flow through the cell,

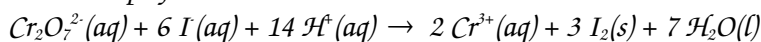
- How many iron (II) ions are oxidised?
- How many permanganate ions are reduced?

4. If the electrodes in the cell represented below are joined by a wire, the colour of one of the solutions gradually fades.



- a) Write the anode half-equation.
- b) Write the cathode half-equation.
- c) Which platinum electrode do we label (+)?
- d) What is the direction of electron flow in the wire?
- e) Which way do the bromide ions move in the cell?
- f) Which way do the  $\text{Fe}^{3+}$  ions move in the solution?
- g) What is the EMF of the cell?
- h) What, if anything, will happen if we mix a solution of iron(III) nitrate and a solution of bromine in water? Write an equation if applicable.
- i) What, if anything, will happen if we mix solutions of iron(II) nitrate and potassium bromide? Write an equation if applicable.

5. Represent all of the reagents and the apparatus required by drawing the cell in which the following reaction could be performed.

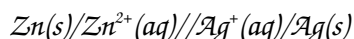


Label the positive and negative electrode; determine the EMF of the cell, and indicate the direction of movement of iodide ions and chromium(III) ions in the cell.

6. a) Explain why silver reacts with nitric acid solutions but not with hydrochloric acid solutions of the same concentration.
- b) Which of the following in aqueous solution oxidise iron but not copper.
  - i) Silver nitrate.
  - ii) Lead(II) nitrate.
  - iii) Bromine.
  - iv) Magnesium sulfate.
  - v) Hydrochloric acid.

7. Care must be taken in the choice of an electrolyte to prepare the salt bridge for a particular cell.

a) Why is a salt bridge containing sodium chloride unsatisfactory for the following cell?



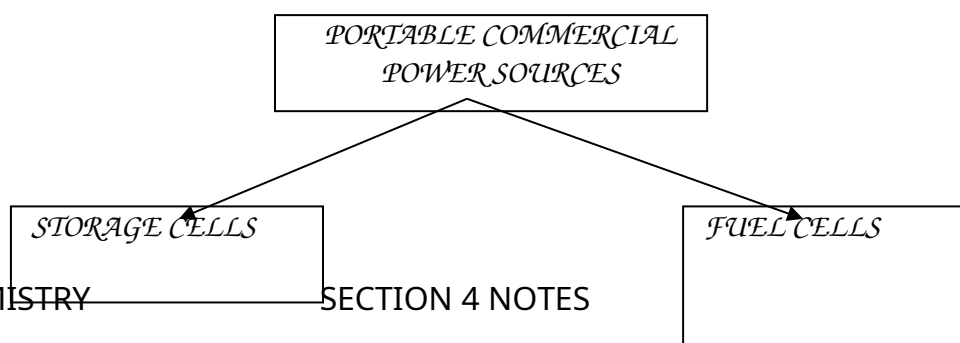
b) Name a cell in which the use of sodium sulfate in the salt bridge is unsatisfactory.

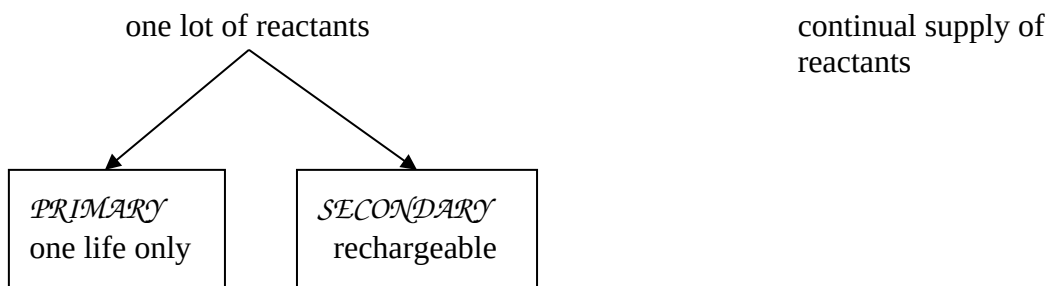
### USES OF ELECTROCHEMICAL CELLS (BATTERIES)

Electrochemical cells are used as portable sources of electricity. These cells are commonly called \_\_\_\_\_.

In each of the batteries below there are structures that each of them have such as; a) 2 e \_\_\_\_\_

- b) an e \_\_\_\_\_
- c) an external c \_\_\_\_\_ and
- d) a r \_\_\_\_\_ reaction producing electricity.





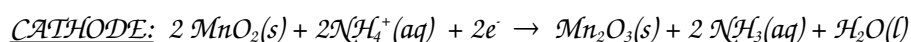
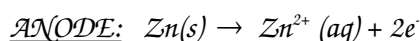
### THE DRY CELL - A PRIMARY CELL

A battery is an electrochemical cell that stores useful energy in the form of an oxidant and a reductant which are capable of releasing energy when required. While any redox reaction could be harnessed as an energy source for a battery, in practice there are certain limitations such as cost, portability, lifetime, etc. which limit the choice of materials.

The two major types of battery are **primary** cells (in which the reaction only occurs once) and **secondary** cells (which can be recharged by passing a current through them).

The most familiar primary cell is the dry cell (or Leclanché cell, after its inventor). The anode consists of a zinc container while the cathode is a graphite rod surrounded by powdered manganese dioxide,  $\text{MnO}_2$ . The space between the electrodes is filled with a moist paste of  $\text{NH}_4\text{Cl}$  and  $\text{ZnCl}_2$ . Is  $\text{NH}_4\text{Cl}$  acidic or basic? \_\_\_\_\_  
Why are some dry cells called alkaline?

The electrode reactions are complex but may be simply represented as

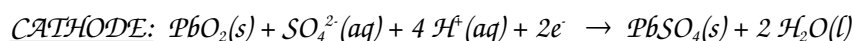
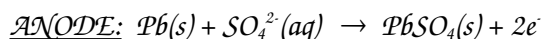


This dry cell has a limited shelf life since the ammonium chloride provides an acidic environment which eventually corrodes the zinc anode. The alkaline batteries overcome this problem to some extent by using a gel of potassium hydroxide as the electrolyte. Both types of dry cell produce a potential difference of around 1.5 volts.

### THE LEAD-ACID BATTERY (LEAD ACCUMULATOR) - A SECONDARY BATTERY

This battery, most commonly found in cars, consists of an anode which is a grid of lead alloy packed with finely divided spongy lead. The cathode is a similar grid packed with lead(IV) oxide powder,  $\text{PbO}_2$ . The electrolyte is a solution which is about 40% sulfuric acid by mass.

At the anode lead is oxidised to  $\text{Pb}^{2+}$  which then combines with the sulfate ions in solution to form insoluble  $\text{PbSO}_4$ . At the anode,  $\text{PbO}_2$  is reduced to  $\text{Pb}^{2+}$  and again  $\text{PbSO}_4$  is produced.





Lead sulfate is formed at each electrode, while sulfuric acid is consumed. As a result the sulfuric acid is diluted and the voltage produced falls. Since sulfuric acid is more dense than water, the extent to which the battery has been discharged can be checked by measuring the density of the electrolyte. The electrolyte in a fully charged battery has a density of around  $1.28 \text{ g mL}^{-1}$  while a flat battery may have an electrolyte density of around  $1.10 \text{ g mL}^{-1}$ .

Unlike the dry cell, the lead-acid battery can be recharged since the products of the cell reaction adhere to the electrodes. If a potential that is larger than the cell voltage is applied to the cell, the electrode reactions can be reversed with  $\text{PbSO}_4$  being reduced to  $\text{Pb}$  at one electrode and oxidised to  $\text{PbO}_2$  at the other.

If a lead-acid battery is recharged too rapidly it may produce hydrogen and oxygen at the electrodes. Not only is there the danger of an explosion, but the electrolysis of water causes water to be lost from the cell and so requires that the cell be topped up from time to time with distilled water. Maintenance-free batteries contain electrodes which are an alloy of lead and calcium. Evolution of hydrogen and oxygen at these electrodes is particularly slow and so there is little electrolysis of water and therefore no need to add water to the battery.

### FUEL CELLS

While recharging can regenerate the oxidants and reductants in secondary cells, it is possible to produce a battery in which the reactants are supplied continuously (and the products removed continuously) to the electrodes. Such a battery is called a **fuel cell**. The most common fuel cell is based on the reaction between hydrogen and oxygen to form water.

The electrodes are porous, compressed carbon containing a suitable catalyst. The electrolyte may be either hydrochloric acid or potassium hydroxide solution. At the anode hydrogen is oxidised to hydrogen ions (in acid electrolyte) or water (in alkaline electrolyte), while at the cathode oxygen is reduced to water (in acid electrolyte) or hydroxide ions (in alkaline media).

ANODE:  $\text{H}_2(\text{g}) \rightarrow 2 \text{H}^+(\text{aq}) + 2\text{e}^-$  (Acid Electrolyte)

CATHODE:  $\text{O}_2(\text{g}) + 4 \text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2 \text{H}_2\text{O}(\text{l})$

The overall reaction is  $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{l})$

Such cells operate continuously as long as the reactants are provided, and because the cell converts the energy of the redox reaction directly to electricity, they are much more efficient than conventional large-scale methods of producing electricity, such as a coal or gas fired power station. However, the major disadvantage of such cells is their expense and while they have been successfully incorporated into some special applications, e.g. spacecraft, they are presently not used for large scale electricity generation.

There are 4 main types of battery needed to know the uses and advantages of are:

<u>TYPE</u>	<u>USES</u>	<u>ADVANTAGES</u>	<u>DISADVANTAGES</u>
Dry Cell			
Alkaline			

Lead Accumulator			
Fuel Cell			

- Write the anode and cathode reactions in the following cells.
  - Nickel-cadmium cell:  

$$\text{Ni}_2\text{O}_3(s) + \text{Cd}(s) + 3 \text{H}_2\text{O}(l) \rightarrow \text{Cd}(\text{OH})_2(s) + 2 \text{Ni}(\text{OH})_2(s)$$
  - Silver oxide-alkaline-zinc cell:  

$$\text{Ag}_2\text{O}(s) + \text{Zn}(s) + \text{H}_2\text{O}(l) \rightarrow 2 \text{Ag}(s) + \text{Zn}(\text{OH})_2(s)$$
- Distinguish between the terms primary cell, secondary cell and fuel cell.
  - Draw and label a typical primary cell, indicating (with equations where relevant) the purpose of each part of the cell.
  - Why does a service station attendant measure the state of charge of your car battery by using a hydrometer to measure the density of the battery fluid? Why does the density of the electrolyte vary?
- In the lead-acid cell, what is the oxidation state of lead in?
  - The anode?
  - The cathode?
  - The anode product?
  - The cathode product?
- What happens to the pH around the cathode as the lead-acid battery is being discharged?
  - What changes in pH might be expected in the region around the cathode of the dry cell?
  - What changes in pH take place around the cathode and the anode during the operation of a fuel cell using hydrochloric acid as the electrolyte?

### STANDARD REDUCTION POTENTIALS

Standard reduction potentials are measured in volts and the emf (electromotive force) of a cell is not a force but a difference in the tendency of one half-cell to attract electrons more than the other. As the emf is a comparison of electron attractions, reduction potentials cannot be measured directly and must be "coupled" to another half-cell. The standard reduction potentials compare each half-cell to the hydrogen half-cell. Why is the hydrogen half-cell potential equal to 0.00 V?

If the  $\text{Cu}^{2+}$  to Cu was the reference cell what would be the e.m.f. of the

- $\text{F}_2$  to F half-cell
- $\text{Na}^+$  to Na half-cell?

The standard reduction potentials are abbreviated as  $E^\circ$  because they are at standard conditions. For a gas = \_\_\_\_\_ pressure and \_\_\_\_\_ temperature and for a solution the concentration = \_\_\_\_\_. What do you think will happen to the voltage if the conditions are not standard?

What are the limitations of the  $E^\circ$  tables?

- 1.
- 2.
- 3.

### SIGN CONVENTIONS

An electrochemical cell has an anode labelled as (-) as it is the source of electrons and the cathode is (+) because electrons are attracted to the source of reduction. However it is not important to remember this, just LEOA and GER. C.

In an electrolytic cell the signs are reversed but again LEOA and GER. C apply.

### CORROSION

Corrosion is a redox reaction where a metal will react with chemicals in its surroundings to form a compound. Usually the chemical reacting with the metal is oxygen gas. For example freshly cut calcium metal will react with oxygen and water to form calcium hydroxide.

GER \_\_\_\_\_ V

LEO \_\_\_\_\_ V

REDOX \_\_\_\_\_ V

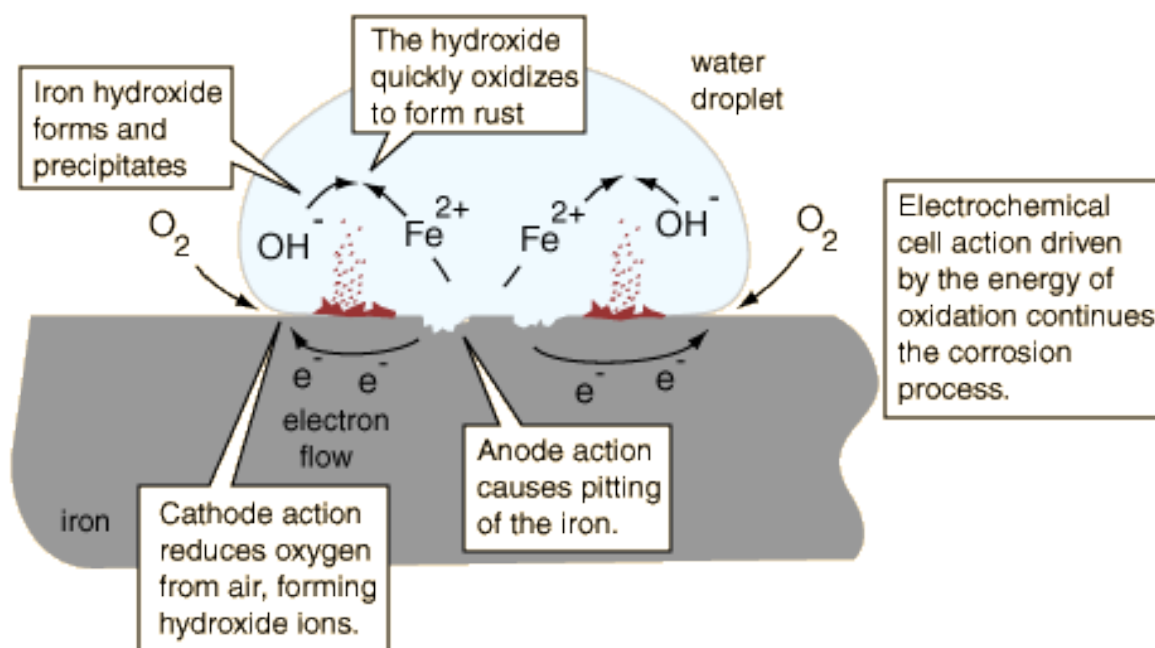
Using the S. R. T. aluminium is a reactive metal, much more reactive than iron but it resists corrosion. Why? \_\_\_\_\_

\_\_\_\_\_

aluminium

iron

Rusting is the name given to the corrosion of iron with oxygen and water. It is an electrochemical and a redox process.



<http://www.chem1.com/acad/webtext/elchem/ec7.html>

*Rusting of iron is 2 steps:*

- Iron is changing to iron (II) and oxygen and water being reduced to hydroxide ions. Write the oxidation and reduction half equations.*
- Iron (II) is further oxidised to form iron (III) oxide monohydrate (\_\_\_\_\_), the structural formula is  $\text{FeO}(\text{OH})$ . Write the full equation.*

*DRAW: labelled diagrams to show the conditions necessary for rusting.*

*Tube A:*

*water and air*

*Tube B:*

*water but no air*

*( boiled water and  
a layer of oil )*

*Tube C:*

*air but no water*

*( Calcium chloride  
to make the air dry )*

*Tube D:*

*ordinary air only*

*Conclusion: It is found that the iron nails in tube A rusted most quickly. Conditions for iron to rust: Both air and water must be present.*

## Methods of preventing rusting

a) PROTECTIVE LAYER: This method of preventing rusting aims to keep water and air from reaching the metal using a layer that covers all the iron. The following are examples of this methods:.

- i) *Painting: applying a coat of paint. For cars, furniture and ships.*
- ii) *Ceramic: coating with a layer of enamel. For pots and lining hot water tanks.*

*One of the most widely used protective layers for steel is another metal. When 2 metals are in contact and exposed to a moist environment you have an electrochemical reaction where one of the metals will be oxidised in preference to the other. Both of the examples below are used to prevent the rusting of iron.*

*iron covered with tin*

*iron covered with zinc*

*If the protective layer is scratched so both metals are exposed to the air only one of the metals will rust. In each example which metal will rust and why?*

—

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iii) *Sacrificial coating. Galvanising is dipping iron into molten zinc to apply a thin layer of zinc to the outside of the iron. Roofing metal.*

iv) *Noble coating. Covering the steel with a metal less reactive than iron will prevent corrosion. Tin - plating: coating with a layer of tin. For food cans.*

b) SACRIFICIAL ANODE. Placing a more reactive metal in contact with iron will mean the reactive metal will be corroded before the steel. Large blocks of zinc are attached to pipelines and ships to prevent the corrosion of the iron.

*Galvanised iron stays shiny and the iron uncorroded for many years.*

*What are 2 reasons for this?*

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c) ELECTRICAL PROTECTION: a D.C. voltage is applied to the steel.

*How does this prevent rusting?*

---

d) ALLOYING IRON: iron is alloyed with other metals. The other metals will corrode and form an oxide layer that covers the iron atoms and makes the alloy more resistant to rusting. Forms a \_\_\_\_\_.

1. *Write the half-equation for the reduction process when iron is corroded by*

a) *Oxygen in a moist environment.*

- b) Dilute sulfuric acid.
- c) If the iron is joined to a piece of copper
- i) What will be the observation in a moist, oxygen-rich environment?
- ii) What differences will be observed if the combination of metals is placed in dilute sulfuric acid?
2. Explain how the corrosion of steel is slowed down by undamaged coatings of
- a) paint;
- b) tin;
- c) zinc.
- Explain what will happen if a scratch is made in each of the above coatings.
3. Explain why rapid corrosion occurs when steel water pipes are joined to copper pipes in Perth.
4. Agricultural fencing wires begin to corrode near joins made by twisting the wire. Explain.
5. Steel wharfs are often protected from corrosion by application of an EMF between the wharf and a lump of suitable metal. Draw a diagram of such a situation, and label the path of the electron flow; the positive and negative terminals of the power supply; the direction of movement of sodium ions in the sea water; the direction of movement of chloride ions in the sea; the anode and cathode. Write the appropriate half-equations for the anode and cathode.
- What would be a "suitable" metal in this process?

### REVISION QUESTIONS FROM TEXTBOOKS

#### **CHEMISTRY FOR WA – STAGE 3**

Review Exercise	Pages	Questions
9.1	265	1-2
9.2	271	1-5
9.3	276	1-4
9.4	286	1-4
9.5	289	1-3
10.1	304	1-6
10.2	308	1-5

End of Chapter Questions	Pages	Questions
Chapter Nine	291	1-24
Chapter Ten	310	1-16

#### **EXPLORING CHEMISTRY – STAGE 3**

Sets 20-23.

#### KEYWORDS

- |                       |                         |                     |
|-----------------------|-------------------------|---------------------|
| 1. Oxidation          | 2. Reduction            | 3. Oxidation Number |
| 4. Redox Reaction     | 5. Oxidising Agent      | 6. Reducing Agent   |
| 7. Metal Displacement | 8. Electrochemical cell | 9. anode            |
| 10. Electrolyte       | 11. Electrode           | 12. Cathode         |
| 13. Salt Bridge       | 14. Anion               | 15. Cation          |
| 16. Storage Cell      | 17. Fuel Cell           | 18. Primary Cell    |

- |                       |                      |                         |
|-----------------------|----------------------|-------------------------|
| 19. Secondary Cell    | 20. Dry Cell         | 21. Electrolysis        |
| 24. Corrosion         | 25. Sacrificial      | 26. Noble Coating       |
| 27. Alloy             | 28. Lead Accumulator | 29. Non-inert electrode |
| 30. Oxidant           | 31. Reductant        | 32. Disproportionation  |
| 33. Standard Solution | 34. Primary Standard | 35. Endpoint            |
| 36. Equivalence Point | 37. Titre            | 38. Aliquot             |

# ANSWERS

PAGE 4

1. a)

b)

8. a) A salt bridge is to carry charge between the 2 halves of the cell but the Cl<sup>-</sup> ion will react with the Ag<sup>+</sup> to form a ppt and no charge will be transferred, so a different electrolyte like KNO<sub>3</sub> would be better.

b)  $Zn(s)/Zn^{2+}(aq)//Pb^{2+}(aq)/Pb(s)$

PAGE 11

1. a)  $Cd(s) \rightarrow Cd^{2+} + 2e^-$   
 $Ni^{3+} + e^- \rightarrow Ni^{2+}$

b)  $Ag_2O(s) + Zn(s) + H_2O(l) \rightarrow 2Ag(s) + Zn(OH)_2(s)$   
 $Ag_2O(s) + Zn(s) + H_2O(l) \rightarrow 2Ag(s) + Zn(OH)_2(s)$

2. a)

b), c)  $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$  +  
 $SO_2(g) + 2H_2O(l) \rightarrow 3H^+(aq) + HSO_4^-(aq) + 2e^-$  -0.17  
+1. V

d)

3. a) Primary - one set of reactants, cannot be recharged.  
Secondary - one set of reactants, can be recharged.  
Fuel - continuous feed of reactants, no need to be recharged.

b)

c) A measure of how much charge is left in the battery is how much sulfuric acid is left. Sulfuric acid is more dense so as the battery uses its acid the electrolyte becomes less dense and less charge is available. The acid is used up during the reaction and if not much acid is left the battery is nearly flat.

4. a) 0 b) +4 c) +2 d) +2

5. a) pH increases, the H<sup>+</sup> are being used and the surrounding solution is becoming more alkaline.

b) pH increases, the acidic NH<sub>4</sub><sup>+</sup> are being used, basic NH<sub>3</sub> is being made and the surrounding paste becomes more alkaline.

c)

6. Which of the following are not redox reactions?

(a)  $SO_2 + 2H_2S \rightarrow 2H_2O + 3S$



- (b)  $3\text{SO}_2 + \text{Cr}_2\text{O}_7^{2-} + 2\text{H}^+ \rightarrow 3\text{SO}_4^{2-} + 2\text{Cr}^{3+} + \text{H}_2\text{O}$   
 (c)  $\text{BaO} + \text{SO}_2 \rightarrow \text{BaSO}_3$   
 (d)  $\text{SO}_2 + 2\text{NO}_3^- \rightarrow \text{SO}_4^{2-} + 2\text{NO}_2$   
 (e)  $2\text{Mg} + \text{SO}_2 \rightarrow 2\text{MgO} + \text{S}$   
 (f)  $2\text{H}^+ + \text{Zn} \rightarrow \text{Zn}^{2+} + \text{H}_2$   
 (g)  $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$   
 (h)  $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$   
 (i)  $2\text{FeCl}_2 + \text{Cl}_2 \rightarrow 2\text{FeCl}_3$   
 (j)  $\text{Cu} + 4\text{H}^+ + \text{SO}_4^{2-} \rightarrow \text{Cu}^{2+} + \text{SO}_2 + 2\text{H}_2\text{O}$

7. Which of the following would not be an oxidation product of  $\text{H}_2\text{S}$ ?

- (a)  $\text{SO}_2$ ; (b)  $\text{S}$ ; (c)  $\text{S}_2$ ; (d)  $\text{H}_2\text{SO}_4$ ; (e)  $\text{Na}_2\text{S}$

8. Which of the following would not be a reduction product of  $\text{HNO}_3$ ?

- (a)  $\text{NO}_2$ ; (b)  $\text{NO}$ ; (c)  $\text{N}_2\text{H}_4\text{NO}_3$ ; (d)  $\text{N}_2$ ; (e)  $\text{N}_2\text{O}$ ; (f)  $\text{N}_2\text{O}_5$ .

9. Which of the following can not act as an oxidant?

- (a)  $\text{Fe}^{2+}$ ; (b)  $\text{Cl}^-$ ; (c)  $\text{CO}$ ; (d)  $\text{SO}_2$ ; (e)  $\text{Cl}_2$ .

10. Which of the following could theoretically act as either an oxidant or reductant?

- (a)  $\text{NO}_2$ ; (b)  $\text{S}_2$ ; (c)  $\text{S}$ ; (d)  $\text{NO}_3^-$ ; (e)  $\text{HCl}$ .

11. Provide partial ionic equations for the following conversions in acid solution:

12.

13. State which of the following reactions are redox reactions (for the redox reactions, provide the partial equations to show both the reductions and the oxidation components):

- (a)  $2\text{Hg}^{2+} + \text{Sn}^{2+} \rightarrow \text{Hg}_2^{2+} + \text{Sn}^{4+}$ ;  
 (b)  $\text{CaCO}_3 + 2\text{H}^+ \rightarrow \text{Ca}^{2+} + \text{CO}_2 + \text{H}_2\text{O}$ ;  
 (c)  $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$ ;  
 (d)  $2\text{CrO}_4^{2-} + 2\text{H}^+ \rightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$   
 (e)  $\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{H}^+ + \text{Cl}^-$ ;  
 (f)  $\text{H}_2\text{O}_2 + \text{NO}_2^- \rightarrow \text{H}_2\text{O} + \text{NO}_3^-$   
 (g)  $2\text{FeCl}_3 + \text{H}_2\text{S} \rightarrow 2\text{FeCl}_2 + 2\text{HCl} + \text{S}$ .

Question 11: Calculate  $x$  in the formula  $\text{FeSO}_4 \cdot x\text{H}_2\text{O}$  from the following data: 12.18 g of iron(II) sulfate crystals were made up to 500 mL acidified with sulfuric acid. 25.0 mL of this solution required 43.85 mL of  $0.01 \text{ mol L}^{-1} \text{KMnO}_4$  for complete oxidation.

Question 12: Given the half-reaction  $\text{NO}_3^-(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{NO}_2^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$

(a) give the ionic equation for potassium permanganate oxidising nitrate(III) to nitrate(V)

(b) 24.2 mL of sodium nitrate(III) [sodium nitrite] solution, added from a burette were needed to discharge the colour of 25 mL of an acidified  $0.025 \text{ mol L}^{-1} \text{KMnO}_4$  solution. What was the concentration of the nitrate(III) solution in grammes of anhydrous salt per L?

Question 13: 2.68 g of iron(II) ethanedioate,  $\text{FeC}_2\text{O}_4$ , were made up to 500 mL of acidified aqueous solution. 25.0 mL of this solution reacted completely with 28.0 mL of 0.02 mol  $\text{L}^{-1}$  potassium permanganate solution. Calculate the mole ratio of  $\text{KMnO}_4$  to  $\text{FeC}_2\text{O}_4$  taking part in this reaction. Give the full redox ionic equation for the reaction.

Question 14: Given the half-cell reaction  $\text{IO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) + 5\text{e}^- \rightleftharpoons \frac{1}{2}\text{I}_2(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$  (see also Q2)

(a) deduce the redox equation for iodate(V) ions oxidising iodide ions.

(b) what volume of 0.012 mol  $\text{L}^{-1}$  iodate(V) solution reacts with 20.0 mL of 0.100 mol  $\text{L}^{-1}$  iodide solution?

(c) (i) Calculate the concentration in g  $\text{L}^{-1}$  of a solution of potassium iodate(V) from the data: 25.0 mL of the potassium iodate solution were added to about 15 mL of a 15% solution of potassium iodide (ensures excess iodide ion). On acidification, the liberated iodine needed 24.1 mL of 0.05 mol  $\text{L}^{-1}$  sodium thiosulfate solution to titrate it. (ii) What indicator is used for this titration?

Question 15: Calculate the molarities of iron(II) and iron(III) ions in a mixed solution from the following data.

(i) 25.0 mL of the original mixture was acidified with dilute sulfuric acid and required 22.5 mL of 0.02 mol  $\text{L}^{-1}$   $\text{KMnO}_4$  for complete oxidation.

(ii) a further 25.0 mL of the original iron(II)/iron(III) mixture was reduced with zinc and acid and it then required 37.6 mL of the  $\text{KMnO}_4$  for complete oxidation.

Question 16: 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 sulfuric acid to give 250 mL of solution. The solution contains  $\text{Fe}^{2+}$  ions from the unrusted iron dissolving in the acid, and,  $\text{Fe}^{3+}$  ions from the rusted iron.

(a) 25.0 mL of this solution required 16.9 mL of 0.020 mol  $\text{L}^{-1}$   $\text{KMnO}_4$  for complete oxidation of the  $\text{Fe}^{2+}$  ions. Calculate the moles of  $\text{Fe}^{2+}$  ions in the sample titrated.

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

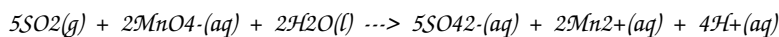
(c) From your calculations in (a) and (b) calculate the ratio of rusted iron to unrusted iron and hence the percentage of iron that had rusted.

13. 10.0 mL of 0.200 mol  $\text{L}^{-1}$   $\text{H}_2\text{O}_2$  exactly reduces 5.00 mL of a  $\text{KMnO}_4$  solution.

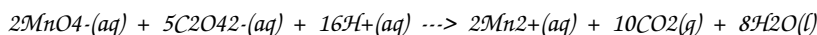
- (a) Find the concentration of the  $\text{KMnO}_4$  solution.  
 (b) Express the concentration found in (a) in  $\text{g L}^{-1}$ .

14. 1.70 g of an impure sample of anhydrous oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4$ , completely reacts with 4.34 mL of  $1.20 \text{ mol L}^{-1} \text{KMnO}_4$ . Find the percentage by mass of oxalic acid in the sample.

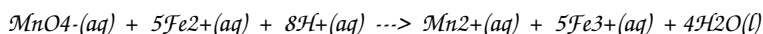
15. The amount of sulfur dioxide in a sample of air can be determined by bubbling the air through acidified potassium permanganate solution.



The excess permanganate can be determined by titration with  $\text{Fe}^{2+}(\text{aq})$  solution. In a typical experiment, 10.0 mL of air, at  $20^\circ\text{C}$  and 1 atm. pressure, was passed through 100 mL of  $\text{KMnO}_4$  solution. The excess  $\text{MnO}_4^-$  was titrated with  $\text{Fe}^{2+}$  solution. A titre of 31.62 mL was obtained. The  $\text{KMnO}_4$  solution was standardised by reacting it with 20.00 mL aliquots of sodium oxalate,  $\text{Na}_2\text{C}_2\text{O}_4$ , solution.



21.68 mL of the permanganate solution was needed. The oxalate solution was made by dissolving 3.390 g of  $\text{Na}_2\text{C}_2\text{O}_4$  in 250 mL of distilled water. The molarity of the  $\text{Fe}^{2+}$  solution was obtained by titrating it with the permanganate solution. 20.00 mL of the  $\text{Fe}^{2+}$  solution needed 19.73 mL of the permanganate solution.



- (a) What are the molarities of the  $\text{Na}_2\text{C}_2\text{O}_4$ ,  $\text{KMnO}_4$ , and  $\text{Fe}^{2+}$  solutions?  
 (b) How much  $\text{MnO}_4^-$  was present before the air was bubbled through it?  
 (c) How much  $\text{MnO}_4^-$  remained after the reaction with  $\text{SO}_2$ ? SO<sub>2</sub> alone?  
 (d) How many mole of  $\text{SO}_2$  was present in the air and what volume was occupied by the  
 (e) What was the percentage, by volume, of  $\text{SO}_2$  in the air?  
 (f) Express the amount of  $\text{SO}_2$  in p.p..