Redox reactions in water

Unit 2 – What makes water such a unique chemical? AOS 1 – How do substances interact with water?

Key knowledge

- Redox (electron transfer) reactions in water
 - oxidising and reducing agents, conjugate redox pairs and redox reactions including writing of balanced half and overall redox equations with states indicated
 - the reactivity series of metals and metal displacement reactions including balanced redox equations with states indicated
 - the causes and effects of a selected issue related to redox chemistry

Redox reactions

Reactions that undergo reduction or oxidation are called redox reactions

- Examples include:
 - Oxidation of food in our bodies
 - Battery reactions
 - Photosynthesis
 - Combustion, explosions



FIGURE 16.1.1 Potassium burning in chlorine gas—a spectacular example of a redox reaction.

Early definition

- Oxidation Combining with oxygen / Addition of oxygen
 - e.g. combustion reactions: $CH_4(g) + 2O_2(g) \rightarrow 2H_2O(g) + CO_2(g)$
 - e.g. metals are exposed to the atmosphere and react with gases and water to form mineral ores: $4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$
- Reduction Loss of Oxygen
 - e.g. extraction of metal from iron ore: (Fe₂O₃ loses oxygen) Fe₂O₃ (s) + 3CO (g) \rightarrow 2Fe (l) + 3CO₂ (g)
- However, this definition is limited to reactions involving oxygen ...

The processes of oxidation and reduction always occur <u>simultaneously</u>

Reduction-loss of oxygen

Undergoes reduction – therefore is reduced. OXIDANT – as it oxidises the other substance

$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$

Oxidation-gain of oxygen

Undergoes oxidation – therefore is oxidised. REDUCTANT – as it reduces the other substance.

Electron Transfer

• The current view of redox reactions now includes many other reactions besides combustion:

e.g.
$$2Mg_{(s)} + O_{2^{(g)}} \rightarrow 2MgO_{(s)}$$

• Here magnesium has lost two electrons:

 $Mg_{(s)} \rightarrow Mg^{2+}(s) + 2e^{-}$

• The definition now involves <u>electron transfer</u>

Oxidation: Electron Transfer

- Oxidation is defined as the loss of *electrons*
 - The substance that is oxidised loses electrons and is therefore an electron donor

$$Mg_{(s)} \rightarrow Mg^{2+}_{(s)} + 2e^{-}$$

$$f$$
Oxidised
Undergoes Oxidation)

Reduction: Electron Transfer

• Reduction is defined as the gain of *electrons*

(U

 The substance that is reduced is one that gains electrons and is therefore an electron acceptor

$$O_2(g) + 4e^- \rightarrow 2O^{2-}(s)$$
Reduced
ndergoes Reduction)



Writing half equations

- A half equation is an equation specifically written for the oxidation OR the reduction reaction
- Electrons are shown in the equation to balance the charges on either side of the equation
 - electrons don't have states

PRACTICE PROBLEM 1

Explain why the following reaction is described as a redox reaction and identify the species oxidised and reduced.

 $\mathbf{Cl_2}\left(\mathbf{aq}\right) + \mathbf{2Br^-}\left(\mathbf{aq}\right) \to \mathbf{Br_2}\left(\mathbf{aq}\right) + \mathbf{2Cl^-}\left(\mathbf{aq}\right)$

PRACTICE PROBLEM 2

For the following equation, write the:

- a. ionic equation
- b. half-equation
- c. conjugate pairs.

 $\mathbf{2AgNO_{3}}\left(\mathbf{aq}\right)+\mathbf{Cu}\left(\mathbf{s}\right) \ \rightarrow \ \mathbf{Cu}{\left(\mathbf{NO_{3}}\right)_{2}}\left(\mathbf{aq}\right)+\mathbf{2Ag}\left(\mathbf{s}\right)$

When sodium metal reacts with chlorine gas (Cl₂), sodium chloride (an ionic compound containing Na⁺ ions and Cl⁻ ions) is formed. The formation of ions can be represented by two half equations. Write their equations and identify the substances oxidised and reduced. Hence write the overall redox equation.

$$\underset{\text{oxidised}}{Na(s)} \rightarrow Na^+(s) + e^- \quad \text{[will need to $\times 2$]}$$

$$\frac{Cl_2(g) + 2e^- \rightarrow 2Cl^-(s)}{\text{reduced}}$$

Half and overall redox equations

half
half

$$2Na(s) \rightarrow 2Na^+(s) + \lambda \lambda^-$$

half
 $Cl_2(g) + \lambda \lambda^- \rightarrow 2Cl^-(s)$
 $\left[2Na(s) + Cl_2(g) \rightarrow 2Na^+(s) + 2Cl^-(s)\right]$
overall
 $2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$

When a strip of copper wire is suspended in a solution of silver ions, long crystals of silver metal can be observed. The solution changes to a pale blue colour, indicating the presence of Cu²⁺ (aq) ions.

Write half equations for this reaction and identify the substances oxidised and reduced. Hence write the overall redox equation.

$$\underbrace{Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}}_{\text{oxidised}}$$

$$Ag^+(aq) + e^- \rightarrow Ag(s)$$

reduced

Overall Redox Equations

- In order to write a full equation it is usual to write the two half equations first and then add them to get an overall equation
- The overall equation should not show any electrons
 - the electrons lost in the oxidation reaction are gained in the reduction equation and therefore cancel out
 - Often you will need to balance the number of electrons
- So for copper and silver ions:

 $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$ $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$ $Ag^{+}(aq) + e^{-} \rightarrow Ag(s) \quad [\times 2]$ $2Ag^{+}(aq) + 2e^{-} \rightarrow 2Ag(s)$ $2Ag^{+}(aq) + 2e^{-} \rightarrow 2Ag(s)$

$$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$$

Write the oxidation and reduction half-equations for the reaction with the overall equation: $2Li(s) + Br_2(l) \rightarrow 2LiBr(s)$

 $2Li_{(s)} + Br_{2}(l) \rightarrow 2Li^{+}(s) + 2Br^{-}(s)$ $\Im Li_{(s)} \rightarrow \Im Li^{+}(s) + \Im e^{-}$ $Li_{(s)} \rightarrow Li^{+}(s) + e^{-} \quad \text{oxidation}$ $Br_{2}(l) + 2e^{-} \rightarrow 2Br^{-}(s) \quad \text{reduction}$

When sodium is oxidised by atmospheric oxygen, the reaction can be represented by the following half equations:

Na (s) \rightarrow Na⁺ (s) + e⁻ O₂ (g) + 4e⁻ \rightarrow 2O²⁻ (s)

• Identify the half equation representing the oxidation reaction and write the balanced overall equation

oxidation

$$4Na(s) \rightarrow 4Na^+(s) + 4e^-$$

$$O_2(g) + 4e^- \rightarrow 2O^{2-}(s)$$

$$\left[4Na(s) + O_2(g) \rightarrow 4Na^+(s) + 2O^{2-}(s)\right]$$

overall $4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$

Potassium metal is oxidised by oxygen gas in air to form solid potassium oxide. Write the half-equations for the reaction and hence write the balanced overall equation.

$$K(s) \rightarrow K^{+}(s) + e^{-} \qquad [\times 4]$$

$$4K(s) \rightarrow 4K^{+}(s) + 4 e^{-}$$

$$O_{2}(g) + 4 e^{-} \rightarrow 2O^{2-}(s)$$

$$4K(s) + O_{2}(g) \rightarrow 4K^{+}(s) + 2O^{2-}(s)$$

$$4K(s) + O_{2}(g) \rightarrow 2K_{2}O(s)$$

Oxidants and Reductants

An oxidant causes another substance to be <u>oxidised</u>.

It itself is simultaneously being reduced, hence undergoing reduction.

A reductant causes another substance to be <u>reduced</u>.

It itself is simultaneously being oxidised, hence undergoing oxidation.

Note: Oxidant = Oxidising agent Reductant = Reducing agent



Exercises:

1. Label the oxidant, reductant, what is oxidised, reduced, undergoing oxidation & reduction in the following equation:

> reductant; $2Cu^{+}_{(aq)} + Br_{2}^{}_{(g)} \rightarrow 2Cu^{2+}_{(aq)} + 2Br^{-}_{(aq)}$ is oxidised; is oxidised: is reduced; undergoing oxidation undergoing reduction

2. Finish the half equation for:

 $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$ oxid<u>n</u> reaction $2H^+(aq) \rightarrow H_2(g) \quad 2H^+(aq) + 2e^- \rightarrow H_2(g) \text{ red}\underline{n} \text{ reaction}$

Which is the oxidation reaction, reduction reaction? Zn, H^+ respectively

- What is being oxidised, reduced?
- What is the oxidant, reductant?
- What is oxidising agent, reducing agent? H^+ , Zn

 H^+ , Zn respectively

Conjugate redox pairs

When a substance is oxidised or reduced, the reactant and the product it forms are referred to the **conjugate redox pair**

- e.g. Zn (s) \rightarrow Zn²⁺ (aq) + 2e⁻
- The conjugate redox pair is Zn²⁺(aq)/Zn(s)
 - The pairs are usually written as oxidant/reductant

 TABLE 16.1.1
 Identifying conjugate redox pairs in a redox reaction

	Example 1	Example 2
Overall equation	$Fe(s) + Sn^{2+}(aq) \rightarrow Fe^{2+}(aq) + Sn(s)$	$Cu(s) + 2Ag^{+}(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$
Oxidation half-equation	$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^{-}$	$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$
Reduction half-equation	$Sn^{2+}(aq) + 2e^{-} \rightarrow Sn(s)$	$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$
Conjugate redox pairs	Fe ²⁺ (aq)/Fe(s) Sn ²⁺ (aq)/Sn(s)	Cu ²⁺ (aq)/Cu(s) Ag ⁺ (aq)/Ag(s)

Balancing More Complex Half Equations – <u>KOHeS</u>

- 1. Balance the Key element
- 2. Balance the Oxygen atoms by adding H_2O to the other side
- 3. Balance the Hydrogen in H_2O by adding H^+ ions to the other side
- 4. Balance the total charge on each side by adding electrons to the more positive side
- 5. Add the States into the final, balanced equation (electrons do not have states)

Oxidation of $Fe^{2+}_{(aq)}$ and reduction of MnO_4^- (permanganate)

• Balance the iron half reaction:

 $Fe^{2+} \rightarrow Fe^{3+} + e^{-}$ [×5]

 $\begin{cases} e^{26} \text{Fe} & \text{electron configuration} \\ 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2 \end{cases} \Rightarrow \text{Fe}^{2+} \& \text{Fe}^{3+} \end{cases}$

• Then balance the manganese half reaction:

 $MnO_{4}^{-} \rightarrow Mn^{2+} + 4H_{2}O$ $MnO_{4}^{-} + 8H^{+} \rightarrow Mn^{2+} + 4H_{2}O$ 7+ 2+ $MnO_{4}^{-} + 8H^{+} + 5e^{-} \rightarrow Mn^{2+} + 4H_{2}O$

²⁵ Mn electron configuration	$\longrightarrow Mn^{2+}$	
$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2 \right\} \Longrightarrow \operatorname{IvIII}$		

• Finally, combine both half equations for the overall redox reaction and add states:

$$5Fe^{2+} \to 5Fe^{3+} + 5e^{-}$$

$$MnO_{4}^{-} + 8H^{+} + 5e^{-} \to Mn^{2+} + 4H_{2}O$$

$$MnO_{4}^{-}(aq) + 8H^{+}(aq) + 5Fe^{2+}(aq) \to Mn^{2+}(aq) + 4H_{2}O(l) + 5Fe^{3+}(aq)$$

Another example

Potassium dichromate $(K_2Cr_2O_7)$ reacts with potassium iodide (KI) in acidified solution. The dichromate ion $(Cr_2O_7^{2-})$ is reduced to form Cr^{3+} , and the iodide ion (I⁻) is oxidised to I₂.

- Write:
 - The half equation for the oxidation of the I^- to I_2
 - The half equation for the reduction of $Cr_2O_7^{2-}$ to Cr^{3+}
 - An overall ionic equation for the reaction
 (the potassium ions are spectators and do not appear in the ionic equation)

$$2I^{-}(aq) \rightarrow I_{2}(s) + 2e^{-} [\times 3]$$

$$Cr_{2}O_{7}^{2-} \rightarrow 2Cr^{3+}$$

$$Cr_{2}O_{7}^{2-} \rightarrow 2Cr^{3+} + 7H_{2}O$$

$$Cr_{2}O_{7}^{2-} + 14H^{+} \rightarrow 2Cr^{3+} + 7H_{2}O$$

$$Cr_{2}O_{7}^{2-} + 14H^{+} + 6e^{-} \rightarrow 2Cr^{3+} + 7H_{2}O$$

$$6I^{-} \rightarrow 3I_{2} + 6 \times^{-}$$

$$Cr_{2}O_{7}^{2-} + 14H^{+} + 6 \times^{-} \rightarrow 2Cr^{3+} + 7H_{2}O$$

 $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6I^-(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3I_2(s)$

PRACTICE PROBLEM 3

Write the half-equation for the oxidation of sulfur dioxide gas, SO₂, to sulfate ions, SO_4^{2-} , in solution.

Practice questions

Complete the questions Ex 12.2 Q 1-10 and 12.2 Quick quiz, pages 473 - 474

So far we have looked at redox reactions in aqueous solutions, or solids/gases involving ionic compounds that can be separated into their constituent ions

- Write the reaction for the combustion of methane in oxygen: $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$
- Is it a redox reaction?

Well, yes, we previously said that it was.

• We can't break the equation into half equations showing electrons, so how can we tell that it is a redox reaction?

Oxidation Numbers 12.3

• When groups of atoms form new compounds, for example,

$$SO_4^{2-} \rightarrow SO_2 + \dots$$

it is often difficult to tell if particular atoms (e.g., S) have lost or gained electrons

- The assigning of <u>Oxidation Numbers</u> (O.N.) to atoms helps to identify whether they have been oxidized or reduced
- An oxidation number is the imaginary charge an atom would have if it was an ion. Oxidation numbers have no physical meaning.
 - Note: e.g., O²⁻ ion has a charge of '2-' (sign goes last) and an oxidation number of '-2' (sign goes first)

Rules for Oxidation Numbers (O.N.)

- 1. The O.N. of an element is 0 (zero) e.g. O.N.(Cu) = 0, $O.N.(O_2) = 0$
- 2. The sum of the O.N. of a compound is 0 (zero) e.g. For CO₂ O.N.(C) + 2 x O.N.(O) = 0
- 3. For **simple** ions: O.N. = charge on ion e.g. O.N.(Cl⁻) = -1, O.N.(S²⁻) = -2
- 4. For **polyatomic** ions, the <u>sum</u> of the O.N. = charge on the ion
- In compounds and polyatomic ions, elements <u>mostly</u> (i.e. not always) have a "fixed" O.N., except for a few cases:
 - a. For hydrogen O.N. = +1 (except in metal hydrides = -1) e.g. H in NaH has an O.N. = -1
 - b. For oxygen O.N. = -2 (except in peroxides = -1) e.g. O in H₂O₂ (hydrogen peroxide) or BaO₂ (barium peroxide) [Note: barium oxide is BaO]

Rules for Oxidation Numbers (continued)

- 5. (continued)
 - c. O.N. of transition elements and non-metallic elements, in compounds, may vary considerably (e.g., N in NH_3 is -3, N in N_2O_5 is +5)

6. The most electronegative element in a compound has the negative oxidation number:

Electronegativity F > O > Cl > N > other elements

- a. Therefore, the oxidation number of F is <u>always</u> -1
- b. Group 1 metals have an oxidation number of +1, and Group 2 metals +2

 $SO_4^{2-} \rightarrow SO_2$ Rule 5b: O.N.(oxygen) = -2 $sO_4^{-2^{2-}} \rightarrow SO_2^{+4-2}$

Rule 2: The sum of the O.N. of a compound is 0 (zero)

Rule 4: For polyatomic ions, the sum of the O.N. = charge on the ion i.e. $O.N.(S) + 4 \times O.N.(O) = -2$ $O.N.(S) + 4 \times (-2) = -2$ O.N.(S) = +6 $\therefore SO_4^{+6} \rightarrow SO_2^{-2}$

The O.N. of S has decreased, therefore S has been reduced.

Exercises

Assign Oxidation Numbers for the elements in:

Mg

(a) H ₂ O	$^{+1}_{H_2} \overset{-2}{O}$	$(2 \times +1 + -2 = 0)$
(b) HNO ₃	+1 +5 -2	
(c) CO ₃ ²⁻	$H N O_3$	$(^{+}1+3\times^{-}2+^{+}5=0)$
(d) F_2O	$^{+4}_{-2}$ $^{-2}_{O_3}$	$(3 \times 2 + 4 = -2)$
(e) Mg	-1 +2	
	$F_2 O$	$(2 \times (1 + (2 \times (2$
	0	
$\begin{array}{cccccc} +4 & -2 & & +2 & -2 & & +4 & -2 \\ C & O_2 & C & O & & C & O_3^{2-} \end{array}$

-3 +1 + NH4

 $^{+5}_{NO_{3}}$ $^{-2}_{NO_{3}}$

 $\overset{+4}{Mn}\overset{-2}{O_2}$

 $^{+7}_{Mn} O_4^-$

? ? -2Mn SO₄ +2 +6 -2 Mn $\int O_4$ polyatomic sum = -2

Cl can have 6 different oxidation numbers

-1, 0, +1, +3, +4, +5, +7

$\begin{array}{cccccccc} +1 & -1 & 0 & +1 & +1 & -2 & +3 \\ H C l & C l_2 & Na C l O & C l \end{array}$

+3 -2 ClO_{2}^{-} chlorite

 $\frac{+4}{Cl} \frac{-2}{O_2}$

+5 +2 $Cl O_3^$ chlorate +7 -2 $Cl O_4^$ perchlorate

Using Oxidation Numbers

- Oxidation involves an \uparrow in oxidation number
- Reduction involves a \downarrow in oxidation number

e.g.
$$2Cu^{+1}(aq) + Br_2(g) \rightarrow 2Cu^{2+}(aq) + 2Br^{-1}(aq)$$

- Oxidation numbers are used in naming of compounds
 - iron(III) chloride (FeCl₃), i.e., $Fe^{3+} = +3$
 - $tin(IV) oxide (SnO_2), i.e., Sn^{4+} = +4$
 - tin(II) oxide (SnO), i.e., Sn²⁺ = +2
 - a permanganate is the general name for compounds containing the manganate(VII) ion, MnO_4^- , i.e., Mn = +7

Identifying Redox Reactions

• If the oxidation numbers of substances have changed, then the reaction is a redox reaction

• HINT: first look for elements - their oxidation numbers are 0 (easiest)

Which reactions are redox?

Identify if redox or not, and give reason:

(a)
$$BaCl_{2} + H_{2}SO_{4} \rightarrow BaSO_{4} + 2HCl$$

 $\stackrel{+2}{Ba} \stackrel{-1}{Cl_{2}} + \stackrel{+1}{H_{2}} \stackrel{+6-2}{S} \stackrel{+2}{O}_{4} \rightarrow \stackrel{+2}{Ba} \stackrel{+6-2}{S} \stackrel{+1}{O}_{4} - 1$
(b) $2Ag + Cl_{2} \rightarrow 2AgCl$
 $\stackrel{0}{Q} \stackrel{0}{O} \stackrel{+1}{O} \stackrel{-1}{O}_{2} \stackrel{+1}{O}_{2} \stackrel{-1}{O}_{2} \stackrel{+2}{O}_{2} \stackrel{-1}{Ag} Cl$ Redox
(c) $2FeCl_{3} + SnCl_{2} \rightarrow 2FeCl_{2} + SnCl_{4}$
 $\stackrel{+3}{2Fe} \stackrel{-1}{Cl_{3}} + \stackrel{+2}{Sn} \stackrel{-1}{Cl_{2}} \rightarrow 2\stackrel{+2}{Fe} \stackrel{-1}{Cl_{2}} \stackrel{+4}{O}_{2} \stackrel{-1}{O}_{4}$ Redox

Review

Complete the following half equations:

Al(s) \rightarrow Al³⁺(aq) $Al^{(s)} \rightarrow Al^{(3+)}(aq) + 3e^{-}$ oxid<u>n</u> $2H^+(aq) \rightarrow H_2(g)$ $2H^+(aq) + 2e^- \rightarrow H_2(g)$ red<u>n</u>

- Which is the oxidation reaction, reduction reaction?
- What is being oxidised, reduced? Al, H^+
- What is the oxidant, reductant? What is oxidising agent, reducing agent? H^+ , Al
- Write the full redox reaction $2Al^{(s)} \rightarrow 2Al^{3+}(aq) + \delta e^{-}$

$$6H^+(aq) + 6 e^- \rightarrow 3H_2(g)$$

 $2Al(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2(g)$

Complete the questions Ex 12.3 Q 1-5 and 12.3 Quick quiz, pages 479 - 480

12.4 Reactivity of metals

- Sodium, magnesium and iron are metals that can be easily oxidised
- Other metals do not oxidise (corrode) as easily



FIGURE 16.2.1 Some metals react with dilute acid to form a salt and hydrogen gas. The reaction between magnesium and dilute acid is extremely vigorous. The reaction between zinc and dilute acid is less vigorous. The reaction between iron and dilute acid is very slow. There is no reaction between lead and dilute acid. Based on this information, the order of metal reactivity from most reactive to least reactive is magnesium, zinc, iron and lead.

Reactivity series

- The reactivity series, or 'electrochemical series', lists metals in order of their reactivity
 - It lists the reduction half equations for metal cations
- As you go down the reactivity series:
 - Metal cations (on the left side) become harder to reduce and therefore less likely to react
 - Metals (right side) become more reactive

CHEMISTRY DATA BOOK

2. Electrochemical series

Reaction	Standard electrode potential (E ⁰) in volts at 25 °C
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.87
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	+1.77
$Au^{+}(aq) + e^{-} \rightleftharpoons Au(s)$	+1.68
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(1)$	+1.23
Br ₂ (l) + 2e ⁻ ≓ 2Br ⁻ (aq)	+1.09
$Ag^{\dagger}(aq) + e^{-} \rightleftharpoons Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$O_2(\mathbf{g}) + 2\mathbf{H}^+(\mathbf{aq}) + 2\mathbf{e}^- \rightleftharpoons \mathbf{H}_2O_2(\mathbf{aq})$	+0.68
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54
$O_2(g) + 2H_2O(1) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$\operatorname{Sn}^{4+}(\operatorname{aq}) + 2e^{-} \rightleftharpoons \operatorname{Sn}^{2+}(\operatorname{aq})$	+0.15
$S(s) + 2H^{+}(aq) + 2e^{-} \rightleftharpoons H_2S(g)$	+0.14
$2H^{\dagger}(aq) + 2e^{-} \rightleftharpoons H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^{-} \rightleftharpoons Pb(s)$	-0.13
$\operatorname{Sn}^{2+}(\operatorname{aq}) + 2e^{-} \rightleftharpoons \operatorname{Sn}(s)$	-0.14
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	-0.25
$Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$	-0.28
$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$	-0.40
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	-0.44
$Zn^{2+}(aq) + 2e^{-} \rightleftharpoons Zn(s)$	-0.76
$2H_2O(l) + 2e^- \Rightarrow H_2(g) + 2OH^-(aq)$	-0.83
$Mn^{2\dagger}(aq) + 2e^- \rightleftharpoons Mn(s)$	-1.18
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	-1.66
$Mg^{2\dagger}(aq) + 2e^- \rightleftharpoons Mg(s)$	-2.37
$Na^{\dagger}(aq) + e^{-} \rightleftharpoons Na(s)$	-2.71
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	-2.87
$K^{\dagger}(aq) + e^{-} \rightleftharpoons K(s)$	-2.93
$Li^{+}(aq) + e^{-} \rightleftharpoons Li(s)$	-3.04

4

Not only metals, but we will just focus on metals for the moment.

CHEMISTRY DATA BOOK

4

2. Electrochemical series

Reaction	Standard electrode potential (E ⁰) in volts at 25 °C
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.87
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	+1.77
$Au^+(aq) + e^- \rightleftharpoons Au(s)$	+1.68
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(1)$	+1.23
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$	+1.09
$Ag^{+}(aq) + e^{-} \rightleftharpoons Ag(s)$	+0.80
$Fe^{3+}(aq) + e^{-} \rightleftharpoons Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq)$	+0.68
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54



Predicting redox reactions

- A more reactive metal (lower right of electrochemical series) tends to be oxidised and donate electrons to the <u>cation of a less reactive</u> <u>metal</u> (top left of the electrochemical series)
- This is called a metal displacement reaction as metals will <u>displace</u> other metals from solutions of their ions
- It is a spontaneous reaction



Note reverse 'Z' shape

Example - Predict if zinc will displace copper from a solution containing copper (II) ions



FIGURE 16.2.2 Reactivity series of metals.

Write the half equations and overall redox equation for the Redox reaction involving Zinc metal and Copper ions

$$Zn(s) \to Zn^{2+}(aq) + 2e$$
$$u^{2+}(aq) + 2e^{-} \to Cu(s)$$

Overall

 $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$



FIGURE 16.2.7 A brown deposit of copper metal is observed forming on the zinc and the blue copper(II) sulfate solution gradually becomes colourless as the concentration of Cu²⁺ ions decreases.

Predicting redox reactions

When a piece of nickel (Ni) is placed in a solution of silver nitrate (Ag⁺), will there be a reaction? Strongest oxidising agent Weakest reducing a

Yes, Ni, being a more reactive metal, will donate electrons to Ag⁺ to become oxidised



Equations

$$Ag^+(aq) + e^- \rightarrow Ag(s)$$
 [×2] NO_3^- is a spectator ion
 $Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$

Overall: $2AgNO_3(aq) + Ni(s) \rightarrow Ni(NO_3)_2(aq) + 2Ag(s)$

Chapter 12.4 questions

Complete 12.4 Quick Quiz and Exercise 12.4 Q 1 - 10, pages 484 - 485

Galvanic cells

Chapter 12.5



 $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

Explanation

When a zinc rod is inserted into a beaker that contains an aqueous solution of copper(II) sulfate, a spontaneous redox reaction occurs: the zinc electrode dissolves to give Zn²⁺(aq) ions, while Cu²⁺(aq) ions are simultaneously reduced to metallic copper. The reaction occurs so rapidly that the copper is deposited as very fine particles that appear black, rather than the usual reddish colour of copper.

Recall - zinc metal will spontaneously displace copper from a solution containing copper (II) ions



FIGURE 16.2.2 Reactivity series of metals.

Galvanic cells

 The reaction, Zn(s) + Cu²⁺(aq) → Zn²⁺(aq) + Cu(s), involves electron transfer and charged particles (ions)

• We can make use of this flow of charged particles to construct a galvanic cell (battery) ...



overall reaction: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$



In the cell

When the switch is closed to complete the circuit, the zinc electrode (the anode) is spontaneously oxidized to Zn²⁺ ions in the left compartment, while Cu²⁺ ions are simultaneously reduced to copper metal at the copper electrode (the cathode).

As the reaction progresses, the Zn anode loses mass as it dissolves to give Zn²⁺(aq) ions, while the Cu cathode gains mass as Cu²⁺(aq) ions are reduced to copper metal that is deposited on the cathode.

Role of the salt bridge

- Completes the electrical circuit by carrying electrical charge, and maintains electrical neutrality in both solutions by allowing ions to migrate between them
- The type of salt in a salt bridge is unimportant, as long as the component ions do not react or undergo a redox reaction under the operating conditions of the cell
- Without such a connection, the total positive charge in the Zn²⁺ solution would increase as the zinc metal dissolves, and the total positive charge in the Cu²⁺ solution would decrease
- The salt bridge allows charges to be neutralized by a flow of anions into the Zn²⁺ solution and a flow of cations into the Cu²⁺ solution. In the absence of a salt bridge or some other similar connection, the reaction would rapidly cease because electrical neutrality could not be maintained.

CHEMISTRY DATA BOOK

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2. Electrochemical series

Reaction	Standard electrode potential (E ⁰) in volts at 25 °C
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.87
$H_2O_2(aq) + 2H^+(aq) + 2e^- \Rightarrow 2H_2O(1)$	+1.77
$Au^{\dagger}(aq) + e^{-} \rightleftharpoons Au(s)$	+1.68
Cl ₂ (g) + 2e ⁻ ≓ 2Cl ⁻ (aq)	+1.36
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(1)$	+1.23
Br ₂ (l) + 2e ⁻ ≓ 2Br ⁻ (aq)	+1.09
$Ag^{\dagger}(aq) + e^{-} \rightleftharpoons Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq)$	+0.68
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$\operatorname{Sn}^{4+}(aq) + 2e^- \rightleftharpoons \operatorname{Sn}^{2+}(aq)$	+0.15
$S(s) + 2H^+(aq) + 2e^- \rightleftharpoons H_2S(g)$	+0.14
$2H^{\dagger}(aq) + 2e^{-} \rightleftharpoons H_2(g)$	0.00
Pb ²⁺ (aq) + 2e ⁻ ≓ Pb(s)	-0.13
Sn ²⁺ (aq) + 2e ⁻ ≓ Sn(s)	-0.14
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	-0.25
$\operatorname{Co}^{2+}(\operatorname{aq}) + 2e^{-} \rightleftharpoons \operatorname{Co}(s)$	-0.28
$Cd^{2+}(aq) + 2e^{-} \rightleftharpoons Cd(s)$	-0.40
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	-0.44
$\operatorname{Zn}^{2+}(\operatorname{aq}) + 2e^{-} \rightleftharpoons \operatorname{Zn}(s)$	-0.76
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	-0.83
$Mn^{2+}(aq) + 2e^{-} \rightleftharpoons Mn(s)$	-1.18
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	-1.66
$Mg^{2+}(aq) + 2e^{-} \Rightarrow Mg(s)$	-2.37
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	-2.71
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	-2.87
$K^+(aq) + e^- \rightleftharpoons K(s)$	-2.93
Li ⁺ (aq) + e ⁻ = Li(s)	-3.04

$Cu^{2+}(aq) + 2q^{-} \Rightarrow Cu(s)$	+0.34
$\operatorname{Sn}^{4+}(\operatorname{aq}) + 2e^{-} \rightleftharpoons \operatorname{Sn}^{2+}(\operatorname{aq})$	+0.15
$S(s) + 2H^+(aq) + 2e^- \implies H_2S(g)$	+0.14
$2H^{+}(aq) + 2e^{-} \Rightarrow H_{2}(g)$	0.00
$Pb^{2+}(aq) + 2e^{-} \Rightarrow Pb(s)$	-0.13
$\operatorname{Sn}^{2+}(\operatorname{aq}) + 2e^{-} \rightleftharpoons \operatorname{Sn}(s)$	-0.14
$Ni^{2*}(aq) + 2e^{-} \Rightarrow Ni(s)$	-0.25
$Co^{2+}(aq) + 2e^{-} \Rightarrow Co(s)$	-0.28
$Cd^{2+}(aq) + 2e^{-} \Rightarrow Cd(s)$	-0.40
$Fe^{2+}(aq) + 2e^- \implies Fe(s)$	-0.44
$Zn^{2+}(aq) + 2e^{-} \rightleftharpoons Zn(s)$	-0.76
AD AMILA → D (ALLAND	-0.23

 $Zn \rightarrow Zn^{2-} + 2e^{-}$ $E^{0} = +0.76 V$ ₆₃



 $Cu^{2+} + Zn(s) \longrightarrow Zn^{2+} + Cu(s)$



No, the fact that it works as well as it does is cool. But as well as it works is not

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Time-lapse (14-hour) photograph

VISIONS

United States

Wedges of an orange generate enough current and electrical juice-3.5 wolta-to power an LED. The fruits citric acid helps electrons flow from gahanized nails to copper wire in this 14-hour exposure.



Only charging a little currency for this show

Talk about coining a new art form. US artist Jonathon Keats pits virtually worthless US and Chinese coins against each other to produce power at New York's Rockefeller Plaza. A US cent is copper coated, while a Chinese fen is aluminium. He places the two coins in saltwater, links them, and the different metals begin to exchange ions, creating electric current. Picture: AFP

Chapter 12.5 Quick quiz

Chapter 12.5 Exercise questions 1 - 10, pages 496 - 497 Review Q 12.6 Q 1 - 10 Page 499 - 500

Lemon battery, and some questions to answer

16.3 Corrosion (theory not covered in class time)

Two types of corrosion

• Dry corrosion (sometimes referred to as 'direct corrosion')

• Wet corrosion

Dry Corrosion

- Occurs as a consequence of a metal reacting with the oxygen in air, to form a metal oxide
 - -e.g. $4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$
- Dry corrosion of aluminium can be useful to protect the metal in situations where maintenance is difficult
 - e.g. Aluminium oxide coating on an aluminium window frame (called 'anodising')
- Dry corrosion in iron, however, forms a coating of iron oxide that flakes off easily, leaving the metal exposed




Wet Corrosion

Can occur in moist air, or through direct immersion in water

FIGURE 16.3.3 Wet corrosion. (a) A piece of steel wool (iron) does not corrode on supermarket shelves. However, once it becomes wet through use, it corrodes quickly. (b) An iron barbecue grill that has been coated with grease shows little sign of corrosion, even after being exposed to the rain for some time. (c) Rust in a car generally starts inside door frames, under mudguards, or in places where the paint has been chipped. (d) Shipwrecks corrode rapidly and will eventually disintegrate. (e) Corrosion occurs more rapidly in cities with a pollution problem, particularly where the pollutants include acidic oxides such as nitrogen dioxide and sulfur dioxide.

Wet Corrosion

In general, corrosion is accelerated by:

- -the presence of water
- impurities such as salt, and acidic pollutants that dissolve in water

The wet corrosion process

Step 1: Iron is oxidised to form Fe²⁺ ions at one region on the iron surface: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^{-}$

At the same time at another region on the surface, using the electrons produced by the oxidation process, oxygen is reduced in the presence of water to hydroxide ions:

 $\mathrm{O_2(aq)} + 2\mathrm{H_2O(l)} + 4\mathrm{e^-} \rightarrow 4\mathrm{OH^-(aq)}$

The overall equation for step 1 is:

 $\begin{aligned} & 2 \mathrm{Fe}(\mathrm{s}) + \mathrm{O}_2(\mathrm{aq}) + 2 \mathrm{H}_2 \mathrm{O}(\mathrm{l}) \to 2 \mathrm{Fe}^{2+}(\mathrm{aq}) + 4 \mathrm{OH^{-}}(\mathrm{aq}) \\ & \mathrm{Step} \ 2\mathrm{:} \ \mathrm{The} \ \mathrm{formation} \ \mathrm{of} \ \mathrm{a} \ \mathrm{precipitate} \ \mathrm{of} \ \mathrm{iron}(\mathrm{II}) \ \mathrm{hydroxide:} \\ & \mathrm{Fe}^{2+}(\mathrm{aq}) + 2 \mathrm{OH^{-}}(\mathrm{aq}) \to \mathrm{Fe}(\mathrm{OH})_2(\mathrm{s}) \end{aligned}$

Step 3: Further oxidation of iron(II) hydroxide occurs in the presence of oxygen and water to produce iron(III) hydroxide, a red-brown precipitate:

 $4\text{Fe(OH)}_2(s) + \text{O}_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 4\text{Fe(OH)}_3(s)$

Step 4: In air, the iron(III) hydroxide loses water to form hydrated iron(III) oxide (Fe₂O₃. xH_2O), which is known as rust.

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Prevention of corrosion

There are several ways to prevent, or reduce, corrosion:

- Surface protection, e.g. covering the metal surface to prevent contact with oxygen and moisture: we can use paint, plastic, oil, grease, etc.
- Alloying: oxidation still occurs but will form a protective layer
- Electroplating: e.g. iron is coated with a thin layer of a less reactive metal such as tin
- Electrochemical protection:
 - Cathodic protection uses low voltage DC to give the iron a negative charge. Iron will be gaining electrons, therefore oxidation is inhibited.
 - Sacrificial protection galvanised iron (iron coated in zinc), used for e.g. roofing. Zinc is more readily oxidised than iron so will undergo oxidation first (it is 'sacrificed')



Prac 22 - Petri dish A

Iron tends to corrode more rapidly at places where the metal lattice has been deformed by stress (bending).

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^{-}$$

$$_{blue/black}$$

$$O^{2-}(aq) + 2H_2O(1) + 4e^{-} \rightarrow AOH^{-}(aq)$$

$$_{pink}$$

Overall:

 $2Fe(s) + O^{2-}(aq) + 2H_2O(l) \rightarrow 2Fe^{2+}(aq) + 4OH^{-}(aq) \quad \left[\rightarrow \text{eventually Fe}_2O_3 \right]$

Prac 22 - Petri dish B

 $|\text{Fe}(s) \rightarrow \text{Fe}^{2+}(aq) + 2e^{-}$ $O^{2-}(aq) + 2H_2O(1) + 4e^- \rightarrow 4OH^-(aq)$ (This reaction occurs at the surface of the copper, which can be a bit harder to see.) **Overall:** $2\text{Fe}(s) + O^{2-}(aq) + 2H_2O(l) \rightarrow 2\text{Fe}^{2+}(aq) + 4OH^{-}(aq)$ \rightarrow eventually orange-brown rust colour The iron corrodes in preference to the copper $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$ $O^{2-}(aq) + 2H_2O(1) + 4e^- \rightarrow 4OH^-(aq)$ (This reaction occurs at the surface of the iron) **Overall**: $|2Zn(s) + O^{2-}(aq) + 2H_2O(l) \rightarrow 2Zn_{N}^{2+}(aq) + 4OH^{-}(aq)$ white $Zn(OH)_{2}$ ZnO The zinc corrodes (sacrificially) in preference to the iron