Chem Factsheet

April 2003 Number 50

Redox Equilibria III - Applications

Before working through this Factsheet you should ensure you understand the redox equilibria covered so far at AS and A2 in Factsheets:
- No. 9 (Equilibrium) – use of the ⇌ sign.
- No. 37 (Redox Equilibria (I)) - cells and standard electrode potentials ($E^{\ominus}$)
- No. 45 (Redox Equilibria (II) – using $E^{\ominus}$values to predict if reactions will take place.

After working through this Factsheet you will:
- have met the concept of 'corrosion/rusting' and be able to explain the processes involved using the $E^{\ominus}$ values and equilibrium processes
- have met the concept of 'storage cells' and seen it applied to the lead acid battery (accumulator) as the specific example.

Exam Hint:- *In this area of the A2 specification you need to learn the basic facts and equations so you can answer questions on the topic. There is no shortcut to learning thoroughly the information given!*

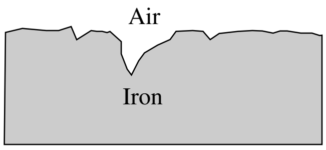
The topics are in most other A2 textbooks – which you could (and should) use in conjunction with the Factsheet to help you gain a full understanding of the work.

The presentation of these topics is designed to be a logical progression from the other Factsheets already mentioned.

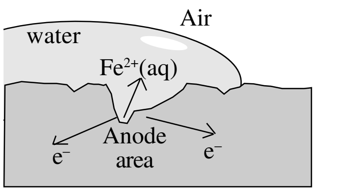
1. Corrosion/rusting - its causes and prevention

Definitions
- **Corrosion** is when a metal is converted into its ions (forming a compound). e.g. M(s) → M^{2+}(aq) + 2e
- This process is **OXIDATION** (oxidation state change from O → + 2
- When iron undergoes this change it is called **RUSTING.**
- Corrosion/rusting is an **ELECTROLYTIC PROCESS** because electron transfer is involved.

Rusting
Overall:
iron + water + oxygen → Fe_2O_3. x H_2O (rust)

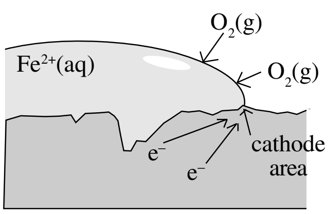
1.


Even the smoothest-looking piece of iron has small pits or pieces of impurities on its surface. These cause small variations in the electrode potential of the iron when water comes into contact with it.

2.


At the anode area (+) the iron atoms dissolve to form iron ions (OXIDATION).

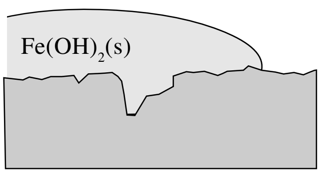
Fe(s) → Fe^{2+}(aq) + $2e^-$

3.


The electrons travel through the iron to where oxygen and water meet the iron – the cathode area (-).

Hydroxide ions are formed

$\frac{1}{2}O_2(g) + H_2O(l) + 2e^- \rightarrow 2OH^-(aq)$

4.


The Fe^{2+} ions react with the OH^- ions to form a precipitate of iron (II) hydroxide.

$Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s)$

At the surface of the water more oxygen converts the iron (II) hydroxide to brown iron (III) oxide.

5. $2Fe(OH)_2(s) + \frac{1}{2} O_2(g) \rightarrow Fe_2O_3(s) + 2H_2O(l)$
(brown 'rust')

Methods of preventing rusting

1. **Barrier methods -** Painting or greasing to prevent air/water reaching the surface of the iron.
2. **Sacrificial Protection** - In this case the iron is covered by a layer of zinc (this is called **GALVANISING**).
   When the zinc is scratched and the iron beneath exposed to air and water, the iron does not rust. This is because of the standard electrode potentials:

   $Fe \rightleftharpoons Fe^{2+} + 2e^-$ $E^{\ominus} = + 0.44$ Volts
   $Zn \rightleftharpoons Zn^{2+} + 2e^-$ $E^{\ominus} = + 0.76$ Volts

   Applying the anti-clockwise rule ('bottom left' i.e. Zn, with 'top right' i.e. Fe^{2+}) gives the reaction,

   $Zn + Fe^{2+} \rightarrow Zn^{2+} + Fe$

   Note Zn that is oxidised i.e. corroded, not the iron.
   The zinc has been 'sacrificed' to protect the iron.

3. **Tin Plating -** 'Tin cans' for foodstuffs are made of iron covered by a layer of tin.

   Look at the standard electrode potentials:

   $Sn \rightleftharpoons Sn^{2+} + 2e^-$ $E^{\ominus} = +0.14$ Volts
   $Fe \rightleftharpoons Fe^{2+} + 2e^-$ $E^{\ominus} = +0.44$ Volts

   If the tin coating is scratched to expose the iron,
   $Fe + Sn^{2+} \rightarrow Sn + Fe^{2+}$ ie. the iron is oxidised ie. rusts.
   so don't buy tins of food which are dented, the iron rusts so the food will not keep!

***Remember** - 'tin plating' is a **barrier method** (**not** sacrificial protection).*

2. Storage cells

Definitions
Cells or **'batteries'** turn chemical energy → electrical energy.
There are two types:

(1) **Disposable** i.e. when the chemical reaction is over they have to be replaced - these are based on non-reversable reactions.
(2) **Rechargeable** – these are called STORAGE CELLS.
In storage cells:
(a) the reactions involved in **discharging** and **charging up** the cell must be **fully reversible.**
(b) the chemicals produced by the redox reactions must be **insoluble.**

The lead acid battery (accumulator)

The lead acid battery is the type used in motor vehicles. It continually discharges (chemical energy → electrical energy) and is continually charged up by the alternator (electrical energy → chemical energy).

Three are two redox reactions involved:

$Pb(s) + SO_4^{2-}(aq) \rightleftharpoons PbSO_4 + 2e^-$ $E^{\ominus} = +0.36$ V

$PbSO_4(s) + 2H_2O(l) \rightleftharpoons PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$ $E^{\ominus} = +1.69$ V

Applying the anti-clockwise rule:

$2PbSO_4 + 2H_2O \rightarrow PbO_2 + 2SO_4^{2-} + Pb + 4H^+$
This is the process of **charging up**.
Note the Pb disproportionates; it is both oxidised (+2 → +4) and reduced (+2 → 0)

In **discharging**, the reaction is reversed:
$PbO_2 + 2SO_4^{2-} + Pb + 4H^+ \rightarrow 2PbSO_4 + 2H_2O$

Questions

1. State what is meant by corrosion of a metal
2. Galvanised iron consists of of iron covered by a layer of zinc. Even if the zinc is scratched, and the iron is exposed to the air, it does not rust.
   (a) Use the data below to explain why
   (b) Comment on the use of tin-plated iron cans for food
   $Zn^{2+} + 2e^- \rightleftharpoons Zn$ $E^{\ominus} = - 0.76$ V
   $Sn^{2+} + 2e^- \rightleftharpoons Sn$ $E^{\ominus} = - 0.14$ V
   $Fe^{2+} + 2e^- \rightleftharpoons Fe$ $E^{\ominus} = - 0.44$ V
3. The NiCad cell has overall cell reaction when discharged

   $NiO(OH)(s) + Cd(s) + 2H_2O(l) \rightarrow 2Ni(OH)_2(s) + Cd(OH)_2(s)$

   State the substance forming the cathode, explaining your choice.

Answers

1. When a metal is converted into its ions/oxidised.
2. (a) Considering the cell is made from zinc and iron we have:
   Zn as the reacting agent $Zn \rightarrow Zn^{2+} + 2e^-$
   Fe as the oxidising agent $Fe^{2+} + 2e^- \rightarrow Fe$
   So overall $Zn + Fe^{2+} \rightarrow Zn^{2+} + Fe$
   so zinc is corroded, not iron
   (b) Since its $E^{\ominus}$ value is less negative, tin will not be corroded in preference to iron, so exposed iron will not be protected. So scratched tin cans may rust.
3. Cadmium (Cd) because it is oxidised 0 → +2

Acknowledgements:
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