Higher

Chemistry

HSN13200
Unit 3 Topic 2

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Topic 2 – Hess's Law, Redox and Electrolysis

Hess's Law

In Unit 1 we used experimental results to calculate enthalpy changes for the Heat of Combustion of ethanol and the Heat of Solution of potassium nitrate. Sometimes we want to find the enthalpy change for a reaction that is difficult or even impossible to carry out. An example is the formation of 1 mole of methane from its elements.

$$C_{(s)} + 2H_{2(g)} \longrightarrow CH_{4(g)} \qquad \Delta H = ?$$

The heat of reaction cannot be measured directly as the reaction does not occur under normal conditions. The enthalpy can, however, be calculated using an alternative route from the reactants to the products. This uses a form of the Law of Conservation of Energy which states energy cannot be created or destroyed. Hess's Law states that:

> The enthalpy change in a chemical reaction depends only on the reactants and products and is independent of the route taken between them.

Its use is best illustrated by using the above example; calculate the enthalpy change for the formation of 1 mole of methane from its elements using the enthalpies of combustion of carbon, hydrogen and methane from the data book.

First write the equation for the reaction whose heat we require:

$$C_{(s)} + 2H_{2(g)} \longrightarrow CH_{4(g)} \qquad \Delta H = ?$$

Now write equations for the information given in the data book:

1 $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H = -394\ \text{kJ mol}^{-1}$

2 $H_2 + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}$ $\Delta H = -286\ \text{kJ mol}^{-1}$

3 $CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + H_2O_{(l)}$ $\Delta H = -891\ \text{kJ mol}^{-1}$

Now use the given information to build up the required equation:

1 $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H = -394\ \text{kJ mol}^{-1}$

2 × 2 $2H_2 + O_{2(g)} \longrightarrow 2H_2O_{(l)}$ $\Delta H = -572\ \text{kJ mol}^{-1}$

3 rev $CO_{2(g)} + H_2O_{(l)} \longrightarrow CH_{4(g)} + 2O_{2(g)}$ $\Delta H = -891\ \text{kJ mol}^{-1}$

adding $C_{(s)} + 2H_{2(g)} \longrightarrow CH_{4(g)}$ $\Delta H = -75\ \text{kJ mol}^{-1}$

Plenty of practice is needed to gain confidence in Hess's Law Problems. There is also a Prescribed Practical which verifies Hess's Law experimentally.

Redox Reactions

Reactions involving oxidation and reduction are called Redox Reactions. We met some redox reactions in Standard Grade Chemistry.

Displacement Reactions
eg zinc metal displaces silver from silver (I) nitrate solution.

We can look at this in terms of these two ion-electron half equations:

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e \qquad \text{Oxidation}$$

$$Ag^{+}_{(aq)} + e \longrightarrow Ag_{(s)} \qquad \text{Reduction}$$

Note
The zinc metal is the reducing agent. It donates electrons and is oxidised.
The silver ion is the oxidising agent. It accepts electrons and is reduced.

The number of electrons lost in the oxidation must balance the number of electrons gained in the reduction. To achieve this we must multiply the second equation by 2. When this is done we can add the 2 half-equations to get the Redox Equation:

$$\begin{array}{rcll} Zn_{(s)} & \longrightarrow & Zn^{2+}_{(aq)} + 2e & \text{Oxidation} \\ Ag^{+}_{(aq)} + e & \longrightarrow & Ag_{(s)} & \text{Reduction} \\ \hline Zn_{(s)} + 2Ag^{+}_{(aq)} & \longrightarrow & Zn^{2+}_{(aq)} + 2Ag_{(s)} & \text{Redox} \end{array}$$

Note that the nitrate ions do not appear in the redox equation. This is because they are spectator ions and are not directly involved in the electron transfer.

Reaction of MAZIT metals with dilute acid.

eg $$Mg_{(s)} + 2H^{+}Cl^{-}_{(aq)} \longrightarrow Mg^{2+}(Cl^{-})_{2(aq)} + H_{2(g)}$$

Again we can write ion electron equations for the oxidation and reduction reactions:

$$\begin{array}{rcll} Mg_{(s)} & \longrightarrow & Mg^{2+}_{(aq)} + 2e & \text{Oxidation} \\ 2H^{+}_{(aq)} + 2e & \longrightarrow & H_{2(g)} & \text{Reduction} \\ \hline Mg_{(s)} + 2H^{+}_{(aq)} & \longrightarrow & Mg^{2+}_{(aq)} + H_{2(g)} & \text{Redox} \end{array}$$

The magnesium metal is the reducing agent and the hydrogen ions are the oxidising agent.

Balancing ion electron half equations

Potassium permanganate ($KMnO_4$) oxidises Fe^{2+} ions to Fe^{3+} ions. During this reaction the MnO_4^{-} ions are reduced to Mn^{2+} ions.

$$Fe^{2+} \longrightarrow Fe^{3+} + e$$

This is balanced

$$MnO_4^{-} \longrightarrow Mn^{2+}$$

This is not so simple to balance and needs some rules

i) Write down the main chemical in its two forms (oxidised and reduced) and balance the main atom(s)

$$MnO_4^- \longrightarrow Mn^{2+}$$

ii) Balance oxygen by adding water molecules

$$MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$$

iii) Balance hydrogen by adding hydrogen ions

$$MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$$

iv) Balance the charge by adding electrons

$$MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O$$

To get the redox equation we must multiply the iron half equation by 5 before adding.

$$\begin{array}{rcll} 5Fe^{2+} & \longrightarrow & 5Fe^{3+} + 5e & \text{Oxidation} \\ MnO_4^- + 8H^+ + 5e & \longrightarrow & Mn^{2+} + 4H_2O & \text{Reduction} \\ \hline MnO_4^- + 5Fe^{2+} + 8H^+ & \longrightarrow & Mn^{2+} + 5Fe^{3+} + 4H_2O & \text{Redox} \end{array}$$

Note that in the previous example the Fe^{2+} ions were the reducing agent and were themselves oxidised to Fe^{3+} ions by donating electrons.

In a different reaction Iodide (I^-) ions can be oxidised to iodine by Fe^{3+} ions. The Fe^{3+} ions are reduced to Fe^{2+} ions.

$$\begin{array}{rcll} 2I^-_{(aq)} & \longrightarrow & I_{2(aq)} + 2e & \text{Oxidation} \\ Fe^{3+}_{(aq)} + e & \longrightarrow & Fe^{2+}_{(aq)} & \text{Reduction} \end{array}$$

So in the previous example, Fe^{2+} was a reducing agent and in this example Fe^{3+} is an oxidising agent. This can be summed up as:

$$\text{Oxidising agent} + \text{electron(s)} \longrightarrow \text{Reducing agent}$$

or

$$\text{Reducing agent} \longrightarrow \text{Oxidising agent} + \text{electron(s)}$$

Redox Titrations

You are familiar with acid base titrations. Redox titrations are similar but involve solutions of oxidising agents reacting with reducing agents. You will do a Prescribed Practical in which the mass of Vitamin C in a tablet is determined by a redox titration. Another common redox titration uses acidified potassium permanganate as an oxidiser; for example it can be used to oxidise Fe^{2+} ions to Fe^{3+} ions. The end point uses the fact that MnO_4^- is purple and Mn^{2+} is colourless.

In this reaction, the acidified potassium permanganate is added from a burette to the solution of iron(II) ions. The iron ions are oxidised and the purple permanganate ions (MnO_4^-) are reduced to colourless Mn^{2+} ions. The equations for this follow the example of balancing half-equations above. The end point is the first permanent pink colour; this indicates the permanganate ions have oxidised all the Fe^{2+} ions and are just in excess.

From the results, the concentration of iron ions in the solution can be calculated as the following example shows.

It takes 20 ml of 0.1 mol l^{-1} permanganate solution to react completely with 25 ml of an iron (II) solution. What is the concentration of the iron (II) ions?

Method A

Let the concentration of iron (II) ions be *x*. We worked out this equation earlier:

$$\underset{\substack{1\text{ mole}\\20\text{ ml; }0.1\text{ mol l}^{-1}}}{MnO_4^-} + \underset{\substack{5\text{ moles}\\25\text{ ml; }x\text{ mol l}^{-1}}}{5Fe^{2+}} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

$$\frac{20\times0.1}{25\times x}=\frac{1}{5}$$

$$x=0.4$$

So the concentration of iron(II) ions is 0.4 mol l^{-1}

Method B

This is an alternative fuller answer which leads you through the problem in steps:

First calculate the number of moles of permanganate used

0.1 mol l^{-1} permanganate means

1000ml contains 0.1 moles of permanganate ions

so 20.0 ml contains $\frac{0.1}{1}\times\frac{20}{1000}$ moles permanganate ions

= 0.002 moles permanganate

Now calculate the moles of iron reacting with the permanganate

The equation tells us that 1 mole of permanganate reacts with 5 moles of iron ions,

so the moles of iron we have = 0.002 x 5 moles iron ions

= 0.01 moles iron ions

so 25 ml Fe^{2+} solution contains 0.01 moles iron(II) ions

so 1000 ml Fe^{2+} solution contains $\frac{0.01}{1}\times\frac{1000}{25}$ moles iron(II) ions

=0.4 moles iron(II) ions

This means that the concentration of the iron(II) ions is 0.4 mol l^{-1}

Electrolysis

We met electrolysis in Standard Grade but only in a qualitative way; in other words we were only interested in what the products were but not how much was formed.

eg we electrolysed copper(II) chloride solution using carbon electrodes. The ions present are $Cu^{2+}_{(aq)}$ and $Cl^{-}_{(aq)}$.

Negative electrode (the cathode)
This attracts Cu^{2+} which gains electrons to become copper metal:

$$Cu^{2+}_{(aq)} + 2e \longrightarrow Cu_{(s)} \qquad \text{Reduction}$$

Positive electrode (the anode)
This attracts the Cl^{-} ions which lose electrons to become chlorine gas

$$2Cl^{-}_{(aq)} \longrightarrow Cl_{2(g)} + 2e \qquad \text{Oxidation}$$

As before the oxidation and reduction ion electron half equations can be added to give the redox equation

$$Cu^{2+}_{(aq)} + 2Cl^{-}_{(aq)} \longrightarrow Cl_{2(g)} + Cu_{(s)} \qquad \text{Redox}$$

We return to electrolysis now but we will be studying it in a quantitative way. In other words we will be interested in how much product is made.

You will carry out a Prescribed Practical in which dilute sulphuric acid will be electrolysed. The aim is to find out what quantity of electricity is required to produce 1 mole of hydrogen gas at the negative electrode. The total quantity of electricity passing in an electrolysis depends on the size of the current and the time the current was passing. The following formula is used:

$$\text{quantity of electricity (coulombs)} = \text{current (amps)} \times \text{time (seconds)}$$

$$Q = I \times t$$

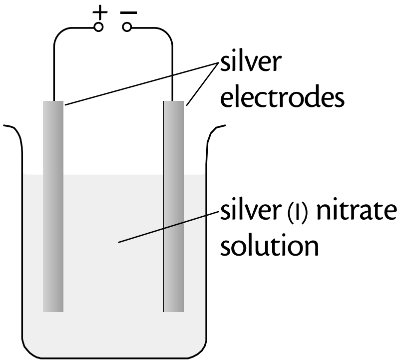
The following are some typical results from similar quantitative electrolyses.

1. Electrolysis of silver (I) nitrate solution

Using silver electrodes the positive electrode dissolves (i) and silver ions are discharged and deposited as silver metal on the negative electrode (ii).

(i) $Ag_{(s)} \longrightarrow Ag^{+}_{(aq)} + e$

(ii) $Ag^{+}_{(aq)} + e \longrightarrow Ag_{(s)}$



The negative electrode is weighed before and after the experiment.

The current, in amps, and the time, in seconds, for which it passed are also noted.

Typical results

Mass of silver deposited = 0.7167 g
Current passed = 0.5 A
Time = 1282 s

$$Q = I \times t = 0.5 \times 1282 = 641 \text{ C}$$

0.7167g of silver are deposited by 641 C

So 107.9g (1 mole) of silver would be deposited by $\frac{641}{1} \times \frac{107.9}{0.7167}$ = 96 500 C

This quantity of electricity, 96 500 C, is called 1 Faraday (1 F).

So 1 Faraday discharges 1 mole of silver ions (Ag^+)

2. Electrolysis of Copper (II) Sulphate

Using copper electrodes, the positive electrode dissolves

$$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e$$

and copper ions are discharged and deposited as copper metal on the negative electrode

$$Cu^{2+}_{(aq)} + 2e \longrightarrow Cu_{(s)}$$

The same measurements are made as in the previous experiment.

Typical results

Mass of copper deposited = 0.1184 g
Current passed = 0.2 A
Time = 1800 s

$$Q = I \times t = 0.2 \times 1800 = 360 \text{ C}$$

0.1184g of copper are deposited by 360 C

So 63.5g (1 mole) of copper would be deposited by $\frac{360}{1} \times \frac{63.5}{0.1184}$ = 193 000 C

This quantity of electricity is 2 Faradays (2 F).

So 2 Faradays are required to deposit 1 mole of copper (II) ions (Cu^{2+})

Electrolysis in General

1 mole of silver ions	$Ag^+ + e \longrightarrow Ag$	requires 1 Faraday
1 mole of copper (II) ions	$Cu^{2+} + 2e \longrightarrow Cu$	requires 2 Faradays
1 mole of aluminium ions	$Al^{3+} + 3e \longrightarrow Al$	requires 3 Faradays
1 mole of hydrogen ions	$H^+ + e \longrightarrow \frac{1}{2}H_2$	requires 1 Faraday
1 mole of bromide ions	$Br^- \longrightarrow \frac{1}{2}Br_2 + e$	requires 1 Faraday

In general, one mole of ions is discharged by nF Coulombs where n is the charge on the ion and F is the Faraday.

Here is a worked example of a typical electrolysis problem.

What mass of nickel is deposited at the negative electrode when a solution of nickel (II) chloride is electrolysed for 25min 30s using a current of 0.4A?

Calculate the total quantity of electricity using

$$Q = I \times t$$

Remember time must be in seconds; 25min 30 s = 1530s

So $Q = 0.4 \times 1530$

$= 612\ C$

Treat this as a calculation from an equation; so start with a balanced equation:

	$Ni^{2+}_{(aq)}$	+	2e	$\longrightarrow$	$Ni_{(s)}$
			2 moles		1 mole
so			2 × 96 500 C		58.7g
therefore			612 C		$\frac{58.7}{1}\times\frac{612}{2\times96500}$ = 0.186g

So mass of nickel deposited = 0.186g