

## Analysis of the copper analyte solution by electrochemical potentials

The Nernst Equation, derived by a German physicist and chemist Walter Nernst (1864–1941) <sup>[1]</sup>, accurately relates the measured electrochemical cell potential of a Daniel Cell to a number of variables including ion concentration of the half cells used, defined by the reaction quotient.

$$E_{cell} = E_{cell}^{\circ} - \left[ \frac{RT}{nF} \right] \ln Q \quad [1]$$

Where <sup>[1]</sup> <sup>[2]</sup>

- $E_{cell}$  = the measured cell potential (V) between two half cells
- $E_{cell}^{\circ}$  = the cell potential (e.m.f) published under standard conditions between two half cells
- $R$  = The Gas constant,  $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
- $T$  = The temperature in kelvin, room temperature (298K) or directly measured
- $n$  = the moles of electrons,  $e^{-1}$ , given by the balanced redox reaction
- $F$  = Faraday's constant,  $96,485 \text{ C mol}^{-1}$
- $Q$  = The reaction quotient

The reaction quotient,  $Q$ , is dependent on the relative amounts of reactants and products present during a reaction at a given time <sup>[3]</sup>. It is, therefore, similar to the equilibrium constant. However, the equilibrium constant,  $K$ , is used for a reaction at equilibrium, rather than any given time. The reaction quotient,  $Q$ , can be determined using a balanced overall equation for the reaction and the known concentrations of the species. Note that when calculating  $Q$ , only species in the same phase are included (aq) <sup>[2]</sup>.

For the general reaction:  $aA + bB \rightarrow cC + dD$  then,  $Q = \frac{c^c D^d}{A^a B^b}$  <sup>[3]</sup>

### How can this be applied to the investigation?

A 50cm<sup>3</sup> sample of the copper(II) analyte solution will be analysed to find its concentration. A collection of electrochemical 'Daniel cells' will be made using a range of different concentrations of copper (II) solution. The 'Daniel cell' is an electrochemical cell consisting of a zinc electrode in a zinc sulfate solution (of known concentration) and a copper electrode in a copper(II) sulfate solution, linked by a salt bridge.

To create the salt bridge, some filter paper will be submerged in a concentrated solution of potassium nitrate(V) <sup>[4]</sup>. Potassium ions and nitrate(V) ions carry current in the salt bridge so there is electrical contact between the two solutions but no mixing. Theoretically there should be an infinite resistance between the two electrodes but this is not achievable in the laboratory. The electrical potential between these two half cells is measured as ' $E_{cell}$ ' in volts using high-resistance voltmeter so that negligible current flows between the half-cells' electrodes <sup>[2]</sup>.

The half reactions occurring during the redox in an electrochemical Daniell cell are <sup>[5]</sup>:

<b>Standard cathode (reduction) half-reaction</b>	<b>Standard electrode potential <math>E^{\circ}</math> (Volts)</b>
$\text{Cu}^{2+}_{(aq)} + 2e^{-} \rightleftharpoons \text{Cu}_{(s)}$	<b>+0.3419</b>
<b>Standard anode (oxidation) half-reaction</b>	<b>Standard electrode potential <math>E^{\circ}</math> (Volts)</b>
$\text{Zn}^{2+}_{(aq)} + 2e^{-} \rightleftharpoons \text{Zn}_{(s)}$	<b>-0.7618</b>
<b>Overall redox reaction</b>	<b><math>E^{\circ}_{cell}</math> (Volts)</b>
$\text{Zn}_{(s)} + \text{Cu}^{2+}_{(aq)} \rightarrow \text{Zn}^{2+}_{(aq)} + \text{Cu}_{(s)}$	<b>1.1037</b>

**Table 3.0:** Standard reduction potentials.  $E^{\circ}_{cell}$  is the difference between the standard reduction potentials of the two half-cells and is always positive [5] [4].

The copper half-cell will be more positive than the zinc half-cell. This means that  $\text{Cu}^{2+}_{(aq)}$  ions are reduced to copper and zinc is oxidised to  $\text{Zn}^{2+}_{(aq)}$  ions. The concentration of  $\text{Zn}^{2+}_{(aq)}$  in the zinc half-cell will increase and so nitrate ions ( $\text{NO}^{3-}_{(aq)}$ ) will migrate from the salt bridge into the zinc half-cell. Conversely, the concentration of  $\text{Cu}^{2+}_{(aq)}$  in the copper half-cell will reduce so potassium ions ( $\text{K}^{+}_{(aq)}$ ) will migrate from the salt bridge into the copper half-cell. [4]

The Daniel cell will be set up for each different concentration of copper(II) half-cell with a separate standard 0.5M zinc sulfate half-cell after each  $E_{cell}$  measurement [4]. All metals strips (of zinc and copper) will be rinsed and dried before use in different half-cells to avoid contamination.

The electrochemical potentials are to be plotted on a graph against the natural log of the ratio between the concentration of  $\text{Zn}^{2+}_{(aq)}$  ions in the negative cell and the concentration of  $\text{Cu}^{2+}_{(aq)}$  ions in the positive cell (i.e.  $\ln\left[\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}\right]$ ). A line of best fit is then plotted and the electrochemical voltage of the copper(II) analyte Daniel cell can be plotted onto the calibration line to find the value of  $\ln\left[\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}\right]$  and hence by rearranging, the concentration of copper(II) in the analyte sample [4]. The justification for the relationship between the ion concentration and the measured electrochemical cell potential is defined by the Nernst equation.

$$E_{cell} = E^{\circ}_{cell} - \left[\frac{RT}{nF}\right] \ln Q$$

$$E_{cell} = 1.1037 - \left[\frac{8.314 * 298}{2 * 96,485}\right] \ln \left[\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}\right]$$

The equation of a graph of electrochemical potentials against  $\ln Q$  will be equal to the Nernst equation. The gradient should thus equal  $-\left[\frac{RT}{nF}\right]$  since  $E_{cell}$  is proportional to  $\ln Q$ .

In the Daniell cell to be used, the natural logarithm of the reaction quotient is approximately equal to the value of  $\ln\left[\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}\right]$ .

In experiment, the electrochemical potentials with the concentration of the zinc half-cells being kept at 0.5M. The calibration curve gives a value of  $\ln Q$  for the copper(II) analyte solution based on the measured electrochemical potential.

Therefore, to find the concentration of copper(II) analyte:

$$\ln Q = \ln\left[\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}\right] \rightarrow Q = \left[\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}\right] \rightarrow [\text{Cu}^{2+}] = [\text{Zn}^{2+}]/Q$$

Where  $Q$  is found by the calculation of  $e^{\ln Q}$

The range of standard concentrations of copper(II) half-cells must fall both above and below the predicted concentration of the copper(II) analyte solution of  $0.109 \text{ mol dm}^{-3}$  (see Section 1.0 - Table 1.0) being sampled in order that the calibration line can be used to interpolate a value. Thus a less accurate extrapolation of the calibration line is avoided, which would have been the case if the concentrations being analysed all fell either side of the concentration of the analyte solution.

## The (standard) Daniell Cell <sup>[4]</sup>

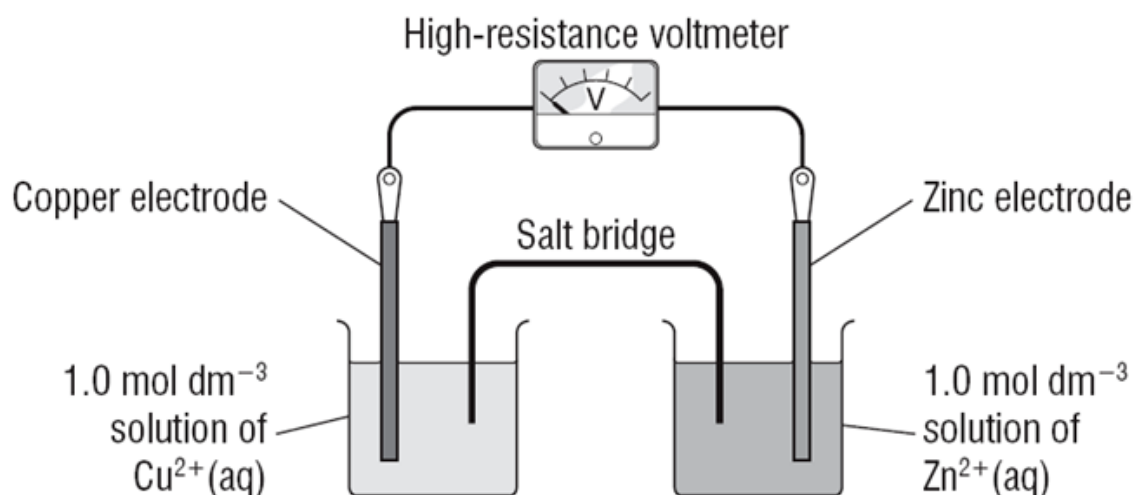


Image sourced from "Oxford-A Level Sciences, Salters Advanced Chemistry, Student Activity sheet DM4 Electrochemistry"

### Practical technique C: Transferring a solution using a graduated burette and suction filter

After rinsing the graduated burette with distilled water, apply a suction filter to the widest end and draw up some ( $< 10\text{cm}^3$ ) of the desired solution into the graduated burette. Hold the graduated burette over a sink drain and remove the suction filter but immediately cover the end where the filter was with your finger to cause a vacuum so the solution does not leave the graduated burette. Invert the graduated burette several times to rinse the inside of it with the solution.

Then reapply the suction filter to the widest end and draw up a volume of the desired solution which is greater than that which is required. Then remove the suction filter but immediately cover the end where the filter was with your finger to cause a vacuum so the solution does not leave the graduated burette. Then facing the graduated burette head on, to reduce parallax error, slowly lift your finger with minute movements as to lower the solution level in the burette until the bottom of the meniscus is in line with the volumetric marking required. Then hold the graduated burette above the desired apparatus which you wish to transfer the solution into and release your finger. Allow the solution to run out the graduated burette and then gently touch the tip of the graduated burette against the surface of the solution you have transferred it to. <sup>[4]</sup>

### What range of copper(II) sulfate concentrations should be used?

The estimated concentration by theoretical calculations of copper(II) in the analyte solution is  $\sim 0.109\text{ mol dm}^{-3}$ . To plot a suitable calibration curve, the range of copper(II) concentrations must cover above and below this value. A range of different concentrations allows for improved accuracy of the calibration curve.

A standard stock solution of 0.4M copper(II) sulfate solution is made up in a  $250\text{cm}^3$  volumetric flask (refer to **method 3.0** later on for details on the masses of copper that will need to be dissolved etc.).

The following quantities of this standard 0.4M copper(II) sulfate solution are diluted using a burette of distilled water and a burette of the 0.4 M copper(II) sulfate solution to make half-cells ID 1 to 5.

Concentration of [Cu <sup>2+</sup> ] (mol dm <sup>-3</sup> )	Volume of stock 0.4M Cu <sup>2+</sup> <sub>(aq)</sub> solution (cm <sup>3</sup> )	Volume of water (cm <sup>3</sup> )	Total volume of Cu <sup>2+</sup> <sub>(aq)</sub> half cell (cm <sup>3</sup> )	Half-cell ID
0.40	50	0	50	1
0.30	37.50	12.50	50	2
0.20	25	25	50	3
0.11	13.75	36.25		4
0.10	12.5	37.50	50	5
Volume of stock 0.4M Cu <sup>2+</sup> <sub>(aq)</sub> solution (cm <sup>3</sup> ) unused	111.25cm <sup>3</sup> of 0.4M Cu <sup>2+</sup> <sub>(aq)</sub> solution remains unused. <b>62.5cm<sup>3</sup></b> of this will be used in a serial dilution to make a 0.1M Cu <sup>2+</sup> <sub>(aq)</sub> solution as described in <b>Table 3.2</b> . The remaining 48.75cm <sup>3</sup> of 0.4M Cu <sup>2+</sup> <sub>(aq)</sub> solution is spare and so can be used for rinsing the burette during the transfer of the solution.			

**Table 3.1:** Formulating the standard Copper(II) sulfate half-cell concentrations (Cell IDs 1 to 5)

A serial dilution is carried out by taking 62.5cm<sup>3</sup> of the 0.4M solution that is unused (refer to **Table 3.1**) and making it up to mark in a 250cm<sup>3</sup> volumetric flask. This will form 250cm<sup>3</sup> of 0.1M copper(II) sulfate solution. The following quantities of ~0.1M copper(II) sulfate solution are used for half-cells 6 to 9.

Concentration of [Cu <sup>2+</sup> ] (mol dm <sup>-3</sup> )	Volume of stock 0.1M Cu <sup>2+</sup> <sub>(aq)</sub> solution (cm <sup>3</sup> )	Volume of water (cm <sup>3</sup> )	Total volume of Cu <sup>2+</sup> <sub>(aq)</sub> half cell (cm <sup>3</sup> )	Half-cell ID
0.09	45	5	50	6
0.08	40	10	50	7
0.07	35	15	50	8
0.06	30	20	50	9
Volume of stock 0.1M Cu <sup>2+</sup> <sub>(aq)</sub> solution (cm <sup>3</sup> ) unused	100 cm <sup>3</sup> of 0.1M Cu <sup>2+</sup> <sub>(aq)</sub> solution remains unused. This is spare and so can be used for rinsing the burette during the transfer of the solution.			

**Table 3.2:** Formulating the standard Copper(II) sulfate half-cell concentrations (Cell IDs 1 to 5)

**Note:** the equation  $c_1v_1 = c_2v_2$  was used to quantitatively calculate the required volumes and concentrations for each half cell. Where  $c$  = concentration (mol dm<sup>-3</sup>) and  $v$  = volume (dm<sup>3</sup>).

### What concentration of zinc sulfate solution is required?

To create a standard zinc half-cell, there should be a ~50cm<sup>3</sup> solution of 0.5M zinc sulfate. A zinc sulfate solution is suitable for use in electrochemistry as zinc sulfate is a soluble salt allowing for the movement of ions <sup>[4]</sup>. For details on the mass of zinc to be dissolved and the volume of the 0.5M standard stock solution, refer to **method 3.2** .

### Method 3.0 – Making the stock 0.4M & 0.1M copper(II) sulfate solutions

Hydrated copper(II) sulfate (**pentahydrate**) will be used in a powder form <sup>[7]</sup>. This is because if anhydrous copper (II) sulfate is used, on the addition of water to make a solution, there would be vigorous heating which could 'spit' (causing loss of solution) or damage glassware.

The formula of hydrated copper(II) sulfate (**pentahydrate**) is  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}_{(s)}$ . The molecular mass ( $M_r$ ) of this compound is  $249.685 \text{ g mol}^{-1}$ . <sup>[7]</sup>

For making the 250cm <sup>3</sup> 0.4 M copper(II) sulfate standard solution		
Value	Calculation	Result
Volume of 0.4 M copper(II) sulfate solution to be made	$250\text{cm}^3 = 0.250 \text{ dm}^3$	
Concentration of stock copper(II) sulfate solution being made	0.4 M	
Moles of copper(II) sulfate	$0.250 \text{ dm}^3 \times 0.4$	0.100 mol
Mass of copper(II) sulfate (pentahydrate / $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}_{(s)}$ )	$249.685 \text{ g mol}^{-1} \times 0.100 \text{ mol}$	<b>24.97 g (to nearest 0.01g)</b>
A serial dilution will then form 250cm <sup>3</sup> of 0.1M copper(II) sulfate standard solution		
Value	Calculation	Result
Volume of 0.1M copper(II) sulfate solution to be made	$250\text{cm}^3 = 0.250 \text{ dm}^3$	
Volume of 0.4M copper(II) sulfate solution to be diluted in order to form a 0.1M solution.	$62.5\text{cm}^3 = 0.0625\text{dm}^3$	
Volume of distilled water required	$187.5\text{cm}^3 = 0.1875\text{dm}^3$ i.e. make the solution up to mark (250cm <sup>3</sup> )	
Moles of copper(II) sulfate	$0.0625 \text{ dm}^3 \times 0.4\text{M}$	0.025 mol
Checking the concentration of copper(II) sulfate is now 0.1M	$\frac{0.025 \text{ mol}}{0.250 \text{ dm}^3}$	0.1 M

**Table 3.3:** Calculating the amounts of copper(II) sulfate to form a standard 0.4M copper(II) sulfate solution and the volume of 0.4M copper(II) solution serial to be used in a serial dilution to form a standard 0.1M copper(II) sulfate solution.

Equipment / reagents	Extra details
Eye protection and lab coat	
Sensitive digital balance	Accurate to 0.01g
Plastic weighing boat	This should be brand new
2 X clean stainless steel spatulas	Rinsed with distilled water and dried with some paper towel
2 X Small clean funnel	Rinsed with distilled water and dried with some paper towel
2 X 250cm <sup>3</sup> volumetric flask with stopper	Clean
Copper (II) sulfate (pentahydrate) powder	The formula is $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}_{(s)}$
Distilled water	In a clean 'wash bottle'
Clean dropper pipette	Rinsed with distilled water.
50 cm <sup>3</sup> pipette with suction filter	Rinsed with distilled water.
10 cm <sup>3</sup> graduated burette with suction filter	Rinsed with distilled water.
5 cm <sup>3</sup> graduated burette with suction filter	Rinsed with distilled water.

To form a stock solution of 250cm<sup>3</sup> 0.4M copper (II) sulfate:

- Place a plastic weighing boat onto the digital balance and zero the balance.
- Weigh out 24.97g of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}_{(s)}$  powder into the weighing boat using a spatula (measuring to the nearest 0.01g).
- Carefully remove the weighing boat from the scales and empty the powder into the 250cm<sup>3</sup> volumetric flask using a funnel if necessary to ensure that no powder is lost. Lightly tap the bottom of the weighing boat and scrape out any powder using a clean spatula. Ensure that the end of the spatula is also tapped on the inside of the funnel.

- Using a wash bottle of distilled water, carefully wash the inside of the funnel, weighing boat and spatula end into the volumetric flask. Continue to add distilled water to make the solution up to mark.

**Note:** When making the volumetric flask up to mark, refer to **practical technique A**

A small clean funnel may be used to do this step. The funnel must be rinsed into the volumetric flask after use to prevent the loss of any copper(II) solution.

- Place a stopper on the volumetric flask containing the copper (II) sulfate solution and invert several times to ensure the solution is homogeneous.

To form a stock solution of 250cm<sup>3</sup> 0.1M copper (II) sulfate:

- Rinse a 50cm<sup>3</sup> pipette, a 10cm<sup>3</sup> and 5cm<sup>3</sup> graduated burettes with distilled water. Then rinse the 50cm<sup>3</sup> pipette, 10cm<sup>3</sup> graduated burette and 5cm<sup>3</sup> graduated burette with a small quantity of the standard 0.4M copper(II) sulfate solution. Carefully follow the steps described in **Practical technique B** in order to transfer 50cm<sup>3</sup> (using the 50cm<sup>3</sup> pipette) from the 250cm<sup>3</sup> volumetric flask to a new clean 250cm<sup>3</sup> volumetric flask. Carefully follow the steps described in **Practical technique C** in order to transfer 10cm<sup>3</sup> (using the 10cm<sup>3</sup> graduated burette) and finally 2.5cm<sup>3</sup> (using the 5cm<sup>3</sup> graduated burette ) of the 0.4M copper (II) sulfate standard solution to the same new volumetric flask.

Using distilled water, a small clean funnel and a dropper pipette, make the solution in the new 250cm<sup>3</sup> volumetric flask up to mark to form a standard solution of 0.1M copper(II) sulfate.

**Note:** When making the volumetric flask up to mark, refer to **practical technique A**.

- Place a stopper on the volumetric flask containing the copper (II) sulfate solution and invert several times to ensure the solution is homogeneous. This will have formed a solution of 250cm<sup>3</sup> of 0.1M copper (II) sulfate.

### Method 3.1 – Making the copper(II) half-cells (ID 1 to 9) and the copper analyte half-cell

Equipment / reagents	Extra details
Eye protection and lab coat	
3 X 50cm <sup>3</sup> burettes	Rinsed with distilled water and a small amount of the solution they are to be filled with.
3 sets of clamp stands, clamps and bosses	Securely mounted to hold a burette vertically in the fume cupboard.
3 X small clean funnels	Rinsed with distilled water and some of the solution they are to be used with.
10 X 100cm <sup>3</sup> glass beakers	Rinsed with distilled water and dried with some paper towel
Marker pen	To label beakers
Standard 0.4M copper (II) sulfate solution	0.4M solution <b>from method 3.0</b>
Standard 0.1M copper (II) sulfate solution	0.1M solution <b>from method 3.0</b>
Copper analyte solution	Analyte solution <b>from method 1.2</b>
Glass rod	Rinsed with distilled water and dried.

- Rinse a 50cm<sup>3</sup> burette with distilled water and then a small quantity of the 0.4M copper(II) sulfate solution (**from method 3.0**). Mount the burette vertically with a clamp stand, clamp and boss. Fill the burette with 0.4M copper(II) sulfate solution and allow some to run out of

- the tap to displace any air. A small funnel may be required. This should be rinsed with distilled water and a small quantity of the solution being transferred.
- Rinse a 50cm<sup>3</sup> burette with distilled water and then a small quantity of the 0.1M copper(II) sulfate solution (**from method 3.0**). Mount the burette vertically with a clamp stand, clamp and boss. Fill the burette with 0.1M copper(II) sulfate solution and allow some to run out of the tap to displace any air. A small funnel may be required. This should be rinsed with distilled water and a small quantity of the solution being transferred.
  - Rinse a 50cm<sup>3</sup> burette with distilled water. Mount the burette vertically with a clamp stand, clamp and boss. Fill the burette with distilled water and allow some to run out of the tap to displace any air. A small funnel may be required. This should be rinsed with distilled water before use.
  - Refer to **Table 3.1** for the volumes of 0.4M copper(II) sulfate solution to be used in half cells 1 to 5.  
Place a clean 100cm<sup>3</sup> beaker beneath the burette containing the 0.4M copper(II) sulfate solution. Run the correct volume of 0.4M copper(II) sulfate into 5 separate beakers according to the volumes shown in **Table 3.1**. A burette is read by facing the burette neck head-on to reduce parallax error. The initial reading on the burette is read and the final reading will be xcm<sup>3</sup> on from this (where x is the value of 0.4M copper(II) sulfate given in **Table 3.1**). The burette is read to the nearest 0.05cm<sup>3</sup> (reading the scale from the base of the meniscus of the solution level).  
Label each beaker using a marker pen with its concentration of copper(II) and its half-cell ID number (both stated in **Table 3.1**).
  - Place each of the beakers from the previous step beneath the distilled water burette. Run the correct volume of distilled water into each of the 5 beakers corresponding to the value shown in **Table 3.1**. Stir each one with a glass rod but ensure the glass rod is cleaned with distilled water and dried before use in each separate solution.
  - Repeat steps 4 and 5, but this time use the **0.1M copper(II) sulfate solution RATHER THAN the 0.4M copper(II) sulfate standard solution**. Refer to the volumes of the **0.1M copper(II) sulfate half-cells** shown in **Table 3.1**. This will produce half cells with ID 6 to 9.
  - There should now be 9 copper(II) sulfate half cells (ID 1 to 9). Each half-cell contains 50cm<sup>3</sup> of copper(II) sulfate solutions in a 100cm<sup>3</sup> glass beakers with concentrations labelled as 0.4M, 0.3M, 0.2M, 0.11M, 0.1M, 0.09M, 0.08M, 0.07M and 0.06M.
  - Label another 100cm<sup>3</sup> beaker, "copper analyte", using a marker pen. Pour 50cm<sup>3</sup> of the copper analyte solution from the 500cm<sup>3</sup> volumetric flask made up in **method 1.2**. The scale on the side of the 100cm<sup>3</sup> beaker can be used to judge 50cm<sup>3</sup>. Accuracy is not essential here because  $E_{\text{cell}}$  values are dependent on the concentration rather than volume. However, the beaker should be faced head-on to minimise excessive parallax error.

### Method 3.2 – Making a standard solution of 0.5M zinc sulfate in order to make 10 X 0.5M zinc sulfate half-cells

Zinc sulfate (ZnSO<sub>4</sub>·7H<sub>2</sub>O) is supplied in the laboratory as a hydrated solid. It is commonly referred to as zinc sulfate heptahydrate. With a molecular mass of this compound is **287.541 g/mol**.<sup>[8]</sup>

500cm<sup>3</sup> of 0.5M zinc sulfate solution will be made. This is such to allow for 10 X 50cm<sup>3</sup> 0.5M zinc sulfate half cells.

Calculations to make 500cm <sup>3</sup> of 0.5M zinc sulfate solution		
Value	Calculation	Result
Volume of zinc sulfate solution	500cm <sup>3</sup> = 0.500 dm <sup>3</sup>	

Concentration of stock zinc sulfate solution	0.5M	
Moles of zinc sulfate	$0.500 \text{ dm}^3 \times 0.5 \text{ M}$	0.25 mol
Mass of zinc sulfate heptahydrate / $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	$287.541 \text{ gmol}^{-1} \times 0.25 \text{ mol}$	<b>71.86 g (to nearest 0.01g)</b>

**Table 3.4:** Calculating the mass of zinc sulfate required to make a 0.5M 500cm<sup>3</sup> standard solution

Equipment / reagents	Extra details
Eye protection and lab coat	
Sensitive digital balance	Accurate to 0.01g
Large plastic weighing boat	This should be brand new
2 X clean stainless steel spatulas	Rinsed with distilled water and dried with some paper towel.
Small clean funnel	Rinsed with distilled water and dried with some paper towel.
500cm <sup>3</sup> volumetric flask with stopper	Clean
Zinc sulfate heptahydrate solid	The formula is $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}(\text{s})$
Distilled water	In a clean 'wash bottle'
Clean dropper pipette	Rinsed with distilled water.
10 X 100cm <sup>3</sup> glass beakers	Rinsed with distilled water and dried with some paper towel.
Marker pen	To label the beakers of zinc sulfate solution

1. Place a large plastic weighing boat onto the digital balance and zero the balance.
2. Weigh out 71.86g of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}(\text{s})$  solid into the weighing boat using a spatula (measuring to the nearest 0.01g).
3. Carefully remove the weighing boat from the scales and empty the powder into the 500cm<sup>3</sup> volumetric flask using a funnel if necessary to ensure that no powder is lost. Lightly tap the bottom of the weighing boat and scrape out any powder using a clean spatula. Ensure that the end of the spatula is also tapped on the inside of the funnel.
4. Using a wash bottle of distilled water, carefully wash the inside of the funnel, weighing boat and spatula end into the volumetric flask. Continue to add distilled water to make the solution up to mark.

**Note:** When making the volumetric flask up to mark, refer to **practical technique A**

A small clean funnel may be used to do this step. The funnel must be rinsed into the volumetric flask after use to prevent the loss of any zinc sulfate.

5. Place a stopper on the volumetric flask containing the 0.5M zinc sulfate solution and invert several times to ensure the solution is homogeneous.
6. Arrange 10 X 100cm<sup>3</sup> clean rinsed beakers. Pour 50cm<sup>3</sup> of the 0.5M zinc sulfate solution into each beaker, using the scale on the side of the 100cm<sup>3</sup> beakers. Each beaker should be faced head-on in order to reduce parallax error. Accuracy is not essential here because  $E_{\text{cell}}$  values are dependent on the concentration rather than volume.
7. There should now be 10 X 100cm<sup>3</sup> beakers containing 50cm<sup>3</sup> of 0.5M zinc sulfate solution. These can be labelled with marker pen with ID 1 to 10.

### Method 3.3 – Method for making saturated potassium nitrate for salt bridges



Potassium nitrate (V) is supplied as an anhydrous white powder <sup>[9]</sup>. The molecular mass of this is 101.1032 g/mol. A saturated solution of 100cm<sup>3</sup> is required to soak 10 strips of filter paper in. These will be used as salt bridges in the Daniell cell.

Calculations to make 100cm <sup>3</sup> of saturated potassium nitrate (V) solution		
Value	Calculation	Result
Volume of zinc sulfate solution	100cm <sup>3</sup> = 0.100 dm <sup>3</sup>	
The solubility of potassium nitrate (V) in water at 25°C (~room temperature) is 38.3g per 100cm <sup>3</sup> of water. This will allow for a maximum saturation of potassium nitrate (V) <sup>[9]</sup>		
Mass of potassium nitrate (V) to be dissolved ( KNO <sub>3(s)</sub> powder )	38.3g X 1	~ 38g

**Table 3.5:** Calculating the mass of potassium sulfate nitrate(V) required for saturating a salt bridge.

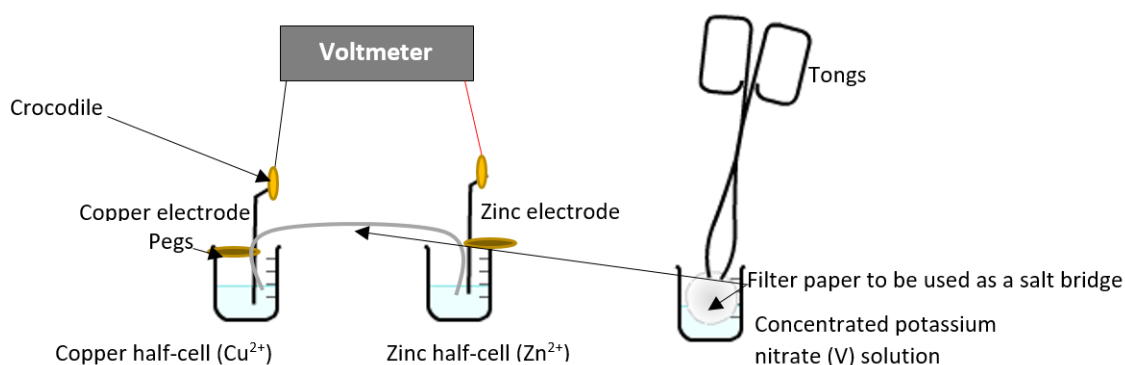
Equipment / reagents	Extra details
Eye protection and lab coat	
Sensitive digital balance	Accurate to 0.01g
10 X strips of filter paper	Cut to roughly 2cm by 15 cm
500cm <sup>3</sup> glass beaker	Rinsed with distilled water and dried with some paper towel.
Glass rod	Rinsed with distilled water and dried with some paper towel.
Potassium nitrate (V) powder	Anhydrous KNO <sub>3(s)</sub> powder
Distilled water	In a clean 'wash bottle'
Sensitive digital balance	Accurate to 0.01g
Plastic weighing boat	This should be brand new
Tongs	To place the salt bridge into the solutions without using your hands

1. Fill the 500cm<sup>3</sup> beaker with 100cm<sup>3</sup> of distilled water (using the scale on the side of the 500cm<sup>3</sup> beaker). Accuracy is not essential for this step.
2. Place a plastic weighing boat onto the digital balance and zero the balance. Weigh out ~38g of KNO<sub>3(s)</sub> solid into the weighing boat using a spatula.
3. Carefully remove the weighing boat from the scales and gradually scrape the KNO<sub>3(s)</sub> powder into the 500cm<sup>3</sup> beaker containing distilled water, stirring simultaneously so that it dissolves. Lightly tap the bottom of the weighing boat and scrape out any remaining powder using a clean spatula.
4. Continue to stir the solution until no more KNO<sub>3(s)</sub> solid dissolves.
5. Using a pair of tongs, submerge all 10 strips of filter paper into the potassium nitrate (V) solution in the 500cm<sup>3</sup> beaker. These will be used as salt bridges in **method 3.4**.

### Method 3.4 - Making the Daniell cells to record E<sub>cell</sub> values

Equipment / reagents	Extra details
Eye protection and lab coat	

10 X salt bridges soaked in saturated potassium nitrate (V) solution	From <b>method 3.3</b>
10 X Half cells of copper(II) sulfate solution	The 50cm <sup>3</sup> samples of varying concentrations of copper(II) sulfate solution and the 50cm <sup>3</sup> copper analyte half-cell from <b>method 3.1</b>
10 X cells of zinc sulfate solution	The 50cm <sup>3</sup> samples of 0.5M zinc sulfate half-cells from <b>method 3.2</b>
Glass rod	Rinsed with distilled water and dried with some paper towel.
Distilled water	In a clean 'wash bottle'
High-resistance voltmeter with two leads	This is high resistance so that negligible current flows between the two half cells in the Daniell Cell.
2 X Crocodile clips for leads	
10 strips of copper metal	Roughly 2cm by 10cm
10 strips of zinc metal	Roughly 2cm by 10cm
2 pieces of emery cloth	Each used to clean metal strips (one for copper and the other for zinc)
2 plastic pegs	To hold the metals strip electrodes to the side of the beaker in the half cells
Tongs	To place the salt bridge into the solutions without using your hands
Paper towel	For drying apparatus



Diagrams made using Microsoft Word 2013 & 'Chemix online', <http://chemix.org/>, developed by Micron developers, © 2007-2017.

- Using tongs, remove a piece of filter paper from the saturated solution of potassium nitrate (V) (**from method 3.3**).
- Clean the 10 copper and 10 zinc metal strips using separate pieces of emery paper (one for the copper and the other for the zinc). Once the metals strips appear shiny and have lost any tarnish, wash them with distilled water to remove any metallic dust or impurities and then dry them with some paper towel.
- Construct a the Daniell cell, whose electrode potential is to be measured, as shown in the diagram above. This is to be done using the 9 X 50cm<sup>3</sup> beakers of copper (II) sulfate half-cells ID1 to 9, the 50cm<sup>3</sup> copper analyte half-cell and the 10 X 50cm<sup>3</sup> 0.5M zinc sulfate half-cells ID1 to 10 (*prepared previously in **method 3.1** and **method 3.2***).
  - The copper strip is placed into the copper (II) half-cell. The zinc strip is placed into the zinc (II) half-cell. In both cases, the metal strip must be submerged as far as possible but it should not touch the inner surface of the beaker or the salt bridge.

- The copper (II) half-cell will form the positive cell and the zinc (II) solution will form the negative cell. Therefore, the positive lead of the high-resistance voltmeter is connected to the top of the copper strip with a crocodile clip. The negative lead of the high-resistance voltmeter is connected to the top of the zinc strip with a crocodile clip. The plastic pegs can be used to securely hold the metal strips to the side of their half-cell beaker.
  - The salt bridge (filter paper soaked in potassium nitrate (V) solution) is to dip into each solution but not touch either electrode. The salt bridge must only be handled using tongs (not hands) and should not come into contact with the surrounding environment (e.g. worktop surfaces) as this will result in contamination that could interfere with  $E_{\text{cell}}$  readings.
4. The electrical potential,  $E_{\text{cell}}$ , is measured between the two half cells for each setup (1 to 9 and the analyte Daniell cell) by reading the value on the high-resistance voltmeter. A graph of  $E_{\text{cell}}$  against the value of  $\ln Q$  is plotted for the Daniell cells that use copper (II) sulfate solutions ID1 to 9.  $\ln Q$  is equal to the value of  $\ln \left[ \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right]$  where  $[\text{Zn}^{2+}]$  is equal to 0.5M for all half-cells and  $[\text{Cu}^{2+}]$  for each half-cell is given in **tables 3.1 and 3.2**.
- 5.

A calibration curve (line of best fit) is drawn onto the graph. The measured electrical potential,  $E_{\text{cell}}$ , for the copper analyte Daniel cell will be used to interpolate a value for  $\ln Q$  from the calibration curve. Therefore, to find the concentration of copper(II) analyte:

$$\ln Q = \ln \left[ \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right] \rightarrow Q = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \rightarrow [\text{Cu}^{2+}] = [\text{Zn}^{2+}] / Q, \text{ Where } Q \text{ is found by the calculation of } e^{\ln Q}$$

This is used to calculate the moles of copper (II) ions in the 50cm<sup>3</sup> sample and then scale this up to account for the total 500cm<sup>3</sup> volume of the analyte solution, thus the moles of copper in the one pence piece.

Using the molecular mass of copper and the total moles of copper in the coin, the mass of copper present in the coin can be calculated. A percentage is then made relative to the mass of the original coin. The percentage mass is then compared to the percentage mass of copper in a standard pre-1992 one pence piece as published by the Royal Mint.

### Risk Assessment for section 3.0

Risk	Hazard	Precaution	Source ID
Copper analyte solution ( $\text{Cu}^{2+}$ , $\text{Sn}^{2+}$ , $\text{Zn}^{2+}$ , $\text{NO}_3^-$ , $\text{H}^+$ )	Acidic solution and nitrates present have oxidising properties so can cause violent reactions with reducing agents. Copper (II) nitrate is harmful if ingested and can irritate the eyes and skin. Zinc ions in solution are harmful and can compounds be irritant to the skin.	Wear eye protection and a protective lab coat. Wash skin well if in contact. Solution should be kept in a fume cupboard encase any further oxidation occurs to release toxic nitrogen dioxide or nitrogen oxide if the solution is dilute. Spills on tabletops, floors etc. should be flooded with water and mopped up. Large spills should be cleared using a mineral absorbent. Do not inhale or ingest. Keep away from reducing agents and other chemicals not needed in the practical. Keep away from any naked flames to prevent toxic fumes.	2a 4 7
Zinc(II) sulfate(VI) solution, 0.5 M	Harmful/Irritant.	Wear eye protection	2a 2b

	Harmful if ingested – may cause nausea and abdominal pain. Risk of serious damage to the eyes	Do not ingest or inhale; use in a well-ventilated lab. Wash skin well if in contact. Spills on tabletops, floors etc. should be flooded with water and mopped up.	
Potassium nitrate (V) solution, concentrated	The solution is an oxidising agent so can cause violent reactions and explosions with reducing agents. May aid combustion of other substances and give off toxic/irritating fumes in fires. Irritating to the skin and eyes. Ingestion can result in abnormal pain, blue skin and dizziness/nausea.	Keep away from reducing agents and other chemicals not needed in the practical. Spills on tabletops, floors etc. should be flooded with water and mopped up. Do not ingest and avoid inhalation; use in a well-ventilated lab. Keep away from any naked flames to prevent toxic fumes. Wash skin well if in contact. Wear eye protection	3a 3b
Copper metal and compounds	Low hazard – dust from cleaning may irritate lungs for those with respiratory problems	Avoid inhaling fine dust during cleaning of the copper strip.	4
Zinc metal and compounds	Low hazard – dust from cleaning may irritate lungs for those with respiratory problems. Zinc dust is highly flammable, it can react with water to produce the highly flammable gas hydrogen in suitable conditions.	Avoid inhaling fine dust during cleaning of the copper strip. Ensure the zinc strip is rinsed with distilled water and dried after cleaning. Keep the zinc dust away from naked flames.	5
Zinc (II) Nitrate (V) formed in the zinc half-cell	Oxidising agent can cause violent reactions with strong reducing agents. Non-combustible but may enhance combustion of other substances when dry. Gives off toxic/irritating fumes in fires. Ingestion results in abdominal pain and nausea.	Keep away from reducing agents and other chemicals not needed in the practical. Spills on tabletops, floors etc. should be flooded with water and mopped up. Do not ingest and avoid inhalation; use in a well-ventilated lab. Keep away from any naked flames to prevent toxic fumes. Wash skin well if in contact. Wear eye protection	6
Potassium Sulfate (VI) formed in the copper half-cell	Low Hazard. May be harmful if ingested: causing Nausea.	Do not ingest. Wash hands if in contact. Wear eye protection.	3a
Copper(II) sulfate compound and solution	Low hazard May be harmful if ingested: causing Nausea.	Do not ingest. Wash hands if in contact. Wear eye protection.	4
Source ID	Institute/name	URL/link	Year
1	CLEAPSS	Hazards: 21,34, 49, 40 <a href="http://www.cleapss.org.uk/resource/Student-Safety-Sheets-ALL.pdf">www.cleapss.org.uk /resource/Student-Safety-Sheets-ALL.pdf</a>	2017
2a	CLEAPSS	Hazcard 49: Zinc & its compounds, <a href="http://www.cleapss.org.uk/resource/Student-Safety-Sheets-ALL.pdf">www.cleapss.org.uk /resource/Student-Safety-Sheets-ALL.pdf</a>	2017
2b	NIOSH > International Chemical Safety Cards (ICSC)	Centres for Disease Control and Prevention, <a href="https://www.cdc.gov/niosh/ipcsneng/neng1698.html">https://www.cdc.gov/niosh/ipcsneng/neng1698.html</a>	2014-2015
3a	CLEAPSS	CLEAPSS Hazcard 34: Sodium & Potassium Salts, <a href="http://www.cleapss.org.uk/resource/Student-Safety-Sheets-ALL.pdf">www.cleapss.org.uk /resource/Student-Safety-Sheets-ALL.pdf</a>	2017
3b	NIOSH > International Chemical Safety Cards (ICSC)	Centres for Disease Control and Prevention, <a href="https://www.cdc.gov/niosh/ipcsneng/neng0184.html">https://www.cdc.gov/niosh/ipcsneng/neng0184.html</a>	2014-2015

4	CLEAPSS	Hazard 40: Copper & its compounds, <a href="http://www.cleapss.org.uk/resource/Student-Safety-Sheets-ALL.pdf">www.cleapss.org.uk /resource/Student-Safety-Sheets-ALL.pdf</a>	2017
5	CLEAPSS	Hazard 49: Zinc & its compounds, <a href="http://www.cleapss.org.uk/resource/Student-Safety-Sheets-ALL.pdf">www.cleapss.org.uk /resource/Student-Safety-Sheets-ALL.pdf</a>	2017
6	NIOSH > International Chemical Safety Cards (ICSC)	Centres for Disease Control and Prevention, <a href="https://www.cdc.gov/niosh/ipcsneng/neng1206.html">https://www.cdc.gov/niosh/ipcsneng/neng1206.html</a>	2014-2015
7	CLEAPSS	CLEAPSS Hazard: 21 Nitric (V) acid, <a href="http://www.cleapss.org.uk/resource/Student-Safety-Sheets-ALL.pdf">www.cleapss.org.uk /resource/Student-Safety-Sheets-ALL.pdf</a>	2017

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