

The Effect of Temperature and Concentration on Galvanic Cells

ABSTRACT

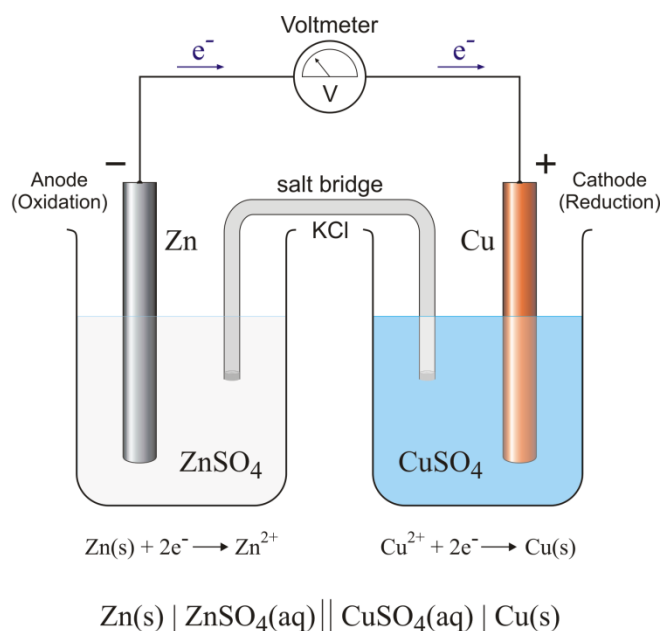
Standard electrode potentials are always specified as the voltage potential under standard conditions (25°C , 1.00 mol L^{-1}), as the voltage is dependent upon both temperature and electrolyte concentration. Here, the effect of temperature and concentration on the voltage of a Daniell cell is quantified. The results were quite dissimilar to that of previous work in this area; this may be due to differences in the salt bridge used. At a constant temperature of 30°C , the electrolyte concentration had a moderate effect on voltage potential – up to 1.3%. The relationship between voltage and temperature was dependent upon the electrolyte concentrations, however all trials showed a strong positive correlation. The maximum change in voltage potential observed was 1.95%, when the temperature of the cell changed from 24 to 69°C . These results may be of importance to manufacturers of batteries or electronic devices that might be used in extreme temperatures.

INTRODUCTION

Galvanic cells, most commonly utilised in the form of batteries, have become one of the most ubiquitous devices in the modern era, and can be found in virtually every portable electronic device. Factors such as the metals constituting the electrodes play a large role in determining the voltage potential of a galvanic cell, however other variables such as concentration and temperature do affect the voltage produced. For this reason, standard electrode potentials are given as the electrode potential under standard conditions, i.e. electrolyte concentrations of 1.000 mol L^{-1} , and a temperature of 25°C (Smith et. al 2010). But how much difference does changing these conditions really make?

The effect of temperature on the potential of a galvanic cell has relevance to all applications that use batteries, as some temperatures may reduce the voltage of the battery to a point where it is unable to perform its intended purpose. Knowing how the voltage of a cell is affected by temperature is important for manufacturers designing electronic devices to be used under extremely hot or cold conditions, in order to incorporate a large enough

Figure 1 – Diagram of a Galvanic Cell

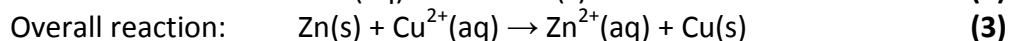
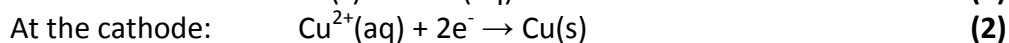
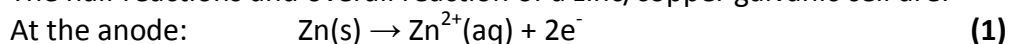


margin that the device can continue to operate.

Galvanic cells convert chemical energy into electrical energy, through redox reactions (Smith et. al 2010). Figure 1 shows the basic elements of a zinc/copper galvanic cell: a zinc electrode in a solution of zinc sulfate, a copper electrode in a solution of copper sulfate, a salt bridge connecting the two solutions, and a wire connecting the two electrodes.

At the anode (negative electrode), zinc is oxidised to zinc ions (Zn^{2+}), and at the cathode (positive electrode), copper ions (Cu^{2+}) are reduced to metallic copper. The salt bridge allows anions (negative ions) to migrate toward the anode, completing the circuit. It also allows cations (positive ions) to migrate toward the cathode, and balance the charge imbalance caused by the movement of anions. The sulfate ion (SO_4^{2-}) is a spectator ion, and does not react.

The half reactions and overall reaction of a zinc/copper galvanic cell are:



The Nernst equation is used to predict the voltage potential of a galvanic cell at non-standard temperatures and concentrations (Wikipedia 2016). The Nernst equation is:

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - (RT/zF) \times \ln(Q_r) \quad (4)$$

where E_{cell} = voltage of cell under non-standard conditions, E_{cell}° = standard cell potential, R = universal gas constant ($8.314472 \text{ J K}^{-1} \text{ mol}^{-1}$), T = temperature in Kelvin, z = no. moles of electrons transferred in reaction, F = Faraday constant ($96,485.34 \text{ C mol}^{-1}$), and Q_r = the reaction quotient.

Predictions from the Nernst equation are shown in Appendix 5.

HYPOTHESIS

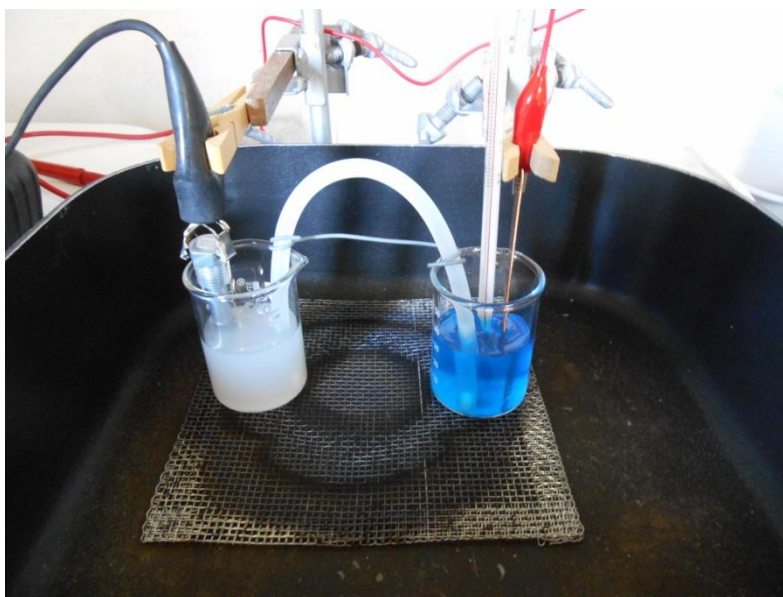
It was hypothesised that the voltage produced by the galvanic cell would decrease as the temperature increases, according to the Nernst equation. Walding (n.d.) reported a slope of $-0.0023 \text{ V/}^{\circ}\text{C}$, and similar results were expected for this experiment.

Furthermore, it was hypothesised that reducing the concentration of either or both electrolytes in the galvanic cell would reduce the voltage of the cell, as there would be less reactants, so the reaction should be slower and produce less electricity.

Figure 2 – The Experimental Setup

PROCEDURE

1. A standard Daniell cell was created, using approximately 35 mL of 1.00 mol L⁻¹ zinc sulfate in one beaker, and about 35 mL of 1.00 mol L⁻¹ copper sulfate in the other. The two half cells were joined with a salt bridge consisting of a piece of rubber tubing, filled with 0.50 mol L⁻¹ sodium sulfate (Na₂SO₄). The ends of the tubing were plugged with small pieces of cotton wool, which allowed ions to pass through, but ensured that the solution inside the tubing did not leak out.
2. The experimental setup is shown in Figure 2.
3. The galvanic cell was placed on a hotplate, and heated to approximately 70°C.
4. At this point, the hotplate was turned off and allowed to gradually cool down.
5. As the cell cooled down¹, the voltage was recorded at approximately every 5°C, using a digital multimeter accurate to 0.001 V. When the display was flicking between two numbers, the average of those numbers was recorded. The temperature at each measurement was also recorded, accurate to 0.5°C, using a thermometer immersed in the copper sulfate solution.
6. The multimeter was disconnected from the circuit when not in use, to ensure that the cell did not run 'flat' over time. Additionally, the salt bridge was not placed into the cell until the maximum temperature was reached.
7. Steps 1 to 6 were repeated using 0.10 mol L⁻¹ solutions of both substances.



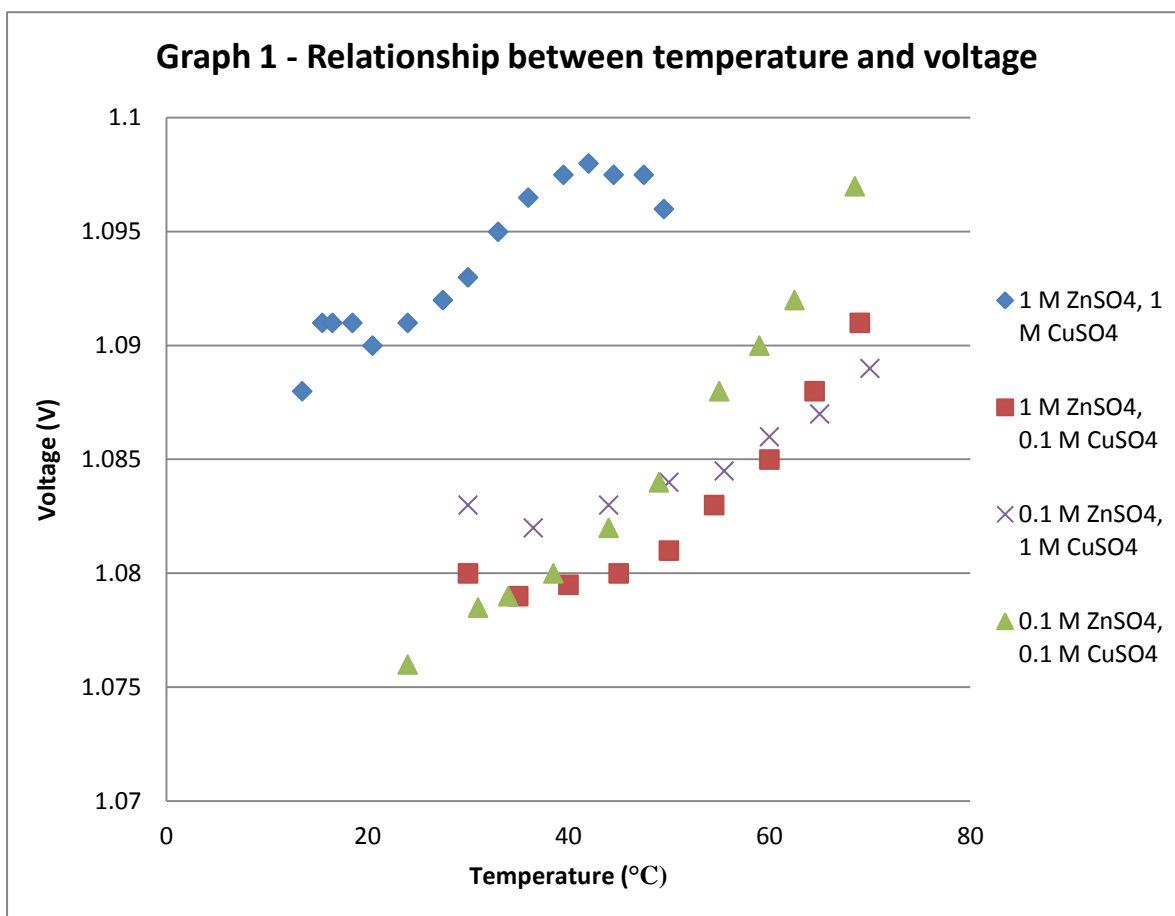
MODIFICATIONS

Temperatures below room temperature were not tested, to reduce the time each trial took. The maximum temperature was raised from 50 to 70°C, so the temperature range tested was large enough to accurately determine the relationship between temperature and voltage. Tubing filled with sodium sulfate was used instead of a paper salt bridge, to prevent the salt bridge drying out, which could bias the results. Concentrations of 0.10 mol L⁻¹ were tested instead of 0.50 mol L⁻¹, in order to maximise any voltage differences.

¹ The voltage of the 1 M ZnSO₄/ 1 M CuSO₄ cell was recorded as the temperature increased.

RESULTS

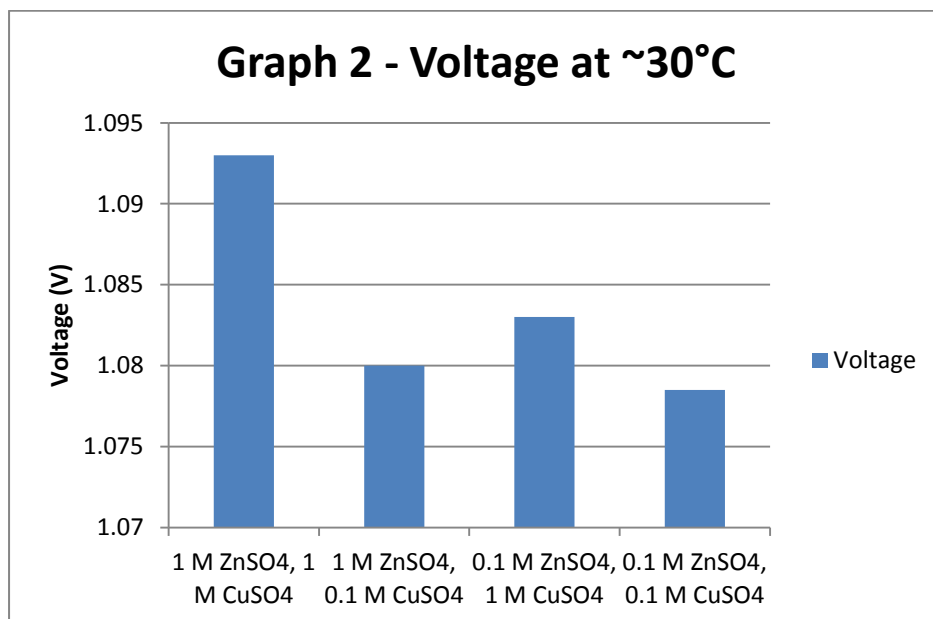
The results are summarised in Graph 1. The raw data collected is available in Appendix 2.



The voltage of each cell at around 30°C is shown in Table 1 and Graph 2 (not all cells were tested at 25°C, which is normally considered the standard temperature).

Table 1 – Voltages at ~30°C

ZnSO ₄ concentration (M)	CuSO ₄ concentration (M)	Voltage (V)	% of 1 M ZnSO ₄ , 1 M CuSO ₄ cell
1.00 M	1.00 M	1.093	100.0%
1.00 M	0.10 M	1.080	98.81%
0.10 M	1.00 M	1.083	99.09%
0.10 M	0.10 M	1.0785	98.67%



DISCUSSION

At 30°C, the voltage of the 1 M ZnSO₄/ 1 M CuSO₄ cell (hereafter referred to as 1 M/ 1 M) was 1.093 V, only 0.6% less than the 1.10 V potential predicted by standard electrode potentials (calculations in Appendix 4). This suggests that the constructed cell was functioning correctly and in a similar fashion to a theoretical cell.

The concentration of the solutions in the half cells had a considerable effect on the voltage potential (Graph 2). At 30°C, the 1 M/ 1 M cell had the highest voltage by a significant margin. The 1 M ZnSO₄/ 0.1 M CuSO₄ and 0.1 M ZnSO₄/ 0.1 M CuSO₄ cells were significantly lower, at 98.81% and 98.67% of the 1 M/ 1 M cell, respectively. The 0.1 M ZnSO₄/ 1 M CuSO₄ cell was slightly higher, at 99.09%.

This suggests that lower concentrations of electrolytes will lower the potential voltage of a cell, as hypothesised. Reactions occur slower at lower concentrations, so the voltage produced might be lower. This could at least partly explain the lower voltage of cells with lower electrolyte concentrations.

Temperature had a much greater effect than concentration. Although the voltage potential of all the cells increased with increasing temperature, none of them exhibited a linear relationship like predicted. Instead, most cells exhibited a quadratic curved relationship, except for the 1 M/ 1 M cell, which was closer to a cubic curve. The lines of best fit are shown in Graph 4, Appendix 3.

This was unexpected, as Walding (n.d.) stated that the voltage potential decreases as temperature increases. In addition, he found an almost linear relationship, whereas this experiment found a more quadratic relationship. In addition, when linear trendlines were fitted to the data (Graph 3, Appendix 3), the magnitude of the change found (0.0003 V/°C)

was over 10 times lower than the change reported by Walding (n.d.), which was $-0.0023 \text{ V}/^\circ\text{C}$. It is unclear why the results were significantly different to previous work, however it may partly be to do with the salt bridge. Walding used a paper strip saturated in KNO_3 , which would probably have a different conductivity from the tubing used as a salt bridge in this experiment. This hypothesis is supported by the fact that at 28°C , Walding's cell had a voltage potential of only 0.959 V , whereas the cell used in this experiment had a potential of 1.092 V at a temperature of 27.5°C – much closer to the theoretical value. Although there may be other explanations, it appears the galvanic cells used here were more accurate models of a theoretical cell. To determine if this is the case, further testing of the voltage potential difference between otherwise identical cells with salt bridges made of paper or tubing is required.

The results also did not align with those predicted by the Nernst equation (see Appendix 5). This is likely due to experimental error, and probably the fact that the Nernst equation is only accurate for relatively dilute concentrations (Wikipedia 2016).

The $1 \text{ M}/1 \text{ M}$ trial was the only one that showed major anomalies – the cluster of temperature around 15°C , and decrease in potential voltage as the temperature continued to increase. The overall relationship displayed by the $1 \text{ M}/1 \text{ M}$ cell did not fit with that of the other cells, which may be due the fact that the voltage was recorded as the temperature increased, rather than as it decreased.

The $0.1 \text{ M}/0.1 \text{ M}$ cell displayed the steepest curve, with a range of about 0.0185 V between 30 and 70°C , while the $0.1 \text{ M}/1 \text{ M}$ showed the shallowest. The $1 \text{ M}/0.1 \text{ M}$ cell had a moderate slope, approximately half way between than that of the other two. The reason behind this difference in steepness is not clear. As the CuSO_4 solution should be getting used up by the reaction, but the ZnSO_4 is not, it could be predicted that the CuSO_4 concentration should make a greater difference than the ZnSO_4 concentration. Although this theory is supported by the voltages at 30°C (Graph 2), there is not a lot of evidence for it in the full dataset (Graph 1), as the 1 M CuSO_4 cells appear to have a shallower slope than the 0.1 M CuSO_4 cells.

The findings are relevant to manufacturers of devices that may experience extreme temperatures, as the battery voltage may vary markedly, depending on the temperature. Manufacturers need to ensure that the voltage of their batteries allow a margin for fluctuations caused by temperature changes. For example, at 69°C , the voltage of the $0.1 \text{ M}/0.1 \text{ M}$ cell was 0.021 V , or 1.95% higher than the voltage at 24°C . Although this difference would likely not affect an electronic device, the voltage difference may be exacerbated by batteries, which consist of multiple galvanic cells. The quadratic-like curved relationships observed in this experiment also suggest that this effect may be more significant at higher temperatures, and vice versa.

There are several limitations to this experiment. Only one trial was performed for each of the four cells, so the data may not be entirely accurate. Multiple trials would be required to accurately examine the relationship between temperature, electrolyte concentration and voltage, as it appears to be quite complex. In addition, it is not clear whether the voltage potential is the same whether the temperature is increasing or decreasing. Further research

in this area could investigate whether the relationship is linear or quadratic, and also look at temperatures below 20°C, which were not investigated in this study.

CONCLUSION

The results supported the hypothesis that lowering the electrolyte concentrations lowers the voltage potential of a galvanic cell. However this effect was not substantial, resulting in voltage differences of up to 1.3%. There was also little difference whether the ZnSO₄ concentration, the CuSO₄ concentration, or both were lowered. This suggests that the electrode metals play a much larger part in determining the voltage potential of a galvanic cell than the concentrations of the electrolytes.

The temperature had a significant effect on the voltage potential, which increased with increasing temperature. There was a noticeable difference between cells containing different electrolyte concentrations, with the 0.1 M ZnSO₄/ 0.1 M CuSO₄ cell displaying the steepest slope, and the 0.1 M ZnSO₄/ 1 M CuSO₄ cell showing the shallowest.

Manufacturers of electronic devices may find this information of use when planning what voltage the battery of a device should be.

REFERENCES

Smith, D, Monteath, S, Gould, M & Smith, R 2010, *Chemistry in use book 1*, Cengage Learning Australia, South Melbourne, Victoria.

Thompson, RB 2008, *Illustrated guide to home chemistry experiments*, O'Reilly Media, Sebastopol, California.

Walding, R n.d., *Senior chemistry – 'Deadly' EEI Ideas*. Available from: <http://seniorchem.com/eei.html>. [17 May 2016].

Wikipedia 2016, *Nernst equation*. Available from: https://en.wikipedia.org/wiki/Nernst_equation. [20 July 2016].

APPENDIX 1 – Risk assessment

The risk assessment for the experiment is shown below.

Potential Risk	Management of the Risk
Copper sulfate is irritating to eyes and skin	Gloves and goggles will be worn at all times.

(Thompson 2008).	
Zinc sulfate is irritating to eyes and respiratory tract (Thompson 2008).	Goggles will be worn, and exposure to the chemical in its powder form will be minimised.
Burns from hot liquid or the hotplate.	A maximum temperature of 70°C will be used, which should prevent any serious burns. Operational procedures will minimise the chance of a burn.

APPENDIX 2 – Raw Data

1 M ZnSO₄, 1 M CuSO₄

Temperature	Voltage
13.5	1.088
15.5	1.091
16.5	1.091
18.5	1.091
20.5	1.09
24	1.091
27.5	1.092
30	1.093
33	1.095
36	1.0965
39.5	1.0975
42	1.098
44.5	1.0975
47.5	1.0975
49.5	1.096

1 M ZnSO₄, 0.1 M CuSO₄

Temperature	Voltage
69	1.091
64.5	1.088
60	1.085
54.5	1.083
50	1.081
45	1.08
40	1.0795
35	1.079
30	1.08

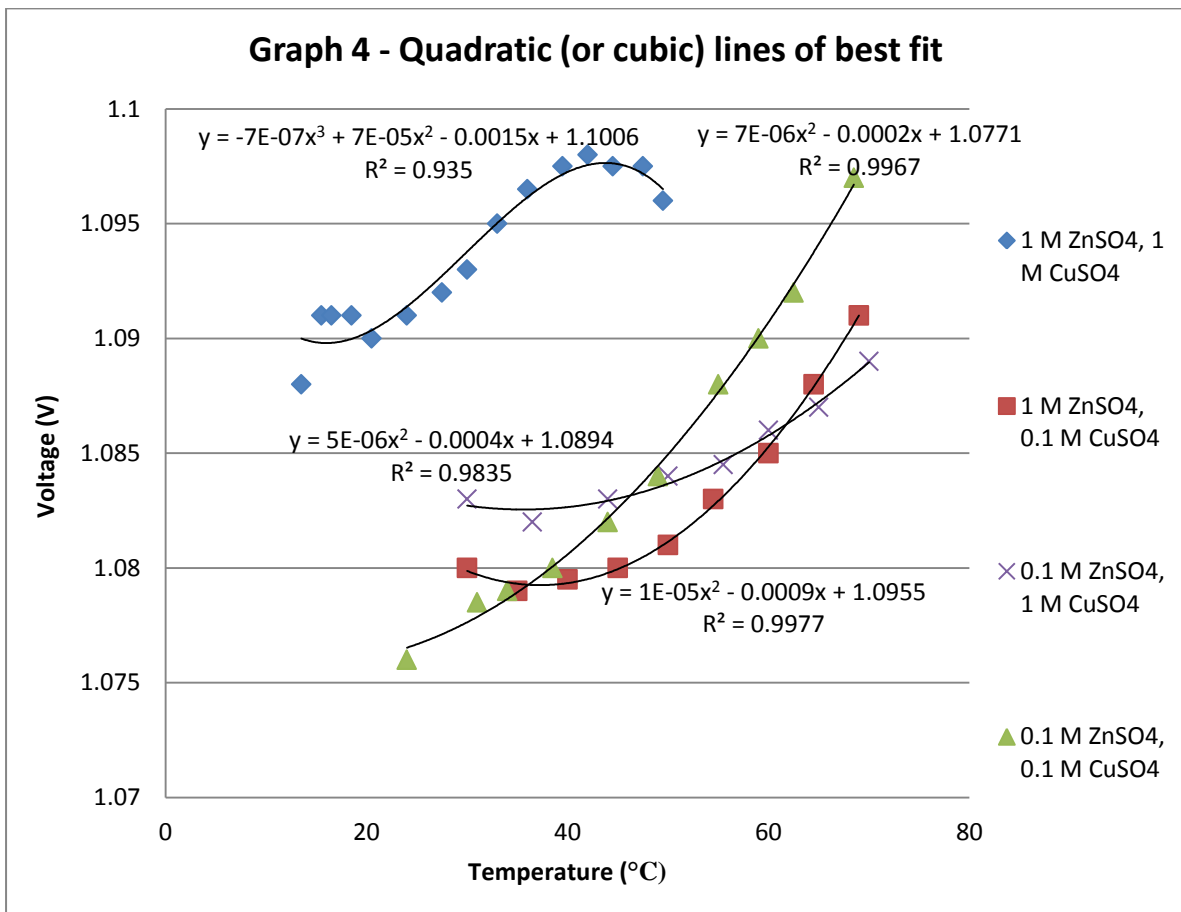
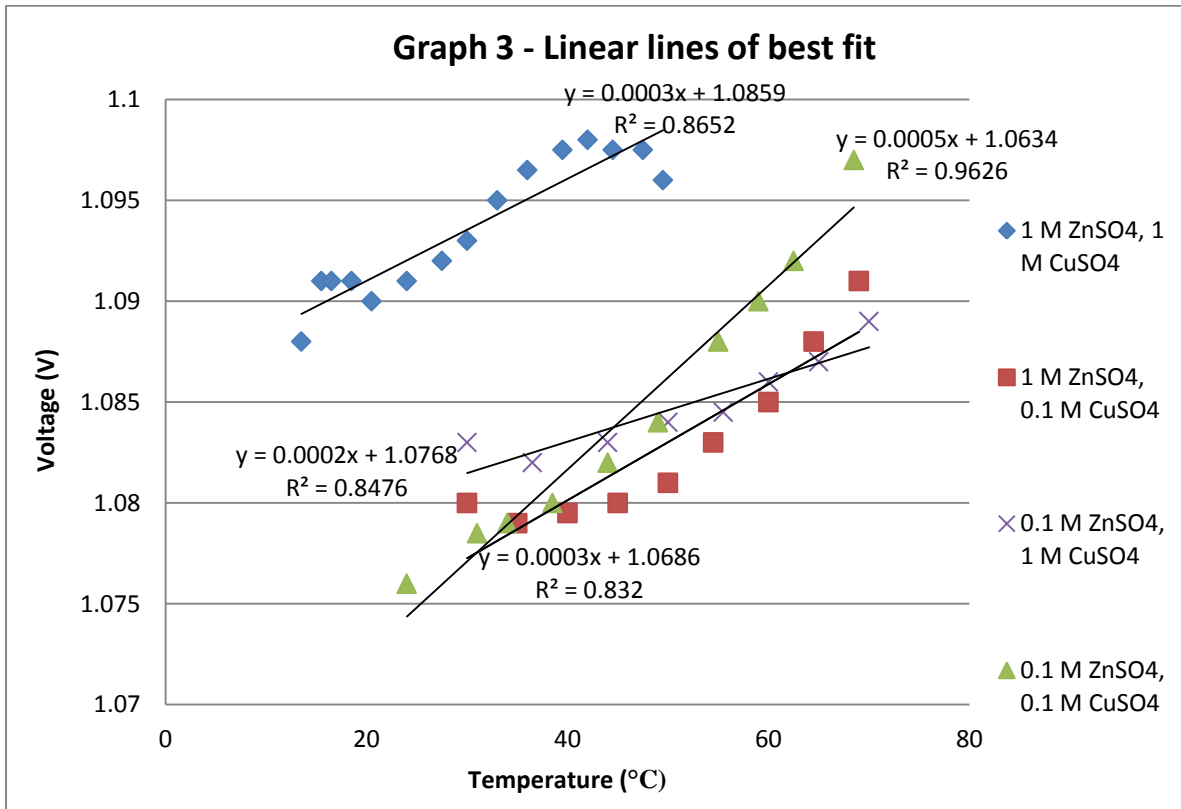
0.1 M ZnSO₄, 1 M
CuSO₄

Temperature	Voltage
10.5	1.093
69	1.09
71	1.093
70.5	1.091
68.5	1.088
65	1.087
60	1.0855
54.5	1.087
50	1.088
45	1.089
40	1.089
34.5	1.088
31	1.087
16	1.0905

0.1 M ZnSO₄, 0.1 M
CuSO₄

Temperature	Voltage
24	1.076
68.5	1.097
62.5	1.092
59	1.09
55	1.088
49	1.084
44	1.082
38.5	1.08
34	1.079
31	1.0785

APPENDIX 3 – Graph with lines of best fit



APPENDIX 4 – Voltage predicted by standard electrode potentials

The standard electrode potential for the reduction of copper is 0.34 V (Smith et. al 2010). As the standard electrode potential for the reduction of zinc is -0.76 V (Smith et. al 2010), the electrode potential for the oxidation of zinc will be 0.76 V – as the oxidation potential is .

The voltage produced by the cell is:

$$EMF_{(total)} = EMF_{(reduction)} + EMF_{(oxidation)}$$

$$EMF_{(total)} = 0.34 \text{ V} + 0.76 \text{ V}$$

$$EMF_{(total)} = 1.10 \text{ V}$$

Therefore, the galvanic cell should theoretically produce 1.10 V at a temperature of 25°C (assuming ZnSO₄ and CuSO₄ concentrations of 1.00 mol L⁻¹).

APPENDIX 5 – Theoretical voltages from Nernst equation

The Nernst equation is:

$$E_{cell} = E^{\ominus}_{cell} - (RT/zF) \cdot \ln(Q_r) \quad (4)$$

where E_{cell} = voltage of cell under non-standard conditions, E^{\ominus}_{cell} = standard cell potential, R = universal gas constant (8.314472 J K⁻¹ mol⁻¹), T = temperature in Kelvin, z = no. moles of electrons transferred in reaction, F = Faraday constant (96,485.34 C mol⁻¹), and Q_r = the reaction quotient.

For a zinc/copper cell, $z = 2$, as there are 2 electrons transferred, as shown in the balanced equation (Equation 3). $E_{cell} = 1.10 \text{ V}$, as shown in Appendix 4. Therefore:

$$E_{cell} = E^{\ominus}_{cell} - [(8.314472 \text{ J K}^{-1} \text{ mol}^{-1} \times T/2 \times 96,485.34 \text{ C mol}^{-1}) \times \ln(Q_r)]$$

$$E_{cell} = 1.10 - (4.3087 \times 10^{-5} \text{ K}^{-1} \times T) \times \ln(Q_r)$$

The reaction quotient (Q_r) will be equal to the concentration of the zinc sulfate (as it is the reactant) divided by the concentration of copper sulfate. Using this value gives the theoretical voltages in Table 2.

Table 2 – Theoretical voltages from Nernst equation

Cell	Temperature (°C)	Theoretical Voltage (V)	Observed Voltage (V)
1 M CuSO ₄ , 1 M ZnSO ₄	30	1.100	1.093
1 M CuSO ₄ , 1 M ZnSO ₄	50	1.100	1.096
1 M CuSO ₄ , 0.1 M ZnSO ₄	30	1.401	1.080

ZnSO ₄				
1 M CuSO ₄ , 0.1 M ZnSO ₄	70	1.440	1.091	
0.1 M CuSO ₄ , 1 M ZnSO ₄	30	0.799	1.087	
0.1 M CuSO ₄ , 1 M ZnSO ₄	70	0.760	1.091	
0.1 M CuSO ₄ , 0.1 M ZnSO ₄	30	1.100	1.0785	
0.1 M CuSO ₄ , 0.1 M ZnSO ₄	70	1.100	1.097	