Determining the effect of electrolyte concentration of the voltage produced by galvanic cells

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Contents

1 Rationale

1.1 Background

Redox

Redox reactions are reactions that involve the transfer of electrons between atoms. These reactions commonly occur within galvanic cells, which within themselves contain two half cells.

Half Cells

Half cells consists of an electrolyte solution and electrode. When two half cells are connected through a load, and a salt bridge, one of these half cells will become the anode, where oxidation occurs, and the other will become the cathode, where reduction occurs. The oxidised cell will transfer its electrons across a wire, where they will then reach and be accepted by the reduced cell.

Each half cell has its own standard electrode potential (E^0) which dictates the magnitude of electron emission, or attraction it has under standard lab conditions.

By measuring the difference in magnitude between half cells, the overall potential between the cells can be quantified.

$$E^0{}_{\text{Cell}} = E^0{}_{\text{Cathode}} - E^0{}_{\text{Anode}}$$

For this experiment, the half cells will be made up of zinc and copper, which have E^0 values of -0.7618V, and $+0.3419$V respectively. Cell's with this composition are also known as "Daniell Cells", and will have a theoretical voltage, under standard conditions, of:

$$(0.3419 - (-0.7618)) = 1.1037\text{V}$$

The Nernst Equation

The Nernst equation is a mathematical equation that allows the theoretical voltage potential of a cell to be quantified under non-standard conditions. While factors such as temperature and pressure throughout the experiment were not modified, the reaction quotient (Q) was indirectly altered by the change in $[CuSO_4]$.

The Nernst equation is defined as:

$$E_{\text{cell}} = E^0 - \frac{RT}{nF} \cdot \ln(Q)$$

Where:

- E = Theoretical electrode potential (voltage)of the cell
- E^0 = Standard electrode potential of the cell
- T = Temperature in kelvin
- R = Universal gas constant
- F= Faraday constant
- z = Number of moles of electrons transferred
- Q = Reaction Quotient

Substituting

$$E_{\text{cell}} = (0.3419 + 0.7618) - \frac{8.31446261815324 \cdot 298}{2 \cdot 96485} \cdot \ln \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$E_{\text{cell}} = (0.3419 + 0.7618) - \frac{8.31446261815324 \cdot 298}{2 \cdot 96485} \cdot \ln \frac{1}{[Cu^{2+}]} \because [Zn^{2+}] \text{ remains constant}$$
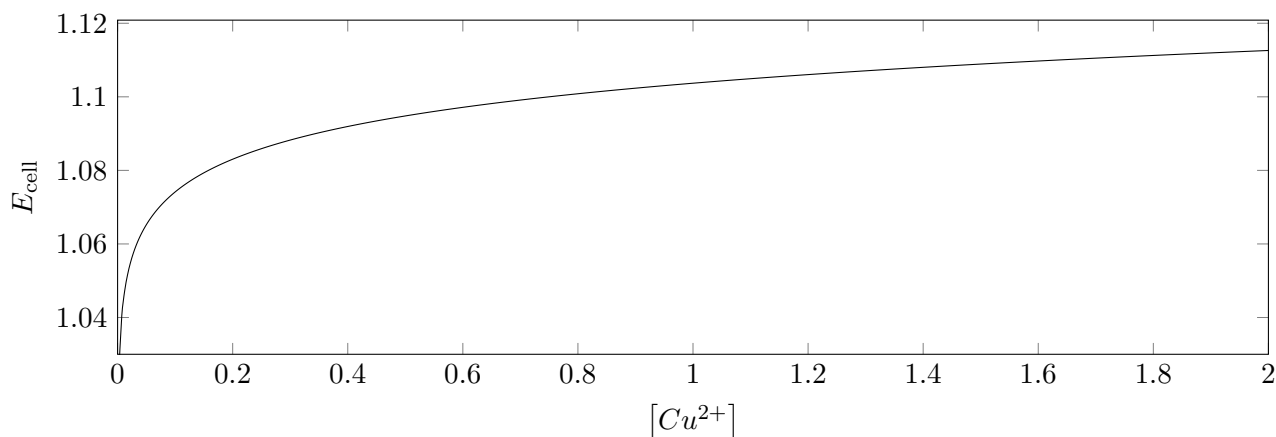
Figure 1: The theoretical relationship between E_{cell} and $[Cu^{2+}]$

Considering Figure 5, the theoretical change in E_{cell} is minuscule in comparison to the change in $[Cu^{2+}]$. When the x-axis increases from 0.5 to 1, a change of only 0.009V is observed. If the relationship is further considered, with domain [0.5, 2], increasing concentration by a factor of 4 only results in an an additional 0.018V. It was questioned whether this relationship held true, especially as $\lim_{x \to 0}$. Investigation of $[Cu^{2+}] = (0, 1]$ would theoretically be the most distinguishable from a logarithmic relationship if the observed relationship diverges due to the distinct curve observed in the area. Clearly $[Zn^{2+}] = [Cu^{2+}] \neq 0$, as this would either result in a division by 0, or ln(0), which are both undefined.

1.2 Research Question

How does altering $[CuSO_4]$ at low concentrations (0-1 mol) affect its voltage output, and does the observed relationship follow the theoretical relationship when applying the Nernst equation.

2 Methodology

2.1 Modifications

The following modifications were made to the original experiment. The original method can be found in the appendix section.

Half Cell Compositions

The results of original experiment indicated that copper and aluminium produced the largest voltage. It was theorised that after multiple trials, the aluminium would oxidise, skewing results.

It was decided that copper and zinc would be more suitable as although they produced a smaller voltage, zinc would take longer to oxidise and therefore producer more consistent results.

Electrodes

Rather than thin strips, larger plates were bent into a "C" shape, slightly smaller than the diameter of the beaker they would be placed in. This maximised the surface area in contact with the electrolyte solution. Furthermore by reusing the same electrodes, this surface area was constant for all trials.

Measurement devices

A digital multimeter was substituted in place of the conventional analog volt meter. Since the digital multimeter uses digital logic to measure voltage, rather than a magnetic field induced by the flow of current, the digital multimeter should reduce the ions 'used up' during each measurement. Furthermore the digital output measures volts to 3 decimal places, leading to reduced uncertainty and increased precision.

Salt Bridge

The salt bridge was unaltered, and still made from filter paper, however, care was taken to ensure consistency in their size.

Procedure

The electrolyte solutions were pre-mixed, labelled, and stored in sealed containers prior to the start of the experiment. This reduced the potential for errors in procedure, as well as the time it took to conduct the experiment, which reduced the influence of environmental factors, such as changes in temperature, on results.

2.2 Method

Materials

- 30ml $CuSO_4$ at concentrations 1.00M, 0.85M, 0.70M, 0.55M, 0.40M, 0.30M, 0.20M, 0.10M
- 240ml 1M $ZnSO_4$
- 20ml KNO_3
- Petri dish
- 50ml Beaker - x2
- Zinc sheet $\approx$ 4cm $\times$ 6cm
- Copper sheet $\approx$ 4cm $\times$ 6cm
- Emery paper
- Filter paper strips $\approx$ 2cm $\times$ 10cm
- Digital Multimeter
- Alligator clips
- 150ml Plastic bottle - x16
- Tweezers
- 1L Distilled water
- Emery paper

Procedure

1. Pour varying amounts of $CUSO_4$ into 150ml plastic bottles and dilute with distilled water to form solutions with concentrations 1.00M, 0.85M, 0.70M, 0.55M, 0.40M, 0.30M, 0.20M and 0.10M.
2. Fill 8 of the 150ml plastic bottles with 30ml of 1M $ZnSO_4$ and set aside with copper solutions.
3. Polish electrodes with emery paper until they their entire surface is free of visible oxidation then connect to alligator clips.
4. Connect alligator clips to multimeter and set to DC voltage mode.
5. Transfer the contents of a $CUSO_4$, and $ZnSO_4$ container into separate beakers.
6. Wet salt bridge with KNO_3 and rest over the lip of both beakers, so that it is partially submerged in both.
7. Add the electrodes to the solution and record result as soon as value settles.
8. Remove electrodes immediately and wash with distilled water. Stir electrolyte solutions with a glass stir rod. Remove salt bridge and dispose of.
9. Reconstruct cell with a new salt bridge, add electrodes back, and repeat measurementation so that there are three trials in total for any given concentration.
10. Safely dispose of electrolyte solutions, wash equipment, and repeat for next $CUSO_4$ concentration.

2.3 Risk assessment

While the electrolytes utilised in this experiment are considered to be harmful if ingested or applied to a persons eyes, there is no risk of injury via inhalation or accidental skin contact as long as appropriate action is taken (ventilation, washing affected area). PPE was worn by all participants to protect their eyes (Lab goggles), body (lab coat) and hands (nitrite gloves). The electrolyte materials are also considered environmental hazards $(CuSO_4, ZnSO_4)$, however since the quantities used were so low, they could safely be disposed of in the sink with after dilution. *For other risks or more details, see risk assessment table attached as an appendix.*

3 Results

$[CuSO_4]$	Voltage			Mean	sigma
	Trial 1	Trial 2	Trial 3		
1	0.703	0.678	0.661	0.681	0.021
0.85	0.664	0.623	0.488	0.592	0.088
0.7	0.557	0.455	0.472	0.495	0.051
0.55	0.457	0.422	0.413	0.431	0.022
0.4	0.438	0.412	0.416	0.422	0.013
0.3	0.498	0.47	0.476	0.481	0.014
0.2	0.458	0.487	0.399	0.4725	0.0145
0.1	0.405	0.456	0.463	0.441	0.029

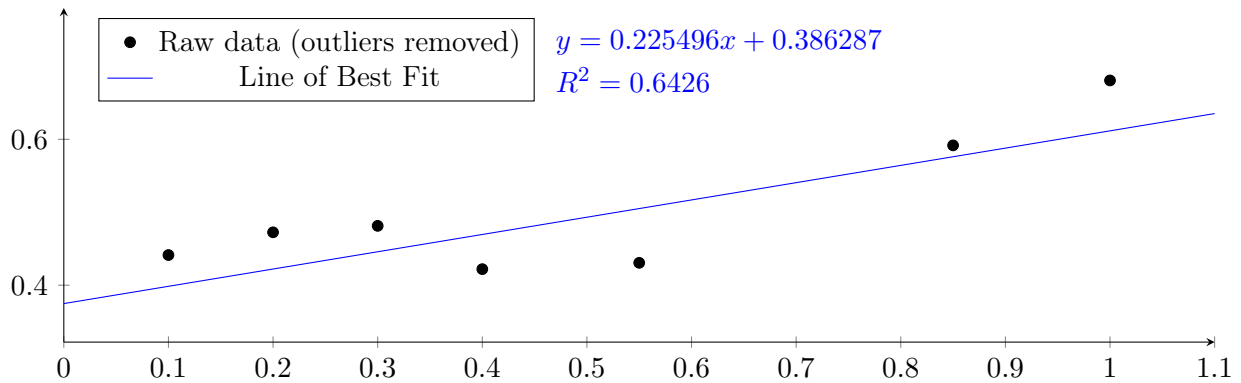Figure 2: Raw data with calculations. Outliers (highlighted in red) **not** included in calculations

Figure 3: Results (outliers removed) with linear line of best fit.
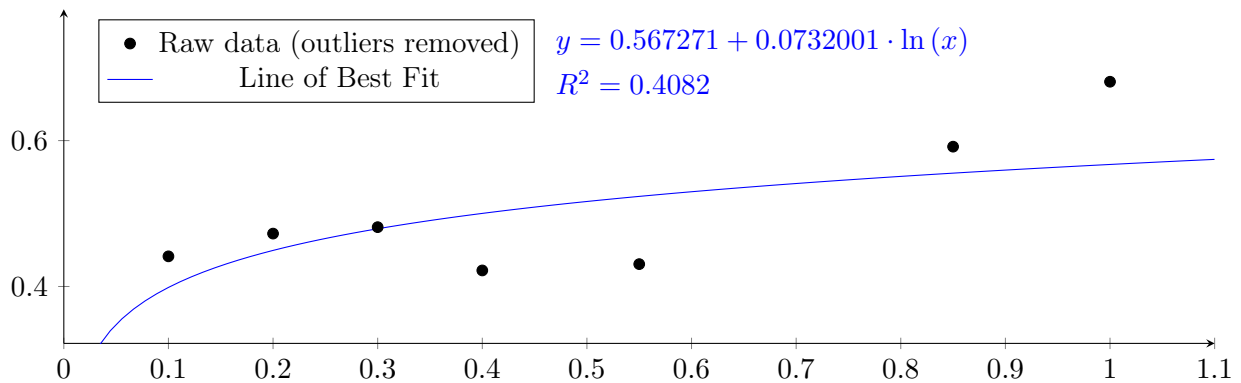

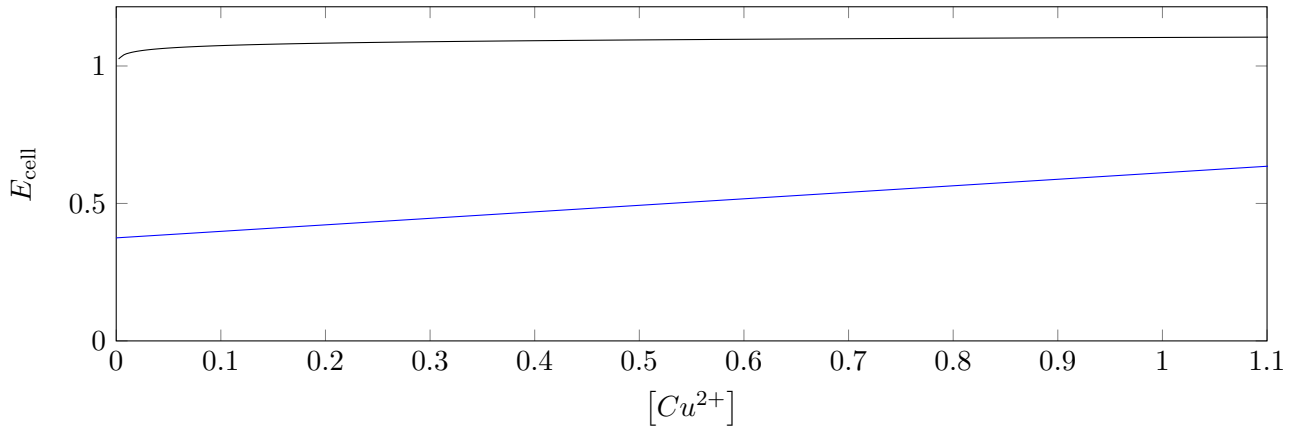Figure 4: Results (outliers removed) with logarithmic line of best fit.

Figure 5: The theoretical relationship between E_{cell} and $[Cu^{2+}]$

3.1 Analysis of Evidence

Identification of relationships and trends.

Across all trials, the voltage produced by the cell was lower than what the Nernst equation predicted. As $[CuSO_4]$ doubles from 0.1 to 0.2, E_{cell} is scaled by a factor of 1.07. As it doubles again from 0.2 to 0.4, it is observed that E_{cell} scales by a factor of 0.89, which is smaller than the initial value. Clearly further investigation is required.

The scatter plot produced using experimental data suggests a linear relationship. Using desmos, linear and logarithmic and linear lines of best fit were found. The linear regression showed a greater correlation than the logarithmic trendline, as $R^2_{\text{Lin}} = 0.6426 > R^2_{\text{Log}} = 0.4082$.

An exponential trendline was briefly considered due to its closer correlation with the data but found to be physically impossible due to the presence of voltage at Considering the components of the Nernst equation, it was considered that

$$E_{\text{cell}} = (0.3419 + 0.7618) - \frac{8.31446261815324 \cdot 298}{2 \cdot 96485} \cdot \ln \frac{1}{[Cu^{2+}]}$$

While the trend observed resembles a linear relationship, divergence from the Nernst equation is what this experiment sought out to investigate, and therefore this result is perfectly valid. It should be noted however that the data is very noisy and does not entirely point to this relationship, as $R^2_{\text{Lin}} = 0.6426 < 1$.

Theory would suggest it should be logarithmic

Compare the nerenst equation

Figure 6 depicts a trend observed where as trials continued, the voltage of each subsequent trial decreased slightly. Procedure was considered and it was theorised that this was due to reuse of the same electrolyte solution over multiple trials. The number of ions left on solution likely decreased as measurements were taken and and differed due to inconsistent duration of the measurement phase. This was theorised to have lead to a smaller voltage. To accurately consider this trend, and evaluate the reliability of the relationship, the average of all data points against what 'trial' they were collected during was considered. While the change in voltage is only on average -0.02V per trial, considering $R^2 = 0.9922$, the linear regression indicates a very high correlation. However due to the large range of values considered, the uncertainty in this relationship is so high that the minimum trendline has a positive gradient, therefore further investigation is required to confirm this.

4 Discussion

4.1 Improvements

Sources of error/improvements

- Alligator clips in solution (floating voltage)
- Inconsistent measurement time. (outlier is main case of this).
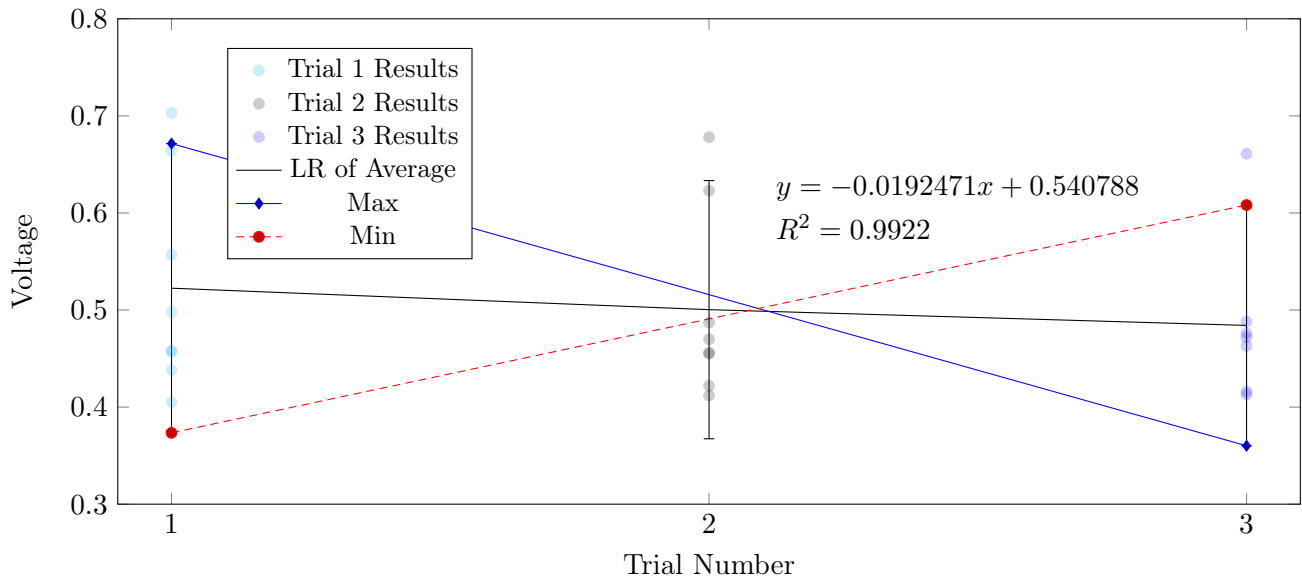- Alligator clips sitting in electrolyte during experiment.

Figure 6: Line of best fit for average voltage over sequential trials (outliers removed)

- Temperature and pressure unknown on day of experimentation. This means that the nerenst equation cannot account for them. Therefore difference in between Nernst equation and actual results n

Item/Substance	Potential Hazards	Standard Handling Procedures	Disposal
Alligator clip with lead	Clip may cause pain and injury if applied to skin.		
Glass beaker	Breakage of beaker. Cuts from chipped rims.	Inspect and discard any chipped or cracked beakers. Sweep up broken glass with brush and dustpan; do not use fingers.	
Metal tweezers	Can be used as a weapon if long and sharply pointed.		
Disposable plastic gloves	May easily be punctured, allowing entry of liquid. Latex gloves may cause an allergic reaction to some people	Take care not to puncture. Check for punctures before use. Use a type of glove that is suitable for the chemicals to be used.	
Lab coat	**Flammable**. Sleeves may catch on objects and knock them over.		
Safety glasses	Scratched or dirty glasses may hinder vision, causing headaches during prolonged use.	**Each person should preferably have own safety glasses**. Check and, if necessary, clean glasses before each use..	
Filter paper	**Flammable. Used filter paper may contain harmful residues**.	After use, dispose of residue and filter paper appropriately.	Dispose of residue and filter paper appropriately.
Copper (sheet)	Not toxic.		<1 kg/day may be placed in the garbage. Larger quantities should be retained for collection by a waste service or metal recycler.
Copper(II) sulfate (>0.94 M)	**Toxic. Irritates skin and eyes**.	<5 mL/day may be poured down the drain. Larger quantities should be placed in a Copper waste container.	
Zinc (pieces)	Not toxic to humans.		**May be placed in the garbage**.
Zinc nitrate (0.79-1 M)	**Toxic. Irritates skin, eyes and lungs. Harmful if swallowed**. Causes skin irritation. **Causes serious eye irritation. Very toxic to aquatic life with long lasting effects**.		<5 mL/day may be diluted with 10 times the volume of water and poured down the drain. Larger quantities should be placed in a Zinc waste container.
Potassium nitrate (0.1-1 M)	**May irritate eyes and skin**. GHS data: Not classified as a hazardous chemical.		<1 L/day may be poured down the drain in a stream of water.
Wash bottle	May be used to spray others.	Preferably use distilled water. Change water regularly to avoid microbial growth.	

Appendices

Risk Assessment