

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

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Contents

1	Rationale	2
1.1	Background	2
1.2	Research Question	3
2	Methodology	3
2.1	Modifications	3
2.2	Method	4
2.3	Risk assessment	5
3	Results	6
3.1	Analysis of Evidence	6
4	Discussion	7
4.1	Improvements	7

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 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 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 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 $+0.3419\text{V}$ respectively. Cell's with this composition are also known as "Daniel Cell's", 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 $[\text{CuSO}_4]$.

The Nernst equation can be 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

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

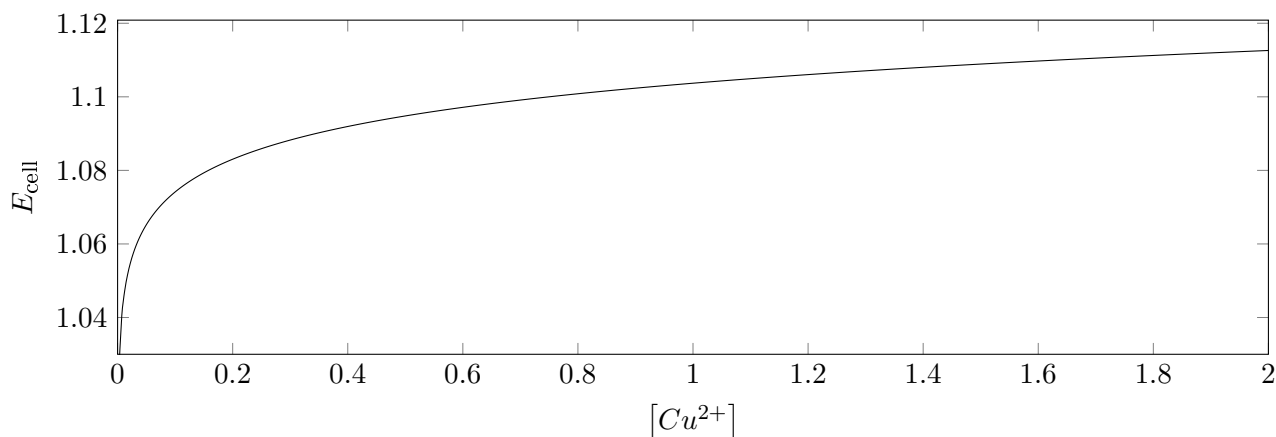


Figure 1: The theoretical relationship between E_{cell} and $[Cu^{2+}]$

Considering figure 1, the theoretical change in E_{cell} is minuscule in comparison to the change in $[Cu^{2+}]$. The 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 $\lim_{x \rightarrow 0}$.

Investigation of $[Cu^{2+}] = [0, 1]$ would theoretically be the most distinguishable from a logarithmic relationship if it differs 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 $\approx 4\text{cm} \times 6\text{cm}$
- Copper sheet $\approx 4\text{cm} \times 6\text{cm}$
- Emery paper
- Filter paper strips $\approx 2\text{cm} \times 10\text{cm}$
- 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 measurement 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

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.
Aluminum (pieces)	Not toxic. Sharp points and edges may cause injury to skin and eyes.		May be placed in the garbage.
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.	
Iron (nails)	Not toxic. Usually mild steel. Sharp edges and points may cause injury.	Store in a dry location to prevent rusting of iron surfaces.	May be placed in the garbage.
Iron(III) chloride (>0.93 M) (ferric chloride)	CORROSIVE TO SKIN, EYES AND LUNGS. May be corrosive to metals. Harmful if swallowed. Causes skin irritation. Causes serious eye damage.	Solubility ~550 g/L at 20°C. Undergoes hydrolysis at low concentrations with precipitation of iron(III) hydroxide.	<200 mL/day may be poured into 10 times the volume of water and poured down the drain in a stream of water.
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.
Aluminum nitrate (>0.5 M)	Irritates skin and eyes, due to acidity as a result of reaction with water. Causes mild skin irritation.		<100 mL/day may be added slowly with stirring to 20 times the mass of water, then poured down the drain in a stream of water.
Spatula	Properties depend on spatula material. A nickel spatula may cause an allergic skin reaction, especially if used repeatedly.	People with nickel allergy should wear gloves if using a nickel spatula.	
Wash bottle	May be used to spray others.	Preferably use distilled water. Change water regularly to avoid microbial growth.	

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

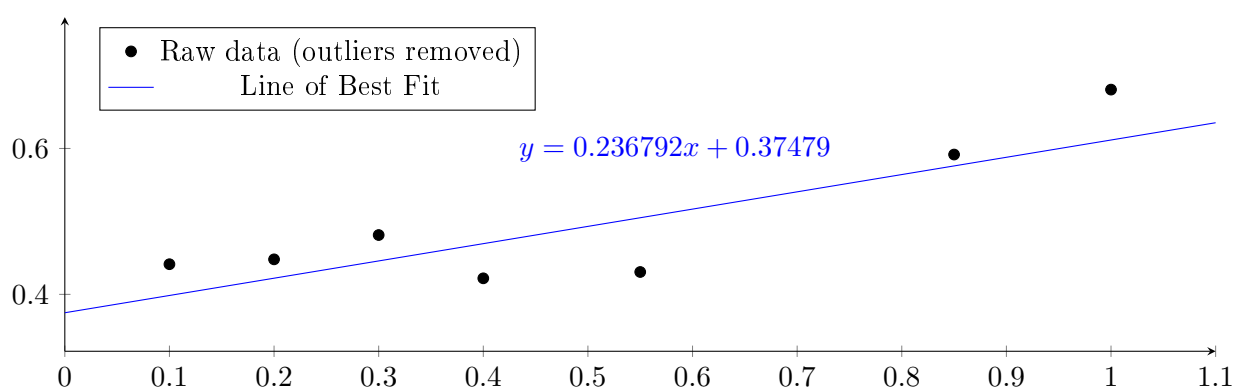


Figure 3: Raw results (outliers removed) with linear line of best fit.

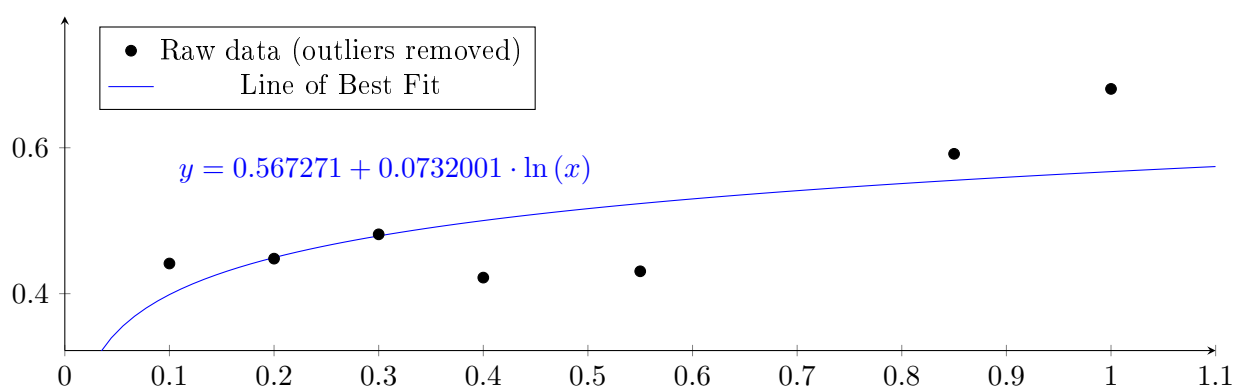


Figure 4: Raw results (outliers removed) with logarithmic line of best fit.

3.1 Analysis of Evidence

The scatter plot produced using experimental data suggests a linear relationship. Using desmos, a linear regression can be utilised to find the line of best fit.

Theory would suggest it should be logarithmic

if we substitute the parameters of the Nernst equation (this part needs more working)

consider half equation $\text{Cu}^{2+} + \text{Zn} \rightarrow \text{Zn}^{2+} + \text{Cu}$ (possibly show how half equation is derived)

finding Q: Since Cu^{2+} and Zn^{2+} are the only aqueous parts of each side of the half equation, they're the only ones counted there's a linear relationship

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

$$(0.3419 + 0.7618) - \frac{8.31446261815324 \cdot 298}{2 \cdot 96485} \cdot \ln \frac{1}{1} \\ = 1.1037\text{V}$$

GRAPH COMPARING THEM

another trend observed was lowering voltage over trials

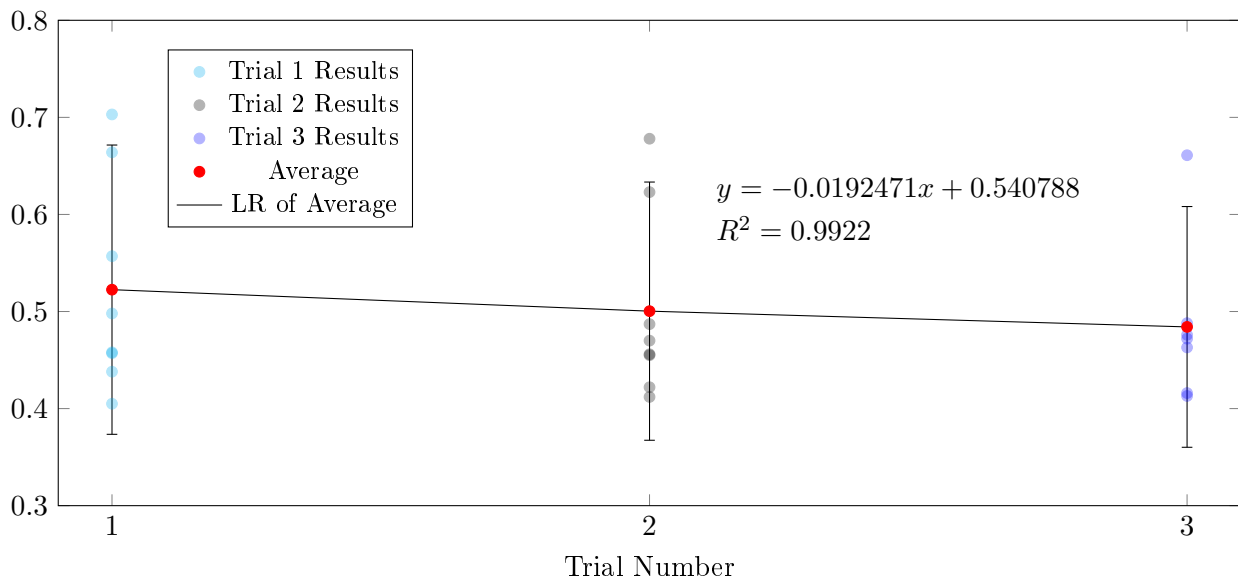


Figure 5: Line of best fit for average voltage over sequential trials (outliers removed)

Figure 5 depicts a trend observed where as trials continued, the voltage of each subsequent trial decreased slightly. Procedure was considered and it was theorized 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 depending on the duration of each trial and measurement phase, which is theorized to have resulted in lower voltage. While the change in voltage is only on average -0.02V per trial, considering $R^2 = 0.9922$, the linear regression has a very high correlation with the average.

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.

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