Report 3:
Galvanic Cells and the Measurement of Cell Potential

Class (e.g. A21, C18, etc.)	Group Number (e.g. Group 1, 2, etc.)
B32	Group 6

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ABSTRACT:
To explore various concepts related to galvanic cells, this experiment was divided into three parts: generating a table of standard reduction potentials, connecting galvanic cells in series, and building a concentration cell.

In the first part, standard reduction potentials were measured for various redox reactions involving different metal ions and zinc to investigate the hypothesis that the standard reduction potentials can be treated as the difference between the cell potential and the oxidation potential. In the experiment, the zinc sheet was used as a cathode in the galvanic cell, and the procedure was repeated with different metal ions as the electrolyte solution near the anode. The cell potential was measured using a digital voltmeter and the electrode potential for Zn was +0.76V. The measured reduction potential was calculated by and compared with the predicted reduction potential. The measured reduction potentials were only to agree with the predicted reduction potentials for half the results when uncertainties from measurement and modelling assumptions were considered and therefore these experimental results could not be used to support the hypothesis in part 1.

In the second part, the cell potentials of three Cu/Zn galvanic cells in series were measured to investigate the hypothesis that the cell potentials in series connections have an additive nature. In this part, three Cu/Zn galvanic cells were connected in series to power an LED, and the overall cell potential was measured by a digital voltmeter. The measured cell potential was compared with the predicted cell potential using the potential of a single Cu/Zn galvanic cell multiplied by three. The measured cell potential did not agree with the predicted cell potential when uncertainties from measurement and modelling assumptions were considered and therefore these experimental results could not be used to support the hypothesis in part 2.

In the third part, the cell potentials of Cu concentration cells were measured to investigate the hypothesis that Nernst equation can be used to model the cell potential of concentration cells. In this part, copper electrodes acted as both cathode and anode, and the procedure was repeated with different combinations of aqueous solutions of copper sulphate ranging from 0.01 M, 0.1 M & 1.0 M. The cell potential was measured using a digital voltmeter and compared with the value predicted by Nernst equation. The ratio of measured cell potentials was agreed with the ratio of predicted cell potentials when uncertainties from measurement and modelling assumptions were considered and therefore these experimental results could be used to support the hypothesis in part 3.

HEALTH & SAFETY INFORMATION

Table 1a: Health and Safety Assessment of the Chemicals used for the Experiment.

Chemical Name & Concentration	Hazard Pictogram(s)	Hazard Phrases
20m 1M KNO3		Corrosive Explosive Toxic Oxidising Harmful to the environment Respiratory irritant Carcinogenic
30ml 1M CuSO4		Corrosive Irritant Harmful Harmful to the environment
10m 1M AgNO3		Irritant Corrosive Toxic
10ml 1M FeSO4		Irritant Harmful
10ml 1M SnCl2		Corrosive Irritant Harmful

30ml1M ZnSO4			Irritant Harmful
DI Water	none		none
Zinc	none		none
Iron	none		none
Tin	none		none
Silver	none		none
Copper	none		none

OBJECTIVES:

The main purpose of this experiment is threefold. Firstly, a table of standard reduction potentials of iron, tin, copper and silver was measured. Secondly, by connecting three batteries in series, it is verified that the voltage of three batteries in series is equal to the total voltage of three batteries. Finally, the concentration cell is prepared by three different concentrations of copper sulfate solution, and then the correctness of Nernst Equation is verified by calculation.

INTRODUCTION:

Part1

First, One kind of chemical reaction in which electrons are moved between reactants is called a redox (reduction-oxidation) reaction. Oxidation and reduction are two processes that happen simultaneously. Oxidation is the process by which a material loses electrons. According to oxidation numbers, an element or compound is considered oxidized when its number rises. An atom has been oxidized, for instance, if it changes from having a positive oxidation state to a zero-oxidation state. Reduction: A material gains electrons during this process. When an element's or compound's oxidation number falls, it is considered reduced. An atom has been reduced, for instance, if it moves from a positive oxidation state to one that is nearer 0.

After that, Electrochemistry is the study of the relationship between electrical energy and chemical energy conversions. It primarily investigates electrolyte solutions, electrode processes in electrolyte solutions, and related phenomena and principles. Then the principle of the galvanic cell is that the electrons lost by the reducing agent in the REDOX reaction are transferred to the oxidant through the external wire, so that the REDOX reaction is carried out on the two electrodes respectively. Electrons pass from the negative electrode to the positive electrode through the wire, and the cation obtains electrons on the positive electrode, forming a loop through the movement of electrons in the circuit and ions in the solution, conducting current. Standard reduction potential refers to the potential of a substance acting as a reducing agent in a REDOX reaction under certain conditions (usually the standard state, including a temperature of 25 degrees Celsius, a pressure of 1 atmosphere, and a solution concentration of 1 mole/liter).

The standard reduction potential can be calculated by this formula:

$$E = E(cathode) - E(anode) \qquad\qquad\qquad \text{Eqn.1}$$

In the experiment, we use Zn as a negative electrode, and the reaction of Zn losing electrons to generate Zn^{2+} provides electrons for the whole galvanic cell. And Zn is a relatively stable and easy to find metal.

Firstly, we discuss the relationship between standard cell potential ($\Delta E°_{cell}$) and standard Gibbs free energy change ($\Delta G°$):

According to the Nernst equation, there is a relationship between standard cell potential and standard Gibbs free energy change:

$$\Delta G° = -nF\Delta E°_{cell} \qquad\qquad\qquad \text{Eqn.2}$$

Where,
$\Delta G°$ is the standard Gibbs free energy change,
$\Delta E°_{cell}$ is the change in standard cell potential,
n is the number of electrons involved in the reaction
F is the Faraday constant.

The standard Gibbs free energy change and standard cell potential are correlated negatively, as this equation demonstrates. A redox reaction is considered spontaneous if its standard Gibbs free energy change is negative ($\Delta G° < 0$) and its standard cell potential changes positively ($\Delta E° > 0$).

After that, we discuss the relationship between equilibrium constant (K)and standard Gibbs free energy change($\Delta G°$)

According to the Gibbs-Helmholtz equation, there is a relationship between the equilibrium constant and the standard Gibbs free energy change:

$$\Delta G° = -RTlnK \qquad\qquad\qquad \text{Eqn.3}$$

Where,
$\Delta G°$ is the standard Gibbs free energy change
R is the gas constant
T is the temperature
K is the equilibrium constant

This formula shows that the standard Gibbs free energy change and the equilibrium constant have a logarithmic connection. A redox reaction's standard Gibbs free energy change will be negative ($\Delta G°< 0$) if its equilibrium constant (K > 1) is greater than 1, suggesting that the reaction promotes the creation of products.

There are lots of advantages of using damp filter paper as salt bridges.
1. Wet filter paper is readily available and inexpensive
2. Wet filter paper has good ion conductivity.
At the same time, it also has many disadvantages.
1. Wet filter paper has a limited-service life.
2. Filter paper has the risk of introducing contaminants or magazines.
3. Filter paper can hold a limited number of ions.
But in general, the advantages of using wet filter paper outweigh the disadvantages.
So, we use wet filter paper as a salt bridge.

Part2
In a galvanic cell, the cell potential (voltage) is generated by the difference in reduction potentials between the two half-cells involved in the cell. When cells are connected in series, their cell potential adds up, leading to an increased overall voltage output.

Light-emitting diodes (leds) are semiconductor devices that can emit light when an electric current flows through them. It can convert most of the electrical energy into light, rather than heat.

Part3

$$E_{cell} = \Delta E°_{cell} - \ln Q \qquad\qquad Eqn.4$$

where,
E_{cell} is the cell potential under non-standard conditions (volts).
$\Delta E°_{cell}$ is the standard cell potential (volts).
R is the gas constant.
T is the temperature.
n is the number of moles of electrons transferred in balanced redox reaction.
Q is the reaction quotient.

To derive the Nernst Equation, we start with the equation for Gibbs free energy (ΔG):

$$\Delta G = -nFE_{cell} \qquad\qquad Eqn.5$$

Using the relationship between Gibbs free energy, equilibrium constant (K), and reaction *quotient* (Q):

$$\Delta G = -RT\ln K \qquad\qquad Eqn.6$$
$$\Delta G = -RT\ln(\frac{Q}{K}) \qquad\qquad Eqn.7$$

Substitute Δ*G* from the first equation into the second equation:

$$-nFE_{cell} = -RT\ln(\frac{Q}{K}) \qquad\qquad Eqn.8$$
$$E_{cell} = \ln(\frac{Q}{K}) \qquad\qquad Eqn.9$$

Since *K* is a constant at equilibrium, and we recognize that $\Delta E°_{cell}$ = lnKc
Finally, it can be written to:

$$E_{cell} = \Delta E°_{cell} - \ln Q \qquad\qquad Eqn.10$$

A concentration cell is a unique kind of electrochemical cell that produces a potential difference depending on how differently the same electrolyte solution is concentrated on its two sides. Instead of using various chemicals to generate electrical energy, this kind of cell uses the concentration gradient. The diffusion of substances in a liquid media, where chemicals tend to diffuse from regions of higher concentration to regions of lower concentration until equilibrium is attained, is the basis for the operation of a concentration cell. This diffusion process causes the ion

concentrations in the electrolyte solution to vary in a concentration cell, which produces an electrical potential and a potential difference.

Concentration batteries work based on ion diffusion and concentration gradients. It usually consists of two half cells, each containing the same kind of electrode material (such as a zinc electrode), but the concentration of the electrolyte solution is different in the two half cells, creating a concentration gradient. If there is a concentration gradient between the two regions, the concentration battery will continue to work. It converts chemical energy (from a concentration gradient) into electrical energy and produces it through ion diffusion and electron flow. Eventually, as the ions continue to spread, the concentrations in the two regions reach equilibrium, and the concentration cell reaches an equilibrium state. In equilibrium, the potential difference and current stop, indicating that the concentration gradient has disappeared.

ASSUMPTIONS:
- The laboratory conditions were constant when doing the experiment.
- All metal electrodes have been polished enough to remove the oxide film before the experiment.
- The galvanic cells are ideal and there were no interactions between the individual cells.
- The electrodes and electrolyte solutions were homogeneous, and any effects of electrode surface area or impurities were negligible.
- The salt bridge contains an ionic substance in a mobile medium which did not participate in the redox reaction.
- The digital voltmeter is accurate enough to read a relatively stable indicator.
- There was no spatter of any solutions when transferring and mixing process.
- The glassware was clean before the experiment started.

APPARATUS
- A digital voltmeter
- 1 M zinc sulphate
- A LED (light-emitting diode)
- Deionised water
- 1M tin sulphate
- Filter paper
- 10ml volumetric flask
- A volumetric pipette
- 1M copper sulphate
- Zn, Fe, Sn, Cu, and Ag electrodes
- Beakers
- 1M iron sulphate
- 1M silver nitrate
- Copper wires and battery clips
- Abrasive paper

PROCEDURE
In the first part, all metal electrodes had been polished before the experiment started. Then, 1 M concentrations of the following ions: Zn^{2+}, Fe^{2+}, Sn^{2+}, Cu^{2+} and Ag^+ were poured into different beakers while Zn, Fe, Sn, Cu, and Ag electrodes were also put into the corresponding beaker. The deionised water was used to wet the filter paper strip which was acted as salt bridges. Then, the digital voltmeter was connected to the zinc sheet and the copper sheet by copper wires and clips. Two ends of the wet filter paper strip were also immersed in two different electrolyte

solutions. The cell potential was recorded in second column in Table 2 when the indicator of the voltmeter changed slowly. This procedure was repeated for 4 different kind of metal ion Fe^{2+}, Sn^{2+}, Cu^{2+} and Ag^+ while the anode of the galvanic cells was kept constant.

In the second part, three Cu/Zn galvanic cells were set following the steps in part 1. The three Cu/Zn galvanic cells were connected in series by copper wires and a LED was also connected in the circuit. Then, the digital voltmeter was connected to the cathode and anode of the Cu/Zn galvanic cells by copper wires and clips. The cell potential was recorded in first column in Table 4 when the indicator of the voltmeter changed slowly.

In the third part, 1M copper sulphate was respectively diluted into 0.1M and 0.01M by using volumetric flask, deionised water, and a volumetric pipette. Then 1M, 0.1M and 0.01M copper sulphate was poured into different beakers. The copper electrodes were immersed in three different combinations of aqueous solutions of copper sulphate ranging from 0.01 M, 0.1 M & 1.0 M. Two ends of the wet filter paper strip were also immersed in two different concentration of copper sulphate solutions. Then, the digital voltmeter was connected to the copper electrodes of the Cu concentration cells by copper wires and clips. The cell potential of three different combinations of copper sulphate ranging from 0.01 M, 0.1 M & 1.0 M was recorded respectively in first column in Table 6 when the indicator of the voltmeter changed slowly.

After the three experiments finished, all the solution in beakers were disposed into the aqueous waste drum and all the glasswares were rinsed thoroughly.

RESULTS:

Table 2. Measured Cell Potentials

Redox Reaction	Measured $E^0{}_{cell}$
$Zn(s) + Fe^{2+}(aq) \rightarrow Zn^{2+}(aq) + Fe(s)$	$+0.60\,V$
$Zn(s) + Sn^{2+}(aq) \rightarrow Zn^{2+}(aq) + Sn(s)$	$+0.52\,V$
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$	$+1.12\,V$
$Zn(s) + 2Ag^{+}(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$	$+1.54\,V$

Table 3. Measured and Predicted Standard Reduction Potentials

Half-Reaction	Measured E^0	Predicted E^0
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	$-0.16\,V$	$-0.44\,V$
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	$-0.24\,V$	$-0.14\,V$
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	$+0.36\,V$	$+0.34\,V$
$Ag^+(aq) + e^- \rightarrow Ag(s)$	$+0.78\,V$	$+0.80\,V$

The standard reduction potential of the cell could be calculated by the difference between the standard reduction potential of the cathode and the standard reduction potential of the anode, which could be represented by

$$E^0_{cell} = E^0_{cathode} - E^0_{anode} \qquad\qquad Eqn.11$$

It could be rearranged as

$$E^0_{cathode} = E^0_{cell} + E^0_{anode} \qquad\qquad Eqn.12$$

Therefore, the measured standard reduction potentials for the half-reactions could be calculated by this equation. As an example, when the measured standard reduction potentials for the cell $E^0{}_{cell}$ was $+0.60\,V$, the measured standard reduction potentials for the half-reactions E^0 could be computed as

$$E^0 = E^0_{cell} + E^0_{anode} = +0.60 + (-0.76) = -0.16\,V \qquad Eqn.13$$

Table 4. Galvanic Cells in Series Measurements

Measured E_{cell}	Predicted E_{cell}
$+2.70\,V$	$+3.30\,V$

The predicted standard reduction potentials for the anode and the cathode in this part of experiment were $-0.76\,V$ and $+0.34\,V$. Therefore, the predicted standard reduction for the single cell could be calculated as

$$E^0_{cell} = E^0_{cathode} - E^0_{anode} = +0.34 - (-0.76) = +1.10\,V \qquad Eqn.14$$

Galvanic cells in series in this experiment were connected with three single cells. Hence, the predicted E_{cell} could be calculated below

$$E_{cell} = 3E^0_{cell} = 3 \times (+1.10) = 3.30\,V \qquad\qquad Eqn.15$$

Table 5. Concentration Cell Measurements

Measured E_{cell}	Predicted E_{cell}
$+0.0236\,V$	$+0.0296\,V$
$+0.0231\,V$	$+0.0296\,V$
$+0.0443\,V$	$+0.0592\,V$

In part 3, the reaction of the concentration cell was

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad\qquad Eqn.16$$

which shows that the number of moles of the electron n is 2.
The reaction quotient Q of this could be calculated by the following equation. For example, when the concentration of the copper ion in copper sulphate $[Cu^{2+}]$ was 1.0 M, the concentration of the copper ion in the diluted copper sulphate $[Cu^{2+}]_{dilute}$ was 0.1 M, the reaction quotient Q could be calculated by

$$Q = \frac{[Cu^{2+}]_{dilute}}{[Cu^{2+}]} = \frac{0.1}{1.0} = 0.1 \qquad\qquad Eqn.17$$

As the standard reduction potential E^0 in this part of the experiment was $0\,V$, the predicted E_{cell} in this example could be calculated by the equation below

$$E_{cell} = E^{\circ} - \frac{0.0257}{n} \ln Q = 0 - \frac{0.0257}{2}\ln(0.1) = +0.0296\,V \qquad\qquad Eqn.18$$

UNCERTAINTY ANALYSIS:
The division value of the voltmeter used in this experiment was 0.0001 V. The maximum uncertainty associated with voltmeter reading could be calculated to be

$$a = \frac{0.0001}{2} = 0.00005\,V \qquad\qquad Eqn.19$$

The uncertainty associated with the measured cell potential could be calculated by the following equation. As an example, for the redox reaction of zinc and iron ions, when the measured cell potential $E^0{}_{cell}$ was +0.60 V, the uncertainty would be calculated as

$$\delta E^0_{cell} = \sqrt{(\frac{a}{\sqrt{3}})^2 + (0.01 E^0_{cell})^2} = \sqrt{(\frac{0.00005}{\sqrt{3}})^2 + (0.01 \times (+0.60))^2} = 0.006\,V \quad Eqn.20$$

The standard uncertainty was calculated to be +/- 0.006 V, which was recorded in Table 5.

The uncertainty associated with standard reduction potentials was assumed to be equal to 0.01V. It would be denoted as $\delta E^0_{cathode}$ because the half-reaction shown in Table 5 occurred at the cathode. Therefore, the uncertainty associated with the calculated standard reduction potential could be calculated by the following equation. As an example, for the redox reaction of zinc and iron ions, the uncertainty

associated with the calculated standard reduction potential δE^0 could be calculated as

$$\delta E^0 = \sqrt{(\delta E^0_{cell})^2 + (\delta E^0_{cathode})^2} = \sqrt{(0.006)^2 + (0.01)^2} = 0.012 \, V \quad Eqn.21$$

The standard uncertainty was calculated to be +/- 0.012 V, which was displayed in Table 5.

In part 2 of this experiment, the uncertainty associated with the measured cell potential for cells in series could be calculated below. As an example, when the measured potential E_{cell} was +2.70 V, the uncertainty associated with the measured cell potential δE_{cell} could be computed as

$$\delta E_{cell} = \sqrt{(\frac{a}{\sqrt{3}})^2 + (0.01 E_{cell})^2} = \sqrt{(\frac{0.00005}{\sqrt{3}})^2 + (0.01 \times (+2.70))^2} = 0.027V \quad Eqn.22$$

The standard uncertainty was calculated to be +/- 0.027 V, which was recorded in Table 6.

The number of cells connected in series, n, was 3. The uncertainty associated with the measured cell potential δE^0_{cell} was 0.011 V. Hence, the uncertainty associated with the predicted cell potential for cells in series δV could be calculated below

$$\delta V = n\delta E^0_{cell} = 3 \times 0.011 = 0.033 \, V \quad\quad Eqn.23$$

The standard uncertainty was calculated to be +/- 0.033 V, which was recorded in Table 6.

In part 3 of this experiment, before calculating the uncertainty associated with predicted cell potential for a concentration cell, the uncertainty associated with $[CuSO_4]$ at the anode $\delta[anode]$ and the uncertainty associated with $[CuSO_4]$ at the cathode $\delta[cathode]$ should be calculated first. The division value of the pipette used in this experiment was 0.01 ml. The maximum uncertainty associated with burette reading could be calculated to be

$$a = \frac{0.01}{2} = 0.005 \, ml \quad\quad Eqn.24$$

Therefore, uncertainty associated with $[CuSO_4]$ at the anode $\delta[anode]$ and the uncertainty associated with $[CuSO_4]$ at the cathode $\delta[cathode]$ could be calculated by the equation below. As an example, when the $[CuSO_4]$ at the anode $[anode]$ was 1.0 M, the $[CuSO_4]$ at the cathode $[anode]$ was 0.1 M, the uncertainty could be calculated as

$$\delta[anode] = \sqrt{2(\frac{a}{\sqrt{3}})^2 + (0.001 V_1)^2 + (0.001 V_2)^2} \quad\quad Eqn.25$$

$$\delta[anode] = \sqrt{2(\frac{0.005}{\sqrt{3}})^2 + (0.001 \times 0)^2 + (0.001 \times 0)^2} = 0.0041 \, M \quad Eqn.26$$

$$\delta[cathode] = \sqrt{2(\frac{a}{\sqrt{3}})^2 + (0.001 V_1)^2 + (0.001 V_2)^2} \quad\quad Eqn.27$$

$$\delta[cathode] = \sqrt{2(\frac{a}{\sqrt{3}})^2 + (0.001 \times 0.001)^2 + (0.001 \times 0.009)^2} = 0.0041\ M \quad Eqn.28$$

Where V1 is the volume of the original 1.0 M solution used to create the new concentration and V2 is the volume of water used to create the new concentration.

As mentioned in the result part, the number of moles of the electron n is 2. Therefore, the uncertainty associated with the predicted cell potential for the concentration cell δE_{cell} could be calculated as

$$\delta E_{cell} = \frac{0.0592}{n} \sqrt{(\frac{\delta[anode]}{[anode]})^2 + (\frac{\delta[cathode]}{[cathode]})^2} \quad Eqn.29$$

$$\delta E_{cell} = \frac{0.0592}{2} \sqrt{(\frac{0.0041}{1.0})^2 + (\frac{0.0041}{0.1})^2} = 0.0012\ V \quad Eqn.30$$

The standard uncertainty was calculated to be +/- 0.0012 V, which was recorded in Table 7.

Table 5. Uncertainty associated with the measured cell potential and calculated standard reduction potential

Redox Reaction	Half-Reaction	δE^0_{cell} (V)	δE^0 (V)
$Zn(s) + Fe^{2+}(aq)$ $\rightarrow Zn^{2+}(aq) + Fe(s)$	$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	0.006	0.012
$Zn(s) + Sn^{2+}(aq)$ $\rightarrow Zn^{2+}(aq) + Sn(s)$	$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	0.005	0.011
$Zn(s) + Cu^{2+}(aq)$ $\rightarrow Zn^{2+}(aq) + Cu(s)$	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	0.011	0.015
$Zn(s) + 2Ag^+(aq)$ $\rightarrow Zn^{2+}(aq) + 2Ag(s)$	$Ag^+(aq) + e^- \rightarrow Ag(s)$	0.015	0.018

Table 6. Uncertainty associated with the measured and predicted cell potential for cells in series

δE_{cell} (V)	δV (V)
0.027	0.033

Table 7. Uncertainty associated with the predicted cell potential for a concentration cell

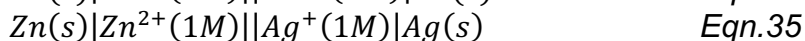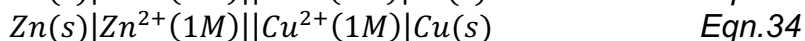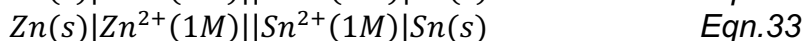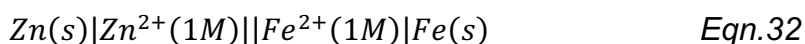| δE_{cell} (V) |
|---|
| 0.0012 |
| 0.012 |
| 0.012 |

DISCUSSION:

For experiment 1, the measured standard reduction potentials, E^0, which indicates the possibility of a substance being reduced is expressed in the form of half-reaction. For example, A is an element, C is the charge:

$$A^{C+} + Ce^- \rightarrow A \hspace{3cm} Eqn.31$$

Based on analysis of Table 2&5, it can be found that none of the measured standard reduction potentials values can coincide with the predicted value of standard reduction potentials. While for the iron and tin, the absolute differences between measured values and predicted values were considerable, which was respectively 0.268 and 0.089. And for copper and silver, the absolute differences between measured values and predicted values were close to 0, specifically, 0.005 and 0.002, which were quite accurate. Thus, the data that gained from the experiment can support the hypothesis which was the overall cell reaction can be thought of as the sum of two half-cell reactions, the measured emf of the cell can be treated as the sum of the electrical potentials at two electrodes, and specifically, in this experiment, one of the electrodes remained as Zn. These results which did not agree with predicted values demonstrated that the measured cell emf of iron and copper were bigger than the predicted values, and the measured cell emf of tin and silver were smaller than which were expected. Moreover, among these values, the differences of iron and tin were substantial. Therefore, the most likely causes of the discrepancies are:

- Non-standard concentration of salt solutions.
  For these four reactions the cell diagram were:

$$Zn(s)|Zn^{2+}(1M)||Fe^{2+}(1M)|Fe(s) \hspace{2cm} Eqn.32$$
$$Zn(s)|Zn^{2+}(1M)||Sn^{2+}(1M)|Sn(s) \hspace{2cm} Eqn.33$$
$$Zn(s)|Zn^{2+}(1M)||Cu^{2+}(1M)|Cu(s) \hspace{2cm} Eqn.34$$
$$Zn(s)|Zn^{2+}(1M)||Ag^+(1M)|Ag(s) \hspace{2cm} Eqn.35$$

The cell diagrams indicated that in ideal situation all the concentration of salt solutions were 1M. According to the definition of electrical energy and free-energy change:

$$Electrical\ energy\ (J) = total\ electrical\ charge(C) \times voltage(V) \hspace{0.5cm} Eqn.36$$
$$\Delta G^0 = -RTlnK \hspace{3cm} Eqn.37$$

Where;
R= gas constant (J/K·mol)
K= the equilibrium constant
T = the temperature of the surroundings (K)

The solving of the relationship between the emf of a galvanic cell and the concentration of reactants and products in a redox reaction, which is known as Nernst Equation, can be found as:

$$E = E^0_{cell} - \frac{RT}{nF}lnQ \hspace{3cm} Eqn.38$$

Where;
F = Faraday constant (J/V·mol)

n = the number of moles of electrons exchanged between the reducing agent and oxidizing agent
Q = the reaction quotient
E_{cell}^0 = standard cell emf (V)

Therefore, the Nernst Equation for these four reactions under the assumption that the temperature of the redox reactions remains at 25 degrees Celsius were:

$$E = E_{cell}^0 - \frac{0.0257V}{n} ln \frac{[Zn^{2+}]}{[Fe^{2+}]} \qquad\qquad Eqn.39$$

$$E = E_{cell}^0 - \frac{0.0257V}{n} ln \frac{[Zn^{2+}]}{[Sn^{2+}]} \qquad\qquad Eqn.40$$

$$E = E_{cell}^0 - \frac{0.0257V}{n} ln \frac{[Zn^{2+}]}{[Cu^{2+}]} \qquad\qquad Eqn.41$$

$$E = E_{cell}^0 - \frac{0.0257V}{n} ln \frac{[Zn^{2+}]}{[Ag^+]^2} \qquad\qquad Eqn.42$$

Since the same $ZnSO_4$ solution used throughout experiment, suppose the concentration of $ZnSO_4$ was exactly 1M, therefore, based on above equations the cause of discrepancies can be found as the concentration of iron ions and copper ions were bigger than 1M, and the concentration of tin ions and silver ions were smaller than 1M.

- The surrounding temperature of the reactions were not stable at 25 degrees Celsius. Due to the assumption of the whole session, the expected oxidation half-reaction potential was + 0.76V, which was used in the calculation of the measured standard reduction potential. When the experiment was been operating, the surrounding temperature was lower than the assumption. This led to the wrong data used in the calculation part.

Based on the Table 3 in the results section, it can be found that the absolutes of differences between measured standard reduction potentials and predicted standard reduction potentials, which indicated the accuracy on predictions against actual results, were respectively 0.28V(Fe), 0.1V(Sn), 0.02V(Cu), 0.02V(Ag). Considering about the approximation of the measurements against predictions which can present the accuracy of the experiment, taking the Fe/Zn galvanic cell as an example, the predicted standard reduction potential was -0.44V, and measured one was -0.16V $\pm$ 0.012V. Therefore, the approximation of the measured value against the predicted value ranged from 33.6% to 39.1%. Similarly, the approximation of the Sn, Cu and Ag were respectively 55.8% ~ 61.1%, 90.7% ~ 98.6%, and 95.3% ~ 99.8%. The accuracy showed the nearness to the 'true' value of the experiment. Based on above analysis, it was obvious that the measured values of Zn-Cu and Zn-Ag were quite close to 0, which showed that the two measurements were accurate. However, for Zn-Fe and Zn-Sn, the measurements were inaccurate.

For experiment 2, three Cu/Zn galvanic cells were connected in series. From Table 4&6, it was obvious that the measured overall cell potential disagreed with the prediction. The result of this experiment demonstrated that the data obtained from the experiment cannot support the hypothesis which was when three Cu/Zn galvanic cells were connected in series, the overall cell potential would be three times the potential of a single Cu/Zn galvanic cell. Considering the relevant uncertainty, it can be found that the measured value of overall cell potential was smaller than the

predicted cell potential. Thus, the reasons why the measured value cannot agree with the predicted value are:

- Internal resistance of the galvanic cell. The three Cu/Zn galvanic cells had different internal resistance, if the internal resistances of the cells were bigger than the standard condition, the potentials that obtained in the experiment would be smaller than prediction.

- Salt solutions' concentrations are nonstandard. In the whole experiment, the concentrations of the salt solutions were supposed to be 1M. Based on the discussion of experiment 1, if $[Zn^{2+}]/[Cu^{2+}] > 1$, the measured value was smaller than the standard value. Therefore, if the concentrations of the $ZnSO_4$ solutions of three cells were bigger than the concentrations of the $CuSO_4$ solutions, the measured cell potential would smaller than the expected result.

- The zinc used in the experiment was of impurity or had not polished before the experiment. One of half-reactions in this redox reaction was:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$ *Eqn.43*

If the impurity in zinc may cause corrosion of the zinc electrode, leading to the formation of unwanted compounds or depletion of the zinc electrode over time, which may lower the potential of the cell.

- The multi-meter was in poor contact.

Based on Table 4, the absolute difference between measured overall cell potential was 0.6, which indicated that the experimental result deviated significantly from the predicted value. Also, the approximation of the measurement against the prediction is 80.2% ~ 83.4%. This meant that the measurement of the experiment was quite inaccurate.
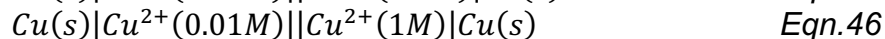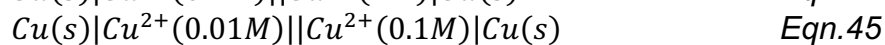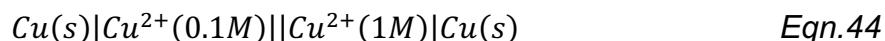
When connecting LED to the circuit, it can be found that if the copper electrode is connected to the negative end of the LED, the LED will not light up. Only if the negative electrode of the LED is connected to the zinc electrode, which is the negative electrode of the galvanic cell, the LED may light up. This is because the characteristic of a light-emitting diode, also known as an LED light, is that inside the LED light, the current is only allowed to flow in one direction. It is a polarized component, which means that it requires the correct polarity and current flow to emit light. When the crocodile clips are connected in the correct orientation, ensuring that the anode terminal of the series galvanic cells is connected to the anode of the LED, and the cathode terminal is connected to the cathode of the LED, the current flows through the LED in the forward bias direction, causing it to emit light. At the same time, the luminous voltage of the light-emitting diode can only be reached when enough Cu/Zn galvanic cells are connected in series.

For experiment 3, taking the uncertainty of the predicted cell potential for a concentration cell into consideration, Table 5 and Table 7 demonstrated that only the measured potential of the second concentration cell, which was formed by 0.1M and 0.01M $CuSO_4$ and copper electrodes, can coincide with the predicted value, while

the rest two measured value, which were respectively made up by 1M and 0.1M solutions, and 1M and 0.01M solutions, cannot agree with the expected results.

The cell diagrams of three concentration cells were:

$$Cu(s)|Cu^{2+}(0.1M)||Cu^{2+}(1M)|Cu(s) \qquad\qquad Eqn.44$$
$$Cu(s)|Cu^{2+}(0.01M)||Cu^{2+}(0.1M)|Cu(s) \qquad\qquad Eqn.45$$
$$Cu(s)|Cu^{2+}(0.01M)||Cu^{2+}(1M)|Cu(s) \qquad\qquad Eqn.46$$

According to the analysis of the discussion section of experiment 1, applying the Nernst Equation to these concentration cells, the emf of the cells were:

$$E_{cell1} = E^0_{cell} - \frac{RT}{nF} ln \frac{[Cu^{2+}]_2}{[Cu^{2+}]_1} \qquad\qquad Eqn.47$$

$$E_{cell2} = E^0_{cell} - \frac{RT}{nF} ln \frac{[Cu^{2+}]_3}{[Cu^{2+}]_2} \qquad\qquad Eqn.48$$

$$E_{cell3} = E^0_{cell} - \frac{RT}{nF} ln \frac{[Cu^{2+}]_3}{[Cu^{2+}]_1} \qquad\qquad Eqn.49$$

Where;
$[Cu^{2+}]_1$= copper sulfate at 1 M concentration
$[Cu^{2+}]_2$= copper sulfate at 0.1 M concentration
$[Cu^{2+}]_3$= copper sulfate at 0.01 M concentration

In this experiment, because the same electrode and the same type of ions were involved in the cell, the E^0_{cell} was 0. Therefore, applying the data of concentration into the above equations, it can be calculated that:

$$E_{cell1} : E_{cell2} : E_{cell3} = 1:1:2 \qquad\qquad Eqn.50$$

From Table 5, the ratio of the potentials of three concentration cells is close to 1:1:2. Therefore, the results obtained from the experiment would support the hypothesis that the principle of chemical potential and the tendency of the system always move towards equilibrium and the whole process would follow the Nernst Equation.

Based on above analysis, the measurements of the cell potentials made up by 0.1M and 1M solutions, and 0.01M and 1M solutions cannot agree with the predictions. Specifically, all the measurements of these three concentration cells were smaller than the expected results. Therefore, the causes of the discrepancies may be:

- Operational error in diluting the solutions. The original solution used to configure the solution was the same, then according to the above analysis, the potential of the concentration cell was related to the concentration ratio of the solution at the two poles, if the temperature and other environmental factors were maintained in the standard state, that was, the temperature was 25 degrees Celsius, the air pressure was 1 atm, when the ratio of concentration was greater than the ideal state, then the absolute value of the natural logarithm of the concentration ratio was less than the prediction, then the resulting potential will be less than the predicted value.
Taking E_{cell1} as an example, suppose the surrounding conditions were 25 degrees Celsius and 1atm air pressure, and the concentration of original solution used in the diluting process was 1M, thus, the potential can be expressed as:

$$E_{cell1} = 0 - \frac{0.0257V}{2} ln \frac{[Cu^{2+}]_2}{1.0} \qquad\qquad Eqn.51$$

In this measurement, the ideal ratio of the concentration was 0.1. Due to the result obtained from the experiment was smaller than the prediction, the actual ratio was bigger than 0.1, in other words, when diluting solution, the added water was less than expected which led to the actual concentration was bigger than 0.1M.

- Uneven mixing or diffusion of the dilute solutions. In concentration cells, ensuring uniform mixing of electrolytes in both half-cells is crucial. The partial mixture in the diluting process can lead to non-uniform concentration gradients and lower the measured potentials.

- The nonstandard temperature of the experiment conditions. Due to the low measured value compared with the predicted value, according to the Nernst Equation, the lower temperature of the experiment compared with the standard condition may be the cause of the unexpected result.

Based on Table 5, it can be found that the absolute differences between measured cell potentials and predicted cell potentials were respectively 0.006, 0.0065, 0.0149. The approximation of measurements against predictions were 76.6% ~ 83.1%, 55.5% ~ 100%, and 62.2% ~ 93.9%. These indicated that the measurements of the experiment were accurate in the first and second concentration cell, while inaccurate in the third concentration cell.

CONCLUSION:
In conclusion, in this experiment which can be divided into three parts, the initial hypothesis of the whole experiment was that the cell potential of a galvanic cell can be measured and correlated with the standard reduction potentials of the half-reactions involved. Meanwhile, for the first part of this experiment, the hypothesis was that the measured emf of the cell can be treated as the sum of the electrical potentials at two electrodes, and the whole cell response can be viewed as the sum of two half-cell reactions. For the second part, the hypothesis was that connecting galvanic cells in series follows the law that the total voltage of a series circuit was equal to the sum of the voltage values of the individual components in series. For the third part of the experiment, the hypothesis was the Nernst Equation would be followed during the entire process due to the principle of chemical potential and the system's constant propensity to move towards equilibrium due to the different concentrations of solutions at two electrodes. Moreover, from the analysis in the discussion section, it can be found that in the part 1&2 of the experiment, after considering the uncertainty, the measurements cannot come within the predictions. Therefore, the data and evidence were not sufficient and direct to support the hypothesis of these two parts. Simultaneously, the discussion section of part 3 shows that although the measured cell potentials cannot meet the predicted values, but the proportional relation can match with the prediction, which indicated that the experiment demonstrated the validity of the hypothesis in the case of the correct ratio had been shown.

For experiment part 1, the main factor that causes the predictions to not match the experimental results was that the salt solutions concentrations are nonstandard, in

other words, are not 1M. According to the accuracy analysis and the uncertainty analysis of the measured values, the best approximation measurements of standard reduction potentials compared with the predictions can respectively reach 39.1%, 55.9%, 98.6%, and 99.8%. This meant that the measured values of the standard reduction potentials of Fe/Zn and Sn/Zn galvanic cells were inaccurate due to the low approximations. While the rest two (Cu/Zn and Ag/Zn galvanic cells) measurements compared with the predictions were quite accurate. Thus, to improve the accuracy and precision of this part of the experiment, the following methods can be taken into consideration:

- Determine the concentration of the electrolyte solution in which the two electrodes are located before the start of the experiment so that both remain at the same concentration. The Nernst Equation shows that the cell potential is related to the quotient of the concentrations of two salt solution. In ideal situation, the quotient would remain as 1.

- Control the temperature of the experiment by using thermotank. The Nernst Equation shows that the temperature would affect the result of the standard reduction potential, therefore, keeping the surrounding temperature at 25 degrees Celsius, which is a standard temperature of the experiment, would help to avoid the system error.

For experiment part 2, the main factor that causes the predictions to not match the experimental results was that the internal resistances of the Cu/Zn galvanic cell were bigger than the ideal situation. Considering the accuracy of the measurement and the uncertainty of the predicted and measured value, it can be calculated that the measurement was about 80.2% ~ 83.4% close to the prediction. This indicates that the measurement of this part was inaccurate. Thus, to improve the accuracy and precision of this part of the experiment, the following methods can be taken into consideration:

- Switch to a higher quality salt bridge. In the experiment, the paper is used to replace traditional slat bridge. Due to the uneven composition of the paper, it is easy to lead to concentration polarization and lead to the bigger resistance of the galvanic cell. Therefore, using a salt bridge made up by high concentration salt solution is helpful.

- Use of electrodes with larger contact areas (copper and zinc). The contact area of the electrode is a factor which may impact the internal resistance of the galvanic cell. Too small surface may lead to low reaction rate. Therefore, use electrodes which have been polished and with larger surface can improve the accuracy of the experiment.

For experiment part 3, the main factor that causes the predictions to not match the experimental results was that the process of diluting had operational error. The added water was less than expectation. Based on the analysis of accuracy and the uncertainty of the predicted values of the concentration cells, it can be found that the best approximation between the measured and predicted values can be achieved to 83.1%, 100%, and 93.9%. This result demonstrated that the measurement of the concentration cell formed by 1M and 0.1M solutions was inaccurate. While the measurement of the concentration cells formed by 0.1M and 0.01M solutions, and 0.01M and 1M solutions were accurate, because the calculated approximations were

higher than 90%. Thus, to improve the accuracy and precision of this part of the experiment, the following methods can be taken into consideration:

- Stirring the solution after diluting. Uneven concentration of diluted solution would more likely lead to the lower measured values compared to the predicted values. Therefore, ensuring uniform mixing of electrolyte solutions to maintain a homogeneous environment around the electrodes can minimize the errors.

- Optimization of electrode preparation: The preparation of electrodes is crucial for the accuracy of the cell potential. It should be ensured that the electrode surface is smooth, uniform and has good electrical conductivity. In addition, metal electrodes should be treated to remove the oxide film to ensure the purity of the electrode surface.