

S.K.H. Lam Woo Memorial Secondary School
F.7 Chemistry Laboratory Report

Name: Chan Ching Wai Class: F.7H (2)

Experiment 5: Investigation of the effect of changes in ionic concentration on the e.m.f of a cell

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Objective:

To investigate the effect of changes in ionic concentration on the e.m.f of a cell and determine the number of electrons involved in the $\text{Fe}^{2+}(\text{aq})/\text{Fe}^{3+}(\text{aq})$ equilibrium.

Introduction:

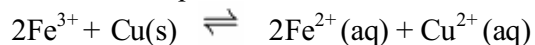
In this experiment, with the $\text{Cu}(\text{s})/\text{Cu}^{2+}(\text{aq})$ half-cell being the reference half-cell, the variation in cell e.m.f was determined by varying the concentration ratio of $\text{Fe}^{2+}(\text{aq})/\text{Fe}^{3+}(\text{aq})$. In this way, the effect of changes in ionic concentration on the e.m.f of a cell and the number of electrons involved in the $\text{Fe}^{2+}(\text{aq})/\text{Fe}^{3+}(\text{aq})$ equilibrium could be found out.

A reference half-cell was needed as the absolute electrode potential for a particular half-cell could not be determined. Yet, the potential difference between the two half-cells connected to form an electrochemical cell could be determined. Then, the relative contributions of any half cell to the cell e.m.f could be measured by arbitrarily choosing one system as the standard. Therefore, in this case, the $\text{Cu}(\text{s})/\text{Cu}^{2+}(\text{aq})$ half cell was taken as the reference half-cell.

In the beginning of the experiment, it was assumed that the copper wire was the negative pole. As the e.m.f measured in all cases showed a positive value, the assumption was correct and copper was the anode in the electrochemical cell. The following was a table showing the details of the electrochemical cell.

	$\text{Cu}(\text{s})/\text{Cu}^{2+}(\text{aq})$ half cell	$\text{Fe}^{2+}(\text{aq})/\text{Fe}^{3+}(\text{aq})$
Polarity	Negative (anode)	Positive (cathode)
Electrode	Copper wire	Nichrome wire
Reaction	Oxidation	Reduction
Half equation	$\text{Cu}(\text{s}) \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-}$	$\text{Fe}^{3+} + \text{e}^{-} \rightleftharpoons \text{Fe}^{2+}(\text{aq})$

The overall equation for the reaction was



The potential difference between the two half-cells drove electrons through the conducting wire from the negative copper wire to the positive nichrome wire. Thus, the chemical energy was converted into

electrical energy. A filter paper soaked with saturated KNO_3 was dipped into the two solutions acting as the salt bridge. It could enable electrical conduction and prevent direct mixing of two solutions at the same time. If the two solutions were directly mixed, spontaneous reactions occurred in one cell and most energy was released as the less useful heat.

With changes in concentration of the chemical species, the equilibrium position for the above half reactions would change. Therefore, the electrode potential of the half-cell would also change. The change in electrode potential could then be predicted by the Nernst equation.

For a $\text{Cu(s)}/\text{Cu}^{2+}(\text{aq})$ half-cell,

$$E = E^0 + \{0.059 \log [\text{Cu}^{2+}(\text{aq})]\} / n$$

E: electrode potential, E^0 : standard electrode potential
n: number of electrons involved

For a $\text{Fe}^{3+}(\text{aq})/\text{Fe}^{2+}(\text{aq})$ half-cell,

$$E = E^0 + \{0.059 \log [\text{Fe}^{3+}(\text{aq})] / [\text{Fe}^{2+}(\text{aq})] / n \}$$

For the overall cell reaction with concentration of CuSO_4 kept at 1M

$$E_{\text{cell}} = E^0_{\text{cell}} + \{0.059 \log [\text{Fe}^{3+}(\text{aq})]^2 / [\text{Fe}^{2+}(\text{aq})]^2 \} / n$$

Given $E^0_{\text{Fe(II)}/\text{Fe(III)}} = +0.77 \text{ V}$ and $E^0_{\text{Cu}/\text{Cu(II)}} = +0.34 \text{ V}$,

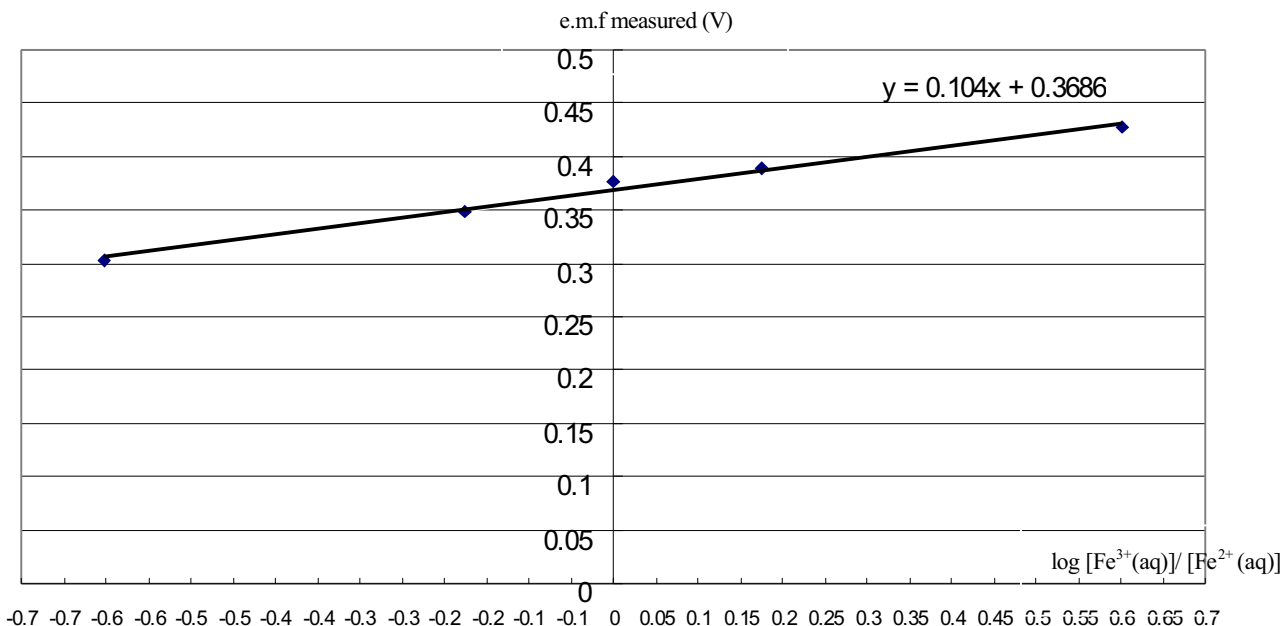
$$\begin{aligned} E_{\text{cell}} &= (0.77 - 0.34) + \{0.059 \log [\text{Fe}^{3+}(\text{aq})]^2 / [\text{Fe}^{2+}(\text{aq})]^2 \} / n \\ &= 0.43 + \{0.059 \times 2 \times \log [\text{Fe}^{3+}(\text{aq})] / [\text{Fe}^{2+}(\text{aq})] \} / n \end{aligned}$$

When a graph of E_{cell} was plotted against $\log [\text{Fe}^{3+}(\text{aq})] / [\text{Fe}^{2+}(\text{aq})]$, the trend of change of cell e.m.f with the variation of concentration ratio $[\text{Fe}^{3+}(\text{aq})] / [\text{Fe}^{2+}(\text{aq})]$ could be investigated. As the slope of the curve equaled to $0.059 / n$, the number of electrons involved in the $\text{Fe}^{2+}(\text{aq})/\text{Fe}^{3+}(\text{aq})$ equilibrium could be found out.

Results:

$\text{Fe}^{3+}(\text{aq})/\text{Fe}^{2+}(\text{aq})$ Half-cell	Number of drops of 1 M $\text{Fe}(\text{NO}_3)_3(\text{aq})$	Number of drops of 1 M $\text{FeSO}_4(\text{aq})$	$[\text{Fe}^{3+}(\text{aq})] /$ $[\text{Fe}^{2+}(\text{aq})]$	$\log \{ [\text{Fe}^{3+}(\text{aq})] /$ $[\text{Fe}^{2+}(\text{aq})] \}$	e.m.f measured
1	10	40	0.250	-0.602	0.303 V
2	20	30	0.667	-0.176	0.348 V
3	25	25	1.000	0	0.376 V
4	30	20	1.500	0.176	0.389 V
5	40	10	4.000	0.602	0.427 V

A graph of emf against $\log \left[\frac{[\text{Fe}^{3+}(\text{aq})]}{[\text{Fe}^{2+}(\text{aq})]} \right]$

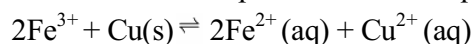


Interpretation:

The above graph was a straight line with negative slope. This showed that with decreasing concentration ratio of $\text{Fe}^{2+}(\text{aq}) / \text{Fe}^{3+}(\text{aq})$, the e.m.f measured decreased.

This agreed with the Nerst equation, $E_{\text{cell}} = 0.43 + \{0.059 \times 2 \times \log [\text{Fe}^{3+}(\text{aq})] / [\text{Fe}^{2+}(\text{aq})]\} / n$, when $[\text{Fe}^{3+}(\text{aq})] / [\text{Fe}^{2+}(\text{aq})]$ decreased, $\log [\text{Fe}^{3+}(\text{aq})] / [\text{Fe}^{2+}(\text{aq})]$ decreased and E_{cell} decreased.

This could also be proved from the equilibrium equation.



When the ratio $[\text{Fe}^{3+}(\text{aq})] / [\text{Fe}^{2+}(\text{aq})]$ decreased and concentration of $[\text{Cu}^{2+}(\text{aq})]$ being unchanged, the proportion of $[\text{Fe}^{3+}(\text{aq})]$ to $[\text{Fe}^{2+}(\text{aq})]$ decreased. Thus, the equilibrium position would shift to the left. The standard electrode potential of the system to be measured refer to reduction and a more positive value of electrode potential meant the reaction tend to proceed in the direction of reduction. Therefore, when the equilibrium position shifted to the left, the electrode potential of cathode and hence the cell e.m.f became less negative.

From the graph, the slope = 0.104

$$\therefore \text{slope} = 0.0592 \times 2 / n$$

$$0.104 = 0.0592 \times 2 / n$$

$$n = 1.14$$

$$\sim 1$$

\therefore The number of electrons involved in the $\text{Fe}^{2+}(\text{aq}) / \text{Fe}^{3+}(\text{aq})$ equilibrium was 1.

This agreed with the equation $\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$.

Discussion:

Criterion for predicting polarities of electrodes

In the beginning of the experiment, it was assumed that the copper wire was the negative pole. As the e.m.f measured in all cases showed a positive value, the assumption was correct and copper was indeed the negative pole and the nichrome wire was the positive pole. For the copper wire, the electrode was negative and had a higher tendency to lose electron to undergo oxidation. As the electrode potential refer to reduction, the electrode potential should be lower. However, if a negative value of cell e.m.f was recorded, the assumption was not true. The copper should be the positive pole and the nichrome wire should be the negative pole instead. The other electrode had a higher tendency to lose electron to undergo oxidation. Then, the electrode potential of copper should be higher than the other.

Discrepancy between literature and experimental value of cell e.m.f

From the graph, y-intercept = 0.3686 V

$$E^0_{\text{cell}} = 0.3686 \text{ V}$$

Given $E^0_{\text{Cu/Cu(II)}} = +0.34 \text{ V}$,

$$\therefore E^0_{\text{cell}} = E^0_{\text{Fe(II)/Fe(III)}} - E^0_{\text{Cu/Cu(II)}}$$

$$E^0_{\text{Fe(II)/Fe(III)}} = E^0_{\text{cell}} + E^0_{\text{Cu/Cu(II)}}$$

$$\begin{aligned}\therefore E^0_{\text{Fe(II)/Fe(III)}} &= 0.3686 + 0.34 \\ &= 0.7083 \text{ V}\end{aligned}$$

Theoretical value = 0.77

$$\text{Percentage error} = (0.77 - 0.7083) / 0.77 \times 100\% = 8.01\%$$

The percentage error may be caused by the following sources and should be improved.

1. The theoretical e.m.f could only be measured in a condition of zero current passing through the electrochemical cell, and hence the cell had zero resistance. However, it was impossible in real case. Resistance present in the electrochemical cell and therefore the cell e.m.f in real case would be smaller.

Yet, the internal resistance could be minimized by using electrodes without much impurities coated on the surface. Also, by moving closer the two electrodes, the internal resistance could also be reduced. Moreover, to have a minimum current passing through the voltmeter, a high impedance voltmeter or a potentiometer could be used.

2. As iron (II) ion was a quite strong reducing agent, it may be oxidized to iron (III) ion even in the air. Therefore, if the iron (II) sulphate solution was placed in room condition for a long time without proper storage, it may be oxidized. Then, even the solutions were added according to the proportion given in the table, $[\text{Fe}^{3+}(\text{aq})]$ was larger and $[\text{Fe}^{2+}(\text{aq})]$ was smaller due to reduction in air. Thus, the ratio of $[\text{Fe}^{3+}(\text{aq})] / [\text{Fe}^{2+}(\text{aq})]$ would be larger than the expected ratio. In this way, the cell e.m.f measured would be larger. To improve, only small volume of iron (II) sulphate solution was poured out into a beaker each time. So that, even it was oxidized in air, only a small amount was oxidized. Moreover, the time for the solution to be exposed to the air could be reduced as all of the solution in the beaker was added in one trial. To further prevent oxidation, the excess iron (II) sulphate solution in the beaker could be discarded each time and use the iron (II) sulphate solution which was freshly

poured out.

3. As the determination of cell e.m.f depended on the concentration of ions inside. Contamination may varied the concentration ratio and hence affect the accurate determination of cell e.m.f. To minimize this error, different plastic containers were used for different trials. Or the plastic containers should be rinsed with distilled water thoroughly after each trial. Otherwise, the ions from the previous trial may remained and affect the concentration ratio. After rinsing, the containers should be dried such that no water remained and diluted the solution. Then, the concentration ratio of $[\text{Fe}^{3+}(\text{aq})]/[\text{Fe}^{2+}(\text{aq})]$ only depended on the specific proportion of $\text{Fe}(\text{NO}_3)_3$ and FeSO_4 added.
4. The volume of $\text{Fe}(\text{NO}_3)_3$ and FeSO_4 added were expressed in term of the number of drop added. Yet, the size of each drop was not necessarily the same. Therefore, the actual volume of solutions added may not be the same as stated in the table. To minimize this error, the force when squeezing the dropper should be approximately constant and the dropper should be held vertically during addition of solution.

Conclusion

From the experiment, it was found out that a decrease in ionic concentration would decreased the cell emf and vice versa. Moreover, the number of electrons involved in the $\text{Fe}^{2+}(\text{aq})/\text{Fe}^{3+}(\text{aq})$ equilibrium was 1.