#### PChem Experiment No. 1

#### The thermodynamics of a galvanic cell

#### 1. Aims

The experiment aims to verify the validity of the Nernst equation, for the EMF of a half cell and for a full galvanic cell. The experiment also aims to find values for ΔS0,ΔH0,ΔG0 from the verified Nernst equations for the cell.

#### 2. Introduction

A Galvanic cell produces a flow of charge across a wire between two half cells due to separate oxidation and reduction reactions taking place in each half cell. The anode of the cell consists of a zinc rid immersed in ZnSo4. The metal is oxidized according to the equation

The cathode consists of a platinum electrode in a mixture of 0.2M potassium ferrocyanide and 0.2M potassium ferricyanide, the relative ratios of which determine the EMF produced by the half-cell. The potassium ferricyanide is reduced according to the equation

Using the Nernst equation, the EMF produced by half cell containing the cathode is given by:

The EMF produced by the whole cell is given by:

In the first part of the experiment the EMF is measured for a range of ratios of ferricyanide to ferrocyanide(1:1, 10:1, 1:10) and the data is used to verify the Nernst Equations above. The second part of the experiment measures a the EMF across the cell for a series of temperatures while the ferri:ferro remains constant at 1:1. EMF is then plotted as a function of temperature. Then using the equation

 may be determined. can be determined from the equation

Then using the attained values for and , can be determined from the equation

#### 3. Experimental Procedure

Part I

100cm3 of 0.2M potassium ferricyanide solution was prepared. The zinc electrode was rinsed in dilute nitric acid solution and then rinsed with deionized water. The cell was assembled and was then placed in a two liter beaker filled with water at room temperature. 10cm3 of 1M ZnSO4 was added to the zinc half-cell. Using the potassium ferrocyanide solution provided, 10cm3 of a 1:1 mixture of ferrocyanide and ferricyanide was prepared and added to the other half cell. The electrodes were connected to the potentiometer and the cell was made sure to be in thermal equilibrium. The temperature of the cell was then recorded to be 294.5oK. The EMF produced by the cell was recorded and then recorded again for ferrocyanide:ferricyanide ratios of 10:1 and 1:10 respectively.

Part II

A mixture of ferrocyanide:ferricyanide of 1:1 was placed in the half-cell containing the Pt electrode. The assembly was placed in the two liter beaker, which contained an ice-water mixture, with a thermometer in the half-cell containing the Pt electrode. At thermal equilibrium the temperature and the EMF across the cell were recorded. The water/ice mixture was then replaced with water at room temperature. The beaker was then placed on a hot-plate with a temperature control. Stirring the water to maintain thermal equilibrium between half-cells, the cell was heated over a temperature range from 275.65oK to 333.15oK and at 5oK intervals the EMF and temperature were recorded.

#### 4. Results

**Part I**

The EMFs were recorded with the varied ratios of ferrocyanide to ferricyanide as follows.

|  |  |
| --- | --- |
| EMF(V) | Ferro:ferri ratio |
| 1.246 | 1:1 |
| 1.173 | 1:10 |
| 1.273 | 10:1 |

Then, the EMF was plotted as a function of .

The results confirm Nernst’s equation in that they demonstrate a linear correlation between Ecell and , which is outlined in the form of the Nernst equation:

In the diagram above m correlates to and C, the intercept, is Hence was found to be 1.2307V. To calculate the value of the standard Gibb’s energy for the cell it was necessary to calculate a value of nF where n=1 and F=96,485.3365(21) C/mol.

 was found to be -237489.0072Jmol-1.

🡪 Do your results confirm Nernst’s equation? Discuss whether this is the case and explain how you reached your conclusions.

🡪 Obtain the best linear fit of your plot and use slope and intercept to determine the cell standard potential E0 and the G0 of the redox reaction taking place in the cell.

**Part II**

The values of EMF changed with temperature as follows.

|  |  |
| --- | --- |
| Temp(oK) | EMF(V) |
| 275.65 | 1.211 |
| 288.15 | 1.193 |
| 293.15 | 1.188 |
| 298.15 | 1.183 |
| 303.15 | 1.177 |
| 308.15 | 1.172 |
| 313.15 | 1.167 |
| 318.15 | 1.161 |
| 323.15 | 1.154 |
| 328.15 | 1.146 |
| 333.15 | 1.137 |

The ratios of oxidant to reductant is 1:1 and as ln(1) is equal to zero, because the rest of the equation above becomes zero.

 can be taken to equal the slope of the plot above. By combining the equations

And

 ,

And assuming that is negligible, is given by

Using this equation the value of was calculated to be -231.5648JK-1. was then be calculated using the value for calculated in part 1, the temperature, T,(294.5oK) from the equation

 was found to be -169293.1736J.

.

#### 5. Discussion and Conclusions

The linear relationship of Ecell and shown in the graph of the data acquired from part 1 of the experiment verified the Nernst equation for a galvanic cell. From the intercept of the plot, Ecell was evaluated to be 1.2307V and from this value the Gibbs’ free energy was calculated to be -138871.2808Jmol-1.

The standard potential for the reaction is given as 0.7618volts (see Vanýsek, Petr (2007). “Electrochemical Series”, in *Handbook of Chemistry and Physics: 88th Edition*) and for the reaction
 it is given as 0.361V(Atkins, P. de Paula J. (2010). Atkin's Physical chemistry. Oxford. W.H Freeman and company. Ninth edition. p928. )(both at 298.15oK). Hence the standard potential reference value for our cell was 1.1228V.By substituting the temperature value of 298.15oK into the equation for our plot of the change in standard potential with respect to temperature, the value for standard potential at 298.15oK was experimentally found to be 1.18802V. This left a discrepancy of 0.065V between the reference value and that obtained through experiment.

Summarize your findings and results. Compare your standard potential results to those you can calculate from reference values at 298.15 K in the electrochemical series (provide the reference: see e.g. Atkins’ *Physical Chemistry* or *CRC Handbook of Physical Constants*). Outline possible sources of errors that might explain any discrepancies between your value and reference values.

#### Answer the following post-practical questions:

1) The dominant contribution to the entropy change of the cell reaction is the reduction of the [Fe(CN6)]3**–** ion to [Fe(CN)6]4**–**. Comment on the possible origin of the relatively large *magnitude* and *sign* of the entropy change that you find in the cell reaction.

The entropy for the cell was calculated to be -231.5648JK-1.The entropy change in the cell correlates to the negative effect of temperature on .

2) Compare the value of the slope obtained from your experiments with that expected from Nernst’s equation and calculate the percentage error of your result with respect to the tabulated value

The slope of the plot of the change in Ecell with was found to be 0.0217.However when calculated from the values it is given by, , the slope was calculated to be 0.02535. The percentage error in the result was 14.4%

3) Given that the standard entropies of Cu and Zn bulk metals are respectively 33.4 and 41.6 JK-1mol-1 and that those for the Cu2+ and Zn2+ ions in aqueous solution are -98.7 and -106.5 JK-1mol-1, calculate S0 for the reaction:

Zn(s) + Cu2+(aq) → Zn2+(aq) + Cu(s)

Comment on why the change in entropy is relatively small.

#### -148.1+132.1=-16 JK-1mol-1

#### The change in entropy is small for the reaction because the reduction of Cu2+(aq) to Cu(s) has a positive entropy change, i.e. it is not favored for that part of the reaction to take place.PChem Experiment 1

#### Pre-practical questions:

1. What is the purpose of the salt-bridge used in this experiment?

The salt bridge allows the flow of charge between cells exclusively in the form of positively charged ions. It allows the flow of charge without allowing the chemicals involved in the respective reduction and oxidation reactions to react with each other.

(2) Write the cell equation (conventional electrochemical specification of the cell) for this cell reaction.

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