Investigating the Effect of Changes in Ionic Concentration on the E.M.F. of a Cell

Student Handout

Purposes

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

Introduction

The Nernst equation is applicable to a half-cell as well as a combined cell.

1. For a metal-metal ion half-cell, the equation has the following form:

$$E = E^{\theta} + \frac{0.059}{n}\log[\text{ion}] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

2. For an ion-ion half-cell, the equation is modified to:

$$E = E^{\theta} + \frac{0.059}{n}\log\frac{[\text{ox}]}{[\text{red}]} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

3. For an overall cell reaction $a(ox)_1 + b(red)_1 \rightleftharpoons c(red)_2 + d(ox)_2$, the equation is

$$E_{\text{cell}} = E^{\theta}_{\text{cell}} + \frac{0.059}{n}\log\frac{[(\text{ox})_1]^a[(\text{red})_1]^b}{[(\text{red})_2]^c[(\text{ox})_2]^d} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

The experiment employs a $Cu(s)/Cu^{2+}(aq)$ couple as the reference half-cell and a $Fe^{2+}(aq)/Fe^{3+}(aq)$ couple for investigation. Variation in cell e.m.f., measured by a digital multimeter, is achieved by varying the concentration ratio of $Fe^{2+}(aq)$ to $Fe^{3+}(aq)$. Overall cell equation for the experiment :

$$2Fe^{3+}(aq) + Cu(s) \rightleftharpoons 2Fe^{2+}(aq) + Cu^{2+}(aq)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad 1\ M$$

According to equation (3),

$$E_{\text{cell}} = E^{\theta}_{\text{cell}} + \frac{0.059}{n}\log\frac{[Fe^{3+}(aq)]^2}{[Fe^{2+}(aq)]^2[1]}$$

$$= (E^{\theta}_{\text{Fe(II)/Fe(III)}} - E^{\theta}_{\text{Cu/Cu(II)}}) + \frac{0.059}{n}(2)\log\frac{[Fe^{3+}(aq)]}{[Fe^{2+}(aq)]}$$

$$= (0.77 - 0.34) + \frac{0.059\times 2}{n}\log\frac{[Fe^{3+}(aq)]}{[Fe^{2+}(aq)]}$$

$$= 0.43 + \frac{0.059\times 2}{n}\log\frac{[Fe^{3+}(aq)]}{[Fe^{2+}(aq)]}$$

A graph of E_{cell} vs $\log\frac{[Fe^{3+}(aq)]}{[Fe^{2+}(aq)]}$ is a straight line the gradient of which is $\frac{0.059\times 2}{n}$. A value for n can be calculated from the gradient of the graph.

Safety

Avoid skin contact with chemicals.

Materials and Apparatus

1 M $CuSO_4$(aq), 1 M $FeSO_4$(aq), 1 M $Fe(NO_3)_3$(aq)

Saturated KNO_3 solution, a coil of nichrome wire and a coil of copper wire each fixed to a trimmed rubber bung, well-plate, plastic pipette, small strips of filter paper, 100 cm^3 beaker, microspatula, digital multimeter (DMM), connecting wires with crocodile clips.

Experimental Procedures

1. Using a clean plastic pipette, transfer 50 drops of 1 M $CuSO_4$(aq) to the central well (see Fig. 1).
2. Using two separate clean plastic pipettes, transfer 10 drops of 1 M $Fe(NO_3)_3$(aq) and 40 drops of 1 M $FeSO_4$(aq) to the well on the right (Well 1).

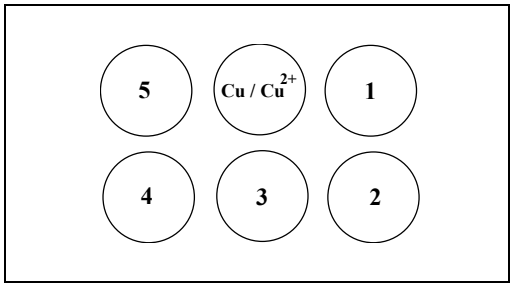

Fig. 1: Positions of Fe^{2+}(aq)/Fe^{3+}(aq) half-cells

3. Wet a small strip of filter paper with saturated KNO_3(aq), lower one end into the central well and the other end into the well on the right.
4. Cover the central well with the rubber bung fitted with a coil of copper wire and the right well with another rubber bung fitted with a coil of nichrome wire.
5. Taking the copper wire as the negative pole and the nichrome wire as the positive pole, measure the e.m.f. of the cell by a DMM (see Fig. 2).
6. Construct four more Fe^{3+}(aq)/Fe^{2+}(aq) half-cells in wells 2 to 5 using the following solution mixtures and measure the e.m.f. of the cells.

Fe^{3+}(aq)/Fe^{2+}(aq) half-cell	No. of drops	
	1 M Fe^{3+}(aq)	1 M Fe^{2+}(aq)
1	10	40
2	20	30
3	25	25
4	30	20
5	40	10

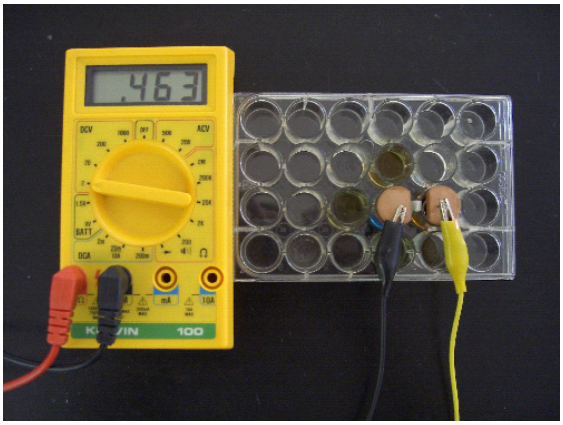

Fig. 2: Cell e.m.f. measurement

Results

Complete the following table:

$[Fe^{3+}(aq)] : [Fe^{2+}(aq)]$	e.m.f./V	$\log\frac{[Fe^{3+}(aq)]}{[Fe^{2+}(aq)]}$
10 : 40		
20 : 30		
25 : 25		
30 : 20		
40 : 10		

Treatment of Data

Enter your results into a spreadsheet software. Highlight the figures in the e.m.f. and $\log\frac{[Fe^{3+}(aq)]}{[Fe^{2+}(aq)]}$ columns and select the Graph Wizard function. Choose the X-Y scattered plot option and label the graph plotted. Evaluate the slope of the best-fit straight line graph using the Trendline function.

Discussion Questions

1. What is the criterion for predicting polarities of electrodes of an electrochemical cell?
2. Describe qualitatively the relationship between a decrease in concentration of the electrolyte around the cathode and cell e.m.f. Explain whether the result agrees with that predicted by the Nernst equation. You can use your experimental results for illustration.
3. From the graph plotted, deduce the E^{θ} value of the $Fe^{3+}(aq)/Fe^{2+}(aq)$ half-cell, given that the $Cu(s)/Cu^{2+}(aq)$ reference half-cell has an E^{θ} value of +0.34V. Compare with literature value. Comment on the discrepancy, if any.