

# Practical 1P3

## Electrode Potentials

### What you should learn from this practical

#### Science

This experiment will familiarise you with the thermodynamics of solutions and show how easily thermodynamic quantities can be obtained from electrochemical measurements.

#### Practical skills

This practical is straightforward, but will introduce certain skills to any students who have not taken A-level chemistry.

#### Overview

The practical has two distinct parts; the first uses cell potential measurements to make measurements of changes in free energy (Gibbs Function),  $G$ , enthalpy,  $H$ , and entropy,  $S$  (where  $G = H - TS$ ) and chemical activity,  $a$ , of cadmium for a cadmium amalgam (solution in mercury).

The second part is essentially a redox titration of an Fe(II) solution using a platinum indicator electrode, but shows that the potential varies with the ratio of  $[Fe^{3+}]/[Fe^{2+}]$  according to the Nernst equation (confirming how  $G$  varies too!).

## Safety

You should note that cadmium and mercury are both toxic, but are safely contained within the cell. There is no reason for you to come into contact with these materials.

The chemical solutions in the second part of the practical are safe provided normal good laboratory practice is followed i.e. do not attempt to pipette by mouth; wear a lab coat and gloves and protect your eyes by wearing safety glasses when handling acids.

## Part I: Gibbs free energy, enthalpy, entropy and chemical activity.

### Theory

The zero-current cell potential,  $E$ , of an electrochemical cell (cell potential difference measured with zero current flow) can be related to the change in the Gibbs function, or free energy change,  $\Delta G$ , for the cell reaction which would occur were the two electrodes to be short circuited:

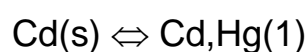
$$\Delta G = -zFE$$

where  $F$  is the Faraday constant ( $96487 \text{ Coulombs mol}^{-1}$ ),  $z$  is the number of electrons transferred in the reaction. (The sign of  $E$  is defined by the direction of the spontaneous reaction.)

For the cell



the cell reaction is:



Cd dissolves as  $\text{Cd}^{2+}$  at the Cd electrode and redeposits as Cd at the amalgam electrode. There is always oxidation at the left-hand electrode and reduction at the right as written. The cell potential is the potential of the right-hand electrode, with respect to that of the left.

$\Delta G$  is the change in Gibbs Function (expressed as  $\text{J mol}^{-1}$ ) which occurs when an infinitesimal amount of Cd is transferred to the existing amalgam i.e. it is not the free energy of mixing (for the formation of the solution from the pure elements), but the change in chemical potential for transfer of cadmium from pure solid cadmium to the liquid amalgam.

The entropy change for the cell reaction can be determined from the temperature coefficient at constant pressure of the cell potential because  $(\partial\Delta G/\partial T)_p = -\Delta S$ . From  $\Delta G$  and  $\Delta S$ ,  $\Delta H$  can easily be found using  $\Delta G = \Delta H - T\Delta S$ .

### **Experimental**

The cell contains three amalgam electrodes containing different concentrations of cadmium (0.5, 1.5, 4.5 wt%) and a pure cadmium electrode, all immersed in 0.1M cadmium sulphate solution. Nitrogen gas is bubbled through the solution in order to avoid oxidation of the cadmium in the amalgams and to suppress oxygen reduction at the electrodes, which would cause a shift in cell potential. Ask a Junior Demonstrator to show you how to use the regulator and valves, before using the nitrogen gas cylinder. The cell is immersed in a thermostatic water bath.

**N.B. Handle the cell with care – the liquid amalgam can easily be spilt from the electrodes!**

Measurements are to be made for all three amalgams by measuring the potential difference between each in turn and the cadmium electrode using a high impedance milli-voltmeter (why does it have to be **high** impedance?). This procedure is repeated at about 5°C intervals for the temperature range 20°C (i.e. room temp.) to 40°C. Note that the results may take some time to steady. (This can take up to 20 minutes for each temperature). Once the readings are stable the values should be recorded. Make sure there is enough solution in the cell and that the thermometer is immersed in the solution. If you are not sure how to operate the thermostat ask a Junior Demonstrator.

## **Analysis of Results**

### **i) State Functions**

Plot graphs of E vs. T for all three amalgams provided and determine  $\Delta G$ ,  $\Delta S$  and hence  $\Delta H$  in each case as outlined below. Estimate the error in these values.

#### **a) Calculation of $\Delta G$ at 298K**

$$\Delta G = -zFE \text{ (values of E in volts)}$$

Values of E at 298 K can be determined from a "best fit" line on the graph, or linear "least squares" regression using a calculator assuming the graph to be a straight line with the equation  $E = a + bT$ .

b) Calculation of  $\Delta S$  :

For each electrode the entropy change can be calculated from the slope,  $b$ , above:

$$\Delta S = zFb$$

c) Calculation of  $\Delta H$

From the definition of  $G$ :  $\Delta H = \Delta G + T\Delta S$

## ii) Activity

When the pressure of an ideal gas is changed from  $p_i$  to  $p_f$  the Gibbs Function changes by an amount:  $\Delta G = RT \ln(p_f/p_i)$ . There is a corresponding change when a species is transferred between two solutions in which it has different "activity",  $a$ ;  $\Delta G = RT \ln(a_f/a_i)$ . In a pure substance activity,  $a = 1$ , so that for transfer from pure Cd to amalgam  $\Delta G = RT \ln(a/1)$ . As  $\Delta G = -zFE$  we can calculate the activity of Cd in each amalgam from the cell potential.

Determine the cadmium activity in each amalgam at 25°C and plot a graph of activity against mole fraction on graph paper or using Excel.

(Relative Atomic Mass of Cd = 112.41; RAM of Hg = 200.61)

Comment on the form of your plot. Which law describes the experimental behaviour?

## Part II: Redox potentials

### Theory

An inert indicator electrode, e.g. platinum, immersed in a solution containing  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  assumes a definite electrical potential, characteristic of the opposing tendencies represented in the equilibrium:

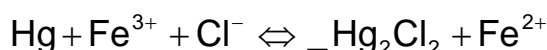


Electron transfer reactions between the electrons in the metal and the ions in solution bring the electrode to a stable potential. Qualitatively it can be argued that the greater the concentration of iron (III) ions, the greater will their tendency be to take electrons from the electrode and thus the more positive its potential will be; a high concentration of iron (II) ions will have the opposite effect. With an "oxidation-reduction potential" (called a "redox potential") the ions do not completely lose, but only change, their charge. Inorganic oxidation-reduction processes can give rise to a reproducible redox potential if the kinetics of the electron transfer reactions are reasonably rapid.

In order to measure this potential we must immerse a second reversible electrode in the solution to complete the circuit. A convenient reference electrode is a saturated calomel electrode (containing Hg and  $\text{Hg}_2\text{Cl}_2$ ). The system can be represented as follows:



The cell reaction is:



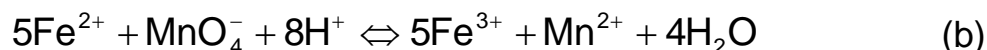
and the cell potential is given by:

$$E = E^{\circ} + 2.3RT/F \log_{10} \left( \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \right) - E(\text{SCE})$$

where  $E(\text{SCE})$  is the electrode potential of the saturated calomel electrode on the hydrogen scale (equal to 0.242 V at 25°C) and  $E^{\circ}$  is the standard potential of the redox couple, also on the hydrogen scale.

### Experimental

A convenient way of preparing a series of solutions with varying Fe(III)/Fe(II) ratios is to titrate a solution of Fe(II) salt with  $\text{KMnO}_4$  solution. This experiment also serves to illustrate the use of measurements of redox potentials for determining the end point of a titration. The oxidation of the  $\text{Fe}^{2+}$  ions occurs according to the following equation:



Using the pipette provided, place 25 ml of 0.1M Fe(II) ammonium sulphate solution (also containing 0.25M sulphuric acid) in a beaker and titrate with approximately 0.02M  $\text{KMnO}_4$  solution in a burette. Carry out the titration first without using the electrodes to determine the end-point of the titration visually, as judged by the first appearance of a pink colour in the solution.

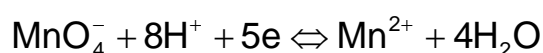
Repeat the titration using the electrodes to obtain an electrical measurement of the end-point of the titration. One electrode is of bright platinum, and the other is a calomel electrode connected to the solution being titrated through a salt bridge filled with saturated KCl. Connect the electrodes to the digital voltmeter.

**NOTE:** The commercial saturated calomel electrode which is used in this experiment contains a saturated KCl salt bridge within its outer casing. Before use, the rubber cap should be removed from the end of the electrode, and the salt bridge junction should be rinsed with distilled water.

Add the  $\text{KMnO}_4$  solution from a burette a few ml at a time to begin with, and in smaller quantities as the end-point is approached. After each addition stir the solution and measure the cell potential.

Plot the cell potential against the volume of  $\text{KMnO}_4$  solution added and discontinue the titration when the cell potential becomes approximately constant for a second time. The potentiometric end-point corresponds to the point of maximum slope in the plot of cell potential against volume added. Estimate the position of this point, and compare it with the visual end-point.

When the end-point has been passed, the cell potential will be determined by the reaction:



It will therefore depend upon the ratio  $[\text{MnO}_4^-]/[\text{Mn}^{2+}]$ , the hydrogen ion concentration, and the standard redox potential for that system. This potential is much higher than that for the Fe(II)/Fe(III) system.

**NOTE:** After use, the reference electrode should again be washed, and the rubber cap must be replaced. Put a few drops of 3M KCl in the rubber cap



before fitting it on the electrode, to prevent the junction from drying out. The platinum electrode should be rinsed in distilled water and dried after use.

### Calculation

From the potentiometric end-point (when volume added =  $V(\text{endpoint})$ ) calculate the molar concentration of the  $\text{KMnO}_4$  solution. (1 mole  $\text{KMnO}_4 \equiv 5$  moles  $\text{FeSO}_4$ ). For each point on the titration curve (volume  $V$  added), calculate the ratio  $[\text{Fe}^{3+}]/[\text{Fe}^{2+}] = V/(V(\text{endpoint}) - V)$ , then plot the observed cell potential against  $\log_{10} [\text{Fe}^{3+}]/[\text{Fe}^{2+}]$ , and see if eqn (a) is obeyed. (Neglect the difference between activity and concentration).

Use your graph to calculate the standard redox potential of the Fe(III)/Fe(II) system. Notice that:

$$E = E^\circ - E(\text{SCE})$$

when  $[\text{Fe}^{3+}] = [\text{Fe}^{2+}]$  (for equal **activity**, an error is introduced if equal concentrations are used (as here)).

### What should be in the report

Write up each of Part I and Part II of this experiment as it is normally done in a scientific paper: Purpose, Experimental method, Results, Discussion & Conclusions.

Do not include more than very brief necessary details of the experimental procedure.

Include details of the calculations and answer the questions as detailed in each section above.

Include graphs of results and diagrams.