Practical 1P8
Electrode Potentials

Prof. Mauro Pasta

HT 2021

What you should learn from this practical **2**
Science . . . 2
Practical skills . . . 2

Overview **2**

Safety **2**

Part I: Gibbs free energy, enthalpy, entropy and activity **2**
Theory . . . 2
Experimental . . . 3
Analysis of results . . . 3
State functions . . . 3
Calculation of ΔG at 298K . . . 3
Calculation of ΔS . . . 3
Calculation of ΔH . . . 3
Calculation of cadmium activity in the amalgam . . . 4

Part II: Redox potentials **4**
Theory . . . 4
Experimental . . . 5
Analysis of results . . . 5

What should be in the lab notebook and scientific report **6**

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 part uses open-circuit cell potential measurements to compute changes in Gibbs free energy, entropy and enthalpy of the formation of a cadmium amalgam (solution in mercury). The activity of cadmium in the amalgam is also determined.
The second part is a potentiometric redox titration of an iron(II) solution with a solution of potassium permanganate. The experiment shows that the potential varies with the ratio of $[Fe^{3+}]/[Fe^{2+}]$ according to the Nernst equation (confirming how ΔG 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 activity

Theory

The open-circuit cell potential ΔE of an electrochemical cell (potential difference measured with zero net current flow) can be related to the change in the Gibbs free energy ΔG of the spontaneous cell reaction:

$$\Delta G = -nF\Delta E \tag{1}$$

where F is the Faraday constant (96485 $Cmol^{-1}$), n is the number of electrons transferred in the reaction.

For the cell:

$$(-)\ Cd_{(s)}|0.1M\ Cd^{2+}_{(aq)}|Cd_xHg_{(l)}\ (+) \tag{2}$$

the cell reaction is:

$$Cd_{(s)} + Cd_xHg_{(l)} \leftrightarrow Cd_{1+x}Hg_{(l)} \tag{3}$$

Cadmium dissolves as Cd^{2+} at the Cd negative electrode and redeposits as Cd in the amalgam of composition Cd_xHg at the positive electrode. By convention, the cell potential is defined by the potential of the positive electrode with respect to the negative electrode:

$$\Delta E = E^+ - E^- \tag{4}$$

ΔG is the change in Gibbs free energy (in $Jmol^{-1}$ when ΔE is expressed in volts) which occurs when an infinitesimal amount of Cd is transferred to the existing amalgam of composition Cd_xHg 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:

$$\left(\frac{\partial \Delta G}{\partial T}\right)_p = -\Delta S \tag{5}$$

From ΔG and ΔS, ΔH can easily be found using:

$$\Delta G = \Delta H - T\Delta S \tag{6}$$

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. The cell is immersed in a thermostatic water bath.

N.B. Handle the cell with care as 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 from room temperature to 40°C. Note that the cell potential may take some time to steady (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.

Analysis of results

State functions

Plot graphs of ΔE vs. T for all three amalgams provided and determine ΔG at 298K, ΔS and hence ΔH in each case as outlined below. Estimate the error in these values.

Calculation of ΔG at 298K

Values of ΔE at 298 K can be determined from the linear "least squares" regression assuming the graph to be a straight line with the equation $E = a + bT$. The corresponding Gibbs free energy change can be calculated according to equation (1).

Calculation of ΔS

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

$$\Delta S = nFb \tag{7}$$

Calculation of ΔH

From the definition of G:

$$\Delta H = \Delta G + T\Delta S \tag{8}$$

Calculation of cadmium activity in the amalgam

The activity (a) represents the "effective concentration" of a species in a solution meaning that the chemical potential of the species in solution depends on its activity in the same way that it would depend on its concentration for an ideal solution:

$$\mu_i = \mu_i^0 + RT \ln a_i \tag{9}$$

At a constant pressure and temperature, the cell potential of the electrochemical reaction under consideration is a function of the activities of pure cadmium (a_{Cd}) and Cd in the amalgam ($a_{Cd(Hg)}$) according to the Nernst equation:

$$\Delta E = \Delta E^0 - RT \ln \frac{a_{Cd(Hg)}}{a_{Cd}} \tag{10}$$

ΔE^0 is the standard cell potential:

$$\Delta E^0 = E_+^0 - E_-^0 \tag{11}$$

where E_+^0 and E_-^0 are the standard reduction potential of the half-reactions occurring at the positive and negative electrode, respectively.
The standard reduction potentials for the two half-reactions in the electrochemical cell under investigation are:

$$E^0_{Cd^{2+}/Cd(Hg)} = -0.3521V$$

$$E^0_{Cd^{2+}/Cd} = -0.4030V$$

The activity of a pure substance is equal to one (i.e. $a_{Cd} = 1$) and therefore the cell potential only depends on the activity of cadmium in the amalgam:

$$\Delta E = \Delta E^0 - RT \ln a_{Cd(Hg)} \tag{12}$$

Determine the cadmium activity in each amalgam at 25°C and plot a graph of activity against mole fraction. The relative atomic masses of cadmium and mercury are 112.41 and 200.61, respectively). 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 Fe^{2+} and Fe^{3+} assumes a definite electrical potential, characteristic of the opposing tendencies represented in the equilibrium:

$$Fe^{3+} + e^- \leftrightarrow Fe^{2+} \tag{13}$$

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 Fe^{3+} 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 Fe^{2+} ions will have the opposite effect. 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 Hg_2Cl_2). The system can be represented as follows:

$$(-)\ Hg_{(l)}|Hg_2Cl_{2(s)}|KCl_{(aq,sat)}|Fe^{3+}_{(aq)}, Fe^{2+}_{(aq)}|Pt\ (+) \tag{14}$$

The cell reaction is:

$$2Hg_{(l)} + 2Fe^{3+}_{(aq)} + 2Cl^-_{(aq)} \leftrightarrow Hg_2Cl_{2(s)} + 2Fe^{2+}_{(aq)} \tag{15}$$

and the cell potential is given by:

$$\Delta E = E^0_{Fe^{3+}/Fe^{2+}} + \frac{2.303RT}{F}\log_{10}\frac{a_{Fe^{3+}}}{a_{Fe^{2+}}} - E_{SCE} \tag{16}$$

where E_{SCE} is the electrode potential of the saturated calomel electrode versus the standard hydrogen electrode (equal to 0.242 V at 25°C) and $E^0_{Fe^{3+}/Fe^{2+}}$ is the standard reduction potential of the redox couple.

Experimental

A convenient way of preparing a series of solutions with varying $[Fe^{3+}]/[Fe^{2+}]$ ratios is to titrate a solution of Fe(II) salt with $KMnO_4$ 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 Fe^{2+} ions occurs according to the following equation:

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O \tag{17}$$

Using the pipette provided, place 25 ml of 0.1M Fe(II) ammonium sulphate, $(NH_4)_2Fe(SO_4)_2$, solution (also containing 0.25M sulphuric acid) in a beaker and titrate with approximately 0.02M $KMnO_4$ 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 $KMnO_4$ solution from a burette a few milliliters 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 $KMnO_4$ 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 half-reaction:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \tag{18}$$

It will therefore depend upon the ratio $[MnO_4]/[Mn^{2+}]$, the proton concentration, and the standard redox potential for that system. This potential is much higher than that for the Fe^{III}/Fe^{II} 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.

Analysis of results

From the potentiometric end-point (when volume added = $V_{end-point}$) calculate the molar concentration of the $KMnO_4$ solution (1 mole $KMnO_4$ = 5 moles $FeSO_4$). For each point on the titration curve (volume V added), calculate the ratio $[Fe^{3+}]/[Fe^{2+}]$:

$$\frac{[Fe^{3+}]}{[Fe^{2+}]} = \frac{V}{V_{end-point} - V} \tag{19}$$

then plot the observed cell potential against $\log_{10} \frac{[Fe^{3+}]}{[Fe^{2+}]}$, and see if equation (a) is obeyed. Neglect the difference between activity and concentration.
Use your graph to calculate the standard redox potential of the $Fe^{III/II}$ system. Notice that:

$$E = E^0_{Fe^{3+}/Fe^{2+}} - E_{SCE} \tag{20}$$

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

What should be in the lab notebook and scientific report

1. You need to include the following records of experiment in your lab book: presentation and completeness of results, data analysis and errors and interpretation of results and conclusions. Include details of the calculations and answer the questions as detailed in each section above.

2. You also need to write up each of Part I and Part II of this experiment as it is normally done in a scientific paper with introduction, methods, results, discussion conclusions (you have already received advice on how to write a scientific report). Include graphs of results and diagrams.