4.04   REDOX POTENTIALS FROM POTENTIOMETRIC TITRATIONS

$$\left(\textbf{4 points}\right)$$

1   Background

1.1   Outline

This experiment is an exercise in simple equilibrium electrochemistry. In it, you will first investigate the Fe^{3+} / Fe^{2+} redox couple by performing an electrochemical titration with Ce^{4+}. This requires the generation of an electrode potential which is monitored as the titration proceeds. In the second part of the experiment the effects of electrode kinetics on the titration are investigated by diluting the solutions. In the final part, potentiometric titrations are used to study metal ions in a lemonade style fizzy drink.

Relevant lecture course: Equilibrium electrochemistry (Trinity term, 1st year). The URL for this experiment is http://ptcl.chem.ox.ac.uk/~hmc/tlab/experiments/404.html

1.2   Safety

You will use moderately concentrated acids, together with salts of cerium and iron in the experiment. These materials do not present any notable hazard, but you should handle them with care and wear safety glasses throughout the experiment. Safety information on the chemicals is available through the URL given above and is also on file in the upper teaching laboratory.

2   Theory

In the simplest electrochemical experiment, a platinum wire is dipped into an aqueous solution containing, for example, Fe^{3+} and Fe^{2+} ions, with a counter anion present to preserve electroneutrality.

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These ions can be interconverted by adding an electron to Fe^{3+} (reduction) or removing an electron from Fe^{2+} (oxidation). A platinum wire can be used to act as a source or sink for a very small number of electrons allowing this interconversion to take place. The following dynamic equilibrium, or *potential determining equilibrium*, is thus established on the surface of the metal, without measurably perturbing the Fe^{3+} and Fe^{2+} concentrations in solution.

$$Fe^{3+} (aq) + e^- (metal) \quad \rightleftharpoons \quad Fe^{2+} (aq)$$

If the equilibrium lies to the left, favouring the formation of Fe^{3+} (aq), then the electrode will bear a slight negative charge and the solution a slight positive charge, and vice versa. There is thus a charge separation, and hence a potential difference, between the metal and the solution. An *electrode potential* is established on the metal wire relative to the solution phase. This experiment is concerned with these electrode potentials, their measurement and application.

Qualitatively, the position of the equilibrium and hence the electrode potential will depend on the relative concentrations of Fe^{2+} and Fe^{3+}. Quantitatively the potential difference for a couple is given by the *Nernst Equation.*

$$\phi_M - \phi_S = \Delta\phi^o - (RT/F) \ln\{[Fe^{2+}]/[Fe^{3+}]\} \qquad (1)$$

where   [A] is the concentration of species A in moles dm^{-3}
                ϕ_M is the potential of the metal electrode
                ϕ_S is the potential of the solution phase
                $\Delta\phi^o$ is a temperature dependent constant.

Equation [1] assumes ideal behaviour. More correctly the Nernst equation should be expressed in terms of activities:

$$\phi_M - \phi_S = \Delta\phi^o - (RT/F) \ln \{a_{Fe}^{2+}/a_{Fe}^{3+}\}$$

where a_A is the activity of species A. However in fairly dilute solutions it is common to assume that the activity of a species is equal to its concentration; we shall make that approximation in the following discussion.

It is not possible to measure the potential of a single electrode directly. Using the example above, how could the potential of the platinum wire dipping into the solution be measured? If a voltmeter were used then one terminal would have to be connected to the electrode, but to what could the other terminal be connected? It is evident that electrode potentials must be measured relative to some reference.

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Arbitrarily, a standard hydrogen reference electrode (SHE) is used as a universal standard and all electrode potentials are quoted relative to this. For example in the case of the Fe^{3+} / Fe^{2+} couple,

$$E^{\ominus} (Fe^{2+} / Fe^{3+}) = 0.77V$$

implying that the cell,

$$Pt \mid H_2(g)\,(p{=}1) \mid H^+(a{=}1) \mid\mid Fe^{2+}(aq)\,(a{=}1), Fe^{3+}(aq)\,(a{=}1) \mid Pt$$

has an emf of 0.77V, with the platinum electrode dipping into the Fe^{2+} / Fe^{3+} solution having a positive potential.

In practice the SHE is inconvenient for everyday use (hydrogen gas needs careful venting and the electrode needs regular plating with platinum black which is highly susceptible to passivation - in other words, deactivation - by organic and biological materials). A convenient alternative is the saturated calomel reference electrode (SCE) which comprises a mercury electrode coated in mercury chloride in contact with a saturated potassium chloride solution. The solution contains potassium chloride crystals to ensure that saturation is maintained and the system is connected to the solution in question by a frit, allowing ion exchange with this solution. The potential determining equilibrium is:

$$\tfrac{1}{2}Hg_2Cl_2(s) + e^- \quad \rightleftarrows \quad Hg(l) + Cl^-(aq)$$
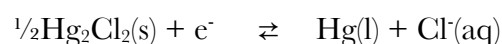
The potential between the mercury metal (M) and the solution (S) is:

$$\phi_M - \phi_S = \Delta\phi^{\ominus} - RT/F \ln a_{Cl^-}$$

It can be seen that the potential of the calomel electrode is dependent only on the chloride ion activity. This is constant as the solution is saturated with chloride ions. The potential of a calomel electrode relative to a standard hydrogen electrode is +0.242V, so if measurements are made using a calomel electrode rather than a hydrogen electrode, this value must be added to the measured voltage.

3 Experimental

3.1 Potentiometric titration of Fe^{2+} with Ce^{4+}

In the first experiment Fe^{2+} is titrated against Ce^{4+}. The potential developed on a platinum electrode immersed in the solution (measured against the SCE) is plotted as a function of the volume of Ce^{4+} added, as described in the calculation section.

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The half equations for this redox reaction are as follows:

$$Fe^{3+}(aq) + e^- \quad \rightleftarrows \quad Fe^{2+}(aq)$$
$$Ce^{4+}(aq) + e^- \quad \rightleftarrows \quad Ce^{3+}(aq)$$
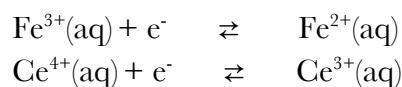
The redox potential of the Ce^{4+} / Ce^{3+} couple is much more positive than that of the Fe^{3+} / Fe^{2+} couple, so if Ce^{4+} is added to a solution containing Fe^{2+}, effectively all of the Ce^{4+} reacts to oxidize Fe^{2+} to Fe^{3+} and the overall reaction is as follows.

$$Fe^{2+}(aq) \; + \; Ce^{4+}(aq) \; \rightarrow \; Ce^{3+}(aq) \; + \; Fe^{3+}(aq)$$
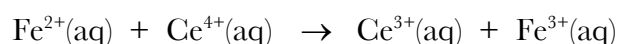
Measurements of the potential of the cell as a function of the volume of Ce^{4+} added during a titration of Ce^{4+} against Fe^{2+} will then lead to a plot with three distinct sections. In the first, all the Ce^{4+} added oxidizes Fe^{2+} to Fe^{3+} so no Ce^{4+} is present in the cell in significant quantity, while both Fe^{3+} and Fe^{2+} are present. Thus, measurements of the emf are made on the Fe^{3+}/Fe^{2+} couple, based on the cell:

$$Hg, Hg_2Cl_2 \mid KCl \mid\mid Fe^{3+}, Fe^{2+} \mid Pt$$

The Nernst equation for this cell is as follows:

$$E = E^\ominus (Fe^{3+}/Fe^{2+}) - E^\ominus_{calomel} - (RT/F) \ln\{[Fe^{2+}]/[Fe^{3+}]\} \qquad (2)$$

The second section in the plot corresponds to the region near the equivalence point. This occurs at the point at which all the Fe^{2+} has been oxidized to Fe^{3+} by the Ce^{4+}. By definition the equivalence point occurs when:

$$[Fe^{2+}]/[Fe^{3+}] = [Ce^{4+}]/[Ce^{3+}] \qquad (3)$$

In the third section, no Fe^{2+} remains to be oxidized by the Ce^{4+}, so measurements are made on the Ce^{4+}/Ce^{3+} couple based on the cell:

$$Hg, Hg_2Cl_2 \mid KCl \mid\mid Ce^{4+}, Ce^{3+} \mid Pt$$

The Nernst equation for this cell is:

$$E = E^\ominus (Ce^{4+}/Ce^{3+}) - E^\ominus_{calomel} - (RT/F) \ln\{[Ce^{3+}]/[Ce^{4+}]\} \qquad (4)$$

Combining the last 3 equations the equivalence point E_{equiv} is found to be:

$$E_{equiv} = \tfrac{1}{2}\{E^\ominus (Fe^{3+}/ Fe^{2+}) + E^\ominus (Ce^{4+}/Ce^{3+})\} - E^\ominus (Hg_2Cl_2 / Cl^-, Hg)$$

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3.2 Potentiometric titration of Fe^{2+} with Ce^{4+} at low concentration: limitations imposed by electrode kinetics

The Nernst equation will only predict the emf of a cell based on the concentrations of the products and reactants if the reaction is under thermodynamic control. The formal electrode potentials alone tell us nothing of the rate at which the equilibria

$$Fe^{3+}(aq) + e^- \quad \rightleftarrows \quad Fe^{2+}(aq)$$
$$Ce^{4+}(aq) + e^- \quad \rightleftarrows \quad Ce^{3+}(aq)$$
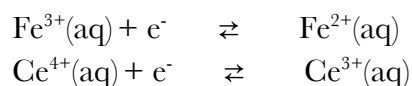
are established. If these reactions are slow, no electrode potential develops and the potentiometric titration approach is useless. At low concentrations of the redox species the kinetics are slower and this places a lower limit on the conditions which can be used in these measurements.

The activation energy for the Fe^{2+}/Fe^{3+} process is lower than that for the Ce^{4+}/Ce^{3+} reaction. Rates of electron transfer can be understood in terms of Marcus Theory, which relates such activation energies to changes in (i) bond lengths and bond angles and (ii) solvation between the reactants, products and the intervening transition state. In the case of Ce^{4+}/Ce^{3+} there is likely to be a significant difference in relative solvation as compared to the Fe^{3+}/Fe^{2+} couple, so explaining the observed kinetic difference.

In this second experiment Fe^{2+} is again titrated against Ce^{4+} but with both redox species in much lower concentrations. The potential developed on a platinum electrode immersed in the solution (and measured against the SCE) is plotted as a function of the volume of Ce^{4+} added to a fixed amount of Fe^{2+}. The potential in this region is ill-defined and likely to fluctuate significantly.

The plot you will determine has two sections - a thermodynamically controlled Fe^{3+}/Fe^{2+} couple as observed earlier, and the Ce^{4+}/Ce^{3+} couple where the kinetics are too slow for equilibrium to be reached, as explained above.

3.3 Finding the electrode potential of the Fe^{2+}/Fe^{3+} couple in a lemonade style soft drink

Irn Bru®, a popular lemonade style drink (at least in Scotland), contains Fe^{3+} as a citrate complex. In this third experiment it is possible to titrate this against Fe^{2+} to find the formal potential of the Fe^{3+} / Fe^{2+} couple, when both ions are complexed to citrate ligands. If a ligand stabilizes a lower oxidation state with respect to the higher, the redox potential increases, and vice versa. It is even possible for a positive redox potential to change sign, for example the redox potential of Fe^{3+}/Fe^{2+} in the presence of EDTA is −0.12V.

4 Procedure

4.1 Potentiometric titration of Fe^{2+} with Ce^{4+}

Clean a bright platinum electrode in a fume cupboard by dipping it in 3M nitric acid, then washing it in demineralized water. Keep the electrode in demineralized water until you need it. Prepare 100 cm^3 of 0.1M Ce(IV) sulfate in 1M sulfuric acid and 0.1M Fe^{2+} in 1M sulfuric acid. Fill the burette with the Ce^{4+} solution.

Important note! There are containers of both Fe(II) and Fe(III), and of Ce(III) and Ce(IV) in the lab; if you are to get correct results from this experiment, it is essential that you use the right chemicals!

Clamp the platinum and calomel electrodes gently so they dip into a clean 250 cm^3 beaker on a stirring plate. Connect the electrodes to a digital voltmeter. Add a magnetic bean, and check it is well clear of the electrodes when in motion. Add to the cell 25 cm^3 of the Fe^{2+} solution; if necessary add some demineralized water so that the electrode is covered, and titrate with the Ce^{4+} solution.

Plot the emf as a function of titrant volume as the titration proceeds. Measure the emf after it has stabilized following the addition of titrant. The plot will show a flat or gently sloping region followed by a steeply rising region. When a second flat or gently sloping region is clearly defined, indicating excess Ce^{4+}, the titration is complete. Do not stop the titration until this second region is properly defined.

4.2 Potentiometric titration of Fe^{2+} with Ce^{4+} in dilute solution

Dilute the Ce^{4+} and Fe^{2+} to 1mM concentrations using 1M sulfuric acid. Rinse the electrodes with demineralized water and repeat the procedure outlined above using the diluted solutions. Plot the emf as a function of titrant volume added for these new concentrations.

4.3 Finding the electrode potential of the Fe^{2+}/Fe^{3+} couple in a lemonade style soft drink

Prepare a fresh solution of Fe^{2+} at about 4mM concentration using Irn-Bru® as a solvent and fill the burette with this solution. Place 50cm^3 of fresh Irn Bru® in a 100cm^3 beaker containing a magnetic bean, and platinum and calomel electrodes as prepared above. Titrate the Fe^{2+} solution into the Irn Bru® in 1 cm^3 portions using up to a total of 6 cm^3. Record the emf as a function of number of moles of Fe^{2+} added. (The concentration of Fe^{3+} in Irn-Bru® is quoted as 0.002% ≈ 7.55×10^{-5} M.)

5 Calculations

5.1

Plot graphs of emf *vs* $\ln\{[Fe^{3+}]\ /\ [Fe^{2+}]\}$ and emf vs $\ln\{[Ce^{4+}]\ /\ [Ce^{3+}]\}$, noting equations [2] and [4], to find the formal redox potentials of the 0.1M Fe^{3+}/Fe^{2+} and $Ce^{4+}\ /\ Ce^{3+}$ couples, in sulfuric acid. Since in different parts of the titration the concentrations of Fe(II) and Ce(IV) are effectively zero, your two graphs will each cover different portions of the titration, one involving the concentrations of cerium ions only and the other iron only.

5.2

Plot a graph of emf *vs* volume of Ce^{4+} added for the 1mM solutions. Comment on the shape of the graph, and compare the equivalence point with that of the more concentrated solution studied in part (a).

5.3

Calculate the standard potential of the Fe^{2+}/Fe^{3+} couple in Irn Bru® by plotting graphs of emf vs $\ln\{[Fe^{3+}]/[Fe^{2+}]\}$, as in section 5.1 above. Compare this result with the standard potential observed in the titration with Ce^{4+} and comment on your results. How could the concentration of iron (III) ammonium citrate in Irn Bru® be accurately measured electrochemically? (Hint: Pure iron (III) ammonium citrate is commercially available.)

6 References

1.   *Electrode Potentials*, OUP, R. G. Compton and G. H. W. Sanders. Oxford University Press, OCP No. 41.
2.   *Electron Transfer Reactions in Organic Chemistry*, Springer-Verlag, 1987, L. Eberson.

7 Recent Physical Chemistry Finals questions in related areas

In recent Finals papers, the following questions covered topics related to those encountered in this experiment: GP I 2004, q1. GP II 2003, q3. GP II 2002 q1. GP II 2001 q2. GP II 2000, q2.