Quantification of Fe (II) and Iodine via amperometric titrations.

Background

Amperometric titration is an electrochemical method where the progress of a titration is followed by monitoring the current passing through the reaction mixture under an externally applied voltage. At the end points of the titration the changes of electrical properties of the solution are sharp. Amperometry employs a *constant potential difference* applied across two electrodes that are immersed in the reaction solution. The current produced under such circumstances is a measure of the actual rate of the electron transfer process at the electrode. The current across the cathode and anode currents are numerically equal and it is the net *faradaic current* passing through the system. The electrode at which the reaction rate is lower determines the overall electron transfer rate, i.e. the faradaic current strength.

When a faradaic current is forced by the externally applied potential difference, oxidation occurs at the anode and reduction at the cathode. The nature of the electrodes for this experiment is also important. At least one of them is an indicator electrode. The rate of these reactions at the indicator electrodes is proportional to the rate at which the reacting species encounters the electrode surface. For a well stirred system the rate of arrival of the material at the electrode surface is proportional to the concentration of the material in the solution.

During a titration the concentrations of the species in the solution will continually change. This results in the change of the faradaic current passing through the solution. If the potential applied is held constant and stirring rate is the same, the current will be proportional to the concentrations of the 'reactant' involved with the slower reaction rate. The shape of the titration curves produced depends on the reversibility of the reaction at the electrode and the configuration of the cell. The two electrode configurations that are in use are;

- Two indicator electrodes
- One indicator electrode (coupled with a reference electrode).

Two titrations will be carried out where the nature of revesibility of the electrode reactions differs.

I. Two indicator (dual polarized) electrodes - both electrode reactions reversible

This part of the experiment will employ the latter electrode configuration.

A Fe (II) solution titrated with Ce (IV) is an example of dual polarized electrodes - both electrode reactions reversible case.

Titration reaction: Fe (II) + Ce (IV) = Fe (III) + Ce (III)

Just after the starting point and before the end point of the titration the solution will contain

Fe(II), Fe(III), and Ce(III). Under the relatively small potential difference applied the reversible electrode reactions possible are:

Cathode: Fe (III) + e = Fe (II)

Anode: Fe (II) = Fe (III) + e

Before the addition of any titrant only Fe (II) is present in solution, making the anodic reaction the only possible oxidation reaction that can occur. To complete the circuit a reduction must occur, at the other electrode. However at this point there is no ion present that is reducible at the applied potential. Therefore the net faradaic current at this point is essentially zero (current, if any observed at this stage is the residual current).

As the titration progresses from the beginning [Fe (III)] will increase. This increase continues up to the half way point because [Fe (III)] limits the current up to this point. Beyond the half way point, [Fe (II)] is less than that of [Fe (III)] and [Fe (II)] will determine the quantity of current passing through. The current begins to decrease. At the end point the current passing is the residual current, because only Fe (III) and Ce (III) are present. Ce (III) oxidation requires a higher positive potential. Beyond the end point, the excess and increasing [Ce (IV)] will raise the current. The second set of electrode reactions shown below comes into play. The variation of current vs. titrant plots changes sharply at the end point enabling its detection.

After the end point with the addition of excess Ce(IV) the possible reversible electrode reactions are;

Cathode: Ce(IV) + e = Ce(III)

Anode: Ce(III) = Ce(IV) + e

Fe(III) reduction requires a lower negative potential. If the applied potential difference is large electrolysis of water would occur.

II. Dual polarized electrodes - one electrode reaction reversible and other irreversible

The titration of thiosulfate vs. iodine is an example of this type.

Titration Reaction: $2S_2O_3^{-2} + I_2 \rightarrow S_4O_6^{-2} + 2I^-$

Under the impressed potential difference, the possible reversible electrode reactions are;

Cathode: $\frac{1}{2} I_2 + e \rightarrow I^-$

Anode: $I^- \rightarrow \frac{1}{2} I_2 + e$

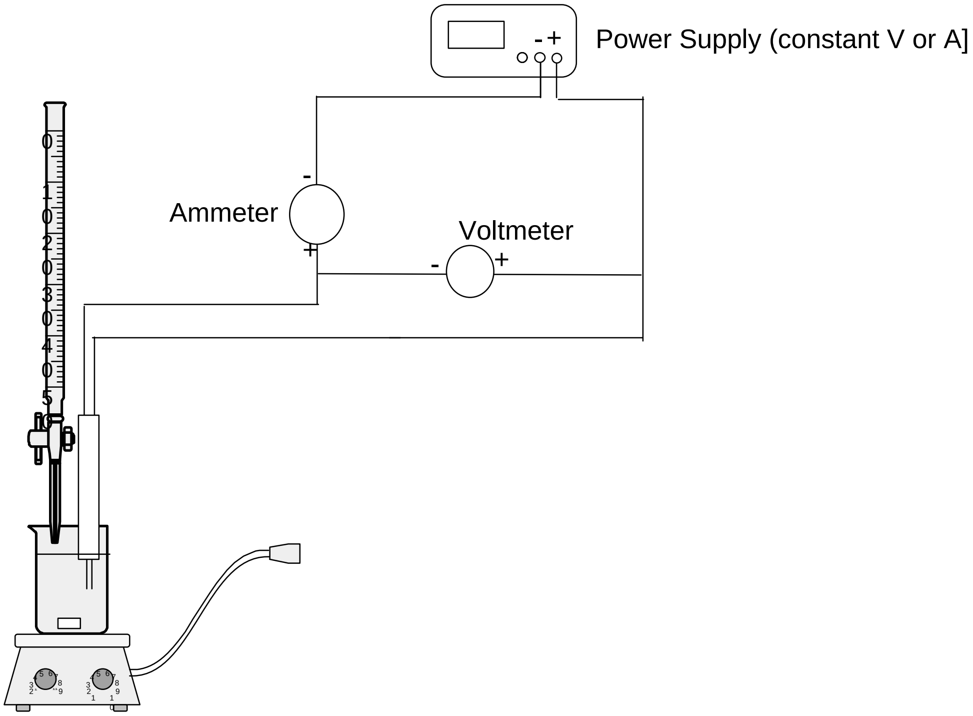
However, there will be no iodine in the reacting solution until the titration passes the endpoint. The thiosulfate, persulfate redox equilibrium is irreversible.

In all situations the concentration of the species present in lower concentration will determine the overall current strength at a given stage of the experiment.

Apparatus:	Platinum electrodes (2), identical; beaker 150 mL, magnetic stirrer, pipette 10 ml, burette 50ml, constant voltage source, connecting cables, DVM (2)
Chemicals:	0.1 M ceric ammonium nitrate (standard); ferrous ammonium sulfate (in 0.1M HCl acid) solution; conc. HCl; 0.025 M sodium thiosulfate (standard), iodine solution in KI (unknown).

Procedure:

In these experiments keep the rate of stirring at the same rate throughout the titration. Set up the circuit shown below using Pt electrodes.



Part I

Titration of Fe(II) vs Ce(IV):

Set up the circuit shown above. The Platinum electrodes immerse in the solution completely.

Pipette 20.00 ml of Fe (II) unknown solution in to a 150 ml beaker, add a few drops of conc. HCl and then add water to cover the electrodes completely. Turn on the magnetic stirrer; keep the stirring rate constant during the experiment. Adjust the applied potential to 0.50V. Titrate the prepared 'unknown' sample with standard Ce (IV) solution. Note the volume of titrant added and the corresponding current through the circuit after each addition of titrant. Make sure to maintain the applied potential at the suggested constant value throughout the run. Repeat this procedure for two other values of applied potentials (see table below). Obtain the data points judiciously, taking care to obtain more data points on either side of the endpoint.

Change the titrant and repeat the titration, at the highest applied potential.

Treatment of data:

1. Tabulate and plot the data for set. (Current vs. volume of the titrant)
2. Interpret the variations obtained in the plots.
3. Calculate the concentrations of the 'unknown' solutions.

Part II

Titration of thiosulfate vs iodine:

Using the same circuit titrate amperometrically 20.00mL of an standard *thiosulfate* solution *vs iodine* (iodine dissolved in KI) solution. Make one trial run with V_{app} = 0.50V.

(Optional) Change the titrant and repeat the titration, at the highest applied potential.

The suggested values for applied potentials for the runs are given below.

Vol. of titrant (ml)	Current (µA)		
	V_{app}= 0.50 V	V_{app}= 0.25 V	V_{app}= 0.05

Treatment of data:

1. Tabulate and plot the data for the three runs of each amperometric determination of the analytes on the same paper (scale).
2. Interpret the variations obtained in the plots.
3. Calculate the concentrations of the 'unknown' solutions.