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BIPOTENTIOMETRIC END-POINT INDICATION OF TITRATION FOR THE
DETERMINATION OF FERROUS ION
(REDOX TITRATION)

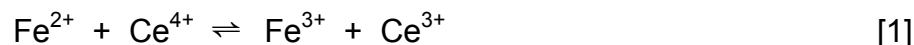
End-point indication using bipotentiometric end-point indication is based on electrochemical setup in which two platinum electrodes are polarized with a constant current and the potential difference between those two electrodes is measured. The method relies on the fact that in the absence of both a reducible and oxidizable species the potential between the electrodes will rise, whereas if both oxidizable and reducible species are present, the potential will be small. As the redox titration proceeds, the amounts and oxidizable and reducible species in the solution change and therefore, potential change tracks the process of the titration. Such a titration, in some aspects similar to the idea of the amperometric titration (your experiment 09), is inherently more accurate than indication using visual indicators. The equipment needs for bipotentiometric titrations are fairly simple. A constant current source (a galvanostat) is needed for the work. Most potentiostats have a switch allowing using the instrument as a galvanostat; however, any potentiostat can be modified to work as a galvanostat.

In bipotentiometry, the current between two identical platinum electrodes is held at a constant value and the resulting potential is measured. In this setup, there is no reference electrode used. Analytical determinations are made from the volume of the titrant delivered. The measured potential, although proportional to concentrations of reducible and oxidizable species, is not used for quantitative purpose, rather, it allows to find the endpoint.

In its conventional and/or most common form, the arrangement for the bipotentiometric titration consists of two polarizable electrodes, *e.g.*, platinum wires, sometimes sealed in a single glass tube to maintain constant spacing during the titration. During the titration experiment the potential between the two electrodes is recorded as a function of the volume of titrant.

There are two potentiostats available in our laboratory; one is the CV-27 voltammograph (a potentiostat) (Bioanalytical Systems, West Lafayette, IN). This one requires a simple modification, as it does not have a switch to use as a galvanostat. The other instrument is the PINE potentiostat, which has the galvanostatic function available via its software. You will be assigned to use the instrument that you have not used in a previous session. The use of these instruments will be illustrated with the titration of ferrous ion using the ceric ion as titrant. Note that the titration procedure is identical to the one used in experiment 09. Use your previous experience to do this work.

The net reaction is given below.



Standards and sample solutions

0.010 mol/l ceric ammonium sulfate in 1.0 mol/l sulfuric acid

0.010 mol/l ferrous ammonium sulfate

0.0010 mol/l ferrous ammonium sulfate

unknown solution (containing iron(II) from the TA

Phenanthroline-ferrous ion indicator solution

(This is supplied by the TA and can be prepared in the following manner:

Dissolve 1.485 g of 1,10-phenanthroline monohydrate in 100 ml of

0.025 mol/l ferrous sulfate solution. CRC handbook, 84th Ed. p. 8-3))

Note: The one molar sulfuric acid in the standards is sufficiently corrosive to harm your eyes, skin and clothing. Wear adequate protection.

Procedure

In a clean beaker, dispense a known volume of the 0.010 mol/l Fe (II) standard solution. Place the bipotentiometric platinum electrode couple in the beaker. Deliver enough deionized water into the beaker to cover the electrodes. However, do not put too much extra water in the beaker. Add 3 drops of phenanthroline indicator to the solution to guide you visually in the process of the titration.

Instruction for the BAS instrument: The instrument needs to be set as a galvanostat and supply current ca. 10^{-5} A. Connect the three electrodes of the CV-27 (**RED**-auxiliary, **BLACK**-working, and **WHITE**-reference) in the following manner: Bridge the auxiliary and the reference electrode inputs with a 15 k Ω resistor. Connect the reference electrode cable to one electrode of the indicator electrode pair and the working electrode cable to the other electrode of the pair. The polarity does not matter. Set the potential on the potentiostat to ca. 0.7 V. With the 15 k Ω resistor the current between the electrodes will be $0.7/15,000=4.6 \times 10^{-5}$ A. Fill clean dry burette with the Ce(IV) titrant solution. Record the initial volume reading. Turn the **CELL MODE** to **STANDBY**. Turn the **POWER** switch to the **ON** position and adjust E1 to +0.7 V. Switch the DISPLAY to I out position. Turn on the magnetic stirrer. Turn the **CELL MODE** switch to **CELL**. Read and record the potential on the attached recorder.

Add 0.50 ml of titrant to the sample solution and record the potential reading from the CV-27. Continue to add the titrant and record the potential at each volume increment. Note the volume of titrant that produces an indicator end-point (from orange to light blue or clear). Continue adding 0.5 ml of titrant and recording the current until 10 ml past the indicator end-point.

Repeat the titration for the 0.0010 mol/l Fe(II) solution, and for the unknown solution. Smaller volume increments may be needed. (Note, if the potential is large (ca.

1.5 to 2 V or more) and does not seem to change much during the titration, you are probably applying too large a current between the indicator electrodes. In that case lower the current and repeat the experiment.)

Instructions for the PINE instrument: The instrument is brand new and some of the details of the operation are still being developed. Much of the procedure is the same as for the BAS CV-27. However, the instrument has its own galvanostat setting. The TA will tell you which electrode connects to which color connection. The operation is computer-driven and should be reasonably obvious.

Results

1. Plot the potential versus volume of the titrant added for all titrations. Determine the end point for the known solutions and compare how the end-point volume agrees with the volume expected for titration with the known cerium standard. Also, how does the bipotentiometric end-point agree with the visual end point as determined by your observation?

2. Calculate and report the Fe(II) concentration in your unknown.

3. Discuss the possible sources of error in your result. Is there any discrepancy between the indicator endpoint and the amperometric endpoint? If so, explain why.

4. Describe how can a potentiostat, which does not have a “galvanostat” switch, be modified to function as a galvanostat. Explain, using an operational amplifier, why does this connection work as a galvanostat.

5. Compare this experiment with the previous titration experiment (09) and highlight advantages, disadvantages and concerns about the two methods.

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