EXPERIMENT 10: POTENTIOMETRIC TITRATION OF IRON IN MOHR'S SALT.
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PURPOSE

- Familiarize with the experimental requirements of a REDOX TITRATION and the calculations necessary to determine the equivalence point of a potentiometric redox reaction.

- Determine the equivalence point of a redox titration using different methods: indicators, midpoint, first derivative and second derivative plots.

THEORY

A redox titration is based upon an oxidation-reduction reaction between the analyte and the titrant. According to the chapter 541 of the USP a successful redox titration is carried out conveniently by the use of a reagent that brings about either oxidation or reduction of the analyte. Many redox titration curves are not symmetric about the equivalence point, and thus graphical determination of the endpoint is not possible or impractical; but indicators are available for many determinations, and a redox reagent can often serve as its own indicator. A **redox indicator** is a compound that changes color when it goes from its oxidized to its reduced state. As in any type of titration, the ideal indicator changes color at an endpoint that is as close as possible to the equivalence point. Accordingly, when the titrant serves as its own indicator, the difference between the endpoint and the equivalence point is determined only by the analyst's ability to detect the color change. A common example is the use of permanganate ion as an oxidizing titrant since a slight excess can easily be detected by its pink color. Other titrants that may serve as their own indicators are iodine, cerium (IV) salts, and potassium dichromate. In most cases, however, the use of an appropriate redox indicator will yield a much sharper endpoint. In some cases it may be necessary to adjust the oxidation state of the analyte prior to titration through use of an appropriate oxidizing or reducing agent; the excess reagent must then be removed, e.g., through precipitation. This is nearly always the practice in the determination of oxidizing agents since most volumetric solutions of reducing agents are slowly oxidized by atmospheric oxygen.

In this experiment, the titration of Fe (II) to Fe (III) with dichromate ion ($Cr_2O_7^{-2}$) will be followed using a platinum- calomel combination electrode. A combination electrode is one that houses in the same body both the working electrode, in this case the platinum redox electrode, and the reference electrode, a silver/silver chloride electrode. In acidic solutions, the dichromate ion is a powerful oxidant that is reduced to chromic ion. Iron (II) is oxidized to iron (III). The half reactions of interest are:

$$Cr_2O_7^{-2} + 14\ H^+ + 6\ e^- \ \rightleftharpoons \ 2\ Cr^{+3} + 7\ H_2O$$

$$Fe^{+2} \ \rightleftharpoons \ Fe^{+3} + e^-$$

The overall redox reaction is:

$$\underset{\text{Colorless}}{6\ Fe^{+2}} + \underset{\text{Orange}}{Cr_2O_7^{-2}} + 14\ H^+ \ \rightleftharpoons \ \underset{\text{Yellow}}{6\ Fe^{+3}} + \underset{\text{Green}}{2\ Cr^{+3}} + 7\ H_2O.$$

The iron content on a sample of ferrous ammonium sulfate (Mohr's salt) can be determined by means of a redox reaction. The ferrous ion may be easily oxidized to the more stable ferric ion using an oxidizing agent such as potassium dichromate. $K_2Cr_2O_7$ may be obtained on a very pure form and may be used as a primary standard. A standard solution used as titrant can be prepared directly and there is no need for standardization. Potassium dichromate is an excellent oxidizing agent for iron(II) since:
- dichromate and iron(II) react quantitatively and with a known stoichiometry
- the reaction is sufficiently fast to be practical for a titration
- the ΔE is large enough to produce a well-defined endpoint.

- standard solutions of potassium dichromate can be prepared from a weighed quantity of the dried solid and need not be standardized; the prepared solutions are very stable.

The titration must be performed in the presence of sulfuric and phosphoric acids. The H_3PO_4 forms a complex with the Fe^{3+}. This reaction lowers the Fe^{3+} concentration and in turns the potential of the Fe^{3+}/Fe^{2+} pair. As a result, the change in potential around the final point region is more drastic.

Mohr's salt is unstable because the Fe^{2+} ion is easily oxidized. The sample should be protected as much as possible from the atmosphere, humidity and high temperatures. For that reason, the sample should not be dried in the oven and should be kept on the desiccator until being used. In this experiment, we will focus our attention to the use of a **redox reaction**. Because, in general, there is no difficulty in finding a suitable redox indicator and most potentiometric titrations are asymmetrical, and time consuming we will perform our titration using diphenylamine sulfonate or its equivalent as a redox indicator for the analysis of an unknown Mohr's salt sample.

A potentiometric titration data set has been made available at the course website for analysis. In this type of titrations the potential difference between two electrodes immersed in the sample solution is plotted against the titrant volume. These electrodes and the solution constitute an electrochemical cell. A buret is used to add the titrant. The potential difference between the electrodes is measured with a pH/mV meter. The potential E of the solution is monitored as a function of the titrant volume by using a proper combination of a reference electrode and a working electrode. The working electrode typically consists of an inert metal like platinum while Silver/Silver Chloride (Ag/AgCl) serves as reference. Both the oxidized and reduced species are usually soluble and their ratio varies throughout the titration. The potential of the indicator electrode will be directly proportional to log (a_{red}/a_{ox}). The potential is then plotted as a function of the volume of titrant added. The equivalence point occurs at the steepest point of the plot **(Figure 1)**.
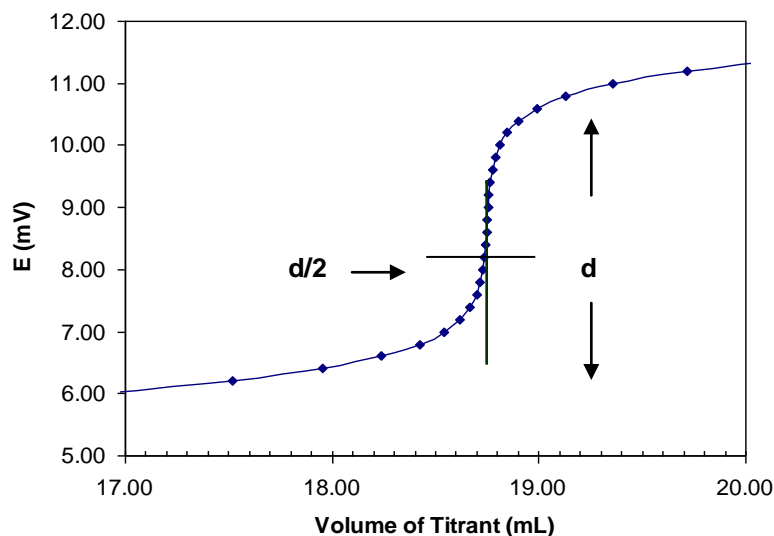
Figure 1: Plot of potential vs. volume of titrant added

Like in a pH titration, the equivalence point can also be estimated as the maximum of a first derivative plot. Since the rate of change of potential has its maximum value at this point, a "spiked" curve is produced and a peak occurs at that point (**Figure 2**).
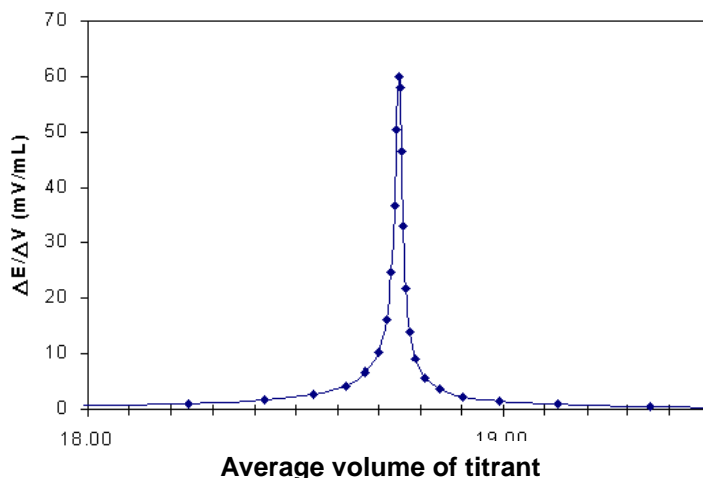
Figure 2: First derivative plot of potential vs. average titrant volume curve.

A redox indicator changes color over a range of $\pm(59/n)mV$, centered at E^0 for the indicator (n is the number of electrons in the indicator half-reaction). The larger the difference in standard potentials between titrant and analyte, the greater the break in the titration curve at the equivalence point. A redox titration is usually feasible if the difference in potentials is >0.2 V. However, the end point of such a titration is not very sharp and is best detected potentiometrically. If the difference in formal potentials is ≥0.4 V, then a redox indicator usually gives a satisfactory end point. Some common redox indicators are diphenylamine, diphenylbenzidine or diphenylamine sulfonate.

PRELABORATORY EXERCISE

Given the half reactions for the iron(II) and dichromate ion titration:
   a. $Cr_2O_7^{-2} + 14 H^+ + 6 e^- \rightarrow 2 Cr^{+3} + 7 H_2O$
   b. $Fe^{+2} \rightarrow Fe^{+3} + e^-$

1. Write the overall redox reaction.
2. Indicate how many electrodes are involved in this redox reaction.
3. Calculate the molarity of a solution prepared by adding 1.2532 g of $FeSO_4(NH_4)_2SO_4.6H_2O$ in a 250 mL volumetric flask and diluting to the mark with water.
4. Calculate the volume of $K_2Cr_2O_7$ (0.02 M) needed to reach the equivalence point when a **0.80 g** sample of <u>pure</u> $FeSO_4(NH_4)_2SO_4.6H_2O$ dissolved in 100 mL of 1N H_2SO_4 is titrated.
5. What is the color change observed when diphenylamine sulfonate is used as an indicator?
6. Read the MSDS of all the reagents used in this experiment and summarize their handling, disposal and health-related precautions.

APPARATUS AND MATERIALS

Magnetic stirrer/stirring bar
50 mL Buret
250 mL beakers

Chemicals:

Potassium dichromate, $K_2Cr_2O_7$ (MW = 294.185)

50% Sulfuric Acid (MW = 98.079; specific gravity =1.84 g/mL)

Mohr's Salt Unknown, $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ (MW = 392.143)

Phosphoric Acid (85%)

Diphenylamine, diphenylbenzidine or diphenylamine sulfonate as indicator (0.3%)

EXPERIMENTAL

A. Preparation of Standard $K_2Cr_2O_7$ (Provided by instructor):

1. Dry a sample of standard $K_2Cr_2O_7$ for an hour at 150 $^{\circ}$C.
2. Allow the sample to cool to room temperature in a desiccator.
3. Accurately weigh about 1.25 g, dissolve in a beaker with 30 or 40 mL of distilled water. Transfer quantitatively into a 250 mL volumetric flask and dilute to the mark. (It is possible that this solution may be already available in the laboratory. In this case your instructor will provide the data about the weight of $K_2Cr_2O_7$ used and the volume of solution prepared).
4. Calculate the exact molarity of this solution.

B. Preparation of 0.5 M H_2SO_4/ H_3PO_4 solution :

1. Add 15 mL of 50% sulfuric acid to 300 mL of distilled water, and mix well. (**Do this slowly and carefully, since the solution will get hot).** Store in a close container.
2. Add 45 mL of phosphoric acid (85%), to the abovementioned mixture and mix thoroughly.

C. Titration Procedure:

Indicator Titration:

1. Obtain a sample of Mohr's Salt unknown from your lab instructor and keep it in a desiccator.
2. Accurately weigh a sample of approximately 0.5000 grams.
3. Dissolve in 100 mL of the sulfuric acid/phosphoric acid solution.
4. Fill the buret with the potassium dichromate solution up to the zero mark.
5. Add 3-5 drops of the diphenylamine sulfonate indicator or its equivalent to the solution.
6. Titrate the sample with the standard dichromate solution until reaching the endpoint.

Potentiometric Titration (optional):
1. Follow Steps 1-5 of the indicator titration procedure.
2. Titrate the sample as follows:
   - Add enough titrant to induce a 10 mV change on the pH meter (~1 mL). The volume of titrant needed to induce a 10 mV change in the observed voltage will decrease as the titration progresses.
   - When the titration is close to the endpoint (≤0.20 mL for a 10 mV change in potential), titrant must be added at 0.10 mL intervals until a hugh jump in voltage is observed (in some cases, between 200- 300 mV). From this point on, larger volumes of titrant will be required to induce a 10 mV change.
   - As soon as the volume of titrant needed to attain a 10 mV change reaches 1.00 mL again, add three 1.00 mL portions of titrant. Record each of these potentials on your notebook
   Repeat the procedure with an additional sample of Mohr's salt.

CALCULATIONS

1. Calculate the exact **molarity** of the potassium dichromate solution from the data on the bottle label.
2. Using the potentiometric data available on the course website, determine the equivalence volume for the potentiometric titration using two different methods:
   - the direct plot of potential versus titrant volume (normal titration curve)

- the first derivative method ($\delta E/\delta V$), where the change in potential is plotted versus the average volume of titrant (first derivative titration curve)

3. Using the equivalence volumes obtained from the graphs; calculate the moles of $K_2Cr_2O_7$ used for each titration, and the moles of Fe on each unknown sample. (Remember that the stoichiometric ratio Fe to $K_2Cr_2O_7$ is 6).

4. Calculate the grams of Fe (atomic weight 55.845) for each sample analyzed using indicators as well as those determined potentiometrically.

5. Calculate the % Fe(II) in each Mohr's salt sample.

6. Calculate the average % Fe.

7. Calculate the relative standard deviation in ppt.

8. Calculate the percent difference between the average indicator and potentiometric results.

QUESTIONS

1. Compare a classical titration (end point determined using an indicator) and a potentiometric titration in terms of:
   - Precision and accuracy
   - Advantages and disadvantages

2. Compare the two graphical methods (normal E vs. Volume, and first derivative curves) used to determine the equivalence point. Which is better, if any, and why?

3. What is the primary function of the phosphoric acid in this titration. What makes potassium dichromate an excellent oxidizing agent for this titration?

4. Is the percent difference between the average indicator and potentiometric results significant? Justiffy your answer.

5. Does the oxidation efficiency of potassium dichromate is pH dependent? Justify your answer.

NOTE: PROPER DISPOSITION OF THE SOLUTIONS CONTAINING POTASSIUM DICHROMATE

DISCARD ALL THE SOLUTIONS INTO THE WASTE BOTTLE LOCATED IN THE SAP AREA AND LABELED AS "Fe / POTASSIUM DICHROMATE-TITRATION EXPT"