Chemistry 201 Laboratory   Summer, 2009

Experiment: Determination of Iron in a Ferrous Ammonium Sulfate Sample (Fe)

This experiment involves the determination of the percentage of ferrous iron in an unknown sample mixture by redox titration with potassium dichromate solution as the standard using:
        (i) ferroin indicator
        (ii) potentiometric titration.

The net ionic balanced equation for the titration is:

$$Cr_2O_7^{2-} \ + \ 6\,Fe^{2+} \ + \ 14\,H^+ \ \longrightarrow \ 2\,Cr^{3+} \ + \ 6\,Fe^{3+} \ + \ 7\,H_2O$$
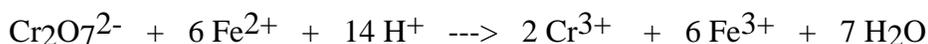
PROCEDURE:

> **DO <u>NOT</u> DRY THE (Fe) SAMPLE IN THE OVEN**
>
> **DO <u>NOT</u> DRY THE POTASSIUM DICHROMATE ($K_2Cr_2O_7$) IN THE OVEN**

Prepare the primary standard:
Use reagent grade potassium dichromate, $K_2Cr_2O_7$ as the primary standard.   Weigh accurately 1.50 g of the primary standard into a 250 mL volumetric flask and dilute to volume with distilled water.

Prepare the unknown:
(Suggestion: Prepare the unknown on the day it will be titrated. The primary standard can be prepared on day 1. Do all titrations on the same day and plan on spending about 30 minutes or more to finish the potentiometric titration).
The preparation of the unknown solution is as follows: Weigh accurately (by difference) a 5 g portion of UNDRIED ferrous sample into about 50 mL 1:1 sulfuric acid solution (i.e. previously prepared with 25 mL concentrated sulfuric acid added slowly to 25 mL distilled water with rapid stirring; solution temperature will reach 80°C) in a 250 mL beaker with vigorous stirring. Cool to a warm temperature, transfer quantitatively to a 100 mL volumetric flask, and make up to volume. Any precipitate if present will dissolve with shaking. Recheck the volume after cooling completely as the solution usually shrinks in volume. If so, adjust it to the correct final volume. To ensure minimum contact of this solution with oxygen, it is recommended that you carry out the titration soon after preparation of the unknown. Otherwise, you need to tightly cover your volumetric flask when you store it in your locker.

TITRATION:
Do three (3) indicator titrations and one (1) potentiometric titration, not necessarily in that order. For the indicator titrations, 20.0 mL aliquots of this unknown solution are titrated with the $K_2Cr_2O_7$ solution using ferroin as the indicator. The color change is from red to yellow green. (The best is just as it changes color which is when it is bluish grey in color).

For the potentiometric titrations, use a the meter in mV mode with a platinum indicator electrode and a calomel reference electrode (set to (+) to have it fall within the scale; if it goes below 0, switch it to make it return to scale). The ferroin indicator is not needed for this titration. Allow the dichromate titrant to drain into a 150 mL beaker provided with a magnetic stirrer. (check with the instructor or GA to make sure you are

using the correct potentiometer). To simplify obtaining a first derivative curve plot, enter the titrant by an approximate, but precisely measured volume:

As an *example* only: *Suppose* that the end point occurs around 15 mL, add the titrant to the following buret *readings* in such a way that you have small volume increments in the vicinity of the equivalence point: For example, 5.00 mL, 10.00 mL, 13.00mL, 14.00, 14.50 , 14.70, 14.80, 14.90, 14.95, 15.00, 15.05, 15.10, 15.20, 15.30, 15.50, 16.00, 17.00 , 20.00, 25.00 mL. (that is, exceed the equivalence point by about 10 mLs.). Remember that as you add the titrant you also pay attention to the stability of the mV reading. When the change increases, make the increments small so you don't miss the actual midpoint of the equivalence point).

To determine the end point in the potentiometric titrations, plot the following curves :
(i) E(mV) vs. volume (v in mL) of titrant,
(ii) $\Delta E/\Delta v$ (mV/mL) vs. average v (mL).

Determine the end point from the latter (first derivative) curve. Compare the results of the two experiments.
Supplementary appendix:
DERIVATIVES OF CURVES:
Acid-base, gravimetric, redox and complexometric titrations usually yield logarithmic curves in plots of the appropriate parameters versus volume of titrant added. (Note: pH and mV are examples of parameters which are logarithmic.). Sometimes, it is difficult to discern the endpoint of the titration, and it is useful to plot the first-derivative value <u>versus</u> the average volume because at the endpoint a sharp change of direction occurs. The tables below show the calculations needed to determine the first and second derivatives for raw data containing a set of mL vs mV. It is recommended that the calculations be done by computer using programs such as Excel.

Table 1: First Derivative

Point	V_i (mL)	mV_i	ΔV^* (mL)	ΔmV	$\Delta mV/\Delta V$ (mL)$^{-1}$	V_{ave} (mL)
1	V_1	mV_1	---	---	---	---
2	V_2	mV_2	$V_2 - V_1$	$mV_2 - mV_1$	$(mV_2 - mV_1)/(V_2 - V_1)$	$(V_2 + V_1)/2$
3	V_3	mV_3	$V_3 - V_2$	$mV_3 - mV_2$	$(mV_3 - mV_2)/(V_3 - V_2)$	$(V_3 + V_2)/2$
4	V_4	mV_4	$V_4 - V_3$	$mV_4 - mV_3$	$(mV_4 - mV_3)/(V_4 - V_3)$	$(V_4 + V_3)/2$
...						

ΔV = difference of the 2 subsequent volumes

A second-derivative curve of a log plot, i.e. $\Delta^2 mV/\Delta V^2$ versus average volume, V_{ave}, yields an even more accurate plot than the first-derivative curve because a transverse line across the volume axis is obtained at the endpoint. (This is optional).

Table 2 : Second Derivative

| Point	V_i	mV_i	ΔV^* (mL)	$\Delta mV/\Delta V$ (mL)$^{-1}$	$\Delta^2 mV/\Delta V^2$ (mL)$^{-2}$	V_{ave} (mL)
1	V_1	mV_1	---	---	---	---
2	V_2	mV_2	$V_2 - V_1$	$mV'_2 = \dfrac{(mV_2 - mV_1)}{(V_2 - V_1)}$	---	$(V_2 + V_1)/2$
3	V_3	mV_3	$V_3 - V_2$	mV'_3	$(mV'_3 - mV'_2)/(V_3 - V_2)$	$(V_3 + V_2)/2$
4	V_4	mV_4	$V_4 - V_3$	mV'_4	$(mV'_4 - mV'_3)/(V_4 - V_3)$	$(V_4 + V_3)/2$
...						

" * " = difference, " ' " = first derivative

Discarding Waste: dichromate ($Cr_2O_7{}^{2-}$) is toxic to the environment. After the experiment, excess $K_2Cr_2O_7$ and the analyte are to be discarded in the designated waste bottles located on the reagent bench.

Concentrated sulfuric acid waste must be placed in the plastic, labeled acid waste container under the acid fume hood. (Alternatively, it may be neutralized with sodium bicarbonate safety solution)
Please ask the instructor or TA if you have any questions.

CALCULATING % Fe in the unknown sample:
We note that the 2 half reactions are:
   a) $Fe^{2+} \longrightarrow Fe^{3+} + e^-$
   b) $Cr_2O_7{}^{2-} + 6\ e^- \longrightarrow 2\ Cr^{3+}$ (unbalanced)
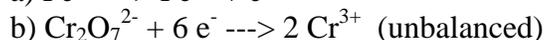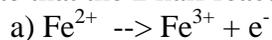
Since at the equivalence point, # equivalents of Fe^{2+} = # equivalents of $Cr_2O_7{}^2$,

we can therefore write: (#moles of Fe^{2+}) x 1= (# moles of $Cr_2O_7{}^2$) x 6

$$M_{Fe2+}V_{Fe2+} = 6M_{Cr2O7}V_{Cr2O7}$$

(alternatively, some write: $N_{Fe2+}V_{Fe2+} = N_{Cr2O7}V_{Cr2O7}$ where N = normality = #gram equiv x molarity. In the case of a redox reactant that transfers n electrons, the normality = n x molarity).
   To determine %Fe in the unknown, the following derivation should help (follow it carefully):

$$\text{and: }\%Fe = \frac{g_{Fe} \times 100\%}{g_{ore}} = \frac{mol_{Fe}\ (\frac{55.85g}{mol})}{g_{ore}} \times 100\% = \frac{6(M_{Cr2O7}V_{Cr2O7})(55.85)(100\%)}{(g_{ore})(\text{fraction titrated})}$$

(Note that the "fraction titrated" is $\frac{V_{Fe,titr}}{V_{Fe,total}}$.)

FURTHER READING:

1. R. B. Dean and W. J. Dixon, Anal. Chem., 23, 636 (1951)

2. W. J. Dixon,   Ann. Math. Stat., 22, 68 (1951)

3. J. S. Fritz and G. H. Schenk, Jr. , "Quantitative Analytical Chemistry" 4th Ed., Allyn and Bacon, Boston (1979)

4. L. Meites, ed., "Handbook of Analytical Chemistry". McGraw-Hill, N.Y. (1963).

Informal report: Date submitted: _____
Experiment: Determination of Iron   Time submitted: _____

Name: _____   Values obtained:

                                                                    (1) _____ %

Locker #_____   (indicator method) (2) _____ %

                                                                    (3) _____ %

                                          (potentiometric method) (4) _____ %

                                    Average value =   _____ %
                              (if applicable) Standard deviation= _____ %

(Note: you may average the values if they are close together. If not decide which is more reliable
before submitting your final value. If you average, enter the standard deviation also)
----

g $K_2Cr_2O_7$ used for standard solution =_____ g

Show calculations:

$[K_2Cr_2O_7]$ =   _____ M

Titration of unknown Fe ore:

g Fe ore (unknown) = _____ g

Titrations: (Ferroin indicator method)   (Potentiometric method)
                          I   II   III   IV
mLs of titrant
added to reach   _____   _____   _____   _____
end point:

% Fe in ore = %Fe   _____   _____   _____   _____

Sample calculation:
N.b. At equivalence point, equivalents, Eq of titrant, A =Eq analyte, B
   #Eq. Fe^{2+} = #Eq. $Cr_2O_7^{2-}$; but: #Eq. Fe = # mol Fe, and #Eq. $Cr_2O_7^{2-}$ = 6x #mol $Cr_2O_7^{2-}$
   So, #mols Fe = 6 x(#mols $Cr_2O_7^{2-}$) ; or, (g Fe)/(AW of Fe) = 6($M_{Cr2O7}V_{Cr2O7l}$)
   => (g Fe) = 6($M_{Cr2O7}V_{Cr2O7l}$)(AW of Fe)   => % Fe = $\dfrac{6M_{Cr2O7}V_{Cr2O7}(AW_{Fe})(100\%)}{(g_{ore})(\dfrac{V_{Fe,titr}}{V_{Fe,total}})}$

   FW of $K_2Cr_2O_7$ = 294.22 g/mol, AW of Fe = 55.85 g/mol