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EFFECT OF FLUORIDE, CHLORIDE, BROMIDE, AND THIOCYANATE
ON POTENTIOMETRIC TITRATIONS OF IRON(II)-TIN(II)
MIXTURES WITH CERIUM(IV)

Y. M. Kwok

MASTER

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Lawrence
Livermore
Laboratory

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EFFECT OF FLUORIDE, CHLORIDE, BROMIDE, AND THIOCYANATE
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ABSTRACT

A two-step curve is expected in the potentiometric titration of Fe(II)-Sn(II) mixtures with Ce(IV) in H_2SO_4 . Each end point should indicate the respective oxidation of Sn(II) and Fe(II). However, experimentally only one end point was found; it corresponded to the total oxidation of Sn(II) and Fe(II). When this oxidation-reduction reaction was carried out in the presence of Cl^- , the theoretical behavior was observed. The present study was done to ascertain if monovalent anions other than Cl^- have a similar effect on this oxidation-reduction system. The monovalent species F^- , Br^- , and SCN^- were selected for this study, and the results indicate that each affects the rate of reaction relative to the ease of oxidation of the individual ions.

INTRODUCTION

The literature contains many references to the potentiometric titration of iron in ores.¹⁻⁴ The method involves an initial reduction of Fe(III) to Fe(II) with $SnCl_2$ in an acid medium. The excess Sn(II) is then removed by oxidation with $HgCl_2$, and the Fe(II) titrated with a standardized oxidant, such as Cr(VI) or Ce(IV), in the presence of a specific indicator.

The excess Sn(II) can also be accounted for quantitatively by direct potentiometric titration with the same oxidant used for Fe(II). The potentials plotted against the volumes of the oxidant is theoretically a

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two-step curve (Fig. 1) with the inflection points indicating the respective oxidations of Sn(II) and Fe(II). Thus, the amount of Fe(II) can be calculated from the difference in volume between the two end points multiplied by the concentration of the oxidant. If we use Ce(IV) as our oxidant, the theoretical potentials for a platinum indicator electrode can be calculated before the first end point by

$$E = 0.15 - \frac{0.059}{2} \log \frac{(\text{Sn}^{2+})}{(\text{Sn}^{4+})} ,$$

at the first end point by

$$E = \frac{2(0.15) + 0.68}{3} ,$$

between the first and the second end points by

$$E = 0.68 - 0.059 \log \frac{(\text{Fe}^{2+})}{(\text{Fe}^{3+})} ,$$

at the second end point by

$$E = \frac{0.68 + 1.44}{2} ,$$

Fig. 1. The theoretical curve for 10 ml of 0.1 M Fe(II) plus 20 ml of 0.05 M Sn(II) titrated with 0.1 M Ce(IV) in 1 M H_2SO_4 .

and after the second end point by

$$E = 1.44 - 0.059 \log \frac{(\text{Ce}^{3+})}{(\text{Ce}^{4+})} .$$

When the oxidation-reduction reaction is carried out with only SnCl_2 and Ce(IV) in 1 M H_2SO_4 , the curve has the same shape as the first half of the theoretical curve. Likewise, the reaction of Fe(II) with Ce(IV) in the same medium yields a curve that matches the second half (see Fig. 2). However, if the solution contains both Sn(II) and Fe(II) , the curve may show only one end point corresponding to the total oxidation of Sn(II) and Fe(II) in the sample (see Fig. 3). This unpredicted result was further studied by Hall.⁵ He observed that if 2 M HCl rather than 1 M H_2SO_4 were used, theoretical behavior resulted. To determine whether monovalent anions other than Cl^- similarly affect this oxidation-reduction system, F^- , Br^- , and SCN^- were selected for testing.

EXPERIMENTAL

MATERIALS

pH Meter

Initially, a Beckman Model G pH meter was used with a platinum indicator electrode and a saturated calomel reference electrode to measure potential. Later, a more responsive Beckman Zeromatic instrument was used.

Fig. 2 Curves for Sn(II) and for Fe(II) titrated with 0.1163 M Ce(IV) in 1 M H₂SO₄ at 23.5°C. (a) The curve for 0.0371 M Sn(II). The end point is reached at 12.75 ml Ce(IV). (b) The curve for 0.0965 M Fe(II). The end point is reached at 8.3 ml Ce(IV).

Fig. 3. Curve for 20 ml of 0.0407 M Sn(II) plus 10 ml of 0.0965 M Fe(II) titrated with 0.1163 M Ce(IV) in 1 M H_2SO_4 at 70 to 74°C. The end point for this mixture is reached at 22.3 ml Ce(IV).

Reagents

All chemicals used were reagent grade.

A standard solution of 0.0167 M potassium dichromate, $K_2Cr_2O_7$, was prepared. The solid was dried at 150 to 200°C for 2 h, cooled in a silica gel desiccator, weighed, and dissolved in 1 M H_2SO_4 .

A 0.1 M solution of iron (II) ammonium sulfate, $Fe(NH_4)_2 \cdot (SO_4)_2 \cdot 6H_2O$, in 1 M H_2SO_4 was prepared and then standardized against the the above $K_2Cr_2O_7$ solution. To accomplish this, a 20-ml aliquot of the 0.1 M $Fe(NH_4)_2 \cdot (SO_4)_2 \cdot 6H_2O$ was diluted to 50 ml with distilled water. To this diluted solution was added 15 ml of concentrated H_3PO_4 and 8 drops of Na-diphenylamine sulfonate indicator. This mixture was then titrated with the standard $K_2Cr_2O_7$ to the end point. Restandardization was done as the molarity of the solution changed.

A 0.1 M solution of cerium(IV) ammonium sulfate, $Ce(SO_4)_2 \cdot 2(NH_4)_2SO_4 \cdot 2H_2O$, in 1 M H_2SO_4 was prepared. It was allowed to stand at room temperature for several days, filtered through Whatman 41 to remove a small amount of precipitate, and standardized against Fe(II). Standardization was done by adding 50 ml distilled water, 10 ml concentrated H_2SO_4 , and 2 drops of iron(II) orthophenanthroline (ferroin), indicator to 20 ml of the $Ce(SO_4)_2 \cdot 2(NH_4)_2SO_4 \cdot 2H_2O$ and titrating with the standard Fe(II) solution.

A 0.0503-M $SnCl_2 \cdot 2H_2O$ solution in 1 M H_2SO_4 was deaerated with N_2 for 2 h to prevent slow oxidation to Sn(IV). The solution then was standardized potentiometrically with Ce(IV) before use.

Solid NaF, NaCl, NaBr, or KSCN was added to the working solution so there was 1 M of the anion in a total solution of 50 ml. Concentrated HCl was added to yield 1 M or 2 M in 50 ml of the working solution.

PROCEDURE

A 10-ml aliquot of standard Fe(II) followed by 20 ml of 1 M H₂SO₄ were pipetted into a 150-ml beaker. To minimize oxidation by air, nitrogen was bubbled through the solution constantly. Then, a known amount of the anion under study was added and dissolved. The solution was deaerated for about 5 min, and 20 ml of Sn(II) solution were pipetted into the beaker. The platinum indicator and saturated calomel reference electrodes were inserted and the solution titrated with Ce(IV). The potential was recorded as a function of Ce(IV) volume.

RESULTS AND DISCUSSION

EFFECT OF CHLORIDE IONS

When both Fe(II) with Ce(IV) in 1 M HCl and in 1 M H₂SO₄ are titrated and the results plotted (Fig. 4), it is seen that they exhibit large changes of potential in the end-point region. Reaction took place in seconds at room temperature; however, the rate appeared to be somewhat faster in the presence of HCl. The use of 1 M NaCl yielded a curve identical with that of 1 M HCl.

The kinetics and mechanism of the reaction were not studied in detail. However from the study of Harbottle and Dodson of the Tl(I)-Tl(III) exchange

Fig. 4. Curves for titration of 0.0965 M Fe(II) with 0.1163 M Ce(IV) in 1 M H₂SO₄, HCl, NaCl, NaBr, NaF, or KSCN at 23.5°C. The end point is reached at 8.3 ml Ce(IV) for each monovalent anion.

reaction,⁶ chloride was found to have a catalytic effect at high concentrations and a retarding effect at low concentrations.

At low concentrations the thallic ion exists as TlCl_2^+ and possibly as TlCl^{2+} . The TlCl_2^+ has a much slower specific exchange with Tl^+ .

At high concentrations the predominant thallic species are probably TlCl_4^- complexes that exchange with Tl^+ at a much higher rate. Silverman and Dodson⁷ also found that chloride catalyzed the $\text{Fe(II)}-\text{Fe(III)}$ exchange reaction. Evidence from the study by Duke and Bornong of the reaction between Tl(III) and Fe(II) showed that chloride increased the rate to a certain extent.⁸ The mechanism is believed to be

Here, Tl(II) -chloride complexes are formed as intermediates.

Duke and Borchers⁹ found that the rate of reaction between Ce(IV) and Tl(I) increased in the presence of Cl^- and was dependent on its concentration. At low Cl^- concentrations, the reaction remained first order in Ce(IV) . At high concentration, the rate depended on the formation of $\text{Ce(IV)}-\text{Cl}^-$ complexes. In titrating Fe(II) with Ce(IV) in this study, the rate of reaction in the presence of Cl^- appears faster than in SO_4^{2-} . It is likely that the $\text{Ce(IV)}-\text{Cl}^-$ complexes are formed and activate the oxidation-reduction reaction.

In the reaction of Sn(II) with Ce(IV), the difference in rates is more obvious in the presence of Cl^- than in SO_4^{2-} . Although the reaction time was based on visual observation only, it was clear that the reaction proceeded immediately when Ce(IV) was added in the presence of Cl^- . The reaction required one or two more seconds after each Ce(IV) addition in a SO_4^{2-} medium. If the reactions are graphed, both have the same shape, except the curve for 1 M H_2SO_4 is displaced slightly to the left (Fig. 5) because the air may oxidize Sn(II) to Sn(IV) as the solution stands; and therefore, the actual concentration of Sn(II) was slightly less than the original concentration.

The slowness of the Sn(II)-Ce(IV) reaction in H_2SO_4 was explained by Brubaker and Court.¹⁰ They said that the major specie of Ce(IV) was the cerium(IV)trisulfate ion, $\text{Ce}(\text{SO}_4)_3^{2-}$, and that of Sn(II) was the ion-pair SnSO_4 . The rate of reaction would be moderately slow compared to a reaction involving Sn^{2+} and $\text{Ce}(\text{SO}_4)_3^{2-}$, in which charge attraction was greater.

Sn was likely in the form of Sn(III) in the intermediate as $\text{SnCe}(\text{SO}_4)_x^{6-2x}$. This intermediate was also proposed by Welton and Higginson.¹¹

When both Sn(II) and Fe(II) were titrated with Ce(IV) in 1 M H_2SO_4 , the curve obtained was as shown in Fig. 3. The reaction was carried out at two different temperatures, and it was slightly faster at 70° than at

Fig. 5. Curves for the titration of 0.0387 M Sn(II) with 0.1163 M Ce(IV) in 1 M H₂SO₄, HCl, NaCl, NaBr, NaF, or KSCN at 23.5°C. The end point is reached at 13.3 ml Ce(IV).

24°C. In the presence of 2 M HCl, the experimental curve approached the theoretical curve (Fig. 6). The discrepancy that occurred between the theoretical curve and the actual curve in sulfuric acid cannot be explained. It is possible that a complex of $\text{Fe(II)}-\text{SO}_4^{2-}-\text{Sn(II)}$ forms in the presence of H_2SO_4 . As Ce(IV) is added to the solution, the Sn(II) is released slowly from the complex and combined with $\text{Ce(SO}_4)_3^{2-}$ to form the stable intermediate $\text{SnCe(SO}_4)_x^{6-2x}$. The Sn intermediate then combines with another $\text{Ce(SO}_4)_3^{2-}$ to give SnSO_4^{2+} and $\text{Ce(SO}_4)_2^-$, as postulated by Brubaker and Court.¹⁰ The rate of reaction going from $\text{Fe(II)}-\text{SO}_4^{2-}-\text{Sn(II)}$ to $\text{SnCe(SO}_4)_x^{6-2x}$ and to the products will depend on the individual rate constants. If we look at the experimental one-end-point curve, the rate seems to be very slow for the reaction of Sn(II) and Ce(IV) in the presence of Fe(II) in H_2SO_4 , and no obvious reaction was detected between Sn(II) and Ce(IV) within 2 to 5 min. Because Ce(IV) is continuously added to the solution, the oxidation-reduction reaction must continue with Fe(II) . No possible complex interfering with the Fe(II) oxidation appeared to form. Stoichiometrically, the only end point corresponds to the total oxidation of Sn(II) and Fe(II) . This implies that Sn(II) may consume two Ce(IV) in the intermediate states, as in the titration of Sn(II) with Ce(IV) when Fe(II) is absent.

Sn(II) forms relatively stable complexes¹² that increase the rate of reaction in Cl^- solution. In the kinetic study of the $\text{Fe(III)}-\text{Sn(II)}$ reaction, Duke and Pinkerton¹² found that the rate of reaction decreased as Cl^- use decreased. The Cl^- may be strongly bound to Fe^{3+} in the activated complex. Electron transfer takes place between the Fe^{3+} and Cl^- . Duke and Pinkerton proposed that the reaction proceeded by a mechanism in which Cl^- was effectively oxidized to Cl^0 , which existed in

Fig. 6. Curves for the titration of a Sn(II)-Fe(II) mixture with 0.0946 M Ce(IV) in either 2 M HCl or 1 M NaBr at 70°C. The Sn(II) in the mixture is 0.0544 M, and the Fe(II) 0.0965 M. The end point of Sn(II) is reached at 11.5 ml Ce(IV) and that of Fe(II) at 21.3 ml.

solution as Cl_2^- or Cl_3^- . The Cl_2^- or Cl_3^- formed was transferred from a ferric to a stannous ion. In early work by Gorin,¹³ the rate of reaction between Fe(III) and Sn(II) in HClO_4 also was much slower than in Cl^- . He found no evidence for a direct reaction between Fe^{3+} and Sn^{2+} . The failure of the two ions, according to Gorin, can be attributed to the high repulsive forces between these polyvalent positive ions. This suggests that formation of an $\text{Fe(III)}-\text{Cl}^--\text{Sn(II)}$ complex allows the electron transfer to occur and thus speeds up the rate of reaction. On the other hand, Remick¹⁴ similarly pointed out that Ce(IV) and Sn(II) react rapidly because of an electrostatic attraction between the positive Ce^{4+} and the negative SnCl_4^{2-} . In conclusion, there is either a $\text{Fe(II)}-\text{Cl}^--\text{Sn(II)}$ complex or a $\text{Ce(IV)}-\text{SnCl}_4^{2-}$ complex formed in the intermediate state that increases the rate rapidly.

EFFECT OF BROMIDE IONS

The presence of Br^- resulted in the rapid oxidation of both Fe(II) and Sn(II) by Ce(IV) at room temperature (Figs. 4, 5). This suggests the catalytic effect of Br^- is greater than Cl^- . The kinetic study of King and Pandow¹⁵ is consistent with the existence of the two activated complexes $\text{Ce(SO}_4)_2\text{Br}_2^{2-}$ and $\text{Ce(SO}_4)_2\text{Br}^-$, which are involved in the electron transfer reaction. In an acid medium, Ce(IV) oxidizes Br^- to free Br atoms, which then combine with Br^- to form Br_2^- in solution. In addition to complexing with Ce(IV) , Br^- also forms stable species with Sn(II) .¹² The $\text{Sn(II)}-\text{Br}^-$ complex is believed to be more active than the corresponding Cl^- complex. Thus, the rate of reaction should be faster in a

Br^- than in a Cl^- solution; experimentally this was the case. The reaction was instantaneous when Ce(IV) was added. Another study¹⁶ on the $\text{Ce(III)}-\text{Ce(IV)}$ reaction proved that the reaction to the higher oxidation state was favored in the presence of Br^- . In the presence of both Sn(II) and Fe(II) in Br^- , the titration curve looked the same as with Cl^- , except the end point was less sharp (see Fig. 6).

EFFECT OF FLUORIDE IONS

In the presence of F^- , the titration of $\text{Sn(II)}-\text{Fe(II)}$ with Ce(IV) resulted in an experimental curve that resembled the titration in the presence of 1 M H_2SO_4 (Fig. 3). There was only one end point, and that corresponded to the total amount of Sn(II) and Fe(II) in solution. At room temperature no reaction was discernable. As the temperature was increased to 70 to 75°C, reaction proceeded slowly (see Fig. 7). At least 2 to 3 min were required for the reaction to be complete and before the next aliquot of Ce(IV) could be added. It appears that a complex or salt may form between the $\text{Sn(II)}-\text{Ce(IV)}$ and inhibit the oxidation-reduction reaction. Fluoride did not seem to inhibit the reaction between Ce(IV) and Fe(II) . Michaille and Kikindai¹⁷ reported that F^- acts as a bridging ligand for metals; FeF^{2+} and FeF_2^+ complexes were formed at low and high F^- concentrations, respectively. They concluded that the presence of F^- catalyzed the $\text{Ce(IV)}-\text{Fe(II)}$ reaction as follows:

Fig. 7. Curves for the titration of a Sn(II)-Fe(II) mixture with 0.0979 M Ce(IV) in the presence of 1 M F^- at 70 to 75°C and at 23.5°C. The Sn(II) in the mixture is 0.0470 M and the Fe(II) is 0.0965 M. A curve for the titration of Sn(II) with Ce(IV) in 2 M HCl at 23.5°C is given for comparison. The end point of the comparison titration is reached with 19.2 ml Ce(IV). The end point of the Sn(II)-Fe(II) mixture is reached at 29.1 ml Ce(IV).

The Fe^{3+} formed reacted with F^- rapidly and thus drove the first reaction to the right. Experimentally, we found that the rate of reaction in the presence of F^- at room temperature is not as fast as in the presence of Br^- or Cl^- , but the titration curves are similar in shape (see Fig. 4).

As Ce(IV) was added to a solution containing Sn(II) alone in the presence of F^- , a white precipitate settled to the bottom of the beaker. This white solid was suspected to be CeF_4 . The potential did not change as the solid formed; there was no indication of oxidation-reduction reaction (See Fig. 5).

EFFECT OF THIOCYANATE IONS

In the presence of SCN^- , the oxidation-reduction reaction between Sn(II) and Ce(IV) was fast. The curve was about as half as sharp as in Cl^- at room temperature (see Fig. 5), but the rate of reaction was about the same. In addition, SCN^- appears to exert a catalytic effect on the $\text{Sn(II)}-\text{Ce(IV)}$ reaction. In the reaction between Fe(II) and Ce(IV) , the potential change at the end point was not well defined (see Fig. 4). The rate of reaction was slower than that for the $\text{Sn(II)}-\text{Ce(IV)}$ titration.

A two-end-point curve identical to the combination of the individual curves for the titration of Sn(II) and of Fe(II) with Ce(IV) was obtained for the titration of Sn(II) and Fe(II) in the presence of SCN^- . As the temperature rose, the rate of reaction did not increase, but the first end point for the Sn(II) disappeared (see Fig. 8). The only end point here does not correspond to the total oxidation of Sn(II) and Fe(II) either. It is possible that the activated complex in the intermediate state was destroyed, because the SCN^- in acid solution usually polymerizes to form SCN_3^- ; the

Fig. 8. Curves for the titration of a Sn(II)-Fe(II) mixture with 0.0946 M Ce(IV) at 45°C and 70 to 73°C in 1 M KSCN. The end points of the mixture at 45°C are reached at 11.3 ml Ce(IV) and 21.5 ml Ce(IV), respectively, for Sn(II) and Fe(II). At 70 to 73°C, the end point is at 18.2 ml.

extent of SCN_3^- formation falls off as the temperature rises.¹⁸ If this is the case, SCN_3^- may be the specie that forms complexes with Sn(II) and Ce(IV) and activates the reaction at room temperature. As the temperature rises, SCN_3^- disappears and its catalytic effect on the reaction is lost. In the oxidation of SCN^- by Cr(IV) as studied by Muirhead and Haight,¹⁹ activated complexes as O_3CrSCN^- and $\text{O}_2\text{Cr(SCN)}_2$ were postulated in the intermediate and activated state.

CONCLUSION

The presence of Cl^- , Br^- , F^- , and SCN^- may either catalyze or retard the oxidation of Sn(II)-Fe(II) mixtures with Ce(IV) . In the presence of Cl^- and Br^- , temperature has little effect on the reactions; in a SCN^- medium, on the other hand, temperature plays an important role. If the temperature is raised, the sharpness of the end point of the Fe(II)-Ce(IV) reaction in the presence of F^- is more pronounced. The rates of reactions correlate with the ease of oxidation of the particular halide used. The rates appear to decrease in the order of Br^- , Cl^- , SCN^- , and F^- . All of these reactions seem to take place between complexed forms of the metal ions. In most of the cases studied, complex formation increases the rate of reaction, except in the case of SO_4^{2-} and F^- . The actual shape of the titration curve may depend on the relative formation constant of the specie involved.

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