THE ELECTROLYTIC BEHAVIOR OF IRON IN A BUFFERED NICKEL SULFATE SOLUTION

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THE ELECTROLYTIC BEHAVIOR OF IRON IN A BUFFERED NICKEL SULFATE SOLUTION

By

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INTRODUCTION

This investigation was carried out to examine the electrochemical behavior of ferrous and ferric ions in a buffered nickel sulfate solution.

Iron is one of the more common impurities found in nickel solutions, and consequently there have been previous studies made on the effect of iron in such solutions. W. D. Gordon has compiled a number of references to these studies (2). H. J. Wiesner found that ferrous iron was fairly soluble even at a pH as high as 6.0 (electrometric), but the solubility of ferric iron decreased considerably at a pH of 2.8 and 3.0 and at a pH of 4.0 or higher it was insoluble (8). Ewing, Brouwer and Werner have completed a study of the effects and removal of iron with respect to several types of nickel solutions from which nickel is electrodeposited (1).

Throughout this investigation a buffered nickel sulfate-chloride solution wasused at pH 2.2. A low pH was necessitated by the fact that at higher pH's ferrous ions are oxidized to the ferric state by aid. Furthermore, the solubility of ferric ions is decreased as the pH is increased (8). Tests were made to assure that no chemical oxidation of the ferrous or reduction of ferric ions took place in the nickel solution.

PROCEDURE

Preparation of the Nickel Stock Solution

The composition of the nickel stock solution which was used throughout the experimental work is as follows:

$Ni\ SO_4.7H_2O$	300 g./l.	40 oz./gal.
$Ni\ Cl_2.6H_2O$	60 g./l.	8 oz./gal.
Total Ni	82 g./l/	11 oz./gal.
pH	2.2	
Temperature	40°C	140°F
Current Density	4.3 amp./dm^2.	40 a.s.f.

The anodes were electrolytic nickel. Except for the case where a porous cup was used all the runs were made with one liter of stock solution. The pH was measured throughout this work with a Beckman Laboratory Model G pH meter, which was checked with 0.05 M potassium acid phtholate, pH 3.97.

Purification of the Stock Solution

Iron, as an impurity, was removed by raising the pH of the solution to 5.3 - 5.5 with nickelous carbonate, bubbling purified air through for twenty-four hours, and then filtering. The iron in the precipitate was in the form of ferric hydroxide. The pH of the solution was then lowered to 2.2 with c.p. grade sulfuric acid. The removal of iron was deemed necessary so that when a run was started the iron could be added as the ferrous or ferric salt without having a mixture of the two.

Preparation of the Cathode

A strip of sheet steel, 5.08 cm. by 9.24 cm. (2 in. by 3.6 in.), was used as the cathode. It was first cleaned with carbon tetrachloride and then electrocleaned for five to ten minutes in an alkaline cleaner of the following composition:

Sodium hydroxide	21	g./l.	2.8	oz/gal.
Sodium metasilicate	15	g./l.	2.0	oz./gal.
Trisodium phosphate	18	g./l.	2.4	oz./gal.
Sodium carbonate	6	g./l	0.8	oz./gal.
Sodium acetate	7	g./l.	0.9	oz./gal.
Sodium lauryl alcohol sulfate	0.05	g./l.	0.0067	oz./gal.
Temperature	90°C		194°F	
Current Density	10.77	amp./dm^2.	100	a.s.f.

The electrocleaner was made up fresh as needed and a steel plate was used as the anode.

After electrocleaning the steel cathode was immersed in a 20% hydrochloric acid solution for one minute, rinsed with iron-free, redistilled water, connected to the negative line from the switchboard with the e.m.f. applied, and placed in the solution midway between the two nickel anodes.

It was important to have the electrical potential applied when the cathode was immersed in the solution so that deposition of the nickel would take place instantaneously and prevent any of the steel from dissolving into the solution. Anodes were placed at each end of the solution with the cathode equidistant from each to avoid having any low current density areas on the cathode.

Analytical Methods

Total Iron. - The method of analysis for small amounts of iron in nickel solutions was devised by E. J. Serfass, et al. (7).

The iron from a 1 ml. sample of the nickel solution was complexed with cupferron, extracted from the nickel solution by amyl acetate, and then in turn extracted from the amyl acetate with nitric acid. After reducing the iron in the nitric acid to the ferrous state and adjusting the pH, o-phenanthroline was added to form a complex iron ion, which is a reddish color. A sample of this solution was placed in a Klett-Sommerson colorimeter with green filter No. 54 and the colorimeter reading was recorded.

This same procedure was repeated without the addition of the sample of the nickel solution to obtain a blank reading. This blank reading was then subtracted from the sample reading.

A calibration curve, Fig. 1, was obtained by analyzing nickel solution samples with known amounts of iron in them and plotting the iron concentration versus the colorimeter reading.

Ferrous Iron. - Two ml. of concentrated sulfuric acid (c.p. grade) were pipetted into a 100 ml. beaker and diluted with approximately the same amount of water (iron-free, redistilled). Five ml. of the solution to be analyzed were then pipetted into the beaker and more redistilled water was added to bring the volume up to 60 - 70 ml.

This solution was then titrated potentiometrically with 0.001 N potassium dichromate (analytical) using a Beckman Laboratory Model G pH meter, with platinum and calomel electrodes, to record the e.m.f. values (3). The solution in the beaker was stirred during the titration.

The e.m.f. values recorded after the addition of each increment of potassium dichromate were plotted versus the volume in milliliters of dichromate. The point on the curve at which the rate of change of the slope was zero was the end point, and the corresponding volume of dichromate solution was recorded.

To avoid repeated calculations, a graph, Fig 2, of milligrams of ferrous iron per liter of nickel solution versus the volume in milliliters of 0.001 N potassium dichromate was drawn. One ml. of the dichromate solution is equivalent to 0.056 mg. of ferrous iron (6). Although a 5 ml. sample was analyzed, it was desired to express the results on a liter basis. Multiplying 0.056 by 1000/5 a conversion factor of 11.2 was obtained. That is, for every milliliter of 0.001 N potassium dichromate used to reach the end point there were 11.2 mg. of ferrous iron per liter of nickel solution.

Standard solutions with various concentrations of ferrous ions were made up and analysed by this method. The analysis was found to be accurate to within ±0.5 mg./liter.

Ferric Iron. - The concentration of ferric iron was obtained by the difference between the total and ferrous iron analyses.

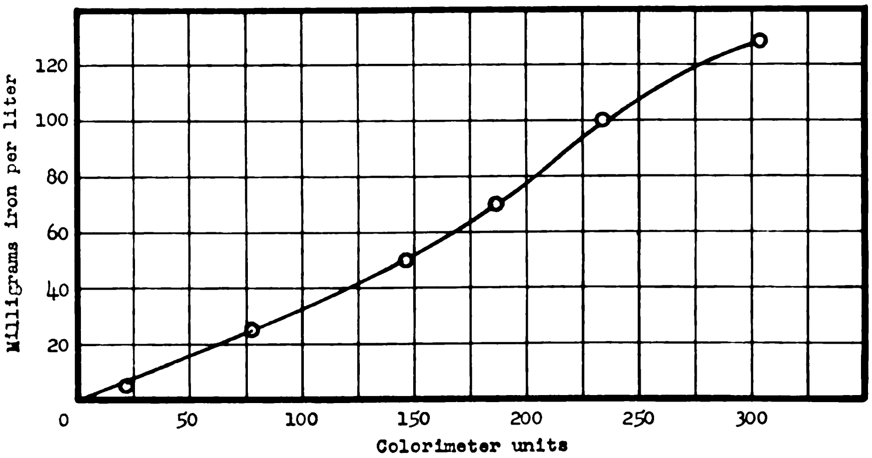

Figure 1. Calibration curve for the determination of iron in nickel solutions. (1.0 ml. sample.)

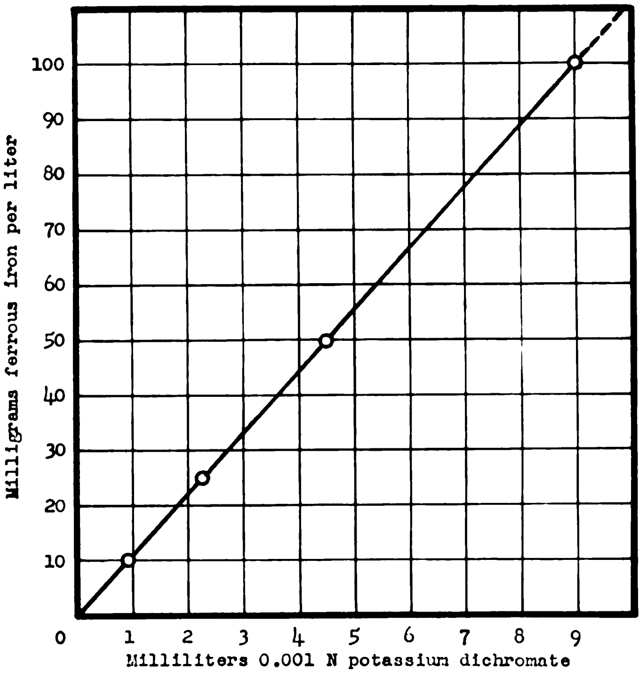

Fig. 2. Calibration curve for the determination of ferrous iron in the nickel solution. (5.0 ml. sample.)

RESULTS

Stability of Ferrous and Ferric Ions in the Nickel Stock Solution

To be sure that there would be no chemical oxidation of ferrous ions or reduction of ferric ions in the nickel solution two tests were made.

First, 100 mg. of ferrous iron, as $FeSO_4.7H_2O$, were added to a liter of the purified stock solution. The solution was analyzed for total and ferrous iron, then allowed to stand for twenty-four hours at 40°C with mechanical agitation as in an actual run except that there was no anode or cathode and no current was flowing. At the end of the prescribed time a sample of the solution was analyzed for total and ferrous iron again. The results from the two sets of analyses were the same and in neither case was there any ferric iron.

A similar test was set up to determine the stability of the ferric iron, added as $Fe_2(SO_4)_3.XH_2O$ to the stock solution. As in the first test, the results of the two sets of analyses were the same, showing that no reduction of the ferric ions took place.

The results of these two tests proved that there was no detectable chemical oxidation of ferrous ions or reduction of ferric ions in the nickel solution. The fact that ferric ions were not reduced is logical since the test was carried out in an oxidizing atmosphere. In the case of the ferrous ions, however, there might be a tendency to expect oxygen in the air to cause oxidation, and such is the case at higher pH's. It should be noted that if a solution of ferrous sulfate be made sufficiently acid it can be, and is, used as a titrating agent which is so slowly oxidized that it need be restandardized only every few days.

Behavior of Ferrous Ions in the Nickel Solution

About 100 mg. of ferrous iron were added to one liter of the purified stock solution and allowed to dissolve. After a sample of the solution had been removed for analysis the current was passed and a properly prepared cathode was immersed in the solution. Thereafter, a sample of nickel solution was withdrawn from the solution every three hours and analyzed for total and ferrous iron. When the concentration of the total iron was below 10 mg. per liter the current was discontinued and the run ended.

Table I shows the data obtained from this run. The concentration of ferrous ions decreased at a faster rate than the total iron, indicating that some ferrous ions were oxidized to the ferric state.

The total iron depletion curve obtained from this run was compared in fig. 3a to the depletion curve obtained by Ewing, et al. from a nickel solution containing ferrous sulfate (1). The curves were nearly identical.

TABLE I

ELECTRO-CHEMICAL REACTIONS OF FERROUS IONS IN THE NICKEL SOLUTION

Time hrs.	Amp. Hrs. per Liter	Fe, total mg./l.	Fe^{+2} mg./l.	Fe^{+3} mg./l.
0.00	0	103	103	0
3.00	12	48	45	3
6.00	24	25	19	6
9.00	36	15	6	9
12.00	48	10	2	8
13.75	55	6	1	5

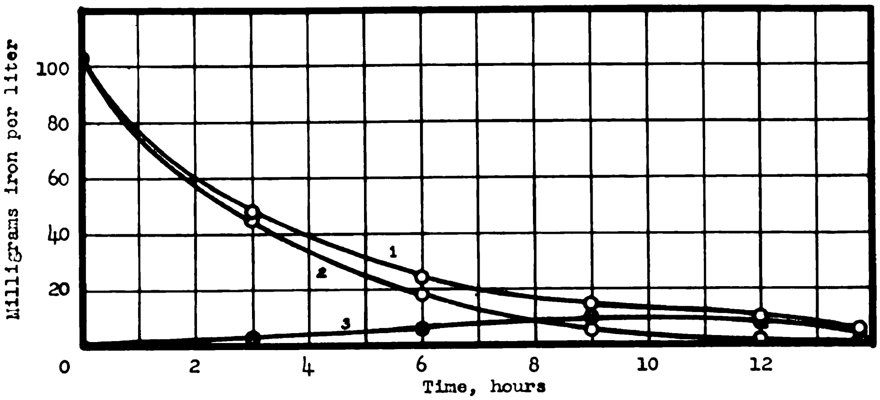

Figure 3. The electrochemical reactions of ferrous iron in the nickel solution. Current density of 4.3 amp./dm^2. pH 2.2 and at 40°C. (1) total iron, (2) ferrous iron, and (3) ferric iron. ○ - experimental; ● - calculated.

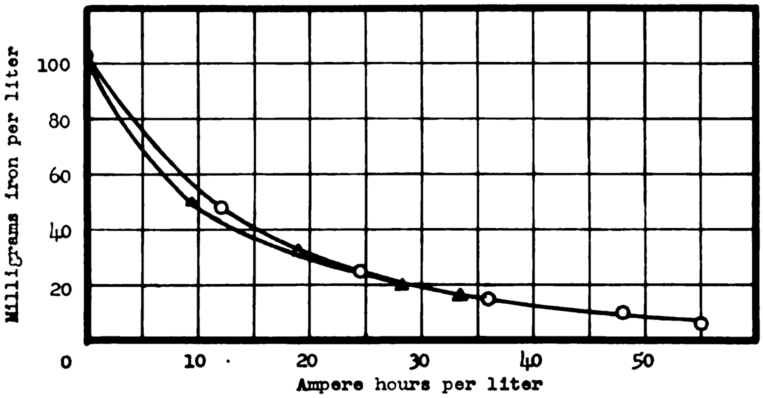

Figure 3a. A comparison of the iron depletion curve from Figure 3 with that obtained by Ewing, et al. (1). ○ - values obtained in this investigation; △ - values obtained by Ewing, et al.

Behavior of Ferric Ions in the Nickel Solution

When work was being initiated in this phase of the investigation the ferric iron was sometimes added to the solution several hours ahead of the time that the current was passed and the cathode put in place. In the analysis of the sample of the solution which was taken just before the run was started it was noted that some of the ferric ions had already been reduced to the ferrous state. Since the only difference between this solution and the solution used in the stability test previously mentioned was that the nickel anodes were immersed in this solution, it appeared that there was an electrochemical reaction between ferric ions and metallic nickel.

To confirm this possibility a purified nickel solution with ferric iron added was allowed to stand with nickel anodes, which were connected externally by a copper wire, but no external e.m.f. was applied. During the run the temperature of the solution was 40°C and agitation was used. Analyses for ferrous and total iron were made on samples taken every three hours, and the results are shown in Table II.

The results proved that there was a reaction between metallic nickel and ferric ions, as would be expected from the following equations:

$$\begin{array}{lllll}
1/2\ \mathrm{Ni^{o}} - e & = & 1/2\ \mathrm{Ni^{+2}} & E^{o} = & +\ 0.250\ \mathrm{v.} \\
\mathrm{Fe^{+3}} + e & = & \mathrm{Fe^{+2}} & E^{o} = & +\ 0.771\ \mathrm{v.} \\
\hline
1/2\ \mathrm{Ni^{o}} + \mathrm{Fe^{+3}} & = & 1/2\ \mathrm{Ni^{+2}} + \mathrm{Fe^{+2}} & E^{o} = & +\ 1.021\ \mathrm{v}
\end{array}$$

The E^{o} values are from Oxidation Potentials and are for acid solutions (5). Since the sign of the E^{o} value for the total reaction is positive the reaction will proceed spontaneously as written. Furthermore, the equilibrium constant, K, is equal to the antilog of (E^{o}) (nF)/(2.3 RT) or, 1.021/0.059, which is equal to 1.93×10^{17}. This means that for all practical purposes the reaction proceeds to completion.

The above values for E and K pertain to an aqueous acid solution, and since in this investigation the reaction was carried out in an almost saturated nickel salt solution the activities of the nickel, ferrous and ferric ions were changed and it is obvious that the e.m.f. and K values were different, but the sign of the e.m.f. value for the reaction remained the same so that the reaction proceeded spontaneously. Also, the reaction went to completion after 9 to 12 hours.

To determine the effect of the above reaction when current was flowing through the nickel solution ferric iron was added and dissolved in the purified stock solution just before the current was passed and the cathode put in place. Results are shown in Table III. From this it can be seen that the ferric ions were reduced rapidly to the ferrous state.

TABLE II

ELECTROLYTIC REACTION OF FERRIC IONS AND NICKEL ANODES IN A NICKEL SOLUTION WITH NO EXTERNAL E. M. F. APPLIED

Time	Fe, total mg./l.	Fe^{+2} mg./l/	Fe^{+3} mg./l.
0 min.	63	0	63
10 min.	63	3	60
30 min	63	14	49
1 hr.	63	18	45
3 hr.	63	49	14
6 hr.	63	59	4
9 hr.	63	62	1
12 hr.	63	63	0

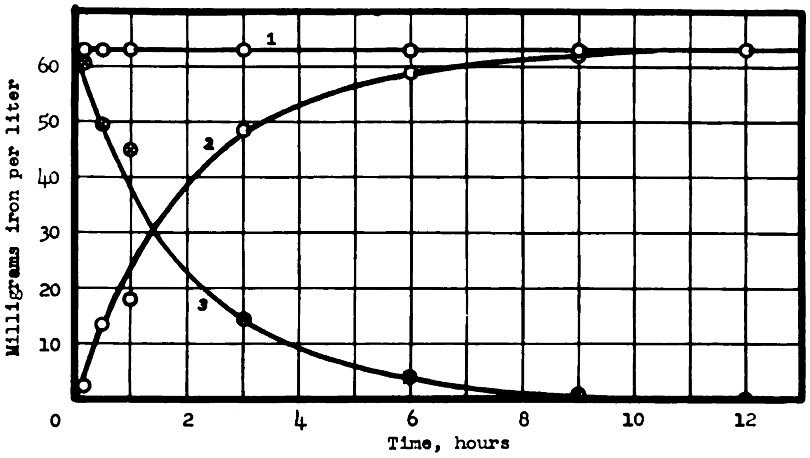

Figure 4. The electrolytic reaction of ferric ions and nickel anodes in the nickel solution with no external e.m.f. applied. pH 2.2 and at 40°C. (1) total iron, (2) ferrous iron, and (3) ferric iron. O - experimental; ● - calculated.

TABLE III

ELECTRO-CHEMICAL REACTIONS OF FERRIC IONS IN A NICKEL SOLUTION

Time	Fe, total mg./l.	Fe^{+2} mg./l.	Fe^{+3} mg./l.
0 min.	70	6	64
15 min	65	22	43
1 hr.	50	23	27
3 hr.	28	21	7
6 hr.	9	8	1
9 hr.	3	3	0
12 hr.	2	2	0

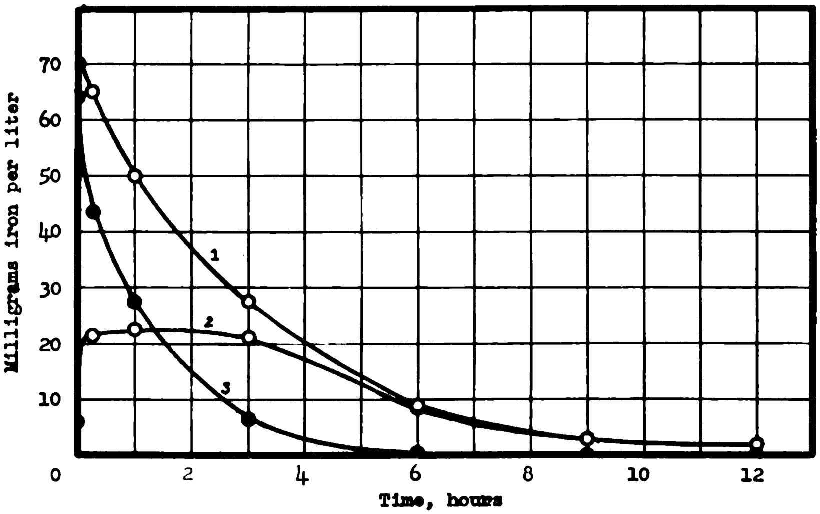

Figure 5. The electrochemical reactions of ferric ions in a nickel solution. Current density of 4.3 amps./dm^2. pH 2.2 and at [illegible]. (1) total iron, (2) ferrous iron, and (3) ferric iron. ○ - experimental; ● - calculated.

Behavior of a Mixture of Ferrous and Ferric Ions in the Nickel Solution

A mixture of approximately equal amounts of ferric and ferrous iron was added to the purified stock solution. Samples were taken every two hours in this run and the results are shown in Table IV. The concentration of the ferrous iron dropped much more slowly than that of the ferric iron, since the ferric iron was continually being reduced to the ferrous state at the nickel electrodes.

Behavior of Ferric Ions When Anolyte and Catholyte are Separated

A porous cup was used to separate the anolyte and catholyte. Ferric iron was added to the catholyte, with results shown in Table V.

There was some ferric iron in the bath which had not been removed when the bath was purified. Ferric iron in the anolyte was reduced to the ferrous state, while very little of the ferric iron in the catholyte was reduced, since it did not come in contact with the nickel anodes.

Agitation was used in the catholyte, but because of lack of space it was not used in the anolyte. Consequently, the ions in the anolyte were not distributed evenly and when samples were withdrawn for analysis they did not necessarily contain a representative amount of iron ions. This was shown by the inconsistent results.

TABLE IV

REACTIONS OF A MIXTURE OF FERROUS AND FERRIC IONS IN A NICKEL SOLUTION

Time hrs.	Fe, total mg./l.	Fe^{-2} mg./l.	Fe^{-3} mg./l.
0	110	51	59
2	79	48	31
4	54	39	15
6	36	28	8
8	28	20	8
10	20	14	6
12	13	7	6

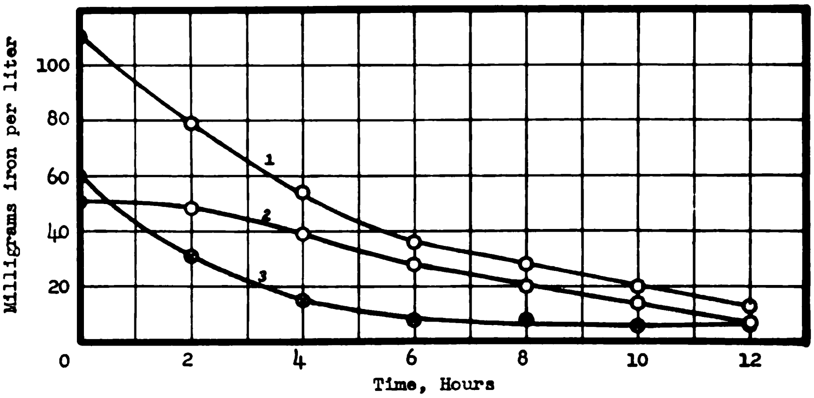

Figure 6. The electrochemical reactions of ferric and ferrous ions in the nickel solution. Current density of 4.3 amps./dm^2. pH 2.2 and at 40°C. (1) total iron, (2) ferrous iron, and (3) ferric iron. ○ - experimental; ● - calculated.

TABLE V

REACTIONS OF FERRIC IONS IN A NICKEL SOLUTION WHEN ANOLYTE AND CATHOLYTE ARE SEPARATED BY A POROUS CUP

Time hrs.	Fe, total mg./l.	Fe^{+2} mg./l.	Fe^{+3} mg./l.
	Anolyte		
0	8	1	7
3	7	6	1
6	9	8	1
9	10	10	0
	Catholyte		
0	49	0	49
3	33	3	30
6	23	4	19
9	16	4	12

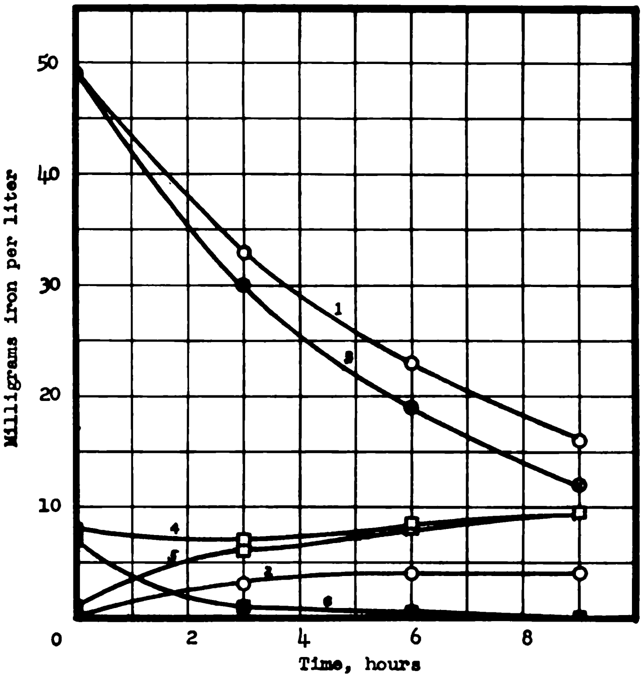

Figure 7. The electrolytic reactions of ferric ions in the nickel solution when anolyte and catholyte are separated by a porous cup. Current density of 4.3 amps./dm^2. pH 2.2 and at 40°C. (1), (4) total iron, (2), (5) ferrous iron, (3), (6) ferric iron. ○, ☐ - experimental; ●, ■ - calculated. ○ - catholyte; ☐ - anolyte.

CONCLUSIONS

In the first run where iron was added as the ferrous salt there was a small amount of ferric ions formed. This was due to ferrous ions being oxidized at the anode and then swept away before they could be reduced again to the ferrous state by the nickel.

Ferric ions in contact with nickel electrodes immersed in the nickel solution while no current was passing were reduced to the ferrous state. This proved that there was galvanic action between metallic nickel and ferric ions. By passing current through the solution of ferric ions the reduction of the ferric ions was accelerated considerably.

By adding a mixture of ferrous and ferric iron to the nickel solution it was possible to compare the behavior of the two forms. The concentration of the ferrous ions decreased slowly, while the concantration of the ferric ions dropped at a rapid rate. Both oxidation states were being electro-deposited at the cathode, but the ferric ions were being reduced to ferrous ions at the nickel anode, thereby depleting the supply of ferric ions and replenishing the ferrous ions.

The use of a porous cup to separate the anolyte and catholyte allowed the reactions of ferric ions in the catholyte to be observed without the interference of the ferric ion nickel reaction. Some of the ferric ions, instead of being reduced completely to the metallic state, were reduced to the ferrous state and then swept away from the cathode. Most of the ferric ions were, however, reduced directly to the metallic state and electro-deposited on the cathode.

The most important result of this investigation was the observation of the ferric ion - nickel galvanic action. There was some ferrous iron oxidized at the anode to ferric iron and the reverse process took place at the cathode, but these reactions were minor as compared to the galvanic cell reaction. After a nickel solution had been electrolyzed for a few hours there was little or no ferric iron present.

It had been hoped to determine whether the ferric ion-nickel reaction were complete or if there were always a few ferric ions present as long as there was iron in the solution. However, it was found that if the concentration of total iron were less than ten milligrams per liter the total iron analysis was not accurate. In some cases there appeared to be more ferric iron than ferrous iron, while in other cases the ferrous iron analysis gave a concentration slightly higher than the total iron analysis. This situation is obviously impossible.

A clue to the answer may be found in the fact that ferric iron was precipitated easily by cupferron, while it was somewhat more difficult to precipitate ferrous iron. It is possible that there was always enough unprecipitated ferrous iron to give a total iron concentration a few milligrams per liter lower than the actual concentration. A study of the total iron analysis at concentrations less than ten milligrams per liter using ferrous iron would be enlightening.

It should be kept in mind that the results of this investigation pertain only to a pH 2.2 nickel solution. At the higher pH's (above 3.0) there is a tendency for the ferrous ions to be oxidized by air, and the ferric ion concentration becomes limited.

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