THE pH AND THE CONDITIONS FOR PRECIPITATION OF SOME METALLIC HYDROXIDES IN CONCENTRATED BUFFERED NICKEL SULFATE SOLUTIONS

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THE pH AND THE CONDITIONS FOR PRECIPITATION OF SOME METALLIC HYDROXIDES IN CONCENTRATED BUFFERED NICKEL SULFATE SOLUTIONS

BY

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A THESIS

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THE pH AND THE CONDITIONS FOR PRECIPITATION OF SOME METALLIC HYDROXIDES IN CONCENTRATED BUFFERED NICKEL SULFATE SOLUTIONS

A study has been made of the factors effecting the formation of the hydroxides of aluminum, cadmium, trivalent and hexavalent chromium, cupric copper, ferrous and ferric iron, and zinc in a strong solution of buffered nickel sulfate with the object of determining the pH values at which the hydroxides began to precipitate, and at which they were completely removed from solution.

Various pH studies of precipitation of metallic hydroxides have been reported in the literature but the only previous extensive investigations similar to the present one are those of Hildebrand (1) and of Britton (2).

Atkins (3) found colorimetrically that ferrous hydroxide precipitated from ferrous sulfate solutions between pH 5.1 and 7.6, while Patton and Mains (4) found the range to be more specifically between pH 5.5 and 6.0. Pickering (5) observed that complete precipitation of ferrous iron had occurred at the pH where the solution was alkaline to phenophthalein.

Miller (6) investigated the composition of the precipitates formed from alum solutions upon addition of alkali. A pH of 5.5 (colorimetric) was given as the value at which the precipitation of aluminum approaches completion. Blum (7) studied the precipitation of aluminum as oxide and from observations made with an hydrogen electrode and suitable indicators, for example, methyl red, found that the precipitation of aluminum hydroxide from aluminum chloride solutions was complete when $[H^+]$ was $10^{-6.5}$ to $10^{-7.5}$. Joffe and McLean (8) found that in the presence of sulfate-ions the aluminum from a 0.0075 M. solution was transformed completely into the gel at pH 4.7 to 4.8. However, in the presence of chloride-ion complete aluminum precipitation occurred at pH 5.4. Prideaux and Henness (9) in studying the precipitation of hydrous aluminum oxide reported visible precipitation from the sulfate solution at about pH 4, but not until about pH 6.5 in chloride solution.

While there is little agreement as to the exact pH values at which aluminum hydroxide starts to precipitate or at which it is removed from solution, the above investigations are in agreement that precipitation from sulfate solution occurs at a lower pH than from the chloride. This supports the general rule that the bivalent sulfate ion has a greater coagulating effect upon a positive colloid than does the monovalent chloride ion.

Hildebrand and Bowers (10) found that zinc was removed at a pH of about 6.3. Kolthoff and Kameda (11) in their studies of the hydrolysis of zinc sulfate titrated various molar concentrations of zinc with sodium hydroxide. They obtained pH values of 6.17 and 6.49 at which zinc starts to precipitate from 0.05M and 0.01M zinc sulfate solution, respectively. Britton (2) reported a pH value of 5.2 for the first appearance of precipitation from a 0.025M solution.

The pH values given by Britton (2) (12) for the precipitation of cadmium, copper and chromium were the only ones found in the literature.

The effect of certain metallic impurities upon cathode effeciency, type of deposit, etc., in nickel plating baths has received considerable attention (13) (14) (15) (16); yet definite information regarding the pH values at which these impurities may be removed is limited.

Thompson and Thomas (24) suggested the following precedure for the removal of zinc from nickel baths; the bath is neutralized with nickel hydroxide or carbonate to pH 6.7, allowed to settle, then filtered, reacidified to pH 5.8, and electrolyzed at high current density for some hours. Blum and Hogaboom (25) discussed the effects of some metallic impurities and the pH's at which they may be removed. Evans (17) described a method of removing chromic acid from nickel plating solutions. In a recent publication, Pinner, Soderberg and Baker (18) have considered methods of removing impurities from nickel baths.

Experimental

Materials and Apparatus: - A stock solution of nickel sulfate was prepared by dissolving 2270 g. of Baker's Analyzed C. P. $NiSO_4 \cdot 6H_2O$ in 8 liters of distilled water. Inasmuch as both ammonium hydroxide and sodium hydroxide were to be used in the work to follow, this solution was divided into two portions; one was treated with ammonium hydroxide, the other with sodium hydroxide solution, approximately 0.5N, until the pH was 6.7 to 6.8. The solutions were heated for one hour at 90° C, allowed to stand twenty-fours, then filtered.

The metals were added in the form of their sulfates, except in the case of hexavalent chromium to give a metal content of approximately 0.5 g/l. Baker's Analyzed Chemicals were used for aluminum, cadmium, iron and nickel sulfates. The $Cr_2(SO_4)_3 \cdot 5H_2O$ and CrO_3 were C. P. grades. The sulfates of copper and zinc were prepared from the pure metals. Boric acid, (Baker's C. P. grade) recrystallized from water was used as the buffer. Each liter of solution contained 37.5 gms of boric acid.

Analyses for cadmium, copper, and zinc were made employing a Leeds and Northrup Electro-Chemograph.

Measurements of pH were made with a laboratory model (G) Beckman pH meter.

Method of Analysis: - For the polarographic determination of cadmium and copper, buffered nickel sulfate solutions served as the supporting electrolyte, but since the zinc and nickel waves come at approximately the same half-wave potential in the sulfate solution the zinc was first separated from the nickel by the method of Fales and Ware (19), the sulfide was dissolved in cold 1:1 hydrochloric acid, evaporated to dryness, taken up in 25 ml. of a solution, 0.1N ammonium acetate and 0.025N potassium thiocyanate, as suggested by Reed and Cummings (20).

Aluminum was determined by use of aurin tricarboxylic acid (20).

Chromium and iron were determined volumetrically using 0.02 and 0.01N potassium dichromate with diphenylamine sodium sulfonate as indicator. Trivalent chromium was oxidized to the hexavalent state with ammonium persulfate, then the above mentioned procedure followed.

Ferric iron was precipitated from the nickel sulfate solution by use of an excess of ammonium hydroxide, filtered, dissolved in warm 1:1 hydrochloric acid and the Zimmerman-Reinhardt method of analysis used. Ferrous iron was first oxidized to the ferric state with hydrogen peroxide, then the hydroxide precipitated with ammonium hydroxide.

Experimental Procedure: - Five hundred ml. of the purified nickel sulfate solution was acidified to a pH of 2.0 - 3.0 by addition of sulfuric acid solution. The weighed quantity of metallic salt was dissolved in the solution, then three 25 ml. samples were withdrawn for analysis. Ammonium hydroxide (1:4) was added dropwise while the solution was being stirred vigorously by means of a motor driven stirrer. A period of five minutes of stirring was allowed after the NH_4OH additions before sampling. At 0.1 - 0.2 pH intervals two 25 ml. samples were withdrawn and pipetted into 7" x 5/8" test tubes. One series of samples was allowed to stand at room temperature (23° - 27° C) for 24 hours with occasional shaking, while the other was heated in a boiling water bath for three hours. The test tubes in this second series were fitted with air condensers in order to minimize evaporation. These were made by almost closing off in a flame one end of a six inch piece of seven mm. tubing.

At the end of these periods observations were made as to the condition of the solutions, the samples filtered through No. 40 or 42 Whatman paper when the nature of the precipitate permitted, and pH measurements again made. Analyses were run on the solutions in the manner described earlier in the thesis.

The above procedure was repeated using 0.2N sodium hydroxide to raise the pH. Each metal was treated in the manner previously described with the exception of ferrous iron in which case it was necessary to keep an inert atmosphere above the solution and samples at all times during the run in order to prevent oxidation.

Nickel carbonate and calcium hydroxide were added to a buffered nickel sulfate solution in order to determine the maximum pH values that could be obtained when the samples were thoroughly agitated at 25° C and when heated for three hours at 100° C.

In the course of this investigation the question of obtaining the equilibrium pH values arose, since during precipitation hydroxyl ions were being removed from solution, thus changing the pH. This precipitation reaction sometimes required considerable time. Accordingly, it was decided that after each addition of base five minutes be allowed for stirring before the samples were collected and their pH determined. The pH's of these samples were again measured after standing 24 hours at room temperature (22° - 28° C) in order to obtain the equilibrium values. Measurements of pH were also made after the second series was heated three hours at 100° C. These data are recorded in the tables.

From a practical standpoint the pH value to which the solution must be raised in order to remove a certain amount of impurity would be most useful. The equilibrium pH values do not always give this information since they are usually from 0.2 - 0.5 pH units lower than the initial values. Thus, in plotting the graphs the initial values were recorded.

Data and Discussion of Results

Buffered Nickel Sulfate Solution Treated with Ammonium or Sodium Hydroxide for Three Hours at 100° C and 24 Hours at Room Temperature (23° - 26° C): - In figures one to four inclusive a single set of conditions is represented on each graph. Each metal which has been studied under a given set of conditions is represented by a curve on the appropriate graph.

From figures one to four inclusive the pH range in which a given metallic hydroxide will precipitate is shown and one can compare directly that range with the range in which the other metals studied come out of solution. By comparing figures one and two and figures three and four it is shown that more rapid precipitation is favored at a lower pH in the heated solutions. In the case of the ferric iron curves in figures one and two it is shown that precipitation of ferric hydroxide begins at a lower pH in the hot solutions than in the cold ones. It may further be observed, however, that at pH 3.5 about the same amount of iron has been removed in both cases. Of course, the case of heating considerable time is saved.

Similar comparisons may be made for the other metals shown in figures one through four.

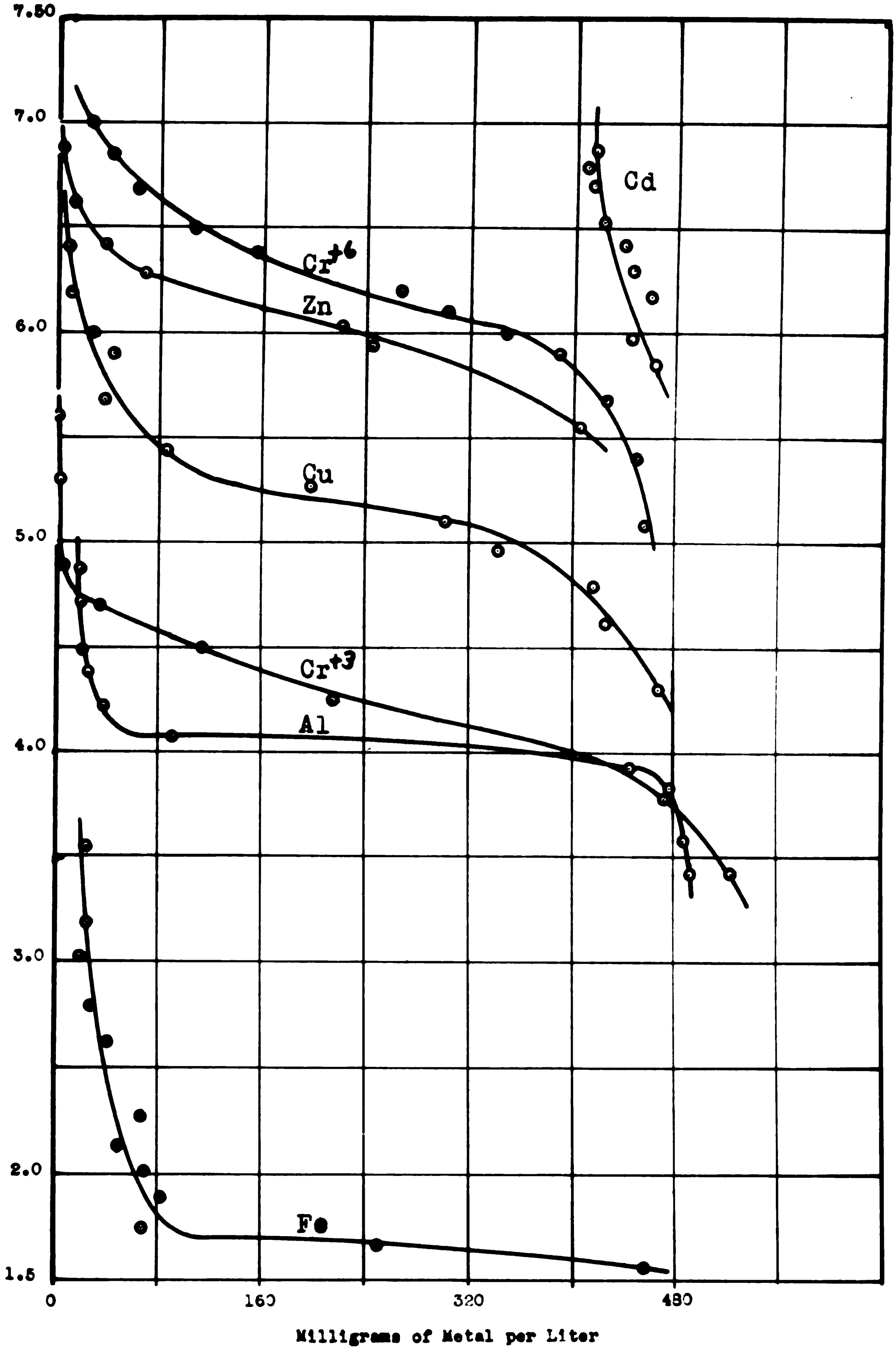

Fig. 1 -Concentration of aluminum, cadmium, chromium (hexavalent), chromium (trivalent), copper, ferric iron, and zinc in buffered nickel sulfate solution treated with ammonium hydroxide and heated three hours at 100° C.

Table 1

Concentration of aluminum, cadmium, chromium (hexavalent), chromium (trivalent), copper, ferric iron, and zinc in buffered nickel sulfate solution treated with ammonium hydroxide and heated three hours at 100°C.

Metal	Initial pH	Final pH	Mg Metal/l
Al	(orig. soln.)	-----	492
	3.42	3.13	492
	3.58	3.14	487
	3.83	3.18	476
	3.93	3.18	445
	4.07	2.75	89
	4.22	2.51	33
	4.33	2.62	25
	4.49	2.71	21
	4.72	2.82	20
	4.88	2.88	19
Cd	(Orig. soln.)	-----	462
	5.85	5.72	462
	5.97	5.73	443
	6.17	5.82	459
	6.30	5.87	445
	6.42	5.93	433
	6.53	6.02	421
	6.70	6.15	413
	6.79	6.24	408
	6.87	6.33	415
Hexa-valent Cr	(Orig. soln.)	------	455
	5.08	5.11	455
	5.40	5.39	448
	5.68	5.58	424
	5.90	5.67	390
	6.00	5.80	346
	6.10	5.84	302
	6.20	5.83	266
	6.39	5.96	154
	6.50	6.02	103
	6.68	6.23	61
	6.85	6.37	42
	7.00	6.51	25
Trival-ent Cr	(Orig. soln.)	-----	524
	3.42	2.62	524
	3.78	2.65	471
	4.25	2.64	214
	4.50	2.63	113
	4.70	2.95	34
	4.90	3.82	5
	5.30	4.90	2
	5.60	5.30	0

Table #1, Cont'd.

Metal	Initial pH	Final pH	mg Metal/l
Cu	(orig. soln.)	------	485
	4.30	4.10	465
	4.62	4.12	424
	4.80	4.32	415
	4.97	4.35	341
	5.10	4.48	301
	5.27	4.55	197
	5.44	4.72	85
	5.68	5.18	37
	5.90	5.56	44
	6.00	5.68	27
	6.19	5.82	9
	6.41	5.97	8
	6.62	6.07	11
Ferric Iron	(orig. soln.)	------	460
	1.56	1.62	455
	1.67	1.62	249
	1.75	1.63	69
	1.89	1.73	83
	2.01	1.78	71
	2.14	1.85	49
	2.27	1.92	69
	2.63	2.04	42
	2.80	2.10	29
	2.93	2.13	39
	3.03	2.18	20
	3.04	2.43	28
	3.19	2.74	25
	3.45	2.95	23
	3.55	3.00	25
Zn	(orig. soln.)	-----	432
	5.55	5.45	403
	5.94	5.61	244
	6.03	5.65	221
	6.23	5.85	67
	6.42	5.92	38
	6.83	6.39	3

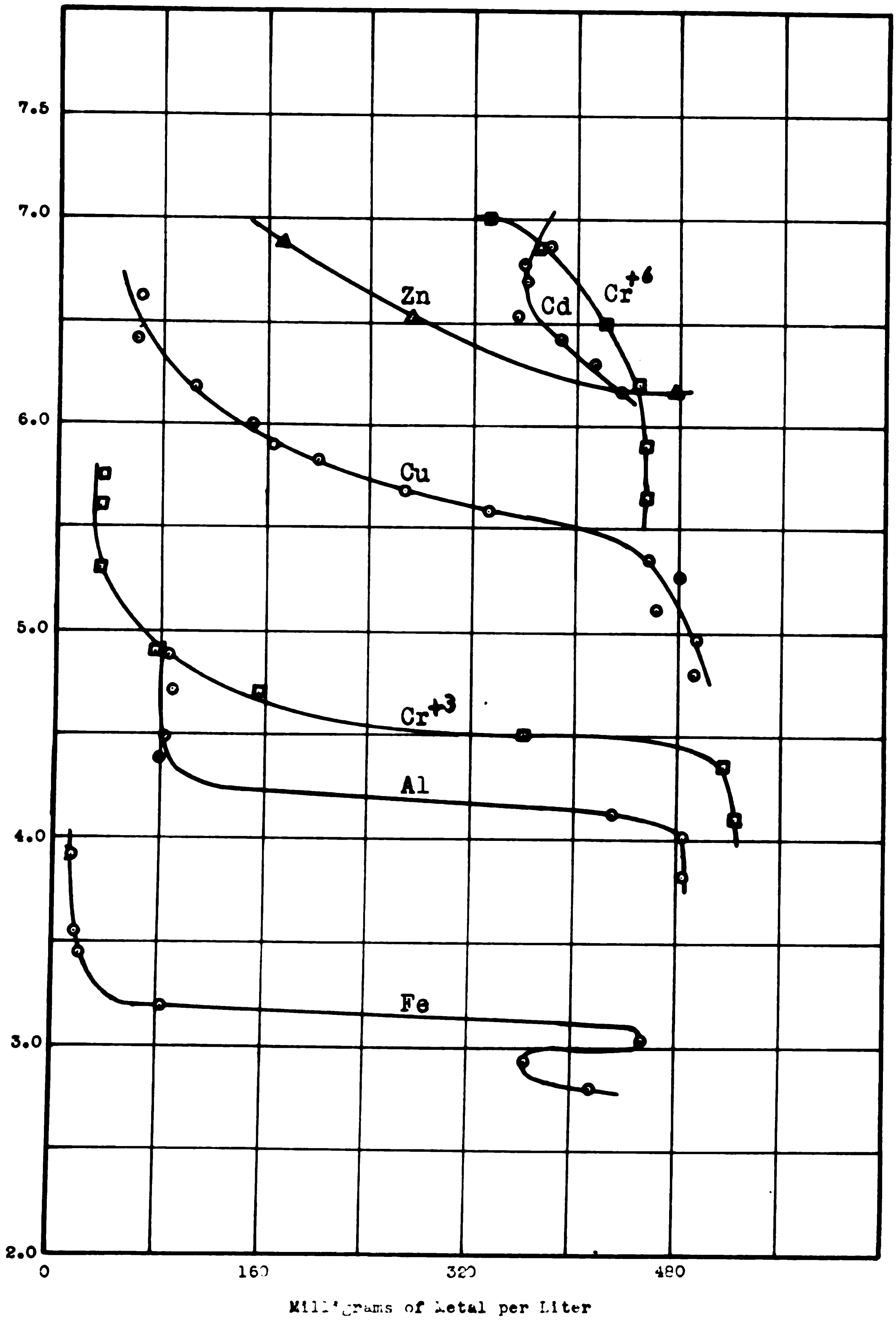

Fig. 2 - Concentration of aluminum, cadmium, chromium (hexavalent), chromium (trivalent), copper, ferric iron, and zinc in buffered nickel sulfate solution treated with ammonium hydroxide and heated 24 hours 23 to 26° C.

Table #2

Concentration of aluminum, cadmium, chromium (hexavalent), chromium (trivalent), copper, ferric iron, and zinc in buffered nickel sulfate solution treated with ammonium hydroxide and heated 24 hours at 23° to 26° C.

Metal	Initial pH	Final pH	Mg Metal/l
Al	(orig. soln.)	---	435
	3.83	3.85	435
	3.93	3.93	425
	4.01	4.05	435
	4.12	4.13	431
	4.33	4.32	79
	4.49	4.45	83
	4.73	4.72	90
	4.88	4.84	86
Cd	(orig. soln.)	---	459
	6.17	6.25	435
	6.30	6.40	415
	6.42	6.42	489
	6.53	6.55	353
	6.70	6.66	362
	6.79	6.73	359
	6.87	6.79	380
Hexavalent Cr	(orig. soln.)	---	454
	5.90	5.87	454
	6.20	6.20	449
	6.50	6.47	423
	6.85	6.85	372
	7.00	7.02	332
Trivalent Cr	(orig. soln.)	---	523
	4.35	4.00	515
	4.50	4.16	361
	4.70	4.46	156
	4.90	4.79	77
	5.30	5.23	33
	5.60	5.62	34
	5.75	5.78	37
Cu	(orig. soln.)	---	485
	4.80	4.62	491
	4.97	4.83	494
	5.10	5.02	464
	5.27	5.20	482
	5.35	5.28	458
	5.58	5.45	334

Table #2, Cont'd

Metal	Initial pH	Final pH	Mg Metal/l
Cu	5.62	5.57	268
(con'd)	5.83	5.70	201
	5.90	5.75	166
	6.00	5.85	151
	6.19	6.00	106
	6.41	6.23	61
	6.62	6.45	64
Ferric	(orig. soln.)	---	460
Iron	2.80	2.80	415
	2.93	2.69	365
	3.03	2.63	455
	3.04	2.79	453
	3.19	3.08	83
	3.45	3.38	20
	3.55	3.50	17
	3.47	3.71	17
	3.92	3.88	15
Zn	(orig. soln.)	---	432
	6.17	6.29	477
	6.52	6.67	273
	6.88	7.01	173

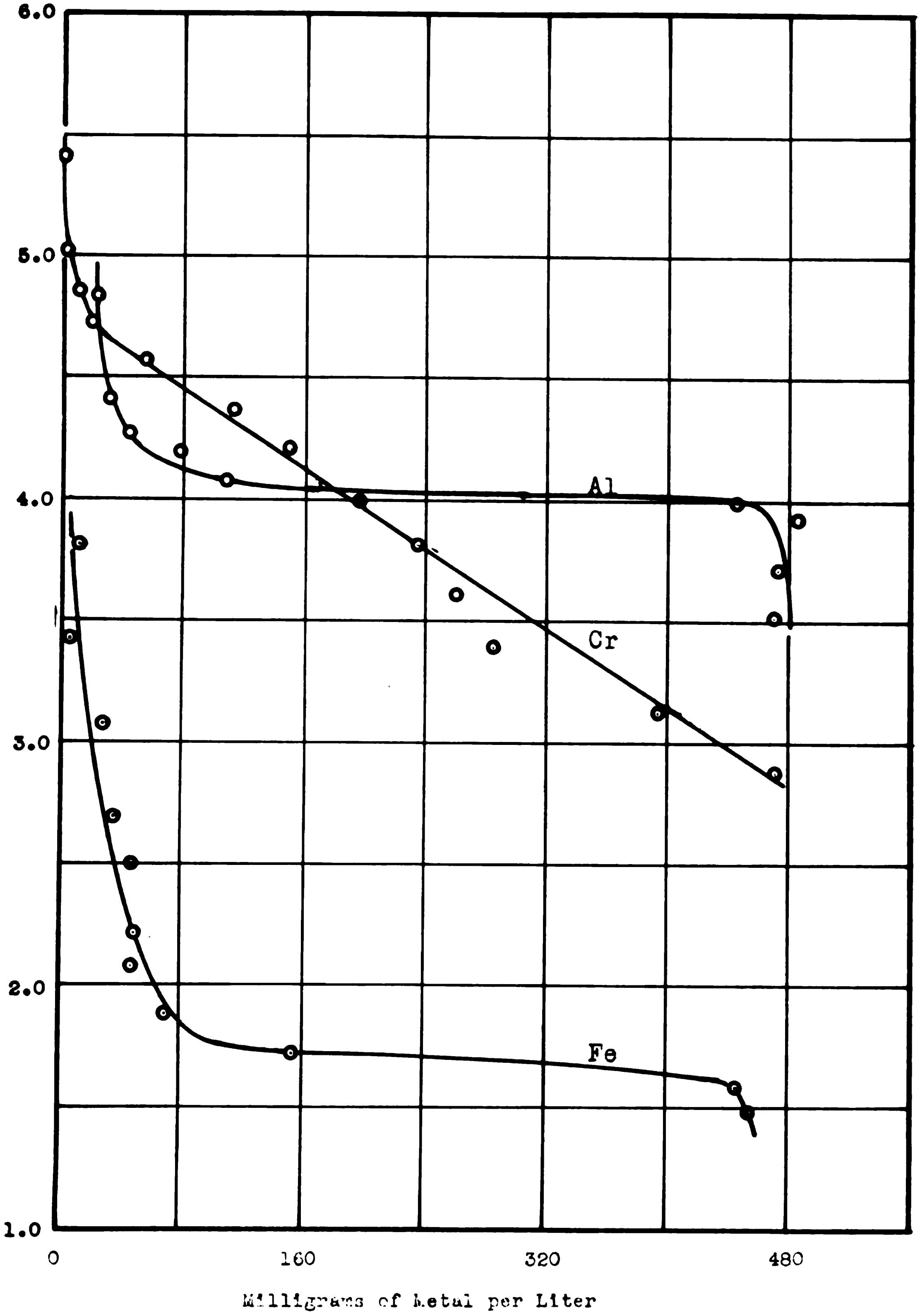

Fig. 3 - Concentration of aluminum, chromium (trivalent), and ferric iron in buffered nickel sulfate solution treated with sodium hydroxide and heated three hours at 100° C.

Table #3

Concentration of aluminum, chromium (trivalent) and ferric iron in buffered nickel sulfate solution treated with sodium hydroxide and heated three hours at 100°C.

Metal	Initial pH	Final pH	Mg Metal/l
Al	(orig. soln.)	---	472
	3.52	3.12	470
	3.72	3.19	473
	3.83	3.13	413 (?)
	3.92	3.17	433
	4.00	3.13	445
	4.09	2.94	107
	4.20	2.62	77
	4.23	2.57	44
	4.42	2.62	30
	4.65	2.75	24
	4.85	2.80	24
Trivalent Cr	(orig. soln)	---	472
	2.89	2.55	472
	3.13	2.53	393
	3.40	2.53	284
	3.62	2.61	259
	3.82	2.61	234
	4.00	2.59	194
	4.23	2.59	150
	4.38	2.61	112
	4.58	2.69	55
	4.74	2.91	19
	4.87	3.17	9
	5.02	3.72	2
	5.30	4.38	0
Ferric Iron	(orig. soln.)	---	455
	1.43	1.50	455
	1.58	1.61	446
	1.72	1.62	154
	1.93	1.71	70
	2.08	1.81	48
	2.22	1.88	50
	2.50	2.02	43
	2.70	2.11	36
	2.82	2.15	31
	2.98	2.19	39
	3.08	2.27	28
	3.06	2.36	20
	3.15	2.69	12
	3.43	2.95	6
	3.82	3.13	12

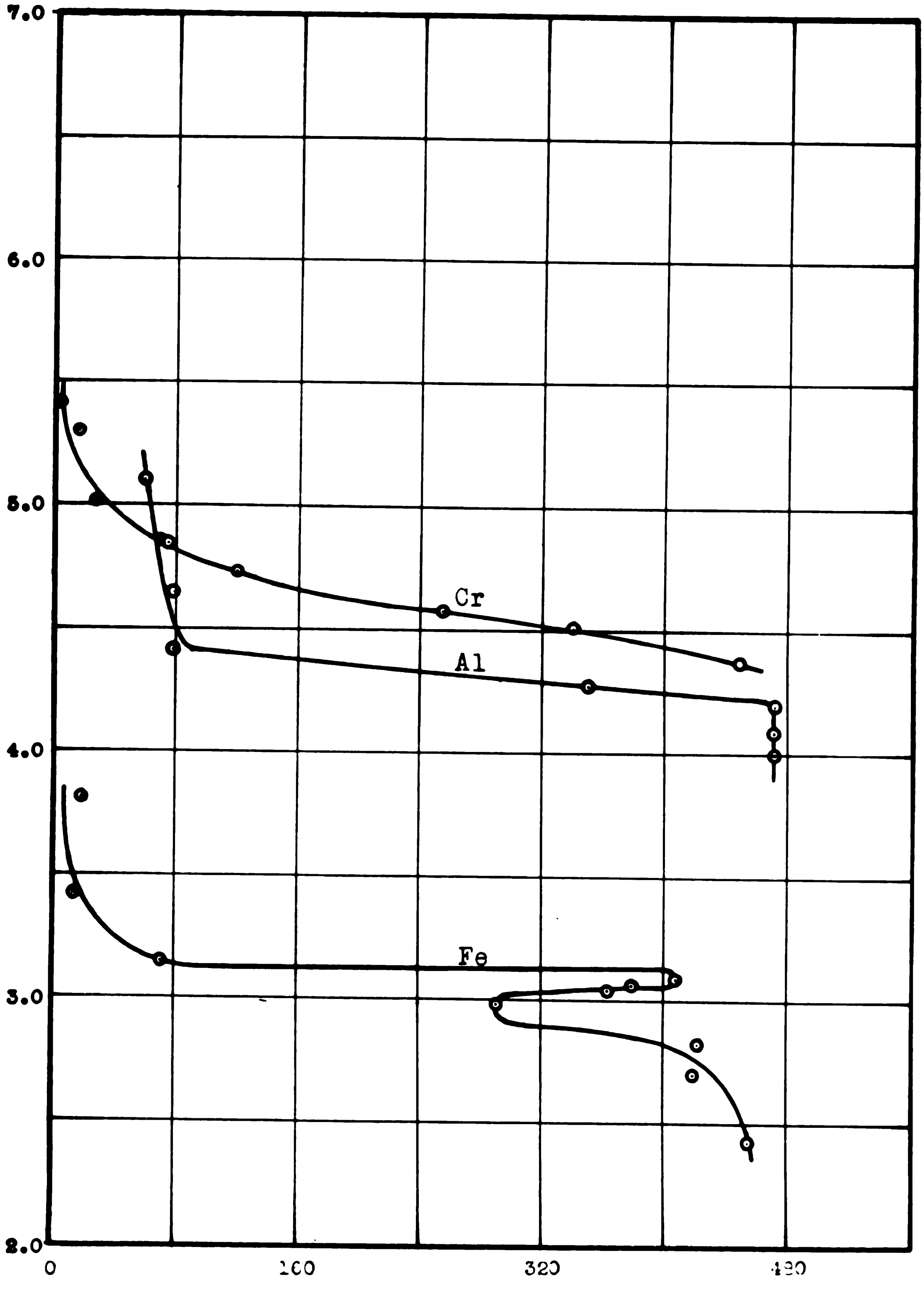

Fig. - 4 Concentration of aluminum, chromium(trivalent), and ferric iron in buffered nickel sulfate solution treated with sodium hydroxide and heated 24 hours at 23° C.

Table #4

Concentration of aluminum, chromium (trivalent), and ferric iron in buffered nickel sulfate solution treated with sodium hydroxide and heated twenty four hours at 25° C.

Metal	Initial pH	Final pH	Mg Metal/l
Al	(orig. soln.)	---	472
	4.00	3.98	472
	4.09	4.06	472
	4.20	4.15	472
	4.23	4.22	350
	4.42	4.37	73
	4.65	4.65	79
	4.85	4.86	75
	5.10	5.08	60
Trivalent Cr	(orig. soln.)	---	468
	4.38	4.02	449
	4.51	4.17	340
	4.58	4.27	255
	4.74	4.43	120
	4.87	4.67	71
	5.02	4.97	28
	5.30	5.23	16
	5.42	5.45	4
Ferric Iron	(orig.soln.)	---	455
	2.43	2.50	455
	2.70	2.74	419
	2.82	2.85	422
	2.93	2.70	292
	3.04	2.68	368
	3.06	2.73	380
	3.08	2.85	408
	3.15	3.01	72
	3.43	3.30	14
	3.82	3.63	20

Treatment with Nickel Carbonate, Calcium hydroxide, and Magnesium oxide: - Since nickel carbonate and calcium hydroxide are often used in purification of nickel plating baths it was thought desirable to determine the maximum pH values that could be obtained with buffered nickel sulfate solutions. Tables A and B show the results of this study. The data in table A were obtained upon treating buffered nickel sulfate solutions with nickel carbonate, calcium hydroxide and magnesium oxide and allowing them to stand at 22° - 27° C with intermittent shaking.

It will be seen that in the buffered nickel sulfate solution nickel carbonate failed to raise the pH to 6.0. Calcium hydroxide did raise the pH above 6.0 in the unheated samples but only to pH 5.4 in the heated samples. The data indicate very definitely that the proper procedure to attain the maximum pH is to allow the nickel carbonate or calcium hydroxide to react with the buffered solution at room temperature. This is in accordance with the fact that the solubilities (27) of calcium hydroxide and nickel carbonate are much less at the higher temperatures. The heated series in table B was carried out by adding the nickel carbonate and the calcium hydroxide at room temperature, then heating to 100° C for three hours. When the solutions were heated to 100° C, the nickel carbonate and the calcium hydroxide added and the heating continued for three hours, the data in table B were obtained.

Table A

pH Values of Buffered Nickel Sulfate Solutions Treated with 5 g/l of Nickel Carbonate and Calcium Hydroxide.

Solution	Reagent	In'tl pH	Time & Temp.	Final pH
Buffered $NiSO_4$	$NiCO_3$	2.70	6 hrs. at 25° C	5.20
Buffered $NiSO_4$	$NiCO_3$	2.70	3 hrs. at 100° C	5.22
Buffered $NiSO_4$	$Ca(OH)_2$	2.70	6 hrs. at 25° C	6.30
Buffered $NiSO_4$	$Ca(OH)_2$	2.70	3 hrs. at 100° C	5.40

Table B

This table gives the data collected when the solutions were heated to 100° C, then the reagent added and the heating continued for three hours at 100° C.

Solution	Reagent	Initial pH	Final pH
Buffered $NiSO_4$	$NiCO_3$	3.00	5.12
Buffered $NiSO_4$	$NiCO_3$	3.04	5.52

Qualitative Effects of the Use of Urea in Raising the pH of Nickel Sulfate Solutions: - Willard and Tang (28) and Willard and Fogg (29) have carried out extensive investigations in the use of urea as an internal method of raising the pH of an aqueous solution. Urea in solution, upon being heated hydrolyses to give ammonium hydroxide and carbon dioxide. If the urea is added to the cold solution which is then vigorously shaken and heated the pH of that solution will slowly and homogeneously be raised.

A very brief exploratory study was made in order to observe the effects of urea on the pH of a concentrated nickel sulfate solution. No boric acid was used in this case. The pH of the nickel sulfate solution was adjusted to 1.5 with sulphuric acid. Small quantities of the urea gradually increased the pH. Further addition of the salt brought about precipitation. A pH of 6.6 was reached. Further additions of urea produced no change in pH until the nickel concentration was greatly reduced, the nickel hydroxide precipitating at pH 6.2 - 6.7.

Some qualitative runs were made with certain metallic ions as impurities (chiefly Fe^{+++}). The precipitate formed was easily removed on the filter, leaving the nickel sulfate solution quite clear.

Additional tests in the presence of the chloride ion indicated that the results were the same.

The chief advantage in the use of urea is that the pH is raised slowly and homogeneously throughout the entire solution, thus avoiding abnormal pH changes in the vicinity of added precipitant.

Discussion of the Individual Ions Studied

Aluminum: - Initial appearance of turbidity upon addition of either ammonium or sodium hydroxide to buffered unheated nickel sulfate solution containing aluminum sulfate was observed at pH 4.4 ± 0.1, although buffer action was encountered at pH 4.0. The solution rapidly became very turbid upon further addition of base and at pH 4.6 - 4.7 coagulation of the hydrous aluminum oxide was noted. As seen from figure 5, the concentration of the aluminum was markedly reduced at pH 4.4 upon standing for 24 hours at 25° C. Figure 5 further shows that heating the samples three hours at 100° C produced heavy precipitation at 0.3 - 0.4 pH units lower, however, the aluminum was not completely removed at pH 4.9. It may also be observed that in the case of the heated samples a considerable drop in pH occurred even where no visible precipitation took place, indicating hydrolysis.

Some difficulty was encountered in the use of aurin tricarboxylic acid for low concentrations of aluminum. In order to have sufficient aluminum (0.1 - 0.5 mg.) for the analysis 20 ml. samples were taken. The high nickel sulfate content caused coagulation and settling of the lake so that it was necessary to shake the colorimeter tubes frequently while making check readings.

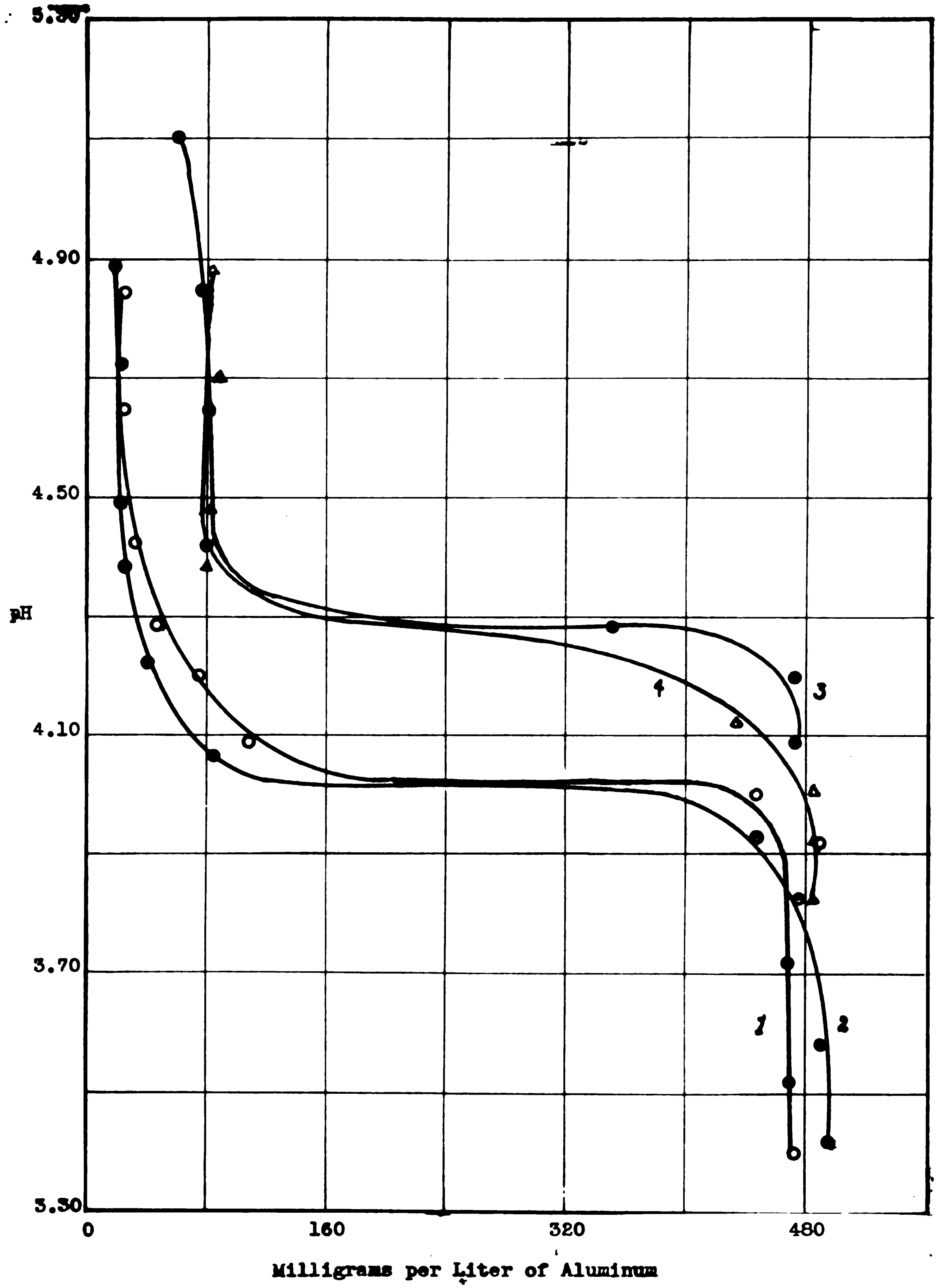

Fig. 5 - Aluminum in buffered nickel sulfate solution at different pH values: 1, NaOH treatment, 3 hrs at 100°C.; 2, NH_4OH treatment, 3 hrs at 100°C.; 3, NaOH treatment, 24 hrs at 25°C.; 4, NH_4OH treatment, 24 hrs at 25°C.

Cadmium: - It may be noted in figure 6 that cadmium is not appreciably removed from a buffered nickel sulfate solution even at a pH of 6.6. In fact it appears that some cadmium returns to the solution above pH 6.7. It was found that in a boric acid solution cadmium is almost entirely removed from solution at pH 7.4, while in a buffered nickel sulfate solution only 50 mg/l of cadmium was removed from solution after it was heated three hours at 100° C.

While making the run with cadmium in the buffered nickel sulfate solution it was observed that between pH 6.2 and 6.3 the solution became very turbid and above 6.3 a large quantity of nickel hydroxide was precipitated. This was about 0.6 pH unit lower than the value at which nickel hydroxide started to precipitate in an unbuffered solution (31). A run was made in which the pH of a buffered nickel sulfate solution was raised with ammonium hydroxide. The results are shown in figure 7.

In view of the heavy precipitation of nickel hydroxide above pH 6.3, the removal of cadmium from the buffered nickel sulfate solution cannot be attributed to the influence of the boric acid since it is entirely probable that some of the cadmium was adsorbed from solution by the nickel hydroxide.

It is evident also that any visual observations as to the pH values at which metallic hydroxides come down are worthless if these values fall within the range where precipitation of nickel hydroxide occurs. In this range a chemical analysis must be made to determine the cadmium present.

Only ammonium hydroxide was used in the study of cadmium due to the dilution factor that would have been encountered had sufficient dilute sodium hydroxide been used to reach the desired pH.

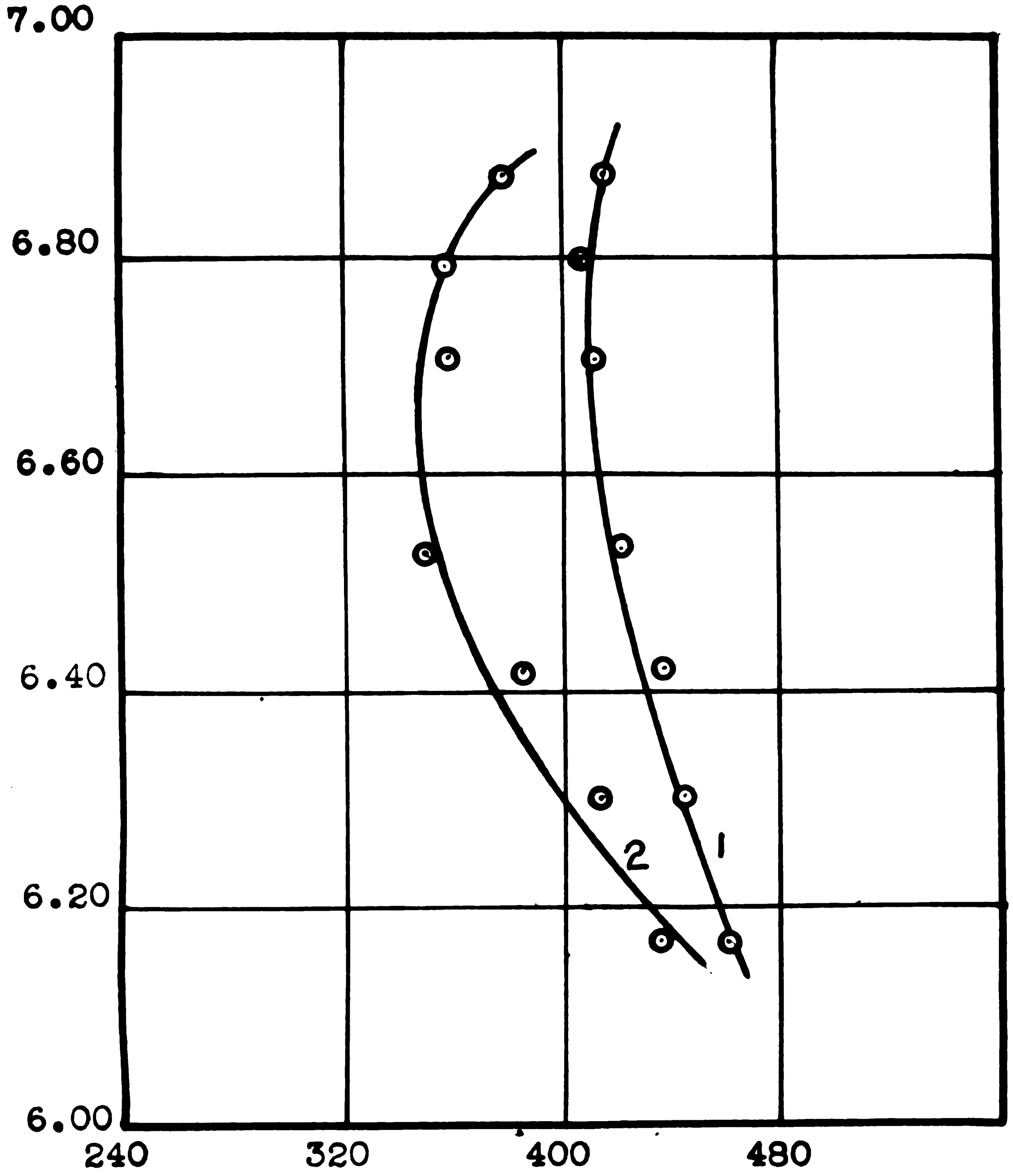

Fig. 6 - Cadmium in buffered nickel sulfate solutions at different pH values: 1, Buffered nickel sulfate solution after NH_4OH treatment, 3 hours at 106°C. 2, Buffered nickel sulfate solution after NH_4OH treatment, 24 hours at 23°C.

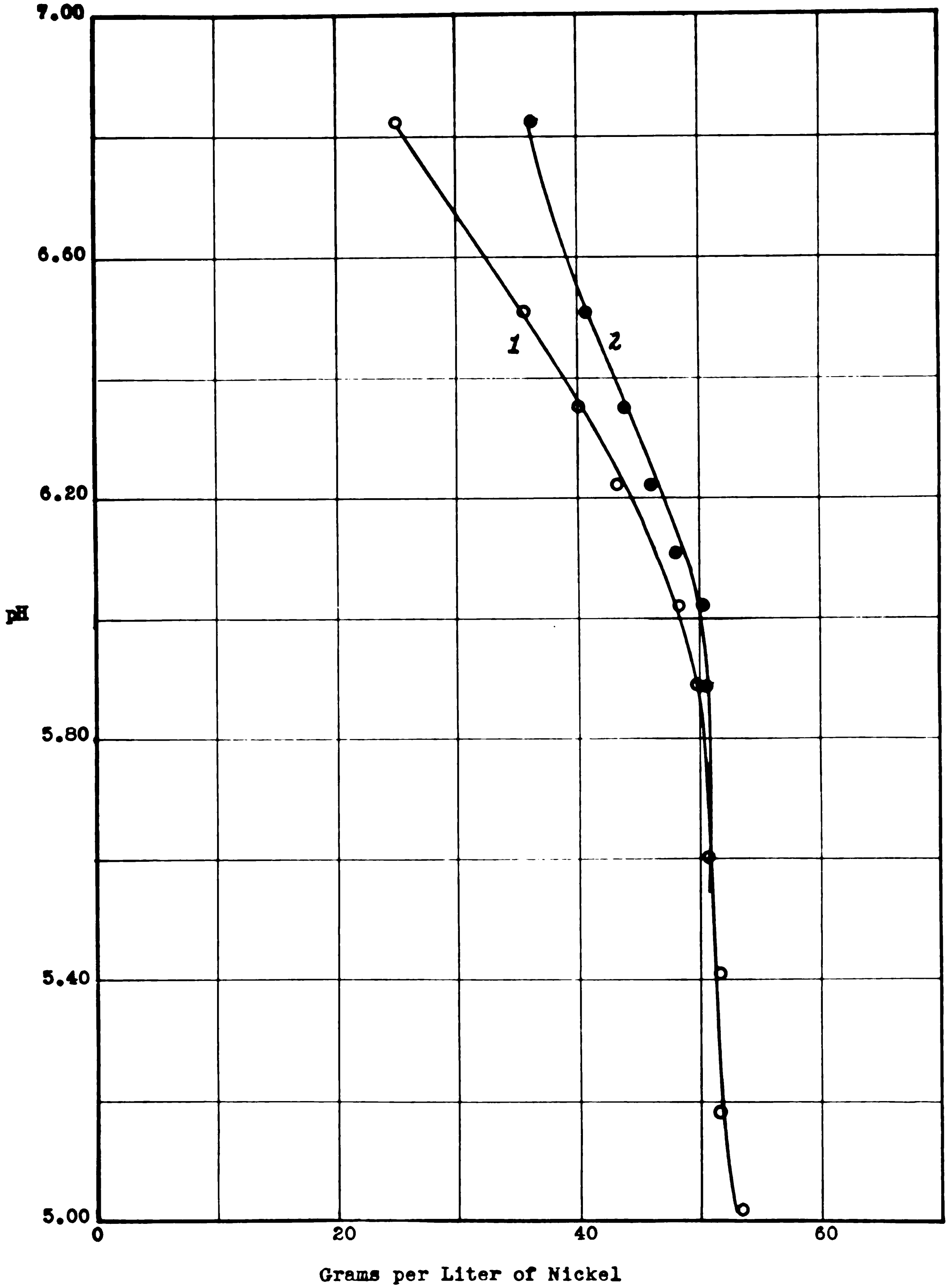

Fig. 7 - Nickel content of buffered nickel sulfate solution at different pH values: 1, NH_4OH treatment, 3 hrs at 100°C.; 2, NH_4OH treatment 24 hrs at 25°C.

Hexavalent Chromium: - A buffered nickel sulfate solution containing 500 mg/l chromium was used. The pH was raised with ammonium hydroxide. As may be seen in figure 8, the break in the curve occurs at pH 5.4 in the case of the heated sample and 5.8 in the cold sample. As shown in figure 8, a pH of 7.0 is required to remove chromium almost completely from solution. It was found that the precipitation from buffered nickel sulfate solutions with ammonium hydroxide (upon heating) is more efficient than in unbuffered solutions. A curve for the unbuffered precipitation approaches that of the buffered solutions above pH 6.8. The voluminous precipitate of nickel hydroxide in the buffered solution probably carries down some chromium with it. It seems doubtful that the boric acid has any influence in this case since it was shown that hexavalent chromium does not precipitate at all from a boric acid solution up to a pH 7.1 when ammonium hydroxide is used as the precipitant.

With sodium hydroxide used as the precipitant, a small quantity of light yellow needles was observed at pH 7.0 after the solution had been heated three hours at 100° C. The solution changed progressively from an orange-red at pH 5 to a light yellow as sodium hydroxide was added, indicating the conversion of the chromic acid to sodium chromate.

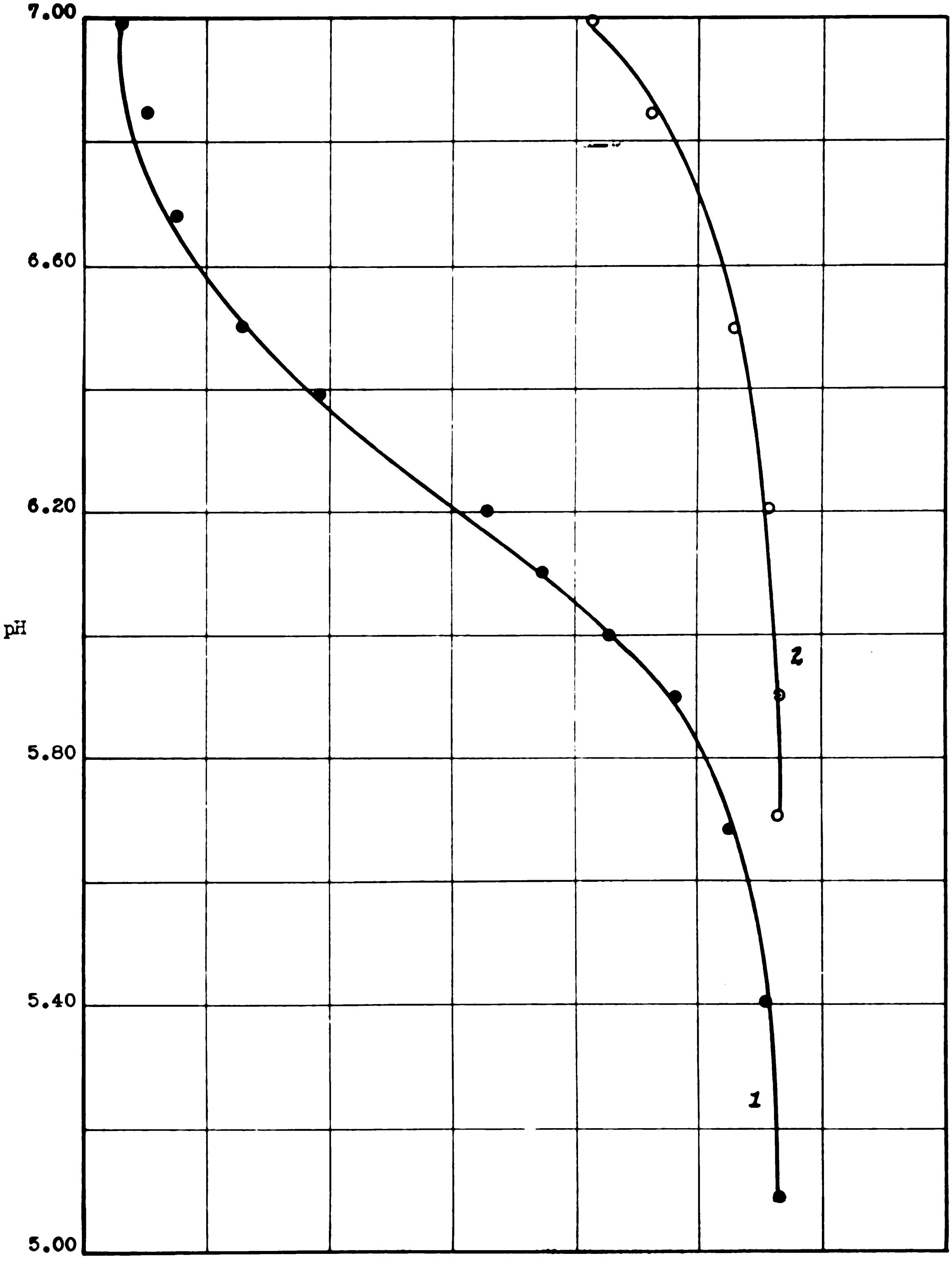

Fig. 8 - Hexavalent chromium in buffered nickel sulfate solution at different pH values: 1, NH_4OH treatment, 3 hrs at 100°C.; 2, NH_4OH treatment, 24 hrs at 24°C.

Trivalent Chromium: - In studying trivalent chromium in the buffered nickel sulfate solutions it was found that initial turbidity, in the case of the heated samples, occurred at pH 2.8 - 2.9 when sodium hydroxide was used and at pH 3.4 - 3.7 when ammonium hydroxide was employed. In the case of the unheated samples turbidity was first noticed at pH 3.4 - 3.5 for both hydroxides. To obtain reproducible data it is necessary to add the hydroxide slowly and with constant agitation. It is quite possible that rapid addition of the base could cause localized changes in pH such that nickel hydroxide would be precipitated, thereby causing turbidity due to nickel hydroxide instead of chromium hydroxide. Of course, this same line of reasoning may be applied to all the metals which start precipitating in pH ranges below the pH at which nickel hydroxide comes out.

As shown by the curves on figure 9, heating the solutions increases their acidity, i. e., precipitation begins at a lower pH value. In the case of the samples heated at 100° C, there was considerable difficulty in obtaining consistant data concerning the minimum pH point at which precipitation occurs after three hours. After five trials using ammonium hydroxide as the precipitant, it was decided that the precipitation probably begins at some pH under 2.0. It is probable that the inconsistent results is due to the rate of hydrolysis of the chromic sulfate.

Britton and Wescott (12) carried out titrations of 0.5 M chromic salts with 2.0N sodium hydroxide. They observed an increase in acidity upon heating the salt solution as shown by the fact that a 0.5 M $CrCl_3 \cdot 6H_2O$ solution had a pH of 2.85, but when heated to boiling and cooled the pH had dropped to 1.2.

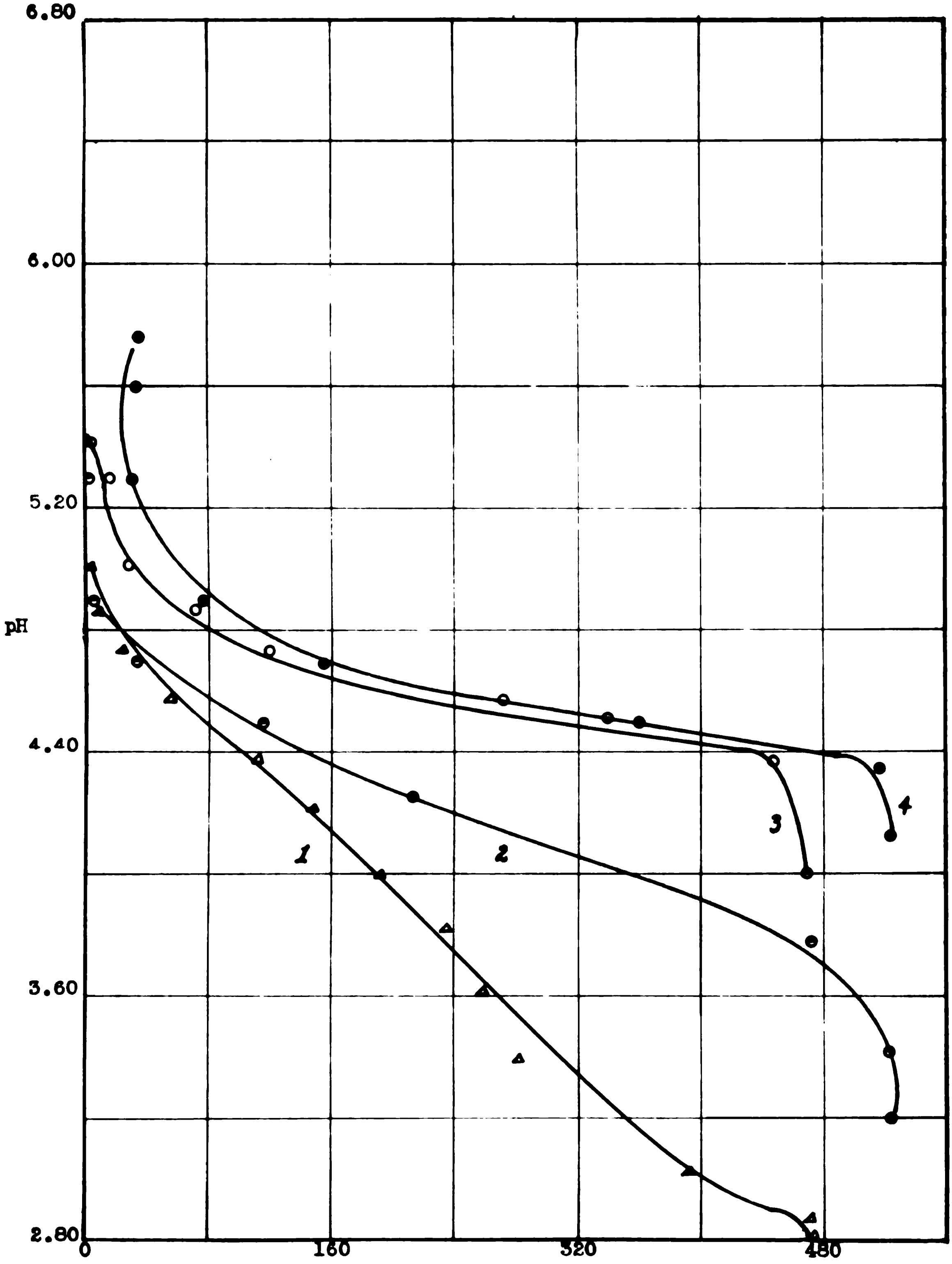

Fig. 9 - Trivalent chromium in buffered nickel sulfate solution at different pH values: 1, NaOH treatment, 3 hrs at 100°C.; 2, NH_4OH treatment, 3 hrs at 100°C.; 3, NaOH treatment, 24 hrs at 23°C.; 4, NH_4OH treatment, 24 hrs at 23°C.

Copper: - In the treatment of copper only ammonium hydroxide was used. In solutions whose pH was 5.6 - 5.7 immediately after the addition of ammonium hydroxide, turbidity was observed in the unheated sample at pH 5.0 - 5.1 and in the heated sample below 4.3. Figure 10 shows quite clearly that copper is more nearly removed from solution in the heated sample. At pH of 6.6, 11 mg/l of copper remains in the heated solution while 64 mg/l remains in the cold sample.

Copper is removed quite rapidly from a boric acid solution at pH 5.4. Recalling that boric acid is used as a buffer it is understandable why the copper behaves as it does in this case.

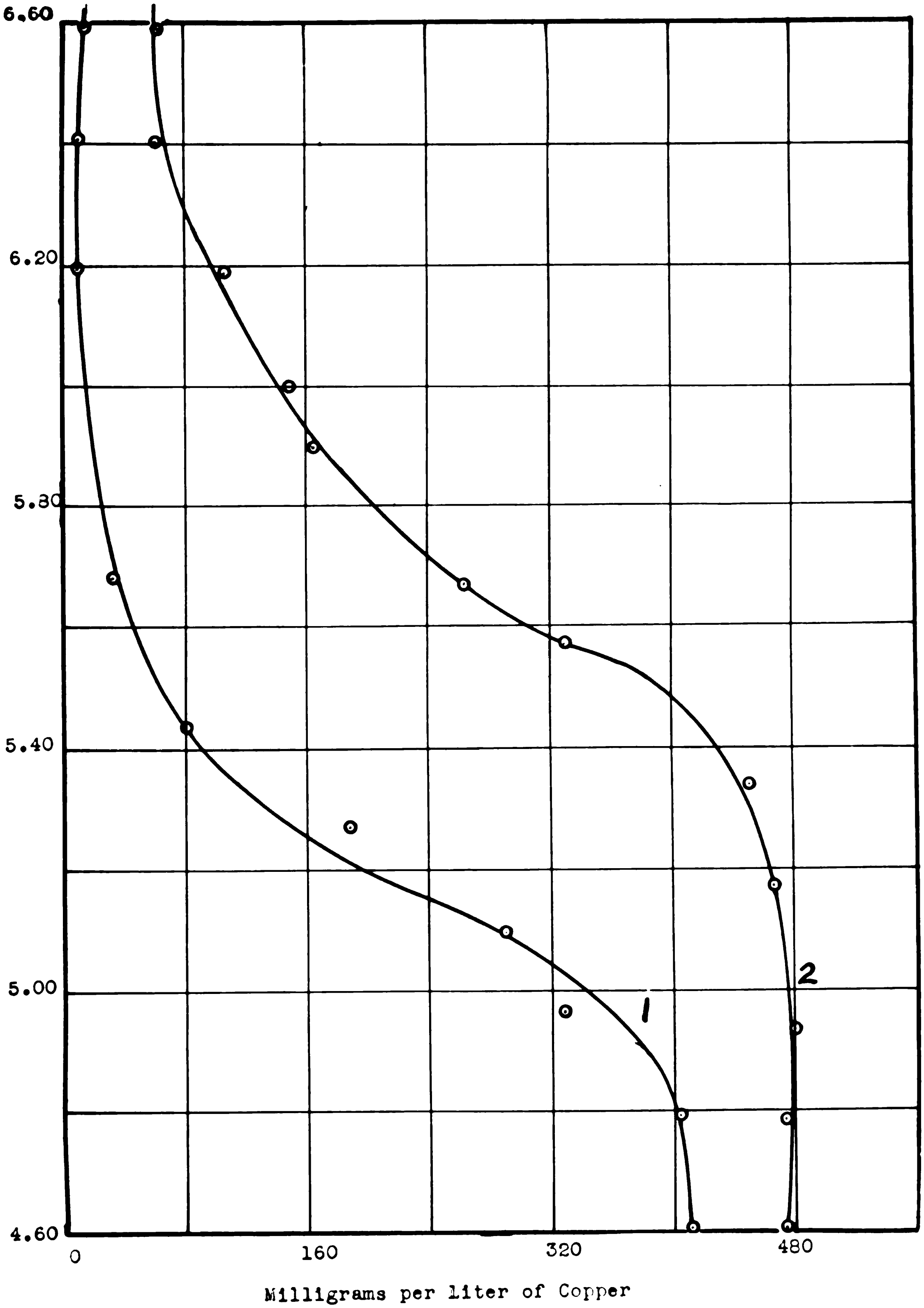

Fig. 10 - Copper in buffered nickel sulfate solutions at different pH values: 1, Buffered nickel sulfate solution after NH_4OH, treatment, three hours at 100°C.; 2, Buffered nickel sulfate solution after NH_4OH treatment, 24 hours at 24°C.

Ferric iron: - The removal of iron from a buffered nickel sulfate solution is of great interest, especially to the electroplating industry. As shown on figure 11, the precipitation of iron from a hot solution begins below pH 1.5 upon the addition of either sodium or ammonium hydroxide. The behavior of a cold solution is quite different. Turbidity becomes evident at pH 2.8 - 2.9 when sodium hydroxide is used and at 2.6 - 2.7 when ammonium hydroxide is added.

Upon heating a series at 100° C coagulation and voluminous precipitation was observed in all samples above pH 1.9 after five minutes in the water bath. Over the period of three hours the samples below this pH showed precipitation down to pH 1.6 - 1.7. Between pH 1.5 and 1.6 the solutions were turbid, but no settled precipitate was present. At pH 1.4 the sample was clear.

From figure 11 it may also be noted that in the case of the unheated samples there is a very narrow pH range (3.0 - 3.1) in which the colloidal ferric hydroxide is quite stable. This stability was found to persist for 36 to 48 hours; however, at pH near 3.5 the iron content in all cases is reduced by 80%. In the case of the heated samples it is lowered by about 80% at a pH as low as 2.0 - 2.1.

The fact that iron is so efficiently removed at such low pH values provides a very convenient method of clearing a Watts Nickel plating bath of iron impurities.

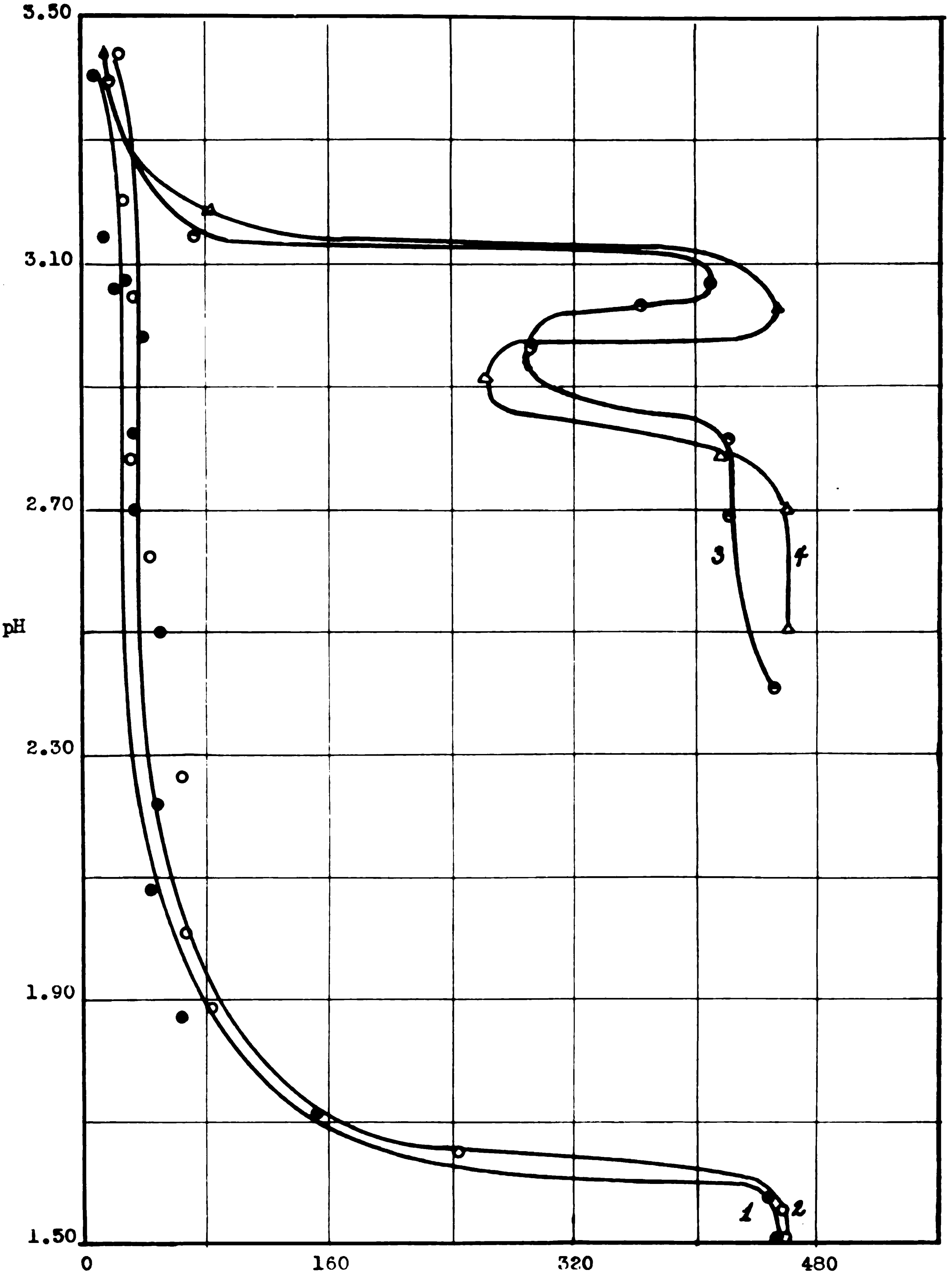

Fig. 11 - Ferric iron in buffered nickel sulfate solution at different pH values: 1, NaOH treatment, 3 hrs at 100°C.; 2, NH_4OH treatment, 3 hrs at 100°C.; 3, NaOH treatment, 24 hrs at 23°C.; 4, NH_4OH treatment, 24 hrs at 23°C.

Zinc: - Zinc was not appreciably removed from the buffered nickel sulfate solution with ammonium hydroxide until a pH of 6.4 was reached as shown in figure 12. At about pH 6.4 the curves break quite rapidly. No sodium hydroxide was used due to a dilution factor, therefore, the two curves shown on figure 12 are for the use of ammonium hydroxide at 100° C and at 25° C. It may be noted that the zinc is removed completely from solution at pH 6.8 in the heated solution.

In this particular case the advantage of the heated process over the cold process is especially obvious.

Again in this case, visual observations were of no value. Analysis showed that in the heated sample zinc was precipitated at a much lower pH in this solution than in nickel sulfate solution alone. The possible effects of the precipitation of nickel hydroxide must not be overlooked.

In carrying out the analysis, which was a combination of the separation method of Fales and Ware (19) and the polaragraphic procedure of Reed and Cummings (20), several points of importance should be noted: (a) In order to have sufficient zinc to work with conveniently at the lower concentrations fifty ml. samples were taken; (b) In the formic mixture, the use of either ammonium chloride or ammonium sulfate was recommended, for this case ammonium chloride was found preferable, since there was a large amount of nickel ammonium sulfate precipitated otherwise, as well as some zinc ammonium sulfate; (c) It was essential that the solution be at pH 2.0 before saturation with hydrogen sulfide gas, otherwise nickel sulfide precipitation was incomplete. A small amount of nickel sulfide is not objectionable since the zinc sulfide may be dissolved in cold 1:1 HCl, leaving the nickel sulfide.

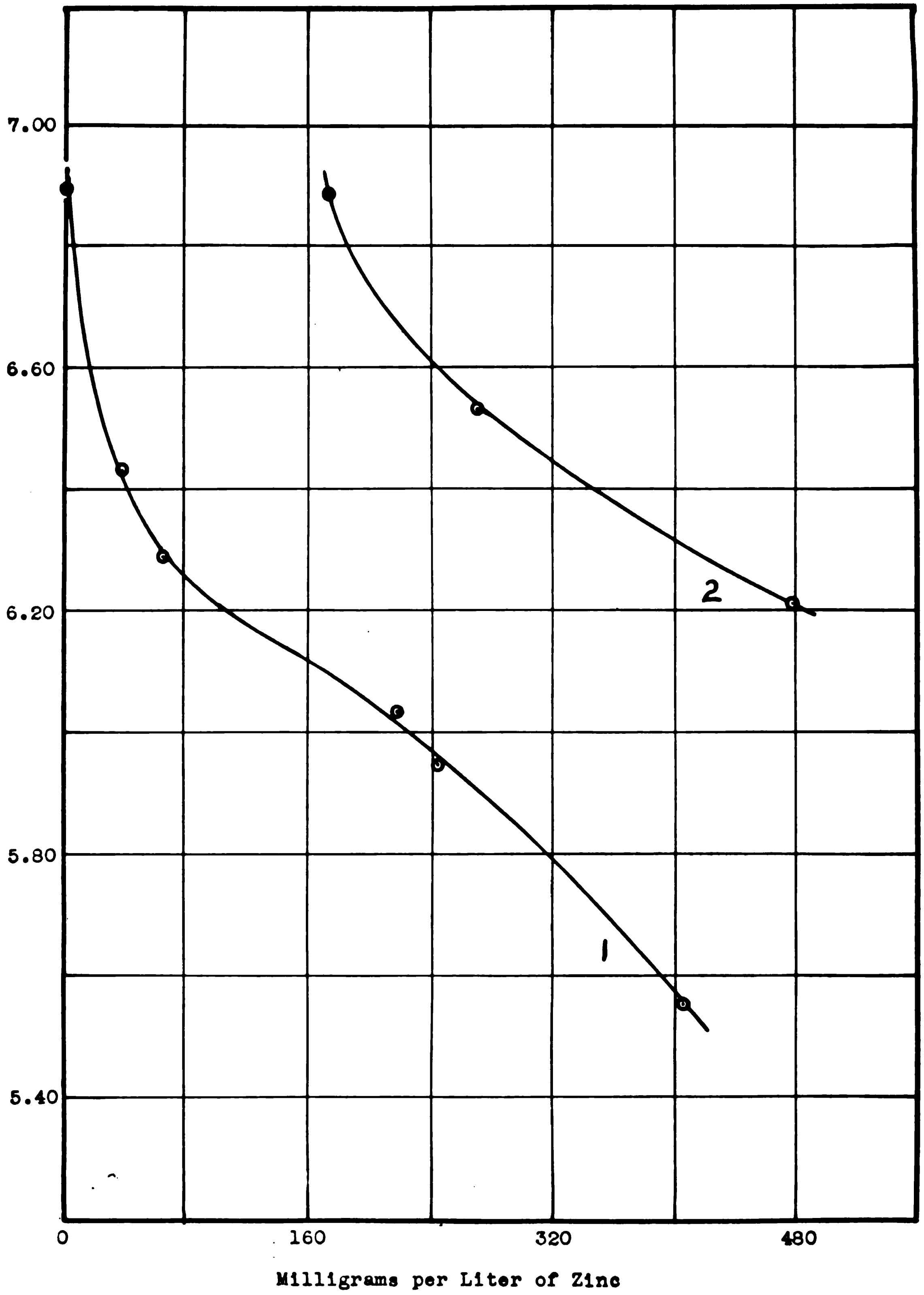

Fig. 12 - Zinc in buffered nickel sulfate solution at different pH values: 1, Buffered nickel sulfate solution after NH_4OH treatment, 3 hours at 100°C. 2, Buffered nickel sulfate solution after NH OH treatment, 24 hours at 25°C.

General Conclusions: - In general the removal of impurities from buffered nickel sulfate starts at a lower pH in heated solutions than in the cold ones. As might be expected, more efficient removal of the impurities was effected in the solutions that were heated for three hours at 100° C, than in those that were allowed to stand at 22° - 27° for 24 hours.

In the case of aluminum, trivalent chromium, copper and ferric iron the hydrolysis process manifest itself in the heated samples in the form of a drop in pH amounting to 0.3 - 2.5 units.

Summary: - The removal of aluminum, cadmium, trivalent and hexavalent chromium, copper, ferrous and ferric iron and zinc from buffered nickel sulfate has been studied at 22° - 27° C and at 100° C using ammonium and sodium hydroxide whenever possible.

The maximum pH values attained when buffered nickel sulfate solutions were treated with 5 g/l of nickel carbonate and calcium hydroxide and thoroughly stirred for six hours at 22° - 27° C or heated for three hours at 100° C were obtained.

Urea was used as an internal agent for the adjustment of pH. It was found that upon heating a nickel sulfate solution to which urea had been added, the pH increased to 6.8 at which point nickel hydroxide separated out.

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