ELECTROLYTIC CHROMIUM, I

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(1) Object of work. (2) Properties of the metal. (3) Results of previous workers. (4) Statement of the chemical problem. (5) Apparatus and method. (6) Electrolysis of chloride solutions. (7) Change in anode solution. (8) Electrolysis of sulphate solutions. (9) Conclusions.

1. *Object of Work.*—The electrodeposition of chromium is of very considerable practical as well as theoretical importance. The element is one of the large number which may be found in either the acid or the basic part of compounds, and which show different valencies in the various compounds. Consequently the results obtained from a study of its electrochemical behavior should be capable of application to many other cases. The present paper will consider only the cases where chromium acts as the base in trivalent compounds; subsequent work will deal with its electrolytic behavior in solutions of chromous salts and also when it forms part of the acid radical.

In many cases electrochemists have been successful in obtaining other metals either in a state of great purity or else in such forms as to open new fields for useful application. Although many processes have been proposed for the electrodeposition of chromium from aqueous solution, they are all, according to Goldschmidt,¹ to be discarded because of the complicated apparatus, high current density, high voltage, low current efficiency and consequent great expense. The statement² has been made however that the electrodeposition of the metal has been carried out successfully on a commercial scale by the Electrochemische Werke, in Bitterfeld, but the method employed is not given.

Even with the drawbacks mentioned above, it seems strange that chemists have not made use of an electrolytic method for the deposition of this metal in order to obtain a better knowledge of the properties of the element and its compounds. Cer-

¹ Zeit. Elektrochemie, 7, 668 (1901).

² Chem. News, 81, 17 (1900); Jahrbuch der Electrochemie, 3, 233.

tainly the method for electrodeposition of the metal must be either unknown or else regarded as difficult, for otherwise the impure metal obtained by the Goldschmidt process would probably not have been used by Hittorf, Ostwald, Luther, Brauer and others in their work if by electrolysis the metal could have been obtained purer and in a form more convenient for working.

The advantages of a pure metal for electrometallurgical work are such that the metal produced by the Goldschmidt thermal process is said to compete quite successfully with the cheaper ferro-chromium, since the latter is less constant in composition.¹ But while from a commercial point of view, the utilization of chromium deposited from aqueous solutions may not be of great importance, some preliminary experiments performed with the object of obtaining the metal gave results so completely at variance with experiments previously recorded, that we have found it necessary to investigate more thoroughly some of the conditions which affect the current yield.

It is necessary to review some of the properties of the metal, physical, chemical and electrochemical.

2. *Properties of the Metal.*—Chromium is a hard white metal, the crystalline variety having a specific gravity according to Moissan of 6.92 at 20°. Its melting-point lies higher than that of platinum. It can be filed with difficulty but is polished quite readily, giving then a reflecting surface as good as that of silver, but more liable to tarnish (Cowper-Coles). Other observers (Hittorf, Moissan) have found however that it keeps its polish in air very well indeed. When deposited electrolytically, it has been found to be more readily scratched than nickel but less readily than silver; it must be remembered, however, that the hardness of a deposit may vary considerably with the conditions of its deposition. When alloyed with certain amounts of chromium, metals such as gold, tin, zinc, lead, copper and iron are made much harder and more resistant to

¹ Le Blanc: "Die Darstellung des Chroms und seiner Verbindungen," p. 58.

strain and friction. These alloys present a very promising field for the metallurgist.

Like iron, nickel and cobalt, the metal occurs in both an active and a passive state. When active, the metal dissolves readily in hydrochloric or hot sulphuric acid to form the chromous salts. Periodicities in the rate of solution of the metal in acids were observed by Ostwald in 1900; the later work of Brauer (1901) showed that these were not observable when the chromium was pure. Hittorf¹ has shown that when the metal is brought into contact with the solution of free chlorine or bromine, with strong nitric acid, *chromic acid*, etc., in other words with the most vigorous oxidizing agents, the metal becomes passive, then acting as a noble metal. This passivity may at all times be destroyed by making the metal cathode in an acid solution. The metal may also become active by contact with highly concentrated solutions of strong acids even at ordinary temperatures; for this purpose may be used hydrochloric, hydrobromic, hydrofluoric, etc. Solutions of the chlorides of the alkalis and the alkaline earths act similarly near the boiling temperature. When made anode in hydrochloric or hydrobromic acid under such conditions that the halogen tends to be set free, the metal dissolves as the chromous salt.² If, however, it is anode under circumstances such that an evolution of oxygen may take place, it dissolves as chromic anhydride (hexavalent), the metal then becoming passive. In other cases as in alcoholic zinc chloride, the metal as anode seems to be trivalent. The effect of temperature on the anodic behavior is very marked; in most solutions where the metal dissolves as chromate, rise of temperature favors solution as the chromic or chromous salt.

In regard to the voltaic relations, it was found that, at ordinary temperatures, the metal was electronegative to zinc, cadmium, iron, nickel, copper, mercury and silver; solutions of mercury chloride and cupric chloride and bromide were reduced at the boiling temperature.

¹ Zeit. phys. Chem. 30, 505 (1899).

² Hittorf: Zeit. phys. Chem. 25, 729 (1898). In these experiments the current density at the anode, and the concentration of the solutions used are not given.

From the results of his experiments, Hittorf concluded that the passivity is not due to a film, as is most probably the case with aluminum, but more probably to some peculiar allotropic (molecular) state of the metal.

3. *Results of Previous Workers.*—The successful electro-deposition of the metal was accomplished by Bunsen¹ when, recognizing the importance of current density and concentration as variable factors, he made use of a two-compartment electrolyzing vessel, the anode of which was a carbon cell which contained the acid, while the cathodic chamber held the chromium solution and the platinum electrode. The electrolyte was a solution of chromous chloride containing some chromic salt, and the electrolysis was carried on in the hot solution with a current density of about 67 amperes per square decimeter. When the current density was lowered, there separated "Wasserfreies Chromoxydoxydul" which dissolved in hydrochloric and sulphuric acids to form the chromous salts, hydrogen being evolved. He was successful in obtaining the metal from the chromic chloride, but this took place more readily when chromous salt was present. Bunsen considered that his "Chromoxydoxydul" had a formula between Cr_4O_5 and Cr_5O_6 ; it has recently been found by J. Férée² to be $\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

In 1890, Placet and Bonnet took out patents in many countries dealing with the electrodeposition of the metal. In the American patent 526,114, September 18, 1894, may be found a summary of their claims, which cover a very wide range. They state that the most important compound from which chromium may be obtained commercially is chromic acid; that at concentrations of from one to two percent the metal may be precipitated but the deposition is more abundant the more concentrated the solution. They have also employed other compounds such as the chromates and bichromates, the sulphate or nitrate of chromium, chrome alum or other chromic salts; in all of these cases they add an alkaline sulphate or an alkaline earth metal to increase the deposition. They state that prior to their invention

¹ Pogg. Ann. 91, 119 (1854).

² Bull. Soc. Chim. Paris (3), 25, 620 (1901).

"it is well known that no articles electroplated with chromium were ever produced."

At the suggestion of Le Blanc, Schick¹ attempted to repeat the experiments with some of the solutions specified by Placet and Bonnet, but obtained mere traces of chromium. Le Blanc states: "Diese Resultate stimmen auch mit gelegentlichen Arbeiten anderer Forscher überein, die ebenfalls beim Arbeiten nach den gegebenen Vorschriften keine Chromniederschläge bekommen konnten.² Danach kann es keinem Zweifel mehr unterliegen, dass das der französischen Akademie von Placet vorgelegte Kilogramm Chrom³ nicht auf dem angegebenen Wege erhalten worden sein kann oder dass wenigstens die zur Erzielung von guten Chromniederschlägen wesentlichen Bedingungen dort nicht angegeben worden sind." A more detailed discussion of this criticism will be given in a later paper.

The patents of Placet and Bonnet were followed by those of Möller and Street (1898) who used in their cathode chamber chrome alum, sodium sulphate, and water, in equal parts by weight. The current density employed was 40 amperes per square decimeter, the range being very limited; the temperature was 90° C. The yield per ampere hour, as given in the English patent, indicates a current efficiency of about thirty percent. The patent claims relate mainly to the byproducts at the anode and the maintenance of the composition of the solution.

In 1900, Cowper-Coles⁴ found that a 25 percent chromic chloride solution at a temperature of 190° F (88° C) and with a current density of 40 to 50 amperes per square foot (approximately 4.3 to 5.3 per square decimeter) gave good deposits of chromium, especially when hydrochloric acid was added to redissolve the precipitated oxide. Other solutions were tried, but with unsatisfactory results.

J. Férée⁴ electrolyzed solutions containing 10 percent hydro-

¹ "Darstellung des Chroms und seiner Verbindungen," p. 16.

² Cowper-Coles: *Chem. News*, 81, 16 (1900); J. Férée: *Bull. Soc. Chim. Paris* (3), 25, 617 (1901).

³ *Comptes Rendus*, 115, 945 (1892).

⁴ l. c.

chloric acid and 16 percent crystalline chromic chloride with current densities of 15 amperes per dcm^2 , obtaining excellent deposits. Using the same current density but a solution containing one-gram molecule of chromic chloride to three gram-molecules of potassium chloride per liter, he again obtained excellent deposits, with a current efficiency of 45 percent; the latter was determined by weighing the metal deposited.

In describing the method used by Bunsen, Borchers¹ states: "The author has frequently repeated this experiment and for the purpose of obtaining large amounts of the metal has altered the conditions of the experiment within certain limits but has always obtained satisfactory results by working within the limits of current density named and by using a high concentration in the cathode cell."

It was however the most recent work on this subject² which, by its unusual results, first attracted our attention to this subject. Neumann's student, Glaser, worked with solutions of chromic chloride, sulphate and acetate in the cathode chamber, while the anolyte consisted of mineral acids or salt solutions. The results for the chloride (100 grams metal per liter) are given in Tables I and II. The first table gives the effect of variation of the current density, the latter being expressed in amperes per square decimeter.

TABLE I

Current density	Products separated	Percent current efficiency
0.9	Chromous-chromic oxide	
1.8	First metal, then chromous-chromic oxide	
3.6	Metal mixed with chromous-chromic oxide	
4.5	Thin metallayer, later chromous-chromic oxide	5.4
7.2	Metal with less chromous-chromic oxide	23.4
9.1	Pure metal	38.4
13.7	Pure metal with crystal projections	38.0
18.2	Pure metal, mostly crystalline	38.6

¹ "Electrometallurgy," p. 366 (1897).

² Neumann: *Zeit. Elektrochemie*, 7, 656 (1901).

As noted above, the work of Férée seems to indicate that the chromous-chromic oxide is not separated.

The manner in which the nature of the deposit is affected by variation in the concentration of the solution is indicated in Table II. The current density is not given but was presumably kept constant.

TABLE II

Grams metallic chromium per liter	Products separated	Percent current efficiency
210	Metallic powder mixed with chromous chloride	—
184	Metallic powder mixed with chromous chloride	—
158	Pure metal	56.6
135	Pure metal	49.0
105	Pure metal	38.4
79	Metal, then chromous-chromic oxide	—
53	Chromous-chromic oxide and hydrogen	—
26	Traces of chromous-chromic oxide, strong hydrogen evolution	—

These results were obtained at room temperature; in speaking of the effect of temperature, Neumann states that above 50° the chromium separated as a black powder, but that the efficiency changed but slightly.

With a different anode solution (not specified) he was able to obtain much higher efficiencies. In regard to this point Le Blanc states (p. 28): "There follows the incomprehensible remark that the current yield was increased from 57 percent to 89.5 percent by changing the anode solution. Or should this read by changing the cathode solution?"

The acetate solutions gave poor deposits and very low efficiencies.

According to Neumann, the electrolysis of chromium solutions would appear comparatively simple, and at first sight might seem to allow of easy duplication. This we have not found to be the case, for some factors which cause variation have not been considered at all. The temperature factor is by no means unimportant. He states nothing as to the length of the tests,

the volume of the solution used, the area of solution exposed to the air, and other factors which in this particular case are of very considerable importance, especially the effect of the presence of the chromous salts formed during the progress of the electrolysis; nor is any statement made in regard to the very important experimental detail of the method of measuring efficiencies. Since many of these factors do not enter into the ordinary problems of deposition of metals, a formulation will now be attempted.

4. *Statement of the Chemical Problem.*—In the electrolysis of chromic chloride in aqueous solutions it is found that in the cathode chamber the current can produce results in the following way:

- (1) Formation of chromous salt.
- (2) Evolution of hydrogen.
- (3) Precipitation of metallic chromium.
- (4) Precipitation of an oxide or hydroxide.

The formation of oxy-salts is also a possibility. Moreover in the solution itself secondary reactions of a purely chemical nature may take place.

(a) Hydrolysis of the chromic salt with liberation of free hydrochloric acid or free base.

(b) Reaction of the chromous chloride with hydrochloric acid, forming chromic chloride and hydrogen.

(c) Absorption of oxygen from the air by the chromous chloride.

(d) Re-solution of the precipitated metallic chromium in the electrolyte, due to the metal being in its most active state.

(e) Diffusion of anode products to the cathode chamber and subsequent reaction.

These reactions change of course with the relative and absolute concentrations of the reacting substances; these are the chromic salts (at least two modifications), chromous salts (probably two modifications), basic salts, and free acid.

To determine then with absolute exactness the nature of the solution, there should be given, or in some way designated, the concentration of the following quantities: chromic chromium,

chromous chromium, and acid radical. In the present work the products have not been analyzed at all stages, but it is hoped that sufficient data are given to allow reproduction of results.

Other variables that enter into the problem are the current density, temperature, solubility of the products of electrolysis, rate of diffusion of anolyte, velocity of the various reactions, and consequently the complete history of previous electrolysis and treatment of the solutions.

The factors that can be controlled more or less readily are the initial concentrations, the presence of air, the temperature and the current density. The control of these has guided us in the choice of the method employed.

5. *Apparatus and Method*—The usual arrangement of a two-compartment cell was used. In a large beaker was placed the porous cup which served as the diaphragm. In the experiments up to 51, the outer chamber was filled with dilute sulphuric acid ($d = 1.12$), the anode being a cylinder of lead. The porous cup which was filled with the chromium solution contained also a copper rod which served as the cathode, its cylindrical shape ensuring uniform current density. The temperature of the cathode solution could be controlled by passing through the glass spiral immersed therein water of any desired temperature. The porous cup had an internal diameter of 4 cm, and a working depth of 7 cm. The cathode wire had a diameter of 4 mm.

The general procedure was to electrolyze, using a well-cleaned copper cathode until 133 cc of hydrogen, corresponding to about 1000 coulombs, had been given off in the alkaline nickel voltameter. This electrode was then replaced by another and the amount of the deposit determined while a second electrode was being plated; in this way many entirely independent determinations were made in long runs on the same solution.

In the earlier stages of the work, the amount of metal deposited was determined by weighing, but a quicker method was soon required and devised. This consists in measuring the volume of the hydrogen evolved when the metal was dissolved in

15 percent hydrochloric acid. Our results confirmed those already recorded in the literature that the metal dissolves to form *chromous* and not chromic chloride, although the latter is formed slowly by the interaction of the acid on the chromous salt. No periodicity in the velocity of solution has been observed; this confirms the work of Brauer who ascribes this phenomena to impurities in the metal.

Previous workers have probably determined the current efficiency by weighing the metal deposited and then applying Faraday's Law, assuming that the metal was trivalent. In this work, we have deposited the metal from a solution in which the metal was trivalent and dissolved it to form a solution in which it is divalent. *To admit of comparisons with the efficiencies obtained by other observers¹*, the volume of hydrogen actually given off on dissolving the metal must therefore be increased by fifty percent. In all the tables given therefore the "efficiency" column indicates three halves of the observed number of cubic centimeters of hydrogen evolved by solution of the metal which was deposited when 100 cc of hydrogen was evolved in the voltameter.

Experimental work was done on solutions of the chloride, sulphate and oxalate of chromium. The experimental results have now to be considered.

6. *Electrolysis of the Chloride Solutions.*—To effect solution, the red insoluble chloride (Bender and Hobein C. P.) was moistened with water and put into the cathode chamber. With a platinum wire as cathode, a current was passed for a short time, causing the formation of a small amount of chromous chloride whose presence as is well known accelerates the velocity of solution of the chromic salt. Another method which we

¹ It is not claimed that either the previous workers or ourselves have applied Faraday's Law to this case correctly when we assume that the trivalent ion is the one from which the metal is deposited; in fact there is every reason to believe that in this case where trivalent and divalent ions are involved in equilibrium relations, the theoretical 100 percent current efficiency must be calculated on the assumption of an intermediate but determinable valency. In view of our present ignorance of this subject, it has seemed advisable to adhere to the previously used methods of calculating efficiencies.

have devised consists in suspending the insoluble salt in water, adding a fragment of electrolytic chromium and a drop of hydrochloric acid and heating for a very short time. The concentrated solutions thus obtained held about one hundred grams of metallic chromium per liter and had a specific gravity of 1.185 at $t = 20^\circ$; two others $d = 1.120$ and 1.260 were also employed when examining the effect of anolyte variation.

Maintaining the temperature constant at 20° , we now determined with the 100 gram solution the effect of current density upon the metallic deposit. The strongest and most adherent deposits were obtained with densities ranging between 10 and 40 amperes per square decimeter. When the range was extended from 40 to 90 amperes, the deposits became very much poorer while platings made between 90 and 200 amperes were so crystalline and had such little adherence that a paper edge could easily brush them away.

The quality of the deposit was greatly improved when the cathode was rotated quite rapidly; in fact the current density could then be doubled and still give a deposit as good as was obtained with the stationary electrode at the lower density.

A rise of temperature to 45° caused greater deterioration in the quality of the deposit than a change in the current density from 30 to 100 amperes.

The range of concentration of the solutions from which the metal may be deposited depends to a great extent upon the temperature. When the variables were properly controlled, it was found possible to obtain the metal from solutions containing one-half to one quarter of the minimum found by Neumann—53 grams per liter, $t = 15^\circ$. Since in his paper he has stated nothing in regard to the control of his temperature, it seems probable that he disregarded the very considerable heating effect due to the high resistance of the more dilute solutions.

The questions at once arise—why has the temperature so marked an effect, and what influence upon the result has the chromous chloride which is formed by reduction?

The 100 gram chromic chloride solution was electrolyzed

for several hours, the efficiency being determined at intervals of ten minutes. The results are given in Table III. The first

TABLE III.—CATHOLYTE, CHROMIC CHLORIDE CONTAINING 100 GRAMS METAL PER LITER

Experiment number	I Tempera- ture	II Current density	III Percent efficiency
1	21°	50	4.5
2	24	51	6.7
3	23	50	9.0
4	23	53	11.2
5	23	51	12.5
6	22	51	16.7
7	22	50	19.5
8	21	50	22.5
9	20	51	25.9
10	20	51	28.0
11	19	50	29.2
12	19	49	28.0
13	21	47	28.0
14	20.5	47	28.0
15	21	49	29.2
16	22	50	29.2
17	22	51	29.2
18	22	51	28.0
19	22	22	23.4
20	22	22	23.4
21	22	70	27.0
22	22	70	30.4

column indicates the temperature, the second the cathode current density per square decimeter, the third the efficiency.

Since the time required for each test was 10 minutes, Curve I plotted from the first eighteen results of Table III uses time in minutes as abscissa, hydrogen efficiency as ordinate. The curve indicates that, while at the outset the efficiency was very low, it steadily increased to the tenth measurement when it remained practically constant. Other and frequent experiments have shown a state of affairs exactly similar to the results obtained in the series ranging from (10) to (18)—that a fairly constant value of the efficiency (about 29 percent) may be main-

tained for long runs provided that the temperature, current density, and concentration are maintained constant. The nineteenth and twentieth tests showed that by lowering the current density the efficiency was lowered, while the last two tests showed that it was increased by raising the density. In these

Fig. 1.

runs, the total chromium content had changed but very little by the removal of the small amounts of metallic chromium from the solution.

To explain the peculiar course of the curve, one may ask what chemical action takes place in the cathode chamber. Reduction of mercuric chloride proved that chromous chloride was formed. This compound, however, absorbs oxygen with very great rapidity. The rate at which this takes place will depend on the concentration of the chromous salt, the area of surface exposed to the air, the agitation and rate of change of the surface and the temperature.

The influence of the temperature was next examined; a chromic chloride solution of the same concentration was used. The current density was constant at 50. The results are detailed in Table IV.

TABLE IV.—CATHOLYTE, CHROMIC CHLORIDE CONTAINING 100 GRAMS METAL PER LITER

Experiment number	Temperature	Percent efficiency
23	52	Several runs, traces of metal
24	52	13.5
25	43	20.0
26	31	25.5
27	31-27	28.5
28	27-24	29.2
29	24-24	33.0
30	16	27.0
31	17	27.0
32	17-27	27.0
33	27-28	30.0
34	40	18.0

Long-continued runs at 50° showed very poor efficiencies under the same conditions which at 22° had given fair efficiency (Table III). Finally as much as 13.5 percent could be obtained at 52°, where at 22°, 28.5 percent had been found. On lowering the temperature the efficiency increased, having a maximum for this concentration at about 24°. At 16° the efficiency is lower than at 22°; other experiments show continuously decreasing efficiencies down to the lowest temperature at which we worked, zero degrees. Neumann has stated that the effect of temperature variation is slight; the results above given show that under some conditions at least this is not the case.

The time runs and the temperature tests offer evidence that the *chromous chloride is necessary to the deposition of the metal and that increase of temperature is not favorable to a high degree of concentration of the chromous salt in the solution.* But more direct evidence of the effect of oxidation was sought.

A solution of chromic chloride of the same concentration was electrolyzed until nearly constant results were obtained. Air and gas were then passed through this at intervals; the results are recorded in Table V and plotted in Curve II. Since

the time required for each test was 10 minutes, the ordinate employed is time. Current density was constant at 70.

Fig. 2.

TABLE V.—CATHOLYTE, CHROMIC CHLORIDE, 100 GRAMS METAL PER LITER

Experiment number	Temperature	Percent efficiency
35	21°C	24.0
36	21	24.0
Air bubbled through the solution		
37	24-22	15.7
38	22	12.4
39	22	10.0
40	20	9.0
Stopped air blowing		
41	19	12.3
42	19	14.7
43	20	16.8
Gas passed		
44	19	15.7
45	19	18.0
46	19	18.0
47	18	16.8
Gas stopped		
48	18	16.8
Air passed		
49	22	11.2
50	20	7.9
51	13	5.7

It will be noticed that when air was passed into the cathode chamber, the efficiency fell continuously; that on stopping the blast it started to rise; that the stirring effect of an indifferent gas did not increase the efficiency materially but that on starting the current of air the yield again fell very decidedly.

Positive evidence as to the occurrence of a vigorous reaction between the air and some constituent of the solution is also given by the sudden rise in temperature of three to four degrees which took place when the air blast was started. The temperature of the air before passing was the same as that of the solution. Recoura¹ has determined the heat of oxidation of chromous chloride and found that very few substances absorb oxygen so vigorously.

There is every indication therefore that the current efficiency is closely connected with the presence in the solution of the chromous chloride. It is not maintained that the oxygen of the air is the only agent which tends to destroy this salt for there is every evidence² that it decomposes in the presence of hydrochloric acid, liberating hydrogen; increase of temperature would probably tend to accelerate this reaction, thus giving a reason for the decreased efficiency after a certain temperature has been reached. If now the efficiency depends upon the presence of the chromous chloride, not merely must the oxygen absorption be eliminated but the conditions for avoidance of the decomposition of the chromous chloride must be discovered. This presents the problem as one of general chemistry, involving the equilibrium and reaction velocities in the system chromium, hydrochloric acid, chromous and chromic chlorides, and hydrogen; the solution of this problem would help materially in advancing our knowledge of the electrochemical deposition of the metal from the chloride solutions.

From the theory of equilibrium the constancy of efficiency noted above is readily explained. It is probable that in the solution ratio of the relative masses of the chromous and chromic compounds has become practically constant. Whatever affects the

¹ *Ann. Chim. Phys.* (6) 10, 18 (1881).

² *Döring: Jour. prakt. Chem.* 66, 65 (1902).

equilibrium, will influence the current yield; and as the equilibrium is affected by many chemical factors so also must be the electrochemical efficiency. This would easily explain the difference in the efficiencies obtained by different observers and indicate how difficult it is to obtain comparable conditions.

7. *Change in Anode Solutions.* In Neumann's paper, the statement was made that the anode chamber held mineral acids or salt solutions. Although nothing is stated as to the nature or the concentration of these anode solutions, the reader is told that by the alteration of the *anode* solution the yield was increased from 57 to 89.5 percent. If this statement be correct—and its accuracy was questioned by LeBlanc—the results produced by variation of the anolyte must indicate some of the factors which increase the efficiency.

To serve as anode solution, the following were made: normal potassium chloride and potassium hydroxide, sulphuric acid of specific gravity 1.13, ammonium ferrous sulphate three hundred grams per liter, ammonium oxalate saturated at room temperature, and ammonium hydroxide of the concentration ordinarily employed in the laboratory.

Since it is almost impossible to clean porous cups in any reasonable time (even by boiling for a week with distilled water changed twice a day), experiments were made at this stage to replace them by parchment fat extractors. These had to be discarded temporarily because of their small size, and the difficulties involved in making efficient cooling coils. Extra care was therefore taken to wash the cups as free as possible from soluble material. After this and before use, the cups were filled with the solution of the chromic chloride which diffused slowly outward.

In the experiments recorded in Table VI, the cathode solution was made from the red sublimed chloride which was dissolved by the methods already described. The density of the solution was 1.120, $t = 18^\circ$; the cathode solution and current density ($D = 57$) were the same in each test, the anode solution along being varied. For the first ten runs an attempt was made

to keep the temperature constant, after which it was allowed to rise. The runs as before were in a continuous series.

TABLE VI.—CATHOLYTE, CHROMIC CHLORIDE SOLUTION,
 $d = 1.120$, $D = 57$

Anolyte, sulphuric acid		Anolyte, ammonium hydroxide		Anolyte, ferrous ammonium sulphate		Anolyte, ammonium oxalate	
Temp.	Percent efficiency	Temp.	Percent efficiency	Temp.	Percent efficiency	Temp.	Percent efficiency
23	10.6	23	8.2	23	8.5	25	6.1
25	10.8	24-27	12.1	24-27	12.3	27	16.5
25	11.2	27	14.7	27	13.9	27	18.0
25	9.0	27	15.7	27	15.7	27	19.1
25	9.0	27	16.9	27	16.9	27	22.5
25	9.0	27	18.0	27	18.0	28	19.6
25	9.0	27	18.6	27	18.3	28	19.1
25	7.5	27	18.0	27	16.9	28	19.6
25	4.5	27	14.7	27	15.7	28	19.2
25	3.4	27	11.2	27	14.7	28	21.4
25-30	9.0	27-45	4.5	27-39	10.8	28-35	20.2
30-35	9.0	—	—	39-44	5.7	35-40	19.6
35-36	9.0	—	—	44-53	3.3	40-43	19.2
36-38	7.9	—	—	53-59	1.1	43-45	19.2
						45-47	19.2
						47-49	16.8

Toward the end of every run, the deposits of metal became very poor. With sulphuric acid in the anode chamber, the deposits became very irregular; with ammonium hydroxide and ammonium ferrous sulphate the deposits were poor after the eighth test, hydroxide being apparently precipitated; with the oxalate the deposit became poor after the tenth test.

From these experiments one conclusion drawn by Neumann is confirmed—the efficiency may be increased very materially by change of the *anode* solution; but the results of Table VI show that in almost every case tried, *the efficiency rises, passes through a maximum and then falls again*. This effect had not been noticed in the electrolysis of the solution $d = 1.185$, with sulphuric acid as anolyte; if it is due to diffusion, it should be less marked the more concentrated the cathode solution.

Runs were now made with a more concentrated chromic chloride solution, $d = 1.260$, $D = 70$. Results are given in Table VII.

TABLE VII.--CATHOLYTE, CHROMIC CHLORIDE SOLUTION,
 $d = 1.260$, $D = 70$

Anolyte, sulphuric acid		Anolyte, ammonium hydroxide		Anolyte, potassium chloride		Anolyte, potassium hydrate	
Temp.	Percent efficiency	Temp.	Percent efficiency	Temp.	Percent efficiency	Temp.	Percent efficiency
24-27	13.5	27	39.4	27	23.7	26	31.5
27	20.3	27	38.3	26	25.9	26	30.3
29	19.1	27	37.0	26	26.4	26	30.3
30	24.1	27	37.0				
29	22.9	30-34	34.2				
29	22.9	34-38	38.3				
29	21.9	38-41	40.5				
28	20.3	41-43	42.7				
28-34	20.3	43-45	46.0				
34-38	13.5	45-46	50.5				
39	12.4	46-48	47.2				
		48-49	48.5				
		41-36	47.2				
		34-32	46.0				
		31	41.5				

With sulphuric acid, the efficiency after first increasing falls off with the time of the run; it is, however, very much greater than with the more dilute chloride solution. With ammonium hydroxide we wished to find the efficiencies when the temperature was not maintained constant; the results showed that there was a decided increase in efficiency as the temperature was raised up to 45° ; in fact the highest efficiency obtained with chloride solutions was found here.

The results of Tables VI and VII indicate that diffusion from the anode solution is a very important factor. The oxygen dissolved therein does not seem to be so very important. This is evidenced by the slight difference between the last three anode solutions in Table VI, but the increase in acidity which

we have previously found to lower the efficiency again appears important. Naturally, the presence of a base which may precipitate the hydroxide must be avoided; but the results seem to indicate that the diffusing base effects the equilibrium relations, perhaps displacing the relative masses of the compounds so as to favor higher efficiencies of metal deposition.

8. *Electrolysis of the Sulphate Solutions.*—Concurrently with the work on the chloride, experiments with the sulphate solutions were made to ascertain if higher efficiencies might be obtained with these.

The solutions used were analyzed, the chromium being determined as chromic oxide, the acid radical as barium sulphate. The salt was found to be strongly basic, having an excess of 14.1 percent of the chromic oxide; this excess is very frequent with the salts of chromium. With this salt, a solution of specific gravity 1.41 (hydrometer) was prepared; it contained 135 grams of chromium per liter. From this supersaturated solution a salt crystallized; the specific gravity of the solution became 1.398, the metallic content dropping to 127 grams per liter, corresponding to a 34 percent solution of the sulphate. A solution of specific gravity 1.250 was found to contain 83 grams per liter, one of specific gravity 1.172 held 59 grams, while for 28.5 grams per liter the specific gravity was 1.087.

In the tests, 100 cc of the solution were used in the cathode chamber, while the anode solution in all of the runs (except in Table XI) consisted of sulphuric acid $d = 1.12$. The current efficiencies were determined in the same manner as before.

In the first tests it was found that solutions holding 29.5 grams per liter (sp. gr. 1.087) yielded only traces of metal even after an hour's run; careful variations would undoubtedly have improved the yield very materially.

Table VIII gives an illustration of results obtained in a continued run when the current density and the temperature were allowed to vary simultaneously. In the next table current density and temperature were maintained constant and the effect of time of run and initial concentration examined. For the more dilute solution (59 grams) the efficiency rises rapidly

TABLE VIII.—CATHOLYTE, CHROMIC SULPHATE SOLUTION,
 $d = 1.142$ at 23°C

	Current density	Temp.	Efficiency
1	55	25°C	21.0
2	55	31	28.5
3	47	27	24.0
4	33	27	21.0
5	33	24	24.0
6	17	20	15.0
7	19	18	19.5
8	35	21	25.5
9	50	24	39.0
10	67	29	51.0
11	67	29	64.5
12	130	31	70.5
13	67	26	51.0
14	67	26	57.0
15	67	25	51.0
16	36	25	46.5
17	36	25	48.0
18	36	20	43.5
19	36	20	48.0

to a maximum, then falls even more rapidly. This cannot be accounted for by a decrease in the amount of metal but is probably due to an increase in the acidity of the solution.

When the solution held 87 grams per liter, very good deposits were obtained from the start. After being electrolyzed for five hours, the solution was put into a stoppered bottle; the next morning it was found to have liberated considerable hydrogen. The efficiency (28) was lower (although the temperature was slightly higher) and continued to fall during the subsequent two hours' electrolysis. But on the removal of the cooling coil (results not detailed in the table) the efficiency rose until at 36° , 40.5 percent efficiency was obtained, while cooling to 20° almost immediately decreased the hydrogen equivalent to 6 percent, then to 2.2 percent. Increase of temperature increased the yield to the figures previously obtained. With the most concentrated solution the current efficiency was at first much lower than with the other two solutions. After the

TABLE IX.—CATHOLYTE, CHROMIC SULPHATE

	59 grams Cr. per liter			87 grams Cr. per liter			135 grams Cr. per liter		
	Current density	Temp.	Percent efficiency	Current density	Temp.	Percent efficiency	Current density	Temp.	Percent efficiency
1	31	19°	6.7	29	17-19°	5.7	30	24-25°	1.1
2	32	19°	9.0	28	17-19°	8.4	30	25-24°	2.4
3	32	19°	12.7	28	17-19°	11.4	30	24-22°	6.1
4	34	19°	12.4	28	17-19°	12.9	30	22-23°	6.9
5	33	19°	15.0	31	17-19°	17.1	31	23-24°	7.9
6	31	19°	15.7	31	17-19°	18.0	31	24-24°	11.7
7	30	19°	17.2	31	17-19°	17.3	32	24-24°	12.9
8	30	19°	17.9	31	17-19°	20.4	32	24-23°	15.1
9	31	19°	19.8	32	17-19°	23.7	31	23-24°	18.1
10	31	19°	22.5	32	17-19°	26.2	32	24-24°	20.5
11	31	19°	28.1	32	17-19°	28.0	32	24-23°	22.1
12	32	19°	30.4	32	17-19°	26.4	31	23-23°	23.5
13	32	19°	22.5	32	17-19°	28.3	30	23-23°	25.3
14	33	19°	18.0	33	17-19°	28.6	30	23-22°	27.0
15	33	19°	14.5	33	17-19°	29.2	30	22-22°	31.5
16	33	19°	10.2	33	17-19°	31.4	34	22-23°	29.8
17				34	17-19°	31.5	32	23-23°	21.9
18				34	17-19°	30.4	32	23-23°	22.8
19				34	17-19°	29.3	31	23-24°	25.3
20				34	17-19°	31.5	31	24-25°	27.0
21				34	17-19°	32.5	32	25-24°	28.1
22				33	17-19°	32.5	33	24-25°	28.1
23				33	17-19°	31.9	34	25-25°	28.1
24				33	17-19°	31.9	33	25-25°	28.1
25				33	17-19°	32.5	34	25-26°	30.3
26				33	17-19°	31.9	—	—	—
27				34	17-19°	31.5	—	—	—
28				33	24	27.0	38	27-26°	33.7
29				33	22	28.6	38	26-26°	36.0
30				34	21	23.5	34	26-25°	36.0
31				32	20	25.9	34	25-25°	36.0
32				32	19	25.9	34	25-24°	36.6
33				30	19	24.7	33	24-22°	36.0
34				31	19	25.9	33	22-26°	37.1
35				31	19	24.9	33	26-29°	37.6
36				31	19	24.7	34	29-33°	38.3
37				30	19	24.7	34	33-35°	40.5
38				31	19	18.0			
39				31	19	18.0			
40				33	19	13.5			

sixteenth test, the solution was removed. Again hydrogen evolution was observed and also a much lower efficiency for the seventeenth test; the efficiency rose slowly as long as the temperature remained constant at 24–25°. Increase of temperature then raised the efficiency—a fact which is very noticeable in dealing with the sulphate solutions. This is also confirmed by the results given in Table X, obtained with a solution containing 87 grams per liter.

TABLE X. — CATHOLYTE, CHROMIC SULPHATE CONTAINING 87 GRAMS METAL PER LITER

Temp.	Current density	Percent efficiency
17–30	60	14.5
26–40	65	24.7
44–49	70	27.0
52–54	70	30.5
60–62	70	37.2
66–67	70	45.0
38–38	70	39.1
30–32	70	34.9

With the same solution it was possible to obtain at temperatures of 40–55° good deposits with a steady current efficiency of 30 percent extending over hours at a time.

In the electrolysis of the sulphate solutions we have not examined the effect of anolyte variation; there seems no doubt, however, that the cathode efficiency will be affected by diffusion, and that a continued high efficiency requires careful control of diffusion.

We have already noted that hydrogen is evolved whenever an electrolyzed solution is allowed to stand and that the current efficiency is invariably lower thereafter. The extent to which the chromic salt is reduced may be noted in the following table for the electrolysis of a solution containing 53 grams of the metal per liter, the gas evolved at the cathode and that evolved on the subsequent solution of the metal being noted. The hydrogen given off in the alkaline voltameter was 133.3 cc; the amount of hydrogen used in reduction is obtained by subtract-

ing from 133.3 cc the sum of the values recorded in the two columns preceding.

TABLE XI.—ELECTROLYTE, CHROMIC SULPHATE CONTAINING 53 GRAMS METAL PER LITER

Temp.	Amps.	cc hydrogen evolved at cathode	(cc hydrogen evolved by chromium) $\times 1.5$	cc hydrogen used in reduction
23-27	3.4	63.0	18.00	52.3
27-32	4.0	69.3	26.25	37.4
32-38	4.1-4.5	61.0	37.5	34.8
35-40	4.5	62.0	44.25	27.1
41-44	4.5	67.0	46.5	19.8
43	4.5	65.6	52.2	15.5

From these and similar experiments the reduction to the chromous salt seems to be favored by low temperatures; on the other hand, we note that the current efficiency for deposition of the metal is increased on raising the temperature.

The effect of air on the sulphate solution was examined in the same way as with the chloride, the solution used being the two-thirds concentrated. With temperature constant at 23°, current of 2.2 amperes, five consecutive runs showed efficiencies of 12.4, 13.5, 15.6, 16.8, and 19.1 percent; when air was blown in at rate of one liter per minute, the temperature remained practically constant, and the efficiencies fell slowly from 18.4 to 15.7, 14.6, 13.9 percent. The lowering of the efficiency was quite marked but by no means so rapid as in the case of the chloride.

A very interesting fact was observed when to avoid oxidation at the surface we added toluene or petroleum ether—the efficiency of metal deposition was reduced in a short time almost to zero.

Preliminary experiments made with both chloride and sulphate solutions showed that with rotating electrodes, better deposits might be obtained over a wide range of current density; since the efficiencies were somewhat lower than with stationary electrode, their use was abandoned. The effect, it will be

noticed, is that of producing more rapid oxidation by the air, which must, of course, be avoided so far as possible.

9. *Conclusions.*—From our experiments the following conclusions are drawn :

(1) The presence of chromous salt appears to be essential to the successful deposition of the metal from its chloride or sulphate solutions. This has been proved by showing (*a*) that the current does work in reducing the chromous to the chromic salts; (*b*) that it is necessary to electrolyze the chromic salts for some time before the metal can be deposited with any considerable efficiency; and (*c*) that the efficiency is destroyed by oxidation of the chromous salt.

(2) Temperature has a very decided influence upon the efficiency of deposition; this result is in direct opposition to those recorded by Neumann. For each especial set of conditions there seems to be a temperature at which the loss in efficiency caused by the decomposition of the chromous salt is balanced by increased efficiency caused by other factors. For example, it was found that after the sulphate had been electrolyzed for some time, rise of temperature increased the efficiency; the same result was observed when the current density was lowered. For a chloride solution between 0° and 16°, the same effects were noticed. As might be predicted, the more concentrated the solution, the higher the temperature which may be advantageously employed.

(3) The nature of the anode solution affects the yield very considerably; that this is probably due to the diffusion of the anolyte into the cathode chamber is indicated by the peculiar results obtained in the continued efficiency runs.

(4) On continued electrolysis of the solutions of chromic salts, the efficiency rises from zero to a value which is practically constant. This may be accounted for by assuming that the absolute and relative masses of the chromous and chromic salts have, under the conditions employed, become practically constant in the solution. Any factor tending to change these relations will affect the current efficiency—for example, change of temperature, increase of acidity, change of concentration and the presence of catalytic agents such as toluene or petroleum ether.

(5) In the ordinary problems of electrochemistry, it is conceivable that in reducing from the higher stages of oxidation, that solution from which metal can be deposited may not be obtained. *For this reason solutions in which the metal shows its lowest valency should in this and in all analogous cases be used when it is desired to obtain good current efficiencies in the deposition of metal.*

We have also noted that the quality of the deposit is always bad when the current efficiency is less than five percent; an acid bath favors hard and strong deposits but causes lower efficiencies.

Any one who will study the electrodeposition of this metal will be impressed by the great number of factors which must be controlled; and it sometimes happens that the exact definition of conditions for the reproduction of the experiments are difficult. With the time at our disposal we have had to restrict the number of variations to be studied, but we believe that we have considered some of the factors which are usually overlooked in electrochemical work but which are of considerable importance.

*Cornell University,
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