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MECHANISM OF CHROMIUM DEPOSITION FROM THE CHROMIC ACID BATH

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ABSTRACT

In commercial electroplating chromium is deposited from baths composed principally of chromic acid in which the chromium is sexivalent. After use, such baths always contain some trivalent chromium, and many of the theories which have been proposed for this process postulate that the chromium is deposited from the trivalent (or possibly bivalent) state, for which the chromic acid serves as a reservoir.

In this paper evidence is presented that the electrolytic deposition of chromium occurs directly from the sexivalent state. The principal evidence is the fact that relatively large additions of compounds of metals such as zinc, nickel, cadmium, iron, and copper have no such effect upon the behavior of the chromic acid bath as would be expected if deposition occurred from the trivalent state. It is shown by cryoscopic and spectrophotometric data that the dichromates of these metals are strongly ionized.

The low efficiency and high polarization in chromium deposition are accounted for, and certain paradoxes are explained. The possible directions for improvement are pointed out, but none of them appears practicable with existing knowledge.

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I. INTRODUCTION

Chromium plating has been developed almost entirely as a result of empirical investigations, which is to be expected in view of the extreme complexity of the reactions upon which the process depends. It is reasonable to expect that if the mechanism were more thoroughly understood, improvements might be effected, for example in the cathode efficiencies and in the range within which bright deposits can be produced. It is the purpose of this and two previous papers (35, 37)¹ on this subject to throw light on the possible nature of the mechanism.

The special aim of this paper is to present evidence that chromium is deposited directly from the sexivalent state, that is, in a single step. An effort is made to explain the mechanism of such a process and to point out plausible solutions of certain paradoxes. The con-

¹ The numbers in parentheses here and throughout the text refer to the references at the end of this paper.

clusion of this analysis is that the chromic acid bath possesses great inherent possibilities thermodynamically even though no method was found to overcome the unfavorable kinetic features in the mechanism of reduction.

II. REVIEW OF PREVIOUS THEORIES

Any complete theory of chromium deposition must answer the following three questions. Why are sexivalent chromium compounds preferable to those of the lower-valence states? Why is an addition agent such as sulphate necessary? By what process is the chromic acid reduced to metal? Numerous authors have advanced theories to cover some of these points.

Carveth and Curry (7), who established the conditions for chromium deposition from the chromic acid bath, concluded that chromium is being deposited directly from the sexivalent state, and, in particular, from a positive sexivalent chromium ion whose concentration is greatly increased by the presence of sulphuric acid. Such a specific effect of sulphuric acid is not borne out by their own experiments, in which they demonstrated that sodium sulphate is also an effective addition agent (which is known in light of present knowledge to be just as effective as sulphuric acid). Moreover, in their hypothesis they assumed that chromic acid is a very weak acid, though actually it is very strong. Whether a positive sexivalent ion is present or important cannot be readily demonstrated. It is possible to show that, if it exists, its concentration must be extremely small. In the absence of definite evidence concerning its existence, it will not be considered.

Liebreich (14, 15, 36, 38) considers that the deposition is the result of successive steps such as $\text{Cr}^{\text{VI}}\text{Cr}^{\text{III}}\text{Cr}^{\text{II}}\text{Cr}^0$, each of which corresponds to a break on his cathode polarization curves. He reports four such breaks instead of the one (shown in fig. 1) that is generally accepted. The final step is the reduction of the chromous ion behind a protecting film of chromous and chromic oxides. He first thought that the sulphate plays no important role, but more recently he ascribed its beneficial effect to the solvent action of sulphuric acid upon the film of basic chromium compounds.

Sargent (13), Haring (16, 19), Ollard (21), and Piersol (28) all assume that deposition occurs from trivalent chromium ions, for the existence of which the presence of the sulphate is favorable. The evidence against this hypothesis is summarized in our first paper (35). Britton and Westcott (29) also consider that deposition occurs from the trivalent state, which is kept in a "suitably ionized condition" by the sexivalent chromium. Carveth and Curry (7) showed that sulphate-free chromic acid is not reduced at high current densities, which was explained by Sargent (13) as a result of the formation on the cathode of a film of reduced chromium compounds, which film he implied was permeable only to hydrogen ions. This idea constitutes the starting point for the explanation of the action of anions (like sulphate) in the next two theories presented.

E. Müller (18, 22, 23, 27, 34) concluded from a study of cathode polarization curves that reduction occurs directly from the sexivalent state. From the fact that the marked jump in potential (such as that shown in fig. 1) starts at a potential that is less negative

than the equilibrium reaction potential for $\text{Cr}^{+++}/\text{Cr}$ (about -0.4 volt), he assumes that the reaction that proceeds on the second part of the curve is one that has a smaller endergic (positive free energy) change (39) than that for $\text{Cr}^{+++}/\text{Cr}$, and in particular that this reaction is $\text{Cr}^{\text{VI}}/\text{Cr}$. Granting that such a relation between the break and the subsequent part of the curve is legitimate, the evidence is not conclusive that the reaction must be $\text{Cr}^{\text{VI}}/\text{Cr}$. This potential jump not only involves the production of chromium but also the liberation of hydrogen, which can occur at potentials considerably less negative than $\text{Cr}^{+++}/\text{Cr}$. Furthermore, the actual deposition of chromium occurs at polarization values that are substantially more negative than that for $\text{Cr}^{+++}/\text{Cr}$. The polarization curve is, therefore, not a true criterion of whether the chromium is being deposited from the sexivalent state.

Another argument that Müller presents in favor of direct deposition from the sexivalent state is that even large additions of trivalent

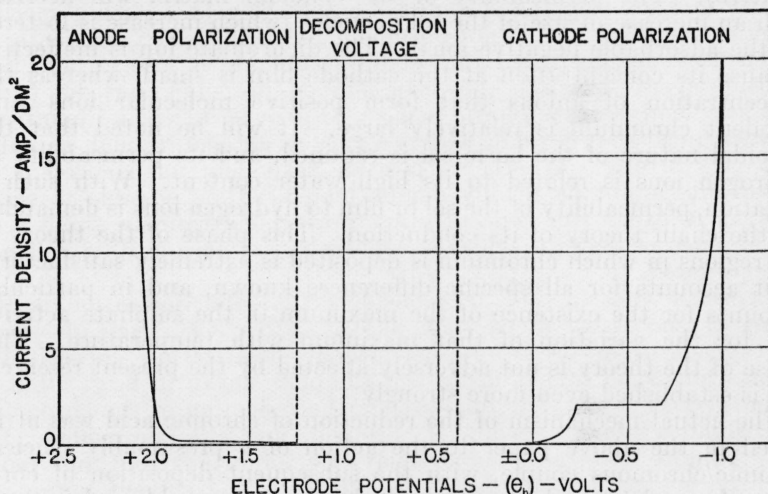


FIGURE 1.—Polarization of the chromic acid bath.

chromium do not have much effect on the cathode efficiency. It will be seen later that this is not a conclusive argument.

The first theory that Müller introduced to explain the action of the sulphate was that the sulphate coagulated the particles of the basic sol that formed the film which would otherwise prevent deposition. This explanation was abandoned by Müller, but a more elaborate version of this phenomenon is the basis of the theory of the action of the sulphate proposed by the present author (35).

In a later paper Müller advanced a second theory of the action of the sulphate. He made the special assumption that the film is composed of molecules of the basic chromate, which are oriented in such a way that the basic part of the molecule faces the cathode, and the acidic part the solution. He attributes the permeability to hydrogen ions to holes in the molecular film, and implies that the rate of exhaustion (by discharge) of the hydrogen ions is greater than the rate of dissolution of the basic molecules. If there exist in the system

negative ions of such a size that they may slip into the interstices, this action would permit hydrogen ions to exist longer in contact with the basic chromate molecules and in that manner effect their dissolution. Objections to this theory are that (a) it fails to account for the specific action of different anions; (b) it fails to account for the maxima in the relation of their activity with concentration; and (c) the consideration of the particles of the basic film (or sol) as molecules is not warranted. His assumption that the ion HSO_4^- is effective is unjustified, as this ion can exist only in a relatively low concentration at a pH of 3, which exists in the cathode film.

In a previous paper by the present author (35) the colloidal nature of the basic chromium chromate was demonstrated, and the range of pH in which it exists was given. Since the formation of a continuous film from sol particles is largely determined by the velocity of the particles, the rate of film formation can be extremely sensitive to the presence of adsorbable negative ions (the sol being electro-positive). The permeability of the colloidal matrix will decrease with an increase in size of the sol particles (which increase is fostered by the adsorbable negative ions). The dichromate ion is ineffective because its concentration at the cathode film is small, whereas the concentration of anions that form positive molecular ions with trivalent chromium is relatively large. It will be noted that the colloidal nature of the basic sol is retained, and its permeability to hydrogen ions is related to its high water content. With such a situation, permeability of the sol or film to hydrogen ions is demanded by the chain theory of its conduction. This phase of the theory in the regions in which chromium is deposited is extremely satisfactory, as it accounts for all specific differences known, and in particular accounts for the existence of the maximum in the sulphate activity and for the variation of that maximum with temperature. This phase of the theory is not adversely affected by the present research, but is established even more strongly.

The actual mechanism of the reduction of chromic acid was attributed in the above paper to the action of a presumably efficient chromic/chromous couple, with the subsequent deposition of chromium from the trivalent state. Such a process could explain most known facts of chromium deposition from the chromic acid bath. For example, it would be insensitive to additions of trivalent chromium because large amounts of trivalent chromium are produced from the dichromate ions. However, subsequent research (37) on deposition from the trivalent and bivalent salts of chromium showed that this couple could not be efficient in the chromic acid bath. Since then, there has been discovered a means of demonstrating that chromium is being deposited directly from the hexivalent state.

It is known that the ions of copper, nickel, zinc, cadmium, and iron can be more readily reduced to the metallic state than can trivalent or bivalent chromium, and that minute amounts of copper interfere with chromium deposition from chromic or chromous salts. There are indications in the literature that even high concentrations of the above ions are without effect upon the deposits from the chromic acid bath. It is upon this difference in behavior of the added ion in the chromic acid and chromic salt bath that the proof given in this paper is constructed. The experimental evidence is presented in the next section.

III. EVIDENCE THAT DEPOSITION OCCURS DIRECTLY FROM THE SEXIVALENT STATE

The evidence must first demonstrate that the state of the ions of copper and other added elements is the same in all systems considered; otherwise there would be no valid basis for comparison. As the existing data on the effects of these ions on the chromic acid bath were not as definite as was desired, they were redetermined. It is clear that if no effect of these added ions is found in the chromic-acid bath, the particular dichromate ions which are reduced to the metallic state do not exist at any time in a state that may be identified as trivalent or bivalent chromium. In the absence of conclusive evidence that chromium exists in other valence states than bi-, tri-, and sexivalent, the following proof shows that the reduction proceeds directly from the sexivalent state.

Although it was apparent from chemical principles that nickel, cadmium, and zinc dichromates are strong ionogens,² it was felt necessary to give a formal proof. Whether copper dichromate is a strong ionogen or exists as a molecular ion was not clear from existing data. The cryoscopic method was employed to demonstrate the nature of these salts and, where applicable, also the spectrophotometric method. The results of the cryoscopic method are given in table 1.

TABLE 1.—Freezing point depressions

Solution number	Metal ion 0.2 M	Chromic acid	Δ		Solution number	Metal ion 0.2 M	Chromic acid	Δ		
			Degrees C	Degrees C				Degrees C	Degrees C	
I.....		M	1.0		IV.....	Zn ⁺⁺	M	1.0	2.34	.75
II.....			0.6	1.59	V.....	Cd ⁺⁺		1.0	2.34	.75
III.....	Cu ⁺⁺		1.0	2.36	VI.....	Ni ⁺⁺		1.0	2.39	.80

Columns 5 and 10 of table 1 show the apparent freezing-point depressions (δ ° C) of the metal dichromates. These values are obtained by subtracting 1.59° (the depression for the residual or free chromic acid) from the total depressions. The expected value of the depressions for complete dissociation is 0.74° C. No particular significance is to be attached to the close agreement between the calculated and experimental values; but the results certainly demonstrate that these salts are strong ionogens and have about the same strength.

Absorption spectra were employed to study the copper and nickel dichromates. A Bausch and Lomb visual spectrophotometer was used and the cells were 2-cm thick. Figure 2 gives the absorbancies ($-\log T$, where T is the transmittancy) of solutions I to (with VI) compositions shown in table 1). The absorbancy of the pure chromic acid solution (no. I) lies below that of the solution containing cadmium (no. V) and above that of the zinc solution (no. IV). The latter relation is caused by the existence of the trichromate ion, $\text{Cr}_3\text{O}_{10}^{--}$, whose concentration is highly dependent on the acidity, and is therefore greater in no. I than in no. IV. The reason that the

² The term "ionogen" refers to an ionizable solute, which is often called an "electrolyte". The latter term will be reserved for the conducting solution.

cadmium solution absorbs more strongly than the pure chromic acid solution is not clear. Whether it is a deformation effect or is caused by true complex-ion formation was not established. With ionic systems the deformation effect can be related to the size and charge of the ions. It is therefore legitimate to assume that the deformations of the dichromate radical produced by the ions of nickel, copper, and zinc are the same, since these ions have identical charge and are close in atomic number.³

It has been known (1, 2, 3, 4, 6, 8, 9), that the absorbancy of the hydrated cupric ion, $[\text{Cu}(\text{H}_2\text{O})_4]^{++}$, is practically independent of its

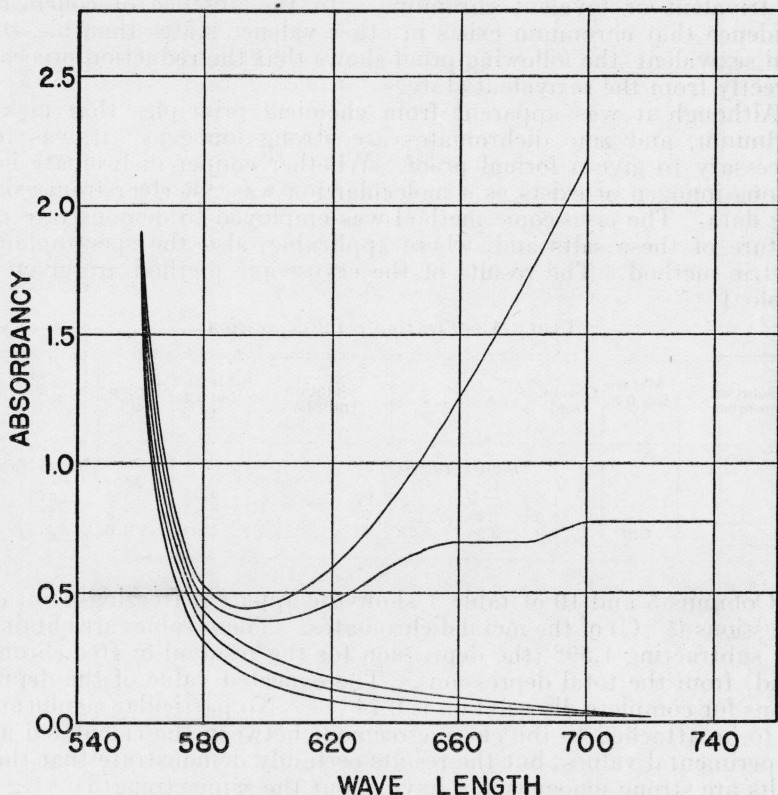


FIGURE 2.—Absorbancies of dichromate solution.

concentration and of the nature of the anion unless true molecular ions are present (such as with the halides). Hence, if we can calculate the absorbancy of the tetra-aquo cupric ion from that of the copper dichromate solution (no. III), positive evidence will be obtained as to whether cupric dichromate is a strong ionogen. The absorbancy of the hexivalent chromium is taken to be equal to that found with the zinc solution (no. IV). Subtracting these values from those of the cupric dichromate solution, the points plotted on figure 3 are obtained.

³ This fact should give these positive ions radii that are very close to each other. X-ray investigations (30) of crystal structure confirm this similarity of nickel and zinc ions. The value reported for copper is much smaller, but has been questioned (probably because it does not fit into the scheme outlined above). The relative sizes of the "bare" (not hydrated) ions are involved.

The curve was calculated from transmission values of a cupric sulphate solution which was 0.2 *M*. The agreement is good except at short wave lengths, where the values are known to be subject to error on account of the extremely low transmission of the cupric dichromate solution. The spectral region used is the only one that can be readily investigated with these solutions. The results with nickel solutions, given in figure 4, indicate that nickel dichromate is also a strong ionogen. The curve was calculated from values obtained with a nickel ammonium sulphate solution. It is known (6, 9, 10) that the absorbancy of the hexa-aquo nickelous ion, $[\text{Ni}(\text{H}_2\text{O})_6]^{++}$, is inde-

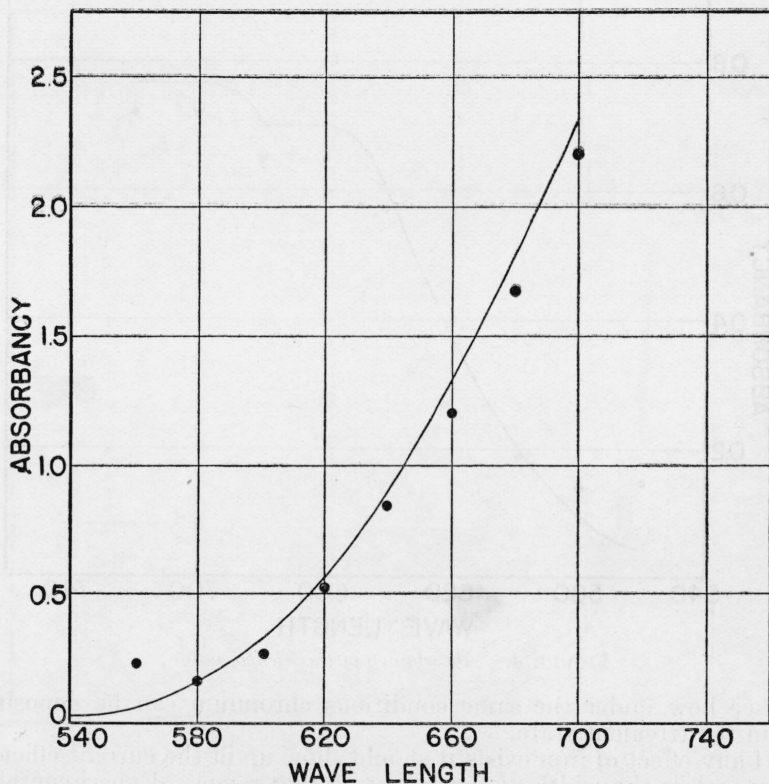


FIGURE 3.—Absorbancy of cupric iron in the presence of sulphate or dichromate anions.

pendent of the anion and of the concentration, provided that true molecular ions are not present.

When iron is present in a chromic acid bath it markedly constricts the bright-plating range at low temperatures. Alter and Mathers (24) and also Schneidewind (20) record that iron is not deposited from the chromic acid bath. Similar statements have been made by Phillips (31) and by Baker (32). Farber and Blum (26) have found that the presence of iron slightly increased the cathode efficiency and throwing power although it slightly contracted the plating range at 45° C. The fact that such a relatively small effect was found is abundant evidence that iron does not participate directly in the deposition.

It appears probable that ferric dichromate is a strong ionogen like chromic dichromate and not, as frequently stated, a colloid.

Trivalent chromium and iron are similar in behavior, though the ferrous ion is a weaker reducing agent than the chromous, and conversely the ferric ion is a more powerful oxidizing agent than the chromic. This situation, coupled with the fact that the ferric ion is a much more powerful oxidizing agent than the chromic ion for the ion-to-metal couple, makes ferric iron a much more favorable case for electrochemical reduction to the metallic state than trivalent chromium. If iron is not deposited to any great extent, it is difficult

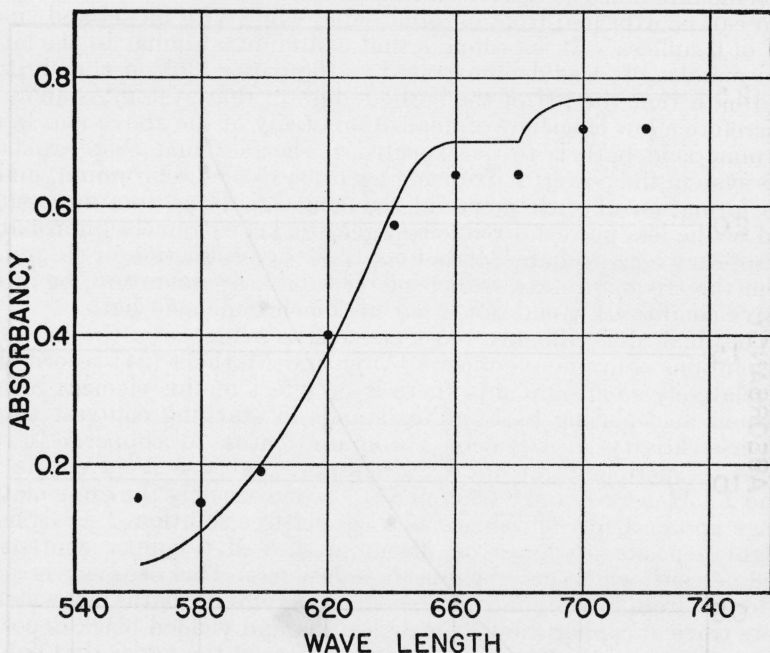


FIGURE 4.—Absorbancy of the nickelous ion.

to see how under the same conditions chromium can be deposited from the trivalent state.

If any effect of iron exists it should show up in the current efficiencies, and in the width of the bright-plating range. Experimentally, it was demonstrated that a solution that was 1 *N* in Fe^{+++} , 2.5 *M* in CrO_3 , and 0.05 *N* in SO_4^{--} did not possess a bright-plating range at 45° C markedly different from that of a similar iron-free solution, with the current efficiencies being approximately the same. Analysis of bright deposits (which were unlikely to retain mechanical inclusions) showed that they contained about 0.10 percent of iron. As Phillips has previously stated, it is difficult to say whether this small content of iron was electrodeposited or was present as inclusions. The practical absence of iron in the deposits is the first evidence that the deposition of chromium occurs from the sexivalent state.

Further evidence is supplied by the effects of zinc, cadmium, and nickel. Experiments were conducted with the usual chromic acid

bath (2.5 M CrO_3 , 0.05 N SO_4^{--}) to which one of the above ions was added in normal (N) concentration. It was found that the bright-plating range was unchanged at 45° C and that the current efficiency at 10 amp/dm² was the same as that obtained from the usual bath. Baker (32) reports that no nickel is present in deposits obtained from chromic acid baths containing nickel. Similar results are recorded by Alter and Mathers (24) for all of these metals.

In the author's paper (37) on trivalent chromium baths it was shown that it is easier to deposit either nickel or zinc than it is to deposit chromium from the chromic or chromous condition. The pH of the cathode film must be not less than 8 before efficient chromium deposition can be expected from chromic salts, while with nickel and zinc a pH of 6 suffices. It is probable that cadmium is similar to the latter two metals. It was demonstrated in the paper (35) on the chromic acid bath that the pH of the cathode film in that system⁴ is about 3. Therefore a low efficiency of deposition of any of the above ions in the chromic acid bath is to be expected. The fact that there exists in this system the powerful oxidizing agent, sexivalent chromium, makes the formation of such powerful reducing agents as zinc impossible, and of the less powerful reducing agent nickel extremely improbable. It appears very probable, therefore, that the production of chromium from the trivalent state (which metal would, by definition, be in the active condition) would not occur in the chromic acid bath.

The final and probably most conclusive evidence is the behavior of solutions containing copper. Alter and Mathers (24) record that in relatively small amounts there is no effect of this element on the chromic acid plating bath. This stands in startling contrast to the hypersensitivity of trivalent chromium baths to copper. In the present experiments at 45° C, a solution that was N in cupric ion (and 2.5 M in CrO_3 and 0.05 N in SO_4^{--}) had sensibly the same plating range and cathode efficiencies as a copper-free solution. Analysis of bright deposits produced on platinum showed a copper content of 0.08 percent, which may be due to inclusions. This behavior is quite different from that found for trivalent chromium baths, in which a mere trace of copper ruined the deposition and yielded black deposits. Since it was demonstrated in the earlier part of the paper that copper dichromate is a strong ionogen, the results indicate quite conclusively that chromium must be deposited directly from a more powerful oxidizing agent than the cupric ion, namely, sexivalent chromium.

As indicated in the first paragraph of this section, the results show conclusively that the particular dichromate ions that are reduced to the metallic state do not exist at any time in a condition that can be identified as trivalent or bivalent chromium, which are the only lower valence states of chromium that are definitely established.

IV. MECHANISM OF REDUCTION

The purpose of this section is to consider the means by which sexivalent chromium is reduced to the metallic state, and to show why the reaction is extremely inefficient and occurs only at very high polarization values. Two paradoxes in the experimental observations will be shown to be consistent with the theory presented.

⁴ This value was obtained from a study of the pH of reduced chromic acid solutions. It was established that solutions with a pH much greater than 3.5 were extremely unstable.

Electrochemists frequently interpret polarization curves on the basis of quasi-thermodynamics, that is, they explain changes in dynamic potential in terms of the change in "effective" ion concentration (or activity) brought about by the passage of the current. The primary utility of thermodynamics is to define the minimum energy conditions that must be satisfied before the reaction can start. Polarization is simply the excess potential that must exist in order that the process proceed at a definite rate, that is, at a definite current density. This problem is to be treated, therefore, in terms of the theory of reaction rates, and the variation of those rates with the electrode potential (33). The electrode potential will influence not only the frequency of collisions but also the absolute rate of reaction.

The attraction of a negative electrode for a positive ion increases the chance of its collision with the electrode, extends the duration of the collision, and effectively reduces the chance of other positive ions of interacting with the cathode. If the positive ions are identical the last factor has no effect, but the first two make the particular reaction more probable.

It may be stated that, under these conditions, this reaction possesses a favorable or high interaction coefficient. A single isolated negative ion would possess, with respect to a cathode, a zero interaction coefficient on account of the repulsive forces involved. However, in systems that contain a mixture of positive and negative ions, the interaction coefficient of the negative ions with the cathode is not zero. The only condition that the action of the cathode imposes is that the net space charge be positive and equal to the charge on the cathode. The extent to which it will deviate from a purely positive space charge will depend upon the force of interaction between the positive and negative ions. If true neutral molecules which involve a reducible radical are present, the existence of that radical at distances from the cathode that are of importance in determining chemical reaction is favored. That such interactions actually exist is shown by the occurrence of reactions that involve the reduction of negative ions at a cathode, and which cannot be explained in terms of favorable "couples." For example, the dichromate ion can be reduced to the trivalent state in alkaline solutions at potentials that entirely exclude the action of the hydrogen/hydrogen ion or the chromous/chromic couple. The nitrate and particularly the nitrite ion can be reduced in alkaline solutions at potentials less negative than that of the hydrogen/hydrogen ion couple (5). Evidently the over-all rate of reduction of a negative ion at a cathode can be finite if the absolute rate of reduction is high enough, even though the interaction coefficient is very small.

The absolute rate of reduction could be determined if it were possible to calculate the potential barrier, the height of which corresponds to the activation energy for the reaction. The potential barrier in this case can be represented by a multidimensional surface, which is a function of the separation and mutual energies of linkage of the atoms involved, their energy in the field, the interaction energy existing between them, and the electron energies, which include the work function of the metal. The height of the barrier represents the energy that the system must possess in order to exist in the configuration that is expressed by other coordinates, that is the relative positions of the particles.

The consideration of the extremely complex case that we shall have to deal with will be qualitative. It is to be borne in mind that the absolute rate of reduction cannot be affected by the existence of other more favorable reactions, but the over-all rate can be influenced to the extent that the more favorable reactions decrease the chance of the less favorable reactions taking place. Furthermore, the existence of the products of the reaction is dependent not only upon a favorable potential barrier for their formation, but also upon the absence of other reactions of sufficiently low and narrow potential barriers that would effect their disappearance.

The standard potentials of the various possible (over all) reactions that may occur are given in table 2. It will be noted that the table does not contain any information concerning the hypothetical quinquevalent and quadrivalent states, as the evidence concerning their existence is unsatisfactory. Even if they did exist, their period of existence would be so short that they could not be rate-determining steps, and therefore they are practically unimportant.

TABLE 2.—Standard Potentials of Reactions

\bar{e} denotes an electron.

These values were taken from Abegg, Handbuch Anorgan. Chem. IV, 1 Ab., 2te Hälfte (1921).

No.	Reaction	Standard potential
		Volts
1.....	$1/2\text{Cr}_2\text{O}_7 + 7\text{H}^+ + 3\bar{e} = \text{Cr}^{+++} + 7/2\text{H}_2\text{O}$	1.3
2.....	$1/2\text{Cr}_2\text{O}_7 + 7\text{H}^+ + 4\bar{e} = \text{Cr}^{++} + 7/2\text{H}_2\text{O}$.9
3.....	$1/2\text{Cr}_2\text{O}_7 + 7\text{H}^+ + 6\bar{e} = \text{Cr} + 7/2\text{H}_2\text{O}$.4
4.....	$\text{H}^+ + \bar{e} = 1/2\text{H}_2$.0
5.....	$\text{Cr}^{+++} + \bar{e} = \text{Cr}^{++}$	-.4
6.....	$\text{Cr}^{++} + 2\bar{e} = \text{Cr}$	-.5
7.....	$\text{Cr}^{+++} + 3\bar{e} = \text{Cr}$	-.5

The reactions in table 2 divide themselves into two groups which involve, respectively, stronger and weaker oxidizing agents than the hydrogen ion/hydrogen couple. From a purely thermodynamic standpoint, reactions that involve more powerful oxidizing couples occur most readily at a cathode. Practically, this need not always be true at finite rates. From this standpoint, however, reaction 3 would be tremendously superior for the production of metal to any process that depends on reactions 5 and 6, or on 7. The experimental evidence indicates that in the chromic acid bath the metal is produced through reaction 3. The loss of much of this "thermodynamic" advantage requires consideration, as it is in the manipulation of the contributing factors that the chance of improvement lies.

In consequence of its negative charge, the dichromate ion possesses an unfavorable interaction coefficient with the cathode. As indicated above, the existence of undissociated molecules of chromic acid and the screening action of positive hydrogen and chromic ions assist the dichromate ion to obtain a finite interaction coefficient, which, however, cannot compare with those exhibited by positive ions. This factor alone could give rise to a low over-all rate for the reaction, which would result in a high polarization for its appreciable occurrence.

Another factor is the order of the reaction. It is known (40) that the deposition of metals does not occur atom by atom but in layers. Even though this reaction is of a very complex order, this phase of metal deposition is generally not the rate-determining step. Deposi-

tion of metal from the chromic acid bath demands that at no time can atomic or active chromium exist, as this is a powerful reducing agent. It is demanded that, since the pH of the cathode film is 3, the chromium must be stable with respect to a solution with that acidity. Since chromium is being produced from the sexivalent state, it is passive even though there is copious evolution of hydrogen. Passivity can have a meaning only when applied to metals in bulk. It is clear that production of metal from sexivalent chromium will be a reaction of a much higher order than the production of metal from the trivalent state, on account of the larger number of electrons involved, and the numbers of hydrogen ions that must enter into the reaction. Reactions of a higher order are generally improbable, but become increasingly possible with increased polarization.

Reverting to the potential barrier, it will be necessary to show what factors could in this case give rise to a reaction requiring a high polarization. On account of the large size and negative charge of the dichromate ion, the potential barrier will tend to be wide, and therefore the activation energy would tend to be large. However, the condition that metal in bulk be formed requires that only those dichromate ions which have a narrow potential barrier produce metal. However, as this is the region in which the most powerful repulsive forces come into play, that barrier will be high. These ions will be, of course, a very small fraction of the dichromate ions in the cathode film. The absolute rate of reduction of these ions to the metallic state can be increased by lowering the height of the barrier, which is accomplished by increasing the energy of the electrons, that is, increasing the cathode potential. The over-all rate will increase if the concentration of favorably situated ions decreases more slowly than the height of the potential barrier increases. The above arguments point to the conclusion that deposition of metallic chromium from the sexivalent state must be a reaction that will require a very high polarization, which is an experimental fact.

Whether the reaction will be efficient depends on whether there exist in the system other reactions which could occur more efficiently at the polarization values required for a definite rate of the reduction of sexivalent chromium to the metallic state. It is known that reaction 4 (discharge of hydrogen) occurs and, in fact, it is the dominant reaction in the system. This is not surprising. The polarization of that reaction is almost one volt. Its interaction coefficient gives rise to a very high effective collision frequency. It is, with the possible exception of reaction 5 ($\text{Cr}^{+++}/\text{Cr}^{++}$), the reaction of the lowest order in the system. By virtue of the favorable interaction coefficient and size of the hydrogen ion, this reaction possesses a relatively narrow potential barrier, the height of which, manifested by the low hydrogen overvoltage on chromium, is low. It is this contrast of factors that gives the chromic-acid bath its very low efficiency, in spite of the fact that the production of metallic chromium from the sexivalent state is a much more favorable reaction thermodynamically than the liberation of hydrogen.

This leads us to the consideration of two paradoxes in the observed phenomena. The first is the liberation of a powerful reducing agent, hydrogen, in the presence of a powerful oxidizing agent, chromic acid. The second is the nondeposition of copper, even though the hydrogen

ion is reduced. These paradoxes will be treated together. As pointed out, it is necessary that, for a definite rate of accumulation of a product, not only must the rate of its formation be high, but it must be higher than the rate of other reactions that tend to effect a re-resolution of the products of the reactions. The stability of the chromium deposit is explained by its existence in the passive state. If, as is probable, hydrogen is discharged internally in the metal, that which escapes will be deactivated, and hence, not reoxidized by the chromic acid. Copper, however, can be discharged only on the surface, where it would in time be reoxidized by the hexivalent chromium. There are three electrochemical facts that make this theory seem plausible—(a) The observations of Pring (11) established that in some cases relatively thick deposits of a metal are necessary before the system acquires the hydrogen overvoltage of that metal in bulk, (b) hydrogen can build up to very high pressures in the interior of metals, and (c) the efficiency of chromium deposition may be affected by the base metal even though the deposit is thousands of atoms thick.

There is good reason to believe that chromium deposition is cyclic, on which basis it is also possible to avoid the paradoxes. Chromium, copper, and hydrogen could be deposited in the favorable phases of the cycle. The hydrogen could be deactivated and escape, but the copper would be reoxidized in the unfavorable phases of the cycle. Chromium, being in the passive condition, would not be reoxidized. Still another explanation is possible, that is that the average concentration of chromic acid in the cathode film is so low that the hydrogen molecules can be deactivated and escape. Copper atoms, however, have no such alternative. It is also possible to explain this behavior by the experimental observation that copper does not deposit on passive chromium. The exact reason for this is unknown.

Reactions 5, 6, and 7, which involve less powerful oxidizing agents than the hydrogen ion/hydrogen couple, belong to two classes. The latter two reactions involve the production of metal while the first does not. While the experimental evidence excluded the possibility that the metal which was produced resulted from reactions 6 and 7, it did not exclude the occurrence of these reactions. They are thermodynamically possible, but the continued existence of the products of the reaction is inhibited not only by the existence in the cathode film of hexivalent chromium, but also of the hydrogen ion itself. It is known as an experimental fact that reaction 5 is easier to perform than 6 or 7, which is also in accord with the analysis presented. It is demanded, therefore, that the over-all rate be increasingly inefficient in the chromic-acid bath as we proceed from reaction 5 to 7.

The basic sol formed at the cathode film tends to inhibit all plating. However, if it can have its electrophoretic velocity lowered, this effect can be minimized. According to the theory proposed (35) the sulphate effects this through adsorption, but the density of anions in the cathode film is normally too low, unless a special means of transport is available. It was pointed out that the positive molecular ions (green complexes) of chromium furnish such a means and give the required differentiation between the ineffective dichromate ion and effective anions such as sulphate. This theory demands that reaction 5 (or a similar reaction) be possible. The absolute rate of reduction is not, as we have pointed out, affected by the existence of other more favor-

able reactions. Since there must be a relatively high concentration of trivalent chromium ions next to the cathode, reaction 5 (the most efficient of the above reactions) can occur to some extent. It has been shown in other researches (12) that the simple chromic ion is more readily reduced than the positive molecular ions of trivalent chromium, though both are of the same order of magnitude. If reaction 5 is possible, the reduction of the green complexes is possible, at least to such an extent that the sulphate ion is liberated at the cathode. There is no doubt that the competing reactions will make the over-all rate very low, but that is not serious because the direct reduction of sexivalent chromium is also inefficient, and it is the relative rate that counts. It is to be borne in mind that we are concerned only with the transient phases of the reaction.

It might be assumed that the deposition of chromium occurs from the trivalent state, for which the interaction coefficient and cathode potentials are favorable, and that the function of the chromic acid is to keep the deposited metal passive and thus prevent its re-solution. However, the formation of any phase (in this case active chromium) from a solution with respect to which it is not stable under the conditions of its formation is contrary to the principle of detailed balancing (17, 25). The supposition that the unstable phase may be converted into a stable one by a further reaction does not avoid the difficulty, and the hypothesis stated, therefore, does not offer any help in the theory of chromium deposition.

The theory of direct deposition of chromium from the sexivalent state in the chromic acid bath accounts for all the important facts of the process. The presence of the chromium in the form of a strong oxidizing agent permits relatively efficient reduction in acid solutions. With the chromic and chromous salt baths the acidity of the cathode film must be so low for relatively efficient deposition that the hydrolysis of the chromic ion produces inferior deposits. The fact that the strong oxidizing agent exists in an acid solution as a large negative ion results in a bath with a very high polarization and low cathode efficiency.

V. POSSIBILITY OF IMPROVING CHROMIUM PLATING

It has been long thought that the inefficiency of the chromic-acid bath is caused by two of the factors that were mentioned in the previous section; namely, poor interaction with the cathode and a high order of the reaction. This conclusion has no doubt led to many of the investigations on trivalent chromium baths. Such systems have good interaction coefficients and the order of the reaction is low. However, the reduction of trivalent chromium is more difficult than that of sexivalent chromium on account of the free energies involved. To some extent the study of low-valence chromium baths has been instigated by the efficient deposition from nickel and zinc baths. It is now certain that for fundamental reasons neither the trivalent nor bivalent chromium baths can approach the efficiencies (with good deposits) that are found in nickel and zinc baths. The advantage of having the chromium in the form of a strong oxidizing agent apparently outweighs any disadvantage of its presence as a large negative ion. It is therefore logical to seek improved operation of the chromic-acid bath by minimizing its disadvantages.

It does not appear possible to change the order of the reaction, but it may be possible to bring about more favorable interaction coefficients. If it were possible to have the sexivalent chromium in a positive molecular ion or in a homopolar molecule that is less dissociated than dichromic acid, $H_2Cr_2O_7$, higher efficiencies might result. Such an attainment of a more favorable interaction coefficient would be at the expense of the thermodynamic ease of reduction.

In the absence of definite information concerning the existence of such complexes, attention was focused on the possible effects of positive ions. It was pointed out that the chromic ion by its screening action undoubtedly assists the sexivalent chromium to reach the cathode. It would be expected that the addition of cations of equal or lower charge would have little effect. These predictions have been confirmed experimentally. The behavior of quadrivalent ions is unknown. It is doubtful, however, whether a dichromate of a quadrivalent ion can exist in any form other than the basic salt at the low acidities existing in the cathode film. The presence of basic salts there would, according to the above theory, restrict the plating range. With stannic hydroxide (metastannic acid), which is only slightly soluble in chromic acid solution, it was found that the current efficiency did not improve and that the plating range was very much restricted.

The most attractive direction for investigation is in the alteration of the structure of the colloidal material in the cathode film. It is to be expected that any positive ion that hydrolyzes at the pH of the cathode film should alter the structure of the colloidal material there. The small effect on the current efficiency and plating range at high temperatures produced by the addition of iron (or ferric hydroxide) is difficult to explain from this point of view. From this result, however, it is predictable that the effect of aluminum (aluminum hydroxide) would also be small. We have confirmed this prediction with experiments made at $45^\circ C$. An agent which may affect the colloidal structure is phosphoric acid. Contrary to statements in the patent literature, pure phosphoric acid is not an effective substitute for sulphate, and, when added in appreciable amount together with sulphuric acid, it prevents plating. The low solubility and easy coagulation of chromium phosphate cause this behavior. Arsenic acid acts similarly.

The use of buffers is another possible avenue of attack, especially to widen the plating range. "Burnt" deposits are caused, first, by the hydrolysis of the chromic ion at the pH then prevailing in the cathode film and, second, by the insufficiency of hydrogen ions to neutralize all of the oxygen ions set free by the reduction of the dichromate radical. A suitable buffer should be effective at a pH between 3 and 4, and it should form no complexes with trivalent chromium. Arsenic acid acts as a buffer at a low pH but it is unsuitable because, as indicated above, chromic arsenate tends to stop plating. Monochloroacetic acid and dichloroacetic acid (which are stable in chromic acid) were tried in concentrations that would be expected to have a buffer action. Their only effect was to impair the quality of the plating. A similar result was obtained for acetic acid. It is probable that the formation of complex ions masks any beneficial buffering effects of these acids.

The theory explains clearly the characteristics that a negative anion must have to be an effective addition agent (that is, a substitute for sulphate). Unfortunately, no anions other than the fluoride and sulphate satisfy all of these criteria. The selenate, for example, has the necessary adsorbability and it forms green complexes, but is not stable, being reduced at the cathode even in chromic acid solutions.

VI. CONCLUSIONS

1. Chromium is deposited in the chromic acid bath directly from the sexivalent state.

2. The liberation of hydrogen probably occurs through discharge within the metal.

3. The liberation of sulphate at the cathode is made possible by a reduction of the chromic to the chromous ion.

4. Improvements in the performance of the chromic acid bath might be produced if it were possible: (a) To have the sexivalent chromium present in a molecule that is less dissociated than dichromic acid, (b) to change the structure of the colloidal material in the cathode film, or (c) to change the buffer characteristics of the cathode film.

Efforts to make improvements over the present chromic acid baths that contain sulphate or fluoride were unsuccessful.

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