Chemistry & Theory of Chromium Deposition: Part I - Chemistry

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Although electrodeposition of chromium has been practiced for 75 years, the mechanism is still open to conjecture. Part of the reason is the complexity of the chemistry of chromic acid and its existence in aqueous solution in the form of coordinated octahedral complexes. These complexes vary both structurally and kinetically at different CrO_3 concentrations. The chemistry of tri- and hexavalent chromium is discussed, including polymerization and related mechanisms relative to the overall deposition mechanism.

Chromium, Cr, also loosely called chrome, is the twenty-first element in relative abundance with respect to the earth's crust, yet is the seventh most abundant element because it is concentrated in the earth's core and mantle. It has atomic number 24 and belongs to group (VI B) of the periodic table. On a tonnage basis, chromium ranks fourth among the metals and thirteenth among all mineral commodities in commercial production.

Chromium was discovered by Vauquelin in 1779 in Siberian red lead, the mineral *crocoite,* $PbCrO_4$. In 1798, he isolated the new metal by reduction of CrO_3 with charcoal at high temperature. The name chromium (from Greek chroma, color) was suggested for the new element because of its many colored compounds. Chromium, relatively recently, was recognized as a biologically necessary trace element. The first conclusive evidence demonstrating a metabolic role for chromium was obtained by Mertz and Schwartz[1] in a series of investigations, the first of which appeared in 1955.

Chromium has a ground state electronic configuration of $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$ $3d^5$, $4s^1$. This distribution of the outermost electrons is favored over $3d^4$ $4S^2$ because of increased stability of the half-filled 3d shell with 1 electron in each of the orbitals. The half-filled shell leads to the "S" state ($L = 0$), which is especially stable, supposedly because of the large amount of exchange energy.[2] The d orbitals project close to the surfaces of the ions, so that the electrons in them interact with the chemical environment.

A typical transition element, chromium forms many compounds that are colored and paramagnetic. Chromium has oxidation states as follows: -2, -1, 0, +1, +2, +3, +4, +5, +6; the highest oxidation state, +6, corresponds to the sum of the numbers of 3d and 4s electrons. The lowest, -2, -1, 0 and +1 are formal oxidation states displayed by chromium in compounds such as carbonyls, nitrosyls and organometallic complexes.

Divalent Chromium

Chromium in the oxidation state +2 was in the past not considered to be of particular interest for electrodeposition mechanisms. It does play a role, however, in the passivation of chromium. Recently, it has been accepted that possibly and probably plays a role in the deposition and dissolution mechanisms; this warrants that it be briefly introduced here. The outstanding characteristic of the Cr^{+2} ion (sky blue in aqueous solution) is its strength as a reducing agent $Cr^{+3} + e^- \longleftrightarrow Cr^{+2}$; $E_0 = 0.41$ V. Because it is easily oxidized by oxygen, preservation of the solution requires exclusion of air. Even under such conditions, the Cr^{+2} ion is oxidized by water with the formation of hydrogen. The rate of oxidation depends on several factors, including the acidity and anions present.

It has been known for some time[3] that pure chromium (usually obtained electrolytically) dissolves in acids to form Cr^{+2} with no (or very little) Cr^{+3}, if the solution is protected from air, of course; impurities apparently catalyze formation of Cr^{+3}. Chromium (+2) solutions may also be obtained by electrolytic reduction of chromium (+3).[4,5] Recently, Leisner *et al.*[6] proposed a chromium dissolution mechanism during anodic dissolution of chromium in chromium plating solutions, postulating $Cr^0 \longrightarrow Cr^{+2}$ oxidation under these conditions. Mandich and Vyazovikina[7] contemplated Cr dissolution in CrO_3 solution as a seven-step mechanism under mixed diffusion-kinetic control. Six steps are single electron electrochemical steps, while the seventh step is associated with desorption of Cr(+6). Dissolution of chromium in acid media (primarily H_2SO_4) is examined extensively in corrosion studies of chromium metal and alloys. Active dissolution yields chromous ions, according to most of the models,[8,9] while in the active-passive transition region, dissolution is associated with the formation of the blocking passive layer.

Trivalent Chromium

Chromium (+3) is the most stable and most important oxidation state of the element. The E_0 values[11] (Table 1) show that both oxidation of Cr^{+2} to Cr^{+3} and the reduction of Cr^{+6} to Cr^{+3} are favored in acidic aqueous solutions. The preparation of Cr^{+3} compounds from either state presents few difficulties and does not require special conditions.[10] In basic solutions, oxidation of Cr^{+3} to Cr^{+6} by oxidants, such as peroxides and hypohalites, occurs with ease. Preparation of Cr^{+6} from Cr^{+3} in basic solutions requires the use of powerful reducing agents, such as hydrazine, hydrosulfite and borohydride, but Fe^{+2}, thiosulfate and sugars can be employed in acid solutions.

The chemistry of Cr^{+3} in aqueous solutions is coordination chemistry. It is demonstrated by the formation of kinetically inert outer orbital octahedral complexes. The bonding can be explained by d^2 sp^3 hybridization; a great number of com-

Table 1
Standard Reduction Potentials for Chromium Ions[11]

Half-Cell Reaction	E_0, V
$Cr^{+3} + 3e^- \longrightarrow Cr$	-0.740
$Cr(OH)^{+2} + H^+ + 3e^- \longrightarrow Cr + H_2O$	-0.058
$Cr^{+2} + 2e^- \longrightarrow Cr$	-0.910
$Cr^{+3} + e^- \longrightarrow Cr^{+2}$	-0.410
$Cr_2O_7^{-2} + 14H^+ + 6e^- \longrightarrow 2Cr^{+3} + 7H_2O$	1.330
$Cr_2O_7^{-2} + 10H^+ + 6e^- \longrightarrow 2Cr(OH)_2 + 3H_2O$	1.100
$CrO_4^{-2} + e^- \longrightarrow CrO_4^{-3}$	0.100

plexes has been prepared. The kinetic inertness results from the $3d^3$ electronic configuration of Cr^{+3} ion.[12] This type of orbital charge distribution makes liquid displacement and substitution reactions very slow and allows separation, persistence and/or isolation of Cr^{+3} species under thermodynamically unstable conditions.

Hydrolysis of Chromium (+3) and Related Processes

Chromium (+3) is characterized by a marked tendency to form polynuclear complexes. Literally thousands of Cr^{+3} complexes have been isolated and characterized and, with a few exceptions, are all hexacoordinate. The principal characteristic of these complexes in aqueous solution is their relative kinetic inertness. Ligand displacement reactions of Cr^{+3} complexes have half-times in the range of several hours. It is largely because of this kinetic inertness that so many complex species can be isolated as solids and that they persist for relatively long periods in solution, even under conditions of marked thermodynamic instability.

The hexaaqua ion $[Cr(H_2O)_6]^{+3}$, which is a regular octahedral, occurs in numerous salts, such as the violet hydrate $[Cr(H_2O)_6]Cl_3$ and in an extensive series of alums, $MCr(SO_4)_2 \cdot 12H_2O$, where M usually is NH_4^+ or K^+ ion. The aqua ion is acidic (pK = 4), and the hydroxo ion condenses to give dimeric hydroxo bridged species:

$$2[Cr(H_2O)_6]^{3+} \underset{H+}{\overset{-H+}{\Leftrightarrow}} 2[Cr(H_2O)_5OH]^{2+} \rightleftharpoons [(H_2O)_4Cr \left\langle \begin{matrix} OH \\ OH \end{matrix} \right\rangle Cr(H_2O_4]^{4+} + 2H_2O \quad (1)$$

On further addition of base, a precipitate is formed that consists of H-bonded layers of $Cr(OH)_3(H_2O)_3$, which readily redissolves in acid. Within a minute, however, this precipitate begins "aging" to an oligomeric or polymeric structure that is much less soluble.[13-15]

Cr^{+3} ion also polymerizes, as a result of hydrolysis and associated reactions, to form bridged complexes with a certain composition, the existence of which is indicated by indirect, but substantial, evidence. Complexes of this type range from dimers through polymers of colloidal dimensions to precipitated Cr^{+3} hydroxide. Except under special circumstances, such reactions are inevitable in neutral and basic solutions and highly probable in slightly acid solutions.

What makes the chemistry of Cr3+ complexes interesting and often tortuous for researchers, is the number of steps and mechanisms possible. The processes include aquation, hydrolysis, olation, polymerization, oxolation and anion penetration, as described briefly as follows:

Aquation

Chromium salts (chloride, sulfate, nitrate, etc.) are aqua complexes characterized by ions such as $[Cr(H_2O)_6]^{+3}$, $[Cr(H_2O)_5Cl]^{+2}$ and $[Cr(H_2O)_4Cl_2]^+$. In aqueous solution, the replacement of co-ordinated groups by water molecules (aquation) is a common reaction:

$$[CrA_5X]^{+2} + H_2O \longleftrightarrow [CrA_5H_2 2O]^{+3} + X^- \quad (2)$$

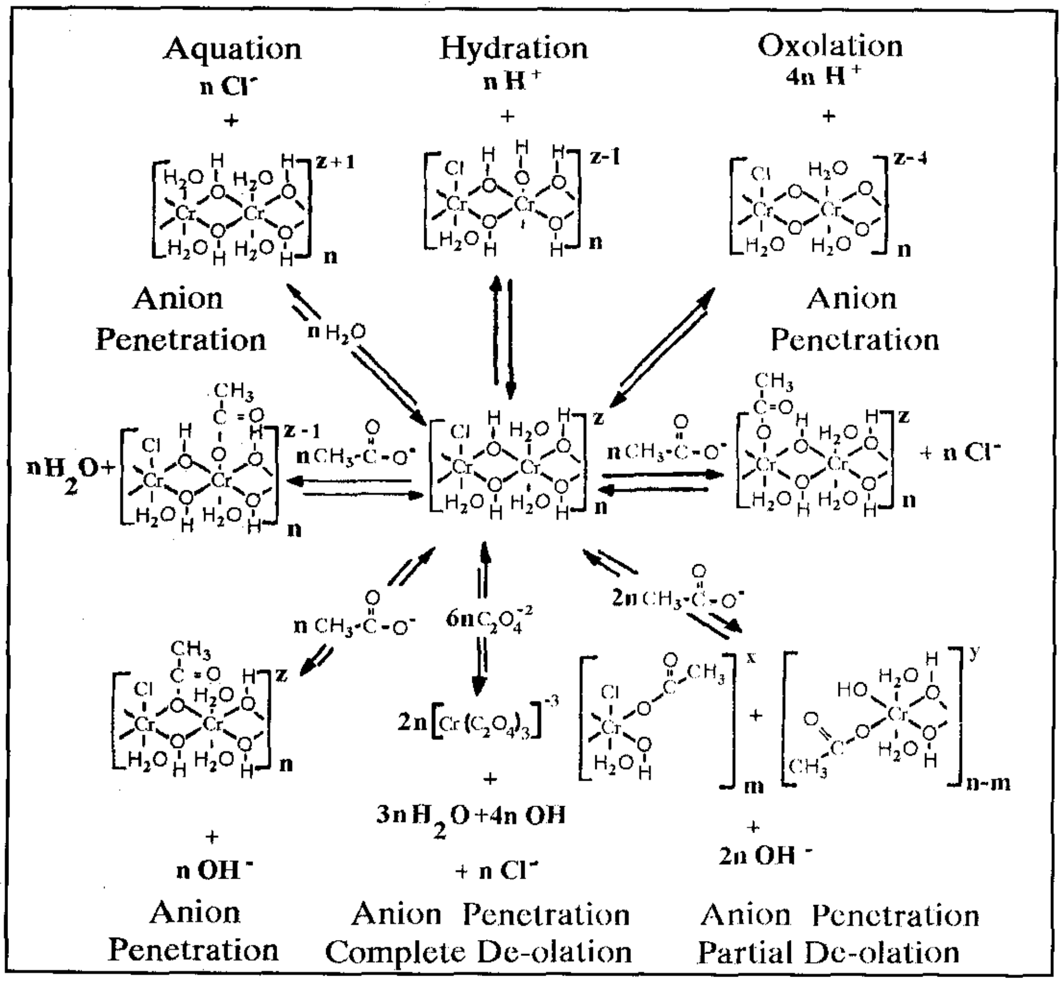


Fig. 1—Reactions of polymeric Cr(III) complexes.[21]

where A is a singly co-ordinated neutral molecule (*e.g.*, H_2O, NH_3) and X is a singly charged co-ordinated negative ion (*e.g.*, Cl, CN, CNS).

The extent of aquation depends on several factors, including the relative co-ordinating tendencies of H_2O and X and the concentration of X. Accordingly, every aqueous solution of Cr^{+3} is potentially a solution of aqua complexes. The Cr^{+2} ion (the complexes of which are labile) catalyzes such reactions, which are usually quite slow otherwise. Electron-transfer reactions between Cr^{+2} and $[Cr(H_2O)_5X]^+$ proceed predominantly through bridged intermediates $\{[Cr\text{-}X\text{-}Cr]^{+4}\}$. Ligand transfer accompanies electron transfer. In the investigations establishing these conclusions, the reaction conditions have generally been characterized by relatively low [Cr^{+2}] and relatively high [H^+]. With relatively high [Cr^{+2}] and relatively low [H^+], another pathway is available[16] with the rate determining reaction involving a hydroxy bridged complex: $[(H_2O)_4\text{-}X\text{-}CrOHCr_6]^{+3}$.

The role of Cr^{+2} is very important, however, in industrial "hard" chromium applications when plating thick layers of chromium or Cr-Ni and Cr-Ni-Fe alloys from trivalent chromium solutions, as an alternative for Cr(VI)-based solutions. Failure to control the transient levels of Cr^{+2} is recognized as the reason for Cr(III)-based solutions not to sustain heavy deposition with an appreciable deposition rate. The problem is recognized as massive olation, catalyzed by a build-up of Cr^{+2} in the high-pH region in the vicinity of the cathode. Although the bulk of the electrolyte can be about pH 2, the diffusion layer can reach pH 4. At this pH and with Cr^{+2}-promoted catalysis, oligomeric species would be released into the bulk of the electrolyte, where they would build up and reduce the level of active species and, consequently, the deposition rate.[17-20]

Hydrolysis

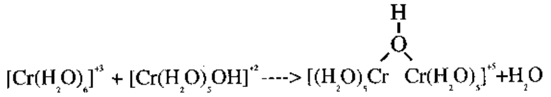
The behavior of aqua complexes as acids leads to far reaching consequences. The acidity of such solutions arises as follows:

$$[Cr(H_2O)_6]^{+3} \text{<---->} [Cr(H_2O)_5OH]^{+2}+H^+ \qquad (3)$$

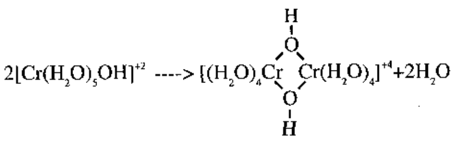
The equilibrium will be displaced to the right by heating and, of course, by the addition of base. The order of magnitude of the first hydrolysis constant is $K = 10^{-4}$. As the pH of the Cr^{+3} solution is raised, the equilibrium is shifted and more of the co-ordinated water molecules may be converted to OH groups, which brings into the picture a new process called olation.

Olation

Olated compounds are complexes in which the metal atoms are linked through bridging with OH groups. Such a group is designated as an *ol* group to distinguish it from the *hydroxo* group (*i.e.*, a co-ordinated OH linked to only one metal atom). The process of formation of *ol* compounds from *hydroxo* compounds is called olation. Olation results from the formation of polynuclear complexes consisting of chains or rings of Cr^{+3} ions connected by bridging OH groups. The first step of this process may be as follows:



$$[Cr(H_2O)_6]^{+3} + [Cr(H_2O)_5OH]^{+2} \text{---->} [(H_2O)_5Cr \overset{\overset{H}{|}}{\underset{/\ \ \backslash}{O}} Cr(H_2O)_5]^{+5}+H_2O \qquad (4)$$



$$2[Cr(H_2O)_5OH]^{+2} \text{---->} [(H_2O)_4Cr \begin{matrix} H \\ | \\ O \\ / \ \backslash \\ \ \\ \backslash \ / \\ O \\ | \\ H \end{matrix} Cr(H_2O)_4]^{+4}+2H_2O \qquad (5)$$

Because the *diol* produced by the reaction shown by Eq. (5) is stabilized by the four-member ring, there is a driving force tending to convert the singly bridged to a doubly bridged complex. This *diol* is produced by polymerization of $[Cr(H_2O)_5OH]^{+2}$, oxidation of Cr^{+2} by molecular oxygen, warming an equimolar mixture of Cr^{+3} and NaOH and boiling an aqueous solution of $[Cr(H_2O)_6]^{+3}$.

The *diol* and any other polynuclear products containing water molecules (or a group that can be displaced by water molecules) can still act as acids, releasing hydrogen ions and leaving co-ordinated OH groups.

Polymerization

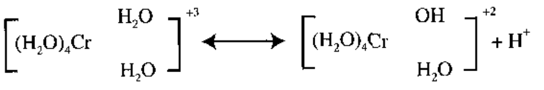
Instead of reaching a definite termination, reaction of Eq. (5) may continue, with the formation of larger and larger molecules, the polymers, as a continued process of olation. This may continue if the product of each successive step contains aqua or *hydroxo* groups. The ultimate consequence is precipitation of chromium hydroxide, $Cr(OH)_3\ X\ H_2O$, a tri-dimensional olated complex.[22] Olation reactions are pH- and time-dependent. At moderate acidity they are quite slow. For higher oligomers to be formed after addition of the base to aqueous Cr^{+3} solution, can take days, but they can subsequently decay, contributing to pH stabilization after a few weeks.[23]

The continued process of olation starts with the hydrolysis of salts of such metals as Al or Cr. The acidity of solution of such salts results from conversion of aqua to hydroxo groups:

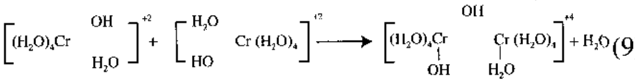
$$[Cr(H_2O)_6]^{+3} \text{<---->} [Cr(H_2O)_5OH]^{+2}+H^+ \qquad (6)$$

$$[Cr(H_2O)_5]^{+2} \text{<---->} [Cr(H_2O)_4OH]^{+}+H^+ \qquad (7)$$

The degree of hydrolysis increases as the temperature is raised and depends on the nature of the anion, and especially on the pH of the solution. If alkali is added to a warm solution of hydrolyzed chromium salt, but not enough for complete neutralization, polymerization occurs instead of precipitation of the basic salt or hydroxide. This can be explained on the basis of a series of hydrolytic and olation reactions. The first step might be presented as:

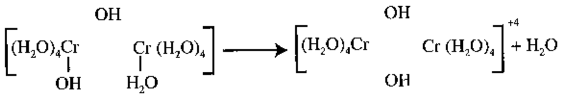


$$\left[(H_2O)_4Cr \begin{matrix} H_2O \\ \\ H_2O \end{matrix}\right]^{+3} \longleftrightarrow \left[(H_2O)_4Cr \begin{matrix} OH \\ \\ H_2O \end{matrix}\right]^{+2} + H^+ \qquad (8)$$



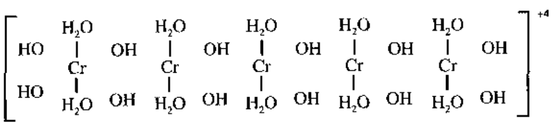
$$\left[(H_2O)_4Cr \begin{matrix} OH \\ \\ H_2O \end{matrix}\right]^{+2} + \left[\begin{matrix} H_2O \\ \\ HO \end{matrix}\ Cr\,(H_2O)_4\right]^{+2} \longrightarrow \left[\underset{\underset{OH}{|}}{(H_2O)_4Cr} \overset{OH}{\ } \underset{\underset{H_2O}{|}}{Cr}\,(H_2O)_4\right]^{+4} + H_2O \qquad (9)$$

If the reacting groups in each ion are in the *cis* positions, a completely olated ion may be formed:



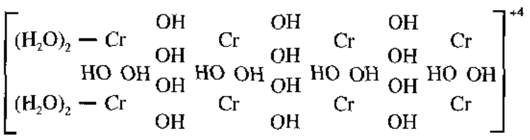
$$\left[\underset{\underset{OH}{|}}{(H_2O)_4Cr} \overset{OH}{\ } \underset{\underset{H_2O}{|}}{Cr}\,(H_2O)_4\right] \longrightarrow \left[(H_2O)_4Cr \begin{matrix} OH \\ \\ OH \end{matrix} Cr\,(H_2O)_4\right]^{+4} + H_2O \qquad (10)$$

Further hydrolysis and olation might result in a polytetrahydroxy-dodecaaquo hexachromium(VI) ion:



$$\left[\begin{array}{ccccccccccc} & H_2O & & H_2O & & H_2O & & H_2O & & H_2O & \\ HO & | & OH & | & OH & | & OH & | & OH & | & OH \\ & Cr & & Cr & & Cr & & Cr & & Cr & \\ HO & | & & | & & | & & | & & | & \\ & H_2O & OH & H_2O & OH & H_2O & OH & H_2O & OH & H_2O & OH \end{array}\right]^{+4} \qquad (11)$$

If the aqua groups are attached to the metal atoms at the end of the chain, cross-linked polymers are formed:



(12)

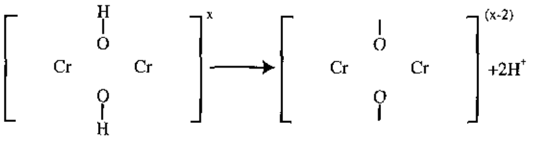
Because of the octahedral configuration of complexes of metals such as chromium, the bonds of a given metal occur in pairs, each of which lies in a plane perpendicular to the planes of the other two pairs. Accordingly, such cross-linked polymers are three-dimensional.

These processes account for the results obtained when a warm solution of a chromium salt is titrated with a base. With the addition of an increment of base, the pH rises immediately, but falls slowly if the solution is allowed to stand before more base is added. This continues with successive increments of base until enough base has been added to precipitate the hydrated oxide. As base is added to the solution, the hydrogen ions are removed. The equilibrium then shifts in the direction of further hydrolysis and olation, with the formation of more hydrogen atoms. In this way, small amounts of base can be added without precipitation; otherwise, precipitation would occur if added all at once.

The process of olation is favored by an increase in concentration, temperature, and basicity. The process reverses slowly when the solution of olated complexes is diluted or when the solution is cooled; (*i.e.*, olation decreases the reactivity of co-ordinated OH groups).

Oxolation

Oxolation may accompany or follow olation, particularly if the reaction mixture is heated. This reaction converts bridging OH^- groups to O^- groups.



(13)

Olation and oxolation account for changes in reactivity of chromium hydroxide as it ages. Freshly precipitated chromium hydroxide usually dissolves quite rapidly in mineral acids, but after standing some hours, it becomes difficult to dissolve. Presumably, olation continues in the precipitate; because bridged OH^- groups react more slowly with acids than singly co-ordinated OH^- groups, the reactivity of the precipitated hydroxide progressively diminishes. If the hydrate is heated, there is a drastic decrease in reactivity as a result of oxolation, a process even more difficult to reverse than olation. While olation and oxolation are both reversible, the long times required for the acidity of solutions, that have been heated and then cooled, to return to the original values, leads to the conclusion that deoxolation is extremely slow. In general, *ol* groups are more readily depolymerized than *oxo* compounds, because protons react more rapidly with *oxo* groups.

Anion penetration

It is well known that the addition of neutral salts to a solution of basic sulfate changes the hydrogen ion concentration. Co-ordinated water molecules, OH^- groups, OH^- bridges or other ligands are replaced by anions in the solution. The extent to which anion penetration occurs with *ol* complexes is determined by the relative coordination tendencies of the entering anions and the groups that they replace, and the length of time that the solutions are allowed to stand.[24] Anions that can enter the co-ordinated sphere easily and displace OH groups can effectively prevent olation. Penetration by anions into basic chromium complexes decreases in the following order:[25]

Oxalate > glycinate > tartrate > citrate > glucolate > acetate > monochloracetate > formate > sulfate > chloride > nitrate > perchlorate

Consequently, if a solution of $[Cr(H_2O)_6]^{+3}$ is required, the only anion should be weakly co-ordinated nitrate or perchlorate, because those of greater co-ordinating tendency may displace one or more of the co-ordinated molecules. In a stock solution of basic chromium sulfate, Serfas *et al.*[24] found ionic species having molecular weights of 68,000.

Reaction Rates

After some parameter of a system containing Cr^{+3} complexes is changed, the corresponding change in composition of the complexes generally occurs only slowly. Heating a solution (or dispersion) of such complexes promotes olation and oxolation, both of which reverse at a low rate when the system is cooled. Reversal of oxolation is much slower than reversal of olation. If the pH of a solution containing olated complexes is reduced to a value at which normally only monometric Cr^{+3} complexes would exist, it may take a long time for the state of aggregation corresponding to the new pH to be attained. The complexity of chromium coordination chemistry is illustrated in Fig. 1.

Hexavalent Chromium

The mechanisms of the electroreduction of chromic acid are of great interest, not only from a theoretical point of view, but for their application in industry as well. The vast majority of decorative, and almost all hard, chromium plating is carried out using CrO_3 as the electrolyte. The fact that chromium can be deposited from Cr^{+6} solutions but not from simple aqueous solutions of lower valency salts is unfortunate for the following reasons:

(1) Because the electrochemical equivalent of Cr in a CrO_3 solution is 0.3234 g/hr and cathode current efficiency is typically 10-20 percent, one A-hr yields only 0.032 to 0.064 g of metal. This is 15-30 times less than for nickel, 18-36 times less than for copper from acid solution and 63-126 times less than for silver. The only way to offset this is to increase the working current density via increase in mass transport and temperature and/or plating time.

(2) The minimum current density at which electrodeposition takes place is two to three orders of magnitude larger than in the case of other metals (Zn, Ni, Sn, Ag, Au, etc.).

(3) The electrodeposition of chromium is more sensitive to operating conditions (temperature and current density) than any other deposition process.

(4) In contrast to other processes, the cathodic current efficiency varies inversely with temperature but is propor-

tional to current density (which causes low throwing power).

(5) Chromium will plate only in the presence of a catalyst (*e.g.*, H_2SO_4), the concentration of which influences the plating rate. In Fig. 2, the influences of temperature and catalyst concentration, expressed as the ratio of CrO_3/H_2SO_4, are shown.[7] Higher temperature and a less than optimum ratio (50:1) are shifting the potential toward more positive values, away from the Cr electrodeposition potential of -1.12 V.

(6) On the positive side, hexavalent chromium electrolytes are relatively less sensitive to the presence of impurities; and the anode material is lead or lead alloys, which can easily be made to conform to any shape.

Despite its paramount technological importance and with all the advances of modern science and instrumentation, exact mechanisms of Cr electrodeposition are still open to conjecture. The main difficulty is the necessary formation and presence of a cathodic film on the surface of the metal being plated. The argument, whether the reduction of Cr^{+6} ions to chromium is direct or indirect, during the last decade developed into a discussion of whether the cathodic film is useful or not (and how it should be modified to improve the process, inasmuch as the existence of this film is no longer in question).

Because of the absence of complete understanding of the deposition mechanism, it is important to understand the chemistry of chromium with all its intricacies of condensation, polymerization, number of different valence states, ability to make anion/cation compounds [*e.g.*, $Cr_2(Cr_2O_7)_3$], existence of a number of double-salts (alums), isomers, oxyhydrates, etc. Virtually all Cr^{+6} compounds contain a Cr-O unit; the halide CrF_7 and unstable hydrides are the sole exceptions.[26] The other Cr^{+6} halides have the formula CrO_2X_2, where X is F, Cl, or Br.

Chromic Acid

The primary Cr-O bonded species is chromium (+6) oxide, CrO_3, which is better known as chromic acid, the commercial and common name. This compound is also known as chromic oxide and chromic acid anhydride. Chromium (+6) forms a large number and considerable variety of oxygen compounds, most of which may be regarded as derived from Cr^{+6} oxide. These include the oxy-halogen complexes and chromyl compounds, chromates, dichromates, trichromates, tetrachromates and basic chromates. All these Cr^{+6} compounds are quite potent oxidizing agents, although kinetically they cover a wide range; Cr^{+6} does not appear to have anywhere near the capability of forming the isopoly anions so characteristic of molybdenum and tungsten.

Chromic trioxide has a molecular weight of 100.01 and forms dark red prismatic crystals belonging to the orthorombic system, the bipyramidal subclass. The density of the solid is 2.79 g/cm³. It melts with some decomposition at 197 °C. CrO_3 is very hygroscopic. Its solubility in water varies from 61.7 percent at 0 °C to 67.5 percent at 100 °C. Oxidation potentials of CrO_3 and chromate solutions are augmented by increasing the acidity of the solution.

Oxidation potentials for chromate ions[26] at 23 °C are listed in Table 3; thermodynamic data[27] for the ions of chromates, dichromates and bichromates at 25 °C are listed in Table 4.

Chromic acid, $HCrO4^-$ or $CrO_3{\cdot}H_2O$, is not known except in solution, where it shows a marked tendency to form polyacids by elimination of water.[28]

$$2H_2CrO_4 \longrightarrow H_2O + H_2Cr_2O_7 \quad \text{(dichromic acid)} \tag{14}$$

$$3H_2CrO_4 \longrightarrow 2H_2O + H_2Cr_3O_{10} \quad \text{(trichromic acid)} \tag{15}$$

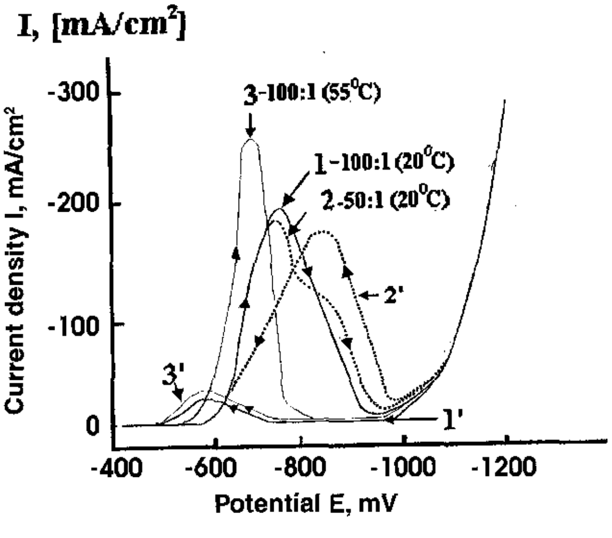


Fig. 2—Linear cyclic polarization (LCP) potential scans for a chromium cathode in a Sargent bath, with concentration ratios of 100:1 (1-1') and 50:1 (2-2') at 20 °C; 50:1 (3-3') at 55 °C; v = 142 mV/sec.

Table 2
Hydrolysis, Equilibrium and Complex Formation Constants[11]

Reaction	Log K
$Cr^{+2} + H_2O \longleftrightarrow Cr(OH)^{+} + H^{+}$	5.3
$Cr^{+3} + H_2O \longleftrightarrow Cr(OH)^{+2} + H^{+}$	-4.2
$Cr^{+3} + 2H_2O \longleftrightarrow Cr(OH)_2 + 2H^{+}$	-10.4
$Cr^{+3} + 3H_2O \longleftrightarrow Cr(OH)_3 + 3H^{+}$	-18.7
$Cr^{+3} + 4H_2O \longleftrightarrow Cr(OH)_4 + 4H^{+}$	-27.8
$2Cr^{+3} + 2H_2O \longleftrightarrow [Cr_2(OH)_2]^{+4} + 2H^{+}$	5.3
$3Cr^{+3} + 4H_2O \longleftrightarrow [Cr_3(OH)_4]^{+5} + 4H^{+}$	-8.7
$4Cr^{+3} + 4H_2O \longleftrightarrow [Cr_4(OH)_6]^{+6} + 6H^{+}$	-13.9
$Cr^{+3} + 3C_2O_4^{-2} \longleftrightarrow [Cr(C_2O_4)_3]^{-3}$	-15.4
$Cr^{+3} + H_2EDTA^{-2} \longleftrightarrow [CrEDTA] + 2H^{+}$	23.4
$Cr^{+3} + SO_4^{-2} \longleftrightarrow CrSO_4^{+}$	1.8
$H_2CrO_4 \longleftrightarrow HCrO_4^{-} + H^{+}$	0.61
$HCrO_4^{-} \longleftrightarrow CrO_4^{-2} + H^{+}$	-5.9
$2HCrO_4 \longleftrightarrow Cr_2O_7^{-2} + H_2O$	2.2
$H_2CrO_4 + Cl^{-} \longleftrightarrow CrO_3Cl^{-} + H_2O$	1.0
$HCrO4^{-} + HSO4^{-} \longleftrightarrow Cr_2SO_7^{-2} + H_2O$	0.60

Table 3
Oxidation Potentials for Chromate Ions[26]

Reaction	E_0, V
$Cr^{+3} + 4H_2O \longrightarrow HCrO_4^- + 7H^+ + 3e^-$	-1.3
$Cr^{+2} + 4H_2O \longrightarrow HCrO_4^- + 7H^+ + 4e^-$	-0.9
$Cr^0 + 4H_2O \longrightarrow HCrO_4^- + 7H^+ + 6e^-$	-0.4
$Cr^{+3} + 4H_2O \longrightarrow CrO_4^{-2} + 8H^+ + 3e^-$	-1.5
$Cr^{+2} + 4H_2O \longrightarrow CrO_4^{-2} + 8H^+ + 4e^-$	-1.1
$Cr^0 + 4H_2O \longrightarrow CrO_4^{-2} + 8H^+ + 6e^-$	-0.6
$HCrO_4^- \longrightarrow CrO_4^{-2} + H^+$	-0.2

Table 4
Thermodynamic Data for Chromate, Bichromate and Dichromate Ions[27]

Ion	Entropy Cal/°K/mol	Entropy of Formation Cal/°K/mol	Heat of Formation Cal/mol	Free Energy of Formation Cal/mol
CrO_4^{-2}	10.5 ±1	-124.5 ±1.0	-208,500	-171,400
$HCrO_4^-$	-	-	-	-180,140
$Cr_2O_7^{-2}$	-	-	-	-305,800

$$4H_2CrO_4 \longrightarrow 3H_2O + H_2Cr_4O_{13} \text{ (tetrachromic acid)} \qquad (16)$$

The change from H_2CrO_4 to $H_2Cr_2O_7$ is rapid, but further polymerization takes measurable time. The color of CrO_3 indicates that it is itself highly polymerized, for it is redder than the di- or trichromates and is approached in color by the tetrachromates. Depolymerization of CrO_3 solution in water is very rapid. It also seems to depolymerize on heating.

Chromic trioxide can be produced by the action of water on chromyl fluoride. It is most commonly produced, however, by action of concentrated sulfuric acid on a chromate, usually sodium dichromate.*

CrO_3 is a powerful oxidizing agent. Bromine has no action on CrO_3 solutions. Iodine, however, turns a solution of CrO_3 black, probably forming a chromium hypoiodite. In the presence of sulfuric acid, iodine is oxidized to iodic acid by CrO_3.

Chromates and Dichromates

Chromates are salts of the hypothetical chromic acid H_2CrO_4. Salts of the hypothetical polybasic chromic acids, $H_2Cr_2O_7$, $H_2Cr_3O_{10}$, $H_2Cr_4O_{13}$, known as dichromates, trichromates, tetrachromates, etc., respectively. Basic salts, derived from hypothetical para and ortho chromic acids H_4CrO_5 and H_6CrO_6 also exist.

Acid solutions of chromic salts are also oxidized to chromates by permanganates and hydrogen peroxide. In alkaline solution, chromic salts are oxidized by hydrogen peroxide, persulfates, oxides of noble metals, hypochlorites, hypobromites, etc. Electrolytic oxidation, in either acid or alkaline solutions, will also convert chromic salts to chromates.

The chromate ion and most of the normal solid chromates are yellow, but on acidifying, the solutions pass through orange to red. The dichromates are red in the solid state and in solution. The higher polychromates are even redder than the dichromate in the solid state. Although the various ions, CrO_4^{-2}, $Cr_2O_7^{-2}$, $Cr_3O_{10}^{-2}$, $Cr_4O_{13}^{-2}$, etc., exist together in equilibrium in solution, the ions higher than dichromate exist only in the most concentrated solutions.[30] Water is easily added to the higher polychromate ions, causing them to revert to the dichromate. On further dilution, even the dichromate ion adds water, forming the chromates. The $HCrO_4^-$ ion exists in quantity only in dilute solution, according to Udy,[28] but more recently, Raman spectroscopy proved non-existence of $HCrO_4^-$ ions in dilute and concentrated solutions.[31]

In basic solutions above pH 6, CrO_3 forms the tetrahedral yellow chromate ion CrO_4^{-2}. Between pH 2 and 6, $HCrO_4^-$ and the orange-red dichromate ion $Cr_2O_7^{-2}$ are in equilibrium; at pH values < 1, the main species is H_2CrO_4. The equilibria are:[27]

$$HCrO_4^- \longleftrightarrow CrO_4^{-2} + H^+ \quad K = 10^{-5.9} \ (F^0 = 8850 \text{ cal}) \qquad (17)$$
$$H_2CrO_4 \longleftrightarrow HCrO_4^- + H^+ \quad K = 4.1 \qquad (18)$$
$$Cr_2O_7^{-2} + H_2O \longleftrightarrow 2HCrO_4^- \quad K = 10^{-2.2} \ (F^0 = 2240 \text{ cal}) \qquad (19)$$

In addition, there are the base-hydrolysis equilibria:

$$Cr_2O_7^{-2} + OH^{-2} \longleftrightarrow HCrO_4^- + CrO_4^{-2} \qquad (20)$$
$$HCrO4^- + OH^- \longleftrightarrow CrO_4^{-2} + H_2O \qquad (21)$$

which have been studied kinetically for a variety of bases.

The pH-dependent equilibria are quite labile and, on addition of a cation that form insoluble chromates (*e.g.*, Ba^{+2}, Pb^{+2} and Ag^+), the chromates, not the dichromates, are precipitated. Moreover, the species present depend on the acid used, and only for HNO_3 and $HClO_4$ are the equilibria as given. With the addition of sulfuric acid, a sulfate complex with chromates is formed in an essentially quantitative conversion:[26]

$$CrO_3(OH)^- + HSO_4^- \longrightarrow CrO_3(OSO_3)^{-2} + H_2O \qquad (22)$$

With polychromates, a heteropoly acid of $Cr_2O_6(OSO_3)^{-2}$ type is formed.[32] Conversion of chromates to dichromates involves formation of an oxygen linkage between chromium atoms. Acid solutions of dichromates are strong oxidants.

$$Cr_2O_7^{-2} + 14H^+ + 6e^- = 2Cr^{+3} + 7H_2O \qquad E_0 = 1.33 \text{ V} \qquad (23)$$

The mechanism of oxidation of Fe^{+2} and other common ions by Cr^{+6} has been studied in detail and, with one- and two-electron reduction respectively, Cr^{+5} and Cr^{+4} are initially formed. The reaction with H_2O_2 in acid solution has a very complex and imperfectly understood mechanism.
The chromate ion in basic solution, however, is a much weaker oxidizer:

$$CrO_4^{-2} + 4H_2O + 3e^- = Cr(OH)_3(s) + 5OH^- \quad E_0 = -0.13 \text{ V} \qquad (24)$$

The crystalline trioxide $(CrO_3)_\infty$ is built of infinite chains formed by the linking of CrO_4 tetrahedra,[33,34] as depicted in

---

* A boiling persulfate solution, in the presence of silver ion as catalyst, oxidizes chromic salts to chromic acid; this method can be used to rejuvenate spent $K_2Cr_2O_7/H_2SO_4$ laboratory "cleaning" solution.[29]

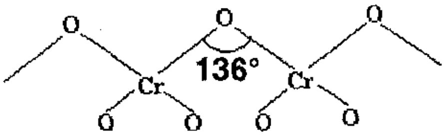


Fig. 3a

Fig. 3b

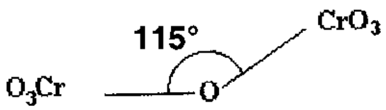


Fig. 3—Structure patterns of simple crystalline chromates.

Fig. 3a. In this bridging, the Cr-O bond has the length of 1.75 Å and the end terminal length is 1.6 Å. There are only Van der Waals forces between the chains, consistent with the comparatively low melting point (197 °C). In simple crystalline chromates,[35] there are tetrahedral CrO_4^{-2} ions in which the Cr-O bond is about 1.6 Å. In $(NH_4)_2Cr_2O_7$, the anion has the structure shown in Fig. 3b.[36]

Polychromates

Polychromates result from sharing corners between CrO_4 tetrahedra, as depicted in Fig. 4. The central Cr-O bonds are found to be much longer (1.91) than the terminal bonds (1.6Å).

Polychromate ions are of particular interest because of their role in chromium plating from hexavalent solutions. It is recognized and accepted that chromium cannot be electrodeposited from Cr^{+6} solutions without the addition of a catalyst, usually in the form of the sulfate. Because the strength of commercial solutions is customarily 1-3 molar, at this concentration, considering the low pH and taking into account the dark red color of the solution, at least the tri- and possibly the tetrachromate ions are present. It should be noted that in the absence of electrical current, the pH of the chromium plating solution is subject to considerable variation, depending on the initial concentration of chromic and sulfuric acids. If the amount of CrO_3 is increased from 10 to 300 g/L (0.1-3 M), the pH changes from 1.4 to 0.08.

Martens and Carpeni,[37] using radioactive chromium, measured the autodiffusion coefficients of isopolychromates at 25 °C in aqueous solution as a function of concentration. Table 5 represents ionic equilibrium dependence on molar concentration. It is evident that in the plating operating ranges (1.5 < C < 3.5 mol/L), the predominant species are di- and trichromate ions.

Table 5
Ionic Equilibrium of CrO_3 in Water[3]

C (conc., mol/L)	Ions in Equilibrium
$C < 10^{-2}$	$HCrO_4^-$
$10^{-2} < C < 10^{-1}$	$HCrO_4^- \longleftrightarrow Cr_4O_7^{-2} + H_2O$
$10^{-2} < C < 1.5$	$Cr_4O_7^{-2}$
$1.5 < C < 3.5$	$3Cr_2O_7^{-2} + 2H^+ \longleftrightarrow 2Cr_3O_{10}^{-2} + H_2O$
$3.5 < C < 7.5$	$Cr_3O_{10}^{-2}$
$7.5 < C < 10$	$4Cr_3O_{10}^{-2} + 2H^+ \longleftrightarrow 3Cr_4O_{13}^{-2} + H_2O$

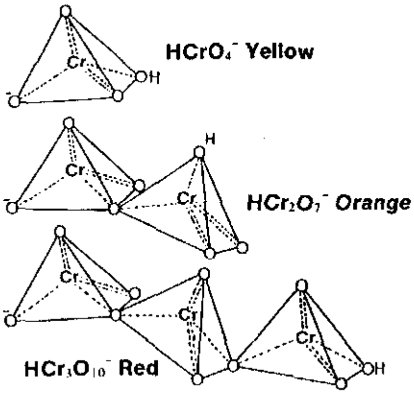


Fig. 4—Structure of polychromates.

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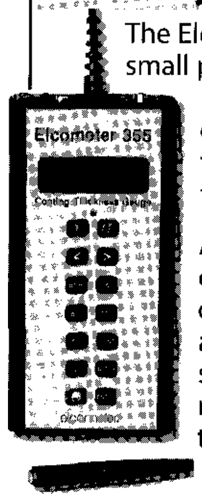

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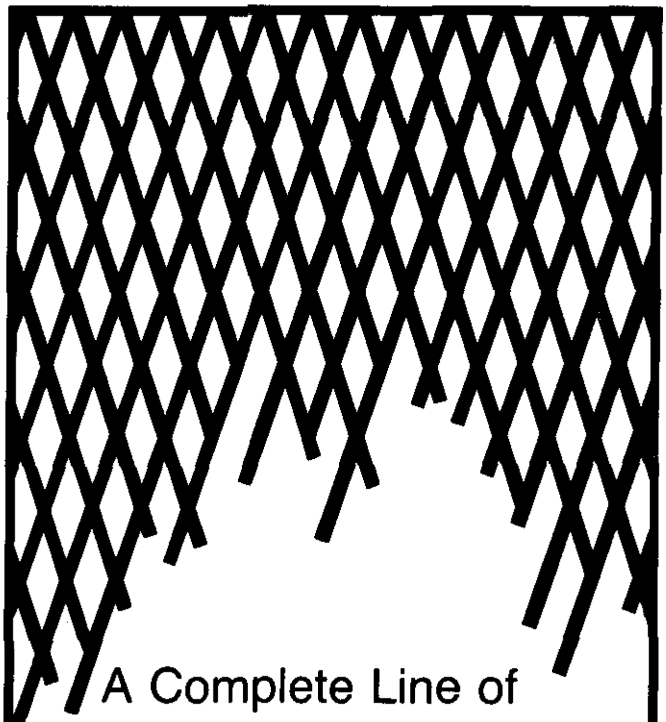

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Interference Coloring of Dual-Anodized Films on Aluminum Containing Electrolytically Deposited Thin Metal Layers

By S. Kawai & M. Yamamuro

This study concerns the properties and structure of oxide films on aluminum, anodized in a sulfuric acid bath, first by DC, and next by AC in the same bath; Sn-Ni metal was then deposited electrolytically into the micropores. Each film showed fine colors that varied from blue, green, and to gold in medium tones as thickness of the AC films increased. EPMA line analyses disclosed that Sn deposited cleanly at the bottom of the micropores, with maximum intensity increasing with the kind of colors. In observations with SEM, the back-scattered electron images proved clearly the difference for AC films; also, the secondary electron images exhibited metal deposition like tree twigs in very fine micropores. The colors obtained indicated good corrosion resistance and light fastness.

Originally, the principle of electrodeposition of anodic films was discovered by Caboni[1] and G. Elssner.[2] Since then, T. Asada[3] invented more practical coloring treatment, and the technology has grown into a large industry because of its superior qualities.

The process consists of two treatments—anodizing of aluminum in sulfuric acid, as usual, to a certain thickness, then Sn or Ni metal deposited electrolytically into the micropores in a conventional plating bath with commercially supplied AC. Finally, dispersed fine metal crystals in the transparent films scatter incident light and produce colors of bronze and black.

One of the authors and a colleague[4] found Sn or Sn-Ni alloy baths that are easy to control for uniform deposits. Also, Keller and Gedde[5] obtained a patent related to the Sn bath. Because of the columnar structure of the deposits, Ni, Co and Fe metals revealed a perpendicular magnetic property.[6]

Durability of Sn colorings was investigated by Gohausen and Schoener,[7] who compared it with Ni and recommended actual applications despite high acid content in the coloring baths. In extensive studies, Baba[8] disclosed that a few H^+ ions penetrate the barrier layer, reach the aluminum base metal, discharge and expand as gas. Moreover, many improved bath compositions and waveforms have been proposed; for example, AC coloring in high-conductivity baths of both Sn and Ni, and DC electrolysis in a Ni bath with extremely low concentration of neutral salts. Unsymmetrical AC, square pulses and anodic DC have been utilized for practical applications.

Recently, composite films anodized in different baths have been of considerable interest. Takahashi *et al.*[9,10] intensively examined pore formations of composite films and pore linking between them.

Optical properties of thin metallic films were studied by Wada *et al.*[11] Meanwhile, Sheasby and Short[12] investigated blue color films generated by optical interference produced by anodizing in sulfuric and phosphoric acids, followed by metal deposition. They noted also that other films produced by anodizing, but beneath metal layers, yielded more light colors. Barba[13] introduced a new process that showed a blue color after anodizing in sulfuric acid, followed by a conditioning treatment in the same bath and by Sn deposition. Recently, many patents related to interference colors have been published, with special interest shown in anodizing by AC.[14]

Preparation of Specimens

1. **Aluminum**
   Specimens were made of sheets of bright mill-finished, 99.9-percent pure aluminum, 100 x 50 x 1 mm.
2. **Pretreatment**

Table 1
Anodizing & Coloring Conditions

Process	Composition g/L		Condition
Anodizing DC (SCR)	H_2SO_4, 150 Al^{+3}, 2		13-16 V 1.0 A/dm² 20 °C 30 min Carbon
Anodizing AC (50 Hz)	As above		3-8 V 1.0 A/dm² 1-8 min Carbon
Coloring AC (50 Hz)	$SnSO_4$	8	10-13 V
	$NiSO_4 \cdot 6H_2O$	25	25 °C
	H_2SO_4	17	2-8 min
	Tartaric acid	10	
	Anti-oxidant	10	
Sealing	$NiSO_4 \cdot 4H_2O$	6	95 °C
	Anhydr. $NaC_2H_3O_2$	2	20 min
	Additive	2	pH 5.8

Table 2
Anodizing Times & Colors

		Specimen Number		
		S-1	S-2	S-3
DC anodizing (min)		30	30	30
AC anodizing (approx. min)		2	4	6
Color		blue	green	gold
CIE	L	58.9	67.5	63.6
	a	-2.8	-6.0	-0.5
	b	-1.0	9.9	26.9