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(Thesis)

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Berkeley, California

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ABSTRACT

Two polynuclear chromium-III species were isolated from refluxed chromic perchlorate and chromic nitrate solutions. The separations were made using an ion-exchange elution. The formulas of the species are believed to be:

$$Cr_2(OH)_2^{4+} \text{ or } Cr_2O^{4+}, \text{ and } Cr_3(OH)_4^{5+} \text{ or } Cr_3O_2^{5+} .$$

Two ion-exchange techniques were especially useful in this identification. In one, the charge per chromium atom was determined from material and charge balance considerations during an elution. In the second, the charge per species was determined from consideration of the equilibrium distribution of the unknown species relative to a known ion between a known amount of resin and a fixed volume of aqueous solution.

Evidence of chromic perchlorate complexing within the resin of these species was found. Similar studies which indicated perchlorate complexing of Fe III, Ce III, Th IV, and La III within the resin were also made.

I. INTRODUCTION

The study of aqueous solutions has long occupied a prominent place in the world of chemistry. In recent years significant advances have been made in understanding the nature of materials dissolved in water, especially metallic ions and the complex ions formed from them. It is now known that even simple $Fe(ClO_4)_3$ dissolves in water to produce a complicated mixture of species.[1] Some of these species contain two, three, or more Fe atoms along with various numbers of O^{2-} or OH^- bridges linking the Fe atoms together. Sillén and coworkers[2] have shown that many other polyvalent metal ions form similar mixtures of polynuclear species in water.

The work on such systems has usually been done by making potentiometric, conductometric, or spectrophotometric measurements on systems in equilibrium. By systematically varying experimental conditions, one can draw conclusions indirectly about the individual species involved. In all cases the original data refer to a mixture of species. It is usually impossible to isolate a single species because most of these species equilibrate rapidly. The relative reactivity of aqueous inorganic species is thoroughly discussed in a review article by Taube.[3]

It was felt that it would be profitable to investigate a system where the component species were inert enough to allow preparation of solutions containing a single species. There are several methods of study possible for single-component solutions which cannot be used when several species are present, while conversely, potentiometric and, to a lesser extent, conductometric techniques do not lend themselves readily to the study of systems that attain equilibrium slowly.

The system of species formed from the +3 oxidation state of chromium was chosen for study. Chromium-III species are very inert in aqueous solution; also there was good reason to think that chromium-III polynuclear hydrolysis products could be prepared. Hall and Eyring observed that upon refluxing, chromic nitrate solutions changed color, became more acidic, and apparently no longer had six water groups around each Cr^{3+} ion.[4] Their studies of the complexing of chromium-III by molybdate ion will be considered in Part V. Much earlier, N. Bjerrum made an extensive investigation of Cr III hydrolysis, and a brief discussion of his work is in order.[5]

Bjerrum obtained the hydrogen ion concentration in Cr III solutions of various compositions by means of EMF measurements. Correcting for the hydrolysis of monomeric species, he calculated the concentration of hydrogen ion arising from the hydrolysis to form polymeric species. With the limited information available, it was not possible to deduce unambiguously both the degree of polymerization and the degree of hydrolysis of the various polymers. Therefore he assumed that species were present with certain degrees of hydrolysis and then calculated their degrees of polymerization from the variation of their equilibrium concentration with the Cr^{3+} concentration. He characterized the system of species thus deduced as being the simplest of those which would explain the data. The degrees of hydrolysis assumed were one OH^- per Cr, two OH^- per Cr, and 2.5 OH^- per Cr. The degrees of polymerization calculated for these three species were, respectively, 2, 6, and 12, in decreasing order of reliability. The corresponding formulas are $(CrOH)_2^{4+}$, $(Cr(OH)_2)_6^{6+}$, and $(Cr(OH)_{2.5})_{12}^{6+}$. Equilibrium constants for the formation of these species were reported.

An investigation somewhat similar to that reported in this thesis was carried on simultaneously by Plane and coworkers.[6,7] A detailed discussion of their results is presented later.

The work reported here consists of (a) the isolation of two polynuclear chromium-III species from refluxed chromic nitrate or chromic perchlorate solutions, (b) the tentative identification of these species as

$$Cr_2(OH)_2^{4+} \text{ or } Cr_2O^{4+}, \text{ and } Cr_3(OH)_4^{5+} \text{ or } Cr_3O_2^{5+},$$

and (c) a preliminary study of the equilibrium between Cr^{3+} and the $Cr_2(OH)_2^{4+}$ species. All work was done with chromium nitrate or chromium perchlorate solutions to avoid complex formation as much as possible.

In the course of the above work, some results bearing on the possible formation of perchlorate complexes in the resin phase of Fe III, Ce III, and Th IV were obtained and are reported.

II. APPARATUS AND EQUIPMENT

All absorption spectra were measured on a Cary recording spectrophotometer Model 11. The wavelength scales were checked against the emission spectra from hydrogen and mercury discharge tubes, and the Fraunhofer lines in the spectrum of the sun. The solution samples were contained in quartz absorption cells while the spectra were being measured. The absorption spectrum of a material was obtained by running a spectrum of a solution containing the material versus air, and then, using the same cell, measuring the absorption of a blank solution versus air. Subtraction of the two curves gave the absorption of the material in solution.

All pH measurements except in the equilibrium experiments were made with a Beckman Model-G pH meter. A calomel electrode will not function properly in a solution containing perchlorate ions because of the formation of a potassium perchlorate precipitate. In order to measure the pH of such solutions it was necessary to immerse the calomel electrode in a saturated potassium chloride solution and connect the potassium chloride solution and the solution to be measured by a salt bridge. This bridge was made by filling 3-mm i.d. glass tubing with agar-agar gel saturated with sodium chloride.

The pH measurements in the equilibrium experiments were made with a Beckman Model-GS pH meter. This meter is sensitive to 0.003 pH unit. The salt bridge used in the equilibrium experiments consisted of a glass tube 1.6 cm i.d. and 7 cm long. The tube was narrowed to a 2-mm orifice at the bottom. The bottom half of the tube was filled with agar-agar gel saturated with sodium chloride, and the top half contained a saturated

potassium chloride solution. The calomel electrode was immersed in the top half of the tube, while the bottom of the tube was placed in the solution to be measured.

Conductivity measurements were made on a standard Leeds and Northrup conductivity bridge.

III. REAGENTS AND ANALYTICAL METHODS

Conductivity water prepared by redistilling distilled water containing alkaline permanganate solution in a Barnstead still was used in the conductivity experiments. Ordinary distilled water was used in all other work.

Most of the ion-exchange experiments were performed with Dowex 50 W, X8, 200 to 400 mesh, analytical-grade, cation-exchange resin. This resin was obtained from Bio-Rad Laboratories, Berkeley, California. Species from refluxed solutions were separated on a special colloidal-size, Dowex 50, X12 resin. This resin was prepared on an experimental basis and is no longer available.

Chromic nitrate solutions were prepared simply by dissolving reagent-grade chromic nitrate in water. A stock solution of chromic perchlorate was prepared by reducing CrO_3 with 30% hydrogen peroxide in the presence of excess perchloric acid.

The solutions prepared in this manner were tested for purity by passing a sample through an ion-exchange column. Frequently the violet band of the Cr^{3+} species was followed by a blue and a green band, indicating the presence of some hydrolyzed chromium products as impurities. These impurities were removed by passing the solution through a column of Dowex 50 W ion-exchange resin. The hydrolyzed impurities were retained on the resin.

Chromous perchlorate was obtained by the reduction of chromic perchlorate on a Jones reduction column.

A stock solution of sodium perchlorate was prepared by treating analytical-grade sodium carbonate with a small excess of perchloric acid

followed by boiling to expel excess carbon dioxide. The pH was adjusted to about 6 with sodium hydroxide.

Cerous perchlorate solutions were prepared from recrystallized, G. F. Smith, primary-standard ammonium hexanitrato cerate by dissolving this ceric salt in dilute hydrochloric acid solution and boiling this solution until the ceric was reduced to cerous chloride. Then the solution was fumed with perchloric acid to remove all chloride.

Thallous perchlorate solutions were prepared by an ion-exchange technique from thallous nitrate. A thallous nitrate solution was passed into a cation-exchange column until the column was completely converted to the thallous form. The column was rinsed with water to remove all traces of nitrate ion. Then a solution of barium perchlorate was introduced into the column. The barium ion has a strong attraction for the resin and displaces all thallous in front of it as it moves down the column. The effect is the same as if a piston were pushing the thallous off the column. The front between the barium and thallous section of the column is very sharp, although usually not level. In this manner pure thallous perchlorate solution was collected as the output of the column. This type of ion-exchange operation will be referred to as a displacement operation throughout this report.

All perchloric acid solutions were prepared by diluting 72% doubly distilled, G. F. Smith perchloric acid. All other chemicals were reagent-grade. They were used without further purification.

Normally, solutions were analyzed spectrophotometrically for chromium as CrO_4^{2-} at 372 mμ with $\epsilon = 4.80 \times 10^3$. Chromium-III was oxidized by

excess 30% hydrogen peroxide in alkaline solution. Reference standards were prepared by diluting weighed samples of $K_2Cr_2O_7$ to known volumes with alkaline solution. Thallous ion interferes with this procedure. The following analytical scheme was worked out for a chromium analysis under conditions where the thallous-ion concentration was about 0.4 M and chromium-III about 10^{-3} M. Ten cc of the solution to be analyzed were placed in a 50-cc beaker along with 2 cc of 0.1 M Na_2SO_4 and made acidic with $HClO_4$. The solution was digested at 90°C for at least 6 hr. (This was to effect complete decomposition of any polynuclear species to Cr^{3+} or a SO_4^{2-} complex.) While the solution was still between 70 and 90°C, 0.5 M KI solution was added dropwise with stirring to precipitate thallous iodide. An excess of about 5% of stoichiometric KI was added. After 10 min digestion at this temperature and 5 min cooling, the solution was filtered through a medium-porosity fritted-glass filter. Five more drops of KI solution were added to the filtrate. After two or more hours, the filtrate was then refiltered. The last traces of thallous ion having now been removed, the solution could be treated as a normal sample for chromium analysis.

In order to test this procedure, five equal portions of chromium solutions were pipetted. To three of these solutions, thallous perchlorate solution was added and the analysis carried out as described. The other two samples were used as controls. The results are shown in Table I. The ratio of the chromium concentration in the control to the chromium concentration in the thallous-containing sample was 1.03. This value was used as a correction factor in every chromium analysis run according to this procedure.

Table I

Test of the chromium analysis of samples containing Tl^+

Optical density,[a] control	Optical density,[a] sample containing Tl^+	Optical density,[b] control	Optical density,[b] sample containing Tl^+
1.226	1.173	1.237	1.191
1.232	1.183	1.236	1.179
	1.213		1.225

[a] Initial solution: $(Cr^{3+}) = 12 \times 10^{-4}$ M, $(Tl^+) = 0.40$ M

[b] Initial solution: $(Cr^{3+}) = 2 \times 10^{-4}$ M, $(Tl^+) = 0.23$ M

Nitrate ion strongly interferes with this procedure. Low values are obtained, probably because chromium is adsorbed on the thallous iodide precipitate. Prolongation of the digestion period after the original thallous iodide precipitation also causes low chromium results. The maximum error of this procedure was estimated to be 3%.

An analysis for total equivalents of charge per unit volume of solution was run several times by using an ion-exchange technique. A column 6 mm in diameter and 25 cm long was packed with Dowex 50W ion-exchange resin. The resin was converted completely to the H^+ form by washing with 2 M HCl solution. This was followed by washing with water until the pH of the output was about 5. A known volume of the solution to be analyzed was added to the top of the column. The added cations displaced H^+ ions at the top of the column, and after the column was thoroughly rinsed with water, all the displaced H^+ ions were washed out. The entire output of the column was collected, and the equivalents of H^+ present determined by titration. The number of equivalents of H^+ displaced is equal to the number of equivalents of charge in the solution added to the column. This value need only be divided by the volume to give the charge concentration. If only one species is present, this method can be used for its determination. Stock $NaClO_4$, $TlClO_4$, $La(ClO_4)_3$, and $Th(ClO_4)_4$ solutions were analyzed by this means.

Thallous solutions containing other species were analyzed by the more conventional potassium bromate oxidation method. It was necessary to have exactly similar endpoint conditions to get reproducible results. The potassium bromate solution was standardized against the $TlClO_4$ stock solution. The thallous concentration in the stock solution was determined

by the ion-exchange method mentioned previously.

Cerrous ion was determined by oxidizing with ammonium peroxydisulfate and titrating sodium oxalate. Ferric ion was determined by the Zimmerman-Reinhardt process, and the hydrogen-ion concentration in ferric solutions was determined by the method of Schumb and Sweetser.[8]

IV. EXPERIMENTAL PROCEDURES

The bulk of the experimental work of this investigation falls into the following categories: (a) the isolation of the components of refluxed chromic nitrate or chromic perchlorate solutions, (b) the determination of the OH^- groups per chromium atom in each of these species, (c) the determination of the charge per chromium atom in each of these species, (d) the determination of the charge per species of each, (e) the determination of the number of molybdenum atoms that can be bound to one chromium atom, as determined by a conductometric titration with ammonium paramolybdate solution, and (f) the study of the equilibrium between Cr^{3+}, H^+, and the blue polynuclear species.

A. Isolation of the Components of Refluxed Chromic Nitrate and Chromic Perchlorate Solutions.

Preliminary experiments were carried out to determine the feasibility of using ion-exchange techniques to separate the components of a refluxed chromic nitrate solution. Chromatographic-type elutions of refluxed chromic nitrate solutions were carried out.

A description of run 4 will indicate the general procedure followed in these experiments. A column 6 mm in diameter and 7 cm long was packed with Dowex 50 x 12 colloidal resin in the Ba^{++} form. A small amount of the same resin was equilibrated ten times with portions of a 0.1 M $Cr(NO_3)_3$ solution which had been refluxed for 1 hr. This resin was then placed on top of the resin in the previously prepared column. Thus before elution began the bottom 95% of the resin was in the Ba^{++} form, while the top 5% consisted of a layer of resin whose exchange sites were filled with

various chromium species. Elution was carried out by passing in a 0.5 M $Ba(ClO_4)_2$ and 2 M $HClO_4$ solution at a flow rate of 0.04 cc per minute. After several hours, five distinct bands could be noticed, all of which were eluted.

Similar experiments using Dowex 50 W, X8, 200 to 400 mesh; Dowex 50, X4, 400-mesh; and Dowex 50, X12, 200 to 400 mesh resins were also carried out, but it was impossible to elute the last green band.

This type of experiment indicated that (a) several species exist in refluxed chromic nitrate solutions, (b) these species are stable for at least several hours, and (c) ion-exchange techniques are feasible for separations.

The chromatographic-type elution used in these experiments had disadvantages. For example, it was impossible to obtain a sample of chromium species that did not also have a high concentration of the eluting species. The fact that only small amounts of material at low concentration could be prepared in this manner was another major drawback.

In order to overcome these drawbacks, a displacement ion-exchange method was used. This procedure was shown to be very effective in the separation of ruthenium species by Cady and Connick.[9] In this type of operation, a column is packed so that the bottom half of the column is filled with resin in the H^+ form and the top half with resin containing chromium species from refluxed chromic perchlorate solutions. A solution containing a strong eluting agent is then introduced into the top of the column. (Such an agent should have a high charge and a small hydrated-ion radius.) The eluting agent completely displaces all chromium species

before it as it moves down the column. The chromium species in turn separate into bands as they move down the column. Care must be taken that enough resin in the H^+ form is used so that all of the most easily eluted chromium species is off the column before any of the second most easily eluted species is eluted.

This type of operation enables one to get fractions containing a single chromium species and no other cationic species except for a small amount of H^+ which is contained in the eluting solution. Any desired concentration can be obtained simply by varying the concentration of the input solution. A fraction was presumed to be pure when both the preceding and following fractions gave the same ultraviolet and visible spectra. The anion concentration of the output fractions is constant throughout a run and is equal to the anion concentration of the input solution. This fact can be readily shown from material-balance considerations. Only if the anion enters into a complexing reaction with the cations present in the resin will this condition fail to hold.

Run 46 was typical of such preparations. Two columns of Dowex 50 x 12 colloidal resin in H^+ form were prepared, each about 20 cm high with a diameter of 8 mm. Into one was passed a solution containing 0.5 M $Cr(ClO_4)_3$ and 0.5 M NaOH which had been refluxed for 6 hr. After complete conversion to chromium and Na^+ forms and a washing with water, this resin was transferred to the top of the previously prepared column of resin in H^+ form. Elution was carried out by passing in a $Th(ClO_4)_4$ solution of total charge concentration equal to 1.10 equivalents per liter at a flow rate of 0.13 cc per minute. Violet, blue, and green bands formed in front of the thorium. All of the green material was not pushed

in front of the thorium, i.e., some of it fell behind the forward front of the thorium and was only gradually eluted. The boundaries separating the various species were quite sharp, but usually were not flat. A flat boundary is very desirable in order to get the maximum yield of pure product. Attempts to flatten the boundaries by using tapered columns, vibrating the columns during elution, and using various techniques for originally packing the column were all uniformly unsuccessful.

Pushing of the green species was only possible when the colloidal resin was used. With other resins the best that could be done was to elute the green species.

The blue species was also prepared by oxidizing chromous perchlorate with oxygen. The products of this oxidation were then purified by ion-exchange methods. This convenient method was developed by Plane and Laswick.[7]

B. Determination of the Number of OH^- Groups per Chromium Atom.

The number of OH^- groups per chromium atom was measured by the following method. The concentration of chromium was determined as well as the concentration of free H^+. (The latter value was obtained from pH measurements and is commented upon later.) The sample was then made alkaline by adding a known amount of sodium hydroxide and oxidized by heating with excess 30% hydrogen peroxide. After oxidation, the alkali content was determined by a potentiometric titration with standardized HCl solution to an end point of about pH 4.2. In this manner any complications due to reaction of the alkali solution with CO_2 were avoided. The correct pH for the end point was determined by running carefully prepared blanks having the same

end-point conditions as the unknowns. The chromium-III species was oxidized according to the following equation:

$$2Cr(OH)_x^{+3-x} + 3H_2O_2 + (8-2x)\ OH^- = Cr_2O_7^{-2} + 7\ H_2O \qquad (1)$$

In writing this equation, the polymerization of the chromium has been omitted for simplicity.

The number of OH^- groups per chromium atom is found from the following equation:

$$\frac{OH^-}{Cr} = \frac{4C + H_1 + H_2 - B}{C}\ , \qquad (2)$$

where C is the number of gram atoms of chromium, B is equivalents of base added, H_1 is equivalents of acid used in titration, and H_2 is equivalents of free H^+ initially present.

This method cannot distinguish between the presence of 2 OH^- groups or a single O^{2-} group. For convenience, all references to results obtained from this type of experiment have been expressed as OH^- per chromium atom, but it should be borne in mind that they might just as well have been expressed in terms of half as many O^{2-} ions per chromium atom.

For both the OH^--per-chromium-atom and the charge-per-chromium-atom experiments, the free H^+ concentration in a solution of the species being studied must be determined. This was done by measuring the pH of the solution. A pH meter measures something that is proportional to the hydrogen-ion concentration,

$$\log^{-1}(-pH) = \gamma\ (H^+), \qquad (3)$$

where (H^+) is the hydrogen ion concentration, and γ is a proportionality constant.

The value of γ for a $Cr(ClO_4)_3$ solution was determined as follows. The same amount of $Cr(ClO_4)_3$ of known concentration was added to each of several 10-ml volumetric flasks. A different, known amount of perchloric acid was added to each flask together with the proper amount of sodium perchlorate to make the perchlorate concentration the same in all samples after dilution to volume. For each sample the following equation is true:

$$Log^{-1}(-pH) = \gamma(H_1^+) + \gamma(H_2^+) + \gamma(H_3^+) , \qquad (4)$$

where (H_1^+) is the concentration of hydrogen ion from the added chromic perchlorate solution, (H_2^+) is the concentration of hydrogen ion from the added perchloric acid, and (H_3^+) is the concentration of hydrogen ions from the hydrolysis of Cr^{3+} to $CrOH^{2+}$. In the preparation of the chromic perchlorate, the exact amount of excess perchloric acid was unknown, and so (H_1^+) was unknown. The value used for (H_3^+) depends on the hydrolysis constant, Q, for the reaction

$$Cr^{3+} + H_2O = CrOH^{2+} + H^+ \qquad (5)$$

$$Q = \frac{(CrOH^{2+})\,(H^+)}{(Cr^{3+})} , \qquad (6)$$

where

$$(H_3^+) = (CrOH^{2+}) = \frac{Q\,(\text{total } Cr^{3+})}{(H^+) + Q} . \qquad (7)$$

The results of the experiment to determine γ for $Cr(ClO_4)_3$ are shown in Table II.

Since (H_1^+) is constant in all samples, a plot of $log^{-1}(-pH)$ versus $(H_2^+) + (H_3^+)$ should give a straight line with a slope equal to γ. A value for Q equal to 1.0×10^{-4} was taken from some work by Bjerrum under

Table II

Factor to convert pH measurements to (H^+)

Sample	pH	H^+ from added $HClO_4$ (M)	Total Cr^{+3} (M)	ClO_4^- (M)
1	2.70	0.00	0.028	0.093
2	2.33	3.11×10^{-3}	0.028	0.093
3	2.13	6.12×10^{-3}	0.028	0.093
4	1.99	9.18×10^{-3}	0.028	0.093

similar conditions.[10] Plotting the results of Table II gave a straight line of slope 0.97, but the value for sample 1 was slightly off the line. A straight line of slope 0.96 through the values for all four samples could be drawn if Q were 0.5×10^{-4}. Even if the value for Q were quite inaccurate, it would not affect the calculation of γ very much. It was assumed that $\gamma = 0.97$ for all the work reported in this thesis. This is a fairly crude procedure, but in the hydroxide-per-chromium-atom experiments the hydrogen-ion concentration can be in error by as much as 10% without seriously affecting the results. Replacing $Cr(ClO_4)_3$ by a chromium, polynuclear, perchlorate salt should not change γ very much, at least not more than 10%, if the perchlorate-ion concentration is kept constant and the hydrogen-ion concentration is about the same. In all pH measurements made to determine free-hydrogen-ion concentrations, the perchlorate concentration was adjusted to be about the same as the solutions shown in Table II.

C. Charge-per-Chromium-Atom Experiment.

1. Method One

The method used by Cady and Connick[9] for the determination of charge per atom of several ruthenium species was initially used to determine the charge per atom for the chromium species. This determination is done simultaneously with the separation of species in a displacement ion-exchange operation. As previously explained, the anion concentration of each fraction is the same as the anion concentration of the input solution to the column. The total charge concentration was determined separately by running the same input solution used in the separations into an ion-exchange column in the H^+ form. Aliquots of the output perchloric

acid solution were then titrated to determine the hydrogen-ion concentration. The hydrogen-ion concentration of the output solution is equal to the total charge concentration of the input solution.

In this method, the aqueous phase contains perchlorate ion at all times. In the experiments reported here, the perchlorate concentration was about 1 M.

2. Method Two

As will be explained later, it was feared that perchlorate complexing might interfere with the results obtained from method 1. In order to avoid this difficulty, the total charge concentration was determined by using the procedure given in Part III, page 10 of this report. In this procedure, the aqueous phase is pure water, and any perchlorate complex present tends to be destroyed.

In both methods, the equation for the calculation of the charge per chromium atom is

$$\text{Charge per chromium atom} = \frac{(x) - (H^+)}{(Cr)} , \qquad (8)$$

where (H^+) is the concentration of free hydrogen ion in the sample studied in M, (x) is the total charge concentration in equiv./l, and (Cr) is the concentration of chromium in the sample studied in g atoms/l.

D. Charge-per-Species Experiments.

An ion-exchange technique similar to that used by Cady and Connick[9] was used to determine the charge per species of the two polynuclear chromium species. The general equation for the distribution of a polyvalent species, M^{n+}, and a monovalent species, B^+, between an aqueous solution and a cation-exchange resin is

$$M^{n+} + \overline{nB^+} = \overline{M^{n+}} + nB^+ . \qquad (9)$$

In this equation, barred symbols denote the resin phase and non-barred symbols the aqueous phase. Equation (9) gives rise to the following equilibrium expression:

$$K_1 = \frac{\overline{M^{n+}}\ (B^+)^n}{(M^{n+})\ \overline{B^+}^n} \quad \frac{\gamma_{\overline{M^{n+}}}}{\gamma_{M^{n+}}} \quad \left(\frac{\gamma_{B^+}}{\gamma_{\overline{B^+}}}\right)^n \quad , \qquad (10)$$

where (M^{n+}) is moles/per liter of solution, and $\overline{M^{n+}}$ is equivalents of M of M per equivalent of resin.

If one could experimentally determine all the concentrations and activity coefficients on the right side, it would be possible to determine both n and K_1 for an unknown species. It would be necessary to perform the experiment under two different conditions. This would give the following pair of independent equations:

$$K_1 = \frac{\overline{M_1^{n+}}\ (B^+)_1^n}{(M^{n+})_1\ \overline{B_1^+}^n} \quad \frac{\gamma_{\overline{M_1^{n+}}}}{\gamma_{M_1^{n+}}} \quad \left(\frac{\gamma_{B_1^+}}{\gamma_{\overline{B_1^+}}}\right)^n \qquad (11)$$

$$K_1 = \frac{\overline{M_2^{n+}}\ (B^+)_2^n}{(M^{n+})_2\ \overline{B_2^+}^n} \quad \frac{\gamma_{\overline{M_2^{n+}}}}{\gamma_{M_2^{n+}}} \quad \left(\frac{\gamma_{B_2^+}}{\gamma_{\overline{B_2^+}}}\right)^n \quad . \qquad (12)$$

Eliminating K_1 between these two equations and solving for n gives:

$$n = \frac{\log \dfrac{(M^{n+})_1\ \overline{M_2^{n+}}}{(M^{n+})_2\ \overline{M_1^{n+}}} + \log \dfrac{\gamma_{(M^{n+})_1}\ \gamma_{\overline{M_2^{n+}}}}{\gamma_{(M^{n+})_2}\ \gamma_{\overline{M_1^{n+}}}}}{\log \dfrac{(B^+)_1\ \overline{B_2^+}}{(B^+)_2\ \overline{B_1^+}} + \log \dfrac{\gamma_{(B^+)_1}\ \gamma_{\overline{B_2^+}}}{\gamma_{(B^+)_2}\ \gamma_{\overline{B_1^+}}}} \quad , \qquad (13)$$

In this study, M^{n+} is always of the form $Cr_x(OH)_{x(3-y)}^{xy+}$, where x is the number of chromium atoms in the species and y is the charge per chromium atom as determined in a separate experiment. Experimentally it was easy to determine the following information about a given equilibration experiment: the total g-atoms of chromium present, the chromium concentration in solution at equilibrium (in terms of g-atoms chromium per liter), the total equivalents of resin, and the total equivalents of balance species B^+. By material-balance considerations, the g-atoms of chromium in the resin phase can be determined as well as the equivalents of species B^+ in the resin, if one knows the average charge per chromium atom. Dividing by the total equivalents of resin present, one obtains the resin-phase concentrations. The concentration of B^+ in solution can also be determined from material-balance considerations. The aqueous concentration of $Cr_x(OH)_{x(3-y)}^{xy+}$ in moles per liter cannot be obtained, but fortunately only the ratio

$$[Cr_x(OH)_{x(3-y)}^{xy+}]_2 \; / \; [Cr_x(OH)_{x(3-y)}^{xy+}]_1 \; ,$$

is required in Eq. (13). This ratio is the same as the known ratio $(Cr)_2/(Cr)_1$, where the concentrations are expressed in g-atoms per liter.

If conditions can be chosen such that the activity-coefficient terms in Eq. (13) are negligible, it can be seen that determination of n by Eq. (13) is experimentally possible.

Experiment 24 was a typical experiment of this type. In order to optimize the accuracy of results, it was necessary to use two monovalent species. The reasons for this step as well as the other factors considered

in designing this experiment will be discussed later. For the first equilibration 15 meq. of resin in thallous form, 28 mmoles of thallous perchlorate, an amount of blue polynuclear chromium species containing 1.4 mg-atoms of chromium, and enough water to make the volume of the aqueous phase 80 cc were mixed in a 300-cc centrifuge bottle. Mixing was provided by stirring at about 300 rpm. Temperature was maintained at 23.0 $\pm$ 0.5°C. After 3 hr, the two phases were separated by centrifuging and two 5-cc samples of the aqueous phase were removed for chromium analysis. Mixing was resumed and the sampling for chromium analysis was repeated again 2 hr later. At that time an additional 50 cc of solution was also withdrawn. These conditions gave $(Tl^+) \cong 0.4\underline{M}$, $\overline{Tl^+} \cong 0.85$ eq/eq resin, $(Cr) \cong 31 \times 10^{-4}$ g-atoms Cr/l, $\overline{Cr} \cong 0.15$ eq/eq resin at equilibrium. The conditions for the second equilibration were established by adding 11 mmoles of thallous perchlorate, 17 mmoles of lithium perchlorate, and water to bring the volume to 80 cc again.

Samples for chromium analysis were taken at 2 and 5 hr, and at 5 hr samples were also taken for thallous analysis. The conditions of this second equilibration gave $(Tl^+) \cong 0.2\ \underline{M}$, $\overline{Tl^+} \cong 0.75$ eq/eq resin, $(Cr) \cong 5.2 \times 10^{-4}$ g-atoms Cr/l, $\overline{Cr} \cong 0.15$ eq/eq resin.

In this experiment, it was necessary to know the number of equivalents of exchange sites present. In the work of Cady and Connick,[9] this was done by noting the weight of H^+ form resin and multiplying by the previously determined equivalent weight of the resin. In practice, the equivalent weight of the resin is not a very precise quantity, since it varies with the amount of water absorbed in the resin. In order to avoid this difficulty the total number of equivalents of exchange sites of a

quantity of resin sufficient for several experiments was determined. The number of exchange sites in the resin used in a particular experiment was determined from

$$E_1 = \frac{W_1}{W} E , \qquad (14)$$

where E_1 is the number of equivalents of resin for an experiment, W_1 is the weight of resin for an experiment, W is the total weight of the resin, and E is the total number of equivalents of resin.

In order to accomplish this, resin in the H^+ form was placed in a column of known weight, and acid-free thallous nitrate solution was passed through until all H^+ had been replaced. After thorough rinsing with water to remove all nitrate and air drying, the weight of the resin was determined by weighing the whole column and subtracting the weight of the empty column. The total number of equivalents of resin was determined by titrating an aliquot of the displaced H^+.

One of the most important factors to be considered in designing a charge-per-species experiment is to make the activity-coefficient term in Eq. 13 negligible, since in general it is not possible to determine all of these values. This can be done if conditions are such that the activity coefficients of both parts of an experiment remain the same. Changes in the resin-phase activity coefficients can be minimized by keeping the composition of the resin phase the same in both experiments. This can be done in any of three ways: (a) holding $\overline{M^{n+}}$ to a low value, so that only a small percentage of the resin exchange sites are occupied by M^{n+}, (b) keeping almost all M^{n+} species in the resin phase, or (c) running preliminary experiments to determine an approximate value of K_1 and

calculating conditions such that the resin concentration of M^{n+} is held constant.

Changes in the aqueous-phase activity coefficients can be minimized by keeping the anion concentration and the ionic strength the same in both parts of the experiment. This can be done in a three-component system, i.e., M^{n+} and two monovalent species. In order to change appreciably the concentration of M^{n+} between the two parts of the experiment, one of the monovalent species must have a much greater attraction for the resin than the other.

It is not possible to maintain a constant anion concentration in the aqueous phase and not vary the composition of the resin. However, it is possible to keep the concentration of M^{n+} in the resin constant so that the percentage of exchange sites occupied by singly charged species remains constant. If the two monovalent species differ greatly in their attraction to the resin, changes in the ratio of the two singly charged species can be minimized. This difference in attraction is given by Q_2 in the following equation:

$$Q_2 = \frac{\overline{B_1^+} \quad (B^+)_2}{(B^+)_1 \quad \overline{B_2^+}} \tag{15}$$

Bonner[11] has measured Q_2 as a function of resin composition for several pairs of singly charged cations, holding the aqueous phase at constant ionic strength. For most pairs of ions considerable change in Q_2 was observed as the resin composition was changed. This indicated that changes occurred in the resin-phase activity coefficients. For $Tl^+ - H^+$ and $Tl^+ - Li^+$, Q_2 was almost independent of the resin composition. Thus

it seems reasonable to believe that changing the ratio of $\overline{Tl^+}$ / $\overline{H^+}$ or $\overline{Tl^+}$ / $\overline{Li^+}$ is less apt to change the resin-phase activity coefficients than changing the ratio for most other pairs. This is the main reason that Tl^+ was chosen rather than any other strongly held ion such as Ag^+. The Q_2 values for $Tl^+ - H^+$ and $Tl^+ - Li^+$ are also far from unity.

It is desirable to have the ratio of $(M^{n+})_1/(M^{n+})_2$ in Eq. 13 as large as possible to minimize error. For example, for n = 4 and the ratio of $(M^{n+})_1/(M^{n+})_2 = 2$, a 10% error in the determination of $(M^{n+})_1$ will cause an error of 0.6 in n, while for $(M^{n+})_1/(M^{n+})_2 = 4$, the same 10% error will cause an error of only 0.3 in the determination of n.

For somewhat the same reason, it is desirable that the known species in the experiment be singly charged rather than doubly or triply charged. If a doubly charged ion is used for the known species, Eq. 13 becomes:

$$\frac{n}{2} = \frac{\log \frac{(M^{n+})_1}{(M^{n+})_2} \frac{\overline{M_2^{n+}}}{\overline{M_1^{n+}}} + \log \frac{\gamma_{M_1^{n+}}}{\gamma_{M_2^{n+}}} \frac{\gamma_{\overline{M_2^{n+}}}}{\gamma_{\overline{M_1^{n+}}}}}{\log \frac{(B^{++})_1}{(B^{++})_2} \frac{\overline{B_2^{++}}}{\overline{B_1^{++}}} + \log \frac{\gamma_{B_1^{++}}}{\gamma_{B_2^{++}}} \frac{\gamma_{\overline{B_2^{++}}}}{\gamma_{\overline{B_1^{++}}}}} \quad . \qquad (16)$$

In the example where n = 4 and with the ratio $(M^{n+})_1/(M^{n+})_2 = 4$, a 10% error in $(M^{n+})_1$ will produce an error of 0.6 in the value of n, while in the previous paragraph it was shown that with a singly charged species the error would be only 0.3.

The amount of any component in the resin phase was determined by subtracting the amount in the aqueous phase from the total amount of that

component. For optimum accuracy, the ratio of the amount in the resin to the amount in the solution for all components should be as large as possible.

However, if the ratio of the amount of resin to the amount of solution becomes too high, erratic results develop. For example, in a test experiment using Cr^{3+} where 20 meq of resin and 40 cc of solution were used, n was calculated to be 2.54. A similar experiment in which 10 meq of resin was used gave n = 2.98.

The attainment of equilibrium was tested by sampling after three and five hours of mixing. In all cases the analyses of the two samples were in close agreement.

E. Molybdenums-per-Chromium Experiment.

The polynuclear species were titrated conductometrically according to the procedure of Hall and Eyring.[4] A solution of chromium-III was titrated with an ammonium paramolybdate solution which was 0.1 M in Mo.

F. Equilibrium Studies.

Equilibrium studies were carried out on the equilibrium between Cr^{3+} and the blue polynuclear species. For this study a series of samples was prepared all having a chromium concentration of 0.03 M, and an ionic strength of 1 (maintained with sodium perchlorate), but each having a different, known amount of added NaOH. Because of the slow reaction rates of the species involved, the studies were carried out at 50°C. The solutions were judged to be at equilibrium when the pH was constant for 24 hours. To be safe, all samples were allowed to remain at least 48 hours in the bath. pH measurements precise to 0.002 pH unit were made at 50°C by using a Beckman pH 4 buffer standardized at that temperature.

After determination of pH, the solutions were quickly cooled to $0^{\circ}C$ in an ice bath and stored thereafter at $4^{\circ}C$. The concentrations of Cr^{3+} and blue polymer were determined by a combination ion-exhcnage and spectrophotometric procedure. The chromium in a known volume of solution was completely absorbed on a column of Dowex 50 W resin. This resin was then transferred to the top of another column of Dowex 50 W resin in the H^{+} form. Thus, before elution began, the bottom half of this second column was in the H^{+} form and the top half was in the Na^{+} and chromium form. A displacement type of elution was then carried out by using a thorium perchlorate solution with total charge concentration equal to 1.1 eq/l. The flow rate was 0.1 cc/min.

The output of this column was collected in four fractions. The first fraction containing only H^{+} and Na^{+} was discarded. The second fraction containing only Na^{+} and violet Cr^{3+} was retained, diluted to a known volume, and analyzed for chromium. The third fraction containing some violet Cr^{3+}, all of the blue, polynuclear, chromium species, and some of the first eluted, green polynuclear species was also retained, diluted to a known volume and analyzed for chromium. The visible and ultraviolet spectrum of this fraction was also measured. From the known spectra of the three chromium species present as well as the total chromium concentration, the concentration of each species in this third fraction was calculated. The presence of chromium species other than the three collected in the third fraction prevented the calculation of the concentration of Cr^{3+} and the blue polynuclear species directly from spectral measurements of the equilibrium solutions.

V. RESULTS AND DISCUSSION

The displacement-type ion-exchange separations were quite successful and provided enough pure material to carry out identification studies. In the preliminary elution experiments, five chromium bands were observed, which came off in the order two violet, one blue, and two green bands. In the displacement-type separations, only three chromium species were isolated. The extra species in the elution experiment might have been ClO_4^- complexes, since the elution was carried out in about 3 M ClO_4^-, while in the displacement-type separations, the ClO_4^- concentration was about 1 M or less. It is also possible that the green material not pushed in the displacement-type separations contained more than one chromium species.

After isolating the new blue and green chromium species, it was necessary to characterize them. It seemed plausible to expect these species to be polynuclear and to carry charges greater than +3. The usual cryoscopic techniques are of little value in such cases. Activity coefficients are not known. In solutions concentrated enough to make accurate measurements, the activity-coefficient errors would make the results meaningless, especially since in an attempt to differentiate between a 4-1 and a 5-1 electrolyte, there is only a difference of 16% in the number of particles per species. Attempts were made to prepare solid samples for x-ray crystallography without success. This matter will be discussed in more detail later.

The ion-exchange techniques Cady and Connick[9] used in the study of ruthenium species were applicable to the study of the chromium species.

From these experiments one gets the average charge per M atom, y, and the charge per species, xy, of any species of the general form $M_x(OH)_{x(3-y)}^{xy+}$. From such information it is possible to determine the number of M atoms in a species. If the oxidation number of M is known, it is also possible to determine how many negatively charged groups are in the species. For example, if for a given species the charge per atom is +2, the charge per species is +4, and the metal is known to be in the +3 oxidation state, the species would have to be $M_2A_2^{4+}$ or M_2B^{4+} where A is a singly charged negative group and B is a doubly charged negative group.

The spectra shown in Fig. 1 are from solutions containing pure Cr species and a perchlorate concentration of 0.1 M. No effort was made to study the effect of (ClO_4^-) on the spectra, other than the qualitative observation that no major change occurs as (ClO_4^-) is changed.

Laswick and Plane have also reported the spectra of these species.[7] Their fraction 2 corresponds to the blue species and fraction 3 probably corresponds to the green species. The curves are quite similar to, but not exactly like, those reported here. For the blue species, Laswick and Plane report peaks at 418 mμ and 528 mμ having absorbances per g-atom of chromium of 22.5 and 18.9, respectively. In this report the peaks are at 416 mμ and 580 mμ, but the absorbancies are 20.1 and 17.2. Such differences are hard to understand. The perchlorate concentration in both studies was about 0.1 M, and both studies were based on samples prepared from the oxidation of Cr^{2+} by oxygen and other samples prepared by isolating the blue species from refluxed Cr^{3+}. The only noticeable difference is the presence of La^{3+} in the solutions studied by Laswick and Plane, but this should not be of any great significance.

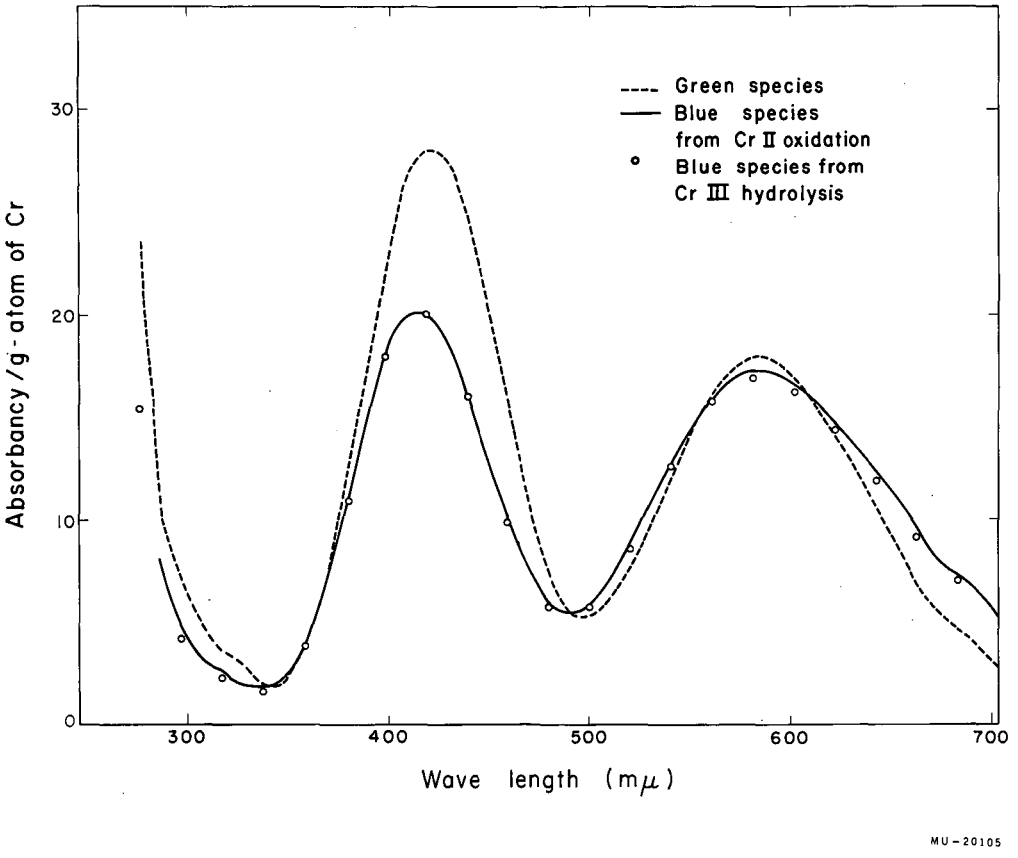


Fig. 1. Spectra of polynuclear Cr III species in 0.1 M perchlorate.

A. The Blue Polynuclear Species.

The bulk of the work on this species was performed on material prepared by the O_2 oxidation of $Cr(ClO_4)_2$. This material is identically the same as that isolated from refluxed Cr^{3+} solutions. Products prepared by the two methods have the same spectra (see Fig. 1), the same OH^--per-chromium-atom value, and the same charge-per chromium-atom value in 1 M ClO_4^- solution.

1. Hydroxyl-ions-per-Chromium-Atom Experiment

The method described in Part IV, B was used to determine the ratio of hydroxyl ions to chromium atoms. Table III gives the values necessary to calculate OH^-/Cr according to Eq. (2). The column headings are the quantities in Eq. (2). There seems little doubt that the true value of the OH^- per chromium atom for the blue species is 1.00.

The uncertainty in the results presented in Tables III and VIII is the maximum error calculated by assuming a 0.5% error in the g-atoms of chromium, a 5% error in the amount of initial free H^+, a 0.2% error in the amount of OH^- added, and an error of 1% in the amount of H^+ used in the titration.

Plane and Ardon[6] titrated a sample of the blue species conductometrically with NaOH. From the break point in the curve, they calculated the charge per chromium atom to be $1.97 \pm .04$, assuming there was no perchlorate complexing.

2. Charge-per-Chromium-Atom Experiments

The first method described in Part IV, C was used initially to determine the charge per chromium atom. In this procedure the aqueous phase contained about 1 M ClO_4^-. It was suspected that under this condition the perchlorate

Table III

Hydroxyl ions per chromium atom for the blue species

Sample source	Mg atom of Cr	Initial meq free H^+	Meq OH^- added	Meq H^+ used in titration	OH^- per Cr atom
Oxidized $Cr(ClO_4)_2$	0.387	0.169	2.000	0.670	$1.00 \pm .05$
Refluxed $Cr(ClO_4)_3$	0.400	0.140	2.000	0.675	$1.04 \pm .05$
Refluxed $Cr(NO_3)_3$[a]	0.108	0.070	1.008	0.594	0.82

[a]This was an early run and the material was not as carefully purified as was the case later. It is probable that an appreciable amount of Cr^{3+} was present.

ion might be complexing the blue species in the resin phase. Thus, further experiments using the second method described in Part IV, C were run. In this case the aqueous phase is pure water. The results of these experiments are given in Table IV.

The uncertainty in the results presented in Tables IV and IX is the maximum error calculated by assuming a 0.5 % error in the chromium concentration, a 5% error in the hydrogen-ion concentration, and a 0.5% error in the total-charge concentration.

The hydroxyl-ion-per-chromium-atom experiments indicated that, if no complexing occurred, the charge per chromium atom would be two. This is in agreement with Experiment 3. However, in Experiments 1 and 2 the charge per chromium atom is less than two, indicating the presence of a perchlorate-complexed species in the resin phase. Unfortunately, it is not possible to determine from these data the amount of complexing in the aqueous phase. This problem will be discussed in the section on the possible complexing by perchlorate ion of Fe III, Ce III, etc.

It should be noted that the perchlorate complex formed with the blue species is fairly labile because it completely broke up within a few minutes during Experiment 3.

3. Charge-per-Species Experiments

From the hydroxyl-per-chromium-atom and the charge-per-chromium-atom experiments, it was expected that a charge-per-species experiment on the blue species would give a value that was an integral multiple of +2. The actual results are given in Table V.

Calculations based on the estimated maximum errors of the measurements made in running the charge per species experiments showed that the probable

Table IV

Charge per chromium atom of the blue species

Experiment	Sample Source	Method	Total charge concentration (equiv/l)	pH[a]	(H^+) M	(Cr) (g atoms/l)	Charge per Cr atom
1	Refluxed $Cr(ClO_4)_3$	1	1.100	1.77	0.172	0.492	1.89 ± .04
2	Oxidized $Cr(ClO_4)_2$	1	1.100	1.69	0.208	0.473	1.89 ± .04
3	Oxidized $Cr(ClO_4)_2$	2	1.176	1.69	0.208	0.473	2.05 ± .04

[a]pH is of the sample diluted 1.016 cc to 10.00 cc.

The eluting solution in the first two experiments was $Th(ClO_4)_4$ prepared from the solid salt and water.

Table V

Charge per species of the blue species and Cr^{3+}

Experiment	Species (preparation)	Total Cr (mg-atoms)	Total Tl^+ (m M)	V (m l)	Equivalents of resin (meq)	(Tl^+) (M)	(Cr) (g atoms/l)	(ClO_4^-) (M)	Charge species
23A[a]	Cr^{3+} (from reduction of CrO_3)	0.226	23.64	38.03	10.01	0.370[c]	20.14×10^{-4}	0.4	2.98
23B[a]		0.175	17.53	42.66	10.01	0.210[d]	5.19×10^{-4}	0.4[e]	
24A[a]	Blue (from oxidized Cr^{2+})	1.413	43.50	79.83	14.98	0.386[c]	30.8×10^{-4}	0.4	3.24
24B[a]		1.197	27.31	79.96	14.98	0.200[d]	5.19×10^{-4}	0.4[f]	
26A[b]	Blue (from oxidized Cr^{2+})	1.415	43.55	79.83	15.03	0.386[c]	32.6×10^{-4}	0.4	3.23
26B[b]		1.185	27.31	79.80	15.03	0.200[d]	5.58×10^{-4}	0.4[f]	

[a] Room temperature

[b] Temperature: 22°C

[c] Calculated from the equation $(Tl^+) = \frac{\text{Total equiv. } Tl^+ - \text{equiv. resin} + \text{equiv. Cr resin}}{\text{liters of solution}}$

[d] Measured

[e] $HClO_4$ used to maintain (ClO_4^-)

[f] $LiClO_4$ used to maintain (ClO_4^-)

error for the blue species would be less than 0.1 of a charge unit. As previously explained, the experiment was carefully designed to eliminate errors due to activity coefficients. The value of 2.98 for the charge per chromium atom obtained by using $Cr(ClO_4)_3$ is an excellent verification of the general validity of this method.

The observed results can be explained by assuming the presence of two chromium species, one of charge +3 and the other of charge +4. It was first suspected that Cr^{3+} might have been present as an impurity. The amount of Cr^{3+} necessary to produce the results of runs 24 and 26 can be calculated. From the Cr^{3+} data of experiment 23 the value of Q_1 of the concentration term of Eq. (10) was calculated to be 1.29. A guess was then made as to the percentage of the chromium atoms present as Cr^{3+}. From Eq. (10), the conditions of experiment 24, the preceding guess, and $Q_1 = 1.29$ for Cr^{3+}, the concentration of Cr^{3+} in both phases can be calculated for both parts A and B of experiment 24.

The concentration of the blue species in each phase was found by subtracting the concentration of Cr^{3+} from the total chromium concentration in a phase. A value of n was then calculated from Eq. 13. The process was repeated, varying the initial assumption about the percent of Cr^{3+} until a value of n = 4.0 was obtained. The results of such calculations show that 20% to 25% of the chromium would have had to have been Cr^{3+}. The OH^- - per chromium-atom experiments indicate that the solutions of the blue species contained very little Cr^{3+}, certainly not 20%. However, these experiments were always run before the charge-per-species experiment, and some slight further decomposition could have occurred. The results might still be explained by Cr^{3+} if decomposition of the blue species

to Cr^{3+} occurred during an experiment. In this case the chromium concentration would be continually changing during each part of the run, but no such changes were observed. Therefore the charge-per-species experiments on the blue material cannot be explained by the presence of Cr^{3+}.

An attempt was made to explain the results by postulating the presence of a +3 perchlorate complex of the blue species. Detailed calculations were made for the conditions of experiment 26. It was assumed that only two chromium species were present, $Cr_2(OH)_2^{4+}$ and $Cr_2(OH)_2\,ClO_4^{3+}$. For this calculation the following equations are necessary:

$$Q_A = \frac{[Cr_2(OH)_2\,ClO_4^{3+}]_a}{[Cr_2(OH)_2^{4+}]_a\,(ClO_4^-)_a} \tag{17}$$

$$Q_B = \frac{\overline{Cr_2(OH)_2^{4+}}_a\,(Tl^+)_a^4}{[Cr_2(OH)_2^{4+}]_a\,\overline{Tl^+}_a^4} \tag{18}$$

$$Q_C = \frac{\overline{Cr_2(OH)_2\,ClO_4^{3+}}_a\,(Tl^+)_a^3}{[Cr_2(OH)_2ClO_4^{3+}]_a\,\overline{Tl^+}_a^3} \tag{19}$$

$$\alpha_a = 2\left(\frac{\overline{Cr_2(OH)_2ClO_4^{3+}}_a}{3} + \frac{\overline{Cr_2(OH)_2^{4+}}_a}{4}\right) \tag{20}$$

$$\beta_a = 2\,[Cr_2(OH)_2ClO_4^{3+}]_a + 2\,[Cr_2(OH)_2^{4+}]_a\,. \tag{21}$$

In Eqs. (20) and (21) α_a is the g-atoms of chromium per equivalent of resin and β_a is the g-atoms of chromium per liter of solution.

In the above equations the subscript "a" indicates the conditions in part A of experiment 26. The equations for part B are not written out because they are exactly the same as above except for the subscript "b" that replaces subscript "a".

The ten equations obtained above can be simplified by eliminating Q_A, Q_B, and Q_C, leaving seven equations. The material-balance equations can be utilized to eliminate all perchlorate terms, leaving only three equations. Further work gives an explicit expression for $\overline{Cr_2(OH)_2^{4+}}_a$.

$$\overline{Cr_2(OH)_2^{4+}}_a = \frac{2\alpha_b \frac{\beta_a}{\beta_b} \left\{ \frac{(Tl^+)_b \; \overline{Tl^+}_a}{\overline{Tl^+}_b \; (Tl^+)_a} \right\} - 2\alpha_a \frac{(Tl^+)_b \; \overline{Tl^+}_a}{\overline{Tl^+}_b \; (Tl^+)_a}}{1 - \frac{(Tl^+)_b \; \overline{Tl^+}_a}{\overline{Tl^+}_b \; (Tl^+)_a}} \quad . \quad (22)$$

For the conditions of experiment 26, this value is 0.026 equivalent per equivalent of resin. Further calculation shows that only 17% of the chromium atoms in the resin could be in the species $Cr_2(OH)_2^{4+}$.

A similar calculation based on the assumption that the two chromium species were $Cr_2(OH)_2^{4+}$ and $Cr_2(OH)_2(ClO_4)_2^{2+}$ gives $\overline{Cr_2(OH)_2^{4+}}_a = 0.0733$ and 48% $Cr_2(OH)_2^{4+}$ in the resin. Calculations involving the dimer complexed by three perchlorates will increase the percentage of $\overline{Cr_2(OH)_2^{4+}}_a$, but not significantly.

The results of the charge-per-chromium-atom experiments can also be explained by the presence of perchlorate complexes. From the value of 1.89 for the charge per chromium atom (Table IV), one calculates that

about 78% of the chromium in the resin phase is in the $Cr_2(OH)_2^{4+}$ form if $Cr_2(OH)_2\ ClO_4^{3+}$ were the only other species. For the pair $Cr_2(OH)_2^{4+}$ and $Cr_2(OH)_2\ (ClO_4)_2^{2+}$, 89% would be $Cr_2(OH)_2^{4+}$. Thus although both types of experiments can be explained individually by perchlorate complexes, they are far from being consistent with each other.

Nonexchange absorption in the resin phase could be another explanation of this experiment. If the amount of chromium absorbed is proportional to the concentration of chromium in solution, in Eq. (13) one would replace $\overline{M_2^{n+}}$ by $\left\{ \overline{M_2^{n+}} - \bar{x} \left[(M^{n+})_2 / (M^{n+})_1 \right] \right\}$ and $\overline{M_1^{n+}}$ by $(\overline{M_1^{n+}} - \bar{x})$ where $\bar{x}$ is a constant. For the conditions of experiment 26, about 38% of the chromium in the resin phase in part A would have to be absorbed to give n = 4. This explanation could be checked by repeating the experiments at lower electrolyte concentrations; if it were valid one would expect larger n values. Such experiments would be difficult to perform because of the low aqueous chromium concentrations which would result. The above calculated result appears to be inconsistent with the charge per atom result, although the experimental conditions differ considerably. Further, the "normal" behavior shown by Cr^{+3} would indicate that more than nonexchange absorption is involved. (See also Section V, C).

Plane and Ardon[6] made a somewhat similar study of the charge per species, using La^{3+} as a balance species, ClO_4^- as an anion, and making observations at three different concentrations. They reported a value for n of 2.96. The n value calculated for the two most concentrated solutions, total (ClO_4^-) = 0.250 M and (ClO_4^-) = 0.174 M, was 0.279, while for the lowest pair, (ClO_4^-) = 0.174 M and (ClO_4^-) = 0.086 M, a high value for n = 2.96 was reported. This trend would be in agreement with complexing.

No attempt was made to keep the ionic strength constant, and a +3 balance species was used, but still their results are not too different from those reported here.

No completely satisfactory explanation of the charge per species results can be presented. A combination of the three possible causes of error presented here seems to be the most plausible explanation. An uncomplexed +4 species fulfills the restriction of the method-two charge-per-chromium-atom experiment in that its charge is a whole number multiple of +2.

Further understanding of the situation could be developed if several charge-per-species experiments could be run with different perchlorate concentrations. The insolubility of thallous perchlorate prevents one from going to higher perchlorate concentrations, and chromium analytical problems become difficult at lower perchlorate concentrations.

4. Molybdenums-per-Chromium-Atom Experiments

Hall and Eyring found that if one followed the addition of an ammonium paramolybdate solution to a Cr^{3+} solution conductometrically, a break occurred at a ratio of 6 molybdenums per chromium. Unlike most reactions of Cr^{3+}, this one was observed to proceed rapidly. When the same procedure was tried on refluxed 0.5 M $Cr(NO_3)_3$ solutions, they found the Mo/Cr ratio dropped to 4.7. In interpreting their results, they assumed that every water in the first coordination sphere of a Cr III species was replaced by a Mo atom or a group containing a Mo atom. If true, this would be a very useful way to determine the number of first-coordination-sphere water molecules in any Cr III species.

This explanation does not tell why the molybdate reaction proceeds rapidly whereas complexing of Cr III is usually very slow. The great speed can be explained if it is assumed that the oxygen atoms in the six water molecules originally surrounding a Cr^{3+} atom are never displaced by a Mo group, but rather the Mo groups displace the protons from the waters and arrange themselves so that the oxygen atoms left are shared by both the Mo and the Cr atoms. The resulting species would have each Mo and Cr atom surrounded by six oxygen atoms arranged octahedrally. Such a species can be visualized by imagining the Mo and Cr octahedrons sharing edges or perhaps faces. A detailed discussion of such structures as well as further comments on the results of Hall and Eyring is given by Baker et al.[12] This idea explains the speed of the reaction by the fact that no Cr-O bonds are broken. For species other than the hexaaquo chromic ion, the relationship between the Mo/Cr ratio and the number of waters is not clear. For example, it might be that no Mo groups would attack a chromium species which did not have at least two cis water groups to provide an edge for sharing. In this case the Mo/Cr would not indicate the number of waters on the chromium.

It would certainly be interesting to determine the Mo/Cr ratio for several known Cr III species. A study using O^{17} as a tracer could be made to see if the Cr-O bonds are broken in the reaction of Cr^{3+} and the molybdate reagent. No matter what the results might turn out to be, the method should be able to provide valuable information about complex ions.

By following the procedure of Hall and Eyring, a value of 2.9 Mo/Cr was obtained for the blue species. Unfortunately only a single determination

was made, but Laswick and Plane[7] reported a value of 2.8, which is in close agreement. Complexing by ClO_4^- was avoided by keeping the ClO_4^- concentration about 0.006 M. Clearcut interpretation of these results awaits further study of the method. Certainly the data cannot readily be explained by saying that there are only three waters per chromium atom in the blue species.

5. Attempts to Prepare a Solid Salt

Considerable effort was made to prepare a solid salt of the blue species. Concentrated HCl, HBr, and $HClO_4$ solutions containing equal portions of the blue species at a concentration such that the chromium was 1 M were prepared with and without added EtOH. These solutions were concentrated by removing water and alcohol on a vacuum line and then cooled to $0^\circ C$. The result was either a thick oil or a decomposition to Cr^{3+}. The oil rapidly picked up water when exposed to air. Solutions of the Br^- salt of the blue species were next prepared by adsorbing the blue species on a cation exchange column and running a displacement-type elution using $LaBr_3$ as an eluting agent. Solutions containing equal portions of its 1 M solution and water, EtOH, acetone, pyridine, and picric acid were prepared. Again, removal of solvent was carried out on a vacuum line, but only oils and Cr^{3+} resulted. Apparently salts of the blue species are just extremely soluble in water. Ardon and Plane do report the preparation of a solid, green, sulfate compound.[6]

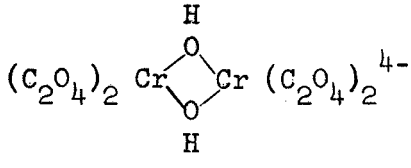
6. Stability Experiments

A few crude experiments on the stability of the blue species at room temperature were carried out by noting the time necessary for the color to change to the violet of Cr^{3+}. In 2.8 M $HClO_4$ this change was

completed in about 2 weeks. In 0.001 M $HClO_4$ no color change could be observed after 3 months.

One somewhat more careful experiment was carried out. A solution of the blue species and $HClO_4$ was prepared such that the chromium concentration was 0.050 g-atoms Cr/l. and the acid was 5.7 M. The ultraviolet spectrum was observed as a function of time. The absorption at 270mμ was chosen to follow since the absorption coefficients of the blue species and Cr^{3+} are quite different at this wavelength. The data are given in Table VI. Figure 2 is a plot of the absorbance of the solution as a function of time. It is clear that two distinct steps are occurring. The curve of the slow step was extrapolated back to zero time, and the extrapolated value found was subtracted from the absorbance to test whether the first part of the curve was first-order in chromium. Figure 3 is a plot of log (A - 0.85) vs time. There are just enough points to show a straight line. Thus there is a rapid initial step which is first-order in chromium, followed by a slower step.

The kinetics of the decomposition of a similar species,



has been studied by Hamm and Grant.[13] They proposed a complicated mechanism involving several steps. It seems likely that the mechanism for the decomposition of the blue species would be equally interesting. Certainly more, and more careful, work should be done to determine the mechanism involved.

Table VI

Decomposition of blue species[a] in $HClO_4$[b] at room temperature

Time	A_λ = 270 mμ	A_λ = 270 mμ -0.85
0	1.630[c]	0.780
4.67 min	1.310	0.460
15.67 min	0.990	0.140
0.77 hr	0.865	
3.85 hr	0.840	
17.07 hr	0.796	
41.67 hr	0.755	
66.88 hr	0.705	

[a]Concentration of blue species = 0.0500 g-atom Cr/l

[b]Concentration of $HClO_4$ = 5.7 M

[c]Taken from extrapolated zero-time value of a duplicate solution containing no $HClO_4$

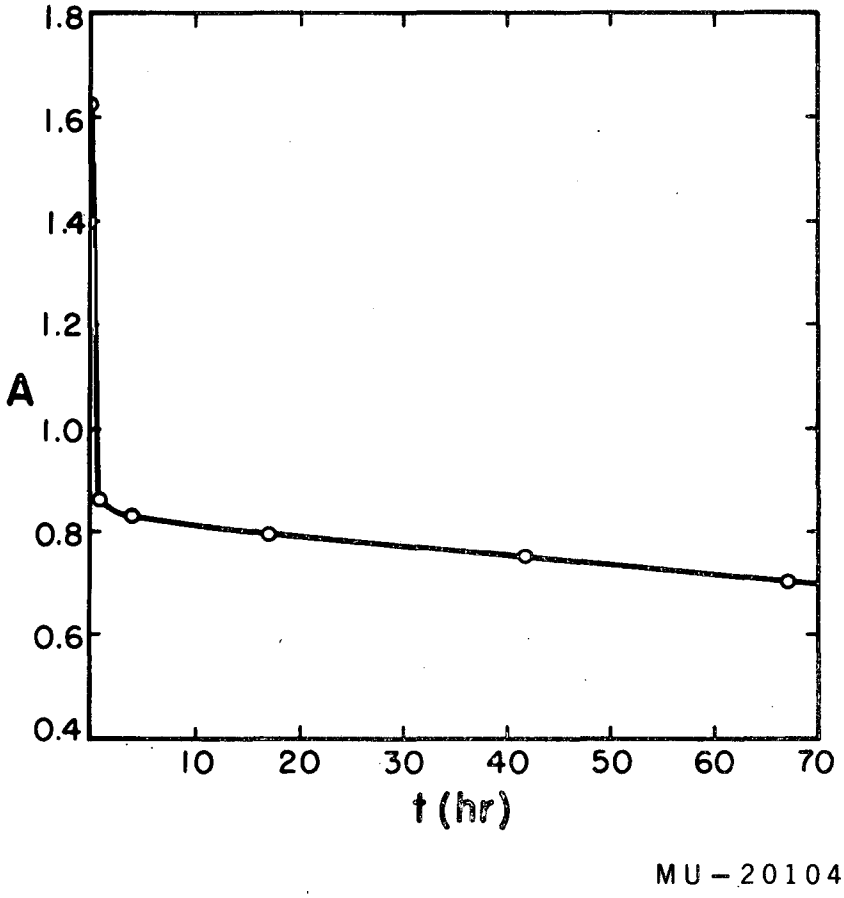


Fig. 2. Change in absorption at 270 mμ of the blue species in 5.7 M $HClO_4$.

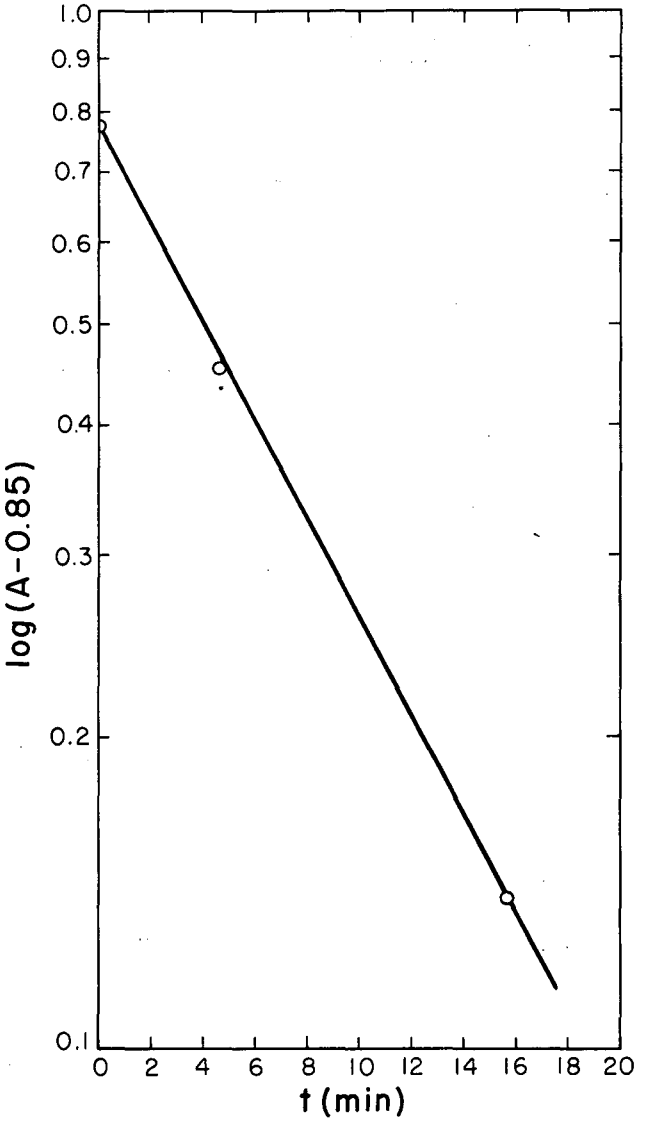


Fig. 3. Test to see if the initial decomposition of the blue species was first-order.

7. Blue Species, Cr^{3+} Equilibrium

The solutions used in the equilibrium studies were prepared in 250-ml volumetric flasks by the addition of 19.94 ml of 0.373 M $Cr(ClO_4)_3$ solution containing less than 0.01 M $HClO_4$, a known amount of NaOH solution, sufficient $NaClO_4$ solution to maintain a ClO_4^- concentration of 1.00 M upon dilution, and water to dilute to 250 ml. The temperature was maintained at 49.8°C. The equilibrium quotient was calculated on the basis of the equation:

$$2\ Cr^{3+} + 2\ H_2O \overset{Q_3}{=} Cr_2(OH)_2^{4+} + 2\ H^+ \ . \qquad (23)$$

The formation of $CrOH^{2+}$ according to Eq. (5) was accounted for by using 3.8×10^{-4} for the value of the hydrolysis equilibrium quotient:[14]

$$Cr^{3+} + H_2O = CrOH^{2+} + H^+ \ . \qquad (5)$$

The results of the equilibrium experiments are shown in Table VII. In the last column are given the values of the concentration equilibrium constant of Eq. (23). $Log^{-1}\ (-pH) = (H^+)$ was used to obtain the (H^+) values in Table VII.

These experiments are preliminary results only. They should be repeated with more care to determine if the trend toward higher Q_3 as the OH^- concentration increases is real. The analytical procedure should be checked by using mixtures of known composition prepared from pure stock solutions. There was not enough pure polymer solution available for this check when these experiments were run. The ion-exchange separation takes several days because of the slow flow rate through the colloidal Dowex-50

Table VII

Blue species, Cr^{3+} equilibrium at 49.8°C and 1 M ClO_4^-

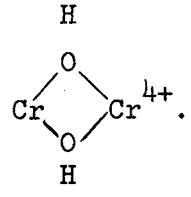
Run	OH^- Added (M)	pH	(H^+) (M)	$(Cr^{3+}) + (CrOH^{2+})$ (M)	(Cr^{3+}) (M)	Blue species concentration (g atoms Cr/l)	Q_3 (M)
1	0.52×10^{-2}	2.180	6.60×10^{-3}	24.8×10^{-3}	23.5×10^{-3}	1.99×10^{-3}	0.78×10^{-4}
2	3.17×10^{-2}	2.609	2.46×10^{-3}	8.4×10^{-3}	7.28×10^{-3}	2.49×10^{-3}	1.42×10^{-4}
3	4.76×10^{-2}	2.716	1.92×10^{-3}	4.97×10^{-3}	4.15×10^{-3}	1.41×10^{-3}	1.52×10^{-4}

resin used. This means that decomposition could occur. It is also difficult to distinguish the boundary between the blue and green species, and this could cause some error.

It would be nice to determine the composition of the equilibrium solutions by spectrophotometric techniques alone. The spectra of the chromium species are not very different, so analysis for a minor constituent of a solution would be very difficult. Unfortunately, it appears that the blue species is always such a minor component. There are also chromium species other than Cr^{3+}, $CrOH^{2+}$, the blue +4 species, and the green +5 species present in the equilibrium mixtures, and of course the spectra of these other species are unknown. The presence of higher chromium polymers can be seen from consideration of the OH^- balance. In run 3, the average OH^- per chromium for the green species is larger than 1.33.

Bjerrum[5] also measured the equilibrium between the dimer and Cr^{3+}, but at 75 and 100°C. Assuming a constant ΔH, one calculates from his data a value for Q_3 at 49.8°C of 1.7×10^{-4} M, which agrees fortuitously well with the last two values of Table VII.

8. Conclusion

The blue species is a dimer of the formula $Cr\text{-}O\text{-}Cr^{4+}$ or  . It probably forms one or more perchlorate complexes, but the formation constants are not known. Any perchlorate complex formed would almost certainly be an outer-sphere complex. A distinction between the two proposed structures could be made from O^{17} tracer studies. Raaman spectrometry might also provide information on this problem.

B. The Green Polynuclear Species.

1. Hydroxyl-ion-per-Chromium-Atom Experiments

The results of the OH^--per-chromium-atom experiments are given in Table VIII. The charge per species of the uncomplexed green material must be a whole number, and must also be a whole-number multiple of 3 - OH^-/Cr atom results. The results given here indicate that the correct OH^--per-chromium value is 4/3 and the charge per species of the uncomplexed green material is therefore an integral multiple of +5.

2. Charge-per-Chromium-Atom Experiments

Results of charge-per-chromium-atom experiments are given in Table IX. Experiments were run in the presence of ClO_4^- (method 1), and in pure water (method 2). The results of the method 2 experiments are in fair agreement with the OH^--per-chromium-atom experiments, indicating that the true charge per chromium atom in the uncomplexed species is 5/3. The uncertainties in the last column were estimated in the same way as for Table IV (see V-A-2). The difference between the results of method 1 and method 2 experiments indicates that the green species is complexed by ClO_4^- in the resin to an even greater extent than the blue species.

3. Charge-per-Species Experiment

Table X gives the result of a charge-per-species experiment run on the green material. The OH^--per-chromium-atom and the charge-per-chromium-atom experiments indicate that the charge per species must be a multiple of +5. This charge per species experiment indicates that the charge per species of the uncomplexed green species is not likely to be +10 or larger and therefore must be +5. The same line of reasoning

Table VIII

Hydroxyl ion per chromium atom for the green species

Sample source	Mg atoms of Cr	Initial meq H^+ free	Added meq OH^-	Meq H^+ used in titration	OH^-/Cr atom
Hydrolyzed $Cr(ClO_4)_3$	0.487	0.157	2.00	0.567	1.38 $\pm$ .05
Hydrolyzed $Cr(NO_3)_3$	0.144	0.070	1.008	0.550	1.31 $\pm$ .05

Table IX

Charge per chromium atom of the green species

Sample	Method	Total charge concentration (equiv/l)	pH	(H^+) (M)	(Cr) (g atom/l)	Charge per Cr atom
1	1	1.100	1.72[a]	0.194	0.599	1.51 ± .04
2	1	1.100	1.72[a]	0.194	0.591	1.53 ± .04
3	1	1.100	1.72[a]	0.194	0.607	1.49 ± .04
2	2	1.211	1.72[a]	0.194	0.591	1.72 ± .04
3	2	0.1274	1.72	0.0197	0.0617	1.74 ± .04

[a]pH is of the sample diluted 1.016 cc to 10.00 cc.

Table X

Charge per species of the green species

Experiment	Total Cr (mg atoms)	Total Tl^+ (mmoles)	V (ml)	Resin (meq)	(Tl^+) (M)	(Cr) (g atoms/l)	(ClO_4^-) (M)	Charge per species
25A[a]	1.179	30.65	59.85	9.021	0.392[b]	11.64×10^{-4}	0.4	3.62
25B[a]	1.120	21.75	59.91	9.021	0.250[c]	2.78×10^{-4}	0.4[d]	

[a] Temp. is 22°C

[b] Calculated from the equation: $(Tl^+) = \frac{\text{Total equiv. } Tl^+ - \text{equiv. resin} + \text{equiv. Cr resin}}{\text{liters of solution}}$

[c] Measured

[d] $LiClO_4$ used to maintain (ClO_4^-)

pursued in the case of the blue species can be pursued to explain the apparent charge per species of less than +5. In this case three perchlorate-complexed species would have to be present in the resin: an uncomplexed +5 species, a singly complexed +4 species, and a doubly complexed +3 species.

4. Molybdenums-per-Chromium Experiment

A single experiment for the green species gave a value of 1.9 Mo/Cr. No drift in the end point was observed. Laswick and Plane[7] report a drifting end point and a value of 1.3 Mo/Cr. A result of two molybdenums per chromium might mean that the Mo groups attack the end chromium atoms of the trimeric green species exactly as they attack chromium atoms in the dimeric blue species, if the green species has the linear structure suggested in part B-6 of this section. The central atoms of the green species would not be attacked at all. This is, of course, only a guess.

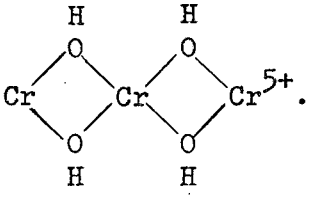
5. Stability Experiments

Crude experiments on the stability of the green species were carried out by noting the time necessary at room temperature for the color to change to the violet of Cr^{3+} under several conditions. No judgment was made as to whether or not the blue species was an intermediate. In 2.8 M $HClO_4$ this change was completed in about a week; in 0.1 M $HClO_4$ the change took about 3 months. As in the case of the blue species, detailed kinetic studies of the formation and decomposition of the green species should be carried out. One of the chief virtues of studying an inert system of hydrolysis polymers like those formed from Cr III is that the reaction mechanisms of the individual species can be studied conveniently.

In a labile system, such as with Fe III, the situation is complicated by both the speed of the reactions and the fact that one must always deal with a mixture of species.

6. Conclusion

The green species is a fairly stable species of the formula $Cr_3(OH)_4^{5+}$ or $Cr_3O_2^{5+}$. Several structures can be envisioned such as $Cr\text{-}O\text{-}Cr\text{-}O\text{-}Cr^{5+}$ or



A three-dimensional ring structure is also quite attractive. This structure would have two chromium octahedra sharing one edge with OH^- groups acting as bridging ligands. The two chromium atoms and the two oxygen atoms of OH^- groups would all be in the same plane. The third chromium atom would be in a second plane parallel to the first plane and passing through the bottom points of the octahedra of the first two chromium atoms. The third chromium atom would be directly below one of the bridging OH^- groups in the first plane. The bottom points of the octahedra of the first two chromium atoms would be OH^- groups bridging to the third chromium atom. There would be four OH^- groups and three chromium atoms. All the chromium atoms would be equivalent; three of the OH^- groups would be shared by two chromium atoms and one by three chromium atoms. As in the case of the blue species, it is not yet possible to distinguish between the $O^=$ and the OH^- structures. However, +3 and +4 outer-sphere perchlorate complexes of this species probably exist in the resin phase.

C. Evidence of Perchlorate Complexing of Other Ions in the Resin Phase.

Evidence of the formation of ClO_4^- complexes in the resin was discovered while running charge-per-chromium-atom experiments on the polynuclear chromium species. It seemed worthwhile to investigate some other species for evidence of ClO_4^- complexing. Table XI gives the results of some of these experiments. These studies were made using the first method described in Section IV C.

It is interesting to note that chromic ion behaves normally, i.e. shows no tendency to complex with ClO_4^- ion. The results of the charge per species experiment (Table V) indicated the same thing. Although the results of Table XI could be interpreted in terms of invasion of the resin by ClO_4^- without complexing, the chromic results indicate a first-coordination sphere interaction for +3 ions at least.

Spectrophotometric evidence for the existence of a $CeClO_4^{2+}$ species in aqueous solution has been reported by Heidt.[15]

A second, less informative, set of experiments was performed on the approximately 0.25 M $Th(ClO_4)_4$, and the approximately 0.33 M $La(ClO_4)_3$ solutions used as eluting agents in the preparation of the chromium species. The total charge concentration of each solution was determined by both methods of Section IV, C. The results are shown in Table XII. Even though the thorium and lanthanum concentrations of these solutions were not determined, the difference in the total charge concentration between the experiments of method I and method 2 clearly indicates that ClO_4^- complexing does take place for both the Th^{4+} and the La^{3+}.

The type of experiment described here gives information about material in the resin phase only. It does not allow one to determine the amount

Table XI

Charge per atom of several M III species in Dowex 50

Salt	Total charge concentration (equiv/l)	(H^+) (M)	$(M(ClO_4)_3)$ (M)	Charge/M atom
$Cr(ClO_4)_3$	0.755	0.010	2.45	3.04
$Ce(ClO_4)_3$	0.868	0.039	0.300	2.76
$Fe(ClO_4)_3$	1.530	0.780	0.266	2.81
$Fe(ClO_4)_3$	1.530	0.780	0.266	2.81

Table XII

Evidence of ClO_4^- complexing of Th IV and La III[a]

Salt	Method	Total charge concentration (equiv/l)
$Th(ClO_4)_4$	1	1.100
	2	1.240
$La(ClO_4)_3$	1	1.000
	2	1.102

[a]The $Th(ClO_4)_4$ solution was prepared from the solid salt and water. No Th assay was run. The $La(ClO_4)_3$ was prepared by neutralizing $La(OH)_3$ with $HClO_4$. No La assay was run. Both solutions should be fairly pure.

of complexing in the aqueous phase. This can be seen by considering the following example. Suppose one had a system containing a species M^{3+} and its ClO_4^- complex $MClO_4^{2+}$. The following equations could be written:

$$M^{3+} + ClO_4^- = MClO_4^{2+} \tag{24}$$

$$2M^{3+} + \overline{3MClO_4^{2+}} = \overline{2M^{3+}} + 3MClO_4^{2+} . \tag{25}$$

If activity coefficients are ignored, these equations give rise to the following equations:

$$Q_4 = \frac{(MClO_4^{2+})}{(M^{3+})(ClO_4^-)} \tag{26}$$

$$Q_5 = \left(\frac{\overline{M^{3+}}}{(M^{3+})} \right)^2 \left(\frac{(MClO_4^{2+})}{\overline{MClO_4^{2+}}} \right)^3 . \tag{27}$$

A third equation can also be written:

$$(M \text{ total}) = (M^{3+}) + (MClO_4^{2+}) . \tag{28}$$

The quantities (M total), $\overline{M^{3+}}$, $\overline{MClO_4^{2+}}$, and (ClO_4^-) can be determined experimentally, but one is still left with four unknowns -- Q_4, Q_5, (M^{3+}), and $(MClO_4^{2+})$ and only three equations. Thus Q_4 cannot be determined.

One could, of course, run a second experiment at a different perchlorate concentration to get the added information necessary. But if the perchlorate concentration were changed enough to do this, the aqueous-phase activity coefficients would also change, and the experiment would have little meaning. What is needed is a way to determine or calculate Q_5 independently. Perhaps a study of several M^{3+}-MCl^{2+} systems would enable one to guess the Q_5 value for the ClO_4^- case.

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