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Howard Hamilton Cady

June 1957

(Ph.D. Thesis)

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Contents

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June 1957

ABSTRACT

A method for the identification of ions in solution has been developed which utilizes the properties of ion exchange resin. It is possible to determine the charge on an ion in solution and its degree of polymerization. The method was checked with known ions and used to isolate and establish the formulas of Ru^{+3}, $RuCl^{++}$, and $RuCl_2^{+}$.

In this investigation the above ions were identified and the existence of uncomplexed Ru(II), and polymeric Ru(IV) were shown. In addition, evidence was found for intermediate oxidation-state compounds of ruthenium with oxidation states between +3 and +4, and between +4 and +5.

Potentiometric titrations were carried out in order to measure the electrode potentials of the various "uncomplexed" ruthenium couples.

I. INTRODUCTION

Even though ruthenium was discovered more than 100 years ago, the chemistry of this element has not been well defined, especially the aqueous solution chemistry of the lower oxidation states. The older literature is well summarized in Gmelin.[1] More recently, Deford[2] has published a critical review of the chemistry of ruthenium, and Schloo[3] has compiled a bibliography on "Properties and Behavior of Ruthenium and its Compounds and Complexes."

With a few exceptions, almost all the quantitative work on ruthenium has been analysis of solid compounds. Recently, Silverman and Levy[4] and Connick and Hurley[5] have established the formulas, the oxidation potentials, and spectra of the upper oxidation state ruthenium species existing in basic solution. Wehner and Hindman,[6,7] Wilson et al.,[8-12] and Niedrach and Tevebaugh[13] have attempted similar investigations on the uncomplexed ruthenium species of lower oxidation state, in acidic solution.

Since the results of the work in acidic media show many peculiarities such as evidence for species with intermediate oxidation states, and in any event did not lead to the establishment of formulas for the species present, it was evident that further research would be necessary before the system could be understood.

It was initially hoped that the uncomplexed or aquo complex ions of ruthenium(III) and (IV) could be purified and identified, and that information on these ions and their reactions could then be used as a base to characterize other ruthenium species. It has been possible to purify and identify the ions Ru^{+3}, $RuCl^{++}$, and $RuCl_2^{+}$. In addition, it has been shown that "uncomplexed" Ru(IV) is polymeric, that there is probably a species in which the average oxidation state is about 4.2, that there is another species with an average oxidation state between 3 and 4, that it is possible to prepare "uncomplexed" divalent ruthenium, and that trifluoroacetic acid complexes Ru(III) if the Ru(III) species is prepared by reduction of RuO_4 in acidic trifluoroacetate solution.

II. APPARATUS AND EQUIPMENT

All absorption spectra were measured on either a Cary Recording Spectrophotometer Model 11 Serial 4, or a Beckman Model DU Spectrophotometer. 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 The absorption spectrum of a material was obtained by running a spectrum of a solution containing 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.

In the experiments in which it was desired to obtain spectral and potentiometric data simultaneously, or where it was necessary to work in an oxygen-free atmosphere, a special quartz cell was used. This cell fitted into the Cary Spectrophotometer and had a 1.09-cm optical path in the light beam of the instrument. Above the optic portion of the cell was a region of larger volume where the solutions were mixed and the electrodes were positioned. Through the top of the cell passed a gold and a platinum electrode, a salt bridge, and a stirrer. A stream of oxygen-free nitrogen blown into the cell was sufficient to exclude oxygen from the air. A representation of the cell is shown in Fig. 1. In some experiments a similar, but much smaller cell without optical windows was used for potentiometric titrations. The numbers indicate:

(1) entrance tube for purified and water saturated nitrogen
(2) wire leads to the potentiometer
(3) graduated pipette

(4) stirrer and combination bearing and plug of teflon

(5) salt bridge

(6) ground glass lip and gasket where the lid is joined to the base of the cell, and

(7) the optical portion of the cell.

Either a Rubicon High Precision Type B potentiometer, or a Beckman Model G pH meter was used for the potential measurements. The potentials were measured against a saturated calomel electrode (s.c.e.).

The salt bridges were of two types, however in both cases contact was made by a solution flowing through a very small orifice. In one case the orifice was formed by standard taper 5/20 ground glass joints, in the other by almost plugging a capillary tube with a tapered glass rod.[*] The ground glass junction allows faster flow of solutions through it with the flow approaching 0.01 ml per hour. The flow through the partly plugged capillary is probably about 0.001 ml per hour.

In titrations involving the addition of RuO_4 solution to another solution it was necessary to use a graduated pipet instead of a burette. A burette could not be used because RuO_4 would react with all the common stopcock greases and it appears to be catalytically decomposed by the ground glass in the stopcock. A "Propipette"[**] was used to control the flow from the pipette and was as satisfactory as a stopcock in that it was airtight.

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[*] This type of junction was developed by Robert H. Wood now at the University of California (Berkeley).

[**] Instrumentation Associates, 17 West 60th Street, New York 23, N. Y.

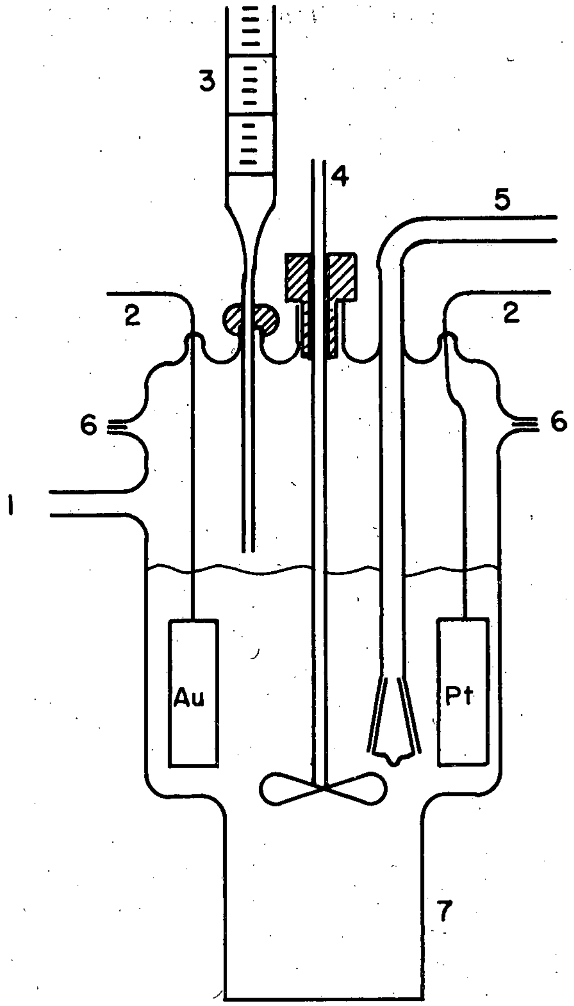

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Fig. 1. Representation of cell used for spectrophotometric and potentrometric titratrons
The numbers indicate:

(1) entrance tube for, purified and water saturated, nitrogen,
(2) wire leads to the potentimeter,
(3) graduated pipette,
(4) stirrer, and combination bearing and plug of teflon,
(5) salt bridge,
(6) ground glass lip and gasket where the lid is joined to the base of the cell, and
(7) the optical portion of the cell.

The continuous-control type potentiostat used to control the electrode potentials in electrolytic oxidation and reduction was similar to that described by Wehner and Hindman.[6]

A Beckman Model G pH meter was used to determine the pH of solutions where direct titration of the hydrogen ion was not practical.

III. PREPARATION OF SOLUTIONS AND ANALYTICAL METHODS

The water used in all experiments was either normal distilled water or conductivity water prepared by redistillation of distilled water from alkaline permanganate solution. In neither case could any evidence for the presence of chloride ion by obtained by precipitation of AgCl. The perchloric acid solutions were prepared by diluting G. F. Smith double vacuum distilled perchloric acid. The trifluoroacetic acid (hereafter called HTFA) was obtained from Minnesota Mining and Manufacturing Co., and purified by fractional distillation. Solutions were made up by dilution, and were standardized by titration with standard carbonate-free sodium hydroxide.

The stock supply of ruthenium chloride was obtained from the A.D. MacKay Company. It was analyzed spectroscopically for metals. The results are shown in Table I.

Table I

Spectroscopic Analysis of Ruthenium Chloride

Al	< 0.01 %	Mo	< 0.01 %	Pt	< 0.1 %
Ca	< 0.01 %	Na	0.01 %	Rh	< 0.05 %
Fe	0.01 %	Os	< 0.1 %	Ru	~ 100 %
Mg	< 0.01 %	Pd	< 0.1 %		

The ruthenium tetroxide solutions were prepared as follows. First the ruthenium chloride was fumed with sulfuric acid to remove the chloride as HCl. Then the ruthenium was oxidized to RuO_4 by permanganate in dilute sulfuric acid. The ruthenium tetroxide was distilled from this solution into a solution of trifluoroacetic or perchloric acid of known concentration. The concentration of the RuO_4 in these acidic solutions was determined spectrophotometrically by use of the molar extinction coefficients determined by Connick and Hurley.[5] The molar extinction coefficients, ϵ, used for most analyses were $\epsilon_{385} = 930$ and $\epsilon_{310} = 2960$, where ϵ_{385} is the ϵ measured at 385 mμ and so on.

The ruthenium concentration in acidic solutions of the lower oxidation states, could be determined from oxidation of the ruthenium to RuO_4 by sodium periodate or ammonium persulfate, followed by spectrophotometric analysis for the ruthenium.[7,11] In general, sodium periodate oxidation was used unless there was an undesirable side reaction involving iodate or periodate.

The reason for avoiding persulfate, where possible, was that it requires heating the solutions to nearly boiling for several minutes, which could lead to loss of RuO_4 by volatilization.

The procedure for ruthenium analysis by periodate was to add ~ 0.03 gram of $Na_3H_2IO_6$ to a sample contained in a quartz absorption cell. It was assumed that this amount of material would not appreciably change the volume of the solution. Ruthenium analyses by persulfate were done in the same manner with about 0.06 gram of $(NH_4)_2S_2O_8$. Sometimes it was necessary to analyze a small volume of a relatively concentrated solution for ruthenium. In these cases the ruthenium solution was diluted to a known volume and oxidized before it was added to the absorption cell.

A qualitative test for the presence of Ru(IV) in a Ru(III) solution was based on the reduction of the higher oxidation states of ruthenium to Ru(III) by iodide ion.[14,15,6] The procedure was to add sodium iodide to the ruthenium solution which was about 1 M in hydrogen ion. After about 20 seconds a solution of colloidal starch was added to the above solution. Evidence of I_2 in this solution was considered to indicate the presence of Ru(IV) in the initial ruthenium solution. Because air oxidizes Ru(II) to Ru(III), it was not necessary to test for Ru(II) in solutions of Ru(III) exposed to the atmosphere.

Ferrous perchlorate solutions were prepared by solution of G. F. Smith ferrous perchlorate in perchloric acid. The ferrous perchlorate was essentially free of chloride ion as tested by silver ion. The chloride ion concentration was about 10^{-4} M in a 0.5 M ferrous perchlorate solution.

Ferrous trifluoroacetate solutions were prepared by dissolving spectroscopic iron in a known excess of the acid. Silver nitrate gave a negative test for chloride ion. After filtration to remove carbon and possible ferric oxide, the ferrous solutions were standardized by titration with permanganate solutions. The primary standards for this titration were sodium oxidate and arsenious oxide. Ferric trifluoroacetate and perchlorate solutions were prepared by adding hydrogen peroxide to a ferrous solution and boiling. The ferric solutions were standardized by reduction to ferrous in a Jones Reductor and titration of the ferrous by permanganate.

A secondary gravimetric standard for iron was ferrous ammonium sulfate hexahydrate that had been stored over a saturated potassium bromide solution.* The determined equivalent weight is 393.0 ± .3

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*Dr. Charles Koch suggested this technique for holding constant the degree of hydration of the ferrous ammonium sulfate.

as compared with a calculated molecular weight of 392.1. This equivalent weight was checked over a period of 2 years and remained constant.

Cupric solutions were prepared by dissolving cupric carbonate in the appropriate acid and filtering to remove insoluble matter. The solutions were standardized by titration using the iodide and thiosulfate method.

Stannous solutions were prepared by passing an acidic cupric solution of known composition through a column of granular tin. These solutions were not standardized, but were assumed to have a final stannous ion concentration equal to that of the initial cupric ion.

Solutions of mercuric ion were prepared by dissolving weighed amounts of mercuric oxide in the desired acid and filtering out any insoluble material. Solutions of mercurous ion were prepared by treating solutions of mercuric ion with mercury metal. The reaction was carried out at about 60°C over a period of more than 2 days. The mercurous ion was standardized by titration with standard sodium chloride. Bromphenol blue was used as the adsorption indicator.[16]

Solutions of titanous trifluoroacetate were prepared by dissolving pure titanium metal in HTFA that contained enough sulfuric acid to initiate the reaction between hydrogen ion and the metal. The reaction was initiated by placing 3 or 4 drops of concentrated sulfuric acid directly on the titanium metal while it was in the HTFA solution. The solutions were protected from air to prevent the oxidation of titanous ion to titanic. Sulfate ion was removed from solution by addition of a slight excess of barium trifluoroacetate followed by centrifugation to remove the resulting barium sulfate.

As titanous ion reacts with perchlorate ion at a finite rate it was not possible to prepare titanous perchlorate solutions by exactly the same method. The procedure used was to dissolve titanium metal in a slight excess of sulfuric acid, cool the solution to 0°C, and precipitate the sulfate by addition of a slight excess of a cold barium perchlorate solution. The solutions were centrifuged to remove the barium sulfate and kept at 0°C to slow the reaction between perchlorate and titanous ions. The concentration of the titanous ion was determined by adding an aliquot of the titanous solution to an acidic ceric solution and titrating the excess ceric with ferrous ion.

Decomposition of recrystallized NH_4VO_3 by heating it in a muffle furnace to 900°C was the method used to prepare pure V_2O_5. This V_2O_5 was dissolved in perchloric acid and reacted with sulfur dioxide or formic acid to prepare VO^{++}. This vanadyl ion was purified by means of an ion exchange column. The vanadyl ion was adsorbed on Dowex 50W x 12 ion exchange resin in a column. After the column was washed with dilute perchloric acid to remove undesirable anions the column was eluted with 4 M perchloric acid and the purified vanadyl perchlorate collected. Vanadyl solutions were standardized by titration with a standard permanganate solution. Vanadous solutions were prepared from vanadyl by use of a Jones Reductor. Vanadic solutions were prepared by air oxidation of the vanadous solutions. The spectra of these ions agreed reasonably well with those obtained by King and Garner,[17] with the exception that the ϵ's for V^{++} were lower in our solutions. A plot of the spectrum of vanadous perchlorate is shown in Fig. 2.

Solutions of dichromate in perchloric acid were prepared by dissolving weighed sodium dichromate. The standardization of these solutions was checked by titration with standard ferrous solutions, with diphenylamine

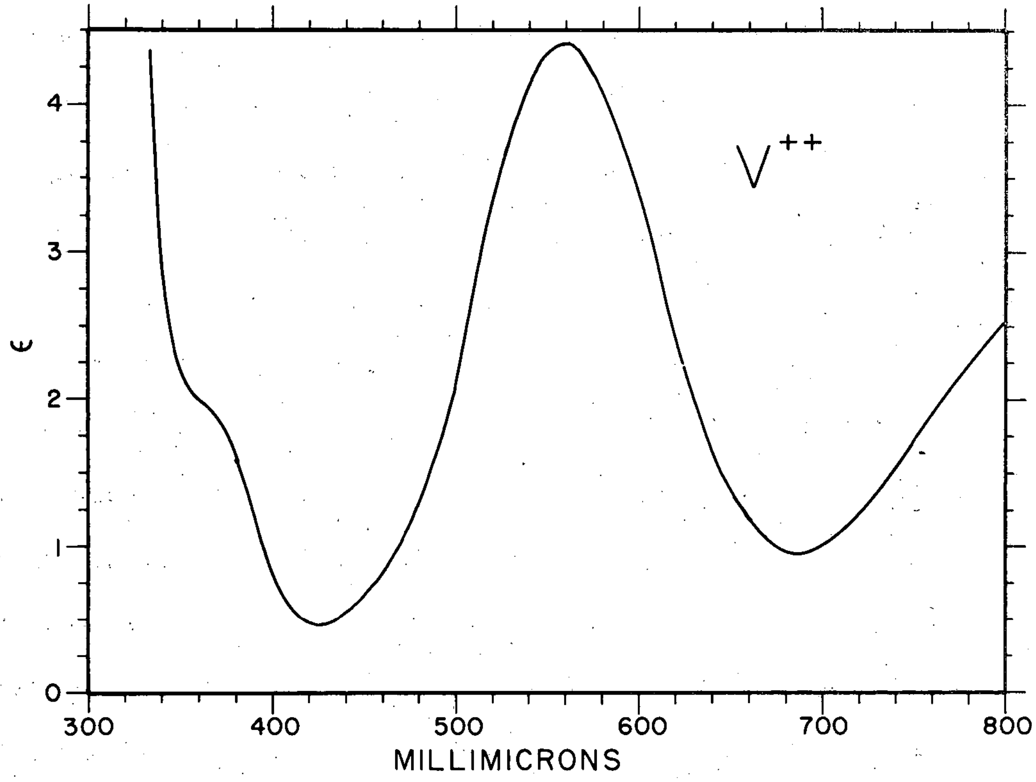

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Fig. 2. Spectrum of vanadons perchlorate in 0.6 M $HC10_4$.

sulfonate as the indicator. Standard chromate solutions were prepared by dissolving a known weight of sodium dichromate in basic solution. Chromic solutions were prepared by hydrogen peroxide reduction of dichromate, or solution of chromic nitrate. Chromic ion was standardized by peroxydisulfate oxidation to dichromate and analysis either by titration with standard ferrous, or spectrophotometrically as chromate ion. The molar extinction coefficient of chromate ion was determined as 4.8×10^3 at 373 mμ. Chromous solutions were prepared by reduction of sodium dichromate or chromic perchlorate solutions by zinc amalgam.

The ceric perchlorate used in titrations was obtained from G. F. Smith as a solution of 0.5 M ceric in 6 M perchloric acid. This solution was standardized by titration with a standard ferrous solution. Cerous perchlorate was prepared from recrystallized G. F. Smith primary standard ammonium hexanitrato cerate. The preparation procedure was to dissolve this ceric salt in dilute hydrochloric acid solution, and to boil this solution until the ceric was reduced to cerous chloride and there were no ammonium or nitrate ions remaining in solution. Then the solution was fumed with perchloric acid to remove the chloride ion as HCl. The cerous solutions were analyzed by oxidation to ceric by peroxydisulfate, and titrated with standard ferrous solution.

Calcium, magnesium, and barium solutions were prepared by solution in perchloric acid of the oxide, hydroxide, or carbonate, whichever was obtainable in the purest form. The concentration of the calcium was determined roughly by hydroxide titration of the acid before and after solution of the basic calcium salt. The difference in the hydrogen ion concentrations was assumed to be twice the calcium ion concentration.

The magnesium was standardized by titration with standard sodium hydroxide with a glass electrode as the indicator. Two breaks occurred in the titration: one for hydrogen ion, the second after the formation of magnesium hydroxide. The barium solutions were roughly standardized by titration with standard sulfate.

The hydrogen peroxide used was obtained as a 30% solution of hydrogen peroxide with no preservatives added. The source of sodium periodate was $Na_3H_2IO_6$ from the Fisher Scientific Company, and the ammonium persulfate (peroxydisulfate) was a Baker's Analyzed reagent.

The ion-exchange resins used were obtained from the Bio-Rad Laboratories as analytical-grade resin. These resins had been processed from Dowex-50W and Dowex-1 ion exchange resins. The resins used were Dowex-50W x 8, Dowex-50W x 12, Dowex-1 x 2, and Dowex-1 x 10 in 200 to 400-mesh particle size. Dowex-50W x 12 colloidal resin was also used. No evidence for the presence of iron or aluminum in these resins was noticed. They were not analyzed spectroscopically, however.

IV. DIVALENT RUTHENIUM

The divalent state of ruthenium is well known in both solid compounds and solution. All the materials that had been previously prepared had one characteristic in common: the ruthenium was complexed. It was hoped that an uncomplexed ruthenium (II) or in reality an aquo complex of ruthenium (II) could be prepared so that it could be used to establish the $Ru^{+2} = Ru^{+3} + e^-$ potential.

Two methods of preparing divalent ruthenium in "noncomplexing" media were attempted. These methods were electrolytic reduction and direct chemical reduction. The solvents used in the preparation were perchloric acid and trifluoroacetic acid. Perchloric acid has the disadvantage that it reacts with the lower oxidation states of ruthenium. The reaction with the trivalent state is slow, but it is much faster with the divalent state. Trifluoroacetic acid does not have this disadvantage of reaction, but it was discovered that it complexes the trivalent state of ruthenium when the ruthenium (III) is prepared by reduction of RuO_4 in HTFA. It was feared that complexing in the divalent state might occur; however this was not demonstrated.

A. Electrolytic Reduction as a Preparative Method

Electrolytic reduction of RuO_4 in perchloric acid was not attempted. The difficulties encountered by Wehner and Hindman in preparing Ru(III) in this medium[6,7] indicated that attempts to prepare Ru(II) by reduction of Ru(IV) were likely to be fruitless. Also, Niedrach and Tevebaugh were unable to prepare Ru(II) by this method.[13]

An attempt was made to prepare Ru(II) in HTFA by electrolytic reduction. Both RuO_4 and chemically prepared Ru(III) were used as starting materials. In neither case was there any indication of the formation of the divalent species. In 1 M HTFA the reduction of Ru(III) appeared to proceed directly to the metal.

B. Chemical Reduction and the Chemistry of Ru(II)

Chemical reduction of RuO_4 to Ru(II) by ionic reducing agents in aqueous solution was attempted in the hope that Ru(II) could be prepared if there was no reactive surface upon which the ruthenium metal could form.

In HTFA RuO_4 reacted with titanous ion to give a product in which the ruthenium had an oxidation state of +2. A solution of $\sim 2.5 \times 10^{-3}$ M RuO_4 in 1 M HTFA was added to a solution of 0.022 M Ti^{+3} in 1 M HTFA. The spectrum of Ru(II) obtained by this method is shown in Fig. 3, Curve 1.

Oxygen from the air reacts with both Ru(II) and Ti^{+3} in HTFA at a rate which would interfere with the stoichiometry of the RuO_4 reduction, if no steps were taken to exclude this oxygen. This reaction with oxygen is faster for Ti^{+3} than for Ru(II), as is shown by the fact that a solution of Ti^{+3} exposed to the air was oxidized in a few hours, while it took about a day to oxidize Ru(II) under the same conditions. Air was not completely eliminated from the reaction vessel during the preparation of Ru(II) but was considerably decreased in concentration by sweeping the system with nitrogen.

The reaction of RuO_4 with Ti^{+3} is rapid and appears to go to completion. Air oxidation of the product formed during the reduction yields Ru(III). The completeness of the reduction is shown by the fact that different RuO_4 preparations and different Ti^{+3} to Ru(II) ratios give essentially the same ϵ's for Ru(II) as long as there is an appreciable amount of Ti^{+3} present.

Other evidence supporting the assumption that Ru(II) is the product is that the titration of Ti^{+3} with RuO_4 in HTFA showed at most a 6.6 electron reduction of the ruthenium to the product called Ru(II). There is an apparent 1.0-electron oxidation of this product to Ru(III) and an apparent 1.2-electron oxidation of Ru(III) to Ru(IV).* If any of the titanous ion was oxidized by oxygen the first end point would appear to indicate that the ruthenium reduction had progressed further than it actually had. The assumption of a six electron reduction of the RuO_4 would require that 9% of the Ti^{+3} had been oxidized by oxygen of the air over a period of 4 hours -- a not unreasonable assumption.

The end points used to determine the oxidation states of the ruthenium were observed spectrophotometrically (Fig. 9) and potentiometrically (Fig. 12).** The abcissas of these figures have been arbitrarily shifted to fit the Ru(III) end point in order to allow for the presumed 9% oxygen oxidation.

In perchloric acid the reduction was not so straightforward as in HTFA. A complicating factor was that $HClO_4$ reacted with Ru(II), or else some ruthenium species was formed that was a catalyst for the reduction of $HClO_4$. Another complication was a direct result of the first. The eventual reduction product of $HClO_4$ is chloride ion and this ion could have led to the formation of ruthenium (II) chlorides. The color of a solution of Ru(II) in HCl is blue.[14] This finding does not necessarily prove that the yellowish brown species formed by Ti^{+3} reduction is not a lower chloride. Better evidence that the species formed is "uncomplexed"

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*See section on tetravalent state for explanation of oxidation from Ru(III) to Ru(4.2).

**The potentiometric behavior of this titration is discussed in the section on potentials.

Ru(II) is that air oxidation of this yellow-brown species yields a colorless ion with no evidence for the formation of the ion $RuCl^{++}$, or any other known ruthenium chloride species.

Three reducing agents were used in attempts to form Ru(II) in perchloric acid. These were Ti^{+3}, V^{++}, and Cr^{+2}. It was necessary to exclude oxygen from the reaction vessel during the reductions. None of the reductions was quantitative, and only qualitative observations are possible.

The reduction of RuO_4 by Ti^{+3} in perchloric acid is similar to the reduction in HTFA in that it is fast, yields a product with a peak at 383 mμ, and has approximately the same ϵ_{383} ; however, the species or proportions of species in $HClO_4$ are not exactly the same as those in HTFA because of the spectral differences at other wavelengths. See Fig. 3, Curve 2 for this spectrum.

Reduction of RuO_4 with vanadous ion as the reducing agent yielded a product that resembled the one obtained by Ti^{+3} reduction in perchloric acid. A spectrum of the Ru(II) obtained in this V^{++} reduction of RuO_4 is shown in Fig. 3, Curve 3. (Note that the scale for ϵ is different than for the other curves.)

Observations of the reaction with V^{++} showed that the RuO_4 was reduced rapidly, but the Ru(II) species was formed slowly. The rate of formation of Ru(II) was dependent upon the concentration of vanadous perchlorate, as was shown by the change in rate with change in vanadous ion concentration. This species might be a chloride complex of Ru(II), since chloride is being formed in the reaction of V^{++} with perchloric acid. The concentration of the Ru(II) species was increasing slowly

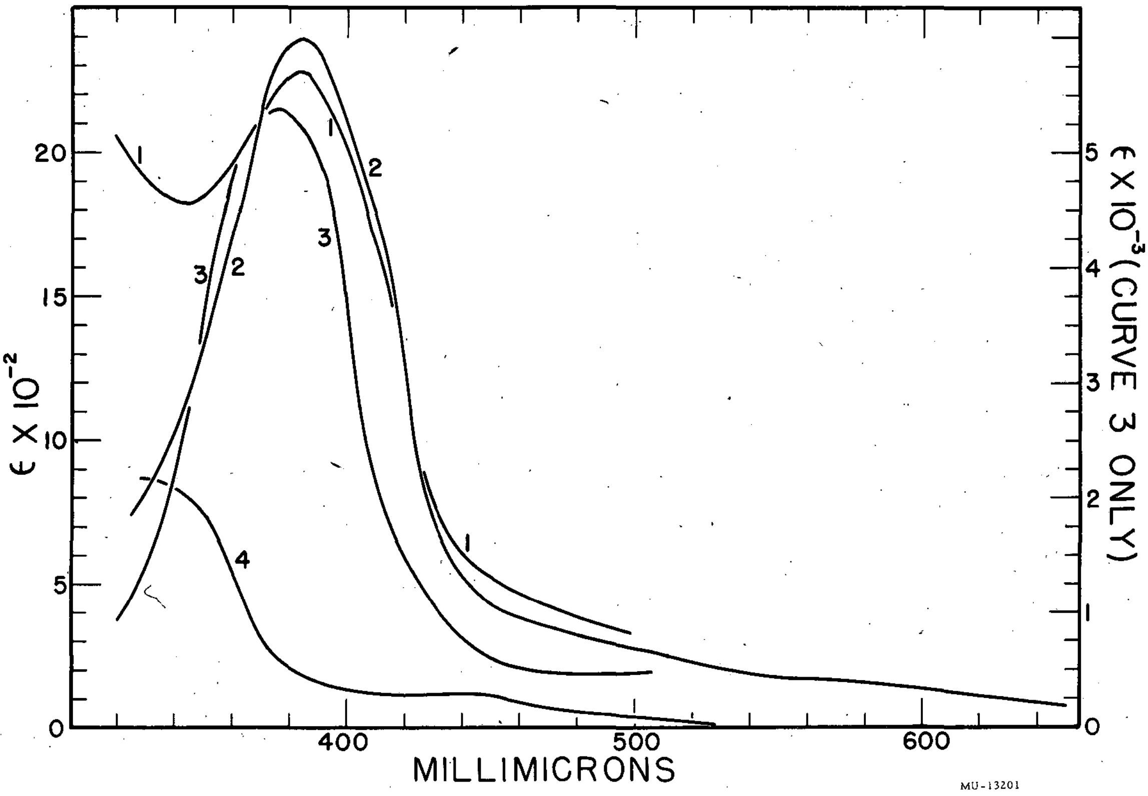


Fig. 3. Curve 1, Spectrum of Ru(II) (Ti^{+3} reduced) in 1M HTFA, Curve 2, Spectrum of Ru(II) (Ti^{+3} reduced) in 0.5M $HClO_4$, Curve 3, Spectrum of Ru(II) (V^{++} reduced) in 1.0 M $HClO_4$, Curve 4, Spectrum of Ru(?) (Cr^{++} reduced) in 1.0 M $HClO_4$.

during the whole of this experiment at the expense of some other colorless ruthenium species. This meant that the apparent ϵ was rising throughout the experiment. The spectrum reported in Fig. 3, Curve 3 is the highest obtained, but not as high as that which would have been obtained at a later time.

The rapid reduction of RuO_4 by Cr^{+2} in $HClO_4$ yielded an entirely different species than the Ti^{+3} or V^{++} reductions. Suggestions of possible species formed could be chromium-ruthenium complexes with oxide, hydroxide, or chloride bridges, Ru(III) instead of Ru(II); or possibly a Ru(I) species. None of these choices is particularly attractive, although the first can be rationalized more easily than the others. A Cr-O-Ru bond system could be kinetically stable because complexes of both Cr(III) and Ru(III) are slow to disproportionate once formed. The bond system could be formed during the reduction if an oxygen atom reacted as a charge-transfer agent. An approximate spectrum of this species obtained by Cr^{++} reduction appears in Fig. 3, Curve 4.

V. TRIVALENT RUTHENIUM

A considerable number of solid compounds of three-valent ruthenium have been prepared.[1,2] In all the compounds that have been well characterized the ruthenium behaves as though it were present in the form of a complex ion. Likewise, almost all the observations on the properties of Ru(III) in solution are observations on the behavior of complex ions.

Until recently the majority of the reports on the aqueous chemistry of this oxidation state consisted of reports on the changes of color observed when different ruthenium species were oxidized or reduced. The oxidation state of the ruthenium was not definitely known for many of the solutions that were assumed to contain Ru(III). Later investigations have shown that often this assumption was in error.[9]

In the more recent investigations there have been attempts to determine exactly what changes were taking place in a ruthenium species during its reaction. There have been efforts to study the aquo complex or complexes of Ru(III)[6,7,13] and to determine what complexes are present when some of the characterized ruthenium compounds are dissolved.[8,9,10] Most of the conclusions from these investigations have been ambiguous to some degree, especially those concerning the uncomplexed or aquo complex of Ru(III).

It seemed desirable to purify and identify some of the ions of Ru(III), particularly the aquo complex and the simpler chloride complexes. These ions could then be used as known starting materials in the study of the chemistry of three-valent ruthenium.

The properties of the ruthenium system make it impractical to purify and identify the species of interest by the conventional methods of crystallization, analysis, and freezing point depression. In order to determine the formulas of the ruthenium species in solution, a method was devised that gave the oxidation state of the ruthenium, the net charge per ruthenium atom in the species, the gross charge per species in solution, and the number of anions, if any, bonded to the ruthenium atom. It was necessary to know both the net charge per atom and the gross charge per species in order to tell if the ruthenium was polymerized, as it is in Ru(IV) solutions. As an example, the hypothetical complex ion $Ru_2Cl_2^{+4}$ would have a charge of +4 per species and +2 per ruthenium atom.

The Ru(III) ions that have been isolated and identified are Ru^{+3}, $RuCl^{+2}$, and probably $RuCl_2^{+}$.

A. Experimental Method

In essence, the classical method for determination of species by analysis and freezing point lowering yields information as to the chemical composition and the degree of dissociation of the species. This information is used to infer the charge on the species in solution and its chemical formula. Other phenomena that depend upon the charge of an ion could be utilized to get the same information. One of these phenomena is the equilibration that occurs between a pair of ions in solution and the same ions in an ion exchange resin. This equilibration phenomenon was the one used to determine the charge per species.

1. Charge per Species

For a cationic resin such as Dowex-50, it is possible to derive the expressions used in the calculation of the charge per species as follows. Given a general reaction

$$A_S^{+n} + n\,H_R^{+} = A_R^{+n} + n\,H_S^{+} \,, \qquad (1)$$

where A is the species of interest, H^+ is a hydrogen ion, n is the charge of species A and the number of hydrogen ions that exchange with it, and S and R stand for solution and resin, respectively. The equilibrium for this reaction can be expressed as

$$\frac{\left[A_R^{+n}\right]\left[H_S^{+}\right]^{n}}{\left[A_S^{+n}\right]\left[H_R^{+}\right]^{n}} = K' \,, \qquad (2)$$

where the brackets stand for activities and K' is the equilibrium constant.

This expression can be approximated by

$$\frac{(A_R^{+n})(H_S^{+})^{n}}{(A_S^{+n})(H_R^{+})^{n}} = K \overset{\sim}{=} K' , \qquad (3)$$

where (A_S^{+n}) and (H_S^{+}) are the concentration of A^{+n} and H^+ in moles per liter of solution, and (A_R^{+n}) and (H_R^{+}) are the concentration of A^{+n} and H^+ in moles per 1000 grams of air-dried, ion-exchange resin.

In order to determine n, the charge per species, it is necessary to have the data from two equilibrations, at different conditions. The expression for the equilibration between the ions in solution and the ions in the resin then becomes

$$\frac{(A_R^{+n})_1(H_S^{+})_1^{n}}{(A_S^{+h})_1(H_R^{+})_1^{n}} \overset{\sim}{=} K' \overset{\sim}{=} \frac{(A_R^{+n})_2(H_S^{+})_2^{n}}{(A_S^{+n})_2(H_R^{+})_2^{n}} \,, \qquad (4)$$

where 1 and 2 stand for the first and second equilibration respectively. It is possible to solve for n when all the concentrations are known.

2. Practical Considerations in Determining the Charge per Species

One of the practical considerations, which simplifies the experimental procedure and calculations, is that it is not necessary to analyze the resin phase for all its constituents. It is possible to calculate the composition of the resin if the capacity, in equivalents of charge per 1000 grams resin, is known, and if the concentration of all but one of the ions absorbed by the resin is known. If there are only two cations in a system it is possible to determine the change in composition of the resin phase from differences obtained by analysis of the solution phase before and after equilibration with the resin.

Since K of Eq. (3) is a function of the composition of the resin, it is desirable to keep the composition of the resin phase nearly constant in the two equilibration experiments. K is a function of composition of the resin, because the activity coefficient of an ion in the resin phase is a function of the composition of the resin. Since this function is not known, it is not possible to calculate activity coefficient corrections. The composition of the resin can be held nearly constant, which eliminates the need of activity corrections, by having a large excess of resin capacity available with respect to the capacity required by A^{+n}, and by arranging conditions in solution so that almost all of species A^{+n} will be absorbed by the resin. This makes $(H_R^{+}) \gg (A_R^{+n})$ and means (A_R^{+n}) does not change appreciably from one equilibration to another.

If the above conditions of $(H_R^{+}) \gg (A_R^{+n})$ is met for both equilibrations, then the value of n that is determined for A^{+n} in solution is uneffected by changes in the degree of hydrolysis of species A between the aqueous and resin phases. This may be seen from the following equation, which allows for a change in the hydrolysis of A:

$$A_S^{+n} + (n-x)\ H_R^{+} + xH_2O = A(OH)_{x_R}^{+n-x} + nH_S^{+}$$

$$K' = \frac{\left[A(OH)_x^{+n-x}\right]\ \left[H_S^{+}\right]^{n}}{\left[A_S^{+n}\right]\ \left[H_R^{+}\right]^{n-x}\ \left[H_2O\right]^{x}} \quad . \tag{5}$$

As long as (H_R^+) is essentially constant this equation has the same form as Eq. (2), and n is still the charge on the aqueous species.

If the degree of complexing of the ruthenium changes between the aqueous and resin phases, then the calculation of n will be in error and will be in error by one unit for each unit of change in the degree of complex formation. For ruthenium the author believes that such a change in the complexes between the aqueous and resin phases is unlikely because of the slowness of the equilibration between the ruthenium complexes. Changes in the degree of polymerization of the ruthenium species between the aqueous and resin phases would also affect the calculation of n. This effect can be detected and corrected for if the species is equilibrated three times with different A_S^{+n}/A_R^{+n} ratios, and the value of H_R^+ is maintained approximately constant.

A fourth consideration is that the method does not need to be very precise since it is only necessary to determine n within one whole unit. That is, ions of fractional charge are unknown. It is this final consideration which makes it practical to use concentrations instead of activities.

3. Charge per Atom

The net charge per ruthenium atom in the complex can also be determined with the aid of ion exchange resin. The method used for this determination is to exchange the ruthenium species, which is absorbed on the resin, for an ion of known charge from a solution of known concentration. Because there is a charge balance in the solution before and after replacement of the ruthenium species, it is possible to calculate the charge per ruthenium atom in the species, as soon as the ruthenium concentration in gram atoms per liter is known for the final solution. For example, if a solution which is 0.10 $\underline{M}$ $HClO_4$ and 0.06 $\underline{M}$ $Ce(ClO_4)_3$ exchanges with a resin containing an ion of unknown charge and this final solution is 0.12 $\underline{M}$ in $HClO_4$ and 0.08 gram atoms per liter in **A**, then the charge per atom of **A** is $\frac{0.10 + 3 \times 0.06 - 0.12}{0.08} = 2.$

As long as the hydrogen ion concentration, as well as A, is measured, the charge per atom in solution will be determined correctly even though the degree of hydrolysis or polymerization of the ruthenium species changes between the aqueous and resin phases. As can readily be seen from Eq. (5), for a species of charge n in solution, n hydrogen ions are exchanged, regardless of the hydrolysis or the resin. A change in the degree of complex formation will affect the calculations. Again this is considered unlikely, because of the slowness of the reaction between the ruthenium and the complex-ion in the aqueous phase.

B. Experimental Procedure

1. Preparation of Ruthenium (III) Species

Several techniques for the preparation of the ruthenium species were attempted. These methods included:

(a) Replacement of the chloride in $K_2RuCl_5 \cdot H_2O$ by metathesis with anhydrous HTFA.

(b) Electrolytic reduction of RuO_4 in HTFA and $HClO_4$.

(c) Chemical reduction of RuO_4 in HTFA and $HClO_4$.

In the first method it was hoped that the chloride would dissociate from the ruthenium and be converted to HCl, which could then be removed from the anhydrous HTFA by volatilization. This method was unsatisfactory because either $K_2RuCl_5 \cdot H_2O$ is too insoluble in anhydrous HTFA or if soluble it does not dissociate readily to yield chloride ions.

Method (b) was also unsatisfactory because there is considerable doubt as to the products formed and because there is danger of forming chloride ion as a by-product when perchloric acid is used as a solvent for the ruthenium. Wehner and Hindman[6,7] used this method and prepared a ruthenium (III) species which is not Ru^{+3}, $RuCl^{++}$, or $RuCl_2^{+}$ nor does it appear to be a higher chloride complex. The most obvious remaining choice is polymerized Ru(III). This is acceptable because it is known that Ru(IV) in solution is polymerized and because Ru(III) complexes are slow to come to equilibrium with their environment. Therefore it is likely that Ru(III) formed by reduction of Ru(IV) would remain polymerized and be held together in the same manner as Ru(IV).

The third method proved the most satisfactory. In HTFA many reagents reduce RuO_4 to Ru(III). The most attractive of these reducing agents was mercurous ion, because mercurous ion and its product mercuric ion can be removed from the Ru(III) solution by electrolysis.

Other satisfactory reducing agents are Fe^{++}, Sn^{++} and Ti^{+3} ions, and some metals. If RuO_4 is in excess during the reaction with a reducing agent Ru(IV) is formed, which is very difficult to reduce further at an appreciable rate, unless the reducing agent is very powerful. Among the reducing agents that reduce Ru(IV) in HTFA at a reasonable rate are metallic tin and titanous ion.

Even when RuO_4 is not in excess it has been found that the Ru(III) solution formed during reduction is composed of several species. In reduction in the presence of chloride ion at least 8 different ruthenium species were formed. Three were Ru^{+3}, $RuCl^{++}$, and $RuCl_2^{+}$, the rest have not been identified, but two of them at least are known to be Ru(IV) species.

It was established that Ru(III) is complexed by HTFA when RuO_4 is chemically reduced in HTFA. When this fact was discovered further work in HTFA was discontinued because of the desire to prepare uncomplexed Ru(III). These complexes with HTFA do not appear to form under all conditions; Rehn and Wilson[8,9,10] have dissolved $K_2RuCl_5 \cdot H_2O$ in dilute HTFA and found no evidence for complex formation. It may be that in the present work the HTFA became attached to the ruthenium during the reduction step.

In $HClO_4$ satisfactory reducing agents were more difficult to find. The reduction must be fast and essentially complete, and must not yield by-products that are likely to interfere with the charge determination experiments. Stannous perchlorate proved the most satisfactory from the standpoint of ease of preparation and completeness of reaction. Incompleteness of reaction eliminated Fe^{++} and Hg_2^{++}. Difficulty of preparation of Ti^{+3} in perchloric acid and the reduction of perchloric acid by Ti^{+3} and V^{++} eliminated the latter two reducing agents. Slowness of reaction eliminated the metallic reducing agents. It was necessary that the reduction be fast and essentially complete because of the oxidation of Ru(III) by perchloric acid.

In practice it was necessary to add RuO_4 slowly to a cold, rapidly stirred solution of stannous ion in perchloric acid. This technique prevents excessive formation of Ru(IV). The stock solution of Ru(III) was oxidized by $HClO_4$ within a day unless this solution was stored in a refrigerator at about 0°C. Under these conditions it would last as long as one week.

Satisfactory reaction yielding Ru^{+3} occurred when the stannous ion was between 0.01 and 0.1 M; the RuO_4 was about 3×10^{-3} M and the perchloric acid was about 0.1 M. The RuO_4 solution could be added until the preparation just began to show signs of Ru(IV) formation although an excess (10 to 50%) of stannous was usually added to eliminate Ru(IV) and to stabilize the Ru(III) with respect to oxidation by perchloric acid or oxygen.

To prepare the chlorides $RuCl^{++}$ and $RuCl_2^{+}$, HCl was added to the stannous solution before the reduction reaction so that it was initially about 0.1 M in HCl, and about 0.05 M in HCl after the reduction.

2. Purification of Species

The ruthenium species were purified on an ion-exchange column at the same time as the net charge per ruthenium atom was determined. The stock solution containing the Ru(III) species and all other products of this reduction reaction was stirred with enough ion-exchange resin to almost fill a column. It was necessary to stir the resin-ruthenium solution for several hours in order to get the ruthenium into the resin phase. This was necessary because the ruthenium would not go onto the resin from this solution rapidly enough so that the solution could be added to the top of a column. On the other hand, the ruthenium equilibrated rapidly after this first absorption. After this stirring the resin was separated from the solution and placed in the column over an amount of the resin in the hydrogen ion form that corresponded to about 3% of the resin stirred.

The foregoing evidence of slow equilibration, combined with the fact that the ruthenium that passed through the ion-exchange columns without absorbtion is always associated with colloidal stannic oxide (which also goes onto the resin slowly), can be explained if one assumes that the ruthenium is trapped in a colloidal particle of stannic oxide. This colloidal particle appeared to break up slowly in the presence of 200 to 400-mesh resin particles, or rapidly in the presence of colloidal Dowex-50.

A solution of known hydrogen ion and cerous ion concentration was then used to elute the ruthenium from the resin. Cerous ion was held so strongly by the Dowex-50 ion exchange resin used in the column that it quantitatively displaced the Ru(III) cations. As cerous ion was added to a column it displaced these cations into lower regions of the column, and is said to "push" them.

As the cations were being pushed they separated from one another. The most tightly held ion being pushed formed a compact band of a pure species on the resin just ahead of the cerous ion. Other bands of ions formed in the column with the most loosely held ion furthermost from the cerous band. Since the cerous solution also contained hydrogen ion and the column was originally in the H^+ form, it was possible for a very loosely held ion to be eluted by the hydrogen ion and never form a compact band that was pushed.

Samples were collected as the bands were pushed out of the column. The uv spectra of these samples were measured on a Cary recording spectrophotometer, and a sample was considered to contain a pure species when the spectra of the two adjacent samples were identical with that of the given sample. The spectra of the pure species Ru^{+3}, $RuCl^{++}$, and $RuCl_2^{+}$ are given in Fig. 4. This method of purification had the advantage that the species are concentrated and purified at the same time.

There were two techniques that helped in the separation of pure species. The first was to vibrate the column during the elution. This kept the resin tightly packed and prevented serious channeling. The second was to taper the column so that it was larger at the top than at the bottom. This permitted the addition to the column of a large amount of the species to be separated, and retained the advantage of a narrow column in that the bands occupied a large vertical distance when they were being eluted from the column.

3. Determination of the Charge per Ruthenium Atom

The principle of charge balance between the elutriant and eluant solutions of the ion-exchange column was used to determine the net charge per ruthenium atom in the complex. The elutriant solution was analyzed for cerous and hydrogen ions, and the eluant solution for ruthenium, hydrogen, tin, and cerous ions. The eluant did not contain detectable amounts of cerium or tin in the samples used for calculation, except in one case where a small amount of cerous ion was present.

The charge per ruthenium atom was calculated based on the assumption of a charge of +3 per cerous ion, a charge of +1 per hydrogen ion, and on the assignment of all the charge necessary to balance the charge between the elutriant and the eluant solutions to the ruthenium species. The results of the experiments on the charge per ruthenium atom are shown in Table II. The ion-exchange resins used were Dowex-50 x 12 for elutions IV-76-5 and IV-76-6, and Dowex-50 x 8 for the rest.

Table II

Charge per ruthenium(III) atom in solution

Elution Number	Elutriant composition (M)		Eluant solution composition (M)			Charge per Ru atom
	Ce^{+3}	H^+	H^+	Ce^{+3}	Ru	
			Species Ru^{+3}			
IV-76-5	0.0420	0.040±.002	0.040±0.002	0.000	0.0436	2.89±.05
IV-76-6	0.0420	0.040±.002	0.040±0.002	0.000	0.0448	2.81±.05
V-50-2	0.0672	0.113±.005	0.120±0.005	0.000	0.0664	2.92±.1
V-50-4	0.0672	0.113±.005	0.120±0.005	0.000	0.0670	2.90±.1
V-50-6	0.0672	0.113±.005	0.120±.005	0.000	0.0666	2.91±.1
			Species $RuCl^{++}$			
V-22-2	0.0420	0.106	0.148	0.000	0.0430	1.95±.1
V-22-3	0.0420	0.106	0.142	0.000	0.0484	1.86±.1
V-22-4	0.0420	0.106	0.138	0.000	0.0480	1.96±.1
V-22-5	0.0420	0.106	0.138	0.000	0.0486	1.93±.1
V-22-6	0.0420	0.106	0.144	0.000	0.0480	1.83±.1

The results are consistent with a charge of +3 per ruthenium atom in the first species and +2 per ruthenium atom in the second.

The eluant solution of elutions IV-76-5 and IV-76-6 actually contained more than a single ruthenium species. The unidentified species adhered to the resin with a greater force than Ru^{+3}, however the low values of charge per ruthenium atom indicate that this species has a charge less than +3 per ruthenium atom. From spectral measurements it was possible to show that at least 70% of the ruthenium in Experiment IV-76-5 was Ru^{+3} and at least 53% of that in Experiment IV-76-6 was Ru^{+3}.

The method for determining the charge per atom was checked with the known ions cupric and chromic. A sample of Dowex-50 x 12, 200 to 400 mesh in the cupric form was equilibrated with a solution containing chromic ions. The initial and final solutions were analyzed and -- on the assumption that cupric ion has a +2 charge -- the results are shown in Table III.

Table III

Charge per chromic ion in solution

Experiment Number	Initial Solution (M) Cr^{+3}	Initial Solution (M) Cu^{+2}	Final Solution (M) Cr^{+3}	Final Solution (M) Cu^{+2}	Charge per Cr^{+3} atom calculated
IV-33	0.1045	0.000	0.027	0.116	3.07

The value of 3.07 for charge per atom checks very well with the actual charge of 3.00.

4. Charge per Ru Species

It was necessary to know several of the properties of the Dowex-50 cation-exchange resins before the charge per ruthenium species could be determined. A summary of the results obtained on air-dried resin is shown in Table IV.

Table IV

Physical constants of air-dried Dowex-50 ion-exchange resin in the hydrogen ion form

	Dowex-50 x 12 200 to 400 mesh	Dowex-50 x 12 Colloidal	Dowex-50W x 8 200 to 400 mesh
Capacity (equivalents/kg)	3.52	3.42	3.86
Wt. resin per ml column volume	0.555 g	0.389	-
Void volume per ml of column volume	0.472	0.655	-
Density of resin	1.18	-	-

In order to solve Eq. (4) for the charge per species in the following quantities were measured for each equilibration: total A present in gram atoms, ΣA; initial hydrogen ion concentration, in moles per liter, before equilibration, $(H_S^+)_{initial}$; total volume of solution present in ml, V; weight of air-dried ion-exchange resin in grams, W; and the gram atoms of A per liter of solution after equilibration, (A_S^{+n}). It was also necessary to know the capacity (C) of the air-dried resin in equivalents of charge per 1000 grams of resin.

From these measurements it is possible to derive the desired values as follows:

(A_S^{+n}) measured

$$(A_R^{+n}) = \frac{\Sigma A - (A_S^{+n})\,V}{W}$$

$$(H_R^{+}) = (C) - n\,(A_R^{+n})$$

$$(H_S^{+}) = (H_S^{+})_{\text{initial}} + \frac{n\,(A_R^{+n})\,W}{V}$$

The quantities (A_S^{+n}) and (A_R^{+n}) can be expressed in gram atoms instead of moles because the units cancel in the calculation. The value of (H_R^{+}), however, depends on the moles of species A in the resin, and therefore a knowledge of the degree of polymerization is required. Because (A_R^{+n}) would always be chosen to be small with respect to (H_R^{+}), the value of (H_R^{+}) actually would not be changed appreciably by the degree of polymerization. Because the value of n determines the concentration of H^+ as well as the power to which it is taken, n must be determined by successive approximations.

In order to test the method, the charge per species of Cr(III) in a solution of chromic nitrate was determined by this batch-equilibration method. The results are presented in Table V. The experimental conditions employed were not ideal; there were two major faults. First, only a small fraction of the chromic ion went into the resin during the first equilibration in 1 M perchloric acid. This led to a large error in the determination of the chromic ion concentration on the resin - estimated at 15% error. The second fault was that after the second equilibration a large fraction of the resin was in the chromic ion form. This is bad because little is known about ionic activities in the resin phase, except that the activity coefficient of an ion is a function of the composition of the resin. This means that a "concentration" equilibrium constant changes with changing resin composition. When these two difficulties are taken into account the calculated charge of 3.16 per chromic ion can be considered to be within satisfactory agreement with the known value of 3.

Table V

Charge per chromic ion in solution

Dowex-50W x 12, 200 to 400 mesh

Equilibration Number	Total Cr^{+n} (mg-atoms)	Initial H_S^+ (M)	V (ml)	W (g)	Total capacity (milliequivalents of charge)	(Cr_S^{+n}) final (M)	Calc. n
IV-38-1	0.131	1.00	100	0.1501	0.529	1.125×10^{-3}	3.16
IV-38-2	0.131	0.100	1000	0.1477	0.520	3.52×10^{-5}	

The determination of the charge per ruthenium species can be consistent with the charge per ruthenium atom only if the charge per species is an integral multiple of the charge per ruthenium atom. This integer is the number of ruthenium atoms in the species.

The results of the determination of the charge per species of ruthenium are summarized in Table VI. The ion-exchange resin used was Dowex-50W x 12 in the first set of experiments, and Dowex-50W x 8 in the rest.

Table VI

Charge per ruthenium species in solution							
Equilibration Number	Total Ru^{+n} (mg-atoms)	Initial H_S^+ (M)	V (ml)	W (g)	Capacity of resin (mequiv.)	(Ru^{+n}) (gram atoms per liter)	Calc. n
			Species Ru^{+3}				
IV-77-1	0.0131	1.035	14.5	0.1738	0.611	2.68×10^{-4}	2.7
IV-77-2	0.0116	0.517	18	0.1738	0.611	4.91×10^{-5}	
V-4-1	0.02015	1.010	15	0.2256	0.868	4.14×10^{-4}	2.8
V-4-2	0.01800	0.5065	20	0.2256	0.868	7.42×10^{-5}	
			Species $RuCl^{+2}$				
V-27-1	0.0121	0.705	14.2	0.2275	0.875	6.47×10^{-4}	1.7
V-27-2	0.00885	0.235	27.2	0.2275	0.875	1.63×10^{-4}	
V-29-1	0.0242	0.750	20	3.124	12.0	4.35×10^{-4}	1.7
V-29-2	0.0242	0.375	40	3.124	12.0	1.56×10^{-4}	

These results indicate one species with a +3 charge, and another of charge +2, to within the experimental uncertainty.

The results from the charge per ruthenium species experiments would be more difficult to interpret if the ruthenium changed its charge per species in going from the aqueous to the resin phase. When this effect was discussed earlier (under Practical Considerations in Determining the Charge per Species), it was considered unlikely that changes in complexing, other than hydrolysis, or in polymerization would take place in this system because ruthenium is so slow to change its species in aqueous solution. Theoretically the results from four different stirring experiments on the same aqueous species would tell if there were a change in species between the aqueous and resin phases. Because of the similarity of conditions actually employed in the equilibrations, it was not possible to eliminate rigorously the possibility of change in the species except for $RuCl^{+2}$, where dimerization of the ruthenium species could be eliminated.

Both Ru(III) species were checked for impurities of Ru(IV) by the iodide method (discussed in the section on Solution Preparation and Analytical Methods).

The only ruthenium ion with a charge of +3 per atom, +3 per species, and an oxidation state of +3 is Ru^{+3}. In addition the perchloric acid experiments gave no evidence of perchlorate complexes of Ru(III) such as $RuClO_4^{++}$. In the pushing experiments on Ru^{+3} with the cation-exchange resin the only bands observed were Ru^{+3} and some tightly held species which may have been Ru(IV).

Since there is no evidence for the formation of a complex between Ru^{+3} and $HClO_4$ in high $HClO_4$ concentration, then the second species of

Table VI cannot be $RuClO_4^{+2}$. This second species must be $RuCl^{++}$, because the only other anion present is chloride and the species has a charge of +2 per species, +2 per ruthenium atom, and an oxidation state of +3 for the ruthenium.

These results agree with the ions hypothesized by A. S. Wilson for the ions present when $H_2RuCl_5 \cdot H_2O$ is allowed to dissociate in HTFA. The spectrum of $RuCl^{++}$ agrees with that obtained by Wilson, but there is a discrepancy in the spectrum of Ru^{+3}. Impurities in his sample could have led to this result.

C. Identification of $RuCl_2^+$

It was found that the method described for determining the charge per ruthenium atom was impractical for $RuCl_2^+$. The acid concentration ($\sim$ 0.1 M) necessary in the preparation of the species, and to prevent hydrolysis and (or) oxidation of the ruthenium, also prevented the formation of a compact band in the pushing experiment. This compact band could not be formed because of the relatively high efficiency of 0.1 M hydrogen ion for elution of this singly charged species, which meant that it was eluted in the normal manner rather than being pushed. This high efficiency of elution coupled with the impracticality of preparing solutions of pure $RuCl_2^+$ approaching 0.1 M in concentration made the determination of the charge per ruthenium atom so difficult that it was not attempted.

Determination of the charge per ruthenium species by the previously described method was still feasible; however, it was decided to obtain this charge information in a different way. The new experimental procedure was as follows. First the resin in an ion exchange column was washed with a solution that contained the two cations H^+ and $RuCl_2^+$

as well as other ruthenium species until the optical absorption in the eluant arising from $RuCl_2^+$ became constant. Then a solution containing only hydrogen ion was added to the top of the column as an elutriant. The H^+ in this solution equilibrated with the ruthenium in the resin near the top of the column and as more solution was added to the column the equilibrated solution passed through the column and was collected. Once the solution reached equilibrium with the treated resin it did not affect the composition of any additional resin that was further down in the column. Just sufficient elutriant was added to flush out the void volume of the column and to give two samples for analysis. The flushing was required because the original stock solution contained several ruthenium species. At least one of these was a neutral or anionic species and would have given erroneous ruthenium analyses if it had not been washed from the void spaces in the column before collecting the first sample.

The composition of the elutriant was changed by increasing the concentration of the hydrogen ion. A sample of this solution was collected and its composition was compared with that of the first sample collected. Since the composition of the resin at the bottom of the column was constant, Eq. (4) simplified to

$$\frac{(H_S^{\ +})_1^n}{(A_S^{\ +n})_1} = K'' = \frac{(H_S^{\ +})_2^n}{(A_S^{\ +n})_2} \quad . \qquad (5)$$

The ruthenium stock solution also contained ruthenium species of charge higher than that of $RuCl_2^+$. It was necessary to adjust conditions so that there was no danger that these species would be eluted from the column while the $RuCl_2^+$ samples were being collected. This was accomplished by using minimal amounts of solution to equilibrate the column initially with $RuCl_2^+$, and to elute the $RuCl_2^+$.

As was previously noted the ruthenium (III) species prepared in the reduction of RuO_4 by stannous ion do not easily equilibrate with ion-exchange resin. The Ru(III) in this solution could be converted to a form that would equilibrate rapidly with Dowex-50 x 8, 200 to 400 mesh, by stirring the stock solution with a small amount of the resin for about 24 hours. This converted solution was run through an ion-exchange column until the spectrum of the eluant solution was constant from sample to sample. At this time the column was considered to be in equilibrium with the $RuCl_2^+$ and the hydrogen ion in this solution.

The results of the experiment are shown in Table VII.

Table VII

Charge per $RuCl_2^+$ species

Equilibration Number	Elutriant solution	Eluant solution	Charge per Species
IV-31-1	0.05 $\underline{M}$ $HClO_4$	0.050 $\underline{M}$ $HClO_4$; 2.48×10^{-4} $\underline{M}$ Ru	0.92
IV-31-2	0.200 $\underline{M}$ $HClO_4$	0.200 $\underline{M}$ $HClO_4$; 8.87×10^{-4} $\underline{M}$ Ru	

This result of a charge of +1 per ruthenium species indicates the presence of $RuCl_2^+$, since the ruthenium is three-valent and the only complexing anion present is chloride. Other possible species could be $Ru_2Cl_5^+$ or any analogous polymeric +1 species. Such a formulation is perhaps less likely than $RuCl_2^+$, because the polymer might be expected to be held quite tightly by the resin in analogy to the case of mercuric and mercurous ions. In any case this species will be referred to as $RuCl_2^+$ in this thesis.

There is a certain amount of ambiguity in the interpretation of the results, because the molar extinction coefficients do not remain in exact agreement from one sample to the next. This lack of agreement is slight, and may be caused by a change in the isomeric ratio of the cis-trans form of $RuCl_2^+$. Another possibility would be the presence of species such as $Ru(OH)_2^+$, $Ru(OH)(Cl)^+$, or $RuCl_3^+$. The last-named ion is a complex of Ru(IV) and cannot be present in an appreciable amount as judged from the iodide test. It is unlikely that hydrolyzed species of Ru(III) exist in 0.2 M $HClO_4$; however, they may exist in 0.05 M acid. This species also agrees with the $RuCl_2^+$ species proposed by A. S. Wilson as one of the species present in a solution of $H_2RuCl_6 \cdot H_2O$ in HTFA which has had time to dissociate.

D. Spectra of Species

The molar extinction coefficients of the three ruthenium species are tabulated in Table VIII. Plots of these data appear in Fig. 4.

Table VIII

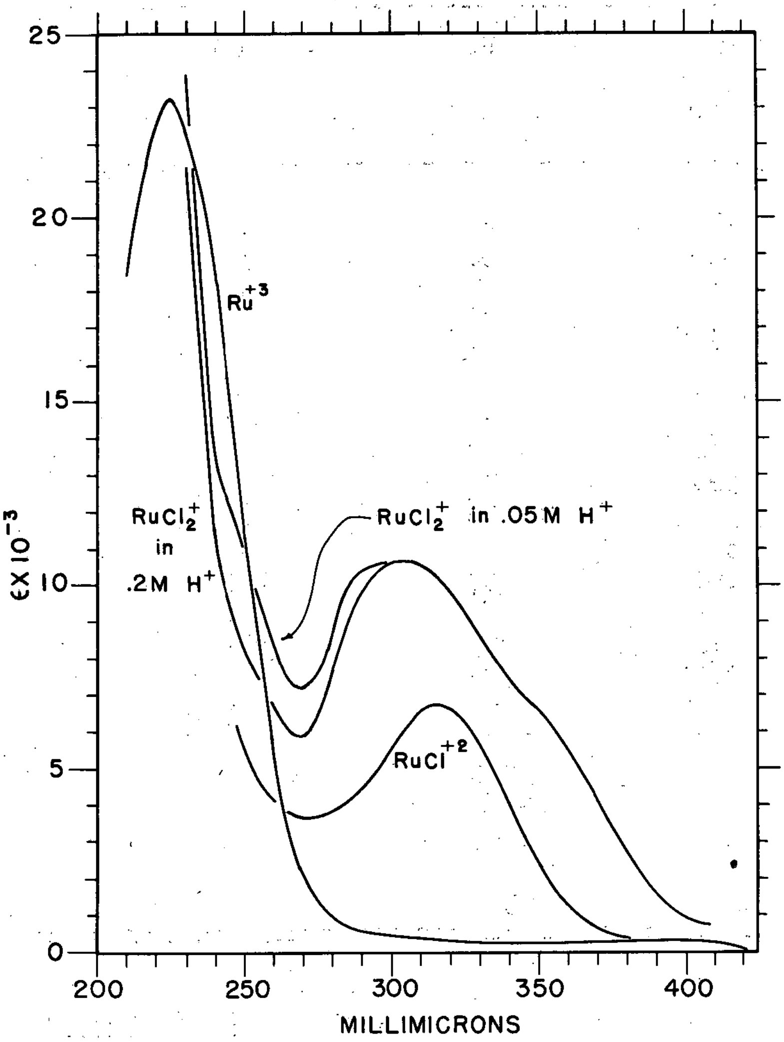
Molar extinction coefficients

mμ	Ru^{+3}	$RuCl^{+2}$	$RuCl_2^+$	
450	∼ 0		0.2 $\underline{M}$ H^+	0.05 $\underline{M}$ H^+
404	29	31	80	79
393	30	31	130	120
382	29	34	242	224
371_5	28	57	400	400
361	26	116	550	550
351	25	236	660	660
340_5	27	402	750	750
330	32	571	880	865
320	37	662	1000	980
310	40	656	1050	1040
300	45	549	1060	1070
290	57	435	970	1040
280	93	382	760	855
270	215	366	590	720
260	575	412	670	844
250	1150	560	840	1100
240	1830		1140	1370
230	2230		2100	2400
220	2260			
210	1850			
315		677 ±		
2240	2320			

E. Additional Chemistry of Ru(III)

1. Oxidation State

One of the most striking characteristics of the aquo or trifluoroacetate complexes of three-valent ruthenium is their lack of color in contrast to the other oxidation states of ruthenium and the other complexes of Ru(III). The colorless species formed in the titration of ruthenium tetroxide with ferrous trifluoroacetate in HTFA had an oxidation state of 3.05 ± .05 as determined by the stoichiometry of the reaction. (See Figs. 7 and 8 in Section VI.)



MU-13202

Fig. 4. Spectra of Ru^{+3}, $RuCl^{++}$, and $RuCl_2^+$ in $HClO_4$.

Oxidometric titration of this colorless species in HTFA by RuO_4 or by ceric ion indicated a spectrophotometric and potentiometric end point after a 1.21 ± .05-electron oxidation. (See Figs. 7 and 8) In perchloric acid ceric oxidation of $RuCl^{++}$ yielded an end point after a 1.01 electron oxidation of the ruthenium.

The spectra of the Ru(IV) obtained in all these titrations agreed with the spectra reported by Wehner and Hindman for Ru(IV) in perchloric acid to within the rather large variabilities they encountered.[6,7]

2. Reaction of $RuCl^{++}$ with Ceric Perchlorate

A brief investigation of the rate of oxidation of $RuCl^{++}$ by ceric ion in perchloric acid yielded some interesting results. The first experiments, which were potentiometric titrations in 0.5 M $HClO_4$ indicated that a slow reaction was taking place after each addition of ceric ion. The potential drift indicated that an oxidizing reagent was disappearing. It was noted that the nearer the $RuCl^{+2}$ - Ru(IV) titration approached the end point the faster was the disappearance of this oxidizing agent. In two identical spectrophotometric studies in 0.5 M $HClO_4$ it was observed that the half time for the spectral changes at 450 mμ was roughly twice as long as at 270 mμ. Further, it was observed that the reaction for the formation of Ru(IV) was as much as tenfold slower in 5 M $HClO_4$ than in 0.5 M. A study of the potentiometric drifts during this reaction in 5 M $HClO_4$ showed a rapid increase in the potential recorded for about 30 seconds, followed by a slow decrease over a period of about 30 minutes. The decrease measured did not fit any simple rate law. Spectral studies of the reaction in 5 M $HClO_4$ indicated that the ceric ion reacted rapidly, almost instantaneously, and that at least some of the early product was RuO_4 (identified by its characteristic vibrational spectrum at ~ 380 mμ). The change in the spectrum, followed as a function of time, indicated that there must be at least two unknown species formed during the later slow stages of the reaction. The species that are formed during the oxidation in 5 M $HClO_4$ differed to an appreciable extent drom those formed in 0.5 M $HClO_4$. Chloride ion was released during the reaction in either acidic solution, as shown by the addition of silver nitrate.

A summary of the results in the two acidic media show that the rates, products, and potentials are different in the different acid concentrations used. The $RuCl^{++}$ and initial Ce^{+4} concentrations were the same in these rate studies, so that the observed variations must depend on the acid medium.

Further study of this reaction probably would be fruitless because of its complexity. The observed formation of RuO_4 in the presence of excess $RuCl^{++}$ was surprising, and was interpreted to indicate that monomeric Ru(IV) is unstable in the system and either disproportionates or reacts very rapidly with ceric ion. In the rapid reaction of Ru(IV) to RuO_4 it is necessary to suppose that the rate of reaction of Ce^{+4} with $RuCl^{++}$ is slower than the corresponding rate with Ru(IV) or that the Ru(IV) species initially formed disproportionates rapidly. A further surprise was the slowness of the rate of reaction of RuO_4 with $RuCl^{++}$. A possible reason for the slow oxidation of $RuCl^{++}$ would be that a forbidden electronic rearrangement is required.

3. Other species

One of the species of Ru(III) that was observed, but not identified was a complex of ruthenium with trifluoroacetate ion. This complex was first detected when an anionic, neutral, and (or) singly charged ruthenium (III) species was not held up appreciably by a Dowex-50 ion-exchange column. The species passed directly through the column without being absorbed from a solution that was less than 1 M in HTFA. This observation was substantiated by several other experiments, in which the Ru(III) had been prepared in different ways. This ruthenium (III) trifluoroacetate complex was prepared by reduction of RuO_4 in HTFA by mercurous ion or stannous ion. Solutions of similar appearance could also be prepared by reduction with ferrous ion as the reducing agent. After long standing, all these solutions are a pale green. The spectrum of the aged solution formed by mercurous reduction is shown in Fig. 5, Curve 5. Both HTFA and perchloric acid were used as elutriants for the HTFA complexed ruthenium with no appreciable difference in the behavior of the columns. By comparison with this result of no hold-up, it takes about 20 cc of 5 M $HClO_4$ to elute any ferric ion from a column of the same size and type of resin whose void volume is about 1.5 ml.

The species formed by mercurous reduction in HTFA was assumed to be a trifluoroacetate complex because reduction under similar conditions of hydrogen and mercurous ion in perchloric acid yeilded uncomplexed Ru^{+3}.

The spectra of several "Ru(III)" solutions that have been formed by reduction of RuO_4 in HTFA are plotted in Fig. 5. The differences in the calculated average molar extinction coefficients are beyond the possible experimental errors. This indicates that more than one species of Ru(III) is formed. Attempts to correct for the traces of

Ru(IV) that are often present do not change the interpretation requiring several Ru(III) species.

Separation and purification of a neutral ruthenium chloride species was attempted, utilizing cationic and anionic exchange resins. A ruthenium-containing species was isolated that was not held up by either resin. This species was present in a solution prepared by refluxing a solution of 0.02 M ruthenium chloride in 0.3 M HCl in the presence of metallic mercury for 40 hours. The spectrum of this neutral species appears in Fig. 6.

The plot of the absorption of the "neutral" ruthenium chloride is not in terms of ϵ, but rather in optical density, because of the uncertainty of the ruthenium analysis in this sample. This analysis shows a concentration of $2.5 \pm .5 \times 10^{-4}$ gram atoms per liter of ruthenium. Since the sample was run in a 1 cm cell the ϵ_{283} is $1.0 \pm .2 \times 10^4$.

Preliminary studies of the higher chloride complexes of Ru(III) in HCl show the existence of two species which are in rapid equilibrium with each other. These species appear to be identical with "$RuCl_6^{-3}$" and "$RuCl_5 \cdot H_2O^=$" as reported by Rhen and Wilson.[12] These ions are prepared by dissolving $K_2RuCl_5 \cdot H_2O$ in various concentrations of HCl. The $K_2RuCl_5 \cdot H_2O$ was not analyzed but was prepared by the method used by Wilson,[9] i.e., reduction by metallic mercury in dilute HCl. The x-ray powder patterns were not identical for the "$H_2RuCl_5 \cdot H_2O$" prepared at different times, but under similar conditions. These patterns showed that the compound could not be $K_4Ru_2Cl_{10} \cdot 0\ H_2O$.

There is evidence for at least two other anions in these solutions of $K_2RuCl_5 \cdot H_2O$. One of these anions shows a peak in its spectrum at

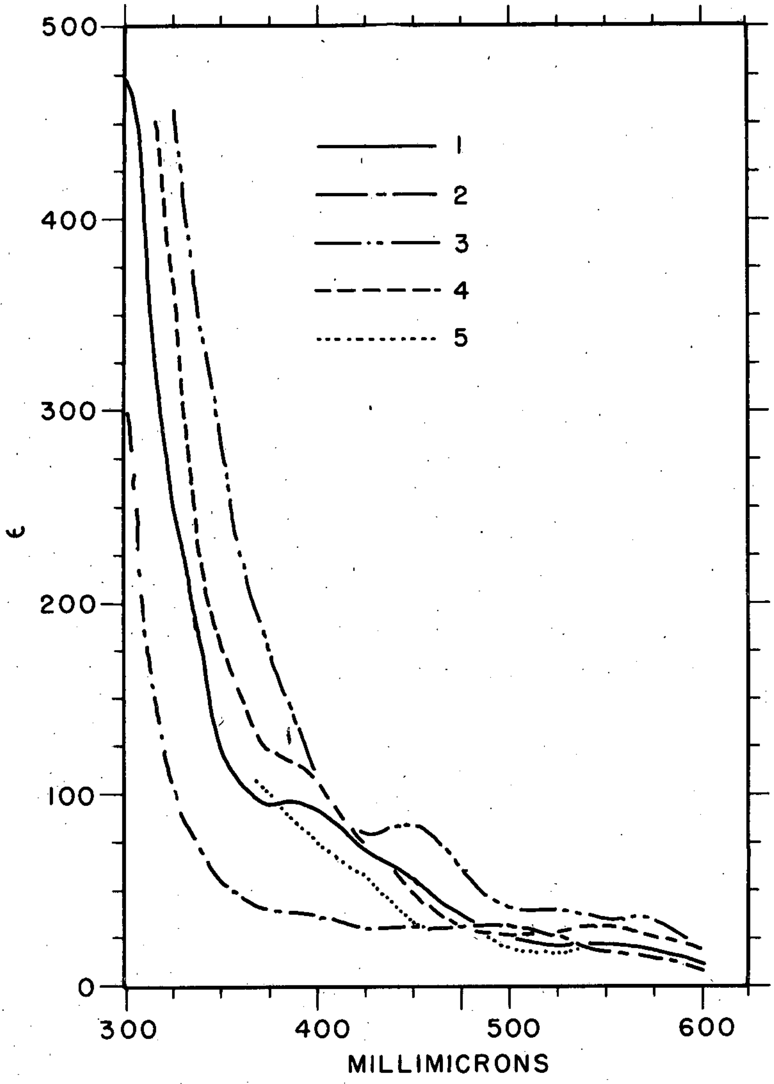


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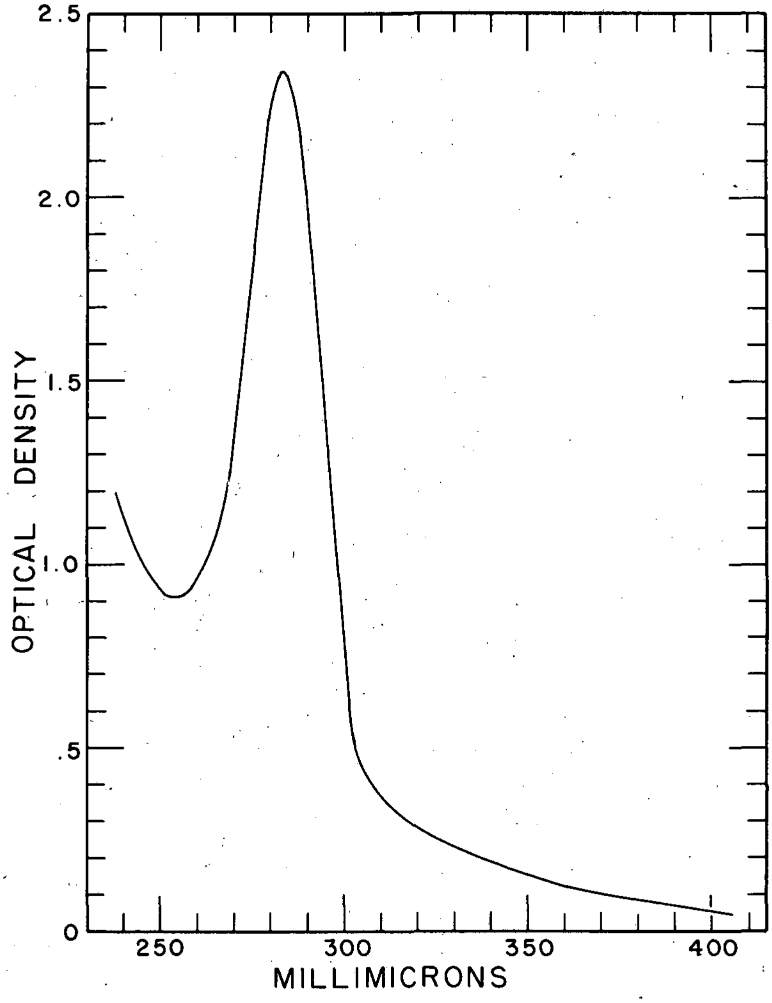
Fig. 5. The spectra of various Ru(III) species in HTFA.

Curve 1. was obtained by stannous trifluoroacetate reduction,
Curve 2. by hydrogen peroxide reduction,
Curve 3, by ferrous trifluoroacetate reduction,
Curve 4, by Ru(II) trifluoroacetate reduction,
Curve 5, by mercurous trifluoroacetate reduction.



MU-13204

Fig. 6. Spectrum of a neutral Ru(III) species in 0.3M HCl.

about 295 mμ with ϵ_{295} between 1.5 and 2.7 x 10^4. The location of the peak is dependent upon the HCl concentration and it shifts from 300 mμ to 290 mμ with a change from 12 to 1 M HCl. Except for this shift the species appears to be resistant to change with changing solution conditions. It has not been shown that this species is three-valent ruthenium, since there is a trace of Ru(IV) present in the $K_2RuCl_5 \cdot H_2O$ preparation.

Several other species were observed, but not identified, during the pushing experiments on Ru^{+3} and $RuCl^{+2}$. In the experiments in which the solutions used for pushing the Ru^{+3} were of low acidity, a species was observed that has a peak at 288 mμ with an ϵ_{288} greater than 1350, assuming a monomer ruthenium species. This species is held more strongly by the resin than is Ru^{+3}, and is held about as strongly as cerous ion. It is probably a hydrolzed and dimerized Ru(III) species, or a mixed oxidation state of Ru(III) and Ru(IV). It converts to Ru(IV) on exposure to air. This species is not converted rapidly to Ru^{+3} by the addition of excess $HClO_4$. It is oxidized to Ru(IV) fairly rapidly by the perchloric acid, however.

During the purification of $RuCl^{++}$ there were a minimum of six additional species being pushed as pure bands, as well as a band of $RuCl_2^+$, which was not pushed, but eluted. Three of these species are probably Ru^{+3}, $RuCl^{+2}$, and the previously mentioned hydrolyzed species. The remainder must be other Ru(III) or Ru(IV) species. There were additional ruthenium species present in the original stock solution, which were held too tightly to be pushed.

4. Rate of reaction of Ru(III) with $HClO_4$

Some workers have reported that perchloric acid oxidized Ru(III), while others report inert behavior.[6,7,8,10,13] In the course of the experiments at this laboratory the following observations were made. Perchloric acid in 0.10 M concentration reacted within 2 days with freshly reduced Ru(III) stock solutions unless the solutions were kept in a refrigerator at about 0°C. The rate of the reaction was stronly dependent upon temperature. A solution of purified Ru^{+3} in 0.1 M $HClO_4$ could be kept at room temperature exposed to light for as long as 2 weeks. This reaction between Ru^{+3} and $HClO_4$ appeared to be autocatalytic. The ruthenium chloride species such as $RuCl^{++}$ reacted more rapidly with $HClO_4$ than did Ru^{+3}. Chloride ion is formed in the reaction between Ru^{+3} and $HClO_4$, and may be responsible for the autocatalysis. Ru(IV) catalyzes the reaction. Oxidation of Ru(III) does not stop at Ru(IV); there is evidence for the slow formation of RuO_4. Finally, the oxidation of Ru^{+3} proceeds rpaidly in both high (6 M) and low ($\leq$ 0.01 M) concentrations of perchloric acid. The increase in rate in low acid concentration is probably due to the rapid rate of oxidation of hydrolyzed Ru(III).

In summary it appears that reactions of Ru^{+3} with perchloric acid are catalyzed by chloride and (or) Ru(IV). This reaction may be retarded by low temperatures and moderate perchloric acid concentration.

VI. TETRAVALENT RUTHENIUM

The observations in this laboratory on the behavior of "uncomplexed" Ru(IV) in both HTFA and $HClO_4$ are in basic agreement with those of Wehner and Hindman,[6,7] and Swanson and Wilson.[12] Evidence for the formation of polymers and intermediate oxidation states is confirmed.

A. Preparation of Ru(IV) and Other Related Species

Several methods of preparation of Ru(IV) were used during the course of the investigation. These methods included:

(a) Electrolytic reduction of RuO_4, and electrolytic oxidation of Ru(III) in HTFA.

(b) Chemical reduction of RuO_4 by ferrous ion, mercurous ion, and hydroger peroxide in both HTFA and $HClO_4$.

(c) Oxidation of Ru(III) by RuO_4, Ce^{+4}, MnO_2, and $HClO_4$ in HTFA and $HClO_4$.

None of these reactions was investigated in great detail, but it is known that the products formed are dependent upon the conditions of the reactions. Some of the variables that seem to affect the properties of the Ru(IV) product are rate of mixing and concentration of reagents, reducing or oxidizing agent employed, and temperature of the solution during reaction.

B. Oxidation States of Species Formed

Comparisons of spectral and potentiometric data gave strong indications of the formation of species that were not Ru(IV), but which apparently had oxidation states near to +4. These species have approximate oxidation numbers of (3.5) and (4.2). The (3.5) species will be discussed later. Wehner and Hindman report evidence for the ruthenium that can be interpreted as indicating the formation of a species having oxidation numbers between 4.2 and 4.5.[6,7] The work in this laboratory confirms their observations on this intermediate oxidation state.

When 100 ml of 2.73 x 10^{-3} $\underline{M}$ RuO_4 was titrated potentiometrically with ~ 0.5 $\underline{M}$ ferrous trifluoroacetate in 1 $\underline{M}$ HTFA, either a gold or a platinum electrode showed two end points near the +4 oxidation state whose difference corresponded to a change of 0.28 in the oxidation number of the ruthenium. The same effect was observed in 4 $\underline{M}$ perchloric acid when 100 ml of 1.17 $\underline{M}$ RuO_4 was titrated with 0.17 $\underline{M}$ ferrous perchlorate, except that the corresponding change in the oxidation state was 0.38. The actual oxidation states of these two species were not known accurately from the experiments because of uncertainty in the ferrous concentration in the titration in HTFA, and because of the possibility of oxidation by perchloric acid in the $HClO_4$ experiments, as well as an unknown loss of RuO_4 by volatilization in both experiments. It was assumed that the lower oxidation state was Ru(IV) in each case, in analogy to the findings of Wehner and Hindman[6,7] for electrolytic reduction of RuO_4. A plot of the potential data is shown in Fig.11,(Section VII). The behavior of the electrodes, etc., is discussed in the section on potentials of the Ru(IV)-RuO_4 couple.

Oxidation of Ru(III) in 1 $\underline{M}$ HTFA also showed evidence for the formation of a species with an oxidation state of approximately 4.2 to 4.4. Two spectrophotometric titrations of 20.3 ml of 6.61 x $10^{-3}$$\underline{M}$

ferrous trifluoroacetate by ~ 1.6 x 10^{-3} M RuO_4 in 1 M HTFA showed a 1.18 change in oxidation state in going from Ru(III) to this higher oxidation state. Figs. 7 and 8 show plots of the data from these titrations. Likewise spectrophotometric titration of 1.15 x 10^{-3} M Ru(III) by 5.05 x 10^{-3} M ceric perchlorate in 1 M HTFA indicated the same change of 1.18 in the oxidation state of the ruthenium. Spectrophotometric and potentiometric titrations of 0.0216 M titanous ion by 2.31 x 10^{-3} M RuO_4 in 1 M HTFA showed evidence for the formation of ruthenium species with oxidation states of 2.0 to 2.1, 3.0, 3.4 to 3.5, and 4.2 to 4.3. Fig. 9, and also Figs. 12 and 13 are plots of the data which indicate these oxidation states.

On the contrary, a potentiometric titration of 8.6 x 10^{-3} M $RuCl^{++}$ by 9.54 x 10^{-3} M ceric perchlorate in 0.5 M perchloric acid showed an end point after a 1.01 change in oxidation state of the ruthenium. This reaction was not a simple electron transfer. The reaction has been discussed in more detail in the section on Reaction of $RuCl^{++}$ with Ceric Ion.

Another possible interpretation of these results, which would explain an average oxidation number of 4.2, but does not involve intermediate oxidation states, would be to assume that a mixture of different products was formed, say with part of the ruthenium in the +5 or +6 oxidation state. The only evidence that would discourage such an interpretation is that one would have to assume that these higher oxidation states are formed in about the same ratio to the Ru(IV), under a variety of reaction conditions. Further, it has not been possible to prepare solutions by these methods in which the average oxidation state of the ruthenium approaches +5 or +6.

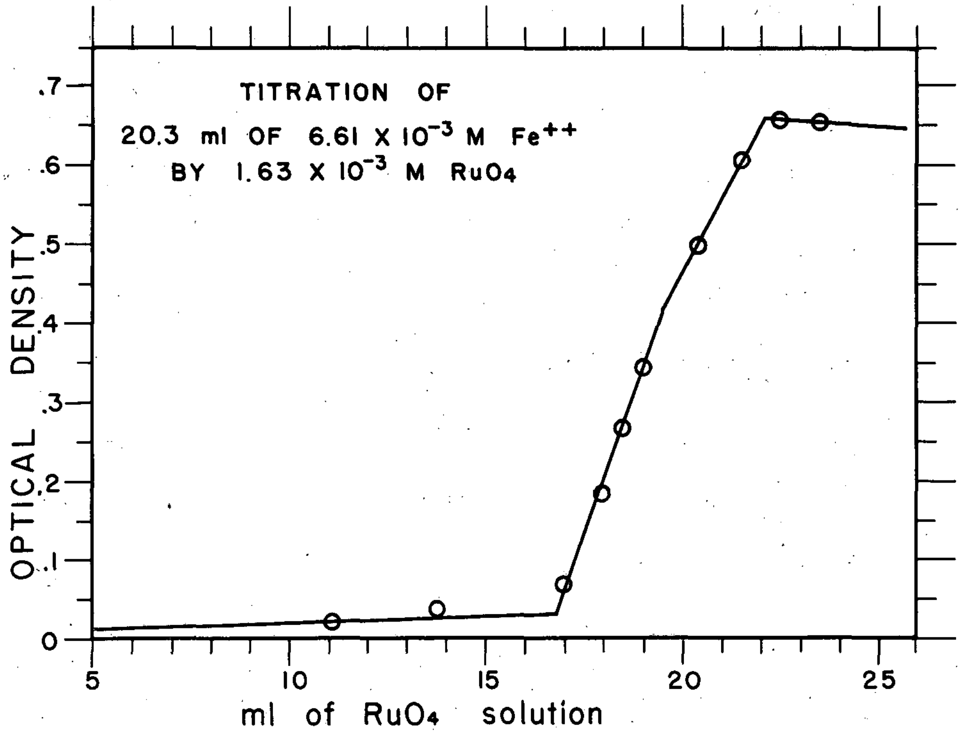


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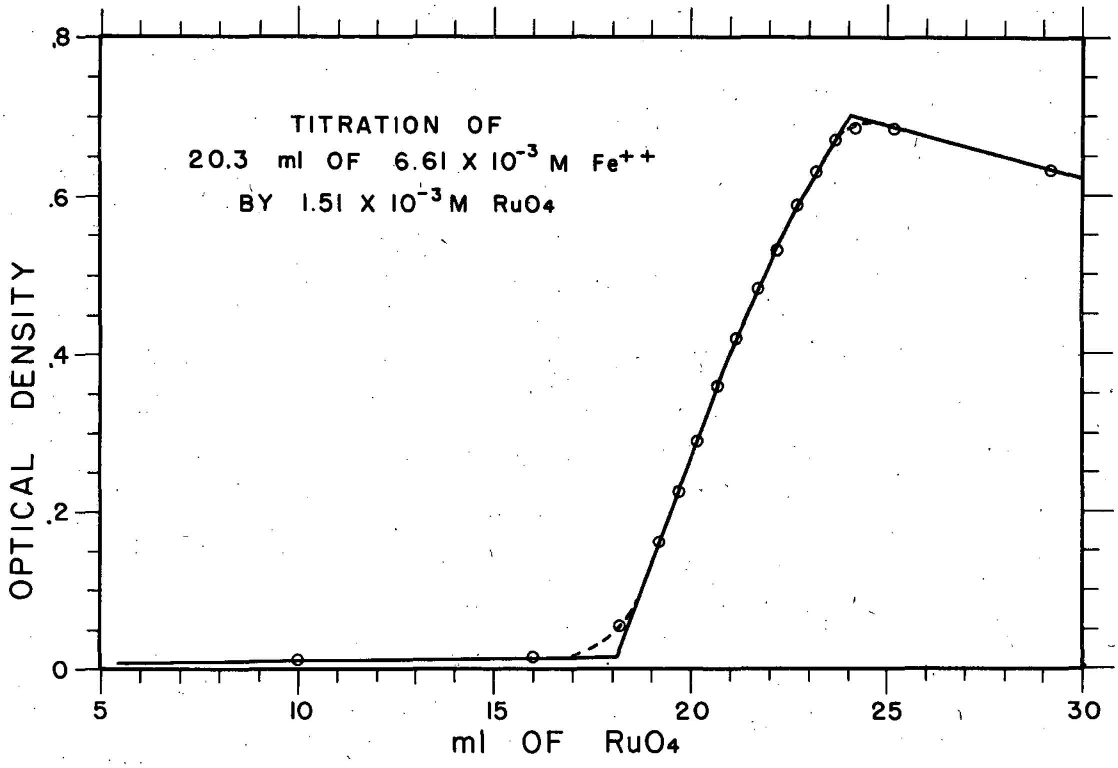
Fig. 7. Spectrophotometric titration of Fe^{++} by RuO_4 in 1M HTFA.



MU-13206

Fig. 8. Spectrophotometric titration of Fe'' by RuO_4 in 1M HTFA.

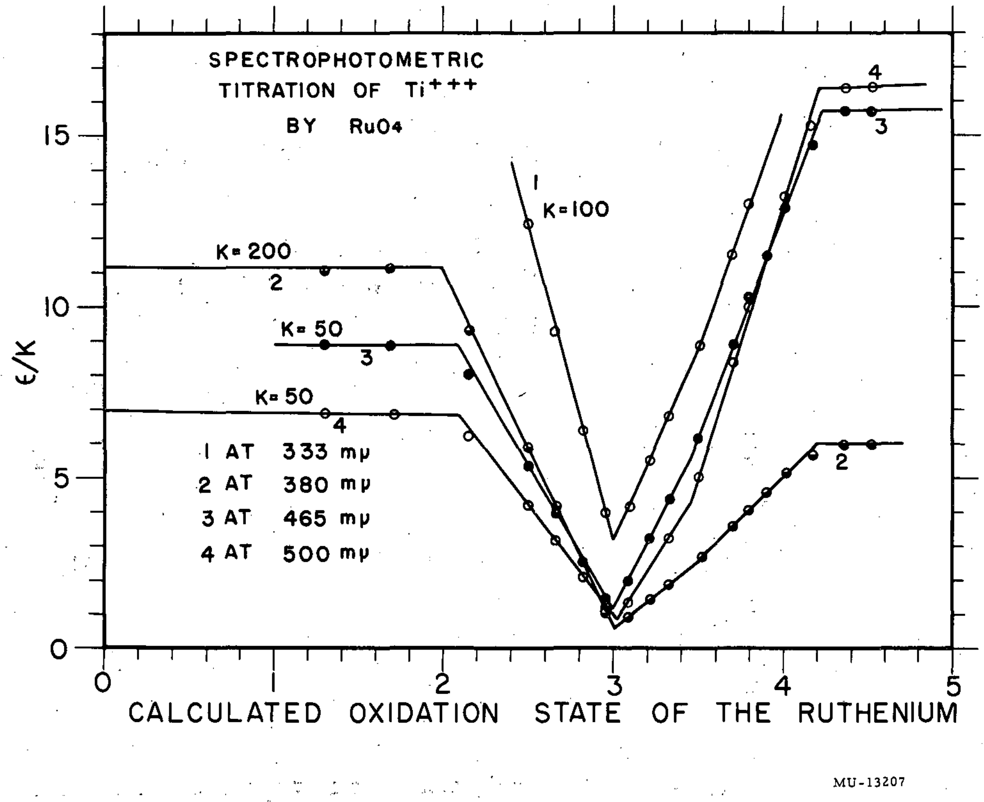


Fig. 9. Spectrophotometric titration of Ti^{+3} by RuO_4 in HTFA.

C. Properties of Ru(IV) and Ru(4.2) in Solution

1. Spectra

The spectrum of Ru(IV) species obtained in solution was not constant from one preparation to the next, but varied appreciably. The Ru(IV) spectra obtained are considered to agree with those obtained by Wehner and Hindman.[6] In Fig. 10, Curves 1 and 2 show two typical spectra obtained for Ru(IV). Curve 1 shows the spectrum of the Ru(IV) prepared by the oxidation of Ru^{+3} by ceric perchlorate. Curve 2 shows the spectrum obtained by the reduction of RuO_4 in HTFA by ferrous trifluoroacetate. Curve 3 is a spectrum of Ru(3.5). The spectrum of the Ru(4.2) species is very similar to that of Ru(IV). The major differences are that the absorption of Ru(4.2) is somewhat higher in the region above 500 mμ and there is no evidence for a plateau at 300 mμ.

2. Polymers

The Ru(IV) and (or) Ru(4.2) species in solution were partially if not completely polymerized. The size of the polymers was to some extent determined by the method of preparation and rate of reaction to the Ru(IV) state. Some of the polymers were of colloidal size as evidenced by the appearance of a Tyndall beam in solutions of Ru(IV). Although some solutions of Ru(IV) did not appear to contain colloidal ruthenium, all the solutions containing Ru(4.2) were colloidal. Ultrafiltration using "Visking" sausage membranes removed the larger colloids, but did not appreciably change the shape of the spectra of the Ru(IV) or Ru(4.2) solutions. The ruthenium species in a solution of Ru(IV) clung tenaciously to Dowex-50 ion-exchange resin. Elution of this material from a column of ion-exchange resin using cerous ion as the elutriant indicated the existence of more than one species of Ru(IV), since some of the Ru(IV) could be removed from the column while some could not.

A solution of Ru(IV) in 1 M HTFA was ultracentrifuged in an attempt to determine the molecular weight of the species present. This solution was prepared by adding 3.24 cc of 0.504 M Fe^{++} solution to 100 cc of 2.73×10^{-3} M RuO_4. Even though ferrous ion is in excess only a small amount of the Ru(IV) was reduced to Ru(III).* The molecular weight of the lightest polymer in this solution was 1000 within the limits of +1000 or -500. This result would indicate a polymeric species consisting of about eight ruthenium atoms, which are probably held together by oxide or hydroxide bridges. The rate of settling was observed using the light absorption method because the solutions were too dilute to use any of the effects involving refraction of light.

3. Chemistry

The chemistry of uncomplexed Ru(IV) in solution is characterized by its inertness to chemical attack by reducing agents. This inertness appeared to be a side effect of the polymerization of the ion since it was possible to reduce RuO_4 to Ru(III) quite easily, provided an excess of the reducing agent was present in a solution at all times and the solution was stirred to insure that the local excesses of RuO_4 dispersed rapidly. If these provisions were not fulfilled a species of Ru(IV) would form which was not easily reduced by the same reducing agents which had been satisfactory earlier. This effect appears to be kinetic

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*We would like to thank Dr. H. K. Schachman of the Virus Laboratory for his help in determining the molecular weight of this ruthenium species.

as the reduction of Ru(IV) to Ru(III) in HTFA would eventually succeed.

This slow rate of reaction was only an inconvenience in HTFA, but makes the reduction of Ru(IV) impractical in $HClO_4$ due to the relatively rapid rate of oxidation of Ru(III) by $HClO_4$, especially since this reaction appears to be catalyzed by Ru(IV).

Ruthenium (IV), in acidic solution reacted rapidly with strong oxidizing agents such as periodate and persulfate to form RuO_4. It also reacted rapidly with anionic reducing agents which complex the ruthenium, for example iodide ion.

D. Ruthenium (3.5)

The presence of a ruthenium species different from Ru(III) or Ru(IV) has been observed in reactions in which the average oxidation state of the ruthenium would be expected to be between 3 and 4. Its exact oxidation state is very uncertain, but there is some evidence supporting the value 3.5. This evidence is from the spectrophotometric titration of titanous ion with RuO_4 in 1 M HTFA. The spectrum of the Ru(3.5) obtained in this titration is shown in Fig. 10, Curve 3. The characteristics that distinguish the spectrum of Ru(3.5) from Ru(IV) are a peak at 340 to 350 mμ and a relative intensification of the peak at 460 mμ compared with the Ru(IV) peak in this region.

Spectral evidence for the formation of this species has been observed in solutions prepared in the following ways (the methods giving high yields are starred):

(a) Reduction of RuO_4 in HTFA solution by excess ferrous trifluoroacetate, and excess mercurous trifluoroacetate;

(b) Reduction of Ru(IV) in HTFA solution by excess ferrous trifluoroacetate and metallic mercury;

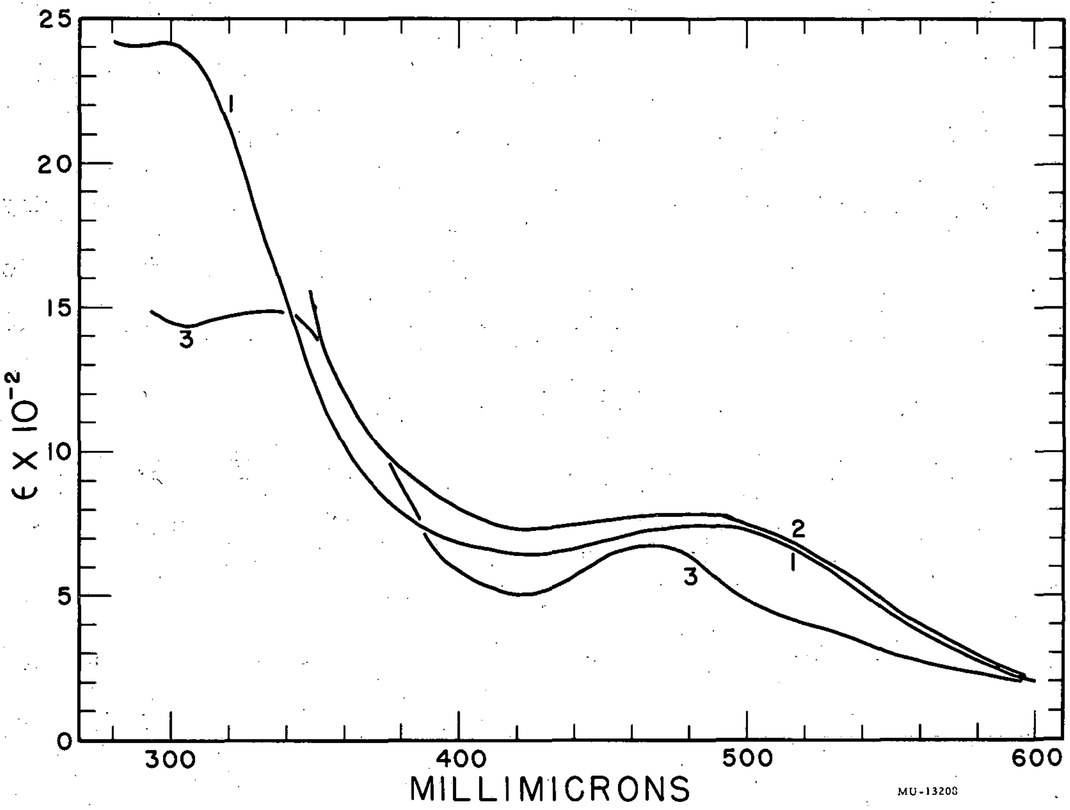

Fig. 10. Curve 1, Spectrum of Ru(IV) in HTFA,
Curve 2, Spectrum of Ru(IV) in HTFA,
Curve 3, Spectrum of Ru(3.5) in HTFA.

(c) Boiling a solution prepared by adding RuO_4 to an excess of H_2O_2 in HTFA;*

(d) Oxidation of Ru(III) in a solution of HTFA by ceric perchlorate, RuO_4,* and MnO_2;*

(e) Oxidation of Ru^{+3} in 0.55 M perchloric acid by ceric ion;

(f) Possibly, oxidation of Ru^{+3} by O_2 or $HClO_4$ in 0.01 M $HClO_4$ solution.

It is not possible to completely eliminate the possibility that this species is a ruthenium(IV) chloride; however, it is known that the total chloride was less than 1% of the total ruthenium, and there was no evidence supporting ruthenium(III) chlorides or ruthenium(IV) chlorides in the initial or final solutions.

The only preparations of this Ru(3.5) species that gave good yields were in HTFA. Since it was known that HTFA complexes Ru(III), and the oxidation state of this species was in doubt, no further observations of its chemistry were made. It may be possible to purify and identify this species by using the same ion-exchange techniques as employed for Ru^{+3} and $RuCl^{++}$.

The most obvious interpretation of this 3.5 species would be a dimer of two ruthenium atoms, with one in the +3 oxidation state and the other in the +4. The dimer would probably be held together by oxide or hydroxide bridges. An analogous interpretation for the 4.2 oxidation state could be a polymeric species containing four atoms of Ru(IV) and one atom of Ru(V), or nine atoms of Ru(IV) and one atom of Ru(VI). If the average oxidation number were higher than 4.2 the ratio of Ru(IV) to Ru(VI) atoms would be decreased.

VII. Potentials

Very little has been published on the ruthenium couples in such common complexing media as hydrochloric, sulfuric, or nitric acids, let alone the relatively noncomplexing media of trifluoroacetic or perchloric acids.

Latimer has estimated the potentials in HCl solutions based on the reported chemical reactions.[18] His estimates for the potentials of interest are

$$\mathrm{Ru} \overset{-0.45}{\overline{\hspace{3em}}} \mathrm{Ru}^{+2} \overset{-0.30}{\overline{\hspace{3em}}} \mathrm{RuCl}_5^{=} \overset{-1.3}{\overline{\hspace{3em}}} \underbrace{\mathrm{RuCl}_5^{-}\,\mathrm{OH}^{=} \overset{-1.75}{\overline{\hspace{3em}}} \mathrm{RuO}_4^{=} \overset{-1.25}{\overline{\hspace{3em}}} \mathrm{RuO}_4}_{-1.5}$$

More recently Backhouse and Dwyer have measured the potentials of the Ru(II)-Ru(III) and Ru(III)-Ru(IV) couples.[19] They report the couples in 1 M HCl to be

$$\mathrm{Ru(II)} \overset{-0.08}{\overline{\hspace{3em}}} \mathrm{Ru(III)} \overset{-0.88}{\overline{\hspace{3em}}} \mathrm{Ru(IV)}.$$

The latter value is in agreement with the report that Cl_2 oxidizes Ru(III) quantitatively to Ru(IV).[14] Using the data of Backhouse and Dwyer one can calculate the chloride-ion and hydrogen-ion dependence of the Ru(III)-Ru(IV) cell, assuming that concentration equals activity. The reaction appears to be $H^+ + 2Cl^- + Ru(III) = Ru(IV) + e^-$, although the only uncertainty is that chloride ion is on the left-hand side of the equation for 0.5 to 6 M HCl.[*] The Ru(II)-Ru(III) couple seems to be independent

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[*] To obtain a potential for the Ru(III)-Ru(IV) reaction the authors attempted to extrapolate the measured potentials to zero chloride concentration. Their interpolation is open to question since they have estimated the Ru(III)-Ru(IV) couple by extrapolation to zero chloride concentration, even though the couple involves chloride ion.

of HCl concentration between 1.5 and 6.8 M HCl, although the authors somehow concluded that there was a chloride dependence.

Wehner and Hindman measured the zero current potentials during the electrolysis of RuO_4, Ru(IV), and Ru(III) in acidic perchlorate solutions.[6] Their potential data, if interpreted assuming rapid equilibration of all ruthenium species, indicate species of +8, +4.3, +4.0, +3.5 to 3.6, and +3 oxidation states. The Ru(III) that they prepared is not Ru^{+3}, nor is it a simple chloride complex, according to their reported spectral information. It may be a polymer of Ru(III), especially as it is known that the complexes of Ru(III) are slow to break up and that the Ru(IV) species being reduced is polymerized. The reported potentials from Wehner and Hindman in 1 M $HClO_4$ are

$$\mathrm{Ru(III)}\ \text{———}\ \overset{(?)}{\mathrm{Ru(3.5)}}\ \text{———}\ \mathrm{Ru(IV)}\ \overset{-1.20}{\text{————}}\ \overset{(?)}{\mathrm{Ru(4.3)}}\ \overset{-1.35}{\text{————}}\ \mathrm{RuO_4}$$

-0.50 -0.65 (from reduction of Ru(IV))

-0.82 -1.12 (from oxidation of Ru(III))

(The value of the saturated calomel electrode is assumed to be -0.24 volt rather than the value of -0.29 volt assumed by Wehner and Hindman.[6]) Obviously the Ru(III)-Ru(IV) electrode was irreversible in their experiments.

Niedrach and Tevebaugh, using polarographic techniques, confirmed Wehner and Hindman's observations that there was a two-step reduction between Ru(IV) and Ru(III) in acidic perchlorate solutions.[13] Niedrach and Tevebaugh report that these steps are irreversible. They further report a reversible wave at more positive potentials corresponding to the formation of Ru(II). They carried out a potentiometric titration of Ru(III) by ceric ion in perchloric acid but reported only the potential at the midpoint, so that it is not known whether they observed two steps by this method. Their results are

Ru(II) —— Ru(III) —— Ru(IV)
+0.10 -0.65 (polarographic)
-0.85 (potentiometric titrations).

It is obvious in reading the reports by these workers that the ruthenium system does not behave ideally, and it is doubtful that the reactions studied were well characterized.

It was hoped that formulas of "uncomplexed" ruthenium species present in acidic perchlorate solutions could be determined by calculations based upon the shapes of the potential curves obtained during the titration of one ruthenium species to another. It would be possible to determine degree of polymerization, change in degree of complex formation, etc., from these curves. It was unfortunate that in practice no conditions were found that would yield potential data of the quality needed for these calculations.

Some of the difficulties encountered were that shiny gold and shiny platinum electrodes, in the same solution, often gave potentials that differed by 0.01 volt. In addition, the potentials being measured in a potentiometric titration, showed a tendency to drift for relatively long periods of time after each addition of titrating agent. This drift could be interpreted as indicating a slow reaction of the titrating agent, a slow equilibration of the products formed, or a slow equilibration of the electrodes with the solution. On top of these difficulties was the one presented by the fact that many of the reactions could be made to proceed in only one direction, e.g., Ru(III) + RuO_4 gives Ru(IV), RuO_4 + Fe^{++}(ex) gives Ru(III), but Ru(IV) + Fe^{++} gives no reaction. It is obvious that the potentials are at best qualitative.

A. Standard-Cell Potentials

The potentials were measured in the cells described earlier in Section II. In all cases the potentials were measured against a Beckman saturated calomel electrode. The value of the calomel potential plus salt bridges was determined from the $E_{1/2}$ in a ferrous-ferric titration. In 1 M HTFA the measured $E_{1/2}$ is -0.474. Using Swift's value for the formal potential for the Fe^{++} - Fe^{+++} couple of -0.732, in 1 M $HClO_4$[15] and assuming this value to hold in HTFA, one obtains the value of -0.258 for the calomel and salt bridges versus the normal hydrogen electrode. Similarly in 0.1 M $HClO_4$ the $E_{1/2}$ Fe^{++} - Fe^{+++} is -0.503 and in 4 M $HClO_4$ it is -0.497. It appears that a value of -0.24 ± .03 for the calomel would be satisfactory for perchloric acid solutions. The saturated calomel electrode will be referred to as the S.C.E. and the normal hydrogen electrode as the N.H.E. $E_{1/2}$ means the voltage obtained at the half-way point of the titration.

B. Potentiometric Titrations

1. Ruthenium Tetroxide - Ru(IV) Potential

Two titrations of RuO_4 to Ru(IV) under different acid conditions gave essentially the same results. The first titration in which ~ 0.5 M ferrous trifluoroacetate was added to 100 ml of 2.75×10^{-3} M RuO_4 in 1 M HTFA, showed two potential breaks. The second potential break at 2.48 ml of ferrous solution indicates an average oxidation state of 3.49 for the ruthenium. No confidence is placed in this value because of uncertainty in the ferrous concentration and unknown volatility losses of RuO_4. The spectrum of the reduced solution showed only the presence of Ru(IV). Excess ferrous ion did not reduce this Ru(IV) rapidly. On the basis of the spectral measurement and Wehner and Hindman's results on electrolytic reduction it was assumed that the second potential break corresponded to Ru(IV). Then the first potential break was at an oxidation number of 4.28. The potentiometric titration data are plotted in Fig. 11 and the $E_{1/2}$ results are summarized in Table IX.

The results of the second titration in which 0.17 M ferrous perchlorate was added to 100 ml of 1.17×10^{-3} M RuO_4 in 4 M perchloric acid are also shown in Fig. 11 and Table IX. In this titration the stoichiometry at the second potential break indicated a 3.9-electron reduction, while the spectral data indicated the presence of only Ru(IV). Volatilization of some RuO_4 would lead to a result of this type. If the second break is, as assumed, at oxidation number 4.00, then the oxidation number of the first break is 4.38. The possibility of a third potential break at 2.54 ml of ferrous solution was indicated by the data, but may be spurious.

The electrode behavior during the titrations was poor at first. There were considerable slow drift; lack of agreement between electrodes; and even in one case a rise of potential, indicating more oxidizing agent after each addition of reducing agent. On the other hand, in the region between Ru(4.3) and Ru(4.0) there was almost no drift, and the potentials used for each electrode were in close agreement.

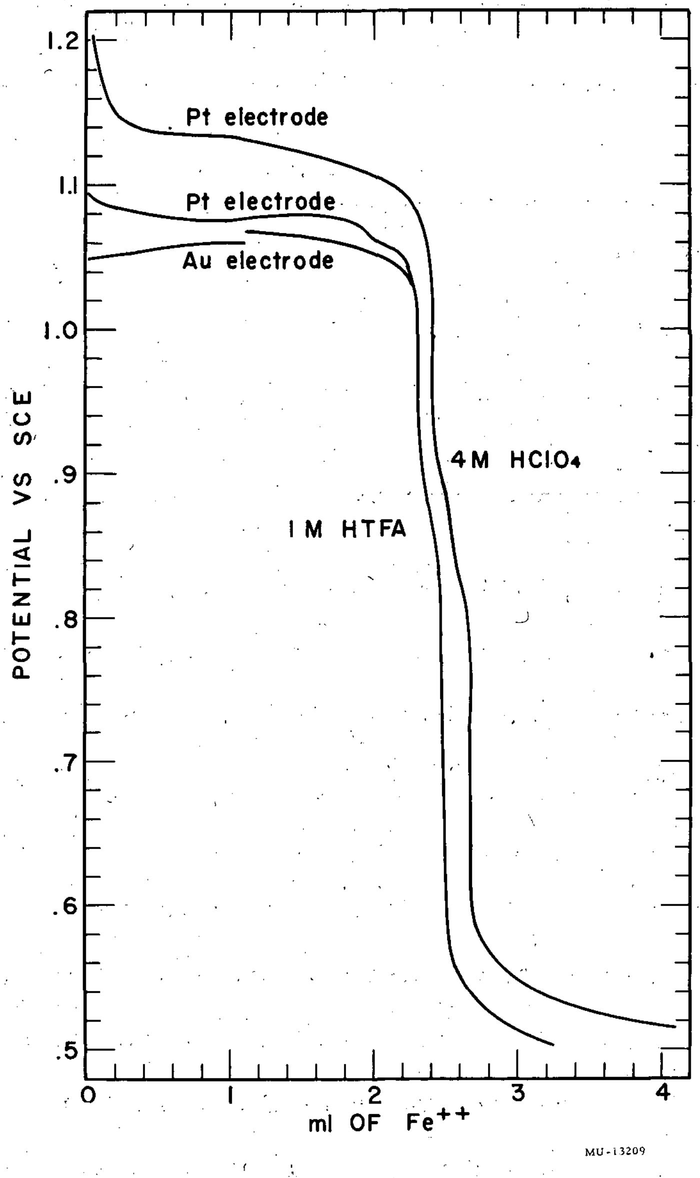

Fig. 11. Potentrometric titration of RuO_4 by Fe^{++}.

Table IX

Potentials of the RuO_4 - Ru(IV) System

Cell	Solvent	Value of S.C.E. + junctions	$E_{1/2}$ measured	$E_{1/2}$ vs N.H.E.
Ru(4.28) - RuO_4	1 M HTFA	-0.26	-1.07	-1.33
Ru(4.38) - RuO_4	4 M $HClO_4$	-0.24	-1.126	-1.33
Ru(4.00) - Ru(4.28)	1 M HTFA	-0.26	-0.88	-1.14
Ru(4.00) - Ru(4.38)	4 M $HClO_4$	-0.24	-0.86	-1.10

For the 4 M perchloric acid solution the potentials vs the N.H.E. were corrected to 1 M H^+ by assuming that four hydrogen ions were consumed in the reduction of RuO_4 to Ru(4.38), and none between Ru(4.38) and Ru(4.0).

2. Ru(III) - Ru(IV) Potential

The potential measurements taken in the Ru(III) - Ru(IV) region are only of qualitative value. The reasons are that the system is irreversible, the products formed are not always the same from one titration to another, and the actual species reacting are not known.

Evidence of irreversibility was shown by the fact that ferrous ion in excess reduced RuO_4 rapidly to Ru(III), but reacted only slowly with Ru(IV). That different products were formed was shown by the fact that the spectrum of the species formed during the oxidation of Ru(III) to Ru(IV) were different if the reaction conditions were changed slightly. Also in reactions where HTFA was the acid medium the degree of complexing of the Ru(III) and Ru(IV) species by trifluoroacetate was not known. There was spectral and possibly slight potential evidence for the formation of a species of oxidation state 3.5. In the titration of $RuCl^{++}$ with Ce^{+4} there was evidence for the initial formation of RuO_4 even though there was a large excess of $RuCl^{++}$. This demonstrated that the reaction was not simply $RuCl^{++} \longrightarrow RuCl^{+++} + e^-$. Also in the titration of Ti^{+3} by RuO_4 in $HClO_4$ there was evidence for the formation of an "inert" Ru(III) as well as a reactive Ru(III). This evidence was that Ti^{+3} reacted initially with RuO_4 to produce Ru(II); the ruthenium must have passed through a reactive Ru(III) state. As more RuO_4 was added it oxidized the Ru(II) to an Ru(III) species that would not completely rereduce to Ru(II) even when there was still an excess of Ti^{+3}. A summary of the Ru(III)-Ru(IV) potentiometric titration results is shown in Table X. The reactions have been assumed to be acid-independent. A plot of the potentiometric titration of Ti^{+3} with RuO_4 in 1 M HTFA in the Ru(III)-Ru(IV) region is shown in Fig. 12. There were large drifts in the potentials being measured at certain points. Fig. 12, Curve 1 shows the location of the last potential measured, i.e., about 8 min after each addition of ferrous solution. Curve 2 shows the estimated final potential based upon extrapolation of the measured potentials to infinite time. Curve 3 represents a theoretical curve for a monomer-monomer, one electron oxidation of Ru^{+3} to Ru^{+4}.

No good potentiometric evidence was obtained during this investigation, for a Ru(3.5) species in $HClO_4$, however, no great effort was made to find it.

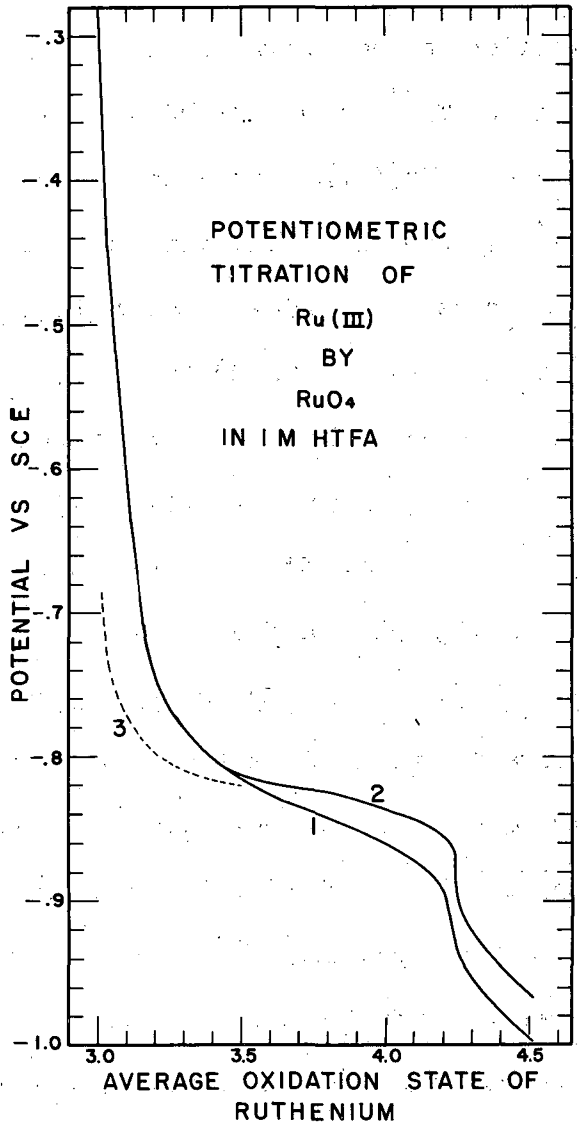

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Fig. 12. Potentrometric titration of Ru(III) by RuO_4 in 1M HTFA in in Ru(III) - Ru(IV) region.

Table X

Potentials in the Ru(III) - Ru(IV) region

Solvent	Oxidizing Agent	Ru(III) species, or preparation method	Probable reaction	Reasoned $E_{1/2}$ vs S.C.E.	$E_{1/2}$ vs N.H.E.
1 M HTFA	Ce^{+4}	RuO_4 added to Fe^{++} ⟶ Ru(III)	Ru(III)⟶Ru(4.2)	-0.82±.01	-1.08±.03
1 M HTFA	RuO_4	Ti^{+3} + RuO_4 ⟶ Ru(II) Ru(II) + RuO_4 ⟶ Ru(III)	Ru(III)⟶Ru(3.5)	-0.77±.01	-1.03±.02
			Ru(3.5)⟶Ru(4.25)	-0.84±.02	-1.10±.02
			or Ru(III)⟶Ru(4.25)	-0.82±.01	-1.08±.02
1 M $HClO_4$	RuO_4	Ti^{+3} + RuO_4 ⟶ Ru(II) Ru(II) + RuO_4 ⟶ Ru(III)	Ru(III)⟶ Ru(IV)?	-0.75±.05	-.99±.07
0.5 M $HClO_4$	Ce^{+4}	$RuCl^{++}$	$RuCl^{++}$ ⟶ ? ⟶ Ru(IV)	-.75±.01	-1.03±.03
0.5 M $HClO_4$	Ce^{+4}	$RuCl^{++}$ + Ag^{+}	$RuCl^{++}$ ⟶ ? ⟶ Ru(IV) +AgCl	-.78±.01	-1.02

3. Ru(II) - Ru(III) Potential

The information obtained on the Ru(II)-Ru(III) couple is also not very definitive. In the potentiometric titration of titanous trifluoroacetate with RuO_4 in HTFA the potential appeared to be -0.20 volt vs the N.H.E.; however, the ferric ion titration of Ru(II) prepared in the same manner indicated a potential of -0.10 volt.

The behavior of the electrode during the titration of titanous with RuO_4 was one of the best observed in any of the ruthenium systems. The electrode responded rapidly to change in the composition of the solution and maintained a steady reading after each change. Analysis of the shape of the potential curve indicated that the reaction was monomer Ru(II) going to monomer Ru(III). It tells nothing about trifluoroacetate complexes, however. This potentiometric titration is shown in Fig. 13.

The titration of titanous perchlorate with RuO_4 in acid perchlorate solution did not yield quantitative information that could be used to calculate anything about the species reacting. The results indicated that the Ru(II)-Ru(III) couple was sufficiently negative so that Ti^{+3} would reduce the ruthenium quantitatively to Ru(II). This result was obtained from spectral data that showed that the amount of Ru(II) present in a solution did not change, although a considerable portion of the Ti^{+3} was being oxidized by perchloric acid. An additional result, which was surprising, was that the reaction of RuO_4 with Ru(II) in perchloric acid apparently yielded a Ru(III) species that was inert to reduction by titanous ion. This was shown by the fact that the average molar extinction coefficient of the ruthenium decreased after each addition of RuO_4 solution even when there was a large excess of

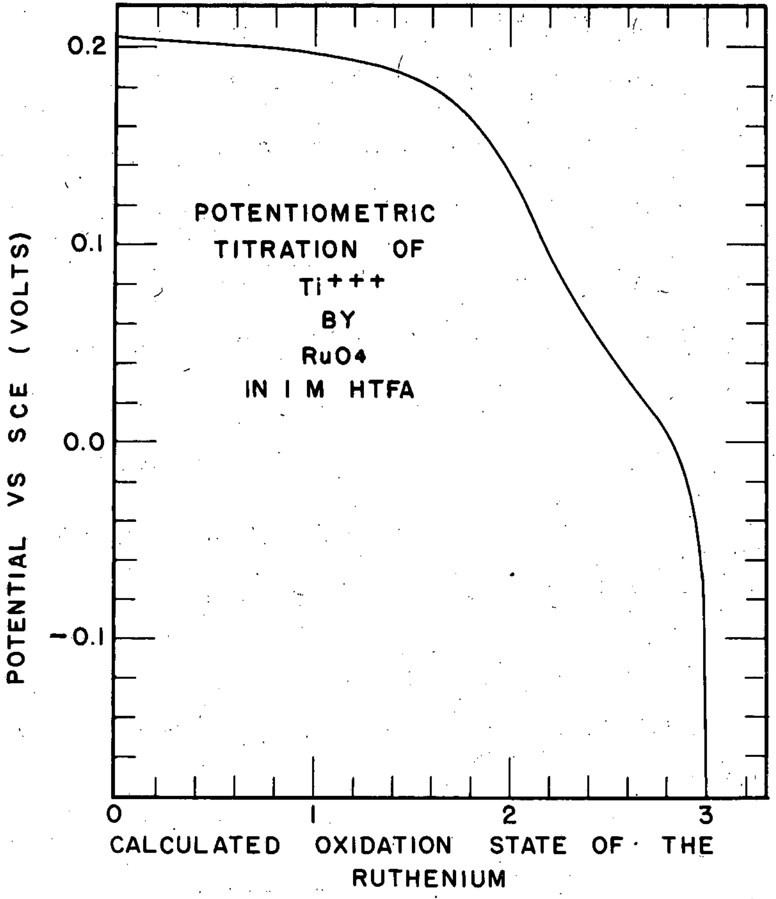

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Fig. 13. Potentrometric titration of Ti^{+3} by RuO_4 in 1M HTFA in the Ru(II) - Ru(III) region.

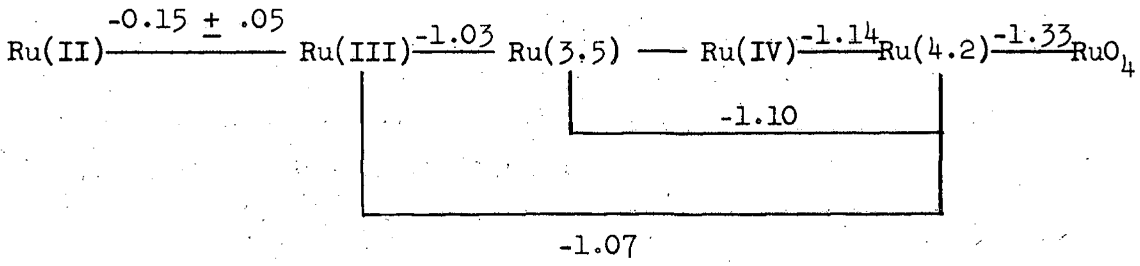
Ti^{+3} present. The potential and spectral data obtained during this titration conflicted with each other and indicated the presence of some unknown oxidizing agent, perhaps one of the earlier products of the perchlorate reduction. The potential chosen for the Ru(II)-Ru(III) couple in perchloric acid is -0.2 volt vs N.H.E.

A diagrammatic summary of the potentials obtained is shown in Table XI. The intermediate oxidation states shown do not necessarily exist, but it is felt that this interpretation fits the data somewhat better than one assuming several species of Ru(IV).

Table XI

Potentials of ruthenium in acidic solution*

1 M HTFA; S.C.E. + junction = -0.26



$$\mathrm{Ru(II)} \xrightarrow{-0.15 \pm .05} \mathrm{Ru(III)} \xrightarrow{-1.03} \mathrm{Ru(3.5)} \text{ — } \mathrm{Ru(IV)} \xrightarrow{-1.14} \mathrm{Ru(4.2)} \xrightarrow{-1.33} \mathrm{RuO_4}$$

1 M $HClO_4$; S.C.E. + junction = -0.24

$$\mathrm{Ru(II)} \xrightarrow{-0.2 \pm .1} \mathrm{Ru(III)} \xrightarrow{-0.99 \pm .07} \mathrm{Ru(IV)} \xrightarrow{-1.10} \mathrm{Ru(4.38)} \xrightarrow{-1.33} \mathrm{RuO_4}$$

*The estimated limits of error are ± 0.02 volt unless indicated otherwise.

These results are considered to agree with those obtained by Wehner and Hindman in the oxidation of Ru(III). They do not agree with those of Niedrach and Tevebaugh, however.

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