at low temperatures were unsuccessful. For example, finely divided plutonium metal was made by the decomposition of plutonium hydride and then slowly fluorinated to the tetrafluoride by reaction with fluorine. After exposure of this material for 25 minutes to PtF₆, no plutonium was found in the vapor phase.

The reaction at room temperature between PtF₆ and neptunium fluoride residues formed by the radiation decomposition of NpF₆ was quantitative. A short exposure of 100 mg. of PtF₆ vapor to a neptunium fluoride residue in a nickel can resulted in the complete disappearance of PtF₆ from the vapor phase with the formation of 67 mg. of NpF₆. NpF₆ is a very stable hexafluoride and does not dissociate into fluorine and a lower neptunium fluoride up to 560°.[31]

The ability of PtF₆ vapor to fluorinate materials at room temperature greatly limits the type of apparatus that this material can be handled in. After our early observation of the formation of NpF₆, all of the studies with PtF₆ were carried out in new systems that had not been used previously in other hexafluoride studies.

Finely divided plutonium metal prepared by the thermal decomposition of plutonium hydride was observed to react rapidly with PtF₆ vapor at room temperature. The solid was brought to red heat by the reaction, and a platinum mirror was deposited on the quartz reaction vessel. No plutonium was found in the excess PtF₆ vapor that was subsequently hydrolyzed and alpha counted. The high temperature of the reaction without the presence of a cold surface to quench any PuF₆ formed

(31) J. G. Malm, B. Weinstock and E. E. Weaver, *J. Phys. Chem.*, **62**, 1506 (1958).

probably was responsible for the failure to find plutonium in the remaining PtF₆ vapor.

Although PtF₆ is quite unstable, the rate of thermal decomposition into fluorine and a lower platinum fluoride is negligible at room temperature. Heating at 90° also produces little thermal decomposition. After 68 minutes at 145–165°, 62 mm. of PtF₆ was found to have decomposed slightly with the formation of 1 mm. of fluorine. After 47 minutes at 260–275°, 60 mm. of PtF₆ had decomposed to the composition 26 mm. of fluorine and 28 mm. of PtF₆. The rate of thermal decomposition of PtF₆ in this temperature range is quite similar to that which has been observed with PuF₆.[11]

The greater reactivity of PtF₆ compared to all the other hexafluorides is evident in its rapid reaction with Pyrex and quartz. It is possible to degas Pyrex and quartz equipment so that there is no reaction with other hexafluorides, including PuF₆. With PtF₆ a general attack on the glass is evident immediately. A similar uniqueness for PtF₆ is observed in the corrosion of nickel and Monel equipment. In spite of prior seasoning, exposure of apparatus to PtF₆ at room temperature results in substantial corrosive attack that continues for periods of time extending into weeks. Under comparable conditions where the order of 1 mg. of PuF₆ would be lost due to seasoning, several hundred milligrams of PtF₆ are lost.

The Chemistry of Ruthenium(IV). I.   Ruthenyl and the Nature of Ru(IV) in Perchloric Acid Solutions[1]

By Frank P. Gortsema[2] and J. W. Cobble

Information has been obtained on the nature of Ru(IV) in perchloric acid through solubility studies. The average charge on the aqueous species is 2. Extensive polymerization has been observed in these solutions and the monomer ruthenyl, RuO⁺⁺, has been identified and isolated as a constituent.

Introduction

Very little previous information has been published on the composition of Ru(IV) in non-complexing media. Wehner and Hindman[3] concluded from spectral and transference studies that Ru(IV) in perchloric acid was largely hydrolyzed, and Niedrach and Tevebaugh[4] proposed two separate species. None of these studies actually succeeded in isolation or identification of any proposed constituents.

(1) This research was supported by the E. I. du Pont de Nemours and Company and the Atomic Energy Commission under Subcontract AX-2271 of AT (07-2)-1.

(2) From the Ph.D. thesis of F. P. Gortsema, Purdue University, 1959.

(3) P. Wehner and J. C. Hindman. *J. Am. Chem. Soc.*, **72**, 3911 (1950).

(4) L. W. Niedrach and A. D. Tevebaugh, *ibid.*, **73**, 2835 (1951).

The purpose of this communication is to report the results of solubility and ion-exchange experiments which have fixed the average charge of Ru(IV) species in perchloric acid as +2 and have further identified ruthenyl, RuO⁺⁺, as a constituent of the system.

Experimental

Materials.—Ruthenium sulfate was prepared from Fisher ruthenium trichloride by treatment of an aqueous slurry of the latter with concentrated sulfuric acid. The resulting mixture was evaporated slowly to fuming and then to semi-dryness on a hotplate at 140–150°. More sulfuric acid was added and the process repeated until the product was chloride-free.[5] Too high a temperature will result in loss of ruthenium by volatilization as RuO₄.

(5) The presence of chloride was tested by means of the test proposed by Wehner and Hindman (reference 3). A few milliliters of ruthenium solution were treated with a strong oxidizing agent and the

Ruthenium tetroxide was prepared by oxidation of ruthenium sulfate with sodium bismuthate and 70% perchloric acid in an all glass distillation apparatus.[6] The RuO₄ vapor was dried by magnesium perchlorate and collected in a liquid nitrogen trap.[7]

Solutions of ruthenium(IV) perchlorate were prepared by the procedure of Yaffe and Voight[8] and Niedrach and Tevebaugh.[4] Pure RuO₄ is dissolved completely in perchloric acid solutions and reduced to the tetravalent state by addition of excess hydrogen peroxide. This reaction yields Ru(IV) in perchloric and nitric acid solutions, although under some conditions Ru(III) can be formed in sulfuric acid.[9] The excess peroxide is destroyed by catalytic decomposition.[10] Too high a Ru/H⁺ ratio will result in precipitation of hydrated ruthenium dioxide.

Solutions of Ru(IV) perchlorate were found to have a spectrum qualitatively similar to that previously reported by others,[3,11] although the quantitative aspects are complicated and will be the subject of a further communication.

Perchloric acid solutions were prepared by dilution of either G. F. Smith 70% doubly vacuum distilled acid or Baker's Analyzed Reagent 70–72% acid with distilled water. Cerous perchlorate solutions were prepared by dissolving G. F. Smith Chemical Company cerous perchlorate hydrate in 0.05 M HClO₄.

Either Mallinckrodt analytical grade 30% hydrogen peroxide was used which had a chloride ion concentration <0.001% or Baker Analyzed 30% (unstabilized), which had a chloride ion concentration <0.005%.

Dowex 50WX12 200–400 mesh resin was used in the ion exchange experiments; it was washed several times, first with 1 M HClO₄ and then with distilled water.

Apparatus.—A Beckman model DU instrument with photomultiplier attachment and thermostated (25.0 ± 0.2°) cell compartment was used for analytical spectrophotometry. Some spectra were obtained with a Cary model 10–11 or 14 recording spectrophotometer. Matched 1 cm. silica cells were used in both cases.

Analytical.—The ruthenium content of some of the solutions was standardized accurately by two independent methods: (a) by precipitation of the ruthenium as the dioxide with ammonium bicarbonate followed by reduction of the hydrate oxide so formed to the metal[12] by hydrogen at 700°, and (b) oxidation of the Ru(IV) solutions with an excess of periodic acid in Beckman stoppered absorption silica cells. The RuO₄ so formed was measured spectrophotometrically at 385 mμ, using an extinction coefficient of 930 as reported by Connick and Hurley.[7] Both methods gave good agreement (within ±1%).

Acidity measurements were carried out by two separate methods. Normal comparative pH values obtained on a Beckman Model G instrument with a glass and calomel electrode could be used for solutions in the approximate pH range of 2.0 to 2.8. For some as yet unexplained reason these or similar electrodes failed to respond correctly at lower pH values (<1.4).[13] In these cases a spectrophotometric method using thymol blue as a H⁺ indicator was used, making proper corrections for the interference by Ru(IV).

In theory the equilibrium [H⁺] also could be calculated from the conditions of the experiment and the solubility,

but the possibility of absorption of some acid on the flocculent precipitate had to be considered.

Cerous sulfate solutions were standardized by oxidation with peroxydisulfate[14] and titrating the ceric so formed with standard ferrous sulfate.

Experimental Procedure.—The solubility measurements were made in a series of 250 ml. three neck, round bottom flasks fitted with mercury seal stirrers and thermostated at 25 ± 0.05°. A predetermined amount of solid RuO₄ was added to 200 ml. of solution in the various flasks each at a different initial pH and allowed to dissolve and reach thermal equilibrium. At that time a four- to ten-fold excess of 30% H₂O₂ was added slowly by means of a syringe over a period of 20 to 80 minutes. The solutions were stirred for approximately 12 hr. before attempting to make any analytical determinations.

Since the RuO₄ is dispersed homogeneously in the aqueous media, it seems reasonable (but not necessary) to assume that the approach to solid RuO₂ is by means of a soluble Ru(IV) species. When the system becomes saturated with respect to this species, RuO₂ precipitates. This method of approaching equilibrium from the supersaturated side has been used successfully before.[15]

Small aliquots of solution were withdrawn by a syringe from the flask from time to time through one of the openings and filtered once or twice through an "ultra-fine" sintered glass filtering crucible.

After the filtrate was allowed to come to room temperature, a known amount was transferred into a volumetric flask and diluted with 0.1 M HClO₄ to give a conveniently measurable optical density. Previous trials had demonstrated that this increase in acid concentration in the Ru(IV) concentration range studied did not significantly affect the quantitative aspects of the absorption curve.

The filtrate resembled a "true" solution in every ordinary sense of the word. It demonstrated, for example, only a very weak Tyndall effect similar to that obtained with filtered water when tested with a Brice–Phoenix light scattering apparatus. The spectra of these solutions were quantitatively reproducible and gave no evidence of spurious scattering indicative of suspended material. Furthermore, there has been no evidence to indicate settling out of any precipitates in some of the solutions which were stored for many months. It was therefore concluded that any ruthenium in solution is present as a true solution, although the possibility of ionic and molecular polymerization was not excluded.

Unfortunately the undersaturation approach to equilibrium could not be used with any great degree of success. In a few cases which were studied in the higher pH range, approach to equilibrium could be inferred from data taken over many weeks in the same apparatus. In these trials, RuO₂ was prepared by reduction of RuO₄ with H₂O₂, thoroughly washed and placed in stirred thermostated flasks containing the desired [H⁺] concentrations for sampling. However, in general, the rate of approach to equilibrium from undersaturation was too slow to be of any practical use, except for the most dilute solutions.

In this respect, the following observations are noted to suggest that the supersaturation approach yielded data which were indicative of equilibrium concentrations: (1) the constancy of absorbancy readings for 10–20 days; (2) the demonstration that the solubility at any given pH was independent of the degree of supersaturation created by varying the initial amounts of RuO₄ used to generate Ru(IV); (3) dilution or partial neutralization with small amounts of concentrated NH₄OH immediately formed a precipitate after which the solution would approach a new equilibrium value consistent with the new pH of the system, and (4) addition of more H₂O₂ only changed the equilibrium solubility proportional to its diluent effect. Representative solubility-time curves are given in Fig. 1 in which some of these effects are illustrated.

The following further observations are of interest: Traces of chloride ion (from impure RuO₄ or HClO₄) will cause erratic and very much higher solubilities than those obtained from otherwise pure Ru(IV) perchlorate solutions; however,

ruthenium removed as RuO₄ by heating. 1 M AgNO₃ solution was added to the resulting solution; a precipitate of AgCl indicates a [Cl⁻] ≥ 10⁻⁴ M.

(6) D. D. Deford, Ph.D. thesis, University of Kansas, 1948, pp. 145–146.

(7) R. E. Connick and C. R. Hurley, *J. Am. Chem. Soc.*, **74**, 5012 (1952). We agree with these authors on the stability of RuO₄ and its solutions in *very clean* glassware. However, we have had exceptionally violent and potentially dangerous explosions with gram quantities of RuO₄ from apparently insignificant traces of catalytic impurities, particularly RuO₂.

(8) R. P. Yaffe and A. F. Voight, *ibid.*, **74**, 2500 (1952).

(9) A. S. Wilson, *J. Inorg. Nuclear Chem.*, **7**, 149 (1958).

(10) A. S. Wilson, private communication.

(11) M. Kilpatrick, M. L. Kilpatrick, R. C. Vogel and E. H. Kobisk, Atomic Energy Commission Unclassified Report AECU-652 (1949).

(12) R. Gilchrist and E. Wichers, *J. Am. Chem. Soc.*, **57**, 2565 (1935).

(13) This may have been due to a poisoning effect on the glass electrode surface.

(14) N. H. Furman, Editor, "Scott's Standard Methods of Chemical Analysis," Vol. I, 5th Ed., D. Van Nostrand Company, Inc., New York, N. Y., 1939, p. 253.

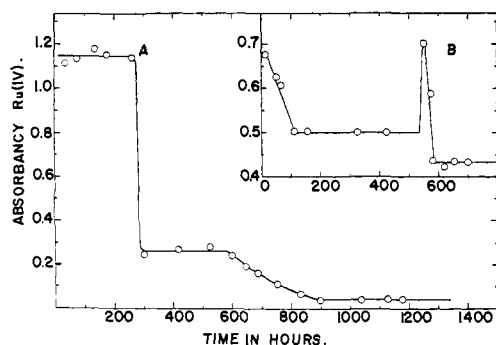(15) M. J. LaSalle and J. W. Cobble, *J. Phys. Chem.*, **59**, 519 (1955).

Fig. 1.—The behavior of typical Ru(IV) solutions upon changing equilibrium conditions. In curve A further 30% H_2O_2 was added to the solution initially at equilibrium, at 300 hr. The drop in concentration is that expected for the new and lower [H$^+$]. At 550 hr. this procedure was repeated, eventually reaching a third equilibrium concentration at approximately 900 hr. In curve B the attainment of equilibrium from the initial *in situ* synthesis of another Ru(IV) solution is indicated to be complete in approximately 100 hr. At 550 hr. more RuO_4 and 30% H_2O_2 was added which resulted in temporary supersaturation of the solution with respect to Ru(IV) but which eventually reached an equilibrium concentration lower than the original as a result of a decrease in the [H$^+$] accompanying the addition of reagents. Analyses were performed on a model DU Beckman spectrophotometer at 487 mμ.

there was no evidence of reduction of the $HClO_4$ solution below approximately 1 M acid in agreement with previously reported observations.[3] Those RuO_4 solutions to which the H_2O_2 was added over a period of an hour gave much more accurate and reproducible results than when the peroxide was added at one time.

Results and Discussion

A. **Solubility Data.**—The solubility results which were obtained from some 15 runs in perchloric acid are illustrated in Fig. 2. No data were omitted except those in which (1) it could be later demonstrated that insufficient RuO_4 to produce saturation had been used, (2) accidental causes or (3) undersaturation data as previously discussed. The results cannot be considered precise. This difficulty is due largely to the almost ceramic-like nature of RuO_2; such behavior has been evidenced in equilibrium data on this material reported by others.[7] A least squares treatment of the data for perchloric acid indicates a slope of 1.94 in the pH range from 0.8 to 2.7. Therefore the perchloric acid solubility experiments of hydrated RuO_2[16] indicate that the solubility behavior is best described by an equation of the type

RuO_2(hydrated) $+ 2H^+ =$
$$[Ru(IV)]^{++} + H_2O(\text{unbalanced}) \quad (1)$$
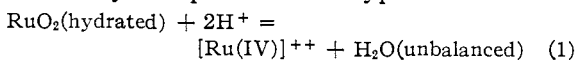
with

$$K_1 = \frac{[Ru(IV)]}{[H^+]^2} = 5.9 \pm 1.1$$

That is, the charge on the species in solution must be $+2$. However, a small percentage of a second

(16) Analysis of solid RuO_2 precipitates similar to the ones obtained in these solubility experiments indicate a hydrate of the form $RuO_2 \cdot 2$-H_2O, or $Ru(OH)_4$. The actual hydrates form of the precipitate does not affect these conclusions (as long as it does not change with pH) as summarized by equation 1. $RuO_2 \cdot 2H_2O$ or a similar hydrate was also the equilibrium species in some basic solutions (reference 7).

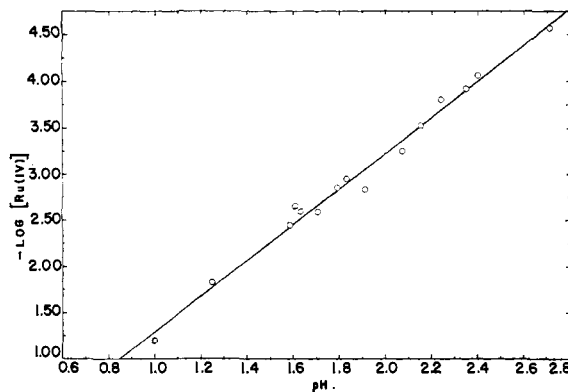Fig. 2.—The solubility of hydrated RuO_2 in perchloric acid, temperature 25°, $\mu = 0.1$.

or even other hydrolyzed species is not definitely excluded, and indeed in this respect these results may be considered to be consistent with the qualitative observations of previous authors.[3,4]

B. **Polymerization.**—In order to test for the possible presence of polymerization, a perchloric acid solution of Ru(IV) was subjected to ultracentrifugation at 59,780 r.p.m. in a Spinco Model E ultracentrifuge. Preliminary results indicated that Ru(IV) in $HClO_4$ was polymerized extensively.

C. **The Existence of Ruthenyl.**—During preliminary ion-exchange experiments with Ru(IV) solutions obtained either from, or similar to, those of the solubility studies, some fractionation of the solutions was obtained. Since the charge on each Ru(IV) unit was $+2$, it appeared possible that the charge density per Ru(IV) species could decrease with increasing polymerization. Thus in many preparations some of the Ru(IV) would not be absorbed by Dowex resin at all; some of the ruthenium that adsorbed could be displaced very slowly by 0.3 M cerous perchlorate or concentrated $HClO_4$ while some of the adsorbed Ru(IV) could only be removed by treatment with 12 M hydrochloric acid.

It was hoped that by successive equilibrations of the displaceable component of these Ru(IV) solutions, one could isolate a species rich in monomeric Ru(IV). The solubility experiments suggested that if this were an appreciable fraction of the Ru-(IV), it would have to have a $+2$ charge.

Therefore quantitative ion exchange experiments similar to those reported previously on other systems by Everest and Salmon[17] and Cady and Connick[18] were employed. If certain physical constants of the resin are known, it is possible to determine the charge per metal atom and charge per species being eluted from ion exchange resin. The ratio of the second to the first gives the degree of polymerization of the species.

1. **The Charge per Ruthenium Atom.**—The determination of the charge per ruthenium atom is based upon the fact that an ion exchange resin has a fixed exchange capacity measured in equivalents of charge per gram. The charge, a, on a metal atom is found by determining the number of equivalents of charge displaced from the resin

(17) D. A. Everest and J. E. Salmon, *J. Chem. Soc.*, 1444 (1955).
(18) H. H. Cady and R. E. Connick, *J. Am. Chem. Soc.*, **80**, 2646 (1958).

divided by the number of gram atoms of metal atom taken up by the resin after exchange occurs. For the particular case of Ru(IV) using a cerous perchlorate elutriant, the reaction is given by

$$Ru_R^{+n} + Ce_S^{+3} = Ru_S^{+n} + Ce_R^{+3} \quad (2)$$

where R and S refer to the species in the resin or solution phase, respectively. If other ions are present, such as H^+, then separate equations must be written to include all of these species. Therefore, in this system the charge per ruthenium atom can be determined as long as the hydrogen ion and ruthenium concentrations are determined, even if the degree of hydrolysis or extent of polymerization of the ruthenium species should change between the aqueous and resin phases.[19]

The charge per ruthenium atom was determined with a "batch" rather than a column technique as used by Cady and Connick,[18] since the rate of movement in a column of the displaceable Ru(IV) species was too slow to be practical. All ion exchange measurements reported here are concerned only with the species eluted with 0.3 M cerous perchlorate. The batch technique suffers from the fact that it is not possible to demonstrate directly that the system under study contains a *single* Ru(IV) species. However, if it can be shown that successive equilibrations with fresh cerous perchlorate solutions always have the same charge per ruthenium atom, then this can be considered evidence to support the presence of only one exchangeable species in the system. The charge per ruthenium atom is calculated from the expression

$$a = \frac{[Ce^{+3}]_i + [H^+]_i - [Ce^{+3}]_f - [H^+]_f}{[Ru(IV)]} \quad (3)$$

where i and f denote the elutriant and eluent, respectively, and a is the charge per ruthenium atom,

The experimental results for four separate determinations of the charge per ruthenium atom are given in Table I. These data demonstrate that it was possible to isolate from a ruthenium(IV) perchlorate solution a species having a charge of +2 per ruthenium atom.

TABLE I

DETERMINATION OF THE CHARGE PER RUTHENIUM ATOM FOR A SPECIES IN Ru(IV) PERCHLORATE SOLUTIONS

Elution no.[a]	Elutriant composition, M [Ce^{+3}]	[H$^+$]	Eluent composition [Ce^{+3}]	M [H$^+$]	[Ru(IV)]	Charge per Ru atom
1A	0.3155	0.0316	0.0846	0.388	0.183	1.85
1B	.3098	.0547	.2189	.0738	.127	2.00
2A	.3098	.0510	.0590	.298	.256	1.97
2B	.3098	.0510	.1801	.0523	.201	1.93

Av. 1.95 ± 0.05

[a] Indicating two separate runs, with two successive equilibrations from the same resin–Ru(IV) system.

2. The Charge per Ruthenium Species.

In order to determine the charge per species, an aqueous ruthenium(IV) perchlorate solution of the same type as above was allowed to equilibrate with a known amount of ion exchange resin in the hydrogen ion form. The reaction then can be represented as
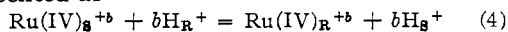
$$Ru(IV)_S^{+b} + bH_R^+ = Ru(IV)_R^{+b} + bH_S^+ \quad (4)$$

where S and R subscripts represent the solution and resin phase, respectively. The equilibrium constant for the reaction is given by

$$K = \frac{(Ru(IV)_R^{+b})(H_S^+)^b}{(Ru(IV)_S^{+b})(H_R^+)^b} \cdot \frac{\gamma Ru_R \cdot \gamma H_S^{+b}}{\gamma Ru_S \cdot \gamma H_R^{+b}} \quad (5)$$

where $(Ru(IV)_S^{+b})$ and (H_R^+) represent the concentrations of Ru(IV) and H^+ in moles per liter in the solution phase; $(Ru(IV)_R)$ and (H_R^+) represent the concentration of Ru(IV) and H^+ in moles per 1000 grams of air dried resin; γRu_R and γRu represent the activity coefficient corrections for the Ru(IV) ion in the resin and solution phase, respectively. To determine b, the ruthenium species must be equilibrated at two different acid concentrations, and the concentrations of all the ions in the resin and aqueous phase must be determined.

In order to solve the expression exactly, it would be necessary to know the activity coefficients for the various species in the aqueous and resin phases. However, there is at the present time no satisfactory method for determining the activity coefficients of ions in the resin phase. Therefore the conditions for the experiment must be fixed so that the composition of the resin phase remains as constant as possible during the equilibration. This is accomplished by having a large excess of resin capacity with respect to the ruthenium species and by arranging the concentrations of the various species in solution so that most of the Ru(IV) is absorbed on to the resin.

For the special case involving two exchanging ions, the determination of the concentrations of the various ions is made considerably easier by first determining the capacity of the air dried resin in milliequivalents per gram (C). To determine b, the quantities that must be measured are: the total amount of Ru(IV) present, Σ Ru(IV); the initial hydrogen ion concentration $(H_S^+)_i$; the total volume of solution in milliliters, V; the weight of air dried resin, W; the concentration of Ru(IV) in gram atoms/liter after each equilibration, Ru(IV). The concentrations of each of the species can then be calculated using the expression given by Cady.[20]

For these experiments, Ru(IV) perchlorate solutions were prepared by using solutions similar to those which had been used to determine the charge per ruthenium atom. Further, the solutions were initially equilibrated with resin and the Ru(IV) then displaced with H^+ to insure that the Ru(IV) used in the charge per species experiments was identical with that just previously characterized as having a +2 charge per ruthenium atom.

The experimental results for the charge per species are given in Table II. These results are consistent with a charge of +2 per ruthenium species. Because of the possibility of adsorption of excess $HClO_4$ into the resin at the higher acid concentrations, the value +2 is probably a lower limit. However, the error so involved is not considered large enough to effect the conclusion.

Since the results of the charge per ruthenium atom and charge per species experiments are the same and must be related to each other by an inte-

(19) Apparently ruthenium polymers are present in the resin phase largely as monomeric species: D. K. Atwood and T. D. De Vries, J. Am. Chem. Soc., 83, 1509 (1961).

(20) H. H. Cady, Ph.D. Thesis, University of California, Berkeley, 1957, p. 28.

ger, a monomeric form of Ru(IV) probably exists in appreciable concentrations in perchloric acid solutions. The most logical formula for such a species is simply ruthenyl, RuO^{++} (or one of its hydrates). It also appears that the ion exchange technique outlined is a good method for concentrating and preparing ruthenyl.

TABLE II

DETERMINATION OF THE CHARGE PER SPECIES FOR RUTHENIUM(IV) PERCHLORATE SOLUTIONS

Ru(IV)$^{+b}$. mg. atom	Initial H$_3$$^+$ (M)	V, ml.	W, g.	Capacity of resin, meq.	Ru(IV)$^{+b}$, g. atom/l.	b
0.0178	1.78	20	0.2047	0.745	2.20×10^{-4}	2.1
.0167	0.763	35	.2047	.745	3.12×10^{-5}	
.0178	1.78	20	.2076	.756	1.60×10^{-4}	2.2
.0170	0.763	35	.2076	.756	1.94×10^{-5}	

Although there was no reason for doubt, it was of interest to prove conclusively that ruthenyl was in the +4 oxidation state. Several ruthenyl solutions were eluted from ion exchange resin for this determination. The normality of the solution was determined by a ceric oxidation potentiometric titration procedure, wherein excess standardized ceric sulfate reacts with ruthenyl; the RuO_4 so formed is volatilized by boiling and the excess ceric titrated potentiometrically with standard ferrous sulfate. The molarity of the solution was determined using the periodic acid oxidation–spectrophotometric method for RuO_4[7] (see Experimental). The results for 4 determinations are given in Table III

TABLE III

EXPERIMENTAL PROOF OF THE OXIDATION STATE OF Ru(IV) SOLUTIONS ELUTED FROM DOWEX 50W × 12 ION EXCHANGE RESIN

Eq./liter	M	Oxidation state	ϵ_{487} mμ
0.3753	0.0939	4.00	706
1.362	.337	3.96	713
1.182	.295	3.99	710
0.0858	.0220	4.11	707
Av.		4.02 ± 0.05	709 ± 3

along with the values obtained for the molar extinction coefficients of the solutions measured at 487 mμ. The ceric oxidation of ruthenium(IV) poly-
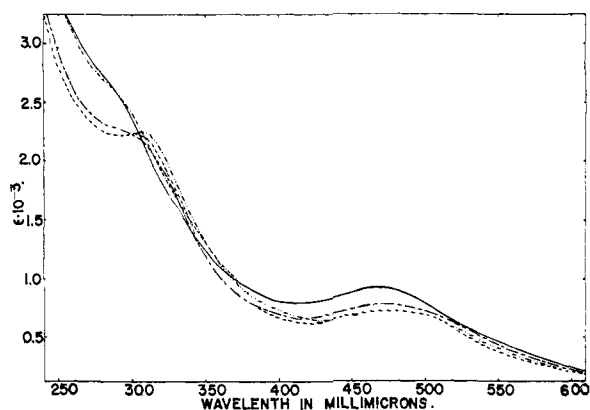

Fig. 3.—The effect of the perchloric acid concentration on the absorption spectrum of ruthenium(IV) perchlorate: ——, 12 M HClO$_4$; ————, 9 M HClO$_4$; ————, 5 M HClO$_4$; ————, 1 M HClO$_4$; ————, 0.1 M HClO$_4$. All spectra taken on freshly prepared solutions with a Cary 14 recording spectrophotometer using 1 cm. cells.

meric solutions is complex, and a preliminary discussion of this reaction already has been published.[21]

D. The Spectra of Ruthenyl Solutions.—Measurements of the effect of hydrogen ion and ionic strength upon Ru(IV) absorption spectra had been carried out previously by Wehner and Hindman[3] who did not have monomeric Ru(IV) solutions. The present study was carried out to repeat the former work, using a pure ruthenyl perchlorate solution prepared by elution from ion exchange resin, and the results at various [H$^+$] are summarized in Fig. 3. It can be seen that the ruthenyl spectra in acid concentrations below 1M are practically identical but that in higher acid concentrations significant changes occur. It is interesting to note that the wave length at which the peak maximum in the visible occurs remains constant in perchloric acid concentrations up to approximately 1M and becomes constant again from 9 to 12 M. This is consistent with an extremely stable oxygenated species, RuO^{++}, which does not lose oxygen or protonate except at very high acid concentrations. Thus ruthenyl is similar in this respect to certain other oxycations such as VO^{++}, VO_2^+, UO_2^{++}, etc. Although the data do not prove it either way, we believe protonation rather than a change into Ru^{+4} is more likely at the highest acid strengths.

(21) F. P. Gortsema and J. W. Cobble, J. Am. Chem. Soc., 81, 5516 (1959).