[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF THE ARGONNE NATIONAL LABORATORY]

The Lower Oxidation States of Ruthenium[1] in Acid Perchlorate Solutions

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Although the chemistry of ruthenium has been explored for some one hundred years, very little is as yet known either about the actual ionic species of the element present in such common complexing media as hydrochloric, nitric and sulfuric acids or about the thermodynamic stabilities, absorption spectra, reaction kinetics and other properties of those species.

In an effort to acquire such information this Laboratory has undertaken an investigation of the solution chemistry of ruthenium. The initial step of this investigation has been concerned with solutions in aqueous perchloric acid, a relatively non-complexing medium. We were unable to find any record in the literature of previous studies of the chemistry of ruthenium in this medium.

It has been found that Ru(IV) and Ru(III) are the only lower oxidation states of ruthenium readily prepared in acid perchlorate solutions. No definite evidence has been obtained for the existence in such solutions of states between Ru(IV) and Ru(VIII) (ruthenium tetroxide). No state lower than Ru(III) has been detected at oxidation–reduction potentials more negative than −0.1 volt.

The preparation of pure solutions of Ru(IV) and Ru(III) in perchloric acid proved to be a problem of considerable difficulty because of the tendency of the ruthenium to form colloidal suspensions and because of the ease with which ruthenium in these states reduces perchloric acid to chloride ion. This paper describes satisfactory electrolytic methods of preparing these lower states and presents preliminary information on their absorption spectra and stabilities. Solutions containing these oxidation states appear to be quite complex and as yet the actual ionic species present have not been identified.

Experimental

Apparatus.—All absorption spectra were measured on a Cary Recording Spectrophotometer, Model 12, Series 8, marketed by the Applied Physics Corporation of Pasadena, California. The wave length scale of this instrument was carefully calibrated against the emission spectra from hydrogen, mercury and neon discharge tubes. Ru(III) solutions were thermostated at 5 to 7° during measurement and the other solutions at 25 ± 0.5°. All samples were contained in quartz absorption cells.

Figure 1 shows the circuit of the continuous-control type potentiostat used to control the electrode potentials during the electrolyses. The instrument described here incorporates a number of desirable features lacking in one or more of such devices previously reported in the literature.[2,3,4] The circuit shown is of high sensitivity and will correct continuously and rapidly any unbalance, positive or negative, between the cathode (or anode) and the reference potential. The unbalance voltage between the reference electrode, E, potentiometer circuit and the cathode (or anode) is developed across the 10-ohm resistor, R_6, and amplified by a Brown amplifier, A. The output voltage of the amplifier actuates motor M, which in turn drives the center tap of the 25-ohm, 100-watt bridge potentiometer, R_2, until the d. c. voltage applied between anode and cathode is such as to reduce the unbalance signal across R_6 to zero. The intrinsic sensitivity of the control circuit is two microvolts across the resistance R_6. Since there is a total resistance of around 1000 ohms in the electrode–reference half cell–potentiometer circuit, the instrument will respond to an unbalance of approximately 0.2 millivolt between the electrode and the reference potential.

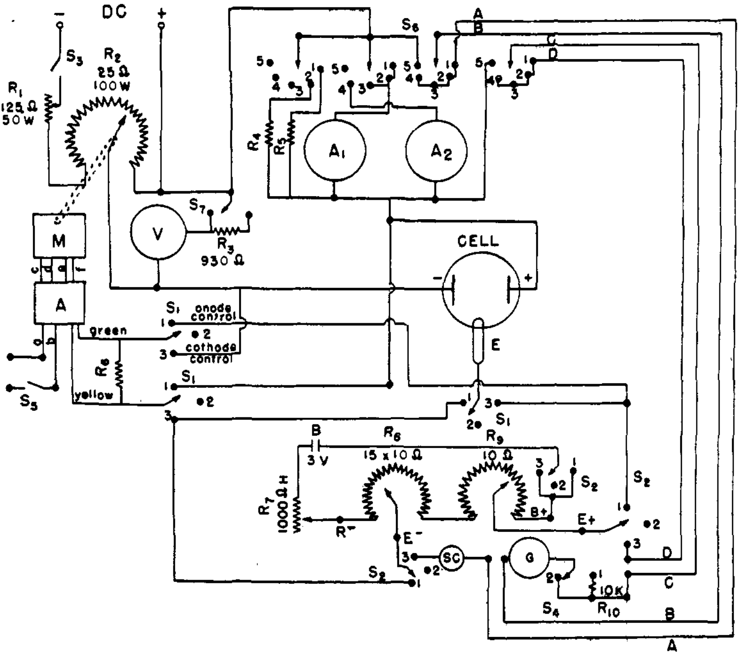

Fig. 1.—Potentiostat circuit.

The Pyrex glass electrolysis cells are shown in Figs. 2 and 3. The compartments of the Fig. 2 cell had capacities of 70 ml. and were separated by a 20-mm. "fine" sintered glass disk. The platinum electrodes consisted of 10-turn coils of 92 mil platinum wire having calculated surface areas of 60 sq. cm. The compartments of the Fig. 3 cell had capacities of 10 ml. and were separated by 10

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[1] Presented in part before the Physical-Inorganic Division of the American Chemical Society at the Atlantic City Meeting in September 1949.

[2] A. Hickling, *Trans. Faraday Soc.*, **38**, 27 (1942).

[3] Caldwell, Parker and H. Diehl, *Ind. Eng. Chem., Anal. Ed.*, **16**, 552 (1944).

[4] J. J. Lingane, *ibid.*, **17**, 332 (1945).

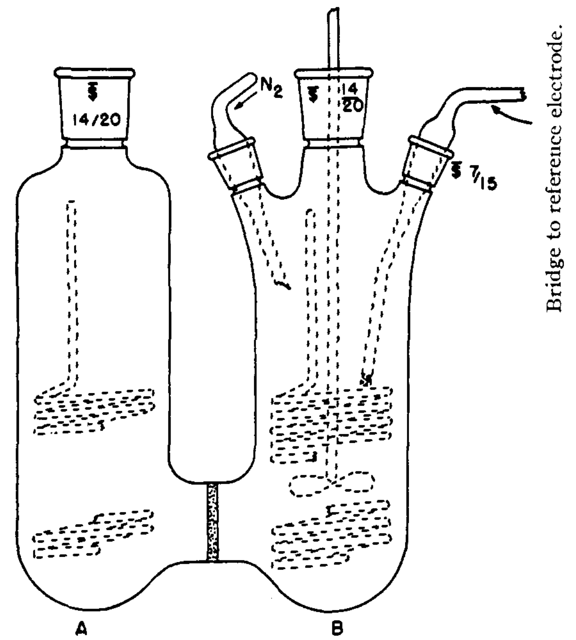

Fig. 2.—Cell for electrolysis of 50 to 60-ml. samples.

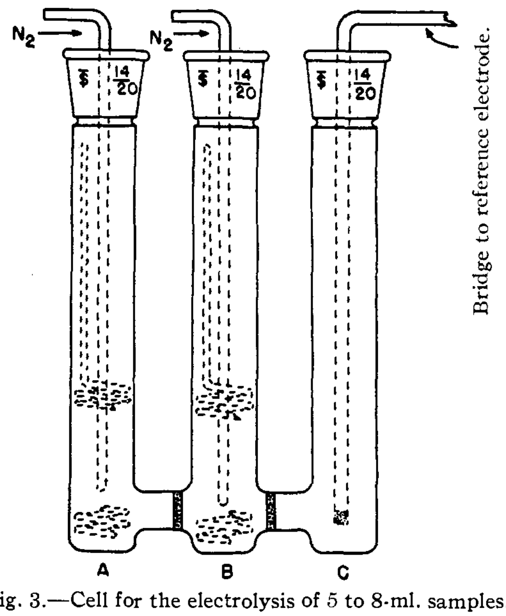

Fig. 3.—Cell for the electrolysis of 5 to 8-ml. samples.

mm. "fine" sintered glass disks. The electrodes were 15-turn coils of 51 mil platinum wire having calculated surface areas of 20 sq. cm. The bridges connecting the catholyte or anolyte with the reference electrode were of the type described by Laitinen[5]; when filled with 1 *M* acid they averaged about 1300 ohms in resistance and when filled with 6 *M* acid, about 800 ohms.

Cathode or anode potentials were established by means of the reference electrodes listed in Table I. For the electrolysis of samples dissolved in 9 *M* perchloric acid the working electrode potentials were based on the 6 *M* acid reference electrodes. The listed potential values were assigned to these electrodes after consideration of the published data[6,7] for the cerous–ceric couple at high ionic strengths and after intercomparison of the electrodes of the same acid molarity. Included in the assigned values are some unknown junction potentials which probably account for the departure of the saturated calomel values from the usually accepted value. Electrode potentials based on these reference half-cells are considered accurate to only ±0.05 volt.

TABLE I

REFERENCE ELECTRODES

No.	Electrode	*E*, volts
1	Pt, $Ce(III)_{0.1M}$, $Ce(IV)_{0.1M}$ in 1 *M* $HClO_4$	−1.68
2	Pt, $Ce(III)_{0.1M}$, $Ce(IV)_{0.1M}$ in 6 *M* $HClO_4$	−1.81
3	Hg_0, $Hg_2{}^{++}{}_{0.1M}$ in 1 *M* $HClO_4$	−0.80
4	Hg_0, $Hg_2{}^{++}{}_{0.1M}$ in 6 *M* $HClO_4$	−0.75
5	S. C. E. (plus satd. NH_4Cl-1 *M* $HClO_4$ junction)	−0.29
6	S. C. E. (plus satd. NH_4Cl-6 *M* $HClO_4$ junction)	−0.28

Valence changes in the electrolytic preparations were determined by means of a gas coulometer of the type described by Lingane.[8]

Analytical Methods.—Solutions of the lower oxidation states of ruthenium were analyzed for total ruthenium content by oxidizing the ruthenium to the tetroxide and determining the tetroxide concentration from the optical density at 385 mμ. The oxidation was accomplished by treatment of a 10-ml. aliquot in 1 *M* perchloric acid with 50 to 100 mg. of ammonium peroxydisulfate (plus a trace of silver sulfate) at 80–90° for 10–15 minutes. A calibration curve, necessary because ruthenium tetroxide in 1 *M* perchloric acid does not strictly obey Beer's law, was obtained from optical measurements on standard solutions, believed to be accurate to 0.4 to 0.5%, prepared by dissolving weighed amounts of tetroxide in perchloric acid. The method of analysis was checked on samples of the standard solutions that had been reduced with mercury and gave results showing an average deviation of approximately 2% from the standard values.

The average oxidation number in solutions of oxidation state higher than Ru(III) was determined by an iodometric method. Previous investigators[9] established, within an accuracy of 1 to 2%, that in hydrochloric acid solutions excess iodide ion reduced ruthenium tetroxide to Ru(III). Our experiments using the standard solutions of tetroxide in perchloric acid showed that the oxidation state change of the ruthenium varied with the iodide and perchloric acid concentrations of the reduction solution (Table II). Since, however, over a narrow range of iodide and acid concentrations the tetroxide gave a reproducible valence change of 5.00 ± 0.02, it is be-

TABLE II

CHANGE IN OXIDATION STATE OF RUTHENIUM IN THE IODOMETRIC TITRATION OF RUTHENIUM TETROXIDE IN PERCHLORIC ACID

[KI], g./100 ml.	[$HClO_4$] moles/liter 0.1	0.6	1
0.5			5.020 ± 0.002[a]
0.7			5.069
1	4.896 ± 0.006[a]	5.022 ± 0.011[a]	5.133 ± 0.012[a]
2		5.082 ± 0.004[a]	

[a] Average values of duplicate or triplicate determinations.

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(5) H. A. Laitinen, *Ind. Eng. Chem., Anal. Ed.*, **13**, 393 (1941).

(6) G. F. Smith and C. A. Getz, *ibid.*, **10**, 191 (1938).

(7) M. S. Sherrill, C. B. King and R. C. Spooner, THIS JOURNAL, **65**, 170 (1943).

(8) J. J. Lingane, *ibid.*, **67**, 1916 (1945).

(9) See, for example, W. R. Crowell and D. M. Yost, *ibid.*, **50**, 374 (1928).

lieved that analyses of states such as Ru(IV) under similar conditions are accurate to ±2%. In the final selected procedure for the iodometric titrations a 0.5 to 2-ml. sample of the ruthenium solution (0.03 to 0.3 *M* in ruthenium) was added to 45–50 ml. of perchloric acid containing 0.5 to 0.6 g. of potassium iodide and 0.5 g. of sodium chloride, and the liberated iodine was titrated potentiometrically under nitrogen with 0.01 *N* thiosulfate. The final acid concentration was 0.5–0.6 molar.

Coulometric measurements during the electrolyses provided an additional means of identifying the lower ruthenium oxidation states. Coulometer readings at the end-points of the electrolyses of Ru(IV) were within 2 to 3% of the theoretical values for reduction to Ru(III) calculated on the basis of the total ruthenium and iodometric analyses for the Ru(IV) state. Measurements during small scale reductions of tetroxide to Ru(IV) in 9 *M* perchloric acid showed that completion of the reduction at a potential of −1.11 v. did correspond, within 1 to 2%, to reduction to Ru(IV), as was shown also by the iodometric method (*cf.* preparation of Ru(IV)). Coulometric analyses based on the oxidation of Ru(IV) and Ru(III) at controlled anode potentials were however usually not feasible (see Discussion). Only in the case of the Ru(III) solutions in 1 *M* perchloric acid that had reached the "equilibrium" state at 0° was the anodic oxidation smooth enough to give reliable coulometric measurements.

Chloride ion, either free or coördinated, was detected in the intensely colored ruthenium solutions in the following manner: to a few ml. of solution were added 1 drop of 1 *M* silver nitrate and just sufficient ceric perchlorate (G. Frederick Smith 0.5 *M* "perchlorato ceric acid" in 6 *M* perchloric acid) to oxidize the ruthenium to the tetroxide. The resulting yellow solution had a distinct turbidity if the concentration of chloride ion was 0.0001 *M* or higher.

Materials.—The perchloric acid solutions were prepared by dilution of either G. Frederick Smith 72% doubly vacuum distilled acid or Merck reagent grade 72% acid.

The source of ruthenium was a solid chloride (37% ruthenium) obtained from the J. Bishop and Company Platinum Works. Spectrographic analysis indicated that the only impurities were manganese (0.01%) and calcium (0.01%).

A chloride-free ruthenium sulfate solution was prepared from the solid chloride by twice precipitating ruthenium hydroxide, washing the hydroxide with 1% sodium sulfate until the washings were chloride-free, and dissolving in hot 25% sulfuric acid. The sulfate solution was then baked under an infrared lamp for 8–12 hours (after the appearance of sulfur trioxide fumes) to ensure removal of traces of chloride ion and osmium after which it was diluted to give a 30 to 50% sulfuric acid solution approximately 0.2 *M* in ruthenium.

Ruthenium tetroxide was prepared by oxidizing an aliquot of the sulfate solution with a two- or threefold excess of sodium peroxydisulfate and a trace of silver sulfate at 70 to 80°. A slow stream of nitrogen carried the tetroxide through a drying tower filled with magnesium perchlorate and into a cold U-trap. The sodium peroxydisulfate was generally added in two or three portions during the course of the distillation.

Preparation of Ru(IV) in 6 *M* Perchloric Acid.—Solutions of Ru(IV) were prepared by the electrolytic reduction of approximately 1.0-g. batches of tetroxide dissolved in 50 ml. of 9 *M* perchloric acid. During the electrolysis a rapid stream of nitrogen was passed through the anolyte and a very slow stream through the catholyte. The reduction was carried out at a cathode potential of −1.11 v. (*vs.* N. H. E.; initial current about 400 ma.) until 85–90% complete, at which point the cell was disconnected and the catholyte diluted with sufficient water to reduce the acid concentration to 6 *M*. (Since it was not convenient to include a coulometer in the circuit in such large scale electrolyses, the point of 85–90% completion was established either by estimation from current–time data or by reducing the cathode potential momentarily to −1.31 v. and noting the current. At 90% completion less than 100 ma. should flow at this potential.) The solution in 6 *M* acid was stored overnight at room temperature, and the electrolysis was then continued at 0° at the cathode potential of −1.11 v. until the current dropped to 1 to 2 ma. Analysis by the total ruthenium and iodometric methods showed that the catholyte was a solution of Ru(IV), approximately 0.08 *M* in ruthenium.

Solutions as strong as 0.3 *M* Ru(IV) were prepared by reducing successive portions of tetroxide, each batch being reduced to 85–90% completion before the next was added. This procedure was necessitated by the limited solubility of ruthenium tetroxide in 9 *M* perchloric acid.

Preparation of Ru(III).—Solutions of Ru(III) were prepared by the reduction (in the cell of Fig. 3) of 0.05 to 0.3 *M* solutions of Ru(IV) in 1 or 6 *M* perchloric acid. Reductions in 1 *M* acid were carried out at 0 to −5°, those in 6 *M* acid at −5 to −10°; prepurified nitrogen was bubbled through both anolyte and catholyte. During electrolyses the cathode potential was continually adjusted to maintain currents of 10 to 20 ma. (initial cathode potential about −0.9 v.). However, at about 80% reduction it became impossible to maintain such currents even though the potential was reduced to −0.1 v. Therefore the electrolyses were completed at −0.3 to −0.4 v. In 1 *M* acid the currents eventually fell to 0.1 to 0.2 ma. and in 6 *M* acid to 1 to 2 ma., and further reduction of the cathode potential to −0.1 v. failed to increase them appreciably. The inability to reach lower residual currents in 6 *M* perchloric acid appeared to be due to a slow reoxidation of the Ru(III) by the acid.

Estimation of Oxidation–Reduction Potentials.—Electrolyses involving the couples $\text{Ru(IV)} \rightarrow \text{RuO}_4 + 4\,e^-$ and $\text{Ru(III)} \rightarrow \text{Ru(IV)} + e^-$ were interrupted at various stages and the cathode or anode potential adjusted until current ceased to flow (as indicated on a 0–100 micro ammeter). The electrode potential and coulometer reading at each such balance point gave the e. m. f. of the ruthenium couple at various ratios of the ruthenium oxidation states. It was found instructive to present the data in the form of a plot showing the faradays of electricity passed (per mole of ruthenium) *versus* the electrode potential. For an electrode process which rapidly attains equilibrium and which involves a reversible couple such a plot assumes the form governed by the equation $E = E_f - (RT/nF) \ln [\text{Ox}]/[\text{Red}]$. However, even for irreversible and/or slow electrode processes such plots are of value, not only for obtaining estimates of the formal potentials but also for obtaining an indication of the magnitude of the overvoltage effect and departure of the electrode process from reversibility. Although the zero-current potentials drifted with time, in most cases they steadied sufficiently after 5–10 minutes to make the readings of significance. Only in the case of the anodic oxidation of Ru(III) to Ru(IV) was the drift sometimes so serious and erratic as to make the readings of little value.

Discussion

Preparation of Ru(IV).—In addition to the electrolytic reduction of ruthenium tetroxide a number of other methods of preparing solutions of Ru(IV) in perchloric acid were investigated. These included: (1) reduction of tetroxide in 1 *M* perchloric acid with mercurous perchlorate; (2) reduction of tetroxide in perchloric acid with mercury, followed by electrodeposition of mercurous ion at controlled cathode potentials; (3) dissolution in perchloric acid of a ruthenium (IV) hydroxide freshly precipitated from a chloride solution; (4) reduction of tetroxide in perchloric acid with hydrogen in the presence of platinized platinum.

These methods failed to yield Ru(IV) solutions that were free of significant amounts of colloidal matter and/or chloride ion. Colloid formation, recognized by Tyndall dispersion and paper chromatography, was particularly severe in method (3) and was evident also when the other methods were employed at acid concentrations as low as 1 *M*. Excessive chloride ion formation was encountered when methods (2) and (4) were used (at room temperatures). This chloride appeared to result from partial reduction to Ru(III) and oxidation of the Ru(III) by perchloric acid. Use of the latter methods at lower temperature, where the formation of chloride ion should be considerably reduced, has not been investigated.

The electrolytic reduction of ruthenium tetroxide in perchloric acid had advantages over the above methods in that it offered greater flexibility and control, and it was therefore investigated in detail. Since preliminary experiments showed that in 1 and 6 *M* acid there was excessive formation of a cathode deposit (presumably a ruthenium oxide), most of the electrolyses were done in 9 *M* acid. The extent of formation of cathode deposit and/or colloidal matter during the reduction in 9 *M* acid was found to depend critically on the cathode potential. Although, as can be seen from Fig. 8, the bulk of the tetroxide can be reduced at a cathode potential of −1.30 v. (*vs.* N.H.E.) in 9 *M* acid in practice excessive amounts of electrode deposition and colloid formation occur under these conditions. (Some evidence indicates the solid material formed is in a higher oxidation state than Ru(IV).) If the reduction is carried out at a more positive potential, −1.11 v., very little cathode deposition occurs and the slight amount of colloid formed largely dissolves if the solutions are stored overnight at room temperature. However, the electrolysis cannot be completed at this potential without the formation of significant amounts of chloride ion. Since experiment confirmed the conclusion drawn from a study of the stability of Ru(IV) in 9 *M* acid that virtually all the chloride was formed during the last 10% of reduction, the final conditions adopted for these electrolyses were reduction to 85–90% completion in 9 *M* acid at −1.11 volts at room temperature and completion in 6 *M* acid at 0°. Excessive colloid formation occurred if the entire reduction was carried out in 9 *M* acid at 0°. Even when these precautions were observed it was difficult to prepare solutions completely free of any trace of chloride ion. Nevertheless, it is possible under these conditions to keep the ratio of chloride to ruthenium as low as 1 to 1000 which is below the 1 to 500 ratio set for a 2% accuracy in the spectral measurements by the extinction coefficients of the stable chloro-complexes of Ru(IV).

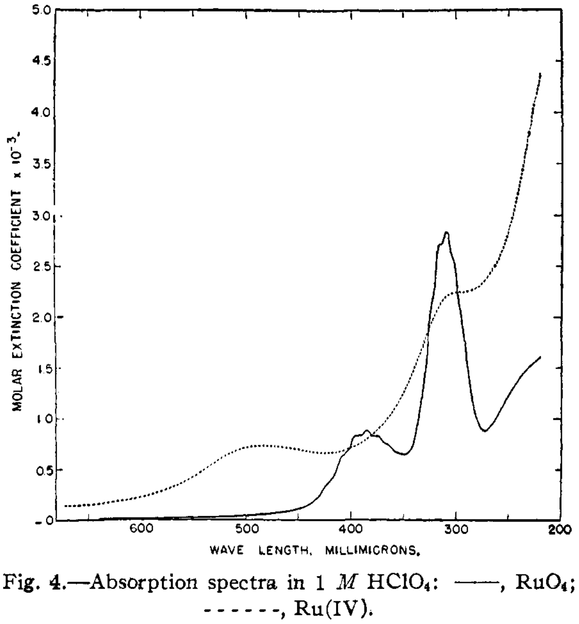

Fig. 4.—Absorption spectra in 1 *M* $HClO_4$: ——, RuO_4; - - - - - -, Ru(IV).

From the results in 9 *M* acid, it is probable that conditions could be found to carry out successful reductions in 6 *M* acid. It is unlikely, however, that satisfactory results can be obtained in 1 *M* acid since the data obtained from other preparative methods indicate that colloid formation is particularly severe at this acidity.

Spectrum of Ru(IV).—The amber-red solutions of Ru(IV) in 1 *M* perchloric acid exhibit the absorption spectrum that is shown in Fig. 4 along with that of the tetroxide.[10] The absorption of various solutions prepared by the electrolytic method generally agreed within 2 to 3% with this spectrum and in both 1 and 6 *M* acid obeyed Beer's law within the accuracy of the measurements (±1–2%) (Fig. 5).

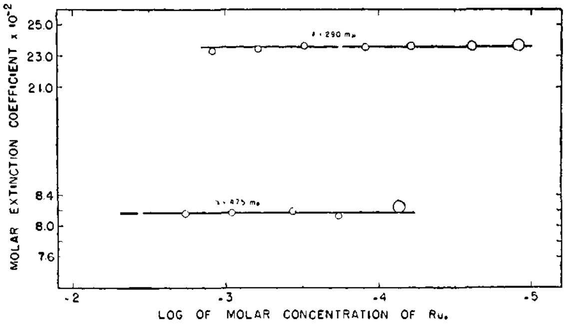

Fig. 5.—Beer's law data for Ru(IV) in 6 *M* $HClO_4$.

Though the spectra of Ru(IV) in 0.12 and 1 *M* acid are nearly identical, definite differences become apparent at acid concentrations above 1 *M* (Fig. 6). The absorption maximum in the visible region is shifted from 480–490 mμ (1 *M* acid) to 475 mμ (6 *M*) and 472 mμ (9 *M*), and the plateau in the ultraviolet is profoundly affected. Studies in mixed perchloric acid–sodium perchlorate solutions showed that the spectral differences

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[10] The λ_{max} of the two main absorption peaks of the tetroxide, 310 and 385 mμ, are in excellent agreement with the published data of B. Qviller for tetroxide vapor (*Tids. Kjemi Bergvesen*, **17**, 127 (1937)).

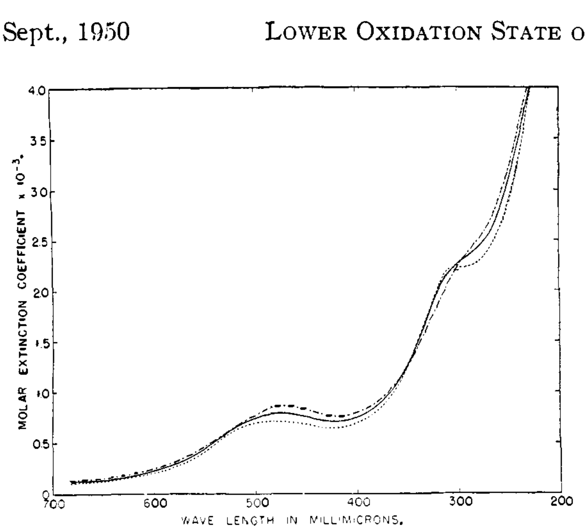

Fig. 6.—Absorption spectrum of Ru(IV) in $HClO_4$: $[HClO_4]$ = — - — -, 9 *M*; ———, 6 *M*; - - - - - - - - -, 1 *M*; . . . ., 0.12 *M*.

between the 1 and 6 *M* acid solutions are almost entirely due to the change in acidity and that those between the 6 and 9 *M* acid solutions may be due in part to ionic strength effects or complex formation as well as change in acidity.

The above results suggest that even at high acid concentrations Ru(IV) exists as hydrolytic products of Ru^{+4}. The potential behavior discussed below supports this conclusion; transference experiments, however, indicate that in 6 *M* acid the species are still cations. In these experiments 0.0118–0.076 *M* solutions of Ru(IV) in 6 *M* perchloric acid were electrolyzed for three hours at 20 ma. in cells of the type described by McLane, Dixon and Hindman.[11] Transference of ruthenium to the cathode compartment occurred and the transported material exhibited a spectrum essentially identical with the starting solution.

Stability of Ru(IV).—Solutions of Ru(IV) (0.001 *M*) in 0.12 *M* and in 1 *M* perchloric acid are quite stable and show no spectral evidence of decomposition after 120 days at room temperature, or in the case of the 1 *M* acid solutions, after eight hours at 75°. On the other hand solutions of Ru(IV) in both 6 and 9 *M* perchloric acid are unstable. Solutions of 0.001 *M* to 0.05 *M* Ru(IV) in 6 *M* acid reach, after about eight hours at 75°, an equilibrium condition in which the oxidation state of the ruthenium is 4.20. Associated with this oxidation is a transformation of the 475 mμ absorption band to a plateau extending from 490–430 mμ. Formation of chloride ion indicates that the perchloric acid is participating in the reaction. At room temperature the oxidation in 6 *M* acid solutions of such concentrations is very slow; spectral changes are apparent only after several weeks and do not reach completion in 40 days. The rate of oxidation is, however, dependent on the ruthenium concentration, for in 0.3 *M* Ru(IV) solutions spectral changes indicate that equilibrium is reached within two weeks. The rate of the oxidation is also considerably higher in 9 *M* perchloric acid, and within 1 to 4 days at room temperature 0.01 *M* Ru(IV) in 9 *M* acid attains an equilibrium oxidation state of 4.24.

Spectrum of Ru(III).—In appearance Ru(III) solutions are pale amber when dilute and blackish-amber when concentrated. The absorption spectrum of freshly prepared material is initially identical in 1 and 6 *M* perchloric acid (Fig. 7); however, when such solutions are stored in an inert atmosphere at 0° changes occur that profoundly alter the spectrum. Interpretation of the spectral changes in the 6 *M* acid solutions is difficult inasmuch as the appearance of large amounts of chloride ion indicates extensive oxidation of Ru(III). In 1 *M* acid, where a well-defined band at 300 mμ reaches an "equilibrium" maximum in 10–15 hours (Fig. 7), the absence of chloride ion and coulometric analysis by anodic oxidation show that the ruthenium is present as Ru(III). The 300 mμ band thus appears to be related to a new Ru(III) species, presumably one that contains fewer hydroxyl groups or oxygen atoms associated with the ruthenium atom. Some support for this postulated change in ionic species is obtained when such "equilibrium" solutions of Ru(III) in 1 *M* acid are oxidized anodically. The Ru(IV) solution obtained shows a spectrum, initially identical in 1 and 6 *M* dilutions, in which the plateau in the ultraviolet is almost completely missing and in which the absorption in the far ultraviolet is considerably higher than that observed in Ru(IV) solutions prepared directly by reduction of tetroxide. When the dilutions in 1 and 6 *M* acid that exhibit this new spectrum are allowed to stand at room temperature for several days, the absorption in the far ultraviolet falls and evidence of the plateau becomes more pronounced.

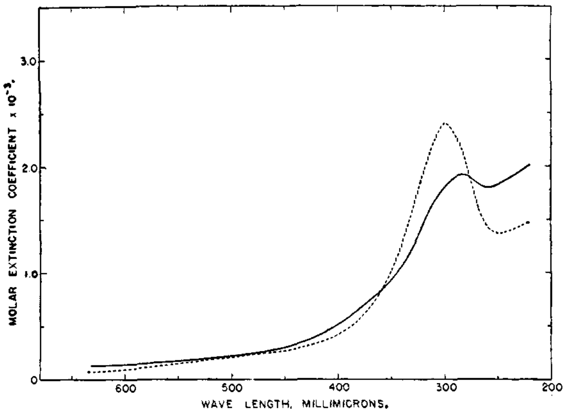

Fig. 7.—Absorption spectrum of Ru(III) in 1 *M* $HClO_4$: ———, freshly prepared; - - - -, after 10–15 hours at 0°.

It is unfortunate that these slow and probably

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[11] C. K. McLane, J. S. Dixon and J. C. Hindman, Paper No. 4.3, Vol. 14B of the Plutonium Project Record of the National Nuclear Energy Series, McGraw-Hill Book Co., Inc., New York, N. Y., 1949.

incomplete changes cannot be studied under more vigorous conditions or for longer times. However, the instability of Ru(III) (and to a lesser extent of Ru(IV)) in perchloric acid does not permit such a study.

Stability of Ru(III).—When solutions of Ru(III) in 1 or 6 *M* perchloric acid are allowed to warm to room temperature, in an atmosphere of nitrogen, spectral changes show that the Ru(III) is oxidized to Ru(IV) with the formation of large amounts of chloride ion. The change is complete within four hours in 6 *M* acid and within twenty-four hours in 1 *M* acid, even for solutions as dilute as 0.0005 *M* in ruthenium. The oxidation is however much slower at 0° and the rate at this temperature is approximately 1% per hour in 6 *M* acid and only a few per cent. in 40 hours in 1 *M* acid.

This ease with which Ru(III) reduces perchloric acid accounts for the fact that all attempts to prepare Ru(III) at room temperature, in either 1 or 6 *M* acid, resulted in incomplete reduction and the formation of large amounts of chloride ion. The stability data are also consistent with the previously known fact that Ru(III) and (less effectively) Ru(IV) act as catalysts in the reduction of perchloric acid by hydrobromic acid.[12]

Oxidation–Reduction Potentials.—Typical curves illustrating the change of the zero-current or "balance" electrode potential during the anodic oxidation of Ru(IV) and the cathodic reduction of ruthenium tetroxide at controlled potentials are shown in Fig. 8. In the reduction of tetroxide in 9 *M* perchloric acid potential breaks occur when 3.7 and when 4 faradays of electricity have been passed through the cell. Because of a slow reoxidation of Ru(IV) by the 9 *M* acid the second break is not too well-defined although there is a very definite current break. However, in 6 *M* acid, where the same general behavior occurs, the second potential break is very definite (see Fig. 8). That the second potential break does indeed correspond to the end-point of the reduction to Ru(IV) is confirmed by iodometric analyses and by coulometric measurements during further reduction to Ru(III). It is, however, difficult to interpret the sharp break at 3.7 faradays. As can be seen from Fig. 8 a corresponding break occurs at about 0.5 faraday in the anodic oxidation of Ru(IV), a behavior observed also in 1 and 6 *M* acid. It is possible that solutions of tetroxide and of Ru(IV) in perchloric acid are both mixtures of several species which are not in rapid equilibrium, or that Ru(IV) and small amounts of tetroxide interact in solution, perhaps by association, to form a fairly stable intermediate state.

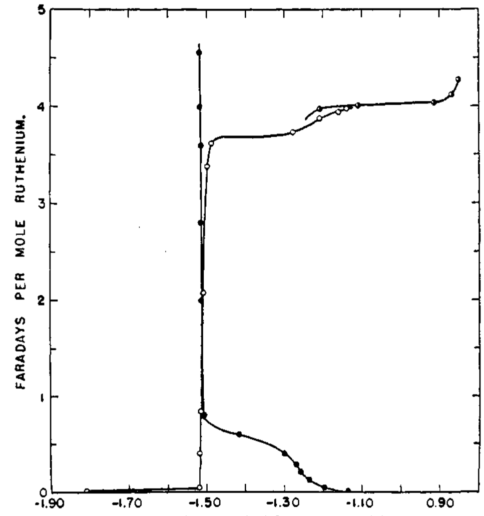

Fig. 8.—Potential behavior during the electrolytic oxidation of Ru(IV) and reduction of RuO_4: ○, reduction of RuO_4 in 9 *M* $HClO_4$ at 25°, c. d. = 1 to 2 ma./sq. cm.; ◑, end-point of reduction of RuO_4 in 6 *M* $HClO_4$ at 0°; ●, oxidation of Ru(IV) in 9 *M* $HClO_4$ at 0°, c. d. = 1 ma./sq. cm.

An interesting feature of the anodic oxidation of Ru(IV) is the absence of a definite end-point. This is true at both 0 and 25° and in 1, 6 and 9 *M* acid. In certain runs 5 faradays were passed without occurrence of a definite end-point, and inspection of the anolyte indicated that significant amounts of Ru(IV) were still not oxidized. Since the electrolyses were carried out at potentials where blank runs indicated that the oxidation of water was not significant, it would appear that ruthenium catalyzes the oxidation of water at a platinum anode.

Despite the above-described pecularities of the electrolyses involving the Ru(IV) → $RuO_4 + 4e^-$ couple, it was felt that reasonable estimates for the formal oxidation–reduction potential[13] of the couple could be obtained from curves of the type in Fig. 8. The potential values listed in Table III were read from the curves at the points corresponding to 2 faradays of electricity passed per mole of ruthenium. Inasmuch as the curves are very steep in this region it is believed these potential values are accurate to within ±0.05 volt

TABLE III

FORMAL POTENTIAL VALUES FOR THE COUPLE

Ru(IV) $\longrightarrow RuO_4 + 4e^-$

[$HClO_4$], moles/liter	Potential values (in volts) obtained during			
	Redn. of RuO_4	Temp., °C.	Oxdn. of Ru(IV)	Temp., °C.
1	−1.40	25	−1.40	0
6	−1.40	25	−1.45	0
			−1.47	25
9	−1.51	25	−1.51	0

The changes in the zero-current or "balance" potential during the course of the reduction of

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[12] W. R. Crowell, D. M. Yost and J. M. Carter, THIS JOURNAL, 51, 786 (1929).

[13] The formal oxidation–reduction potential of this couple is defined as the potential of the couple at equal concentrations of RuO_4 and Ru(IV).

Ru(IV) in 1 and 6 *M* perchloric acid are shown in Fig. 9. While a definite current-break end-point occurs in the electrolysis in 6 *M* acid, the potential curve in Fig. 9 does not indicate this, apparently because near the end-point the rate of the slow oxidation of Ru(III) by the 6 *M* acid is nearly equal to the rate of reduction of the Ru(IV). The curves of Fig. 9 indicate that Ru(IV) in both 1 and 6 *M* acid is a mixture of at least two species, neither of which behaves reversibly during the reduction. The displacement of the 1 *M* acid curve toward more positive potentials is consistent with the interpretation that the constituents are hydrolytic species in which the ruthenium is associated with hydroxide ion or oxygen.

Attempts to determine the potential behavior during the anodic oxidation of freshly prepared Ru(III) to Ru(IV) were generally not successful. In the oxidation of such Ru(III) in either 1 or 6 *M* perchloric acid, the zero-current potentials drifted so badly and erratically that no significant data could be obtained. The behavior of the Ru(III) ⟷ Ru(IV) couple in such oxidations was one of great irreversibility, and in order to complete the oxidations at an appreciable rate eventually anode potentials as negative as −1.30 to −1.40 volts had to be used. Under these conditions very poor end-points were obtained, presumably because the anode potential was sufficiently negative to oxidize appreciable amounts of Ru(IV) to the tetroxide. However, in the oxidation of the "equilibrium" Ru(III solutions (see discussion of Ru(III) spectrum) the zero-current potentials adjusted more satisfactorily and a definite end-point occurred. The change in zero-current potential during such an oxidation is also shown in Fig. 9. The large displacement of this anodic curve from the cathodic curves is indicative of the profound change that has taken place in the Ru(III) solution. It would also appear from this anodic curve that even the "equilibrium" Ru(III) solution consists of a mixture of ionic species.

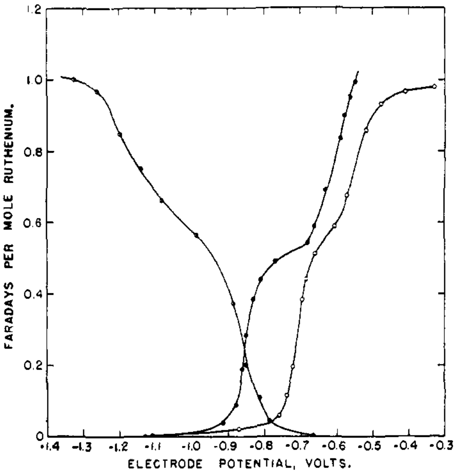

Fig. 9.—Potential behavior during the electrolytic reduction of Ru(IV) and oxidation of Ru(III): ●, reduction of Ru(IV) in 6 *M* $HClO_4$ at −5 to −10°, c. d. = 1 to 2 ma./sq. cm.; ○, reduction of Ru(IV) in 1 *M* $HClO_4$ at 0 to −5°, c. d. = 0.5 to 1 ma./sq. cm.; ◑, oxidation of "equilibrium" Ru(III) in 1 *M* $HClO_4$ at 0°, c. d. = 0.5 to 1 ma./sq. cm.

Table IV gives approximate values for the formal potentials of the couple Ru(III) → Ru(IV) + e^-.[14] These potential values were obtained at the mid-points of the waves in the curves shown in Fig. 9. In view of the apparent irreversibility of the couple and the changes that occur in Ru(III) solutions the values obtained from the cathodic curves can be considered only as positive limits and the values obtained from the anodic curve only as negative limits of the real values. It is interesting to compare the data of Table IV with the formal potentials reported by Grube and Fromm[15] for the Ru(III) ⟷ Ru(IV) couple in hydrochloric acid. These workers found by static potential measurements that in this complexing medium at room temperature the couple had the following values: −0.908 v. (0.5 *M* HCl), −0.874 v. (1.1 *M* HCl) and −0.858 v. (2 *M* HCl). The data of Grube and Fromm indicate preferential complexing of the Ru(IV) by chloride ion, and it might be estimated from the data that in perchloric acid the formal potential of the Ru(III) ⟷ Ru(IV) couple should be as negative as −0.95 v. It is not surprising that the potentials given in Table IV are not in close agreement with this estimated value since it is certain that equilibrium was not established among the various Ru(IV) and Ru(III) species during the electrolytic oxidations and reductions in perchloric acid. Unfortunately the instability of these lower oxidation states of ruthenium in perchloric acid render it almost impossible to carry out extensive measurements under true equilibrium conditions.

TABLE IV

FORMAL POTENTIALS OF THE COUPLE

Ru(III) ⟶ Ru(IV) + e^- at 0 to −5°

$[HClO_4]$, moles/liter	E_f in volts From redn. of Ru(IV) Species 1	 Species 2	From oxdn. of "equilibrium" Ru(III) Species 3	 Species 4
1	−0.7	−0.55	−1.17	−0.87
6	− .85	− .6		

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(14) L. W. Niedrach and A. D. Tevebaugh of the Knolls Atomic Power Laboratory, General Electric Company, and E. Turk of the Chemical Engineering Division, Argonne National Laboratory, have independently obtained data concerning this couple in perchloric acid. Niedrach and Tevebaugh concluded from the behavior of Ru(IV) at the dropping mercury cathode and from a slight reduction of Ru(IV) by mercury that the potential of the couple was E = −0.68 v. From a polarographic study using a stationary graphite microelectrode, Turk found that Ru(IV) is reduced in two steps at half-wave potentials of −0.68 v. and −0.43 v. (*vs.* N. H. E.) in 1 *M* perchloric acid (μ = 2 *M*).

(15) G. Grube and G. Fromm, *Z. Elektrochem.*, **47**, 208 (1941).

Summary

Controlled potential electrolyses have been used for the preparation of Ru(III) and Ru(IV) in perchloric acid. The analytical identification, absorption spectra and stabilities of these states are described. Conditions for the oxidation of Ru(III) and Ru(IV) by perchloric acid are discussed.

Evidence from absorption spectra and electrode behavior is cited for the complex nature of the ionic species present in solutions of Ru(III) and Ru(IV). The slowness of equilibria involving these species is discussed. Limits have been placed on the formal oxidation potential of the Ru(III) → Ru(IV) + e⁻ couple.

The formal oxidation potential of the couple Ru(IV) → RuO_4 + e⁻ has been estimated as −1.40 ± 0.05 v. (1 *M* $HClO_4$), −1.43 ± 0.05 v. (6 *M* $HClO_4$) and −1.51 ± 0.05 v. (9 *M* $HClO_4$).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Effect of Ionic Strength on Polarographic Half-wave Potentials[1]

BY DONALD D. DEFORD AND DONALD L. ANDERSEN[2]

The half-wave potential for the polarographic reduction of simple ions of metals soluble in mercury is given[3,4,5] by the equation

$$E_{1/2} = E_a^0 + \frac{RT}{nF}\ln f_s - \frac{RT}{2nF}\ln\left(\frac{D_s}{D_a}\right) \qquad (1)$$

where E_a^0 is the standard potential of the metal amalgam electrode, f_s is the activity coefficient of the metal ions in the solution, D_s is the diffusion coefficient of the metal ions in the solution and D_a is the diffusion coefficient of the metal atoms in the mercury. In the derivation of this equation it has been assumed that both the activity of the mercury and the activity coefficient of the metal atoms in the amalgam are equal to unity. Since the amalgams formed at the dropping mercury electrode are extremely dilute, these assumptions are reasonable. It has also been assumed that the Ilkovic equation is valid for the reduction under consideration.

If the measurement of the half-wave potential is made in the customary manner by employing an external reference electrode as the anode, the observed half-wave potential will also include the junction potential between this reference electrode and the solution being studied. Furthermore, even though one selects a supporting electrolyte which has very little tendency to form complexes with the reducible metal ion, it is often impossible to find a suitable supporting electrolyte which exhibits completely negligible tendency toward complex-formation. If complex-formation does occur, the half-wave potential is shifted by an amount which is given[6] by

$$\Delta E_{1/2} = \frac{RT}{nF}\ln\left(1 + \frac{C_x^p f_x^p f_s}{K_c f_c}\right) \qquad (2)$$

where C_x represents the concentration of the complex-forming substance, K_c represents the dissociation constant of the complex, p represents the number of moles of complex-forming substance per mole of metal ion in the complex, and f_x, f_s and f_c represent the activity coefficients of the complex-forming substance, of the simple (hydrated) metal ion and of the complex, respectively.

If the effects of liquid-junction potential and of complex-formation are included in the equation for the half-wave potential, equation (1) becomes

$$E_{1/2} = E_a^0 + \frac{RT}{nF}\ln f_s - \frac{RT}{2nF}\ln\left(\frac{D_s}{D_a}\right) - E_L - \frac{RT}{nF}\ln\left(1 + \frac{C_x^p f_x^p f_s}{K_c f_c}\right) \qquad (3)$$

where E_L is the liquid junction potential. Since the values of f_s, D_s and E_L are functions of the ionic strength and of the ionic environment, it may be expected that the half-wave potential will be significantly affected by changes in ionic strength or ionic environment.

The only previous study of the effect of ionic strength on half-wave potentials is that of Lingane,[1] who studied the half-wave potentials of thallous, zinc, lead and cadmium ions in a supporting electrolyte of potassium nitrate. The range of ionic strengths studied was quite narrow, 0.02 to 1.0 *M*, but the data indicated that the influence of ionic strength on the half-wave potentials was indeed significant.

The present paper reports the results of measurements of the half-wave potential of cadmium in various nitrate supporting electrolytes for a range of ionic strengths extending up to 12 *M*. Cadmium was chosen as the reducible ion since it is particularly easy to study by the polarographic method. Nitrates were chosen as supporting electrolytes in order to keep complex-formation at a minimum.

Experimental

A Sargent Model XXI visible recording polarograph was used for recording all polarograms. The initial and span voltages of the polarograph were measured by means of a

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[1] Presented before the Atlantic City Meeting of the American Chemical Society, September 1949.

[2] School of Chemistry, University of Minnesota, Minneapolis, Minnesota.

[3] J. J. Lingane, THIS JOURNAL, **61**, 2099 (1939).

[4] M. v. Stackelberg, *Z. Elektrochem.*, **45**, 466 (1939).

[5] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941.

[6] D. D. DeFord and D. N. Hume, to be published.