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I. THE CRYSTAL STRUCTURE OF POTASSIUM PERRUTHENATE

II. STUDIES OF THE UPPER VALENCE STATES OF RUTHENIUM IN AQUEOUS SOLUTIONS

M. D. Silverman and H. A. Levy

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I. THE CRYSTAL STRUCTURE OF POTASSIUM PERRUTHENATE

II. STUDIES OF THE UPPER VALENCE STATES OF RUTHENIUM IN AQUEOUS SOLUTIONS

A THESIS

Submitted to
The Committee on Graduate Study
of
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---

by

Meyer David Silverman

August, 1950

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PREFACE

The chemistry of ruthenium is complicated by the fact that the element can exist in all oxidation states from zero to eight. For the most part, the work reported in the literature is concerned with the study of lower valent ruthenium complexes and other compounds in acid solution. This dissertation describes research directed toward clarification of the chemistry of the upper valence states, especially in basic solution, a field which heretofore has received relatively little attention. The studies include determination of a crystal structure, examination of spectrophotometric properties of several solution species and some of their reactions, measurement of oxidation potentials and investigation of an acid ionization equilibrium.

At the beginning of this investigation, an effort was made to obtain pure compounds as starting materials for further studies. Among other compounds, pure crystalline potassium perruthenate was obtained. Because this substance possesses a simple crystal structure and is a representative upper-valence state compound, an investigation of its crystal structure was undertaken.

As oxidation-reduction potentials in solution offer an excellent means for interpreting the chemistry of an element, an initial attack was made in this direction. However, efforts toward realizing equilibrium in systems containing ruthenate, perruthenate and ruthenium dioxide, either in electrolytic cells or otherwise, were unsuccessful because of the long-term instability of these systems.

Since the polarograph offered a method for obtaining approximate oxidation potentials in unstable systems where concentrations cannot be measured accurately, work was directed along these lines.

In order to clarify the nature of the species present in solutions of ruthenium tetroxide, its acid ionization constant was measured.

Some of the non-equilibrium reactions of ruthenium in its VI, VII, and VIII oxidation states were explored by means of spectrophotometric studies, taking advantage of the intense characteristic color of these solutions.

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CHAPTER I

A SURVEY OF THE CHEMISTRY OF RUTHENIUM IN ITS UPPER VALENCE STATES

A. Introduction

Although ruthenium was discovered over one hundred years ago, it has remained one of the less familiar elements. The chemistry of its upper valence states, especially in solution, has received particularly little study.

Ruthenium is the only element which is known to exist in all oxidation states from zero to eight. The more common valences which it exhibits are III, IV, VI, and VIII. The lower valent compounds are found in acid solution; in basic solution they hydrolyze to give precipitates of ruthenium hydroxide and hydrous ruthenium dioxide. On the other hand, dissolved ruthenates and perruthenates are stable only in basic solution; in acid solution they disproportionate to give ruthenium tetroxide and the hydrous dioxide. Of the upper valent compounds, only the tetroxide is stable in acid solution.

Ruthenium, in common with other heavy Group VIII elements, forms an extremely large number of complex compounds; as Pauling[1] states:

> The metals of the palladium and platinum groups have little tendency to form positive ions, but prefer to remain

---

(1) Pauling, Linus, "The Nature of the Chemical Bond," Second ed., Cornell University Press, Ithaca, N. Y., 1940, p. 257.

neutral or even become negative; this characteristic is indicated by their position in the electronegativity scale. In consequence, these elements can form covalent octahedral complexes not only with cyanide, ammino, hydroxide and related groups, but also with chlorine, bromine and even iodine atoms.

One would consequently expect the chemical behavior of ruthenium to be quite complicated, and this is indeed the case. Nevertheless, for an interpretation of its chemistry, analogies can be drawn to the known chemistry of other elements which possess properties similar to those of ruthenium in a given valence state. For example, in acid solution ruthenium resembles the transition element iron in its bivalent and tervalent states. Ruthenium tetroxide is similar to osmium tetroxide in its chemical behavior and the alkali ruthenates in solution behave very much like the manganates.

The French treatise, "Traité de Chimie Minérale,"(2) has been used generously as a source of information whenever an article in the literature was unavailable and as a reference work which critically summarizes the literature on the chemistry of ruthenium according to valence state.

B. The Ruthenates and Perruthenates

The ruthenates and perruthenates are the respective salts of the hypothetical acids H_2RuO_4 and $HRuO_4$. The perruthenates of sodium

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(2) Charonnat, R., "Traité de Chimie Minérale," Vol. XI, Masson and Cie, Paris, 1932, p. 383.

and potassium are the only salts of heptavalent ruthenium that have ever been isolated.[3] They may be prepared by oxidizing concentrated ruthenate solutions with chlorine until the orange-red color changes to a dark green. However, a better method and one which avoids contamination by other ions is to absorb an excess of ruthenium tetroxide in a concentrated ruthenate solution and allow the mixture to stand at 0°.

Debray and Joly [4] were the first to isolate greenish-black, octahedral crystals of potassium perruthenate and find that they are stable in air. Goniometric measurements by Dufet showed these crystals to be of tetragonal symmetry and not isomorphous with those of potassium permanganate.[5] The perruthenates are only slightly soluble in water at room temperature; their dark-green neutral aqueous solutions are not stable, but disproportionate rapidly to give ruthenium tetroxide and ruthenium dioxide according to the equation:

$$2\,H_2O + 4RuO_4^- \longrightarrow 3RuO_4 + RuO_2 + 4OH^-$$

Excess hydroxide easily reduces perruthenate to ruthenate, with simultaneous evolution of oxygen.[6]

---

(3) Debray, H., and Joly, A., Compt. rend., 106, 1494 (1888).

(4) Debray, H., and Joly, A., loc. cit.

(5) Dufet, M., Bull. Soc. franc. Mineral, 11, 216 (1888).

(6) Debray, H., and Joly, A., op. cit., p. 1498.

In complete analogy to the manganates, the alkali ruthenates may be prepared in the dry way by fusing the powdered metal or dioxide with an excess of the appropriate alkali and a strong oxidizing agent such as alkali nitrate or peroxide.[7] [8] The latter reagent avoids contamination by other ions. The color of the melt is green, indicating that the VII oxidation state has been attained; however, dissolution of the melt gives a deep orange-red colored solution characteristic of ruthenate, with evolution of oxygen. An alternative method for the preparation of pure ruthenates is the absorption of ruthenium tetroxide in concentrated aqueous alkali;[9] the tetroxide is reduced first to perruthenate and then to ruthenate with evolution of oxygen. Ruthenates are also formed when powdered ruthenium metal or lower valent ruthenium salts are oxidized by permanganate or hypochlorite in strongly alkaline solutions.[10]

A number of alkaline earth and heavy metal ruthenates, slightly soluble in water, have been prepared.[11] In contrast to the perruthenates, the alkali ruthenates are very soluble in water and can be obtained only by evaporation of concentrated solutions. The

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(7) Gutbier, A., Angew. Chem., 22, 487 (1909).

(8) Krauss, F., Z. anorg. allgem. Chem., 132, 301 (1924).

(9) Howe, J. L., and Mercer, F. N., J. Am. Chem. Soc., 47, 2926 (1925).

(10) Ruff, O., and Vidic, E., Z. anorg. allgem. Chem., 136, 49 (1924).

(11) Debray, H., and Joly, A., Compt. rend., 106, 1494 (1888).

ruthenates are very hygroscopic; they decompose on standing in air to ruthenium dioxide.[12] [13] The analogy with the manganates does not hold as far as structure is concerned, for the ruthenates, eg., $BaRuO_4 \cdot H_2O$ and $K_2RuO_4 \cdot H_2O$, crystallize with water of hydration.[14] Concentrated ruthenate solutions have been reported to be unstable, slowly depositing ruthenium dioxide on standing. However, during the present work ruthenate solutions as high as 0.1 M have been stored for as long as several months without any sign of decomposition. Ruthenates are easily reduced to the hydrous dioxide with organic reducing agents such as ethyl alcohol. Upon acidification ruthenates disproportionate to give the tetroxide and the hydrous dioxide.[15] [16] [17]

Krauss[18] claimed to have prepared an ammonia complex of ruthenium (VI) by evaporation of a solution formed from the reaction

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(12) Debray, H., and Joly, A., Compt. rend., 106, 1494 (1888).

(13) Krauss, F., op. cit., p. 308.

(14) Debray, H., and Joly, A., op. cit., p. 1497.

(15) Gutbier, A., Leuchs, G. A., and Wiesmann, H., Z. anorg. allgem. Chem., 95, 177 (1916).

(16) Gutbier, A., and Ransohoff, F., ibid., 45, 241 (1905).

(17) Wöhler, L., Balz, P., and Metz, L., ibid., 139, 205 (1924).

(18) Krauss, F., ibid., 132, 301 (1924).

of ammonia with a concentrated ruthenate solution. He characterized the small black crystals as having the formula $RuO_2(OH)_2(NH_3)_2$. The salt was slightly soluble in water and dilute sulfuric acid, but quite soluble in hydrochloric acid. Concentrated hydrochloric acid reacted with this compound to give a brown aquo salt whose formula was given as $[RuO_2(H_2O)_2(NH_3)_2]Cl_2$; the chlorine atoms are ionizable. Brizard[19] however, noted that potassium ruthenate oxidized ammonia with the formation of nitroso compounds of ruthenium (III) and (IV). The question is therefore raised as to whether Krauss really obtained a compound of ruthenium (VI).

Aoyama[20] prepared microscopic crystals of an acid, characterized as $H_2RuO_2Cl_4 \cdot 3H_2O$, from the reaction of dry chlorine and hydrochloric acid with ruthenium tetroxide. The crystals, similar in appearance to potassium permanganate, were extremely hygroscopic and hydrolyzed very rapidly in water and alcohol to give a black colloidal substance (no doubt the hydrous dioxide). Concentrated hydrochloric acid decomposed the acid, with evolution of chlorine, to yield a compound corresponding to H_2RuCl_6. Ammonium chloride reacted with the acid yielding ruthenium tetroxide and a mixture of $(NH_4)_2RuCl_6$ and $(NH_4)_2RuCl_5$.

---

(19) Brizard, L., Ann. chim. et phys., (7), 21, 311 (1900).

(20) Aoyama, S., Z. anorg. allgem. Chem., 138, 249 (1924).

Howe[21] apparently prepared the rubidium and cesium salts of the above oxychloro acid, $H_2RuO_2Cl_4$. These compounds, soluble in dilute hydrochloric acid, were recrystallized in the cold from this solution unchanged, even in the presence of alcohol. Water instantly decomposed these substances, giving a black liquid having the odor of ruthenium tetroxide. Neither Krauss[22] nor Aoyama[23] were able to duplicate the preparation of these compounds.

C. The Oxides of Ruthenium

In spite of the fact that ruthenium possesses all oxidation states between zero and eight, only two oxides, the dioxide and tetroxide, have ever been isolated. The latter is by far the more interesting compound.

The properties of the two oxides are in direct contrast to one another: Ruthenium dioxide has properties similar to and behaves chemically like manganese dioxide, while ruthenium tetroxide acts very much like osmium tetroxide. Whereas the dioxide is stable in air and can be heated to 600° before a reaction with oxygen

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(21) Howe, J. L., J. Am. Chem. Soc., 23, 775 (1901).

(22) Krauss, F., Z. anorg. allgem. Chem., 117, 111 (1921).

(23) Aoyama, S., ibid., 138, 249 (1924).

begins,[24] the tetroxide is extremely unstable in the presence of light and moisture and is easily reduced to the dioxide by traces of organic matter.[25] [26] No melting point has ever been observed for the dioxide; on the other hand, the tetroxide melts at 25°.[27] [28] The dioxide is very insoluble in water; the crystalline form, extremely refractory, is not attacked by any acid or mixture of acids,[29] while the hydrous dioxide, when freshly precipitated, easily dissolves in hydrochloric acid but is still insoluble in both nitric and sulfuric acids. The tetroxide, however, is soluble enough to give a 0.12 M. solution at room temperature;[30] it is rapidly reduced to the tervalent and tetravalent states by the halogen acids.

Crystalline ruthenium dioxide is obtained only by dry methods of preparation; for example, by heating the sulfate in air at

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(24) Debray, H., and Joly, A., Compt. rend., 106, 1494 (1888).

(25) Joly, A., ibid., 111, 693 (1891).

(26) Claus, C., Bull. Acad. Sci., St. Petersburg, (3) 1, 100 (1860).

(27) Debray, H., and Joly, A., Compt. rend., 106, 328 (1888).

(28) Krauss, F., Z. anorg. allgem. Chem., 131, 348 (1923).

(29) Joly, A., in Fremy, "Encyclopedie Chimique," Vol. III, No. 17, Part I, Paris, 1900, p. 218.

(30) Remy, H., Angew. Chem., 39, 1061 (1926).

600°[31] [32] or the chloride or chloro-complexes in air or oxygen at 500-700°.[33] [34] [35] It can also be formed by heating powdered ruthenium metal in oxygen at 1000°[36] or by roasting the disulfide or hydrous oxide in air at high temperatures.[37] [38] [39] The hydrous oxide of ruthenium, whose composition corresponds approximately to the formula $RuO(OH)_2$[40] is formed when tetravalent species precipitate by hydrolysis. It may be prepared by neutralizing a solution of ruthenium (IV) chloride with aqueous alkali, or by the air oxidation of lower valence hydroxides. It is also formed by the reduction of ruthenates and perruthenates in basic media, and from the reduction of

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(31) Gutbier, A., and Ransohoff, F., Z. anorg. allgem. Chem., 45, 241 (1905).

(32) Lunde, G., ibid., 163, 345 (1927).

(33) Aoyama, S., Science Reports, Tohoku Imp. Univ. I 16, 27 (1927).

(34) Aoyama, S., Z. anorg. allgem. Chem., 138, 249 (1924).

(35) Wöhler, L., Balz, P., and Metz, L., ibid., 139, 205 (1924).

(36) Remy, H., and Köhn, M., ibid., 137, 365 (1924).

(37) Claus, C., Bull. Acad. Sci., St. Petersburg (2), 5, 241 (1847).

(38) Müller, E., and Schwabe, K., Z. Electrochem., 35, 170 (1929).

(39) Wöhler, L., Balz, P., and Metz, L., op. cit., p. 205.

(40) Charonnat, R., Ann. chim., (10) 16, 5 (1931).

ruthenium tetroxide in solution, either catalytically, by autodecomposition, or reduction with hydrogen peroxide and many other reducing agents.

The steel-blue crystals of the dioxide possess the rutile type structure and the density, based on X-ray data, is 6.97 g./cc.[41] [42] The dioxide can be reduced to the metal by hydrogen[43] or by carbon monoxide on heating.[44] By reaction with a mixture of carbon monoxide and chlorine it may be converted to the trivalent chloride. Ruthenium tetroxide is formed when the dioxide is heated in air or oxygen above 600°.

Ruthenium tetroxide is usually prepared in the wet manner in an all-glass apparatus by distillation from an acid solution containing a strong oxidizing agent such as potassium permanganate or periodic acid; the distillate is collected in an ice-cooled receiver which may contain water, aqueous acid or aqueous alkali.[45] [46] [47] [48] [49] The

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(41) Goldschmidt, V. M., Barth, T., Holmsen, D., Lunde, G., and Zachariasen, W., Skrifte Norske Videnkapsacad. Oslo, Mat.-Nat. Kl. 1, 16 (1926).

(42) Krauss, F., and Schrader, G., Z. anorg. allgem. Chem., 176, 385 (1928).

(43) Sainte-Claire Deville, H., and Debray, H., Ann. chim., (3) 56, 385 (1859).

(44) Remy, H., and Wagner, T., Z. anorg. allgem. Chem., 157, 339 (1926).

(45) Crowell, W., and Yost, D. M., J. Am. Chem. Soc., 50, 374 (1928).

(46) Gutbier, A., Angew. Chem., 22, 487 (1909).

(47) Howe, J. L., J. Am. Chem. Soc., 23, 775 (1901).

(48) Krauss, F., Z. anorg. allgem. Chem., 131, 348 (1923).

(49) Ruff, O., and Vidic, E., ibid., 136, 49 (1924).

solid material obtained may be purified by washing with water, drying over magnesium perchlorate, and redistilling *in vacuo*. Two apparently different crystalline forms of the tetroxide are known: reactive yellow needle-like crystals and an orange-brown amorphous solid. Krauss[50] believed that these two forms are different crystalline modifications; however, Remy,[51] basing his opinion on the fact that both solids have identical melting points and solubilities in water, stated that the two crystalline forms are not any more different than are snow and ice. The boiling point of the tetroxide has never been determined because it decomposes explosively at 106° to 110°.[52] [53] [54] [55] Its solubility in water has been measured by Remy over the temperature range 0° - 75°;[56] at room temperature its solubility is about 21 g./l. Absorption bands in the visible and near ultra-violet have been observed for the gaseous tetroxide even at low pressures.[57] [58]

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(50) Krauss, F., *Z. anorg. allgem. Chem.*, *131*, 348 (1923).

(51) Remy, H., *Angew. Chem.*, *39*, 106 (1926).

(52) Krauss, F., *op. cit.*, p. 350.

(53) Debray, H., and Joly, A., *Compt. rend.*, *106*, 328 (1888).

(54) Saint-Claire Deville, H., and Debray, H., *ibid.*, *80*, 457 (1875).

(55) Joly, A., in Fremy, "Encyclopedie Chimique," Vol. 3, No. 17, Part 1, Paris 1900, p. 218.

(56) Remy, H., *op. cit.*, p. 1062.

(57) Krasikov, S. E., Filippov, A. N., and Chernyaev, I. I., *Ann. secteur platine Inst. chim. gen.* (U.S.S.R.), *13*, 19 (1936).

(58) Qviller, B., *Tidskrift for Kjemi og Bergvesen*, *8*, 137 (1937).

Ruthenium tetroxide is reduced to the tetravalent chloride by hydrochloric acid, to a mixture of the (III) and (IV) bromides by hydrobromic acid and to the tri-iodide by hydriodic acid.[59] The latter reaction is the basis for a quantitative method of analysis for ruthenium. The tetroxide is reduced slowly by hydrogen peroxide to the hydrous dioxide[60] and to the insoluble disulfide by hydrogen sulfide. Potassium ruthenocyanide, isomorphous with the ferrocyanide, may be prepared by adding a mixture of potassium cyanide and potassium hydroxide to ruthenium tetroxide.[61] When the tetroxide is absorbed in aqueous alkali, either ruthenate or perruthenate solutions are formed, depending on the alkalinity. Conductivity measurements by Krauss[62] involved experimental difficulties and the data obtained afford little information as to the state of the oxide in aqueous solution. Krauss[63] claimed to have prepared a salt of ruthenium (VIII), the compound $(NH_4)_2RuO_5$, from the reaction of ruthenium tetroxide with concentrated ammonia; however, Trenkner[64] using the same procedure obtained a compound which he characterized as $RuO(OH)_2 \cdot 2NH_3 \cdot 2H_2O$.

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(59) Ruff, O., and Vidic, E., Z. anorg. allgem. Chem., 136, 49 (1924).

(60) Wöhler, L., Balz, P., and Metz, L., ibid., 139, 204 (1924).

(61) Joly, A., op. cit., p. 222.

(62) Krauss, F., Z. anorg. allgem. Chem., 131, 348 (1923).

(63) Krauss, F., ibid., 119, 217 (1921).

(64) Trenkner, K., Dissertation, "Neue Untersuchungen über das Ruthenium," Erlangen, 1905.

CHAPTER II

THE CRYSTAL STRUCTURE OF POTASSIUM PERRUTHENATE

A. Introduction

Although potassium perruthenate was first prepared in 1876, its crystal structure until the present work has not been determined. The original preparation[1] was first reported to be isomorphous with potassium permanganate; Deville and Debray described the perruthenate as black, brilliant orthorhombic octahedra, derived from a prism of 117°. In 1888, Debray and Joly[2] also prepared the perruthenate and submitted samples for crystallographic observation to Dufet[3] who reported from goniometric measurements that the crystal is tetragonal with axial ratio c/a 2.31086; moreover, the perruthenate was described as black, tetragonal octahedra, stable in air, and not isomorphous with potassium permanganate.

Hiortdahl[4] first recognized the similarity of crystal form of sodium periodate and calcium tungstate (scheelite), as well as of some periodates of other univalent metals and some tungstates and molybdates

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(1) Sainte-Claire Deville, H., and Debray, H., Compt. rend., 83, 926 (1876).

(2) Debray, H., and Joly, A., ibid., 106, 1494 (1888).

(3) Dufet, M., Bull. Soc. franc. Mineral, 11, 216 (1888).

(4) Hiortdahl, T., Z. Kryst. Min., 12, 411 (1887).

of other bivalent metals. To these, Barker,[5] from morphological data published in Grothe,[6] added the compounds potassium perruthenate and potassium osmiamate, $KOsO_3N$, and discussed the bearing of such cases of isomorphism on valence theory. These crystals are all tetragonal, and have axial ratios ranging from 2.155 to 2.315.*

Since the first determination of the structure of scheelite in 1926,[7] some thirty other crystals have been found to possess this structure type, e.g., potassium iodate, sodium perrhenate, ammonium pertechnetate, calcium molybdate, lead tungstate, cesium fluorochromate $CsCrO_3F$, and tetragonal bismuth arsenate. Wykoff[8] points out that in the half-dozen cases of complete structure examination among these compounds, different parameters for the oxygen atoms have been reported in every case. These parameters are of interest for the information they give about the interatomic distances in crystals, thus aiding our understanding of the forces which bind atoms in crystals.

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*The original report gave axial ratios of 1.521 to 1.634, which are related to those quoted above by a factor of $1/\sqrt{2}$, and are therefore based upon a different but equivalent choice of a-axis corresponding to a face-centered rather than a body-centered unit cell.

(5) Barker, T. V., J. Chem. Soc., 101, 2487 (1912).

(6) Grothe, P., "Chemische Krystallographie," Engelman, Leipzig, 1908, vol. 2, pp. 175, 393.

(7) Vegard, L., Phil. Mag., 1, 1151 (1926).

(8) Wyckoff, R. W. G., "The Structure of Crystals," Supplement to Second Edition, Reinhold Corp., New York, 1935, p. 68.

B. Preparation of Crystals and X-ray Patterns

Essentially pure potassium perruthenate was first prepared by the method of Debray and Joly.(9) The starting ruthenium salt, a mixture of ruthenium trichloride and ruthenium tetrachloride, was fumed several times with concentrated sulfuric acid to eliminate chlorides. After the addition of potassium permanganate as oxidizing agent, ruthenium tetroxide was distilled from the sulfuric acid solution into 1 M. potassium hydroxide. The solution of the distillate was orange-colored due to ruthenate ion (which was first formed) and gradually changed to the dark green color of the perruthenate as more tetroxide was absorbed. Small black crystals were deposited on the walls of the receiver; this crystalline material was washed with ice-cold freshly distilled water, and was finally dried *in vacuo* over anhydrous calcium sulfate.

Copper radiation Debye-Scherrer photographs of this preparation, after grinding to $>$ 300 mesh in a mortar, were taken in Norelco cameras of two sizes, 5.73 cm. and 11.4 cm. diameter, respectively. The larger picture is shown in Fig. 1 and the data taken from it are listed in Table I. These patterns provided confirmation of the scheelite structure type as described in the next section.

The lattice constants for the perruthenate were obtained with greatest precision from reflections in the back-reflecting region on a

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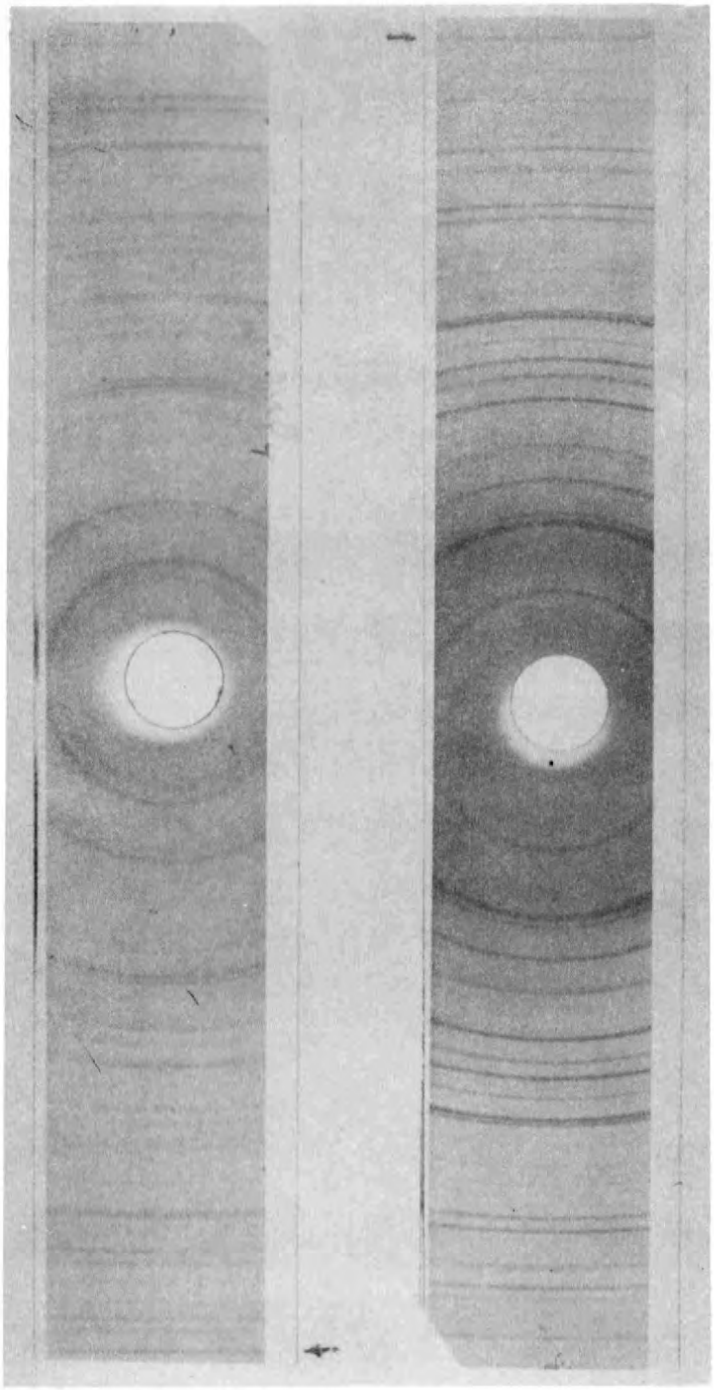
(9) Debray, H., and Joly, A., *Compt. rend.*, *106*, 1494 (1888).



Debye-Scherrer Pattern for Potassium Perruthenate

Fig. 1

TABLE I

INTENSITIES AND INTERPLANAR DISTANCES FOR POTASSIUM PERRUTHENATE FROM POWDER DIFFRACTION DATA[a]

Indices	Intensity[b]	$d_{obs.}$[c]	$d_{calc.}$
101	S	5.145	5.139
112	VS	3.380	3.378
004	W+	3.225	3.241
200	M+	2.790	2.799
202	VW	2.567	2.570
114	VW	2.506	2.507
211	W	2.452	2.456
213	VW	2.165	2.164
204	M+	2.113	2.119
220	W	1.976	1.979
116 222	M	1.892	1.896 1.892
215	W	1.799	1.801
303 206 312	S	1.708	1.712 1.709 1.707
224	M	1.685	1.690
008	VW	1.619	1.620
321	W	1.542	1.541
305	W	1.515	1.518
217	W	1.486	1.490
323 226	W	1.461	1.461 1.460
208 400	M	1.400	1.403 1.399
109			1.395
316 402	M+	1.369	1.369 1.368
411	VW	1.350	1.350
325	VW	1.333	1.331
307	VW	1.313	1.315
413 332	W	1.292	1.296 1.292
404	VW	1.284	1.284
228 420 219	M	1.251	1.253 1.252 1.249

TABLE I

INTENSITIES AND INTERPLANAR DISTANCES FOR POTASSIUM PERRUTHENATE FROM POWDER DIFFRACTION DATA[a] (continued)

Indices	Intensity[b]	$d_{obs.}$[c]	$d_{calc.}$
1.1.10 422	W	1.230	1.231 1.229
3.1.10 1.1.12 514	W	1.043	1.046 1.044 1.040
521	VW	1.037	1.037
435 505	VW	1.028	1.029 1.029
2.0.12 3.0.11	VW	1.003	1.009 0.9975
440	W	0.9895	0.9894
516	W	0.9783	0.9786
532 2.2.12	VW	0.9485	0.9489 0.9486
602	VW	0.9232	0.9232
446	VW	0.8998	0.8990
620	VW	0.8849	0.8849
536 622	VW	0.8769	0.8769 0.8767
1.0.15 624	W	0.8536	0.8537 0.8537
448	VW	0.8440	0.8443
5.1.10	W	0.8368	0.8370
633 626 4.2.12	W	0.8186	0.8190 0.8190 0.8190
00.16	W	0.8102	0.8103
712 552 30.15	W+	0.7855	0.7853 0.7853 0.7853
628 640	W+	0.7762	0.7765 0.7762

[a]These data are taken from Fig. 1.

[b]The symbols in this column have the following meaning: VW = very weak, W = weak, M = medium, S = strong, and VS = very strong.

[c]These data have been corrected for camera errors by comparing the d values obtained with the known d values of sodium chloride in a photograph of a mixture of the two substances.

Debye-Scherrer pattern in which sodium chloride was mixed with the perruthenate in order to provide calibrating lines.

Single crystals of the salt, required for the assignment of parameters to the oxygen atoms, were obtained in a new preparation by distilling ruthenium tetroxide into an alkaline solution of potassium ruthenate, placing the mixture in a refrigerator for several days, and washing the crop of small black crystals as described above.

Several crystals, whose shapes were approximately that of an elongated tetragonal octahedron, about 0.03 x 0.02 cm., were mounted on glass fibers by using rubber cement. The initial orientation of the crystal on the fiber was made purely from its external shape; usually the crystal was several degrees off from one of its axes.

Two specimens were mounted in two positions: one, parallel to the long axis of the specimen (the c axis of the crystal), and the other, perpendicular to this long direction (parallel to the b axis). The final adjustments of the crystal to place the c and b axes accurately parallel to the rotation axis were guided by making a series of X-ray oscillation photographs. Two of these photographs, each covering a range of from 10 to 15°, were taken 180° apart from each other on the same film; by making one exposure of much longer duration than the other, it was possible to ascertain in what direction the crystal was tipped from its axis. Rocker arms, set at 90° to each other on the goniometer head, were used to adjust the position of the crystal. Two centering screws, also on the goniometer head, served to center the crystal on its rotation axis after each rocker arm adjustment. A series

of these oscillation photographs were made until the crystal position was accurately parallel to the rotation axis; then before taking a Weissenberg photograph, a complete (360°) rotation exposure was made to insure the exact position of the crystal. The final criteria for this position is the non-splitting of the layer lines on the rotation photograph.

The first series of Weissenberg photographs were taken with unfiltered copper X-radiation. The shape of the spots on the photographs indicated that absorption of radiation by the crystal was considerable and that structure factors derived from the observed intensities were not to be trusted. Calculations (given in Appendix I) verified this indication; accordingly, new equatorial Weissenberg photographs, using unfiltered molybdenum radiation, were taken about the c and b axes. These photographs are shown in Figs. 2 and 3 and the data are summarized in Tables II and III.

To facilitate the visual estimation of intensities of spots, the multiple film technique of de Lange, Robertson, and Woodward[10] was used; that is, three Kodak non-screen X-ray films were placed one behind another in the Weissenberg camera, interleafed with two sheets of silver foil, one 2.5 mils thick between the first and second films, and the other 3.0 mils between the second and third films. All three films were exposed simultaneously; the constant ratio of exposures of

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(10) de Lange, J. J., Robertson, J. M., and Woodward, I., Proc. Roy. Soc. (London), A 171, 398 (1939).

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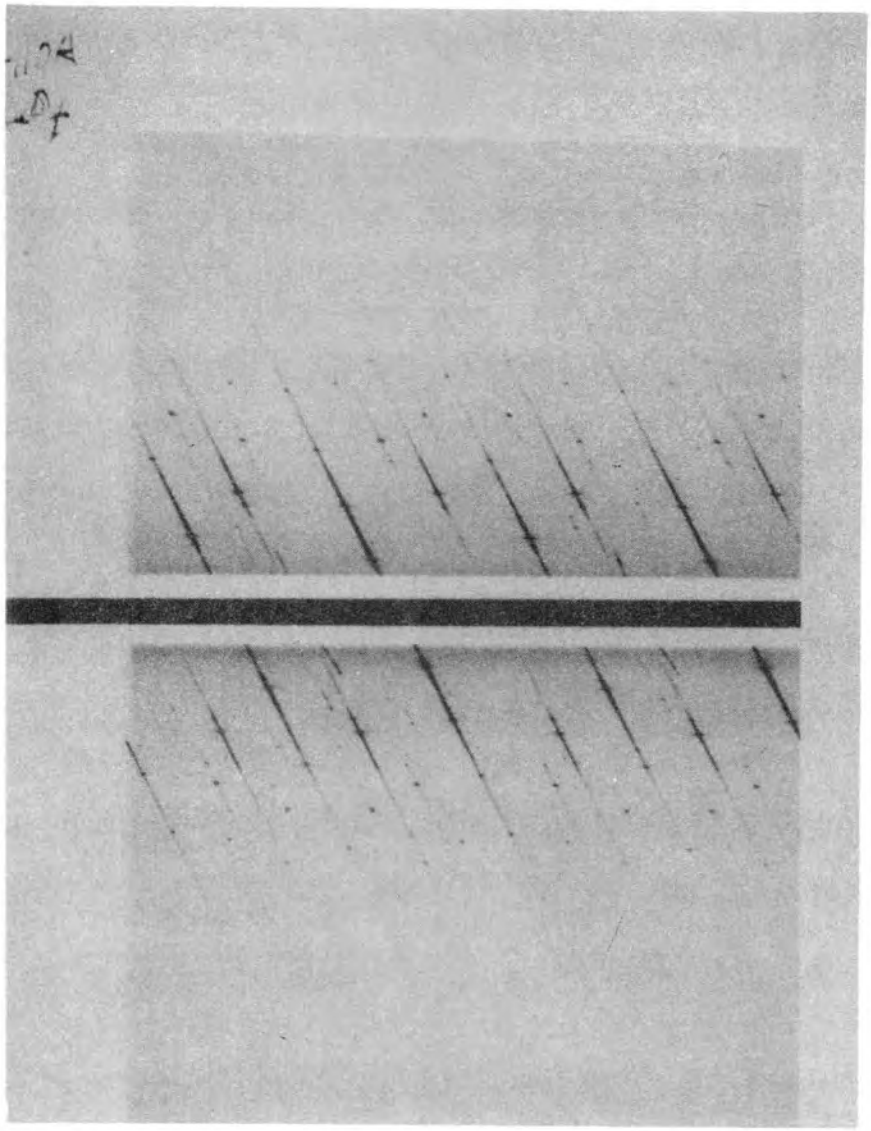


Weissenberg Photograph of hkO Reflections
Fig 2

TABLE II

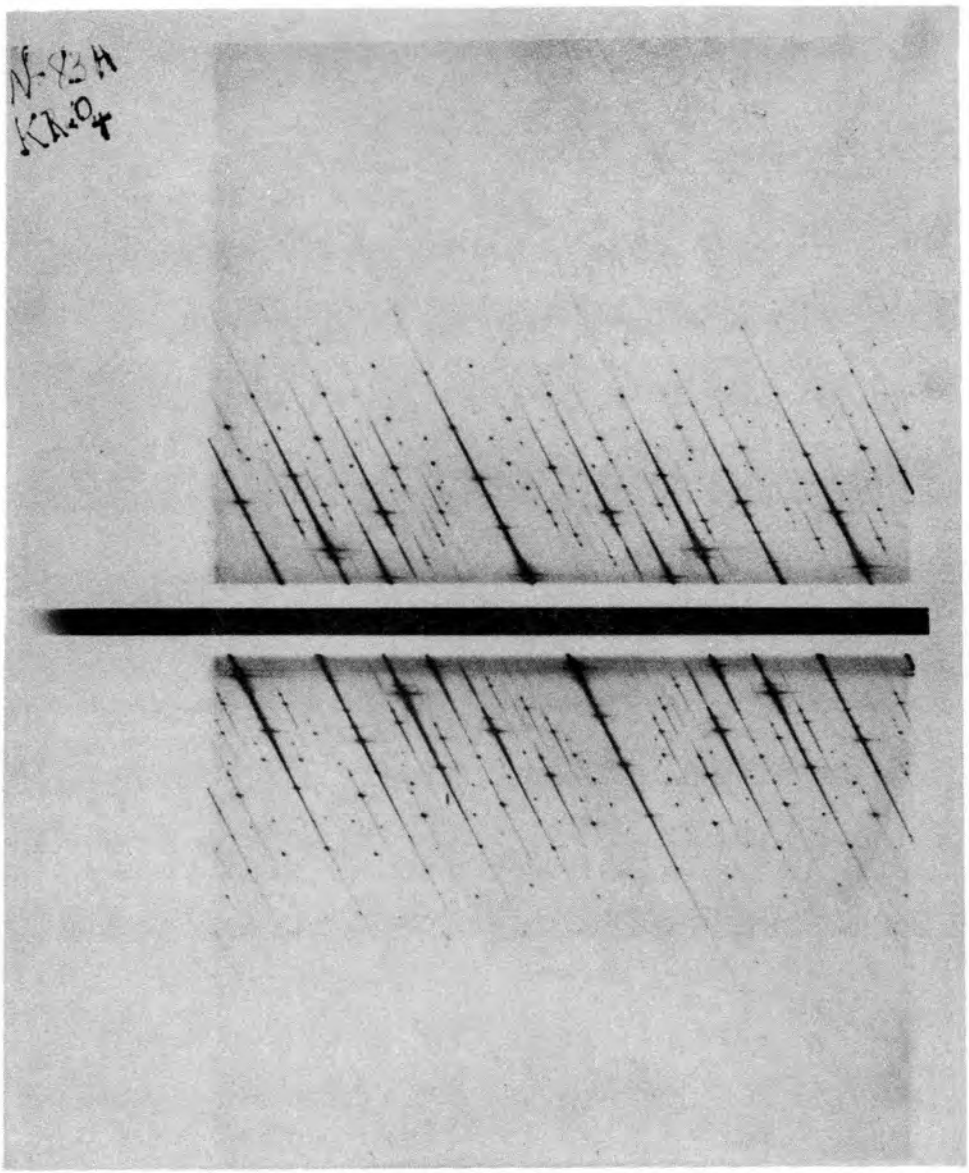
CALCULATED AND OBSERVED hk0 STRUCTURE FACTORS FOR POTASSIUM PERRUTHENATE[a]

hk0	$\frac{\sin\theta}{\lambda}$	$I_{obs.}$	$\lvert F_{obs.}\rvert$[b]	$F_{calc.}$[c]
200	0.179	185	37.2	-33.9
220	0.253	155	40.6	-34.7
400	0.358	38	24.8	+27.5
420	0.400	40	27.2	+28.5
240	0.400	45	28.8	-29.9
440	0.506	9	14.9	+12.4
600	0.537	7.5	14.2	-12.9
620	0.566	9.5	16.5	-15.7
260	0.566	7.5	14.7	-14.4
640	0.645	3.4	10.9	-12.2
460	0.645	4.2	12.1	+12.5
800	0.715	2.8	10.6	+11.1
280	0.738	1.7	8.5	- 7.4
820	0.738	1.3	7.4	+ 6.8
660	0.760	1.7	8.7	- 8.1
840	0.800	0.85	6.4	+ 6.2
480	0.800	0.90	6.5	+ 6.4
10.0.0	0.895	0.37	4.5	- 4.0
860	0.895	0.30	4.0	+ 3.7
680	0.895	0.25	3.6	- 3.2
10.2.0	0.913	0.26	3.8	- 3.8
2.10.0	0.913	0.24	3.6	- 3.5
10.4.0	0.965	0.23	3.6	- 4.0
4.10.0	0.965	0.20	3.4	+ 3.7

[a]These data are taken from Fig. 2.

[b]Computed from the equation $I_{obs.} = S^2 \lvert F\rvert^2_{obs.} \times \frac{1 + \cos^2 2\theta}{\sin 2\theta}$.

[c]Calculated for the final model whose parameters are x = 0.006, y = 0.117, z = 0.802, with separate Debye-Waller temperature corrections for Ru, K, and O; see p. 36 of text.



Weissenberg Photograph of hOl Reflections

Fig. 3

TABLE III

CALCULATED AND OBSERVED $h0\ell$ STRUCTURE FACTORS FOR POTASSIUM PERRUTHENATE[a]

$h0\ell$	$\frac{\sin\theta}{\lambda}$	$I_{obs.}$	$\lvert F_{obs.}\rvert$[b]	$F_{calc.}$[c]
103	0.146	165	25.4	+20.5
004	0.154	500	45.4	-39.7
200	0.179	260	35.4	-34.1
202	0.195	14	8.53	- 8.9
105	0.212	2.4	3.78	- 4.7
204	0.236	260	41.1	+39.7
301	0.270	6.1	6.7	- 8.6
107	0.284	4.1	5.67	- 6.4
303	0.292	8.5	8.35	- 7.3
206	0.293	1.25	3.23	+ 2.9
008	0.309	50	20.8	+20.3
305	0.329	12	10.6	+12.7
208	0.356	135	37.3	-31.2
400	0.358	70	27.1	+27.3
109	0.358	6.8	8.47	+ 9.4
402	0.366	2.3	4.94	- 7.6
307	0.380	8.0	9.45	+11.0
404	0.389	45	22.7	-24.5
2.0.10	0.425	1.20	3.9	+ 4.1
406	0.426	0.50	2.56	+ 2.8
1.0.11	0.434	3.3	6.58	+ 6.3
309	0.439	4.2	7.44	- 7.2
501	0.448	3.9	7.25	+ 6.8
0.0.12	0.463	40	23.9	-25.1
503	0.472	1.3	4.33	+ 4.1
408	0.472	28	20.25	+19.4
505	0.486	4.1	7.92	- 8.9
2.0.12	0.496	15	15.25	+16.2
3.0.11	0.501	1.9	5.49	- 6.7
1.0.13	0.508	4.0	7.98	- 8.0
507	0.522	2.3	6.21	- 7.3
4.0.10	0.526	0.85	3.8	+ 4.7
600	0.536	8.5	12.1	-13.1
602	0.542	0.1	<1.3	- 1.3
604	0.558	10	13.5	+15.9
509	0.566	0.85	4.0	+ 4.5
3.0.13	0.568	0.80	3.9	+ 4.1
2.0.14	0.568	0.1	<1.4	+ 0.3
606	0.584	0.1	<1.4	+ 0.5

TABLE III

CALCULATED AND OBSERVED $h0\ell$ STRUCTURE FACTORS FOR POTASSIUM PERRUTHENATE[a] (continued)

$h0\ell$	$\frac{\sin\theta}{\lambda}$	$I_{obs.}$	$\lvert F_{obs.}\rvert$[b]	$F_{calc.}$[c]
4·0·12	0.584	8.5	12.9	-13.9
1·0·15	0.586	1.7	5.8	- 6.5
5·0·11	0.615	1.4	5.5	+ 5.6
0·0·16	0.617	7.5	12.7	+14.3
608	0.619	8.5	13.5	-14.3
701	0.626	0.70	3.9	- 4.2
703	0.636	1.3	5.4	- 5.0
3·0·15	0.637	0.42	3.0	+ 3.2
2·0·16	0.641	6.0	11.6	-10.8
4·0·14	0.648	0.1	<1.5	+ 0.5
705	0.654	0.75	4.2	+ 3.4
6·0·10	0.660	0.1	<1.5	+ 1.0
1·0·17	0.662	0.37	3.0	+ 3.3
5·0·13	0.672	0.37	3.0	- 2.9
707	0.681	0.85	4.6	+ 3.5
3·0·17	0.708	0.38	3.1	- 3.8
6·0·12	0.708	2.8	8.5	+ 7.9
4·0·16	0.713	2.7	8.4	+ 8.9
800	0.715	2.9	8.7	+11.3
709	0.716	0.39	3.2	- 3.8
2·0·18	0.718	0.1	<1.6	- 1.2
802	0.719	0.1	<1.6	0
5·0·15	0.731	0.20	2.3	- 2.3
804	0.732	2.75	8.6	- 7.7
1·0·19	0.739	0.21	2.4	+ 2.9
806	0.751	0.1	<1.5	0
7·0·11	0.756	0.15	2.1	- 2.5
6·0·14	0.760	0.1	<1.7	0
0·0·20	0.772	2.1	7.9	- 5.1
808	0.778	1.6	6.9	+ 5.2
3·0·19	0.780	0.18	2.3	- 2.8
4·0·18	0.781	0.1	1.7	- 1.9
2·0·20	0.792	2.2	8.2	+ 7.4
5·0·17	0.794	0.23	2.6	+ 3.2
7·0·13	0.802	0.1	1.8	+ 2.7
901	0.805	0.21	2.6	+ 3.0
903	0.812	0.12	1.9	+ 2.9
8·0·10	0.812	0.1	<1.8	0
1·0·21	0.816	0.1	1.8	- 1.9
6·0·16	0.818	1.2	6.2	- 5.3
905	0.827	0.13	2.0	- 1.4
907	0.848	0.12	2.0	- 1.3

TABLE III

CALCULATED AND OBSERVED $h0\ell$ STRUCTURE FACTORS FOR POTASSIUM PERRUTHENATE[a] (concluded)

$h0\ell$	$\frac{\sin\theta}{\lambda}$	$I_{obs.}$	$\lvert F_{obs.}\rvert$[b]	$F_{calc.}$[c]
4.0.20	0.850	0.85	5.3	-5.1
7.0.15	0.852	0.1	1.83	+2.4
8.0.12	0.853	0.90	5.5	-6.2
3.0.21	0.853	0.1	1.83	+2.4
5.0.19	0.859	0.1	1.83	+1.9
2.0.22	0.869	0.1	<1.85	-0.5
909	0.876	0.1	<1.86	+1.7
6.0.18	0.876	0.1	<1.86	-0.4
1.0.23	0.892	0.1	<1.88	-1.3
10.0.0	0.894	0.80	5.30	-4.0
8.0.14	0.895	0.1	<1.88	0
10.0.2	0.897	0.1	<1.88	0.8
7.0.17	0.906	0.1	<1.88	-1.4
10.0.4	0.906	0.45	4.01	+4.1
9.0.11	0.910	0.1	<1.89	+1.6
4.0.22	0.921	0.1	<1.90	-0.7
10.0.6	0.923	0.1	<1.90	+0.3
5.0.21	0.925	0.1	<1.90	-1.8
0.0.24	0.926	0.50	4.25	+3.8
3.0.23	0.927	0.1 ?	<1.90	+1.8
6.0.20	0.940	0.40	3.82	+4.2
8.0.16	0.945	0.45	4.06	+4.1
2.0.24	0.945	0.30	3.32	-3.5
10.0.8	0.945	0.34	3.60	-3.7
9.0.13	0.948	0.1	<1.92	-2.0
7.0.19	0.964	0.1	<1.93	-1.5
1.0.25	0.970	0.1 ?	<1.93	+1.6
10.0.10	0.973	0.1	<1.93	0.7
11.0.1	0.984	0.1	<1.93	-1.1
11.0.3	0.990	0.1	<1.93	-1.3
9.0.15	0.990	0.1	<1.93	-1.8
4.0.24	0.992	0.22	2.86	+2.7
5.0.23	0.994	0.1	<1.93	-1.6
8.0.18	0.996	0.1	<1.93	0

[a]These data are taken from Fig. 3.

[b]Computed from the equation $I_{obs.} = S^2 |F|^2_{obs.} \times \frac{1 + \cos^2 2\theta}{\sin 2\theta}$.

[c]Calculated for the final model whose parameters are x = 0.006, y = .117, z = .802, with separate Debye-Waller temperature corrections for Ru, K, and O; see p. 36 of text.

corresponding spots on the first and second films was 7.5 : 1, and for the second and third films, 12.5 : 1. These ratios were obtained by making carefully timed test exposures of different duration and comparing the exposure times of spots of equal intensity on the three films.

C. Unit Cell, Space Group and Structure Type

The powder pattern of potassium perruthenate was shown to be closely similar to the pattern of scheelite with the help of nomographs devised by Frevel.[11] These "nomographs" are plots of the relative intensities of the strongest lines as a function of the Bragg angle for the various tetragonal crystal types.

The powder pattern was successfully indexed on the basis of a body-centered tetragonal lattice. The interplanar spacing of all reflections allowed by the selection rules for this lattice type[12] (i.e., $h + k + \ell$ even) were calculated by means of the formula

$$\frac{d}{n} = \frac{1}{\sqrt{\left(\frac{h}{a_o}\right)^2 + \left(\frac{k}{b_o}\right)^2 + \left(\frac{\ell}{c_o}\right)^2}} \quad . \qquad (1)$$

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(11) Frevel, L. K., Rinn, H. W., and Anderson, H. C., Ind. Eng. Chem., Anal. Ed., 18, 83 (1946).

(12) "International Tables for the Determination of Crystal Structures," Gebruder Borntraeger, Berlin, 1935, p. 163.

The calculated d/n values are listed in Table I along with the corresponding observed reflections of Fig. 1 and their estimated intensities; the observed d/n values were calculated from observed scattering angles 2θ by means of the Bragg formula

$$n\lambda = 2\,d\,\sin\theta\,. \qquad (2)$$

The most precisely observed lattice spacings were used to estimate the size of the unit cell. These reflections and the derived a_o and c_o axial lengths are tabulated below.

hkℓ	a_o, A.	c_o, A.
440	5.6089	
620	5.6089	
640	5.6083	
0·0·16		12.991

The values adopted are: $a_o = 5.609 \pm 0.002$ A, $c_o = 12.991 \pm 0.002$ A, based on a_o for sodium chloride equal to 5.683 A.

The pattern shows the following systematic absences in accord with the scheelite structure; hkℓ when $h + k + \ell$ is odd, corresponding to a body-centered lattice; hk0 when h or k is odd; 00ℓ when ℓ is not a multiple of 4. These absences and no others are required by the space group $C_{4h}^{6} = I\,4_1/a$, which is the space group to which

scheelite and its isomorphs belong.* The same absences are characteristic of space group $C_4^6 = I\ 4_1$ which differs from the former by the absence of a center of symmetry. The symmetry and absences in an X-ray picture can never distinguish between two space groups so related. We have proceeded under the assumption that potassium perruthenate belongs to the same space group as scheelite and its isomorphs and the successful assignment of parameters as described in this chapter confirms the validity of this assumption.

The symmetry of this space group requires that four molecules of potassium perruthenate be present in the unit cell, with ruthenium and potassium occupying the four-fold positions (a) and (b) as listed in the International Tables (Tabellen).(13) The sixteen oxygen atoms can be placed in two sets of eight-fold positions (c), (d) or (e), or in general positions (f). The former are not consistent with observed intensity data, nor do they lead to a chemically plausible structure.

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*These symbols have the following meaning: C_{4h}^6 is the Schoenflies notation for a particular tetragonal bipyramidal space group. The remaining symbols, $I\ 4_1/a$, refer to the Hermann-Mauguin notation and give a complete description of the symmetry: I indicates a body-centered lattice; 4_1 that the principal axis is a four-fold screw rotation axis parallel to c_0; /a indicates the presence of a glide reflection plane, the glide being $\frac{1}{2}\ a_0$, perpendicular to the screw axis.

(13) "International Tables for the Determination of Crystal Structures," Gebruder Borntraeger, Berlin, 1935, p. 163.

D. Determination of the Structure

To complete the determination of the structure of potassium perruthenate, it is necessary to evaluate the three parameters x, y, and z which give the positions of the sixteen oxygen atoms in the unit cell. This evaluation is made by comparing structure factors estimated from the observed intensities $|F|_{obs}$ with those calculated for various assumed values of x, y, and z.

1. Observed Structure Factors

Estimations of the relative intensities of reflections were made by comparing densities of spots on the three negatives exposed simultaneously, as previously described. Before reliable values of structure factors can be derived from intensity data, a determination must be made of whether absorption of radiation in the crystal specimen has substantially affected the relative values of the intensities of the various reflections. Accordingly, an estimate of the effect of absorption on various reflections was made in a manner described in Appendix I. The conclusion was reached that relative corrections to the observed intensities would not be larger than $\pm$ 5 per cent for hk0 and $\pm$ 7 per cent for h0ℓ. Consequently, the observed intensities were used for calculating structure factors without making corrections for absorption.

Values of the observed structure factor $|F|_{obs}$ were obtained by the following equation, which applies to equatorial reflections:

$$I = S^2 |F|^2_{obs} (1 + \cos^2 2\theta) / \sin 2\theta \qquad (3)$$

where $\underline{I}$ is the intensity, $\underline{\theta}$ is the Bragg angle and $\underline{S}$ is a proportionality constant usually determined from the data. In this work, $\underline{S}$ was estimated by adjusting the values of $|F|_{obs}$ to the same scale as $|F|_{calc}$; this estimation was simultaneous with an estimation of the temperature factor as described below.

2. Calculated Structure Factors

The general expression for the structure factor as given in Zachariasen[14] for crystals with a center of symmetry at the origin of coordinates is:

$$F^{o}_{hk\ell} = \sum_{i} f_i \cos 2\pi (hx_i + ky_i + \ell z_i) \qquad (4)$$

where the summation is carried out over all atoms in the unit cell and accordingly contains twenty-four terms. In this expression, $\underline{f_i}$ is the atomic scattering factor of the ith atom and x_i y_i z_i are parameters, measured in fractions of the corresponding cell edges, describing the location of the ith atom in the unit. This expression assumes that all atoms are stationary; actually, they undergo temperature motion which has an important effect on the X-ray intensities.

Accordingly, in order to calculate structure factors for comparison with $|F|_{obs}$ the following information is necessary: (a) atomic

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(14) Zachariasen, W. H., "Theory of X-ray Diffraction in Crystals," John Wiley and Sons, Inc., New York, N. Y., 1945, p. 99.

scattering factors for potassium, ruthenium, and oxygen, and (b) corrections for the effect of the temperature motion of the atoms in the crystal. Each of these factors will be discussed in the ensuing paragraphs.

a. Atomic scattering factors. The atomic scattering factor f is the factor with which the expression given by J. J. Thomson for the amplitude of the radiation scattered by one free electron must be multiplied to obtain the amplitude of the radiation scattered by the stationary atom under consideration. This scattering factor has been found experimentally to depend not only on the chemical element involved and on the effective interplanar distance or $\sin \theta/\lambda$ value, but also to some extent on the wave-length and on the state of chemical combination. In general, these latter effects are not very great (except when the wave-length of the incident radiation is close to the K-edge of the atom); for each atom or ion a function of $\sin \theta/\lambda$ can be given which usually represents the scattering power to within about two units. This function is obtained from theoretical expressions for the electron distribution in the atom, or empirically from X-ray data from crystals of known structure.

Three independent methods for the calculation of electron distributions in atoms and ions have been developed. Of these the most accurate is that based on Hartree's theory of the self-consistent field.[15] Values calculated by this method together with interpolated

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(15) Hartree, D. R., Proc. Cambridge Phil. Soc., 24, 89, 111 (1928).

values for light atoms and ions are given in a paper by James and Brindley.[16]

The approximate treatment of Thomas[17] and Fermi[18] leads to scattering factors which are usually used for heavy atoms. Pauling and Sherman[19] have calculated f values with the use of hydrogen-like eigenfunctions and suitable screening constants. A comparison of the f values obtained by the different methods suggests that the values for light atoms and ions obtained directly by Hartree's method are accurate to a few tenths of a unit, and that the interpolated values have a somewhat larger possible error.*

The atomic scattering factors for potassium, ruthenium, and oxygen will to some extent, especially for small values of sin θ/λ, depend on the distribution of electrons in their neighborhood. Potassium is doubtless singly positively charged; the Hartree values of f for $K^{\oplus}$ were taken directly from the Tabellen.[20] The distribution of electrons in the perruthenate ion is, in all likelihood,

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*The above three paragraphs have been taken from the Tabellen and are included here for the sake of completeness.

(16) James, R. W., and Brindley, G. W., Phil. Mag., 12, 81 (1932).

(17) Thomas, L. H., Proc. Cambridge Phil. Soc., 23, 542 (1927).

(18) Fermi, E., Z. Physik, 48, 73 (1928).

(19) Pauling, L., and Sherman, J., Z. Krist., 81, 1 (1932).

(20) "International Tables for the Determination of Crystal Structures," Gebruder Borntraeger, Berlin, 1935, p. 571.

intermediate between a pure ionic configuration, $Ru^{+7}(O^{=})_4$, and a pure non-polar distribution $Ru^{-1}O_4$. Values of *f* corresponding to the intermediate distribution $Ru^{+3}(O^{-})_4$ have been used for this work. This choice is consistent with the positions of ruthenium and oxygen in the scale of electronegativities.(21)

Values for O^{-} were obtained by interpolating between the Hartree values for O and $O^{=}$ given in the Tabellen.(22) The atomic scattering factor for Ru^{+3} was derived by modifying the Thomas-Fermi values for Ru^{0} given in the Tabellen(23) so that the value at $\sin \theta/\lambda = 0$ is 41 (corresponding to 41 electrons) and joins smoothly into the Ru^{0} curve at $\sin \theta/\lambda = 0.4$. This behavior is suggested by the Hartree curves for $S^{=}$, S^{0}, and S^{+6}. For values of $\sin \theta/\lambda$ greater than 0.4, the Thomas-Fermi values for Ru^{0} were employed. Corrections of +0.2 and -1.9 for the wave length dependent anomalous scattering by the K-electrons, obtained from Compton and Allison(24) after Hönl,(25) were added to the scattering factors of potassium and ruthenium, respectively. A plot of the scattering factors for ruthenium, potassium, and oxygen is given in Fig. 4 .

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(21) Pauling, L., "Nature of the Chemical Bond," Second Edition, Cornell University Press, Ithaca, N. Y., 1940, p. 65.

(22) "International Tables for the Determination of Crystal Structures," Gebruder Borntraeger, Berlin, 1935, p. 571.

(23) "International Tables for the Determination of Crystal Structures," ibid., p. 572.

(24) Compton, A. H., and Allison, S. K., "X-Rays in Theory and Experiment," Second Edition, Van Nostrand, New York, N. Y., 1935, p. 315.

(25) Hönl, H., Z. Physik, 84, 1 (1933); Ann. Physik 5, 18, 42 (1933).

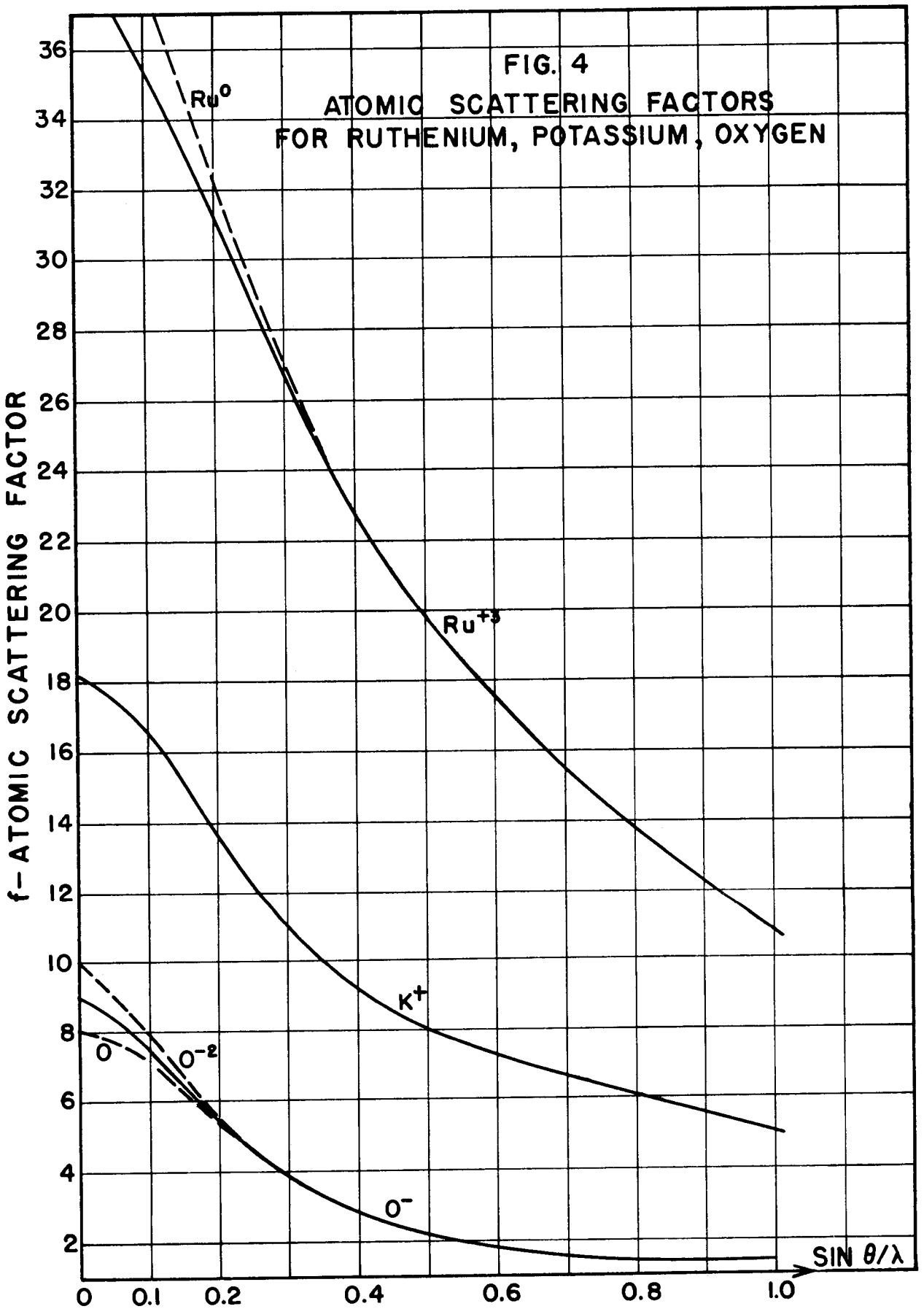
FIG. 4
ATOMIC SCATTERING FACTORS
FOR RUTHENIUM, POTASSIUM, OXYGEN
f- ATOMIC SCATTERING FACTOR
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
0.1
0.2
0.4
0.6
0.8
1.0
SIN θ/λ
Ru⁰
Ru⁺³
K⁺
O
O⁻²
O⁻

b. Temperature factor. The effect of the thermal motion of atoms in crystals is to decrease the amplitude of the scattered radiation and is usually taken into consideration by the use of a temperature-corrected structure factor, F, obtained my multiplying F^o, the structure factor without temperature correction, by the Debye-Waller[26][27] temperature factor in the equation

$$F = F^o \; e^{-B} \left(\frac{\sin \theta}{\lambda}\right)^2 \quad . \qquad (5)$$

The B term in the above equation may be related to the Debye characteristic temperature, Θ. Using the value for sodium chloride of Θ equal to 281°, the Debye-Waller formula gives $B = 1.43 \times 10^{-16}$. Actually separate temperature corrections should be made for the two ions corresponding, according to Waller and James,[28] to $B = 1.55 \times 10^{-16}$ for Na^+ and 1.25×10^{-16} for Cl^-. This example illustrates the approximation involved in using the value of B calculated from the characteristic temperature and a mean atomic mass.

In this work the temperature factor was estimated from the data by use of the following equation; it is very similar to (5) above, with the additional factor S, the scale factor, in order to normalize values of $|F|_{obs}$ with those of $|F|_{calc}$.

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(26) Debye, P., Ann. Physik, 43, 49 (1914).

(27) Waller, I., Z. Physik, 17, 398 (1923); Uppsala Univ. Årsskrift, 1925; Ann. Physik, 83, 153 (1927).

(28) Waller, I., and James, R. W., Proc. Roy. Soc., A 117, 214 (1927).

$$S\left|F\right|_{obs} = \left|F\right|_{calc} \exp - B\left(\frac{\sin\theta}{\lambda}\right)^2 \quad . \tag{6}$$

Rearranging this equation and taking the logarithm of both sides,

$$\log \frac{\left|F\right|_{obs}}{\left|F\right|_{calc}} = -\frac{B}{\lambda^2}\left(\sin^2\theta\right) - \log S \quad . \tag{7}$$

A plot of $\log \frac{\left|F\right|_{obs}}{\left|F\right|_{calc}}$ versus $\sin^2\theta$ should give a straight line whose slope is equal to $-\frac{B}{\lambda^2}$ and an intercept equal to $\frac{1}{S}$.

The values of $\underline{B}$ and $\underline{S}$ were determined several times by comparing the $\left|F\right|_{obs}$ values with those calculated for successively closer models. The final value obtained from hk0 data was $\underline{B}$ equal to 1.76×10^{-16}, and this figure gave fairly good agreement for the hk0 reflections. However, satisfactory agreement using this value of $\underline{B}$ could not be obtained for the h0ℓ reflections.

For these reflections the plot of $\log\left[\left(\left|F\right|_{obs}\right)/\left|F\right|_{calc}\right]$ for parameter values near the final ones tended to define two approximately straight lines characterized by a single intercept but having two distinctly different slopes. One of these was defined by reflections for which h0ℓ is even; the other for which h0ℓ is odd. For the even reflections, potassium and ruthenium scatter X rays in phase, resulting in reinforcement, while in odd reflections the scattering is out of phase, resulting in interference. If different temperature factors are appropriate for potassium and ruthenium, similar to those for sodium chloride discussed above, exactly this behavior is to be expected. Quantitatively, $\underline{F}_{even}$ and $\underline{F}_{odd}$ are given by the following

equations, except for the contribution of the oxygen atoms, which is relatively small:

$$F_{even} \cong f_{Ru} \exp M_{Ru} + f_K \exp M_K \tag{8}$$

and

$$F_{odd} \cong 0.707 \left(f_{Ru} \exp M_{Ru} - f_K \exp M_K\right) , \tag{9}$$

where f_{Ru} and f_K are the atomic scattering factors and exp M the temperature factor with M being equal to $-\frac{B}{\lambda^2}(\sin^2 \theta)$.

Equations (8) and (9) may be rearranged to give

$$\frac{F_{even}}{f_{Ru}} \cong \exp M_{Ru} + \frac{f_K}{f_{Ru}} \exp M_K$$

and

$$1.414 \frac{F_{odd}}{f_{Ru}} \cong \exp M_{Ru} - \frac{f_K}{f_{Ru}} \exp M_K$$

The factor f_K / f_{Ru} is nearly independent of sin θ with the approximate value 0.45. Hence a plot of $|F|_{obs} / f_{Ru}$ should approximately define functions expressible as the sum for even h0ℓ and difference for odd h0ℓ of two exponentials in $\sin^2 \theta$. The sum of these two functions then gives exp M_{Ru} and their difference gives exp M_K. This procedure is similar to that by which Waller and James[29] analyzed the temperature dependence of sodium chloride

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(29) Waller, I., and James, R. W., Proc. Roy. Soc., A 117, 214 (1927).

data. The values of B obtained were 1.61×10^{-16} for ruthenium and 2.28×10^{-16} for potassium. Use of these separate values of B substantially improved the agreement between calculated and observed structure factors for $h0\ell$ and slightly increased the agreement for hk0 reflections.

The difference in B values is reasonable inasmuch as potassium, the lighter atom, should undergo more violent temperature oscillation than the heavier ruthenium. The expected B value for oxygen is not easily estimated; although it is a much lighter atom, which would increase the value of B, it is much more strongly bound, which would tend to decrease B. However, the contribution of oxygen to the structure factor is relatively small and the effect of refinements in its temperature factor is not observable. Therefore the average value of B equal to 1.76×10^{-16} was employed for oxygen.

3. Determination of Parameters

The four ruthenium atoms were placed in fourfold positions at 1/4, 0, 7/8; 1/4, 1/2, 1/8; 3/4, 1/2, 3/8; 3/4, 0, 5/8; and the four potassium atoms at 1/4, 0, 3/8; 1/4, 1/2, 5/8; 3/4, 1/2, 7/8; 3/4, 0, 1/8, these positions corresponding to those listed as (a) and (b) respectively in the Tabellen.* The sixteen oxygen atoms are

*The atomic positions listed in the Tabellen for this space group are based on an origin of coordinates placed at the point of symmetry S_4 which is the position of the ruthenium atom in the structure. The center of symmetry is then described by the coordinates 1/4, 0, 7/8, and corresponding positions. We have chosen to base our working coordinates on an origin at the center of symmetry in order to utilize real expressions for the structure factor expressions. For the final reporting of parameters we have converted our parameters to the system described in the Tabellen.

then placed at x y z; 1/4 - y, 3/4 + x, 3/4 - z; 1/2 - x, $\bar{y}$, z; 1/4 + y, 1/4 - x, 3/4 - z, and those related to these by a center of symmetry at the origin and a body center translation, which are the general positions of the space group corresponding to (f). Inserting these atomic positions in the general expression given in equation (4), simplified expressions for the contribution of potassium, ruthenium, and oxygen can be derived.

a. Determination of x and y. The hk0 data were employed for the determination of x and y. Use was made of the fact that pairs of reflections hk0 and kh0 occur at the same Bragg angle and therefore the same temperature factor and atomic scattering factors apply to both. Furthermore, the contributions of potassium and ruthenium to each reflection of a pair are the same and the differences in $|F|_{obs}$ are entirely due to oxygen contributions. The difference in the observed structure factor therefore directly gives an inequality showing the relative contribution of oxygen to the members of the pair; the sign of F is in every case determined by the contribution of ruthenium which is in a known position, and it must be taken into account in interpreting this inequality.

Each inequality is consistent with a restricted portion of x-y space. In Fig. 5, a map showing the boundaries of these regions is presented. Only that part of the x-y plane with $0 < x < 0.25$ and $0 < y < 0.25$ is included. The remainder of the plane is related by symmetry. It is seen that the only region in which the oxygen contributions are consistent with observed inequalities is included

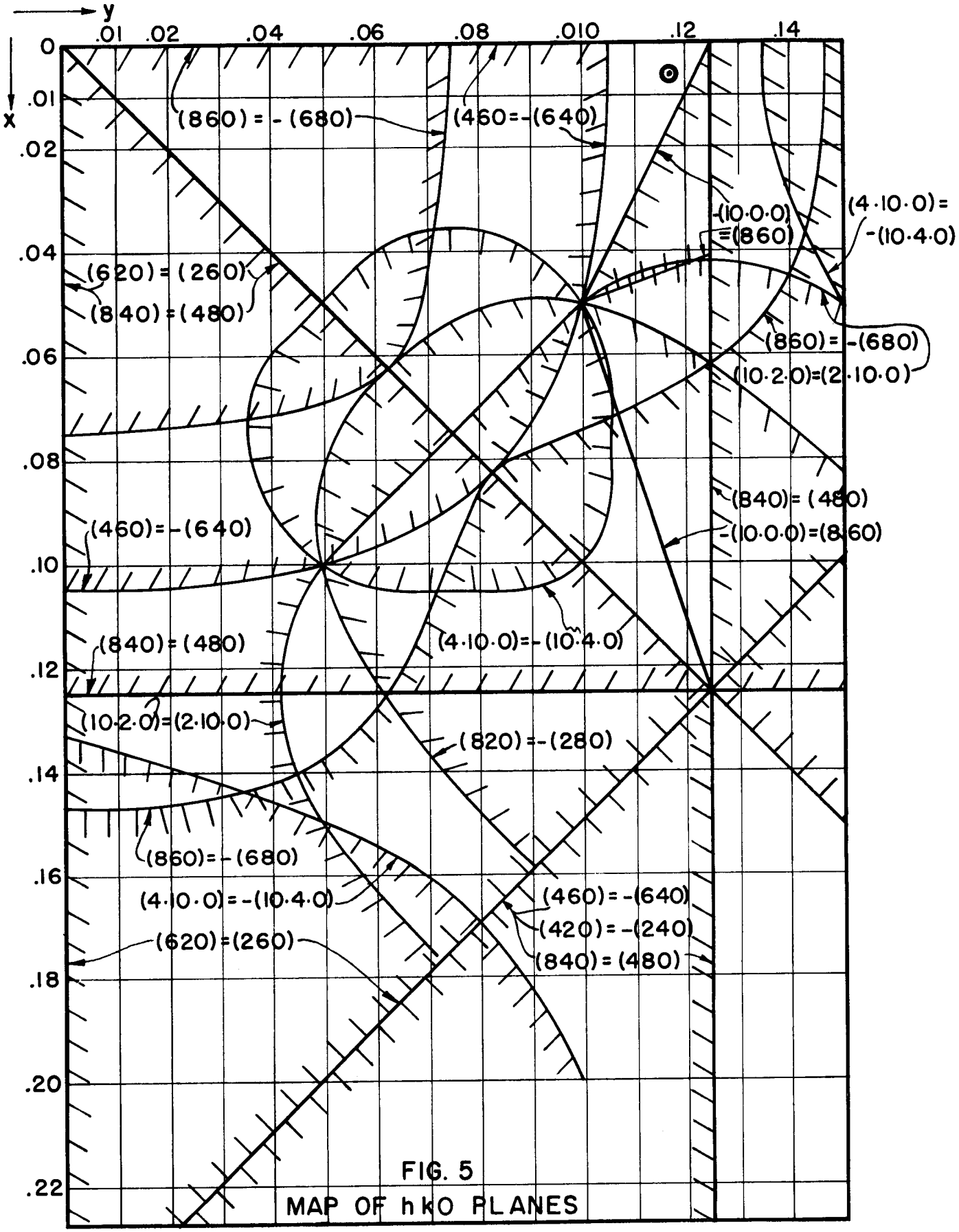

FIG. 5
MAP OF hkO PLANES

⊙ FINAL PARAMETERS x = .006, y = .117

in a rough triangle in the region x from 0 to 0.05 and y from 0.105 to 0.125. The final set of parameters $x = 0.006$, $y = 0.117$ was assigned by computing F_{hk0} for several pairs within this triangle and choosing the one which gave best agreement as indicated by a least squares calculation.[30] The comparison of $|F|_{obs}$ and $|F|_{calc}$ for hk0 is presented in Table II.

Having established the x and y parameters, the determination of the z parameter was carried out by similar methods, using agreement of the $h0\ell$ intensities as the criterion for improvement. The agreement obtained between the calculated and observed structure factors for $z = 0.802$ is shown in Table III.

Described with reference to the coordinate system listed in the Tabellen, the atomic positions are transformed to the following:

Ru at $0, 0, 0;\ 0, \frac{1}{2}, \frac{1}{4};\ \frac{1}{2}, \frac{1}{2}, \frac{1}{2};\ \frac{1}{2}, 0, \frac{3}{4};$

K at $0, 0, \frac{1}{2};\ 0, \frac{1}{2}, \frac{3}{4};\ \frac{1}{2}, \frac{1}{2}, 0;\ \frac{1}{2}, 0, \frac{1}{4};$

O at $x, y, z;\ \bar{x}, \bar{y}, z;\ x, \frac{1}{2} + y, \frac{1}{4} - z;\ \bar{x}, \frac{1}{2} - y, \frac{1}{4} - z;$
$\bar{y}, x, \bar{z};\ y, \bar{x}, \bar{z};\ \bar{y}, \frac{1}{2} + x, \frac{1}{4} + z;\ y, \frac{1}{2} - x, \frac{1}{4} + z,$

and those related by the body center translation. In this system the values of the parameters are

$$x = 0.756, \quad y = 0.117, \quad z = 0.927 .$$

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(30) Hughes, E. W., J. Am. Chem. Soc., 63, 1737 (1941).

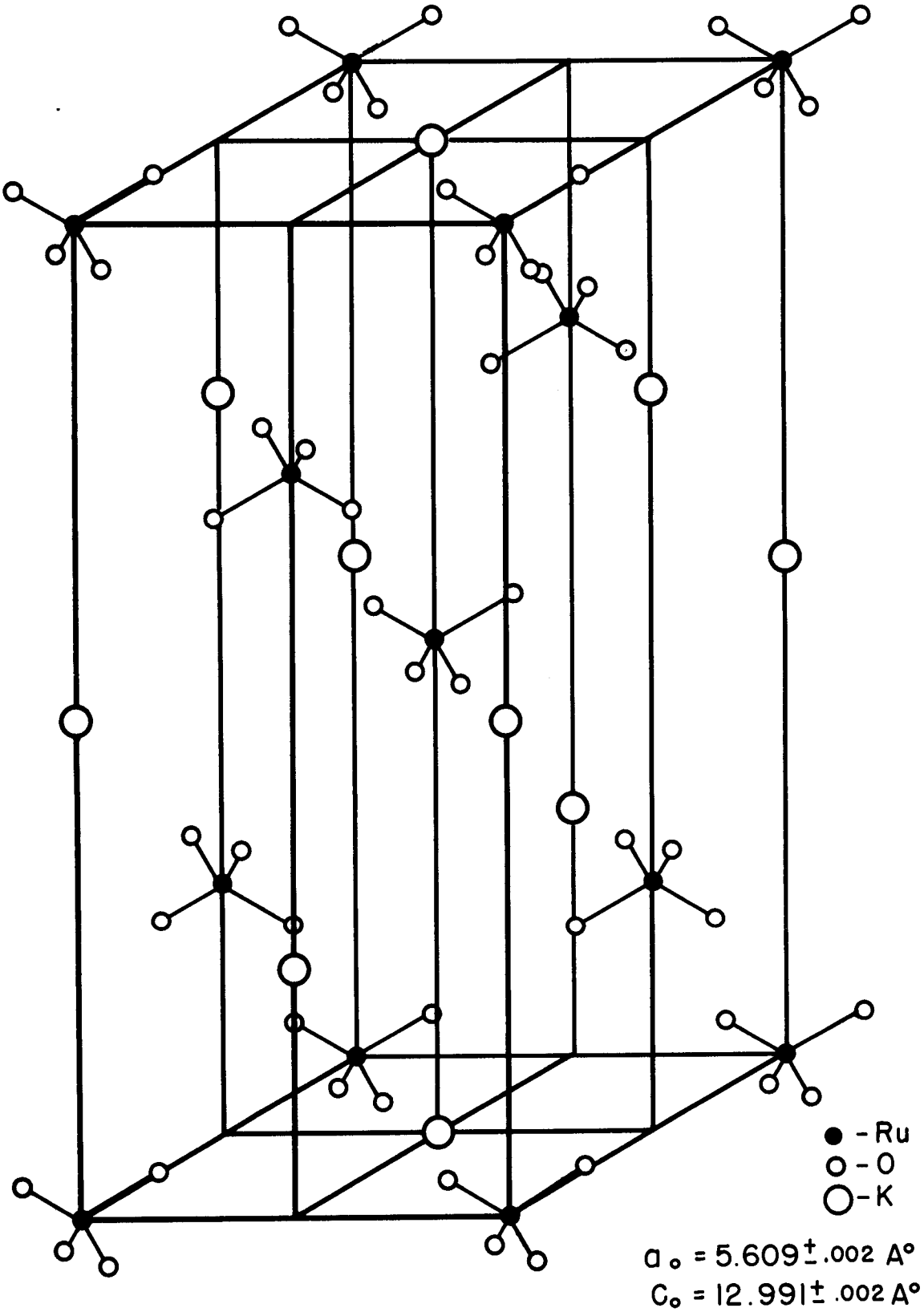

FIG. 6

CRYSTAL STRUCTURE OF $KRuO_4$

TABLE IV

INTERATOMIC DISTANCES AND BOND ANGLES IN $KRuO_4$ AND OTHER ABO_4 COMPOUNDS HAVING THE SCHEELITE STRUCTURE

		Interatomic Distances in A.				
Compound	Bond Angle O-B-O	B-O	A-O	Same Group O-O	Neighboring Group O-O	A-B
$KRuO_4$	106° 18'	1.79	2.75 2.79	2.86 3.04	3.11 3.40	3.97 4.29
KIO_4 (31)	104° 30'	1.80	2.76 2.81			4.07 4.29
$NaIO_4$ (32)		1.792	2.573 2.577		2.67	
$KOsO_3N$ (33)		1.62	3.04 3.07			4.00 4.36
$KCrO_3F$ (34)		1.58	2.80 2.89	2.50 2.62	3.07	

(31) Hylleraas, E., Z. Physik, 39, 308 (1926).

(32) Hazlewood, E. A., Z. Krist., (A) 98, 439 (1938).

(33) Jaeger, F. M., and Zanstra, J. E., Rec. Trav. Chim. Pays-Bas, 51, 1013 (1932).

(34) Ketelaar, J. A. A., and Wegerif, Frl. E., ibid., 57, 1269 (1938).

E. Discussion of the Structure

A diagrammatic sketch of the potassium perruthenate unit cell is shown in Fig. 6. Employing the parameters obtained above, interatomic distances and bond angles may be calculated. These data are given in Table IV, along with those available in the literature for compounds ABO_4 of similar structure.

Four oxygen atoms, at a distance 1.79 A., are coordinated around the very small central ruthenium ions to form the corners of a tetragonal bisphenoid; the latter is very close to a regular tetrahedron slightly compressed in the direction of the c-axis. The Ru-O distance is essentially equal to the I-O distance in KIO_4 and $NaIO_4$ in which iodine is also heptavalent. Apparently the effective radii of Ru^{7+} and I^{7+} are the same in these compounds.

Each potassium ion is surrounded by eight perruthenate ions, four at the corners of a square with K-Ru distances of 3.97 A. and the other four at the corners of a tetrahedron with K-Ru distances of 4.29 A. Similarly, each perruthenate ion is in turn surrounded by eight potassium ions with like coordination. The oxygens, at the corners of two dissimilar interpenetrating tetrahedra, form an eightfold coordination group about each potassium atom, the two K-O distances being 2.75 A. and 2.79 A. Evidently the packing is determined by the potassium-oxygen contacts rather than the oxygen-oxygen contact, since the latter distance is greater than the sum of the Van der Waals radii for oxygen.

Wyckoff[35] gives a calculated ionic radius of 0.60 A. for Ru^{4+}. The magnitude of the correction to Ru^{7+} may be estimated by comparison with the values listed for Mn^{4+} and Mn^{7+} which are 0.52 A. and 0.46 A., respectively; an ionic radius of 0.54 is thus estimated for Ru^{7+}. If the Ru-O bond is purely ionic in character, the expected distance between these atoms should be the sum of the ionic radii, 1.94 A., using the value of 1.40 A. given for $O^{=}$ in Pauling.[36] Since the observed Ru-O distance is 1.79 A., we may conclude that the bond is not ionic. In fact, as has been noted previously, the electronegativity of ruthenium suggests that the bond is largely covalent. No covalent radius for heptavalent ruthenium is available; however, the single-bond radius, 1.24 A., derived by Pauling[37] from the distances in metallic ruthenium, together with that for oxygen, 0.66 A., give the value 1.90 A. Double bond character might reduce the expected distance to about 1.80 A., which is close to that observed. Whether this agreement is significant is a question that must await further evidence.

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(35) Wykoff, R. W. G., "Crystal Structures," Interscience Publishers, Inc., New York, N. Y., Section I, 1948.

(36) Pauling, L., "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., Second Edition, 1940, p. 346.

(37) Pauling, L., J. Am. Chem. Soc., 69, 542 (1947).

CHAPTER III

EQUILIBRIUM AND SPECTROPHOTOMETRIC STUDIES OF UPPER VALENT RUTHENIUM IN BASIC SOLUTION

A. Introduction

In Chapter I it was stated that, for a study of upper valent ruthenium chemistry in aqueous solution, analogies would be drawn to the known chemistry of upper valent manganese. Equilibrium constants have been reported for the disproportionation of manganate to yield permanganate and manganese dioxide; furthermore, potentials have been measured for the manganate, permanganate and permanganate, manganese dioxide couples, respectively. Similar information for ruthenium systems would give a clearer picture of upper valent ruthenium chemistry than is now generally known.

It has been reported(1) that perruthenate ion disproportionates in aqueous medium to give ruthenium tetroxide and ruthenate, along with deposition of ruthenium hydroxide:

$$2KRuO_4 \longrightarrow RuO_4 + K_2RuO_4 \quad .$$

The ruthenate which is formed soon decomposes in the absence of alkali. It is also stated that excess alkali will react with perruthenate to

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(1) Charonnat, R., "Traité de Chimie Minérale," Vol. XI, Masson and Cie, Paris, 1932, p. 399.

yield ruthenate along with evolution of oxygen, a reaction which appears to be completely analogous in the case of manganese:

$$2KRuO_4 + 2KOH \longrightarrow 2K_2RuO_4 + \tfrac{1}{2}O_2 + H_2O \quad .$$

Preliminary tests indicated that ruthenate ion might disproportionate in a manner similar to manganate; therefore a preliminary investigation was undertaken to determine whether equilibrium data could be obtained for systems containing ruthenate, perruthenate, and ruthenium dioxide. Since ruthenium solutions are highly colored, spectrophotometric techniques were frequently employed.

Unfortunately, equilibrium data could not be obtained for the disproportionation of ruthenate; however, valuable qualitative information, largely derived from spectrometric studies to be discussed in a later section, was obtained which made it clear why equilibrium could not be attained in these systems. Because past work on manganese systems served as a guide to the study of upper valent ruthenium chemistry, a review of the pertinent literature on upper valent manganese is being given here.

Sackur and Taegener[2] investigated the conversion of permanganate to manganate in excess alkali and the disproportionation of manganate in water according to the following reactions:

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(2) Sackur, O., and Taegener, W., Z. Electrochem., 18, 718 (1912).

$$2KMnO_4 + 2KOH \longrightarrow 2K_2MnO_4 + \tfrac{1}{2}O_2 + H_2O \qquad (1)$$

$$3K_2MnO_4 + 2H_2O \rightleftharpoons 2KMnO_4 + MnO_2 + 4KOH \qquad (2)$$

Reaction (1) can be expressed as a pair of electrochemical couples:

$$2MnO_4^- + 2e \rightleftharpoons 2MnO_4^{=} \qquad (1a)$$

$$2OH^- - 2e \rightleftharpoons H_2O + \tfrac{1}{2}O_2 \qquad (1b)$$

The potential of the oxygen couple in 1 M. potassium hydroxide (1b) is known to be 0.40 volts. Hence, a measurement of the manganate-permanganate potential can be combined with this value to obtain the equilibrium constant for reaction (1).

Sackur and Taegener employed the following cell and obtained the value 0.61 volts for the manganate-permanganate couple:

$$Pt;\ K_2MnO_4,\ KMnO_{4(1.5\ M.\ KOH)} \,\|\, KOH_{(0.8\ M.)},\ HgO_{(s)};\ Hg_{(l)}$$

The equilibrium constant for reaction (1) was calculated from these data to be 2.8×10^3 and the dissociation pressure of oxygen to be 6×10^{13} atmospheres; reaction (1) is therefore irreversible.

Similarly, reaction (2) may be expressed as the sum of two couples:

$$2MnO_4^{=} \rightleftharpoons 2MnO_4^- + 2e \qquad (2a)$$

and

$$2H_2O + MnO_4^{=} \rightleftharpoons MnO_2 + 4OH^- - 2e \qquad (2b)$$

The potential of (2a) was obtained above; hence it was only necessary to obtain the potential for couple (2b) to calculate the equilibrium constant for reaction (2). For this purpose the following cell was employed:

$$Pt;\ MnO_{2(s)};\ K_2MnO_4 \,\|\, KOH_{(4\text{-}8\ \underline{M}.)},\ HgO_{(s)};\ Hg_{(\ell)} \quad .$$

Sackur and Taegener experienced considerable difficulty in obtaining reproducible potentials for this cell, probably due to the irreversibility of the manganese dioxide electrode; moreover, junction potentials were very high (several hundredths of a volt). They obtained an approximate potential of 0.50 volt for couple (2b). This potential yielded the value 1.4×10^{-4} for the equilibrium constant of equation (2) and a potential of 0.54 volts may be calculated from the above values for the couple $MnO_4^{=}$, MnO_2.

Ruby[3] in 1921 assayed the work of Sackur and Taegener; he concluded that the potential for the manganate-permanganate couple (0.61 volts) was fairly reliable, but that the potential of 0.50 for equation (2b) was only a very rough approximation. Ruby investigated directly the equilibrium given by equation (2), where

$$K = \frac{(MnO_4^{-})^2\ (OH^{-})^4}{(MnO_4^{=})^3} \quad . \qquad (3)$$

After filtering out manganese dioxide, volumetric methods were used for analysis of the species present in solution.

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(3) Ruby, C. E., J. Am. Chem. Soc., 43, 294 (1921).

Experimental errors made in the determination for manganate and permanganate increased the error in the determination for hydroxyl ion because of the analytical method employed. The equilibrium was investigated from both directions; values obtained for the equilibrium constant, starting from the manganate side, varied from 23 to 90, and gave an average of 54.6; on the other hand, those obtained from the opposite direction varied from 16 to 81, with a fortuitously close average of 51.6. Using the overall average value of 53 for the equilibrium constant and the potential of 0.61 volts obtained by Sackur and Taegener for the manganate, permanganate couple, Ruby calculated a potential of 0.66 volts for the manganate, manganese dioxide couple, and a potential of 0.65 volts for the permanganate, manganese dioxide couple.

Several years later, Schlesinger and Siems[4] investigated this equilibrium problem with a novel approach. These authors used a similar reaction to (2) above:

$$3BaMnO_{4(s)} + 2H_2O \rightleftharpoons Ba(MnO_4)_2 + 2Ba(OH)_2 + MnO_2 . \quad (4)$$

Their method is based on the fact that barium manganate is insoluble; hence, errors due to decomposition of permanganate or manganate are avoided, because these ions are in equilibrium with solid barium manganate and its decomposition in solution is compensated by further

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(4) Schlesinger, H. I., and Siems, H. B., J. Am. Chem. Soc., 46, 1965 (1924).

reaction of the solid with water. Schlesinger and Siems employed the following analytical methods for the measurement of the concentration of the three species in solution: (1) barium was determined by a sulfate precipitation; the manganate concentration was then calculated from the solubility product of barium manganate (measured independently); (2) permanganate was measured colorimetrically; and (3), hydroxyl ion was determined by conductimetric titration with standard barium hydroxide after adding excess sulfuric acid to the filtered equilibrium mixture. Schlesinger and Siems obtained values of 10 to 25 for the equilibrium constant of reaction (2); the average of all values was 16.

Andrews and Brown[5] in 1935 investigated the permanganate, manganese dioxide couple. They prepared a manganese dioxide electrode by first dipping platinum foil in manganous nitrate and then heating the foil in nitric and perchloric acids. This foil served as the electrode for the permanganate couple in the following cell:

$$Pt,\ MnO_{2(s)};\ MnO_4^- \ \|\ KOH,\ HgO_{(s)};\ Hg_{(\ell)} \quad .$$

These workers obtained a (IV)-(VII) potential of 0.588 volts from measured cell potentials reproducible to 1 millivolt. Whether or not the couple is reversible is open to question, despite the reproducibility of the potentials and their adherence to the Nernst equation. Employing Schlesinger and Siems' value of K = 16 for the equilibrium

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(5) Andrews, L. V., and Brown, D. J., J. Am. Chem. Soc., 57, 254 (1935).

discussed above, potentials of 0.564 and 0.600 volts were calculated for the manganate, permanganate and manganate, manganese dioxide couples, respectively.

To summarize, it may be noted that a potential for the manganate, permanganate couple and an equilibrium constant for the disproportionation of manganate were obtained. These values were then employed to calculate the potentials for other upper valent manganese couples.

B. Experimental

Attempts were made to attain equilibrium from both directions for the disproportionation of ruthenate according to the following equation:

$$3Na_2RuO_4 + 2H_2O \longrightarrow 2NaRuO_4 + 4NaOH + RuO_2 \quad . \qquad (5)$$

Initially, the approach was from the ruthenate side. Sodium ruthenate solutions were prepared by distilling ruthenium tetroxide into carbonate-free alkaline solutions. To these solutions, water or perchloric acid was added, as the case might be, to adjust the solution to the required pH and ionic strength. The solutions were put into flasks, the latter sealed, and then placed in a thermostat at 25° for five to seven days. The flasks were opened in a carbonate-free atmosphere (dry box), the solutions centrifuged to bring down any ruthenium dioxide and samples were taken for analysis.

Analyses for ruthenate and perruthenate were made in the following manner. A sample of the centrifuged reaction mixture was pipetted into a cold solution of potassium iodide in 2 N. hydrochloric acid. Ruthenium was reduced to the (III) state and the liberated iodine was titrated with 0.01 N. sodium thiosulfate. Total ruthenium was first determined by the thiourea method developed by DeFord.[6] In this method, upper valent ruthenium is reduced to the (IV) state with alcohol; the resulting hydrous oxide precipitate is dissolved in concentrated hydrochloric acid and ruthenium is reduced to the (III) state with potassium iodide. The addition of thiourea yields a stable complex of Ru(III) which can be analyzed for spectrophotometrically. Later, this was supplemented by a spectrophotometric method in which all the ruthenium was brought to the ruthenate (VI) state by pipetting samples of the centrifuged reaction mixture into 1 M. sodium hydroxide containing bromate ion. Readings were taken for ruthenate on the Beckman spectrophotometer at 4650 A. The use of the broad absorption band of ruthenate ion in this wave length region was first suggested as a possible analytical tool by this author;[7] later, Marshall and Rickard[8] developed the analytical method in detail. The pH was

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(6) DeFord, D. D., Dissertation, "The Chemistry of Ruthenium," University of Kansas, Lawrence, Kansas, 1948.

(7) Silverman, M. D., and Swartout, J. A., Atomic Energy Commission Report No. MonN-432, "Quarterly Report of the Chemistry Division, Oak Ridge National Laboratory," September through November, 1947, p. 105.

(8) Marshall, E. D., and Rickard, R. R., Ind. Eng. Chem., Anal. Ed., 22, 795 (1950).

determined by using a Beckman pH meter with a high pH blue glass electrode calibrated against standard buffers. It is estimated that the pH values obtained were accurate to $\pm$ 0.03. Hydroxyl ion activity was calculated from the pH and the dissociation constant of water taken as 10^{-14}.

Attempts to approach equilibrium from the perruthenate side were made in the following manner: Solid potassium perruthenate and ruthenium dioxide were put into carbonate-free alkaline solutions, the flasks sealed and then placed in a thermostat. Ruthenium dioxide was prepared in a manner similar to that employed by Schlesinger and Siems[9] for manganese dioxide, i.e., by neutralizing an alkaline ruthenate solution with carbon dioxide so that ruthenium dioxide forms by disproportionation; the filtered precipitate was washed with water. Potassium perruthenate was prepared by the method described in the previous chapter. The reaction mixtures were handled and analyzed as described above.

The results are given in Tables V and VI, which also summarize the measurements made in attempts to approach equilibrium from either direction. Two columns of figures in each table are listed under the heading "Titre $Na_2S_2O_3$," with subheadings "as ($RuO_4^{=}$)" and "as (RuO_4^{-})"; these figures were calculated by assuming that (a) all of the oxidizing power in the centrifuged solution was due to ruthenate, and (b) that all

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(9) Schlesinger, H. I., and Siems, H. B., J. Am. Chem. Soc., 46, 1965 (1924).

TABLE V

THE ALKALINE DISPROPORTIONATION OF RUTHENATE
(Test for Equilibrium Approached from Ruthenate)

Sample Number	pH	Ionic Strength, Molarity[a]	Conc., Molarity x 10^4		Titre $Na_2S_2O_3$		K (if any)
			OH^-[e]	Total Ru (Thiourea)	As[b] $(RuO_4^=)x10^4$	As[c] $(RuO_4^-)x10^4$	
1	11.00	0.007	10.1	1.61	1.24	0.93	None
13	11.25	.011	17.9	1.82	1.43	1.08	None
14	10.60	.11	3.26	2.72	2.21	1.66	None
6	11.20	.108	20.7	2.93	2.07	1.55	None
11	10.35	.037	2.26	3.41	4.48	3.38	$2.4x10^{-7}$
12	10.90	.037	8.00	2.58	3.05	2.29	$6.1x10^{-10}$
3	11.80	.024	63.5	14.7	10.2	7.65	None
4	11.75	.024	56.7	14.0	9.8	7.35	None
5	12.10	.018	127	13.8[d] 8.9	10.5	7.85	$7.9x10^{-5}$
9	10.95	.20	8.98	31.6	43.8	32.8	None
10	10.80	.26	6.35	31.3	44.5	33.4	None
8	11.96	.40	91.9	50.8	67.7	50.8	None
7	12.20	.21	160	95.8	128	96.5	$2.6x10^{-1}$

[a]The concentration of added sodium perchlorate.

[b,c]The figures in these columns have been obtained by assuming that the entire titre is due to (b) ruthenate; (c) perruthenate.

[d]Two widely different analytical results on duplicate samples.

[e]The values given in this column are activities and not concentrations.

TABLE VI

THE ALKALINE DISPROPORTIONATION OF RUTHENATE
(Test for Equilibrium Approached from Perruthenate)

Sample Number	pH	Conc., Molarity x 10^4		Titre $Na_2S_2O_3$		K[c]
		OH^d	Total Ru (Thiourea)	As[a] $(RuO_4^{=})x10^4$	As[b] $(RuO_4^{-})x10^4$	
5	9.55	0.358	7.0	11.9	8.45	None
6	9.55	0.358	7.75	12.3	9.65	None
1	10.05	1.13	7.32	11.3	9.20	None
2	10.20	1.60	8.11	12.8	8.28	None
3	10.48	3.04	8.28	12.3	8.90	None
4	10.50	3.19	7.59	11.0	9.20	None
7	11.56	3.66	8.75	12.0	9.00	None
8	11.63	4.30	10.33	13.9	10.4	None
9	10.62	4.20	4.15	6.13	4.60	None
10	10.64	4.40	4.43	5.94	4.45	None
11	10.38	2.42	31.4	55.5	41.6	None
12	10.40	2.53	30.4	51.5	38.6	None

[a,b]The figures in these columns have been obtained by assuming that the entire titre is due to (a) ruthenate; (b) perruthenate.

[c]In each case the ionic strength was adjusted to 0.15 M. with sodium perchlorate.

[d]The values given in this column are activities and not concentrations.

of it was due to perruthenate. The analyses for total ruthenium listed in a third column should give values falling intermediate between those calculated for ruthenate and perruthenate if these were the only ruthenium species in the centrifuged solution. However, this was seldom the case; in the few experiments where this occurred, equilibrium constants, as shown in the last column of each table, were calculated by means of the equation

$$K = \frac{(RuO_4^-)^2 (OH^-)^4}{(RuO_4^=)^3} , \qquad (6)$$

where concentrations are employed except for OH^-, for which activity values were used. The four values obtained show too wide a spread to be of any significance. The following facts are noteworthy:

(1) When the reaction proceeded from ruthenate, analyses for total ruthenium by the thiourea method almost always showed more ruthenium present in solution than was consistent with the iodometric titre. This could be accounted for by the presence of colloidal ruthenium dioxide which was not completely centrifuged out of the reaction mixture. This dioxide would dissolve in the hydrochloric acid-potassium iodide solution and thus contribute both to the iodometric titre and to total ruthenium, though more strongly to the latter.

(2) When the reaction proceeded from the perruthenate side of the equation, lower results for total ruthenium were obtained by the thiourea method than were consistent with the iodometric titre on the assumption that ruthenate and perruthenate were the only species present in solution. This could only be accounted for if there were a

higher valent species of ruthenium present in solution, presumably, ruthenium tetroxide. This belief that ruthenium tetroxide was present in the reaction mixture was later verified by spectrophotometric data.

(3) Gas formation was noticed in a number of runs, especially those at the higher pH values. That this gas was oxygen, formed by the following side reaction, was confirmed later by spectrophotometric data.

$$2KRuO_4 + 2KOH \longrightarrow 2K_2RuO_4 + \tfrac{1}{2}O_2 + H_2O \quad .$$

(4) Greater accuracy in the analyses for the various constituents is desirable. The thiourea method for total ruthenium is not infallible and reproducibility is not always easily obtained. Furthermore, errors made in the determination of ruthenate and total ruthenium became additive, since the calculation of the concentration of perruthenate in solution involved both values. The error in determining the hydrogen ion concentration by means of pH measurements to $\pm$ 0.03 gives an error in the OH^- concentration of $\sim$ 7 per cent.

Further work along lines similar to those employed for manganese systems was not continued for several reasons. Initially, it appeared that side reactions occurred at rates that would make it impossible to attain equilibrium data for the disproportionation of ruthenate. The presence of these side reactions was substantiated by spectrophotometric data reported in the next section. No effort was made to prepare an electrode having a surface layer of ruthenium dioxide, as was done in the case of manganese dioxide, for the ruthenium compound is more insoluble and, in addition, is very refractory when prepared at elevated

temperatures. Finally, spectrophotometric data revealed the instability of perruthenate in solution so that no attempt was made to obtain potentials involving this ion by means of thermodynamic cells.

C. Spectrophotometric Studies of Upper Valent Ruthenium Systems

1. Ruthenate

Because solutions of upper valent ruthenium are all highly-colored, it appeared likely that spectrophotometric methods could be employed to advantage in this problem.

Potassium ruthenate solutions were obtained by absorbing gaseous ruthenium tetroxide (whose distillation has been described in the previous chapter), in a 1 M. solution of potassium hydroxide. Confirmation of the valence state was assured by iodometric titration and total ruthenium analyses. The absorption spectrum of ruthenate ion in 1 M. KOH, stable for at least twenty-four hours, was determined with a Beckman spectrophotometer, using a 1 cm. cell and a slit width of 0.02 mm. The first published curve for the absorption spectrum of ruthenate ion in aqueous solution was presented by this author in an earlier report.[10] A more precise plot for this spectrum is given in Fig. 7. Two broad absorption peaks are present in the visible and near

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(10) Silverman, M. D., and Swartout, J. A., Atomic Energy Commission Report No. MonN-432, "Quarterly Report of the Chemistry Division, Oak Ridge National Laboratory," September through November, 1947, p. 105.

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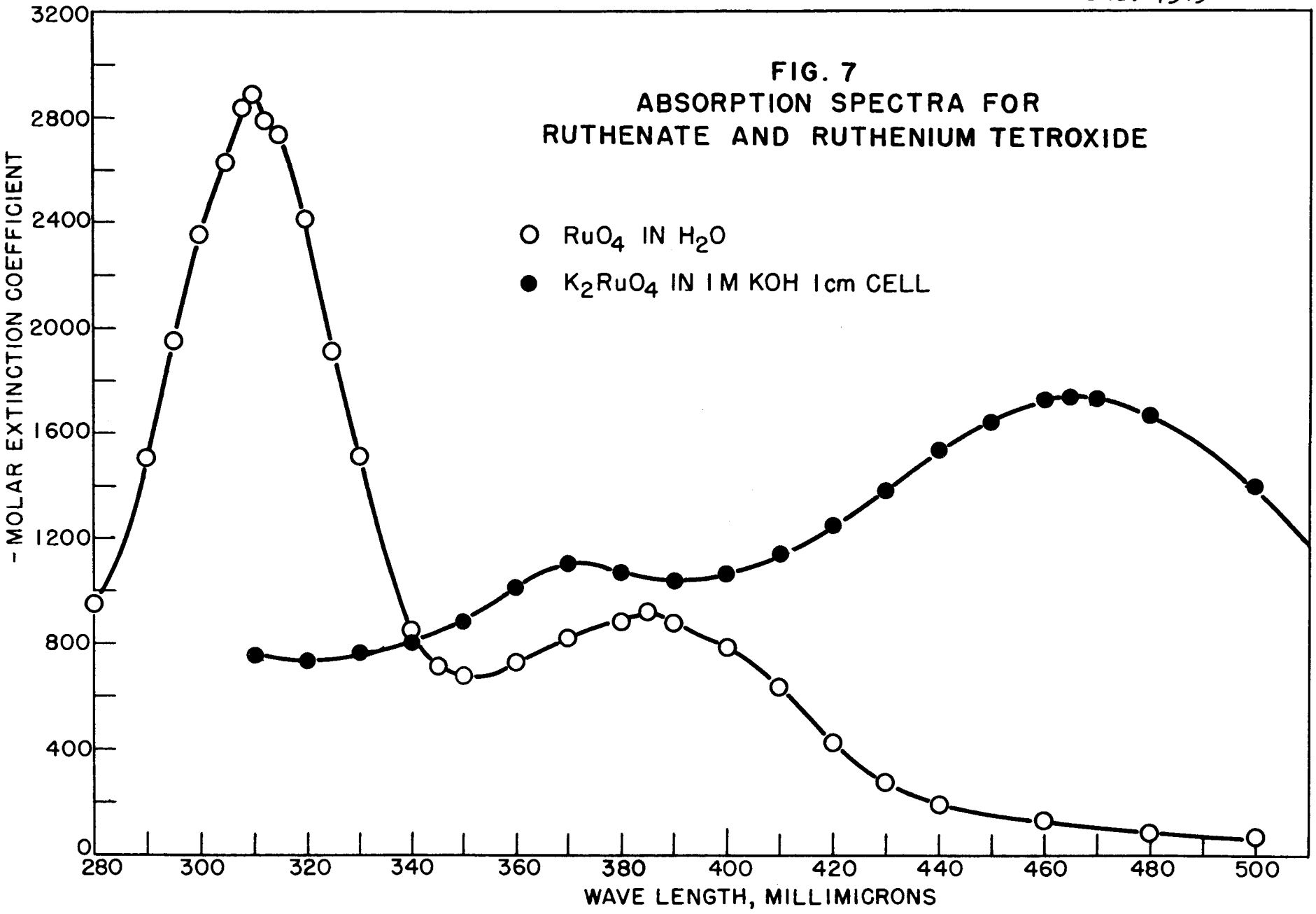

ultra-violet spectrum, a small one with a molar extinction coefficient of ~1100 at 3700 A. and a broad band with a molar extinction coefficient of 1735 at 4650 A. Since this early curve was published, Marshall and Rickard[11] have investigated and verified the use of this broad peak at 4650 A. as a satisfactory analytical method for ruthenium.

Ruthenate solutions are unstable below pH 12; the absorption spectrum of such a solution shows the rapid growth of two absorption peaks in the neighborhood of 3100 A. and 3850 A. The same type of spectra is observed for potassium perruthenate solutions at pH 10.65 (Curve III, Fig. 8). It therefore appears that ruthenate disproportionates to yield ruthenium dioxide and perruthenate which, in turn (as will be shown in the next section), gives rise to ruthenium tetroxide. However, at pH $\leqslant$ 10, the ruthenate peak at 4650 A. completely disappears; a curve similar to that shown in Fig. 7 for pure ruthenium tetroxide is obtained, with one exception: the ratio of the peak height at 3100 A. to that at 3850 A. is lowered to ~1.5 because of continuous absorption in the spectrum by solid ruthenium dioxide.

Some additional experimental observations might be noted here. When ruthenate solutions disproportionate below pH 12, dark greenish-colored solutions characteristic of perruthenate are obtained. These solutions are not stable, but decompose further, depositing ruthenium dioxide and evolving ruthenium tetroxide; the latter may be detected in

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(11) Marshall, E. D., and Rickard, R. R., Anal. Chem., 22, 795 (1950).

very low concentration by its strong ozone-like odor. The rate of decomposition of these solutions appears to be strongly dependent on the pH, increasing rapidly as the pH is lowered.

From the spectrophotometric data and experimental observations, the following reactions appear to take place:

$$3Na_2RuO_4 + 2H_2O \longrightarrow 2NaRuO_4 + 4NaOH + RuO_2 \qquad (7)$$

$$4NaRuO_4 + 2H_2O \longrightarrow 3RuO_4 + RuO_2 + 4NaOH\ . \qquad (8)$$

2. Ruthenium Tetroxide

The absorption spectrum of ruthenium tetroxide in aqueous solution has been examined and is also shown in Fig. 7. The data are quite similar to those obtained by other workers for gaseous ruthenium tetroxide and its solution in carbon tetrachloride.[12][13] Two absorption peaks are present, a small broad peak at 3850 A. with a molar extinction coefficient of 920 and a sharp peak at 3100 A. with a molar extinction coefficient of 2870. The spectrum changed very slowly with time, but this change was due to loss of the volatile tetroxide from solution since the ratio of the peak heights remained the same. These

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(12) Qviller, B., Tidskrift for Kjemi og Bergvesen, 8, 137 (1937).

(13) Krasikov, S. E., Filippov, A. N., and Chernyaev, I. I., Ann. secteur platine Inst. chim. gen. (U.S.S.R.), 13, 19 (1936).

data are in accord with those of Wehner and Hindman[14] who, in addition, determined the spectrum of ruthenium tetroxide in 1 M. and 6 M. perchloric acid. Aqueous solutions of ruthenium tetroxide, whose concentrations were determined by iodometric titration and total ruthenium analyses, were found to obey Beer's law in the approximate concentration range 0.4 to 8.0 x 10^{-4}, as shown by these data:

Molarity x 10^4	Molar Extinction Coefficient 3100 A.	3850 A.
7.62	2860	905
3.05	2885	925
1.84	2870	925
0.795	2870	920
0.381	2860	910

3. Perruthenate

Pure potassium perruthenate was prepared as described in Chapter II and its identity verified by analysis and X-ray diffraction. Therefore, it was possible to start with a pure compound of the (VII) state. However, attempts to obtain a spectrum for pure perruthenate ion were unsuccessful because the spectrum changed rapidly with time. Neutral solutions of potassium perruthenate decompose over a period of several minutes. This decomposition is easily observed, for the dull green

(14) Wehner, P., and Hindman, J. C., Atomic Energy Commission Report No. ANL-4215, "Quarterly Report of the Chemistry Division, Argonne National Laboratory," July through September, 1948.

solution first formed quickly blackens, and particles of hydrous ruthenium dioxide are deposited from solution. Moreover, the odor of ruthenium tetroxide may be detected above the solution.

Further attempts to obtain an absorption spectrum were made by adjusting the pH of the water with carbonate-free potassium hydroxide before dissolving the perruthenate. Spectrophotometric observations in these experiments at various pH values is presented by a plot in Fig. 8, where the nominal molar extinction coefficient is plotted against the wave length in millimicrons. Curves I, II and III were taken on a recording Beckman spectrophotometer, while the other two curves were taken with the standard instrument, using a 1 cm. cell with a slit width of 0.03 mm. All spectra were measured within fifteen minutes after preparing the solutions.

Two absorption peaks are present in Curves I, II, and III (lower pH values), the smaller one at 3850 A. and the larger one at 3130 A. The latter is not completely shown on the graph because the recording instrument was not adjusted to take readings below 3200 A; however, several readings taken below 3200 A. on the standard instrument confirmed this absorption peak. The ratio of these peak heights is of the order of unity, whereas it may be noted that in the case of ruthenium tetroxide, whose spectrum has peaks at the closely similar wave lengths of 3100 A. and 3850 A., the ratio of the peak heights is 3.1.

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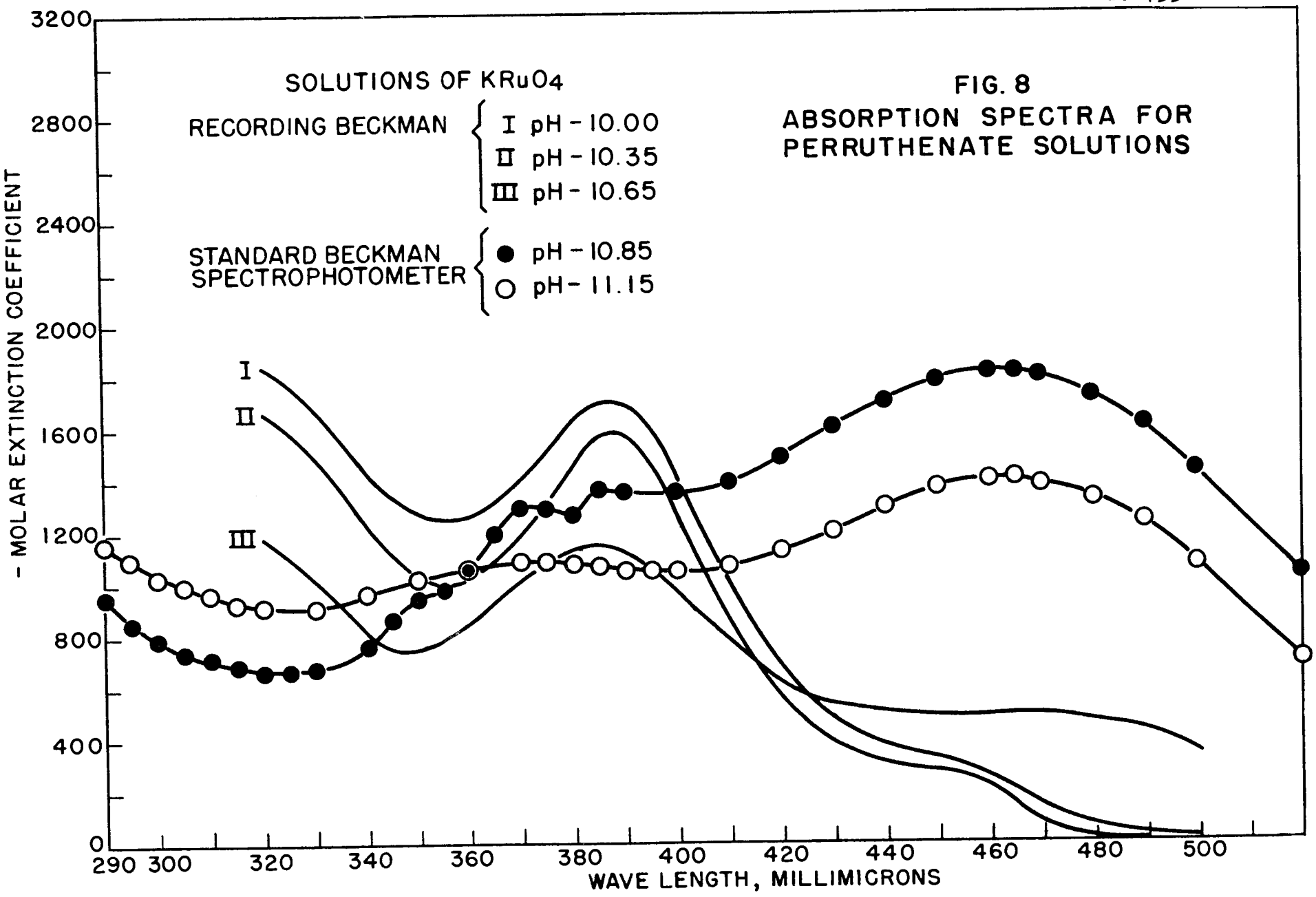

FIG. 8
ABSORPTION SPECTRA FOR PERRUTHENATE SOLUTIONS

It is believed that the absorption at 3130 A. cannot be ascribed to perruthenate for this peak completely disappears at pH 10.85, whereas some absorption is still present in the 3850 A. region. Ruthenium tetroxide may be mainly responsible for the absorption in this region. The high absorption at 3850 A. for Curves I and II cannot be due entirely to ruthenium tetroxide, ruthenate, or a combination of these. A possible and likely explanation is that perruthenate ion has a strong absorption peak at this wave length. Ruthenate ion does not appear to be present in solution at pH 10 and pH 10.35, as indicated in Curves I and II, but the higher absorption in the 4650 A. range in Curve III indicates that ruthenate is starting to form at pH 10.65.

The curves for higher pH in Fig. 8 indicate that conversion of perruthenate to ruthenate is favored by raising the pH of the dissolving solution. The disappearance of the peak at 3130 A. and the shift of the 3850 A. peak to a much lower one at 3700 A. indicate that at pH 11.15 practically no ruthenium (VIII) is present and that most of the perruthenate has been converted to ruthenate. The low ratio of peak heights at 4650 A. and 3700 A. suggests that there is a species that shows weak continuous absorption throughout the spectrum and this is what would be expected if colloidal ruthenium dioxide is present.

At all pH values investigated the spectrum changed with time, this change being in the direction of continuous absorption

characteristic of a colloid. The rapidity of this change increased with decreasing pH.

From the spectrophotometric data, it is believed that, depending on the pH, two competing reactions take place when solid perruthenate dissolves in aqueous solution. These are:

$$4KRuO_4 + 2H_2O \longrightarrow 3RuO_4 + RuO_2 + 4KOH \qquad (8)$$

$$2KRuO_4 + 2KOH \longrightarrow 2K_2RuO_4 + \tfrac{1}{2}O_2 + H_2O \qquad (9)$$

To summarize, at pH < 10, reaction (8) proceeds so rapidly that perruthenate ion is present in solution only for a period of minutes and solid ruthenium dioxide can be visually detected in the solution. In the pH region 10 to 10.65, this reaction takes place more slowly over a period of hours and the dioxide is present as a colloid. At pH $\sim$ 10.65, reaction (9) begins; as the pH is raised above this figure, the reaction proceeds at a much faster rate and the dark-green color of the perruthenate gradually turns to orange, visual evidence of ruthenate ion. However, traces of ruthenium dioxide still appear in the solution upon standing unless the pH is raised above 12. Either reaction (8) still takes place to a slight extent until pH $\sim$ 12 or, as appears more likely, traces of ruthenium dioxide appear due to decomposition of ruthenate.

In view of these spectrophotometric data, it is not surprising that equilibrium data could not be obtained for the disproportionation of ruthenate.

CHAPTER IV

POLAROGRAPHIC STUDIES - OXIDATION POTENTIALS FOR THE UPPER VALENCE STATES OF RUTHENIUM

A. Introduction

Unsuccessful attempts to obtain physical measurements on ruthenium (VI), (VII), and (VIII) systems at equilibrium have been described in the previous chapter. Spectrophotometric studies showed that irreversible side reactions, such as the oxidation of water yielding ruthenium dioxide, occur at rates comparable to the approach to the equilibria of interest. Furthermore, the simultaneous determination of ruthenate, perruthenate, ruthenium tetroxide and ruthenium dioxide in their mixtures, by spectrophotometric methods or others, proved difficult. Consequently, no further attempt was made to obtain equilibrium data, either by electrolytic cells or otherwise. Since the polarograph offers a method for obtaining approximate oxidation potentials in unstable systems where concentrations cannot be measured accurately, work was directed along these lines.

The polarographic method is based on the interpretation of the current-voltage relations that are obtained when solutions of electroreducible or oxidizable substances are electrolyzed. One electrode is made with a small area and operated highly polarized; it often consists of mercury falling dropwise from a very fine bore capillary glass tube. The other electrode, usually the standard reference saturated calomel

electrode, has a large area so that polarization effects are negligible. Automatic instruments are available which register automatically the changes in current observed when the electromotive force is applied between the two electrodes.

The current is usually plotted as the ordinate versus the applied potential. A typical current-voltage curve or polarogram is reproduced in Fig. 9 and is seen to be similar to a typical potentiometric titration curve. The midpoint of both curves represents the characteristic potential of the particular oxidation-reduction system illustrated. However, the conditions under which these curves are obtained are quite different. In the polarographic method the ratio of oxidant to reductant present at the microelectrode interface is altered by means of the electric current, whereas in the potentiometric method the ratio is changed throughout the entire solution by adding a titrating agent. A supporting electrolyte is added to the cell solution in a concentration about one hundred-fold that of the electroactive material so that the latter can reach the electrode surface only by diffusion.

When the reaction occurring at the small electrode is reversible, the potential at any point on the wave is given approximately by the Nernst equation; at 25°

$$E = E_0 - \frac{0.0591}{n} \log \frac{a_{red}}{a_{oxid}} \qquad (1)$$

where a_{oxid} and a_{red} are the activities of the oxidant and reductant, respectively, as they exist at the electrode interface rather than in the body of the solution, E_0 is the standard oxidation potential and

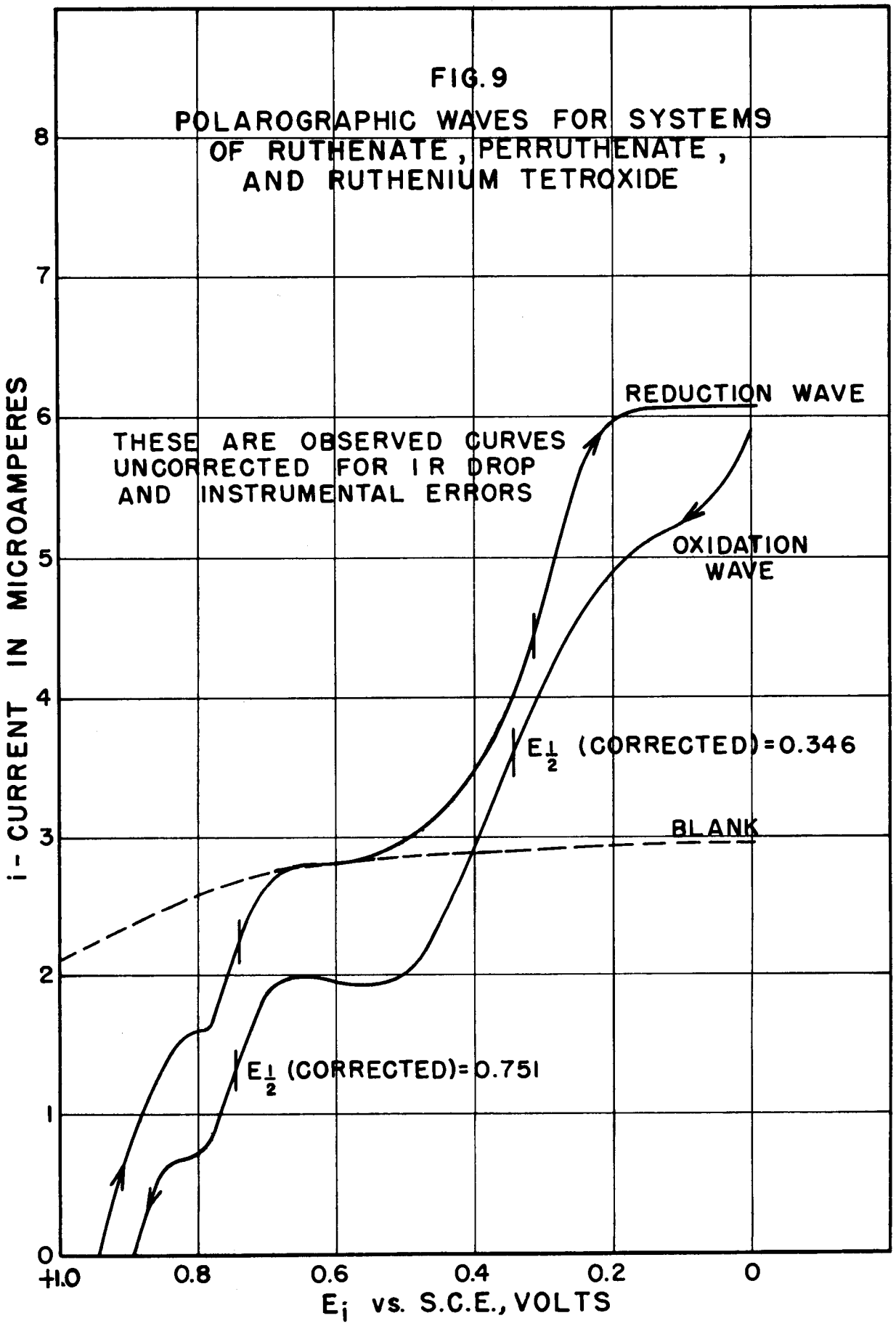
FIG. 9
POLAROGRAPHIC WAVES FOR SYSTEMS OF RUTHENATE, PERRUTHENATE, AND RUTHENIUM TETROXIDE
THESE ARE OBSERVED CURVES UNCORRECTED FOR I R DROP AND INSTRUMENTAL ERRORS
REDUCTION WAVE
OXIDATION WAVE
$E_{\frac{1}{2}}$ (CORRECTED) = 0.346
$E_{\frac{1}{2}}$ (CORRECTED) = 0.751
BLANK
i - CURRENT IN MICROAMPERES
0
1
2
3
4
5
6
7
8
+1.0
0.8
0.6
0.4
0.2
0
E_i vs. S.C.E., VOLTS

$\underline{E}$ is the observed potential. The equation relating $\underline{E}$ to the current $\underline{i}$, whose derivation may be found in Kolthoff and Lingane,[1] is, for a reduction wave:

$$E(i) = E_o - \frac{RT}{nF} \ln \frac{f_{red}\, k_{oxid}}{f_{oxid}\, k_{red}} - \frac{RT}{nF} \ln \frac{i}{i_d - i} \qquad (2)$$

In this equation, $\underline{f}_{oxid}$ and $\underline{f}_{red}$ are the activity coefficients of the oxidized and reduced species, and $\underline{i}_d$ is the asymptotic current approached as the applied potential is increased, the current being then determined by the rate of diffusion of the species being electrolyzed to the electrode (hence the term diffusion current); $\underline{k}_{oxid}$ and $\underline{k}_{red}$ are constants characteristic of the oxidized and reduced species respectively, known as diffusion current constants, and are related to diffusion coefficients. The half-wave potential, $\underline{E}_{\frac{1}{2}}$, is defined as the value of $\underline{E}(i)$ at the midpoint of the wave where $\underline{i} = \frac{i_d}{2}$. The last logarithm term in equation (2) then becomes zero so that

$$E_{\frac{1}{2}} = E_o - \frac{RT}{nF} \ln \frac{f_{red}\, k_{oxid}}{f_{oxid}\, k_{red}} \qquad (3)$$

and at 25°

$$E_{\frac{1}{2}} = E_o - \frac{0.0591}{n} \log \frac{f_{red}\, k_{oxid}}{f_{oxid}\, k_{red}} \quad . \qquad (4)$$

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(1) Kolthoff, I. M., and Lingane, J. J., "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 142.

Hence at any point on the wave,

$$E(i) = E_{\frac{1}{2}} - \frac{0.0591}{n} \log \frac{i}{i_d - i} \qquad (5)$$

This fundamental equation of the polarographic wave was first derived by Heyrovsky and Ilkovic.[2] It is evident from equation (5) that a plot of $E(i)$ versus $\log \frac{i}{i_d - i}$ should produce a straight line with a slope equal to $\frac{0.0591}{n}$ volts at 25°, and the potential where the log term becomes zero should be the half-wave potential. The linearity of this plot and the slope of $\frac{0.059}{n}$ volts serve as a test for the reversibility of the electrode reaction. In the above equations, the signs have been adjusted to conform with the polarographic convention, e.g., positive sign denotes oxidizing power relative to hydrogen ion (opposite to the Latimer[3] convention usually used for reporting oxidation potentials).

The most satisfactory indicator microelectrode for polarographic work is the dropping mercury electrode because it possesses the following advantages: (1) its surface is reproducible, smooth and continually renewed; (2) the current assumes a steady value immediately and is reproducible; and (3) the value of the overvoltage of hydrogen is highest on mercury, about -1.5 volts being required to discharge hydrogen from neutral solution, so that much

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(2) Heyrovsky, J., and Ilkovic, D., Collection Czechoslov. Chem. Communications, 7, 198 (1935).

(3) Latimer, W. M., "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938.

work can be done in acid solutions and at large negative potentials without interference from the evolution of hydrogen.

The dropping mercury electrode can be used in neutral potassium chloride in the approximate range 0.0 to -1.5 volts, versus the saturated calomel electrode; however, when used as an anode mercury readily dissolves. For anodic use, a noble metal is indicated. A smooth platinum electrode has been successful employed both as cathode and anode; it offers a much lower hydrogen over-voltage, the hydrogen coming off at approximately -0.8 volts, but an anodic potential to about +1.0 volt is permissible before oxygen is discharged.

Since the potentials for the upper valence states of ruthenium are in the anodic region, the platinum electrode was used in this investigation. Previous workers have shown that reproducible half-wave potentials and diffusion currents can be obtained with a solid electrode such as platinum or carbon, using either manual or automatic recording methods. The effect of different variables on the results obtained with the automatic recording polarograph using solid electrodes has been studied in some detail by Rogers, Miller, Goodrich and Stehney.[4] Because solid electrodes have not been often used, some of their conclusions are summarized. These workers showed that the size of the electrode does not affect the half-wave potential; however, smaller electrodes are more suitable for higher concentrations of the reducible

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(4) Rogers, L. B., Miller, H. H., Goodrich, R. B., and Stehney, A. F., Ind. Eng. Chem., Anal. Ed., 21, 777 (1949).

ion and vice versa. They noted that the rate of polarization (rate of applied voltage) did not affect the half-wave potential, but faster rates of polarization did produce larger diffusion currents. Although stirring tended to avoid maxima* in the current voltage curve, it markedly decreased the reproducibility of both the half-wave potential and the diffusion current. In the experiments described below, no stirring was employed because of these effects; an even stronger reason for avoiding stirring was the fact that it accelerated the decomposition of ruthenium solutions, as evidenced by discoloration of the solutions and precipitation of the hydrous dioxide.

B. Experimental

1. Procedure

Two oxidation-reduction couples were investigated: the ruthenate-perruthenate couple and the perruthenate-ruthenium tetroxide couple. Each was studied in both oxidation and reduction. In a given experiment, a dilute solution of the appropriate ruthenium species, ruthenate, perruthenate or ruthenium tetroxide, in sodium perchlorate as supporting electrolyte, was placed in the polarographic cell. A double bridge whose arms contained sodium perchlorate of the same concentration, and saturated ammonium chloride, respectively, connected this cell to a

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*The polarographic maximum is the occurrence of an anomalously large current in certain voltage regions. This phenomenon will be discussed in a later section.

saturated calomel half-cell. In terms of the usual notation used to describe electrolytic cells, the two polarographic systems may be shown by the following diagrams:

$$Pt;\ RuO_4^-,\ RuO_4^{=},\ NaClO_{4(0.1\ \underline{M}.)} \Big\| NaClO_{4(0.1\ \underline{M}.)} \Big\| NH_4Cl_{(sat)}$$
$$Hg_2Cl_2,\ KCl,\ Hg;\ Pt$$

$$Pt;\ RuO_4,\ RuO_4^-,\ NaClO_{4(0.1\ \underline{M}.)} \Big\| NaClO_{4(0.1\ \underline{M}.)} \Big\| NH_4Cl_{(sat)}$$
$$Hg_2Cl_2,\ KCl,\ Hg;\ Pt$$

A Sargent automatic polarograph connected to a Brown recorder was used in all these experiments. Each wave was studied under a variety of conditions of pH, ruthenium concentration, and sodium perchlorate concentration.

2. Reagents and Solutions

All chemicals used in the investigation were of reagent grade and all solutions were prepared with water distilled from alkaline potassium permanganate solutions. Sodium perchlorate was adopted as the supporting electrolyte after it was found that chloride ion, a more usual supporting electrolyte, catalyzed the decomposition of ruthenium solutions. The instability of these solutions, as evidenced by darkening of the solution and the formation of solid ruthenium dioxide, was a prime source of difficulty throughout this investigation.

The ruthenium concentration was adjusted by adding any one or a combination of the following to a solution of the desired pH; namely, solid potassium perruthenate, a concentrated solution of potassium ruthenate or a concentrated solution of ruthenium tetroxide. The pH of the mixture was adjusted by adding carbonate-free sodium hydroxide.

To avoid interference due to cathodic reduction of oxygen, the polarographic solutions were de-aerated with tank nitrogen which was first freed of oxygen by passing the gas through a series of four wash bottles, the first three containing an ammoniacal cuprous chloride solution and strips of copper foil, and the fourth wash bottle 6 N. sulfuric acid which removed ammonia from the nitrogen stream. The acid was renewed from time to time to insure complete removal of ammonia.

3. Apparatus

The polarographic cell consisted of a 50-ml. beaker containing the dilute solution of ruthenium in sodium perchlorate. Through one opening of a two-hole rubber stopper a platinum electrode was inserted in the solution; the second opening contained a glass bridge filled with sodium perchlorate which connected the cell solution with a second solution of sodium perchlorate (of the same concentration) in another 50-ml. beaker. A second glass bridge, filled with a mixture of saturated ammonium chloride and agar, connected this latter solution with the saturated calomel half-cell containing potassium chloride. A platinum contact was used for the calomel electrode. This double-

bridged system was used in order to avoid contact between ruthenium solutions and chloride ion. Junction potentials were kept very small (<1 mv.) by using the same concentration of sodium perchlorate in both beakers and the bridge, and saturated ammonium chloride in the second bridge; the specific advantages of this latter material have been demonstrated by Murray and Acree.[5] The platinum electrodes (~ 1 mm. long and 0.03 cm.^{2}) were made by fusing platinum wire into a soft glass tube and making contact in the usual way by filling the tube with mercury. The electrodes were cleaned by dipping them in an alkaline solution of periodic acid.

In order to correct for potential drop across the cell (IR drop), the resistance of the cell was measured before each run with a conductivity bridge, Model RC-1B, made by Industrial Instruments, Inc. The pH was determined with the Beckman pH meter, Model G, using the high pH glass electrode.

All experiments were carried out at room temperature, which was $24.5^{\circ} \pm 0.5^{\circ}$. Closer control of the temperature was not considered necessary for the precision desired in this work.

4. Data

The polarographic data are summarized in Tables VII through X. Tables VII and VIII summarize the data obtained in dilute concentrations of sodium perchlorate (i.e., 0.1 M. and 0.04 M.); Tables IX and X

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(5) Murray, C. N., and Acree, S. F., J. Res. Nat. Bur. Standards, 7, 713 (1931).

summarize earlier data obtained in 3 M. sodium perchlorate. Under the column headed "Solution" are listed the ruthenium compounds which served as starting materials. In all cases, after making up the solution enough time was allowed to elapse so that other species which are stable at the predetermined pH would be present; e.g., when dissolving potassium perruthenate in a solution of pH 10.90, enough time was allowed in order that some of the perruthenate would be converted to ruthenate. Thus, both oxidation and reduction waves could be run on the same system.

In the early part of this investigation, considerable difficulty was experienced in keeping a low IR drop across the two-bridged system. For this reason, 3 M. sodium perchlorate was used in the first bridge, and the earlier data in Tables IX and X were taken at this concentration of supporting electrolyte. Later, when more experience was gained with these systems, it was found that dilute concentrations of sodium perchlorate could be effectively utilized.

The $E_{\frac{1}{2}}$ values listed in the last two columns of each table are the observed half-wave potentials (versus hydrogen) corrected for instrumental errors and IR drop. Unless considerable decomposition of the solution had already occurred, oxidation and reduction were run on the same system, using the same electrode. It may be noted that in Tables IX and X, which are earlier data, this occurrence was often the reason why only a single wave was obtained; hence one $E_{\frac{1}{2}}$ value is reported. The average half-wave potentials obtained are summarized in Table XI.

TABLE VII

POLAROGRAPHIC POTENTIALS FOR THE RUTHENATE, PERRUTHENATE COUPLE

μ = 0.1 M. ($NaClO_4$)

Run	Solution[a]	pH	$E_{\frac{1}{2}}$ in Volts Oxidation Wave	Reduction Wave
M-1	$KRuO_4$	12.1	0.607	-
M-8	$KRuO_4$	11.9	-	0.619
M-9	$KRuO_4$	11.2	.607	.623
M-10	RuO_4 + $KRuO_4$	11.0	.590	.602
M-11	$KRuO_4$	10.8	.574	.602
M-13	$KRuO_4$	10.8	.592	-
M-14	$KRuO_4$	10.7	.592	.615
M-16	$KRuO_4$	10.6	.601	.620
M-17	$KRuO_4$	10.6	.603	.617
M-18	$KRuO_4$	10.6	.598	.606
M-19	RuO_4 + K_2RuO_4	11.0	.620	.558
M-20	RuO_4 + K_2RuO_4	10.6	.610	.636
M-21	RuO_4 + K_2RuO_4	10.8	.603	.583
M-22	RuO_4 + K_2RuO_4	10.5	.601	.619
M-23	RuO_4 + K_2RuO_4	11.0	.594	.592
M-24	RuO_4 + K_2RuO_4	9.5	-	.593
M-25	RuO_4 + $KRuO_4$	9.0	-	.620
M-26	RuO_4 + $KRuO_4$	11.6	.629	.575
Average			.604	.607
		μ = 0.04 M. ($NaClO_4$)		
N-1	$KRuO_4$	10.8	.592	.583
N-2	RuO_4 + $KRuO_4$	9.0	.596	.608
N-3	RuO_4 + $KRuO_4$	10.7	.598	.619
N-4	$KRuO_4$	10.6	.599	.609
N-5	$KRuO_4$	10.3	.581	.609
Average			.594	.605

[a]The compounds listed in column were the starting materials; in almost all cases both Ru(VI) and Ru(VII) species were present in solution when the potential was applied. The ruthenium concentration varied from 10^{-4} to 10^{-3}.

TABLE VIII

POLAROGRAPHIC POTENTIALS FOR THE
PERRUTHENATE, RUTHENIUM TETROXIDE COUPLE

Run	Solution[a]	pH	$E_{\frac{1}{2}}$ in Volts Oxidation Wave	Reduction Wave
		μ = 0.1 M. ($NaClO_4$)		
M-1	$KRuO_4$	12.1	0.973	-
M-2	$KRuO_4$	12.0	0.966	-
M-3	$KRuO_4$	12.0	1.016	-
M-8	$KRuO_4$	11.9	-	1.011
M-10	RuO_4 + $KRuO_4$	11.0	-	1.015
M-11	$KRuO_4$	10.8	-	1.025
M-14	$KRuO_4$	10.7	1.005	1.000
M-16	$KRuO_4$	10.6	1.007	1.005
M-17	$KRuO_4$	10.6	1.024	1.012
M-18	$KRuO_4$	10.6	0.998	0.998
M-19	RuO_4 + K_2RuO_4	11.0	1.009	1.008
M-20	RuO_4 + K_2RuO_4	10.6	1.002	1.008
M-21	RuO_4 + K_2RuO_4	10.8	0.989	1.034
M-22	RuO_4 + K_2RuO_4	10.5	1.002	1.005
M-23	RuO_4 + K_2RuO_4	11.0	1.000	0.997
M-24	RuO_4 + K_2RuO_4	9.5	1.016	0.998
M-25	RuO_4 + $KRuO_4$	9.0	1.003	0.986
M-26	RuO_4 + $KRuO_4$	11.6	1.006	-
Average			1.001	1.005
		μ = 0.04 M. ($NaClO_4$)		
N-1	$KRuO_4$	10.8	1.000	1.025
N-2	RuO_4 + $KRuO_4$	9.0	1.007	1.018
N-3	RuO_4 + $KRuO_4$	10.7	1.002	1.003
N-4	$KRuO_4$	10.6	0.998	-
N-5	$KRuO_4$	10.3	1.006	1.008
Average			1.003	1.010

[a]The compounds listed in this column were the starting materials; in almost all cases both Ru(VII) and Ru(VIII) species were present in solution when the potential was applied. The ruthenium concentration varied from 10^{-4} to 10^{-3}.

TABLE IX

POLAROGRAPHIC POTENTIALS FOR THE
RUTHENATE, PERRUTHENATE COUPLE

μ = 3.0 M. ($NaClO_4$)

Run	Solution[a]	pH	$E_{\frac{1}{2}}$ in Volts Oxidation Wave	Reduction Wave
F-9	$KRuO_4$	10.5	-	0.619
F-10	$KRuO_4$	10.9	0.577	-
F-11	$KRuO_4$	10.2	.589	-
F-13	$KRuO_4$	10.9	.583	-
F-14	$KRuO_4$	10.2	-	.600
F-15	$KRuO_4$	10.8	.579	-
F-17	$KRuO_4$	10.2	.589	-
F-18	$KRuO_4$	10.5	-	.575
F-22	$KRuO_4$	10.2	-	.577
H-1	RuO_4	11.6	-	.634
H-4	RuO_4	11.6	-	.613
H-5	RuO_4	11.3	-	.620
I-4	Na_2RuO_4	11.5	.583	-
I-6	Na_2RuO_4	11.5	-	.564
I-9	Na_2RuO_4	>12	.597	-
J-1,2	RuO_4	11.2	.620	.607
J-5	RuO_4	11.0	-	.606
J-6,7	RuO_4	11.2	.602	.597
L-1	$KRuO_4$	11.2	.614	-
L-2	$KRuO_4$	10.9	.601	-
L-3	$KRuO_4$	10.9	-	.625
L-4	$KRuO_4$	10.8	-	.579
L-5,6	$KRuO_4$	11.0	.609	.589
Average			.595	.600

[a]The compounds in this column were the starting materials; in most cases the solutions were not stable long enough to run both oxidation and reduction waves on the same sample. The ruthenium concentration varied from 10^{-4} to 10^{-3}.

TABLE X

POLAROGRAPHIC POTENTIALS FOR THE
PERRUTHENATE, RUTHENIUM TETROXIDE COUPLE

$\mu = 3.0\ \underline{M}\ (NaClO_4)$

Run	Solution[a]	pH	$E_{\frac{1}{2}}$ in Volts Oxidation Wave	Reduction Wave
F-9	$KRuO_4$	10.5	-	0.994
F-13	$KRuO_4$	10.9	1.007	-
F-15	$KRuO_4$	10.8	0.983	-
F-16	$KRuO_4$	10.9	0.980	-
G-3	RuO_4	12.0	-	0.956
H-2	RuO_4	11.3	-	0.997
H-4	RuO_4	11.6	-	0.987
H-5	RuO_4	11.3	-	0.976
I-2	$KRuO_4$	11.0	1.019	-
I-4	Na_2RuO_4	11.5	0.948	-
J-1	RuO_4	11.2	0.952	-
J-5	RuO_4	11.0	-	0.986
K-1	Na_2RuO_4	-	-	1.001
L-3	$KRuO_4$	10.9	-	0.996
L-4	$KRuO_4$	10.8	-	0.966
L-6	$KRuO_4$	11.0	0.959	-
Average			0.978	0.984

[a]The compounds in this column were the starting materials; in most cases the solutions were not stable long enough to run both oxidation and reduction waves on the same sample. The ruthenium concentration varied from 10^{-4} to 10^{-3}.

TABLE XI

SUMMARY OF POLAROGRAPHIC POTENTIALS

Conc. $NaClO_4$	$E_{\frac{1}{2}}$ in Volts Ru(VI), Ru(VII)	Ru(VII), Ru(VIII)
0.04 M.	0.60 ± 0.02	1.01 ± 0.02
0.10 M.	0.61 ± 0.02	1.00 ± 0.02
3.0 M.	0.60 ± 0.03	0.98 ± 0.03

C. Discussion

The half-wave potential $E_{\frac{1}{2}}$ observed in these experiments is related to the thermodynamic potential E_o by equation (3), given earlier in this chapter. At the half-wave point, the concentration of oxidized species multiplied by the diffusion current constant k_{oxid} for that species is equal to the corresponding product for the reduced species. Thus the half-wave potential is closely related to the formal potential E_o° characteristic of equal concentrations of oxidized and reduced species:

$$E_o^{\circ} = E_{\frac{1}{2}} - \frac{0.059}{n} \log \frac{k_{red}}{k_{oxid}} , \qquad (6)$$

and in fact, the two are equal if the ratio k_{red}/k_{oxid} is unity. This has often been found true when the oxidized and reduced species are structurally similar even though differing in charge, as for example in the case of UO_2^{++} and UO_2^{+},[6] and $Fe(CN)_6^{\equiv}$, $Fe(CN)_6^{\equiv}$.[7] In any case the effect of this term on E_o° is small. In what follows, the term involving this ratio will be neglected, so that $E_{\frac{1}{2}}$ will be directly interpreted as E_o°.

Polarographic maxima (mentioned earlier) were observed intermittently during this investigation. This phenomenon was frequently noted when oxidation waves were run on high pH (near 12) solutions containing mainly ruthenate. The common practice of introducing

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(6) Kraus, K. A., Private Communication.

(7) Kolthoff, I. M., and Lingane, J. J., "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 436.

suppressing agents, which are usually organic materials, could not be employed in this work because upper valent systems of ruthenium are easily reduced to ruthenium dioxide. Maxima occurred very infrequently during reduction runs. Kolthoff and Lingane[8] have discussed maxima in some detail; they state that the height of a maximum of a given electroreducible substance is greatly dependent upon its concentration, but that there appears to be no simple relation between them. Rogers and coworkers [9] also, in their investigations with silver using the stationary platinum electrode, could not reach any conclusions regarding the effect of concentration on maxima. The rounded maxima obtained (similar to those observed in this work) were, in their belief, primarily due to the time lag in reaching a state of diffusion equilibrium. In this investigation, whenever large maxima were obtained the data were discarded; in other cases, the current plateau was evaluated from the measurements beyond the maximum.

It should be noted that the values obtained for the half-wave potentials for the ruthenate-perruthenate and perruthenate-ruthenium tetroxide couples are independent of the pH of the cell solution. This is to be expected in the case of the former couple, where the couple involves no hydrolysis of either species:

$$RuO_4^- + e \rightleftharpoons RuO_4^{=} .$$

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(8) Kolthoff, I. M., and Lingane, J. J., "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 124.

(9) Rogers, L. B., Miller, H. H., Goodrich, R. B., and Stehney, A. F., Ind. Eng. Chem., Anal. Ed., 21, 777 (1949).

The fact that this is also noted in the case of the other couple is verification for the belief that ruthenium tetroxide is largely present in solution as a neutral species. The acid ionization constant value of 1.3×10^{-12} for the tetroxide (discussed in the following chapter) substantiates this view.

The reproducibility of the data is in accord with that reported by Rogers and coworkers[10] for the solid platinum electrode. Although the instrumental limits of accuracy were less than $\pm$ 0.01 volt, the limits of reproducibility of the experimental measurements were somewhat wider; therefore the potentials are reported in Table XI. as being accurate to $\pm$ 0.02 volt. However, they are reported to be accurate to $\pm$ 0.03 volt in 3 M. sodium perchlorate because these earlier data are believed to be not as reliable for reasons already discussed.

The two criteria for the reversibility of a polarographic couple are: (1) the shape of the wave obtained, so that a plot of $\log \frac{i}{i_d - i}$ versus E(i) gives a straight line whose reciprocal slope is 0.059/n volts where n is the number of electrons involved in the reaction; and (2), that the value for the half-wave potential obtained from a cathodic wave be the same as that obtained from an anodic wave. Within the limits of experimental error, a large number of runs satisfy this latter condition. Moreover, the first

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(10) Rogers, L. B., Miller, H. H., Goodrich, R. B., and Stehney, A. F., Ind. Eng. Chem., Anal. Ed., 21, 777 (1949).

criterion is also fairly well satisfied as shown by the plot in Fig. 10. Values of 0.051, 0.050, and 0.048 volts are obtained for the reciprocal slope of the three lines given in this plot. These differ somewhat from the theoretical slope of 0.059 volts, but are in accord with the experience of other workers who have studied the solid platinum electrode.[11]

The relationship between the standard thermodynamic potential E_o and the formal potential E_o° is

$$E_o = E_o^{\circ} + \frac{0.059}{n} \log \frac{f_{red}}{f_{oxid}} \quad . \qquad (7)$$

Hence, for the calculation of E_o, some estimation must be made for the activity coefficients of the oxidized and reduced species. For this purpose, the modified form of the Debye-Huckel limiting law for individual ions

$$- \log f = \frac{0.509\ z^2 \sqrt{\mu}}{1 + 2\sqrt{\mu}}$$

will be employed, since there are no experimental data for ruthenate and perruthenate solutions which can be used. Using this expression, the following activity coefficients may be calculated for ruthenate and perruthenate:

	Activity Coefficient	
Species	$\mu = 0.04$	$\mu = 0.1$
RuO_4^-	0.845	0.796
$RuO_4^=$	0.489	0.404

(11) Rogers, L. B., Private Communication.

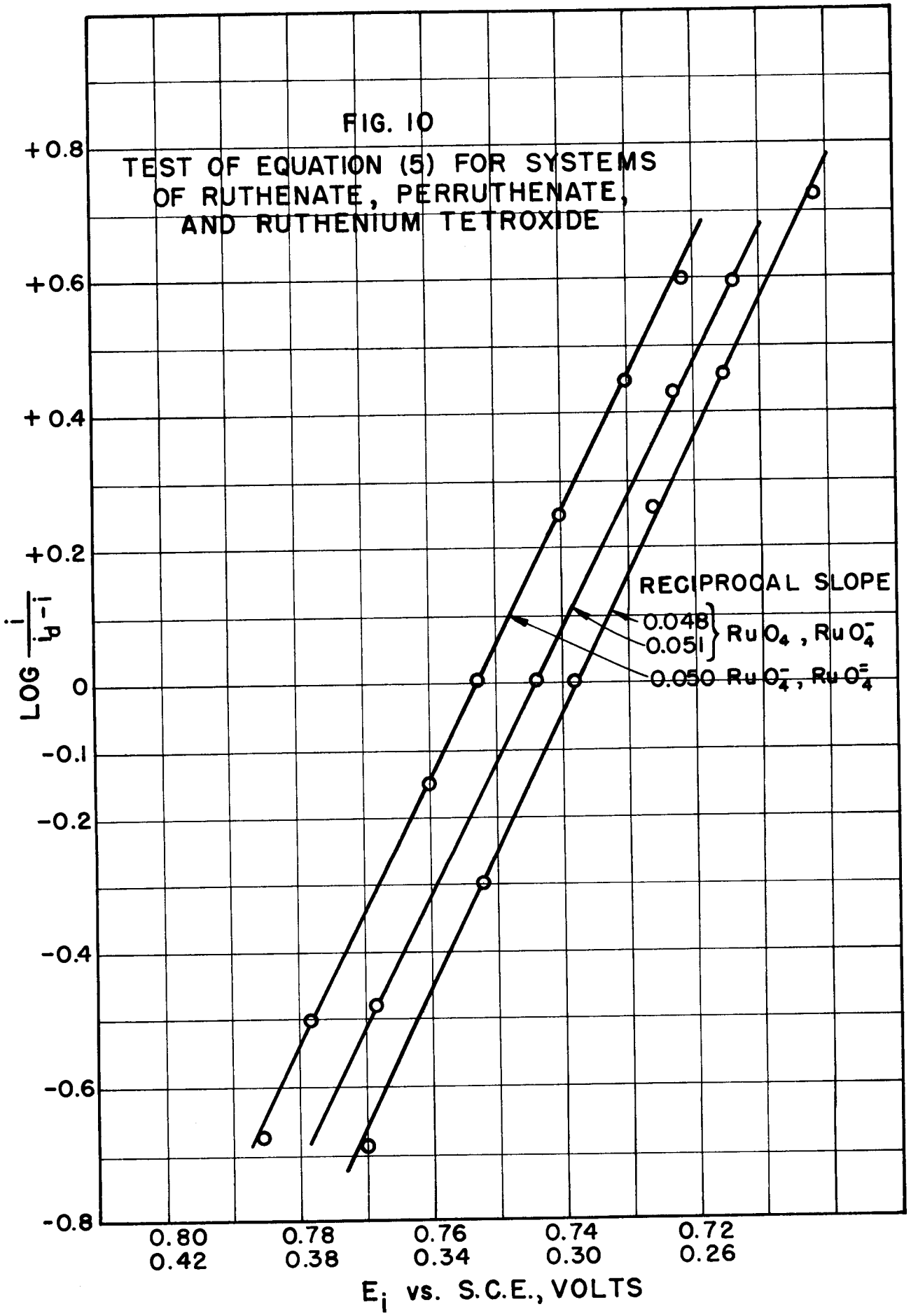
FIG. 10
TEST OF EQUATION (5) FOR SYSTEMS OF RUTHENATE, PERRUTHENATE, AND RUTHENIUM TETROXIDE
RECIPROCAL SLOPE
0.048
0.051
RuO4 , RuO4-
0.050 RuO4-, RuO4=
+0.8
+0.6
+0.4
+0.2
0
-0.1
-0.2
-0.4
-0.6
-0.8
LOG i/(i_d - i)
0.80
0.42
0.78
0.38
0.76
0.34
0.74
0.30
0.72
0.26
Ei vs. S.C.E., VOLTS

The activity coefficient of ruthenium tetroxide is taken as unity, since this species is uncharged.

Employing these values for the activity coefficients at the appropriate ionic strength, and using the average values of E_o° ($\cong E_{\frac{1}{2}}$) given in Table XI, the following potentials, in volts, are obtained.

Couple	$\mu \cong 0.04$		$\mu \cong 0.1$	
	E_o°	E_o	E_o°	E_o
Ruthenate-perruthenate	0.60	0.59	0.61	0.59
Perruthenate-ruthenium tetroxide	1.01	1.00	1.00	1.00

These values are in very good agreement with the values of 0.60 and 1.0 volts predicted by Latimer[12] for these couples.

With these data we may compute the equilibrium constant, K, for the following reactions:

	K	$p(O_2)$ atm.
$2RuO_4 + 2KOH \longrightarrow 2KRuO_4 + \frac{1}{2}O_2 + H_2O$	1.3×10^{10}	1.7×10^{20}
$2KRuO_4 + 2KOH \longrightarrow 2K_2RuO_4 + \frac{1}{2}O_2 + H_2O$	1.4×10^{3}	2.0×10^{6}
$RuO_4 + 2KOH \longrightarrow K_2RuO_4 + \frac{1}{2}O_2 + H_2O$	4.5×10^{6}	2.0×10^{13}
$2KRuO_4 \longrightarrow K_2RuO_4 + RuO_4$	1×10^{-7}	

The values obtained for the dissociation pressure of oxygen, $p(O_2)$, (when all other components are at unit activity), indicate that the first three reactions listed are irreversible.

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(12) Latimer, W., "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., p.216.

The value obtained for $\underline{K}$ in the last reaction indicates that this reaction will not take place to an appreciable extent; this is in accord with the deductions made from spectrophotometric data in the last chapter, and in contrast to previous information given in the literature.[13]

To complete the picture for all upper valent ruthenium potentials, a value of the potential for the ruthenate, ruthenium dioxide couple is needed. Attempts were made to obtain this potential at various pH and ruthenate concentrations by polarographic examination of the following couple:

$$RuO_4^{=} + 2H_2O + 2e \longrightarrow RuO_2 + 4OH^- \quad .$$

The half-wave potential in reduction showed proper dependence on pH but not on ruthenate concentration; furthermore, the shape of the wave and a plot of $\underline{E}(i)$ versus $\log \frac{i}{i_d - i}$ were not indicative of a reversible couple. Oxidation waves could not be obtained because of the insolubility of ruthenium dioxide. It is therefore concluded that the ruthenate, ruthenium dioxide couple is irreversible.

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(13) Charonnat, R., "Traité de Chimie Minérale," Vol. XI, Masson and Cie, Paris, 1932, p. 399.

CHAPTER V

THE ACID IONIZATION CONSTANT OF RUTHENIUM TETROXIDE

A. Introduction

In the chapter on polarographic studies, a potential was obtained for the perruthenate-ruthenium tetroxide couple. This potential was found to be independent of the pH of the solution, indicating that the (VIII) state is essentially neutral within the pH limits (9-11) employed. Except for this evidence, the nature of the species present in ruthenium tetroxide solutions has never been ascertained. Using water whose specific conductance was 2.7×10^{-6}, Krauss[1] obtained values of 16.6 to 69.1×10^{-6} for the specific conductance of a 0.007 M. solution of ruthenium tetroxide; the conductivity measurements involved experimental difficulties and Krauss stated that the data obtained afford little information as to the state of the oxide in aqueous solution. Krauss[2] claimed to have prepared a salt of ruthenium (VIII), the compound $(NH_4)_2RuO_5$, from the reaction of the tetroxide with concentrated ammonia; however, Trenkner[3]

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(1) Krauss, F., Z. anorg. allgem. Chem., 131, 348 (1923).

(2) Krauss, F., ibid., 119, 217 (1921).

(3) Trenkner, K., Dissertation, "Neue Untersuchungen über das Ruthenium," Erlangen, 1905.

characterized the compound he obtained using the same procedure as one of ruthenium (IV) having the composition $RuO(OH)_2 \cdot 2NH_3 \cdot 2H_2O$. Remy[4] measured the solubility of the tetroxide in water over the temperature range 0° to 75°. The solubility rises until the melting point (25°) is reached; it then falls, passes through a minimum at about 40°, and then rises slowly. Remy claimed this indicates that a chemical reaction occurs between ruthenium tetroxide and water; however, Charonnat[5] states that the shape of the curve (solubility plotted against temperature) corresponds to the reciprocal miscibility of two liquids having a critical point and that it does not demonstrate the existence of a hydrate.

Hofmann, Ehrhart and Schneider,[6] using water whose conductance was 5×10^{-6}, obtained a value of 10.9×10^{-6} for the specific conductance of a 0.04 M. solution of osmium tetroxide. Tschugaeff[7] succeeded in obtaining a well-defined series of compounds of the following types:

$OsO_4 \cdot 2KOH$,	$OsO_4 \cdot RbOH$,	$OsO_4 \cdot CsOH$,	$2OsO_4 \cdot CsOH$
$(K_2H_2OsO_6)$	$(RbHOsO_5)$	$(CsHOsO_5)$	$(CsHOs_2O_9)$

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(4) Remy, H., Angew. Chem., 39, 1061 (1926).

(5) Charonnat, R., "Traité de Chimie Minérale," Vol. XI, Masson and Cie, Paris, 1932, p. 397.

(6) Hofmann, K. A., Ehrhart, O., and Schneider, O., Ber., 46, 1657 (1913).

(7) Tschugaeff, L., Compt. rend., 167, 162 (1918).

These compounds, formed by the addition of a very concentrated solution of the alkali to a saturated solution of osmium tetroxide, are clearly crystalline and are orange or brown in color. They are strongly hydrolyzed in aqueous solution and can be titrated with a mineral acid using methyl orange as an indicator. Tschugaeff[8] therefore claims that these compounds represent salts corresponding to different acids formed from the anhydride osmium tetroxide. Krauss and Wilken[9] have also prepared salts similar to the above by pouring a solution of the appropriate base over solid osmium tetroxide. Moreover, addition salts of the type $OsO_4 \cdot 2CsF$ were similarly prepared; these authors state that the Werner[10] theory claiming ruthenium and osmium tetroxide are coordinately saturated is not borne out by the above facts. Yost and White[11] demonstrated that osmium tetroxide behaves as a very weak acid in aqueous solution and measured its ionization constant; they suggested the name perperosmic acid[12] for the acid species. The following work involves a procedure similar to that used by these investigators.

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(8) Tschugaeff, L., Compt. rend., 167, 162 (1918).

(9) Krauss, F., and Wilken, D., Z. anorg. allgem. Chem., 145, 151 (1925).

(10) Werner, A., "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," Fifth ed., Brunswick, 1923.

(11) Yost, D. M., and White, R. J., J. Am. Chem. Soc., 50, 81 (1928).

(12) Yost, D. M., and White, R. J., loc. cit.

B. Theory

The experimental method depends on the extraction of ruthenium tetroxide by an organic solvent, carbon tetrachloride, from both neutral and alkaline aqueous phases. The distribution coefficients obtained can be substituted in the following equation to calculate the acid constant, K_A, of the tetroxide:

$$K_A = K_W(r_W - r_S) \Big/ r_S(OH^-), \qquad (1)$$

where K_A is defined to be

$$(H^+)(HRuO_5^-) \Big/ \left[(RuO_4) + (H_2RuO_5)\right] ; \qquad (2)$$

K_W is the ionization constant of water equal to 1.0×10^{-14}; r_W is the distribution ratio of RuO_4, organic to neutral aqueous phase; and r_S is the distribution ratio for RuO_4, organic to alkaline aqueous phase in which the hydroxide concentration is (OH^-). Here, following Yost and White,[13] we have assumed Ru(VIII) to be partially hydrated with one water per RuO_4; other assumptions as to the degree of hydration would make no essential change in equation (1). Concentrations are used throughout this treatment as representing thermodynamic activities.

This equation can be derived in the following manner. If ruthenium tetroxide acts as an acid, and assuming one molecule of

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(13) Yost, D. M., and White, R. J., J. Am. Chem. Soc., 50, 81 (1928).

water is involved, the following equilibria exist:

$$RuO_4 + H_2O \rightleftharpoons H_2RuO_{5\ aq.} \rightleftharpoons H^+ + HRuO_5^- \ . \qquad (3)$$

From the mass action law, the true ionization constant is

$$K_A' = (H^+)(HRuO_5^-)\Big/(H_2RuO_5) \ . \qquad (4)$$

The distribution of ruthenium tetroxide molecules between carbon tetrachloride and water can be expressed by a simple ratio

$$r_w' = (RuO_4)_{org.}\Big/(RuO_4)_{aq.} \text{ , a constant,} \qquad (5)$$

and the hydration in the aqueous phase by

$$(H_2RuO_5)_{aq.}\Big/(RuO_4)_{aq.} = k \text{, also a} \qquad (6)$$

constant, so that

$$(RuO_4)_{org.}\Big/\Big[(RuO_4)_{aq.} + (H_2RuO_5)_{aq.}\Big] = r_w'\Big/(k + 1) = r_w \ . \qquad (7)$$

No essential change in the expression is made if ruthenium tetroxide is partially hydrated in the organic phase as long as it is substantially unionized. We now assume that H_2RuO_5 is a very weak acid so that the measured distribution ratio with a neutral aqueous phase gives the value of r_w. Similarly, for extractions involving an alkaline aqueous phase a part of the acid will be ionized according to the equation

$$H_2RuO_5 + OH^- \rightleftharpoons HRuO_5^- + H_2O, \qquad (8)$$

and we can write for the measured distribution ratio

$$r_s = (RuO_4)_{org.} \Big/ \left[(RuO_4)_{aq.} + (H_2RuO_5)_{aq.} + (HRuO_5^-)_{aq.}\right]. \qquad (9)$$

Dividing (9) by (8),

$$r_s/r_w = \left[(RuO_4)_{aq.} + (H_2RuO_5)_{aq.}\right] \Big/ \left[(RuO_4)_{aq.} + (H_2RuO_5)_{aq.} + (HRuO_5^-)_{aq.}\right], \qquad (10)$$

from which

$$(HRuO_5^-) = \left[(RuO_4)_{aq.} + (H_2RuO_5)_{aq.}\right]\left[(r_w - r_s)/r_s\right]. \qquad (11)$$

Substituting this result in equation (4), and combining with equations (2) and (6),

$$K_A = K_A^{\circ}\left[k/(k + 1)\right] = (H^+)(r_w - r_s)/r_s , \qquad (12)$$

and since $K_w = (H^+)(OH^-)$, the final result is

$$K_A = (K_w)(r_w - r_s)/(r_s)(OH^-). \qquad (1)$$

C. Experimental

Preliminary experiments were conducted as follows. Portions of a water solution of ruthenium tetroxide were pipetted into known volumes of mixtures of carbon tetrachloride and water or aqueous sodium hydroxide. The mixtures were shaken for one minute at 25°, and samples were withdrawn from both phases and analyzed for Ru(VIII) by the iodometric method described in Chapter III. The hydroxyl ion concentration was determined before extraction by

titration of a sample with standard acid. The short extraction time was necessary to avoid appreciable reduction of ruthenium tetroxide to lower valent species. The initial results left much to be desired. Values of K_A varied from 1.5×10^{-12} to 2×10^{-11} for pH values of 12.7 to 11.05; the latter value was obtained at the lower pH. It appeared that several factors could bring about this spread in results. Initially, the ruthenium tetroxide solution was not freshly made but had stood in a refrigerator for several weeks prior to its use; consequently, it was possible that some reduction of the tetroxide had taken place, i.e., oxidation of water by some reaction such as

$$RuO_4 + H_2O \longrightarrow RuO_4^{=} + 2H^{+} + \tfrac{1}{2}O_2 \qquad (13)$$

Colloidal ruthenium dioxide might be present in the aqueous phase and contribute to its titer giving anomalously strong acid constants. Secondly, reduction of ruthenium tetroxide to ruthenate might take place in alkaline solution during the extraction according to the equation

$$RuO_4 + 2OH^{-} \longrightarrow RuO_4^{=} + H_2O + \tfrac{1}{2}O_2 \qquad (14)$$

Finally, reduction of the tetroxide in the carbon tetrachloride layer was noticed in a number of cases (color change, traces of precipitate upon centrifugation). This could occur by means of a catalytic decomposition,

$$RuO_4 \longrightarrow RuO_2 + O_2 \ . \qquad (15)$$

Data from these decomposed samples were not used; however, it is conceivable that some decomposition (not readily visible) had started in some of the samples analyzed.

To avoid these possible errors, a number of precautions were taken. Fresh ruthenium tetroxide was prepared in the usual manner, i.e., distillation from a solution of ruthenium sulfate in sulfuric acid, from which all chloride had been removed by repeated fuming, using periodic acid as the oxidizing agent. The tetroxide which distilled was passed through magnesium perchlorate to remove water and then redistilled <u>in vacuo</u> into small glass bulbs. These bulbs of dry, pure tetroxide were used in the later experiments.

A second series of extractions was made employing the procedure described above but breaking a bulb of dry ruthenium tetroxide into the reaction mixture instead of pipetting a solution of the material. The values obtained for K_A in this series of extractions varied from 1.1 to 7.8×10^{-12}. Again, the high values were obtained with solutions of low alkalinity.

Spectrophotometric observations showed that the formation of ruthenate was not an important factor; i.e., the rate of reaction (14) was too slow to interfere with the extraction. Furthermore, there was no evidence of reduction in the carbon tetrachloride layer. Finally, spectrophotometric data showed the ruthenium

tetroxide concentration in pure water did not change quickly with time, indicating the rate of reaction (13) was too slow to interfere with the extraction.

On the other hand, solutions in pure water of these dry preparations of ruthenium tetroxide were found to give pH values of $\sim$3.5 - 5. From the data presented above showing that ruthenium tetroxide is a very weak acid, it was impossible to ascribe these low pH values to ionization of H_2RuO_5. An obvious answer to this question was that traces of a stronger acid, entrained with the tetroxide during distillation were carried through all the subsequent purification steps. However, to clarify the problem completely further experiments were conducted.

A possible alternative mechanism for the formation of the high concentration of hydrogen ion is suggested by equation (13). Under such conditions, the appearance of hydrogen ion should be coincident with the reduction of ruthenium tetroxide in solution. However, this possibility was eliminated by making pH measurements immediately after ruthenium tetroxide samples were dissolved in water, with both a Leeds Micromax recording pH meter and a glass electrode connected to a vibrating reed electrometer. It was found that the acid appeared within five seconds, or as fast as the tetroxide dissolved. In order to investigate the possibility of a very fast reaction between ruthenium tetroxide and potassium chloride from the calomel electrode (which might account for the sudden appearance of hydrogen ion), spectrophotometric techniques were again

employed. The concentration of ruthenium tetroxide in solution did not change appreciably when electrodes were placed in the solution for fifteen to thirty seconds; however, pH measurements indicated that acid was already present. Hence it was concluded that the acid must have been present when ruthenium tetroxide was dissolved in solution and that it must have been carried through from the original preparation, either by entrainment or distillation. As corroboration that it was not formed by reduction of ruthenium tetroxide, no correlation could be obtained between the pH of the solution and the concentration of ruthenium tetroxide therein when separately distilled samples of the tetroxide were dissolved. These considerations suggest that results from solutions of low alkalinity are probably unreliable since pH was not measured after the extraction, and it is here that a small amount of entrained strong acid could make the greatest change in the final pH.

A third series of extractions was then made, employing only concentrations of alkali high enough to avoid effects due to acid present with the ruthenium tetroxide. The hydroxyl ion concentration was determined by titration of the aqueous phase before extraction; pH measurements before and after extraction showed no change within the sensitivity of the instrument (0.01 in pH). This series gave reasonably concordant values of K_A, which are reported in Table XII along with the higher alkalinity measurements of the previous series. The average of all the values for neutral extractions gives a distribution coefficient r_w equal to 40.8. This

TABLE XII

DETERMINATION OF THE ACID CONSTANT OF RUTHENIUM TETROXIDE

Sample No.	RuO_4 Conc. in Millimoles/Liter In CCl_4 Layer	In Aq. Layer	Aqueous Layer	Distribution Coefficient[a]	K_A[b] x 10^{12}
2A	2.04	0.0618	H_2O	42.7	
2B	1.89	0.0510	H_2O	37.0	
3A	2.40	0.0541	H_2O	44.3	
4A	2.67	0.0650	H_2O	44.1	
			NaOH		
5A	0.496	0.0737	0.0337 N	6.75	1.50
6A	0.815	0.113	0.0337 N	7.23	1.38
9B	3.18	0.232	0.0167 N	13.7	1.19
2	5.10	0.130	H_2O	39.2	
3	5.20	0.136	H_2O	38.2	
4	1.35	0.0317	H_2O	42.6	
9	2.07	0.0520	H_2O	39.8	
11	5.10	0.121	H_2O	42.1	
			NaOH		
5	0.835	0.0716	0.0200 N	11.65	1.25
6	1.87	0.144	0.0185 N	13.0	1.16
7	0.354	0.0480	0.0408 N	7.4	1.11
10	0.380	0.0570	0.0425 N	6.7	1.20
14	2.11	0.108	0.01066 N	19.5	1.03
15	0.419	0.0270	0.01066 N	15.4	1.55

[a]Average r_w = 40.8.

[b]Average K_A = 1.3 x 10^{-12}.

Standard deviation of K_A = 0.18 x 10^{-12}

.1213

.05

.0035

.0313

.06

figure was used to calculate the K_A values (from equation (1) above) listed in the last column of the table. The average of all these results gives the value 1.27×10^{-12} for the first ionization constant, K_A, of perperruthenic acid.

D. Discussion

It is estimated that the value 1.3×10^{-12} obtained for the ionization constant of perperruthenic acid may be in error by as much as 25 per cent. The principal sources of error in the determination are the following: (1) the determination of the end point of the titration, especially since the titer was usually quite small, and (2) the possible occurrence of side reactions such as (14) and (15). The starch-iodine end point is difficult to see in the presence of ruthenium (III) which is formed by the reduction of upper valent species; it is a change in color from a grayish-blue to a deep rose. Dilute concentrations of ruthenium were employed to avoid excessive Ru(III) color, consequently necessitating the use of extremely dilute thiosulfate solutions. Errors due to the occurrence of side reactions were discussed in the foregoing section.

Perperruthenic acid is very slightly stronger than perperosmic acid,[14] whose first ionization constant is 8.0×10^{-13}; this

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(14) Yost, D. M., and White, R. J., J. Am. Chem. Soc., 50, 81 (1928).

is what one would expect from the relative places of ruthenium and osmium in the periodic table. Moreover, the acid ionization constants obtained fall in line with the values noted above for the conductances obtained for these two very weak acids. That no salts of perperruthenic acid have been obtained, in contrast to the case of perperosmic acid, may be attributed to the instability of ruthenium tetroxide; ruthenium tetroxide will oxidize water, as noted in the previous chapter on polarographic studies.

A theory of the ionization constants of inorganic oxygen acids has been presented by Kossiakoff and Harker,[15] based on the assumption that the free energy change associated with ionization is substantially the electrostatic work involved in the transfer of a proton from the acid to the solvent. A semi-empirical equation was developed whose parameters were determined from considerations of the charge distribution and structures of the acid and ion. Constants were calculated for twenty-six acids, and reasonable agreement with observed values ($\pm$0.5 in log K) was obtained.

Ten years later Ricci,[16] in a critical analysis of the Kossiakoff-Harker theory, presented arguments showing that while the charge distribution of the acid is essential to the success of the Kossiakoff-Harker theory, the detailed structures of acid and ion are

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(15) Kossiakoff, A., and Harker, D., J. Am. Chem. Soc., 60, 2047 (1938).

(16) Ricci, J., ibid., 70, 109 (1948).

not. He proposed as a simplification the following empirical expression

$$pK \simeq 8.0 - m(9.0) + n(4.0) \qquad (16)$$

where K is the acid ionization constant of the species H_aMO_b, whatever its net or total charge, m is the formal charge of M, and n is b - a, the number of non-hydroxyl oxygen atoms.

The acid ionization constant of perperruthenic acid predicted by the Ricci equation depends upon the degree of hydration assumed for the acid species. The following are the possibilities:

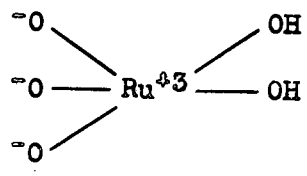
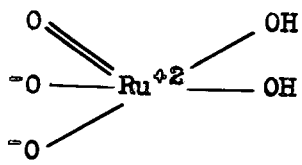
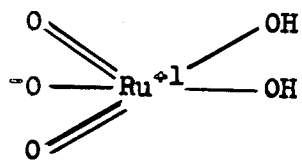
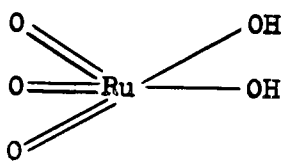
Formula	n	m	pK
$Ru(OH)_8$	0	0	8
$RuO(OH)_6$	1	1	3
$RuO_2(OH)_4$	2	2	-2
$RuO_3(OH)_2$	3	3	-7

This comparison would appear to offer the possibility of distinguishing the degree of hydration of the acid species. This conclusion is however unsound for the following reason.* Ricci has taken the parameter n as the number of non-hydroxyl oxygens. If, however, Kossiakoff and Harker's fundamental assumption that the free energy of ionization is essentially an electrostatic work term is

*The following argument and extension of Ricci's equation was proposed by Dr. H. A. Levy.

correct, this parameter should more generally be described as the number of oxygen atoms bearing a singly negative formal charge. The two numbers are identical if all non-hydroxyl oxygen atoms are singly bonded to the central ruthenium. On the other hand, if one or more are doubly bonded, these oxygens will bear a zero formal charge, and to the rather crude approximation of the theory have no effect in hindering ionization.

Octavalent ruthenium possesses ample orbitals to make possible formation of a number of double bonds. For example, for the structure of the single-hydrate species there are the following possibilities, with corresponding values of _m_ and _n_ according to the above revised definition, and of _pK_.

Structure	m	n	pK
	$^{+}3$	3	-7
	$^{+}2$	2	-2
	$^{+}1$	1	3
	0	0	8

Thus, according to this revised interpretation of Ricci's equation, any of the hydrates could be predicted to have a pK of 8, and this value is associated with a ruthenium formal charge of zero. In view of the position of ruthenium on the electronegativity scale, this appears the most likely value.

The observed pK of 12 is much larger than the highest predicted value. The discrepancy appears to be a strong indication that the dissolved species is largely unhydrated, the hydration constant (k in equation (6)) being of the order of 10^{-2} to 10^{-4}.

SUMMARY

SUMMARY

The crystal structure of potassium perruthenate has been determined to be of the scheelite type, space group C_{4h}^{6} - I $4_1/a$; the unit cell, containing four molecules of $KRuO_4$, has the dimensions $a_o = 5.609 \pm 0.002$ A. and $c_o = 12.991 \pm 0.002$ A. The parameters of the oxygen atoms have been determined by using equatorial Weissenberg photographs. The atomic positions are Ru at (000), K at (0, 0, $\frac{1}{2}$), O at (xyz) and crystographically equivalent positions with $x = 0.75_6$, $y = 0.11_7$, $z = 0.92_7$, accurate to about 0.002. The ruthenium coordination is a tetrahedron slightly flattened along the c-axis, with a Ru-to-O distance of 1.79 A.

The disproportionation of ruthenate to perruthenate and ruthenium dioxide does not reach stable equilibrium. Aqueous perruthenate ion is unstable, decomposing by disproportionation at pH below 10.65 or by discharging oxygen at pH above 10.65.

Potentials of 0.59 and 1.00 volts have been obtained for the ruthenate-perruthenate and perruthenate-ruthenium tetroxide couples, respectively, by polarographic methods using a solid platinum electrode. These potentials have been used to calculate equilibrium constants for several reactions.

The acid ionization constant of ruthenium tetroxide has been determined to be 1.3×10^{-12} by a method involving the extraction of the tetroxide from aqueous and alkaline solutions with carbon tetrachloride. The value obtained is discussed with particular reference to theories for the ionization constants of inorganic oxygen acids.

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APPENDIX

APPENDIX

ABSORPTION OF RADIATION BY A CRYSTAL

Absorption of radiation by a crystal can be calculated in the following manner. If a beam of X rays of intensity I_o is allowed to pass through a layer of material of thickness d, then I is the intensity of the exit beam according to the equation

$$I = I_o \exp(-\mu d) \quad , \qquad (1)$$

where μ is called the linear absorption coefficient. The total absorption coefficient for crystal measurements is $\mu = \tau + \sigma$, where τ is that part of the absorption due to the transformation of the radiation into photoelectrons, and σ that due to scattering. For all but the very light elements σ is a small fraction of the whole absorption.

For a crystal having a simple chemical composition such as potassium perruthenate, μ is easily calculated by means of the formula

$$\mu = \frac{n}{V} \sum \mu_a \quad , \qquad (2)$$

where μ_a is the atomic absorption coefficient, or the absorption per atom; n is the number of molecules in the unit crystal cell and V is the volume of the crystal cell in cubic centimeters. The summation is taken over all the atoms of the molecule. Values of μ_a are given in the Tabellen.

The calculation for a potassium perruthenate crystal using copper radiation is:

$n = 4$ $\qquad$ $\mu_a \times 10^{23}$ for Ru $= 3090$

$V = (5.609)^2\ (12.991) = 40.87 \times 10^{-23}$ $\qquad$ $\mu_a \times 10^{23}$ for K $= 923$

$d = 0.0266$ cm. $\qquad$ $\mu_a \times 10^{23}$ for 4(O) $= 134.4$

$\sum \mu_a \times 10^{23} = 4147.4$

$$\mu = \frac{4 \times 4147.4 \times 10^{23}}{40.87 \times 10^{23}} = 406 \text{ cm.}$$

Using equation (1) above for a typical path length d = 0.0266 cm., estimated from the dimensions of the crystal, the reduction of intensity of the beam is so great (greater than 99 per cent) that a small variation in path length would yield large relative changes in the intensity of the transmitted beam.

Consequently, the Weissenberg photographs were retaken using unfiltered molybdenum radiation. A similar calculation to that above indicated that the transmitted beam would have an intensity greater than 25 per cent of that of the incident beam.

An estimation of the relative effect of absorption of molybdenum radiation on various reflections was made graphically in the following manner. Large scale drawings of the external shape of the crystal were made after measuring the dimensions of the crystal with a tool-maker's microscope. The direction of the incident and reflected beam were plotted for a given reflection. The length of path of the beam through various parts of the crystal was measured and the corresponding

absorption factors computed. These were appropriately averaged to give an effective absorption factor for this reflection.

Graphical estimates were made in this manner for a number of hk0 and h0ℓ reflections; absorption corrections were neglected when it was found that relative $|F|^2_{obs}$ values would not be disturbed more than $\pm$ 5 per cent for hk0 or $\pm$ 7 per cent for h0ℓ reflections, corresponding to errors in $|F|_{obs}$ of 2.5 and 3.5 per cent, respectively.

Some typical values of I/I_o so estimated are tabulated below:

h0ℓ	105	109	1·0·13	800	10·0·0	3·0·17	6·0·20
I/I_o	0.469	0.474	0.484	0.417	0.446	0.447	0.455

hk0	420	240	640	460	440	600
I/I_o	0.315	0.340	0.333	0.345	0.337	0.321