

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY, AND THE DEPARTMENT OF CHEMISTRY UNIVERSITY OF TENNESSEE]

## Crystal Structure of Potassium Perruthenate, $\text{KRuO}_4^{1,2}$

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The crystal structure of potassium perruthenate has been determined to be of the scheelite type, space group  $C_{4h}^2 - I_{41}/a$ ; the unit cell, containing four molecules of  $\text{KRuO}_4$ , has the dimensions  $a_0 = 5.609 \pm 0.002 \text{ \AA}$ . and  $c_0 = 12.991 \pm 0.002 \text{ \AA}$ . The atomic positions are Ru at (000), K at (0, 0,  $1/2$ ), O at ( $xyz$ ) and crystallographically equivalent positions with  $x = 0.244$ ,  $y = 0.117$ ,  $z = 0.073$ , accurate to about 0.002. The ruthenium coordination is a tetrahedron slightly flattened along the  $c$ -axis, with a Ru-O distance of 1.79  $\text{ \AA}$ .

Deville and Debray<sup>3</sup> first described potassium perruthenate as black brilliant orthorhombic octahedra crystals, derived from a prism of  $117^\circ$ . A later preparation<sup>4</sup> was examined by Dufet,<sup>5</sup> who reported from goniometric measurements that the crystal is tetragonal with axial ratio  $c/a$  2.31086 and not isomorphous with potassium permanganate. The compound appears as black, tetragonal octahedra, stable in air. Barker<sup>6</sup> recognized  $\text{KRuO}_4$  to be isomorphous with scheelite,  $\text{CaWO}_4$ .

### Preparation of Samples. Unit Cell and Space Group

Essentially pure potassium perruthenate was first prepared by the method of Debray and Joly.<sup>4</sup> Small black crystals of the salt were ground to pass a 300 mesh screen and copper-radiation Debye-Scherrer photographs of the powder were taken in cameras of 5.73 cm. and 11.4 cm. diameter.

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.<sup>7</sup> The lattice constants for the perruthenate were obtained with greatest precision from reflections in the back reflecting region on a Debye-Scherrer pattern in which sodium chloride was mixed with the perruthenate in order to provide calibrating lines. The values adopted are:  $a_0 = 5.609 \pm 0.002 \text{ \AA}$ .,  $c_0 = 12.991 \pm 0.002 \text{ \AA}$ ., based on  $a_0$  for sodium chloride equal to 5.638  $\text{ \AA}$ .

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 with the mother liquor and ice-cold distilled water. Specimens whose shapes were approximately tetragonal octahedra about  $0.03 \times 0.02 \text{ cm}$ . were chosen for X-ray study.

Equatorial Weissenberg photographs, using unfiltered molybdenum radiation were taken about the  $c$ - and  $b$ -axes. The observed structure factors are listed in Table I, with calculated signs given by the final parameters. The multiple film technique of de Lange, Robertson and Woodward<sup>8</sup> was employed for the visual estimation of intensities. Absorption corrections were estimated graphically and applied to the observed intensities.

(1) From the doctorate thesis of M. D. Silverman, 1950. This document is based on work sponsored by the Atomic Energy Commission, under the resident graduate program of the Oak Ridge National Laboratory, the Oak Ridge Institute of Nuclear Studies, and the University of Tennessee.

(2) Presented before the Division of Physical and Inorganic Chemistry, 115th National Meeting, American Chemical Society, San Francisco, Calif., March, 1949.

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

(4) H. Debray and A. Joly, *ibid.*, **106**, 1994 (1888).

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

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

(7) L. K. Frevel, H. W. Rinn and H. C. Anderson, *Anal. Chem.*, **18**, 83 (1946).

(8) J. J. de Lange, J. M. Robertson and I. Woodward, *Proc. Roy. Soc. (London)*, **A171**, 398 (1939).

TABLE I  
OBSERVED STRUCTURE FACTORS FOR  $\text{KRuO}_4$

$hkl$	$F_{\text{obsd.}}$	$hkl$	$F_{\text{obsd.}}$	$hkl$	$F_{\text{obsd.}}$
200	-37.2	0-0-12	-23.9	3-0-19	-2.3
220	-40.6	503	+4.3	4-0-18	-1.7
400	+24.8	408	+20.2	2-0-20	+8.2
420	+27.2	505	-7.9	5-0-17	+2.6
240	-28.8	2-0-12	+15.2	7-0-13	+1.8
440	+14.9	3-0-11	-5.5	901	+2.6
600	-14.2	1-0-13	-8.0	903	+1.9
620	-16.5	507	-6.2	8-0-10	<1.8
260	-14.7	4-0-10	+3.8	1-0-21	-1.8
640	-10.9	600	-12.1	6-0-16	-6.2
460	+12.1	602	<1.3	905	-2.0
800	+10.6	604	+13.5	907	-2.0
280	-8.5	509	+4.0	4-0-20	-5.3
820	+7.4	3-0-13	+3.9	7-0-15	+1.8
660	-8.7	2-0-14	<1.4	8-0-12	-5.5
840	+6.4	606	<1.4	3-0-21	+1.8
480	+6.5	4-0-12	-12.9	5-0-19	+1.8
10-0-0	-4.5	1-0-15	-5.8	2-0-22	<1.8
860	+4.0	5-0-11	+5.5	909	<1.9
680	-3.6	0-0-16	+12.7	6-0-18	<1.9
10-2-0	-3.8	608	-13.5	1-0-23	<1.9
2-10-0	-3.6	701	-3.9	10-0-0	-5.3
10-4-0	-3.6	703	-5.4	8-0-14	<1.9
4-10-0	+3.4	3-0-15	+3.0	10-0-2	<1.9
103	+25.4	2-0-16	-11.6	7-0-17	<1.9
004	-45.4	4-0-14	<1.5	10-0-4	+4.0
200	-35.4	705	+4.2	9-0-11	<1.9
202	-8.5	6-0-10	<1.5	4-0-22	<1.9
105	-3.8	1-0-17	+3.0	10-0-6	<1.9
204	+41.1	5-0-13	-3.0	5-0-21	<1.9
301	-6.7	707	+4.6	0-0-24	+4.2
107	-5.7	3-0-17	-3.1	3-0-23	<1.9
303	-8.3	6-0-12	+8.5	6-0-20	+3.8
206	+3.2	4-0-16	+8.4	8-0-16	+4.1
008	+20.8	800	+8.7	2-0-24	-3.3
305	+10.6	709	-3.2	10-0-8	-3.6
208	-37.3	2-0-18	<1.6	9-0-13	<1.9
400	+27.1	802	<1.6	7-0-19	<1.9
109	+8.5	5-0-15	-2.3	1-0-25	<1.9
402	-4.9	804	-8.6	10-0-10	<1.9
307	+9.4	1-0-19	+2.4	11-0-1	<1.9
404	-22.7	806	<1.5	11-0-3	<1.9
2-0-10	+3.9	7-0-11	-2.1	9-0-15	<1.9
406	+2.6	6-0-14	<1.7	4-0-24	+2.9
1-0-11	+6.6	0-0-20	-7.9	5-0-23	<1.9
309	-7.4	808	+6.9	8-0-18	<1.9
501	+7.2				

### Determination of the Structure

The space group for potassium perruthenate, in accord with the structure of scheelite and its iso-

types, is  $C_{4h}^6 - I_4/a$ ; systematic absences in the photographs verified this assignment.

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 "Internationale Tabellen."<sup>9</sup> The sixteen oxygen atoms can be placed in two sets of eightfold 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.

Values of  $F_{\text{calcd.}}$  were obtained from the general expression for crystals with a center of symmetry at the origin

$$F_{hkl} = \sum_i f_i [\exp -B(\sin \theta/\lambda)^2] \cos 2\pi(hx_i + ky_i + lz_i)$$

Scattering factors for ruthenium and oxygen were interpolated from Thomas-Fermi and Hartree values, respectively, to approximate  $\text{Ru}^{+3}$  and  $\text{O}^-$  distributions. Hartree values for  $\text{K}^+$  were employed. Anomalous scattering corrections for potassium and ruthenium of +0.2 and -1.9,<sup>10</sup> respectively, were applied. The resulting values for ruthenium and oxygen are

$\sin \theta/\lambda$ $\times 10^{-3}$	0	0.1	0.2	0.4	0.6	0.8	1.0
$f_{\text{Ru}}$	39.1	35.3	31.2	22.8	17.7	13.7	10.8
$f_{\text{O}}$	9	7.5	5.4	2.8	1.8	1.5	1.35

Approximate values of the oxygen parameters were easily obtained by trial. Temperature and scale factors were then estimated in the usual way. It became apparent that separate temperature factors for potassium, ruthenium and oxygen were required to produce satisfactory agreement for the  $h0l$  reflections. The procedure by which these were estimated was similar to one described by Waller and James.<sup>11</sup> The values of the temperature factor coefficients ( $\times 10^{-16}$ ) derived are: Ru, 1.61; K, 2.28; and O, 1.76.

Parameter values were refined first by trial and error. Agreement of pairs of reflections  $hk0$  and  $h\bar{h}0$  at the same Bragg angle were given greatest weight. Final values of  $x$  and  $y$  were obtained by a simple least squares refinement,<sup>12</sup> employing the same pairs of reflections. The observation equations were

$$F_{\text{calcd}}(hk0) \pm F_{\text{calcd}}(h\bar{h}0) = F_{\text{obsd}}(hk0) \pm F_{\text{obsd}}(h\bar{h}0)$$

for  $(hk0) = 420, 620, 640, 820, 840, 860, 10\cdot2\cdot0$  and  $10\cdot4\cdot0$ , the sign being positive when the pair of structure factors are of opposite sign and *vice versa*. This procedure reduces the effect of temperature factor uncertainties. Refinement of the parameter  $z$  was by trial and error after refinement of  $x$  and  $y$  was complete. The values obtained are  $x = 0.244$ ,  $y = 0.117$ ,  $z = 0.073$ . The estimated probable error is 0.002.

(9) "Internationale Tabellen zur Bestimmung von Kristallstrukturen" Gebrüder Borntraeger, Berlin, 1935.

(10) A. H. Compton and S. K. Allison, "X-Rays in Theory and Experiment," Second Edition, D. Van Nostrand Co., Inc., New York, N. Y., 1935, p. 315; H. Z. Hönig, *Z. Physik*, **84**, 1 (1933); *Ann. Physik*, [5] **18**, 42 (1933).

(11) I. Waller and R. W. James, *Proc. Roy. Soc. (London)*, **A117**, 214 (1927).

(12) E. W. Hughes, *THIS JOURNAL*, **68**, 1737 (1941).

These parameters yield structure factors in good agreement with observed values. The discrepancy factor  $\Sigma|F_{\text{calcd}} - F_{\text{obsd}}|/\Sigma|F_{\text{obsd}}|$  is 8.2% for the  $hk0$  reflections and 10.9% for the  $h0l$  values, invisible reflections omitted. All calculated values corresponding to invisible reflections are below the indicated upper limits except 9.013, which calculates 2.0.

## Discussion

Interatomic distances and bond angles were calculated from the parameters given above and are presented in the Table II, along with values for other  $\text{ABO}_4$  compounds of similar structure.

TABLE II  
INTERATOMIC DISTANCES AND BOND ANGLES IN  $\text{KRuO}_4$   
AND OTHER  $\text{ABO}_4$  COMPOUNDS HAVING THE SCHEELITE  
STRUCTURE

Compound	Bond angle O-B-O	Interatomic distances in Å.				
		B-O	A-O	Same group O-O	Neighboring group O-O A-B	
$\text{KRuO}_4$	$106^\circ 18'$	1.79	2.75	2.86	3.11	3.97
			2.79	3.04	3.40	4.29
$\text{KIO}_4^{13}$	$104^\circ 30'$	1.80	2.76			4.07
			2.81			4.29
$\text{NaIO}_4^{14}$		1.792	2.573		2.67	
			2.577			
$\text{KOSO}_3\text{N}^{15}$		1.62	3.04			4.00
			3.07			4.36
$\text{KCrO}_3\text{F}^{16}$		1.58	2.80	2.50	3.07	
			2.89	2.62		

Four oxygen atoms, at a distance 1.79 Å., are co-ordinated 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  $\text{KIO}_4$  and  $\text{NaIO}_4$  in which iodine is also heptavalent. Apparently the effective radii of  $\text{Ru}^{7+}$  and  $\text{I}^{7+}$  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 Å. and the other four at the corners of a tetrahedron with K-Ru distances of 4.29 Å. Similarly, each perruthenate ion is in turn surrounded by eight potassium ions with like coördination. The oxygens, at the corners of two dissimilar interpenetrating tetrahedra, form an eightfold coördination group about each potassium atom, the two K-O distances being 2.75 and 2.79 Å. 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<sup>17</sup> gives a calculated ionic radius of 0.60 Å. for  $\text{Ru}^{4+}$ . The magnitude of the correction to  $\text{Ru}^{7+}$  may be estimated by comparison with the values listed for  $\text{Mn}^{4+}$  and  $\text{Mn}^{7+}$  which are 0.52 and 0.46 Å., respectively; an ionic radius of 0.54 Å. is thus estimated for  $\text{Ru}^{7+}$ . If the Ru-O bond

(13) E. Hylleraas, *Z. Physik*, **39**, 308 (1926).

(14) E. A. Hazlewood, *Z. Krist.*, [a] **98**, 439 (1938).

(15) F. M. Jaeger and J. E. Zanstra, *Rec. trav. chim.*, **51**, 1013 (1932).

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

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

were purely ionic in character, the expected distance between these atoms would be the sum of the ionic radii, 1.94 Å., using the value of 1.40 Å. given by Pauling.<sup>18</sup> The observed distance 1.79 Å. is

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

appreciably shorter, possibly being indicative of a covalent link, as suggested by the electronegativity of ruthenium. Double bond character may also contribute to a short interatomic distance.

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## Polarographic Studies of Ruthenium in Oxidation States IV, VI, VII and VIII<sup>1,2</sup>

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Standard potentials of  $-0.59$  and  $-1.00$  volt have been obtained polarographically for the ruthenate-perruthenate and perruthenate-ruthenium tetroxide couples, respectively, using a stationary platinum electrode.

With the exception of the work of Connick and Hurley,<sup>3</sup> very little new information on the aqueous solution chemistry of ruthenium in the VI, VII and VIII oxidation states has been accumulated during the past 25 years. The older literature is well summarized in Gmelin<sup>4</sup> and also by Charonnat.<sup>5</sup>

Concurrent with this work, Connick and Hurley<sup>3</sup> measured potentials of cells containing ruthenium-(VI) and -(VII) in alkaline solution and obtained a standard potential for the couple in excellent agreement with the polarographic result here reported. They also measured an approximate equilibrium constant for the disproportionation of ruthenate into perruthenate and ruthenium dioxide and from these data calculated a potential for the (IV)-(VI) couple. These investigators, and also the present authors,<sup>6</sup> have previously established by spectrophotometric studies the pH ranges in which the various oxidation states are experimentally accessible.

Polarographic studies involving ruthenium have previously been limited to the lower oxidation states.<sup>7-9</sup> In the present work, two oxidation-reduction couples were successfully investigated, the ruthenium(VI)-(VII) couple and the (VII)-(VIII) couple. Each was studied in oxidation and reduc-

tion over a range of total ruthenium concentration and pH, and at two concentrations of supporting electrolyte (NaClO<sub>4</sub>).

Attempts to obtain the ruthenium(VI)-(IV) potential polarographically were unsuccessful. Half-wave potentials from reduction waves showed proper dependence on pH, (corresponding to four hydroxyl ions liberated per RuO<sub>4</sub><sup>2-</sup> reduced), but not on ruthenate concentration; furthermore, the shape of the wave (plot of  $E_i$  vs.  $\log i/(i_d - i)$ ) was not indicative of a reversible couple. Oxidation waves could not be obtained.

### Experimental

The starting materials for preparation of the solutions were solid potassium perruthenate, a stock solution of potassium ruthenate (*ca.* 0.02 *M*) in *ca.* 0.1 *M* KOH, and an aqueous solution of ruthenium tetroxide. From a solution of spectrographically pure ruthenium chloride, freed of chloride by repeated fuming with sulfuric acid, ruthenium tetroxide was distilled using potassium permanganate as an oxidizing agent. The tetroxide was kept for periods up to several weeks as a solution in ice-cold distilled water, or as crystalline solid in the ice-box. Potassium perruthenate was prepared<sup>10</sup> by absorbing the tetroxide in dilute potassium hydroxide. Small black crystals which were deposited after standing overnight in the ice-box were filtered and washed with ice-cold distilled water. Chemical analysis of the crystals after drying *in vacuo* confirmed their identity as potassium perruthenate. Potassium ruthenate stock solution was prepared by dissolving crystals of the perruthenate, or by absorbing distilled ruthenium tetroxide, in 1 *M* potassium hydroxide. All other chemicals employed were of reagent grade.

The solid platinum electrodes used throughout this investigation were prepared in a manner described by Rogers and co-workers.<sup>11</sup> Whenever deposition of RuO<sub>2</sub> on the Pt electrode was noted a fresh electrode was used. A Sargent automatic polarograph, model XX, was used. The resistance of the cell was measured before each run with a conductivity bridge (model RC-1B, Industrial Instruments, Inc.). The pH was measured with a Beckman model G pH meter, using the high pH type E glass electrode. All experiments were carried out at  $24.5 \pm 0.5^\circ$ .

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 the arms of which contained sodium perchlorate of the same concentration, and saturated ammonium chloride, respectively, connected this cell to a saturated calomel half-cell.

(10) H. Debray and A. Joly, *Compt. rend.*, **106**, 1994 (1888).

(11) L. B. Rogers, H. H. Miller, R. B. Goodrich and A. F. Stehney, *Anal. Chem.*, **21**, 777 (1949).

(1) From the doctorate thesis of M. D. Silverman, August, 1950. This document is based on work sponsored by the Atomic Energy Commission under the resident graduate program of the Oak Ridge National Laboratory, the Oak Ridge Institute of Nuclear Studies, and the University of Tennessee.

(2) Presented before the Division of Physical and Inorganic Chemistry, 115th National Meeting, American Chemical Society, San Francisco, Calif., March, 1949.

(3) R. E. Connick and C. R. Hurley, *THIS JOURNAL*, **74**, 5012 (1952).

(4) "Gmelin's Handbuch der anorganischen Chemie," 8 Auflage, Verlag Chemie, Berlin, 1938.

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

(6) M. D. Silverman and J. A. Swartout, Quarterly Reports of the Chemistry Division, Oak Ridge National Laboratory, CNL-37 (April, 1948) and ORNL-286 (September, 1949); also unclassified report ORNL-746 (August, 1950).

(7) D. D. DeFord and A. W. Davidson, *THIS JOURNAL*, **73**, 1469 (1951).

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

(9) E. Turk, Quarterly Reports of the Chemical Engineering Division, Argonne National Laboratory, ANL-4292 (March, 1949), 4329 (June, 1949), and 4372 (September, 1949).