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THE HIGH-TEMPERATURE CHEMISTRY OF
FISSION-PRODUCT ELEMENTS

SUMMARY REPORT

AUGUST 1, 1962, THROUGH JULY 31, 1963

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GENERAL ATOMIC
DIVISION OF
GENERAL DYNAMICS

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GA-4500

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FISSION-PRODUCT ELEMENTS**

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AUGUST 1, 1962, THROUGH JULY 31, 1963

This research was carried on by General Atomic Division of General Dynamics Corporation, and was supported in part by the U. S. Atomic Energy Commission under Contract No. AT(04-3)-164.

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CONTENTS

I. INTRODUCTION	1
II. RESULTS AND DISCUSSION	2
High-temperature Chemistry of the Ruthenium-Oxygen System	2
Mass-spectrometric Study of Gaseous Rhodium Oxides	3
Vaporization of Iridium in Oxygen	7
Iridium Oxychloride	8
Dissociation of Palladium Oxide	10
Dissociation of Rhodium Oxide	15
Dissociation of Iridium Oxide	17
X-ray Studies of the Trichlorides of Platinum-group Metals	20
REFERENCES	25

I. INTRODUCTION

The high-temperature chemistry of metal chlorides and metal oxides in the temperature range 500° to 2000°C is being investigated under joint support of the Atomic Energy Commission (Contract AT(04-3)-164) and General Atomic.

Since its inception, the program has supplied considerable fundamental chemical and thermodynamic information in previously undefined areas of chemistry. Several important features of metal chloride and oxide chemistry have been revealed. For example, a gaseous polymer, $\text{Pd}_5\text{Cl}_{10}$, which would hardly have been predicted, and a previously unknown gaseous molecule, RuCl_4 , were identified. Previously reported solid RhCl_2 , RhCl , IrCl_2 , and IrCl were shown not to exist, and solid OsCl_3 was found to exhibit a wide range of solid solution with excess chlorine.

The work was particularly fruitful during the past year owing to the utilization of a recently acquired mass spectrometer manufactured to General Atomic's specifications by Consolidated Electrodynamics Corporation. For example, through use of this instrument, evidence was found for the vapor species RhO . Apparently, this is the first experimental evidence for a gaseous monoxide of a platinum-group metal. Another highlight of the past year was the discovery of an iridium oxychloride vapor species.

In the following sections, progress made since the issuance of our last summary report (GA-3398) is described.

II. RESULTS AND DISCUSSION

HIGH-TEMPERATURE CHEMISTRY OF THE RUTHENIUM-OXYGEN SYSTEM

A study of the ruthenium-oxygen system in the temperature range 800° to 1500° C and in the oxygen pressure range 0.01 to 1.0 atm has been completed. Condensed phases and vapor species were identified, dissociation and vapor pressures were measured, and thermodynamic data were calculated from the pressure data. An account of the work⁽¹⁾ has been accepted for publication in The Journal of Physical Chemistry.

Results show that solid RuO₂ is the only stable condensed oxide under the conditions of the study. The dissociation pressure of the oxide reaches 1 atm at 1540° C. Thermodynamic quantities

$$\Delta H_{298}^{\circ} = -72.2 \pm 2.0 \text{ kcal/mole}$$

and

$$\Delta S_{298}^{\circ} = -43.3 \pm 2.0 \text{ e. u.}$$

for the reaction

were derived from a study of the temperature dependence of the dissociation pressure of RuO₂(s).

A study of the effect of oxygen pressure on vapor pressure showed the important vapor species to be RuO₃ and RuO₄, and a study of the effect of temperature on vapor pressure yielded

$$\Delta H_{298}^{\circ} = -18.0 \pm 4.0 \text{ kcal/mole}$$

$$\Delta S_{298}^{\circ} = -16.6 \pm 4.0 \text{ e. u.}$$

for the vaporization reaction

and

$$\Delta H_{298}^{\circ} = -46.7 \pm 5.0 \text{ kcal/mole}$$

$$\Delta S_{298}^{\circ} = -39.3 \pm 5.0 \text{ e. u.}$$

for the reaction

Our results are in good agreement with the results of Schäfer, Tebben, and Gerhardt. (2)

In addition, a mass-spectrometric investigation of this system has been completed, and an account of the work (3) is being submitted for publication in The Journal of Physical Chemistry. The results are summarized below.

Mass spectra were measured in the temperature range 877° to 1252°C and over an oxygen pressure range from about 2×10^{-5} to 5×10^{-4} atm. Mass peaks attributable to Knudsen-cell effusate corresponded to O_2^+ , RuO^+ , RuO_2^+ , and RuO_3^+ . The ions RuO^+ and RuO_2^+ were shown to be fragments of the ion RuO_3^+ as a result of a study of the effect of oxygen pressure on ion intensities. This indicates that RuO_3 was the only gaseous species of importance under the conditions of the study.

From a study of the effect of temperature on RuO_3^+ intensity at constant cell O_2^+ intensity, the heats $\Delta H_{1250}^\circ = -17$ kcal/mole for the reaction

and $\Delta H_{1250}^\circ = +54$ kcal/mole for the reaction

were derived. These values are in line with the heats -13.9 and +54.7 kcal/mole calculated for the respective reactions at the mean temperature (1250°K) from data reported by Schäfer, et al., (2) and the heats -17.0 and +51.6 kcal/mole derived from transpiration studies of the ruthenium-oxygen system performed at General Atomic (1) and summarized above.

MASS-SPECTROMETRIC STUDY OF GASEOUS RHODIUM OXIDES

A mass-spectrometric study of the rhodium-oxygen system is being conducted to determine the important vapor species at oxygen pressures around 10^{-4} atm. The procedure being used is similar to that used in the earlier study of the ruthenium-oxygen system. (3)

In the current study, a rhodium-metal sample is held in an alumina Knudsen cell which is mounted in the mass spectrometer. The cell, which is fitted at the bottom with an alumina oxygen-feed tube, is held in a

molybdenum cup and is covered with two layers of 5-mil molybdenum. The assembly is heated by electron bombardment and temperatures are measured by means of optical pyrometry.

Mass spectra have been measured over the temperature range 1550° to 1795° C and over an oxygen pressure range from about 10^{-6} to 10^{-4} atm. Mass peaks attributable to Knudsen-cell effusate corresponded to O^+ , O_2^+ , Rh^+ , RhO^+ , and RhO_2^+ .

Appearance potential curves were measured for the oxide ions and the rhodium ion. The values obtained, which were corrected by using a mercury measurement as a standard, were as follows:

$$Rh^+ = 7.4 \text{ volts}$$

$$RhO^+ = 9.3 \text{ volts}$$

$$RhO_2^+ = 10.0 \text{ volts}$$

The value of 7.4 volts for Rh^+ is in good agreement with values in the literature.

The ions RhO^+ and RhO_2^+ , produced by 20-volt electrons, were shown conclusively not to be fragment ions as a result of a study of the effect of oxygen pressure on ion intensities. In this study, oxide ion intensities were measured as a function of oxygen ion current at 1795° C. Figures 1 and 2 are log-log plots of the data. The data for RhO^+ show a slope near 0.5 and those for RhO_2^+ a slope near 1.0. This indicates that RhO^+ is not a fragment of RhO_2^+ and that under the experimental conditions the important vaporization reactions are

and

Temperature dependences of Rh^+ , RhO^+ , and RhO_2^+ intensities at constant O_2^+ intensity were measured in the range 1252° to 1557° C. The data are shown in Figs. 3 and 4. From the slope of lines drawn through the data, we calculate $\Delta H_{1950} = +126$ kcal/mole for the vaporization of rhodium, $\Delta H_{1950} = +84$ kcal/mole for reaction (6), and +40 kcal/mole for reaction (7), where 1950°K is the mean temperature of the measurements.

Fig. 1--Log I_{RhO^+} as a function of $\log I_{\text{O}_2^+}$
at 1795°C

Fig. 2--Log $I_{\text{RhO}_2^+}$ as a function of $\log I_{\text{O}_2^+}$
at 1795°C

Fig. 3--Temperature dependence of Rh^+ and RhO^+ intensities

Fig. 4--Temperature dependence of RhO_2^+ intensities

VAPORIZATION OF IRIDIUM IN OXYGEN

The volatility of iridium in oxygen in the temperature range 1000° to 1500° C has been studied previously by Alcock and Hooper,⁽⁴⁾ Schäfer and Heitland,⁽⁵⁾ and Cordfunke and Meyer.⁽⁶⁾ The transpiration method was used in each of these studies.

Because of some disagreement in the results of these investigators, a cursory study of the vaporization of iridium in oxygen has been conducted in our laboratory. The results are given in Table 1.

Table 1
VAPOR-PRESSURE DATA FOR IRIDIUM-OXYGEN SYSTEM

Temp. (°C)	Oxygen Pressure. (atm)	IrO ₃ Pressure (atm × 10 ³)	Flow Rate (mmole O ₂ /min)
1204	0.993	1.08	0.017
1303	0.986	1.31	0.024
1304	0.987	1.31	0.043
1303	0.986	1.21	0.096
1403	0.991	1.43	0.042
1404	0.493	0.47	0.0188
1404	0.248	0.208	0.0112
1505	0.991	1.51	0.047

All investigators agree that the major vapor species is IrO₃. Iridium metal is the condensed phase under the conditions of study. Therefore, the vaporization reaction of importance is

For this reaction the various investigators found the following $\log K_p$ (atm) versus $1/T$ relationships:

Alcock and Hooper

$$\log K_p = -\frac{1812}{T} - 4.72$$

Schäfer and Heitland

$$\log K_p = -\frac{1784}{T} - 4.707$$

Cordfunke and Meyer

$$\log K_p = - \frac{2034}{T} - 4.465$$

Present Investigators

$$\log K_p = - \frac{1930}{T} - 4.54$$

Curves corresponding to these relationships are shown in Fig. 5.

The curves in Fig. 5 show that our data agree within the uncertainty of the results with the data of Cordfunke and Meyer, and that the data of Alcock and Hooper and of Schäfer and Heitland are somewhat lower. In the opinion of Cordfunke and Meyer, the difference could be caused by insufficient saturation of the carrier gas in the earlier studies. They point out that a high surface area is necessary for complete saturation of the carrier gas. Our limited flow-rate data (see Table 1) suggest that this may be the case.

IRIDIUM OXYCHLORIDE

As a result of vaporization studies in which mixtures of oxygen and chlorine gas are passed over iridium metal in the temperature range 1300° to 1500° C, evidence has been found for an iridium oxychloride gaseous molecule.

The transpiration method is being employed in these studies. The carrier gases are passed over the samples contained in mullite reaction tubes. Effluent chlorine gas is collected in potassium iodide solution and oxygen gas is collected in a gas buret above the solution. The radionuclide 75-d Ir¹⁹², produced by irradiation of iridium-metal powder in a TRIGA reactor, is used as a tracer for analytical purposes.

Iridium metal is the condensed phase under the conditions of these studies, and if we assume one iridium atom per gaseous molecule, the vaporization reaction is

From the equilibrium constant for this reaction, we obtain

$$\frac{x}{2} \log P_{\text{O}_2} + \frac{y}{2} \log P_{\text{Cl}_2} - \log P_{\text{IrO}_x \text{Cl}_y} = K \quad (10)$$

Fig. 5--Comparison of equilibrium constants for $2 \text{Ir(s)} + 3 \text{O}_2 = 2 \text{IrO}_3(\text{g})$ as a function of temperature, found by four investigators

and it can be seen that a study of the effect of oxygen pressure and chlorine pressure on oxychloride pressure will lead to identification of the species.

The vapor-pressure data obtained thus far are given in Table 2. Partial pressures of the oxychloride species were obtained by subtracting partial pressures of IrO_3 and IrCl_3 , derived from the results of previous studies in our laboratory (described in the previous section and GA-3398), from the measured total pressure.

The results in Table 2 show that the oxychloride is the predominant species under the conditions studied. Application of Eq. (10) to the experimental data indicates that x is 2 and y is probably 1. Therefore, on the basis of these limited data, the oxychloride species is provisionally identified as IrO_2Cl . At this stage, x can be evaluated more reliably than y because the partial pressure of oxygen has been varied over a much wider range than the partial pressure of chlorine.

DISSOCIATION OF PALLADIUM OXIDE

The dissociation of palladium oxide is under investigation. This work was undertaken after a review of the literature showed conflicting values for the heat of formation of the compound.

The stable solid oxide of palladium appears to be established as PdO . Wöhler⁽⁷⁾ and Schenck and Kurzen,⁽⁸⁾ using static methods, measured the dissociation pressure of the compound. Data of the two investigations are in agreement, and we derive from these data a value of about -26 kcal/mole for the heat of formation (at 298°K) of PdO(s) . This value is not in agreement with the value of -20.4 kcal/mole obtained by Wöhler and Jockum,⁽⁹⁾ who used a calorimetric method. Wöhler and also Schenck and Kurzen noted a dependence of dissociation pressure on the composition of the oxide. Wöhler attributed this behavior to the existence of a solid-solution region, whereas Schenck and Kurzen attributed it to impurities in the palladium metal.

In the present investigation, dissociation pressures were measured by both static and dynamic (transpiration) methods, using techniques similar to those described in Ref. 1. In the static method, the oxide sample was contained in a dead-end quartz tube, and dissociation pressures were read on a mercury manometer. In the transpiration method, helium served as the carrier and the effluent helium-oxygen mixture was analyzed gas chromatographically.

Dissociation-pressure values measured over the range 552° to 872°C are plotted against $1/T$ in Fig. 6. The pressure values represent oxygen

Table 2

PRESSURE OF OXIDE, CHLORIDE, AND OXYCHLORIDE VAPOR SPECIES IN EQUILIBRIUM WITH
IRIDIUM METAL AND OXYGEN-CHLORINE GASEOUS MIXTURES

Temp. (°C)	P_{O_2} (atm)	P_{Cl_2} (atm)	Total Vapor Pressure (atm $\times 10^3$)	P_{IrO_3} (atm $\times 10^3$)	P_{IrCl_3} (atm $\times 10^3$)	$P_{IrO_x Cl_y}$ (atm $\times 10^3$)
1303	0.314	0.678	9.2	0.22	0.64	8.3
1303	0.483	0.891	17.0	0.43	0.94	15.6
1403	0.076	0.966	3.31	0.03	1.50	1.78
1403	0.341	0.648	9.8	0.28	0.82	8.7
1403	0.452	0.913	16.4	0.42	1.40	14.6
1403	0.457	0.918	16.6	0.43	1.40	14.8

Fig. 6--Dissociation pressure of palladium oxide

pressures in equilibrium with two phases, palladium oxide and palladium metal. Results obtained by the static and dynamic methods agree within the expected uncertainty. The data show linearity and indicate that the dissociation pressure reaches 1 atm at 867°C.

In Fig. 7, data of Wöhler and of Schenck and Kurzen are compared with our data, the line representing our data being taken from Fig. 6. The three sets of data are in agreement, and on this basis it would appear that the dissociation pressure of palladium oxide is established.

On the other hand, the composition of the palladium oxide phase in equilibrium with palladium metal has not yet been established. Consequently, the dissociation-pressure reaction cannot be written. As mentioned above, others have observed an effect of oxide composition on dissociation pressure. This effect has also been observed in our laboratory, and experiments are being conducted to measure dissociation pressures as a function of oxide composition at various temperatures.

To check on the possible formation of a lower oxide phase, a mixture of Pd(s) and PdO(s) was made in which palladium and oxygen were in the atom ratio 2 to 1. The mixture was sealed in a small, evacuated quartz tube, annealed at 750°C for 72 hr, quenched, and then analyzed by X-ray techniques. Diffraction lines were found only for Pd(s) and PdO(s).

The fact that the dissociation-pressure data (Fig. 6) are linear with $1/T$ suggests either that the solid-solution region is not wide or that the composition of the oxide in equilibrium with the metal does not change in composition with temperature.

Let us calculate thermodynamic quantities assuming that the oxide is stoichiometric PdO and that the dissociation reaction is

From the slope of the line in Fig. 6, we obtain at the mean temperature (950°K)

$$\Delta H_{950}^{\circ} = -25.8 \text{ kcal/mole} ,$$

and from this we obtain

$$\Delta S_{950}^{\circ} = -22.5 \text{ e. u.}$$

for reaction (11). From heat-capacity equations given by Kelley, ⁽¹⁰⁾ we

Fig. 7-- Comparison of dissociation-pressure data for palladium oxide

derive

$$\Delta C_p = -6.08 + 12.32 \times 10^{-3} T + 0.20 \times 10^{-5} T^{-2}$$

for reaction (11), and using this we calculate

$$\Delta H_{298}^{\circ} = -26.8 \text{ kcal/mole}$$

and

$$\Delta S_{298}^{\circ} = -23.6 \text{ e. u.}$$

The heat of formation is considerably higher than the value of -20.4 kcal/mole found calorimetrically by Wöhler and Jockum.

Combining ΔS_{298}° with standard entropies for palladium ($9.06 \pm 0.05 \text{ e.u.}$) and oxygen ($49.01 \pm 0.01 \text{ e.u.}$) given by Kelley and King⁽¹¹⁾ yields $S_{298}^{\circ} \text{ PdO(s)} = 9.9 \text{ e.u.}$ This value seems reasonable when compared with standard entropy values given by Kelley and King for similar oxides: 10.19 ± 0.05 for CuO, 9.08 ± 0.04 for NiO, 13.5 ± 0.3 for SnO, 8.31 ± 0.04 for TiO, and 9.3 ± 0.2 for VO. On the other hand, the value seems low when compared with the value of 13.2 e.u. calculated for PdO using Latimer's tables.⁽¹²⁾

DISSOCIATION OF RHODIUM OXIDE

The dissociation pressure of rhodium oxide as a function of temperature has been measured using static and dynamic methods. According to the literature, Rh_2O_3 is the stable solid oxide of rhodium. Analyses of samples which we have prepared are in agreement.

To check for intermediate oxides, a sample of Rh(s) and Rh_2O_3 (s) was prepared in which rhodium and oxygen were in the atom ratio 1 to 1. The sample was placed in a small quartz tube, annealed at 885°C for 70 hr, quenched, and then analyzed by X-ray techniques. Diffraction lines only for Rh(s) and Rh_2O_3 (s) were found.

Dissociation-pressure values were measured over the temperature range 730° to 1125°C . A $\log p$ versus $1/T$ plot of the data is shown in Fig. 8; within experimental error, the pressure values fall on a straight line. The dissociation pressure reaches 1 atm at 1125°C .

From the slope of the line, we calculate at the mean temperature (1170°K)

$$\Delta H_{1170}^{\circ} = -95.3 \text{ kcal/mole}$$

Fig. 8--Dissociation pressure of rhodium oxide

and

$$\Delta S_{1170}^{\circ} = -63.5 \text{ e. u.}$$

for the reaction

From heat-capacity data given by Kelley⁽¹⁰⁾ for $\text{M}_2\text{O}_3(\text{s})$ -type compounds, we estimate the heat capacity of Rh_2O_3 to be 30 cal/deg-mole. Combining this with known heat capacities for Rh(s) and $\text{O}_2(\text{g})$, we obtain $\Delta C_p = 4.3$ cal/deg-mole. Using this value, we calculate

$$\Delta H_{298}^{\circ} = -98.6 \text{ kcal/mole}$$

and

$$\Delta S_{298}^{\circ} = -69.4 \text{ e. u.}$$

for reaction (12).

Combining the ΔS_{298}° value with standard entropies for rhodium ($7.53 \pm 0.05 \text{ e. u.}$) and oxygen ($49.01 \pm 0.01 \text{ e. u.}$) given by Kelley and King,⁽¹¹⁾ we obtain $S_{298}^{\circ} \text{Rh}_2\text{O}_3(\text{s}) = 19.2 \text{ e. u.}$ This value may be compared with the standard entropy values 12.18 ± 0.03 for Al_2O_3 , 19.4 ± 0.3 for Cr_2O_3 , 20.90 ± 0.10 for Fe_2O_3 , 30.7 ± 0.2 for La_2O_3 , 26.4 ± 0.5 for Mn_2O_3 , 18.83 ± 0.09 for Ti_2O_3 , and 23.5 ± 0.3 for V_2O_3 given by Kelley and King, and with a value of 26.5 e. u. calculated from Latimer's tables.⁽¹²⁾

DISSOCIATION OF IRIDIUM OXIDE

According to Cordfunke and Meyer,⁽¹³⁾ iridium metal is appreciably soluble in solid IrO_2 at temperatures above 800°C . These investigators determined the width of the solid-solution region from X-ray analyses of annealed samples of Ir(s) and $\text{IrO}_2(\text{s})$. Their results indicate that the ratio O/Ir is only 1.6 at 1050°C . We hope to check their observations by the use of X-ray techniques and also by the determination of dissociation pressures as a function of composition at various temperatures. Information on solid-solution behavior is, of course, necessary to define the dissociation reaction.

Thus far in our studies of iridium oxide, dissociation pressures as a function of temperature have been measured using a static method. Measurements were attempted by a dynamic (transpiration) method, but the results indicated that equilibrium was not attained. Figure 9 shows the

Fig. 9--Comparison of three sets of data on the dissociation pressure of solid iridium oxide

dissociation-pressure data (measured by the static method) plotted against reciprocal temperature. The values are representative of three-phase (oxygen, iridium metal, and iridium oxide) equilibria.

Cordfunke and Meyer also measured the dissociation pressure of iridium oxide, and their data are included in Fig. 9. They report two sets of pressure values, the lower set being representative of three-phase equilibria and the higher set being representative of the dissociation of stoichiometric IrO_2 . Their lower set of data fall only slightly above a line drawn through our data.

Let us neglect nonstoichiometric behavior and assume that the three-phase equilibrium is represented by the reaction

and on this basis calculate thermodynamic data. From the slope of the line drawn through our data in Fig. 9, we obtain at the mean temperature (1250°K)

$$\Delta H_{1250}^\circ = -53.8 \text{ kcal/mole} \quad ,$$

and from this obtain

$$\Delta S_{1250}^\circ = -39.0 \text{ e. u.}$$

for reaction (13). Using $\Delta C_p = +6.1 \text{ cal/deg-mole}$, estimated from heat-capacity data given by Kelley, ⁽¹⁰⁾ we calculate

$$\Delta H_{298}^\circ = -59.6 \text{ kcal/mole}$$

and

$$\Delta S_{298}^\circ = -47.7 \text{ e.u.}$$

The ΔH_{298}° value may be compared with the value of -40.1 kcal/mole determined calorimetrically by Wöhler and Jockum. ⁽⁹⁾ Combining the ΔS_{298}° value with standard entropies for iridium and oxygen (8.48 ± 0.04 and 49.01 ± 0.10 , respectively), we obtain $S_{298}^\circ \text{IrO}_2(\text{s}) = 9.8 \text{ e. u.}$ This value is not unreasonable considering that the uncertainty is 2 or 3 e. u. We would estimate the standard entropy of the compound to be around 12 e. u. on the basis of standard entropy values given by Kelley and King ⁽¹¹⁾ for similar oxides.

As mentioned above, Cordfunke and Meyer report a set of data (the upper set of data in Fig. 9) which they consider to be representative of the dissociation pressure of stoichiometric IrO_2 . They calculate from these data

$$\Delta H_{298}^{\circ} = -64.0 \text{ kcal/mole}$$

for reaction (13). A further calculation performed using their data and the ΔC_p value cited above yields

$$\Delta S_{298}^{\circ} = -51.9 \text{ e. u.}$$

Combining this with standard entropies for the elements given above, we obtain $S_{298}^{\circ} \text{ IrO}_2(\text{s}) = 5.7 \text{ e. u.}$ This value is unreasonable when compared with the expected value of around 12 e. u. The result indicates that heat and entropy values calculated from the particular set of data in a second-law calculation are questionable.

X-RAY STUDIES OF THE TRICHLORIDES OF PLATINUM-GROUP METALS

The metals ruthenium, rhodium, and iridium form solid trichlorides. Osmium apparently forms a trichloride, but the compound appears to have a wide range of composition. Chemical analyses of osmium chloride samples have given chlorine contents which vary from 3.13 to 3.94 chlorine atoms per osmium atom. Palladium trichloride is not stable, but palladium dichloride is known. The chlorides of platinum have not yet been defined.

Structural parameters found in single-crystal X-ray studies of chromium trichloride by Wooster⁽¹⁴⁾ and in similar studies of ruthenium trichloride by Stroganov and Ovchinnikov⁽¹⁵⁾ are identical within the limits of error given. This suggests that the two compounds are isostructural. The data are shown in Table 3.

To compare unit-cell dimensions for all the trichlorides, X-ray powder photographs were obtained using samples of RuCl_3 , RhCl_3 , IrCl_3 , $\text{OsCl}_{3.13}$, and $\text{OsCl}_{3.93}$ (in the remainder of this section $\text{OsCl}_{3.13}$ and $\text{OsCl}_{3.93}$ will be referred to as OsCl_3 and OsCl_4 , respectively). The X-ray patterns were taken with a 114.6-mm Straumanis-loading Debye-Scherrer camera filled with hydrogen.

The structural parameters given in Table 3 were used to obtain the intensities of all lines which might contribute to powder patterns for the trichlorides. By use of these intensities, it was possible to index the lines for all the compounds. With the aid of an analytical extrapolation method and a least-squares FORTRAN program written by Vogel and Kempter,⁽¹⁶⁾

lattice constants and their standard deviations were calculated from the photographs. The results are given in Table 4.

Table 3
STRUCTURAL PARAMETERS FOR CrCl_3 AND RuCl_3 ^a

Space group $P3_112$ - 6 MCl_3 per unit cell. Two metal ions at 5/9, 7/9, 0 and 8/9, 4/9, 0 (3-fold positions) and 3 chloride ions at 5/9, 7/9, 0.26; 8/9, 4/9, 0.26; and 2/9, 1/9, 0.26 (6-fold positions).

Compound	a_0 (Å)	c_0 (Å)
CrCl_3	6.02 ± 0.05	17.3 ± 0.1
RuCl_3	5.97 ± 0.04	17.2 ± 0.1

^a Data of Wooster⁽¹⁴⁾ and of Stroganov and Ovchinnikov.⁽¹⁵⁾

Table 4
LATTICE CONSTANTS OBTAINED FOR METAL TRICHLORIDES

Compound	X-ray Wave Length	a_0 (Å)	c_0 (Å)	c/a
RuCl_3	2.2909	5.983 ± 0.004	17.171 ± 0.007	2.870 ± 0.002
RhCl_3	2.2909	5.942 ± 0.002	17.054 ± 0.003	2.870 ± 0.001
	1.5418	5.942 ± 0.002	17.063 ± 0.009	2.872 ± 0.002
OsCl_3	2.2909	6.047 ± 0.002	17.151 ± 0.004	2.836 ± 0.001
	1.5418	6.048 ± 0.002	17.147 ± 0.004	2.835 ± 0.001
IrCl_3	1.5418	6.015 ± 0.002	17.019 ± 0.006	2.829 ± 0.001

Although no definitive conclusions can be drawn without knowing atom coordinates in these crystals, it is interesting to note similarities in the c/a ratios of RuCl_3 and RhCl_3 and of OsCl_3 and IrCl_3 . The latter pair approach the c/a ratio which would be produced by ideal cubic closest packing of anions, $\sqrt{8} = 2.828$. Volumes of the unit cells also appear to show periodic behavior, with similar changes in size from RuCl_3 to RhCl_3 (532.3 to $521.5 \text{ \AA}^3$) as from OsCl_3 to IrCl_3 (543.1 to $533.3 \text{ \AA}^3$).

As representative of the best patterns obtained, observed $\sin^2 \theta$ values for CrK_α radiation and their deviations from calculated values are given for RhCl_3 and OsCl_3 in Table 5. Relative peak heights were obtained with a microphotometer by conversion of percent transmission to density. Observed peak heights are also shown for OsCl_4 in Table 5, and it can be seen that all except the 114, 118, 300, 0012, 224, and 228 lines are significantly weaker than their OsCl_3 counterparts. Furthermore, no new lines could be detected in the OsCl_4 pattern. Prominent peaks obtained for OsCl_4 with CuK_α radiation are given in Table 6; other peaks occurred, but none exceeded the height of neighboring listed peaks. The deviations from observed $\sin^2 \theta$ values are given for a primitive, cubic unit cell with $a_0 = 2.4685 \pm 0.0005 \text{ \AA}$.

These results suggest that OsCl_4 crystals do not belong to the trigonal CrCl_3 space group, but rather simulate a NaCl -type structure with $1/4 \text{ Os}^{+4}$ at each cation position on the average. Although this statistical space group is not a primitive one ($\text{Fm}3\text{m}$), one-half the possible lines are not observed because of the near equality of X-ray scattering by $1/4 \text{ Os}^{+4}$ and Cl^- ions. Such is the case for KCl crystals, and CuK_α intensities for this salt ($a_0 = 6.293 \text{ \AA}$, ASTM 4-0587) are listed in Table 6 for comparison. It appears, then, that the unit cell for OsCl_4 is cubic with $a_0 = 4.937 \pm 0.001 \text{ \AA}$.

The principal difference between crystals of OsCl_3 and OsCl_4 lies in their cation distributions. This can be understood if we let C stand for a layer of cations and A for a layer of anions. Then the sequence along the trigonal c -axis is ACAACA... in OsCl_3 and ACACAC... in OsCl_4 .

Comparison of the two unit cells can be made by computing "cubic" unit-cell lengths from the trigonal OsCl_3 dimensions. If we denote the trichloride lattice constants by A_0 and C_0 , then the distance between Cl^- ions in the (001) plane may be obtained from the parameters in Table 3 as $A_0 \sqrt{27/81} = A_0 / \sqrt{3}$. For the face-centered Cl^- ion arrangement in OsCl_4 , the closest Cl^- - Cl^- distance is one-half of the face diagonal $a_0 / \sqrt{2}$, where a_0 is the "cubic" lattice constant. By equating Cl^- - Cl^- distances, we obtain a relationship between the two unit cells, $a_0 / \sqrt{2} = A_0 / \sqrt{3}$, or $a_0 = A_0 \sqrt{2/3}$. The cube diagonal of the OsCl_4 cell, $a_0 \sqrt{3}$, traversed three layers of Cl^- ions, while six layers are traversed by C_0 in OsCl_3 . Thus, we obtain a second relationship $C_0 = 2a_0 \sqrt{3}$, or $a_0 = C_0 / \sqrt{12}$. From the first

Table 5

X-RAY DATA (CrK_α) FOR OSMIUM AND RHODIUM CHLORIDES

h k l	$\text{OsCl}_{3.13}$				RhCl_3				$\text{OsCl}_{3.93'}$
	Observed Peak Height	Calc. Intensity	Observed $\text{Sin}^2\theta$ $\times 10^4$	Observed- Calc. $\text{Sin}^2\theta$ $\times 10^4$	Observed Peak Height	Calc. Intensity	Observed $\text{Sin}^2\theta$ $\times 10^4$	Observed- Calc. $\text{Sin}^2\theta$ $\times 10^4$	Observed Peak Height
0 0 3	68	100	0398	-2	92	100	0405		25
1 0 0		16			18	14	0499		
1 1 1	58	19	1477	1	48	16	1540		9
0 0 6	} 7	2	1603	1		0			} 3
1 1 2		3		-7		0			
1 1 4	100	29	2147	2	100	37	2219		100
1 1 5	26	6	2546	-0	12	4	2623		3
0 0 9		2			} (2)	1	3673		
1 2 2		2				1			
1 1 7	40	7	3622	5	21	8	3707	-8	5
1 1 8	} 86	8	4305	19	37	9	4391	1	} 74
3 0 0		17		2	49	21	4478	2	
3 0 3	32	15	4704	0	26	14	4878	-3	4
2 2 1	12	2	5783	-0	9	2	6006	2	
3 0 6	9	3	5903	-6		-1			5
1 3 0		1			(2)	1/2	6462	9	
0 0 12	23	3	6412	-8	16	3	6512	4	} 31
2 2 4	30	5	6446	-7	23	6	6678	-1	
1 1 11	42	4	6825	-5	13	4	6954	-2	
2 2 5		2			(2)	1	7082	-2	
4 0 0		1			(2)	1/2	7939	4	
3 0 9	} 34	6	7925	8	} 14	3	8147		20
2 2 7		4		-0		4			
2 2 8	35	6	8585	-0	20	8	8830	-7	
1 1 13	14	2	8962	-0	(3)	1	9116	2	

relationship we calculate $a_o = 6.047\sqrt{2/3} = 4.937 \pm 0.002 \text{ \AA}$, which is identical with the value $4.937 \pm 0.001 \text{ \AA}$ found for OsCl_4 . On the other hand, from the second relationship we obtain $a_o = 17.151/\sqrt{12} = 4.951 \pm 0.002 \text{ \AA}$, which is significantly larger than the a_o value found for OsCl_4 . This indicates the occurrence of a uniaxial expansion along the trigonal z-axis in passing from OsCl_4 to OsCl_3 .

Table 6
X-RAY DATA ($\text{CuK}\alpha$) FOR OsCl_4 COMPARED WITH
ASTM DATA FOR KCl

h k l ^a	OsCl_4			KCl	
	Observed Height	Observed $\sin^2\theta \times 10^4$	Observed-Calc. $\sin^2\theta \times 10^4$	KCl	
				I/I _o	h k l
1 1 4	100	976	-3	100	2 0 0
1 1 8 } 3 0 0 }	68	1950	-5	59	2 2 0
2 2 4 } 0 0 12 }	19	2935	5	23	2 2 2
2 2 8	7	3910	4	8	4 0 0
4 1 4 } 3 0 12 }	17	4878	-2	20	4 2 0
4 1 8 } 1 1 16 } 3 3 0 }	12	5852	-3	13	4 2 2
2 2 16 } 6 0 0 }	5	7811	7	2	4 4 0
5 2 4 } 3 3 12 } 1 1 20 }	7	8785	7	6	{ 4 4 2 6 0 0
5 2 8 } 4 1 16 }	6	9750	-2	2	6 2 0

^a P3_112 indices are given to show relationship with OsCl_3 .

Calculated intensities based on $2/3 \text{ Os}^{+3}$ at $5/9, 7/9, 0; 8/9, 4/9, 0; 2/9, 1/9, 0$ and Cl^- ions in originally listed P3_112 positions account for all observed $\text{CrK}\alpha$ lines for OsCl_3 , so disorder within (001) cation planes is not excluded. IrCl_3 , in fact, exhibits the (100) line while OsCl_3 does not, which perhaps indicates that this type of disorder is present in the latter.

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