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THE HIGH-TEMPERATURE CHEMISTRY OF
FISSION-PRODUCT ELEMENTS

SUMMARY REPORT

August 1, 1961, through July 31, 1962

Cont ATC04-3) -164

August 23, 1962

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GENERAL ATOMIC
DIVISION OF
GENERAL DYNAMICS

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REACTOR DIVISION

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I. INTRODUCTION

During the past year the study of the osmium-chlorine system, mentioned in the last Summary Report,^{(1)*} has been continued, and studies of the iridium-chlorine and ruthenium-oxygen systems have been undertaken. A paper giving an account of our work on the rhodium-chlorine system has been published,⁽²⁾ and a paper on the chemistry of the transition metal chlorides has been presented at a regional meeting of the American Chemical Society.⁽³⁾

Several unexpected and interesting developments have resulted from our studies. We found that the solid chloride of osmium exhibits a wide homogeneity range. Such behavior is rare for chlorides. We have been able to show that previously reported IrCl_2 and IrCl do not exist. We have found that both osmium and iridium show a refractory behavior that we have not observed with the other platinum metals studied.

In this report, the current work is summarized and then discussed in detail in the appendixes. However, it seems worthwhile to briefly outline the work which has been completed and reported on.

II. WORK COMPLETED

Studies of the high-temperature chemistry of the chlorides of ruthenium, rhodium, and palladium have been completed and published.^(2, 4-6) For each of these metal-chlorine systems, condensed phases and vapor species were identified, dissociation and vapor pressures were measured, and thermodynamic data were calculated from the pressure data.

A discussion of diffusion effects in the transpiration method of vapor-pressure measurement has been published.⁽⁷⁾ A discussion of kinetic effects in the transpiration method has been written,⁽⁸⁾ and an extensive review of the method has been issued.⁽⁹⁾

Papers have been presented at a Gordon Conference⁽⁸⁾ and at a meeting of the International Congress of Pure and Applied Chemistry.⁽¹⁰⁾

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*References are given on the last page of this section.

Some work was performed using infrared techniques to study inorganic vapors, (11) and a review was written of the ligand field theory and its application to the chemistry of transition metal chlorides. (1)

III. CURRENT STUDIES

THE OSMIUM-CHLORINE SYSTEM

Studies of the osmium-chlorine system in the temperature range 400° to 1500°C are almost complete. The results are summarized below and are discussed in detail in Appendix A.

Osmium exhibits a refractory nature that we have not encountered with the other platinum metals studied (we have recently found similar behavior in iridium); consequently, this has been a difficult system to study. The metal could not be chlorinated directly; the chloride could be made only by vapor condensation. In the temperature range 550° to 1100°C , we could not obtain equilibrium vapor pressures even though various schemes were tried.

It is of particular interest that the condensed phase in the osmium-chlorine system was found to be a solid chloride with a wide range of homogeneity-- $\text{OsCl}_{3.1}$ to $\text{OsCl}_{3.9}$. Wide ranges of homogeneity are very unusual for chlorides, niobium chloride being the only other chloride reported to exhibit such behavior. (12) X-ray powder photographs of OsCl_{3+z} , CrCl_3 , RuCl_3 , RhCl_3 , and IrCl_3 show many lines in common; thus, it appears likely that these compounds are isostructural. We found that solid OsCl_{3+z} decomposes to the metal under a chlorine pressure of 1 atm at about 575°C .

The effect of chlorine pressure on vapor pressure indicates that the important vapor species are OsCl_4 , OsCl_3 , and OsCl_2 . Over the solid chloride, OsCl_4 appears to be the important vapor species. Above 575°C , where osmium metal is the stable condensed phase, the partial pressure of OsCl_4 decreases and the partial pressures of OsCl_3 and OsCl_2 increase with increasing temperature.

THE IRIDIUM-CHLORINE SYSTEM

The iridium-chlorine system is being investigated in the temperature range 600° to 1500°C . This investigation is estimated to be 50% complete. A summary of the results is given below, and a detailed account of the work is given in Appendix B.

Solid IrCl_3 appears to be the only stable condensed chloride of iridium under the conditions studied. We find no evidence of a homogeneity range. In disagreement with results reported by other investigators, ⁽¹³⁾ our results show that the lower chlorides IrCl_2 and IrCl do not exist. We have measured the dissociation pressure of $\text{IrCl}_3(\text{s})$ over the temperature range 615° to 770°C by two methods. The compound is found to decompose under a chlorine pressure of 1 atm at 768°C .

Several vapor-pressure determinations have been made over the temperature range 650° to 1500°C and a chlorine-pressure range of 0.2 to 1.0 atm. Difficulties were encountered in obtaining equilibrium vapor pressures in the temperature range 768° to 1300°C . It is interesting to note that this refractory behavior in an intermediate temperature range is similar to the behavior exhibited by osmium. Results on the effect of chlorine pressure on vapor pressure suggest that IrCl_3 is the only important vapor species under the conditions studied.

THE RUTHENIUM-OXYGEN SYSTEM

The ruthenium-oxygen system in the temperature range 800° to 1500°C is being investigated. The investigation is estimated to be two-thirds complete. The work is summarized below and a detailed account of the work is given in Appendix C.

There appears to be no dissociation-pressure data in the literature on the ruthenium-oxygen system. There is a small amount of reported vapor-pressure data, but a disagreement exists with regard to the important vapor species.

Solid RuO_2 appears to be the only stable condensed oxide of ruthenium. The compound does not show a measurable homogeneity range. The dissociation pressure of the compound has been measured over the temperature range 1100° to 1500°C , using two different methods. The dissociation pressure is found to be 1 atm at 1540°C .

Vapor pressures have been measured both as a function of oxygen pressure and of temperature. Studies of the effect of oxygen pressure on vapor pressure at 1453° and 1503°C indicate the important vapor species to be RuO_3 . Curvature in the $\log p_v$ versus $1/T$ curve in the region 900° to 1100°C suggests a higher oxide vapor species, probably RuO_4 .

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Appendix A

THE OSMIUM-CHLORINE SYSTEM AT HIGH TEMPERATURE

by

W. E. Bell, M. Tagami, R. E. Inyard, P. K. Gantzel, and J. M. Dixon

The high-temperature chemistry of the osmium-chlorine system has been studied for the purpose of identifying condensed phases and vapor species, measuring dissociation and vapor pressures, and determining thermodynamic quantities for the various reactions and species involved.

Osmium proved to be much more refractory than the other metals of the platinum group (ruthenium, rhodium, and palladium) which have been studied in this Laboratory. Direct chlorination of the metal could not be accomplished; we were able to make the solid chloride only by condensation of the chloride vapor. Dissociation pressures could not be measured; under some temperature and chlorine pressure conditions, equilibrium vapor pressures could not be achieved.

A paper by Ruff and Bornemann^{(A. 1)*} appears to be the only literature reference of note on the high-temperature chemistry of the osmium-chlorine system. They report the preparation of the solid chlorides OsCl_4 , OsCl_3 , and OsCl_2 , and describe the properties of these compounds.

EXPERIMENTAL

DISSOCIATION PRESSURES

Dissociation pressure measurements were attempted by both the static and the transpiration methods as described in an earlier report. (A. 2)

VAPOR PRESSURES

Vapor pressures were measured by the transpiration method essentially as described in Ref. A. 3. Mullite reaction tubes were used above 1000°C and both mullite and quartz tubes were used below that temperature. Chlorine

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* References appear at the end of each appendix.

served as the carrier gas. To determine the quantity of osmium condensed, the condensing region was broken up and placed in a nitric acid solution. The osmium was separated as the volatile oxide and determined colorimetrically using the thiourea method.

As an aid in achieving equilibrium vapor pressures, the transpiration experiments were conducted using low flow rates of ~ 0.01 millimole Cl_2/min (mmole/min) and large metal (or chloride) samples of ~ 2.5 g. These conditions may be compared with flow rates of ~ 0.03 mmole/min and sample weights of ~ 0.3 g which have been satisfactory in our work on other metal-chlorine systems. As an added aid in achieving equilibrium, the metal samples used in most of the experiments were pretreated with hydrogen at high temperature. As will be described in a later section, other experimental parameters were varied in an attempt to achieve equilibrium.

The vaporization results gave no indication of a diffusion-effect problem. A check on the importance of diffusion can be obtained by using Merten's treatment of diffusion effects in the transpiration method. (A. 4) In applying this treatment, one estimates the importance of vapor diffusion by evaluating the term $\exp(-v\lambda/DA)$ where v is the volumetric flow rate, λ is the length of the capillary, A is the area of the capillary, and D is the interdiffusion coefficient. We apply Merten's treatment at 1500°C since diffusion is more important at higher temperatures. Based on diffusion-effect studies made earlier, (A. 5) it is expected that D is no greater than $2.0 \text{ cm}^2/\text{sec}$ at 1500°C and 1 atm pressure. Using this value for D , the flow rate 0.01 mmole/min cited above, and the capillary dimensions 2 cm long by 0.1 cm in diameter, we calculate $\exp(-v\lambda/DA) = 10^{-1.34} = 0.046$. Thus, under conditions where one would expect diffusion effects to be the greatest in our experiments, the diffusion error appears to be $< 5\%$. From calculations of this type, it was recognized that diffusion could be a problem at the higher temperatures, therefore we conducted most of the experiments in the temperature range 1300° to 1500°C at flow rates higher than 0.01 mmole/min .

GENERAL

Osmium sponge (Johnson-Matthey, 99.995% purity), ammonium chloroosmate (Engelhard Industries), and $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$ (Engelhard) were employed in the condensed-phase studies. Johnson-Matthey osmium sponge or osmium chloride made from the sponge were the solid reactants used in all but one of the vapor-pressure experiments. Engelhard osmium metal (made from the ammonium chloroosmate) was used in one vapor-pressure experiment at 798°C . Matheson chlorine gas (99.85% minimum purity) was used. The chlorine flowed through a sulfuric acid bubbler and P_2O_5 powder before entering the reaction tube. Tube furnaces and Pt-Pt-10% Rh thermocouples were used as described in Ref. A. 3. Temperature uncertainties are believed to range from $\pm 2^\circ$ at 500°C to $\pm 4^\circ$ at 1500°C .

RESULTS AND DISCUSSION

CONDENSED PHASES

Considerable effort was devoted to an attempt to make pure osmium chloride. It was found that direct chlorination of the metal proceeds very slowly. This is shown by the results of an experiment in which osmium metal sponge and chlorine gas at 1 atm pressure were allowed to react for 18 hr at 500°C. The product contained only enough chlorine to be $\text{OsCl}_{0.4}$. (Analyses of the chlorides were performed gravimetrically by hydrogen reduction.)

Dehydration of commercial $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$ in a chlorine stream at 400°C gave material which was contaminated with oxides.

Several attempts were made to produce the chloride from commercial ammonium chloroosmate, $(\text{NH}_4)_2\text{OsCl}_6$. Samples of the chloroosmate were heated in a chlorine stream at temperatures ranging from 350°C to 550°C for as long as 15 hr; none of the products, however, was entirely free of ammonia.

It was found that osmium chloride can be made by condensation of the chloride vapor. This can be done by heating the underside of a quartz reaction tube containing osmium metal in a chlorine atmosphere. The chloride forms on the hot surface of the metal, vaporizes, and condenses on the inside upper surface of the reaction tube. Chemical analyses consistently showed material made in this manner to have a chlorine content close to $\text{OsCl}_{3.9}$. The material condenses in the form of a grayish-black crust which does not appear to be hygroscopic.

Attempts were made to prepare pure $\text{OsCl}_3(\text{s})$ from samples of $\text{OsCl}_{3.9}(\text{s})$ made in the manner just mentioned. Samples of $\text{OsCl}_{3.9}$ were held at 550°C and 1 atm chlorine pressure for periods as long as 30 hr. The lowest chloride obtained was $\text{OsCl}_{3.1}$. This behavior suggests that the solid chloride has a wide homogeneity range, $\text{OsCl}_{3.1}$ to $\text{OsCl}_{3.9}$, which seems to be substantiated by the following results obtained from X-ray analyses and density measurements.

X-ray powder photographs of OsCl_{3+z} , CrCl_3 , RuCl_3 , RhCl_3 , and IrCl_3 show many lines in common; thus, it appears likely that these compounds are isostructural. Single crystal X-ray studies of CrCl_3 and RuCl_3 were carried out by Wooster(A. 6) and by Stroganov and Ovchinnikov(A. 7); within their limits of error, identical structural parameters were found for the two compounds. We have found that hexagonal lattice constants of $a_0 = 6.04$ and $c_0 = 17.1$ Å give a reasonable fit for the $\text{OsCl}_{3.1}$ pattern.

The spacings for $\text{OsCl}_{3.9}$ are identical with those for $\text{OsCl}_{3.1}$, but most of the weaker lines are faint or absent in the photograph of $\text{OsCl}_{3.9}$. Although the lowest order line (003) remains in the $\text{OsCl}_{3.9}$ pattern, almost all other lines may be indexed on the basis of a primitive cubic cell with sides of $2.466 \pm 0.001 \text{ \AA}$ (8 lines). The presence of the (003) line indicates that the P3_112 -unit cell is probably maintained by random osmium vacancies resulting in a nonintegral number of cations per unit cell in OsCl_{3+z} . The observed c/a ratio is almost exactly equal to $\sqrt{8}$, the value given by cubic closest packing.

Table 1 compares the theoretical (X-ray) densities with the measured densities of chlorides of various compositions produced by decomposition of $\text{OsCl}_{3.9}$ in 1 atm chlorine pressure at 550°C . The theoretical densities were calculated on the basis of 18 chloride ions and a variable number of osmium ions per hexagonal unit cell. It was hoped that there would be better

Table 1
COMPARISON OF THEORETICAL WITH MEASURED
DENSITIES OF OSMIUM CHLORIDE

Composition, Cl:Os Ratio	Theoretical Density (g/cm^3)	Measured Density (g/cm^3)
3.13	5.32	4.97
3.41	5.05	4.92
3.68	4.82	4.87
3.94	4.63	4.41

agreement between the measured and the theoretical densities; nevertheless, the measured densities change with composition as one would expect for a chloride of nonstoichiometric behavior.

Solid OsCl_{3+z} appears to decompose slowly and completely to metal in 1 atm chlorine pressure at temperatures above 575°C . This indicates that lower chlorides, such as $\text{OsCl}_2(\text{s})$ and $\text{OsCl}(\text{s})$, do not exist as stable phases.

Ruff and Bornemann^(A. 1) reported the preparation of $\text{OsCl}_4(\text{s})$ by slow cooling of vapor produced by passing chlorine gas over osmium metal at 650° to 700°C . This compound was produced in the form of a black, brittle crust. On rapid cooling of the vapor, they found that $\text{OsCl}_3(\text{s})$ formed. These investigators attempted to make $\text{OsCl}_3(\text{s})$ by decomposition of ammonium chloroosmate in a chlorine stream at high temperature; however, they found that the product consistently contained 6% to 7% of ammonium

chloride. $\text{OsCl}_3(\text{s})$ was found to be a dark brown, porous, hygroscopic powder. These authors also reported the preparation of $\text{OsCl}_2(\text{s})$ by heating $\text{OsCl}_3(\text{s})$ at about 500°C and 0.46 atm chlorine pressure, or in vacuum; they reported the dichloride to be a dark brown, water-insoluble powder. As mentioned above, we found no evidence for lower chlorides.

DISSOCIATION PRESSURES

Dissociation-pressure measurements were attempted with samples of $\text{OsCl}_{3.9}$ made in the manner described above. In measurements at several temperatures using the transpiration method, we were able to get fairly constant partial pressures of chlorine in the argon carrier gas, but the pressure values did not show a reasonable temperature dependence. In static measurements, it was found that equilibrium conditions could not be achieved. Inability to measure dissociation pressures is undoubtedly caused by the slowness of the decomposition and formation reaction.

IDENTIFICATION OF VAPOR SPECIES

On the basis of the condensed-phase studies, the stable condensed phases are $\text{Os}(\text{s})$ and $\text{OsCl}_{3+z}(\text{s})$; therefore, the solid-vapor equilibria to be considered are:

From the equilibrium constant for reaction (A. 1), we obtain

$$\log p_{\text{Os}_x \text{Cl}_y} = \frac{y}{2} \log p_{\text{Cl}_2} + \log K. \quad (\text{A. 3})$$

A similar expression is obtained for reaction (A. 2), and we see that $y/2$ and $[y - (3+z)x]/2$ can be evaluated by studying the effect of chlorine pressure on vapor pressure. Providing both equilibria can be studied under temperature conditions where the same vapor species can be studied over both condensed phases, x and y can be evaluated. However, this could not be done in this study because of kinetic difficulties.

Chlorine pressure-dependence data measured at 1104° , 1304° , and 1506°C are shown in Fig. A. 1 a. The pressure data were plotted assuming one gaseous molecule per osmium atom condensed. In Fig. A. 1 a, we have

Fig. A. 1--Effect of chlorine pressure on vapor pressure, assuming one gaseous molecule per osmium atom condensed: (a) at 1104°, 1304°, and 1506°C; (b) at 498°C

shown the results of all experiments conducted at 1506°C. At 1104°C and 1304°C, it was necessary to discard several vapor-pressure values that obviously were not equilibrium values. At 1104°C and 0.1 atm chlorine pressure, we were unable to obtain a value that seemed reasonable.

Equation (A. 3) applies to the data of Fig. A. 1 a since reaction (A. 1) is the vaporization reaction in the temperature range 1104°C to 1506°C under the chlorine pressure conditions used. The slopes of the curves are 1.3, 1.2, and 1.1 at 1104°C, 1304°C, and 1506°C, respectively; thus, y varies from 2.6 to 2.2 over this temperature range. The fact that this is not a whole number and the fact that y decreases with increasing temperature are interpreted to mean that the vapor is composed of both $\text{Os}_x\text{Cl}_2(\text{g})$ and $\text{Os}_x\text{Cl}_3(\text{g})$. For this combination of species, one would expect the observed pressure-dependence curves to show more upward concavity than they do. In explanation of this, it is presumed that the measured vapor pressures are slightly less than the saturation pressures. The data do not permit an unambiguous evaluation of x ; however, it seems probable that $x = 1$.

The chlorine pressure-dependence data obtained at 498°C are shown in Fig. A. 1 b. The vapor-pressure value (19.9×10^{-3} atm) at 0.99 atm chlorine pressure was obtained using the flow rate 0.01 mmole/min and was selected from several values obtained from experiments conducted under various flow-rate conditions. The other pressure values were the only determinations made at the respective chlorine pressures and were obtained using flow rates of approximately 0.01 mmole/min.

At 498°C and in the chlorine pressure range studied, reaction (A. 2) is the vaporization reaction. The data in Fig. A. 1 b show a slope of 0.6; thus, $[y-(3+z)x]/2 = 0.6$ and $y = 1.2 + (3+z)x$. It seems likely that the stable condensed chloride is OsCl_3 , even though the lowest condensed chloride obtained was $\text{OsCl}_{3.1}$; and it seems probable that $x = 1$. Therefore, $y = 4.2$. Our interpretation of this result is that OsCl_4 is the important vapor species over solid osmium chloride. Analogously, in the ruthenium-chlorine system we found $\text{RuCl}_4(\text{g})$ to be the important species over solid ruthenium trichloride.(A. 8)

We were unable to achieve equilibrium vapor pressures in the temperature range 550°C through 1100°C; therefore, the effect of chlorine pressure on vapor pressure could not be studied in this temperature region.

TEMPERATURE DEPENDENCE OF VAPOR PRESSURE

From the results so far mentioned, we surmise that

is the important reaction at lower temperatures where the solid chloride is the stable condensed phase, and that

are the important reactions at higher temperatures where Os(s) is the condensed phase.

Figure A. 2 shows the $1/T$ dependence of observed vapor pressures in equilibrium with the stable condensed phase, Os(s) or OsCl₃(s), at 1 atm chlorine pressure. The points represent total vapor pressures and were plotted assuming one gaseous molecule per osmium atom condensed.

Let us first consider the vapor-pressure data in the low temperature region 398° to 548° C ($10^3/^\circ\text{K} = 1.490$ to $10^3/^\circ\text{K} = 1.218$). Sources of the data in this region are as follows: The pressure value at $10^3/^\circ\text{K} = 1.490$ was selected from the results of several experiments conducted to find the effect, at this temperature, of variation in flow rate and solid reactant on the observed vapor pressures. The pressure value at $10^3/^\circ\text{K} = 1.297$ was taken from the chlorine-pressure-dependence curve in Fig. A.1 b. The values at $10^3/^\circ\text{K} = 1.387$ and $10^3/^\circ\text{K} = 1.218$ represent the results of the only experiments conducted at these two temperatures. A slight correction to 1 atm chlorine pressure was necessary for each of the observed values due to the fact that the measurements were made at chlorine pressures of ~0.98 atm.

The four vapor-pressure values in the low-temperature region fall on a straight line and appear to be equilibrium values. From the slope of the line we obtain $\Delta H_{750}^\circ = +23$ kcal/mole and from this $\Delta S_{750}^\circ = +22$ e. u. for reaction (A. 4). These thermodynamic values seem reasonable when compared with the values $\Delta H_{1000}^\circ = +33.4$ kcal/mole and $\Delta S_{1000}^\circ = +24.2$ e. u. that we obtained for a similar reaction in the ruthenium-chlorine system. (A. 8)

Let us skip, temporarily, the intermediate temperature region and consider only the data in Fig. A.2 above $10^3/^\circ\text{K} = 0.728$ (1100° C). The pressure values at $10^3/^\circ\text{K} = 0.726$, 0.634, and 0.562 were taken from the curves in Fig. A.1 a. The value 74×10^{-3} atm at $10^3/^\circ\text{K} = 0.677$ is the result obtained at a flow rate of 0.01 mmole/min. Values obtained at this temperature and at higher flow rates were 73×10^{-3} atm at 0.037 mmole/min and 28×10^{-3} atm at 0.069 mmole/min. The point at $10^3/^\circ\text{K} = 0.596$ was the result of the only experiment conducted at this temperature. All the values were corrected to 1 atm chlorine pressure.

Fig. A.2--Temperature dependence of vapor pressure, assuming one gaseous molecule per osmium atom condensed

The vapor-pressure values in the region above $10^3/^{\circ}\text{K} = 0.728$ (1100°C) fall on a smooth curve. This observation coupled with the results of flow-rate studies conducted at 1205°C suggest that equilibrium was achieved in this temperature region.

Thermodynamic information cannot be derived from the curve in the high-temperature region because the relative contributions of $\text{OsCl}_2(\text{g})$ and $\text{OsCl}_3(\text{g})$ to the total vapor pressure are unknown.

Let us consider the temperature region 550° to 1100°C ($10^3/^{\circ}\text{K} = 1.215$ to $10^3/^{\circ}\text{K} = 0.728$). As can be seen in Fig. A.2, many vapor-pressure values were obtained in this region but because of kinetic difficulties which prevented the attainment of equilibrium the values are scattered, and for the most part are very unreasonable. Since the data are unreliable, the $1/T$ dependence curve in this temperature region was drawn (dashed curve of Fig. A.2) to blend with the data and with the lower and higher temperature curves. The break occurs at $1/T = 1,200$ (560°C), and this temperature approximates the temperature at which the solid chloride decomposes under 1 atm chlorine pressure. This result may be compared with the temperature 575°C approximated from condensed-phase studies. The dashed curve was drawn so that at the break the slope changes by about -45 kcal/mole, which is Brewer's estimated value for the heat of formation of $\text{OsCl}_3(\text{s})$.^(A.9)

The curve in the intermediate temperature region is concave because three reactions (A. 5), (A. 6), and (A. 7) prevail. Reaction (A. 7) becomes less important and reactions (A. 5) and (A. 6) become more important as the temperature increases. The ruthenium-chlorine system shows similar behavior in an intermediate temperature region.^(A.8)

Various experimental schemes were tried in the temperature region 550° to 1100°C in the hope that a way could be found to overcome the kinetic difficulties and achieve equilibrium pressure values. Pressure values which were obtained from these experiments together with values obtained using usual experimental procedures are included in Fig. A.2. The experimental techniques used in measuring each of the values are as follows:

1. The "a" points are the results of two experiments in which the carrier gas was allowed to flow through a 1-in. layer of osmium metal powder packed into the reaction tube. These experiments were performed to find the effect of maximizing the surface area of metal exposed to the carrier gas. The results show little effect.
2. The "b" point was obtained from an experiment at 798°C in which Engelhard osmium metal powder was used as the solid reactant in place of the normally used Johnson-Matthey metal powder. This result shows that using osmium metal from a different source had little effect.

3. The "c" point is the result of an experiment at 798°C in which the chlorine carrier gas flowed through metal powder at 800°C before it entered the reaction tube. This experiment was performed with the hope that the carrier gas would be "cleaned up" before it entered the reaction tube. This procedure seemed to aid the approach to equilibrium.
4. The "d" point was obtained from an experiment in which the chlorine carrier gas was saturated with vapor by passing it over osmium metal powder at 550°C ; the gas was then passed over osmium metal powder at 798°C . This experiment was performed to determine the effect of approaching equilibrium from the high-vapor-pressure side. It is interesting to note that this procedure had no effect, which suggests that $\text{OsCl}_4(\text{g})$ reaches its equilibrium vapor pressure rapidly, but that equilibrium between the gaseous species is not easily established.
5. The "e" points are the results of experiments at 648° , 798° , and 948°C ($10^3/^{\circ}\text{K} = 1.086, 0.934, \text{ and } 0.819$, respectively) in which the chlorine carrier gas was saturated with vapor at 1200°C and then passed over metal powder at the temperature of interest. The positions of the "e" points relative to the dashed curve (which is the expected temperature-dependence behavior) indicate that they approach equilibrium values more closely than the other points. The "e" points at 648° and 798°C appear too high, but this is understandable since equilibrium was being approached from the high-pressure side.

The remainder of the points in the 550° to 1100°C region are the results of experiments conducted in the manner outlined in the Experimental section.

Another experimental observation was made which relates to the kinetic problem. A transpiration experiment was performed at 800°C in which 1 atm of oxygen was used as the carrier gas. This experiment showed that the oxides of osmium are very volatile--much more volatile than the chlorides--and the result tends to remove the possibility that the passivity of osmium might be caused by an oxide coating on the metal.

Looking at the data of Fig. A. 2 from an over-all viewpoint, it can be seen that equilibrium vapor pressures of $\text{OsCl}_4(\text{g})$ were achieved at temperatures as low as 398°C , but equilibrium vapor pressures of $\text{OsCl}_3(\text{g})$ and $\text{OsCl}_2(\text{g})$ were achieved only at temperatures above 1100°C . It appears, therefore, that a large difference exists between the rates at which the various gaseous chlorides form and that equilibrium between the gaseous species is not easily established at the lower temperatures.

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Appendix B

THE IRIIDIUM-CHLORINE SYSTEM AT HIGH TEMPERATURE

by

W. E. Bell and M. Tagami

The results which have been obtained so far in the study of high-temperature chemistry of the iridium-chlorine system are described and analyzed. The investigation is approximately 50% complete.

Previous investigators^{(B. 1)(B. 2)} have studied condensed chlorides of iridium and have reported dissociation pressure data. There appear to be no vapor pressure data in the literature. Brewer^(B. 3) estimates that IrCl_4 , IrCl_3 , and IrCl_2 are important vapor species in the range 700° to 1200°C.

EXPERIMENTAL

DISSOCIATION-PRESSURE STUDIES

Dissociation pressures were measured as described in Ref. B.4. Both static and dynamic (transpiration) methods were used.

VAPOR-PRESSURE STUDIES

Vapor pressures were determined by the transpiration method essentially as described in Ref. B.5. Mullite reaction tubes were used. Chlorine served as the carrier gas and was collected in a potassium iodide solution.

To determine the quantity of iridium condensed, a radioactive-tracer method of analysis was used. The radio-tracer 75-d Ir^{192} was produced by irradiation of iridium metal powder in the TRIGA reactor. Gamma-ray spectra of the irradiated metal agreed with spectra reported for Ir^{192} .

At the end of each transpiration experiment, the mullite condensing tube was crushed, placed in a plastic vial, and counted in a NaI(Tl) well counter. Optimum counting was obtained by counting the 0.31 Mev peak through a window. For standards, samples of the radioactive metal were

weighed, mixed with crushed mullite, and counted in the same manner as the unknowns. Under these counting conditions, the specific activity of the metal sample was only about 100 cpm/mg; the activities of the unknowns ranged from about 5 to 300 cpm. The background stabilized at about 18 cpm.

The specific activity of the metal sample that we have used was too low to obtain accurate data in the region of low vapor pressures. We plan to continue the work with a metal sample which will be irradiated for a longer period to reach a higher specific activity.

GENERAL

The materials used were iridium sponge (Johnson-Matthey, 99.995% purity); chlorine gas (Matheson, 99.85% minimum purity); and argon gas (Liquid Carbonic, 99.9% minimum purity). The gases were dried and purified as before. (B. 5)

A platinum-wound tube furnace and Pt-Pt-10% Rh thermocouples were used as described in Ref. B. 5. Temperature uncertainties are believed to range from $\pm 2^\circ$ at 700° to $\pm 4^\circ$ at 1500°C .

RESULTS AND DISCUSSION

CONDENSED-PHASE STUDIES

Crystals produced by direct reaction of iridium sponge and 1 atm of chlorine gas at 600°C during a 12-hr period show a chlorine content, as determined gravimetrically by hydrogen reduction, within 0.7% of the theoretical value for IrCl_3 . Crystals produced in this manner are olive green. Crystals produced by vapor deposition are also IrCl_3 but they are red. Both the olive green and red modifications give the reported $\text{IrCl}_3(\text{s})$ X-ray powder pattern. (B. 6) On the basis of the powder pattern for IrCl_3 , it appears likely that the compound is isostructural with the solid trichlorides CrCl_3 , RuCl_3 , and RhCl_3 .

To test for the existence of lower chlorides, IrCl_2 and IrCl_2 , a mixture of $\text{Ir}(\text{s})$ and $\text{IrCl}_3(\text{s})$ was made in which iridium and chlorine were in a mole ratio of 1 to 1. The mixture was sealed in a small evacuated quartz tube, annealed overnight at 775°C , and then analyzed by X-ray techniques. Diffraction lines were found only for $\text{IrCl}_3(\text{s})$ and $\text{Ir}(\text{s})$. This result indicates that lower chlorides do not exist under the conditions of the experiment. Further evidence that lower chlorides are not stable under our experimental conditions is described under Dissociation-pressure Studies.

Wöhler and Streicher^(B. 1) claim to have shown the existence of $\text{IrCl}_3(\text{s})$ and also the lower chlorides $\text{IrCl}_2(\text{s})$ and $\text{IrCl}(\text{s})$ under conditions similar to ours. However, since they failed to demonstrate the homogeneity of the phases separated and in light of the present results, it would seem that there may be an error in their conclusions regarding IrCl_2 and IrCl .

DISSOCIATION-PRESSURE STUDIES

Our dissociation-pressure data for $\text{IrCl}_3(\text{s})$ together with the data of Wöhler and Streicher^(B. 1) and Remy and Kohn^(B. 2) are plotted in Fig. B. 1. Our data were measured using both a static and a transpiration method. The other investigators used a static method.

It can be seen in Fig. B. 1 that at pressures above 0. 2 atm our data and the data of Wöhler and Streicher are in good agreement, whereas the data of Remy and Kohn appear too high. At pressures below 0. 2 atm, the pressure data of the other investigators veers away from our experimental curve. It is noteworthy that our lowest static point lies above the curve (this point resulted from a measurement made when the chlorine content of the sample was at a maximum). This behavior suggests a systematic error that causes the static data to be too high at the lower pressures.

Both Wöhler and Streicher and Remy and Kohn reported that the degree of sintering of the solid chloride affected the dissociation pressure by as much as 0. 2 atm. Much of the spread in their data is attributed to this effect. We have not found evidence of such behavior.

In our static measurements, the chlorine content of the sample varied from essentially the content of IrCl_3 to less than one chlorine atom per iridium atom. At the end of the measurements, it could be seen that the sample was composed of metal and chloride phases with a clear demarcation between the two phases. The transpiration measurement at 689°C ($10^3/^\circ\text{K} = 1. 039$) was continued to complete decomposition of the chloride and only one pressure plateau was observed. It seems clear, therefore, that chlorine content of the sample has little effect on the dissociation-pressure data. These results suggest also that $\text{IrCl}_3(\text{s})$ is the only stable condensed chloride.

Our data in Fig. B. 1 follow a linear relationship between $\log p$ and $1/T$ within experimental error. The dissociation pressure of $\text{IrCl}_3(\text{s})$ is shown to be 1 atm at 768°C (1041°K).

From the slope of the line in Fig. B. 1, we calculate that at the mean temperature of the measurements (950°K)

$$\Delta H_{950}^\circ = -62.5 \text{ kcal/mole}$$

Fig. B. 1--The dissociation pressure of $\text{IrCl}_3(\text{s})$; comparing General Atomic data with data of other investigators

and

$$\Delta S_{950}^{\circ} = -60.0 \text{ e. u.}$$

for the reaction (uncertainties have not yet been assigned to the thermodynamic data)

Using $\Delta C_p = 4.5 \text{ cal/mole } ^{\circ}\text{K}$, estimated from a rough rule given by Kubaschewski and Evans,^(B. 7) we calculate:

$$\Delta H_{298}^{\circ} = -65.5 \text{ kcal/mole},$$

$$\Delta S_{298}^{\circ} = -65.3 \text{ e. u.},$$

$$\log p_{\text{Cl}_2} = \frac{-9.751}{T} - 1.510 \log T + 13.90.$$

Combining ΔS_{298}° with standard entropies $S_{298}^{\circ} \text{ Ir} = 8.48 \pm 0.04 \text{ e. u.}$ and $S_{298}^{\circ} \text{ Cl}_2 = 53.29 \pm 0.01 \text{ e. u.}$, given by Kelley and King,^(B. 8) we obtain $S_{298}^{\circ} \text{ IrCl}_3(\text{s}) = 23.1 \text{ e. u.}$ This value may be compared with experimental values for isostructural compounds: $S_{298}^{\circ} \text{ RhCl}_3 = 27.1 \pm 3.0 \text{ e. u.}$, obtained by Bell, Tagami, and Merten,^(B. 9) $S_{298}^{\circ} \text{ RuCl}_3(\text{s}) = 30.5 \pm 2.5 \text{ e. u.}$, obtained by Bell, Garrison, and Merten;^(B. 4) and $S_{298}^{\circ} \text{ CrCl}_3(\text{s}) = 29.4 \pm 0.2 \text{ e. u.}$, reported by Kelley and King;^(B. 8) based on low-temperature heat-capacity data.

Wöhler and Streicher^(B. 1) reported dissociation-pressure data for IrCl_2 and IrCl ; however, as mentioned above, we find no evidence for the lower chlorides.

VAPOR-PRESSURE DATA

The vapor-pressure data which have been accumulated to the present time are given in Table B. 1. The data were obtained under various conditions of flow rate, chlorine pressure, and temperature.

The effect of flow rate on the observed vapor pressure values is considered first. In studies made at 702° , 1302° , and 1402°C , flow rates were varied over the range of ~ 0.02 to $0.13 \text{ mmole Cl}_2/\text{min}$. These rates may be compared with flow rates of $\sim 0.03 \text{ mmole Cl}_2/\text{min}$ ordinarily used in our transpiration experiments.

Table B. 1

IRIDIUM CHLORIDE VAPOR-PRESSURE VALUES
UNDER VARYING CONDITIONS OF TEMPERATURE,
CHLORINE PRESSURE, AND FLOW RATE

Temp. (°C)	$1/^\circ\text{K} \times 10^3$	Flow Rate (mmole Cl_2 /min)	Chlorine Pressure (atm)	Vapor Pressure (atm $\times 10^3$)
651	1.082	0.027	0.993	0.0027
702	1.026	0.020	0.747	0.0139
702	1.026	0.033	0.991	0.013
702	1.026	0.057	0.991	0.011
700	1.028	0.122	0.989	0.010
753	0.975	0.030	0.995	0.057
901	0.852	0.034	0.987	0.121
1102	0.727	0.105	0.989	0.34
1302	0.635	0.040	0.988	1.13
1302	0.635	0.054	0.989	0.80
1302	0.635	0.128	0.989	0.58
1402	0.597	0.021	0.989	1.60
1402	0.597	0.061	0.987	1.59
1402	0.597	0.123	0.988	0.85
1503	0.563	0.006	0.248	0.30
1503	0.563	0.030	0.490	0.71
1503	0.563	0.055	0.989	2.2

It can be seen in Table B. 1 that the observed vapor pressures are not independent of flow rate and that the greatest effect occurs at 1302°C. This indicates that a problem exists in achieving equilibrium and that the problem is most pronounced at intermediate temperatures. This behavior is analogous to the behavior of the osmium-chlorine system discussed in Appendix A.

It seems clear that in order to study the vaporization of iridium chloride it is necessary to work at the lowest practical flow rates (bearing in mind diffusion effects) and to take other appropriate steps that will aid in the approach to equilibrium.

IDENTIFICATION OF VAPOR SPECIES

Next we consider the effect of chlorine pressure on vapor pressure and its use in identifying vapor species.

Since Ir(s) and $\text{IrCl}_3\text{(s)}$ appear to be stable condensed phases under

our temperature and chlorine pressure conditions, the vaporization reactions are:

From the equilibrium constant for reaction (B. 2), we obtain

$$\log p_{\text{Ir}_x \text{Cl}_y} = \frac{y}{2} \log p_{\text{Cl}_2} + \log K . \quad (\text{B. 4})$$

A similar expression is obtained from reaction (B. 3), and it can be seen that $y/2$ and $(y - 3x)/2$ can be evaluated from a study of the effect of chlorine pressure on vapor pressure providing the same vapor species can be studied over both condensed phases.

Figures B. 2 and B. 3 show the data obtained so far in our studies of the effect of chlorine pressure on vapor pressure. The data were taken from Table B. 1. The slope of the 1503°C isotherm (Fig. B. 2) is 1.5; thus, $y/2 = 1.5$ and $y = 3$. Therefore, it appears that the important vapor species at temperatures around 1500°C is IrCl_3 . We assume $x = 1$ based on the behavior of other platinum metal chlorides.

If $\text{IrCl}_3\text{(g)}$ is the only vapor species of importance, we would expect the isotherm in the temperature region where $\text{IrCl}_3\text{(s)}$ is the condensed phase to show a slope of zero, which is to say that $(y - 3x)/2 = 0$. The data (two points) that have been obtained so far at 702°C (Fig. B. 3) are in line with this expectation.

Therefore, based on the small amount of data so far obtained, we surmise that IrCl_3 is the only important vapor species under the experimental conditions of this work.

TEMPERATURE DEPENDENCE OF VAPOR PRESSURE

Since IrCl_3 appears to be the important vapor species under our temperature and chlorine pressure conditions, the vaporization reactions to be considered are:

Reaction (B. 5) is related to (B. 6) by reaction (B. 1).

Fig. B. 2--Effect of chlorine pressure on vapor pressure at 1503°C, assuming one gaseous molecule per iridium atom

Fig. B. 3--Effect of chlorine pressure on vapor pressure at 702°C, assuming one gaseous molecule per iridium atom

Figure B. 4 shows the temperature dependence of observed vapor pressures at 1 atm chlorine pressure; the data were taken from Table B. 1. All data at 1 atm chlorine pressure, including data obtained in flow-rate studies, are plotted in Fig. B. 4.

On the basis of the flow-rate studies discussed and of the behavior of the osmium-chlorine system (see Appendix A), we assume that the vapor-pressure points at $10^3/^\circ\text{K} = 0.852$ and $10^3/^\circ\text{K} = 0.727$ are not equilibrium values. We further assume that the point at $10^3/^\circ\text{K} = 0.563$, the low flow-rate point at $10^3/^\circ\text{K} = 0.597$, the points at $10^3/^\circ\text{K} = 1.082$ and 0.975 , and the low flow-rate point at $10^3/^\circ\text{K} = 1.026$ are equilibrium values.

Assuming that $\text{IrCl}_3(\text{g})$ is the only important vapor species in the temperature range studied, the vapor pressure is expected to vary with temperature in the form of two straight lines (neglecting heat-capacity effects) intersecting at $10^3/^\circ\text{K} = 0.961$ (768°C), the temperature at which $\text{IrCl}_3(\text{s})$ dissociates under 1 atm chlorine pressure. On the basis of this assumption the curves in Fig. B. 4 were drawn through the observed vapor pressure points that were assumed to be equilibrium values.

If our method of deriving the curves is valid, curve A represents the temperature dependence of the vapor pressure of IrCl_3 over $\text{Ir}(\text{s})$ at 1 atm chlorine pressure and curve B represents the temperature-dependence data where $\text{IrCl}_3(\text{s})$ is the condensed phase.

From the slope of curve A, we calculate

$$\Delta H_{1041}^\circ = +16.5 \text{ kcal/mole},$$

and from this we obtain

$$\Delta S_{1041}^\circ = -2.8 \text{ c. u.}$$

for reaction (B. 5). For convenience, we assign the temperature 1041°K (768°C) to the thermodynamic quantities since this temperature is the dissociation temperature of $\text{IrCl}_3(\text{s})$ at 1 atm chlorine pressure.

Using $\Delta C_p = -1.1 \text{ cal/mole } ^\circ\text{K}$ estimated from values for similar halides given by Kelley, (B. 10) we calculate

$$\Delta H_{298}^\circ = +17.3 \text{ kcal/mole},$$

$$\Delta S_{298}^\circ = -1.5 \text{ e. u.}$$

Fig. B. 4--Temperature variation of IrCl_3 vapor pressure

for reaction (B. 5). Combining the ΔS_{298}° value with standard entropies for Ir(s) and $\text{Cl}_2(\text{g})$, we obtain $S_{298}^{\circ} \text{IrCl}_3(\text{g}) = 87.0 \text{ e. u.}$ This value seems reasonable when compared with the value 85.3 e. u. calculated from an empirical equation given by Kubaschewski and Evans^(B. 7) and with the value $S_{298}^{\circ} \text{RhCl}_3(\text{g}) = 89.3 \pm 4.0 \text{ e. u.}$ obtained by Bell, Tagami, and Merten.^(B. 9)

From curve B (Fig. B. 4), we calculate

$$\Delta H_{1041}^{\circ} = +56.1 \text{ kcal/mole ,}$$

$$\Delta S_{1041}^{\circ} = +35.2 \text{ e. u.}$$

for reaction (B. 6). Using $\Delta C_p = -5.6$, obtained by combining ΔC_p 's for reactions (B. 1) and (B. 5), we calculate

$$\Delta H_{298}^{\circ} = +60.2 \text{ kcal/mole ,}$$

$$\Delta S_{298}^{\circ} = +42.2 \text{ e. u.}$$

for reaction (B. 6). Combining ΔS_{298}° with $S_{298}^{\circ} \text{IrCl}_3(\text{s}) = 23.1 \text{ e. u.}$, calculated from dissociation-pressure data given previously, we calculate $S_{298}^{\circ} \text{IrCl}_3(\text{g}) = 65.3 \text{ e. u.}$ This value seems unreasonably low compared with values cited above. This suggests that errors are involved in the data used in obtaining curve B or that vapor species other than IrCl_3 are important at low temperature.

A further check on the vapor-pressure data is made as follows: Combining the respective ΔH_{1041}° and ΔS_{1041}° values for reactions (B. 5) and (B. 6), we obtain $\Delta H_{1041}^{\circ} = -39.6 \text{ kcal/mole}$ and $\Delta S_{1041}^{\circ} = -38.0 \text{ e. u.}$ for reaction (B. 1). These values are not in agreement with the values $\Delta H_{1041}^{\circ} = -62.2 \text{ kcal/mole}$ and $\Delta S_{1041}^{\circ} = -59.6 \text{ e. u.}$ calculated from dissociation-pressure measurements.

These discrepancies suggest that our low-temperature vapor-pressure data are in error or that the interpretation is incorrect. We suspect that errors exist in the vapor-pressure measurements. A systematic error could have occurred here since the activities of the unknowns, under our counting conditions, were only about 10 cpm above background. We plan to repeat the low-temperature vapor-pressure measurements using an iridium metal sample having a higher specific activity.

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Appendix C

HIGH-TEMPERATURE CHEMISTRY OF THE RUTHENIUM-OXYGEN SYSTEM

by

Wayne E. Bell and M. Tagami

The results so far obtained in studies of high-temperature chemistry of the ruthenium-oxygen system will be discussed. The work was undertaken for the purpose of identifying condensed phases and vapor species, measuring dissociation and vapor pressures, and calculating thermodynamic values from the pressure data.

We have completed measurements of the dissociation pressure of $\text{RuO}_2(\text{s})$. We are currently studying condensed oxides and measuring oxide vapor pressures as a function of temperature and oxygen pressure. The investigation is estimated to be two-thirds complete.

Reported data on the ruthenium-oxygen system are meager, and to some extent discordant. Alcock and Hooper^(C. 1) reported a small amount of vapor-pressure data on the ruthenium-oxygen system. In measurements at 1280°C using a transpiration method, they found the pressure of the gaseous oxide to be proportional to $p_{\text{O}_2}^{1/2}$. From this they deduced the vapor species to be Ru_xO . On the basis of estimated data on solid RuO_2 reported by Brewer^(C. 2), they assumed the condensed phase to be ruthenium metal under their conditions.

Schafer, Gerhardt, and Tebben^(C. 3) observed (they reported no quantitative data) the dissociation pressure of RuO_2 to be much less than Brewer estimated. Accordingly, they stated that Alcock and Hooper should have taken the condensed phase to be RuO_2 rather than ruthenium metal and that the 0.5 power oxygen-pressure dependence suggests the vapor species Ru_xO_3 rather than Ru_xO .

EXPERIMENTAL

DISSOCIATION-PRESSURE STUDIES

Dissociation pressures were measured by both static and dynamic (transpiration) methods using techniques similar to those described in

Ref. C. 4. In the static method, the oxide sample was contained in a dead-end mullite reaction tube that was connected through a small sulfuric acid manometer to a vacuum pump, oxygen supply, and mercury manometer. Equilibrium oxygen dissociation pressures were readily obtained. A mullite reaction tube was used for the transpiration method (see Ref. C. 5). Helium served as the carrier gas and the effluent helium-oxygen mixture was analyzed chromatographically.

VAPOR-PRESSURE STUDIES

Vapor pressures were determined by the transpiration method using techniques similar to those described in Ref. C. 5. Mullite reaction tubes were used, and oxygen served as the carrier gas. The effluent oxygen gas was collected over mercury in a known volume at reduced pressure.

Flow rates ranged from 0.02 to 0.10 mmole O_2 /min, depending on temperature and oxygen pressure conditions. The results of flow-rate studies conducted at 1303° and 1453°C indicate that at the flow rates used diffusion and kinetic effects were not important.

In order to minimize diffusion effects and also to permit working at partial pressures as low as 0.01 atm at temperatures of $\sim 1500^\circ C$, we have tried using argon-oxygen mixtures as carrier gases. A difficulty arises, however, in the use of gas mixtures; the oxygen content of the mixture changes very appreciably, 20% to 30%, in passing through the reaction tube. This depletion in oxygen is caused by the production of ruthenium oxide vapor, part of which is carried through the capillary and part of which diffuses to the cold sections at each end of the reaction tube.

A radio-tracer method of analysis was used to determine the quantity of ruthenium condensed. The ruthenium metal used was irradiated in the TRIGA reactor to produce the radionuclide 41-d Ru^{103} . Two different metal samples were used having activities of about 5,000 cpm/mg under our counting conditions. Gamma-ray spectra of the samples agreed with spectra reported for Ru^{103} . At the end of each experiment, the mullite condensing region was crushed, placed in a plastic vial, and counted in a well counter. Optimum counting conditions were obtained by counting the main gamma-energy peak of Ru^{103} (0.50 Mev) through a window. To minimize geometry problems, each sample was counted at least five times with shaking between each count. Statistical counting errors were less than 2% standard deviation. For standards, samples of the radioactive metal were weighed, mixed with crushed mullite, and counted in the same manner as the unknowns. Activities of the unknowns ranged from about 300 to 25,000 cpm. The background stabilized at about 20 cpm.

GENERAL

The materials used were ruthenium metal sponge (Johnson-Matthey, 99.995% purity), oxygen gas (Matheson, research grade), and helium gas (Liquid Carbonic). The oxygen gas flowed through a sulfuric acid bubbler and P_2O_5 before entering the reaction tube. The helium gas was purified by passage through a charcoal trap held at liquid-nitrogen temperature. A platinum-wound tube furnace and Pt-Pt-10% Rh thermocouples were used. Temperature uncertainties are believed to range from $\pm 2^\circ$ at 800° to $\pm 4^\circ$ at 1500°C .

RESULTS AND DISCUSSION

CONDENSED-PHASE STUDIES

Solid RuO_2 appears to be the stable condensed oxide under the temperature and oxygen-pressure conditions of this work. We have found that prolonged heating of ruthenium in oxygen at 950°C yields an oxide having an oxygen content within 1% of the theoretical value for RuO_2 . Other investigators have reported the preparation of $\text{RuO}_2(\text{s})$.^{(C. 6)(C. 7)}²

To test for lower oxides and also to determine oxygen solubility in the metal, a sample of the oxide contained in a dead-end mullite tube was decomposed at 1450°C and at an oxygen pressure that was a few millimeters below the dissociation pressure at 1450°C . The sample was then sealed off, quenched in air, and analyzed gravimetrically. The resulting material was obviously metal and had an oxygen content of less than 0.40 atom-% oxygen.

DISSOCIATION PRESSURES

The dissociation-pressure data, measured over the range 1107° to 1503°C by two different methods, are plotted in Fig. C. 1. The data are linear on the $\log p$ versus $1/T$ plot within experimental error and extrapolate to 1 atm oxygen pressure at 1540°C .

From the slope of the line drawn through the points in Fig. C. 1, we calculate, at the mean temperature of the measurements (1570°K),

$$\Delta H_{1570}^{\circ} = -67.4 \pm 1.0 \text{ kcal/mole ,}$$

and from this we obtain

$$\Delta S_{1570}^{\circ} = -37.2 \pm 1.0 \text{ e. u.}$$

Fig. C. 1--Dissociation pressure of $\text{RuO}_2(\text{s})$

for the reaction

Using $\Delta C_p = 3.7 \text{ cal/mole } ^\circ\text{K}$, estimated from values for similar oxides given by Kelley, (C. 8) we calculate

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

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

The heat of formation agrees with $\Delta H_{298}^\circ = -73.1 \pm 1 \text{ kcal/mole}$ obtained calorimetrically by Shchukarev and Ryabov. (C. 9)

Combining ΔS_{298}° with standard entropies $S_{298}^\circ \text{ Ru} = 6.82 \pm 0.05 \text{ e. u.}$ and $S_{298}^\circ \text{ O}_2 = 49.01 \pm 0.01 \text{ e. u.}$, given by Kelley and King, (C. 10) we calculate $S_{298}^\circ \text{ RuO}_2(\text{s}) = 12.5 \pm 2.0 \text{ e. u.}$ This value seems very reasonable when compared with standard entropy values for similar oxides 12.68 (MnO_2), 11.06 (MoO_2), 13.0 (NbO_2), 12.04 (TiO_2), 12.3 (VO_2), 12.12 (ZrO_2) given by Kelley and King.

Remy and Kohn^(C. 11) reported dissociation pressure data for RuO_2 in the narrow temperature range 923° to 932°C . Their pressure values exceed our values in this temperature range by more than two orders of magnitude. They observed a change in dissociation pressure with oxygen content. We have observed similar behavior. At the beginning of our static dissociation-pressure measurements, it was necessary to pump off a small amount of oxygen from the oxide sample before a point was reached where further oxygen removal had no effect. This behavior could possibly be attributed to adsorbed oxygen or to a small homogeneity range in the oxide.

IDENTIFICATION OF VAPOR SPECIES

Since Ru and RuO_2 are the stable condensed phases in the temperature range and in the oxygen-pressure range studied, the solid-vapor equilibria to be considered are

From the equilibrium constant for Eq. (C. 2), we obtain

$$\log p_{\text{Ru}_x\text{O}_y} = \frac{y}{2} \log p_{\text{O}_2} + \log K. \quad (\text{C. 4})$$

A similar expression is obtained for Eq. (C. 3), and it can be seen that $y/2$ and $(y-2x)/2$ can be evaluated, and thus the vapor species identified, by studying the effect of oxygen pressure on vapor pressure.

Oxygen-pressure dependence data measured at 1453° and 1503°C are shown in Fig. C. 2. The curves were drawn with slopes of 0.5 and 1.5 with breaks occurring at the dissociation-pressure points as fixed by the dissociation-pressure data given previously. The data fit these curves nicely; thus, $y/2 = 1.5$ and $(y - 2x)/2 = 0.5$, $y = 3$, and $x = 1$. It is therefore apparent that the principal vapor species is $\text{RuO}_3(\text{g})$.

As yet, we have no oxygen-pressure dependence data that can be used to identify vapor species in the low-temperature region 900° to 1100°C . However, curvature in the temperature-dependence curve (see Fig. C. 3) in this temperature region suggests that a higher oxide vapor species, probably RuO_4 , becomes important at temperatures below 1100°C .

TEMPERATURE DEPENDENCE OF VAPOR PRESSURE

Figure C. 3 shows the temperature dependence of observed vapor pressures in equilibrium with $\text{RuO}_2(\text{s})$ at 1 atm oxygen pressure. The curve drawn through the data points shows linearity in the high-temperature region $10^3/^\circ\text{K} = 0.728$ to $10^3/^\circ\text{K} = 0.563$ (1100° to 1503°C). As has been shown, the vapor species around 1500°C is $\text{RuO}_3(\text{g})$; therefore, the vaporization reaction in the high temperature region is

From the slope of the linear (high temperature) portion of the curve in Fig. C. 1, we calculate at the mean temperature (1650°K)

$$\Delta H_{1650}^\circ = +48.7 \text{ kcal/mole},$$

and from this

$$\Delta S_{1650}^\circ = +21.0 \text{ e. u.}$$

for reaction (C. 5) (uncertainties have not yet been assigned to these thermodynamic quantities).

Fig. C. 2--Effect of oxygen pressure on vapor pressure at 1453° and 1503°C, assuming one gaseous molecule per ruthenium atom

Fig. C. 3--Observed total vapor pressure over RuO₂(s) at 1 atm oxygen pressure

We estimate ΔC_p for reaction (C. 5) to be $-6 \text{ cal/mole } ^\circ\text{K}$, and assuming it to be constant over the range 298° to 1650°K we calculate

$$\Delta H_{298}^\circ = +56.8 \text{ kcal/mole ,}$$

$$\Delta S_{298}^\circ = +31.2 \text{ e. u.}$$

Combining ΔS_{298}° , $S_{298}^\circ \text{ RuO}_2(\text{s}) = 12.5 \pm 2.0 \text{ e. u.}$ calculated above and $S_{298}^\circ \text{ O}_2 = 49.01 \pm 0.01 \text{ e. u.}$, given by Kelley and King, (C. 10) we obtain $S_{298}^\circ \text{ RuO}_2(\text{g}) = 68.2 \text{ e. u.}$ This value may be compared with the estimated value 75.9 e. u. , calculated from an empirical equation given by Kubaschewski and Evans. (C. 12)

The curve in Fig. C. 3 in the low-temperature region $10^3/^\circ\text{K} = 0.850$ to $10^3/^\circ\text{K} = 0.728$ shows a decreasing slope with decreasing temperature. As mentioned above, this behavior suggests that a higher oxide vapor species becomes important at low temperatures.

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