240 pg
21.5168
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IN-1013
January 1968

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IDAHO NUCLEAR CORPORATION
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U. S. ATOMIC ENERGY COMMISSION

Printed in the United States of America
Available from
Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U. S. Department of Commerce
Springfield, Virginia 22151
Price: Printed Copy $3.00; Microfiche $0.65

IN-1013
Issued: January 1968
Waste Disposal and Processing
TID 4500

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U. S. Atomic Energy Commission Research and Development Report
Issued Under Contract AT(10-1)-1230
Idaho Operations Office

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ABSTRACT

The partial pressure of ruthenium tetroxide over ruthenium dioxide as a function of oxygen partial pressure was measured in the temperature range 453 to 723°C, extending earlier data at higher temperatures. Best current values for $\Delta H^\circ_{f,298}$, $\Delta F^\circ_{f,298}$, and C_p for the oxides of ruthenium are given.

SUMMARY

The volatilization of ruthenium in the temperature range 453 to 723°C was studied by the transpiration technique. With oxygen as the carrier gas, the volatile tetroxide of ruthenium was formed by the reaction $RuO_2(s) + O_2 = RuO_4(g)$. The equilibrium constant for this reaction can be expressed as $\text{Log } K = -4764T^{-1} - 0.236$. These results are in good agreement with measurements made by others at higher temperatures. The recommended heats of formation, free energies of formation, absolute entropies at 298°K, and the heat capacities of the ruthenium oxides are given.

Based on this work, a calculation of ruthenium volatilization as ruthenium tetroxide from the calciner in the Waste Calcining Facility was made. It suggested that either nonequilibrium concentrations of $RuO_4(g)$, very fine particulate matter, or another ruthenium vapor species plays an important role in ruthenium volatilization in the calciner, since the partial pressure of ruthenium tetroxide accounted for only a few percent of the observed volatility.

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THE RUTHENIUM DIOXIDE-OXYGEN-RUTHENIUM TETROXIDE EQUILIBRIUM

I. INTRODUCTION

Ruthenium-106, a fission product that is present in essentially all high-level radioactive waste solutions, is volatilized to some degree in nearly all waste treatment processes that convert radioactive liquid to solid forms at elevated temperatures. This volatile ruthenium has been removed successfully from the off-gas stream in the Waste Calcining Facility (WCF) at the Idaho Chemical Processing Plant by using silica gel adsorbers to retain the volatile species. To better understand the mechanism of this removal and to assist in developing more efficient methods for removing ruthenium from off-gas streams, a study was undertaken to identify the volatile species in the ruthenium-oxygen system at 500 to 600°C and to study the equilibrium:

$$RuO_2(s) + O_2 = RuO_4(g). \tag{1}$$

The reaction of Equation (1) has been studied previously by Bell and Tagami [1] in the temperature range 800 to 1400°C and by Schäefer et al [2] in the temperature range 800 to 1600°C. Their results are in fair agreement. Both of these studies were at temperatures at which there were significant partial pressures of both RuO_3 and RuO_4. In the present work the above reaction was studied in the temperature range 453 to 723°C to obtain information on the reaction without the interference of other gas species and to obtain more reliable thermodynamic data for the reaction at temperatures of current interest.

II. EXPERIMENTAL TECHNIQUES

RuO_2 was prepared by adding excess NaOH to a solution of $RuCl_3$ containing 0.44 mCi of Ru^{106}, followed by filtration of the $Ru(OH)_3$, and oxidation with H_2O_2. The solid RuO_2 was then filtered, washed, and dried. The RuO_2 was heated to 600°C in an oxygen atmosphere to dry the sample further and to vaporize trace amounts of the NaCl impurity. The concentration of ruthenium in an aliquot portion of the chloride solution was determined spectrophotometrically as the thiourea complex[3].

The RuO_2 prepared in the above fashion had an initial specific activity of 3.4 x 10^{11} dpm per gram-atom of ruthenium. The identity of the $RuO_2(s)$ was confirmed by its X-ray powder pattern [4].

The reaction was studied using the transpiration technique. Oxygen, maintained at a constant pressure by a fine control pressure valve in conjunction with a standard gage control valve, was allowed to flow over the RuO_2 sample and was finally condensed in a trap cooled with liquid nitrogen. The flow rate of oxygen, varying from 0.1 to 10 cc/min (STP), was controlled by means of interchangeable capillary orifices placed between the reaction vessel and the exit trap. The pressure of oxygen in the system was measured with a mercury manometer. Runs were initiated by placing a preheated furnace around the reaction vessel with the gas flowing in a reverse direction while the sample was coming to an equilibrium temperature. During the measurement, the RuO_4, formed by reaction of RuO_2 with O_2, decomposed on glass wool in the exit tube. At the end of each run the deposited ruthenium was dissolved in hydrofluoric acid. The resulting solution was counted in a well-type scintillation counter with a counting efficiency of 21 percent for the particular sample geometry used. The standard deviation in the observed counting rate was in all cases less than 10 percent. The data are given in Table I.

TABLE I

EXPERIMENTAL $RuO_4(g)$ PRESSURES AND EQUILIBRIUM CONSTANTS FOR THE REACTION $RuO_2(s) + O_2 = RuO_4(g)$

Temperature (°C)	P_{O_2} (mm)	$10^3/T$ (°K^{-1})	P_{RuO_4} (mm)	K_p
453	657	1.385	6.23 x 10^{-5}	9.49 x 10^{-8}
476	646	1.342	2.32 x 10^{-4}	3.59 x 10^{-7}
500	653	1.300	3.03 x 10^{-4}	4.65 x 10^{-7}
553	660	1.217	6.37 x 10^{-4}	9.65 x 10^{-7}
603	645	1.148	7.08 x 10^{-4}	1.10 x 10^{-6}
610	655	1.139	1.62 x 10^{-3}	2.47 x 10^{-6}
652	650	1.087	2.46 x 10^{-3}	3.79 x 10^{-6}
652	433	1.087	1.82 x 10^{-3}	4.21 x 10^{-6}
652	207	1.087	8.77 x 10^{-4}	4.24 x 10^{-6}
723	649	1.009	6.12 x 10^{-3}	9.42 x 10^{-6}

III. RESULTS AND DISCUSSION

Pressures of RuO_4 were measured as a function of O_2 pressure at 652°C. It was confirmed that RuO_4 is the major vapor species at that temperature (Table I). The pressure of RuO_4 was measured in the temperature range 453 to 723°C at an oxygen pressure of about 650 mm to determine the thermodynamic properties of the reaction $RuO2 + O_2 \rightleftharpoons RuO_4(g)$. The observed equilibrium constant was dependent upon flow rate only at the lowest temperature. Data below 453°C were discarded for this reason. The experimentally determined $RuO_4(g)$ pressures, oxygen pressures, temperatures, and calculated equilibrium constants are shown in Table I. Results of the transpiration experiments are shown in Figure 1 along with the results of Schäefer et al, and Bell and Tagami. There is good agreement among the data. The equation of the least square line through the data points on Figure 1 is:

$$\log \frac{P_{RuO_4}}{P_{O_2}} = -4764T^{-1} - 0.236 \quad \text{(standard deviation in } \log K_P = 0.127\text{)}. \tag{2}$$

The constants in Equation (2) correspond to values of $\Delta H° = -21.8$ kcal/mole and $\Delta S° = -1.1$ e.u./mole. From the free energy function for the reaction, derived from the free energy functions for RuO4 [5], the decomposition pressures of RuO_2 [1], the heat of formation of RuO_2 [6], the heat capacity and entropy of Ru [7], and the free energy functions for oxygen [7], Equation (3) was derived which adequately gives the free energy functions for the reaction $RuO_2 + O_2 = RuO4(g)$ in the temperature range 298 to 1000°K:

$$\Delta H^o_{298} = 12.02T - 8.98 \times 10^{-3}T^2 + 3.54 \times 10^{-6}T^3 - 4.576T \quad \log \frac{P_{RuO_4}}{P_{O_2}} \tag{3}$$

A third law correlation of the experimental results gives a $\Delta H°298 = 28.8 \pm 0.3$ kcal/mole. This is in good agreement with the value of 28.0 kcal/mole reported by Schäefer and in fair agreement with the value of 25.5 ± 3 kcal/mole reported by Bell and Tagami. In Table II, the recommended thermodynamic properties of ruthenium oxides which have been derived from this and other work are listed.

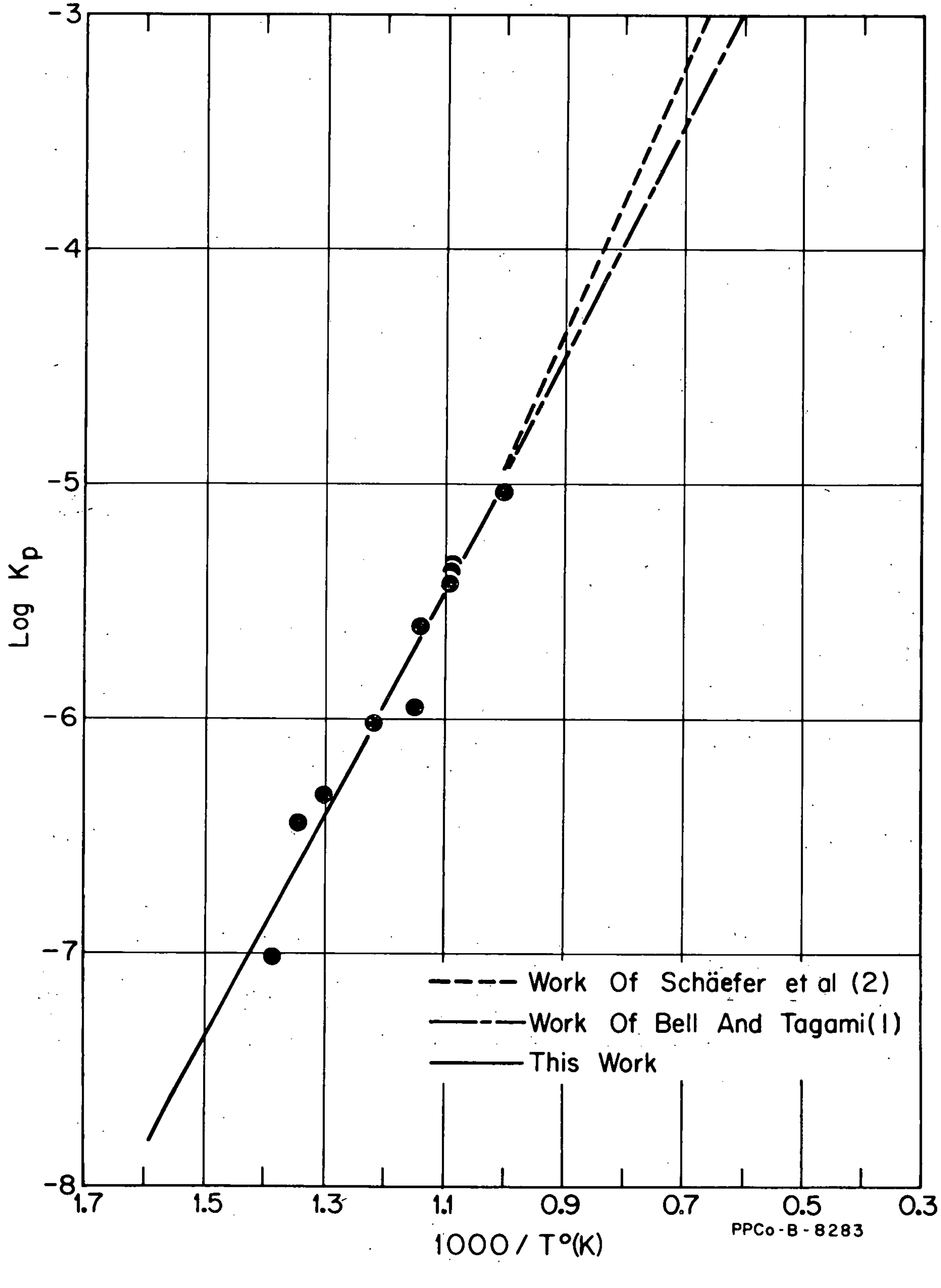

FIG. 1 TEMPERATURE DEPENDENCE OF THE EQUILIBRIUM CONSTANT K_P FOR THE REACTION $RuO_2(s) + O_2 = RuO_4(g)$.

TABLE II

THERMODYNAMIC PROPERTIES OF RUTHENIUM OXIDES

Oxide	Property	Heat of Formation $\Delta H^o_{f,298}$ kcal/mole	Free Energy of Formation $\Delta F^o_{f,298}$ kcal/mole	Entropy S^o_{298} e.u.	Heat Capacity C_p cal/mole ^oK
RuO_4	gas	-45	-34.2	68.8	[a] [e]
	liquid[d]	-54	-36.6	46.7	33
	solid[d]	-59.6	-36.6	27.9	20
RuO_3	gas	-14	-10.2	68	[b]
RuO_2	solid	-73	-60	12.5	[c]

[a] $23.04 + 2.156 \times 10^{-3}\ T - 4.647 \times 10^5\ T^{-2}$

[b] $18.13 + 1.16 \times 10^{-3}\ T - 3.32 \times 10^5\ T^{-2}$

[c] $11.6 + 6.0 \times 10^{-3}\ T$

[d] Calculated from information presented in Reference 8.

[e] Calculated from information presented in Reference 5.

IV. ESTIMATION OF RUTHENIUM VOLATILITY IN THE WASTE CALCINING FACILITY

Using Equation (3), the partial pressure of RuO_4 was predicted for the gas stream leaving the calciner in the WCF during an actual production run. Operating data for the temperature, gas flow rate, and off-gas composition were taken from the report of the first WCF campaign [9]. The ruthenium carry-over, predicted only from the vapor pressure of ruthenium tetroxide, accounted for only a few percent of the ruthenium observed to be leaving the calciner. Values for predicted RuO_4 and total observed ruthenium leaving the calciner vessel were, respectively, 1×10^3 mCi/day and 9×10^4 mCi/day. This calculation strongly indicates that the species RuO_4 in equilibrium with oxygen is only partially responsible for ruthenium transport from the calciner vessel. Other possible paths by which ruthenium could be transported include another vapor species, particulate matter, or nonequilibrium concentrations of RuO_4 [with respect to Equation (1)] attained by reaction of ruthenium with oxides of nitrogen during calcination. The other vapor species have not yet been identified; but certainly the effectiveness of various vapor filtration devices, such as glass wool, for ruthenium decontamination suggests that particulates are frequently associated with ruthenium tetroxide vapor.

V. REFERENCES

1. W. E. Bell and M. Tagami, "High-Temperature Chemistry of the Ruthenium-Oxygen System", J. Phys. Chem., 67 (1963) pp 2432-2436.

2. H. Schäefer, A. Tebbern, W. Gerhardt, "Chemistry of the Platinum Metals. V. Equilibriums with $Ru_{(s)}$, $RuO_{2(s)}$, $RuO_{3(g)}$, and $RuO_{4(g)}$", Z. Anorg. Allgem. Chem., 321 (1963) pp 41-55.

3. G. H. Ayers and F. Young, "Spectrophotometric Study of the Ruthenium-Thiourea Complex", Anal. Chem., 22 (1950) pp 1277-1280.

4. L. K. Frevel, H. W. Rinn, H. C. Anderson, "Tabulated Diffraction Data for Tetragonal Isomorphs", Ind. Eng. Chem., Anal. Ed., 18 (1946) pp 83-93.

5. M. H. Ortner, C. J. Anderson, P. F. Campbell, Research and Development Studies on Waste Storage Process, IDO-14504 (May 1961).

6. S. A. Schukarev and A. N. Pyakov, Russ. J. Inorg. Chem., 5, 941 (1960).

7. A. Glassner, The Thermochemical Properties of the Oxides, Flourides, and Chlorides to 2500°K, ANL-5750 (1957).

8. S. Lawroski (Div. Director), Chemical Engineering Division Summary Report for January, February, and March, 1950, ANL-4463 (1959). (Secret)

9. R. E. Commander et al, Operation of the Waste Calcining Facility with Highly Radioactive Aqueous Waste, IDO-14662 (June 1966).