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MASS-SPECTROMETRIC STUDY OF THE
RUTHENIUM-OXYGEN SYSTEM

Ru-O

by

J. H. Norman, H. G. Staley, and W. E. Bell

August 16, 1963

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**MASS-SPECTROMETRIC STUDY OF THE
RUTHENIUM-OXYGEN SYSTEM¹**

by

J. H. Norman, H. G. Staley, and W. E. Bell

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MASS-SPECTROMETRIC STUDY OF THE RUTHENIUM-OXYGEN SYSTEM

Recent studies^{2, 3, 4} of the ruthenium-oxygen system in the temperature range 1000° to 2000° K and at oxygen pressures around 1 atm have shown RuO_2 to be the important condensed phase and RuO_3 and RuO_4 to be important vapor species. In the present work, the ruthenium-oxygen system has been investigated in a mass spectrometer to determine the important vapor species at oxygen pressures around 10^{-4} atm...

EXPERIMENTAL PROCEDURES

A Consolidated Electrodynamics Corporation 21-703 mass spectrometer modified for Knudsen-cell experiments was employed for this work. A quartz Knudsen cell 1 in. high by $3/4$ in. in diameter and having a 0.7-mm-diameter orifice was used. The cell, fitted at the top with a quartz oxygen-feed tube, was held in a close-fitting molybdenum cup and was covered with three layers of tantalum. The assembly was heated by electron bombardment using tungsten filaments mounted on the side of the cell and above the cell. (A detailed description of the assembly will be presented in a later publication.) Oxygen flowed into the cell through a viscous-flow inlet from a large reservoir. Oxygen pressure in the cell was fixed by the pressure in the reservoir. Temperatures were measured by means of two Pt-Pt, 10%-Rh thermocouples attached to the inside of the molybdenum

(2) H. Schäfer, G. Schneidereit, and W. Gerhardt, Z. anorg. u. allgem. Chem., 319, 327 (1963).

(3) H. Schäfer, A. Tebben, and W. Gerhardt, Z. anorg. u. allgem. Chem., 321, 41 (1963).

(4) W. E. Bell and M. Tagami, accepted for publication in J. Phys. Chem.

cup, one near the top and the other near the bottom. Temperatures were equalized at the thermocouple points by adjusting the potential applied across the top-mounted tungsten filament. Reported temperatures are believed to be accurate to $\pm 10^\circ$.

RESULTS AND DISCUSSION

Mass spectra were measured over a temperature range from 1150° to 1525°K and an oxygen pressure range of 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^+ .

Appearance-potential curves were measured for the oxide ions in an attempt to distinguish parent and fragment ions; however, the results were inconclusive. It is worthy of note that the appearance potentials of RuO^+ and RuO_2^+ were found to be respectively 1 and 3 e. v. higher than the appearance potential of RuO_3^+ .

The ions RuO^+ and RuO_2^+ produced by 20-volt electrons were shown conclusively to be fragment ions as a result of a study of the effect of oxygen pressure on ion intensity. In this study, oxide ion intensities were measured as a function of oxygen ion current at 1190° and 1240°K . Figure 1 is a log-log plot of the data. At 1240°K , slopes of the RuO_3^+ , RuO^+ , and RuO_2^+ isotherms are 1.52, 1.52, and 1.58, respectively. Within the uncertainty of the data, these values are 1.5; thus, the intensity of each ion is proportional to $P_{\text{O}_2}^{3/2}$. This shows that RuO^+ and RuO_2^+ are fragment ions formed from $\text{RuO}_3(\text{g})$ and that under the experimental conditions the important vaporization reaction is

At 1190°K , the RuO_3^+ isotherm (Fig. 1) shows a slope close to 0.5. This indicates that $\text{RuO}_2(\text{s})$ was the condensed phase in the oxygen pressure

Fig. 1-- $\log I_{\text{RuO}_x}$ as a function of $\log I_{\text{O}_2^+}$

range used and that the important vaporization reaction is

Maximum values of the equilibrium constants described by the following reactions can be estimated from the studies of the observed ruthenium-oxygen ion intensities:

At 1240°K, the equilibrium constants for reactions (3) and (4) are not larger than $10^{-3.5}$ and $10^{-6.3}$, respectively. These numbers reflect detection limits of the partial pressures of RuO_2 and RuO species and do not indicate that the species have been observed.

The vapor pressure of RuO_4 as determined by Bell and Tagami⁴ is around 10^{-8} atm under the conditions of this study. While 10^{-8} atm of RuO_4^+ should be detectable if RuO_4^+ is a major ionization product of RuO_4 , the presence of RuO_4 gaseous species was not established.

Logarithmic plots of the ion currents of RuO_3^+ times $T^{1/2}$ and times $T^{-1/2}$ as a function of reciprocal temperature ($1/T$) are shown in Fig. 2. The $I_{\text{RuO}_3^+} T^{1/2}$ relationship is used to determine the heat of reaction (2) because this function is proportional to the equilibrium constant for the reaction at constant $I_{\text{O}_2^+}$:

$$\frac{P_{\text{RuO}_3}}{P_{\text{O}_2}^{1/2}} \propto \frac{I_{\text{RuO}_3^+} T}{I_{\text{O}_2^+}^{1/2} T^{1/2}} \propto I_{\text{RuO}_3^+} T^{1/2}$$

For similar reasons, the $I_{\text{RuO}_3^+} T^{-1/2}$ relationship is proportional to the equilibrium constant for reaction (1).

Fig. 2--Logarithms of the RuO₃⁺ currents times T^{-1/2} and times T^{1/2} as a function of reciprocal temperature

Temperature dependence of the RuO_3^+ intensity at constant cell O_2^+ intensity was measured in the range 1150° to 1525°K . The ion-intensity data showed a break at 1267°K . Using this temperature in an equation for the dissociation pressure of $\text{RuO}_2(\text{s})$ given by Bell and Tagami,⁴ we calculate that the oxygen pressure in the Knudsen cell was about 3×10^{-4} atm during the measurements. From slopes of lines drawn through the data, we calculate $\Delta H_{1250} = 54$ kcal/mole for reaction (2) and $\Delta H_{1250} = -17$ kcal/mole for reaction (1). These values are in good agreement with ΔH_{1250} values of +54.7 and -13.9 kcal/mole calculated for the respective reactions from data reported by Schäfer, et al.,² and ΔH_{1250} values of +51.6 and -17.0 kcal/mole calculated for the respective reactions from data reported by Bell and Tagami.⁴