nitrate and excess sodium ferrate(III) in a short 20 mm. i.d. tube having one end closed off and terminated in a ground glass joint at the other. This was attached to a system having a mercury displacement gas buret for maintaining the pressure at about 1 atm. while the reaction proceeded. A trap was included in the system for transferring the nitric oxide to the system by means of a liquid nitrogen bath. A furnace surrounding the reaction chamber was brought to 250° and then slowly raised to 400°. Progress of the reaction was followed by change in the mercury level of the gas buret. It was found that the rate of the reaction was strongly pressure dependent, and fell rapidly as the reaction approached completion. With the nitric oxide pressure regulated at 760 ± 200 mm., the reaction was 99% complete in 48 hours at a temperature of 400 ± 10°. The temperature was then reduced to 360° for 72 hours. The furnace was then cooled, nitric oxide removed from the system, and the reaction chamber removed for extraction of the sodium nitrite with dry methyl alcohol. The use of methyl alcohol instead of water was necessary since an excess of water-hydrolyzable sodium ferrate(III) was employed. The weight of nitrite product compared to that of the nitrate reactant indicated 99.8% conversion. Titration with permanganate confirmed the product as sodium nitrite of better than 99.9% purity.

These results are confirmed by a few rough measurements which indicate that the equilibrium constant for reaction 1 at 400° is such as to give about 99.95% nitrite under a nitric oxide pressure of one atm.

Calcium nitrite was similarly prepared as represented by eq. 3

$$Ca(NO_3)_2 + 2CaFe_2O_4 + 4NO = 3Ca(NO_2)_2 + 2Fe_2O_3 \qquad (3)$$

This reaction took place most readily at 275° under one atmosphere of nitric oxide pressure. The reaction required about 48 hours for 99% completion.

Potassium nitrite could not be prepared by this method.

Discussion

Due to the slowness of the reaction at lower temperatures and pressures and the unfavorable equilibrium constant at higher temperatures, the optimum conditions described above are incapable of giving complete quantitativeness with respect to nitric oxide. However, by having the final gas volume small, quantitative conversions with respect to nitric oxide can be very nearly attained.

STANFORD, CALIFORNIA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF THE UNIVERSITY OF CONNECTICUT]

The Preparation of a Strontium–Iridium Oxide Sr_2IrO_4[1,2]

BY JOHN J. RANDALL, JR., LEWIS KATZ AND ROLAND WARD

RECEIVED AUGUST 16, 1956

The preparation of strontium–iridium oxide, Sr_2IrO_4, is effected by heating mixtures of iridum metal powder and strontium oxide at 1200° in air. The compound has been shown to be isotypic with K_2NiF_4 No compound of the perovskite type could be obtained in this system despite the fact that the ionic radii of strontium and iridium are favorable.

One of the few ternary oxides of the platinum metals to be prepared and characterized is the hexagonal $Ba_3Pt_2O_7$.[3,4] A phase with a similar structure is obtained upon heating strontium oxide and platinum dioxide at 700°. When the preparation of analogous compounds of iridium was attempted, a phase having an entirely different structure was formed in the strontium–iridium–oxygen system.

Experimental

Strontium–iridium oxide is obtained readily by the reaction between iridium metal powder and strontium oxide, carbonate, nitrate or hydroxide at 1200° in air. In using the nitrate or hydroxide, the temperature must be brought slowly to 1200° to prevent spattering. The reaction occurs rapidly compared with most solid phase reactions, a pure product being obtained upon heating for 15 min., regrinding the sample and reheating for 15 min. The reactions were carried out in platinum or zirconium silicate combustion boats.

It was found that the X-ray powder diffraction pattern of the product could be assigned to a tetragonal unit cell, a = 3.89 Å., c = 12.92 Å. The density of the product was 7.45 g./cm.^{3}. This indicated that the unit cell could contain two formula weights of Sr_2IrO_4 (calculated density 7.44 g./cm.^{3}). Examination of the products obtained by heating mixtures with atomic ratio Sr/Ir = 1.5 revealed that iridium metal had settled out of the product to form a thin layer on the surface of the zirconium boat. When mixtures of lower atomic ratio were used, some iridium remained dispersed in the sample as revealed by X-ray analysis. With mixtures containing an atomic ratio Sr/Ir = 2, the presence of strontium oxide could not be detected by X-ray analysis, nor could any change in lattice constant be observed.

Chemical Analysis.—The compound was found to be soluble upon prolonged digestion with hydrochloric acid. The iridium was determined first by the method of Delépine[5] which involves the reduction of Ir^{+4} with excess iodide and titration of the liberated iodine with thiosulfate. Calcd. for Sr_2IrO_4: Ir, 44.67. Found: Ir, 44.12.

Because of the marked color change on reducton of $IrCl_6^{-2}$ (red-brown) to $IrCl_6^{-3}$ (light yellow-green), it was thought that a photometric method would also be appropriate. The solution containing $IrCl_6^{-2}$ was treated with chlorine, the excess being removed by boiling. Using a Fisher model Electrophotometer with a filter covering the absorption peak for $IrCl_6^{-2}$ (~495 mμ), a solution containing about 1 mg. of iridium in 200 ml. was titrated with 0.004 N ferrous ammonium sulfate solution. A plot of the optical density *vs.* ml. of ferrous solution added is shown in Fig. 1. This procedure gave % Ir = 44.52.

By first separating iridium according to the method of Gilchrist (precipitation as the hydroxide, ignition to the oxide and reduction to the metal)[6] it was possible to determine strontium by titration with Versene according to the method of Cheng.[7] The percentage of strontium was 39.77% (calculated for Sr_2IrO_4, 40.53%).

From these data, the formula Sr_2IrO_4 appears to be confirmed.

Structure Determination.—The unit cell dimensions for Sr_2IrO_4 are very close to those of K_2NiF_4.[8] Sr_2IrO_4: a = 3.89, c = 12.92 Å.; K_2NiF_4: a = 4.00 Å., c = 13.07 Å. Observation of systematic absences for the X-ray powder

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[1] Taken in part from a Master's Thesis submitted by John J. Randall, Jr., to The University of Connecticut, 1956.

[2] This research was supported by the Office of Naval Research. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[3] M. G. Rousseau, *Compt. rend.*, **109**, 144 (1889).

[4] W. O. Statton, *J. Chem. Phys.*, **19**, 40 (1951).

[5] M. Delépine, *Ann. chim.*, **7**, 277 (1917).

[6] R. Gilchrist, *J. Research Natl. Bur. Standards*, **12**, 295 (1934).

[7] K. L. Cheng, private communication.

[8] D. Balz and K. Plieth, *Z. Elektrochem.*, **59**, 545 (1951).

diffraction pattern showed that $h + k + l = 2n$, the requirement for a body centered lattice. This is consistent with the space group possibilities for K_2NiF_4.[8] By analogy with this structure the z parameters for oxygen and strontium were assigned the values $z_O = 0.151$ and $z_{Sr} = 0.347$. The calculated relative intensities are compared with the observed intensities in Table I. No correction was made for absorption. The agreement is good and appears to establish the structure of Sr_2IrO_4 as the K_2NiF_4 type.

TABLE I

OBSERVED AND CALCULATED INTERPLANAR SPACINGS AND INTENSITIES (FORWARD REFLECTIONS)

hkl	d/n(obs.)	d/n(calcd.)	I(obsd.)	I(calcd.)
002	6.48	6.42	m^{+}	41.8
101	3.72	3.72	m^{-}	22.7
004	3.23	3.23	$w^{=}$	1.2
103	2.88	2.89	s^{+}	100.0
110	2.74	2.75	s^{-}	55.5
112	2.53	2.53	w	4.6
105	2.143	2.148	m^{+}	13.1
006		2.150		16.6
200	1.942	1.944	m	27.6
202	1.859	1.861	w	5.7
211	1.720	1.722	w	4.7
116	1.689	1.692	m^{-}	22.2
204	1.667	1.665	$w^{=}$	0.7
107		1.667		0.1
213	1.612	1.612	s^{-}	51.5
215	1.441	1.442	m	6.9
206		1.443		19.0
118	1.392	1.392	w	3.3
220	1.374	1.374	w	3.1
222	1.345	1.344	w^{+}	0.2
109		1.346		8.5
301	1.288	1.289	$w^{=}$	0.9
217	1.264	1.265	$w^{=}$	0.4
224		1.265		0.1
303	1.242	1.241	w^{++}	8.4
208		1.242		5.2
310	1.229	1.229	w^{++}	10.9
312	1.207	1.208	w^{-}	3.9
226	1.158	1.158	w^{++}	8.7
305		1.158		1.7
1,0,11	1.124	1.124	w	3.5

Discussion

The formation of Sr_2IrO_4 as a pure phase by the reaction of mixtures containing excess strontium indicates that all of the excess strontium oxide is volatilized at 1200° since no change in lattice constant was observed. With less than stoichiometric quantity of strontium, the excess iridium is liberated and the pattern of Sr_2IrO_4 again shows no change in spacing. The compound Sr_2IrO_4 is therefore assumed to be stoichiometric.

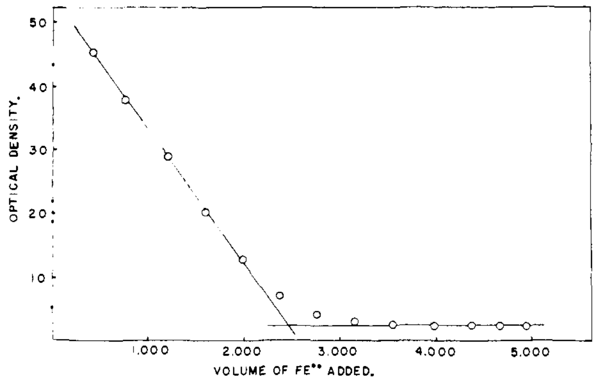

Fig. 1.—Typical photometric titration curve for $(IrCl_6)^{-4}$.

Other transition metals which have been shown to give A_2BO_4 phases are titanium, manganese and molybdenum.[8] Each of these elements also gives a perovskite-type oxide with strontium but all attempts to prepare a phase of this type in the strontium–iridium–oxygen system have failed. Lower temperatures and reactions in which only stoichiometric amounts of oxygen were allowed to react have been tried without success. This cannot be explained on the basis of relative ionic radii since the Goldschmidt radius of Ir^{+4} is 0.66, which lies close to the range covered by the other elements ($Ti^{+4} = 0.64$, $Mn^{+4} = 0.52$, $Mo^{+4} = 0.62$). The tolerance factor for the perovskite structure $t = [(R_A + R_O)/\sqrt{2}\ (R_B + R_O)]$ for iridium is 0.95, well within the common range.

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STORRS, CONN.

[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY, CHEMISTRY DIVISION]

The Solubility of Several Metal Sulfates at High Temperature and Pressure in Water and in Aqueous Uranyl Sulfate Solution[1]

BY ERNEST V. JONES, M. H. LIETZKE AND WILLIAM L. MARSHALL

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The solubility of several metal sulfates at high temperature and pressure has been determined in H_2O and in aqueous UO_2SO_4. In most of the systems investigated a large increase in solubility of the metal sulfate is observed at a given temperature as a function of increasing UO_2SO_4 concentration. This type of behavior points to a considerable degree of complexing in the saturated solutions. Several heats of solution have been determined and a possible relationship between these values and the amount of complexing is suggested.

Introduction

Two general methods are available for the determination of the solubility of salts at elevated temperature. In the analytical method saturated solutions are prepared and separated from the solid phase at the equilibrium temperature, and analyzed. In the synthetic method known ratios of salt and water are heated and the temperature

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[1] This document is based on work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory.