[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Reaction Occurring on Thoriated Cathodes[1]

BY MICHAEL HOCH AND HERRICK L. JOHNSTON

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The vapor pressure of thorium dioxide was determined by the method of Knudsen, between 2398 and 2677°K. ThO_2 vaporizes mostly undissociated as $ThO_2(g)$, the heat of vaporization being $\Delta H^0_{298} = 170 \pm 1$ kcal./mole. Some of the material (2–10%) vaporizes as ThO. No reaction occurs between ThO_2 and W. The study of the reaction $Th(l) + ThO_2(s) \rightleftarrows 2ThO(s)$ by a high temperature X-ray diffraction technique showed the formation at 2150°K. of solid ThO. The ThO has a cubic, face-centered lattice, with $a = 4.31$ Å. The formation of thorium on the thoriated cathodes is thus due to the decomposition of the ThO_2 to ThO at 2500°K. and above; the ThO disproportionates to Th and ThO_2 on cooling to 2000°K.

Introduction

The reaction between ThO_2 and W, or the question of what occurs on a thoriated cathode, how the thorium (which is assumed to be the emitter) is formed, is still unsolved, although many investigators have attacked the problem. All the work was done, however, on filaments, and the main interest was to improve the emission. Langmuir[2] reported a heat of vaporization of ThO_2 of 184 kcal. and a heat of reduction of 138 kcal. Shapiro[3] measured rates of evaporation with or without emission and found them equal. He obtained a heat of vaporization for ThO_2 of 171 kcal. Fan[4] studied the emission of ThO_2 alone, and of ThO_2 + W, and found them equal. He measured a heat of vaporization of 184 kcal. for ThO_2 and 46 kcal. for Th. The emission characteristics of thoriated cathodes have been reviewed by Danforth.[5]

In this work we first determined the rate of evaporation of ThO_2 by the Knudsen effusion method. The material vaporized was collected on two collectors: a cold collector at room temperature and a hot collector, the temperature of which was about 2000°K. The purpose of the two collectors was the following: If only molecules which are stable at room temperature (such as ThO_2 or Th) evaporate, then the X-ray diffraction patterns of the material on the two collectors should be identical. If a molecule which is unstable at room temperature (such as ThO) evaporates, on the cold collector we will obtain an amorphous substance due to the rapid cooling of the gas molecule (similar to the case of SiO).[6] If this molecule hits the hot collector, the temperature of which is low enough that the ThO molecule is not stable, but high enough that the ThO molecule can disproportionate to Th and ThO_2, then the X-ray diffraction patterns of the materials on the two collectors should be different. The chemical analyses of the two materials would be identical.

The rate of evaporation over a ThO_2 + W mixture was determined in a manner similar to that used over ThO_2.

The reaction $ThO_2(s) + Th(l) \rightleftarrows ThO(s)$ was studied by taking X-ray diffraction patterns at elevated temperatures. The formation of a new compound is shown by the appearance of a new set of diffraction lines. From the new diffraction pattern the lattice constant and crystal structure of the compound can be determined.

Apparatus and Experimental Procedure

Two tantalum Knudsen cells, dimensions 0.5 in. diameter, 0.75 in. high with an orifice diameter of 0.0625 in., were used for the vapor pressure measurements. The area of the orifice was corrected for thermal expansion by using the thermal expansion coefficient of tantalum determined previously in this Laboratory.[7] ThO_2 was introduced into the first cell; after the data on pure ThO_2 were taken, an equimolecular mixture of ThO_2 and W was introduced into the same cell. Into the second cell only the ThO_2 + W was introduced, and data taken. Both cells were degassed for two hours at 2000° before the runs were made.

A new metal vapor-pressure cell was built, similar to the one used on our calorimeter,[8] and is shown in Fig. 1. The power was supplied by a 20-kw. General Electric heater, equipped with grid control. The temperature was measured with a disappearing-filament optical pyrometer, calibrated against a standard tungsten-ribbon lamp. The standard tungsten lamp had been calibrated by the National Bureau of Standards and, in the range of the present investigation, was reported to have a maximum uncertainty of 8°.

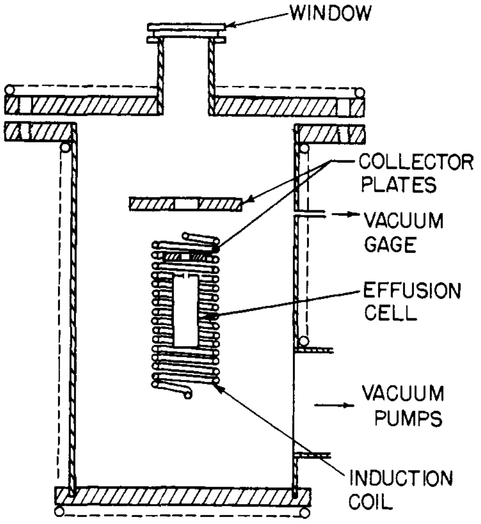

Figure 1.

When the cells were degassed, the initial heating was only about 5 seconds (negligible compared to the length of the run), due to the high pumping speed. The power input into the cell was very constant, and possible small temperature fluctuations were masked in the uncertainty of the temperature readings. Thus the temperature was taken as the average of the readings, and straight time was used to compute the pressures.

In the temperature range where the experiments were carried out, tantalum, the cell material, has a low though

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[1] This work was supported in part by the Office of Naval Research under contract with The Ohio State University Research Foundation.

[2] I. Langmuir, *Phys. Rev.*, **22**, 357 (1923).

[3] E. Shapiro, THIS JOURNAL, **74**, 5233 (1952).

[4] H. Y. Fan, *J. Applied Phys.*, **20**, 682 (1949).

[5] W. E. Danforth, *Advances in Electronics*, **5**, 170 (1953).

[6] M. Hoch and H. L. Johnston, THIS JOURNAL, **75**, 5224 (1953).

[7] J. W. Edwards, R. Speiser and H. L. Johnston, *J. Applied Phys.*, **22**, 424 (1951).

[8] M. Hoch and H. L. Johnston, to be published.

measurable vapor pressure. Blank runs on the empty cells were carried out, and the weight losses of thorium dioxide were corrected for the weight loss of the empty cell. The weight loss of the empty cell was always less than 10% of the weight loss due to thorium dioxide.

To correct for the thickness of the effusion hole (0.01 in.) all weight losses due to ThO_2 were multiplied by the factor $1/0.89 = 1.1236$.[9,10]

The cold collector plates were made of Pyrex 1.5 in. in diameter with a 0.25-in. hole in the middle. The hot collector was made of tantalum, 0.5 in. in diameter, with several 0.0625-in. holes drilled into it and several slits in the side to regulate its temperature. The material from the cold collector was scraped off, fastened with some "radio cement" to a thin glass rod, and X-ray diffraction patterns photographed in the Norelco–Phillips X-ray camera. The evaporating material slowly filled up the holes of the hot collector plates. The material was broken off with a pair of tweezers and put into the X-ray diffraction camera.

The high-temperature X-ray diffraction patterns were photographed in our high-temperature camera.[11] The technique was the same as that described elsewhere[6,12] except that the X-ray diffraction patterns were obtained in a high vacuum, with an exposure time of 30 minutes. The use of a vacuum was necessary because, at the high temperatures involved, arcing occurred in helium and argon atmospheres.

The thorium dioxide was obtained from the Maywood Chemical Works, the thorium from the Fairmount Chemical Co., and the tungsten from the Callite Tungsten Corp.

Experimental Results and Discussion of Data

Vapor Pressure Data.—The experimental data for pure ThO_2 are presented in Table I, and those for the ThO_2 + W mixture are given in Table II. The data from the two tables are plotted in Fig. 2. The pressure was calculated from the rate of effusion, using the equation $p = m\sqrt{2\pi RT/M}$, where p is the pressure in atmospheres, R is the molar gas constant, T is the absolute temperature, m is the rate of effusion in g./sq. cm./sec. and M is the molecular weight of the vapor.

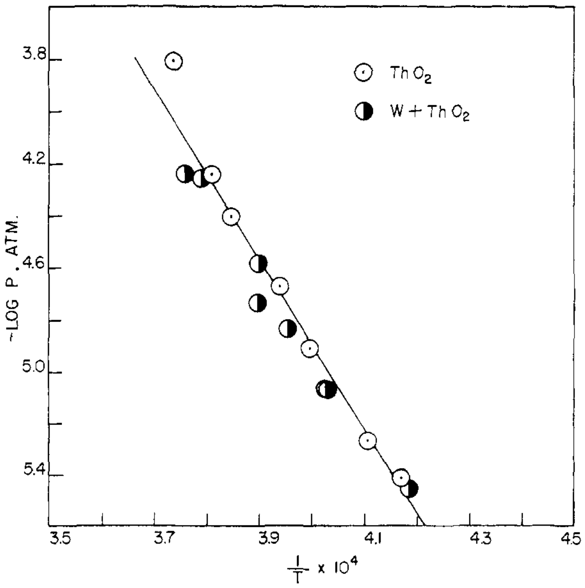

Figure 2.

TABLE I

VAPOR PRESSURE OF ThO_2

Run	Temp., °K.	Eff. time, sec.	Area, cm.^{2}	Wt. loss, g.	Evapn. rate × 10^5, g./cm.^{2}/sec.	P × 10^6 atm.	−log P
1	2398	25200	0.0195	0.0250	5.7046	3.878	5.411
6	2435	14400	.0196	.0197	7.8506	5.378	5.269
5	2502	7200	.0196	.0223	17.805	12.363	4.908
3	2539	10800	.0196	.0573	30.415	21.275	4.672
4	2600	7200	.0196	.0702	55.897	39.565	4.403
2	2625	7200	.0196	.1017	80.859	57.510	4.240
7	2676	1800	.0196	.0683	217.02	155.839	3.807

TABLE II

VAPOR PRESSURE OF ThO_2 + W

Run	Temp., °K.	Eff. time, sec.	Area, cm.^{2}	Wt. loss, g.	Evapn. rate × 10^5, g./cm.^{2}/sec.	P × 10^6, atm.	−log P
1	2389	25200	0.0195	0.0228	5.2049	3.532	5.452
6	2481	5400	.0196	.0116	12.376	8.557	5.068
8	2484	9000	.0196	.0196	12.472	8.629	5.064
5	2529	4500	.0196	.0166	21.132	14.753	4.831
3	2564	3600	.0196	.0283	37.087	26.071	4.5838
7	2566	3600	.0196	.0166	26.402	18.567	4.7313
4	2639	2910	.0196	.0397	78.030	55.643	4.255
2	2661	4500	.0196	.0634	80.577	57.700	4.239

The rates of evaporation are equal in both cases, indicating that no reaction between W and ThO_2 occurs. The X-ray diffraction photographs taken of the material condensed on the cold collector showed only the ThO_2 pattern. The material from the hot collector showed the ThO_2 pattern very strongly, and the Th pattern weakly. The visual intensity ratio was from 50:1 to 10:1. This indicates that ThO_2 vaporizes as ThO_2(g) with a slight dissociation to ThO.

If ThO_2 would vaporize completely as ThO and O, and then recombine on the collector plates, the X-ray diffraction pattern of the material from the cold collector would have, besides ThO_2 lines, a strong amorphous background which it does not have. No diffraction lines of tungsten or tungsten oxide were found on any collector.

To obtain ΔH and the equation for the vapor pressure, our data were treated by a sigma plot. The necessary specific heat data were taken from Kelley[13] for solid ThO_2($C_p = 15.84 + 2.88 \times 10^{-3}T - 1.60 \times 10^{-5}T^{-2}$); and we estimated, for gaseous ThO_2, C_p = 10.5 cal./mole/deg. Thus we obtain ΔH^0_{298} = 170.3 kcal./mole, and

$$\Delta H = 172{,}491 - 5.34T - 1.44 \times 10^{-3}T^2 - 1.60 \times 10^{-5}T^{-1}$$

The vapor pressure can be expressed by the relation

$$\log p \text{ (atm.)} = -37695T^{-1} - 7.82 \times 10^{-4}T + 12.145$$

A comparison of our data with Shapiro's shows that the heats of vaporization agree very well; however, our pressures are about 40 times as large as his. At 2000°K. we have 4×10^{-6} mm. and Shapiro has 1×10^{-7} mm. The discrepancy corresponds to a temperature difference at 200°, due probably to the fact that the loosely attached ThO_2 does not reach the temperature of the heating wire, although the pyrometer gives the temperature of the latter.

High-Temperature X-Ray Diffraction Data.—The high temperature X-ray diffraction studies of

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(9) P. Clausing, *Ann. Physik*, **12**, 961 (1932).

(10) S. Dushman, "Scientific Foundations of Vacuum Technique," John Wiley and Sons, Inc., New York, N. Y., 1949, 96 pp.

(11) J. W. Edwards, R. Speiser and H. L. Johnston, *Rev. Sci. Instr.*, **20**, 343 (1949).

(12) M. Hoch and H. L. Johnston, THIS JOURNAL, **76**, 2560 (1954).

(13) K. K. Kelley, "High Temperature Heat Content and Entropy Data for Inorganic Compounds," Bur. of Mines Bull. 476 (1949).

an equimolar mixture of Th + ThO_2 showed, at 1850°, the almost complete disappearance of the ThO_2 and Th diffraction lines and the appearance of a new set of diffraction lines. On cooling this new set of diffraction lines disappeared and the Th and ThO_2 pattern reappeared. The new diffraction lines could be indexed with a face-centered cubic pattern with a_0 = 4.31 Å. Interplanar distances are given in Table III. This new diffraction pattern is that of thorium monoxide, indicating that above 1850° the reaction $ThO_2(s) + Th(l) \rightleftarrows 2ThO(s)$ goes to the right.

TABLE III

X-RAY DIFFRACTION LINES OF ThO AT 1850°

(a_0 = 4.31 Å.)

$\sin^2\theta$	d in Å.	Indices h,k,l
0.0967	2.47	1,1,1
.1280	2.14	2,0,0
.2540	1.52	2,2,0
.3491	1.30	3,1,1
.3785	1.25	2,2,2
.5238	1.06	4,0,0
.6229	0.974	3,3,1

Conclusion.—We can now answer the last question, what happens on a thoriated filament, when it is activated at 2600°K., then cooled to 1800–1900°K. At 2600°K. some of the ThO_2 dissociates to gaseous and solid ThO, which disproportionates to Th and ThO_2 on cooling to 1900°K. For the heat of reduction of ThO_2, Langmuir[2] gave 138 kcal. The heat of formation of ThO_2 from Th and O_2 is 293 kcal.[14] Thus the value of 138 kcal. is very probable for the reaction

$$ThO_2(s) \longrightarrow ThO(s) + {}^1/_2O_2(g)$$

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COLUMBUS, OHIO

[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY, BROWN UNIVERSITY]

The Hydrolysis and Aggregation of the Beryllium Ion

BY G. MATTOCK[1]

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The complexity of aqueous solutions of beryllium is shown by a discussion of previous work, and the system is examined experimentally by means of the glass electrode in perchlorate medium. Use of a general expression involving all possible ion species (neglecting any perchlorate complex formation) enables calculation of the following constants from the pH data: $[BeOH^+][H^+]/[Be^{2+}] = (0.3 \pm 0.1) \times 10^{-6}$; $[Be_2OH^{3+}][H^+]/[Be^{2+}]^2 = (0.31 \pm 0.06) \times 10^{-3}$; in a 1.0 molar perchlorate medium at 25 + 0.02°. The pH characteristics of the system are discussed in terms of a number of possible combinations of polynuclear species, and it is concluded that description by means of only a few ionic types is incomplete. It is shown that a large number of different ionic species of increasing polynuclear complexity co-exist in hydrolyzed solutions of beryllium.

It has long been known that beryllium ions are hydrolyzed and aggregated in aqueous solution. Thus Britton,[2] in 1925, considered that beryllium salt solutions are colloidal in nature, while shortly afterwards Sidgwick and Lewis[3] suggested the existence of $[Be(OBe)_4]^{2+}$ aggregates. Milda Prytz[4] inferred that addition of sodium hydroxide to $BeSO_4$ and $BeCl_2$ causes stagewise hydrolysis, with formation of $BeOH^+$ and Be_2O^{2+}. Assuming that the predominant hydrolysis reaction is one involving condensation to Be_2O^{2+}, she obtained average values for $[Be_2O^{2+}][H^+]^2/[Be^{2+}]^2$ of 5.9 $\times 10^{-7}$ and 4.4 $\times 10^{-7}$ for bromide and iodide solutions respectively.[5]

J. Bjerrum[6] examined the hydrolysis in ammonium nitrate–ammonia buffers, and explained the variation in Prytz's constants with metal ion concentration as being due to the presence of a Be_2OH^{3+} ion. Prytz's assumption of dimerization being the only reaction at the point of half-neutralization to the $BeOH^+$ turning point (from which region the data were drawn) is rather arbitrary, however, and Bjerrum[6] mentions the possibility of a trinuclear species. On the other hand, Schaal and Faucherre[7] postulate a $[Be_4O_2]^{4+}$ (or $[Be_4(OH)_4]^{4+}$) ion as being involving in the hydrolysis.

Recently the ion exchange of beryllium perchlorate solutions was studied[8] by means of radioactive tracers. At an ionic strength of 0.1 and a temperature of 37°, polymerization of beryllium was observed in 10^{-5} molar solutions at a pH 4.5. At pH 5.5 the solutions were colloidal. The effect of time, pH, electrolytes, solvents and stirring on the coagulation of carrier-free Be^8 at 10^{-9} molar concentrations in dilute nitric acid have also been studied.[9]

This survey of the literature shows that beryllium ions readily hydrolyze in solution and form condensed species containing more than one beryllium atom. It appears that as the concentration of beryllium increases and the acidity decreases, these condensation products increase in size to become colloidal and finally to precipitate. Apart from the work of Prytz, no quantitative idea of the tendencies to hydrolyze and aggregate is available, however, and it was considered worthwhile to ob-

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[1] Present address: Chemistry Department A, Technical University of Denmark, Copenhagen, Denmark.

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[8] I. Feldman and J. R. Havill, THIS JOURNAL, **74**, 2337 (1952).

[9] G. K. Schweitzer and J. W. Nehls, *ibid.*, **75**, 4354 (1953).