fluoride as one salt component and zinc, cobalt, copper, cadmium and nickel fluoride as the other. Novoselova[3] has studied systems containing ammonium, aluminum and beryllium fluorides. As part of a general program of research on inorganic fluorides, we have studied the system ammonium fluoride–potassium fluoride–water at 25°. The system is a simple one; no double salts are formed, the solid phases being ammonium fluoride, potassium fluoride and potassium fluoride dihydrate.

Experimental

The Schreinemakers wet residue method, as discussed by Purdon and Slater,[4] was used. The C. P. materials were weighed into polyethylene cups fitted with rubber stoppers bearing entrance tubes for a pipet and for a motor-driven lucite stirrer. Samples were withdrawn

(3) Novoselova, *J. Gen. Chem. U. S. S. R.*, **9**, 1063 (1939); **10**, 1547 (1940); *C. A.*, **33**, 7687 (1939); **35**, 3186 (1941).

(4) Purdon and Slater, "Aqueous Solutions and the Phase Rule," Edward Arnold and Co., London, 1946, p. 63.

through a paper filter held onto the end of a glass pipet by a lucite cap. Teflon pipets were used at first, but it was found that glass contributed no observable error if the samples were handled quickly.

The solutions and wet residues were analyzed for ammonium ion and potassium ion. Ammonia was determined by distillation from strongly alkaline solution into boric acid and titration with standard hydrochloric acid. Potassium was determined by ignition with sulfuric acid, followed by treatment of the sulfate with ammonium carbonate at 600°.

Results

The results of the analyses of the solution and wet residues are given in Table I and representative points have been plotted in Fig. 1.

Summary

The system ammonium fluoride–potassium fluoride–water has been studied at 25°.

No new compound is formed by the two fluorides.

The Oxidation of Zirconium at High Temperatures[1]

BY DANIEL CUBICCIOTTI

Zirconium metal can react with oxygen in two ways: (a) to form a solid solution of oxygen in the metal phase and (b) to form a new phase of zirconium dioxide. When oxygen is admitted at pressures of a micron or less to a sample of zirconium at 1000 to 1500°, the oxygen dissolves in the metal and no new phase is formed. DeBoer and Fast[2,3] have established the solubility of oxygen in the metal to be about 38 atom per cent. This reaction has been studied to determine the "gettering" power of the metal. Thus Ehrke and Slack[4] and Hukagawa and Nambo[5] measured the residual pressures of gas over a heated zirconium filament. Guldner and Wooten[6] found that no new phase was formed until after the metal was saturated with oxygen.

Hickman and Gulbransen[7] found a new phase of monoclinic zirconium dioxide formed on the surface of the metal at 600° under an oxygen pressure of 1 mm. At the lower temperature and higher pressure of this experiment the rate of reaction of the metal with oxygen is apparently greater than the rate of solution of the oxide into the metal phase, and a new phase is formed on the metal surface. Gulbransen and Andrew[8] give an excellent

(1) This research was conducted under the sponsorship of the Office of Naval Research.

(2) DeBoer and Fast, *Rec. trav. chim.*, **55**, 459 (1946).

(3) DeBoer and Fast, *ibid.*, **59**, 161 (1940).

(4) Ehrke and Slack, *J. Applied Phys.*, **11**, 129 (1940).

(5) Hukagawa and Nambo, *Electrotech. J. (Japan)*, **5**, 27 (1941).

(6) Guldner and Wooten, *Trans. Electrochem. Soc.*, **93**, 223 (1948).

(7) Hickman and Gulbransen, *Anal. Chem.*, **20**, 158 (1948).

(8) Gulbransen and Andrew, *AIME, J. of Metals*, **185**, 515 (1949); *J. Electrochem. Soc.*, **96**, 364 (1949).

review of the literature on the reactions of zirconium with gases.

The present investigation of the oxidation was made to study the reaction in the intermediate temperature range of 600 to 900°. The two types of reactions, one occurring at low temperatures, the other at high temperatures, indicate that at some intermediate temperature there must be a point at which both reactions occur simultaneously.

Experimental

Method.—To measure the rate of reaction between zirconium and oxygen, the rate of consumption of oxygen by a specimen of metal at high temperature was measured. The apparatus consisted of two silica glass bulbs, connected by de Khotinsky-cemented rubber connectors to a glass manometer system, which was connected through stopcocks to a vacuum system and a gas buret. The silica bulbs were kept at constant high temperature by an electric muffle furnace regulated with a Wheelco Capacitrol. The manometer fluid was a commercial non-volatile oil, Amoil, with a density of 0.93 g. per cc. The pressure in the bulb containing the sample was prevented from dropping to a low value by periodic additions of oxygen, in known amounts, to the bulb.

In a typical run, a piece of 0.0054" thick sheet zirconium about 3 × 15 mm. was cleaned with acetone, rubbed shiny with a clean cloth, weighed and its surface area measured. The sample was placed in one of the silica glass bulbs which was then connected to the glass system with a rubber connector and cemented. The system was evacuated to about 10^{-5} mm. and the furnace brought to temperature, oxygen at known low pressure was admitted to the two bulbs. The decrease of pressure due to the consumption of the oxygen by the sample was measured with the Amoil manometer. When the pressure in the bulb dropped by 0.05 cm. of mercury below the original value, additional oxygen was admitted to the bulb and

the change in the manometer observed. From this observation, the pressure changes measured during the run could be converted into volume of oxygen consumed. As a check, the total amount of oxygen consumed by the metal was determined by the weight increase of the sample.

X-Ray diffraction pictures of some of the oxide scales formed were made with a General Electric XRD-1 unit and powder camera. An edge of the oxidized metal was centered in the camera so that half the X-ray beam was diffracted by the sample. Diffraction lines appeared on half the film. This method was superior to one using the powdered sample since most of the diffraction of X-rays occurred at the surface of the sample—the region of interest.

Materials.—Ductile zirconium metal 0.0054 inch thick was obtained from Foote Mineral Company. A typical analysis of the material is

Hf	2.5 to 3.0%
Fe	0.04%
O_2	0.03%
N_2	0.01%
Zr	balance

Commercial oxygen of 99.6% purity was used.

Results

Type of Oxidation.—Measurements of the rates of consumption of oxygen by zirconium were made from 593° to 921° at pressures ranging from 0.1 to 20 cm. In Figs. 1 and 2 are shown the results of the measurements for several runs. The amounts of oxygen consumed are plotted against the square root of time to show the degree to which the oxidations conform to the parabolic law [(amount of reaction)^2 = constant $\times$ time] since these oxidations were found to fit this law more closely than the linear or the logarithmic law.[9]

The runs below 880° were all found to conform to the parabolic law—that is, graphs of the amount of oxygen

TABLE I

THE PARABOLIC RATE CONSTANTS FOR THE OXIDATION OF
ZIRCONIUM

Run	Temp., °C. ± 5°	Press. of O_2 cm. Hg ± 0.05	Rate constant, k $\left(\dfrac{\text{g. } O_2 \text{ consumed}}{\text{sq. cm. metal surf.}} \right)^2 \dfrac{1}{\text{min.}}$
31	593	2.2	1.1×10^{-9}
45	597	20.3	1.0×10^{-9}
43	633	21.1	2.6×10^{-9}
44	650	20.0	4.8×10^{-9}
42	655	20.1	4.3×10^{-9}
35	683	0.4	9.2×10^{-9}
8	687	0.7	1.1×10^{-8}
7	690	1.9	1.2×10^{-8}
5	690	4.9	9.0×10^{-9}
10	690	7.4	1.1×10^{-8}
38	763	0.3	2.2×10^{-8}
39	757	0.4	1.8×10^{-8}
37	757	0.9	1.8×10^{-8}
36	759	5.0	1.6×10^{-8}
41	757	13.5	1.3×10^{-8}
40	759	20.2	2.2×10^{-8}
14	822	0.9	5.3×10^{-8}
17	845	0.3	1.0×10^{-7}
19	876	0.1	8.5×10^{-8}
24	916	0.2	1.2×10^{-7}
28	918	0.3	9.2×10^{-8}
23	918	0.6	1.4×10^{-7}

(9) For a discussion of the types of oxidation laws see Gulbransen, *Trans. Electrochem. Soc.*, **91**, 573 (1947).
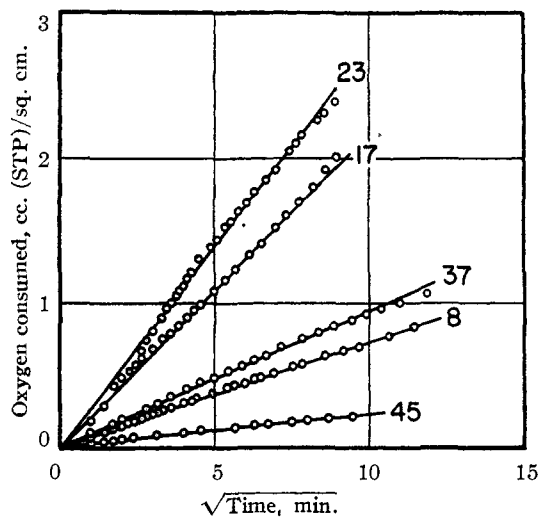

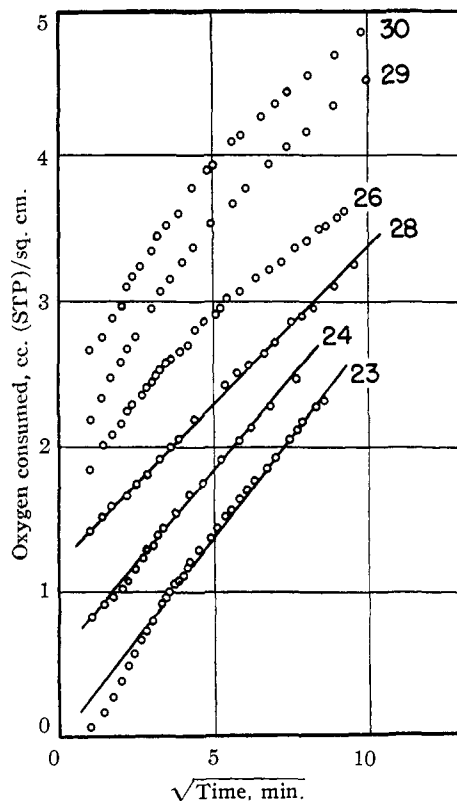Fig. 1.—The oxidation of zirconium at 597, 687, 757, 845 and 918°. Numbers indicate run numbers.

Fig. 2.—The oxidation of zirconium at 920°. The numbers indicate run numbers. The zeros of the ordinates are shifted.

consumed *versus* the square root of time were straight lines. Thus the results of each run below 880° were fitted to the parabolic equation and the rate constants so calculated are given in Table I, together with the temperature and pressure of each run.

The reproducibility of the measurements may be seen from the data at 690° and those at 760°. At 690°, the range of constants is from 9.0 to 12 $\times 10^{-9}$ or a variation of about 30% in the constants. At 760° the greatest dif-

ference in constants is about 60%. The discrepancy between runs at constant temperature may have been due to errors in measurement of the dimensions of the specimens. In addition there may have been differences in the surface roughness from one sample to another and small differences in the temperature of the oxidation.

The only measurements made above 880° were at about 920°. The data obtained at this temperature are shown in Fig. 2. The graphs of the amount of oxygen consumed *versus* the square root time for runs 23, 24 and 28 were almost linear. However similar graphs for runs 26, 29 and 30 show a distinct curvature. To obtain rate constants that could be compared with the lower temperature data, runs 23, 24 and 28 were assumed to be parabolic and rate constants calculated.

The Temperature Coefficient.—The effect of temperature on the course of the oxidation may be seen in Table I and Fig. 1. In the 320° temperature range studied, the rate constant changed by about a hundred-fold. The effect of temperature is seen in Fig. 3, in which the logarithm of the rate constant is plotted as a function of the reciprocal of the absolute temperature for each run.
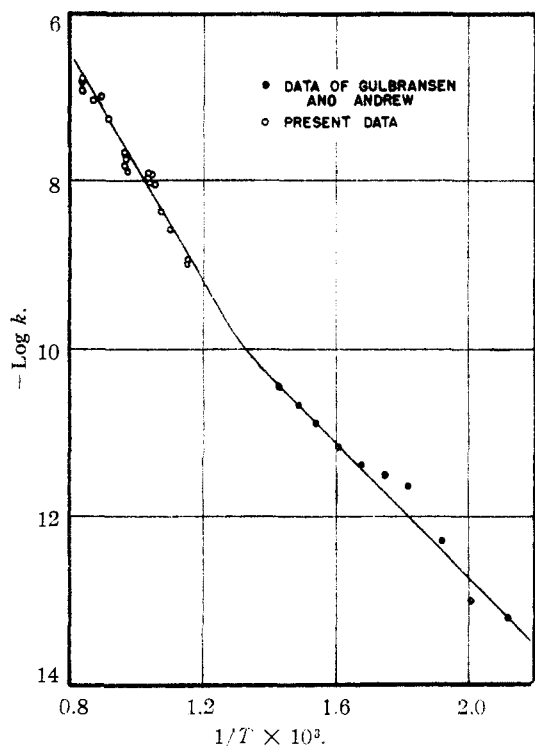

Fig. 3.—The logarithm of the rate constants *versus* reciprocal of temperature.

The Pressure Effect.—From Table I one may see the effect of the pressure of oxygen on the rate constant. At 690° the pressure was varied from 0.4 to 7.4 cm.; however, no trend in the rate constants appeared that may be related to the pressure of the oxygen. At 760° the pressure was varied by a factor of 70, and the rate constants showed no trend as the pressure was increased. Therefore, within the accuracy of these experiments, there was no observable effect of pressure on the rate constants.

Properties of the Oxide Formed.—At the end of each run, the sample was cooled in vacuum and then examined. When only a small amount of oxygen had been allowed to react with the metal, the resultant sample had a shiny, black coating which was very hard and adhered to the metal. When larger amounts of oxygen had been allowed to react, white spots appeared on the black coating. When about half as much oxygen as was required to oxidize the

sample completely was allowed to react with the metal, a shiny, white outer layer appeared on the sample. Between this outer white layer and the metal phase there was a layer of dull black material. In every case the final sample was very brittle in contrast to the original metal which was ductile. When the metal was completely oxidized, a pink or yellowish powder was obtained.

X-Ray diffraction pictures were taken of samples with black coatings, with white coatings and with white-spotted black coatings, and pictures of the unreacted metal were also made for reference. The diffraction pattern of the metal corresponded closely to the interplanar spacings given for zirconium metal on Card 2941 issued by the American Society for Testing Materials.[10] The patterns observed for all the oxide scales X-rayed, whether white, black or spotted, corresponded to the spacings of zirconium metal plus the spacings given on Cards II-1163 and II-1513.[11] These cards were made from a monoclinic and a tetragonal modification, respectively, of zirconium dioxide. Although patterns were made from samples oxidized at several temperatures, no differences in the spacings or relative intensities of the diffraction lines were apparent; and so there were no great differences in the oxide phases formed at different temperatures.

Discussion

In Table II a comparison is made of the parabolic rate constants for the oxidation of several metals, ranging from the rapid-oxidizing metal iron to the very slow-oxidizing beryllium. The rate constant for the oxidation of zirconium is larger than those of beryllium and nickel and slightly smaller than that of cobalt.

TABLE II

COMPARISON OF THE PARABOLIC RATE CONSTANTS FOR THE OXIDATION OF SEVERAL METALS

Metal	Constant $\left(\dfrac{\text{g. oxygen consumed}}{\text{sq. cm. metal surface}}\right)^2 \dfrac{1}{\text{min.}}$ 800°C.	900°C.	Ref.
Fe	3.3×10^{-6}	1.7×10^{-6}	(12)
Cu	5.3×10^{-7}	2.1×10^{-6}	(12)
Co	5.5×10^{-8}	3.7×10^{-7}	(12)
Zr	4.4×10^{-8}	1.2×10^{-7}	
Ni	1.5×10^{-9}	1.2×10^{-8}	(12)
Be	2.7×10^{-12}	3.6×10^{-11}	(13)

Gulbransen and Andrew[8] have studied the oxidation of zirconium from 200 to 425°. The material they used was 5 mil sheet supplied by Foote Mineral Company; that is exactly the same type of metal as used in the present work. Their method differs from the present one in that they used a micro balance technique, and they took great pains to clean the surface of the metal samples.

Gulbransen and Andrew report that their oxidation curves on a parabolic plot were not initially parabolic, but tended toward the parabolic as the reaction proceeded. They give parabolic rate constants, apparently derived from such plots, which may readily be compared to the present

(10) Am. Soc. Testing Mat., "Original Set of X-Ray Diffraction Patterns," 1942.

(11) Ibid., "First Supplementary Set," 1944.

(12) Wagner, "Handbuch der Metallphysik," Vol. I, pt. II, pp. 123–154, 1940, Akad. Verlag., Leipzig.

(13) Cubicciotti, THIS JOURNAL, 72, 2084 (1950).

data.[14] This comparison is made in Fig. 3. Through each set of data a straight line may be drawn. The lines are of markedly different slope; however, they do join smoothly between the two sets of data. Thus the activation energies given by the two sets of measurements are different; however, the two sets of rate constants complement each other.

Since some of the present oxidations were not exactly parabolic, a further check was made on those that were. For a parabolic oxidation a graph of the log of oxygen consumed *versus* the log of time should be a straight line with slope equal to two. Thus the present data were plotted in that manner. Figure 4 shows such plots for the runs shown in Fig. 2. The data of runs 8, 17, 37 and 45 fall on straight lines with slopes 2.0, 2.0, 2.0 and 2.2, respectively. The curve for run 23 shows an initially curved line; however, after about the first twelve minutes, the curve becomes linear with slope 2.0. This graph constitutes a confirmation of the parabolic nature of the oxidations.

McAdam and Geil[15] have measured the rate of growth of oxide thickness on zirconium, as compared with several other metals, by an interferometric method at temperatures below 400°. It is not possible to compare the rate constants of the present experiments with their work; however, they give an order of oxidation rates for the metals. They found zirconium to be oxidized more rapidly than nickel and only somewhat less rapidly than cobalt and iron at about 350°, that is, the same order of reaction rates as shown in Table II.

The activation energy from the present data may be calculated from the slope of the line of Fig. 3. The value obtained is 32 kcal. per mole. Gulbransen and Andrew give the much lower value of 18.2 kcal. per mole from their data.

It is possible to calculate an activation energy for the reaction from the data of McAdam and Geil.[15] They give the time required to form a first order blue on the metal at temperatures from 200 to 350°. If one assumes their oxidations were parabolic, then the parabolic rate constants are in-

(14) Gulbransen and Andrew have expressed their rate constants in sq. cm./sec. assuming that a layer of 1 g./cm. of zirconium dioxide has a thickness of 0.615 cm. To convert their rate constants into the units used in the present work, one must multiply the constants by $60/(0.615).^2$

(15) McAdam and Geil, *J. Research, Natl. Bur. Stand.*, **28**, 593 (1942).
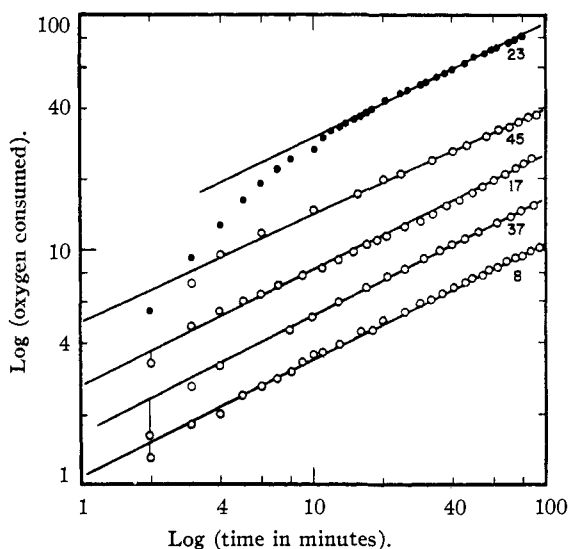

Fig. 4.—The log of oxygen consumed *versus* log time for several runs. Run numbers are indicated on the curves. The ordinates have been multiplied by arbitrary constants.

versely proportional to the time required to form the blue. From such calculations one estimates a value of 35 kcal. per mole from their data.

An explanation of the deviations of some of the oxidations from the parabolic law may possibly be found in the fact that zirconium can absorb large proportions of oxygen into the metallic phase. Thus if the metal were absorbing oxygen as well as forming the dioxide, the total consumption of oxygen with time could be represented as the sum of two terms: one almost linear, corresponding to the absorption by the metal, the other parabolic, corresponding to the formation of the dioxides. Further work is needed to investigate this point.

Summary

The rate of consumption of oxygen by ductile zirconium metal has been studied in the range 600 to 920°. The oxidation curves were parabolic at all temperatures except 920°, where a small deviation toward linear was observed. The oxidation rates were not affected by changing the oxygen pressure from 0.1 to 20 cm. The temperature coefficient of the parabolic rate constant gave an activation energy of 32 kcal. per mole.