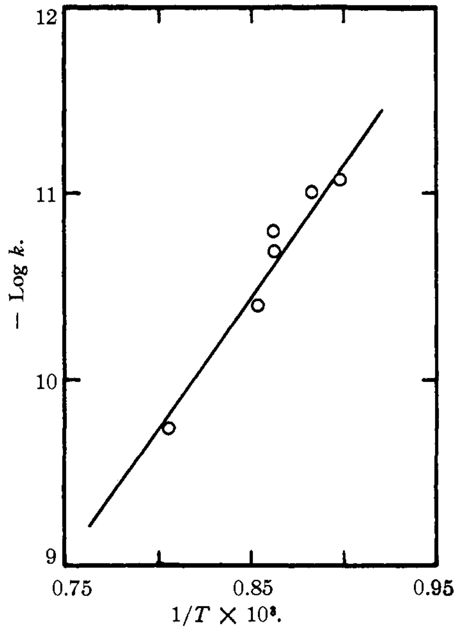

Fig. 2.—The dependence of the logarithm of the rate constant on reciprocal of absolute temperature.

points fall very close to a straight line, as seen from the figure. The largest deviation from the straight line drawn corresponds to a 20% deviation in the rate constant. Such a deviation may be considered within experimental error as mentioned above. Because the oxidation curves were all parabolic and the log K *vs.* $1/T$ plot is linear, it is reasonable to state that the same mechanism for oxidation holds over the temperature range studied. The activation energy for this oxidation process determined from the slope of the line of Fig. 2 is 62 kcal. per mole.

Since the oxidation curves are parabolic, the rate determining step in the oxidation process is the diffusion of some species through the growing oxide film.[3,4,5] Thus the activation energy observed should correspond to the activation energy of diffusion through the oxide. Barrer[13] has tabulated the activation energies of diffusion of some ions through salts. Those values are all less than 50 kcal. per mole. Gulbransen[2] has given the activation energies observed in the oxidation of several metals obeying the parabolic law at high temperatures. The largest activation energy of his data is 45.7 kcal. per mole. It appears that the activation energy observed in the present study is exceptionally large for the type of reaction considered.

The species that can diffuse through the beryllium oxide scale are $O^{=}$, Be^{++}, and e^{-}. In view of its relatively large size, it is not likely that the $O^{=}$ ion diffuses sufficiently rapidly to account for any large fraction of the reaction rate. Of the other species, it is not possible at present to decide which has the smaller rate and is thus rate determining in the reaction. The further study of the mechanism of the reaction should prove interesting in view of the high activation energy and small rate.

Summary

The rate of the reaction between beryllium metal and oxygen gas has been studied from 840 to 970°. The oxidation was found to proceed according to the parabolic law with much smaller rate constants than for other similar reactions. The energy of activation for the reaction was found to be 62 kcal. per mole.

(13) Barrer, "Diffusion in and Through Solids," Cambridge University Press, Cambridge, England, 1941, p. 274.

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[CONTRIBUTION FROM THE RESEARCH SECTION, DIVISION OF CHEMICAL ENGINEERING, TENNESSEE VALLEY AUTHORITY]

Azeotropy in the System Phosphoric Oxide–Water

BY GRADY TARBUTTON AND M. E. DEMING

Although Tilden and Barnett[1] reported vapor density measurements which they interpreted to indicate that metaphosphoric acid (88.75% P_4O_{10}) exists in the vapor state as the dimeric molecule $H_2P_2O_6$, Balareff[2] has reported data that indicate that the meta acid dissociates on vaporizing. He found that the residue from the distillation of metaphosphoric acid in a gold vessel contained 89 to 93.4% phosphoric oxide. It should be noted that the materials investigated by Tilden and Barnett[1] contained about 90% phosphoric oxide, which is significantly greater than the phosphoric oxide content of metaphosphoric acid. Balareff[2] concluded that the rate of loss of water by metaphosphoric acid and the eventual composition of the acid apparently depend on the temperature and duration of heating and on the partial pressure of water vapor in the system.

Zagvozdkin, Rabinovich and Barilko[3] measured the "dehydration" pressure of orthophosphoric acid (72.4% P_4O_{10}) at temperatures between 150 and 300°, and determined the amounts of ortho-, pyro- and metaphosphoric acids in the residues. They reported that the residue obtained at 300° contained a total of 88.68% phosphoric oxide, composed of 96.10% meta- and 4.62% ortho-

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(1) W. A. Tilden and R. E. Barnett, *Trans. Chem. Soc.* (*London*), **69**, 154–160 (1896).

(2) D. Balareff, *Z. anorg. Chem.*, **102**, 34–40 (1917).

(3) K. I. Zagvozdkin, Yu. M. Rabinovich and N. A. Barilko, *J. Applied Chem.* (*U. S. S. R.*), **13**, 29–36 (1940).

phosphoric acid, and had a vapor pressure of 0.5 mm. They stated that no measurable amount of phosphoric oxide was volatilized in any of their experiments.

The present study was undertaken to determine whether phosphoric oxide and water form any congruently boiling compounds, and to establish other properties of the system in the region of high phosphoric oxide concentration.

Experimental

The apparatus is shown in Fig. 1. In a few experiments in which attempts were made to determine the compositions of the distillates, the condenser was modified by attaching ampoules to the bottom of the condenser with short lengths of glass tubing. By manipulation of the condenser through the motion permitted by the spherical joints, individual ampoules were placed to act as receivers; when a sample was collected, the ampoule was sealed off and removed.

Orthophosphoric acid solution (85% H_3PO_4) lost water rapidly when it was heated to 475° in a stream of dry nitrogen; the residue had a phosphoric oxide content that corresponded approximately to metaphosphoric acid. On further heating at 475° for six hours, the composition of the residue remained unchanged, and no distillate condensed at room temperature. These results indicate that the mixtures approximating metaphosphoric acid in composition are stable at 475° and have a very low vapor pressure at that temperature. At higher temperatures, both water and phosphoric oxide were volatilized from this material, but at such rates that the residue became richer in phosphoric oxide. At 750°, for example, the phosphoric oxide content of successive fractions of the distillate increased from 79 to 90%, and the residue contained 91% phosphoric oxide. In contrast to Balareff's conclusions,[2] however, the composition of the residual phosphoric acid tended to approach a definite composition of about 92% phosphoric oxide when the temperature or the duration of heating was increased. When samples were heated for short periods at various temperatures, the phosphoric oxide content of the residues increased from 82.4 to 92.2% as the temperature was increased from 300 to 800°. When samples that contained about 88% phosphoric oxide were heated to 600° for various periods, the phosphoric oxide content of the residues increased from 88.3 to 91.7% as the duration of heating was increased from forty-five minutes to seventeen hours. After forty-two hours heating at 600°, the residue contained 92.1% phosphoric oxide. To approach the apparent limiting concentration from the other direction, samples that contained approximately 98% phosphoric oxide were heated at various temperatures between 500 and 870°. All the residues contained less than 98% phosphoric oxide. The residue obtained at 870° contained approximately 92% phosphoric oxide; it distilled at approximately 870° without change in composition under atmospheric pressure (750 mm.).

The results show that, in agreement with Balareff,[2] metaphosphoric acid does not distil congruently at atmospheric pressure. They show that the phosphoric oxide–water system forms either a compound or an azeotropic mixture that contains approximately 92% phosphoric oxide and boils congruently at about 870° at 750 mm. A series of experiments was made to determine whether the product was a compound or an azeotropic mixture.

The test material was prepared by evaporating the water from orthophosphoric acid in a platinum dish until the phosphoric oxide content of the residue was about 88.8%. Samples of the residue were distilled under atmospheric and reduced pressures in platinum crucibles in the apparatus shown in Fig. 1 until the boiling point was reached. The residues were analyzed by the gravimetric magnesium pyrophosphate method; duplicate analyses checked within 0.1%. The apparatus was cold at the beginning of each experiment, and an inert gas was passed slowly through the apparatus during each distillation. In the experiments at atmospheric pressure, dry nitrogen was admitted at the top of the apparatus. When the pressure in the system was below atmospheric, sufficient air was drawn into the apparatus through the imperfect joints to serve as a carrier for the volatile products. The boiling point was taken as the liquid temperature that remained constant while the temperature of the surrounding furnace continued to rise. Distillation was continued for at least five minutes after the temperature of the sample became constant.

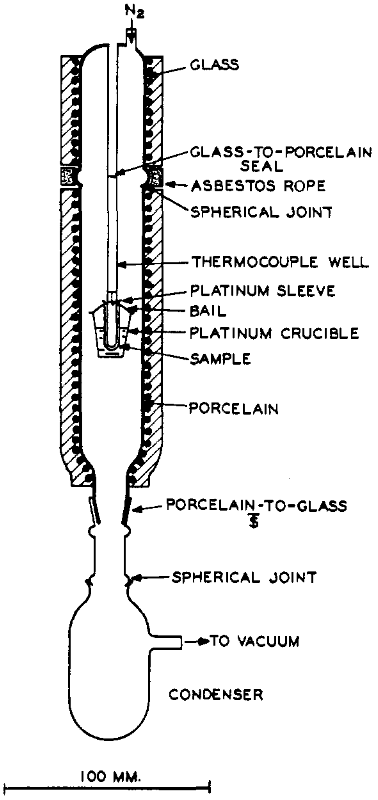

Fig. 1.—Distilling apparatus.

The results are summarized in Table I. The vapor pressure–temperature relationship is plotted in Fig. 2, and the composition–pressure relationship is plotted in Fig. 3. The pressure–temperature data were reproducible within the limits of

TABLE I

TEMPERATURE–VAPOR PRESSURE–COMPOSITION RELATIONSHIPS OF CONSTANT-BOILING COMPOSITIONS IN THE P_4O_{10}–H_2O SYSTEM

Temp., °C.	Press., mm.	P_4O_{10} content of residue Wt. %	Mole fraction
694	104	91.1	0.393
737	181	91.5	.406
773	280	91.6	.409
777	283	. .	. . .
796	377	91.8	.415
801	380	92.0	.422
837	552	. .	. . .
840	555	92.0	.422
869	753	92.1	.425

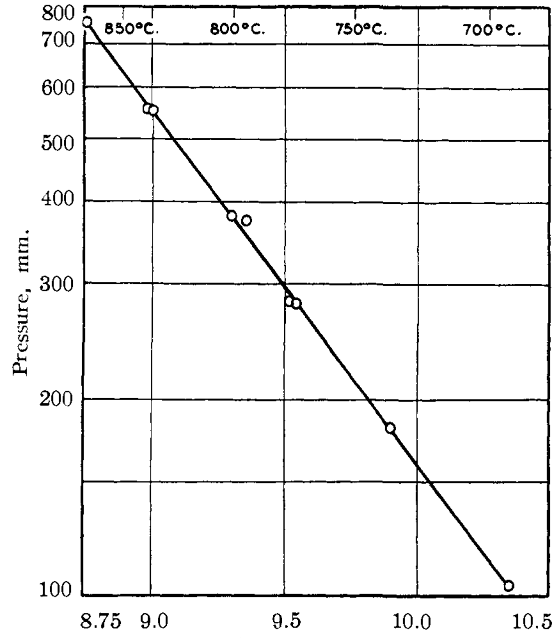

Fig. 2.—Temperature–vapor pressure relations in the system P_4O_{10}–H_2O, mixtures containing 91.1 to 92.1% P_4O_{10}.

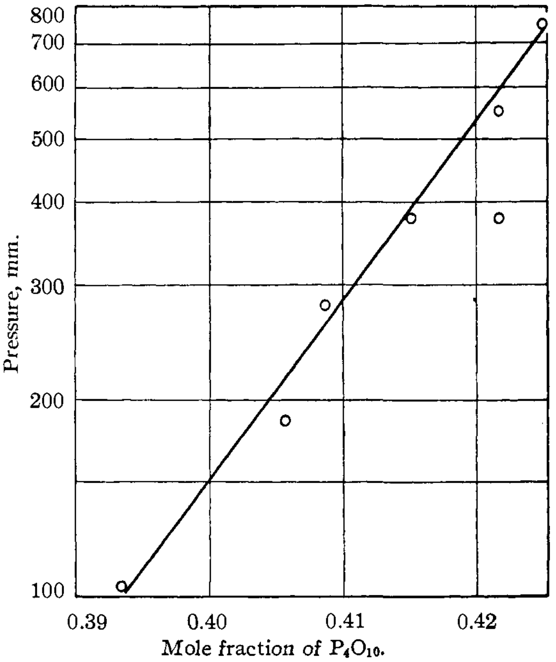

Fig. 3.—Composition–vapor pressure relations in the system P_4O_{10}–H_2O, constant-boiling mixtures at temperatures of 694 to 869°.

the measuring instruments. Although only a few duplicate experiments were made, the composition–pressure data appeared to be about as precise as the chemical analyses. The relationship between log $p_{\text{mm.}}$ and $1/T$ of mixtures in the phosphoric oxide–water system that contain 91.1 to 92.1% phosphoric oxide is very nearly linear, and this might be interpreted as indicating a congruently boiling compound. This linear relationship, however, is also the normal behavior of a two-component azeotropic mixture,[4] and the data show that the composition of the congruently boiling mixture varies with the pressure on the system. In general, two-component azeotropic mixtures obey approximately the linear relationship illustrated by the line in Fig. 3.[4]

From the earlier observation of the slow rate of distillation at 475°, it was evident that the vapor pressure of a mixture containing approximately 88.8% phosphoric oxide is low at that temperature. The vapor pressure of such a mixture is calculated from the equation of the line in Fig. 2 ($\log p_{\text{mm.}} = -5459/T + 7.6547$) to be about 2 mm at 475°. Although the large extrapolation is subject to question, it lends some support to the earlier observation.

It is concluded, on the basis of the data given in Table I and plotted in Figs. 2 and 3, that phosphoric oxide and water form no congruently boiling compounds, but that the system is azeotropic.

Acknowledgment.—T. M. Jones and J. F. Shultz contributed to the study through helpful suggestions and performance of some of the experimental work.

Summary

An exploratory study was made of the phosphoric oxide–water system in the region of high phosphoric oxide content. The results show that when water is distilled from orthophosphoric acid and the temperature is raised to 475°, the residue has a composition approximately that of metaphosphoric acid. The vapor pressure of this residue is about 2 mm. at 475°. The phosphoric oxide content of the system increases as the temperature is increased, although both water and phosphoric oxide are vaporized, until an azeotropic mixture is obtained. The azeotropic mixture varies in composition from 91.1 to 92.1% phosphoric oxide as the pressure on the system at its boiling temperature increases from 104 to 753 mm. The corresponding boiling points increase from 694 to 869°. The azeotropic mixture that boils at 869° and 753 mm. was obtained from samples both richer and poorer in phosphoric oxide.

WILSON DAM, ALABAMA RECEIVED MAY 20, 1949

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(4) E. A. Coulson and E. F. G. Herington, *J. Chem. Soc.*, 597–607 (1947).