[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Influence of Combustion Conditions on the Density of Water Formed from Commercial Hydrogen and Oxygen

BY W. HEINLEN HALL AND HERRICK L. JOHNSTON

It was suggested in an earlier paper[1] that conditions at the time of combination of hydrogen and oxygen might influence the density of the water formed, particularly if the two gases were not present in the stoichiometric proportions. A further check on this point appeared of interest because of the possible significance of such an effect in the determination of isotope ratios.

To accomplish this a number of experiments have been carried out, with oxygen and hydrogen from commercial tanks. The gases were either combined by ignition in a small blowtorch of glass, to produce a flame, or the mixed gases reacted on a catalyst surface of platinized asbestos. The water vapor was condensed, the water purified[2] and its density determined to roughly 1 p. p. m. by the submerged float method. Precautions[3] were taken to avoid possible errors due to barometric variations or to changes in weight or volume of the glass float. Combustions were made out of contact with air.

The results of these experiments are given in Table I, where they are classified with respect to the conditions of combustion. As shown, the catalyst was employed under three sets of conditions. III represents conditions similar to those in our earlier work,[4] in which the catalyst chamber was heated to 300° and the mixed gas passed slowly through a loose plug of the platinized fiber. Reaction took place over a large area of catalyst[5] surface, without incandescence, and there was relatively long contact between the mixture of steam and the gas introduced in excess. The conditions in IV were similar, except that the catalyst chamber was not heated. An approximate temperature of 100° was maintained by the heat of reaction. In the experiments listed under II the mixed gases were directed onto a small area of the catalyst by a capillary which almost touched the asbestos. This resulted in a much more localized reaction with the result that incandescence was produced in a small zone adjacent to the capillary. In reality combustion probably occurred as a homogeneous gas phase reaction in a thin flame adjacent to the catalyst surface. In this series of experiments the walls of the catalyst chamber were cooled with water, which condensed the steam and thus removed it from the active zone.

TABLE I

Condition of combustion	Volume of O_2 per unit volume of H_2	Sample	Densities relative to normal water	
			ΔT	Δd (p. p. m.)
I Flame at tip of glass blowtorch				
(a) Stoichiometric proportions	0.5	A3	+0.010	+2.6
(b) Oxygen in excess	4	A1	+ .010	+2.6
	0.7	B2	+ .012	+3.1
(c) Hydrogen in excess	.06	A2	+ .006	+1.6
II Glowing catalyst in water-cooled copper tube				
(a) Oxygen in excess	0.75	A5	+0.013	+3.4
(b) Hydrogen in excess	.2	A4	+ .013	+3.4
III Catalyst at 300° in heated Pyrex tube				
(a) Oxygen in excess	1.0	A8	−0.002	−0.5
	1.0	B3	− .020	−5.2
(b) Hydrogen in excess	0.1	A6	+ .018	+4.7
	.16	A7	+ .021	+5.5
	.25	B5	+ .021	+5.5
IV Catalyst at 100° in uncooled Pyrex tube				
(a) Oxygen in excess	1	B4	−0.014	−3.7
(b) Hydrogen in excess	0.125	B1	+ .025	+6.5

The columns in the table refer to: proportions in which the gases were supplied from the tanks, measured by flowmeters; identifying sample numbers, with the letters A and B used to distinguish two different pairs of oxygen and hydrogen tanks used in the investigations; and the temperatures of floating equilibrium and corresponding density increments, relative to purified samples of Columbus city water.

Interpretation and Discussion of Results

The low density of sample A2 may indicate a slight effect, due to excess hydrogen, in the flame experiments. However, the effect, if present, is no greater than the limits of error of the determination. Nor is the density of the water pro-

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(1) Hall and Johnston, THIS JOURNAL, **57**, 1515 (1935).

(2) Snow and Johnston, *Science*, **80**, 210 (1934).

(3) Johnston, THIS JOURNAL, **57**, 484 (1935).

(4) The same lot of platinized asbestos was used in all of the catalyzed experiments of the present work as was used in the early investigation.

(5) Analysis of the gas which came from the catalyst in one experiment, with an initial mix of 27 parts oxygen to 73 of hydrogen, showed that the oxygen removal was 95% complete.

duced from the "B" pair of tanks significantly different from that of the "A" pair. We take 2.5, the average of the four samples secured in the flame combustions, as the value best representative of the hydrogen and oxygen in the tanks and use this as a reference point to measure the effect of the various conditions accompanying the catalytic experiments.

The consistently high values (2 to 4 parts per million relative to the flame experiments) obtained with excess hydrogen in series III and IV are well outside the experimental error and are opposite in sign to effects which might be anticipated on the basis of comparative reaction velocities of light and heavy hydrogen.[6] They may be accounted for by the exchange reaction

$$H_2O(g) + HD = HDO(g) + H_2 \qquad (1)$$

for which platinum is observed to be a catalyst.[7] Equilibrium constants for this reaction are 2.0 and 1.38 at 100 and 300°, respectively.[7b] Table II records the relative densities to be expected with equilibrium fully attained.[8]

TABLE II

EQUILIBRIUM DENSITIES (CALCULATED) FOR THE RUNS WITH HYDROGEN IN EXCESS

Sample	Hydrogen steam ratio	Density above normal water, p. p. m.
A6	4.0	7.6
A7	2.1	6.7
B5	1.0	5.4
B1	3.0	13.5

Failure to attain full equilibrium, particularly at the lower temperature, is to be expected since the time of contact with the catalyst was much shorter than that found by A. and L. Farkas[7b] for complete equilibrium.

With excess oxygen, under the conditions pertaining to series III and IV, densities are consistently low (3 to 8 parts per million). Although the exchange reaction

$$H_2O^{18} + O^{16}O^{16} = H_2O^{16} + O^{16}O^{18} \qquad (2)$$

would lead, qualitatively, to water of low density, the quantitative effect of this reaction could not exceed approximately 0.3 p. p. m. in the experiment at 300°, or about 1 p. p. m. at 100°.[9] The low densities must therefore be the result of higher reaction velocities of $O^{16}O^{16}$ as compared with $O^{16}O^{18}$. It is evident that platinum is a much poorer catalyst for the exchange of oxygen with water than for the exchange of hydrogen with water.

The results in Series II are probably to be accounted for on the theory that here we are dealing with a homogeneous gas phase reaction in which the isotope proportions remain unchanged, as in the flame, and that rapid removal of water vapor from the gas phase prevents a subsequent hydrogen exchange with sample A4.

The Density of Atmospheric Oxygen

These experiments confirm a reinterpretation[10] of an observation reported in our previous paper.[1] The fact that tank hydrogen burned in air (flame) produced water of higher density than that resulting from reaction of the same tank hydrogen with oxygen from normal water (catalyst) was attributed by us to the relative proportions in which the gases were brought together in the two combustions. On the basis of the present work we see that the density of samples 4(a, b) of the earlier work were probably *high* to the extent of about 2.7 parts per million due to the hydrogen exchange reaction on the catalyst. With this correction applied the discrepancy between samples (4) and (5) of that work is *increased* to give a difference of 6.6 p. p. m. The combustion in atmospheric oxygen gave the water of higher density. This is in good agreement with independent work of Dole,[10] who reports 6.0 p. p. m. greater density for water produced by combustion of hydrogen with atmospheric oxygen than for water produced by combustion of the same hydrogen with oxygen from normal water.

The conclusions in the earlier paper respecting the O^{18} and O^{17} enrichment of water from commercial electrolytic cells are not changed by the results reported here. Since the conditions of combustion were the same with samples 2 and 3 (a, b) the influence of the hydrogen exchange reaction must have canceled out in the comparisons of densities.

Summary

Density comparisons of water produced by

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[6] H. W. Melville, *J. Chem. Soc.*, 797 (1934).

[7] (a) Horiuti and Polanyi, *Nature*, **132**, 819 (1933); (b) A. and L. Farkas, *Trans. Faraday Soc.*, **30**, 1071 (1934).

[8] The hydrogen was produced by electrolysis of water and should be nearly normal unless the electrolyte was newly prepared. The oxygen was produced by the fractionation of air and might be expected to contribute, in itself, a density abnormality of about 6 p. p. m. (*cf. seq.*) except for some probable isotope separation in its production. For purposes of this computation we have taken the hydrogen as normal (H/D ratio of 5800) and have credited the 2.5 p. p. m. abnormality to the oxygen alone.

[9] This calculation is based on the enrichment factors computed by Urey and Greiff [THIS JOURNAL, **57**, 321 (1935)] and on an O^{16}/O^{18} ratio of approximately 500.

[10] Malcolm Dole, *J. Chem. Phys.*, **4**, 268 (1936).

combustion of hydrogen and oxygen from commercial cylinders show: (1) that the proportions in which the gases are brought together for reaction results in no significant change in the isotopic composition of either hydrogen or oxygen if the combustion occurs in a flame.

(2) That changes of isotopic composition sufficient to affect the density of the resulting water by several parts per million may occur if the combination takes place on a platinum catalyst. With oxygen in excess the density of the resulting water may be low and appears to be accounted for by lower reaction velocities of oxygen molecules containing the heavier isotopes. With hydrogen in excess the resulting water was found, under certain conditions, to be high in density. This appears to be the consequence of an incomplete exchange reaction between steam and the excess hydrogen.

An exchange reaction between steam and molecular oxygen does not appear to be significantly catalyzed by platinum at 300°.

Previous data[1] corrected for the hydrogen exchange are in quantitative agreement with Dole's discovery[10] that water produced from hydrogen and atmospheric oxygen is denser by about 6 parts per million than water produced by combination of the same hydrogen with oxygen obtained from normal water.

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Kinetics of the Vapor Phase Reaction of Mercury and Halogens

BY RICHARD A. OGG, JR., HENRY C. MARTIN AND PHILIP A. LEIGHTON

There appears to have been but little study of the familiar combination of mercury with halogens. In particular, no evidence has as yet been adduced to show that such a reaction can take place other than at the surface of liquid mercury. It is desired to report the preliminary results demonstrating the occurrence of a rapid vapor phase combination of mercury and bromine and to discuss the kinetics of this process.

The method previously described[1] for demonstrating visually the evaporation of mercury was extended to observe qualitatively the reaction of mercury vapor with halogens. A dish of warm liquid mercury was interposed between a mercury "resonance" lamp and a fluorescent screen. The ascending vapor was manifested as a dark shadow on the screen. Introduction of a small dish containing liquid bromine or warm iodine crystals into the space above the liquid mercury caused the shadows to vanish, only to reappear after removal of the halogen.

Estimates of the rate of the mercury–bromine reaction were made by an adaptation of the "diffusion flame" method employed by Frommer and Polanyi[2] in their studies of sodium vapor reactions. Mercury vapor (at a known partial pressure of some 0.01 to 0.1 mm.) carried in dry air at atmospheric pressure was allowed to flow through a nozzle into a reaction cell filled with air at atmospheric pressure and bromine vapor at a partial pressure of some 10 to 40 mm. The reaction zone was maintained at approximately 110°.

Quartz windows allowed a beam of light from a mercury "resonance" lamp to traverse the reaction zone and by means of quartz lenses an image of the nozzle and surrounding region was cast upon a fluorescent screen. With suitable rates of flow (a linear nozzle velocity of about 1 cc./sec.) the reaction "flame" was observed as a circular shadow projecting from the nozzle image. Visual estimation was made of the light absorption in various parts of the "flame," and compared with that in blank experiments in which air containing mercury vapor at various known concentrations was allowed to flow into the bromine-free cell. In this manner a rough estimate could be made of the total number of mercury atoms present in the mercury–bromine "flame." The reciprocal of the mean life of the mercury atoms in the "flame" divided by the bromine concentration yields the bimolecular velocity constant.

The mercury–bromine reaction appeared to be one of the first order with respect to each reactant. Upper and lower limits for the velocity constant under the above conditions were estimated as

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(1) P. A. Leighton and W. G. Leighton, *J. Chem. Education*, **12**, 139 (1935).

(2) L. Frommer and M. Polanyi, *Trans. Faraday Soc.*, **30**, 519 (1934).