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Summary

A manometer has been developed which is capable of measuring by electrical means pressure differentials of an inch of mercury with an accuracy of one part in 1000 at a pressure of 3000 lb. per sq. in. The instrument is direct reading and requires neither calibration nor the use of very clean mercury.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

THE THERMAL HYDROGEN–OXYGEN COMBINATION. FORMATION OF HYDROGEN PEROXIDE, AND THE INFLUENCE OF SURFACE NATURE[1]

BY ROBERT N. PEASE[2]

Hydrogen peroxide has not before been reported as a product of the slow reaction between hydrogen and oxygen which takes place in the neighborhood of 550° and 1 atm. Indeed Rowe[3] states that none could be detected by the sensitive titanium sulfate test. This paper reports the results of some flow experiments in which easily detectable quantities were obtained. In addition there are reported some data on the effect of the nature of the reaction tube surface on the hydrogen–oxygen reaction.

The experiments were of the flow type. Compressed hydrogen and oxygen were passed through flowmeters and a drying system to a cylindrical reaction tube of pyrex glass to the ends of which were sealed 2-mm. capillaries. The off-gas passed through a weighing tube cooled to $-79°$. The reaction tube was contained in an electrically heated furnace the temperature of which was automatically controlled to about $\pm 2°$. Hydrogen peroxide was determined by washing out the weighing tube and titrating the product with 0.02 normal potassium permanganate in sulfuric acid solution.

The Reaction at Atmospheric Pressure.—The data of Table I refer to experiments in which the reaction tube was approximately 1.7 cm. in diameter and 10 cm. long and had a volume of 20.8 cc.   The cleaning of the reaction tube is an important point.   In this case the tube was rinsed out twice with hot concd. nitric acid, and then a dozen times with distilled water.   The total gas flow was usually 40 cc. per minute at 25° and atmospheric pressure (about 760 mm.).   Since the reaction rate is subject to considerable variation, each set of data was bracketed with sets to which it was to be compared.   The average of three separate determinations is given in each case.   Results are expressed in terms of milligrams of products formed per half-hour, and also as exit-gas concentrations (in 0.01 atm., calculated for 25° and 1 atm. total pressure).   In most of the runs the entering gases were saturated with water vapor at 0°, as the behavior of the reaction was somewhat more steady under these conditions.   This water was subtracted from the total found in the weighing tube.   Complete conversion of 10 cc. per minute of hydrogen in a half hour would yield 220 mg. of water.

TABLE I

WATER AND HYDROGEN PEROXIDE FROM HYDROGEN AND OXYGEN

Temp., °C.	Reactants cc./min.		Formed mg. per half hour		Exit-gas concns. in 0.01 atm.	
	H_2	O_2	H_2O	H_2O_2	H_2O	H_2O_2
Effect of Drying						
540	30	10				
Dried at		0°	56.8	2.04	6.41	0.13
Dried at		−79°	47.5	1.83	5.38	.11
Dried at		0°	51.1	1.92	5.79	.12
Effect of Heating Time						
540	10	10	61.0	0.77	13.8	0.09
	30	30	19.3	1.95	1.46	.08
	10	10	67.5	0.90	15.3	.11
Effect of Composition						
540	10	30	13.0	1.19	1.47	0.07
	30	10	50.3	2.15	5.70	.13
	10	30	6.6	0.92	0.74	.06
Effect of Temperature						
540	10	30	4.8	0.68	0.54	0.04
550			16.9	1.29	1.91	.08
540			1.3	0.63	0.15	.04
540	30	10	35.3	1.64	4.37	.10
530			16.7	1.08	1.89	.06
540			36.4	1.61	4.12	.10

In spite of the irregularity of the results, certain conclusions as to the formation of water and hydrogen peroxide may be drawn.   It is, first of all, clear that the initial presence of traces of water vapor is not essen-

tial. When the heating time is cut to one-third by tripling the gas flow, the off-gas concentration of water vapor is cut to one-tenth while that of the peroxide is not measurably altered. The reaction is clearly auto-accelerated so far as water formation is concerned. The peroxide appears to attain an approximate steady-state concentration. One cannot conclude from these data that hydrogen peroxide is the sole primary product but the results point in that direction.

Experiments on the effect of hydrogen–oxygen ratio show clearly that formation of both products is more rapid with excess of hydrogen. Water formation is again the more affected. A rise of 10° in reaction tube temperature increases the yield of water 2- to 4-fold, and about doubles the peroxide formed over the range studied. The temperature coefficient appears to depend on the $H_2:O_2$ ratio.

These results may be taken to indicate that hydrogen peroxide is a primary product of the hydrogen–oxygen reaction, that water is formed auto-catalytically, and that the reaction is favored by a high ratio of hydrogen to oxygen as well as by high temperature.

There are many other conclusions that might be drawn from these and the quantities of other data on the reaction which we have obtained. Aside from the above, however, the only certainty is that the highly capricious behavior of the reaction mixture in pyrex reaction vessels has made this a most unsatisfactory reaction to deal with. According to Hinshelwood,[4] the reaction in silica vessels is very similar in behavior, glazed porcelain being rather more satisfactory to work with.

The Reaction at Low Pressures.—Hinshelwood[5] has reported the extraordinary fact that hydrogen–oxygen mixtures become unstable and explode within a restricted low-pressure range at temperatures above about 450°. It was of interest to confirm this by a somewhat different method and especially to determine whether the formation of hydrogen peroxide could be detected. Accordingly the flow apparatus was altered to include a three-way stopcock before the reaction tube, a reaction tube about 1 cm. in diameter by 10 cm. long into which the reaction gases passed via a drawn-out capillary, and a vacuum pump and gage for reducing and reading the pressure at the outlet end. With these alterations a number of runs were made. Results are recorded in Table II.

The results are essentially in agreement with those of Hinshelwood as to the existence of an upper pressure limit. There was immediate (but not complete) reaction up to a certain pressure and then a rapid decrease in reaction rate at higher pressures. A significant feature of the results is that no trace of hydrogen peroxide was detectable in the region of rapid action. Nevertheless, at higher pressures with only small amounts of

[4] Gibson and Hinshelwood, *Proc. Roy. Soc.* (London), **119A**, 591 (1928).
[5] Thompson and Hinshelwood, *ibid.*, **122A**, 610 (1929).

TABLE II

HYDROGEN–OXYGEN REACTION AT LOW PRESSURES

Gas rates, 20 cc./min. for each gas (measured at 25° and 1 atm.); reaction tube volume about 7 cc.

Temp., °C.	Press., mm.	Mg. of H_2O per 10 min.	
500	5 to 10	Nil	
	25	Nil	
525	5 to 10	42.4	
	25	43.0	
	50	9.0	H_2O_2 less than 0.05 mg.
	75	Nil	
550	5 to 10	86.8	
	25	83.2	
	50	79.4	
	75	63.4	
	400 (approx.)	1.6	$- H_2O_2 = 0.28$ mg.

water being formed, hydrogen peroxide was obtained in easily detectable amounts. In this connection it is to be remembered that the exposure time was shorter in proportion at the lower pressures. The failure of hydrogen peroxide to escape from the reaction tube at the low pressures in the explosion region might be ascribed to the high temperatures attained in the gas. It is not unlikely, however, that the peroxide is itself accountable for the explosivity. A possibility is that a freshly-formed peroxide molecule is subject to dissociation yielding atomic oxygen. If the molecule enters into collision with a normal molecule within a minimum time after formation, it is stabilized. Failing this, it dissociates and produces the chain of results characterizing the explosion. High pressures would favor stabilization, while low pressures would permit of dissociation.

Effects Due to Surface.—Hinshelwood[4,5] has shown that the hydrogen–oxygen reaction is repressed when the reaction vessel is packed with broken wall-material, in the case of porcelain and silica vessels. Data showing that this is also true for pyrex reaction vessels are given in Table III. In addition, the importance of the nature of the surface is brought out by data in this table. When either an empty or a packed reaction tube is rinsed out with a potassium chloride solution, the reaction rate is subject to a marked decrease. Thus, whatever the action of the glass surface may be in suppressing reaction, this action is enhanced by coating the glass with a film of potassium chloride. The special feature of this effect is that it is so marked in the empty tube. Although no direct comparison was made, the rate must be reduced about 2000-fold by the coating.

Without detailing the results, it may be said that treatment with potassium hydroxide solution is about equally as effective as treatment with potassium chloride. In addition, treatments with solutions of aluminum nitrate, barium nitrate, arsenious chloride or phosphoric acid were

TABLE III

HYDROGEN–OXYGEN COMBINATION.   EFFECT OF PACKING AND COATING

Gases flowing at 20 cc. per minute each.   Reaction-space volume, 20.0 ± 0.5 cc.

| Temp., °C. | Empty tube | | Packed tube | |
	Cleaned with HNO₃	Rinsed with KCl soln.	Cleaned with HNO₃	Rinsed with KCl soln.
	Mg. water plus hydrogen peroxide formed per minute			
510	0.02			
520	.07			
530	.22			
540	.63			
550	Explos.		0.13	0.02
575			.65	.03
590		0.06		
600		.19	5.34	.07
610		.58		
625		Explos.	10.4	.43
650				.63

all more or less effective.   This is in comparison with the same tube when rinsed first with nitric acid and with water.   Treatment with a copper nitrate or chromic acid solution caused a marked increase in rate, due no doubt to positive surface catalysis.   Yet even in these cases it is significant that no hydrogen peroxide was formed, and that the kinetics were so altered as to suggest that the original reaction had again been suppressed. It may be mentioned that no treatment gave better yields of hydrogen peroxide than the original one with hot concd. nitric acid.

Summary

1.   The hydrogen–oxygen combination in pyrex reaction vessels has been studied by the flow method.

2.   It has been found that hydrogen peroxide is formed in readily detectable amounts along with water.   The former may be the primary reaction product.

3.   The reaction mixture becomes unstable at low pressures and reacts explosively, but yields no peroxide under these conditions.

4.   Reaction may be partially suppressed by filling the reaction vessel with broken pyrex glass or better by coating its inner surface with any one of a number of substances, among which is potassium chloride.

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