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The Low Pressure Hydrogen-Oxygen Reaction on Platinum

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In a study of the reaction between hydrogen and oxygen at low pressures on platinum wires, Tanner and Taylor³ report that "considerably more oxygen disappears than corresponds to water formation" and to account for this abnormal consumption of oxygen suggest that hydrogen peroxide is formed directly on the surface of the platinum catalyst. In view of the partial separation, due to differential diffusion, obtained on handling a $3\text{H}_2:1\text{N}_2$ gas mixture at low pressures,⁴ the possibility suggested itself that the abnormal disappearance of oxygen in the hydrogen-oxygen reaction might be an apparent rather than a real abnormality. Enrichment of the gaseous mixture in hydrogen, due to its higher diffusion rate as compared with that of oxygen, on admitting the hydrogen-oxygen mixture to the reaction system could account for the results obtained. The object of this work was to determine the ratio of hydrogen and oxygen reacting at low pressures on platinum wire under conditions such that no separation of hydrogen and oxygen could possibly occur and to study the effect of the usual methods of handling gases on this ratio.

Experimental Details

The apparatus employed is indicated diagrammatically in Fig. 1 and is essentially the same as that of Tanner and Taylor. It was constructed entirely of 15 mm. diameter soft glass tubing. The stopcock K leading to the main line and pumps was of the vacuum type with a 4 mm. opening. The mercury cut-offs, with the McLeod gage between them, permitted obtaining various pressures of hydrogen, oxygen and mixtures of the gases. The reaction cell was made of 15 mm. diameter tubing and contained 45 cm. of 0.1 mm. diameter platinum wire suspended in the form of two loops from 1 mm. platinum leads which were glass coated except at the tips. The electrically heated catalyst was made one arm of a Wheatstone bridge and the resistance determined at various temperatures from 20 to 360°. During an experiment the current flowing through the platinum wire was adjusted so that the resistance, corresponding to the temperature desired, remained constant. Temperatures of 100–300° were used.

The Pirani gage consisted of 52 cm. of 0.05 mm. diameter tungsten wire silver soldered to 1-mm. platinum leads. This wire, in the form of two loops, was rigidly supported in 15-mm. glass tubing and was made one arm of a second Wheatstone bridge. The gage was immersed in an ice-bath and the current required to keep the wire at a constant resistance, corresponding to 50°, was measured on a milliammeter. The gage was calibrated against the McLeod gage on hydrogen and oxygen after every experiment. These carefully purified gases and a $2\text{H}_2:1\text{O}_2$ mixture, prepared by properly mixing pure H_2 and O_2 , were stored in flasks attached at H. In many experiments pure hydrogen was obtained by gently heating with a small gas flame a palladium-welded-to-

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(3) Tanner and Taylor, *THIS JOURNAL*, **53**, 1289 (1931).

(4) Wiig and Kistiakowsky, *ibid.*, **54**, 1806 (1932).

platinum tube which was sealed in at a point between D and E. The hydrogen used made no difference in the results. The traps C, G were surrounded by liquid air and the ratio of the volume AD to AF determined by pressure measurements on the McLeod gage while C was cooled in liquid air. The volume AD was *ca.* 160 cc. and DK, including the McLeod gage, *ca.* 135 cc.

The procedures used will be indicated in connection with the results.

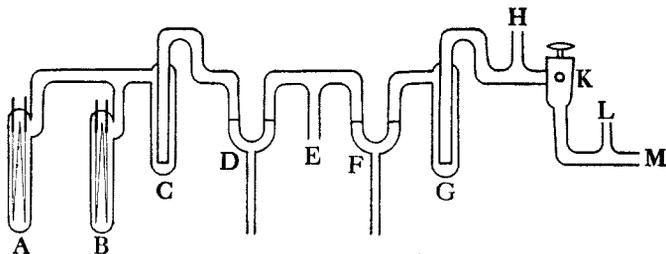


Fig. 1.—Apparatus: A, Pirani gage; B, reaction vessel; C, G, traps; D, F, mercury cut-offs; E, to McLeod gage; H, L, to hydrogen-oxygen storage bulbs; M, to pumps.

Experimental Results

Hydrogen and Oxygen Admitted Separately into the Reaction System.—In order that there might be no possibility of a change in concentration in the reaction mixture, hydrogen and oxygen were admitted separately at measured pressures and then mixed. The procedure was as follows. The system was thoroughly evacuated, the platinum wire glowed, after which one of the gases, say hydrogen, was admitted and the pressure adjusted, by removing excess gas by the pump, until the desired pressure of hydrogen was trapped in AF. This pressure of hydrogen was read on the McLeod gage. The mercury cut-off D was now raised, trapping hydrogen at the measured pressure in AD. DEF was now evacuated and oxygen admitted to the proper pressure. The cut-off D was lowered allowing the two gases to mix in AF and the total pressure read. From the total pressure, the pressure of hydrogen and the change in hydrogen pressure on expanding from AD to AF, the composition of the mixture is known. The gas mixture in the volume AF, after being allowed to mix for ten to three hundred minutes, was in general caused to react on the platinum wire. In some experiments the gases were allowed to mix for fifteen to twenty-two hours, the cut-off D raised and the reaction run in AD with identical results. There was no “clean-up” of gas on heating the platinum wire in either hydrogen or oxygen alone. The course of the reaction was followed with the Pirani gage. At the conclusion of the reaction, the pressure and nature of the residue were determined from the McLeod and Pirani gage readings. From these data and the original pressures, the ratio of hydrogen and oxygen which had reacted were calculated. The results are given in Table I. Figure 2

shows a rate curve, which is of the same form as that found by Tanner and Taylor.

TABLE I
RATIO H_2/O_2 REACTING AT LOW PRESSURES ON PLATINUM WIRE

Expt.	Reaction mixture, microns		Residue, microns		Ratio H_2/O_2
	H_2	O_2	H_2	O_2	
1	55.1	22.0	12.2	...	1.95
2	5.5	7.0	...	0.5	0.85 ^a
3	46.4	19.1	6.5	...	2.09
4	11.8	5.7	0.4	...	2.00
5	18.4	9.0	.9	...	1.94
6	6.9	8.9	...	5.7	2.16
14	26.5	11.6	3.1	...	2.02
20	29.8	11.6	6.4	...	2.02
24	29.2	12.0	4.0	...	2.10
25	39.2	18.7	3.1	...	1.93
27	15.8	7.4	0.2	...	2.11
28	42.7	19.7	2.6	...	2.04
29	43.1	24.5	1.4	...	1.87
30	24.4	15.3	...	2.7	1.87
31	15.3	13.1	...	6.2	2.22
33	15.0	9.7	...	2.7	2.14
34	35.6	19.2	...	1.4	2.00
35	42.6	19.6	7.0	...	1.83
36	40.7	21.0	1.94
37	29.7	14.6	0.1	...	2.03
38	28.4	16.6	...	2.0	1.95

Average 2.02

^a Omitted from average.

The average ratio of the amount of hydrogen reacting with oxygen is 2.02 from twenty experiments. The low values were all obtained in experiments in which oxygen was admitted to the reaction system first and, conversely, all the high values in those experiments in which hydrogen was the first gas admitted. In Expts. 7-13 the Pirani gage was not used to determine the nature of the residue but it was assumed to be the same as the gas present in excess at the start of the experiment. The ratios obtained were very erratic and varied from 1.5 to 9.0. Later it was found that the residue, even after long-continued heating of the platinum wire, often consisted of a mixture of hydrogen and oxygen, instead of pure hydrogen or oxygen. This accounts for the balance of the experiments omitted from the table.

The ratio 0.85 obtained in Expt. 2 might seem to corroborate Tanner and Taylor's statement that considerably more oxygen disappears than corresponds to water formation. This is the *only* experiment in which a low value was obtained and is the *second* experiment performed with the platinum wire. Langmuir⁵ has found that platinum must first be ac-

(5) Langmuir, THIS JOURNAL, 40, 1394 (1918).

tivated by heating it in a hydrogen-oxygen mixture before oxygen will react with oxidizable impurities in the platinum, that is, show an abnormal disappearance of oxygen. Expt. 1, in which there was an excess of hydrogen at the start, served to activate the catalyst and in the next experiment nearly all of the excess oxygen present disappeared. Presumably it reacted with oxidizable impurities in the wire, as suggested by Langmuir's results. Tanner and Taylor quote Langmuir as attributing, in later experiments, the abnormal disappearance of oxygen to the evaporation of oxygen atoms from the surface and their subsequent combination

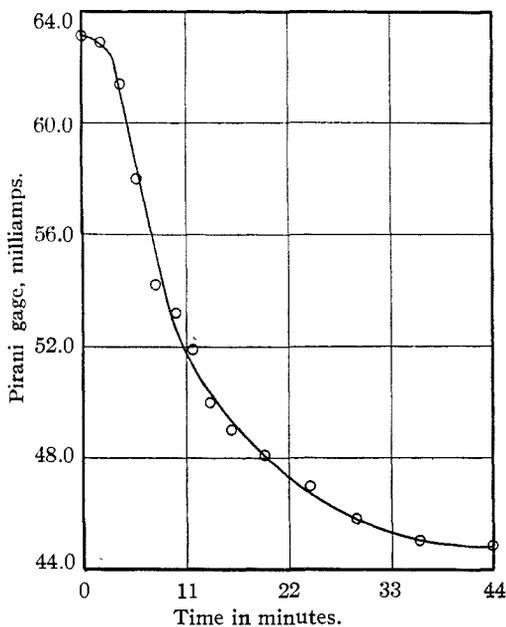


Fig. 2.—Rate of reaction of H_2 and O_2 on Pt wire at 150° (Expt. 20).

with oxygen to form ozone, or with water vapor on the bulb walls to form hydrogen peroxide. These later experiments, however, were performed with the catalyst heated to much higher temperatures (1200 – 1600°) than those used in Langmuir's earlier experiments (275°), in Tanner and Taylor's experiments (380°) and in the present work (300°).

The results obtained in the experiments reported here show that hydrogen and oxygen at low pressures react on platinum in the ratio of 2:1 when care is taken to prevent separation of the gas mixture through differential diffusion. The next section indicates the results that may be obtained

when the gas mixture is handled by the usual methods.

$2H_2:1O_2$ Admitted into Reaction System.—When admitting a $2H_2:1O_2$ gas mixture into the reaction system, one may admit exactly the amount desired or an excess may be passed into the reaction system and then reduced to the proper pressure. The method used may have a considerable effect on the result obtained.

The storage bulb containing the gas mixture was first located at H (Fig. 1), being connected through a short piece of glass tubing of small volume and a stopcock. When a few mm. of the gas mixture was admitted into this tube and then expanded into the evacuated reaction system, the desired low pressures were obtained. The ratios of H_2/O_2

reacting obtained in this way varied from 1.81–2.00, the average being 1.88.

In the experiments of Tanner and Taylor the bulb containing the electrolytic gas was located on the other side of the stopcock K and so the storage flask was shifted to the position L. The gas mixture had now to expand through the stopcock K into the evacuated reaction system. The results obtained in these experiments, which were all run in AF, are given in Table II.

TABLE II
RATIO H_2/O_2 REACTING AT LOW PRESSURES ON PLATINUM WIRE

Expt.	Pressure ($2H_2:1O_2$), microns	Residue, H_2 , microns	Apparent ratio H_2/O_2
46	47.8	5.1	1.67
48	43.3	6.3	1.55
49	32.5	6.9	1.35
50	16.8	1.9	1.66
68	52.8	4.1	1.77
55	101.6	5.3	1.84
67	100.3	0.4	1.99
51	138.0	1.1	1.98

At pressures of about 0.1 mm. the ratio H_2/O_2 is about 2.0, but is much smaller at lower pressures. The average of the five experiments at pressures less than 0.053 mm. is 1.60. The explanation must be that the reaction mixture has been enriched in hydrogen due to differential diffusion. If this is correct, then a ratio greater than 2.0 should be obtained by reversing the procedure so that an excess of hydrogen may diffuse out of the system.

Pressures of gas mixtures ($2H_2:1O_2$) of 0.1–0.3 mm. were admitted into AK and the pressure in AF reduced to less than 0.05 mm. by expanding the gas mixture from AD, AF or AK into the evacuated main line leading to the pumps. The volume of the main line, however, was only *ca.* 45 cc. as compared with *ca.* 300 cc. for AK. Seven experiments gave in each case 2.0 for the ratio H_2/O_2 . When an additional volume of approximately the same size as AK was added to the main line, the results given in Table III were obtained. Expansion of the gas mixture from AD or AF instead of AK gave ratios of 2.0.

TABLE III
RATIO H_2/O_2 REACTING AT LOW PRESSURES ON PLATINUM WIRE

Expt.	Pressure ($2H_2:1O_2$), microns		No. of expansions	Residue, O_2 , microns	Apparent ratio H_2/O_2
	Initial	Reduced			
58	147	28.4	3	3.6	3.20
62	167	31.0	3	3.1	2.82
63	167	35.1	3	3.1	2.72
64	223	45.9	3	3.5	2.59
66	326	36.0	4	4.1	3.04

Average 2.85

Discussion

The results with mixtures of hydrogen and oxygen made up in the reaction system with known amounts of the gases indicate that the ratio of hydrogen to oxygen reacting at low pressures on platinum wire is 2.0. Lower values, however, were apparently obtained on admitting exactly the desired pressure of a $2\text{H}_2:1\text{O}_2$ mixture from a storage bulb attached to the main line beyond the stopcock separating the reaction system from the pumps. Hydrogen diffuses much more rapidly than oxygen and at low pressures an enrichment of the gas mixture in hydrogen might occur. This accounts for the low H_2/O_2 ratios. A calculation of the composition of the gas mixture which must have been present at the beginning of Expt. 49 indicates that the percentage of hydrogen by volume was 77.3 instead of 66.7 as assumed in calculating the apparent H_2/O_2 ratio. Thus the more rapid diffusion of hydrogen as compared with oxygen has caused an error of about 15.9 and 31.8% in the hydrogen and oxygen compositions, respectively.

The high ratios in Table III are similarly accounted for by an enrichment of the gas mixture in oxygen due to the diffusion out of the reaction system of more hydrogen than corresponds to $2\text{H}_2:1\text{O}_2$. The maximum change obtained occurred in Expt. 58 and calculation shows the oxygen concentration to have been 41.8% by volume at the beginning of the run instead of the 33.3% assumed.

Abnormal H_2/O_2 ratios were obtained only at pressures less than about 0.05 mm. However, this limiting pressure and the values of the abnormal ratios probably depend on various characteristics of the system employed, such as size and type of stopcock, volume ratios, size of connecting tubing, densities of the gases used, etc. A study of the effect of these factors in bringing about a change of composition in gas mixtures during manipulation at low pressures is projected for the near future. The present experiments serve to emphasize the importance of considering the possible occurrence of differential diffusion in handling gas mixtures at low pressures.

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Summary

Hydrogen and oxygen at low pressures have been found to react in the ratio of 2:1 by volume on platinum as a catalyst when care is taken to eliminate any possibility of a change in concentration of the gaseous mixture due to differential diffusion. Considerable deviations of the ratio H_2/O_2 from 2.0 were obtained as a result of the partial separation of the gases during their manipulation. The results indicate that the possi-

bility of a separation by diffusion must be considered when a mixture of gases of widely different densities is handled at low pressures.

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Changes of Chemical Potential in Concentrated Solutions of Certain Salts¹

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The chemical potential of a component in a homogeneous mass or phase was defined by Willard Gibbs² by the following equation

$$\mu_1 = \left(\frac{dE}{dm_1} \right)_{S, V, m_2, m_3, \dots} \quad (1)$$

where μ_1 is the chemical potential of component 1, E is the total intrinsic energy, S the total entropy, and V the total volume of that mass of the phase which contains $m_1, m_2, m_3 \dots$, grams of the various components. From the two laws of thermodynamics Gibbs showed that necessary and sufficient conditions for the coexistence in equilibrium of two or more phases in contact with each other were that the pressure and the temperature should be the same throughout all the phases and that the chemical potential of each component substance, as defined above, must have the same value in all the phases of which it is an actual component.³ Furthermore, it may be demonstrated rigorously that in any phase the chemical potential of a component is a function of the pressure, the temperature and the composition of the phase and of these variables only.⁴

In a phase of two components such as an aqueous salt solution one independent variable, *e. g.*, the weight fraction, x , of one or other component is sufficient to determine the composition so that

$$\begin{aligned} \mu_1 &= F_1(P, T, x_1) \\ \text{or } \mu_2 &= F_2(P, T, x_2) \end{aligned} \quad (2)$$

An outstanding practical problem in inorganic chemistry, namely, a determination, as complete as possible, of all the conditions under which a given set of phases in any particular system will coexist at equilibrium, resolves itself into the empirical determination of the chemical potentials of the components in each of the phases as functions of the temperature, the pressure and the composition. When this knowledge is at hand, it is a relatively simple matter to find the combinations of pressure, temperature

(1) Read before the Washington Section, American Chemical Society, April 14, 1932.

(2) J. Willard Gibbs, "Collected Works," Longmans, Green and Co., 1928, Vol. 1, p. 63.

(3) Gibbs, Ref. 2, p. 65.

(4) It is assumed that conditions are so chosen that effects due to capillarity, gravitational or electrostatic forces are negligibly small.