tube window, although the cathode rays have a range of 20 cm. under these conditions. This corresponds to the roughly exponential manner in which the energy of the beam falls off as one proceeds away from the window of the tube.

Ozone is both formed and decomposed under the influence of cathode rays. With continued raying a steady state is reached with an ozone concentration of 1 molecule to 1700 of oxygen. This concentration is independent of the tube current. This value compares with the concentration of 1 in 12 obtained with the silent discharge. Cathode rays have a much greater decomposing action than the silent discharge.

The maximum yield of ozone is 825 cc. of gas, measured under standard conditions and obtained with a tube current of 0.0010 ampere at 180 kv.

It has not been possible to check the results of Krüger and Utesch, who determined the amount of ionization by a saturation current method. Saturation was never observed in any of the experiments—the current in the ionization chamber increasing regularly as the applied field increased.

SCHENECTADY, NEW YORK

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

COMBINATION OF HYDROGEN AND OXYGEN UNDER THE INFLUENCE OF CATHODE RAYS

BY ABRAHAM LINCOLN MARSHALL

RECEIVED JUNE 23, 1928 PUBLISHED DECEMBER 10, 1928

The reaction between hydrogen and oxygen presented itself as the simplest oxidation reaction occurring in the gas phase which could be investigated. Hinshelwood and Thompson[1] have shown that it is possible to study a homogeneous thermal reaction between these substances in the range 550–600° with velocities increasing in rate up to explosions. It is well known that when flames of hydrogen and oxygen impinge on a cold surface hydrogen peroxide can be detected as one of the products of reaction. Marshall[2] has found that in the case of the photochemical reaction sensitized by mercury vapor the reaction proceeds by way of the peroxide stage and that this product can be obtained in the pure state. Scheuer[3] has studied the combination of hydrogen and oxygen (electrolytic gas) under the influence of α-particles and in all cases reported hydrogen peroxide as one of the products of the reaction, amounting in one case to 16% of the combined hydrogen.

In a previous paper[4] on the ozonization of oxygen the cathode ray tube

[1] Hinshelwood and Thompson, *Proc. Roy. Soc.*, **118**, 170 (1928).

[2] Marshall, *J. Phys. Chem.*, **30**, 1078 (1926).

[3] Scheuer, *Compt. rend.*, **159**, 423 (1914).

[4] Marshall, THIS JOURNAL, **49**, 2763 (1927).

installation and general technique for high voltage work was described. One point, however, which is important for the technical success of this investigation was not mentioned, namely, the temperature of the window during the operation. Coolidge[5] reports a few measurements on window temperature during operation; with 200 kv. and 0.6 milliampere, the window reached 132° in five seconds, and with 1.3 milliamperes it reached 340° in ten seconds. Mixtures of hydrogen and oxygen explode when heated to about 600° so that one is strictly limited as to the amount of energy one can use for successful operation by the temperature of the window. If the filament does not give a uniform distribution of energy over the focal area, it is quite possible for a very small area to be receiving considerably more than its quota of electrons and to form a hot spot on the window. During the early part of the investigation, the tube was operated at 180 kv. and 1 milliampere, and on several occasions, due to a slight increase in current, disastrous explosions occurred. The system was finally operated at 180 kv. and 0.80 milliampere and was stabilized by means of a very sensitive relay connected in the grounded side of the high voltage line. This relay opened the remote control in the power line supplying the transformers when the tube current rose to 0.90–1.00 milliampere. During several months' work it functioned on a number of occasions and no further troubles were experienced from this source.

The reacting gases were taken from the high pressure supply lines of electrolytic hydrogen and oxygen available in the Laboratory and were used without further purification. It was possible to obtain rates of flow up to 1500 liters per hour of each gas. They were circulated through a cylindrical glass cell $3^1/_2''$ in diameter by $10''$ long. In all the experiments the pressure was kept at 91 cm. of mercury. The effluent gases were analyzed for hydrogen peroxide, water vapor and ozone. In order to make this analysis, it was necessary to dry the gases as completely as possible before use. It was found that the use of liquid-air traps for this purpose was entirely ineffective; the moisture was frozen out in the trap in the form of snow which would then be blown out of the trap, due to the high rate of gas passage. The most effective drying agent was found to be concentrated sulfuric acid. Two large gas scrubbing bottles of the type used in the previous investigation for absorbing ozone were connected in series and filled with sulfuric acid. The first scrubber did practically all of the work even at the fastest rates of flow, the purpose of the second being to remove that water vapor which the first could not absorb, due to an increase in its aqueous tension brought about by dilution and heating. It was found after some time that a slight mist of sulfuric acid was being carried over from the scrubbers, which deposited on the walls of the reaction chamber and gave rise to erratic analytical results by absorbing

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[5] Coolidge, *J. Franklin Inst.*, December, 1926.

some of the peroxide and water vapor formed in the reaction chamber. A long column of powdered potassium hydroxide was then introduced into the system and a plug of absorbent cotton, which was dehydrated by warming gently and passing a current of dry gas. Separate drying trains were used in each gas line. With this system it was possible to pass gas at 1500 liters per hour and collect less than 1 mg. of material in a liquid-air trap in the exit line over a fifteen minute period. This amount was within the experimental error of the analytical method used.

Method of Analysis

The gas mixture from the reaction vessel was led through a glass coil, C, in Fig. 1, which was immersed in a carbon dioxide–ether mush to freeze out the hydrogen peroxide and water vapor formed during the reaction. The gas, before it entered the gas scrubbers D and D′, was then passed through another spiral, not shown in the figure, which was immersed in warm water. D contained distilled water to absorb any peroxide not caught in C, and D′ alkaline potassium iodide to absorb ozone. The coil C was connected to the rest of the apparatus by means of two ground-glass joints, A and A′. After an experiment, the trap was disconnected at A and A′ and while still in the cooling mixture, dry air was passed slowly through it to remove the hydrogen and oxygen. The stopcocks B and B′ were then closed, the male parts of the ground joints carefully wiped free from grease and the coil warmed up to room temperature and dried in a blast of compressed air. The coil was then carefully wiped with a linen cloth and weighed. The coil weighed about 180 g. and was balanced to the nearest milligram. During a series of experiments, the weight of the coil might drift 10–15 mg. but it was always found possible to check its weight to within one milligram when it was merely chilled, allowed to warm up and dried. It was absolutely necessary to displace the hydrogen and oxygen before weighing and to make sure that the coil was properly chilled before closing the stopcocks.

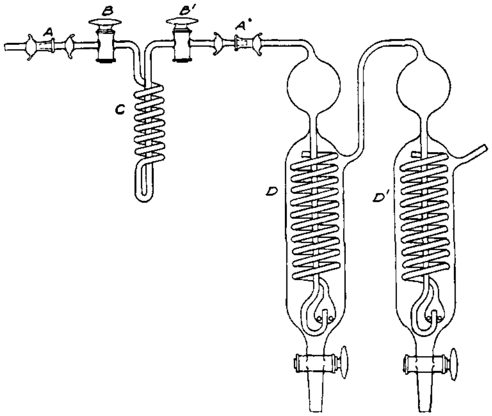

Fig. 1.

TABLE I

PROOF THAT RATIO H_2O_2/H_2O IS UNCHANGED BY PASSAGE THROUGH TRAP

Rate of circulation, 1400 liters/hour of H_2; 240 liters/hour of O_2

Coil 1		Coil 2			
Weight incr., g.	$KMnO_4$, cc.	Weight incr., g.	$KMnO_4$, cc.	Ratio weight	Ratio titer
0.089	27.6	0.011	1.3	8.1	21.2
.033	24.8	.002	2.0	16.5	12.4
Rate of circulation, 450 liters/hour of H_2; 60 liters/hour of O_2					
0.069	14.7	0.026	6.8	2.65	2.16
.034	14.3	.018	7.5	1.89	1.91
.030	13.9	.016	7.4	1.87	1.88

After weighing, the coil was washed out and the peroxide collected titrated with standard permanganate solution; any peroxide collected in D was then added and the total titer obtained. It was found that practically all of the material collected in Coil C was caught in the first two turns; however, some of this was blown through the coil in the form of snow and this was collected in D. From a knowledge of the two titers and the weight of material caught in C, it was possible to calculate the total amount of peroxide and water vapor formed. The physical properties of these two substances are almost identical and thus the ratio of peroxide to water in the coil was the same as that in the scrubber. To be certain of this point, a few experiments were made using a second coil; it was shown that the ratio of materials in Coil 2 was the same as in Coil 1. These results are tabulated in Table I.

The second experiment and the last two are the most reliable and in these it is easy to see that the ratios are the same within experimental error, which proves the desired point as only a small fraction of the material caught in the trap is peroxide.

Having obtained a reliable method of analysis, a study was next made of the effect of adding a small amount of water vapor on the yield of hydrogen peroxide. The results justify the conclusion that peroxide formation does not proceed *via* water vapor. Hydrogen, from an electrolytic generator producing 12.5 liters per hour, was passed through a water saturator at 22° and then led into the dry gas stream on its way to the reaction vessel. The gases were streaming at the rate of 1400 liters per hour of hydrogen and 240 liters per hour of oxygen. In blank experiments about 0.045 g. of water was collected in the coil in 15 minutes; with the tube operating the total material collected averaged 0.081 g., whereas without the water added 0.033 g. were collected. This latter consisted of approximately 85% hydrogen peroxide, so that the addition of the saturator has increased the water vapor concentration about ten-fold. The average of 6 experiments without water addition gave 41.2 cc. of hydrogen peroxide formed in fifteen minutes and the same amount was formed in the presence of the added water vapor.

Several series of experiments were performed using approximately the same concentrations of hydrogen and oxygen throughout the series but varying the rate of circulation. The results given in Table II are taken from the earlier part of the work and are not so reliable as those in Table III, which, however, are for a different concentration.

TABLE II

VARIATION IN REACTION PRODUCTS WITH RATE OF FLOW

Rate of circulation, liters per hour		Product formed in one hour, cc.			
H_2	O_2	H_2O_2	H_2O	O_3	$H_2O_2 + H_2O$
1400	240	116.8	166.0	13.6	282.8
800	120	100.8	188.8	11.2	289.6
1400	240	115.2	164.4	..	279.6
450	60	83.2	218.8	8.0	302.0
800	120	97.2	211.2	..	308.4
1400	240	114.0	167.6	..	281.6

Each set of values is the average of 4 or 5 experiments and while the peroxide determinations are easily reproducible, those for the water vapor in some cases show considerable divergences, typical sets of data being 44.7, 46.2, 37.0, 36.6 and 55.2, 46.0, 41.4, 46.2. This, however, is to be expected, since all the errors of the analysis are placed on the water vapor value, which is obtained by a difference method.

The second half of Table III gives a résumé of all the data obtained for a single set of conditions and is typical of all the results to be reported in this paper.

TABLE III

VARIATION IN REACTION PRODUCTS WITH RATE OF FLOW

Rate of circulation, liters per hour		Product formed in one hour, cc.			
H_2	O_2	H_2O_2	H_2O	O_3	$H_2O_2 + H_2O$
1450	1280	214.0	293.6	108.4	507.6
865	780	198.4	304.4	103.2	502.8
345	300	153.6	353.6	70.0	507.2
865	780	214.0	313.2	122.0	
		212.0	360.0	122.4	
		187.6	306.8	91.6	
		192.0	272.8	92.0	
		174.6	302.4	71.2	
		206.4	316.8	121.6	
		193.1	254.8	92.4	
		193.9	284.2	96.0	
		212.2	327.8	118.8	

It will be noted that the yield of peroxide for a given concentration of hydrogen and oxygen decreases as the rate of flow is decreased. There is a roughly linear relation between the concentration decreases and the water vapor increases, the sum of the two remaining constant. This means that at the lower rates of flow where the concentration of the products is higher, some of the peroxide is decomposed forming water vapor. The total amount of reaction for a given energy input is constant and hence the sum of the peroxide plus water vapor formed is independent of the rate of flow. This is the best proof available that both peroxide and ozone are decomposed as well as formed by high velocity electrons. The amount of water vapor primarily formed by the radiation is constant, independent of the rate of circulation, and the observed increases at lower rates of flow are due to secondary decomposition of hydrogen peroxide.

Influence of Changing Concentrations

Another very interesting study in an investigation of this kind is the kinetics of the reaction. Five different concentrations were used and the gases were circulated at the fastest rate available in an attempt to avoid as much decomposition of hydrogen peroxide as possible. About twenty experiments were made at each concentration and the extreme values of the peroxide and ozone determinations did not vary more than (±)5% from the mean and, in most cases, agreed much closer than this; in the case of the water vapor determinations, the extremes were (±)18% in a few cases with most of the values coming within better than 10% of the mean. The results are given in Table IV.

TABLE IV

VARIATION IN REACTION PRODUCTS WITH CONCENTRATION

Rate of flow, liters per hour		Product formed in one hour, cc.			
H_2	O_2	H_2O_2	H_2O	O_3	$H_2O_2 + H_2O$
1450	300	173	128	24	301
865	1500	167	428	152	595
1450	780	199	211	68	410
345	2000	99	528	256	627
1450	1280	197	269	105	466

These results can be compared with those obtained by Lind[6] raying similar mixtures in a static system with α-particles. Lind gives values for

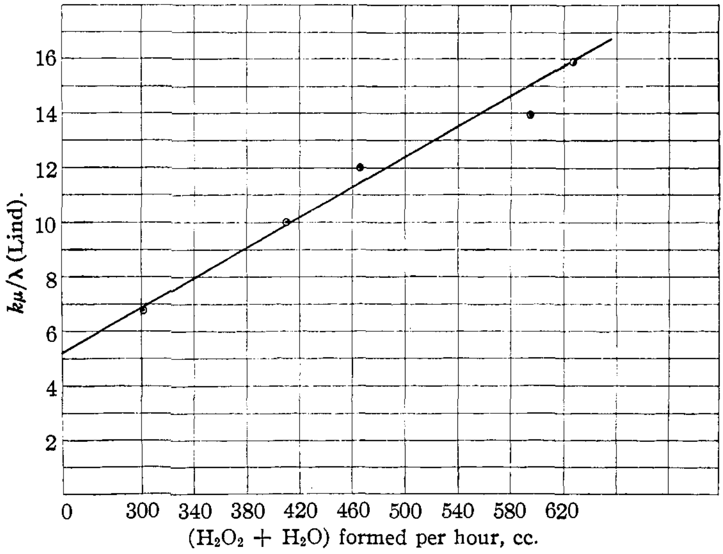

Fig. 2.

$k\mu/\lambda$, the velocity constant obtained with α-particles, for a number of concentrations of hydrogen and oxygen. These velocity constants are all reduced to values for a cell of given volume and plotted as a function of the concentration. This reduction is possible since Lind has shown that the velocity constant varies inversely as the square of the diameter of the sphere in which the reaction is proceeding. From the smoothed curve of

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[6] Lind, THIS JOURNAL, **41**, 543 (1919).

the reaction velocity–concentration diagram, values are read off corresponding to the concentrations used in this investigation. In Lind's experiments in a static system, the final product would be water vapor with only traces of peroxide and ozone; hence the sum of the peroxide and water vapor formed in a given time in the cathode ray experiments should be proportional to Lind's reaction velocity constant if the mechanism in the two cases is similar. The comparison is given in Fig. 2 and it is seen that any discrepancies lie well within the limits of experimental error in the two investigations.

The rate of peroxide formation is very insensitive to changes in concentration; at 15% hydrogen it has dropped to half the maximum value and at 83% hydrogen it has decreased 13% from the maximum. The rates of formation of water vapor and ozone seem to parallel one another very closely as evidenced by Fig. 3, which shows that over the range investigated the relationship is almost linear. We know that with pure oxygen the curve must return to zero amount of water vapor formed, so that it is possible to guess the result in the concentration region not investigated. This seems to indicate that the mechanisms responsible for water vapor and ozone formation are closely connected and quite different from that which produces hydrogen peroxide.

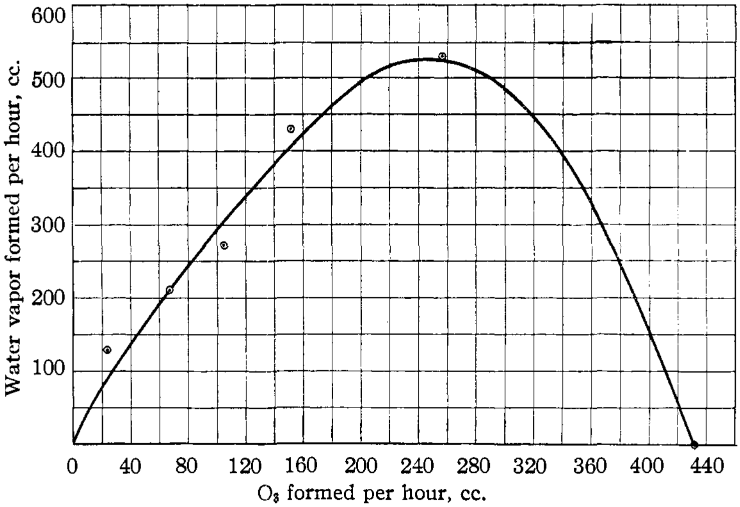

Fig. 3.

Summary

A method has been developed for analyzing gas mixtures containing small quantities of hydrogen peroxide, water vapor and ozone.

In the reaction between hydrogen and oxygen under the influence of cathode rays, it has been shown that peroxide, water vapor and ozone are formed as primary products.

A kinetic study at varying concentrations of hydrogen and oxygen shows that the rate of peroxide formation is almost independent of concentration, whereas the rate of water vapor formation varies over a five-fold range, and ozone over a ten-fold range.

The rates of formation of ozone and water vapor parallel one another very closely at all the concentrations studied, suggesting that the same primary mechanism is responsible for the formation of both.

The gross rate of reaction parallels that observed by Lind for the same reaction under the influence of α-particles.

SCHENECTADY, NEW YORK

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE IN AN ACID CHLORINE-CHLORIDE SOLUTION. II. AN INTERPRETATION OF THE RATE MEASUREMENTS IN CONCENTRATED SOLUTION

BY ROBERT LIVINGSTON

RECEIVED JUNE 29, 1928 PUBLISHED DECEMBER 10, 1928

The velocity of decomposition of hydrogen peroxide in an acid chlorine-chloride solution can be represented, with approximate accuracy, by the following equation[1]

$$v = \chi(H_2O_2)(H^+)(Cl^-)f^2_{HCl} \qquad (1)$$

where χ is a constant (0.00010) and f_{HCl} is the activity coefficient of hydrochloric acid. In dilute solutions the equation apparently represents the experimental data within the limits of error; in more concentrated solutions the value of χ decreases systematically to a value of 0.00005 at an ionic strength of 5μ. Equation 1 may be considered as a simplified form of the general reaction velocity equation, presented by J. N. Brönsted.[2] The exact form of the Brönsted equation for this reaction is

$$v = K\, H_2O_2(H^+)(Cl^-)f^2_{HCl} \cdot f_{H_2O_2}/f_x \qquad (2)$$

where f_x is the activity coefficient of the "reaction complex," ($H_2O_2{\cdot}HCl$), If we assume that $f_{H_2O_2}/f_x$, the ratio of the activity coefficients of two neutral molecules, is equal to unity, Equation 2 reduces to the form of Equation 1.

It has been demonstrated, both on theoretical[3] and on experimental[4]

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[1] Livingston and Bray, THIS JOURNAL, **47**, 2069 (1925); **48**, 405 (1926).

[2] (a) Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); (b) "The Velocity of Ionic Reactions," Columbia Press, 1927.

[3] Debye and McAuley, *Physik. Z.*, **26**, 22 (1925).

[4] A review of existing data has been recently presented by Randall and Failey, *Chem. Reviews*, **4**, 271, 285 (1927). This summary demonstrates that the formula holds