and Wells.[1] The different samples, A, B, and C, all give essentially identical results.

It appears, then, that if the atomic weight of silver is taken as 107.93 (O = 16.000), the atomic weight of lead is 207.19, nearly three tenths of a unit higher than the value now in use. If the atomic weight of silver is 107.88, a value probably nearer the truth than 107.93, lead becomes 207.09, a number still much higher than that depending upon Stas's syntheses, as is to be expected.

We are greatly indebted to the Carnegie Institution of Washington for assistance in pursuing this investigation, also to Dr. Wolcott Gibbs and to the Cyrus M. Warren Fund for Research in Harvard University for many indispensable platinum vessels.

CAMBRIDGE, MASS.,
October 18, 1907.

CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE UNDER HIGH PRESSURES OF OXYGEN.[2]

BY E. B. SPEAR.

Received October 12, 1907.

Introduction.

The mechanism of catalysis by means of the metals in their different forms and especially their decomposing effect on hydrogen peroxide has been the subject of a great deal of very thorough experimental investigation. Since Bredig published his work on the preparation of colloidal solutions by electrical[3] means, the study of catalysis has had an additional impetus, and our knowledge of the subject has been greatly increased by the investigations of this author and his co-workers, Müller v. Berneck,[4] K. Ikeda,[5] W. Reinders,[6] Fortner,[7] Teletow[8] and v. Antropoff.[9]

It has been conjectured by several authors that the *dissolved* or *chemically* bound oxygen in the metal phase plays a necessary part in the catalytic decomposition of hydrogen peroxide. The experiments of Haber and S. Grinberg,[10] Euler,[11] and of Engler and Wöhler[12] indicate

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[1] *Loc. cit.*

[2] Dissertation, Heidelberg (1907).

[3] Z. angew. Chem., 1898, p. 951.

[4] Z. physik. Chem., **31**, 258.

[5] *Ibid.*, **37**, 2.

[6] *Ibid.*, **37**, 323.

[7] Ber., **37**, 798.

[8] Z. Elektrochemie, **12**, 581.

[9] *Ibid.*

[10] Z. anorg. Chem., **18**, 37.

[11] Oefers af. K Vetenskaps Förhandl., 1900, p. 267.

[12] Z. anorg. Chem., **29**, 1.

that the presence of oxygen is necessary before many of these catalytic processes take place.

Bredig and Müller v. Berneck[1] attempted to investigate the influence of the dissolved or chemically bound oxygen on the catalytic decomposition of hydrogen peroxide by subjecting their colloidal solutions to reduced pressure before using them as catalyzers. They were not able, however, to discover any marked difference in either the rate of reaction or in the reaction constant as a result of this treatment. Bredig,[1] therefore, concluded that the decrease in catalytic effect observed by Gernez, after he had boiled his colloidal solutions, or had heated his platinum black, was caused by some change that the *metal* had undergone, rather than by the loss of oxygen. This assumption of Bredig's agrees very well with the experimental facts, at least in the case of colloidal solutions, because of the coagulating effect of the boiling. Again, if the loss of oxygen were the only cause of the observed retardation in the rate, the colloid must very quickly regain its original activity because oxygen is a product of the decomposition of hydrogen peroxide. It is doubtful if this is the case.[2] It might be pointed out, however, that if a *compound* of platinum and oxygen is an essential factor in the catalysis it does not necessarily follow that this compound will be destroyed by pumping out the *dissolved* oxygen unless it has an appreciable dissociation pressure and a rapid rate of decomposition. Bredig's experiments are not conclusive, they indicate that the *dissolved* oxygen does not play a vital part in the reaction. This latter statement is in accordance with the results given in this article.

Liebermann and Genersich[2] endeavored to investigate the rôle of the oxygen in the decomposition of peroxide by boiling their colloidal solutions or by bubbling gas through them in order to free them from oxygen. They then treated different portions of the catalyzer thus prepared with oxygen, hydrogen and nitrogen gas respectively and compared the effectiveness of each portion with that of the original colloidal solution. Unfortunately we are not able to conclude very much from their experiments because they worked with much too concentrated solutions (about 3 per cent. hydrogen peroxide). Their reaction mixture must have been saturated with oxygen as a product of the catalysis itself before they could make a single titration to learn the progress of the reaction. Their gasometric method also does not give us the necessary information, for the difference in height of the two columns of mercury is not an accurate measure of the amount of decomposition during the first few moments of the reaction because of supersaturation. But it is precisely this amount that we wish to know.

[1] *Loc. cit.*, p. 336.

[2] Liebermann and Genersich (Arbeiten aus den hy. Institut der Universität Budapest; Archiv. ges. Physiol., 104, 139) state that their platinum solutions regained their original activity in a few instances.

The object of the work described here was to ascertain experimentally the effect of increasing the concentration of oxygen on the catalytic decomposition of hydrogen peroxide. This was accomplished by means of the apparatus described on page 198.

Experimental.

Preparation of the Solutions.—The colloidal solutions used in this work were prepared by Bredig's well-known electrical method. The pure metals were obtained from Heraeus, Hanau. The colloidation of platinum took place in neutral, that of all the other metals mentioned in dilute M/1000 alkaline solutions as free as possible from carbonate. The concentrations of the platinum, palladium, iridium and gold solutions were determined by precipitating the metals with hydrogen sulphide in dilute sulphuric acid solution, heating the sulphides to constant weight and weighing as pure metal. The colloidal silver solutions were analyzed by dissolving the metal in concentrated nitric acid, evaporating almost to dryness, diluting and titrating with a potassium sulphocyanate solution according to the method of Volhard. The hydrogen peroxide solutions were prepared by diluting a 30 per cent. preparation from Merck with pure water.

The water used in the preparation of the solutions was purified by Hulett's method.[1] The conductivity of the water thus prepared was not determined because these measurements are not sufficiently delicate to be regarded as a safe criterion for the absence of many of the so-called *poisons* for colloidal platinum; furthermore, many of these poisons are non-electrolytes.

Cleansing of the Glass Apparatus.—Experience teaches that reproducable results cannot be obtained with metal catalysis unless the glass with which the solutions come in contact has been cleaned with extreme care. New vessels should be boiled for some time with concentrated hydrochloric acid and then with pure water. Vessels not in use should be carefully cleaned and placed in pure water. Immediately before they are required they should be well steamed out, using pure water to generate the steam.

In spite of the most careful manipulation, however, one often obtains irregular results that cannot be repeated. This is especially the case where the experimental difficulties preclude the possibility of preventing occasional poisoning effects. If many irregular results were obtained with a particular set of solutions they were thrown out, the glassware thoroughly cleaned and new solutions made up.

Description of the Bomb.—The experiments under pressure were carried out in a bomb made of "Rotguss" (see Fig. 1, *a*, p. 198). The ring *c* was for screwing the lid *b* on to body of the bomb *a*. The manipulation is much

[1] Z. physik. Chem., 21, 297.

more difficult when the ring *c* and the lid *b* consist of one piece as in the case of bomb *b* Fig. 3, p. 204. The compressed gas was conducted into the bomb through the metal tube *e*. The detachable tube *f* was connected with the glass tube *g* by a piece of rubber tubing *p*. The glass tube *g* dipped into the reaction mixture contained in the glass vessel *d* and served as a siphon through which small portions of the liquid in *d* could be taken out at will and analyzed. The short metal tubes *t* and *q* were soldered on to the lid. The bomb was made gas-tight by means of a steel ring, *m*, and two rings of soft lead, *l*, which were each about 2 mm. thick. This arrangement is not entirely satisfactory and difficulty was experienced in keeping the bomb from leaking at high pressures. The original plan of the author seems much preferable, but owing to a misunderstanding it was not carried out by the firm that made the bomb (see Fig. 1, *b*). Here there is only *one* lead ring employed and no plain surface between the body of the bomb and the lid. The under side of the thread *w* on the bomb and the upper side of the thread on the ring *c* should be right-angled and not beveled as it is in the figure.

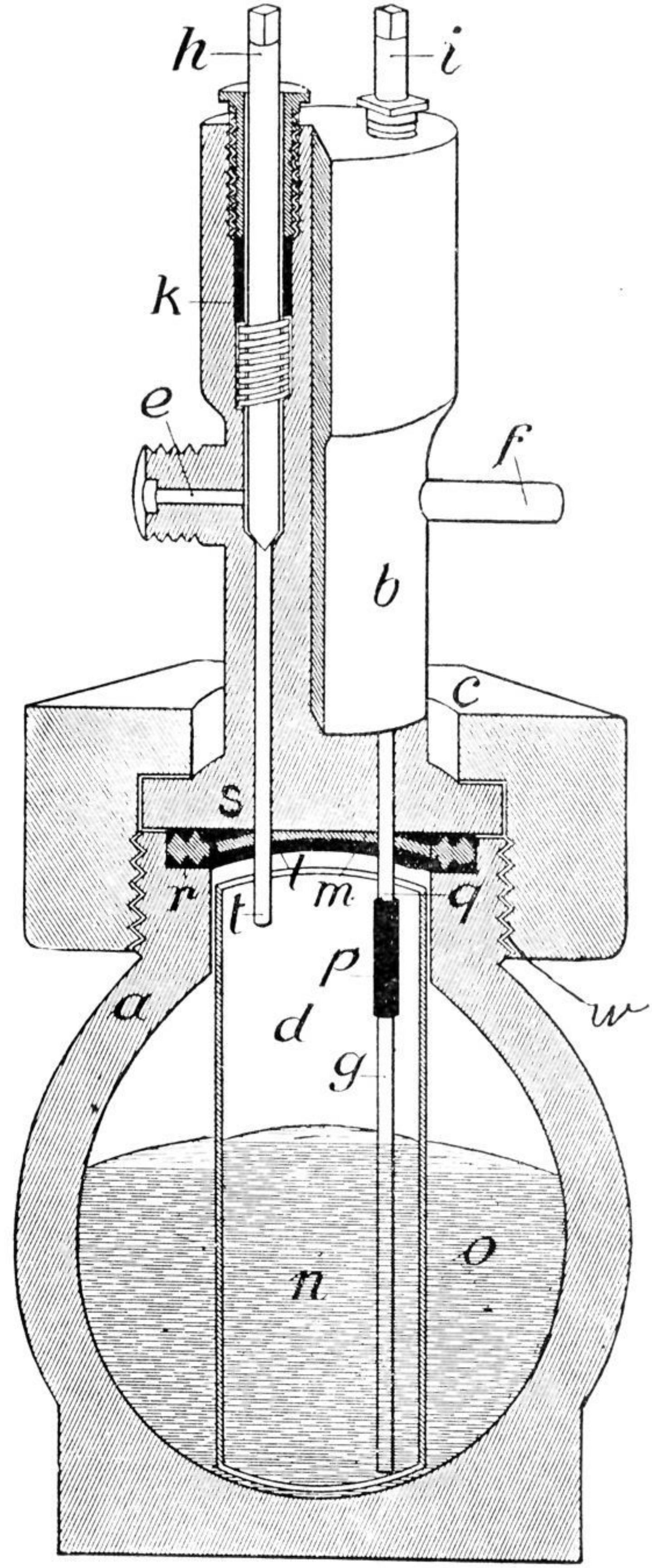

Fig. 1(*a*).

The bomb was placed in a thermostat and partially filled with water in order that the reaction mixture might rapidly come to and remain

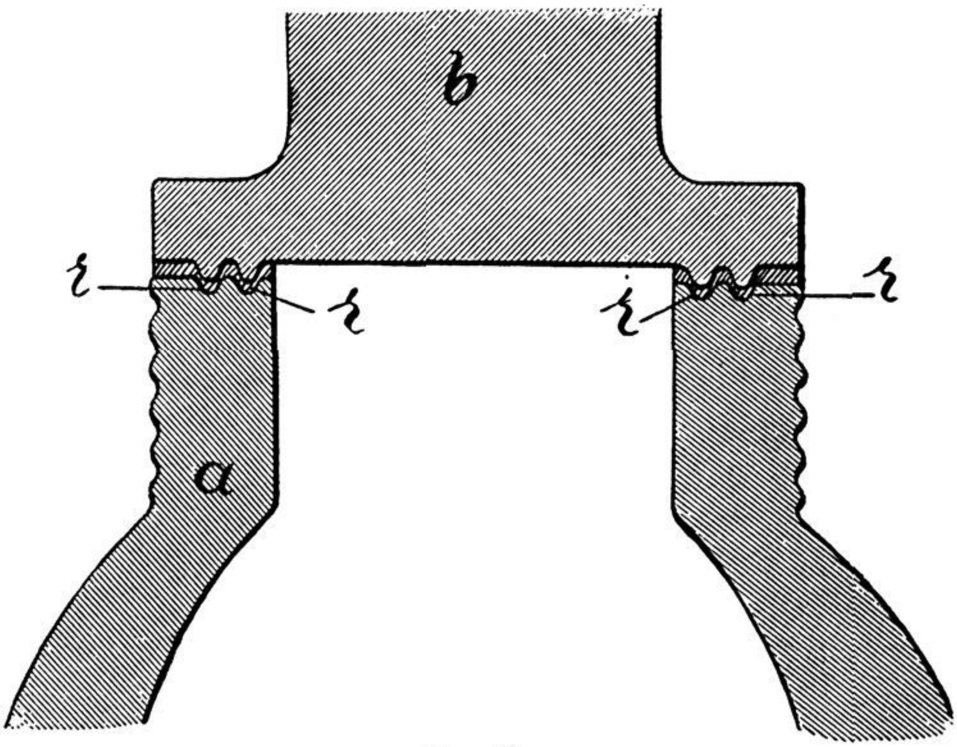

Fig. 2(*b*).

at the temperature of the thermostat. The tube *e* was connected with a manometer by means of a bent metal tube *z*, Fig. 3, p. 204 and the manometer was in turn connected with an ordinary oxygen bomb. By means of this arrangement a pressure of 1–100 atmospheres of oxygen gas could be obtained at will in the reaction-bomb. It was found possible to open the valve *i* so slowly that the liquid ran out of *f* drop by drop or in a gentle stream. At very high pressures (100–250 atmospheres) the liquid came out as a spray, owing to the expansion of the dissolved gas.

Blank experiments without a catalyzer proved that a small portion of the hydrogen peroxide was decomposed on being forced out through the metallic tube *f*. This difficulty was overcome by coating the inside of the tube with paraffin which was accomplished by filling the tube with a saturated alcoholic solution of paraffin and then sucking air through. It was found necessary to renew the coating every two or three days. These precautions prevented the decomposition of the hydrogen peroxide even when the solution was allowed to stand some time in the tube.

Analytical Method.—The progress of the reaction was followed by the method so often employed by Bredig and his co-workers, *viz.*, by titrating the still undecomposed hydrogen peroxide in a known volume with a dilute solution of potassium permanganate (0.24 gram per liter) after the addition of a few cubic centimeters of dilute sulphuric acid. Occasionally it was found necessary to add a drop of manganous sulphate to start the reaction.

Operation under Pressure (1–100 Atmospheres).—The colloidal solutions were diluted to the desired concentration and kept at 25° for at least twelve hours before the experiment because very irregular results are obtained, if freshly diluted solutions are employed for catalytic purposes. The hydrogen peroxide solutions were also warmed to 25° before the mixing took place.

The desired amounts of the different solutions were now placed in the reaction vessel and thoroughly mixed by stirring with a glass rod. Two cc. were immediately pipetted out and titrated. In many cases, however, the first titration was made after the pressure had been applied. The lid was then placed on the bomb and quickly screwed down. The bomb was connected with the source of pressure as quickly as possible and the pressure slowly applied. In about ten minutes after the first titration the valve *i* was slowly opened and 5 to 10 cc. of the liquid were allowed to run out before the second sample for analysis was collected in order that no liquid that had remained in the tube *f* might be titrated and possibly cause an error in the result. The sample thus obtained was violently shaken to free the liquid from gas before the usual 2 cc. were measured for titration.

The compressed oxygen used was that generally employed for analytical purposes. In order to ascertain if it contained anything poisonous to colloidal platinum, the gas was bubbled through a hydrogen peroxide solution for one-half hour. No difference in the rate could be detected resulting from this treatment. One dare not bubble gas through the colloidal solutions.[1] In later experiments the possibility of poisoning by the compressed oxygen was reduced very greatly by the use of the glass vessel described on p. 202.

In order to compare the results obtained under pressure with those under ordinary circumstances, experiments with the same solutions in the same vessel on the same day were carried out in the bomb at atmospheric pressure. The solutions were mixed as already described and the first titration made as usual. The glass vessel containing the reaction mixture was then placed in the bomb and the lid screwed on. In about ten minutes a pressure of 1–3 atmospheres was applied and a sample run out as before. The pressure in the bomb was then relieved.

Catalysis with Colloidal Platinum.—In the course of this investigation irregular results were occasionally obtained and the reactions were considered poisoned or accelerated if they could not be repeated under the same experimental conditions. More than 200 measurements were made with colloidal platinum, a few of which are given below.

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[1] Liebermann and Genersich, *Loc. cit.*

In this article:

t = time in minutes;

Titer = number of cubic centimeters of the potassium permanganate solution used to titrate the undecomposed hydrogen peroxide.

P = pressure in atmospheres;

Conc. = concentration;

Atm. = atmospheres;

Exp. = experiment;

k = reaction constant calculated from the integrated formula,

$$k = \frac{1}{t_2 - t_1} \, ln \, \frac{A - x_1}{A - x_2},$$

where A is the titer at the beginning of the reaction, x_1 and x_2 the amount of hydrogen peroxide decomposed at the time t_1, t_2 expressed in cubic centimeters of potassium permanganate solution. In every case, *k* has been calculated from pairs of consecutive measurements. The concentration of the metal in the reaction mixture is expressed in gram atoms, that of the hydrogen peroxide in gram mols. per liter.

TABLE 1.

	Expt. 63(*a*). P = 70.		Expt 63(*b*). P = 1.			Expt. 121. P = 70.		Expt. 122. P = 1.	
Concentrations.	*t*.	0.4342 *k*.	*t*.	0.4343 *k*.	Concentrations.	*t*.	0.4343 *k*.	*t*.	0.4343 *k*.
	30.5	0.0028	29	0.0023					
$Pt = \frac{1}{145,000}$	62.5	0.0029	60.5	0.0024	$Pt = \frac{1}{100,000}$	10	0.0176	10	0.0150
$H_2O_2 = \frac{1}{30}$	76.5	0.0029	76	0.0024	$H_2O_2 = \frac{1}{30}$	20	0.0169	21	0.0186
						30	0.0187	35	0.0174
Duplicates of	Expt. 64. P = 70.		Expt. 65. P = 1.			Expt. 125. P = 70.		Expt. 126. P = 1.	
63 (*a*) & (*b*)	39	0.0024	29	0.0021	$Pt = \frac{1}{2,000,000}$	80	0.00028	29	0.00047
	77	0.0027	67	0.0025		236	0.00023	71	0.00028
	109.5	0.0027	111.5	0.0027	$H_2O_2 = \frac{1}{30}$	382	0.00020	..	..
	Expt. 80. P = 70.		Expt 81. P = 1.		Duplicate of			Expt. 127. P = 1.	
$Pt = \frac{1}{150,000}$	29	0.0040	29	0.0037	126			118	0.00022
$H_2O_2 = \frac{1}{30}$	74.5	0.0059	63	0.0047				359	0.00011
	126.5	0.0042	106.5	0.0052					
	167	0.0051							
	Expt. 119. P = 70.		Expt. 120. P = 1.						
$Pt = \frac{1}{200,000}$	14.5	0.0069	18	0.0057					
$H_2O_2 = \frac{1}{30}$	34.5	0.0067	40	0.0061					
	56.5	0.0070	63	0.0065					
	78.5	0.0069	90	0.0063					

Although a gas does not dissolve very rapidly in a motionless liquid we may safely assume that the concentration of the oxygen in the mixture was very much greater towards the end of the reaction in the experiments under high pressure than in those at a pressure of one atmosphere, yet the constants in the two cases are almost identical. Quantitative experiments with regard to the amount of dissolved oxygen will be given later.

The objection might be raised to the foregoing results that the compressed oxygen contained a poison or an accelerator for the reaction whose influence exactly counterbalanced the effect of the increased concentration of the oxygen. This possibility was very much reduced by the use of the glass vessel described below. By this arrangement the surface of contact between the gas and the reaction mixture was reduced to very small dimensions, so that not very much of the outer gas could get into the reaction mixture during the experiment, while the chemically pure oxygen that had been generated by the catalysis could get out of the liquid only under high pressure. By beginning with the corresponding concentration of hydrogen peroxide in the reaction mixture it was possible to obtain any desired concentration of oxygen, while the outer compressed gas served to keep the generated oxygen from escaping from the liquid.

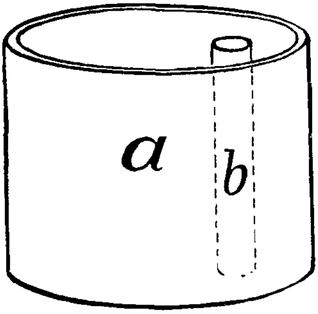

Fig. 2.

a (Fig. 2) is a glass vessel (ca. 3 cm. deep) that exactly fitted into the vessel in which the reaction was carried out. The siphon tube *g* (Fig. 1) fitted just as neatly into tube *b* (Fig. 2). Vessel *a* was placed on the surface of the reaction mixture and was free to sink as the liquid was siphoned out for analysis. If the glass was free from grease the liquid rose between the sides of the inner and outer vessels to the upper edge of vessel *a*. A series of results obtained by this method is given in Table 2.

TABLE 2.

	Expt. 250. P = 1.		Expt. 251. P = 60.			Expt. 252. P = 1.		Expt. 253. P = 70.	
Concentrations.	*t*.	0.4343 *k*.	*t*.	0.4343 *k*.	Concentrations.	*t*.	0.4343 *k*.	*t*.	0.4343 *k*.
Pt = $\frac{1}{200,000}$*	10	0.0072	10	0.0072	Pt = $\frac{1}{200,000}$	10	0.0055	10	0.0038
$H_2O_2 = \frac{1}{25}$	30	0.0087	30	0.0072	$H_2O_2 = \frac{1}{3}$	30	0.0060	30	0.0037
	60	0.0091	60	0.0081		60	0.0064	60	0.0041
	92	0.0094	90	0.0076		127	0.0061	..	...

* Preparation several months old.

Duplicates of	Expt. 256. P = 1.		Expt. 257. P = 70.		Duplicates of	Expt. 254. P = 1.		Expt. 255. P = 70.	
254 & 255	11	0.0050	10	0.0055	252 & 253	10	0.0059	12	0.0054
	30.5	0.0065	30	0.0066		30	0.0074	30	0.0060
	60	0.0070	60	0.0080		60	0.0074	60	0.0073
	117	0.0064	139	0.0094		120	0.0078	177	0.0089
	188	0.0053	169	0.0122					

If all the oxygen generated in Expts. 255 and 257 remained in solution the pressure toward the end of the reaction must have been 120 atmospheres. We may, therefore, safely assume that the partial pressure of the free oxygen in solution was 30 to 40 times as great as in the corresponding experiments, 254 and 256, yet we see that the rate was practically the same in both cases.

The influence of still greater oxygen concentrations (100 to 200 atmospheres) was investigated by the aid of the apparatus shown in Fig. 3. As the author could not obtain the use of a pump suitable for the purpose, the high pressure was obtained by allowing liquid oxygen to evaporate. *a* is the reaction bomb already described. It was placed as usual in a thermostat and was connected with a manometer for high pressures (1–1000 atmospheres). The manometer was in turn connected with the bomb *b*. If now a calculated amount of liquid oxygen was put into bomb *b* and allowed to evaporate, the corresponding pressure was obtained in the reaction bomb *a*.

It was impossible to pour liquid oxygen into the bomb without cooling it before hand if the liquid came into contact with the metal, because the heat capacity of the latter is so great that the liquid evaporated in a very few minutes. Cooling the bomb before introducing the oxygen was too expensive and impracticable. This difficulty was overcome by pasting strips of asbestos paper on the inner walls of the bomb and blowing a glass bulb inside it. The narrow space between the glass and the metal was filled with zinc oxide. With this arrangement the liquid oxygen (ca. 400 cc.) evaporated completely within thirty minutes, consequently, the high pressure was obtained quickly enough for the purposes of the experiment.

Details of the Experiments at High Pressure.—The experiment was begun in the usual manner and a pressure of 70–80 atmospheres was obtained in the reaction bomb from the usual source. The liquid oxygen was next poured into the bomb *b*, and the whole apparatus connected as in the figure. As soon as the pressure in the bomb, *b*, had risen to 70–80 atmospheres, bomb *a* was connected with the source of pressure by opening valve *d* (Fig. 3). The pressure rose to its maximum in about thirty minutes but occasionally fell somewhat towards the end of the experiment because the apparatus was not always gas-tight.

An analysis of the gas obtained from the liquid oxygen gave a content of 93.5 per cent. of oxygen. The remainder consisted principally of nitrogen. The results are given in Table 3.

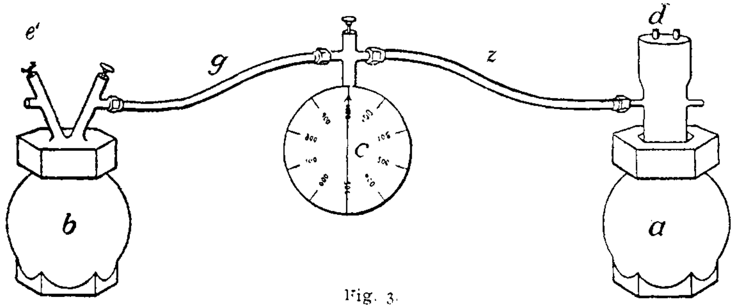

Fig. 3.

In Experiments 259 and 267 an open glass vessel was used in bomb *a*, while in Experiment 268 the vessel described on p. 202 was used. We see quite clearly from these results that a high concentration of oxygen has no perceptible effect on the catalysis.

TABLE 3.

	Expt. 259. P = 160 → 140.		Expt. 263. P = 70.			Expt. 266. P = 1.		Expt. 267. P = 200 → 100.	
Concentrations.	*t*.	0.4343 *k*.	*t*.	0.4343 *k*.	Concentrations.	*t*.	0.4343 *k*.	*t*.	0.4343 *k*.
$Pt = \frac{1}{200,000}$	10.5	0.0042	9	0.0026	$Pt = \frac{1}{350,000}$	10	0.0020	12.5	0.0020
$H_2O_2 = \frac{1}{2}$	32	0.0050	30	0.0047	$H_2O_2 = \frac{2}{3}$	30.5	0.0026	32	0.0028
	63.5	0.0049	60	0.0050		67	0.0029	62	0.0030
	107	0.0052	120.5	0.0047		151.5	0.0025	99	0.0026
	193	0.0050	197.5	0.0049		346.5	0.0021	174	0.0023
	256	0.0052	..	..				269	0.0019

	Expt. 268. P = 200 → 160.		Expt. 269. P = 1.	
$Pt = \frac{1}{350,000}$	10	0.0025	10	0.0033
$H_2O_2 = \frac{1}{3}$	26.5	0.0024	30	0.0036
	60	0.0030	60	0.0032
	120	0.0022	120	0.0022
	231	0.0019	..	..

The effect of increasing the concentration of the oxygen was tried where the *k* decreased from the beginning of the reaction. In such cases it is generally assumed that some one of the solutions contains a poison for the catalysis. Experiments 270 and 271 were carried out with the same solutions 8 days later than 260–3.

TABLE 4.

	Expt. 260. P = 1.		Expt. 261. P = 70.			Expt. 262. P = 1.		Expt. 263. P = 70.	
Concentrations.	*t*.	0.4343 *k*.	*t*.	0.4343 *k*.	Concentrations.	*t*.	0.4343 *k*.	*t*.	0.4343 *k*.
$Pt = \frac{1}{200,000}$	10	0.0075	10	0.0069	Duplicates	10	0.0047	9	0.0026
$H_2O_2 = \frac{1}{20}$	30	0.0068	29	0.0060	of 260 & 261	32.5	0.0037	30	0.0047
	60	0.0055	60	0.0057		121.5	0.0036	60	0.0050
	120	0.0050	117.5	0.0052		207.5	0.0024	120.5	0.0047
								197.5	0.0049

	Expt. 270. P = 1.		Expt 271. P = 70.	
$Pt = \frac{1}{200{,}000}$	10	0.0043	9	0.0044
$H_2O_2 = \frac{1}{4}$	31	0.0042	30	0.0040
	59	0.0043	61	0.0042
	137	0.0035	126	0.0038
	215	0.0032	..	..

Many authors have thought that the platinum becomes more active through the presence of the hydrogen peroxide or of the oxygen. A glance at the tables given above will reveal the fact that the *k* often increases in value until the very end,[1] while in many experiments (usually with different colloidal solutions) *k* goes through a maximum.[2] A large number of experiments not given here were carried out and in every case no relation was found between the amount of dissolved oxygen and the rate of reaction, or the course of ***k***.

Experiments with Colloidal Gold under Pressure.—The gold catalysis of hydrogen peroxide at ordinary pressure has been studied by Bredig and Reinders.[3] Experiments under high pressures of oxygen gave similar results to those obtained with platinum.

The reaction mixture was made alkaline because the rate in neutral or dilute acid solutions is very slow. The alkaline solution was made according to Paul's method by dissolving freshly cut sodium in water that had been boiled to free it from carbon dioxide.

TABLE 5.

	Exp. 155. P = 1.		Exp. 157. P = 80			Exp. 168. P = 1.		Exp. 169. P = 80.	
Concentrations.	*t*.	0.4343 ***k***.	*t*.	0.4343 ***k***.	Concentrations.	*t*.	0.4343 ***k***.	*t*.	0.4343 ***k***.
$Au = \frac{1}{200{,}000}$	22.5	0.0017	20	0.0027	$Au = \frac{1}{200{,}000}$	20	0.0045	20	0.0040
$NaOH = \frac{M}{55}$	40	0.0025	40	0.0027	$NaOH = \frac{2M}{55}$	40	0.0045	40	0.0051
$H_2O_2 = \frac{1}{30}$	70	0.0033	70	0.0026	$H_2O_2 = \frac{1}{30}$	60	0.0079	60	0.0056
	100.5	0.0046	95	0.0044		80	0.0045	..	..
	$96.7 = t_{A/2}$		$100 = t_{A/2}$			$52.3 = t_{A/2}$		$55.6 = t_{A/2}$	
$Au = \frac{1}{400{,}000}$	Expt. 154. P = 1.		Expt. 160. P = 80.		$Au = \frac{1}{400{,}000}$[4]	Expt. 162. P = 1.		Expt. 163. P = 1.	
$NaOH = \frac{1}{55}$	19.5	0.0020	20	0.0017	$NaOH = \frac{2M}{55}$	20	0.0021	21	0.0019
$H_2O_2 = \frac{1}{30}$	70	0.0027	50	0.0024	$H_2O_2 = \frac{1}{30}$	40	0.0011	60	0.0011
						60	0.0011		
					Duplicates	Expt. 164. P = 60.		Expt. 163. P = 80.	
					of 162 & 3	20	0.0018	21	0.0019
					under pres.	40	0.0012	60	0.0015
						60	0.0016	81	0.0013
						80	0.0013	..	...

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[1] See Experiments 65, 80, 81, 121, 250, 253, 254, 255, 257, 244, 245.

[2] See Experiments 232, 237, 266, 267, 268, 269.

[3] *Loc. cit.*

[4] Partly coagulated.

Experiments with colloidal gold more dilute with respect to alkali than $\frac{M}{100}$ gave very irregular results, very probably because of the presence of a varying amount of carbon dioxide. It is very difficult under complicated experimental conditions to prevent errors from this source.

As Bredig and K. Ikeda have pointed out, the metal catalysis of hydrogen peroxide in alkaline solutions does not follow the simple law for first-order reactions. Nevertheless, the values of k given in the table above have been calculated according to this law because they serve as a method of comparison if the same intervals of time are considered. Wherever it was practicable the time $t_{A/2}$ necessary to decompose one-half the hydrogen peroxide has been calculated by interpolation.

Experiments with Colloidal Palladium under Pressure.—The decomposition of hydrogen peroxide by colloidal palladium under ordinary pressure has been studied by Bredig and Fortner. The reaction under high pressures of oxygen has been followed by the author in precisely the same manner as in the case of gold. The results are very regular and show that the palladium solutions used were very much more active than those of the other metals having the same concentration.

TABLE 6.

	Expt. 175. P = 1.		Expt. 176. P = 80			Expt. 177. P = 1.		Expt. 178 P = 70.	
Concentrations.	t.	$0.4343\,k$.	t.	$0.4343\,k$.	Concentrations.	t.	$0.4343\,k$.	t.	$0.4343\,k$.
$Pd = \frac{1}{1,200,000}$	20	0.0073	20	0.0069	Duplicates of	20	0.0067	20	0.0082
$H_2O_2 = \frac{1}{30}$	40	0.0088	43	0.0092	175 & 176	40	0.0104	40	0.0107
$NaOH = \frac{1}{55}$	60	0.0093	60	0.0093		60	0.0110	60	0.0134
	$38 = t_{A/2}$		$38.7 = t_{A/2}$			$36.1 = t_{A/2}$		$34.4 = t_{A/2}$	

	Expt. 179. P = 1.		Expt. 180. P = 80.	
Duplicates	20	0.0070	20	0.0072
of 175 & 6	40	0.0095	43.5	0.0092
			60	0.0100
	$37.4 = t_{A/2}$		$38.1 = t_{A/2}$	

Investigation with Colloidal Iridium.—The catalytic properties of colloidal iridium have not yet been carefully worked out.[1] It has been the object of the following experiments to go into the question only in so far as it was necessary in order to ascertain the effect of high concentrations of oxygen on the catalytic decomposition of hydrogen peroxide by colloidal iridium.

The electrical colloidation of iridium is much more difficult than that of the other metals used in these experiments. Iridium is brittle and the wires often fuse together because of the large amount of current required (14–16 amperes, 70 volts).

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[1] Experiments on this problem are being carried out by Dr. Brossa, in Heidelberg.

No experiments were carried out with iridium in acid or neutral solution. Those in dilute alkaline solution show the remarkable fact that the reaction very nearly follows the law for first-order reactions. No very great weight should be laid on this result until the subject has been thoroughly investigated, because all the following experiments with colloidal iridium were carried out with a single preparation.

TABLE 7.

	Expt. 182. P = 1.		Expt. 183. P = 70.			Expt. 184. P = 70.		Expt. 185. P = 1.	
Concentrations.	t.	0.4343 k.	t.	0.4343 k.	Concentrations	t.	0.4343 k.	t.	0.4343 k.
$\mathrm{Ir}=\frac{1}{60,000}$[1]	20	0.0054	20	0.0048	Duplicates	21	0.0062	21	0.0049
$\mathrm{NaOH}=\frac{1}{55}$	40	..	40	0.0052	of 183 & 182	60	0.0049	40	0.0052
$H_2O_2=\frac{1}{30}$	60	0.0060	60	0.0058				60	0.0051
						$56.3=t_{A/2}$		$60=t_{A/2}$	
Duplicates	Expt. 186. P = 70.		Expt. 187. P = 1.			Expt. 189. P = 1.		Expt. 190. P = 1.	
of 183 & 182	20.5	0.0043	20.5	0.0049	$\mathrm{Ir}=\frac{1}{60000}$[2]	20	0.0018	20	0.0018
	42	0.0050	40.5	0.0045	$\mathrm{NaOH}=\frac{1}{220}$	49.5	0.0019	51	0.0019
	60	0.0062	60	0.0050	$H_2O_2=\frac{1}{30}$	93.5	0.0020	104.5	0.0022
	$61=t_{A/2}$		$60=t_{A/2}$			147.0	0.0022		
$\mathrm{Ir}=\frac{1}{60,000}$	Expt. 191. P = 1.		Expt. 192. P = 1.		$\mathrm{Ir}=\frac{1}{60,000}$	Expt. 193. P = 1.		Expt. 194. P = 1.	
$\mathrm{NaOH}=\frac{1}{55}$	20	0.0023	20	0.0024	$\mathrm{NaOH}=\frac{2}{55}$	20	0.0021	20	0.0021
$H_2O_2=\frac{1}{30}$	40	0.0025	40	0.0026	$H_2O_2=\frac{1}{30}$	50	0.0021	50	0.0021
	85	0.0025	80	0.0026		80.5	0.0020	80	0.0021
	169	0.0028	166	0.0028					

Experiments with Colloidal Silver under Pressure.—MacIntosh[3] measured the rate of decomposition of hydrogen peroxide by colloidal silver and found that the constant calculated from the equation for first-order reactions decreased, whereas it increases in the case of gold, platinum, etc. He explains this phenomenon by assuming that colloidal silver is slowly dissolved by hydrogen peroxide. The author's experiments verify MacIntosh's results. It was found necessary to work in dilute alkaline solutions because the silver dissolved very rapidly even in neutral solutions of hydrogen peroxide. For instance, the decomposition of a $\frac{M}{15}$ solution of hydrogen peroxide by a $\frac{1}{20,000}$ gram atom solution of colloidal silver became immeasurably slow after 20 minutes.

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[1] Professor Bredig has very kindly informed the author that subsequent investigation in his laboratory has shown that the method of analysis employed here for iridium gives faulty results. These figures do not, therefore represent the true concentrations.

[2] Partly coagulated.

[3] J. Phys. Chem., 6, 15.

TABLE 8.

	Expt. 221. P = 60.		Expt. 222. P = 1.			Expt. 223. P = 60.		Expt. 224. P = 1.	
Concentrations.	*t*.	0.4343 *k*.	*t*.	0.4343 *k*.	Concentrations.	*t*.	0.4343 *k*.	*t*.	0.4343 *k*.
$Ag = \frac{1}{50,000}$	7	..	7	..	$Ag = \frac{1}{50,000}$	5.5	..	5	...
$NaOH = \frac{M}{100}$	17	0.0189	17	0.0181	$NaOH = \frac{1}{200}$	15.5	0.0128	15.5	0.0135
$H_2O_2 = \frac{1}{40}$	37.5	0.0165	40	0.0151	$H_2O_2 = \frac{1}{40}$	36.5	0.0094	35.0	0.0128
	77	0.0126	103	0.0119		75.5	0.0088	75	0.0117

	Expt. 225. P = 1.		Expt. 226. P = 50.	
$Ag = \frac{1}{100,000}$	5	..	6.5	..
$NaOH = \frac{1}{50}$	16.5	0.0111	16.0	0.0146
$H_2O_2 = \frac{1}{30}$	36.5	0.0101	36	0.0118
	76.5	0.0076	76	0.0097

Theoretical Considerations.

If we make the reasonably safe assumption that the reaction takes place in a heterogeneous system let us consider under what conditions high oxygen concentrations would appreciably affect the catalysis.

Because the reaction under pressure goes completely as far as we can determine by ordinary analytical means, any chemical equilibrium between hydrogen peroxide, oxygen and water may be left out of consideration. It has been suggested by several authors that the oxygen forms an intermediate compound with the metal or, perhaps, a solid solution. Neither of these hypotheses preclude the existence of a layer of condensed oxygen on the surface of the solid phase.

Suppose, then, the first step of the reaction is represented by the equation

$$\text{I.} \qquad yO + nM = M_nO_y,$$

where M_nO_y is either a *chemical* compound or a solid solution and that this step is followed by a second according to the equation

$$\text{II.} \quad M_nO_y + yH_2O_2 = nM + yO_2 + yH_2O.$$

Nernst and Brunner[1] have shown that the measured rate will be affected by the rate of the *chemical* reaction in heterogeneous systems only when the latter is slow in comparison to the rate of diffusion of the substance undergoing decomposition. In the light of these considerations, pressure would have an effect on the measured rate of reaction when:

(1) The activity of the platinum-oxygen phase in the second step of the reaction changes with increasing concentration of oxygen.

(2) The rate with which the chemical compound or solid solution M_nO_y in the first step of the reaction is formed, varies with the concentration

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[1] Z. physik. Chem., 51, 95 and 494.

of the oxygen. As the experimental results given in this article prove definitely that pressure has no measurable effect on the rate, we are forced to conclude either, that the two above cases do not exist, or that the chemical reactions are rapid in comparison to the rate of diffusion of the hydrogen peroxide. The latter hypothesis agrees very well with the experimental results obtained by J. Teletow.[1]

Pressure would also have no appreciable effect on the reaction if an active platinum compound were formed directly from the union of platimum and hydrogen peroxide and not from platinum and oxygen, even if the rate of union were *not* rapid.

Summary.

The chief results of this article are: A method has been worked out whereby rates of reaction may be measured under high gas pressure.

It has been experimentally determined that the catalytic decomposition of hydrogen peroxide by colloidal solutions of platinum, palladium, iridium, gold and silver is unappreciably affected by increasing the pressure of oxygen gas above the reaction mixture from 1 to 200 atmospheres.

This investigation was carried out in the chemical laboratory of the University of Heidelberg during the years 1905–6, under the direction of Prof. Bredig to whom my sincere thanks are due for friendly and valuable advice.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
October 9, 1907.

A METHOD FOR THE SEPARATION OF IRON FROM INDIUM.

BY F. C. MATHERS.

Received December 16, 1907.

One of the most difficult steps in the purification of indium is its separation from iron. Winkler[2] obtained a separation by the fractional precipitation of the sulphide, the indium sulphide being less soluble than the iron sulphide. A more satisfactory method was devised by Bayer,[3] who treated a solution of the mixed chlorides with sodium sulphite. Basic indium sulphite is precipitated from this solution upon boiling. The precipitate, after filtration, was dissolved in a solution of sulphurous acid and basic indium sulphite was again precipitated by boiling. This solution and reprecipitation was repeated several times to completely purify the indium. The Bayer method was tested in this laboratory, but gave unsatisfactory results. Weselsky[4] treated the chlorides of indium and iron with sulphur dioxide or sodium thiosulphate and then

[1] Dissert., Heidelberg, 1906.

[2] J. pr. Chem., 94, 1 (1865).

[3] Bayer, Lieb. Ann., 158, 372 (1871).

[4] J. pr. Chem., 94, 443 (1865).