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THE IGNITION TEMPERATURES OF HYDROGEN-OXYGEN MIXTURES.

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HISTORICAL INTRODUCTION.

THE determination of the ignition temperature of detonating gas has formed the subject of a number of experimental investigations.[1] In general, one of two methods was employed. Either the gas was enclosed in a sealed bulb and plunged into a bath of known temperature, or it was passed through a tube which was heated from without to a definite temperature. By means of the former method, V. Meyer, first with Krause and later with Askenasy, found the ignition temperature (absolute) of pure detonating gas to lie between 791° and 879° (or 518°–606° C.), whereas Emich obtained a fairly constant result of 862° (or 589° C.). For mixtures containing an excess of oxygen up to 80.4 per cent., Emich found 844°–881° (or 571°–608° C.) and with an excess of hydrogen up to 67.7 per cent. 848°–880° (or 575°–607° C.). A number of the values found for the mixture $2H_2+O_2$ by the use of the second method are as follows:

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[1] Mallard et Le Chatelier: Compt. rend. 91, 825; Bull. soc. chim. 39, 2; Helier: Ann. chim. phys. [7] 10, 521; Gautier et Helier: Compt. rend. 122, 566; V. Meyer und Krause: Ann. 264, 85; V. Meyer und Askenasy: Ibid. 269, 49; V. Meyer und Freyer: Ber. 25, 622; V. Meyer und Raum: Ibid. 28, 2804; Mitscherlich: Ibid. 26, 163; Bodenstein: Z. physik. Chem. 29, 665; Emrich: Monatsh. 21, 1061; and others.

Mallard and Le Chatelier	823°	(or 550° C.)
Bodenstein	926°–983°	(or 653°–710° C.)
Mitscherlich	947°	(or 674° C.)
V. Meyer and Freyer	about 973°	(or 700° C.)
Gautier and Helier	1113°	(or 840° C.)
Helier	1118°	(or 845° C.)

The results obtained by these methods differ greatly, owing to the uncertain method of heating the gas, to the catalytic action of the walls of the vessel, and to the possibility of some combination taking place before ignition. A more detailed discussion will be gone into later in connection with some new experimental data.

THEORY.

With regard to the question of ignition temperatures, Professor Nernst gave me the following suggestions:

"Let us consider a given mass of inflammable gas of uniform temperature, the catalytic action of the containing walls being eliminated, as for example in the manner shown in the experimental portion of this paper. The ignition temperature is defined as the temperature at which the gas would ignite if left entirely to itself for some time.

"The temperature of the gas will rise on account of the heat of reaction. On the other hand, the cooling of the gas will tend to neutralize this rise. Considering unit volume in the interior of the gaseous mass, from the law of mass action, the heat evolved would be

$$Q_1 = qkC_1^{v_1}C_2^{v_2} \ldots\ldots\ldots,$$

while the heat given off by conduction and radiation would be

$$Q_2 = \alpha(T - T_0) + \beta(T - T_0)^4,$$[1]

where q is the heat of reaction, k the specific reaction-velocity, C_1, C_2 the concentrations of the reacting substances, T the temperature of the gas and T_0 that of the surroundings. For the ignition temperature to be reached $Q_1 > Q_2$. If the volume of gas is very large, the particles in the inner portions would not lose an appreciable amount of heat, and the larger the volume the lower would be its ignition temperature. In the latter case, the time required for actual ignition would also be increased. In other words, an inflammable gas of infinitely large volume would ignite spontaneously, independently of the lowness of its initial temperature, although only after a great interval of time. If the

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[1] See Nernst: Physik. Z. 5, 777 (1904).

gas occupies a finite moderate volume, cooling by conduction and radiation would proceed very rapidly, and consequently the heat of reaction per unit volume must be large in order to cause ignition. If Q_1 is greater than Q_2 by not too small an amount, the temperature of the gas would rise rapidly under these conditions. Consequently the ignition temperature would be higher the smaller the volume of the gas, and also the time required for ignition to take place would be less.

"Without developing these views further, attention may be called to the important fact that Q_1 increases with much greater rapidity than Q_2 with increase in temperature. This leads to the conclusion that with a small mass of gas the ignition temperature increases only slightly with decrease in volume, and that an increase in the initial pressure of the gas, acting evidently in the same manner as increasing the initial volume, would exert only a small influence on the ignition temperature."

The preceding views are confirmed by the experiments to be described in the following pages.

In order to overcome the objections to the methods used heretofore in determining the ignition temperatures of gaseous mixtures, Professor Nernst suggested developing the heat necessary to ignite the gas by the adiabatic compression of the gas itself. This investigation was undertaken to determine the practicability of this method.

DESCRIPTION OF APPARATUS.

In order to heat the gas whose ignition temperature was to be determined, it was necessary to enclose it in a small vessel supplied with a device for allowing the gas to be compressed instantaneously. Two pieces of apparatus were constructed on the same plan, but of different sizes.[1] A section vertically through the center is shown in the figure. A steel cylinder, *AA*, was screwed into a wrought iron plate, *LL*, so as to fit absolutely air-tight. The piston head *B* fitted closely into the cylinder *AA*. The piston rod *CC* was made a little narrower (about 2 mm.) than *B*. The piston head together with the piston rod was made of one piece of steel. It was topped by an iron plate *D*, screwed on to the piston rod. In order to have the piston head slide into the cylinder

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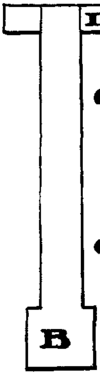
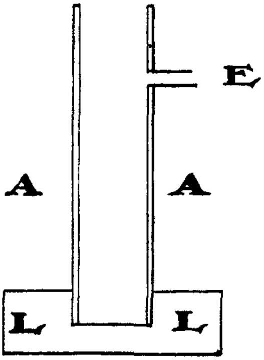
[1] I wish to take this opportunity of thanking Mr. Schlüter for his advice and assistance in planning and constructing the apparatus, and Mr. Schlicht for his great aid in carrying out the experiments.

and at the same time permit no leakage, three circular grooves each 1 mm. wide and 1 mm. deep were cut into the former and wound with hemp. The cylinder was filled with the gas to be studied through *E*, a brass tube 5 mm. in diameter soldered to the cylinder. The compression was obtained after enclosing the gas in the cylinder and pushing the piston down below the opening *E* so as to shut off access to the air by allowing a weight to fall on the plate *D*. By increasing the size of the weight and the distance of its fall, as great a compression, and consequently as high a temperature as was desired, could be obtained. A brass ring, 1 cm. in width, was fitted on the piston rod so that it could be moved up and down only by the use of some force. This served to show the smallest volume of gas in the cylinder during a compression, as the ring was pushed up by the walls of the cylinder as the piston descended, and then remained fixed in position when the piston moved upward again, thus indicating the lowest point reached by the piston. Knowing the dimensions of the apparatus, the volume reached by the compression could then be calculated. Lanoline was found to be the best lubricant for the piston, and was used throughout this work.





The dimensions were as follows:

Apparatus I.—Length of cylinder, *AA*, 20.82 cm.; inner diameter of cylinder, 2.50 cm.; thickness of walls of cylinder, 0.51 cm.; distance from lower inner edge of inlet tube to bottom of cylinder, 14.22 cm.; thickness of wrought iron plate, *LL*, 3.24 cm.; thickness of wrought iron plate directly beneath the cylinder, 1.22 cm.; diameter of piston head, 2.50 cm.; length of piston (including piston head and piston rod), 26.04 cm.; thickness of upper plate, *D*, 2.30 cm. The plate *LL* was firmly bolted to a heavy board.

69.8 cc. gas measured at atmospheric pressure were used in each experiment with this apparatus. To effect the compression a weight of 25 kg. was used, and the height which it was allowed to fall varied from 48 to 86 cm.

Apparatus II.—Length of cylinder, *AA*, 23.06 cm.; inner diameter of cylinder, 4.40 cm.; thickness of walls of cylinder, 0.73 cm.; distance from lower inner edge of inlet tube to bottom of cylinder, 18.67 cm.; thickness of wrought iron plate, *LL*, 4.95 cm.; thickness of wrought iron plate directly beneath the cylinder, 1.02 cm.; diameter of piston head, 4.40 cm.; length of piston (including piston head and piston rod), 26.25 cm.; thickness of upper plate, *D*, 1.97 cm. The upper plate was fastened by means of two chains to a heavy iron plate on which the apparatus was placed so as to prevent the piston from flying out of the cylinder after an explosion.

283.9 cc. gas measured at atmospheric pressure were used here in each experiment. A 38 kg. weight was dropped a distance varying from 90 to 130 cm.

The following test will serve to show how air-tight apparatus II was. The piston was pushed past the inlet tube, allowed to come to rest, and the distance from the top of the upper plate to the floor measured. A 25 kg. weight was then placed on the upper plate, the air in the cylinder being compressed to a smaller volume. If the piston did not fit in the cylinder so as to be air-tight, the air within, being under pressure, would be forced out between the piston and the cylinder. From time to time the weight was removed and the piston pushed back to its original position by the compressed air within. The distance from the top to the floor was measured each time. In the following table *h* represents these distances and *t* the intervals of time in minutes from the beginning of the test to the successive removals of the weight.

In eight hours the height decreased 1.09 cm. or the volume 16.6 cc. As in the ignition experiments 283.9 cc. gas measured at the ordinary pressure were present. Apparatus I was not quite as tight as this, but it may safely be assumed that there was no escape of gas during the rapid compression which was used to cause ignition.

h (cm).	t (minutes).
39.69	0
39.58	25
39.66	70
39.40	120
39.27	155
39.18	190
38.80	315
38.74	440
38.60	480

In the experiments to be described, only mixtures of hydrogen and oxygen were studied. These were obtained by the electrolysis of a 10 per cent. solution of caustic soda by means of a current having a potential of 110 volts, sufficient resistance being put in the circuit to give a density of about 3 amperes. The electrodes were made of nickel. For the mixture $2H_2+O_2$ one cell was taken. For mixtures containing more hydrogen or more oxygen, U-tubes were put in series with the first cell, and the gas required taken from the corresponding arm of the U-tube. In this way by using the right number of cells, the following mixtures were obtained: $4H_2+O_2$, $2H_2+O_2$, H_2+O_2, H_2+2O_2, H_2+4O_2. The gas was evolved only when required. The glass tubes through which it was necessary to pass the gas were connected by means of thick rubber tubing. In order to have comparable conditions under which to determine the ignition temperatures of the different mixtures, it was decided to saturate the gas in all cases with water vapor at the ordinary temperature. This was done by allowing it to bubble through two or three small wash-bottles filled with water.

METHOD OF EXPERIMENTING.

The method of making a determination was as follows: The mixture to be ignited was led into the cylinder by means of a thin rubber tube which passed through the inlet tube, reaching to the bottom of the cylinder. This rubber tube was connected to the glass tube coming from the generating cells right at the edge of the inlet tube. The piston was clamped in position so that the lower edge of the piston head was just above the opening of the inlet tube in the cylinder. In this way the gas was run into the bottom of the cylinder, the displaced air passing out through the inlet tube around the rubber tubing. Owing to the diffusion which was bound to take place the gas was passed in for an hour before each experiment.[1] After the air had been displaced and the required mixture was present in the cylinder, the rubber tube was withdrawn rapidly, and the piston pushed down past the opening of the inlet tube. The mixture was now confined in the cylinder. The distance from the top of the cylinder to the ground was then measured. This was accomplished in apparatus I by means of a pointer fastened to the plate *D* which marked its height on a blackened plate clamped in position, and in apparatus II by measuring directly the distance from the top of the plate *D* to the upper edge of the lower plate *LL*. Knowing the dimensions of the apparatus, the height h_1 of the volume of gas enclosed in the cylinder was known.. The weight was then allowed to fall on the piston, causing a sudden compression of the gas within. The gas was heated in this way to its ignition point, and as soon as this was reached, exploded. The force of the explosion was great enough to stop the downward motion of the piston, even when the kinetic energy supplied by the weight was not entirely exhausted.[2] This was shown most plainly by means of apparatus I with the mixture $2H_2+O_2$ where the same results were obtained independently of the height from which the weight fell. From the movable brass ring on the piston rod, already described, the height h_2 of the volume of gas at the moment of explosion was determined. Owing to the high temperature attained by the explosion, some of the lanoline was invariably decomposed. This did not interfere with the determinations as it was only desired to obtain the ignition temperature. There was never any decomposition when no explosion had taken place, although in some cases the ignition temperature was almost reached. The initial temperature of the gas was taken to be that of the room temperature. The initial pressure of the gas was always greater than one atmosphere. Since, in pushing the piston past the inlet tube, the compression began when the piston passed the lower edge of the inlet tube, the distance from this lower edge

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[1] A number of experiments in which the gas had been led into the cylinder three to four hours gave no different results.

[2] The terrific force of the explosion can perhaps be better appreciated from the fact that in apparatus I, in an early experiment with the mixture $2H_2 + O_2$, a piece was blown out of the cast-iron base plate *LL* 0.5 cm. in thickness. The plate was then made of wrought iron and thicker. In apparatus II, where a larger amount of gas was used, the weight (38 kg.) was hurled to a height of 60 to 80 cm. by every explosion.

to the bottom of the cylinder divided by h_1 would be the initial pressure in atmospheres. For apparatus I we have $14.22/h_1$ and for apparatus II $18.67/h_1$.

METHOD OF CALCULATING.

In the experiments recorded in the following pages, h_1 represents the initial height in centimeters of the volume of the mixture under examination.

h_2, the final height in centimeters of the volume of the mixture, that is, at the ignition point.

T_1, the initial temperature (absolute) of the mixture.

T_2, the ignition temperature (absolute).

p_1, the initial pressure of the gas in atmospheres.

p_2, the pressure of the gas in atmospheres at the ignition temperature.

l, the distance in centimeters the weight fell (only used with apparatus I for the mixture $2H_2+O_2$).

The values h_1, h_2, T_1, and p_1 were obtained directly from the experiments. To calculate T_2 and p_2 the equation for adiabatic changes

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{k-1} \text{ and } \frac{p_2}{p_1} = \left(\frac{v_1}{v_2}\right)^{k}$$

were made use of.

Since the diameters of the cylinders were constant, by substituting h_1 for v_1 and h_2 for v_2 we have

$$\frac{T_2}{T_1} = \left(\frac{h_1}{h_2}\right)^{k-1} \text{ and } \frac{p_2}{p_1} = \left(\frac{h_1}{h_2}\right)^{k}$$

For k, the ratio of the specific heats of the gases at constant pressure and constant volume, 1.4 was taken. There are no data which define this value accurately under the necessary conditions. The ignition temperatures did not exceed 600° C. in most cases, and although a small decrease in k has been observed at this temperature, the increase in pressure in the present experiments may compensate this, as k increases slightly with the pressure. At any rate, all the determinations are affected equally, and if in future a more exact value for k is found, the correction of the data here presented would be a simple matter. The equations therefore reduce to

$$\log T_2 = \log T_1 + 0.4\ (\log h_1 - \log h_2)$$

and

$$\log p_2 = \log p_1 + 1.4\ (\log h_1 - \log h_2).$$

The measurements were made with a steel measuring rod carrying a vernier, so that direct readings to a tenth of a millimeter could be made.

Perhaps the source of greatest inaccuracy lay in the reading of the final height h_2 of the gas. With apparatus I a difference in reading of 0.1 mm. of this height would produce a difference of 5° to 6° in the ignition temperature T_2, while with apparatus II, 0.1 mm. difference in h_2 would mean 3° difference in T_2.

EXPERIMENTAL RESULTS.

The results obtained are shown in the following tables: first for apparatus I for the mixtures: $4H_2+O_2$, Table I; $2H_2+O_2$, Table II; H_2+O_2, Table III; and then for apparatus II for the mixtures: $4H_2+O_2$, Table IV; $2H_2+O_2$, Table V; H_2+O_2, Table VI; H_2+2O_2, Table VII; H_2+4O_2, Table VIII.

The average values of T_2 and of p_2/p_1 are also given for each series of determinations.

TABLE I.

$4H_2 + O_2$. Apparatus I.

h_1 (cm.).	h_2 (cm.).	p_1 (atm.).	p_2 (atm.).	T_1 (abs.).	T_2 (abs.).	p_2/p_1.
10.78	0.66	1.32	65.9	293.	896.	49.9
10.48	0.70	1.36	60.0	291.	859.	44.1
8.78	0.52	1.62	84.7	293.	908.	52.3
8.60	0.64	1.65	62.8	294.	831.	38.1
				Average,	874.	46.1

TABLE II.

$2H_2 + O_2$. Apparatus I.

h_1 (cm.).	h_2 (cm.).	l (cm.).	p_1 (atm.).	p_2 (atm.).	T_1 (abs.).	T_2 (abs.).	p_2/p_1.
8.86	0.74	48.1	1.61	51.9	292.	788.	32.2
8.55	0.59	......	1.66	70.2	293.	854.	42.3
8.51	0.59	63.2	1.67	70.1	293.	852.	42.0
8.17	0.62	63.2	1.74	64.3	293.	822.	37.0
8.05	0.59	......	1.77	68.6	293.	833.	38.8
7.74	0.57	67.2	1.84	70.8	290.	823.	38.5
7.60	0.59	52.7	1.87	68.6	292.	809.	36.7
7.24	0.63	63.2	1.96	59.9	293.	778.	30.6
7.12	0.58	......	2.00	66.8	293.	799.	33.4
6.88	0.54	67.8	2.07	72.9	293.	811.	35.2
6.57	0.56	86.0	2.16	68.0	293.	785.	31.5
6.53	0.46	67.8	2.18	89.3	292.	844.	41.0
6.30	0.55	74.7	2.26	68.5	290.	769.	30.3
6.16	0.56	52.7	2.31	66.3	295.	770.	28.7
5.91	0.44	63.2	2.38	91.7	293.	828.	38.5
4.78	0.38	63.2	2.98	103.0	293.	807.	43.5
					Average,	811.	36.3

TABLE III.

$H_2 + O_2$. Apparatus I.

h_1 (cm.).	h_2 (cm.).	p_1 (atm.).	p_2 (atm.).	T_1 (abs.).	T_2 (abs.).	p_2/p_1.
10.47	0.86	1.36	44.9	290.	788.	33.0
9.98	0.79	1.43	49.6	290.	800.	34.7
6.54	0.61	2.18	60.2	290.	749.	27.6
6.29	0.49	2.26	80.6	290.	805.	35.7
				Average,	786.	32.8

TABLE IV.

$4H_2 + O_2$. Apparatus II.

h_1 (cm.).	h_2 (cm.).	p_1 (atm.).	p_2 (atm.).	T_1 (abs.).	T_2 (abs.).	p_2/p_1.
14.91	0.97	1.25	57.4	293.	874.	45.9
14.82	1.00	1.26	54.9	297.	873.	43.6
14.81	0.96	1.26	58.2	294.	878.	46.2
13.45	0.80	1.39	72.2	296.	915.	51.9
12.58	0.75	1.48	76.8	296.	913.	51.9
10.71	0.66	1.74	86.2	296.	902.	49.5
				Average,	893.	48.2

TABLE V.

$2H_2 + O_2$. Apparatus II.

h_1 (cm.).	h_2 (cm.).	p_1 (atm.).	p_2 (atm.).	T_1 (abs.).	T_2 (abs.).	p_2/p_1.
15.07	1.24	1.24	40.9	293.	796.	33.0
15.06	1.17	1.24	44.3	292.	811.	35.7
15.04	1.06	1.24	50.9	293.	847.	41.0
15.03	1.08	1.24	49.6	293.	840.	40.0
14.71	1.16	1.27	44.5	293.	809.	35.0
14.67	1.11	1.27	47.2	293.	823.	37.2
14.22	1.02	1.31	52.5	293.	841.	40.1
13.83	1.10	1.35	46.7	293.	807.	34.6
13.74	1.06	1.36	49.1	293.	817.	36.1
12.65	1.01	1.47	50.8	293.	805.	34.6
12.30	0.91	1.51	58.1	291.	825.	38.5
12.18	0.92	1.53	57.0	293.	823.	37.3
11.57	0.89	1.61	58.5	291.	812.	36.3
9.31	0.70	2.01	75.1	292.	822.	37.4
				Average,	819.	36.9

TABLE VI.

$H_2 + O_2$. Apparatus II.

h_1 (cm.).	h_2 (cm.).	p_1 (atm.).	p_2 (atm.).	T_1 (abs.).	T_2 (abs.).	p_2/p_1.
14.98	1.24	1.25	40.8	295.	799.	32.6
14.95	1.28	1.25	39.0	296.	791.	31.2
14.38	1.24	1.30	40.1	296.	789.	30.9
13.91	1.17	1.34	43.0	296.	797.	32.1
13.66	1.21	1.37	40.7	298.	786.	29.7
13.41	1.12	1.39	45.0	296.	799.	32.4
11.95	0.97	1.56	52.6	296.	808.	33.7
				Average,	796.	31.8

TABLE VII.

$H_2 + 2O_2$. Apparatus II.

h_1 (cm.).	h_2 (cm.).	p_1 (atm.).	p_2 (atm.).	T_1 (abs.).	T_2 (abs.).	p_2/p_1.
14.32	1.16	1.30	44.0	296.	809.	33.9
14.16	1.15	1.32	44.3	299.	816.	33.6
13.84	1.19	1.35	41.9	299.	798.	31.0
13.17	1.06	1.42	48.3	294.	806.	34.0
13.09	1.05	1.42	48.8	296.	812.	34.4
12.69	1.05	1.47	48.2	296.	802.	32.8
12.11	1.00	1.54	50.6	296.	803.	32.8
11.81	0.93	1.58	55.5	296.	818.	35.1
				Average,	808.	33.5

TABLE VIII.

$H_2 + 4O_2$. Apparatus II.

h_1 (cm.).	h_2 (cm.).	p_1 (atm.).	p_2 (atm.).	T_1 (abs.).	T_2 (abs.).	p_2/p_1.
15.05	1.09	1.24	49.0	296.	846.	39.5
13.83	1.00	1.35	53.4	296.	848.	39.6
13.63	0.98	1.37	54.6	296.	848.	39.9
12.79	0.93	1.46	57.3	296.	845.	39.3
12.43	0.87	1.50	60.8	296.	858.	40.5
				Average,	849.	39.8

Whether the rise in temperature produced by the adiabatic compression is the only source of heat entering into question in these experiments may be answered affirmatively. The compression is so rapid that there is no chance for radiation to the walls of the vessel. There is no heat developed by friction which could affect the mixture, for even if the sliding of the piston in the cylinder would produce such heat, it would not be in contact with the enclosed volume of gas.

DISCUSSION OF RESULTS.

The ignition temperatures (absolute) obtained for the different mixtures are as follows:

	Apparatus I.	Apparatus II.
$4H_2 + O_2$	874.	893.
$2H_2 + O_2$	811.	819.
$H_2 + O_2$	786.	796.
$H_2 + 2O_2$	......	808.
$H_2 + 4O_2$	......	849.

The pressures at which these temperatures were determined were all greater than 39 atmospheres. It is evident from the tables that differences in pressure over 39 atmospheres produce no appreciable difference in the ignition temperatures.

The effect of the initial temperatures on the inflammability is of great interest. Direct experimental values for the ignition temperatures of the different mixtures when the initial temperatures were higher than the room temperature could not be obtained, because the lanoline used to insure the tightness of the apparatus as well as to act as lubricant, melted, thus permitting leakage between the piston and the cylinder. No other lubricant could be found to answer the purpose at these higher temperatures.

A little consideration will show, however, that the effect of changing the initial temperature is included in the data given. Let us take the state of affairs in an experiment at the instant when the piston in descending reaches a point half way between the starting point and the bottom of the cylinder. At this moment $h_2 = \frac{1}{2} h_1$ and

$$\log T_2 = \log T_1 + 0.4 (\log h_1 - \log \tfrac{1}{2} h_1)$$
$$= \log T_1 + 0.12041.$$

If $T_1 = 290°$, T_2 would be equal to 383°.

We can now consider this value of T_2 as the initial temperature of the mixture, which, on being further adiabatically compressed, explodes when the ignition temperature is reached. This is evidently the same ignition temperature which was found when the experiment was considered as starting from the room temperature. This method of treating the problem is permissible since the only other factor which changes during an experiment is the pressure and this, as we have seen, does not influence the ignition temperature under the given conditions. In a similar manner, by dividing a single experiment into an infinite number of separate ones in which T_1 (the initial temperature) is successively increased by a small amount, the initial temperatures of all the mixtures can be considered to be varied from the ordinary up to the ignition temperature.

We can sum up briefly by stating that, from the experimental results obtained, the ignition temperature is independent of the final pressure of the gas for pressures greater than 39 atmospheres (this was the least pressure at which the ignition temperature was determined; this constancy probably extends to pressures much less than this), and that the ignition temperature under the conditions described is entirely independent of the initial temperature of the gas. It must be borne in mind that the values for p_2/p_1

do change depending on the initial temperatures. Those given in the tables refer simply to the cases in which the gas was at the room temperature when p_1 was measured.

Considering the difference in size between apparatus I and II the agreement in the ignition temperatures is as close as could be expected. Perhaps the values obtained by means of apparatus II are the more accurate, as here a larger volume of gas was used, and the errors arising from the measurements play a smaller part. The discussion of the results will therefore be limited to the experimental values obtained with this apparatus.

The ignition temperature of the mixture H_2+O_2 lies lower than that of any of the other mixtures studied. This minimum in temperature, corresponding to a maximum affinity, is shown most clearly by means of the accompanying curve in which the relative volumes of hydrogen and oxygen in the different mixtures are plotted as abscissae and the temperatures of ignition as ordinates. The most evident explanation for this is, that in the combination of hydrogen and oxygen, the first product formed is hydrogen peroxide which may or may not be then decomposed, the conditions determining how complete this second reaction is. This theory is not new but up to the present has lacked experimental verification. It was first put forward by Mendeléeff:[1] "....it may be admitted that, in the combination of hydrogen with oxygen, hydrogen peroxide is first formed (equal volumes of hydrogen and oxygen) which is decomposed by the heat evolved into water and oxygen. This explains the presence of traces of hydrogen peroxide in almost all cases of the combustion or oxidation of hydrogenous substances, for it cannot be supposed that water is first formed and then the peroxide of hydrogen, because up to now such a reaction has not been observed, while the formation of H_2O from H_2O_2 is very easily reproduced." The

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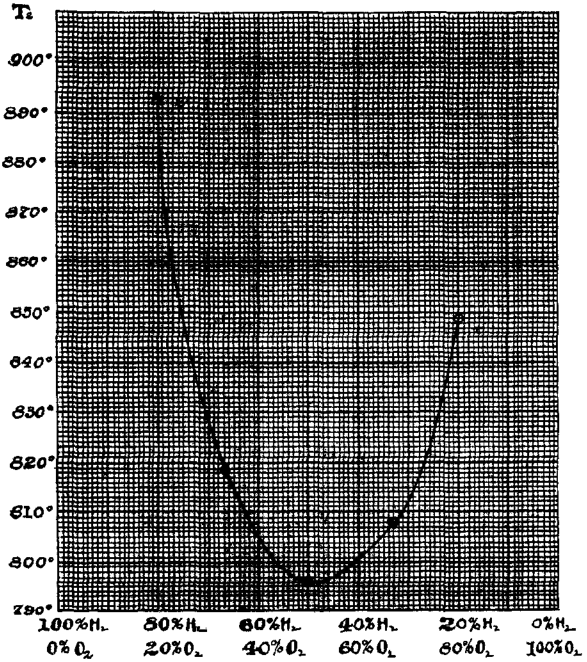
[1] This extract is from "The Principles of Chemistry," by Mendeléeff, the English translation of the sixth Russian edition, Vol. I, page 312. The foot-note on the same page states: "This opinion which I have always held (since the first editions of this work), as to the primary origin of hydrogen peroxide and of the formation of water by means of its decomposition, has in later days become more generally accepted, thanks more especially to the work of Traube . . . . perhaps the theory of the explosion of detonating gas itself and of the combustion of hydrogen will gain in clearness and truth, and we take into consideration the preliminary formation of hydrogen peroxide and its decomposition."

experimental work of Traube[1] and more recently that of Engler[2] have done much to forward this view.

Emich[3] in an article published in 1897 described a series of experiments in which he determined the length of spark (by measuring the distance between two electrodes) which would just ignite mixtures containing varying amounts of hydrogen and oxygen. He found the greatest inflammability (the inflammability varying inversely as the spark length) with the mixture containing equal volumes of hydrogen and oxygen. On diluting this mixture with hydrogen and then with oxygen, he found that twice as much oxygen was required to cause the same increase in spark length as hydrogen, or that beginning with the mixture of greatest inflammability—$H_2 + O_2$—and adding equal volumes first of oxygen and then of hydrogen, the inflammability of the resulting mixture was decreased twice as much by the hydrogen



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[1] Traube: Ber. 15, 657; 16, 1201; 18, 1881; 22, 1496; 26, 1471.

[2] Engler and Weissberg: "Vorgänge der Autoxydation."

[3] Emich: Monatsh. 18, 6.

as by the oxygen. As will be seen from the figures on page 1527, the same result was obtained in this work, the ignition temperature being increased approximately twice as much by the addition of hydrogen as by the addition of the same volume of oxygen, beginning with the mixture having the lowest ignition temperature—H_2O_2. Emich speaks of the probability of the primary formation of hydrogen peroxide, but in a second paper[1] he appears to have abandoned this view as the result of having determined directly the ignition temperatures of the different mixtures by enclosing them in sealed bulbs and plunging them into baths of known temperature. He found very little difference in the ignition temperatures of the mixtures and concluded that there was no simple relation between this temperature and the thickness of the gaseous layer which could just be ignited by a spark. Mention may be made of some of the other relations found by Emich. The presence of moisture had no influence on the spark length necessary for ignition. When inert gases such as nitrogen or carbon dioxide were added, the inflammability depended solely upon the partial pressures of the hydrogen and the oxygen present.

The work here described shows that ignition temperature and inflammability as measured by Emich do bear a simple relation to each other, and are in fact inversely proportional.

In comparing the results by the method described in this paper with the results obtained by other methods, the ignition temperature of detonating gas only can be discussed. The temperature found in this work is 819°. V. Meyer and co-workers found it to lie between 791° and 879° while Emich found 862° by enclosing the gas in sealed vessels and plunging them into baths of known temperature. Here evidently the whole mass of gas was not heated to the ignition temperature simultaneously. The heat passing through the walls of the vessel would cause catalytic action on the inner surface first, and in the time which, although perhaps very short, it would take the whole mass of gas to reach the required temperature, a certain amount of combination would have taken place. The water which is formed in this way, diffusing into the interior, might also affect the reaction. The pressure in the vessel would be diminished, perhaps below atmospheric pressure, the expansion due to the heating acting in the opposite direction. From the theory of the ignition temperature

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[1] Emich: Monatsh. 21, 1061.

developed by Professor Nernst, decrease in pressure would mean a slightly higher ignition temperature. Here we have a considerably higher ignition temperature. The amount of combination before ignition in these experiments is very indefinite, and the condition of the gas at the moment of explosion is entirely undetermined.

With regard to the ignition temperature as determined by passing the gas through a tube heated to a known temperature, Mallard and LeChatelier found an average of 823°. Other investigators obtained much higher values than this, due doubtless to the fact that the gas did not reach the temperature of the tube when less heat was employed in their determinations. Catalytic action and combination before ignition must act in these experiments as well, while the gas would be under atmospheric pressure all the time. The result found agrees very well with the result obtained here, a slightly higher temperature being found as the theory requires. It is surprising that the catalytic action of the walls has so slight an influence on the ignition temperature.

From the theoretical considerations, these ignition temperatures apply only to moderate volumes of gas, such as are generally worked with in the laboratory. With very minute or very large volumes, other conditions obtain, as shown in the theoretical portion of this paper.

THE EXPLOSION WAVE.

In order to produce an explosion wave, a gaseous mixture must be heated to a definite temperature, a constant velocity of propagation of the chemical reaction being then attained. In the explosion wave this temperature results from the progressive adiabatic compression of the gas, the velocity of the wave being constant when a certain compression and, consequently a certain temperature, is reached.[1] The absolute final compression for any gaseous mixture need not be a constant; only the ratio of the final to the initial pressures should be.

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[1] This theory of the explosion wave was first put forward by Mallard and Le Chatelier; Recherches expérimentales et théoriques sur la combustion des mélanges gaseux et explosives, Ann. mines—September to December, 1883. Recently the fact that the explosion wave is purely a hydrodynamical phenomenon has been clearly set forth by Nernst: "Physikalischchemische Betrachtungen über den Verbrennungsprogess in den Gasmotoren," pages 21-31.

In the work described in this paper, the ignition temperatures were reached by adiabatic compression. We have practically the phenomenon of the explosion wave in this compression, chemical action being produced by the rise in temperature brought about by adiabatic compression. We should then expect p_2/p_1 to be constant for any one mixture. This is found to be approximately the case from the tables on pages 19–22. The average values for p_2/p_1 are given here.

	Apparatus I.	Apparatus II.
$4H_2 + O_2$	46.1	48.2
$2H_2 + O_2$	36.3	36.9
$H_2 + O_2$	32.8	31.8
$H_2 + 2O_2$	......	33.5
$H_2 + 4O_2$	......	39.8

The mathematical theory of the explosion wave has been worked out by E. Jouquet in very complete form.[1] It is impossible to give even a general account of this interesting work here. His calculations of the velocity of the explosion wave for a number of reactions agree remarkably closely with the values found by Berthelot and by Dixon, especially when the approximate nature of some of the data which he was forced to use is taken into account. He also shows just how near the formulas of Berthelot and of Dixon for calculating these velocities approach the true ones, and why the results calculated from these agree in many cases with the experimental values.[2]

Some of the calculations of Jouquet may perhaps be applied directly to the results here obtained.[3] He puts forward two hypotheses with regard to the actual combination of the gases in the mixtures: first, "la combustion est nulle dans la quasi-onde de choc," and secondly; "cette combustion est notable." Not to enter into details, it may be stated that for the mixture $2H_2+O_2$, p_2/p_1 would be equal to 34.29 in the former case, and to 17.15 in the latter. Jouquet states expressly that this is true only after the wave has been set up and is moving with constant velocity, and not during the period of its formation. Perhaps he referred to the usual manner of setting up an explosion wave by slow preliminary combustion, and not to the method here described. At

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[1] E. Jouquet: "Sur la propagation des réactions chimiques dans les gaz," J. mathémat. 1905, 347, and 1906, 5.

[2] Second paper, page 76.

[3] Second paper, page 80.

any rate the value found experimentally is 36.6 which is very close to the value deduced by Jouquet from the first hypothesis.

In conclusion, I wish to express my thanks to Professor Nernst at whose suggestion this investigation was undertaken, for his interest and encouragement throughout the course of the work.

BERLIN, August, 1906.

THE POLARIZATION CAPACITY OF IRON AND ITS BEARING ON PASSIVITY.[1]

BY C. MCCHEYNE GORDON AND FRIEND E. CLARK.

Received August 29, 1906.

THIS paper contains an account of some measurements of the polarization capacities of iron electrodes. It was expected that a comparison of the capacity values in a number of different solutions would give some evidence for or against the oxide film explanation of passivity. As will be set forth below, the results found lead us to the conclusion that the oxide film theory is after all the correct explanation.

Finkelstein[2] measured the polarization capacity of iron in concentrated nitric acid by the same method that we have employed, with the same end in view, but came to the opposite conclusion. On the whole his capacity measurements, however, were not necessarily in conflict with the film theory, his main reasons for rejecting this theory being based on his measurements of the potentials of iron.

The method is that first used by Gordon,[3] at the suggestion of Nernst,[4] and later by Scott[5] and others in Nernst's laboratory. It is a comparison of the electrode capacity with that of a metallic condenser in the Wheatstone bridge, with a telephone receiver as the zero instrument. In most cases the method gives a sharp telephone minimum only for small measuring currents, near the limit of audibility of the telephone. In series with the metallic condenser it is necessary to have a variable resistance, in order to balance the resistance of the electrolyte, which is in series

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[1] Presented in abstract at the Ithaca Meeting of the American Chemical Society.

[2] Z. physik. Chem. 39, 91 (1902).

[3] Gordon: Z. Elektrochem. 3, 153 (1896); Wied. Ann. 61, 1 (1897).

[4] Nernst: Z. physik. Chem. 14, 622 (1894).

[5] Scott: Wied. Ann. 67, 388 (1899).