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STUDY ON THE EXPLOSIVE REACTION BETWEEN HYDROGEN AND OXYGEN.

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I. Introduction.

The reaction between hydrogen and oxygen has been investigated in detail by many workers, such as N. Semenoff and his co-workers[1], N. Hinshelwood and his co-workers[2], B. Lewis and von Elbe[3], and Haber and Alyea[4], etc. In this country W. Jono's[5] and R. Goto's[6] papers on this subject were published. Many workers discussed the reaction mechanism kinetically, basing on the analysis of the pressure-time curves of the reaction. The knall gas mixed in appropriate ratio reacts explosive or slowly by various methods of ignition. It is well-known that these reactions have two critical pressure limits of explosion above and below which no explosion occurs, and that a flame is observed in the explosive reaction. There are few who investigated the relations between the process of the reaction and the flame intensity. It is very interesting and may be useful for us to clarify their relations experimentally. The emission spectrum of the flame was studied by Bonhoeffer[7], and W. Jono[5], and as the results OH radical was found, but since the radical is found in the spectrum of water, it is not always considered that OH radical should be introduced in the mechanism of the reaction. In any way it is necessary to observe the reaction from different angles in order to clarify the reaction mechanism which appears simply, but in fact complicated.

According to the studies above mentioned, the combination between hydrogen and oxygen is one of the typical chain reactions and explained completely from the branching chain theory. But the relations between the explosion and the slow reaction remain in question. R. Goto[6] emphasizes that the chains initiate on the surfaces in both reactions from his experimental results and W. Jono[5] supposes that as the reaction velocity is accelerated near the critical pressure limit of

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1) N. Semenoff, *Chemical Kinetics and Chain Reactions*, 1935, Oxford.

2) C. N. Hinshelwood and A.T. Williamson, *The Reaction Between Hydrogen and Oxygen*, 1934, Oxford.

3) Lewis and von Elbe, *Combustion, Flames and Explosions of Gases*, 1934, Cambridge.

4) *Z. physikal. Chem.*, **B10**, 193 (1930).

5) *J. phys. Chem. Japan*, **9**, 1 (1935).

6) ibid., **16**, 101, 141, 152 (1942).

7) *Z. Elektrochem.*, **42**, 449 (1936).

explosion and at last becomes infinite, the relations between the explosion and the slow reaction are continuous. However, from another point of view, it may be supposed that the surface reaction and the gaseous reaction can occur independently and simultaneously. The relations between the pressure change and the flame intensity were investigated in this paper.

II. Experimental Methods.

The experimental apparatus was the same one that W. Jono[5] used in studying the explosive reaction between hydrogen and oxygen. The pressure change in the reaction was recorded through the three elements type's electromagnetic oscillograph made by Yokogawa by means of the mica-membrane monometer of an electric condenser, whose capacity varied with the change of pressures and whose motion was calibrated by desired pressure before and after every experiment. The elements were of D–type.

The photo-cell, NEC V–3–C, was used to record the intensity of a flame produced in an explosion, which was emitted from the tale of the reaction vessel and connected to the oscillograph. Its connection is shown in Fig. 1.

The reaction vessel made of Terex glass has a volume of about 113 cc and a diameter of 3 cm.

Commercial electrolysed hydrogen and oxygen were used and purified through the Pt–asbestos heated at 450°C. The temperature of the electric furnace was measured by means of a quartz mercury thermometer interposed in it, or a milli-voltmeter with a Pt–Rh thermo-couple.

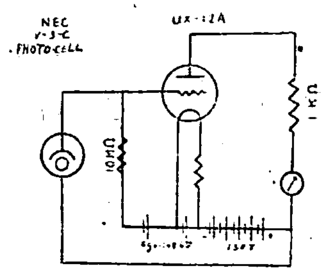

Fig-1

The ratio of a mixture of hydrogen and oxygen was almost 3 : 1, because this ratio was the most convenient for experiments. The initial pressures were adjusted to explode at 550°C within the explosion peninsula of this ratio in a mixture of hydrogen and oxygen.

The experimental procedure was as follows: while hydrogen and oxygen heated independently at 550°C in the reaction vessel were abruptly mixed by breaking an inner vessel, the oscillograph moved automatically.

III. Experimental Results.

a) Relation between the pressure change-time and the flame intensity-time curves.

Fig. 2 (a) shows a simultaneous record of the typical pressure change-time curve and the flame intensity-time curve, where A is the former, B the latter, and C the time-mark.

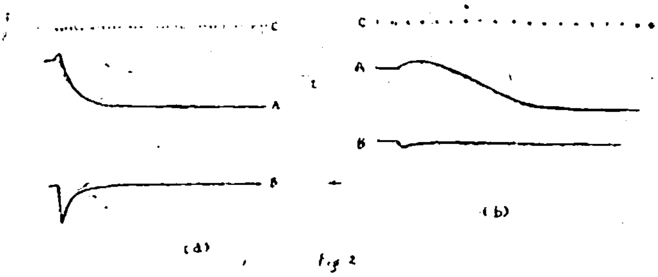

Fig 2

These pressure change-time curves in this experiment contain simultaneous change due to the molecular numbers and the reaction heat in the reactions, and the flame intensity-time curves show purely change of light intensity. As the both curves show, the changes of the pressure and flame intensity correspond to each other: the flame intensity increases with the pressure increase by the reaction heat, and gradually decreases with the pressure decrease. Compared with them. in more details, 1) the point of the initiation of the pressure increase and the flame agrees completely with each other, on the contrary the time required to their maximum points does not strictly correspond, but the maximum point of the pressure-time curve comes later: 2) the flame intensity decreases with the pressure decrease: with the pressure decrease: 3) both slopes of the increasing curves are steeper than those of the decreasing ones. In order to ascertain the results above obtained the curve taken by about three folds of rotation velocity of the film-drum is shown in Fig. 2 (b). Both curves clearly correspond to each other. But at the maximum of the pressure the flame intensity curve is inclined to show decrease in its light intensity, and other parts are analogous.

The flame intensity curve falls slowly according as the pressure decreases remarkably, and the former returns to the zero-point after about 1/12 sec., though the latter continues to change. Thus it was experimentally shown that during explosion the light of the flame continued to be emitted. If the explosion finished at the maximum point of the pressure rise, the light of the flame would not appear at the part of the pressure decrease. However, it seems that there happened no reaction recognized in the pressure-time curve after the light had disappeared, but very slow pressure decrease was observed. This fact means that the reaction is still proceeding after the explosion has finished. Thus it is supposed that in this reaction the explosion and the slow reaction proceed simultaneously.

b) The reaction velocity in the part of the explosive reaction.

The cooling velocity should be taken into account when the reaction velocity of the explosive reaction is calculated from the pressure rise by the reaction heat. Assuming that the heating velocity constant is equal to the cooling constant in the pressure-time curve, that the gases of the reaction are ideal gases, and that water is not yet produced in the primary reaction, the temperature rise which corresponds to the pressure at that moment is calculated from the following expression:

$$\triangle T=\triangle P\cdot T/P \qquad (1)$$

where $\triangle T$ is the temperature rise, $\triangle P$ the pressure increase, T the temperature of the reaction vessel, and P the initial pressure. From the calculated values of $\triangle T$ the relation between $d\triangle T/dt$ and $\triangle T$ is a straight line, as shown in Fig. 3: that is, the following equation,

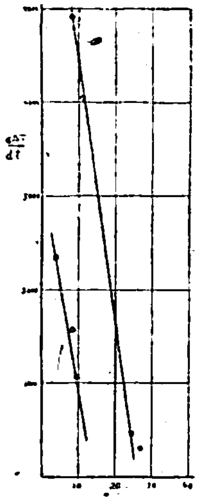

Fig. 3

$$d\triangle T/dt=k\triangle T \qquad (2)$$

where k is the heating constant. From the inclination of this straight line k's are found to be 224 and 259.4. Therefore the mean value of k is 241.7. In this equation the heating velocity is proportional to $\triangle T$. The number of mole of water to be produced, corresponding to $\triangle T$, is shown in the following equation,

$$\triangle T(C_{vH_2}n_{H_2}+C_{vO_2}n_{O_2})=QN_{H_2O} \qquad (3)$$

where C_{vH_2} and C_{vO_2} are the molecular specific heat of hydrogen and oxygen in constant volume: n_{H_2}, n_{O_2}, and N_{H_2O} the number of mole of hydrogen, oxygen and water at the moment respectively; Q is the heat of formation per mole of water. Differentiating (3) by t, that becomes

$$\frac{dN_{H_2O}}{dt}=\frac{(C_{vH_2}n_{H_2}+C_{vO_2}n_{O_2})}{Q}\frac{d\triangle T}{dt} \qquad (4)$$

Taking the cooling velocity into consideration in (4) and calibrating, the following equation is obtained

$$\frac{dN_{HO_2}}{dt}=\frac{(C_{vH_2}n_{H_2}+C_{vO_2}n_{O_2})}{Q}\left(\frac{d\triangle T}{dt}+k\triangle T\right) \qquad (5)$$

where k is the cooling constant.

The reaction velocity was calculated from (5). Strictly speaking, the number of moles of hydrogen and oxygen to decrease with the formation of water is to be calibrated in (5). The reaction velocity below the zero point of the pressure

Table. 1 (a). $T=550°C$, $P_i=57.3$ m.m Hg $H_2:O_2=3:1$

t (1/120 sec.)	$T°C$	$d\triangle T/dt$	$d\triangle T/dt+k\triangle T$	$dN/dt\times10^6$
0.3	10.8	4320	6940	80.50
0.5	19.1	4980	9200	106.72
0.7	24.4	3180	9077	105.29
1.0	11.5	5160	7940	92.10
1.2	0	6900	6900	80.04

(b)

t (1/120 sec.)	P_{H_2O}	$\triangle P$	N	$dN/dt\times10^6$
1.5	0.18	0.18	—	121.2
2.0	0.60	0.42	0.941	225.8
2.5	0.96	0.36	0.806	193.4
3.0	1.20	0.36	0.806	193.4
3.5	1.52	0.32	0.717	172.1
4.0	1.84	0	0.717	172.1
5.0	2.26	0.42	0.941	112.9
6.0	2.52	0.26	0.582	69.8
7.0	2.72	0.20	0.448	53.8
8.0	2.82	0.10	0.224	26.9
9.0	2.96	0.14	0.314	37.7
10.0	3.0	0.04	0.090	10.8
11.0	3.04	0.04	0.090	10.8
12.0	3.05	0.01	0.022	2.7
13.0	3.06	0.01	0.022	2.7
14.0	3.07	0.01	0.022	2.7
15.0	3.072	0.002	0.004	0.5

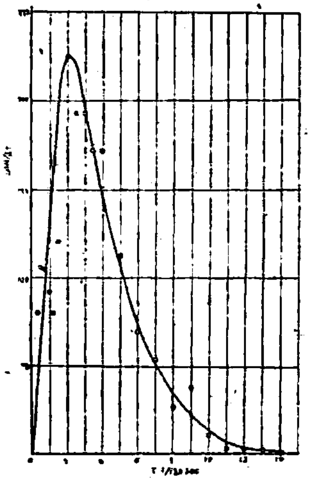
Fig. 4.

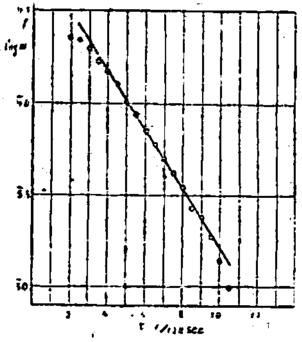

Fig. 5.

was calculated without any calibration. Table 1 and Fig. 4 showed these results. Kowalsky[8] reported that at the initial stage an induction period was recognized, but in the present experiments any induction period was not observed. In the case of Kowalsky's experimental method a cold mixture of reaction gases was introduced to the reaction vessel. Therefore, if a heated mixture had been introduced, any induction period would have not been observed. The reaction velocity gradually decreases after it has suddenly reached a maximum.

Now if log ω is plotted against the time t where ω denotes the reaction velocity, a straight line is obtained after the maximum of ω, as shown in Fig. 5, that is,

$$2.3 \log \omega = kt \quad \text{or} \quad \omega = e^{-kt} \qquad (6)$$

where k is the constant. This expression corresponds to N. Semenoff's formula, and also the relation between the flame intensity and time. But the maximum point of the pressure displaces from that of the flame. As shown in Fig. 6, if $d\Delta I/dt$ is plotted against ΔI which denotes the photo-intensity change after it has reached the maximum, a straight line is obtained:

$$d\Delta I/dt = k\Delta I \qquad (7)$$

Integrating (7)

$$\ln \Delta I = kt \qquad (8)$$

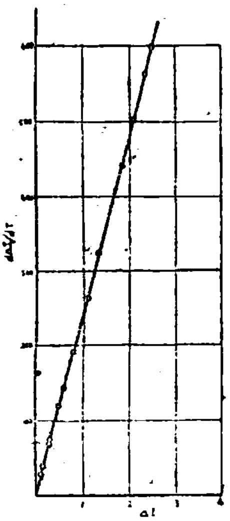

Fig. 6.

As for the displacement of the maximum, it seems that there exist following suppositions: i) if the pressure and photo-intensity change completely correspond to each other, the former has essentially a time lag; ii) owing to construction of the apparatus itself a time lag appears in the pressure change. Now the time taken for photo-intensity to reach a maximum is about 1/240 sec., while it is about 1/60 sec. in the pressure increase. It may be rather considered that the lag is ascribed to the construction of the manometer used. Thus the reaction velocity and the photo-intensity completely correspond to each other.

c) Mean length and numbers of the chain.

Photo-intensity of the flame reaches a maximum at t_m sec., and disappears at t_0 sec. Now the mean time required to produce one water molecule τ is t_0/N,

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[8] *Phys. Z. d. Sowjetunion*, 4, 723 (1933).

where N is the number of water molecules produced at t_0 sec. This shows the apparent mean length of the chain. Therefore, the numbers of the chain produced by t_m sec. are t_m/τ, as shown in Table 2, which are almost of the same order regardless of the ratio of the mixtures. This fact means that the probability of the production of activated particles is constant regardless of the ratio of the mixtures in the primary reaction.

Table 2.

Exp. No.	t_m sec.	t_0 sec.	N_{H_2O} at t_0 sec.	$\bar{\tau}=t_0/N$	$t_m/\bar{\tau}$	$O_2 : H_2$
1	1/240	1/15	$62.5\times6.06\times10^{16}$	1.76×10^{-19}	2.4×10^{15}	1 : 3
2	1/360	5.7/120	$35.5\times6.06\times10^{16}$	2.21×10^{-19}	1.3×10^{16}	1 : 2.8
3	1/300	5.3/120	$53.0\times6.06\times10^{16}$	1.38×10^{-19}	2.4×10^{16}	1 : 3.4
4	1/300	17/120	$60.0\times6.06\times10^{16}$	3.89×10^{-19}	9.9×10^{16}	1 : 4.1
5	1/300	9.6/120	$120.0\times6.06\times10^{16}$	1.10×10^{-19}	3.0×10^{16}	1 : 4.5
6	1/300	9.6/120	$102.0\times6.06\times10^{16}$	1.21×10^{-19}	2.6×10^{16}	1 : 3.9
7	1/300	9.6/120	$71.50\times6.09\times10^{16}$	1.85×10^{-19}	1.8×10^{16}	1 : 5.1

IV. Conclusion.

In the explosion the time taken for the flame to appear and disappear is about 1/12 sec., but after the explosion the reaction slowly continues to proceed. The residual pressure of the mixture is enough to explode again, but no explosion is observed. If fresh hydrogen or oxygen is introduced into the reaction vessel, the explosion will occur again. The number of the water molecules produced when the rate of the reaction reaches a maximum is of the same order regardless of the ratio of the mixtures. The ΔI–t and ΔP–t curves correspond completely to each other. These facts may suggest that the explosion and the slow reaction will probably occur simultaneously and independently. In other words, the explosion is purely a reaction in the gaseous phase, and the slow reaction proceeds on the surface. The ΔP–t curves obtained in the experiments are superposed by the pressure changes of both reactions and the ΔI–t curves show the process of the explosion.

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