SPONTANEOUS COMBUSTION OF HYDROGEN

Translations from articles by
W. Nusselt and by P. Pothmann

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NOTE.—Destruction of Zeppelins, by ignition of hydrogen while filling, formed the occasion of these experiments. Nusselt's conclusion that electrification may be caused by dust carried along in the gas, as well as Pothmann's conclusion that suspended moisture will have the same effect, have been verified by recent experiments in the Physical Laboratory of the Bureau of Mines at Pittsburgh.
It is shown by the author's experiments that hydrogen which escapes to the atmosphere through openings in the system may burn spontaneously if it contains dust. Purely thermal reasoning cannot account for the combustion. It seems to be rather an electrical ignition. The dust particles in the escaping hydrogen were charged by friction against the walls at the vent. It was clearly shown by an investigation (described below) that the visible discharge at the end of such vent caused an electrical ignition of the explosive gaseous mixtures formed by diffusion. In order to determine whether the cause of the spontaneous ignition was thermo-mechanical, thermo-chemical, or thermo-electrical, the experiments
listed in this paper were performed.

(1) In a first series of experiments, the effect of friction was studied in bringing about combustion. Gas under pressure was allowed to flow through a sharp edged nozzle and then through an opening 3 millimeters in diameter. Gaskets of iron and wood were used. Pressures were varied. Results were negative. (Fig. 1.)

(2) In a second series of experiments, the friction of the escaping hydrogen was increased by the addition of fine particles (ferric oxide, ferrous hydroxide, and mixtures of sand and iron filings). Chamber "B" (Fig. 1), was the mixing compartment. "B" was charged through opening "a". Gas was admitted through a right angled tube, "b", stirring up the particles. The gas-solid mixtures escaped as in Experiment 1. Results negative.

(3) In a third series of experiments, the above arrangement was modified by omitting the 3-millimeter opening but
forming a vent ("technical leak") between flange and gasket.

Various types of gasket were tried. Rubber was used first, inasmuch as it was believed that this might encourage spontaneous ignition. Results were negative. "Klingerite" was tried next, in the same apparatus. Results were positive. These could be reproduced and made more pronounced by tapping the mixing chamber and stirring up the particles within. Upon ignition, the hydrogen gas burned with a yellow flame. This was due to the suspension of ferric oxide. Positive results were also obtained when lead was used as a gasket, and also when no gasket was used.

Another series of experiments were carried on with the above flange arrangement, using rough particles (ferrous oxide, ferrous hydroxide). Ferrous oxide gave positive results; ferrous hydroxide and emory gave negative results.
From the above it is seen that the ignition is not entirely thermo-mechanical, inasmuch as such rough particles as emory give negative results; nor entirely thermo-electrical, inasmuch as ignition took place with the flange uninsulated. The author thought that the ignition might be thermo-chemical in nature.

The following assumptions were, thereupon, made by the author, namely that:

(a) Heat is developed at the vent of the apparatus due to friction.

(b) Atmospheric oxygen diffuses into the stream of hydrogen and is set off by the heated catalyst, \((\text{Fe}_2\text{O}_3)\).

(c) Ferric oxide is partially reduced, giving up some of its oxygen, forming an explosive mixture with the hydrogen in the stream. This might also be set off by the heated catalyst.

(d) Combustion may be brought about by the formation of pyrophoric iron. This reaction usually takes place when hydrogen is passed over iron oxide at about 500°C. (Pyrophoric iron has the property of igniting immediately upon being exposed to the air.

To test the above assumptions, the following experiments were performed.
A porcelain crucible containing some ferric oxide was placed into a spherical bomb. An explosive mixture of hydrogen and oxygen under 10 atmospheres pressure was introduced. No change was noticed. The same was left standing for several weeks at room temperature. No change took place. The temperature was then raised to 100°C. No change was noted.

The apparatus consisted of two hemispherical steel shelves, pressure gauge, bath, and thermometer.

In Experiment 2, a cylindrical bomb was used. This apparatus was charged with ferric oxide and was evacuated. It was then tested for leaks by admitting the explosive gaseous mixture (an excess of hydrogen was used) under several atmospheres pressure and allowing it to stand for some time. If no drop in pressure was observed, no leak. Tests were made at 200°C, 300°C, and 360°C. Upon heating, there was
a gradual rise in pressure due to an increase in temperature. This rise continued until a maximum was reached. The pressure dropped slowly then, due to combustion, until it remained constant. At this point, all the oxygen had been consumed. At 200°C, 9 hours was necessary for complete combustion. At 300°C, combustion took place ten times as fast. In these experiments, combustion took place, but without any violent explosion.

The apparatus used consisted of a steel tube soldered at one end, a pressure gauge, needle valve, heating coil, and a bath of some liquid which could be raised to at least 450°C. (Fig. 4.)

(3) In a third series of experiments, the effect of moving the hydrogen against the ferric oxide, or moving of the ferric oxide against the hydrogen was studied to see whether such action would increase the catalytic effect of the catalyst (Fe₂O₃).
A rotating calorimeter was used, (Fig. 5), which consisted of a horizontal tube set on bearings about which it could be rotated. The tube was wound with an electric coil. A pressure gauge was attached to one end of this tube. Within were strips of sheet metal to stir up contents. Upon rotating the apparatus and increasing the temperature to 400°C., the mixture was gradually consumed but not explosively.

From this third series of experiments it follows that the spontaneous ignition of hydrogen was not due to the catalytic action of ferric oxide.

(4) A series of experiments was then carried on to see whether pyrophoric iron might not cause such ignition. It was believed that this substance formed at the vent of the flange, especially in cases where ignition took place. An "Iron-cap" arrangement was set over a small "Ignition-head", which is attached to one end of the tube. (Figs. 7 to 10). To the cap was
attached a tube 20 meters long and 3/4" in diameter. The
"Ignition-head" arrangement was removed first from position
and a hydrogen-dust mixture was swept through the apparatus.
No spontaneous combustion took place. The "Ignition flange"
was next set into position to test whether efflusion into the
air would cause ignition. Combustion ensued. The cap and
long tube were then set into position and an explosive gaseous
mixture was sent through the system, but the anticipated effect
did not take place. If the cause of the combustion was due to
the formation of pyrophoric, the hydrogen-pyrophoric mixture
should have ignited spontaneously upon reaching the atmosphere
after its journey through the long tube. This was not the case.

(5) However, in running another test on the apparatus, in the dark
in Figure 1, the author noted a dull beam of light in the path
of the gas jet. This was increased upon forcing out some more-
particles along with the gas. Wire mesh was then placed about the flange. This did not prevent the illumination. The author modified this apparatus with the addition of a double-right-angled copper tube brought to a point (Fig. 11). The rod was so arranged that the point could be set in any desired position. In these experiments, the point was set 20 millimeters from the vent in the flange. With this rod in place, sparks were noted, but no burning. With the rod out of position, there was combustion.

Some authorities believe that explosive mixtures may be ignited by brush discharges. In order to study this question, the author carried on additional experiments, using a Hempel explosion-pipette (Fig. 13). One platinum wire was fused into a glass bulb, terminating in the center of it. This wire was connected to one of the poles of a Toepler machine; the other was immersed in the quicksilver of a leveling vessel. After exciting the machine a "brush-discharge" appeared at the end of the platinum wire. If
the pipette had previously been filled with an explosive mixture, a stream of it might have been permitted to escape without producing ignition. Ofttimes, however, an ignition did take place. This was due to the "self-induction" of the streaming jet of gas, which produced electrical stress which resulted in the formation of sparks.

The above experiments (1 to 5), proved that ignition was not due to thermal, thermal-chemical, or pyrophoric conditions, but due to electrical charges.

It was further attempted to find out whether ionization has any effect upon the ignition of an explosive mixture. For this purpose a thorium compound was placed in the apparatus (Fig. 3). An explosive mixture was then passed into the chamber. The thorium preparation produced an ionizing effect on the gaseous mixture. After allowing the mixture to stand for some time it
was ignited by a spark from an induction coil. The actual lapse of time of the combustion was noted by means of an optical indicator. Ionization apparently did not increase the velocity nor the capacity for ignition.

The results of the entire investigations can be summed up briefly in the following: (1) Pure hydrogen passing through a vent in a tube cannot be ignited spontaneously; (2) Ignition can be brought about only if small dust particles are admitted with the hydrogen. In this movement the dust becomes electrically charged by friction. At the vent it is discharged, and ignition ensues.

In conclusion the author adds the following practical suggestions:

In order to prevent spontaneous combustion of hydrogen when used in balloons, pains should be taken to have it dust-free. This can be accomplished to some extent by the use of filters.
Most particles found in the system consist mainly of rust (Fe₂O₃). In ordinary hydrogen cylinders of a few liters capacity about 300 g of rust was found. This is very remarkable inasmuch as rust will form only when water and simultaneously with oxygen come in contact with the iron. In an atmosphere of hydrogen under high pressure rust may form with water alone.

The moisture in the hydrogen may be taken out by inserting a portion of the line in a freezing mixture.

The safest path to follow in order to avoid spontaneous combustion is to use helium instead of hydrogen.
Fig. 1.
Ignition flange.

Fig. 2.
Mixing chamber.

Fig. 3.
Explosion bomb.

Fig. 4.
Oil thermostat.

Figs. 5, 6.
Rotating calorimeter.

Figs. 7-10.
Small ignition head with cap.

Figs. 11, 12.
Large ignition flange and ground wire.

Fig. 13.
Hempel explosion pipette.

Nusselt’s “Spontaneous Combustion of Hydrogen.”
THE SPONTANEOUS COMBUSTION OF ESCAPING HYDROGEN

by

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AN ABSTRACT

The author was influenced, in performing the work described in this paper, by a series of similar experiments performed with hydrogen by Russelt. The work of the latter convincingly proved that the spontaneous ignition of hydrogen traces back to the operation of an electric field. Pothmann, working independently, tackled the proposition from another angle, namely, "Moisture Electricity". No dust was used in his experiments. The experiments were performed in the dark.

(1) A steam jet which escaped under pressure into the air was found to be negatively charged. The maximum charge was located at the center of the jet, at some distance from the orifice. The charge, the potential of which drops with a dropping pressure, seems to be bound by the presence of droplets of water. Dry steam is uncharged. The electric field may be examined and
demonstrated by means of an electroscope set at several meters distance from the jet.

(2) Carbon dioxide escaping from a cylinder likewise shows an electric charge.

(3) Dry compressed air was then allowed to escape through a flange and then through a high pressure tube into the air. The initial pressure of 200 atmospheres was dropped to 80 atmospheres at the point of discharge. There was no sign of an electric field. No dull light was noted in the dark.

(4) Finally a mixture of gas and steam was allowed to flow through a flange. The potential between the center of the jet and the ground was measured by means of "spark-length". (Fig. 1). The steam valve \( v_1 \) and the gas valve \( v_2 \) were opened and a mixed jet of air and moisture was allowed to escape through the flange. After closing the steam valve the proportion of moisture in the gas-jet mixture was cut down and the proportion of air was increased until finally nothing but air escaped. A constant pressure was maintained throughout.

**Results.** The potential of the mixed jet, at a distance of 100 millimeters from the discharge vent, is:

(a) Higher than for pure moisture.
(b) A function of the discharge pressure.
(c) Of the same order of magnitude as pure water (at the same discharge pressure), even when the water content is small. (At 5 atmospheres pressure, the voltage is about 1000 volts).

(d) Independent of the chemical nature of the mixed gases (air and hydrogen were used).

(5) Three liters of water were poured into seven steel cylinders (40 liters capacity). Into each of these compressed air was admitted, each under a different pressure. The cylinders were set in an air bath and heated to about 200°C so that the water within was vaporized. After opening the cylinder valves a mixture of air and dry steam escaped. The potentials were measured.

Result.— No electric field was noted in any of the above combinations.

(6) For the following experiments a gas cylinder wagon (14 cylinder type) with a capacity of 3000 cubic meters was used. Fig. 2 (grounded) shows one of the two sets of seven steel cylinders which were filled with gas to a pressure of 200 atmospheres. Each cylinder has a valve by means of which the gas could be admitted to a manifold, to which was attached a "T" shaped fitting which served as a discharge vent. The cylinder was partly filled with water and then a pipe admitted gas into it, until its internal pressure was brought up to 150 atmospheres. The grounded wires as well as a wire
d₁, on account of the strong electric field developed by the escaping jet were suspended by means of porcelain insulation pieces in the path of gas stream. A spark measuring device F was attached to d₁. Several valves v₁ and a water valve v₂ were opened. The air which had been moistened was allowed to escape. The addition of water could be controlled very well by the valve arrangement. The experiments were performed at night.

Results.—The observations may be summarized as follows:—

(a) An electric charge appeared in the gas-jet mixture.
(b) At low escaping pressures (2 atmospheres) with a very slight addition of water, the top end of the grounded wires showed a faint light.
(c) At higher pressures (10 to 20 atmospheres) the light was more pronounced, and small sparks shot across rod f. —
(d) At still higher pressures (40 atmospheres) a dull light appeared at the orifice of the ejector.
(e) At 80 atmospheres the luminous beams became very intense, increasing in length to about 50 centimeters. They were of striated formation, bent towards the jet. (Fig. 3). After closing the valve the striation disappears. This dull light does not have the power to ignite hydrogen.
(f) Electric sparks 70 mm in length were developed in the afore mentioned tests.

(7) Wires were so placed in the gas jet (Fig. 4) that sparks could be produced. With this arrangement escaping hydrogen could be ignited.
(8) Increasing the temperature of the water gave an increase in the intensity of the spark until at a temperature of about 100°C, an extremely strong electric field was developed. The relationship between the temperature and electric charge of the jet at various discharge pressures was studied. The discharge pressure at the different temperatures was so regulated that the spark was maintained at a constant length of 3 millimeters. Such experiments were carried on with hydrogen and air, working on the assumption that the electrical phenomenon was independent of the nature of the gas.

Points A₀ and A₁ and A₂ Fig. 5 represent hydrogen. A₃ and A₄ represent air. The curve shows that the potential varies with the temperature and discharge pressures but is independent of the nature of the gas.

Results Fig. 5 shows that escaping gases, especially hydrogen, produce intense electrification at low pressures and high temperatures if water or vapor is present, on the other hand at high pressures and low temperatures, the danger of spontaneous combustion is especially great if water or ice is mixed with hydrogen.

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Fig. 1
Electric charge of a gas-moisture mixture

Fig. 2
Electric charge of a gas-water jet

Fig. 3
Dim light at orifice

Fig. 4
Ignition of hydrogen in its own electric field

Fig. 5
Graph of constant potential (1000 volts) of an escaping water-gas mixture.