

## THE MECHANISM OF THE UPPER LIMIT OF INFLAMMATION OF ELECTROLYTIC GAS MIXTURE.

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It is well known that the development of the chain theory is very closely connected with the phenomena of the upper and lower limits of inflammation. The velocity of the chain reaction  $w = \frac{n_0}{1 - \alpha}$  can be constant only when  $\alpha < 1$ . With  $\alpha \geq 1$  the velocity of the chain reaction automatically grows larger and leads to an explosion. In cases of very small  $n_0$  the transition from practically no reaction at all to a very rapid reaction is a very sharp one.  $\alpha$  is a function of the pressure  $p$  of the gas mixture. If  $\alpha$  grows with  $p$ , reaches a certain maximum and then again diminishes, then we have two pressure limits,  $p_1$  and  $p_2$ , with  $\alpha(p_1) = 1$ , and  $\alpha(p_2) = 1$ . This means that the velocity of reaction being immeasurably small at  $p < p_1$  and  $p > p_2$  becomes infinitely large at  $p_2 > p > p_1$ . That is the theory of the upper and lower limit of inflammation as given by Semenoff<sup>1</sup> and Hinshelwood.<sup>2</sup>

The first growth of  $\alpha$  with pressure was explained very well by the breaking-up of the chains on the walls of the vessel. The theory of the lower limit was given by Semenoff and proved by several experimenters for different reactions. It was much more difficult to explain the diminution of  $\alpha$  at further pressure growth. Hinshelwood<sup>3</sup> and later Semenoff<sup>4</sup> supposed that this is connected with the breaking-up of the chains in the gas volume. By a certain hypothesis about the mechanism of reaction the probability of the break-up of chains in the gas volume grows at large pressures, and therefore  $\alpha$  diminishes as the pressure increases.

F. Haber and N. Alyea<sup>5</sup> have proved that in the case of the reaction  $H_2 + O_2$  the chains begin on the walls of the vessel. But not all kinds of walls can be initial centres of reaction. Aluminium, for instance, is not capable of serving as such, and therefore in aluminium vessels there occurs no inflammation at all of  $H_2 + O_2$  at low temperatures.

Haber and Alyea concluded, as is known, from their experiments that the upper limit is not connected with the nature of the gas, but only with the properties of the surface. At pressures corresponding to the upper limits there occur some changes in the gas adsorption on the walls, so that these become incapable of further production of initial

<sup>1</sup> *Z. physik. Chem.*, **1B**, 192, 1928.

<sup>2</sup> *Proc. Roy. Soc.*, **122**, 1929.

<sup>3</sup> *Ibid.*, **122**, 610, 1929.

<sup>4</sup> *Z. physik. Chem.*, **6B**, 307, 1930.

<sup>5</sup> *Ibid.*, **193**, 10, 1930; *Naturwiss.*, **441**, 1930.

centres. In several articles, Hinshelwood<sup>6</sup> argues against such a conclusion, and points out several indirect data which are in contradiction to the point of view of Haber and Aleya, and seem to prove the conception of Hinshelwood and Semenov.

Haber and Oppenheimer,<sup>7</sup> on mixing with oxygen a stream of hydrogen that has been passed over hot tungsten and therefore contains atomic hydrogen, observed inflammation of the mixture at temperatures much lower than that of self-inflammation. But they did not observe in this experiment the phenomenon of the upper limit. It seems, therefore, that this phenomenon vanishes when there is a due number of artificially generated initial centres (in this case hydrogen atoms). This experiment seems to prove the correctness of the theory of Haber and

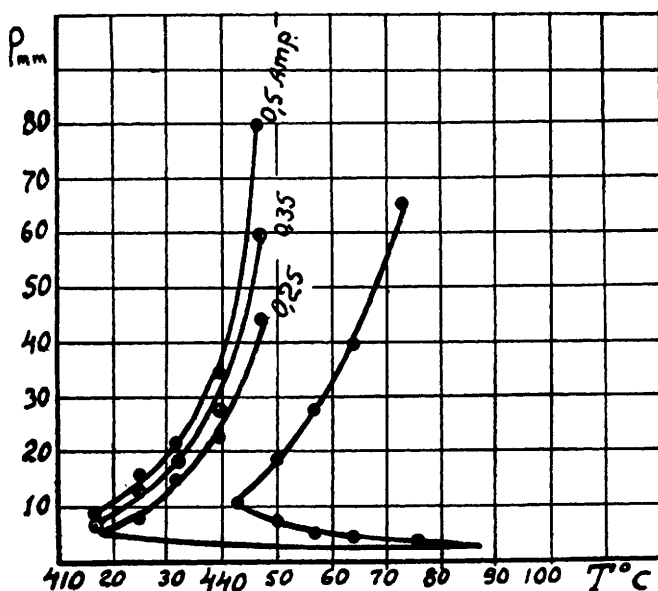


FIG. 1.

Aleya. But the last experiments which we made in Leningrad show just the contrary.

A discharge tube, containing hydrogen at pressures of about 0.4 mm., was heated in a furnace. After passing the discharge through the tube for several seconds (the concentration of H-atoms was about 10-50 per cent.) it was turned off and by a quick turn of the stopcock the mixture,  $H_2 + O_2$ , at a certain pressure, was let in. With this arrangement the region of inflammation of  $H_2 + O_2$  in mixtures containing a constant amount of hydrogen atoms was studied. The results received (see Fig. 1) show that the presence of hydrogen atoms enlarges the region of inflammation but does not change its characteristic form (that of a peninsula). The upper limit remains very sharp, with increase of the current, *i.e.*, with increase of the H-atom concentration the peninsula grows larger, but not very much so. We suppose that the discrepancy of our results with those of Haber and Oppenheimer is connected with the fact that

<sup>6</sup> *Proc. Roy. Soc.*, **130A**, 670, 1931.

<sup>7</sup> *Z. physik. Chem.*, **16B**, 773, 1932.

in their experiments the concentration of hydrogen atoms increased with the hydrogen pressure.

In agreement with others we found no self-inflammation when the surface of the discharge tube was covered with aluminium. But in presence of H-atoms there occurred an inflammation, and an upper limit was observed (Fig. 2). This proved that we observed not a surface effect but a volume effect.

We have performed analogous experiments with ions as initial centres. A stream of the mixture  $H_2 + O_2$  passed at first an electrodeless discharge, and then entered a long heated tube. By the stream method

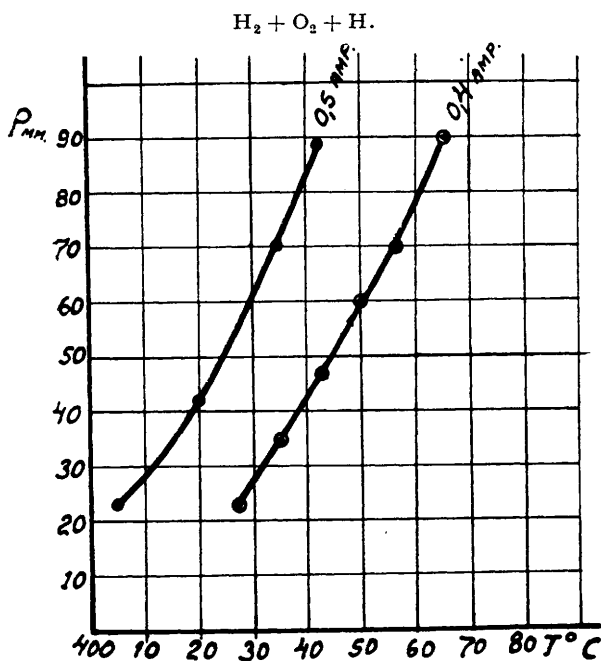


FIG. 2.

in the same manner as the experiments of Haber and Oppenheimer.<sup>9</sup>

In the same apparatus, but without a discharge, we performed some further experiments. At a given pressure of the stream we increased the temperature until there occurred an inflammation and a stationary ignition region was obtained. If the ignition took place at low pressures, the flame heated the gas only to a few tens of degrees. This could be determined by calculation as well as directly with a thermo-couple,<sup>10</sup> which was placed in a thin capillary glass tube in the ignition region. While continuing to let the burning stream go we lowered the temperature of the oven. The temperature of the burning region also decreases. At last the flame went out at a certain temperature of the burning region. Using this fact we were able to determine the dependence of the temperature of extinction of the flame upon the pressure. Fig. 4 shows the curve of inflammation (A) and of the extinction (B).

<sup>8</sup> Kowalsky, *Z. physik. Chem.*, **11**, 56, 1930.

<sup>9</sup> *Z. physik. Chem.*, **16**, 773, 1932.

<sup>10</sup> Dubowizky, *Physik. Z. Sowjetunion*, **1**, 586, 1932.

the inflammation region was determined in absence and in presence of the discharge.

We see from Fig. 3 that the inflammation region has become larger, but has conserved its form. The upper limit is seen sharply. (The curve I., the region of self-inflammation, the region II. of inflammation in electrical discharge.)

The form of the curve in the case of inflammation by a condensed spark<sup>8</sup> can be explained

We see that the second curve has a much larger area than the first but is of the same form. The upper limit exists not only for the inflammation, but also for the extinction of the flame.

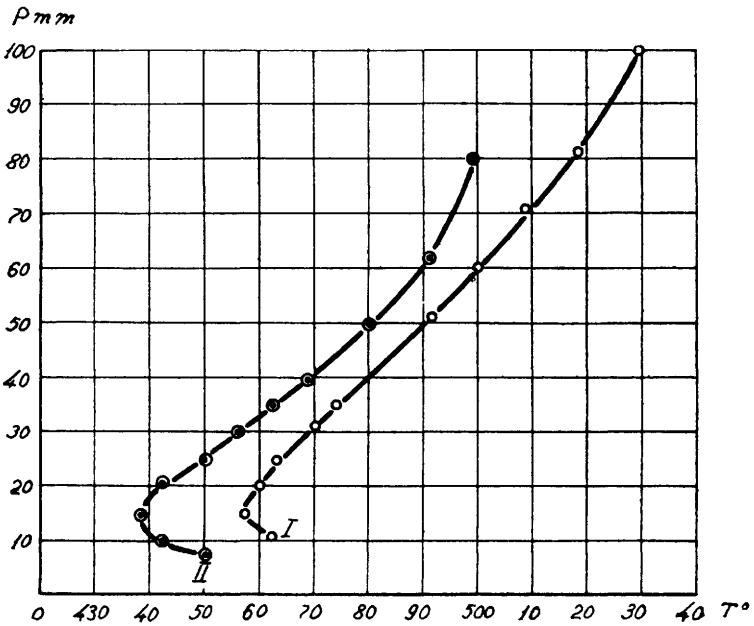


FIG. 3.

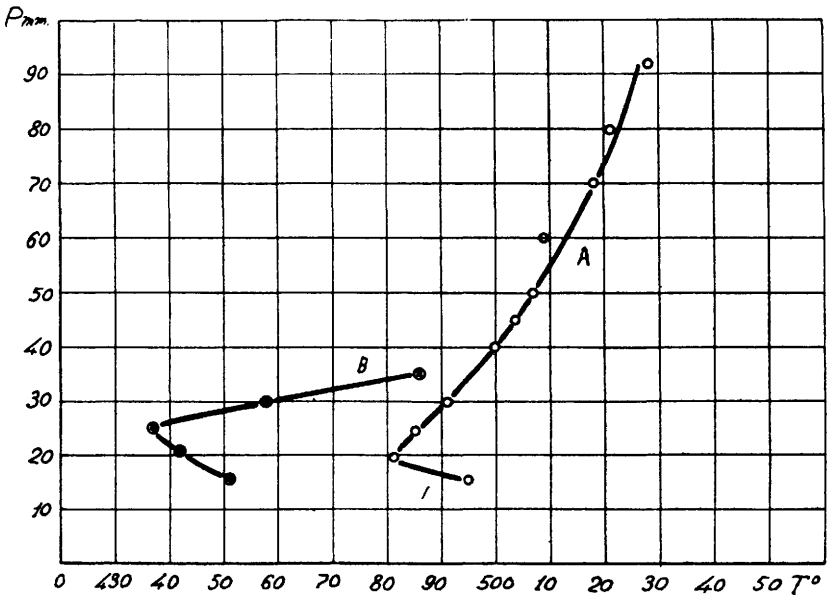


FIG. 4.

It seems to us that all these data prove finally the fallacy of the point of view of Hinshelwood and Semenov. It must be said, however, that the inflammation limits depend in some way upon the number of initial centres. The chain theory of inflammation has to be restricted, namely,  $\alpha$  must itself depend upon the number of active centres. In other words, we must include in the theory the interaction of the chains.<sup>11</sup>

We have now begun experiments on the inflammation of  $H_2 + O_2$  by atomic oxygen. Atomic oxygen seems to act much more strongly than atomic hydrogen. Immeasurably small concentrations of O are enough to lower the inflammation temperature 80-100 degrees. The lower limit, which is very low for high  $T$ , increases quickly for  $T$  about  $420^\circ C$ . In our experimental arrangement we could not determine the upper limit, but the form itself of the curve (Fig. 5) shows that there

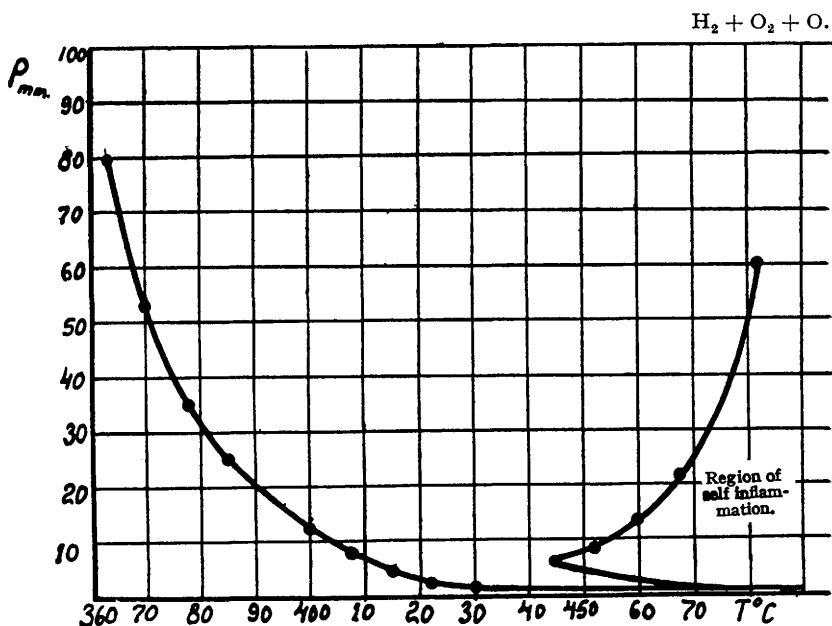
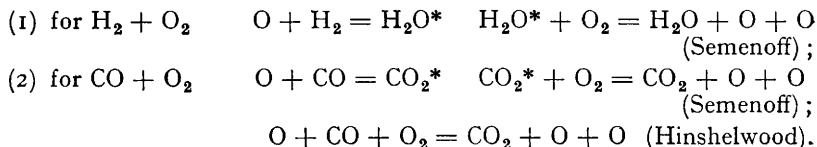


FIG. 5.

exists an upper limit. Such a strong action of O-atoms seems to prove the validity of the hypothesis first proposed by Semenov<sup>12</sup> and later by Hinshelwood,<sup>13</sup> that the mechanism of the chain development inside the peninsula of inflammation is

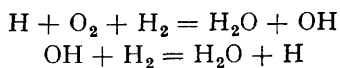


<sup>11</sup> *Physikalische Zeitschrift Sowjetunion*, No. 4, 1932.

<sup>12</sup> *Z. physik. Chem.*, 6, 307, 1930.

<sup>13</sup> *Proc. Roy. Soc.*, 138, 297, 1932.

The mechanism proposed by Haber



seems to be correct only for pressures larger than  $p_2$ , that is the region of stationary chain reactions.

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