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THE PROBLEM OF THREE LIMITS OF INFLAMMABILITY

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-USSR-

[Following is the translation of an article entitled "K voprosu o trekh predelakh vosplameneniya" (English version above) by Academician N. N. SEMENOV in Doklady Akademii Nauk SSSR (Reports of the Academy of Sceinces USSR), Vol LXXXI, No 4, Moscow, 1951, pages 645-648.]

Between 1926 and 1934, Soviet physical chemists discovered branching chain reactions and developed their theory (1). At the basis lay nee facts discovered by them in the domain of inflammability limit phenomena in oxygen of phosphorus vapor, sulphur, carbon monoxide, hydrogen, etc.

Qualitatively, one of the most characteristic phenomena for the chain inflammability is, one may note, the presence of a so-called peninsula of inflammability in the p-T plane. (See Fig. 1, where the cross-hatched region is the inflammable one). The chain theory of the peninsula of inflammability was given by N. N. Semenov in 1934 (1). The curve abc of the peninsula may be expressed by means of a quadratic equation, or (depending on the condition of termination of the chain) by a third degree equation, having two positive roots for $T > T_k$ and none for $T < T_k$. To every temperature (for $T > T_k$) correspond two limits: the lower one p_1 (below which there is no combustion) and the upper one p_2 (above whichthere is no combustion).

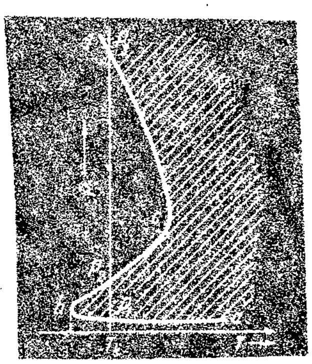

Fig. 1

In many cases there may be observed yet a third limit (curved) situated appreciably higher than p_2. This limit, because of its nature, is called the thermal limit (1, 2). In practice, in many cases, with appreciable pressure increase, above the upper limit ensues a reaction whose rate increases with pressure, which on further pressure increase is inevitably brought into thermal ignition. It is because of that, that the third limit received its name.

In 1938, Lewis (3) gave the chain theory of the third limit for the case of the hydrogen-oxygen reaction. From our analysis of this work it was clear that chain inflammation at the third limit may take place only if very special conditions are satisfied, not at all like a general phenomenon.

In 1943, N. S. Akulov (4) made an attempt to put forward a general theory of chain inflammability at the third limit. However, one of his basic and unproven premises against kinetic considerations was that the division of the chain increases with pressure according to the relation $a_o + a_1p^2$.

In an article in 1945, N. S. Akulov (5) showed another method of explaining the chain reaction at the third limit. He criticized his previous work, writing: "In the case of the previous method for the case of larger C we had to take in addition one unproven assumption with respect to a quadratic dependence of chain division from concentration. In the case of the new method, this becomes unnecessary."

Akulov chooses an arbitrary, uncommon type of chain reaction, which is such that one of the chain elongation reactions proceeds trimolecularly in bulk and simultaneously on a surface together with the precipitation of a new radical in the bulk. The chain termination takes place on a surface.

In order to state it formally, after Akulov, we write for the reaction of oxidation of hydrogen disulphide the following three kinetic equations:

$$\frac{d(O)}{dt} = -[k_{11}(H_2S)C + k_{11}'\sigma](O) + k_{12}(O_2)(SO) + k_{13}(O_2)(S),$$

$$\frac{d(SO)}{dt} = -k_{12}(O_2)(SO) + k_{13}(O_2)(S),$$

$$\frac{d(S)}{dt} = [k_{11}(H_2S)C + k_{11}''\sigma](O) - [k_{13}(O_2) + k_{13}'\sigma](S).$$

Here (O), (S), (SO), H_2S), and (O_2) are concentrations of the respective atoms, radicals, and molecules; C is the concentration of the initial combustible mixture, $C + (H_2S) + (O_2)$; σ = the ratio of surface area to volume, of the vessel. Decrease in concentration of sulphur atoms on the surface is at a rate $k_{13}'\sigma(S)$ and the consumption rate of the oxygen atoms proceeds at a rate $\lambda_{11}\sigma(O) = (k_{11}' - k_{11}'')\sigma(O)$, where $k_{11}''\sigma(O)$ is the rate of the heterogeneous phase reaction $O + H_2S_{surface} = H_2O + S_{bulk}$.

For the solution of the system of equations Akulov adopts (without quoting the source) a method worked out by me in 1943 (6). At the moment the only thing of interest to us is the fact that the equation for the limits is gotten by equating to zero of the determinant A of the system of algebraic equations

$$\frac{d(C)}{dt} = \frac{d(SO)}{dt} = \frac{d(S)}{dt} = 0.$$

This determinant is stated in Akulov's article in formula (9). Akulov obtains an equation for the determination of the limits and maintains that it gives three roots, corresponding to three limits of chain inflammability. But, in fact, one is able to show that this equation in Akulov's case is in no case able to give three positive real roots, but only one such root. In fact, dividing A by $k_{12}(O_2)$, we obtain from formula (9) of Akulov's article the equation for the limits, as shown:

$$\frac{A}{k_{12}(O_2)} = k_{11}k_{13}C(O_2)(H_2S) + (2k''_{11}-k'_{11})k_{13}\,\sigma(O_2) -$$

$$- k_{11}k'_{13}\sigma C(H_2S) - k'_{11}k'_{13}\sigma^2 = 0.$$

Setting $C = p$; $(O_2) = p(1-\gamma)$, $(H_2S) = p\gamma$, after dividing by the coefficient of p^3 we obtain

$$p^3 - bp^2 + cp - d = 0,$$

where $$b = \frac{k'_{13}}{k_{13}(1-\gamma)}, \quad c = \frac{(2k''_{11} - k'_{11})}{k_{11}\gamma}\sigma, \quad d = \frac{k'_{11}k'_{13}\sigma^2}{k_{11}k_{13}\gamma(1-\gamma)}$$

hence $$bc = \frac{2k''_{11} - k'_{11}}{k'_{11}}\,d = \frac{k''_{11} - \lambda'_{11}}{k''_{11} + \lambda'_{11}}\,d = \alpha d,$$

where $\alpha < 1$.

Thus, in the equation for the limits by Akulov, the inequality $bc < d$ is always satisfied. As d is the product of the three roots, and bc is the product of the sum of the roots with the sum of their pairwise products, so on the assupmtion that the three positive and real roots exist, the product bc should be always greater than d. The condition $bc < d$ means that the equation may bot have three positive and real roots, but only one root. (Note: We are considering the case $2k''_{11}-k'_{11}=k''_{11}-\lambda'_{11}>0$, that is $c>0$. With $2k''_{11}-k'_{11}<0$ and $c<0$ -- what is physically obvious and should take place -- two out of the three roots are negative, which follows from the consideration of the signs of the coefficients of the third degree equation.)

Not only are there not three roots, but there are not even the two usual ones. The formula (11) for the induction period obtained by Akulov makes no sense either, because it contains imaginary quantities.

In discussing the problem one should sometimes turn his attention to one very simple scheme which illustrates Akulov's results:

$$X_1 \xrightarrow{k_1(A)} xX_2 \xrightarrow{k_2(B)} \begin{matrix} X_1 \rightarrow \text{ and so forth} \\ X_3 \xrightarrow{k_3(A)c} X_1 \rightarrow \end{matrix}$$

With the calculation of the chain termination on the walls of the vessel, this scheme leads to the system of equations:

$$\frac{dx_1}{dt} = k_1(A)x_1 + k_2(B)x_2 + k_3(A)cx_3,$$

$$\frac{dx_2}{dt} = xk_1(A)x_1 - (b_2\sigma + k_2(B))x_2,$$

$$\frac{dx_3}{dt} = k_2(B)x_2 - (b_3\sigma + k_3(A)c)x_3.$$

Constructing the determinant and dividing it by $k_1(A)$ we obtain an equation of the third degree for the limits:

$$(2x - 1)k_2k_3\gamma(1 - \gamma)p^3 - b_2\sigma k_3\gamma p^2 + (x - 1)b_3\sigma k_2(1 - \gamma)$$

$p - b_2b_3\sigma^2 = 0$, or, dividing by the coefficient of p^3:

$$p^3 - bp^2 + cp - d = 0,$$

where $b = \dfrac{b_2\sigma}{(2x - 1)k_2(1 - \gamma)}$, $c = \dfrac{(x - 1)b_3\sigma}{(2x - 1)k_3\gamma}$,

$$d = \frac{b_2b_3\sigma^2}{(2x - 1)k\,k\,(1 - \gamma)\gamma}.$$

Hence, $bc = \dfrac{x - 1}{2x - 1}d$. As $x > 1$ [see note], so $bc < d$ and obviously also this equation may at most have only one positive real root.

(Note: In the case when $x < 1$, the coefficient c in the equation is negative, and this means that two roots of the equation are negative, that again there is only one limit (if $x < \frac{1}{2}$, then $c > 0$, and b and d are negative, and thus the equation does not have even one positive root.)

There arises a problem of whether the third limit exists in general. The answer is yes, it may, but under very special assumptions with respect to the mechanism of the chain reaction. Let us take an ordinary case of hydrogen oxidation, at the present time experimentally studied by Soviet scientists(7).

1) $H + O_2 = OH + O$; 2) $OH + O_2 = H_2O + H$; 3) $O + H_2 = OH + H$;

4) H + wall — decrease of H; 5) $H + O_2 + M = HO + M$;

6) $HO_2 + H_2 = H_2O + H$; 7) HO_2 + wall — decrease of HO_2.

Expressing the above system with four equations and equating the determinant A to zero, we obtain the equation for the limits:

$$2k_1k_6(O_2)(H_2) + 2k_1k_7(O_2) - k_4k_6(H_2) - k_4k_7 - k_5k_7(O_2)C = 0,$$

or

$$2k_1k_6\gamma(1-\gamma)p^2 - k_5k_7(1-\gamma)p^2 + 2k_1k_7(1-\gamma)p - k_4k_6\gamma p - k_4k_7 = 0$$ [See note].

(Note: The constant k_5 itself depends on γ, because in the expression for the constant of trimolecular collisions enter molecule velocities, specifically for O_2 and H_2.)

Let us note that this second-degree equation gives only two roots, corresponding to the first and second limit. Thus, there is no third limit in this case. However, if we assume that HO_2 very well clings to the wall and that the constant k_7 defines the diffusion rate, that is $k_7 = a/p$, then three limits are possible. Thus we have obtained a third-degree equation

$$2k_1k_6\gamma(1-\gamma)p^3 - k_5\alpha(1-\gamma)p^2 + 2k_1\alpha(1-\gamma)p - k_4k_6\gamma p^2 - k_4\alpha = 0,$$ or

$$p^3 - \frac{k_4k_6\gamma + k_5\alpha(1-\gamma)}{2k_1k_6\gamma(1-\gamma)}p^2 + \frac{2k_1\alpha(1-\gamma)}{2k_1k_6\gamma(1-\gamma)}p - \frac{k_4\alpha}{2k_1k_6\gamma(1-\gamma)} = 0.$$

Here the product bc d, and so the possibility of three limits is not excluded. This possibility is connected with a very special assumption as to the constants (k_6 is small, k_7 depends on p, etc.).

Even in the case of the reaction $H_2 + O_2$ as V. V. Voyevodskiy and A. B. Nalbandyan have shown on the basis of investigation of toehrs' experiments (7) and as have clearly shown the experiments of V. A. Poltorak and V. V. Voyevodskiy (8), the third chain limit exists only in the case of washing the walls of the glass vessel with salt solutions of the type KCl, which, as is known, appreciably increases the probability of capture of radicals by the wall. In clean systems, as was shown previously by D. A. Frank-Kamenetskiy(9), and was confirmed by Poltorak and Voyevodskiy, chain inflammanility does not exist at the third limit and instead, a thermal explosion takes place.

CONCLUSIONS:

1) From three roots of Akulov's equation (for the limits determination), two are always imaginary (for $c > 0$) or negative (for $c < 0$). Thus, the attempt to give the chain theory of the third limit, one must conclude, is a failure.

2) The third chain limit of inflammability, as was shown by Voyevodskiy, is sometimes possible. However, it may be seen that it may come about only, as a rule, under very special conditions for the reaction to proceed, and only for a reaction sustained with the aid of a very rarely occuring chain mechanism.

3) The reason for the spreading of the third limit is the inevitability of a thermal explosion at a sufficiently high pressure. The third limit, in general, has a thermal nature.

4) What applied to the chain theory of the first and second limits and so often was noted in branching chain reactions (in the form of the inflammability peninsula), today remains the Semenov theory (1929-1934), confirmed and consolidated by all later experiments.

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