# THE IGNITION OF GASES BY LOCAL SOURCES

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Although the ignition of gases by local sources (mainly electric sparks) has been the subject of extended experimental investigations, there has been very little theoretical consideration of this topic. A paper by Taylor-Jones, Morgan, and Wheeler (7), one by Silver (6), and another by Mole (2) exhaust the list. At present the literature on ignition seems to consist mainly of an enormous collection of experimental data with insufficient theoretical basis to coördinate the data, to indicate the significance of experimental results, or to supply a ground for prediction. It was therefore felt that a theoretical study, even if only partially correct, might indicate lines of research that would help to eliminate the somewhat confused state of the literature on the subject.

## PHYSICAL ASSUMPTIONS

In order to treat the problem mathematically, it is necessary to adopt a definite physical mechanism for the process. We conceive of the problem of the ignition of gases as follows: In a combustible gaseous mixture contained in a large vessel there is an arrangement for rapidly releasing energy within a small volume at a distance from the walls, for example, by passing an electric spark. It is assumed that the energy instantaneously heats up a small spherical volume and also creates active particles. These active particles are the chain carriers of the chain-reaction theory; it is not necessary to state whether they are ions, atoms, molecules with an excess of energy, or something else. It is also not necessary to specify the mechanism by which these active particles are created, but simply to assume that the release of energy does create them. The following processes then take place: There is a heat-generating reaction which is assumed to proceed at a rate proportional to the concentration of active particles, but this concentration varies with distance and time because the active particles are diffusing through the gas, and in addition are increasing in number at a rate proportional to their concentration; that is, chain branching is occurring. We are interested mainly in temperature, and so the chemical reaction enters the picture only insofar as it generates heat; it is not necessary to make any statements about the mechanism of the reaction except that it proceeds at a rate proportional to the concentration of active particles. Similarly, no particular mechanism for chain branching need be introduced.

Now the temperature at the center of the sphere tends to fall because of conduction of heat away from it, and to rise because of the heat generated. In some cases it rises continuously, and in others it shows a drop after a time (figure 1). Some criterion for ignition is needed, and the most natural one to use is the requirement that the temperature at the center of the sphere shall never fall. This can be justified by the fact that both the rate of the heat-generating reaction and of chain branching increase with increasing temperature, so that a temperature drop would slow them down, thus causing a further drop in temperature, and eventually making the reaction stop altogether.

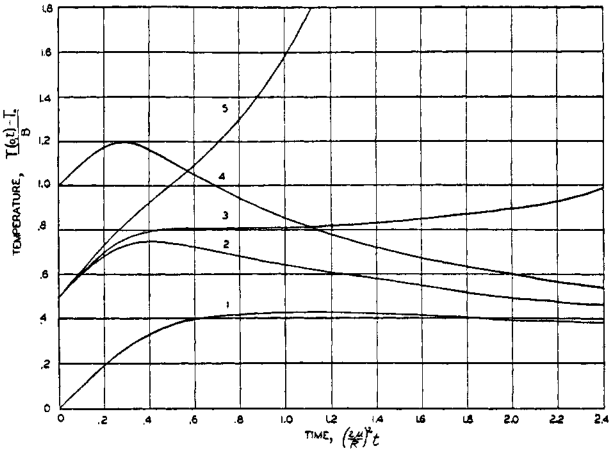

FIG. 1. Temperature at the origin for various values of $A$ and $m$

| | $A$ | $m$ | |
|---|---|---|---|
| Curve 1. | 0 | 0 | No ignition |
| Curve 2. | 0.5 | 0 | No ignition |
| Curve 3. | 0.5 | 0.64 | Ignition, at limit |
| Curve 4. | 1 | 0 | No ignition |
| Curve 5. | 0.5 | 1 | Ignition |

$$B = \frac{Qn_0R^2}{4k}$$

In the following section the partial differential equations for the concentration of active particles and for temperature are stated and solved. Then the criterion for ignition is applied, giving a relation between the physical constants which must hold for ignition to take place.

It is assumed that the diffusion coefficient of the active particles is equal to the thermometric conductivity (thermal conductivity divided by specific heat per unit volume) of the gas through which they diffuse. If the active particles and the gas are the same molecular species, this is the result given by the elementary kinetic theory of gases (1). This is not quite exact, but the difference is not serious; experimental values for the ratio of diffusion coefficient to thermometric conductivity lie between 0.7 and 1. It is not impossible to solve the equations without this assumption, but the result is not enough closer to physical reality to justify the greatly increased complications.

It is obvious that many factors have been omitted from the picture given above. The rates of the heat-generating reaction and of chain branching are not merely proportional to the concentration of active particles, but are also functions of temperature. The effects of changes in pressure and of the presence of burned gas have also been left out of consideration. However, an attempt is not being made to set up a mechanism for the complete course of the reaction. This discussion is concerned only with a condition for ignition, and since the question as to whether ignition takes place or not is decided within a very short time, it is reasonable to assume that these omitted factors do not change very greatly within this time.

## SOLUTION OF EQUATIONS

To make clear exactly what is involved, we restate in more general terms the problem which is treated here.

Consider a heat-conducting medium of infinite extent which is initially at temperature, $T_0$, except within a sphere of radius, $R$, where the initial temperature is $T_1$. At the start this sphere is filled with active particles in the concentration $n_0$ per unit volume. These active particles diffuse through the medium; each generates $Q$ units of heat in unit time and they increase in number at a rate proportional to their concentration. We wish to determine the relation that must exist among the physical constants for the temperature at the center of the sphere never to decrease.

The differential equation for the concentration of active particles is

$$\frac{\partial n}{\partial t} = \mu^2 \nabla^2 n + \alpha n \tag{1}$$

with the initial condition

$$\left.\begin{aligned} n &= n_0 \text{ for } 0 \leqslant r < R \\ n &= 0 \text{ for } \quad r > R \end{aligned}\right\} \quad \text{when } t = 0 \tag{2}$$

where $n = n(r, t)$ is the concentration of active particles at a distance $r$ and time $t$,

$\mu^2$ = diffusion coefficient,

$\nabla^2$ = Laplacian differential operator, here $\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right)$

$\alpha$ = branching coefficient, and

$n_0$ = initial concentration in the sphere of radius $R$.

Equation 1 is merely the diffusion equation (4) with the additional term $\alpha n$ giving the rate of increase of active particles.

To solve this put $n = e^{\alpha t} f(r, t)$. Then $f(r, t)$ satisfies the diffusion equation (that is, equation 1 without the branching term $\alpha n$) and the same initial condition. This has the solution (5)

$$f(r, t) = n_0 U(r, t)$$

where

$$U(r, t) = \frac{1}{2}\left[\operatorname{erf}\left(\frac{R + r}{2\mu\sqrt{t}}\right) + \operatorname{erf}\left(\frac{R - r}{2\mu\sqrt{t}}\right)\right] + \frac{\mu}{r}\sqrt{\frac{t}{\pi}}\left[e^{-\left(\frac{R+r}{2\mu\sqrt{t}}\right)^2} - e^{-\left(\frac{R-r}{2\mu\sqrt{t}}\right)^2}\right] \quad (3)$$

$$\operatorname{erf} x = \frac{2}{\sqrt{\pi}} \int_0^x e^{-s^2}\, ds \quad (4)$$

being the error function or probability integral. Then

$$n(r, t) = n_0 e^{\alpha t} U(r, t) \quad (5)$$

is the solution of equations 1 and 2.

Since the function $U(r, t)$ is to be used again, it is worth noting its meaning. As here introduced, $U(r, t)$ gives the concentration of diffusing particles in an infinite medium when the initial concentration is 1 within a sphere of radius $R$, and 0 outside this sphere. Since the heat conduction equation (3) is of the same form as the diffusion equation, $U(r, t)$ also gives the temperature in an infinite medium due to an initial temperature of 1 within the sphere and of 0 outside.

$U(r, t)$ can also be regarded in a slightly different manner. Instead of considering an initial temperature distribution, consider an instantaneous spherical volume source of heat which generates enough heat to raise the temperature of the sphere from 0 to 1. If this generation of heat occurs at time $t = 0$, the temperature will be given by $U(r, t)$. If it occurs at time $t = \tau$, the temperature at any later time will be given by $U(r, t - \tau)$.

These considerations will be used in finding the temperature distribution in the gas.

The partial differential equation for temperature is

$$\frac{\partial T}{\partial t} = \mu^2 \nabla^2 T + \frac{Q}{c} n(r, t) \tag{6}$$

with initial condition

$$\left.\begin{aligned} T &= T_1 \text{ for } 0 \leqslant r < R \\ T &= T_0 \text{ for } \quad r > R \end{aligned}\right\} \quad \text{when } t = 0 \tag{7}$$

where $T = T(r, t)$ is the temperature at distance $r$ and time $t$,
$\mu^2$ = thermometric conductivity (The same symbol is used as for diffusion coefficient because these are assumed equal as explained above.),
$Q$ = quantity of heat generated in unit time by the action of each active particle,
$c$ = specific heat of unit volume,
$T_1$ = initial temperature of the sphere of radius $R$, and
$T_0$ = initial temperature outside this sphere.

Equation 6 is the heat conduction equation (3) with the additional term $\frac{Q}{c}n(r, t)$, which gives the rate of temperature rise due to the heat produced by the action of the active particles.

This may be solved as follows. Put

$$T = T_0 + (T_1 - T_0)\, U(r, t) + V(r, t) \tag{8}$$

Then $T_0 + (T_1 - T_0)\, U(r, t)$ satisfies the heat conduction equation (that is, equation 6 without the term $\frac{Q}{c}n$) and the initial condition. $V(r, t)$ must then satisfy equation 6 and vanish everywhere when $t = 0$; it is the temperature due to a heat source generating $Qn(r, t)$ units of heat in unit time.

Now, as noted before, the temperature due to an initial distribution can be reinterpreted as that due to an instantaneous heat source. The temperature due to a spherically symmetric initial distribution, $\phi(r)$, is (5)

$$\frac{1}{2\mu r\sqrt{\pi t}} \int_{-\infty}^{\infty} \phi(\rho)\, e^{-\left(\frac{\rho - r}{2\mu\sqrt{t}}\right)^2} \rho\, d\rho^{*} \qquad (\text{with } \phi(-\rho) \text{ put equal to } \phi(\rho))$$

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* $U(r, t)$ is, of course, obtained by putting
$\phi(\rho) = 1$ for $-1 < \rho < 1$
$\phi(\rho) = 0$ elsewhere

Then the temperature due to an instantaneous volume source which generates $Qn(r, t)$ units of heat at time $t = \tau$ is

$$W(r, t; \tau) = \frac{1}{2\mu r\sqrt{\pi(t-\tau)}} \int_{-\infty}^{\infty} \frac{Q}{c} n(\rho, \tau)\, e^{-\left(\frac{\rho - r}{2\mu\sqrt{t-\tau}}\right)^2} \rho\, \mathrm{d}\rho \tag{9}$$

Since $W(r, t; \tau)$ is the temperature at $r$ and $t$ due to a source at time $\tau$, the temperature due to the continuous source $Qn(r, t)$ can be obtained by integrating $W(r, t; \tau)$ for $\tau = 0$ to $\tau = t$. Thus,

$$V(r, t) = \int_0^t W(r, t; \tau)\, \mathrm{d}\tau \tag{10}$$

The reasoning by which this result has been obtained has been more physical than mathematical. A more rigorous proof of the fact that $V(r, t)$ satisfies equation 6 can be given along the following lines. First note that $W(r, t; \tau)$ satisfies

$$\frac{\partial W}{\partial t} = \mu^2 \nabla^2 W \tag{11}$$

for all $\tau < t$, as can be shown by direct calculation. Then

$$\frac{\partial V}{\partial t} = \int_0^t \frac{\partial W}{\partial t}\, \mathrm{d}\tau + \lim_{\tau \to t} W(r, t; \tau) \tag{12}$$

It can be shown that

$$\lim_{\tau \to t} W(r, t; \tau) = \frac{Q}{c} n(r, t) \tag{13}$$

as follows: Put $\rho = r + 2\mu\sqrt{t - \tau}\,\lambda$ and substitute in equation 9; then

$$\begin{aligned} W(r, t; \tau) &= \frac{1}{r\sqrt{\pi}} \int_{-\infty}^{\infty} \frac{Q}{c} n(r + 2\mu\sqrt{t-\tau}\,\lambda, \tau)\, e^{-\lambda^2} (r + 2\mu\sqrt{t-\tau}\,\lambda)\, \mathrm{d}\lambda \\ &= \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \frac{Q}{c} n(r + 2\mu\sqrt{t-\tau}\,\lambda, \tau)\, e^{-\lambda^2}\, \mathrm{d}\lambda \\ &\qquad + \frac{2\mu\sqrt{t-\tau}}{r\sqrt{\pi}} \int_{-\infty}^{\infty} \frac{Q}{c} n(r + 2\mu\sqrt{t-\tau}\,\lambda, \tau) \cdot e^{-\lambda^2}\, \lambda\, \mathrm{d}\lambda \end{aligned}$$

Putting $\tau = t$, the second integral vanishes and the first is

$$\frac{Qn(r, t)}{c} \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-\lambda^2}\, \mathrm{d}\lambda = \frac{Qn(r, t)}{c}$$

giving equation 13. Then,

$$\mu^2 \nabla^2 V(r, t) = \mu^2 \int_0^t \nabla^2 W(r, t; \tau)\, \mathrm{d}\tau = \mu^2 \int_0^t \frac{\partial W}{\partial t}\, \mathrm{d}\tau \tag{14}$$

from equation 11.

From equations 12, 13, and 14 it follows that

$$\frac{\partial V}{\partial t} = \mu^2 \nabla^2 V + \frac{Q}{c} n(r, t)$$

showing that $V(r, t)$ satisfies equation 6.

Substituting the value of $n(r, t)$ from equation 5 in equation 9 and carrying out the integration[1] there results

$$W(r, t; \tau) = \frac{Q n_0 e^{\alpha\tau}}{c} U(r, t) \tag{15}$$

It is worth noting the physical reason for this simple result. $U(r, t)$ is the temperature distribution due to an instantaneous spherical volume source at $t = 0$. Since our source,

$$\frac{Q}{c} n(\rho, \tau) = \frac{Q n_0}{c} e^{\alpha\tau} U(\rho, \tau)$$

has the value of $U$ at time $\tau$ (except for the factor $e^{\alpha\tau}$), it follows that it will have the same value as $U$ at any later time.

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[1] The following definite integrals are involved

$$\int_{-\infty}^{\infty} \operatorname{erf}(a + bx) e^{-x^2} \, dx = \sqrt{\pi} \operatorname{erf}\left(\frac{a}{\sqrt{1 + b^2}}\right)$$

$$\int_{-\infty}^{\infty} \operatorname{erf}(a + bx) x e^{-x^2} \, dx = \frac{b e^{-a^2/(1+b^2)}}{\sqrt{1 + b^2}}$$

These can be established as follows: Let

$$I(a, b) = \int_{-\infty}^{\infty} \operatorname{erf}(a + bx) e^{-x^2} \, dx$$

$$\frac{\partial I}{\partial a} = \frac{2}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-(a+bx)^2 - x^2} \, dx = \frac{2}{\sqrt{\pi}} e^{-a^2/(1+b^2)} \int_{-\infty}^{\infty} e^{-\left(\sqrt{1+b^2}\, x + \frac{ab}{\sqrt{1+b^2}}\right)^2} dx$$

$$= \frac{2}{\sqrt{1 + b^2}} e^{-a^2/(1+b^2)}$$

Then,

$$I(a, b) = \sqrt{\pi} \operatorname{erf}\left(\frac{a}{\sqrt{1 + b^2}}\right) + f(b)$$

but $I(0, b) = 0$, since

$$\int_{-\infty}^{0} \operatorname{erf}(bx) e^{-x^2} \, dx = -\int_{0}^{\infty} \operatorname{erf}(bx) e^{-x^2} \, dx$$

so that $f(b) = 0$. Similarly for the other integral.

From equation 10 there results

$$V(r, t) = \frac{Qn_0}{c}\frac{e^{\alpha t} - 1}{\alpha} U(r, t) \tag{16}$$

and finally, from equation 8

$$T(r, t) = T_0 + \left(T_1 - T_0 + \frac{Qn_0}{c}\frac{e^{\alpha t} - 1}{\alpha}\right) U(r, t) \tag{17}$$

giving the desired temperature distribution.

### CONDITION FOR IGNITION

To obtain the condition for ignition, consider the temperature at the origin

$$T(0, t) = T_0 + \left(T_1 - T_0 + \frac{Qn_0}{c}\frac{e^{\alpha t} - 1}{\alpha}\right)\left(\operatorname{erf}\frac{R}{2\mu\sqrt{t}} - \frac{R}{\mu\sqrt{\pi t}} e^{-R^2/4\mu^2 t}\right) \tag{18}$$

This changes with time at the rate

$$\frac{\partial T(0, t)}{\partial t} = -\left(T_1 - T_0 + \frac{Qn_0}{c}\frac{e^{\alpha t} - 1}{\alpha}\right)\frac{R^3}{4\sqrt{\pi}\,\mu^3 t^{5/2}} e^{-R^2/4\mu^2 t} + \frac{Qn_0}{c} e^{\alpha t}\left(\operatorname{erf}\frac{R}{2\mu\sqrt{t}} - \frac{R}{\mu\sqrt{\pi t}} e^{-R^2/4\mu^2 t}\right) \tag{19}$$

To determine the relation which holds between the physical constants when

$$\frac{\partial T(0, t)}{\partial t} \geqslant 0$$

put

$$x = \frac{R}{2\mu\sqrt{t}}$$

$$\alpha = m\left(\frac{2\mu}{R}\right)^2$$

$$A = \frac{4(T_1 - T_0)k}{Qn_0 R^2} \qquad (k = \text{thermal conductivity} = \mu^2 c)$$

then,

$$\frac{\partial T(0, t)}{\partial t} = \frac{2Qn_0}{c} x^5 e^{-x^2}\left[-A - \frac{e^{m/x^2} - 1}{m} + \frac{e^{\frac{m}{x^2} + x^2}}{x^5}\left(\frac{\sqrt{\pi}}{2}\operatorname{erf} x - xe^{-x^2}\right)\right] \tag{20}$$

The function

$$F(x) = \frac{e^{\frac{m}{x^2}+x^2}}{x^5}\left(\frac{\sqrt{\pi}}{2}\operatorname{erf} x - xe^{-x^2}\right) - \frac{e^{\frac{m}{x^2}} - 1}{m}$$

approaches $+\infty$ as $x$ approaches 0 or $\infty$ for $m > 0$. By differentiation it is found that $F(x)$ has a single minimum given by the following relation between $x$ and $m$.

$$m = x^2\left[x^2\left(\frac{\operatorname{erf} x + \frac{2}{\sqrt{\pi}}\,xe^{-x^2}}{\operatorname{erf} x - \frac{2}{\sqrt{\pi}}\,xe^{-x^2}}\right) - \frac{5}{2}\right] \tag{21}$$

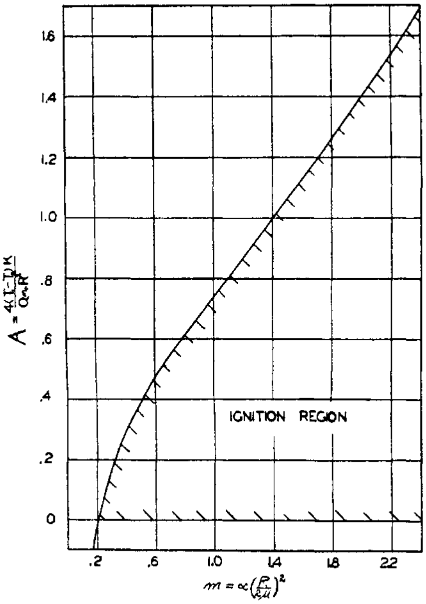

FIG. 2. Condition for ignition

From this there can be found the value of $x$ which makes $F(x)$ a minimum for a given $m$, and then the value of $F(x)$ for this minimum. If $A$ is not greater than this value, then from equation 20,

$$\frac{\partial T(0, t)}{\partial t} \geqslant 0$$

for all $t$.

This then gives the desired relation which must be fulfilled for a nondecreasing temperature at the origin. It is that

$$A = \frac{4(T_1 - T_0)k}{Qn_0 R^2}$$

must be less than or equal to a value depending on $\alpha$, since $m$ is merely $\alpha$ expressed in convenient units. The ignition limit is, of course, given by the equality in this relation.

Figure 2 is a graph of the relation between $A$ and $\alpha$, and figure 1 shows the course of the temperature at the origin for five pairs of values of $A$ and $\alpha$.

## SIGNIFICANCE AND APPLICABILITY OF THE THEORY

Unfortunately the result obtained in the last section cannot be tested by direct comparison with experiment, because the quantities which enter have not been measured in experiments on the ignition of gases. In fact, they may be incapable of direct experimental determination. However, certain conclusions can be drawn from this theoretical result as it stands, and it should be possible to perform experiments which will give some information about the needed quantities.

From figure 2 it can be seen that ignition does not occur if $\alpha = 0$; that is, chain branching must take place for ignition to occur. This could have been expected to follow from the physical assumptions; because if the active particles do not increase in number, they eventually become very thinly spread out owing to diffusion and cannot generate enough heat to cause much rise in temperature. According to von Elbe and Lewis (8) the chain-branching reaction in the oxidation of hydrogen is negligible at low temperatures. Our conclusion would then be that ignition of a hydrogen–oxygen mixture by a local source can only occur if the source raises some volume to a high enough temperature for branching to be significant. This statement sounds very similar to those made by the proponents of a thermal theory of ignition. However, it is obvious that our theory does not state that ignition is assured by merely raising some volume to a sufficiently high temperature. The statement above is simply a limitation in the case where branching is known not to occur at low temperatures.

There is one set of experimental data which, though not exactly fitting the conditions assumed here, can be shown to give at least qualitative agreement with the theory. Silver (6) has studied ignition by shooting heated spheres of platinum and quartz into gases. He gives the minimum temperature to which spheres of various sizes must be heated to cause ignition in mixtures of 10 per cent coal gas, 3 per cent pentane, and 20 per cent hydrogen, each in air.

It is possible to relate Silver's experimental data to the considerations of this paper as follows. From figure 1 the condition for ignition is that

$$A = \frac{4(T_1 - T_0)k}{Qn_0R^2}$$

have a value which depends on

$$m = \frac{R^2}{4\mu^2}\alpha$$

The relation between $A$ and $m$ is, over a considerable range, close to a straight line passing through the origin, so that

$$A = \text{constant} \times \frac{R^2}{4\mu^2}\alpha$$

is the ignition relation. Now $\alpha$ depends on temperature according to

$$\alpha = \text{constant} \times e^{-\frac{E_1}{RT}}$$

also $Q$, being proportional to a reaction rate follows a similar relation,

$$Q = \text{constant} \times e^{-\frac{E_2}{RT}}$$

The initial concentration of active particles probably depends on a surface reaction and can, therefore, also be assumed to be proportional to $e^{-\frac{E_3}{RT}}$. Then

$$\frac{T - T_0}{R^4} = \text{constant} \times e^{-\frac{E_1+E_2+E_3}{RT}}$$

and the graph of $\log\left(\frac{T - T_0}{R^4}\right)$ against $\frac{1}{T}$ should be a straight line. This graph is shown in figure 3 and it can be seen that the experimental values satisfactorily approximate a straight line.

The variation of $k$ and $c$ with temperature has been neglected. Inclusion of this factor would make no real difference in the appearance of figure 3; the slopes of the lines would be slightly increased.

Silver gave a theoretical discussion of his work, using as a criterion for ignition the requirement that the initial rate of heat production by the reaction shall be greater than the rate of heat loss by conduction. This led to the conclusion that the graph of $\log \frac{T - T_0}{R}$ against $\frac{1}{T}$ should be a straight line with a slope equal to the activation energy of the reaction.

The experimental points fell as close to straight lines as in the present analysis, but the slopes of the lines were approximately equal, whereas pentane and hydrogen have very different activation energies. The slopes of our lines are also not very different, but this is not contrary to the theory, since they should be proportional to $E_1 + E_2 + E_3$.

In the experiments just discussed, $T_1$, the initial temperature of the sphere, was determined directly. This is one of the quantities needed to test the theory, but in the case of an electric discharge it appears to be impossible to relate $T_1$ to measured quantities. This suggests that it might be worth while to perform experiments with an energy source that released a known amount of energy, perhaps something like a percussion cap. It should then be possible to make statements about $T_1$. This would be of value not only for testing the present theory, but should also put an end to the controversy over the thermal theory of ignition by giving a direct answer to the questions involved.

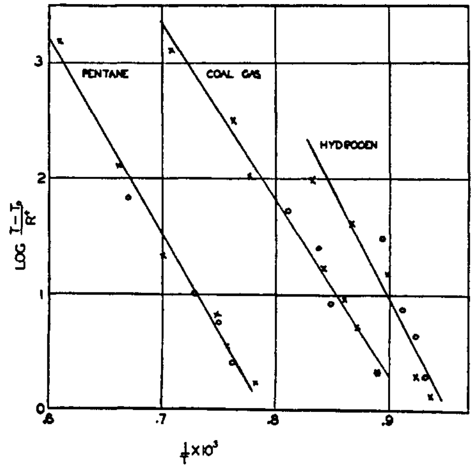

FIG. 3. Data of R. S. Silver (6) on ignition of gases by heated spheres. Experimental values: ×, platinum spheres; ○, quartz spheres.

To test the present theory it is also necessary to have information about $n_0$, the initial concentration of chain carriers. This requires a knowledge of the kinetics of the reaction and of the physical mechanism of the creation of these initial chain carriers.

If such information were available, it would be possible to make statements such as the following. Suppose $T_1$ is held constant, then for a given mixture $\alpha$ and $Q$ should be constant. Let $R$ and $n_0$ vary, then from

$$\frac{4(T_1 - T_0)k}{Qn_0 R^2} = \text{constant} \times \frac{R^2}{4\mu^2}\alpha$$

a relation of the form, $n_0 R^4 =$ constant, follows.

Again, if $T_1$ is constant and pressure, $p$, and $R$ vary, a relation between $p$ and $R$ is obtained. The form of the relation depends on the kinetics of the reaction. Suppose that chain branching, $\alpha$, requires the collision of $m_1$ molecules, that the heat-producing reaction involves $m_2$ molecules, and that the creation of the initial active particles involves $m_3$ molecules; then $\alpha$ = constant $\times p^{m_1}$, $Q$ = constant $\times p^{m_2}$, $n_0$ = constant $\times p^{m_3}$. Also $\mu^2$ is inversely proportional to density, hence inversely proportional to pressure. So that the relation is $p^{m_2 + m_2 + m_3 + 1} R^4$ = constant.

If the theory could be verified for reactions for which the kinetics is fairly well established, it should be useful to test hypotheses about the mechanism of other reactions.

## SUMMARY

When energy is released by a local source such as an electric spark in a combustible gaseous mixture, it is assumed to heat instantaneously a small volume and also to create active particles, chain carriers, which diffuse through the gas and increase in number by chain-branching processes at a rate proportional to their concentration. The heat-producing reaction proceeds at a rate proportional to concentration of active particles. Taking as a criterion for ignition the requirement that the temperature at the point of ignition shall never decrease, the following condition for ignition is obtained:

$$A = \frac{4(T_1 - T_0)k}{Qn_0 R^2}$$

must be less than or equal to a value depending on $\alpha$, the relation being given in figure 1.

The significance and applicability of this result are discussed.

This problem was suggested by Guenther von Elbe and Bernard Lewis. The author gratefully acknowledges his indebtedness to them and to M. A. Mayers of this laboratory for many helpful suggestions during the course of the work.

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## *DISCUSSION*[2]

Louis S. Kassel (Universal Oil Products Company, Chicago, Illinois): This paper certainly represents an interesting attempt to provide a mechanism for this important process. It may be worth while, however, to point out one feature of Landau's treatment that is perhaps oversimplified.

This is the assumption that the branching rate is independent of temperature; this admittedly incorrect proposition is justified by the statement that "the question as to whether ignition takes place or not is decided within a very short time." Inspection of figure 1, however, shows that when ignition fails the temperature at the origin may have risen, owing to the reaction, by 20 to 50 per cent as much as it had owing to the local source. Thus it is apparently required to assume that the branching rate is constant over a temperature interval of something like 100°C. It is to be expected that a theory which assumes a reasonable temperature coefficient for the branching rate will give a more rapid determination of whether ignition is to occur, and that failure to ignite will be preceded by only slight temperature rises. Even for these intervals, however, the increase of branching rate with temperature seems an essential feature of the theory, since it is only the effect of this increase which limits the abortive rise to a range over which one might think the branching rate could be considered constant.

[2] Received September 17, 1937.