REPORT No. 337

THE GASEOUS EXPLOSIVE REACTION
AT CONSTANT PRESSURE—THE REACTION ORDER
AND REACTION RATE

By F. W. STEVENS
Bureau of Standards
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SUMMARY

This investigation was carried out at the Bureau of Standards at the request of and with the financial assistance of the National Advisory Committee for Aeronautics.

1. In the case of the gaseous explosive reaction at constant pressure, the data given in this report show that the statistical expression, \( r = \left( \frac{D}{I} \right)^{1/2} K \), derived from the order of the stoichiometric equation written for complete combustion of a fuel, is proportional to the spatial rate at which an equilibrium is established in the gaseous explosive system, and that this relation is found to hold for high reaction orders where very complex hydrocarbon fuels are involved in the transformation.

2. The above relation, since it is based solely upon the initial and final condition of the transformation, is independent of the microprocesses, whatever these may be, resulting in the final union of the initial active components in the proportions required by the reaction constant \( K \) for the temperature and pressure at which the reaction takes place.

3. The data also provide interesting confirmation of the assumption that high-order reaction processes consist of many simultaneous simpler ones each running its course within the reaction zone “according to its own order and mechanism independently of any other reactions occurring at the same time.” The probability of the correctness of this assumption is chiefly shown by the fact that the equivalent reaction order of a composite fuel may be determined from the reaction orders of its components, and further, that the velocity constant, \( k \), of the fuel may also be determined from the velocity constants of those components.

4. The data given in this report all cover the “explosive limits” of the fuels investigated. Incidental to the purpose of the investigation here reported, the “explosive limits” will be found to be expressed for the condition of constant pressure, in the fundamental terms of concentrations (partial pressures) of fuel and oxygen. It may be seen from the results given that a fundamental relation clearly exists between explosive range and the magnitude of \([F]_{\text{max}} \) of the fuel.

The reaction order is given by the stoichiometric equation. This equation expresses quantitatively the equality of masses existing between the initial components and final products of the completed chemical transformation. In the case of a gaseous explosive reaction between a fuel of known composition and oxygen, the equation may thus express the proportions in terms of (atmospheric) partial pressures of the fuel and of the oxygen necessary for complete combustion, but without reference to the ultimate processes by which the transformation is effected. The composition of the final products resulting from the reaction in any particular case is dependent on temperature and pressure and is expressed by the reaction constant \( K \) for those conditions:

\[
K = \frac{[A]^m [B]^n [C]^p}{[A]^q [B]^s [C]^t} \ldots \ldots
\]

and

\[
\left( \frac{\partial \ln K}{\partial T} \right)_p = \frac{U_p}{RT^2}
\]

(Reference 1, p. 223.)

Besides the above thermodynamic relations based on the initial and end conditions of the transformation, the stoichiometric equation has, in connection with the kinetic theory of gases, furnished suggestion for a possible mechanism by which the initial molecular condition of the active components becomes the final condition of the equilibrium products. Following the suggestion made by van’t Hoff (Reference 2, p. 13), this kinetic view of the transformation and of its equilibrium condition is indicated in the equation by the use of a modified sign of equality \( \Rightarrow \), expressing the direction of the opposed simultaneous reactions that characterize transformations. By this view the total reaction resulting in this thermodynamic equilibrium is the summation of separate simultaneous reactions each having its characteristic order and “each running its course independently of any other reactions occurring at the same time.” (Reference 3, p. 877.)

In the case of the simplest reaction orders, and where the reaction may be so conditioned as to run its
course as free as possible from the effects of the container, of variable temperature and concentrations, the correspondence between reaction order and reaction mechanism is usually found to be very close (Reference 4, p. 634, Reference 5, p. 109, Reference 6, p. 281b), and in those cases where a lack of agreement was found, the discrepancy has usually been traced to local changes in concentrations, to impurities, and even to secondary reactions not indicated in the stoichiometric equation which represents only the result of the total chemical change (Reference 7, p. 289).

But in the case of nominally higher reaction orders, where large numbers of molecules may be involved in the transformation, the actual processes taking place are rarely found to follow a mechanism indicated by the reaction order of the stoichiometric equation, although the equilibrium condition agrees with it and the reaction constant is expressed in its terms. The processes taking place in these high-order reactions are found to follow simpler orders. It is found that even trimolecular reactions are rare and that the processes taking place in polymolecular transformations proceed by simultaneous uni, bi, rarely, trimolecular orders. (Reference 4, p. 653.) Moreover, the advance in modern physics has greatly changed the older and cruder concepts of molecular transformations and shown that the microprocesses of a reaction are much more refined than a simple kinetic theory of gases is able to formulate.\(^1\)

The above considerations apply in general to gaseous reactions occurring below ignition temperature where the processes referred to as taking place in a homogeneous gaseous system proceed uniformly throughout the entire mass of active gases. It is assumed that like relationships should apply also to molecular transformations occurring within the zone of explosive reaction, since the initial conditions and final equilibria in both these reaction forms are the same for like conditions of temperature and pressure.

But where the gaseous transformation is brought about by the explosive form of reaction—and this is the form employed in industrial uses of the reaction as a source of power—the gross mechanism of the reaction on which its industrial value depends corresponds more closely with the stoichiometric equation than does the form of reaction below ignition temperature. This is because the rate of transformation of the gaseous system, as brought about by the spatial propagation of the reaction zone within it, is expressed in terms of the spatial rate at which the completed reaction is established in the gases, without reference to the mode or way by which the equilibrium is attained within the reaction zone. Likewise the stoichiometric equation is written for the completed reaction without reference to simultaneous reactions of simple orders that, whatever they may be, lead to the same thermodynamic result; that is, the unknown microprocesses ultimately bring about the union of the active components in the required proportion to produce the resulting equilibrium. This proportion of the active components required for the completed reaction, determines the reaction order. The reaction order then represents a definite final condition and not a process.\(^2\)

If a kinetic interpretation be given the reaction order an expression results that is statistical in form but whose factors are drawn from thermodynamic relations that are independent of the processes involved in the transformation. Nevertheless the empirical kinetic expression obtained from the reaction order possesses this necessary and fundamental requirement: It is consistent with the thermodynamic equilibrium and the reaction constant \(K\) is expressed in its terms. If the possible rate \(\Gamma\) indicated by it is seldom consistent with the total rate resulting from unknown microprocesses and simple simultaneous reactions, it does give an expression proportional to their total effect.

In the case of the gaseous explosive reaction at constant pressure the spatial rate \(s\) at which an equilibrium is established in the gaseous system is directly determined; so that the proportionality factor \(k_1\) between the probable indicated rate \(\Gamma\) of the reaction order and the actual observed rate \(s\) may in any case be found:

\[^1\text{It should be appreciated that even in the case of a complicated set of simultaneous reactions the individual steps of the total process are themselves simple reactions of definite order and mechanism, so that a study of the theory of isolated reactions is the natural preliminary for the study of all branches of chemical kinetics.}\] (Reference 7)

\[^2\] It has always been found difficult to deduce a reliable dynamic expression from a relation essentially static in its nature, e.g. Jouguet, "Vitesse de Reaction et Thermo-dynamique," Ann. de Physique, v. 5-7 (1928). "The two energy laws may be made use of in the construction of a static system but they may not be employed in the construction of a dynamic one," Marcolin, "Contribution à l’Etude de la Cinétique Physiochimique," Ann. de Physique III, 190-221 (1915).
condition of the reaction. is the observed spatial rate at which the reaction is completed in the gaseous system, at constant pressure, by the reaction zone. It represents the continuous summation of the effect of all processes, whatever they may be, simultaneously taking place within the reaction zone. The empirical expression \( s = k_1 \left[ \text{CO} \right]^2 \left[ \text{O}_2 \right] \) is essentially thermodynamic in its origin, as is the stoichiometric equation from which it is derived; the determining time factor in the equation is contained in the value of \( s \) which is directly determined. The rate at which the union of 2CO and \( \text{O}_2 \) is accomplished in consequence of unknown processes occurring within the reaction zone is

\[
s = k_1 \left[ \text{CO} \right]^2 \left[ \text{O}_2 \right],
\]

where

\[
k_1 = \frac{s}{\Gamma} = \frac{r^3}{2} [\text{CO}]^2 [\text{O}_2].
\]

The final volume of reaction products represented by \( r' \) at initial pressure, but at the temperature due to the explosive reaction, corresponds to the reaction constant \( K \) for that pressure and temperature

\[
K = \frac{[\text{CO}]^2}{[\text{O}_2]}
\]

In obtaining the experimental values of \( s = s' r^3 \) for the explosive reaction of these gases at constant pressure it was found that \( k_1 = \frac{s}{\Gamma} \) not only remained constant for any particular reaction, it was also found in this case to be a fair constant (=691) for all values of \( \Gamma \) that would support a zone of explosive reaction. Figure 1, lower curve, shows the close agreement between the observed values of \( s \), represented in the figure by solid dots , and the values obtained from the statistical relation, \( s = k_1 \left[ \text{CO} \right]^2 \left[ \text{O}_2 \right] \), represented by open circles and continuous line.

The above example shows that the reaction order in this case gives little or no insight as to the processes occurring in the transformation, but it gives reliable information as to their result. The statistical expression based on the reaction order is seen to be proportional to the spatial rate at which the reaction completes itself within the gaseous system. From a practical standpoint such a relationship based on the initial and end points of the transformation is an advantage, for in the use of hydrocarbon fuels as a source of power in the gas engine the fuels employed are not only composite but their components for the most part consist of heavy hydrocarbon molecules. The stoichiometric equations for complete combustion of these hydrocarbons represent unusually high reaction orders, involving, as is supposed, complicated sets of simultaneous reactions. The reaction order provides for these cases a statistical expression proportional to the total effect of the unknown microprocesses.

On the assumption that the resulting reaction is the summation of simultaneous reactions each following its own order and mechanism independently of other reactions occurring at the same time within the reaction zone, a stoichiometric equation for complete

\[
2\text{C}_2\text{H}_4 + 3\text{O}_2 \rightarrow \text{2CO} + 2\text{H}_2\text{O} + 2\text{O}_2
\]

is given in A. A. C. A. Technical Report No. 176 and in J. Am. Chem. Soc. 45, 1923 (1926). The diagrammatic figure here shown and described will be sufficient to indicate the relation of the factors used in the text. If an explosive reaction is initiated by an induction spark within a homogeneous mixture of explosive gases at rest and unconfined the zone of explosive reaction originating at this point propagates itself, for moderate velocities below the velocity of sound, in all directions at constant linear speed, \( r' \). The reaction zone thus forms a spherical shell of flame including the reaction products as formed and expanding at constant linear rate \( r' \). If \( r' \) represents a sphere of initial active components ignited at the center, and \( r' \) the resultant sphere of reaction products at the instant the reaction is completed, and \( t \) the time interval between the ignition and the completion of the explosive process, the constant rate of movement of the reaction zone in space will be given by

\[
\frac{r'}{t} = \frac{r'}{t} = \text{rate of propagation of the reaction zone in space within the gaseous system.}
\]

This is not, however, the rate of propagation of the reaction zone relative to the gases as if they were at rest, \( r_0 \), the spatial rate of their transformation is

\[
r_0 = \frac{r'}{t} = \text{rate of propagation of the reaction zone within the gaseous system.}
\]
combustion of a composite fuel of known components may be written as a simple reaction:

\[ n_1F + n_2O_2 = n_4CO_2 + n_4H_2O \]

The equivalent order of this reaction, \( n_1+n_2 \), is determined from the relative importance of the orders of the separate components of the fuel mixture. The statistical expression derived from this order is:

\[ r = \frac{[F]^{n_1}[O_2]^{n_2}}{[F]} \]

The rate of propagation of the reaction zone within the explosive mixture of these gases is

\[ s = k_1[F]^{n_1}[O_2]^{n_2} \]

The maximum value of \( s \) in this expression should be found for the partial pressures of \( F \) and \( O_2 \) as stated below:

\[ s_{\text{max}} = k_1 \left[ \frac{n_1}{n_1+n_2} \right]^{n_1} \frac{[F]}{[O_2]} \]

Experimental data illustrating the relations observed between reaction order and reaction rate in the explosive reaction at constant pressure of composite fuels are given in the tables and coordinate-figures that follow.

**EXPERIMENTAL RESULTS**

The heaviest hydrocarbon fuel found suitable for use at initial atmospheric conditions with a constant pressure bomb was butane, \( \text{C}_4\text{H}_{10} \). The stoichiometric equation written for complete combustion of this fuel is

\[ 2\text{C}_4\text{H}_{10} + 13\text{O}_2 = 8\text{CO}_2 + 10\text{H}_2\text{O} \]

The reaction order is 15. A kinetic interpretation of so high a reaction order would give a probable reaction rate of \( \Gamma = [\text{C}_4\text{H}_{10}]^{15}[\text{O}_2]^{13} \), the probability of so large a number of molecules meeting together being remote. The observed rate of explosive reaction of these gases, however, is high. This would indicate that the total reaction consists of many simpler simultaneous ones, with the result that the fuel and oxygen are found at the completion of the processes to be united, as stated by the equation. How much greater the actual spatial rate \( s \) is at which the transformation is effected in the gaseous system than the value of the molecular rate indicated by \( \Gamma \) is

\[ k_1 = \frac{s}{\Gamma} \]

The observed rate \( s \) expressed in terms of the initial partial pressures of the active gaseous components is

\[ s = k_1 \text{C}_4\text{H}_{10}^{15} \text{O}_2^{13} \]

In Table I are recorded the experimental values of \( s = \frac{s}{\Gamma} \) for those mixtures of butane and oxygen that will ignite. There is also given for each mixture ratio of these gases the corresponding value of \( \Gamma \) and of \( k_1 = \frac{s}{\Gamma} \). The value of \( k_1 \) found is 172,430 so that \( s_{\text{max}} = 172,430 \times 0.133 \times 0.867 = 477 \text{ cm/sec} \).

**TABLE I.—OBSERVED RATE OF FLAME PROPAGATION IN 2C,H_{10}+13O_2 → EXPLOSIVE REACTION AT CONSTANT PRESSURE**

<table>
<thead>
<tr>
<th>Record 9-10-38 No.</th>
<th>Partial-pressure atmospheres</th>
<th>( \Gamma = [\text{C}<em>4\text{H}</em>{10}]^{15}[\text{O}_2]^{13} )</th>
<th>( s = \frac{\Gamma}{\Gamma} ) cm/sec</th>
<th>( s = \frac{s}{\Gamma} ) cm/sec</th>
<th>( k_1 = \frac{s}{\Gamma} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 to 22</td>
<td>[C,H_{10}] [O_2]</td>
<td>0.040</td>
<td>0.090</td>
<td>0.000942</td>
<td>1.720</td>
</tr>
<tr>
<td>33 to 40</td>
<td></td>
<td>0.500</td>
<td>0.950</td>
<td>0.01283</td>
<td>2.764</td>
</tr>
<tr>
<td>41 to 44</td>
<td></td>
<td>0.600</td>
<td>0.940</td>
<td>0.01610</td>
<td>3.587</td>
</tr>
<tr>
<td>45 to 48</td>
<td></td>
<td>0.070</td>
<td>0.930</td>
<td>0.01910</td>
<td>4.590</td>
</tr>
<tr>
<td>49 to 59</td>
<td></td>
<td>0.080</td>
<td>0.920</td>
<td>0.02183</td>
<td>5.520</td>
</tr>
<tr>
<td>57 to 60</td>
<td></td>
<td>0.090</td>
<td>0.910</td>
<td>0.02374</td>
<td>6.214</td>
</tr>
<tr>
<td>61 to 65</td>
<td></td>
<td>0.100</td>
<td>0.900</td>
<td>0.02559</td>
<td>6.810</td>
</tr>
<tr>
<td>69 to 75</td>
<td></td>
<td>0.109</td>
<td>0.891</td>
<td>0.02662</td>
<td>7.372</td>
</tr>
<tr>
<td>73 to 80</td>
<td></td>
<td>0.120</td>
<td>0.880</td>
<td>0.02733</td>
<td>8.133</td>
</tr>
<tr>
<td>81 to 84</td>
<td></td>
<td>0.129</td>
<td>0.871</td>
<td>0.02762</td>
<td>8.700</td>
</tr>
<tr>
<td>85 to 92</td>
<td></td>
<td>0.140</td>
<td>0.860</td>
<td>0.02759</td>
<td>8.885</td>
</tr>
<tr>
<td><strong>Av. ( k_1 )</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>172,430</td>
</tr>
<tr>
<td>93 to 96</td>
<td></td>
<td>0.150</td>
<td>0.850</td>
<td>0.02719</td>
<td>8.380</td>
</tr>
<tr>
<td>97 to 104</td>
<td></td>
<td>0.160</td>
<td>0.840</td>
<td>0.02655</td>
<td>8.049</td>
</tr>
<tr>
<td>106 to 108</td>
<td></td>
<td>0.186</td>
<td>0.834</td>
<td>0.02905</td>
<td>7.523</td>
</tr>
<tr>
<td>109 to 116</td>
<td></td>
<td>0.180</td>
<td>0.820</td>
<td>0.02455</td>
<td>6.847</td>
</tr>
<tr>
<td>117 to 120</td>
<td></td>
<td>0.190</td>
<td>0.810</td>
<td>0.02334</td>
<td>5.988</td>
</tr>
<tr>
<td>121 to 124</td>
<td></td>
<td>0.200</td>
<td>0.800</td>
<td>0.02195</td>
<td>4.988</td>
</tr>
<tr>
<td>133 to 140</td>
<td></td>
<td>0.220</td>
<td>0.780</td>
<td>0.01910</td>
<td>2.760</td>
</tr>
<tr>
<td>141 to 144</td>
<td></td>
<td>0.228</td>
<td>0.772</td>
<td>0.01787</td>
<td>2.118</td>
</tr>
<tr>
<td>145 to 152</td>
<td></td>
<td>0.240</td>
<td>0.760</td>
<td>0.01625</td>
<td>1.749</td>
</tr>
</tbody>
</table>
The results given in the table are shown graphically in the upper left-hand curve of Figure 1. Ordinates in this figure are values of \( s = \frac{s'}{\tau} \); abscessas are partial pressures of fuel and oxygen. Experimental values are represented by dots, ●. Values of \( s = 172,430 \) \([\text{CO}]^2[\text{O}_2]^1\) are shown by open circles and continuous line. The lower curve in this figure represents in a similar way experimental values obtained from records of the explosive reaction \( 2\text{CO} + \text{O}_2 \rightarrow \) already mentioned. For this reaction the value of \( k_1 = \frac{s}{\Gamma} \) was found to be 691. Values corresponding to the equation \( s = 691 \) \([\text{CO}]^2[\text{O}_2] \) are represented by open circles and continuous line. The maximum value of \( s \) is 691 = \([0.667]^2[0.333]^1 = 103 \text{ cm/sec} \). Table II gives the experimental values found for this reaction.

**TABLE II.—OBSERVED RATE OF FLAME PROPAGATION IN 2CO + O_2 → EXPLOSIVE REACTION AT CONSTANT PRESSURE**

<table>
<thead>
<tr>
<th>Record 9-7-27 No.</th>
<th>Partial pressure atmosphere</th>
<th>( \Gamma = [\text{CO}]^2 [\text{O}_2] )</th>
<th>( s^2/\tau ) cm/sec</th>
<th>( s' = s' \Gamma ) cm/sec</th>
<th>( k_1 = \frac{s}{\Gamma} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 to 3</td>
<td>0.224</td>
<td>0.776</td>
<td>0.0389</td>
<td>191</td>
<td>27.6</td>
</tr>
<tr>
<td>4 to 7</td>
<td>0.288</td>
<td>0.760</td>
<td>0.0590</td>
<td>226</td>
<td>34.7</td>
</tr>
<tr>
<td>8 to 11</td>
<td>0.310</td>
<td>0.721</td>
<td>0.0681</td>
<td>279</td>
<td>37.5</td>
</tr>
<tr>
<td>12 to 15</td>
<td>0.331</td>
<td>0.700</td>
<td>0.0853</td>
<td>335</td>
<td>45.3</td>
</tr>
<tr>
<td>16 to 19</td>
<td>0.355</td>
<td>0.675</td>
<td>0.1013</td>
<td>386</td>
<td>50.3</td>
</tr>
<tr>
<td>20 to 23</td>
<td>0.359</td>
<td>0.641</td>
<td>0.0826</td>
<td>343</td>
<td>55.5</td>
</tr>
<tr>
<td>24 to 27</td>
<td>0.338</td>
<td>0.612</td>
<td>0.0921</td>
<td>347</td>
<td>58.3</td>
</tr>
<tr>
<td>28 to 31</td>
<td>0.416</td>
<td>0.584</td>
<td>0.1011</td>
<td>561</td>
<td>71.1</td>
</tr>
<tr>
<td>32 to 35</td>
<td>0.490</td>
<td>0.540</td>
<td>0.1140</td>
<td>632</td>
<td>80.3</td>
</tr>
<tr>
<td>36 to 39</td>
<td>0.491</td>
<td>0.509</td>
<td>0.1227</td>
<td>660</td>
<td>84.8</td>
</tr>
<tr>
<td>40 to 43</td>
<td>0.528</td>
<td>0.477</td>
<td>0.1304</td>
<td>714</td>
<td>88.4</td>
</tr>
<tr>
<td>44 to 47</td>
<td>0.674</td>
<td>0.426</td>
<td>0.1404</td>
<td>794</td>
<td>96.8</td>
</tr>
<tr>
<td>48 to 51</td>
<td>0.622</td>
<td>0.378</td>
<td>0.1463</td>
<td>858</td>
<td>100.6</td>
</tr>
<tr>
<td>52 to 55</td>
<td>0.638</td>
<td>0.332</td>
<td>0.1480</td>
<td>870</td>
<td>102.8</td>
</tr>
<tr>
<td>56 to 59</td>
<td>0.726</td>
<td>0.274</td>
<td>0.1449</td>
<td>949</td>
<td>101.9</td>
</tr>
<tr>
<td>60 to 63</td>
<td>0.775</td>
<td>0.225</td>
<td>0.1351</td>
<td>814</td>
<td>92.2</td>
</tr>
<tr>
<td>64 to 67</td>
<td>0.810</td>
<td>0.190</td>
<td>0.1247</td>
<td>733</td>
<td>88.4</td>
</tr>
<tr>
<td>68 to 71</td>
<td>0.840</td>
<td>0.160</td>
<td>0.1129</td>
<td>632</td>
<td>79.2</td>
</tr>
<tr>
<td>72 to 75</td>
<td>0.848</td>
<td>0.152</td>
<td>1.0968</td>
<td>614</td>
<td>77.1</td>
</tr>
<tr>
<td>76 to 79</td>
<td>0.883</td>
<td>0.117</td>
<td>0.912</td>
<td>463</td>
<td>63.9</td>
</tr>
<tr>
<td>80 to 83</td>
<td>0.903</td>
<td>0.097</td>
<td>0.791</td>
<td>420</td>
<td>60.1</td>
</tr>
<tr>
<td>Av. ( k_1 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Mixtures of these two gases, carbon monoxide and butane, that differ widely in reaction characteristics, as reaction speed, reaction order, and velocity constant \( k_1 \) were made up in various proportions into composite fuels \( F \) and examined in the same way as the above simple gases. There is no way to distinguish the time-volume photographic figures of the explosive reaction at constant pressure of different homogeneous explosive mixtures. There is only one reaction zone in any case, and at constant pressure it is propagated at constant speed for moderate velocities below the rate of sound in the gases. To what extent the reaction characteristics of a composite fuel may be predicted from the reaction characteristics of its components on the assumption that the simultaneous reactions occurring within the explosive reaction zone, where each runs its course according to its own order and mechanism "independently of any other reactions occurring at the same time," is shown in the experimental results given below.

A composite fuel \( F \) was made up of the two gases in the following proportions: 95 parts by volume of carbon monoxide and 5 parts by volume of butane. The equivalent reaction order of the resulting fuel should then be

\[
\begin{align*}
0.05 \text{ part CO, order } 3 & = 2.85 \\
0.05 \text{ part C}_4\text{H}_{10}, \text{ order } 15 & = .75 \\
\text{Equivalent reaction order} & = 3.60
\end{align*}
\]

The amount of oxygen necessary for complete combustion of one part of the fuel is

\[
\begin{align*}
0.95 \text{ CO} + 0.475 \text{ O}_2 & = 0.95 \text{ CO}_2 \\
0.05 \text{ C}_4\text{H}_{10} + .325 \text{ O}_2 & = .20 \text{ CO}_2 + 0.25 \text{ H}_2\text{O}
\end{align*}
\]

\[1 \text{ F + .8 O}_2 = 1.15 \text{ CO}_2 + .35 \text{ H}_2\text{O}\]

The stoichiometric equation for this fuel of order 3.6 would be

\[2 \text{ F + 1.6 O}_2 = 2.3 \text{ CO}_2 + 0.5 \text{ H}_2\text{O}\]

Table III gives the experimental values found for this fuel. \( k_2 = \frac{s}{\Gamma} = 2.647 \cdot \Gamma = [F]^3 \cdot [\text{O}_2]^{1.5} \cdot s_{\max} \) should then be found for \( s = 2.647 \) \([0.555]^3[0.445]^{1.5} = 223 \text{ cm/sec} \). Figure 2 shows these results expressed graphically. Observed values of \( s = s' \frac{\tau}{\Gamma} \) are shown in the figure by dots ●. Calculated values of \( s = 2.647 \) \([F]^3[\text{O}_2]^{1.5} \) are shown by open circles, ○, and continuous line.
TABLE III.—OBSERVED RATES OF FLAME PROPAGATION IN A FUEL F, CONSISTING OF 95 PARTS BY VOLUME OF CARBON MONOXIDE AND 5 PARTS BUTANE, WITH OXYGEN

<table>
<thead>
<tr>
<th>Record 10-24-28 No.</th>
<th>Partial-pressure atmospheres</th>
<th>$\Gamma=\frac{[F][O_2]}{\text{cm/sec}}$</th>
<th>$s=\frac{t}{\Gamma}$ cm/sec</th>
<th>$s=\frac{t}{\Gamma}$ cm/sec</th>
<th>$s=\frac{t}{\Gamma}$ cm/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 to 7</td>
<td>0.265</td>
<td>0.735</td>
<td>0.04291</td>
<td>848</td>
<td>105.6</td>
</tr>
<tr>
<td>8 to 11</td>
<td>0.317</td>
<td>0.683</td>
<td>0.05658</td>
<td>1.262</td>
<td>138.0</td>
</tr>
<tr>
<td>12 to 15</td>
<td>0.389</td>
<td>0.631</td>
<td>0.06926</td>
<td>1.624</td>
<td>178.0</td>
</tr>
<tr>
<td>16 to 19</td>
<td>0.412</td>
<td>0.688</td>
<td>0.07248</td>
<td>1.810</td>
<td>198.0</td>
</tr>
<tr>
<td>20 to 23</td>
<td>0.483</td>
<td>0.547</td>
<td>0.08417</td>
<td>2.184</td>
<td>215.0</td>
</tr>
<tr>
<td>24 to 27</td>
<td>0.515</td>
<td>0.486</td>
<td>0.08831</td>
<td>2.379</td>
<td>223.0</td>
</tr>
<tr>
<td>28 to 31</td>
<td>0.571</td>
<td>0.429</td>
<td>0.09159</td>
<td>2.526</td>
<td>233.0</td>
</tr>
<tr>
<td>32 to 35</td>
<td>0.622</td>
<td>0.378</td>
<td>0.09638</td>
<td>2.661</td>
<td>233.0</td>
</tr>
<tr>
<td>36 to 39</td>
<td>0.674</td>
<td>0.322</td>
<td>0.10136</td>
<td>2.800</td>
<td>243.0</td>
</tr>
<tr>
<td>Av. $kr$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40 to 43</td>
<td>0.733</td>
<td>0.267</td>
<td>0.06495</td>
<td>1.733</td>
<td>155.0</td>
</tr>
<tr>
<td>44 to 47</td>
<td>0.770</td>
<td>0.230</td>
<td>0.06833</td>
<td>1.654</td>
<td>121.0</td>
</tr>
</tbody>
</table>

In like manner the equivalent order of a fuel consisting of 90 parts by volume of carbon monoxide and 10 parts butane would be

- 0.90 part CO, order 3, 2.70
- 0.10 part C4H10, order 15, 1.50

Equivalent order of fuel, 4.20

Its stoichiometric equation written for order 4.2 would be

$$2F + 2.2 O_2 = 2.6 CO_2 + H_2O$$

Table IV gives the experimental values obtained with this fuel. The value found for $kr=\frac{s}{\Gamma}$ is 4,652.

The amount of oxygen necessary for complete combustion of one part of this fuel is

$$0.90 \text{ CO } + 0.45 \text{ O}_2 = 0.90 \text{ CO}_2$$
$$0.10 \text{ C}_4\text{H}_{10} + 0.65 \text{ O}_2 = 0.40 \text{ CO}_2 + 0.5 \text{ H}_2\text{O}$$
$$1F + 1.1 \text{ O}_2 = 1.3 \text{ CO}_2 + 0.5 \text{ H}_2\text{O}$$

In Figure 3 the curve represented by a continuous line corresponds to the equation $s = 4,652 \left[\frac{[F][O_2]}{\Gamma}\right]^{0.33}$. Observed values of $s$ are shown by the mark *. $s_{\text{max}} = 4,652 [0.476]^{0.33} [0.524]^{0.33} = 254 \text{ cm/sec}$.
A fuel whose composition is 80 parts by volume carbon monoxide and 20 parts butane has an equivalent reaction order of 5.4. Its stoichiometric equation written for this order and for complete combustion would be

$$2F + 3.4 O_2 = 3.2 CO_2 + 2 H_2O$$

The experimental results obtained from the explosive reaction of this fuel are given in Table V. The value for $k_\gamma = \frac{\varepsilon}{\Gamma} = 12,136$. The value for $r_{\text{max}}$ would then be

$$s_{\text{max}} = 12,136 \left(0.370\right)^2 \left(0.630\right)^{1.4} = 345 \text{ cm/sec}.$$ 

These results are also shown graphically in Figure 4. Observed values of $s$ are marked •. Calculated values of $s = 12,136 \left[F\right]^2 \left[O_2\right]^{1.4}$ are given by the curve marked by a continuous line.
A composite fuel made up of 70 parts by volume of carbon monoxide and 30 parts butane has an equivalent reaction order of 6.6. Its stoichiometric equation for this order and for complete combustion will be

$$2F + 4.6O_2 = 3.8CO_2 + 3H_2O$$

Table VI gives the experimental results obtained from the explosive reaction of this fuel. The value for $k_F = \frac{\dot{\gamma}}{\gamma}$ is $[F]e\ [O_2]^{4.4}$. The value for $k_F = \frac{\dot{\gamma}}{\gamma} = 21,848$. The value for $\xi_{max}$ is

$$\xi_{max} = 21,848 \times [0.300]^{4} \times [0.700]^{4.4} = 381 \text{ cm/sec.}$$

These results are shown graphically in Figure 5. Observed values are marked •. The locus of the equation $21,848 [F]^2 [O_2]^{4.4}$ is shown by the continuous curve.

TABLE VI.—OBSERVED VALUES OF THE RATE OF FLAME PROPAGATION IN A FUEL F, MADE UP OF 70 PARTS BY VOLUME OF CARBON MONOXIDE AND 30 PARTS BUTANE, WITH OXYGEN

<table>
<thead>
<tr>
<th>Record 11-4-28 No.</th>
<th>Partial-pressure atmospheres</th>
<th>$\Gamma = [F]^2 [O_2]^{4.4}$</th>
<th>$\dot{\gamma} = \frac{\dot{\gamma}}{\gamma} \text{ cm/sec}$</th>
<th>$\dot{\gamma} = \frac{\dot{\gamma}}{\gamma} \text{ cm/sec}$</th>
<th>$k_F = \frac{\dot{\gamma}}{\gamma}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 to 4</td>
<td>0.063 [O_2]</td>
<td>0.005975</td>
<td>1.181</td>
<td>139</td>
<td>22,230</td>
</tr>
<tr>
<td>5 to 8</td>
<td>0.063 [O_2]</td>
<td>0.068382</td>
<td>2,010</td>
<td>193</td>
<td>25,090</td>
</tr>
<tr>
<td>9 to 12</td>
<td>0.063 [O_2]</td>
<td>0.103696</td>
<td>2,474</td>
<td>225</td>
<td>21,300</td>
</tr>
<tr>
<td>13 to 16</td>
<td>0.063 [O_2]</td>
<td>0.12650</td>
<td>2,992</td>
<td>254</td>
<td>20,990</td>
</tr>
<tr>
<td>17 to 20</td>
<td>0.063 [O_2]</td>
<td>0.13920</td>
<td>4,177</td>
<td>308</td>
<td>22,120</td>
</tr>
<tr>
<td>25 to 28</td>
<td>0.063 [O_2]</td>
<td>0.16330</td>
<td>5,321</td>
<td>332</td>
<td>20,450</td>
</tr>
<tr>
<td>29 to 32</td>
<td>0.063 [O_2]</td>
<td>0.17090</td>
<td>6,340</td>
<td>372</td>
<td>21,800</td>
</tr>
<tr>
<td>33 to 36</td>
<td>0.063 [O_2]</td>
<td>0.17410</td>
<td>6,932</td>
<td>395</td>
<td>22,170</td>
</tr>
<tr>
<td>37 to 40</td>
<td>0.063 [O_2]</td>
<td>0.17430</td>
<td>6,303</td>
<td>390</td>
<td>22,380</td>
</tr>
<tr>
<td>Av. $k_F$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>21,848</td>
</tr>
<tr>
<td>41 to 44</td>
<td>0.063 [O_2]</td>
<td>0.17410</td>
<td>6,056</td>
<td>365</td>
<td>20,970</td>
</tr>
<tr>
<td>45 to 47</td>
<td>0.063 [O_2]</td>
<td>0.17320</td>
<td>6,087</td>
<td>359</td>
<td>20,720</td>
</tr>
<tr>
<td>48 to 50</td>
<td>0.063 [O_2]</td>
<td>0.17140</td>
<td>5,875</td>
<td>330</td>
<td>19,260</td>
</tr>
<tr>
<td>53 to 56</td>
<td>0.063 [O_2]</td>
<td>0.16180</td>
<td>5,438</td>
<td>309</td>
<td>19,190</td>
</tr>
<tr>
<td>57 to 60</td>
<td>0.063 [O_2]</td>
<td>0.15090</td>
<td>4,820</td>
<td>260</td>
<td>16,560</td>
</tr>
<tr>
<td>61 to 64</td>
<td>0.063 [O_2]</td>
<td>0.15530</td>
<td>3,145</td>
<td>174</td>
<td>13,720</td>
</tr>
<tr>
<td>65 to 68</td>
<td>0.063 [O_2]</td>
<td>0.12010</td>
<td>2,177</td>
<td>168</td>
<td>13,160</td>
</tr>
<tr>
<td>69 to 72</td>
<td>0.063 [O_2]</td>
<td>0.10890</td>
<td>1,117</td>
<td>66</td>
<td>6,264</td>
</tr>
</tbody>
</table>
Table VII gives results observed in the reaction of a fuel made up of 60 parts by volume of carbon monoxide and 40 parts butane. The equivalent reaction order of this fuel with oxygen for complete combustion is 7.8. Its stoichiometric equation written for this order is

$$2F + 5.8 \text{O}_2 = 4.4 \text{CO}_2 + 4 \text{H}_2\text{O}$$

In this case, $$P = \frac{[F]^7 \times [\text{O}_2]^{1.8}}{r} = 36,870$$. The value for $$s_{\max}$$ should then be

$$s_{\max} = 36,870 [0.256]^{7} [0.744]^{1.8} = 435 \text{ cm/sec}$$

Figure 6 expresses these results in graphic form. Observed values determined from the photographic figures, $$s = s_{\max}^{\frac{1}{r}}$$ are marked •. Values calculated from the statistical relation $$s = 3,687 [F]^{4.4} [\text{O}_2]$$ are marked by the continuous curve.

**TABLE VII—OBSERVED VALUES OF THE RATE OF FLAME PROPAGATION IN A FUEL F, MADE UP OF 60 PARTS BY VOLUME OF CARBON MONOXIDE AND 40 PARTS BUTANE, WITH OXYGEN**

<table>
<thead>
<tr>
<th>Record, 11-4-25 No.</th>
<th>Partial pressures</th>
<th>$$P = \frac{[F]^7 \times [\text{O}_2]^{1.8}}{r}$$</th>
<th>$$s = s_{\max}^{\frac{1}{7}}$$</th>
<th>$$s = s_{\max}^{\frac{1}{r}}$$</th>
<th>$$k_{1} = \frac{r}{P}$$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 to 4</td>
<td>0.069</td>
<td>0.931</td>
<td>0.003142</td>
<td>1.046</td>
<td>122</td>
</tr>
<tr>
<td>5 to 8</td>
<td>0.066</td>
<td>0.935</td>
<td>0.003055</td>
<td>1.172</td>
<td>137</td>
</tr>
<tr>
<td>9 to 12</td>
<td>0.119</td>
<td>0.851</td>
<td>0.006792</td>
<td>2.246</td>
<td>252</td>
</tr>
<tr>
<td>13 to 16</td>
<td>0.145</td>
<td>0.855</td>
<td>0.008185</td>
<td>3.854</td>
<td>303</td>
</tr>
<tr>
<td>17 to 20</td>
<td>0.171</td>
<td>0.829</td>
<td>0.009861</td>
<td>5.066</td>
<td>351</td>
</tr>
<tr>
<td>21 to 24</td>
<td>0.196</td>
<td>0.806</td>
<td>0.010798</td>
<td>5.293</td>
<td>391</td>
</tr>
<tr>
<td>26 to 30</td>
<td>0.210</td>
<td>0.790</td>
<td>0.011230</td>
<td>5.523</td>
<td>418</td>
</tr>
<tr>
<td>29 to 32</td>
<td>0.225</td>
<td>0.775</td>
<td>0.011540</td>
<td>6.220</td>
<td>420</td>
</tr>
<tr>
<td>33 to 36</td>
<td>0.238</td>
<td>0.764</td>
<td>0.011600</td>
<td>6.422</td>
<td>423</td>
</tr>
<tr>
<td>37 to 40</td>
<td>0.245</td>
<td>0.755</td>
<td>0.011750</td>
<td>6.663</td>
<td>422</td>
</tr>
<tr>
<td>41 to 44</td>
<td>0.255</td>
<td>0.745</td>
<td>0.013000</td>
<td>6.903</td>
<td>420</td>
</tr>
<tr>
<td>Av. $$k_{1}$$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>36,870</td>
</tr>
<tr>
<td>45 to 48</td>
<td>0.263</td>
<td>0.737</td>
<td>0.011790</td>
<td>6.500</td>
<td>420</td>
</tr>
<tr>
<td>49 to 52</td>
<td>0.275</td>
<td>0.725</td>
<td>0.011700</td>
<td>6.007</td>
<td>408</td>
</tr>
<tr>
<td>53 to 56</td>
<td>0.284</td>
<td>0.706</td>
<td>0.011280</td>
<td>6.065</td>
<td>350</td>
</tr>
<tr>
<td>57 to 60</td>
<td>0.299</td>
<td>0.671</td>
<td>0.010896</td>
<td>5.223</td>
<td>311</td>
</tr>
<tr>
<td>61 to 64</td>
<td>0.355</td>
<td>0.645</td>
<td>0.009910</td>
<td>4.413</td>
<td>267</td>
</tr>
<tr>
<td>65 to 68</td>
<td>0.375</td>
<td>0.622</td>
<td>0.008660</td>
<td>3.351</td>
<td>188</td>
</tr>
<tr>
<td>69 to 72</td>
<td>0.408</td>
<td>0.592</td>
<td>0.007166</td>
<td>2.087</td>
<td>115</td>
</tr>
<tr>
<td>73 to 76</td>
<td>0.423</td>
<td>0.577</td>
<td>0.007372</td>
<td>9.199</td>
<td>60</td>
</tr>
</tbody>
</table>
When the composite fuel consists of equal parts by volume of the components carbon monoxide and butane, its equivalent reaction order is 9. A stoichiometric equation written for this order and for complete combustion is

\[
2F + 7O_2 = 5CO_2 + 5H_2O
\]

The values for \( \Gamma \) will then be written \( \Gamma = [F]^9 [O_2]^7 \), and the value for \( k_F = \frac{8}{\Gamma} = 52,757 \). \( s_{\text{max}} \) will be

\[
s_{\text{max}} = 52,757 [0.222]^9 [0.778]^7 = 450
\]

Figure 7 is a graphic statement of these results and their relation drawn from the experimental values given in Table VIII.

**TABLE VIII.** OBSERVED RATE OF PROPAGATION OF REACTION ZONE IN A FUEL F, CONSISTING OF 50 PARTS BY VOLUME OF CARBON MONOXIDE AND 50 PARTS BUTANE WITH OXYGEN

<table>
<thead>
<tr>
<th>Record 11-13-49 No.</th>
<th>Partial-pressure atmospheres</th>
<th>( \Gamma - [F]^9 [O_2]^7 )</th>
<th>( s - s' )</th>
<th>( s - s'' )</th>
<th>( s_{\text{max}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 to 4</td>
<td>0.049</td>
<td>0.00169</td>
<td>0.0460</td>
<td>0.0340</td>
<td>51,430</td>
</tr>
<tr>
<td>5 to 8</td>
<td>0.075</td>
<td>0.00326</td>
<td>0.0756</td>
<td>0.0566</td>
<td>51,870</td>
</tr>
<tr>
<td>9 to 12</td>
<td>0.096</td>
<td>0.00468</td>
<td>0.0760</td>
<td>0.0566</td>
<td>51,870</td>
</tr>
<tr>
<td>13 to 16</td>
<td>0.135</td>
<td>0.00814</td>
<td>0.0757</td>
<td>0.0566</td>
<td>51,870</td>
</tr>
<tr>
<td>17 to 20</td>
<td>0.165</td>
<td>0.00721</td>
<td>0.0655</td>
<td>0.0464</td>
<td>52,200</td>
</tr>
<tr>
<td>21 to 24</td>
<td>0.166</td>
<td>0.00774</td>
<td>0.0642</td>
<td>0.0464</td>
<td>53,100</td>
</tr>
<tr>
<td>25 to 28</td>
<td>0.165</td>
<td>0.00771</td>
<td>0.0640</td>
<td>0.0464</td>
<td>53,100</td>
</tr>
<tr>
<td>29 to 32</td>
<td>0.196</td>
<td>0.00856</td>
<td>0.0757</td>
<td>0.0566</td>
<td>51,870</td>
</tr>
<tr>
<td>33 to 36</td>
<td>0.209</td>
<td>0.00847</td>
<td>0.0749</td>
<td>0.0566</td>
<td>53,100</td>
</tr>
<tr>
<td><strong>Av. ( k_F )</strong></td>
<td></td>
<td></td>
<td>52,757</td>
<td>0.0566</td>
<td>53,100</td>
</tr>
<tr>
<td>41 to 44</td>
<td>0.230</td>
<td>0.00849</td>
<td>0.0741</td>
<td>0.0566</td>
<td>49,180</td>
</tr>
<tr>
<td>45 to 48</td>
<td>0.237</td>
<td>0.00803</td>
<td>0.0733</td>
<td>0.0566</td>
<td>46,110</td>
</tr>
<tr>
<td>49 to 52</td>
<td>0.259</td>
<td>0.00788</td>
<td>0.0745</td>
<td>0.0566</td>
<td>49,180</td>
</tr>
<tr>
<td>55 to 58</td>
<td>0.289</td>
<td>0.00891</td>
<td>0.0759</td>
<td>0.0566</td>
<td>53,100</td>
</tr>
<tr>
<td>57 to 60</td>
<td>0.314</td>
<td>0.00613</td>
<td>0.0685</td>
<td>0.0464</td>
<td>54,440</td>
</tr>
<tr>
<td>61 to 64</td>
<td>0.346</td>
<td>0.00609</td>
<td>0.0674</td>
<td>0.0464</td>
<td>53,030</td>
</tr>
<tr>
<td>65 to 68</td>
<td>0.380</td>
<td>0.00598</td>
<td>0.0620</td>
<td>0.0464</td>
<td>53,030</td>
</tr>
</tbody>
</table>

When the composition of the fuel is 30 parts carbon monoxide by volume and 70 parts butane, the equivalent reaction order is 11.4. The stoichiometric equation written for the fuel of this order and for complete combustion is

\[
2F + 9.4O_2 = 6.3CO_2 + 7H_2O
\]

\( \Gamma = [F]^{11.4} [O_2]^{7.4} \), \( k_F = \frac{8}{\Gamma} = 92,978 \) and \( s_{\text{max}} \) will be found for the relation

\[
s_{\text{max}} = 92,978 [0.175]^{11.4} [0.824]^{7.4} = 467
\]

Table IX gives the experimental results obtained from the reaction of this fuel. Figure 8 is their graphic representation where observed values of \( s = s' \) are marked by dots ● and calculated values \( s = 92,978 [F]^{11.4} [O_2]^{7.4} \) are marked by a continuous line.
Table IX.—Observed Rates of Flame Propagation in a Fuel F Consisting of 30 Parts by Volume of Carbon Monoxide and 70 Parts Butane, with Oxygen

<table>
<thead>
<tr>
<th>Record 11-15-26 No.</th>
<th>Partial-pressure atmospheres</th>
<th>$\Gamma = [F]_0 [O_2]^{1.4}$</th>
<th>$s^2 = \Gamma \frac{d}{d \text{cm/sec}}$</th>
<th>$s = s^2 \sqrt{a}$</th>
<th>$k_F = \frac{s}{\Gamma}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 to 4</td>
<td>0.0427</td>
<td>0.9673</td>
<td>0.001211</td>
<td>1.010</td>
<td>109</td>
</tr>
<tr>
<td>5 to 8</td>
<td>0.0452</td>
<td>0.9548</td>
<td>0.001222</td>
<td>1.356</td>
<td>129</td>
</tr>
<tr>
<td>9 to 12</td>
<td>0.0508</td>
<td>0.9392</td>
<td>0.002052</td>
<td>2.041</td>
<td>204</td>
</tr>
<tr>
<td>13 to 16</td>
<td>0.0562</td>
<td>0.9148</td>
<td>0.003141</td>
<td>3.305</td>
<td>305</td>
</tr>
<tr>
<td>17 to 20</td>
<td>0.1110</td>
<td>0.8680</td>
<td>0.004077</td>
<td>5.582</td>
<td>379</td>
</tr>
<tr>
<td>21 to 24</td>
<td>0.1320</td>
<td>0.8360</td>
<td>0.004944</td>
<td>8.035</td>
<td>445</td>
</tr>
<tr>
<td>25 to 28</td>
<td>0.1570</td>
<td>0.8430</td>
<td>0.004924</td>
<td>8.035</td>
<td>445</td>
</tr>
<tr>
<td>29 to 32</td>
<td>0.1700</td>
<td>0.8800</td>
<td>0.005015</td>
<td>7.995</td>
<td>428</td>
</tr>
<tr>
<td>Av. $k_F$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>33 to 36</td>
<td>0.1800</td>
<td>0.8200</td>
<td>0.005015</td>
<td>7.362</td>
<td>403</td>
</tr>
<tr>
<td>37 to 40</td>
<td>0.2050</td>
<td>0.7850</td>
<td>0.004888</td>
<td>6.958</td>
<td>365</td>
</tr>
<tr>
<td>41 to 44</td>
<td>0.2200</td>
<td>0.7710</td>
<td>0.004653</td>
<td>6.442</td>
<td>323</td>
</tr>
<tr>
<td>45 to 48</td>
<td>0.2560</td>
<td>0.7440</td>
<td>0.004084</td>
<td>4.619</td>
<td>258</td>
</tr>
<tr>
<td>49 to 52</td>
<td>0.2800</td>
<td>0.7200</td>
<td>0.003860</td>
<td>3.808</td>
<td>209</td>
</tr>
<tr>
<td>53 to 56</td>
<td>0.3060</td>
<td>0.6940</td>
<td>0.003024</td>
<td>1.887</td>
<td>102</td>
</tr>
</tbody>
</table>

For a composite fuel made up of 10 parts by volume of carbon monoxide and 90 parts butane the equivalent reaction order is 13.8. Its stoichiometric equation written for this order and for complete combustion is

$$2F + 11.8O_2 = 7.4CO_2 + 9H_2O$$

Table X gives the observed results obtained from the reaction of this fuel. $\Gamma = [F]_0 [O_2]^{1.4}$. $k_F = \frac{s}{\Gamma} = 143,020$, $s_{\text{max}} = 143,020 [0.145]^5 [0.855]^{1.4} = 473$.

Figure 9 represents these results graphically. Observed values are marked ●. Values obtained from the equation $143,020 [F]_0 [O_2]^{1.4}$ are represented by the continuous line on the figure.
TABLE X.—OBSERVED RATES OF FLAME PROPAGATION IN A FUEL F, CONSISTING OF 10 PARTS BY VOLUME OF CARBON MONOXIDE AND 90 PARTS BUTANE, WITH OXYGEN

<table>
<thead>
<tr>
<th>Record 11-27-26 No.</th>
<th>Partial-pressure atmospheres</th>
<th>$F=F^0 [O^2]^4$</th>
<th>$s'=-e_i$</th>
<th>$e=e_i$</th>
<th>$s=s_i$</th>
<th>$k_F$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$P$</td>
<td>$t_i$</td>
<td>$t_i$</td>
<td>$C_m$</td>
<td></td>
</tr>
<tr>
<td>5 to 8</td>
<td>.050</td>
<td>.980</td>
<td>0.001384</td>
<td>2.412</td>
<td>195</td>
<td>142,600</td>
</tr>
<tr>
<td>9 to 12</td>
<td>.070</td>
<td>.990</td>
<td>0.002082</td>
<td>4.259</td>
<td>307</td>
<td>148,200</td>
</tr>
<tr>
<td>13 to 16</td>
<td>.090</td>
<td>.910</td>
<td>0.002650</td>
<td>6.670</td>
<td>373</td>
<td>140,600</td>
</tr>
<tr>
<td>17 to 20</td>
<td>.111</td>
<td>.889</td>
<td>0.003073</td>
<td>8.660</td>
<td>452</td>
<td>135,600</td>
</tr>
<tr>
<td>21 to 24</td>
<td>.130</td>
<td>.870</td>
<td>0.003864</td>
<td>8.839</td>
<td>458</td>
<td>130,900</td>
</tr>
<tr>
<td>29 to 32</td>
<td>.160</td>
<td>.860</td>
<td>0.003906</td>
<td>8.856</td>
<td>459</td>
<td>132,000</td>
</tr>
<tr>
<td>33 to 36</td>
<td>.150</td>
<td>.980</td>
<td>0.003304</td>
<td>7.881</td>
<td>398</td>
<td>120,900</td>
</tr>
<tr>
<td>37 to 40</td>
<td>.170</td>
<td>.830</td>
<td>0.002208</td>
<td>7.476</td>
<td>364</td>
<td>113,600</td>
</tr>
<tr>
<td>41 to 44</td>
<td>.186</td>
<td>.814</td>
<td>0.000349</td>
<td>6.494</td>
<td>297</td>
<td>97,520</td>
</tr>
<tr>
<td>45 to 48</td>
<td>.206</td>
<td>.791</td>
<td>0.002748</td>
<td>5.500</td>
<td>236</td>
<td>82,150</td>
</tr>
<tr>
<td>49 to 52</td>
<td>.233</td>
<td>.761</td>
<td>0.002276</td>
<td>3.256</td>
<td>158</td>
<td>68,430</td>
</tr>
<tr>
<td>53 to 56</td>
<td>.264</td>
<td>.736</td>
<td>0.001873</td>
<td>1.476</td>
<td>75</td>
<td>41,130</td>
</tr>
<tr>
<td><strong>AV. $k_F$</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>143,020</td>
</tr>
</tbody>
</table>

A relation was also sought connecting the $k_F$ value of the fuel with the $k_i$ values of the fuel's components. Such a relation is found to be a simple one for the case where the reaction orders of the fuel's components are all the same. The reaction order of any fuel consisting of these components will then be the same as that of the components. (Reference 8, p. 15) so that

$$s = k_F [F]^n [O_2]^m$$

All of the factors to the right in the above equation may be known from the velocity coefficients of the reaction zone of the components and the mixture ratio of $F$ and $O_2$. That is, the rate of propagation of the reaction zone in any mixture ratio of $F$ and $O_2$ may be deduced for any composite fuel made up of components having the same reaction order.

When, however, the reaction orders of the components of the fuel differ greatly, the equivalent reaction order of the various possible mixtures made of these components will vary between the least and greatest reaction order to be found among its components. This may be seen from the records given above, and made more evident by the curve in Figure 10.

In order to show that the relations given above hold for composite fuels made up of many known components, there is given below one example of a set of results obtained from a fuel made up of three components—carbon monoxide, methane, and butane. In the example given, the fuel consisted of equal parts by volume of these components. The equivalent reaction order of this fuel is

$$0.333 \text{ part CO, order } = 1$$
$$0.333 \text{ part CH}_4 \text{ order } = 3 = 1$$
$$0.333 \text{ part C}_4\text{H}_{10} \text{ order } = 5 = 15$$

Equivalent order of fuel $F = 7$

The proportion of $O_2$ necessary for complete combustion of one part fuel is

$$0.333 \text{ CO } + 0.167 \text{ O}_2 = 0.333 \text{ CO}_2$$
$$0.333 \text{ CH}_4 + 0.667 \text{ O}_2 = 0.333 \text{ CO}_2 + 0.667 \text{ H}_2\text{O}$$
$$0.333 \text{ C}_4\text{H}_{10} + 2.165 \text{ O}_2 = 1.333 \text{ CO}_2 + 1.667 \text{ H}_2\text{O}$$

$$1 \text{ F } + \text{ 3 O}_2 = 2 \text{ CO}_2 + 2.33 \text{ H}_2\text{O}$$

Its stoichiometric equation written for order 7 is

$$1.75 F + 5.25 O_2 = 3.5 CO_2 + 4.04 H_2O$$

Observed results for this reaction are given in Table XI. $F = [F]^{1.75} [O_2]^{5.25}, k_F = \frac{s}{t} = 23,532$. The value for $s_{max}$ is

$$s_{max} = 23,532 [0.25]^{1.75} [0.75]^{5.25} = 460 \text{ cm/sec}$$

These results, plotted in the same manner as those already given, are shown in Figure 11.
TABLE XI.—OBSERVED VALUES OF THE RATE OF FLAME PROPAGATION IN A FUEL F, MADE UP OF 33.3 PARTS BY VOLUME OF CARBON MONOXIDE, 33.3 PARTS METHANE, AND 33.3 PARTS BUTANE WITH OXYGEN

<table>
<thead>
<tr>
<th>Record 4-30-29 No.</th>
<th>Partial-pressure atmospheres</th>
<th>$P_0$</th>
<th>$O_2$</th>
<th>$v = \frac{1}{k} \times 10^{-2}$</th>
<th>$s = \frac{r_0}{r_1}$</th>
<th>$v = \frac{1}{k} \times 10^{-2}$</th>
<th>$s = \frac{r_2}{r_1}$</th>
<th>$k = \frac{s}{r}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 to 8</td>
<td>0.050</td>
<td>0.920</td>
<td>0.00777</td>
<td>1.545</td>
<td>164</td>
<td>21.600</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9 to 12</td>
<td>0.110</td>
<td>0.880</td>
<td>0.01140</td>
<td>2.792</td>
<td>275</td>
<td>424</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13 to 16</td>
<td>0.140</td>
<td>0.840</td>
<td>0.01451</td>
<td>3.746</td>
<td>340</td>
<td>29.430</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16 to 19</td>
<td>0.181</td>
<td>0.810</td>
<td>0.01761</td>
<td>4.696</td>
<td>414</td>
<td>26.600</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 to 23</td>
<td>0.204</td>
<td>0.795</td>
<td>0.01859</td>
<td>6.614</td>
<td>448</td>
<td>25.970</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23 to 26</td>
<td>0.223</td>
<td>0.777</td>
<td>0.01911</td>
<td>7.538</td>
<td>485</td>
<td>25.820</td>
<td></td>
<td></td>
</tr>
<tr>
<td>27 to 30</td>
<td>0.238</td>
<td>0.762</td>
<td>0.01948</td>
<td>8.431</td>
<td>486</td>
<td>25.930</td>
<td></td>
<td></td>
</tr>
<tr>
<td>31 to 34</td>
<td>0.250</td>
<td>0.750</td>
<td>0.01950</td>
<td>9.450</td>
<td>485</td>
<td>25.820</td>
<td></td>
<td></td>
</tr>
<tr>
<td>35 to 38</td>
<td>0.257</td>
<td>0.748</td>
<td>0.01950</td>
<td>9.528</td>
<td>485</td>
<td>25.820</td>
<td></td>
<td></td>
</tr>
<tr>
<td>39 to 42</td>
<td>0.280</td>
<td>0.720</td>
<td>0.01921</td>
<td>6.955</td>
<td>391</td>
<td>20.360</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Av. $k_F$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>23.590</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

REMARKS

Deviations from statistical equation, $s = k_F [F]^{n} [O_2]^{m}$.—It will be noticed in all of the tables as well as in all of the coordinate figures given—except those for the $2CO + O_2 \rightarrow$ reaction—that the observed values of $s - s_{max}$ after passing the mixture ratio for $s_{max}$ and that this deviation from a theoretical value increases with increasing amounts of the hydrocarbon in excess of the theoretical amount of oxygen for complete combustion. The stoichiometric equation is written for complete combustion of the fuel. Complete combustion does not take place when the fuel is excess of the required amount of oxygen. Besides, the excess of a hydrocarbon or of carbon in the highly heated products of combustion containing water vapor is not an inert substance, as is an excess of CO in the equilibrium products, $CO_2$ of the $2CO + O_2 \rightarrow$ explosive reaction, nor the excess of $O_2$, always present, in the reaction products below the reaction for $s_{max}$. A reaction takes place between the excess of the hydrocarbon and water vapor that is not accounted for in the stoichiometric equation written for complete combustion, nor in the statistical expression that determines the theoretical curve. Similar deviations from a theoretical reaction constant $K$, due to the presence in the reacting system of an inert gas or to the dissociation of the products of reaction, led finally, when the causes of these deviations were better understood and suitable devices provided for their investigation and measurement, to the determination of specific heats of gases and the degree of dissociation of combustion products at the high temperatures at which the working fluid of the engine is employed. (Reference 9, p. 536, Reference 10, p. 513, Reference 11, p. 641.)

The deviations from a kinetic expression, $s = k_F [F]^{n} [O_2]^{m}$, here noticeable and measurable in the results given above, may prove of similar value concerning a more efficient combustion of hydrocarbon fuels in the gas engine. (Reference 8, p. 16.) The problem here is of the same order as the problem of the determination of an equilibrium in an autoclave used in the industrial synthesis of fuels: Given the pressure and temperature within the container, the composition of the hydrocarbon and the other gases of the mixture,
to determine the resulting products (equilibrium) at the temperature and pressure of the autoclave.

**Explosive limits.**—Quite incidental to the line of study that is the subject of this report, the results here given, together with many other results obtained with other gases and with other fuel combinations in the study of the kinetics of the gaseous explosive reaction at constant pressure, cover the range of "explosive limits" of those gases for the conditions of constant pressure imposed on the reaction. The subject is referred to here because investigations having in view the determination of explosive limits and seeking for the results obtained a fundamental relationship between fuel composition and range of inflammability have employed constant volume methods that involve great changes in pressure during the transformation and produce in the active gases the flame is entering not only indeterminate changes in their concentrations but also violent and erratic movement of the gases carrying the flame. There is no way under these (constant volume) conditions to distinguish between the flame movement due to the mass movement of the gases it is transforming and the essential part of its motion—namely, its motion relative to the gases themselves.

The marked disagreement noticeable in the results of different investigations carried out under conditions of constant volume called forth the following observation concerning the experimental procedure by constant volume methods that has usually been followed: "The spread of the ordinary flame through the explosive gaseous mixture depends in every respect upon the influence of experimental conditions imposed on the reaction. It is, therefore, little to the point to speak of explosive limits or of flame velocity in terms of percent composition of the explosive gases; every set of numerical results so obtained depends in large measure upon the mode of ignition and its position, upon the form and material of the inclosing container and upon the way by which the reaction runs its course—in short, upon the conditions imposed upon the reaction by the experimental device and method used. Under the same set of constant physical conditions, the same set of numerical results may well be obtained. The explosive limits of a number of gaseous mixtures have been repeatedly investigated, often under very different conditions and in consequence yielding very different results." (Reference 12, p. 637.)

The above observation may well apply to all kinetic studies of gaseous explosive reactions made under constant-volume conditions. Under these conditions indeterminate pressure changes set up in the active gases by the explosion and by reflected impulse waves render the concentrations of the active gases the flame may be entering at any instant indeterminate also.

So far as the writer is aware, no investigations with a view of finding a relation, if such exist, between explosive range and fuel composition have been carried out by constant-pressure methods. Without going into detail it may be seen that the results given in this report all cover the explosive range of the fuels studied. These experimental results, as well as the theoretical figures accompanying them, all clearly point to a fundamental relation connecting the magnitude of explosive range with the value of the partial pressure of the fuel for maximum energy \([F]_{\text{max}}\). Stated in general terms the relation is: The greater the value of \([F]_{\text{max}}\), the greater is the explosive range. The curves for the heavier hydrocarbons are all narrow, since their complete combustion requires so much oxygen. The actual experimental curves are still narrower, owing to the effect of the secondary reaction on the rich side. The curve for the CO, O, reaction is broad, since little oxygen is required for complete combustion. These statements may be expressed numerically:

\[
[F]_{\text{CO} \text{ max}} = 0.667, \text{its explosive range is } 0.93 - 0.20 = 0.73 \\
[F]_{\text{CH}_4 \text{ max}} = 0.333, \text{its explosive range is } 0.47 - 0.14 = 0.33 \\
[F]_{\text{CH}_3\text{OH max}} = 0.133, \text{its explosive range is } 0.24 - 0.04 = 0.20
\]

**Fuels of intermediate \([F]_{\text{max}}\) values show intermediate explosive ranges.**

**Bureau of Standards,**  
**Washington, D.C., May 9, 1929.**

**REFERENCES**