changes. Experimental details are given for the analytical work, for the determination of molecular refraction and for the measurement of absorption bands. In the case of neodymium perchlorate, increasing concentration has been found to be associated with an increase in volume and refraction, and a slight shift toward the red of the absorption bands. Such results agree with deductions from the Clausius–Mosotti theory of dielectrics and are in accordance with recent observations of Fajans and of Ephraim.

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[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION OF THE U. S. BUREAU OF MINES]

A CHAIN REACTION THEORY OF THE RATE OF EXPLOSION IN DETONATING GAS MIXTURES[1]

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RECEIVED MAY 9, 1930 PUBLISHED AUGUST 5, 1930

It is well known that when an explosive gas mixture is ignited at one end of a tube, the initial flame speed, after undergoing a rapid acceleration, acquires a maximum and constant value which does not alter, regardless of the length of the column of gas. Given certain conditions as to temperature, pressure and composition, each gas is characterized by a definite speed of propagation ranging between 1000 and 4000 meters per second. The term detonation wave is usually given to the flame propagated at these velocities.

Theories for the High Rates of Explosions.—Several attempts have been made to account for these high rates of explosions. Berthelot and Vieille[3] compared the speed of a detonation wave to the mean kinetic speed of the molecules in the burned gases. This speed can be readily computed from the temperature attained in the combustion. In many instances the speeds thus calculated differ widely from the experimentally determined velocities of the detonation wave. Dixon[4] likened the speed of the detonation wave in gas mixtures to the velocity of propagation of sound in the same gas at the high temperatures created by the combustion. Although in some cases the velocities calculated agree with those actually found, in others they differ quite widely. It was soon recognized that the "sound-wave theory" was defective and inadequate.[4]

A more satisfactory and hydrodynamical theory was developed independ-

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[3] Berthelot and Vieille, *Compt. rend.*, **93**, 18, 1881; **94**, 149 (1882).

[4] Dixon, *Trans. Roy. Soc.* (London), **184**, 97 (1893); *J. Chem. Soc.*, **97**, 665 (1910).

ently by D. L. Chapman[5] and E. Jouguet.[6] Their theory utilizes Riemann's and Hugoniot's equations for the propagation of shock waves in fluids where no chemical change occurs. The excellent agreement which Chapman finds seems to be due, at least in part, to the use of specific heats which were derived from the velocity of the detonation wave itself. The early calculations of Jouguet, using old specific heat data, show much better agreement with experiment than when the latest values of specific heats are employed; in fact, the divergences are marked until allowances are made for dissociation of the gases at the high temperatures developed.[7]

Because of the degree of success which the Chapman–Jouguet theory enjoys, it deserves more detailed consideration and exposition. Space will be devoted to this subject elsewhere.[7]

While the following treatment does not possess the distinct advantage of the mathematical theory of Chapman and Jouguet, and for this reason may be said to be more limited in the scope of its application, it does attempt to present pictures of the microscopic molecular mechanisms of propagation from one layer of gas to the next. For instance, the reaction

$$2CH_4 + 3O_2 = 2CO + 4H_2O$$

involving as it does a quintuple collision, cannot be considered to occur to any appreciable extent in a detonation wave which is traveling some 2500 meters per second. Any picture which is capable of visualizing the individual interactions, and at the same time accounts for the velocity of propagation, is a distinct step in advance.

Obviously, the molecular mechanism should involve some connecting link between the layers of gas through which the explosion front is moving. Furthermore, there is evidence in some cases that the reaction in the latter is incomplete. Accordingly, adopting a kinetic analysis, the writer has sought to account for the high velocities of explosions by making use of the conception of chain reactions which is now generally believed to constitute the means by which explosions occur.[8] This concept permits one to understand how certain interactions may proceed sometimes with velocities enormously greater than can be deduced from a consideration of the initially impressed force. Thus, a single interaction between two molecules may generate a product which reacts with the next suitable molecule it encounters, the process continuing in like manner from layer to layer by reason of regenerated active products through a large number of steps or a chain of reactions.

[5] D. L. Chapman, *Phil. Mag.*, **47**, 90 (1899).

[6] E. Jouguet, *J. de Mathématique*, 347 (1905); 6 (1906); "Mécanique des Explosifs" Paris, **1917.**

[7] To be published.

[8] N. Semenoff, *Z. Physik*, **46**, 109 (1927); **48**, 571 (1928); C. N. Hinshelwood and co-workers, *Proc. Roy. Soc.* (London), (1928 and 1929).

Calculation of Rates of Explosions.—The chain theory is adopted in the following attempt to calculate the rates of explosions. The separate links in the chain are usually exothermic in character and of types which occur with reasonable probability. The energy evolved in each step is divided equally among the several degrees of freedom of the products.[9] Some of the products are shot out in the direction of propagation with a velocity corresponding to the energy in their three degrees of translation. The active atom or molecule (hereafter called the "carrier") carries its energy over to the next reaction, accumulating more energy with each succeeding step in the chain. Finally, the energy on the carrier reaches a maximum limit which remains constant, regardless of the number of subsequent steps in the chain. As the time for each single chemical change to occur can be neglected, that part of the maximum energy which is energy of translation determines the velocity of the explosion. It is understood that it is not the same carrier which operates throughout the chain as it proceeds down the length of the tube, but a new and similar one which is regenerated in each successive reaction.

Three typical cases will now be illustrated showing the type of mechanism involved. After an examination of the best available specific heat data at high temperatures and the total number of degrees of freedom possible, the actual average number of degrees of freedom selected for the products in all reactions is as follows: monatomic, 3; diatomic, 8; triatomic, 11.

1. **The Explosion of Hydrogen and Chlorine.**—It is known that in the presence of atoms the reaction proceeds by a long series of steps[10] of the type

$$H + Cl_2 = HCl + Cl \qquad (1)$$
$$Cl + H_2 = HCl + H \qquad (2)$$
$$\text{etc.} \qquad (1)$$

Each reaction generates a product which serves as a reactant in the next step in the chain.

The following thermochemical data are adopted

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[9] As the products consist of mono-, di- and tri-atomic systems and the last two are capable of absorbing energy of vibration and rotation, it was decided, as a first approximation, not to divide the energy according to the mass, that is, in equal momenta. The only justification, for the present, for the use of the above method is that when used consistently for many reactions, correct values for rates of propagation can be calculated. At the high temperatures developed where many active degrees of freedom come into play, the energy should be divided amongst all and this seems to offer the simplest method of doing so.

[10] In the photochemical formation of hydrogen chloride the chain lengths have been measured at about a half million [Porter, Bardwell and Lind, THIS JOURNAL, **48,** 2603 (1926)]. The chain is terminated by the removal of the atoms by combination with themselves. In the case of an explosion traveling down a tube, the chains must be indefinitely long, because the atoms which are shot out in the direction of propagation continue to meet molecules of chlorine and hydrogen.

$$\begin{aligned} H_2 + Cl_2 &= 2HCl + 44 \text{ Kcal.} \\ H_2 &= 2H - 103.5 \text{ Kcal.} \\ Cl_2 &= 2Cl - 57 \text{ Kcal.} \end{aligned}$$

Ignition by the spark causes the formation of a certain number of H atoms. Then there follows

$$\begin{array}{l} H + Cl_2 = HCl + Cl + 45.25 \text{ Kcal.} \\ \text{(3/11 of 45.25 Kcal. or 12.34 Kcal. is taken up by the Cl atom)} \\ Cl^{12.34} + H_2 = HCl + H - 1.25 + 12.34 = 11.09 \\ H^{3.024} + Cl_2 = HCl + Cl + 45.25 + 3.024 = 48.274 \\ Cl^{13.16} + H_2 = HCl + H + 11.91 \\ H^{3.25} + Cl_2 = HCl + Cl + 48.50 \\ Cl^{13.23} + H_2 = HCl + H + 11.98 \\ H^{3.27} + Cl_2 = HCl + Cl + 48.52 \\ Cl^{13.235} + H_2 = HCl + H + 11.985 \\ H^{3.271} + Cl_2 = HCl + Cl + 48.521 \\ Cl^{13.235} \end{array}$$

We shall represent the final carrier of the chain as a chlorine atom possessing 13.235 Kcal. of translational energy. The velocity is given by

$$^1/_2\, Mv^2 = 13235 \times 4.18 \times 10^7$$

$$v = \sqrt{\frac{2 \times 13235 \times 4.18 \times 10^7}{35.5}} = 1763 \text{ meters per second}$$

The average experimental value for a mixture $H_2 + Cl_2$ is 1765 meters per second.

2. The Explosion of Hydrogen and Oxygen.—The thermochemical data adopted are: heat of formation of OH = +7.5 Kcal.;[11] H_2 = +103.5 Kcal.; H_2O = +57.8 Kcal.

We shall assume that the spark causes the formation of OH molecules

$$\begin{array}{l} H_2 + O_2 = 2OH + 15 \text{ Kcal.} \\ OH^{7.5} + H_2 = H_2O + H - 1.25 + 7.5 = 6.25 \text{ Kcal.} \\ H^{1.34} + O_2 + H_2 = H_2O + OH + 117.25 + 1.34 = 118.59 \text{ Kcal.} \\ OH^{50} + H_2 = H_2O + H + 48.75 \\ H^{10.45} + O_2 + H_2 = H_2O + OH + 127.70 \\ OH^{53.8} + H_2 = H_2O + H + 52.55 \\ H^{11.26} + O_2 + H_2 = H_2O + OH + 128.51 \\ OH^{54.1} + H_2 = H_2O + H + 52.85 \\ H^{11.33} + H_2 + O_2 = H_2O + OH + 128.58 \\ OH^{54.15} \text{ etc.} \end{array}$$

3 of the 8 degrees of freedom of OH are translational.

The final carrier is an OH molecule possessing $^3/_8$ of 54.15 or 20.3 Kcal. of translational energy.

$$v = \sqrt{\frac{2 \times 20300 \times 4.18 \times 10^7}{17}} = 3160 \text{ meters per second}$$

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[11] D. S. Villars, *Proc. Nat. Acad. Sci.*, **15**, 709 (1929).

The experimental speed for a mixture of $2H_2 + 1O_2$ is 2819 meters per second. Addition of excess oxygen decreases the velocity. This can be explained by the following deactivating reaction

$$H^{11.33} + O_2 = OH + O - 6.25 \text{ Kcal.}$$

The effect of N_2 in lowering the velocity is probably due to inelastic collisions. Addition of excess H_2, on the other hand, increases the speed which may be due to the increased probability of occurrence of

$$OH + H_2 = H_2O + H$$

The maximum speed attained is 3532 meters per second for a $8H_2 + 1O_2$ mixture.

If a value of −3.5 Kcal. is used for the heat of formation of OH[11a] the velocity is 3080 meters per sec.

3. The Explosion of Carbon Monoxide and Oxygen.—The thermochemical data adopted are: heat of formation of CO = +26.5 Kcal.; CO_2 = +94.5 Kcal.; O_3 = −34 Kcal.; O_2 = +131 Kcal.[12]

We shall assume that the spark causes the reaction

$$2CO + O_2 = 2CO_2 + 136 \text{ Kcal.}$$

and that one carbon dioxide molecule collides with a carbon monoxide molecule, the latter emerging with 29 Kcal.

$$CO^{29} + O_2 = CO_2 + O + 2.5 + 29 = 31.5 \text{ Kcal.}$$

$$O^{6.75} + O_2 \xrightarrow{\text{CO or } O_2} O_3 + O_2 + 31.5 + 6.75 = 38.25 \text{ Kcal.}$$

(This reaction takes place in triple collision)

$$O_3^{22.13} + CO + CO = 2CO_2 + O + 104.5 + 22.13 = 126.63 \text{ Kcal.}$$

$$O^{15.2} + O_2 \xrightarrow{\text{CO or } O_2} O_3 + O_2 + 46.7$$

$$O_3^{27.03} + CO + CO = 2CO_2 + O_2 + 131.53$$

$$O^{15.78} + O_2 \longrightarrow O_3 + O_2 + 47.28$$

$$O_3^{27.38} + CO + CO = 2CO_2 + O + 131.88$$

$$O^{15.83} + O_2 \longrightarrow O_3 + O_2 + 47.33$$

$$O_3^{27.40} + CO + CO = 2CO_2 + O + 131.90$$

$$O^{15.83} + O_2 \longrightarrow O_3 + O_2 + 47.33$$

$$O_3^{27.40}$$

Three of the eleven degrees of freedom of O_3 are translational. The translational kinetic energy is 7.47 Kcal. and the corresponding velocity is

$$v = \sqrt{\frac{2 \times 7470 \times 4.18 \times 10^7}{48}} = 1140 \text{ meters per second}$$

The experimental average of Berthelot's and Dixon's results is 1135 meters per second. Should the foregoing mechanism be modified so that the fourth reaction is split up into two steps, namely

$$O_3 + CO = CO_2 + O_2$$

[11a] R. Mecke, *Z. physik. Chem.*, **7B**, (1930).

[12] G. Herzberg, *ibid.*, **4B**, 223 (1929); J. Kaplan, *Phys. Rev.*, **35**, 436 (1930); R. T. Birge, *Trans. Faraday Soc.*, **25**, 707 (1929); R. Mecke, *Naturwiss.*, **17**, 996 (1929).

and

$$O_2 + CO = CO_2 + O$$

the final velocity turns out to be 1100 meters per second, which is in good agreement with Berthelot's average of 1103 meters per second. All other possible mechanisms give final velocities which deviate by over 150% from the observed values.

It can be shown that whatever the initial reaction caused by the ignition, or the initial amount of energy therefore on the carbon monoxide molecule, the final results are identical provided that the same subsequent mechanism is adhered to. For instance, if the ignition brings about the reaction

$$CO + O = CO_2 + 133.5$$

followed by

$$\begin{aligned}
&CO_2^{133.5} + CO = CO^{56.2} + CO_2^{77.3}\\
&CO^{56.2} + O_2 = CO_2 + O + 2.5 + 56.2 = 58.7 \text{ Kcal.}\\
&O^{12.58} + O_2 \xrightarrow{\text{CO or } O_2} O_3 + O_2 + 31.5 + 12.58 = 44.08\\
&O_3^{25.5} + CO + CO = \text{etc.}
\end{aligned}$$

the final O_3 carrier will still possess 27.40 Kcal. of energy. Furthermore, should the ignition process impart a large amount of energy to the initial carriers, causing them to travel with a velocity greater than the final constant value, the chain mechanism indicates how these highly energized carriers are deprived of some of their energy. The final carriers will possess energy corresponding exactly to the velocity characteristic of the mixture. This deceleration of the detonation wave has been shown by C. Campbell and D. W. Woodhead[13] in the case of the ignition of a hydrogen–oxygen mixture by another hydrogen–oxygen mixture possessing a greater characteristic velocity. It is possible, though not certain, that photographs published by W. A. Bone and R. P. Fraser[14] can be interpreted in this light.

It is noteworthy that the chain theory explains the acceleration or deceleration of the explosion wave front to the final constant velocity characteristic of the mixture.

In proceeding as above, the writer has imposed conditions which would tend to lower the calculated results. However, for a given mechanism and carrier the velocity calculated represents a maximum—that is, on the basis that each reaction in the chain occurs before the carrier is deactivated.[15]

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[13] Campbell and Woodhead, *J. Chem. Soc.*, 3010 (1926).

[14] Bone and Fraser, *Trans. Roy. Soc.*, (London) **A228**, 197–234 (1929), Plate 10, No. 37, Plate 11, No. 38.

[15] The substitution of inert gases such as helium and argon for an excess of one of the constituents would normally be expected to lower the rate. We have shown,[7] however, that helium causes a marked increase in the rate when it is added to a mixture of $2H_2$ and $1O_2$, whereas the addition of argon lowers it. If helium and argon behaved differently in the transfer of energy by collision, the former giving up energy of translation to the carrier and the latter removing energy, this could be accounted for. De-

This is directly comparable with the experimental values about to be given in the accompanying table, since it contains those values for the optimum composition of a combustible gas mixture which gives the maximum velocity. For instance, the maximum value for the H_2–O_2 explosion is for an $8H_2 + O_2$ mixture.

Attention is directed to the fact that the final carrier in a given mechanism has been rather arbitrarily selected. For instance, in the H_2–Cl_2 explosion the atomic hydrogen carrier indicates a velocity of 5200 meters per second. This offers no difficulty in accounting for the high rate of the explosion. The case would be different were no carrier present possessing a final velocity equal to at least the experimental velocity of the detonation wave. The carriers listed in Table II were selected because the velocities calculated from them are close to the true values. In a few cases they represent the highest velocity carrier. If the microscopic chemical process was the only factor which determined the velocity of the detonation wave, it would be difficult to understand why the velocity is not that of the fastest carrier. It is possible that a fusion of the present theory and the Chapman–Jouguet theory in a manner indicated elsewhere[7] is desirable for an understanding of two striking phenomena in explosions, namely, the high speed of the detonation wave and the extreme rapidity of chemical reaction in the wave front.

Before presenting the table of results it may prove of interest to include a few mechanisms for the reactions occurring in the explosion wave front for other explosions; these are given briefly in Table I.

TABLE I

REACTION MECHANISMS

Explosion	Mechanism adopted
CH_4 and O_2	$O + O_2 + CH_4 = C + 2H_2O + O$
C_2H_4 and O_2	$O + O_2 + C_2H_4 = 2C + 2H_2O + O$ $O + O_2 + C_2H_4 = CO_2 + 2H_2 + C + O$
H_2 and N_2O	$H + N_2O = N_2 + OH$ $OH + H_2 = H_2O + H$
C_2H_6 and O_2	$O + O_2 + C_2H_6 = 2C + 2H_2O + H_2 + O$
CS_2 and O_2	$O_2 + CS_2 = SO_2 + C + S$ O_2 $S + O_2 \rightarrow SO_2 + O_2$
O_3	$O + O_3 = 2O_2$ $O_2 + O_3 = 2O_2 + O$

Table II contains a summary of calculated and experimental velocities. It is not maintained that the mechanisms selected are correct. Suffice it to remark that they are plausible and possible, and that the carriers selected

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spite the difference in their atomic weights, there is no real evidence for this assumption. On the other hand, it will be shown that the inverse behaviors of helium and argon are readily explained by the Chapman–Jouguet theory (cited).

give the correct velocities while others give values far removed from those found. The experimental values are those of Dixon and others.[16]

TABLE II

SUMMARY OF CALCULATED AND EXPERIMENTAL VELOCITIES

Explosion	Carrier	Vel. calcd., meters/sec.	Vel. observed, meters/sec.	Deviation, %
$H_2 + O_2$	OH	3160	3532	−10.5
$H_2 + Cl_2$	Cl	1763	1765	−0.11
$CO + O_2$	O_3	1140	1135	+0.44
$C_2N_2 + O_2$	N	2780	2728	+1.9
$CH_4 + O_2$	O	2480	2513	−1.3
$C_2H_4 + O_2$	O	2530	2559	−1.1
$C_2H_2 + O_2$	O	2947	2941	+0.20
$NH_3 + O_2$	O	2435	2390	+1.9
$H_2 + N_2O$	OH	2840	>2732	+<3.9
$C_2H_2 + N_2O$	O	2635	2580	+2.1
$C_2H_2 + NO$	O C N_2	2773 3435 } 2866 2390	2850	+0.6
$C_2H_6 + O_2$	O	2010	2363	−15.0
$CS_2 + O_2$	O_2	1960	1802	+8.8
$2O_3 \longrightarrow 3O_2$	O_2	2240	Not measured; calcd. by Jouguet theory, 2123	

In some explosions it is difficult to picture a mechanism in the flame front because there is little or no knowledge concerning the degree to which the reaction progresses in it. Where marked deviations below the observed values occur it is possible that some unknown mechanism is in operation. Despite this, however, the concordance is exceptionally good in most cases.

Summary

An attempt has been made to calculate the velocity of propagation of gaseous explosions employing the concept of reaction chains. Fourteen explosive mixtures were investigated, mechanisms developed and the calculated velocities compared with known experimental values. The agreement is exceptionally good in most cases.

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[16] See Bone and Townend, "Flame and Combustion in Gases," **1927**, pp. 511–518.