Cresol red shows a salt error of +0.29 unit when applied to the solution used by the Committee. Phenol red shows an error of 0.09 P_H unit.

In dilute solution, monoammonium phosphate has a P_H of 4.35.

A simple, inexpensive type of rocking electrode has been described.

ST. LOUIS, MISSOURI

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

EXPLOSIONS IN DETONATING GAS MIXTURES. I. CALCULATION OF RATES OF EXPLOSIONS IN MIXTURES OF HYDROGEN AND OXYGEN AND THE INFLUENCE OF RARE GASES[1]

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Historical

In the year 1881, Berthelot and Vieille[4] and independently Mallard and Le Chatelier[5] announced the discovery of the propagation of explosions in gas mixtures with speeds enormously greater than had been measured previously. These investigators were able to measure the speeds in a number of different mixtures by means of chronoelectric[6] and photographic[7] methods, respectively. Since then, Dixon and others[8] have continued these studies and have measured the velocity of propagation of the detonation wave in a large number of gas mixtures.

Properties of the Detonation Wave.—When certain inflammable gas mixtures are ignited at one end of a uniform tube, the initial slow movement of the flame is rapidly accelerated to a high speed, which remains constant, regardless of the length of the tube. The term "detonation wave" is applied to the propagation of a disturbance at this constant

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[1] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.) Read before American Chemical Society at Atlanta, Georgia, April, 1930.

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[4] Berthelot and Vieille, *Compt. rend.*, **93**, 18 (1881).

[5] Mallard and Le Chatelier, *ibid.*, **93**, 145 (1881).

[6] Berthelot and Vieille, *ibid.*, **94**, 101, 149, 822 (1882); **95**, 151, 199 (1882); *Ann. chim. phys.*, **28**, 289 (1883).

[7] Mallard and Le Chatelier, *Ann. des Mines*, [8] **4**, 274, 335 (1883); *Compt. rend.*, **130**, 1755 (1900); **131**, 30 (1900).

[8] H. B. Dixon, *Phil. Trans. Roy. Soc.*, **184A**, 97 (1893); **200A**, 315 (1903). See Bone and Townend, "Flame and Combustion in Gases," 1927, pp. 511–518, for more complete list of references.

speed. The following are among its more important properties. (1) When established, the detonation wave propagates with a constant velocity which depends upon the chemical and percentage composition of the gas mixture. (2) The speed is independent of the material of which the tube is made. (3) The speed is independent of the diameter of the tube, if this is larger than a small limiting value. (4) The speed is practically independent of the initial pressure and temperature of the gas mixture. A three-fold variation in pressure near atmospheric or a variation in temperature from 10 to 100° introduces only a slight alteration in speed. (5) The speed is independent of conditions in the rear of the wave. It is immaterial whether inflammation is started at the closed or open end of the tube and whether ignition is produced by a flame, spark, detonator, shock wave or by some other means.

Therefore, the speed with which a detonation wave propagates is a physical constant of the particular gas mixture. It should be noted, however, that the period of combustion immediately preceding the establishment of the detonation wave is markedly influenced by many factors such as initial pressure, temperature, condition of the interior surface of the tube, diameter of the tube, composition of the mixture or method of ignition.

Theories of the Detonation Wave.—Berthelot and Vieille compared the speed of a detonation wave to the mean kinetic velocity of the molecules in the burned gases. This can be computed readily from the temperature attained in the combustion, but in many instances the speed thus calculated differs widely from the experimentally determined velocity of the detonation wave.

Dixon identified the speed of the detonation wave in gas mixtures with the velocity of propagation of sound at the high temperature created by the combustion. Although, for some cases, the calculated velocities agree with those actually found, for others they differ rather widely. It was soon recognized that the "sound-wave theory" was defective and inadequate.[9]

Very recently, Lewis[10] has developed a theory of the propagation by means of reaction chains. The complete reaction consists of a number of steps. The product of any one step is shot forward with a velocity corresponding to the energy of translation acquired by it and it then becomes a reactant in the next step. A similar active product or "carrier" is continually regenerated. The velocity of the "carrier" is shown to increase to a constant value, which is identified with the velocity of the detonation wave in the appropriate mixture. Consider, for example, a series of explosive mixtures of hydrogen and oxygen. It is found experimentally that the velocity of the detonation wave depends upon the concentrations of

[9] H. B. Dixon, *J. Chem. Soc.*, **97**, 665 (1910).

[10] Bernard Lewis, THIS JOURNAL, **52**, 3120 (1930).

hydrogen and oxygen and reaches a maximum value for a certain optimum composition, $8H_2 + O_2$. The final velocity of the "carrier" as computed by the chain-reaction theory is compared with the velocity of the detonation wave in this mixture of optimum composition. The calculated values agree very well with those found experimentally for a considerable number of different explosive mixtures. Although this picturization of the molecular mechanism in reaction chains is a step in advance, it is not easy to predict quantitatively velocities slower than that corresponding to the optimum composition mentioned above. This theory is, therefore, not to be regarded as complete, but rather as an attempt to visualize the chemical reactions occurring in the detonation wave.

A widely applicable theory was developed independently by Chapman[11] and Jouguet.[12] This theory is essentially hydrodynamical and furnishes no satisfactory explanation of the extreme rapidity with which chemical reactions occur in gaseous explosions. It would seem that a fusion of the chain reaction and the Chapman–Jouguet theories is necessary for an understanding of two striking phenomena in explosions. These are (1) the extreme rapidity of chemical reaction in the wave front, and (2) the high speed of the detonation wave. The view is held[10,13] generally that explosive reactions occur in a series of chains in which an active product of one reaction is continually used and regenerated in succeeding reactions. The chain-reaction theory is able to account rather generally for very high rates of chemical reaction.[13] Granted a high rate of chemical reaction, the Chapman–Jouguet theory is able to predict the velocity of the detonation wave. In this fusion of the two theories it is only necessary to find a "carrier" in a reaction chain that will propagate the chemical reaction through an infinitesimal element of volume in a period not greater than that required for the detonation wave to sweep across this volume. This combination of the two theories will introduce no change in the equations developed in the Chapman–Jouguet theory.

The velocities calculated by Jouguet[12] agreed reasonably well with those found experimentally. However, his more recent calculations[14] using specific heat data given by Kast, in some instances, give velocities in less satisfactory agreement with experiment than the earlier calculations.

In view of the importance of the problem of the mechanism of deto-

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

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

[13] C. N. Hinshelwood and co-workers, *Proc. Roy. Soc.* **1928** and **1929**; N. Semenoff, *Z. Physik.*, **46**, 109 (1927); **48**, 571 (1928); F. Haber, and H. D. von Schweinitz, *Sitzb. preuss. Akad. Wiss.*, **1928**, 499; L. Farkas, P. Goldfinger and F. Haber, *Naturwiss.*, **17**, 674 (1929); R. Mecke, *Z. physik. Chem.*, **7B**, 108 (1930); L. Farkas, F. Haber and P. Harteck, *Naturwiss.*, **12**, 266 (1930).

[14] E. Jouguet, *Compt. rend.*, **181**, 546 (1925).

nations in gases, it has seemed worth while to repeat these calculations using the best specific heat data of today and taking into account dissociation of the products. Because in this paper we deal solely with the combustion of hydrogen and oxygen mixtures, either by themselves or admixed with inert gases, the dissociations which occur to an appreciable extent at the temperatures developed and which will be considered are

$$2H_2O \rightleftharpoons 2H_2 + O_2 \qquad (1)$$

$$2H_2O \rightleftharpoons H_2 + 2OH \qquad (2)$$

$$H_2 \rightleftharpoons 2H \qquad (3)$$

The Chapman–Jouguet Theory.—To facilitate an understanding of the method used to calculate the velocity of the detonation wave, it seems desirable to give a brief account of the Chapman–Jouguet theory.[15] Consider a plane explosion wave traveling in a tube with velocity V. The coördinate axes will be assumed to move with the wave front, which is consequently stationary in this coördinate system. AB and CD in Fig. 1 are two planes immediately ahead of and behind the wave front. Let p_1, v_1, T_1, u_1 and E_1 be the pressure, specific volume, absolute temperature, velocity with respect to the moving coördinate system, and specific internal energy of the unburned gases, respectively; and p_2, v_2, T_2, u_2 and E_2 the corresponding quantities for the burned gases. Since it is assumed that the unburned gases are at rest in a stationary system of coördinates, $u_1 = -V$. The experimental results indicate that the detonation wave is of permanent type. Assuming that this is the case, it is immediately possible to write the following three equations which state that the mass, momentum and energy of the matter contained between the planes AB and CD do not change with time

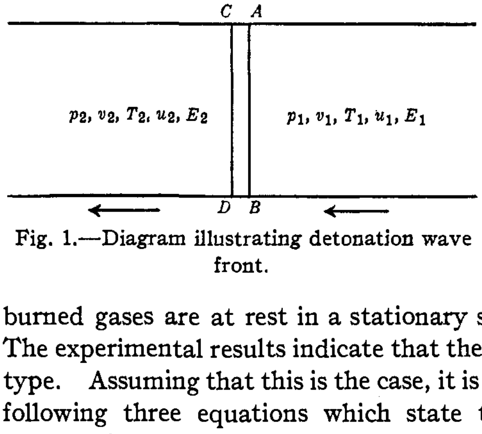

Fig. 1.—Diagram illustrating detonation wave front.

$$\text{Mass} \qquad \frac{u_1}{v_1} = \frac{u_2}{v_2} \qquad (1)$$

$$\text{Momentum} \qquad \frac{u_1^2}{v_1} + p_1 = \frac{u_2^2}{v_2} + p_2 \qquad (2)$$

$$\text{Energy} \qquad E_1 + \frac{u_1^2}{2} + p_1v_1 = E_2 + \frac{u_2^2}{2} + p_2v_2 \qquad (3)$$

It will be initially assumed also that the chemical reaction proceeds to completion and that the composition of the burned gases is consequently

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[15] In view of the equivalence of the relations developed by Chapman and Jouguet, it seems preferable to refer to the Chapman–Jouguet theory rather than the Jouguet theory, even though Chapman's investigations are less comprehensive. An excellent account of this theory is given by R. Becker, *Z. Physik*, **8**, 321 (1922).

known. This furnishes the value of n_2, the number of moles per gram to be used in the equation of state

$$p_2v_2 = n_2RT_2 \tag{4}$$

These four equations give four relations between the five unknowns, V (or $-u_1$), u_2, v_2, p_2 and T_2, and an additional relation is consequently needed for their complete determination. Considerations based on mechanics and thermodynamics led Jouguet to the conclusion that the required relation is

$$\frac{p_2 - p_1}{v_1 - v_2} = -\left(\frac{\partial p_2}{\partial v_2}\right)_{\text{ad}} \tag{5}$$

The additional relation which was obtained by Chapman from different considerations has been shown to be equivalent to this.

If it is assumed that the internal energy of the burned gases is a function of the temperature only, it follows that

$$E_2 - E_1 = \bar{c}_v(T_2 - T_1) - Q \tag{6}$$

where $\bar{c}_v$ is the mean specific heat of the burned gases between T_2 and T_1 and Q is the heat liberated by the reaction at constant volume, per gram of the explosive mixture. Also

$$\left(\frac{\partial p_2}{\partial v_2}\right)_{\text{ad}} = -\frac{\gamma_2 p_2}{v_2} \tag{7}$$

where γ_2 is the ratio of the specific heats for the burned gases at the temperature T_2. If

$$\mu = \frac{v_1}{v_2} \tag{8}$$

the equations given can be transformed to the forms

$$\mu^2 - \left(1 + \frac{1}{\gamma_2}\right)\mu + \frac{n_1T_1}{n_2T_2\gamma_2} = 0 \tag{9}$$

$$\bar{c}_v(T_2 - T_1) - Q - \frac{R}{2}(\mu - 1)\left(n_2T_2 + \frac{n_1T_1}{\mu}\right) = 0 \tag{10}$$

$$V = \mu\sqrt{\gamma_2 n_2 RT_2} \tag{11}$$

$$\frac{p_2}{p_1} = \mu\frac{n_2T_2}{n_1T_1} \tag{12}$$

It will be seen that Equation 11 states that the velocity of the detonation wave is μ times the velocity of sound in the burned gases.

For the computation of V in the case of no dissociation, it is assumed that the combination of hydrogen and oxygen to form water vapor proceeds to completion. A value for T_2 is assumed and γ_2 for this temperature is calculated from the specific heats of the burned gas. These values for T_2 and γ_2, together with the known values of n_1, n_2 and T_1, are substituted in Equation 9, which is solved for μ. This value of μ is introduced in Equation 10, which is then solved to give an improved value of T_2. The calculations are repeated until values of μ and T_2 are found which satisfy both (9) and (10). The velocity of the detonation wave can then be found from (11) and the pressure, p_2, from (12).

The velocities for detonation waves were also calculated on the assumption that the chemical composition of the burned gases corresponds to equilibrium at the temperature and pressure attained in the wave front. The dissociation of water vapor into hydrogen and oxygen and into hydrogen and hydroxyl, and the dissociation of molecular into atomic hydrogen were considered.

Three additional variables are required to specify the chemical composition of the burned gases and three more equations are furnished by the conditions of equilibrium. By an extension of the method[16] of calculation outlined above, values for T_2, μ and the three variables which specify the composition of the burned gases are found which satisfy Equations 9 and 10 and the three conditions of equilibrium. These values can then be used to determine the velocity from Equation 11.

Two interpretations of $(\partial p_2/\partial v_2)_{\text{ad}}$ are possible when dissociation is considered. In the first, $(\partial p_2/\partial v_2)_{\text{ad}}$ is taken to mean the adiabatic change of pressure divided by change of volume for a gas of the invariable chemical composition found from the conditions of equilibrium. This interpretation leaves unchanged the equations which have been given and is the one which has been used for the calculation of velocities. The other interpretation is that $(\partial p_2/\partial v_2)_{\text{ad}}$ is to be taken on the assumption that the chemical composition of the gas changes during the adiabatic compression, so as to be in chemical equilibrium at all stages of the infinitesimal compression.

Consideration of the theory indicates that the second assumption is the one which should be used. The equations which have been given are valid for the first assumption; consequently, a strict interpretation of the theory requires that they be suitably modified in order to be in agreement with the second interpretation of $(\partial p_2/\partial v_2)_{\text{ad}}$. We have therefore calculated the velocity of detonation in a mixture of $2H_2 + O_2$ and in mixtures of $2H_2 + O_2$ diluted with six moles of hydrogen or five moles of oxygen, nitrogen, helium or argon, in two different ways. In one we have used the equations that are valid for the first interpretation of $(\partial p_2/\partial v_2)_{\text{ad}}$, and in the other, the equations that are valid for the second interpretation. In all these cases the differences between the velocities calculated in these two ways are less than 0.4%. We have therefore made all the other calculations using the first interpretation, because it is much simpler mathematically.

Choice of Data.—Eastman[17] has made an exhaustive critical study of the existing data on the specific heats of gases at high temperatures. The experimental data for diatomic gases are on the whole reasonably satisfactory up to 3000°K. As the calculated temperatures in the detonation

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[16] Lack of space prevents a detailed description of the method used for dealing with the three-fold dissociation. It may prove desirable to treat this separately in another place.

[17] E. D. Eastman, Tech. Paper 445, U. S. Bureau of Mines, 1929.

wave are often considerably in excess of this temperature a certain amount of extrapolation is necessary. The final equations which we have adopted for the specific heats of hydrogen, oxygen and nitrogen were formulated on the basis that the specific heats at constant volume reach a value of 7 at 3000°K. and remain constant thereafter. The equations used in this investigation are

$$C_{v_{\mathrm{H}_2}} = 4.65 + 0.492 \times 10^{-3}T + 0.319 \times 10^{-6}T^2 - 0.074 \times 10^{-9}T^3$$
$$C_{v_{\mathrm{N}_2 \text{ or } \mathrm{O}_2}} = 4.74 + 0.408 \times 10^{-3}T + 0.486 \times 10^{-6}T^2 - 0.1234 \times 10^{-9}T^3$$

up to 3000°K. For higher temperatures the constant value, 7, is employed. The specific heats obtained from these formulas are in substantial agreement with those given by Eastman's equations.

The experimental data on the specific heat of water vapor at high temperatures are not in as satisfactory a condition. Eastman has made this the subject of a special study and has kindly sent us a copy of his unpublished manuscript. His new equation follows closely the best experimental data up to about 2700°K., reaches a maximum for C_v of 12.18 at 2800°K., and then falls off slowly at higher temperatures. There is no experimental or theoretical basis for the falling off of specific heats at high temperatures. Furthermore, Wohl and von Elbe[18] have made a few new determinations which agree with Pier's results on which Eastman's formula is based mainly, but their numerical values do not agree with Eastman's, due to different considerations in the calculations. There is every indication that the specific heat approaches an asymptotic value. We have, therefore, adopted Eastman's formula and assumed that the maximum value reached at 2800°K. remains constant at higher temperatures. The formula is

$$C_{v_{\mathrm{H}_2\mathrm{O}}} = 6.33 - 6.53 \times 10^{-4}T + 2.70 \times 10^{-6}T^2 - 6.145 \times 10^{-10}T^3$$

The values for the heat content of water vapor calculated from this equation agree to within less than 6% with the values given by Wohl and von Elbe for temperature up to 5000°K.

Equilibrium Constants.—The equilibrium constant for the dissociation of water vapor into hydrogen and oxygen was recalculated, using the specific heat data given above. The free energy of water vapor has been calculated by several methods by Eastman.[19] His average value at 298°K. is $\Delta F_{298} = -54{,}467$ Cal. The heat of formation of water is $\Delta H_{291} = -57{,}826$ Cal.[20]

Three equations are necessary to cover this temperature range because of the form of the specific heat equations. The final equations used are

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[18] K. Wohl and G. von Elbe, *Z. physik. Chem.*, 5B, 241 (1929).

[19] E. D. Eastman, Information Circular 6125, U. S. Bureau of Mines, 1929.

[20] "International Critical Tables," Vol. V, 1929, p. 176. The minus sign represents the evolution of energy.

Valid up to 2800°K.

$$\log K_{H_2O} = +\frac{57{,}295}{4.573T} - 0.848 \log T - 1.474 \times 10^{-4}T + 7.78 \times 10^{-8}T^2 - 8.72 \times 10^{-12}T^3 + 0.0616$$

Valid between 2800 and 3000°K.

$$\log K_{H_2O} = \frac{14{,}412}{T} + 2.0975 \log T - 7.610 \times 10^{-5}T - 2.047 \times 10^{-8}T^2 + 2.473 \times 10^{-12}T^3 - 10.4417$$

Valid above 3000°K.

$$\log K_{H_2O} = \frac{13317.3}{T} + 0.34492 \log T - 4.3285$$

The following data have been used to calculate the equilibrium constant for the dissociation of molecular into atomic hydrogen; entropy,[21] $S_{H_2\,(298)} = 31.25$; $S_{H\,(298)} = 27.4$; and $\Delta H_{298} = 103{,}500$ cal.[22]

The following equations are obtained from these data

Valid up to 3000°K.

$$\log K_{H_2} = -\frac{102{,}534}{4.573T} + 1.673 \log T - 0.5375 \times 10^{-4}T - 1.16 \times 10^{-8}T^2 + 1.350 \times 10^{-12}T^3 + 0.322$$

Valid above 3000°K.

$$\log K_{H_2} = 6.1622 - \frac{23{,}179}{T} + 0.4885 \log \frac{T}{3000}$$

An equation expressing the equilibrium constants for the dissociation of water vapor into H_2 and OH has been given by Wohl and von Elbe[18] and has been adopted here. F in the following equation is the Einstein function for the free energy of an harmonic oscillator. The figures in brackets are the values of $(h/k)\nu = \beta\nu$ calculated from the frequency of the absorption maxima in the infra-red.[23]

$$\log K_{OH} = -\frac{128{,}000}{4.573T} + 2.5 \log T + \frac{1}{4.573T}\,[F(6140) + 2F(5100) - 2(F(2280) + 2F(5330))] - 0.44$$

Wohl and von Elbe's equation has not been modified to conform with the specific heats used in this investigation because of the uncertainty in the heat of decomposition into OH and H_2.

It is to be emphasized that the specific heat data used in this investigation have not been calculated from the observed velocities of detonation waves, as was done by Chapman. If specific heats obtained in this way are used, it is to be expected that the calculated and observed velocities will be in close agreement. Our data have been derived from the independent sources mentioned above. Hence, the close agreement which we have found (see below) between the calculated and observed velocities for a number of explosive mixtures would seem to substantiate both the Chapman–Jouguet theory and the specific heat data used.

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[21] These are unpublished values of Giauque, and were given to us through Dr. Eastman.

[22] F. R. Bichowsky and L. C. Copeland, This Journal, 50, 1315 (1928).

[23] Landolt–Börnstein, fifth edition, first supplementary volume, pp. 702–704.

Results of the Calculation.—Tables I, II and III show a comparison between the calculated and experimental values. The first column contains the explosive mixture obtained by adding the indicated number of moles of gas to a stoichiometric mixture of hydrogen and oxygen—namely,

TABLE I

CALCULATED AND EXPERIMENTAL VELOCITIES OF DETONATION WAVE IN HYDROGEN AND OXYGEN DILUTED WITH NITROGEN

Explosive mixture	Calculated velocity Without dissocn., m./sec.	With three-fold dissocn., m./sec.	Experimental velocity, m./sec.	Deviation, %
$2H_2 + O_2$	3278	2806	2819	−0.43
$+ 1N_2$	2712	2378	2407	−1.2
$+ 3N_2$	2194	2033	2055	−1.07
$+ 5N_2$	1927	1850	1822	+1.15

TABLE II

CALCULATED AND EXPERIMENTAL VELOCITIES OF DETONATION WAVE IN HYDROGEN AND OXYGEN DILUTED WITH OXYGEN

Explosive mixture	Calculated velocity Without dissocn., m./sec.	With three-fold dissocn., m./sec.	Experimental velocity, m./sec.	Deviation, %
$2H_2 + O_2$	3278	2806	2819	−0.43
$+ 1O_2$	2630	2302	2319	−0.73
$+ 3O_2$	2092	1925	1922	+0.16
$+ 5O_2$	1825	1735	1700	+2.06

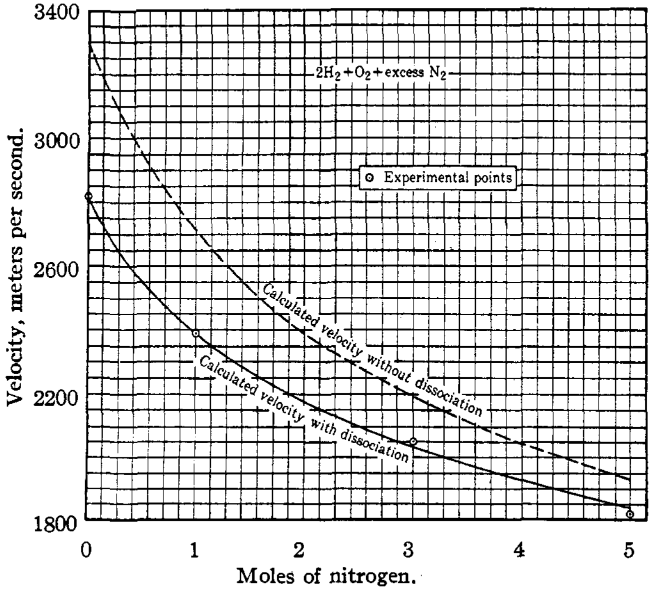

Fig. 2.—Calculated velocities of detonation wave with excess nitrogen.

$2H_2 + O_2$. The second column contains the calculated velocity assuming that no dissociation occurs in the detonation wave. The third column contains the calculated velocity assuming three-fold dissociation as given above. The fourth column gives the experimental velocity determined by Dixon and others.[24] The fifth column gives the percentage deviation of the values in the third column from the experimental values.

Figures 2 and 3 show the data graphically. The circles represent the experimental points. It is seen that the agreement with the theory is exceptionally good.

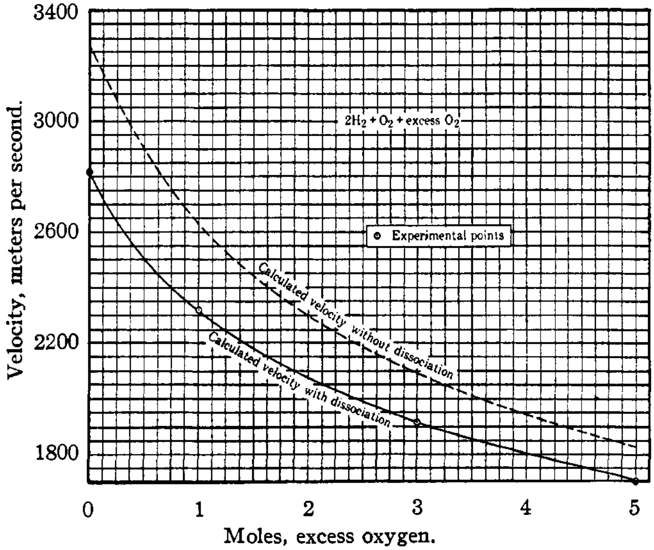

Fig. 3.—Calculated velocities of detonation wave with excess oxygen.

The velocities for the mixtures $2H_2 + O_2$ and $2H_2 + 6O_2$ were also calculated by assuming that equilibrium is attained for the reaction $2H_2 + O_2 \rightleftharpoons 2H_2O$ and neglecting the other two dissociations previously considered. The values calculated in this way are 3023 and 1793 meters per second, which are in much less satisfactory agreement than the values obtained by considering all three dissociations. These results indicate that it is important to consider dissociation in explosion phenomena. If the specific heat and free energy data are correct, the close agreement between the calculated and observed velocities would appear to justify the conclusion that *the explosion occurs as if equilibrium were reached for the three dissociations we have used.*

Table III and Fig. 4 show the results with excess hydrogen.

The agreement in the case of a large excess of hydrogen is not quite as

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

TABLE III

CALCULATED AND EXPERIMENTAL VELOCITIES OF DETONATION WAVE IN HYDROGEN AND OXYGEN DILUTED WITH HYDROGEN

Explosive mixture	Calculated velocity Without dissocn., m./sec.	With three-fold dissocn., m./sec.	Experimental velocity, m./sec.	Deviation, %
$2H_2 + O_2$	3278	2806	2819	−0.43
$+ 2H_2$	3650	3354	3273	+2.48
$+ 4H_2$	3769	3627	3527	+2.83
$+ 6H_2$	3802	3749	3532	+6.15

good. There are several possible reasons for this discrepancy. The experimental values for the mixtures with a large amount of excess hydrogen may be somewhat low. On the other hand, dissociation is almost negligible for these mixtures if equilibrium is assumed. It is quite possible that complete combustion is not realized in the wave front at these high speeds. If this is the case, the calculated values would be lower and more nearly in agreement with the observed. The incompleteness of the reaction may easily be enough to account for the difference. That there is incomplete reaction in the wave front is borne out by some direct photographs we have taken of the explosion with excess hydrogen. The photographs indicate a fair amount of combustion occurring behind the wave front, although not nearly as much as in an explosion of a $2H_2 + 1O_2$ mixture where the equilibrium falls far short of complete reaction.

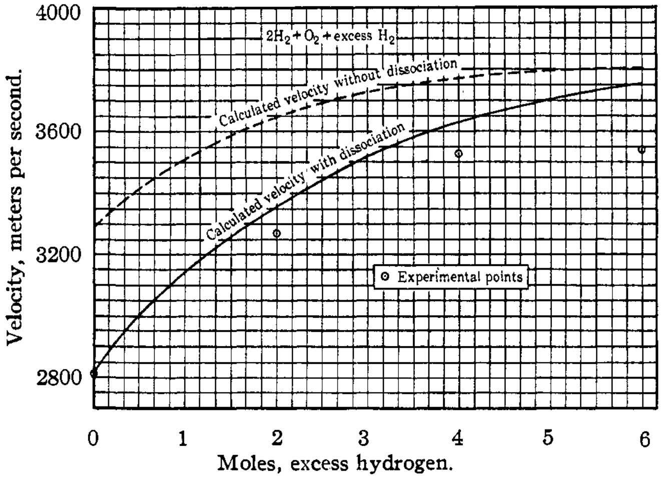

Fig. 4.—Calculated velocities of detonation wave with excess hydrogen.

The Effect of Helium and Argon.—The addition of helium and argon to the explosive mixture furnishes another means of checking the correctness of the Chapman–Jouguet theory. The theory indicates that the velocity of the detonation wave is proportional to the density of the gas mixture after combustion and to the absolute temperature reached in the wave front. If the inert gas helium be added to a mixture of $2H_2$ and $1O_2$, the velocity should increase as a result of the decreased density. On the other hand, argon, because of its greater density, should be expected to effect a decrease in the velocity. We have here the ordinarily unexpected result that two inert monatomic gases differing in atomic weight but identical in every chemical respect affect the velocity of the explosion in opposite directions. For the same quantities of added inert gas, the degree of dissociation and the heat capacities, and consequently T_2, γ_2 and μ, are the same. The calculated velocities for mixtures with an equal number of moles of helium and argon are therefore inversely proportional to the square root of the density of the burned gases.

To test the theory it is highly desirable to eliminate all variable factors except one. By adding helium or argon, or mixtures of helium and argon, to the explosive mixture it is possible to keep all factors constant with the exception of the density and to determine whether the dependence of velocity upon density is, or is not, of the form predicted by the theory.

No experimental values for the velocities of the detonation wave in mixtures of hydrogen and oxygen diluted with helium and argon were found in the literature. For this reason we have undertaken to determine their velocities.

Experimental Method

The velocities for mixtures diluted with helium and argon were obtained from direct and Schlieren photographs[25] taken on films attached to a drum moving with a peripheral speed of about 60 meters a second. Figure 5 is a sketch of the arrangement for the direct photographs. The explosion tube consisted of a thick-walled lead tube with an inside diameter of 19 mm. and of sufficient length to insure setting up the detonation wave of constant velocity. This was joined to a heavy pyrex glass tube of the same bore for the direct photographs and to a steel tube with a slit covered by a cellophane window for the Schlieren photographs. Both ends were closed by rubber stoppers which subsequently were blown out by the force of the explosion. An explosion traveling with constant velocity produces an inclined straight line on the film. The velocity of the detonation wave can be readily computed from the slope of this line, the speed of the drum and the constants of the optical arrangement.

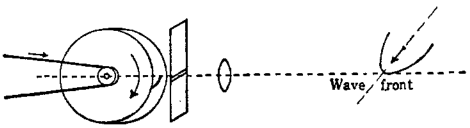

Fig. 5.—Apparatus for obtaining direct photographs of detonation waves.

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[25] Töpler, *Wied. Ann.*, **131**, 33 (1867).

The gases were taken from cylinders and mixed over water. The hydrogen and oxygen were of a high degree of purity, while the helium and argon contained (by analysis) 2.95 and 4.65% nitrogen, respectively, and no combustible gases, carbon dioxide or oxygen.

Figure 6 is a reproduction of a typical direct photograph. The dark vertical lines are due to strips of opaque paper placed at certain distances on the explosion tube. The upper inclined straight line represents the movement of the wave front. The lower straight line sloping in the opposite direction represents the wave reflected from the end of the tube. This travels with a reduced velocity in the partly burned medium. The photograph is an interesting one, for it can be used to give an estimate of the velocity of the gases in the rear of the wave. This velocity is obtained from the slope of the striations close to the upper straight line. Although the slope of the striations cannot be measured accurately because of its rapid rate of change, the value found for the velocity of the burned gases agrees reasonably well with the value calculated from the Chapman–Jouguet theory. The theoretical value for the velocity of the burned gases in a fixed coördinate system is

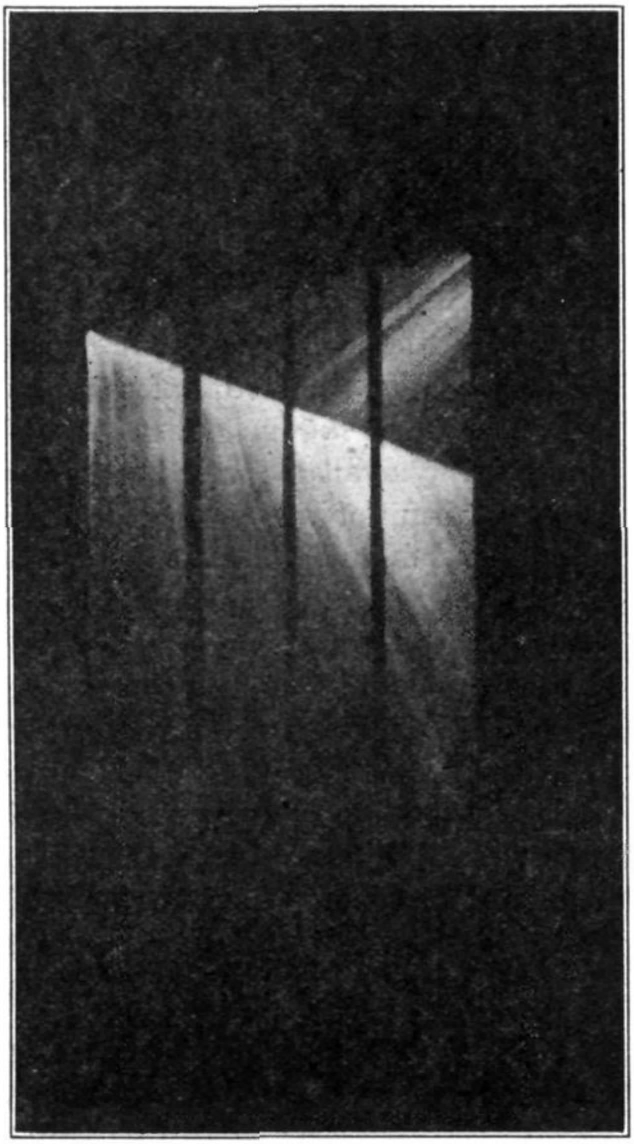

Fig. 6.—Photograph of explosion.

$$D = V - u_2 = \frac{\mu - 1}{\mu} V$$

The passage of the reflected detonation wave causes more intense combustion in the burning gases. The directions of the wave and the burned gases are completely reversed. It will be observed that near the point where the reflection occurs, the velocity of the gases emitted from the reflected wave are nearly zero, due to the balancing effect of velocity of the gases from the original wave traveling in the opposite direction; but as the reflected wave meets gases with smaller and smaller velocities, the velocity of the gases emitted from it increases, as is clearly shown in the photograph. Here again the velocity of the gases falls off with time.

The Schlieren method depends upon the refraction of a beam of light as it passes through a medium of different density. The alteration of the density in the wave front is sufficient to change the direction of the beam from an arc lamp, causing it to enter the camera instead of impinging on a diaphragm. Schlieren photography has been used by W. Payman and his associates[26] in explosion experiments and will not be described in detail here. A steel tube was used, a narrow slit being cut at one end for a length of about 33 cm. to permit passage of the beam of light. The slit was covered with a cellophane window which was strong enough to remain intact until the detonation wave had passed.

The velocity of the detonation wave is determined from the slope of the inclined straight line in Fig. 6. The slopes obtained with the apparatus found readily available were not great enough, especially for the fast mixtures, to permit of any great precision in the determination of the velocity. The values obtained for a stoichiometric mixture of hydrogen and oxygen and also for mixtures containing excess oxygen and excess hydrogen are somewhat lower than those given in the literature. For this reason the results about to be given are to be considered preliminary in character and too great weight should not be attached to the lack of agreement between the calculated and observed velocities for mixtures diluted with helium and argon. With certain changes in technique that are contemplated, better experimental values can be obtained.

The experimental results in Table IV are an average of the velocities determined by both methods. They are compared with the calculated velocities with and without dissociation.

TABLE IV

CALCULATED AND EXPERIMENTAL VELOCITIES OF DETONATION WAVE IN HYDROGEN AND OXYGEN DILUTED WITH HELIUM AND ARGON

	Calculated velocity			
Explosive mixture	Without dissocn., m./sec.	With three-fold dissocn., m./sec.	Experimental velocity, m./sec.	Deviation, %
$2H_2 + O_2$ + 1.5 He	3772	3200	3010	+6.2
+ 3 He	3990	3432	3130	+9.65
+ 5 He	4083	3613	3160	+14.45
+ (2.82 He + 1.18 A)	3012	2620	2390	+9.62
+ (1.5 He + 1.5 A)	2741	2356	2330	+1.12
+ 1.5 A	2500	2117	1950	+8.45
+ 3 A	2212	1907	1800	+6.12
+ 5 A	1992	1762	1700	+3.95

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[26] Payman and Robinson, Safety in Mines Research Board Paper No. 18; Payman and Shepherd, *ibid.*, Paper No. 29. Payman, *Proc. Roy. Soc.* (London), **120A**, 90 (1928).

It is observed that the predictions of the theory are verified qualitatively. In view of the preliminary nature of the experimental results this is perhaps all that could be expected. It is interesting to note, however, that the differences are in such a direction as to be accounted for by failure to attain equilibrium in the wave front. As more inert gas is added the dissociation is repressed owing to the lower temperature in the explosion. This effect is not as marked as it is with excess hydrogen, but it is possible that the presence of a large amount of inert gas prevents the attainment of equilibrium in the wave front, especially for those mixtures that possess a high velocity.

Acknowledgment.—The writers wish to acknowledge with pleasure their appreciation to W. C. F. Shepherd, investigator from the Safety in Mines Research Board, Great Britain, for his aid in taking these photographs and to D. B. Gawthrop for permission to use the Schlieren apparatus constructed by him and W. Payman of the Safety in Mines Research Board.

Summary

1. Velocities for the detonation wave in explosive mixtures of hydrogen and oxygen diluted with several gases have been calculated on the basis of the Chapman–Jouguet theory. Velocities have been computed for each of the two following assumptions: (a) the composition of the burned gases corresponds to complete combustion; (b) the composition of the burned gases corresponds to chemical equilibrium for the dissociation of water vapor into hydrogen and oxygen, and into hydrogen and hydroxyl, and for the dissociation of molecular into atomic hydrogen.

2. The calculated values for mixtures diluted with nitrogen and oxygen agree exceptionally well with the experimental values when dissociation is considered.

3. The calculated values for mixtures diluted with hydrogen are in good agreement for amounts of excess hydrogen up to four moles, but about 6% high for 6 moles of excess hydrogen. Possible reasons for the difference are suggested.

4. These results indicate the importance of dissociation phenomena in explosions.

5. The satisfactory agreement for these mixtures suggests further tests of the Chapman–Jouguet theory for mixtures diluted with helium and argon.

6. Direct and Schlieren photographs have been taken for mixtures containing various amounts of these inert gases, and the velocity of the detonation wave has been determined from them.

7. There is less satisfactory agreement with the theory than for the other mixtures. Although the predictions of the theory are verified qualitatively, the average difference between observed and calculated velocities

is about 8%. At least a part of this difference may be due to experimental error.

8. Further work is contemplated to obtain better experimental results.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

QUENCHING OF THE FLUORESCENCE OF NITROGEN DIOXIDE

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Of late the photochemical decomposition of nitrogen dioxide into nitric oxide and oxygen has been the object of several investigations.[2] That the absorption spectrum of nitrogen dioxide in the visible and near ultraviolet regions of the spectrum is discrete is well known.[3] Recently, Mecke[4] and Henri[5] have noted that predissociation occurs in this gas, the bands first becoming diffuse between 3800 and 3700 Å. The light absorption process in this region corresponds to the beginning of formation of an excited molecule followed by immediate dissociation into nitric oxide and oxygen. Fluorescence is to be expected in nitrogen dioxide at sufficiently low pressures when one illuminates with wave lengths above the limit of predissociation. Indeed, due to the ineffectiveness of blue light, 4358 Å., in causing photodecomposition, Norrish was led to conclude that all of this light must be reradiated. Norrish[6] succeeded in obtaining the expected fluorescence which appears as a faint yellowish luminescence when nitrogen dioxide is illuminated with the 4358 and 4047 Å. lines of the mercury arc. The spectra emitted are identical under excitation by either λ4358 or 4047, consisting of two wide maxima at 6400 and 5900 Å., except that the intensity of the 5900 band is relatively more intense with the shorter wave length. With λ3660 there is only an extremely feeble fluorescence, also in this same region. The almost complete absence of fluorescence by this light is indeed in keeping with the idea that immediately after light absorption, dissociation of the excited molecule takes place.

The object of the present investigation is the study of the intensity of the fluorescence as a function of the pressure both of nitrogen dioxide itself and of added gases. Such measurements afford quantitative data concerning the efficiencies of deactivating collisions, quantities of considerable importance in chemical kinetics.

[1] National Research Fellow in Chemistry.

[2] Norrish, *J. Chem. Soc.*, 761 (1927); Dickinson and Baxter, THIS JOURNAL, **50**, 774 (1928); Norrish, *J. Chem. Soc.*, 1158, 1604, 1611 (1929).

[3] Harris, *Proc. Nat. Acad. Sci.*, **14**, 690 (1928).

[4] Mecke, *Naturwissenschaften*, **17**, 996 (1929); *Z. physik. Chem.*, **7B**, 108 (1930).

[5] Henri, *Nature*, **125**, 202 (1930).

[6] Norrish, *J. Chem. Soc.*, 1611 (1929).