[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Kinetics of the Hydrogen–Oxygen Low Pressure Explosion

BY ARTHUR A. FROST AND HUBERT N. ALYEA

The theory that explosion of hydrogen–oxygen mixtures occurs when the rate of branching of reaction chains exceeds the rate of breaking of these chains[1,2] gives the following expression for the explosion limit

$$\frac{\text{Chain branching}}{\text{Chain breaking}} = 1 = \frac{k_2p^ye^{-E_2/RT}}{k_1p^xe^{-E_1/RT} + k_3p^ze^{-E_3/RT}} \qquad (1)$$

where the different terms represent the rates of elementary processes as discussed below. It is found to satisfy the empirical results[2,3] when $x<y<z$ and $E_1<E_2>E_3$. At sufficiently low pressures the term in p^z may be neglected and at sufficiently high pressures the term in p^x may be neglected. This gives rise to an upper and a lower explosion limit, respectively, for both of which there is a linear relationship between log p and $1/T$ as has already been pointed out.[4]

For the lower limit Hinshelwood and Moelwyn-Hughes[5] have employed the expression

$$\frac{\text{Chain branching}}{\text{Chain breaking at wall}} = 1 = \frac{K_2N\dfrac{p_{H_2}p_{O_2}}{p_{H_2} + (k_b/k_a)p_{O_2}}}{K_1N\dfrac{1}{p_{H_2} + D_{O_2}p_{O_2} + D_ip_i}} \qquad (2)$$

N is the number of chains in progress. In this the chain branching is assumed to have a certain constant probability of occurring during such a cycle as

$$X_O + H_2 \longrightarrow X_H + \dots \quad (k_a)$$
$$X_H + O_2 \longrightarrow X_O + \dots \quad (k_b)$$

They assume that $k_a = k_b$. The factor for chain breaking at the wall is controlled by the relative abilities of hydrogen, oxygen, and various inert gases, $(1, D_{O_2}, D_i)$, in hindering diffusion of the chain carriers to the wall. It is seen that their expression corresponds to equation (1) with $x = -1$; $y = +1$; and K_2 and K_1 include the temperature dependence.

We propose to extend this theory to include the upper limit. Now y has a value of unity in equation (1), and z must therefore be greater than one. But since a rate process depending upon p^z is to be interpreted as a collision of the chain carrier with z other molecules, and since any collision involving more than three molecules is unlikely, z is uniquely determined to have the value 2. Equation (1) then becomes:

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(1) Semenoff, *Z. Physik*, **48**, 571 (1928); Bursian and Sorokin, *Z. physik. Chem.*, **B12**, 247 (1931).

(2) Thompson and Hinshelwood, *Proc. Roy. Soc.* (London), **A122**, 610 (1929).

(3) Dixon, Harwood and Higgins, *Trans. Faraday Soc.*, **22**, 267 (1926).

(4) Kopp, Kowalsky, Sagulin and Semenoff, *Z. physik. Chem.*, **B6**, 307 (1930).

(5) Hinshelwood and Moelwyn-Hughes, *Proc. Roy. Soc.* (London), **A138**, 311 (1932). This was adopted by Thompson for the spark explosion at room temperature, *Trans. Faraday Soc.*, **28**, 299 (1932).

$$\frac{k_2 \dfrac{p_{H_2} p_{O_2}}{p_{H_2} + (k_b/k_a) p_{O_2}} e^{-E_2/RT}}{k_1 \dfrac{e^{-E_1/RT}}{p_{H_2} + D_{O_2} p_{O_2} + D_i p_i} + k_3 p_{H_2} p_{O_2} e^{-E_3/RT} + k_4 p_{O_2}^2 e^{-E_4/RT} + \text{other terms in } p^2} = 1 \tag{3}$$

The following measurements of the explosion limits, when the hydrogen/oxygen ratio is varied over a wide range, were carried out to determine the validity of this relationship.

Experimental

A Pyrex reaction vessel 20 mm. in diameter and 200 mm. long was heated in an electric furnace, the temperature being controlled by a hand operated variable resistance to within ±1° as recorded on a chromel–alumel thermocouple. Capillary tubing, used to diminish the effect of unmixed gases, connected the reaction vessel with a mercury manometer. Tank hydrogen was led over platinized asbestos, dried by passing through calcium chloride and magnesium perchlorate, and stored in a two-liter Pyrex flask. Oxygen and nitrogen were similarly dried.

In order to inhibit the slow reaction which otherwise intruded upon the accuracy of the subsequent measurement of the explosion limit, the Pyrex vessel was initially rinsed with 10% potassium chloride solution. While this produces perhaps a 2000-fold decrease in the rate of the slow reaction,[6] it has only a relatively small influence on the explosion limit and should not alter the kinetics appreciably. It was also found necessary before each experiment to exhaust the reaction vessel to less than 10^{-3} mm. of mercury as read on a McLeod gage.

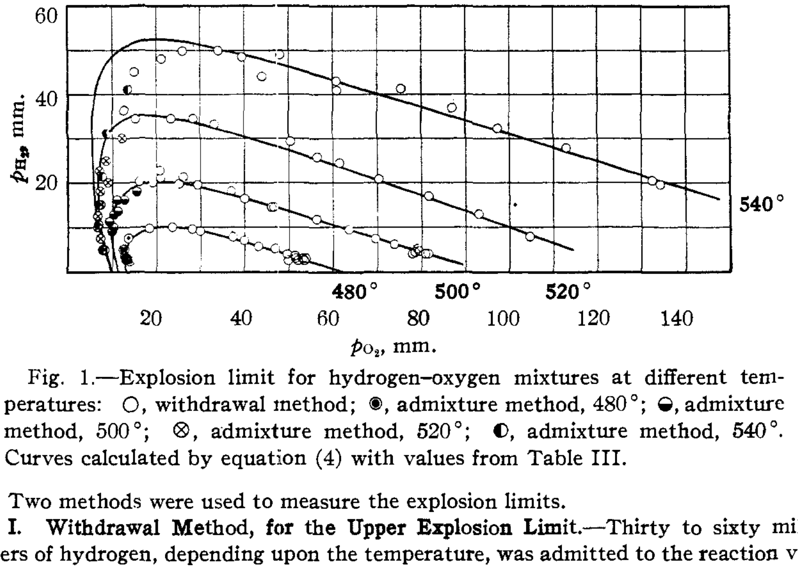

Fig. 1.—Explosion limit for hydrogen–oxygen mixtures at different temperatures: ○, withdrawal method; ◉, admixture method, 480°; ◒, admixture method, 500°; ⊗, admixture method, 520°; ◐, admixture method, 540°. Curves calculated by equation (4) with values from Table III.

Two methods were used to measure the explosion limits.

I. Withdrawal Method, for the Upper Explosion Limit.—Thirty to sixty millimeters of hydrogen, depending upon the temperature, was admitted to the reaction vessel, under which condition subsequent addition of oxygen does not give explosion. Oxygen was then added to give the desired composition. After waiting one minute for the gases to mix, the mixture was slowly pumped out and the pressure below which explosion occurred was recorded.

II. Admixture Method, for the Lower Limit and Transition Region.—Hydrogen

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[6] Pease, *Proc. Nat. Acad. Sci.*, **14**, 472 (1928).

was admitted to the reaction vessel to a pressure sufficiently below the explosion limit. Oxygen was then added slowly, to allow complete mixing, until the explosion limit was reached. At this point the pressure suddenly decreases. In experiments with nitrogen an oxygen–nitrogen mixture was added to the hydrogen.

Experimental Results

The explosion regions for varying hydrogen–oxygen ratios at different temperatures are given in Fig. 1. The effect of nitrogen at 500 and 520° and at different concentrations is given in Figs. 2 and 3. The experimental data for 500° are presented in Tables I and II.

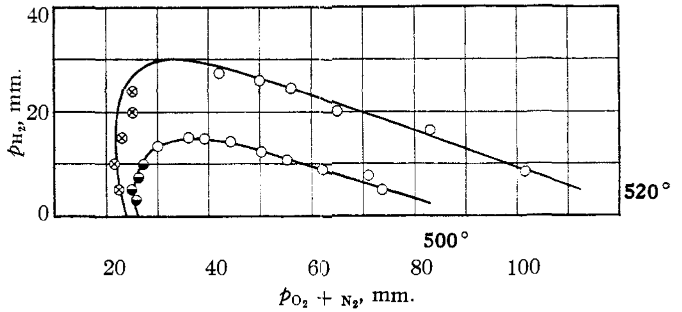

Fig. 2.—Effect of nitrogen at different temperatures: $p_{O_2} = p_{N_2}$; ⊙, withdrawal method; ◒, admixture method, 500°; ⊗, admixture method, 520°. Curves calculated by equation (4) with values from Table III.

The measurements were extended as far toward zero hydrogen pressure as possible. In this neighborhood the gas mixture is so weak in hydrogen that only a slight pressure change occurs during explosion.

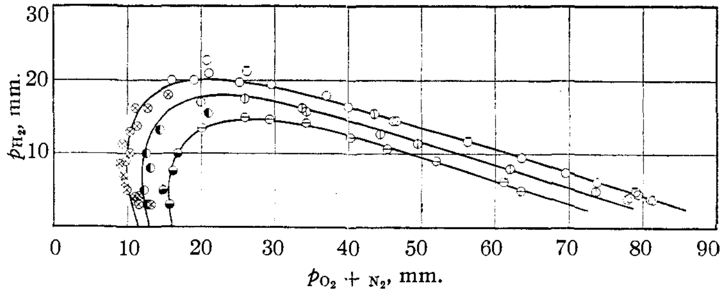

Fig. 3.—Effect of varying oxygen/nitrogen ratio at 500°: $p_{O_2}/p_{N_2} = \infty$; ⊙, withdrawal method; ⊗, admixture method; $p_{O_2}/p_{N_2} = 3$; ⦶, withdrawal method; ◐, admixture method; $p_{O_2}/p_{N_2} = 1$; ⊖, withdrawal method; ◒, admixture method. Curves calculated by equation (4) with values from Table III.

It is apparent that the curves are closed to the p_{H_2} axis and open to the p_{O_2} axis. They cannot be even approximately expressed by equation (3) if it is assumed that $k_a = k_b$ as was found for uncoated Pyrex at 550° at

TABLE I

EXPLOSION LIMIT OF H_2–O_2 MIXTURES AT 500°

Expt.	Method	p_{H_2}, mm.	p_{O_2}, mm.
1	A	7.0	9.5
2	A	13.7	11.3
3	A	8.5	8.8
4	A	3.5	11.0
5	A	9.0	9.7
6	A	16.3	10.9
7	A	11.2	9.3
8	A	18.0	15.5
9	A	4.0	11.0
10	A	16.2	12.8
11	A	13.0	10.2
12	A	3.0	13.2
13	A	10.0	10.3
14	A	4.3	11.5
15	A	6.0	9.5
16	W	19.8	16.2
17	W	21.2	26.3
18	W	19.6	29.4
19	W	20.1	18.9
20	W	17.9	37.1
21	W	22.4	20.6
22	W	11.8	56.2
23	W	21.0	21.0
24	W	19.8	25.2
25	W	6.2	73.8
26	A	3.0	11.5
27	W	9.5	63.5
28	W	14.5	46.0
29	W	14.5	46.5
30	W	7.5	69.5
31	W	4.6	79.4
32	W	4.1	77.9
33	W	4.3	78.7
34	W	5.0	79.0
35	W	4.1	80.9
36	W	3.9	81.3
37	W	16.6	39.9
38	A	5.0	9.8

TABLE II

EXPLOSION LIMIT OF H_2–O_2–N_2 MIXTURES AT 500°

Expt.	Method	p_{O_2}/p_{N_2}	p_{H_2}	$p_{O_2} + p_{N_2}$
1	W	3	15.6	43.4
2	W	3	8.0	62.0
3	W	3	12.8	44.2
4	W	3	16.2	33.8
5	W	3	17.6	25.9
6	W	3	15.8	34.2
7	W	3	17.1	19.9
8	A	3	10.0	12.5
9	A	3	8.0	13.0
10	A	3	5.0	12.7
11	A	3	3.0	12.9
12	A	3	13.0	14.3
13	A	3	15.5	21.0
14	W	3	5.1	73.4
15	W	3	11.5	49.5
16	W	1	4.9	63.6
17	W	1	6.3	61.2
18	W	1	9.2	51.8
19	W	1	10.8	45.2
20	W	1	12.3	40.2
21	W	1	14.3	34.2
22	W	1	14.7	29.3
23	W	1	13.4	20.1
24	W	1	15.1	25.9
25	A	1	10.0	16.8
26	A	1	5.0	14.7
27	A	1	7.5	16.2
28	A	1	3.0	15.8

A = Admixture.
W = Withdrawal.

<4 mm. total pressure by Hinshelwood and Moelwyn-Hughes. On the other hand, the assumption that $k_a \gg k_b$ then reduces equation (3) to

$$\frac{k_2 p_{O_2} e^{-E_2/RT}}{k_1 \dfrac{e^{-E_1/RT}}{p_{H_2} + D_{O_2} p_{O_2} + D_{N_2} p_{N_2}} + k_3 p_{H_2} p_{O_2} e^{-E_3/RT} + k_4 p_{O_2}^2 e^{-E_4/RT} + k_5 p_{N_2} p_{O_2} e^{-E_5/RT}} = 1 \qquad (4)$$

That this expression gives satisfactory agreement with the experimental data is shown in Fig. 4. In order to simplify the calculations, D_{O_2} is arbitrarily set equal to unity. This is permissible since in the absence of nitrogen, D_{O_2} is a measure of the slope of the extremity of the lower explosion limit curve, in which neighborhood the dispersion of the experimental results is too great to give it a precise value. In the absence of nitrogen, equation (4) may be written in the form

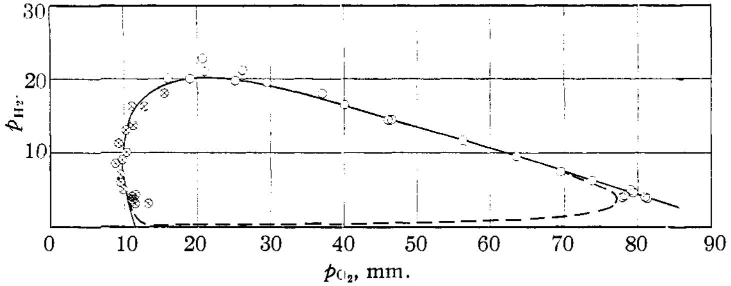

Fig. 4.—Explosion limit for hydrogen–oxygen mixtures at 500°: ○, withdrawal method; ⊗, admixture method. Curves calculated by equation (3): —— $k_a = \infty\ k_b$, with K values from Table III; – – – $k_a = 100\ k_b$, with $K_1 = 111$, $K_2 = 0.0328$, $K_4 = 0.0090$.

$$p_{O_2}(p_{H_2} + p_{O_2}) = K_1 + K_3 p_{H_2} p_{O_2}(p_{H_2} + p_{O_2}) + K_4 p^2_{O_2}(p_{H_2} + p_{O_2}) \qquad (5)$$

where $K_n = k_n/k_2 e^{-(E_n - E_2)/RT}$ and $n = 1, 3, 4$. By choosing three representative experimental points along the explosion limit at any given temperature and substituting the values of p_{O_2} and p_{H_2} in equation (5), three simultaneous linear equations were obtained. From these K_1, K_3 and K_4 were evaluated. From Fig. 3, D_{N_2} and K_5 at 500° could be calculated. Assuming D_{N_2} independent of the temperature, which is a satisfactory first approximation both experimentally and theoretically,[7] the value of K_5 at 520° could be calculated from Fig. 2. The results of these calculations are presented in Table III.

TABLE III

CONSTANTS FOR EQUATION (4)

		Constants		Pressures in mm. of Hg		
T, °C.	D_O	D_{N_2}	K_1	K_3	K_4	K_5
480	1	..	137.3	0.0457	0.0157	...
500	1	1.25	112	.0328	.0104	0.0146
520	1	1.25	95.7	.0217	.0078	.0098
540	1	..	96.0	.0158	.0050	...

From Fig. 5, the plot of log K_n against $1/T$°K., the following relative values of the activation energies and specific rate constants may be obtained.

$E_2 - E_1 = 10{,}700$ cal. $\qquad k_1/k_2 = 0.453$
$E_2 - E_3 = 21{,}900$ $\qquad k_3/k_2 = 2.17 \times 10^{-8}$
$E_2 - E_4 = 22{,}300$ $\qquad k_4/k_2 = 5.70 \times 10^{-9}$
$E_2 - E_5 = 24{,}200$ $\qquad k_5/k_2 = 2.30 \times 10^{-9}$

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(7) Melville and Ludlam, *Proc. Roy. Soc.* (London), **A132**, 108 (1931).

If E_5, being the smallest, is chosen to be zero, the values become

$$E_1 = 13{,}500 \text{ calories} \qquad E_3 = 2300 \text{ calories}$$
$$E_2 = 24{,}200 \text{ calories} \qquad E_4 = 1900 \text{ calories}$$

Equation 4 is then

$$\frac{k_2p_{O_2}e^{-24,200/RT}}{\frac{0.453k_2e^{-13,500/RT}}{p_{H_2} + p_{O_2} + 1.25p_{N_2}} + 2.17 \times 10^{-8}k_2p_{H_2}p_{O_2}e^{-2300/RT} + 5.70 \times 10^{-9}k_2p_{O_2}^2e^{-1900/RT} + 2.30 \times 10^{-9}k_2p_{O_2}p_{N_2}e^{-0/RT}} = 1 \qquad (6)$$

An activation energy of 24,200 calories determines the rate of *chain branching*, and not the actual explosive reaction rate. The term obviously represents a process

$$x_1 + O_2 \longrightarrow x_2 + x_3 + \ldots$$

where the x's are chain carriers.

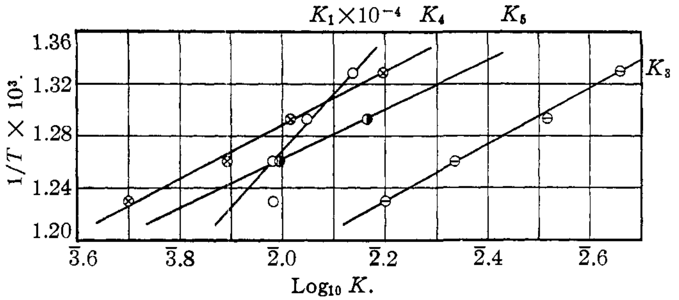

Fig. 5.—Temperature dependence of rate processes: ○, $K_1 \times 10^{-4}$; ⊖, K_3; ⊗, K_4; ◑, K_5.

The rate of *chain breaking at the wall* besides being influenced by the rate of diffusion of the chain carriers may also be dependent upon the fraction of surface effective at any given moment. The calculated activation energy of 13,500 calories is therefore probably only an apparent value.

The following process harmonizes with the three terms representing *chain breaking in the gas phase* x + O_2 + M ⟶ products incapable of continuing the branching chain, where M may be any molecule of the gas mixture.

It should be emphasized that equation 4, despite its large number of constants which are chosen so as to fit best the experimental results, cannot be made to pass through an arbitrary set of points by adjusting the constants. This is evident from the fact that equation 4 does not express the experimental results in Fig. 1 for the transition region at 540°. This divergence is not due to any drift in experimental results since the values obtained by withdrawal and by admixtures are concordant. A possible interpretation is that above 520° another chain breaking process with a high activation energy comes into effect.

Summary

1. The upper and lower limits of the low pressure thermal explosion of hydrogen–oxygen mixtures were measured between 480 and 540° in a potassium chloride-coated Pyrex vessel over the range 0.04–0.9 mole fraction of hydrogen.

2. The effect of nitrogen on the explosion limits was investigated.

3. A kinetic expression (equation 6) represents our experimental results for both limits. It requires that: (a) branching of reaction chains involves a collision of a chain carrier, x_1, with an oxygen molecule: $x_1 + O_2 \longrightarrow x_2 + x_3 + \ldots$; $E = 24{,}200$ calories. (b) Breaking of reaction chains at the wall depends upon a diffusion of the chains to the wall. Apparent $E = 13{,}500$ calories. (c) Breaking of reaction chains in the gas phase occurs by a triple collision: $x + O_2 + M$, the products of which are incapable of continuing the chain. $E < 4000$ calories.

PRINCETON, NEW JERSEY

RECEIVED APRIL 25, 1933
PUBLISHED AUGUST 5, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Preparation and Purification of Methyl Borate and Ethyl Borate[1]

BY STEWART H. WEBSTER AND L. M. DENNIS

Schiff[2] prepared ethyl borate by digesting boric oxide with absolute alcohol for twenty-four hours in a copper digestor at a temperature slightly below 120°.

Etridge and Sugden,[3] after testing various methods that had been described in the literature for the preparation of these borates, selected as the most suitable procedure the heating of boric oxide with the proper alcohol, methyl or ethyl, in a pressure bottle at 120° for twelve hours.

Experimental

Since the methods used for preparing and purifying these two compounds were quite similar, only that for methyl borate will be described in detail.

Methyl Borate.—When boric oxide is added to anhydrous methyl alcohol and the flask is gently shaken, a violent reaction takes place in a few seconds.

The following procedure makes possible the control of the speed of the reaction and avoids the use of a pressure bottle or digestor such as were employed in the two methods cited above. It has the further advantage of shortening the time of preparation and increasing the yield.

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[1] The work upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[2] Schiff, *Ann.*, Suppl., **5**, 158 (1867).

[3] Etridge and Sugden, *J. Chem. Soc.*, 989 (1928).