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

Equation for Hydrogen-Oxygen Explosion Limits[1]

BY H. H. STORCH[2] AND C. W. MONTGOMERY[3]

Frost and Alyea[4] write an equation to represent the data on the upper and lower limits for hydrogen–oxygen mixtures which, in the absence of diluents such as nitrogen, may be written as

$$p(O_2) = K_1 + K_3p(O_2)(H_2) + K_4p(O_2)^2$$

where p = total pressure, (O_2) = oxygen pressure, (H_2) = hydrogen pressure.

An equation similar to (1) may be derived from the following assumptions. 1. The rate of chain branching is directly proportional to the oxygen pressure. 2. The rate of chain breaking is the sum of a term which is inversely proportional to the total pressure (representing chain breaking at the walls), and of terms involving "square" products (representing chain breaking by triple collisions in the gas phase).

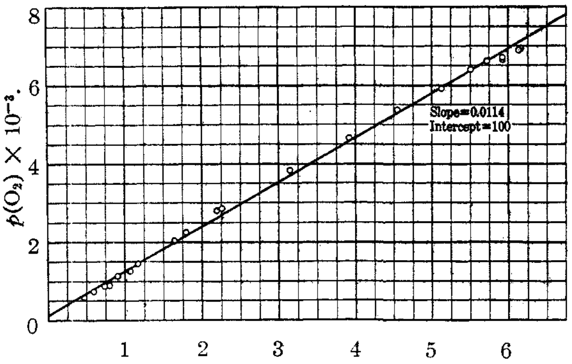

Fig. 1.—Frost and Alyea's upper limit data.

At the explosion limits the rates of 1 and 2 are related as follows

$$K_1(O_2) \gtreqless K_2(H_2)(O_2) + K_2'(O_2) + K_2''(H_2) + K_3/p \quad (1)$$

or

$$(O_2)p \gtreqless \frac{K_2}{K_1}(H_2)(O_2)p + \frac{K_2'}{K_1}(O_2)^2p + \frac{K_2''}{K_1}(H_2)^2p + \frac{K_3}{K_1} \quad (2)$$

This equation may be greatly simplified by assuming that $K_2 = 2\,K_2' = 2\,K_2''$. Then we have

$$p(O_2) \gtreqless \frac{K_2}{K_1}p^3 + \frac{K_3}{K_1} \quad (3)$$

which is the equation of a straight line if one considers $(O_2)p$ and p^3 as the variables.

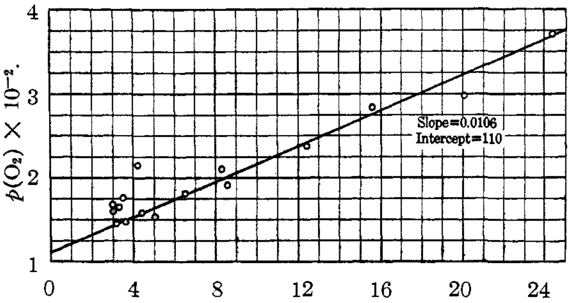

Fig. 2.—Frost and Alyea's lower limit data.

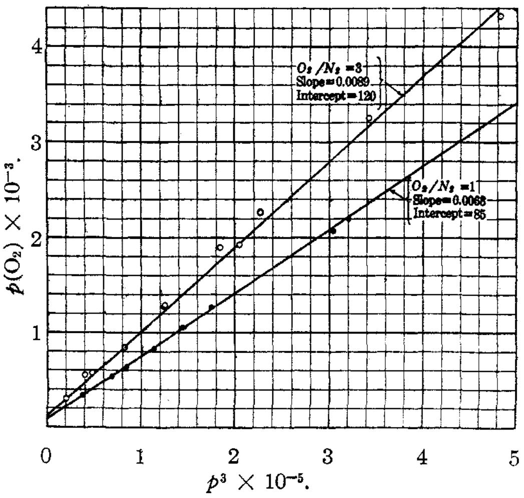

Fig. 3.—Frost and Alyea's upper limit with nitrogen dilution.

In Figs. 1, 2, 3 and 4 all of Frost and Alyea's[4] data for the hydrogen–oxygen limits at 500° are plotted. It will be noted that, excepting a few points at high O_2/H_2 ratios for the lower limit, the data are well represented by equation (3). The slopes and intercepts of the lines of Figs. 1 and 2, representing data for the upper and lower limits, respectively, are the same within 10%. Figures 3 and 4 are the lines obtained for the upper and lower limits with nitrogen dilution. These latter figures are consistent in the sense that an increasing O_2/N_2 ratio decreases the slopes and intercepts by approximately the same amount for both limits. Similar lines may be obtained

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[1] Published by permission of the Director, U. S. Bureau of Mines, and presented at the Cleveland meeting of the American Chemical Society, September 12, 1934. (Not subject to copyright.)

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[4] Frost and Alyea, THIS JOURNAL, **55**, 3227 (1933).

using data taken from the curves given by Frost and Alyea[4] for 480, 520 and 540°. The data for 480° fit equation (3) very well, but those for 520 and 540° deviate from equation (3) for high H_2/O_2 ratios, the points lying below the line drawn through the medium and low H_2/O_2 ratio data. These deviations are considered to be due to the increasing influence at the higher temperatures of the hydrogen pressure on the rate of chain branching. This point will be further discussed below when a possible series of chain-branching reactions is presented. Introducing a hydrogen term in the left-hand member of equations (2) and (3) one obtains

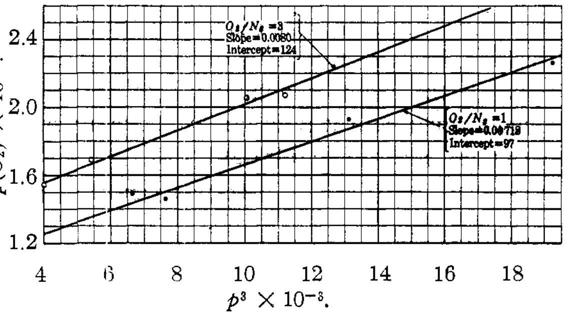

Fig. 4.—Frost and Alyea's lower limit with nitrogen dilution.

$$\left(O_2 + \frac{K_1'}{K_1} H_2\right) p \gtreqless \frac{K_2}{K_1} p^3 + \frac{K_3}{K_1} \qquad (4)$$

and by assuming that $K_1'/K_1 = 0.1$ at 520°, and 0.2 at 540°, the lines of Fig. 5 were obtained. It will be noted that the upper and lower limits at these temperatures are well represented by equation (4).

Data by Grant and Hinshelwood[5] for the upper explosion limit of hydrogen–oxygen mixtures at 550° in quartz vessels are well-fitted by equation (4), if one assumes $K_1'/K_1 = 0.4$. This value is somewhat larger than one would predict for this temperature from the Alyea and Frost data.[4] The slope of the line is, however, close to the value obtained by extrapolating the latter data.

The data presented by Hinshelwood and Moelwyn-Hughes[6] on the lower limit for hydrogen–oxygen explosions at 550° in quartz vessels do not fit equations (3) or (4) even approximately. This discrepancy, as well as the deviation of the high O_2/H_2 points for the lower limit at 500° in Frost and Alyea's[4] data, is probably connected with the function of adsorbed hydrogen in both the chain-breaking and chain-branching processes. The data for the lower limit in quartz where the discrepancy is very large are, however, too meager to permit any detailed consideration of this possibility.

While it is perhaps futile at this time to write a series of chemical reactions from which equations (3) and (4) may be derived, it is nevertheless satisfying to be able to present the following reactions, which are qualitatively consistent with these equations

Chain initiation

$$\left\{\begin{array}{ll} O_2 = O_2' & \text{(a)} \\ O_2' + H_2 = 2OH + 15{,}000 \text{ cal.} & \text{(b)} \end{array}\right.$$

Chain propagation

$$\left\{\begin{array}{ll} H + O_2 = HO_2 + 40{,}000 \text{ cal.} & \text{(c)} \\ HO_2 + H_2 = H_2O_2 + H - 2000 \text{ cal.} & \text{(d)} \end{array}\right.$$

Chain branching

$$\left\{\begin{array}{ll} OH + H_2 = H_2O + H + 200 \text{ cal.} & \text{(e)} \\ H + O_2 = OH + O - 1000 \text{ cal.} & \text{(f)} \\ O + H_2 = OH + H + 13{,}200 \text{ cal.} & \text{(g)} \end{array}\right.$$

Chain breaking

$$\left\{\begin{array}{ll} O_2 + 2OH = H_2O_2 + O_2 + 20{,}900 \text{ cal.} & \text{(h)} \\ H_2 + 2OH = H_2O_2 + H_2 + 20{,}900 \text{ cal.} & \text{(i)} \\ 2H_2 + O = H_2O + H_2 + 116{,}200 \text{ cal.} & \text{(j)} \\ H_2 + O + O_2 = H_2O + O_2 + 116{,}200 \text{ cal.} & \text{(k)} \end{array}\right.$$

Other reactions leading to water formation

$$\left\{\begin{array}{ll} H_2O_2 + H_2 = 2H_2O + 82{,}300 \text{ cal.} & \text{(l)} \\ 2H_2O_2 \longrightarrow 2H_2O + O_2 + 44{,}000 \text{ cal.} & \text{(m)} \end{array}\right.$$

If e, f and g occur only rarely as compared with c and d and if f is much slower than e and g, then chain branching will be proportional to oxygen concentration. At the higher temperatures, however, one would expect the rate of f to approach those of e and g, and hence both oxygen and hydrogen partial pressures must appear in the

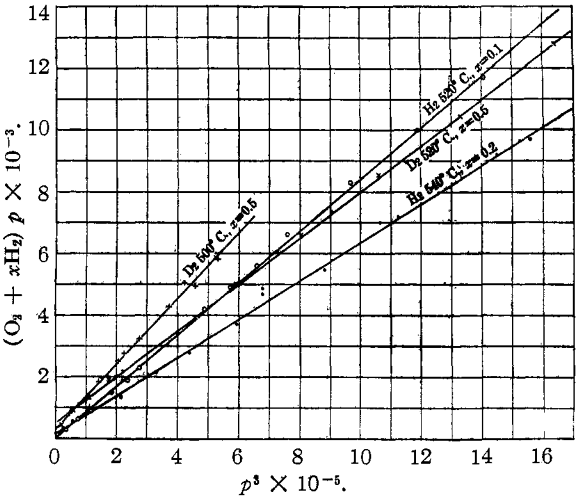

Fig. 5.—Data for deuterium and hydrogen at higher temperatures.

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[5] Grant and Hinshelwood, *Proc. Roy. Soc.* (London), **A141**, 29 (1933).

[6] Hinshelwood and Moelwyn-Hughes, *ibid.*, **A138**, 311 (1932).

chain-branching rate expression. Similarly, if deuterium is substituted for hydrogen, one would expect the rates of reactions e and g to be decreased much more than that of reaction f. Hence one expects the deuterium pressure to appear in the chain branching rate expression at lower temperatures than those at which the hydrogen pressure appears. Using the data of Frost and Alyea[7] for deuterium–oxygen explosions and a value of 0.5 for K_1'/K_1 of equation (4) the lines of Figure 5 for D_2 were obtained. It is apparent that the substitution of D_2 for H_2 practically obliterates the temperature effect observed for H_2.

The authors wish to express their sincere appreciation for many helpful criticisms made by Dr. L. S. Kassel.

Summary

An equation has been suggested for representing the explosion limits of hydrogen–oxygen mixtures as a function of the partial pressures of the reactants. This equation is shown to be qualitatively consistent with a series of possible reactions for the chain branching and chain breaking mechanisms; and it is in quantitative agreement with most of the available data.

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[7] Frost and Alyea, THIS JOURNAL, **56**, 1251 (1934).

NOTES

Boron Arsenate

BY WALTER C. SCHUMB AND WINSLOW H. HARTFORD

In connection with our study of the compounds of boron described elsewhere,[1] we have prepared the relatively little known boron arsenate,[2] and have determined certain of its properties. The method of Meyer[3] for the preparation of boron phosphate was employed, but modifications were necessary due to the greater tendency of boron arsenate to hydrolyze. The best results were obtained by the following procedure: 100 g. of arsenic acid was dissolved in water, the solution was filtered from any suspended matter, heated to boiling, and 20 g. of boric acid then was added. The liquid was maintained at the boiling point until, suddenly, a viscous, white precipitate formed, which was washed rapidly by decantation, filtered and dried; 24.5 g. of a pure white product was obtained. This product still contained a small amount of boric acid, but when boiled with ethyl alcohol, in which boric acid is somewhat soluble and hydrolysis does not occur, a substance was obtained which analysis showed to be very nearly pure boron arsenate. Boron and arsenic were determined on separate samples, using the standard Chapin method for boron, and the U. S. Department of Agriculture method for arsenic.[4] *Anal.* Calcd. for $BAsO_4$: B, 7.27; As, 50.34. Found: B, 7.21, 7.27; As, 50.17, 50.07, 50.20.

The ready hydrolysis of boron arsenate is indicated by the facts that in contact with water the substance was wholly decomposed after three days, and that even in acid solution hydrolysis slowly progressed.

The specific gravity of this substance was found to be, at room temperature, 3.40, a fact which, taken in comparison with the much lower specific gravities of the reactants, indicates a highly condensed internal structure. Its index of refraction (n_D) was 1.66. It is readily decomposed by hot water or warm solutions of sodium carbonate or sodium hydroxide; concentrated hydrochloric acid dissolves it on warming, forming arsenic trichloride and liberating chlorine. It is soluble in dilute sulfuric acid but not in the cold, concentrated acid. It is slowly dissolved by dilute or concentrated nitric acid. At red heat it is slightly decomposed without melting.

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[1] Schumb and Hartford, THIS JOURNAL, **56**, 2613 (1934).

[2] Berger, *Compt. rend.*, **170**, 1492 (1920); Schulze, *Naturwiss.*, **21**, 562 (1933); *Z. physik. Chem.*, **B24**, 215 (1934); Gruner, *Z. anorg. allgem. Chem.*, **219**, 181 (1934).

[3] Meyer, *Ber.*, **22**, 2919 (1889).

[4] Chapin, THIS JOURNAL, **30**, 1687 (1908); U. S. Dept. of Agriculture, Bull. 107, p. 239.

Occurrence and Position of the Principal Inflection Point in Certain Acid–Base Titration Curves

BY E. D. EASTMAN

This note comprises a refutation of the statements of P. S. Roller[1] concerning my previous

[1] Roller, THIS JOURNAL, **54**, 3485 (1932).