from 95% alcohol, toluene and absolute alcohol, the bromide forms slightly brownish plates which soften above 129° and melt at 133–5°. It is soluble in the cold in acetone or chloroform and sparingly so in alcohol, toluene, or ether.

Kjeldahl: 0.3393 g. subst.; 12.7 cc. 0.1 *N* HCl.
Calc. for $C_{11}H_{14}O_2NBr$: N, 5.15%. Found: N, 5.24%.

***p*-Acetaminophenoxypropyl Cyanide (*p*-Acetaminophenyl-γ-cyanopropyl Ether, *p*-Acetaminophenoxybutyronitrile).**—The cyanide was prepared as in the case of the *ortho* isomer, the yield from 27.3 g. of the bromide being 19.5 g. Recrystallized from absolute alcohol, it melts at 98–100° with preliminary softening. It dissolves readily in alcohol or acetic acid, difficultly in benzene.

Kjeldahl: 0.2957 g. subst.; 27.0 cc. 0.1 *N* HCl.
Calc. for $C_{12}H_{14}O_2N_2$: N, 12.84%. Found: N, 12.79%.

***p*-Amino-γ-phenoxybutyric Acid Hydrochloride.**—After saponification of the nitrile the reaction mixture was cooled to 0° and the salt filtered off. 10 g. of the nitrile yielded 6.3 g. of the hydrochloride. Recrystallized twice from 1 : 1 hydrochloric acid, using bone-black, it forms flat, grayish prisms which darken above 180° and melt at 191–4° to a brown liquid. It is sparingly soluble in the cold in absolute alcohol and, in aqueous solution, gives a deep violet color with ferric chloride.

0.1828 g. subst.; 0.1125 g. AgCl.
Calc. for $C_{10}H_{13}O_3N.HCl$: Cl, 15.32%. Found: N, 15.22%.

***p*-Amino-γ-phenoxybutyric Acid.**—The free acid crystallized from an aqueous solution of the salt on adding sodium acetate solution. Recrystallized from a small volume of water, using bone-black, the acid forms lustrous, slightly brownish scales which melt at 145.5–6° (corr.) to a brown liquid. It is sparingly soluble in cold alcohol and in hot benzene. The amino acid is readily diazotized, coupling with R-salt to give a deeper red dye than is formed from the simple aminophenoxyacetic acids.

Kjeldahl: 0.3215 g. subst.; 16.45 cc. 0.1 *N* HCl.
Calc. for $C_{10}H_{13}O_3N$: N, 7.18%. Found: N, 7.17%.

NEW YORK CITY.

[CONTRIBUTION FROM THE PHARMACOLOGICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN.]

SOME OBSERVATIONS ON THE EFFECT OF THE PARTIAL PRESSURE OF OXYGEN ON COMBUSTION.

BY H. C. DOLLWIG, A. C. KOLLS AND A. S. LOEVENHART.

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The nature of combustion has aroused the curiosity of man from the earliest times and the fundamental theories of chemistry at different periods have centered around the views held regarding it. A large amount of work has been done on the subject and no fact concerning its more general aspects can be without interest.

Many investigators have observed the effect on combustion of varying the partial pressure of the oxygen in the atmosphere and the effect of mixing various gases with air on the property of supporting the flame. It is generally held that the facility with which a chemical reaction may be induced and the velocity of the reaction are increased by an increase in the active mass of the reacting substances. In the vast majority of instances in the literature of oxidation this has been found to hold. The following two instances may be cited to show that an increase in the oxygen pressure lowers the ignition point.

Thenard[1] showed that fir wood burns in pure oxygen only when a temperature of 350° is reached but it burns at 252° in oxygen under a pressure of 2.6 m. of mercury. Mallard and LeChatelier[2] found that the ignition point of a mixture of carbon monoxide and oxygen is 630–680°. Diluting the mixture with carbon dioxide raised the ignition point to 695–725°. There are several remarkable exceptions to the rule, however, instances in which an increase in the oxygen pressure decreases the facility and the velocity of oxidation. Thus, Fourcroy[3] found that pure oxygen at ordinary conditions of temperature and pressure does not act at all on phosphorus. This observation has been confirmed by Pflüger[4] and many others. Van Marum[5] found that phosphorus ignites spontaneously in oxygen at diminished pressure. Thorpe and Tutton[6] showed that phosphorus oxide when sealed in a tube with oxygen oxidizes more rapidly after a part of the oxygen is absorbed and the pressure is lessened. This they attribute to the increased volatility of the oxide at diminished pressure. Dixon[7] has shown that the addition of oxygen to electrolytic gas hinders the explosion more than a similar admixture of nitrogen. The same holds true for a mixture of cyanogen and oxygen. Dixon found that the retardation of the explosion wave by an excess of oxygen or by nitrogen is proportional to the volume of the inert gas and to its density.

Several investigators have determined the composition of the residual air when various combustibles are allowed to burn within a confined space until the atmosphere will no longer support their combustion. Since

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[1] *Ann. chim. phys.*, **44**, 181 (1830).

[2] *Compt. rend.*, **91**, 825 (1880).

[3] "Memoires de l'academic des Science," 1788, cited by Ewan, *Z. physik. Chem.*, **16**, 315 (1895).

[4] *Arch. ges. Physiol.*, 10, 251 (1875).

[5] "Verhandlelingen uitgegeeven door Tylers Tweede Genoopschap," 10 (1798); *Phil. Mag.*, [1] **4**, 83 (1799).

[6] *J. Chem. Soc.*, **55**, 571 (1890).

[7] *Ber.*, **38**, 2419 (1905).

most of the combustibles investigated contained carbon the question has repeatedly arisen as to the amount of carbon dioxide required to extinguish the flame and there has been a wide difference of opinion on this point. Thus various investigators place the amount of carbon dioxide required to extinguish the flame at from 3 to 25%.[1] The question as to the amount of oxygen required to support the flame possesses special importance in connection with the hygiene of mines. There long existed a popular belief that when the atmosphere of a mine supports combustion it is respirable and will support life whereas if it will not support combustion it is not respirable and will not support life. This belief was undoubtedly founded on the view that oxidation within the body is essentially the same as combustion. Both of these propositions have been proved to be wrong; an atmosphere which will not support combustion may still support life, and an atmosphere which will support combustion may not support life. In 1845, Leblanc[2] investigated the atmosphere of certain mines. He found that an atmosphere containing 17% of oxygen would not support the combustion of the miner's lamp and that it mattered not whether the reduction of the oxygen percentage resulted from an increase of carbon dioxide or of nitrogen. He stated that air containing oxygen 17.55%, carbon dioxide 0.3%, nitrogen 82.15%, does not support the flame but is respirable though "deficient." He recorded that the miners continue to work on in the dark when the oxygen is 4 to 5% below the normal. He concluded, "C'est la proportion d'oxygen disparu qui détermine la resistance à la combustion." Leblanc's excellent work has been neglected by many subsequent workers. Clowes[3] investigated the composition of atmospheres which are just insufficient in oxygen to support the combustion of various substances. In his experiments an enclosed volume of air contained in a glass cylinder was employed. He allowed material to burn in the normal atmosphere and when the flame was extinguished he determined the composition of the residual atmosphere. He also prepared artificial mixtures by diluting air with nitrogen and carbon dioxide and determined the degree of admixture required to extinguish the flames of various combustible materials. He found that more nitrogen than carbon dioxide had to be added to air in order to produce an extinctive mixture. He studied both wick-fed flames using absolute ethyl alcohol, methyl alcohol, paraffin, candle, etc., and also the flame from a jet of the following gases: hydrogen, carbon monoxide, methane, ethylene, coal gas. He found that with all of the wick-fed flames a reduction of the oxygen percentage in the atmosphere to 16.2–

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[1] Pelet and Jomini, *Bull. soc. chem.*, [3] **29**, 197 (1903).

[2] *Ann. chim. phys.*, [3] **15**, 488 (1845).

[3] *Proc. Roy. Soc. London*, **56**, 2 (1894); "The Detection and Measurement of Inflammable Gases and Vapours in the Air," London, 1896.

17.2% sufficed to extinguish them when nitrogen served as the diluent. In the case of the jet flames there is a marked variation in the composition of the atmosphere required to support the flame. Thus, Clowes found that the methane flame is extinguished when the oxygen percentage falls to 17.4%, carbon monoxide at 15.1%, coal gas at 11.3% and the hydrogen flame only when the oxygen percentage falls to 6.3%. Clowes apparently used in his work an ordinary glass cylinder of about 8 liters' capacity which was closed by means of a ground-glass plate. The desired volume of the gases were introduced into the cylinder by displacing a definite volume of water and a light xylonite ball was used to mix the gases. Clowes believes that the extinction of both jet and wick-fed flames in atmospheres poor in oxygen is due primarily to a fall in the temperature of the flame until it drops below the ignition point. In the case of wick-fed flames Clowes holds that the fall in temperature lessens the vaporization so that the flame may be extinguished as the result of a lack of combustible material. The remarkably small reduction in the oxygen content of the atmosphere required to extinguish the flame has led to the suggestion that this might be used to prevent dust explosions in mines, mills, etc.[1] Our interest in the problem arose in connection with certain other work in which we were engaged. We were exposing small animals such as rabbits, small dogs, etc., to atmospheres low in oxygen at atmospheric pressure in order to determine whether a reduction of the oxygen pressure alone has the same physiological effect as a reduction of the barometric pressure. The work indicated that the physiological effect of lowered partial pressure of oxygen is the same regardless of the method of lowering the oxygen pressure. In this connection we were led to compare the effects on combustion of reducing the oxygen in the atmosphere by the same two methods, namely, 1st, by diluting air with nitrogen and working at atmospheric pressure, 2nd, by partially evacuating the vessel thus reducing both the oxygen and nitrogen pressures. The candle and ethyl alcohol lamp were used exclusively in the work.

Experimental Part.

Work at atmospheric pressure: In this part of the work we used a galvanized iron chamber of approximately 382 liters' capacity. The chamber was provided with three windows. An electric fan placed in the chamber insured a uniform mixing of the gases. A spark from a high tension coil was so disposed that a wick could be lighted without opening the chamber and the electric fan enabled us to extinguish the flame. Using this apparatus we obtained results quite similar to those of Clowes so far as we repeated his work. When the oxygen is reduced to 15%, the alcohol wick-fed flame burns while the spark is on but gradually goes out

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[1] Harger, *J. Soc. Chem. Ind.*, 31, 413 (1912); Brown, *J. Ind. Eng. Chem.*, 9, 269 (1917); Brown and Clement, *Ibid.*, 9, 347 (1917).

within five seconds after turning off the spark. This would indicate that the lowered temperature of the flame in the atmosphere poor in oxygen is responsible for the extinction of the flame. In other words the heat of the reaction under these conditions is not sufficient to make the reaction continuous. At the temperature of the spark it burns in this atmosphere. A pledget of cotton saturated with ether and lighted in the air is immediately extinguished on introducing it into an atmosphere of 13.6% oxygen. At 13% oxygen, the flame from a jet of Madison illuminating gas was extinguished.[1] When the oxygen content of the atmosphere fell to 6.63% the flame of a jet of hydrogen ceased to burn.

In order to reduce the oxygen content of the chamber used in the work at atmospheric pressure to any desired point we made use of a second smaller chamber in which a jet of hydrogen was kept burning and the atmosphere of the large chamber was forced through the small chamber by means of a Crowell blower immersed in oil. This blower circulated the air at a rate of from 32 to 52 liters per minute, depending on the speed of the blower. The air was forced through concentrated sulfuric acid and a large drum filled with soda lime and then returned to the large chamber. Hence there was no accumulation of carbon dioxide or water vapor in the atmosphere of the chamber. The apparatus has been described in a preceding paper.[2] During the reduction of the oxygen content by the hydrogen flame the large chamber communicated with the outside air through a glass tube about 15 cm. long and with a bore of about 6 mm. in order to maintain atmospheric pressure in the chamber.

In the work with the candle we employed the tallow candle and two grades of the cheaper paraffin candle. The results were approximately the same with all three candles. A typical experiment may be given.

Dec. 17 Barometric pressure 736.7 mm.
Temperature of room 21.7°.
11 A.M. Started reducing the oxygen in the chamber by means of the hydrogen flame.
11.10½ Oxygen = 18.7%.
11.17 Candle lighted and placed in the chamber.
11.31 Flame extinguished. Candle relighted—flame gradually diminished in size and in 10 seconds was extinguished. Candle lighted and placed in the chamber, flame extinguished in 10 seconds.
Atmosphere of chamber O_2 = 16.1% = 118.6 mm. Hg. Oxygen pressure.

Ethyl Alcohol Wick-fed Flame.—The ethyl alcohol used was 99.8%. An asbestos wick was used.[3] As the oxygen diminished the flame "climbed

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[1] The average composition of Madison illuminating gas is as follows: Benzene 7%, ethylene 3%, carbon monoxide 33%, hydrogen 40%, ethane 2%, methane 8%, oxygen 1%, carbon dioxide 3%, nitrogen 3%. Private communication from Professor Otto Kowalke.

[2] Kolls and Loevenhart, *Am. J. Physiol.*, 39, 67 (1915).

[3] It was found that although the flame from a cotton wick was neater and more vigorous apparently in the air, in atmospheres of low oxygen content it was always extinguished first.

up the wick" until the flame was only on top of the wick and finally there was a space of 1 to 2 mm. between the top of the wick and the very small flame. It was evident that only the vapor of the alcohol was burning. The flame was extinguished when the oxygen fell to 15.1% = 111.2 mm. Hg. Oxygen pressure.

Experiments at Reduced Barometric Pressure.—In this work we employed a cylindrical chamber of 19.64 liters' capacity made of 3 mm. boiler plate steel. It is 37.5 cm. high and 26 cm. in diameter and is provided with a circular window 5 cm. in diameter of heavy plate glass held in a steel frame. The frame of this window screws on to a casting welded to the chamber and it can be put in place or removed very quickly. The joint is made perfectly tight by means of a rubber gasket. Through this window the candle or lamp was placed in the chamber and the flame observed during the experiment. There is a fixture at the top of the chamber for attaching the pressure hose leading to the vacuum pumps. A mercury manometer is inserted in this line between the chamber and the vacuum pumps. In the evacuation of the chamber a Crowell pump and a May-Nelson rotary pump were used in combination. The chamber could be evacuated to less than 100 mm. of mercury within 30 seconds. In the experiments the window was removed, the lamp or candle placed in the chamber through the window and the wick lighted. The pumps were started immediately and then the window was put in place. The duration of the experiment was counted from the time that the window was closed. Prior to that time the ventilation was excellent and there was practically no increase of carbon dioxide or decrease of oxygen in the atmosphere of the chamber. The pressure in the chamber dropped very rapidly during the first few seconds and then more and more gradually.

The pressure at which the flame was extinguished was noted. The experiments rarely lasted over one minute. The following results were obtained with three different kinds of candles. The same candles were used in experiments at atmospheric pressure.

No.	Candle.	Barometric pressure. Mm. Hg.	Duration of experiment. Seconds.	Residual pressure in chamber when flame was extinguished. Mm. Hg.
1	Tallow	737.4	41	94.4
2	Tallow and paraffin	741	47	90
3	Tallow and paraffin	741	46	88
4	Paraffin	741	44	92
5	Paraffin	741	43	94
			Average,	91.7

In Expt. 1, an analysis was made of the residual air of the chamber. It was found to contain O_2 = 19%, CO_2 1.22%. The increase of about 0.6% in the unabsorbable residue is probably due to the production of a small amount of carbon monoxide or the distillation of hydrocarbons from the candle.

Accordingly, under these conditions the oxygen pressure must drop to approximately 19 mm. Hg before the flame is extinguished. As previously noted at atmospheric pressure the flame is no longer supported when the oxygen pressure falls to 118.6 mm. Hg. Hence we may say that the ratio 19 : 118.6 represents the relative efficiency of oxygen in supporting the flame at atmospheric and at the reduced pressure of 91.7 mm. or, in other words, at this reduced pressure only one-sixth of the oxygen pressure is required to support the flame as at atmospheric pressure. In one experiment we filled the chamber with pure oxygen and carried out the experiment in the usual way. We found the candle was extinguished at a residual pressure of 26 mm. Hg. This agrees, as well as could be expected in an experiment of this kind, with the result when air was used. In this experiment it was found that the residual air contained 13.25% carbon dioxide.

Experiments with Alcohol at Reduced Barometric Pressure.—The ethyl alcohol used in these experiments was 99.8%. The same material was used as in the experiments at atmospheric pressure.

Date.	Wick.	Barometer.	Duration. Seconds.	Observed negative pressure.	Residual pressure at which flame was extinguished. Mm. Hg.
12/2/14	Asbestos......	741	30	601	140
12/2/14	Asbestos......	741	36	617	124
12/2/14	Asbestos......	741	37	619	122
12/2/14	Asbestos......	741	38	611	130
					Average, 129

Calculated on the basis that the residual air had the same composition as the outside air at the end of the experiment, this would correspond to an oxygen pressure of 27 mm. Hg. At atmospheric pressure, using a mixture of oxygen and nitrogen, it requires more than 111.2 mm. Hg oxygen pressure to support the alcohol wick-fed flame. It therefore requires approximately four times as high an oxygen tension to support the flame at atmospheric pressure as in the air at 129 mm. of mercury.

We were surprised to find that it requires a lower pressure to extinguish the candle flame than the alcohol flame, whereas at atmospheric pressure the candle flame is extinguished first by a gradual lowering of the oxygen pressure.

These observations would seem to confirm the view that the cause of the extinction of the flame at atmospheric pressure on even a slight lowering of the oxygen pressure is due to the cooling of the flame by the nitrogen present so that the temperature falls below the ignition point. Since the flame of the alcohol lamp will not withstand as low a pressure as that of the candle we should conclude that the increased volatility of the combustible at diminished pressure plays only a minor role in tending to maintain the flame at lower oxygen pressures. It has been noted at great altitudes that fuels burn less vigorously than at lower levels. Thus the oil burnt in an asbestos wick lamp in a given time was 2.193 g. at 760 mm. Hg and 1.9119 g. at 360 mm. Hg.[1]

Summary.

1. In mixtures of oxygen and nitrogen at atmospheric pressure the flame of the candle and of the ethyl alcohol (99.8%) lamp are extinguished at the following partial pressures of oxygen: Candle, 116 mm. Hg; alcohol lamp, 112.7 mm. Hg.

2. On evacuating a chamber filled with air the flames of the candle and alcohol lamp are extinguished at the following partial pressures of oxygen: Candle, 19 mm. Hg; alcohol lamp, 27 mm. Hg.

Conclusions.

1. The principal reason for the great difference between the concentration of oxygen required to maintain combustion under the two sets of conditions is probably that the excess of nitrogen which has to be heated cools the temperature below the ignition point. It may be that the presence of the inert gas also interferes with the access of oxygen to the flame by reducing the rate of diffusion. If the latter factor really plays no role then the power of an inert gas to extinguish the flame should be proportional to its specific heat.[2] The roles of convection currents and of diffusion in supporting the flame by supplying oxygen remain as unknown factors for the present. We hope at some future time to determine these various factors experimentally.

MADISON, WIS.

[CONTRIBUTION FROM THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY OF THE UNIVERSITY OF ILLINOIS.]

A STUDY OF THE NORMAL METABOLISM OF THE GUINEA PIG.

BY L. MILLARD SMITH AND HOWARD B. LEWIS.

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Since the discovery in 1907 by Holst and his pupils[3] that guinea pigs on certain types of restricted diets were affected by disorders of nutrition closely akin to human scurvy, a large amount of experimental evidence

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[1] Leonard Hill, "Recent Advance in Physiology and Biochemistry," London, 1908, p. 212.

[2] The extinction of the flame by the nitrogen is analogous to the extinction of a furnace fire by mixing cinders with the coal. In this case we should expect the cinders to extinguish the flame in consequence of their cooling effect and also by interfering with access of oxygen.

[3] Holst, A., and Frölich, T., *J. Hyg.*, 7, 634 (1907); *Z. Hyg.*, 72, 1 (1912); *Ibid.*, 25, 334 (1913).