8. The decay of the oxygen afterglow is unlike that of the nitrogen afterglow, the former coming to an abrupt termination.

9. Unlike the nitrogen afterglow the oxygen afterglow is not enhanced at the temperature of liquid air. As far as can be observed the oxygen glow is quenched.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

ACTIVE NITROGEN. III. THE MUTUAL EFFECT OF NITROGEN AND OXYGEN ON THEIR RESPECTIVE AFTERGLOWS[1,2]

BY BERNARD LEWIS[3]

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Introduction

In the course of an investigation[2b] dealing with the influence of surface on the nitrogen afterglow and the influence of the impurity oxygen in this phenomenon, it was observed that as the pressure of a certain mixture of nitrogen and oxygen was decreased, changes occurred not only in the duration and intensity but also in the character of the afterglow. Studies were therefore made with different mixtures of nitrogen and oxygen at various pressures. Among other things the results to be presented will enable one to establish readily any experimental condition desired (within the limits of pressure employed) involving the production of the nitrogen or oxygen afterglow.

It is well known that when oxygen is subjected to the action of an electric discharge, a yellowish-green glow is observed whose spectrum is continuous in character from the reds to the blues.[2c,4] Nitrogen, on the other hand, gives rise to the characteristic orange-yellow afterglow (α-bands).[5] While the nitrogen afterglow lasted longer than four minutes under suitable conditions in these experiments, the maximum duration of afterglow observed in pure oxygen was about thirty-six seconds.

When a mixture of the gases is subjected to the discharge, the type of afterglow one observes is dependent upon the total pressure and the per-

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[1] Read before the Midwest Regional Meeting of the American Chemical Society at Minneapolis, June 8, 1928.

[2] (a) Part I, THIS JOURNAL, **50**, 27 (1928); (b) Part II, *ibid.*, **51**, 654 (1929). (c) also *Nature*, **121**, 938 (1928).

[3] National Research Fellow in Chemistry.

[4] J. J. Thompson, *Phil. Mag.*, **32**, 321 (1891); E. P. Lewis, *Ann. Physik*, **2**, 459 (1900); R. J. Strutt, *Proc. Phys. Soc.*, **23**, 66 (1910) (glow obtained in nitrogen–oxygen mixture); G. Herzberg, *Z. Physik*, **46**, 878 (1928); J. Kaplan, *Proc. Nat. Acad. Sci.*, **14**, 258 (1928).

[5] E. P. Lewis, ref. 4; *Physik. Z.*, **5**, 546 (1904); R. J. Strutt (Rayleigh), *Proc. Roy. Soc.*, (1911–1916).

centage of the components. For example, consider a gas mixture containing 40% of oxygen and 60% of nitrogen between the limits of pressure employed (*ca.* 1.8 mm. to 0.01 mm.). As the pressure is decreased the color of the afterglow undergoes the following metamorphoses: yellowish-green, greenish-yellow, blue (several shades), lilac-blue, gradual disappearance of the blue and appearance of the orange-yellow nitrogen afterglow.[6] Indeed, all other conditions being equal, at the same certain total pressure a gas containing 20% of oxygen will exhibit the nitrogen afterglow, whereas a mixture containing 35% of oxygen will show only the oxygen afterglow. It is therefore quite comprehensible that Hagenbach and Frey[7] should have observed the N_2 afterglow in air while Strutt observed only the oxygen afterglow. The apparent contradiction is accounted for by the fact that the observations were made at different pressures; above 0.75 mm. the greenish-yellow glow is in evidence while below 0.3 mm. the orange-yellow glow is prominent. The curves which follow will make this clear.

Apparatus, Material and Method

The electrodeless discharge was employed in order to avoid the contaminating influence of metallic electrodes. The electrical arrangement was the same as described in Part II of this series.[2] Conditions as to current, temperature, etc., were maintained as constant as possible. The discharge tube, which was about 20 cm. long and 7 cm. in diameter, was connected in the usual way to a mercury-vapor, high-vacuum pump system and also to a Hyvac oil pump through a small dosing tube. The latter was connected to a bulb and a mercury manometer in which the desired mixture of gases was prepared. Pure oxygen prepared from potassium permanganate and tank nitrogen (containing 0.3% of oxygen by analysis) were used. Each gas was maintained at liquid-air temperature for an hour before making up the mixture. A small amount of the mixed gases was maintained at liquid-air temperature in a trap in the dosing tube before its admittance to the discharge chamber. The lower part of the trap was kept in liquid air throughout a run in order to avoid any possible diffusion of mercury vapor. At each pressure a discharge lasting half a second was passed and several readings of the duration of the afterglow were taken after the cessation of the discharge. Pressures were read on a McLeod gage. Simultaneously, observations were made on the character of the afterglow with a small spectroscope. Readings were made in a completely darkened room. No attempt was made to estimate intensities except in a qualitative manner. The intensity curve follows only approximately the duration curve.

Results

Within the pressure limits employed, a maximum may be observed in the oxygen afterglow down to about 12% of oxygen. With decreasing percentages of oxygen (beginning with pure oxygen) the maximum flattens out and finally diappears and with it also the oxygen afterglow. From 100 to 60% of oxygen only the oxygen afterglow is observed even down

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[6] In general the same sequence of colors was observed by Constantinides, *Phys. Rev.*, **30**, 95 (1927), as the partial pressure of oxygen was changed. Herzberg (ref. 4) records similar changes.

[7] Hagenbach and Frey, *Physik. Z.*, **18**, 544 (1917); see also Herzberg, ref. 4.

to very low pressures (*ca.* 0.05 mm.). However, in a mixture containing less than 60% of oxygen, in addition to the above maximum, a sharp minimum is observed (blue afterglow) at a somewhat lower pressure, at which point the intensity and duration become quite small. In the region of this minimum, usually just preceding it, the lilac color begins to appear, which is an indication that the nitrogen α-bands have just become visible. Here the spectroscope shows also the blue continuous background.[8] As the pressure is reduced further, the α-bands become more prominent, the blue portion disappearing, until finally only the former are visible. The nitrogen afterglow rises to a duration maximum at very low pressures (0.035–0.04 mm.).

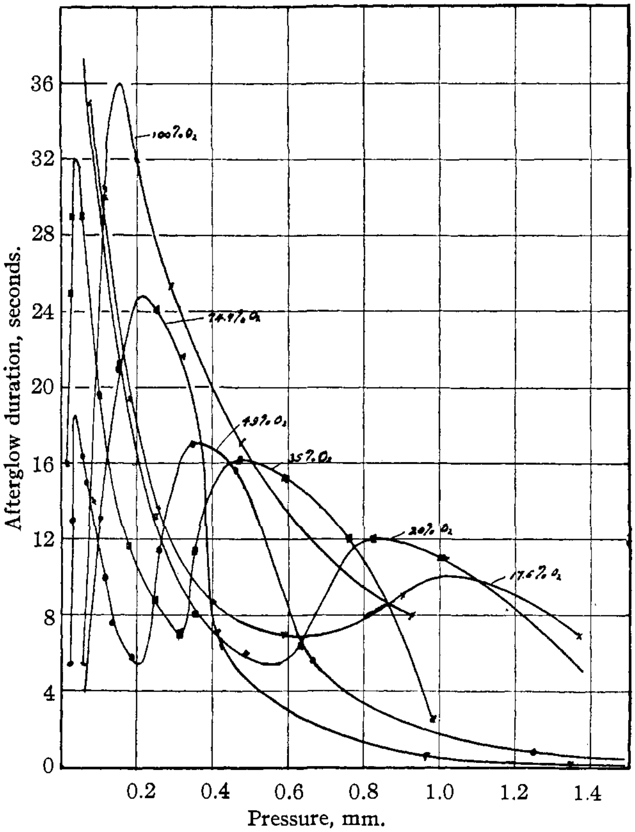

Fig. 1a.

The maximum in the oxygen afterglow, the minimum following it

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[8] A curious phenomenon was observed in the region of this minimum [*Nature*, **122**, 241 (1928)], namely, that entirely different afterglows can be obtained in the same mixture and at the same pressure merely by varying the length of time of discharging.

and the point at which the α-bands are just visible are displaced toward lower total pressures as the percentage of oxygen in the mixture is increased.

The maximum in the nitrogen afterglow duration occurs (within experimental error)[9] at about the same pressure. A few characteristic curves are given in Figs. 1a and 1b to illustrate these points.

If one multiplies the percentage of oxygen by the total gas pressure at the maxima, the minima and the points at which the α-bands appear, constants are obtained. This means that these points always occur at the same partial pressure of oxygen. These oxygen pressures are: maxima, 0.161 mm.; minima, 0.111 mm.; α-bands, 0.123 mm. The following equations, which represent rectangular hyperbolas, are satisfied: $xy = a = 0.161$; $xy = b = 0.111$; $xy = c = 0.123$, in which x is the total gas pressure and y the percentage of oxygen. In Fig. 2 a rectangular hyperbola is

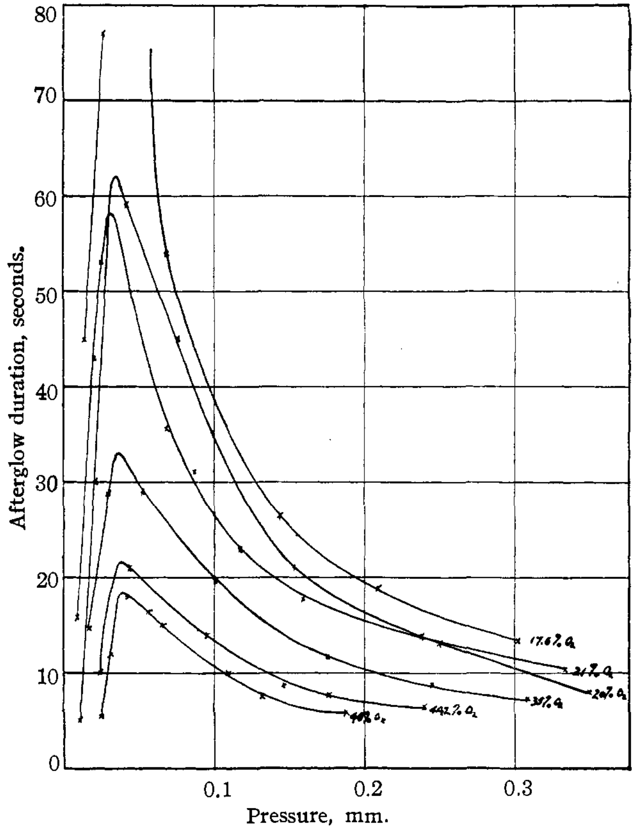

Fig. 1b.

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[9] Phosphorescence of the glass at lower pressure sometimes prevents an accurate determination of the duration.

plotted for each of these three equations and the experimental points for the maxima, minima and α-bands are laid out on them. The coincidence is very good. Another way of emphasizing this is to plot $1/p$ against percentage of oxygen, from which good straight lines are obtained. It is unnecessary, however, to show this. It will be observed (Fig. 2) that for small percentages of oxygen there is a greater divergence between the pressures at which the maxima and minima occur. This means that the maxima should flatten out and become less prominent with decreasing percentage of oxygen. Fig. 1a shows this well. Actually the maxima become so flat as to disappear entirely. Since the oxygen concentration for any set of points is constant, the observed shifts must be due to active nitrogen.

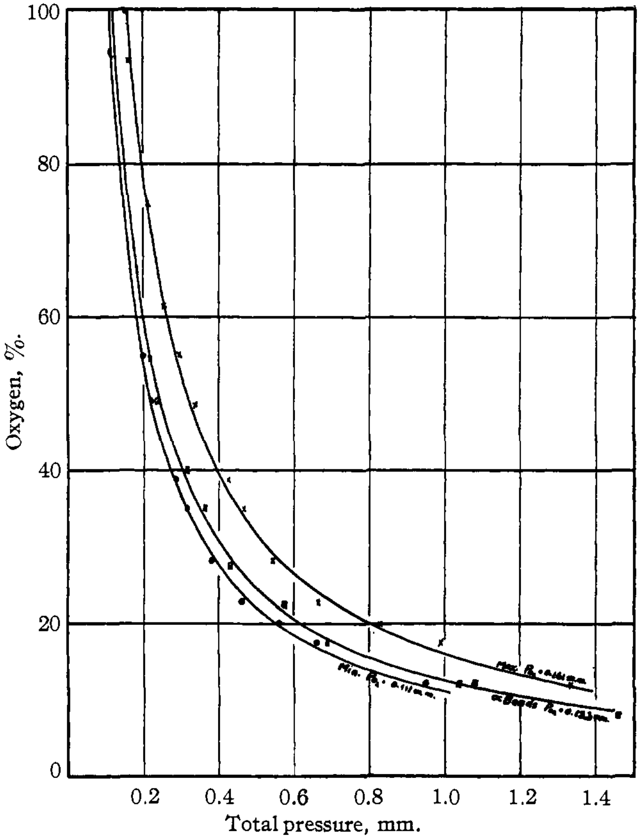
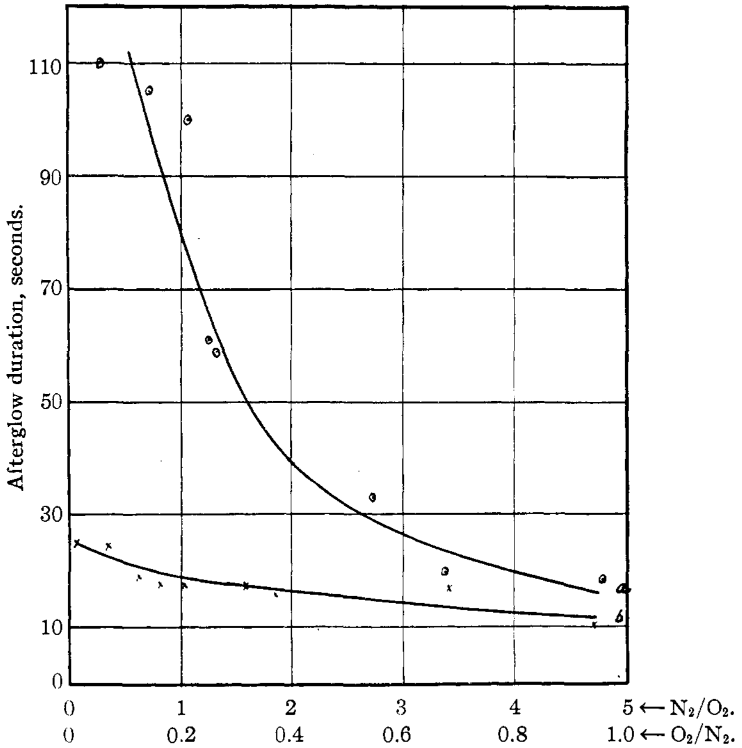


Fig. 2.

In Fig. 3a the duration of the nitrogen afterglow at the maxima is plotted against the ratio of the oxygen concentration to the nitrogen concentration and in 3b the duration of the oxygen afterglow at the maxima is plotted against the ratio of the nitrogen concentration to the oxygen concentration. These curves are only approximately correct since the surface of the discharge chamber was changed after each run by heating and evacuating. It is seen that whereas the influence of oxygen on the nitrogen afterglow is very marked,[10] that of nitrogen on the oxygen afterglow is certainly very slight (the ratio in the latter varied 70-fold). In agreement with this Herzberg[4] finds that nitrogen led into a stream of glowing oxygen is without effect. It may be concluded that whereas normal oxygen molecules have a marked quenching action on the nitrogen afterglow, normal nitrogen molecules do not affect the oxygen afterglow. Since in these experiments both gases were activated together, the slight quenching action of the oxygen afterglow is probably due to the action of the nitrogen afterglow carriers or active nitrogen molecules or both. It is evident, therefore, that the effect of active nitrogen in quenching the oxygen afterglow is far



a = maximum N_2; b = maximum O_2.

Fig. 3 (a and b).

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[10] Compare Constantinides' (ref. 6) and Strutt's (ref. 9) experiments in which a very rapid quenching is observed on passing oxygen into a stream of glowing nitrogen. The amount of quenching is practically proportional to the oxygen concentration.

less than the effect of active oxygen in quenching the nitrogen afterglow. Thus even when the concentration of nitrogen is five times that of oxygen (Fig. 3b), the nitrogen afterglow is effectively quenched, the oxygen afterglow being the only one visible.

Discussion

In presenting the following discussion, the author realizes that no exact formulation of the processes occurring can be attempted at this stage due to the complexity of the system when exposed to the electric discharge. The manifold possibilities are not by any means exhausted in the following list of reactions.

Normal oxygen molecules must be mainly responsible for the quenching of the nitrogen afterglow or, in other words, the removal of nitrogen atoms.[11a] There are several ways in which this could take place

$$N + N + O_2 = N_2 + O_2 + 263{,}000 \text{ cal.}[11b] \tag{1}$$
$$N + O_2 + \text{third body} = NO_2 + 124{,}000 \text{ cal.} \tag{2a$_1$}$$
$$N + O_2 = NO + O + 29{,}000 \text{ cal.} \tag{2a$_2$}$$
$$N + NO_2 = N_2 + O_2 + 140{,}000 \text{ cal.} \tag{2b$_1$}$$
$$N + NO_2 = 2NO + 97{,}000 \text{ cal.} \tag{2b$_2$}$$
$$N + NO = N_2 + O + 72{,}000 \text{ cal.} \tag{2c}$$
$$N + O + \text{third body} = NO + 191{,}000 \text{ cal.} \tag{3}$$

No indication is made of excited states of the products.

It is seen that all these reactions are possible from an energy standpoint and it is probable that all of them contribute to the extinction of the nitrogen afterglow. If the product condensed out in liquid air is nitrogen peroxide,[12] it is probable that $2a_1$ contributes to the quenching in a large measure.[13]

[11a] Kaplan and Cario, *Nature*, **121**, 906 (1928), believe that the excited nitrogen molecule (11th vibrational state in level B) from which the α-bands proceed is brought about by a collision between a metastable nitrogen molecule in level A [8 volts] and a metastable N atom (3.56 volts) in which the energy of the latter is transferred to the former. For a discussion of this see H. O. Kneser, *Ann. Physik*, **21**, 707 (1928).

[11b] From recent work by H. O. Kneser, [*Ann. Physik*, **21**, 707 (1928)] it appears very probable that the mechanism of α-band emission involves a triple collision between two atoms of nitrogen and a third body. The results of his experiments are not in accord with similar results of Bonhoeffer and Kaminsky [*Z. physik. Chem.*, **127**, 385 (1927)], which earlier led them to doubt the triple collision hypothesis. The most recent value for the heat of dissociation of nitrogen is 9.5 volts (or about 218,000 calories) [Gaviola, *Nature*, **122**, 313 (1928); Birge and Mulliken, **122**, Dec. (1928)]. This new value in no way invalidates the theory of Sponer regarding the origin of the α-bands. The process may still be thought of as occurring between a normal nitrogen atom and a metastable nitrogen atom (2.4 volts) in triple collision with a third body.

[12] Majewska and Bernhardt, *Z. Physik*, **48**, 137 (1928). If a discharge is passed through a mixture of the gases, a gas is condensed out at −85° (see Part II). This gas cannot, therefore, be O_3, NO nor N_2O.

[13] There is also, of course, the possibility of formation of NO_2 by the action of O_3 on NO.

It has been mentioned that normal nitrogen molecules do not affect the oxygen afterglow. Nitrogen atoms could remove oxygen atoms by collision with a third body and thus quench the glow but the concentration of nitrogen atoms is probably too small for this to be marked. It will be assumed for want of evidence as to the intensity distribution in the continuous spectrum in pure oxygen as compared with that in the continuous spectrum in air or in that produced by the oxidation of nitric oxide by ozone, that the oxygen afterglow is due to the emission of radiation (see Thompson, ref. 4) when two oxygen atoms, possessing any velocity, combine. This may occur in a two body collision,[14] so that competition for the reactions N + O + third body and O + O is in favor of the latter. The small quenching effect of the oxygen afterglow by active nitrogen may easily be due to the active nitrogen molecular species.

It would be valuable from the standpoint of atomic kinetics to make calculations at the minima, where the α-bands appear, of the collisions between the various species present in the glowing gas, to determine if possible at what concentration of atomic nitrogen the α-bands become visible. In view of the complicated system of reactions which may be occurring, the uncertainties involved in the fractions of oxygen and nitrogen which are dissociated by the discharge and the fruitfulness of such collisions as between two nitrogen atoms, it is doubtful whether the calculation would have much meaning. One may simplify the problem by considering only the reactions $2a_1$ and $N + N = N_2' \longrightarrow \alpha$-bands. In a mixture containing 20% of oxygen, the minimum occurs at 0.56 mm. Assuming 1% dissociation of nitrogen, which may be high,[15] and disregarding dissociation of oxygen, we find the number of collisions between N and O_2 ($\sigma_N = 1.77$ Å. and $\sigma_{O_2} = 1.44$ Å.) equal to 2.77×10^{20} per cc. per sec. Since this requires the intervention of a third body and the ratio of triple to double collisions is[16] about $^1/_{1000}$, this becomes roughly 3×10^{17} collisions per cc. per sec. The number of collisions between N and N is 1.7×10^{19} per cc. per sec. This calculation shows at least that such an encounter as between two nitrogen atoms results in a molecule very infrequently, for otherwise it would be possible to see the α-bands at a much higher pressure than corresponds to the minimum. One arrives at the same result from classical theory. It is believed that only atoms possessing certain velocities can combine.[17] In fact the temperature coefficient of the

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[14] Oxygen has a continuous absorption spectrum beginning at λ1751 and can emit continuously by electron transition.

[15] Crew and Hulbert, *Phys. Rev.*, **30**, 124 (1927).

[16] At atmospheric pressure, Herzfeld, *Z. Physik*, **8**, 132 (1921).

[17] Indeed, the persistence of the oxygen afterglow even in the presence of "active" nitrogen at pressures of nitrogen many times that of oxygen, is probably due to the ease with which two oxygen atoms combine as compared with the combination of two nitrogen atoms.

nitrogen afterglow (between room temperature and liquid air temperature) can be accounted for if one assumes that only atoms combine which possess velocities below some small critical value. Since the α-bands just become visible in the region of the minimum it is evident that a sufficient number of these fruitful collisions are taking place. These must increase in number as the pressure is reduced, for the intensity of the α-bands increases. In a general way this can be understood, for the fraction of nitrogen molecules dissociated by the discharge increases as the pressure is reduced[15,18] and the number of suitable collisions between N and N must therefore increase faster than deactivating collisions.

I am indebted and thankful to Professor S. C. Lind for his constant interest and advice during the tenure of this Fellowship and for placing at my disposal the facilities of his laboratories.

Summary and Conclusions

A study is made with the electrodeless discharge of the nitrogen and oxygen afterglows in mixtures of nitrogen and oxygen at various pressures. A sequence of changes in the character of the afterglow is recorded as the pressure is reduced in the same mixture This may be divided roughly between the oxygen afterglow at higher pressures and the nitrogen afterglow at lower pressures with a maximum in each and a minimum between the two. Within the limits of pressure employed (*ca.* 1.8 mm. to 0.01 mm.) and from 100 to 60% of oxygen, only the oxygen afterglow with its maximum is observed. At lower percentages of oxygen the minimum appears and also the nitrogen afterglow. Below about 12% of oxygen, the oxygen afterglow maximum disappears and with it also the oxygen afterglow. The α-bands just become visible at a total pressure slightly higher than that at the minimum.

The oxygen maxima, the minima and the points at which the α-bands just appear are displaced toward lower total pressures as the percentage of oxygen increases. It is found that these points always occur at a constant partial pressure of oxygen: oxygen maxima, 0.161 mm.; minima, 0.111 mm.; α-bands, 0.123 mm. The experimental points fit the corresponding hyperbolas very well. The nitrogen afterglow rises to a duration maximum at a pressure of about 0.035–0.04 mm. *The curves and data presented enable one to determine any experimental condition desired (within the pressure limits employed) involving the production of the nitrogen or oxygen afterglows.*

It is concluded that normal oxygen molecules have a marked quenching action on the nitrogen afterglow but that normal nitrogen molecules have no effect on the oxygen afterglow. The slight quenching action in the oxygen afterglow is probably due to active nitrogen molecules.

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[18] This is also evident from the fact that with decreasing pressure in either pure nitrogen or oxygen the glow becomes more intense and of longer duration.

Calculations show that the fruitfulness of collisions between two nitrogen atoms to form a molecule is small. The temperature coefficient of the afterglow in nitrogen can be explained on the basis that only atoms possessing velocities below some critical value can combine on colliding.

MINNEAPOLIS, MINNESOTA
BERLIN, GERMANY

[CONTRIBUTION FROM THE PHYSICAL CHEMICAL LABORATORY OF MCGILL UNIVERSITY]

THE PROPERTIES OF PURE HYDROGEN PEROXIDE. VI

BY G. L. MATHESON AND O. MAASS

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The following paper is one of a series[1] that deals with the properties of pure hydrogen peroxide. In it several new freezing-point curves are described and the existence of compounds between hydrogen peroxide and a number of organic bases is investigated. The measurements of the heat of decomposition, the molecular weight in the vapor phase and the explosion temperature of pure hydrogen peroxide are described.

Pure hydrogen peroxide was prepared in much the same manner as was set forth in the first paper of this series with a few slight modifications. The concentration, by evaporation *in vacuo*, was carried out until the strength was about 98% by weight. The distillate produced in the final stages of evaporation was saved. The final purification was carried out as before by means of fractional crystallization.

Freezing-Point Curves.—This section of the experimental work deals with the solubility and freezing-point curves of various substances in pure hydrogen peroxide. These experiments are of interest in comparison with corresponding water systems. The apparatus employed consisted of a long test-tube set in a bath of ether in a transparent Dewar flask. A stirrer was provided in the tube and the bath was stirred by bubbling air through it. Its temperature could be controlled by adding carbon dioxide snow or by changing the rate of flow of air. The temperature was measured by a thermometer placed in the bath. The materials were added in the most convenient manner for each substance. The chemicals used were all carefully purified to remove foreign substances which might decompose the peroxide. The temperatures are those recorded just as the last crystals disappeared when the bath was slowly warmed.

In Table I the results are recorded for potassium chloride, sodium fluoride, potassium sulfate and methyl alcohol, and these systems are plotted in Figs. 1 and 2, with the corresponding water systems.

The data for the water curves are taken from the literature with the exception of the one for sodium fluoride, for which the following points

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[1] Maass and Hatcher, THIS JOURNAL, **42**, 2548 (1920).