radium includes the correction determined by Hönigschmid for the temperature of the radium salt. This was overlooked in the earlier tables. The value for thorium is that obtained by Hönigschmid in his most reliable series.[17]

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ACTIVE NITROGEN. II. THE INFLUENCE OF SURFACE ON THE AFTERGLOWS IN NITROGEN AND OXYGEN[1,2]

BY BERNARD LEWIS[3]

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It has been contended by some workers[4] that pure nitrogen subjected to the action of an electric discharge shows no afterglow but that its restoration is effected by the addition of a trace of oxygen. Other investigators[5] have shown that pure nitrogen undoubtedly could give rise to an afterglow, which, however, is intensified by the addition of oxygen or certain other impurities. More recently Bonhoeffer and Kaminsky[6] have concluded that pure nitrogen is glowless but the introduction of certain optimum amounts of such impurities as oxygen, hydrogen sulfide and methane into the discharge mixture produces a glow of maximum intensity.

The action of the impurities has been thought to be due to the formation of a layer of gas on the surface of the vessel which inhibits the catalytic combination of nitrogen atoms thereon. The atoms must now combine in the gas phase with consequent emission of the α-bands. It was the purpose early in these experiments to ascertain whether the impurity, oxygen, entered into the mechanism of afterglow production. The possibility could not be entirely excluded that oxygen was necessary in some physical action to induce the afterglow in the gas phase, notwithstanding results by Bonhoeffer and Kaminsky, namely, that different impurities are without effect on the character of the afterglow.

[17] Hönigschmid *Sitz. Kaiser. Akad. Wien,* [IIa] **125,** 1 (1916).

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

[2] Bernard Lewis, Part I, THIS JOURNAL, **50,** 27 (1928).

[3] National Research Fellow in Chemistry.

[4] Compte, *Physik. Z.,* **14,** 74 (1913); Tiede, *Ber.,* **46,** 340 (1913); Tiede and Domcke, *ibid.,* **46,** 4095 (1913); **47,** 420 (1914).

[5] Von Mosengeil, *Ann. Physik,* **20,** 833 (1906); Strutt, *Proc. Roy. Soc.,* **85,** 219 (1912); *Physik. Z.,* **14,** 215 (1913); König and Elöd, *ibid.,* **14,** 165 (1913); *Ber.,* **47,** 523 (1913); König, *Z. Elektrochem.,* **21,** 278 (1915); Baker and Strutt, *Ber.,* **47,** 801, 1049 (1914); Baker, Tiede, Strutt and Domcke, *Nature,* **93,** 478 (1914); Strutt, *Proc. Roy. Soc.,* **91,** 303 (1915).

[6] Bonhoeffer and Kaminsky, *Z. physik. Chem.,* **127,** 385 (1927).

Initial Experiments.[7]—Accordingly, pure nitrogen was introduced into a liter bulb[8] into the center of which pure oxygen could be admitted more or less uniformly in all directions through an inner tube perforated at one end. In impure nitrogen the active species which eventually give rise to the glow remain for some time after the cessation of the discharge. If similar circumstances exist in pure nitrogen (assuming it is glowless) and provided the presence merely of ordinary oxygen is required to create the afterglow, then the glow may be expected to appear if oxygen is introduced immediately after discontinuing the discharge.

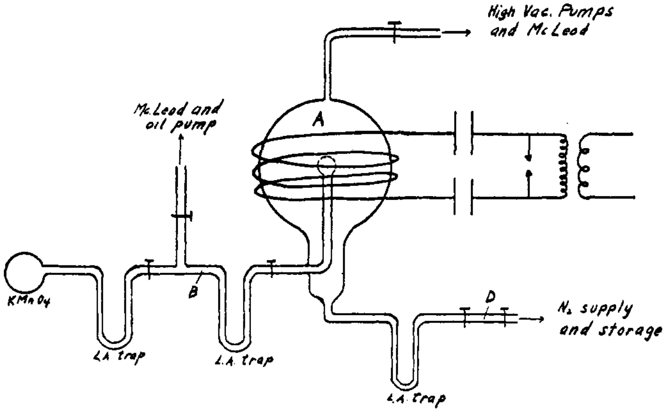

Fig. 1.

The apparatus given in Fig. 1 requires no explanation. Pure oxygen was prepared from potassium permanganate and pure nitrogen by two methods: (1) from bromine water and ammonia,[9] and (2) by heating sodium trinitride (NaN_3). Water vapor was removed from the gases in liquid-air traps. In the first method the nitrogen, prepared in a special generator, was also stored over phosphorus pentoxide to remove ammonia. The electrodeless discharge was employed in all experiments, thus eliminating a possible contaminating influence of metallic electrodes. A static method was used.

For some time it was impossible to produce absolutely glowless nitrogen, even though utmost precaution had been taken to ensure the complete absence of oxygen and other impurities. Only after thoroughly baking out the bulb at high temperature and under high vacuum as well as the occasional passage of the discharge was a glowless pure nitrogen obtained[10] (nitrogen pressure about 0.1 mm. of mercury). Upon the

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[7] Bernard Lewis, *Nature*, **121**, 938 (1928).

[8] The bulb and all connecting tubes, made of pyrex, were carefully cleaned with hot chromic acid and subsequently heated almost to melting before assembling the apparatus.

[9] Waran, *Phil. Mag.*, **42**, 246 (1921); Kenty and Turner, *Nature*, **120**, 332 (1927).

[10] With this treatment the glow gradually disappeared. It must be remarked that in using a static system in a glass vessel, it is not easy to remove the glow entirely by heating alone. It was noted on several occasions that whereas no glow was evident after the discharge was discontinued, during the passage of the latter the characteristic nitrogen glow could be observed, though weak, to extend about 1.5 cm. into the wide tubing directly below the bulb.

introduction of pure, dry oxygen (1%, the pressure was adjusted in dosing tube B) in the manner described above, *no glow was produced.* This was repeated several times using nitrogen from both sources with similar results. Furthermore, after the oxygen had been admitted and the mixture subjected to the discharge, little or no glow was discernible.[11] This seemed very strange indeed in view of the previous work of Strutt, Bonhoeffer and Kaminsky and others. It is evident that neither ordinary oxygen molecules nor "active" oxygen takes part in the excitation process which produces the luminosity. This conclusion is not at variance with Bonhoeffer and Kaminsky's observation mentioned above regarding the effect of impurities on the afterglow spectrum.

Further Experiments.—The electrical arrangement was modified somewhat in order to increase the energy in the coil wrapped around the bulb, so that the discharge could be passed at higher gas pressures. A spark gap made with heavy zinc electrodes 4 cm. in diameter was connected in series with two condensers (each of 10 double-thickness glass plates 18 × 20 inches, immersed in transformer oil) which in turn were in series with the coil. The latter (4 turns) and leads (which were made as short as possible) consisted of 0.25-inch copper rod. The secondary of a transformer was connected across the spark gap, which was 2.5 to 3 cm. wide. The secondary voltage was about 50,000 volts and the primary current 21.5 amperes. A glass tube 20 cm. long and about 7 cm. in diameter was substituted for the bulb. Two liquid-air traps protected the tube from stopcock grease. Nitrogen could be obtained at will from sodium nitride or from a nitrogen cylinder (containing 0.3% of oxygen by analysis) and the oxygen was obtained from potassium permanganate. All gases entered the discharge tube by way of the dosing Tube B in which water vapor, etc., was removed with liquid air. In all of the experiments to be described the discharge tube was initially baked out at a temperature of 350–470° from six to eighteen hours under high vacuum. All connecting tubes were heated frequently almost to melting. Unless otherwise stated, (1) the gas admitted was previously deprived of water vapor by long standing (six to twenty-four hours) at liquid-air temperature and (2) both traps in direct communication with the discharge tube were immersed in liquid air.

During the progress of the following work a paper appeared by G. Herzberg[12] on the influence of the walls on the nitrogen and oxygen afterglows. The results recorded here, in so far as the two works overlap, substantiate Herzberg's observations. The method employed to restore the afterglow was unlike that used by him. Some interesting new phenomena in temperature and pressure effects have also been found.

A.—Tank nitrogen was admitted at a pressure of 0.704 mm. The glow was weak and lasted for fourteen seconds.[13] Normally in an unbaked vessel and with water removed from the entering gas, the afterglow lasted for about 130 sec. and with greater intensity. With intermittent discharging the duration and intensity of the glow gradually diminished to < 0.5 sec. The vessel now being evacuated to 0.31 mm., no glow was visible. Upon removing the liquid air from both traps the glow reappeared,

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[11] It will be shown in a subsequent contribution (Part III) that a mixture containing 1% of oxygen at a pressure of about 0.1 mm. gives rise to an intense afterglow of long duration under ordinary circumstances.

[12] G. Herzberg, *Z. Physik*, **46**, 478 (1928).

[13] Observation of the enhanced afterglow at the liquid-air trap with a spectroscope indicated the presence of α-bands.

lasting for eighteen sec. (Under ordinary conditions and at this pressure the glow would last for 190 sec.) By the same procedure (discharging[14] with liquid air on the traps) the glow could again be eliminated, a pressure decrease < 0.01 mm. being recorded on the McLeod gage. Thus it is evident that some gas is being condensed out.

B.—Tank nitrogen was admitted at a pressure of 0.318 mm. The glow lasted for twelve sec. Fresh tank nitrogen was admitted at a pressure of 0.349 mm., the glow lasting for ten seconds. This was increased to twenty sec. when the liquid air was removed from both traps. This is to be expected, since in a system containing a given amount of active gas, the glow is enhanced at liquid-air temperature resulting in a more rapid removal of the glow-producing species. Ordinary tank nitrogen (moist) was now admitted, with the following results:

Pressure (mm.)	0.357	0.290	0.129
Duration (sec.)	90	130	160

The vessel was evacuated and fresh moist tank nitrogen admitted:

Pressure (mm.)	1.3	0.328	0.205
Duration (sec.)	72	115	140–150

Liquid air was replaced on both traps and this gas (0.205 mm.) was subjected to the discharge, the glow becoming weaker and of shorter duration until finally it disappeared entirely. The pressure had decreased to 0.16 mm.[15] In this glowless condition fresh, dry tank nitrogen was admitted at about 3 mm. and the vessel evacuated to a pressure 0.22 mm. *Practically no afterglow was observed.* If any was present it was exceedingly faint and lasted less than a fourth of a second (possibly due to weak phosphorescence of the glass, which is sometimes observed). Repetition of the above on other occasions failed to show any glow whatsoever. When the liquid air was removed the glow reappeared with its usual intensity and endured for 117 sec. These experiments indicate conclusively that even in the presence of sufficient oxygen to produce a very marked glow under ordinary conditions, the afterglow can be eliminated if the vessel is treated as outlined above.

[14] Herzberg also found that in order to eliminate the afterglow in a glass vessel, completely, the discharge had to be passed, for only in this way can the last traces of water vapor or other occluded gas be removed from the walls.

[15] It is not understood why such a decrease in pressure should have occurred unless it be due to the usual "clean-up" effect. In the initial experiments recorded above, this pressure decrease was so marked at times, after long discharging, that the discharge ceased to pass. Thus it was observed that the pressure sometimes decreased from 0.1 to 0.001 mm. The gas could be recovered by removing the liquid air and heating the bulb. Some investigation of this was carried out but the results are not sufficient to warrant mention here. Herzberg also noted this extraordinary "self-evacuation."

C. I.—Experiment B was repeated but the traps were cooled to a temperature of only −85° (carbon dioxide and ether). Dry tank nitrogen showed a weak glow lasting for nine sec. which disappeared as before after some discharging. The condensate therefore cannot be ozone, nitric oxide or nitrous oxide. Other possibilities are water, nitrogen peroxide, nitric acid, and nitrogen pentoxide. We are interested here in the substance which, when removed, causes the glow to disappear. Since (1) the glow can be eliminated even in the presence of oxygen, (2) the same effect takes place in pure nitrogen (see Section D) and (3) the glow, it will be shown, can be restored by addition of small amounts of water vapor to pure or tank nitrogen, it is probable that the effective substance is water vapor. The last traces of water which adhere tenaciously to the glass walls are liberated by the discharge and condensed. It is quite possible that nitrogen peroxide also is condensed out from tank nitrogen as Majewska and Bernhardt believe.[16]

C. II. **Reversed Pressure Effect with Tank Nitrogen.**—Fresh dry tank nitrogen was admitted to the vessel in the condition as left in C I.

Pressure (mm.)	0.390	0.267
Duration (sec.)	1	0.6

The carbon dioxide–ether baths were removed and replaced by liquid air after the trap had warmed up. The glow which appeared (seven sec.) was removed completely by discharging. Fresh, dry tank nitrogen was admitted again.

Pressure (mm.)	>1.0	0.40	0.275
Duration (sec.)	7	1.4	<0.25

The vessel was evacuated and fresh, dry tank nitrogen admitted again. At a pressure of 0.148 mm. there was no glow. This procedure was repeated; at a pressure of 0.445 mm. the glow lasted for one sec., while at 0.210 mm. there was no glow.

These results are in agreement with those in Section B as long as the pressure of nitrogen is low (about 0.20 mm). However, when the pressure is increased, an afterglow undoubtedly appears even though of short duration. This may be explained as follows. At higher pressures some of the clean surface is poisoned by adsorption of the gases (both oxygen and nitrogen). The combination of nitrogen atoms on the walls being somewhat hindered, more combinations can occur in the gas phase and give rise to the afterglow. At lower pressures the decreased adsorption exposes more free surface for atomic combination. The same effect is observed when pure nitrogen is used (see Section D).

The interesting fact established is, that *with a "clean" surface a pressure effect is observed which is reversed from that observed with an "unclean"*

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[16] Majewska and Bernhardt, *Z. Physik*, **48**, 140 (1928).

surface. That is to say, with the latter the afterglow increases in duration and intensity with reduction in pressure (see Section B and also Part III), whereas with the former the duration and intensity decrease with pressure.

D. Reversed Pressure Effect with Pure Nitrogen.—Pure dry nitrogen (from sodium nitride) was admitted.

Pressure (mm.)	1.7	0.260	0.158
Duration (sec.)	12	5	3.5

Thus the reversed pressure effect is also evident with pure nitrogen. In this case also the glow disappeared completely by passing the discharge. As mentioned in Section C this is probably due to the removal of the last traces of adsorbed water. However, even under these circumstances, the admittance of a fresh supply of pure nitrogen at higher pressures causes a short glow to appear.

Pressure (mm.)	1.43	0.152
Duration (sec.)	4	<0.25

E. Restoration of the Afterglow by Water Vapor.—These experiments were designed to ascertain whether the introduction of water vapor sufficient to cover the surface could restore the afterglow in pure nitrogen. A small glass tube containing distilled water whose dissolved oxygen was removed by boiling, was connected through a stopcock to the discharge vessel. The water could be maintained at any desired temperature and the vapor pressure above ice calculated from the equation of Nernst[17]

$$\log_{10} p_{\text{mm.}} = -\frac{2611}{T} + 1.75 \log T - 0.00210\, T + 6.5343$$

which has been substantiated experimentally down to 100°*K*. by Weber.[18] Nitrogen at a pressure of 0.26 mm. gave only a faint glow lasting for three sec. in the thoroughly baked vessel (liquid air removed from traps). The vessel and water tube were now thoroughly evacuated, the latter being maintained at liquid-air temperature. The liquid air was replaced by a carbon dioxide-alcohol mixture at $-39°$ and water vapor at a pressure 0.11 mm. was admitted to the discharge vessel. The excess water vapor in the gas phase was condensed out in a liquid-air trap and then pure dry nitrogen admitted. A bright afterglow lasting for 75–80 sec. was observed at 0.190 mm. pressure.[19] The whole procedure was repeated, this time admitting water vapor at a pressure 1.2×10^{-3} mm. (ice at $-73°$) with the following results:

Pressure (mm.)	1.2	0.54	0.158
Duration (sec.)	37	70	93–100

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[17] Nernst, *Verh. deut. Phys. Ges.*, **11**, 313 (1907).

[18] Weber, *Comm. Phys. Lab. Univ. Leyden*, **14**, 150A (1915).

[19] Herzberg was able to restore the glow by the addition of small amounts of hydrogen.

It should be noted in the last table that the normal pressure effect is again in evidence with a covered surface.

By discharging with liquid air on one trap the glow was reduced from one hundred sec. to nineteen sec. This was not carried on long enough to diminish the glow further. There was no measurable pressure decrease. Removal of the liquid air caused the restoration of the glow to 140 sec. Thus the afterglow is present or not depending upon the presence of water vapor on the walls. It was found that too much water vapor in the gas phase was prejudicial to the afterglow, a fact also observed by E. P. Lewis.[20]

F.—These experiments will show that the effects in Section E are reproducible with tank nitrogen and that the presence of 0.3% of oxygen has no effect in prolonging the glow over that observed in pure nitrogen. After the same treatment as in Section E, water vapor at 2.2×10^{-3} mm. (ice at $-69°$) was admitted.

1. Dry pure nitrogen	Pressure (mm.)	1.23	0.27
	Duration (sec.)	36	90

Vessel evacuated.

2. Dry tank nitrogen	Pressure (mm.)	0.88	0.24
	Duration (sec.)	63	100

The increase of ninety to one hundred sec. is to be anticipated on reducing the pressure from 0.27 to 0.24 mm. Note the normal pressure effect in both cases.

G. Reversed Temperature Effect.—It is well known that when an untreated vessel containing nitrogen which gives rise to a long afterglow at room temperatures is heated, the afterglow is considerably reduced both in intensity and duration. For example, in one experiment it was found that the afterglow was diminished from 160 to two sec. at a pressure of nitrogen of 0.155 mm. when the vessel was heated from room temperature to approximately 250° (Bunsen burner used). However, in the course of this work it was found that in vessels which were treated as outlined in this paper, a different phenomenon prevails, namely, that not only is the afterglow not diminished by heating but the duration is increased and the intensity slightly enhanced. Many and varied experiments were carried out both with pure and tank nitrogen; but one example will be given. Pure nitrogen at 0.152 mm. pressure in a baked-out vessel gave rise to a glow lasting for one-half sec. When the vessel was heated with a free flame, it lasted for two and one-half sec. Tank nitrogen at 0.20 mm. pressure showed a glow which lasted for three sec. at room temperature and five and one-fifth sec. when heated. After the vessel had cooled, the glow lasted for two and four-fifth sec. and on heating again for three

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[20] E. P. Lewis, *Ann. Physik*, **2**, 459 (1900).

and four-fifth sec. The effect is very noticeable if the glow be eliminated completely by discharging with the liquid-air traps in operation. Here the glow can be restored to last almost one second on heating the vessel.

This reverse temperature effect can easily be explained by assuming that when the discharge is passed in a vessel whose walls are "clean," a layer of nitrogen atoms is adsorbed on the surface. Other atoms colliding with the wall will nearly always meet an adsorbed atom and combine to form a molecule. However, when heat is applied much more of the surface is free and atoms will not always "find" an adsorbed atom on colliding with the wall. This leads to many more favorable collisions in the gas phase and thus we observe an enhanced afterglow.

Finally, two sets of data will be given to show simultaneously both the reversed and normal effects of pressure and temperature.

1. Tank nitrogen. Baked vessel.

Pressure (mm.)	1.5	0.20
Duration (sec.)	17	3
After heating, duration (sec.)		5.2

2. Tank nitrogen after admittance of 2 × 10^{-3} mm. of water vapor.

Pressure (mm.)	1.35	0.29	0.155
Duration (sec.)	4	100	160
After heating, duration (sec.)			2–3

H. The Effect of a Paraffined Surface.—A bulb of 250-cc. capacity and about the same diameter as the discharge tube (a new tube was used which had never been baked out) was coated on the inside with paraffin and sealed to the latter tube. The afterglow was observed through a small opening made by warming the paraffin locally. It was found that with a pressure of tank nitrogen of 0.29 mm. the afterglow in the discharge vessel and the paraffined bulb was of the same intensity and duration (275 sec.). Apparently, therefore, not only does the paraffin effectively poison the surface but it does not itself act as a catalyzer for atomic combination.

Experiments with Oxygen

It was shown above that the nitrogen afterglow is made observable only after the surface of the vessel has been effectively poisoned by the adsorption of a layer of gas.

The results of the following experiments show that the afterglow in oxygen likewise is dependent on the surface condition. This may be expected if the view expressed by Thompson[21] is correct that the after-

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[21] J. J. Thompson, *Phil. Mag.*, **32**, 321 (1891); E. P. Lewis, *Ann. Physik*, **2**, 549 (1900); R. J. Strutt (Lord Rayleigh), *Proc. Phys. Soc.*, **23**, 66 (1910). It is not certain that the afterglow observed in pure oxygen is the same as the continuous spectrum in air observed by Lord Rayleigh, which he attributed to the oxidation of NO by O_3 (formed in the discharge) to NO_2. G. Herzberg, *Z. Physik*, **46**, 878 (1928); J. Kaplan, *Proc. Nat. Acad. Sci.*, **14**, 258 (1928); B. Lewis, *Nature*, **121**, 938 (1928).

glow observed in pure oxygen is due to the emission accompanying atomic recombination, which is strengthened by the fact that the observed spectrum is continuous.[21] The presence of atoms has been demonstrated by Crew and Hulbert[22] and Copeland.[23] The duration of the afterglow in oxygen is considerably shorter than in nitrogen. This may be attributed to the possibly greater facility with which oxygen atoms combine.[24]

The experimental procedure was the same as outlined above. Pressures were read on a McLeod gage connected to the dosing tube. Observations were made in a completely darkened room, a small spectroscope being used to observe the character of the afterglow. Pure oxygen was prepared from potassium permanganate.

Results

In a discharge tube which had been thoroughly cleaned (hot chromic acid followed by distilled water and heating the glass almost to melting), pure oxygen showed an afterglow whose spectrum was continuous in character and whose duration changed with the pressure as follows:

Pressure (mm.)	0.925	0.475	0.285	0.19	0.15	0.115[25]
Duration (sec.)	8	17.2	25.2	32	36	30.4

Upon discontinuing the discharge, the intensity of the afterglow decreased gradually but after a time it suddenly came to an abrupt end. This is quite unlike the prolonged gradual decay of the nitrogen afterglow. Herzberg[12] recorded a similar observation.

The discharge tube was baked out in a furnace at a temperature of 400–440° for eight hours under high vacuum. Both traps were then immersed in liquid air and pure, thoroughly dried oxygen was admitted. At various pressures between 1 mm. and 0.216 mm. not the slightest indication of an afterglow was visible. A glow was still absent after the removal of the liquid air. This was the first experiment with oxygen. In later work this extreme success merely by baking the vessel was never completely realized.

In another representative experiment in a baked-out vessel a faint afterglow was observed lasting about half a second at a pressure of oxygen of about 1.8 mm. (The first two short discharges showed no glow.) At a pressure of 0.24 mm. the duration was two and one-half seconds. When the liquid-air traps were removed the duration was three and one-half seconds.[26]

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

[23] Copeland, *ibid.*, **31**, 1113A (1928); Bichowsky and Copeland, *Nature*, **120**, 729 (1927).

[24] Bernard Lewis, THIS JOURNAL, **51**, 665 (1929).

[25] This pressure is below the duration maximum of the oxygen afterglow at about 0.16 mm. (ref. 24).

[26] This may have been due in part to the adsorption of ozone condensed by liquid air.

With the liquid air replaced, only a little discharging was required to cause the glow to disappear entirely. Ordinarily in an untreated vessel the oxygen afterglow is destroyed by heat but when heat is applied to a treated vessel containing glowless oxygen, the glow appears. In the present instance it lasted about a quarter of a second. After cooling, it disappeared only to reappear again on heating. This *reversed temperature effect* in a vessel with "clean" walls was also observed in the nitrogen afterglow. The explanation advanced for the latter also applies here.

A fresh supply of pure dry oxygen was admitted to the discharge tube which previously contained oxygen whose glow had been removed by discharging. At a pressure of 0.66 mm. there was practically no glow (less than a tenth of a second) and at 0.26 mm. no glow at all. It is quite evident that an afterglow cannot be obtained with pure oxygen in a vessel whose walls are "clean." A "reversed pressure effect" cannot definitely be said to exist due to the exceedingly faint and short afterglow.

An attempt was made to see whether the glow could be restored by the introduction of water vapor sufficient to cover the surface. The general procedure was the same as given above. It was shown first that pure dry oxygen produced only a very faint glow in the baked-out vessel. Water vapor at a pressure 8×10^{-3} mm. (ice at $-60°$) followed by pure oxygen was then admitted. A bright afterglow was produced[19] whose duration is given in the following table.

Pressure (mm.)	0.66	0.314	0.226	0.111[25]
Duration (sec.)	3	11.4	15	13

Too much water in the gas phase is prejudicial to the afterglow. Thus at a pressure of oxygen of 0.25 mm. and of water vapor of 0.135 mm. (ice at $-37°$) the glow lasted less than one second; after condensing most of the water vapor in liquid air the duration was 7 seconds.

The results with air in a baked-out vessel indicated also that the afterglow is considerably weakened in intensity and duration. It will be shown elsewhere[21,24,27] that the afterglow in air undergoes several changes as the pressure is decreased. In a vessel which was baked out but which was not subjected to the discharge treatment, these changes were still observed but the glows were exceedingly weak. At the minimum separating the oxygen afterglow from the nitrogen afterglow, the glow disappeared entirely.

Finally the effect of a paraffin surface was studied. It was found that the afterglow behaved similarly in the paraffined vessel as in the discharge vessel. The durations and intensities were identical and the same abrupt termination of the afterglow was observed in each.

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[27] Constantinides, *Phys. Rev.*, **30**, 95 (1927), and Bernard Lewis, *Nature*, **121**, 938 (1928).

When liquid air was placed on one of the traps the afterglow intensity was not enhanced near the surface of the liquid air, as is the case with the nitrogen afterglow. Instead, it seemed as if it was reduced in intensity or even extinguished. One could not be certain about this last point since the tube was always slightly frosted over. However, it may be noted that Herzberg (ref. 21 p. 892) reports that when the discharge tube is cooled with liquid air no glow is observed.

Summary and Conclusions

The experiments described above show that:

1. Ordinary oxygen or "active" oxygen takes no part in the excitation process which gives rise to the nitrogen afterglow.
2. Pure nitrogen prepared from sodium nitride and nitrogen containing 0.3% of oxygen show intense afterglows of long duration in an ordinary glass vessel. Pure oxygen shows a characteristic green afterglow (continuous spectrum) in a similar vessel.
3. Pure nitrogen or nitrogen containing 0.3% of oxygen at about 0.2 mm. pressure can be made to show no glow if the vessel is thoroughly baked out and subjected to the action of the electric discharge. Above this pressure a short glow appears. The afterglow in oxygen disappears in a similarly treated vessel.
4. Admittance of water vapor (*ca.* 10^{-3} mm.) enough to cover the surface of the vessel causes a restoration of the glow to its usual intensity and duration both in pure nitrogen and nitrogen containing 0.3% of oxygen. The afterglow in oxygen may similarly be restored by water vapor. Too much water vapor is prejudicial to the nitrogen and oxygen afterglows.
5. *The condition of the surface of the containing vessel is a determining factor which governs the visibility of the afterglow in nitrogen or oxygen.*
6. Two new phenomena are described, namely, *reversed pressure effect* and *reversed temperature effect.* Whereas in an untreated vessel the duration and intensity of the nitrogen afterglow increase (within the pressure limits employed, *ca.* 1.8 mm. to 0.1 mm.) as the pressure is reduced, in a treated vessel a decrease takes place. Similarly, heat markedly decreases the intensity and duration of the afterglow in an untreated vessel, whereas in a treated vessel the duration increases and the intensity is slightly enhanced with heating. These phenomena are explained. A reversed temperature effect is observed in the oxygen afterglow in a treated vessel, the restored glow being weak and of short duration.
7. Paraffin effectively poisons the surface and does not itself catalyze the removal of the active constituents. The intensity, duration and type of decay of the nitrogen and oxygen afterglows are the same in an ordinary as in a paraffin-coated vessel.

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.

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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).