Studies on the Discharge Reaction in Liquid Air. III
On the Mechanisms of Nitric Oxide- and Ozone-Formation*

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Synopsis

The emission spectra and the current-wave forms were obtained from the discharge in liquid oxygen, liquid nitrogen and liquid air. From the results obtained, the mechanisms of NO- and ozone-formation were discussed. It was concluded that NO was produced by the reaction between $N_2(B\,^3\Pi_g)$ and O_2 (ground), and that ozone was formed by the reaction between O (ground) and O_2 (ground) at a very early stage of the spark discharge characterized by the emission of the continuous spectrum, being hardly formed through the exothermic arc discharge.

I. Introduction

Many observations of emission spectrum and voltage-current relation characteristic to discharge in the atmospheric air, gaseous oxygen and nitrogen under various conditions have been reported, while those in the liquid states of these gases are very few. G. D. Liveing and J. Dewar(1), and M. Curie(2) reported the spectra of visible region obtained in discharge experiment in the liquids with a glass spectrograph. The research for the spectrum of ultraviolet region is wanted. In the previous papers(3)(4), the natures of the discharge reaction products and the secondary thermal reactions taking place during and after discharge were reported, and it was ascertained that NO and ozone were the primary stable products in the discharge. In the present study, the mechanisms of the formations of these primary products were examined from the experimental results of emission spectrum and current-wave forms in the discharge.

II. Experimental

The apparatus used for the discharge experiment is shown in Fig. 1. The high voltage source employed was a transformer or an induction coil. The Lyeden jar used was of the capacity of about 1/1000 μF. The observation of spectrum was made with Hilger E2 quartz spectrograph which covered the visible and ultraviolet regions. In uncondensed discharge with a transformer, the exposure of about 2 hours was necessary, while in uncondensed discharge with an induction coil or in condensed discharge with either of these sources for high tension,

* The 748th report of the Research Institute for Iron, Steel and Other Metals.

(1) G. D. Liveing and J. Dewar, Collected Papers on Spectroscopy, p. 423.
(2) M. Curie, Compt. Rend., **177** (1923), 1022.
(3) E. Kanda and Y. Nomura, Sci. Rep. RITU, **A 5** (1953), 1.
(4) Y. Nomura, Sci. Rep. RITU, **A 5** (1953), 8.

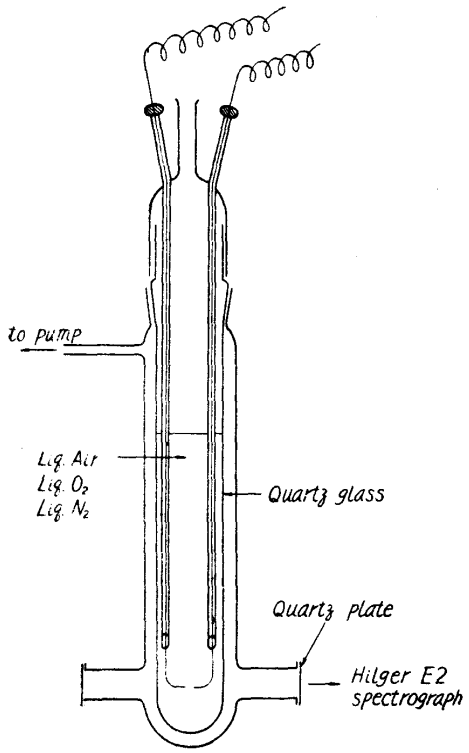


Fig. 1

about 30 minutes sufficed for the exposure owing to the strong emission. The photographs of current-wave form were obtained by using an electro-magnetic oscillograph camera, where a discharge gap was inserted in series in the oscillograph-circuit. The characteristic frequency of the vibrator was adjusted to 6500 cycles. The conditions under which the photographs were taken are shown in the table, in which the Roman numerals refer to the spectrum photos and the alphabet to those of current-wave forms.

III. On the nitric oxide-formation

It is well known that a continuous absorption spectrum of oxygen exists in the region where NOγ-bands appear, and that NOγ-bands are very persistent even if nitrogen is contaminated with traces of oxygen. Therefore, the information of nitric oxide-formation process can be obtained from the spectrum of the discharge in liquid nitrogen contaminated with a minute amount of oxygen rather than in liquid air. The feature of spectrum depends on whether a transformer or an induction coil was used, and also on whether Lyeden jar was inserted or not. A strong continuous spectrum was observed in a certain case. In general, a continuous spectrum means the existence of free atoms or atomic ions. In accordance with E. J. B. Willey[5] and O. H. Wansbrough-Jones[6], however, the NO-formation process involving atoms (N, O) or atomic ions (N^+, O^+) generally seems to be very unlikely. Therefore, it is considered that in discharge reaction either with a transformer or with an induction coil the same kind of active molecules play a part in the NO-formation, and that they should exist at the stage of arc discharge at which nitrogen oxides are produced most effectively.

It is a well-known fact that, in the spectrum of discharge in gaseous nitrogen contaminated with a minute amount of oxygen, there appears strong NOγ-bands in the region from 2800 Å to 2200 Å besides the nitrogen second positive bands (N_2II-bands) and the nitrogen negative bands (N_2^+-bands). In the discharge spectrum in the liquids, however, NOγ-bands are recognized very feebly only in the uncondensed discharge with a transformer under high voltage (Photos. VII, VIII), while the intensities of N_2II- and N^+_2-bands are comparable to those of the spectrum obtained in the gaseous phase. From these facts, it may be considered that NOγ-bands can be emitted when the initially formed unexcited NO is subjected to a certain

(5) E. J. B. Willey, Proc. Roy. Soc., **A 159** (1937), 247.
(6) O. H. Wansbrough-Jones, Proc. Roy. Soc., **A 127** (1930), 511.

secondary excitation.

A view regarding the NO-formation process has been proposed by E. J. B. Willey[5]. According to his view $O_2(A\,^1\Sigma_g)$ plays an important roll in NO-formation, and the following energy relation has been obtained. N_2(ground) + $O_2(A\,^1\Sigma_g, v = 0)$ = 2NO(ground) + 1.37eV, where v is the vibrational quantum number. NO-molecule formed could not be in the state $A\,^2\Sigma^+$ necessary to emitt NOγ-bands, even if it absorbs the whole of the energy liberated by this reaction, because NO $(A\,^2\Sigma^+)$ is in the energy relation: NO$(A\,^2\Sigma^+, v=0)$ = NO(ground) + 5.4eV. Consequently, though Willey's view is convienient to the explanation of our result, it has an undiserable point. $O_2(A\,^1\Sigma_g)$ may be produced easily by various kinds of excitations as it is in the energy relation: $O_2(A\,^1\Sigma_g, v = 0)$ = O_2(ground) + 1.62eV, and, therefore, NO may be formed even by the way not so energitic as a discharge. In fact, atmospheric-band[7] (7710 Å~5380 Å), which are observable in the absorption spectrum of atmospheric air, are attributed to the excitation, O_2(ground)$\rightarrow O_2(A^1\Sigma_g)$, and if Willey's view is right, a considrable amount of nitrogen dioxide would be found in air, but it is not the case.

Another view is that N^+_2 and O_2 directly react upon each other to form NO_2 as the final product, and this view was supported by O. H. Wansbrough-Jones[6], J. W. Westhaver and A. K. Brewer[8], and M. W. Feast[9]. As already ascertained, the initially formed nitrogen oxide is not NO_2 but NO. If NO instead of NO_2 is produced through the reaction between N^+_2 and O_2, NO will be supposed to be in the excited state to emit NOγ-bands for the following reasons: N^+_2(ground) is 15.6 eV richer in energy than N_2(ground) and a greater part of this amount may be available for the excitation of NO. In fact, the above mechanism is not difficult to explain the spectroscopic results obtained from the discharge in gaseous phase, where NOγ-bands always appear. This mechanism, however, is not appropriate to our experimental results obtained through discharge in the liquid phase, in which no NOγ-band was observed in a certain case.

In the following, we shall propose another mechanism. N_2II-bands are emitted through the transition $N_2(C\,^3\Pi_u) \rightarrow N_2(B\,^3\Pi_g)$, and N_2I-bands through $N_2(B\,^3\Pi_g)$ $\rightarrow N_2(A\,^3\Sigma^+_u)$. It is worthy of notice that N_2I-bands are comparatively distinct in the discharge under high voltage (Photos. VII, VIII), and are apt to disappear under low voltage (Photos. V, VI). Even in the latter case, as N_2II-bands are recognizable, $N_2(B\,^3\Pi_g)$ apparently exists, and of course nitrogen oxides were obtained in both cases under high and low voltage. Therefore, no occurrance of the transition $N_2(B^3\,\Pi_g) \rightarrow N_2(A\,^3\Sigma^+_u)$ in the case of low voltage suggests that $N_2(B\,^3\Pi_g)$ is consumed for NO-formation. Adopting $N_2(B\,^3\Pi_g, v)$ with $v = 8$ from the ordinarily observable upper value in the vibrational structure of N_2II-bands, and assuming that it combines with O_2(ground) into NO, the following energy relation is obtained: O_2(ground) + N_2 $(B\,^3\Pi_g, v = 8)$ = 2NO (ground) + 2 × 4.4 eV.

(7) M. N. Saha, Proc. Roy. Soc., **A 160** (1937), 155.
(8) J. W. Westhaver and A. K. Brewer, Jour. Phys. Chem., **34** (1930), 554.
(9) M. W. Feast, Proc. Phys. Soc., **A 63** (1950), 563.

Thus, NO molecules produced through this mechanism can not be excited to NO($A\,^2\Sigma^+_1$ $v = 0$) state necessary to emit NOγ-bands. This mechanism will hold even in the case of $v > 8$, because the increase of the vibrational energy with v is small, and it seems to be more reasonable to explain our experimental results.

IV. On the ozone-formation

Hitherto[10]-[14], the discrete spectra attributed to oxgen, namely, O (excited or unexcited), O^+(excited or unexcited), O_2(excited), O_2^+(excited or unexcited), etc., have been taken into consideration in the spectroscopic investigation of ozone-formation, but according to our spectroscopic evidences, this standpoint seems unreasonable. As reported in our first paper, in the discharge experiments in liquid air the amount of ozone produced was larger when an induction coil was used as a high tension source than when a transformer was used, and in the latter case it increased with the decreasing applied voltage. Considering the above tendencies of ozone-formation and the characteristics of the spectra in the discharge, the following fact can be ascertained: in dependent of the kinds of electric sources, the stronger the continuous spectrum appears, the more the ozone is produced. In the condensed discharge in liquid oxygen, the continuous absorption spectrum extends from about 3100Å to the shorter region (Photos. XII, XV, XVII) and this is attributed to ozone, because ozone shows strong absorption in the region shorter than 3100Å. From this result, the condensed discharge seems favourable to the formation of ozone.

The remarkable relation between current-wave form and spectrum is as follows: when the current-wave form of the initial stage of the discharge appears more frequently, especially when only the oscillatory current appears without arc discharge current (Photos. A, E, F, J, L, M), the continuous spectrum is emitted more strongly. E. O. Lawrence and F. G. Dunjngton[15], and L. Bilitzer and W. M. Cady[16] studied the time-resolved emission spectra of condensed spark discharge in atmospheric air, and reported that at a very early stage of the discharge (less than $10^{-6}\sim10^{-8}$ sec.) a continuous spectrum accompanied with O^+- and N^+-lines appeared and that they faded with the appearance of the lines of the electrode metal. From their results, it was supposed that the continuous spectrum would appear strong in the photographs when the initial stage of spark was repeated by the effective cooling action of liquid, and it was the case in our present experiment. The oscillatory current of about 3000 cycles was observed in the whole run of the basic current both in the condensed and the uncondensed discharges with a transformer (Photos. A and J). Each oscillation of them may be considered

(10) J. K. Hunt, Jour. Amer. Chem. Soc., **51** (1929), 30.
(11) N. Nekrasov and I. Stern, Acta Physicochim., U. S. S. R. **4** (1936), 283.
(12) L. A. M. Henry, Bull. Soc. Chem. Belg., **40** (1931), 295.
(13) W. H. Otto and W. H. Bennett, Jour. Chem. Phys., **8** (1940), 899.
(14) O. H. Wansbrough-Jones, Proc. Roy. Soc., **A 127** (1930), 530.
(15) E. O. Lawrence and F. G. Dunjngton, Phy. Rev., **35** (1930), 396.
(16) L. Blitzer and W. M. Cady, Jour. Opti. Soci. America, **41** (1951), 440.

to show a very early stage of the spark. Consequently, it will be considered that ozone is not produced in the whole run of spark, but only in its initial stage. E. Briner and E. Durand[17], G. A. Gorodetskiĭ[18], etc., reported that ozone was not produced through spark but through silent discharge occurred simultaneously with the spark. If the silent discharge is equal in nature to the spark discharge in the very initial stage, the view of E. Briner and others may be admissible.

E. C. G. Stueckelberg[19] pointed out that among the potential curves of oxygen molecule-ion there was one so shallow that the dissociation-ionization process of oxygen, $O_2 \rightarrow O(\text{ground}) + O^+(\text{ground}) + e$, occurred very easily. This will lead to the conclusion that in a very initial stage of spark in liquid oxygen the dissociation-ionization process of molecule takes place to produce atom and atomic ion both in ground state. W. H. Crew and E. O. Fulburt[20], F. L. Mohler[21], and W. Finkelnburg[22] considered that the continuous spectrum was emitted by the recombination of free electron and atomic ion forming neutral atom excited to various energy states. On the other hand, it is a well known fact that ozone is formed by the reaction between O-atom (ground) and O_2-molecule (ground). Thus, it will be reasonable to suppose that the ozone-formation takes place simultaneously with emission process of the continuous spectrum.

In general, little or no production of ozone takes place by arc discharge which is strongly exothermic. This fact, as suggested by M. W. Feast[9], may be explained from the view that ozone, even if it might be produced, would almost entirely be decomposed by the thermal action of arc. As continuous spectrum hardly appears in arc discharge, however, it is concluded from our stand point that ozone will not be formed by arc discharge. The electric power and also the heat evolved in the discharge with a transformer is larger than with an induction coil and, consequently, the discharge with a transformer apts to change into arc stage, especially without Lyeden jar. Therefore, the smaller production of ozone with a transformer than with an induction coil must not be explained from the thermal decomposition of ozone by larger heat evolution with a transformer.

In conclusion the author wishes to express his hearty thanks to Prof. Eizô Kanda for his kind guidance in the course of this investigation. The research has been aided by the fund from the Scientific Research Expenditure of the Department of Education.

(17) E. Briner and E. Durand, Compt. Rend., **145** (1907), 248.
(18) G. A. Gorodetskiĭ, Jour. Applied Chem. U. S. S. R., **12** (1939), 1637.
(19) E. C. G. Stueckelberg, Phys. Rev., **34** (1929), 65.
(20) W. H. Crew and E. O. Hulburt, Phys. Rev., **28** (1926), 936.
(21) F. L. Mohler, Phys. Rev., **31** (1928), 187.
(22) W. Finkelnburg, Zeit. f. Phys., **88** (1934), 297, 768; Phys. Rev., **45** (1934), 341; ibid, **46** (1934), 330.

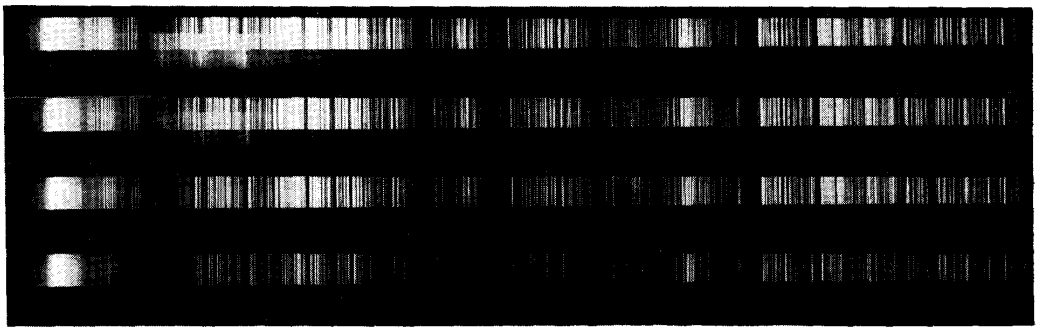
Table for the discharge conditions and for the

Photo	Medium	High voltage source	Volts (Pimary side)	Amperes (Pimary side)	d (mm)
I	liq. O_2	T	48	1.2	0.5
II	"	"	72	2.2	"
III	"	"	80	2.9	"
IV	"	"	92	3.3	"
A	"	"	50	1.4	"
B	"	"	80	2.6	"
V	liq. N_2	T	44	1.2	0.5
VI	"	"	56	1.6	"
VII	"	"	74	2.4	"
VIII	"	"	88	2.7	"
C	"	"	50	1.4	"
D	"	"	80	2.6	"
IX	liq. O_2	I	10	(1.5)	0.5
X	liq. N_2	"	"	"	"
XI	liq. air	"	"	"	"
E	"	"	"	(3)	"
F	"	"	"	"	"
G	at. air	"	"	6	"
H	"	"	"	"	"
I	"	"	"	4.5	12
XII	liq. O_2	T + C	70	(2)	0.5
XIII	liq. N_2	"	"	"	"
XIV	liq. air	"	"	"	"
XV	liq. O_2	"	100	—	"
XVI	liq. N_2	"	"	—	"
J	liq. O_2	"	60	(2)	0.2
K	liq. N_2	"	"	"	"
XVII	liq. O_2	I + C	10	(6)	0.5
XVIII	liq. N_2	"	"	"	"
XIX	liq. air	"	"	"	"
L	liq. O_2	"	"	"	"
M	liq. N_2	"	"	"	"

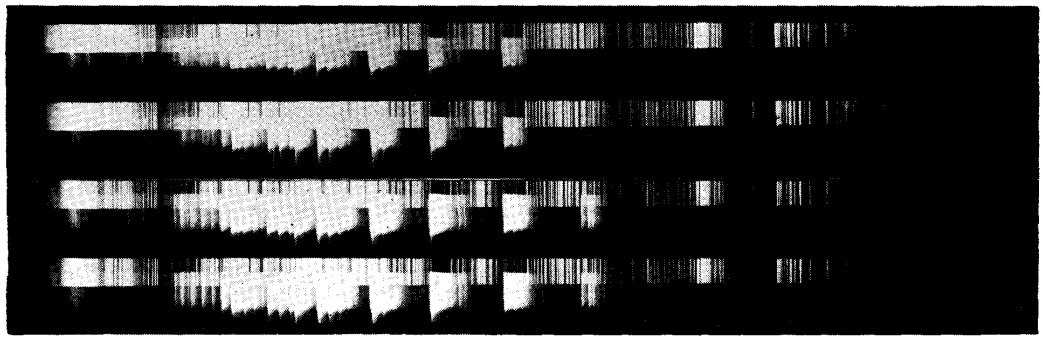
Abbreviation: liq. = liquid, at. air = atmospheric air, T = transformer, I = induction coil, T + C or I + C = condensed discharge with T or I, d = gap between electrode points, ( ) in the array of "Amperes" means its value fluctuated to some extent, b. sp. = band spectra, c. sp. = continuous spectra, osc. cur. = oscillating current.

features of spectra and current-wave forms.

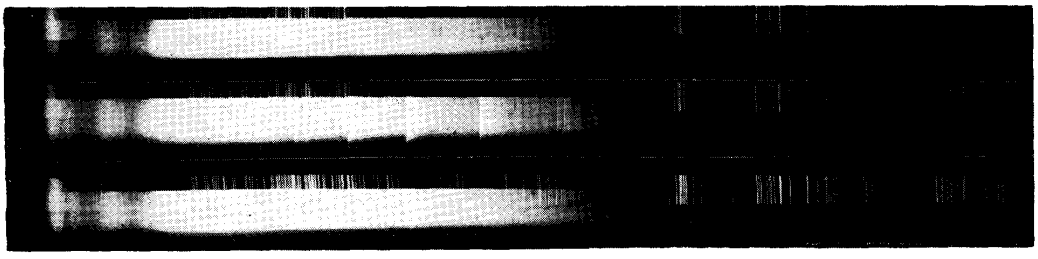
General features or special conditions of discharge	Features of spectra and current-wave forms
[discharge was stable]	b. sp. was absent, at lower voltage O- and O^+-lines as well as c. sp. became stronger, at higher voltage they appeared very weakly in the original plate.
	A was characterised by 3 KC osc. cur. and corresponded to the case accompanied by c. sp., B was almost same to atmospheric discharge.
[discharge was stable]	b. sp. appeared strongly, in V c. sp. with N^+-lines appeared in the region of N_2I-bands, while in VIII N_2I-bands became clear, at higher voltage $NO\gamma$-bands appeared weakly in the original plate.
	alike to atmospheric discharge, osc. cur. as well as c. sp. was difficult to appear comparing with the case of liq. O_2.
[discharge was somewhat unstable comparing with the cases of T.]	c. sp. were similar with each other, in IX and XI, absorption by oxygen appear.
at the begining of discharge at some time after the begining of discharge at the begining of discharge at the stage with red heat electrodes with large d to avoid red heat electrodes	in the case of liquid arc discharge which appeared ordinarily in the atmospheric discharge was hardly maintained.
[discharge was unstable, and was maintained under high voltage]	c. sp. and lines became more recognizable in all cases comparing with uncondensed cischarge.
the voltage was applied intermittently	in both cases only strong c. sp. with brodened lines appeared.
with small d to stabilize the discharge	osc. cur. as well as c. sp. appeared more easily in liq. O_2.
[discharge was very unstable, and was maintained only at high currents]	c. sp. with very brodened lines had same feature in all cases, excluding the difference due to absorption of O_2 and O_3.
	osc. cur. were also same in both cases.



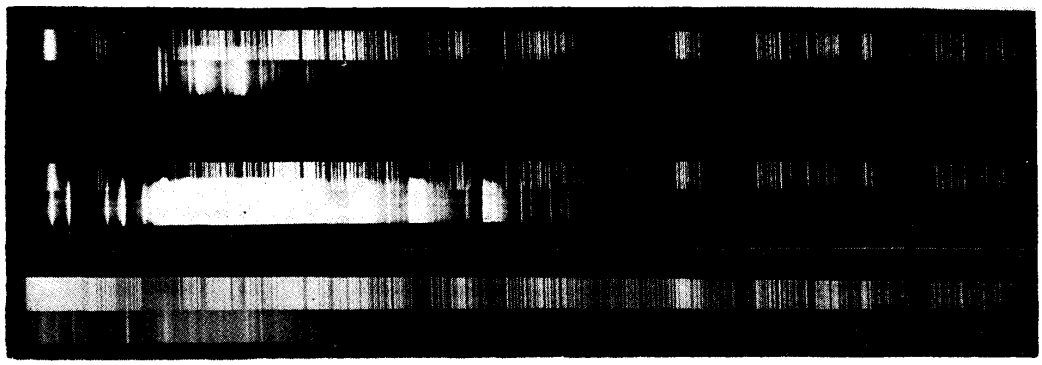
Uncondensed discharge with transformer in liquid oxygen.



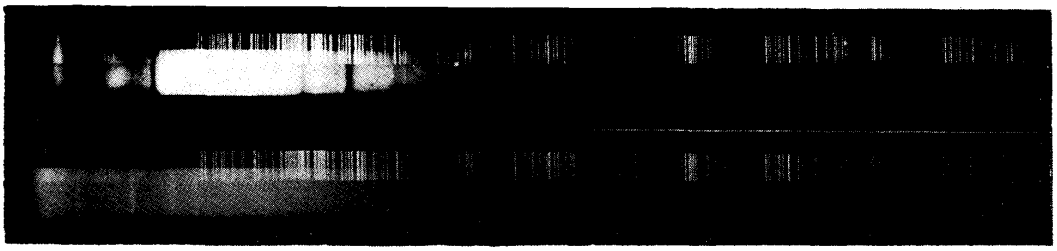
Uncondensed discharge with transformer in liquid nitrogen.



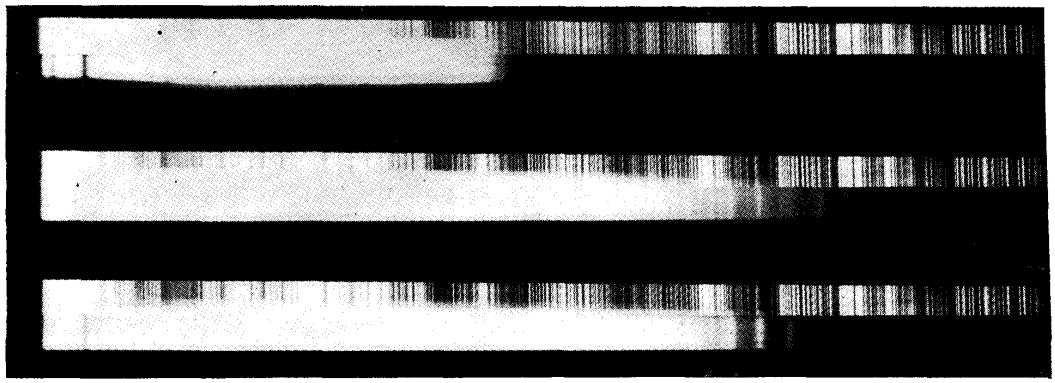
Uncondensed discharge with induction coil.
IX : liquid oxygen, X : liquid nitrogen, XI : liquid air.



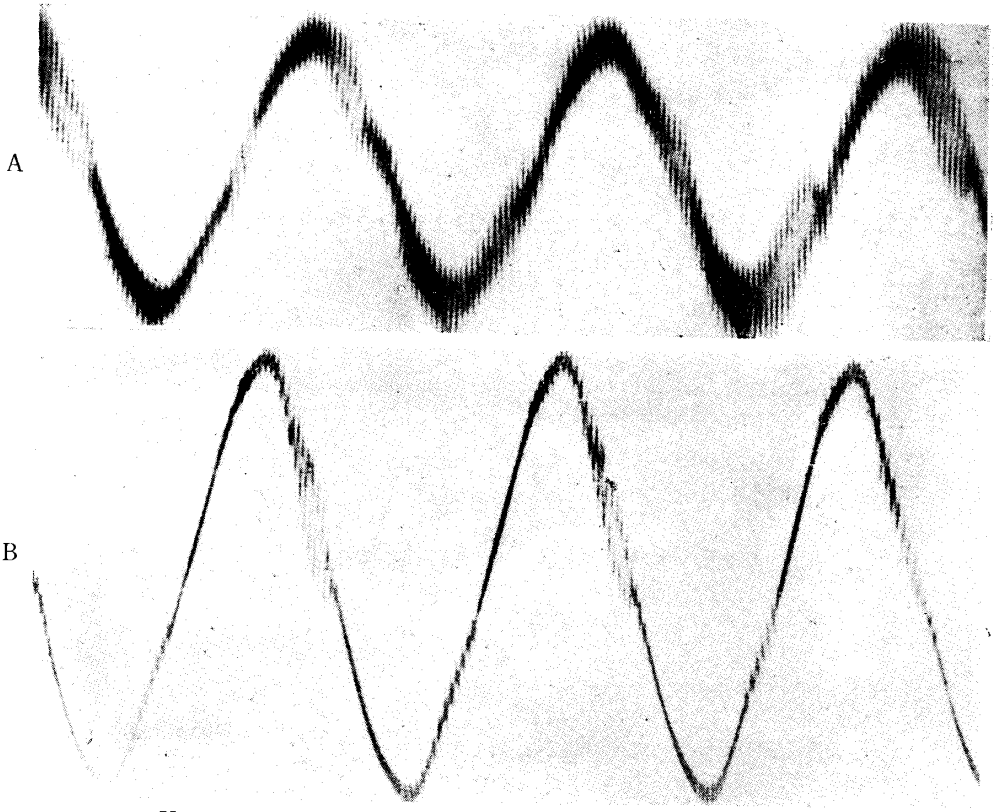
Condensed discharge with transformer.
XII : liquid oxygen, XIII : liquid nitrogen, XIV : liquid air.



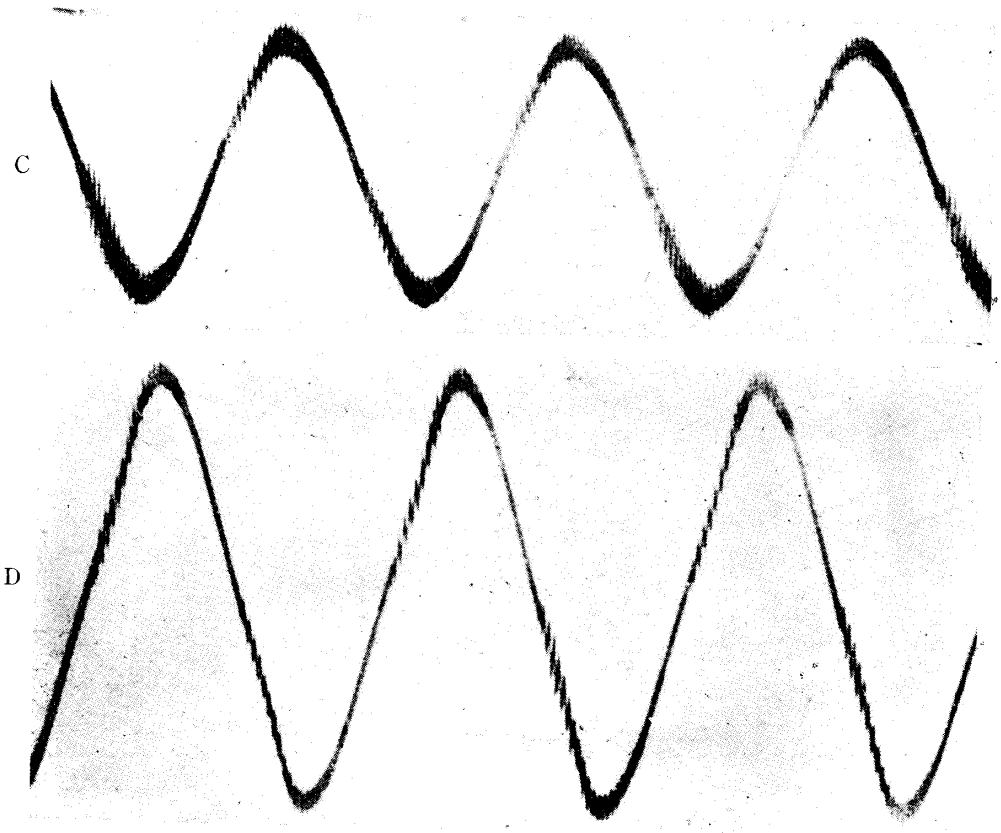
Condensed discharge with transformer applying the voltage intermittently.
XV : liquid oxygen, XVI : liquid nitrogen.



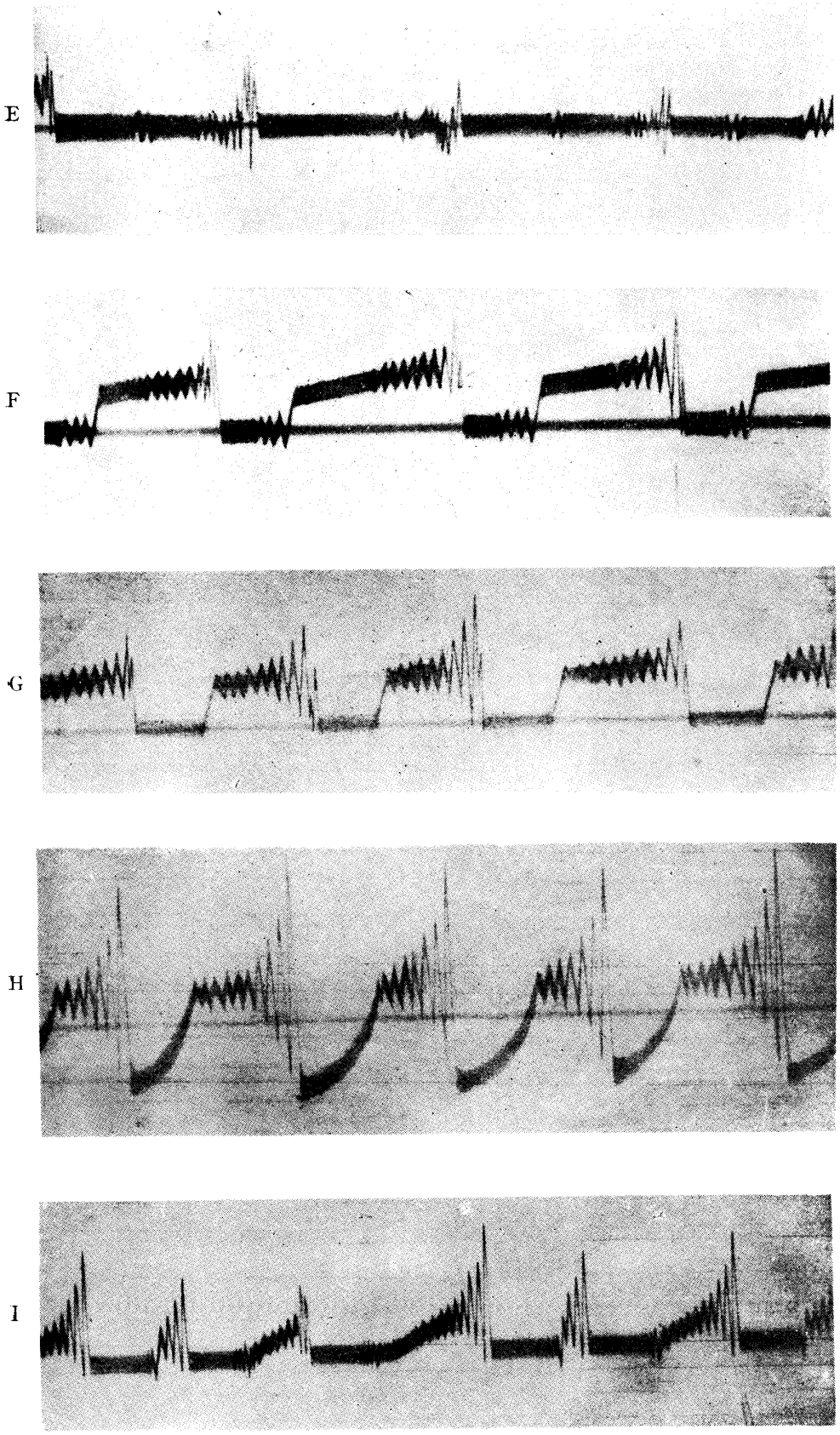
Condensed discharge with induction coil.
XVII : liquid oxygen, XVIII : liquid nitrogen, XIX : liquid air.



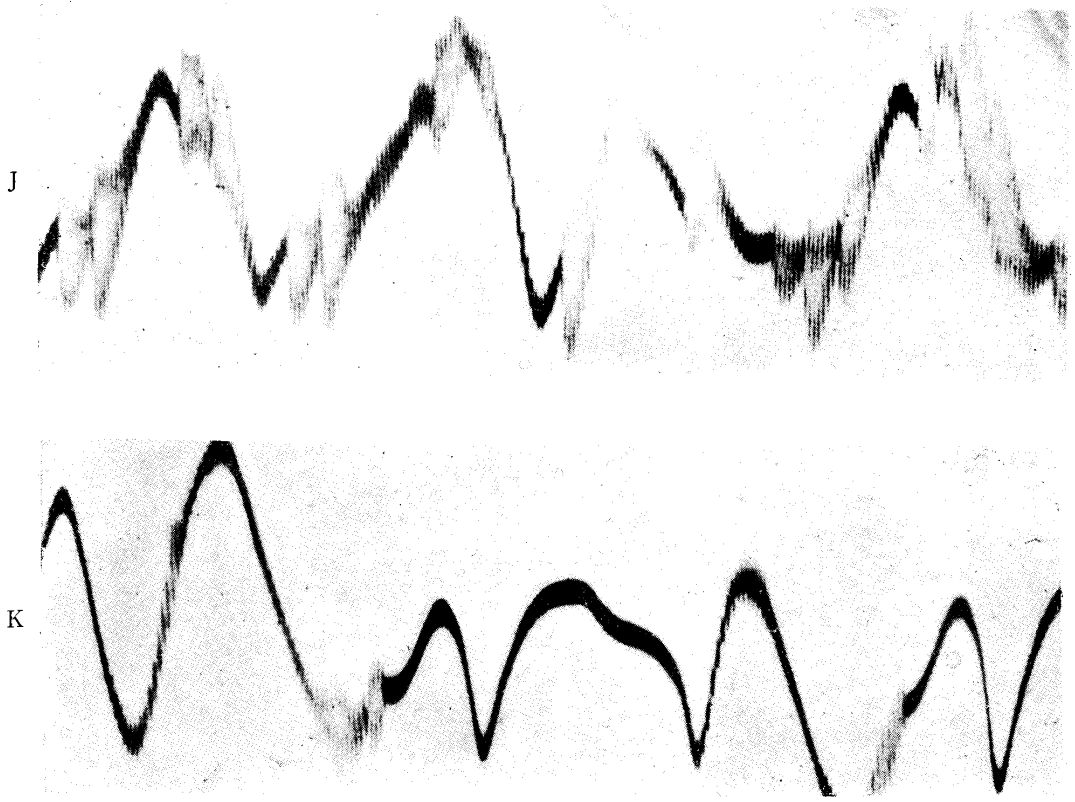
Uncondensed discharge with transformer in liquid oxygen.



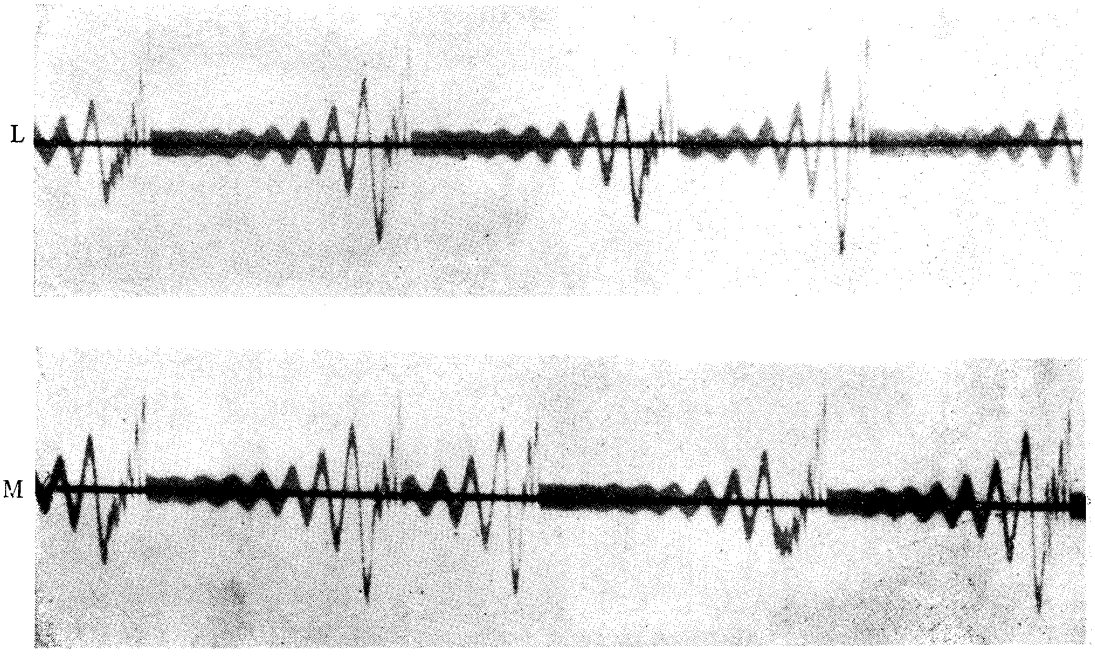
Uncondensed discharge with transformer in liquid nitrogen.



Uncondensed discharge with induction coil.
E～F : liquid air, G～I : atmospheric air.



Condensed discharge with transformer.
J : liquid oxygen, K : liquid nitrogen.



Condensed discharge with induction coil.
L : liquid oxygen, M : liquid nitrogen.