

# ON THE CHEMICAL REACTION OF GLOW DISCHARGE IN THE ATMOSPHERE\*

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The chemical reaction of glow discharge<sup>1)</sup> in the atmosphere is of interest in the fundamental fact that this discharge is such one that is between ozonizer discharge and arc discharge with respect to field (electron temperature), electron density, discharge current and gas temperature. In this paper the fixation of atmospheric nitrogen by glow discharge is obtained under various conditions, having on every one of which the air flow coaxially to the positive column.

In general, the reaction should occur in both the cathode fall and the positive column. These can be separated in accordance with the nature of the cathode fall voltage holding it at a constant value under various currents. As a result of separation, the yield in the former is negligibly small comparing with the latter. This is naturally due to the small thickness ( $10^{-4}$  cm) of the former. The experimental data are summarized in Figs. 1~5. The unit of the yield of NO "y" is  $\text{HNO}_3$  g/KW hr.

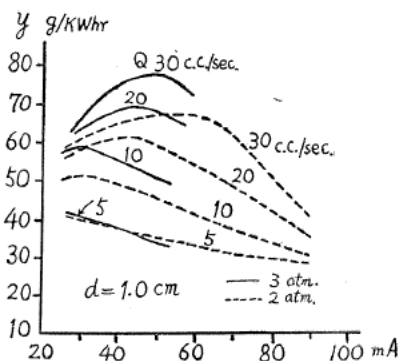
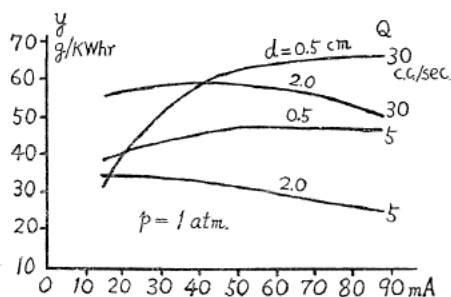
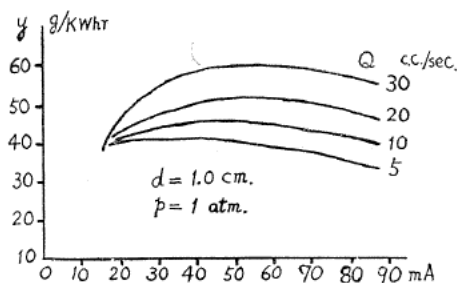


FIG. 1 (upper left). Effects of current and rate of air flow.

FIG. 2 (lower left). Gap effect.

FIG. 3 (right). Pressure effect.

\* Abstracted and translated from the paper published in Japanese (1947-1948) in J. I. E. E. of Japan.

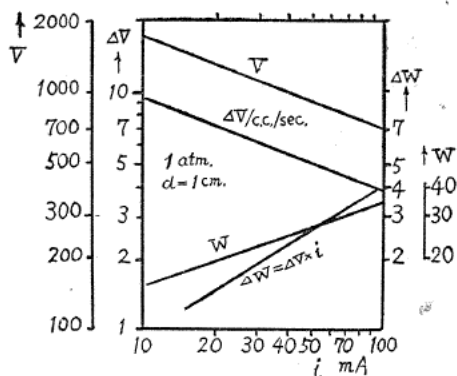
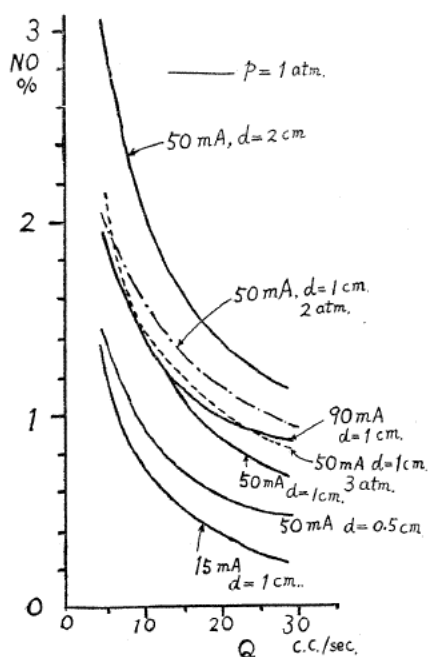


FIG. 4 (left). Concentration of NO.  
 FIG. 5 (right).

1. *Effect of Current*: The yield  $y$  has maximum ( $y_m$ ) at a certain value of current ( $I_m$ ), which becomes larger in case the rate of air flow increases. The decrease of  $y$  at the low current is due to the fall of gas temperature by the air flow. The decrease at the high current seems to suggest the inefficiency of discharge acting on the flowing air.

2. *Effect of the Rate of Air Flow "Q"*: As the speed of air flow increases, the burning voltage  $V$  (or field  $E$  or input power per unit length  $W$ )<sup>2)</sup> rises, and in general  $y$  increases owing to the quick removal of NO from the discharge region prior to the occurrence of the dissociation by discharge. The increment of voltage  $\Delta V$  is proportional to the rate of flow  $Q$  cc/sec.

3. *The Effect of the Gap Length of Electrodes  $d$*  is not remarkable. The longer the gap length  $d$  becomes, the smaller  $I_m$  becomes. The reason of this is as follows; when the gap length becomes larger, the flowing air may have a longer time of contact to the discharge, because of the axial flow, that fact is equivalent to the decrease of the rate of flow.

4. *The Effect of Pressure* shall not be substantially expected, as the gas reaction is of equimolecular:  $N_2 + O_2 = 2NO$ . But in this results, the yield is improved and  $I_m$  grows smaller when pressure rises. Taking it into account that the rate of flow in this case is reduced at 1 atm., one must discuss the position of maximum yield.

5. *Frequency Effect*: The yields and the spectra of high frequency discharges of 10 M.C. and 200 M.C. are not much differ from the case of D.C., as shown in Table 1.

TABLE 1. Emission Spectrum in the Atmosphere

	Positive column	Negative glow
D.C. <100 mA	N <sub>2</sub> first positive    weak N <sub>2</sub> second positive    weak N <sub>2</sub> <sup>+</sup> medium NO( $\gamma$ )                        strong OH	N <sub>2</sub> second positive N <sub>2</sub> <sup>+</sup> N NO( $\gamma$ )
D.C. >100 mA	N <sub>2</sub> <sup>+</sup> NO( $\gamma$ ) O <sub>2</sub> -Runge OH	N <sub>2</sub> second positive N <sub>2</sub> <sup>+</sup> N NO( $\gamma$ )
10 M.C.	same as the case of D.C.	similar to the case of D.C. NO( $\gamma$ ): stronger
200 M.C.	similar to the case of D.C., but with the small gap length, the spectra of positive column resemble to that of negative glow of D.C.	

- 1) In the report of Briner (Helvetica Chimica Acta 19, 287 (1936) etc.) on the fixation of atmospheric nitrogen by high frequency arc (10 M.C.), the positive column seems to be the same as what is here treated.
- 2)  $E = (V - V_c) / d$  where  $V_c$  = cathode fall potential, assuming 350 V for the air, and  $d$  = gap length.  $W = EI$ .