common, that they destroy the chemical or physical integrity of the cortex of the egg."

*It is stated by Just\(^3\) (p. 316): "It has not been satisfactorily proved that the failure of self-fertilization in Ciona is not due to blood," etc. This is obviously untrue since self-sterility has been abundantly shown to be present in eggs laid normally—not artificially removed (cf. Castle, Morgan or the data in this paper).

\(^2\) East and Parks, Genetics, 2, 505 (1917).
\(^3\) Just, Protoplasma, X, 300 (1930).
\(^4\) Fuchs, Arch. Entw-mech., 40, 205 (1914).
\(^5\) Morgan, J. Exp. Zool., 1, 135 (1904).
\(^6\) Lillie and Just, General Cytology, Chicago (1924).

THE AMMONIA DISCHARGE TUBE

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During the past few years a number of studies of the chemical properties of atoms and radicals have indicated that considerable clarification of reaction mechanism may be achieved by such methods.\(^1\) Wood\(^2\) and Bonhoeffer\(^3\) have demonstrated the preparation of atomic hydrogen. The work of Taylor and Lavin\(^1\) and of Lavin and Stewart\(^4\) indicates that one of the products of a water vapor discharge tube is the hydroxyl radical. Gaviola and Wood\(^5\) have shown that the radical NH, produced by the action of excited mercury on ammonia or on mixtures of nitrogen and hydrogen, may exist for an appreciable length of time. Thus it seemed probable that this radical might be drawn from an ammonia discharge tube and studied in a manner similar to that used with atomic hydrogen.

Experimental.—The experimental procedure was exactly that employed in the work with hydrogen and with water vapor. The accompanying diagram shows the method of placing the metal wound thermometers in the active gas stream. Small iron cylinders were attached to the end of the thermometers and by means of an electromagnet they could be moved in and out of the reaction zone without opening the apparatus.

The ammonia was taken from a tank where it was stored over sodium. Tank oxygen, nitrogen and ethylene were used.

Experimental Results.—Preliminary work\(^6\) showed that when ammonia was flowed through a discharge tube, under the same conditions used to obtain atomic hydrogen, an active gas was obtained. This gas had in part the properties of atomic hydrogen; it was reducing in character and
small solid particles along the exit of the discharge tube were heated to incandescence. But, in addition, in the liquid air trap, 1.5 meters from the discharge tube, there was an intense green glow. This glow emanated from the solid ammonia condensed in the trap, and under optimum conditions could be brought to sufficient intensity to be seen in a lighted room. This glow did not appear when solid ammonia in the trap was bombarded with atomic hydrogen or active nitrogen. It could, however, be produced by the admission of suitable quantities of ammonia to active nitrogen.

The possible active products in the exit tube of an ammonia discharge tube are atomic hydrogen, active nitrogen, NH and NH₂.

The bands at 3370Å - 3360Å which are characteristic of a discharge in ammonia and which have been ascribed to the NH molecule were sought in the afterglow, but were never found to be emitted. The absorption spectrum of a two-meter tube of the active gas also gave no trace of these bands. Relative intensity measurements of the bands, excited by an electrodeless discharge, in pure ammonia, and in ammonia activated by the discharge, proved impossible, due to the superposition of the strong O—O band of the second positive group of nitrogen, which was formed by the action of the discharge. The failure of spectroscopic methods to give direct evidence of NH led to a study of the chemical properties of the active gas.

Solid Surfaces.—The introduction of various solids into the gas stream showed that there was considerable difference in their ability to remove the luminescence in the trap. As has been mentioned, the metal wires were wound around the bulb end of the thermometer and placed at either position A or at B. The results may be summarized in the following table.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Effect on Glow at Distance of 35 cm. from Tube</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO</td>
<td>Immediately extinguished</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>Immediately extinguished</td>
</tr>
<tr>
<td>Sn</td>
<td>Induction period</td>
</tr>
<tr>
<td>Ni</td>
<td>Induction period</td>
</tr>
<tr>
<td>Cu</td>
<td>Induction period</td>
</tr>
<tr>
<td>Fe</td>
<td>Induction period</td>
</tr>
<tr>
<td>Pt</td>
<td>Induction period</td>
</tr>
<tr>
<td>Mo</td>
<td>Little effect</td>
</tr>
<tr>
<td>W</td>
<td>Little effect until cleaned by atomic hydrogen</td>
</tr>
<tr>
<td>ZnO₄Cr₂O₉</td>
<td>Little effect, increasing with time</td>
</tr>
</tbody>
</table>

Both copper oxide and iron oxide extinguished the glow immediately on being placed in the active gas stream (at A). The metals affected the luminescence after varying periods of time. The exact induction periods have not yet been determined. As the metals became active in removing the luminescence, sputtering took place. As a result of this action, portions of the metal were deposited on the walls of the exit tube and there
gave rise to a glow. When this condition was reached the glow in the trap was entirely extinguished.

If the solid was removed to the side tube, away from the active gas stream, the luminescence of the sputtered material on the walls decreased in intensity and finally died away altogether. Simultaneously, the glow in the trap was restored. In some cases the glow could be seen to travel the length of the tube, apparently being re-sputtered and condensed many times.

It has been shown that the zinc catalyst is effective in removing atomic hydrogen almost entirely from a gas stream. Since this substance has little effect on the glow in the trap it is possible to remove atomic hydrogen by placing the zinc catalyst at A (Fig. 1) and then studying the other active component by inserting a coated thermometer at B. Copper oxide at B quenched the glow immediately, while copper began to give an effect only after about fifteen minutes induction period. The rate of temperature rise of copper oxide under these circumstances is about seven times as great as that of copper. Copper oxide at A gives a rise thirty times as great as when it is at B and the zinc chromate at A. Hence, very little atomic hydrogen reaches B, and the greater rise of copper oxide can be ascribed to the removal of the glow-producing component.

Experiments with Gases.—Ethylene was led into the stream of active gas through a side tube about 50 cm. from the discharge tube. The reaction took place with the emission of a yellow luminescence extending for about two centimeters. The glow was photographed with a Hilger quartz spectrograph and was found to consist of bands due to CH, C≡C and CN.

At the end of the run it was found that a white solid had been condensed in the trap. The substance was very hygroscopic and had an intense odor of cyanides. It very quickly changed over to a brown-black oil and then to a solid. The inorganic test for cyanides was positive. Admission of the ethylene extinguished the green glow in the trap; there was still a feeble luminescence but it was yellow in color. The walls near
the reaction zone became quite hot, and a surface luminescence was observed. If the ethylene was shut off and the discharge stopped sufficiently to allow the tube to cool, and then the discharge turned on again the walls became hot once more. A surface luminescence was now present. The green glow was no longer present, but reappeared when the walls were cleaned, just as in the case of the sputtered metals.

The reaction with oxygen was accompanied by a blue-green glow; the luminescence in the trap was extinguished. The luminous zone with oxygen was very much longer than with ethylene, extending practically to the trap. When the supply of oxygen was cut off the glow did not go back into the trap but appeared on the tube just above. The phenylene di-amine test for nitrites was obtained.

Discussion.—The results show that active gases streaming from a discharge in ammonia consist of atomic hydrogen and some nitrogen-containing radical or atom, which cannot be identified with certainty, but which is in all probability some lower radical hydride of nitrogen, NH or NH₂. The possibility that the active gas consists of a mixture of active nitrogen and atomic hydrogen seems ruled out by the fact that the former alone gives none of the observed effects and that the active gas, with hydrogen atoms removed, retains its characteristic properties. The observation that copper oxide is so much more effective in removing the glow than metallic copper again points to a nitrogen hydride.

The specificity of the surfaces in their action, together with the induction period and sputtering, offers some points of catalytic interest. Since copper and iron oxides are very effective in removing the glow, we cannot ascribe the induction period to oxide removal by atomic hydrogen. It is closely related to the sputtering, which produces an active surface, especially on the walls where great activity is to be expected because of the fine subdivision of the sputtered material. The same effect is observed on catalysts employed in ammonia oxidation. Also, catalysts used in ammonia synthesis do not possess full activity when new but show an induction period with increasing activation.

The inability of hydrogen atoms or molecules to react with NHₓ on a surface of the zinc catalyst is also of interest in relation to the results of Taylor and Lavin who showed it to be extremely effective in removing hydrogen atoms. It suggests that zinc oxide catalysts may not be efficient in the recombination of H and OH, a point which up to the present has eluded experimental test owing to the great efficiency of such surfaces for hydrogen atom recombination.

The authors wish to thank Professor Hugh S. Taylor for his continued interest and many constructive criticisms.

Summary.—1. A preliminary study has been made of the gases flowing from the exit of an ammonia discharge tube.
2. The active gas seems to consist of atomic hydrogen and NH or NH₂.
3. Catalytic effects of certain substances and characteristic luminescences at various surfaces have been observed.

1 Bonhoeffer and Haber, Z. physik. Chem., A137, 263 (1928); Bonhoeffer and Har-teck, ibid., 139, 64 (1928); Von Wartenburg and Schulze, ibid., B2, 1 (1929); Paneth, Ber., 62B, 1335 (1929); Taylor and Jones, J. Am. Chem. Soc., 52, 1111 (1930); Taylor and Lavin, ibid., 52, 1910 (1930); Steiner, Z. Elektrochem., 36, 807 (1930).

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THE SEPARATION OF THE TWO TYPES OF IODINE MOLECULE AND THE PHOTOCHEMICAL REACTION OF GASEOUS IODINE WITH HEXENE

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Soon after Dennison had deduced from the specific-heat curve that ordinary hydrogen gas consists of a mixture of two types of molecule, the so-called ortho and para hydrogen, a similar state of affairs in the case of iodine gas was demonstrated by direct experiment by R. W. Wood and F. W. Loomis. In brief, these experimenters found that the iodine bands observed in fluorescence stimulated by white light differ from those in the fluorescence excited by the green mercury line λ 5461, which happens to coincide with one of the iodine absorption lines. Half of the lines are missing in the latter case, only those being present which are due to transitions in which the rotational quantum number of the upper state is an even integer. In other words, in the fluorescence spectrum excited by λ 5461 only those lines appear which are due to what we may provisionally call the "ortho" type of iodine molecule.

It is evident than that by irradiating iodine gas with the green mercury line it is possible to selectively activate molecules of the "ortho" type. Furthermore, as shown by these experiments, a molecule of the "ortho" type has an average life time in this form longer than the time it remains in the activated condition before emitting radiation.

It occurred to one of us that these facts might be made use of in effecting