bodies round up into small spheres which soon begin to swell and behave actively as contractile vacuoles. Since a fresh vacuole frequently starts up where one has disappeared it is possible that the evacuated membrane of one condenses to form the primordium of another. There is good reason to believe that sugar in the above concentrations enters the cytoplasm, where, by some process that we do not understand, it is probably concentrated in the contractile vacuoles, the resulting swelling and bursting being explicable simply as osmotic and surface tension phenomena. When, owing probably to high viscosity of the external surface of the protoplasm induced, *e.g.*, by chromates, etc., the vacuoles fail to burst, the cytoplasm becomes thickened into a foamy mass.

There are suggestions in the literature that an origin of vacuoles from similar bodies may be the rule in widely different cell types. For example, the production of secretory vacuoles from the so-called "Golgi apparatus" in cells of the Epididymis as described by Nassonov[4] and Ludford.[5] Now in *Spirogyra* one phase of the polymorphic myelin growths answers every description of the "Golgi apparatus." Mention may also be made of Bensley's account[6] based on a study of fixed materials of the evolution of the central vacuoles in onion roots from a canaliculate system which might well be identical with what we have described in the living cell.

To summarize, in the origin of vacuoles a portion of the living protoplasm which is enclosed in a film of lipoid substance enlarges in volume by the intake of water. At what stage the diluted protoplasmic substance ceases to be alive or whether the central vacuole may be part of the living system thus becomes a question analogous to that of the cell wall. There are grounds, however, for regarding the limiting film as not altogether dependent on the life of the cell for some of its most characteristic behaviors. As regards its growth the resemblances to the physical growths of lecithin is remarkable, and as regards semipermeability the lining of the sap cavity, which gives a similar lipoid reaction, may retain this property long after the cell is dead. This has been known since De Vries's "Plasmolytischen Studien," but we have recently observed extreme examples of the fact. In cells "killed" by iodine with eosin the vacuolar membrane contracted in concentrated glycerine; thereafter for 8 days it underwent slow deplasmolysis retaining its smooth contour, and, for a part of the time, maintaining a high concentration of eosin, indeed much higher than on the outside. Recently we have noted that the tonoplast can retain its smooth contour also after sufficient treatment with osmic acid vapor to flocculate the contents (in part) of the central vacuole.

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[4] Nassonov, D., Archiv. fur mik. Anatomie, *100*: 1924.

[5] Ludford, R. J., Proc. Roy. Soc. B. *98*: 354, 1925.

[6] Bensley, R. R., through Cowdry's "General Cytology," p. 343.

THE TRANSFER OF EXCITED ENERGY FROM OZONE TO HYDROGEN AND NITROGEN

FRANCK and Cario[1] have shown that energy may be transferred from photosensitized mercury atoms to hydrogen at low pressures. The behavior of the excited hydrogen leads these workers to conclude that the active gas is hydrogen atoms. Bonhoffer[2] has made a study of the decomposition of ozone by photosensitized chlorine and bromine to determine a relation between the absorbed radiant energy. Rideal and Norrish[3] have used the photosensitization of ozone decomposition by chlorine in a determination of the kinetics of the reaction between hydrogen and oxygen. Taylor and Marshall[4] give the results of their work on the reaction of hydrogen atoms, produced by excited mercury atoms, with a variety of gases, including nitrogen. The hydrogen and nitrogen used was freed from oxygen. Mixtures of nitrogen with excess hydrogen when illuminated with resonance radiation in the presence of mercury vapor showed little or no change in pressure and the tests with Nessler's reagent at the close of the runs were negative. However, Noyes[5] reports that ammonia is formed in mixtures of hydrogen and nitrogen by transference of excited energy from mercury atoms to the molecules of the above gases. In the report by Noyes we are not informed if special precautions were taken to remove oxygen except in his investigation using mixtures of hydrogen and nitrogen in contact with vapor of boiling mercury. In this case no ammonia was formed when oxygen had been removed from the gas mixture previous to its contact with mercury vapor. Dickinson[6] by using the method of Franck and Cario for making atomic hydrogen has shown that excited hydrogen atoms combine with oxygen at 45° C. This work has been extended by Mitchell,[7] who finds that the rate of the reaction between illuminated hydrogen and oxygen in presence of mercury vapor depends upon the pressure of the oxygen; and also that this reaction is retarded in the presence of argon. In the conclusion, he suggests the possibility that the active hydrogen is not atomic. These investigations described above have been conducted largely at low pres-

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[1] *Zeit. Physik.*, *12*, 162 (1922).

[2] *Zeit. Physik.*, *13*, 94 (1923).

[3] *Jr. Chem. Soc.*, *127*, 787 (1925).

[4] *Jr. Physical Chem.*, *29*, 1140 (1925).

[5] *Jr. Am. Chem. Soc.*, *47*, 1003 (1925).

[6] Proc. Nat. Acad. Sci., *10*, 409 (1924).

[7] Proc. Nat. Acad. Sci., *11*, 458 (1925).

sures and with the gases in the field of light during the period that the transfer of excitation has occurred.

Marshall and Taylor[8] find that active hydrogen produced by the Wood's method in a high tension discharge at low pressures will react with unilluminated chlorine to form hydrogen chloride. In a further study of this reaction Marshall[9] concludes that more hydrogen chloride is formed than can be accounted for by the number of hydrogen atoms entering the reaction tube. He explains these results by means of a chain mechanism. But Wendt and Landauer[10] show that active hydrogen, other than atomic, is formed in a low pressure high tension discharge. Polyatomic hydrogen in a higher quantum state may be a factor to be considered in accounting for the abnormal results obtained by Marshall.

Results have been obtained by Venkataramaiah[11] which indicate that hydrogen is activated by continuous burning of oxygen in hydrogen. He considers that when the combustion is once initiated by spark discharge the reaction activates the hydrogen. Probably electrons of high kinetic energy capable of ionizing hydrogen are emitted by the reacting molecules. This very interesting work of Venkataramaiah's suggested the investigation the results of which are reported in the present communication.

Since active hydrogen is formed in the combustion of oxygen in hydrogen at the temperature of the flame, we might expect the same reaction to take place, but at a much lower velocity, if the temperature was lowered. But hydrogen and oxygen do not combine very readily at ordinary temperatures without the intervention of a catalyst. The problem was to increase the velocity of combination of hydrogen and oxygen at ordinary temperatures without using a solid catalyzing agent. Pickel[12] reports that ozone reacts with hydrogen appreciable below 100° C; also that the union of active oxygen with hydrogen takes place faster than the reversion of ozone to oxygen. It has long been known that ozone is formed in flames, and it was thought that ozone might play a part in the activation of hydrogen in the flame as described by Venkataramaiah. The active hydrogen produced by corona discharge,[13, 14] by electrolysis,[15, 16] and by the displacement of hydrogen from an acid by a metal,[17] will react with nitrogen with the formation of ammonia. Therefore there seemed to be some probability of catalyzing the reaction of hydrogen with nitrogen by using a high concentration of ozone evolved into a mixture of the two gases.

A solution of sulphuric acid sp. gr. 1,213, at 15°, was electrolyzed, using a current of 6.2 amperes. The drop of potential across the electrodes was nine volts. A piece of platinum foil 5 sq cm in area served as a cathode. The anode was a platinum wire .5 mm in diameter and 31 mm in length.

A stream of hydrogen and nitrogen at atmospheric pressure mixed approximately in a ratio of three to one, respectively, and at a velocity close to eight liters per hour, was led directly down over the anode at which the ozonized oxygen evolved at a very rapid rate. The escaping gas mixture was washed with ammonia free water in an absorption bulb such as described by Duane and Wendt.[18]

The gases and sulphuric acid solution were previously tested with Nessler's reagent and found to be ammonia free. The nitrogen was purified in system used by Mr. A. S. Ellis, who is making a study in this laboratory of current density in relation to percentage of active hydrogen produced at cathodes of various metals.

Runs of fifteen minutes' duration were made, and in every case so much ammonia was found upon Nesslerizing the absorbing liquid that the color was too deep for a quantitative estimate. To obtain the quantity of ammonia formed the absorbing solution was diluted with ammonia free water to a definite volume and an aliquot part taken for the Nesslerization. Tests were made on the absorbing liquid for decomposition products of sulphuric acid but none were found.

Runs were made duplicating conditions of those described, except that no hydrogen was mixed with the nitrogen in the gas stream led down over the anode. In every trial the absorbing liquid was free from ammonia. This seems to indicate that the ozone was transferring its excitation to the hydrogen, which in turn was capable of uniting with nitrogen to form ammonia.

Weigert[19] reports that in the dark there is no appreciable reaction between ozone and hydrogen within an hour. It was thought that diffused light might have some influence upon this reaction between ozone, hydrogen and nitrogen; also we wished to learn if this reaction was accompanied by light phenomena such as are associated with the Strutt active nitrogen. Runs were made for fifteen minutes in the dark under the same conditions as described for mixtures of hy-

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[8] *Nature*, *112*, 937 (1923).

[9] *Jr. Physical Chem.*, *29*, 842 (1925).

[10] *Jr. Amer. Chem. Soc.*, *42*, 930 (1920).

[11] *Jr. Am. Chem. Soc.*, *45*, 261 (1923).

[12] *Zeit. Inorg. Chem.*, *38*, 307 (1904).

[13] Wendt and Grubb, *Jr. Amer. Chem. Soc.*, *42*, 937, (1920).

[14] Anderegg, *Jr. Am. Chem. Soc.*, *47*, 2429 (1925).

[15] Grubb, *Nature*, *111*, 671 (1923).

[16] Venkataramaiah, *Nature*, *112*, 57 (1923).

[17] Grubb, SCIENCE, *57*, 696 (1923).

[18] *Phy. Rev.*, *10*, 116 (1917).

[19] *Zeit. Physik. Chem.*, *90*, 189, 1915.

drogen, nitrogen and ozone. Careful observations were made for light phenomena but none were noticed. The amount of ammonia formed seemed to check very well with that for previous runs and apparently there is very little if any decrease in the velocity of the reaction due to the absence of light. There are a number of factors which need investigating to throw light upon the mechanism of this transfer of excited energy. In the formation of the ammonia we might assume that the reaction is preceded by the ionization of the reacting constituents. The hydrogen may be ionized by the energy transferred during a collision with an excited ozone molecule. The hydrogen ions would then be free to combine with hydrogen molecules to give a polyatomic group. A reaction between hydrogen molecules and ionized hydrogen has been suggested by Smyth[20] and by Hodgness and Lunn[21] in a study of ionization potentials. These workers find that at very low pressures the percentage of polyatomic groupings is very small, but that higher pressures favor the reaction $H_2 + H^+ = H_3^+$.

Whether the ozone transfers any excitation to the nitrogen has not been determined. Lowry[22] found that ozone did not react with nitrogen sufficiently to form an acid unless the nitrogen had been subjected to an electronic discharge previous to mixing with ozone. However, this only shows that the ozone does not transfer energy to nitrogen in sufficient quantities under Lowry's experimental conditions to ionize the nitrogen and form the oxide. But the ozone will react with nitrogen that has been excited to a higher quantum state by electronic bombardment.

Griffith and Shutt,[23] in a study of "Photochemical Reactivity of Ozone in Presence of Other Gases," find evidence for an abnormal reactivity of ozone and hydrogen when compared with the reactivity of ozone and nitrogen, or ozone and other gases. They have plotted the change in pressure against the initial ozone concentration and find that the curve contains both a minimum and a maximum. The pressure decreases with increasing percentage of ozone to 1.5; then an increase of pressure occurs up to 9.5 per cent. of ozone. These two points, where the minimum and maximum are located, would indicate pressure equilibrium for two or more reactions. In explaining these results the authors have assumed that the hydrogen remains in the molecular state and reacts with atomic oxygen to form water. We have obtained evidence which indicates that the hydrogen is also excited and is capable of combining with nitrogen. It would seem, then, that the reaction between ozone and hydrogen is more complicated than the mechanism offered by Griffith and Shutt.

In the formation of ammonia the combination of an atom of nitrogen with three atoms of hydrogen indicates that the sum total of transfer of excitation has been sufficient to not only ionize the nitrogen but also to dissociate it into atoms. This is probably not the result of a single collision of a nitrogen molecule with an excited group. If we consider Euchen's[24] values for the heats of dissociation of nitrogen 440 kg. cal. of oxygen, 425 kg. cal. of hydrogen 90 kg. cal., respectively, in relation to each other, we might expect the excited ozone capable of transferring enough energy upon collision with the hydrogen molecule to produce hydrogen atoms, but this same relation would probably not be true for nitrogen. However, if nitrogen atoms were produced we should expect some nitrates to be formed in the presence of such a high concentration of ozone. A careful search was made, but no nitrates were found. This is what we might predict from the relation of the above heat values. Also we find experimentally that nitrogen is much more readily reduced than it is oxidized.

In extending the theory of Klein and Rosseland[25] relating to collisions of the "second kind" Franck[26] has postulated that during a collision of an excited group with an unexcited molecule the energy of excitation may be transferred to the colliding molecule without the emission of light. Some of the resultant energy may be manifest as chemical. Probably a part of the energy of formation of water and of ammonia is transferred as chemical. The formation of ammonia probably results from cumulative excitation during collisions of the "second kind." If we assume that the active constituent in excited hydrogen at atmospheric pressure is the H_3 group, then two successive collisions of the nitrogen molecule with H_3 groups would probably tend to give two molecules of ammonia.

It was noticed that during the course of this preliminary work a variation in the velocity of the gas stream gave inverse variations in the quantity of ammonia formed. Any changes in velocity of gas stream would produce variations in the concentration of ozone in the gas mixture and also increase or decrease the time of contact of ozone with other gases before entering absorption bulb. These factors are being investigated further.

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[20] *Phy. Rev.*, *25*, 452 (1925).

[21] *Phy. Rev.*, *26*, 44 (1925).

[22] *Jr. Chem. Soc.*, *101*, 1152 (1912).

[23] *Jr. Chem. Soc.*, *124*, 2760 (1923).

[24] *Ann. der Chemie*, *440*, 111 (1924).

[25] *Zeit. für Physik.*, *4*, 46 (1921).

[26] *Zeit. für Physik.*, *9*, 259 (1922).