of discharge tubes, etc., which play a major part in laboratory sources. Even in astronomical sources its applicability is very limited, since it requires that the energy available for excitation must increase in a prescribed way as the density is increased.

Comparing the density of radiation given by the mechanism postulated by (2) with that of complete thermodynamic equilibrium, it is evident that at low electron densities the permitted (A_{21} large) and forbidden (A_{21} small) lines depart equally from the equilibrium case. At high electron densities, however, de-excitation by collision causes the forbidden lines to depart much farther from the equilibrium case than the permitted lines.

Which of these treatments, M constant or M proportional to density, one uses is largely a matter of personal preference, since neither can lay claim to any uniqueness in describing either astronomical or laboratory phenomena. Indeed equally strong claims can be made for considering the intensity coming from unit volume, in which case the number of atoms capable of being excited (N_1 in 2) also increases with the density. M then becomes roughly proportional to the square of the density, and an even greater increase of I with the density is obtained than that given by (2).

The important facts which hold true in all of these cases are:

(1) At low densities where de-excitation by collision is negligible, the number of quanta emitted is practically equal to the number of atoms excited regardless of whether the lines are permitted or forbidden. Because of the lower excitation potential of the forbidden lines, they become under these conditions the true resonance lines of the atoms or ions concerned. The forbidden lines therefore take a very major role since a large part of the available energy is transferred to them.

(2) At high densities the excitation of the forbidden lines remains large. Because, however, of the very high probability of de-excitation by collision compared to the probability of spontaneous emission, only a negligible fraction of the atoms excited succeeds in emitting forbidden lines. Under these conditions, therefore, practically all of the available energy appears in the permitted lines.

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Photochemistry of Ammonia

THE mechanism of the photochemical decomposition of ammonia has been the subject of considerable discussion lately¹, from which it would appear that the nature of the reaction is almost completely elucidated. The experiments to be mentioned below were designed to settle the few remaining uncertain points regarding the reaction. In point of fact, however, they have opened the results to a new interpretation.

The relevant experimental evidence, discussed in the references cited above, may be summarized thus. From the diffuse nature of the absorption spectrum

and the absence of fluorescence, it was concluded that each molecule on absorbing a quantum dissociated into NH_2 and H . The low quantum yield—for example, 0.3 at 20° C. and 100 mm. pressure—was interpreted as due to a back reaction, which was supported by the fact that atomic hydrogen inhibited the reaction. Using para hydrogen to measure the stationary concentration of atomic hydrogen, it was found that this concentration was much smaller than that calculated on the assumption that H atoms disappear by the reactions $\text{H} + \text{H} + \text{X} \rightarrow \text{H}_2 + \text{X}$ and $\text{H} + \text{NH}_2 + \text{X} \rightarrow \text{NH}_3 + \text{X}$, where X is a third body. This anomaly was explained by assuming that NH_2 radicals combine to form hydrazine, which in turn rapidly reacts with atomic hydrogen, thereby maintaining a low stationary atom concentration.

In order to compute the magnitude of this latter process, the effect has been measured of hydrazine on the stationary atomic hydrogen concentration (estimated by para hydrogen conversion) produced by photo-excited mercury atoms. The results showed that the low concentration is not due to hydrazine, for the pressure of hydrazine required to account for the low concentration of hydrogen atoms could not possibly be formed during the course of a normal ammonia experiment.

This point was made doubly sure in the following way. If hydrazine is responsible for the low concentration, then ammonia undergoing photo-dissociation should also inhibit the para hydrogen conversion photo-sensitized by mercury atoms. A mixture of ammonia and para hydrogen was therefore exposed first to a mercury resonance lamp and then simultaneously to the lamp and to a zinc spark which dissociated the ammonia. There was no appreciable inhibition of para conversion when the ammonia was being dissociated, even though conditions were such that inhibition of ammonia decomposition by atomic hydrogen could be detected.

The conclusions to be drawn from these experiments are that the low hydrogen atom concentration is not due to the presence of hydrazine, which substance plays no significant part in the photo-chemistry of ammonia, except under special conditions, and that the secondary reactions only involve $\text{H} + \text{H} \rightarrow \text{H}_2$, $\text{NH}_2 + \text{NH}_2 \rightarrow 2\text{H}_2 + \text{N}_2$ and $\text{H} + \text{NH}_2 \rightarrow \text{NH}_3$.

Another series of experiments gave the probable clue to the dilemma. Using the same intensity of radiation for exciting mercury atoms and for dissociating ammonia, it was observed that the ratio of the rates of para hydrogen conversion is very nearly equal to that expected if only one quarter of the ammonia molecules absorbing light yield the products NH_2 and H .

These experiments therefore suggest that only a fraction (given approximately by the quantum yield) of the ammonia molecules undergo primary dissociation to H and NH_2 , which react in the fashion mentioned above. The remainder lose their energy by chemically ineffective processes.

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¹ Taylor, H. S., *J. Phys. Chem.*, 42, 783 (1938). Leighton, P. A., "The Determination of the Mechanism of Photochemical Reactions", 27 (Paris: Hermann et Cie).