4. It is pointed out again that the magnitude of the salt effect on velocity of reaction between ions is very great in dilute solutions, and that at low concentrations changing salt concentration during the course of a reaction may mask the true character of the reaction.

II. Finally, it is shown that in the case of the reaction $S_2O_8^{--} + C_2O_4^{--} \xrightarrow{Ag^+} 2SO_4^{--} + 2CO_2$, the velocity is not as predicted from the other reactions.

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FLUORESCENCE IN MIXTURES OF AMMONIA AND MERCURY VAPOR

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Introduction

While making experiments on the decomposition of ammonia by optically excited mercury vapor, Dickinson and Mitchell[1] observed a greenish fluorescence which appeared when a mixture of ammonia at a few millimeters' pressure and mercury vapor at room temperature was illuminated by the radiation from a cooled quartz mercury arc; they showed that the resonance radiation 2537 Å. was necessary to the production of this fluorescence. Observations with a direct vision spectroscope showed the fluorescence to be a diffuse band with a maximum around 5100 Å. Photographs with a quartz prism spectrograph showed an additional diffuse band in the ultraviolet with a maximum around 3370 Å. The green fluorescence was also observed visually when nitrogen was used instead of ammonia.

In the present experiments the ultraviolet fluorescence and the conditions under which it is excited were examined further.

Experimental Arrangement

A spherical resonance vessel (volume about 500 cc.) with a plane quartz window sealed to one end with sealing wax was connected to a vacuum system. About 2 cc. of mercury was placed in the resonance vessel to give a partial pressure of mercury corresponding to its vapor pressure at room temperature. Ammonia, nitrogen, hydrogen and argon could be admitted to the apparatus in the desired amounts and their pressures read on a McLeod gage. The method of purifying and admitting the gases to the resonance vessel was the same as that described by Mitchell

[1] Dickinson and Mitchell, *Proc. Nat. Acad. Sci.*, **12**, 692 (1926).

and Dickinson.[2] Light from a quartz mercury arc, cooled by water at a definite temperature, was allowed to shine on the quartz window of the resonance vessel. In some cases a light filter consisting of a quartz cell containing 3 mm. thickness of a 25% solution of acetic acid was used. This filter was found to cut out radiation below 2400 Å., which was shown[1] to decompose ammonia photochemically, giving rise to hydrogen as a product. As the amount of hydrogen formed per unit time in the direct photochemical decomposition was known to be several times as great as the amount formed in the sensitized decomposition, it was thought necessary to use the filter. However, on account of the intensity of the light (distance from the window 10 cm.) and the short time of exposure, very little decomposition took place. One experiment made using no filter (see Fig. 2) gave substantially the same results as when the filter was used. The filter was only used in cases where relative intensities were desired, except in the above-mentioned case. A small Hilger quartz prism spectrograph was used for photographing the ultraviolet band.

In cases where intensity measurements were desired, calibration spots were placed on the plate by exposing portions of it to light from a small flash light bulb at different distances for the same length of time used in the fluorescence exposures (1 minute). The plates were measured on a microphotometer and the galvanometer deflections plotted against the square of the distance to the light. The relative intensities of the bands were obtained by recording the minimum galvanometer deflections (corresponding to the maximum of intensity of the band) and reading off the intensities from the plot. A small correction for the blackening of the plate in the region from 3180 to 3650 Å., due to scattered light from the window, was made by subtracting the intensity at zero ammonia pressure from each of the intensities at higher pressures.

Experimental Results

With 7 mm. of ammonia in the vessel, the green fluorescence was observed and photographs showed the diffuse bands stretching from 3170 to 3650 Å., with a maximum around 3370 Å.

Experiments made with the same pressure of nitrogen showed green fluorescence but photographs showed no ultraviolet band. The plate showed, incidentally, a line or perhaps a band-head at about 3370 Å., near the mercury line 3342 Å. which was reflected from the quartz window.

Experiments made with 7 mm. of argon, 40 mm. of argon and 7 mm. of hydrogen showed neither green nor ultraviolet bands. Indeed nothing was visible on the plate except the mercury lines reflected from the window, the fluorescent band of quartz between 4046 and 4358 Å., and the 2537 Å. resonance line of mercury.

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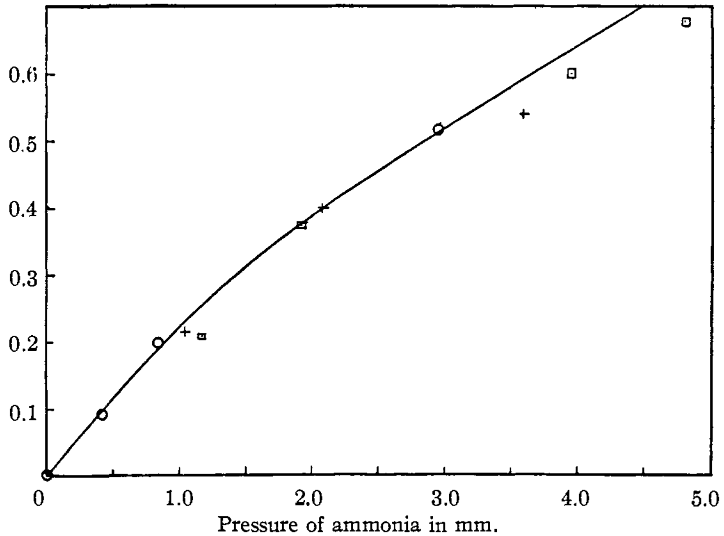
[2] Mitchell and Dickinson, THIS JOURNAL, **49**, 1478 (1927).

Photographs with an uncooled arc and ammonia showed neither green nor ultraviolet bands.

Photographs were taken with different ammonia pressures in the vessel, using the cooled arc, and the plates were photometered. The relative intensities of the ultraviolet band were plotted against the pressures of ammonia as shown in Fig. 1. On Fig. 1 are also plotted rates of decomposition of ammonia, in arbitrary units, as a function of the ammonia pressure.



○ Intensity of fluorescence. + ⊡ Rate of decomposition.

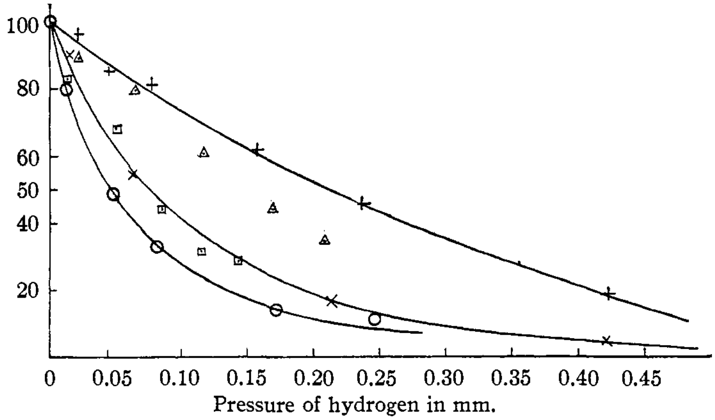
Fig. 1.

Finally, experiments were made in which a constant pressure of ammonia was kept in the vessel and various amounts of hydrogen were added. Small amounts of hydrogen were found to decrease the intensity of the ultraviolet band to a marked degree. The plates were photometered and the results are shown in Fig. 2. Relative intensities are plotted as ordinates against pressure of hydrogen as abscissas for three different ammonia pressures, namely, 5.04 mm., 3.00 mm. and 2.82 mm. Fig. 2 also contains results of experiments on the effect of hydrogen on the rate of sensitized decomposition of ammonia.[2]

Discussion of Results

The above experiments show that mercury atoms, excited by the absorption of the resonance line 2537 Å. of mercury, are necessary for the production of the ultraviolet and green bands, since no bands were observable when the lamp was run hot so that the center of the line was reversed. Confining our attention to the ultraviolet band for the moment, the experiments show that this band occurs when ammonia is present. Hence, ammonia and mercury atoms in the 2^3P_1 or 2^3P_0 states are necessary for the production of the band.

It will be seen from Fig. 1 that the dependence of the intensity of fluorescence on the pressure of ammonia agrees quite well with the dependence of the rate of sensitized decomposition on ammonia pressure. The possibility of so adjusting the scale of ordinates that the fluorescence and the rate curves coincide shows that there is a proportionality between the intensity of fluorescence and the rate of decomposition of ammonia. The proportionality between the intensity of fluorescence and the rate of sensitized decomposition can be accounted for on the assumption that excited ammonia molecules are responsible for both the fluorescence and the decomposition.



+ Quenching of fluorescence, P_{NH_3} = 5.04 mm.; ○ Quenching of fluorescence, P_{NH_3} = 2.82 mm.; × Quenching of fluorescence (no filter), P_{NH_3} = 3.0 mm.; △ Rate of decomposition, P_{NH_3} = 5.06 mm.; ☐ Rate of decomposition, P_{NH_3} = 3.22 mm.

Fig. 2.

From Fig. 2 it will be seen that small amounts of hydrogen have a marked effect in decreasing the fluorescence and that the relative effect is greater, the smaller the ammonia pressure. If the sole role of the hydrogen were to take activation from the mercury atoms, we should expect that at very low pressures of ammonia the amount of hydrogen necessary to decrease the intensity of fluorescence to one-half would be the same as that necessary to decrease the resonance radiation of mercury by the same amount. This pressure of hydrogen was shown by Stuart[3] to be 0.2 mm. However, from Fig. 2 it is to be noticed that at pressures of ammonia as high as 3 mm. only 0.05 mm. of hydrogen is necessary to decrease the intensity of the

[3] Stuart, *Z. Physik*, **32**, 262 (1925).

fluorescence to one-half. The proportionality between the intensity of fluorescence and the rate of sensitized decomposition is even more striking in Fig. 2, since the curves there show considerably more curvature than those of Fig. 1. The explanation of the large effect of hydrogen on the rate of decomposition, that hydrogen can take activation from excited ammonia molecules by collision of the second kind, is applicable to the intensity of fluorescence if ammonia be assumed to be the emitter.

Rayleigh[4] and Houtermans[5] have found that diffuse bands are emitted by distilling mercury vapor which has been radiated by the light from a cooled quartz mercury arc. One band, with a maximum at 3370 Å., bears a striking similarity to the band described in this paper; however, another band occurs at 2539 Å., which is not observed in mixtures of ammonia and mercury. If it is assumed that the 3370 Å. band from boiling mercury is identical with that from mercury-ammonia mixtures it becomes difficult to explain the above facts, since it is not easy to see how the fluorescence would then depend on the pressures of ammonia and hydrogen in the way it does. In particular it is difficult to see how the explanation given by Houtermans for the bands in distilling mercury vapor could be made to fit the facts observed in the case of the fluorescence of mercury and ammonia at room temperature. However, the dependence of the intensity of fluorescence on the pressure of ammonia and hydrogen is readily explained on the assumption that the emitter is an ammonia molecule which has been activated by collision of the second kind with an excited mercury atom.

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Summary

The intensity of the diffuse band, with a maximum at 3370 Å., emitted when mixtures of ammonia and mercury vapor at room temperature are irradiated with mercury resonance radiation 2537 Å., has been found to vary with ammonia and hydrogen pressures in the same manner as the rate of sensitized decomposition of ammonia. It is suggested that excited ammonia molecules are responsible for both emission and decomposition.

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[4] Rayleigh, *Proc. Roy. Soc.* (*London*), **111**, 456 (1926).

[5] Houtermans, *Z. Physik*, **41**, 140 (1927).