ever, the ferric iron may be detected *qualitatively* in the presence of much higher concentrations of copper. For example, a small excess of reagent was added to a solution containing Fe^{+++} 8 p. p. m. and Cu^{++} 40 p. p. m. A white precipitate was formed which settled upon standing for a few minutes, giving a dark green supernatant solution showing the presence of ferric iron. Salts that easily hydrolyze, such as those of tin or titanium, interfere with the color matching unless their concentration is very low.

We desire to express our thanks to G. D. Searle and Co., Chicago, Ill., who furnished us with the 7-iodo-8-hydroxyquinoline-5-sulfonic acid used in this investigation. J. D. Riedel-E. deHaën A. G., Hannover, Germany, supplied a number of pure salts of the rare elements, for which we are very grateful.

Summary

7-Iodo-8-hydroxyquinoline-5-sulfonic acid is a very sensitive colorimetric reagent for ferric iron, its yellow aqueous solution changing to blue or green upon the addition of ferric ions. It gives no color reaction with ferrous ions nor with a large number of other ions. The reagent is sensitive to 1 part of ferric iron in 10 million parts of solution when the observation is made in a 50-ml. (210 mm. to mark) Nessler tube. The reaction is best carried out in a solution acid to methyl orange paper. The color is stable to light (an advantage over the thiocyanate method) but is destroyed by strong acids and bases. Salts that hydrolyze easily or yield colored ions should not be present unless in very low concentration.

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[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY OF BROWN UNIVERSITY]

PHOTOCHEMICAL STUDIES. XV. GERMANE. SOME REMARKS ON THE DECOMPOSITION OF AMMONIA SENSITIZED BY MERCURY VAPOR

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The photochemistry of germane has not been investigated previously. It should be of interest because of the similarity between this compound and methane. Taylor and Hill[1] found the latter compound, in contrast to other saturated hydrocarbons, not to undergo reaction under the influence of excited mercury atoms. Bates[2] found also that excited cadmium atoms transferred their energy to methane without producing reaction. Bates[3] also investigated thoroughly the quenching of the resonance radiation of mercury by methane and found it to have an exceedingly

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[1] Taylor and Hill, THIS JOURNAL, **51**, 2922 (1929).

[2] Bates, *Proc. Nat. Acad. Sci.*, **14**, 849 (1928).

[3] Bates, THIS JOURNAL, **52**, 3825 (1930).

small effective cross section for quenching. He observed a peculiar effect of methane in producing increasing transparency of mercury vapor at pressures higher than forty or fifty millimeters. These properties and others show that methane is in many respects analogous to the noble gases.[4]

The absorption spectrum of methane in the Schumann region has been investigated by Leifson,[5] who found continuous absorption below 1800 Å. at high pressures and a series of bands below 1600 Å. at low pressures.

In studying the sensitized decomposition of germane it was desired to have some control reaction which would serve to determine the constancy of the intensity of resonance radiation. For this purpose the sensitized decomposition of ammonia was chosen. Both the sensitized and unsensitized decompositions of this gas have been investigated repeatedly.[6] This reaction proved not to be well adapted to the purpose at hand and it will be given only brief mention. Certain conclusions with regard to the mechanism of the sensitized reaction are, however, possible.

I. Experimental

The germane used in these experiments was prepared by the action of ammonium bromide on magnesium germanide in liquid ammonia solution.[7] It was purified by reaction with sodium in liquid ammonia to produce sodium germanyl ($NaGeH_3$), the germane being regenerated by causing the latter substance to react with ammonium bromide in liquid ammonia solution. In this way the higher hydrides of germanium are broken down. Final purification consisted in repeated fractional distillations with liquid air. To test the purity samples were decomposed thermally, leading to the reaction $GeH_4 = Ge + 2H_2$. For example, in one experiment the initial pressure of the germane was 0.1221 mm. and the final pressure of the hydrogen 0.2446 mm., calcd., 0.2442. The agreement with the theoretical is within experimental error, although if the impurity is assumed to be Ge_2H_6 the purity calculated from the figures is 99.7 mole per cent.

The ammonia was dried by sodium and purified by fractional distillation.

(a) **Attempt to Obtain the Absorption Spectrum of Germane.**—A condensed discharge through hydrogen at a pressure of a few millimeters served as a source of radiation.[8] A Hilger E3 spectrograph and plates sensitized either with Nujol or with a special sensitizing solution furnished by the Eastman Kodak Co. were used. Exposures were made in two tubes, one twenty centimeters in length and the other three hundred and fifty centimeters in length, at pressures varying from a few millimeters to approximately one atmosphere. Aside from a slight continuum at the short wave lengths which seemed to disappear upon further purification of the germane, no absorption was observed between 2130 and 7000 Å. As will be shown later it is possible,

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[4] See Glockler, This Journal, **48**, 2021 (1926).

[5] Leifson, *Astrophys. J.*, **63**, 73 (1926).

[6] For recent work on the unsensitized reaction see Wiig and Kistiakowsky, This Journal, **54**, 1806 (1932). This article contains references to earlier work on both types of reaction.

[7] E. Seaton Carney, Thesis, Brown University, 1928; G. K. Teal, Thesis, 1930. The authors wish to express their appreciation to Dr. Teal for preparing the germane used in these experiments.

[8] Chalonge and Lambray, *Rev. d'optique*, **8**, 332 (1929).

however, to obtain photochemical decomposition of germane by radiation transmitted by thin layers of quartz. It appears probable that germane does absorb at some place in the range of wave lengths between about 1800 and 2100 Å. Further studies with a vacuum grating will be made at a later date.

Two attempts yielding negative results were made to obtain the Raman spectrum of germane. Failure was caused undoubtedly by the fact that it was impossible to use sufficiently high pressures to give the requisite light scattering.

As a check on the method of obtaining absorption spectra the predissociation bands of ammonia were photographed.

(b) **The Sensitized Decompositions of Germane and of Ammonia.**—Customary technique was used for these studies. The mercury arc was a horizontal type operated with the mercury reservoirs under water. Two reaction vessels were placed above the lamp in such a way that one could be used as a control. The pressure of the mercury vapor was maintained constant by separating the reaction vessels from the rest of the apparatus by traps immersed in ice-water mixtures. Pressures below 0.2 mm. were read on ordinary McLeod gages. For runs at higher pressures a modified McLeod gage was used. In the case of ammonia the rate was determined by measuring the pressure of the gas uncondensed by liquid air. The vapor pressure of germane is not negligible at the temperature of liquid air and varies considerably between the boiling point of oxygen and the boiling point of nitrogen. Empirical corrections were made for the vapor pressure of germane, using the observed vapor pressure of the pure material at the beginning of a run.

Careful determinations were made to show that the sensitized reactions were not greatly complicated by the direct photochemical reactions. This was accomplished by removing the mercury vapor by means of a trap immersed in solid and liquid ammonia (−77°). In both cases not more than 5% of the observed rate could be ascribed to the unsensitized reaction.

(c) **The Unsensitized Decomposition of Germane.**—The radiation from the hydrogen discharge tube was used in these experiments. The discharge tube was waxed directly to the window of the reaction vessel, eliminating any air path and giving a thickness of quartz traversed by the radiation of less than one millimeter. Mercury vapor was removed as before by solid–liquid ammonia mixtures. In some experiments a second reaction vessel was placed so as to receive radiation which had traversed the first in order to ascertain the completeness of absorption. Results in the second vessel were always negative even with the first vessel evacuated due, undoubtedly, to the greater thickness of quartz traversed by the radiation.

These experiments on the unsensitized reaction are, therefore, very qualitative and serve merely to show that the general course of the reaction is not greatly different from that of the sensitized reaction.

II. Results

(a) **The Photosensitized Decomposition of Germane.**—Figure 1 shows the course of a typical reaction. The upper curve represents the total pressure and the lower curve the pressure of the gas uncondensed by liquid air corrected for the vapor pressure of germane and the cooling of the system. The latter pressure is due to the hydrogen formed during the reaction.

Several runs were carried to complete decomposition. One would predict from the equation $GeH_4 = Ge + 2H_2$ that the final pressure would be twice the initial pressure. This was never found to be the case, indicating an appreciable clean-up of hydrogen on the walls. Actually the pressure at the end of the run averaged 1.81 times the initial pressure. Pumping out the hydrogen and flaming the walls led to an evolution of gas very closely equal to the amount cleaned up.

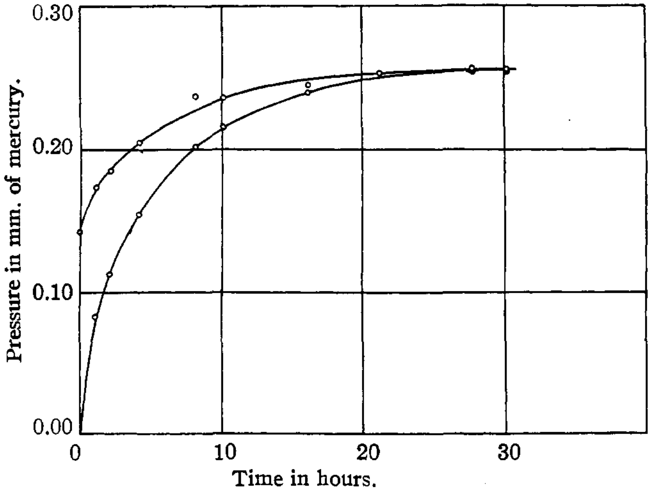

Fig. 1.—Photosensitized decomposition of germanium hydride.

If P_1 is the initial pressure of germane, P_t the total pressure at time t, P_g the pressure of germane at time t and P_H the pressure of hydrogen at time t, we may write

$$P_g = P_t - P_H \tag{1}$$

If the fraction of the hydrogen cleaned up by the walls is assumed to be constant during a run we may write

$$P_H = 1.81(P_1 - P_g) \tag{2}$$

Hence

$$P_g = (1.81P_1 - P_t)/0.81 \tag{3}$$

and

$$P_H/(P_t - P_1) = 2.23$$

Table I shows data illustrating the validity of this relationship.

TABLE I

PHOTOSENSITIZED DECOMPOSITION OF GERMANE

Time, hrs.	P_t, mm.	P_H, mm.	$P_H/(P_t - P_1)$
0	0.1413	0.0000	..
1	.1718	.0701	2.30
2	.1846	.1000	2.30
4	.2040	.1425	2.27
8	(.2370) (?)	.1896	1.98
10	.2360	.2034	2.15
16	.2441	.2257	2.19
30	.2544	.2560	2.26
			Av. 2.21

The average value of this ratio found for all runs is 2.25 and this figure will be used.

The dependence of the rate of decomposition on the pressure of the germane was investigated over a range of pressures from 0.01 mm. to several millimeters. In a given run it was sometimes difficult to decide definitely whether the data fitted best a first or second order equation. When constants at various pressures were compared the constants for both types

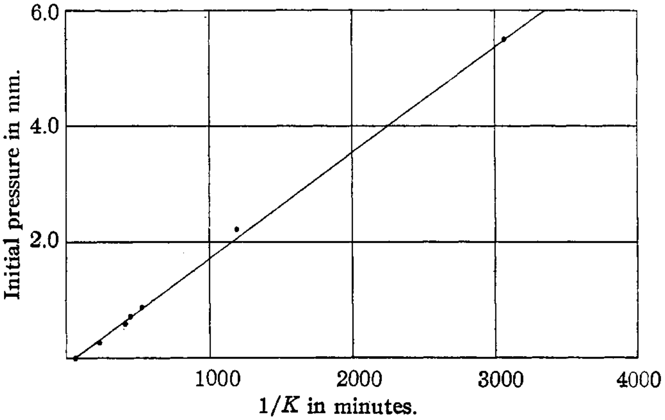

Fig. 2.

TABLE II

RATE OF PHOTOSENSITIZED DECOMPOSITION OF GERMANE

Time, hrs.	Pressure of germane, mm.	K (first order), hrs.$^{-1}$	K (second order), mm.$^{-1}$ hrs.$^{-1}$
0	0.1413		
		0.24	2.2
2	.1036		
		.17	2.2
4	.0878		
		.16	4.2
10	.0245		
		.15	16.1
21	.0046		
	....		
0	.0560		
		.052	227.4
1.02	.0496		
		.042	207
2.03	.0449		
		.038	207
3.03	.0411		
		.035	207
4.08	.0377		

were found to vary markedly with pressure, although those for the first order equation varied less than the others. Figure 2 shows a plot of the reciprocal of the first order constant against the pressure of the germane at the beginning of the run. A similar plot for the second order constants gave a hyperbolic curve. It seems necessary to conclude, therefore, that a mechanism leading to a first order equation as a limiting case is most nearly applicable. Table II shows calculations of the two constants for two runs.

The deposit of germanium on the walls of the cell gradually decreased the amount of light transmitted. In making intercomparisons in a series of runs it became necessary to use some standard of comparison. This was done by alternating runs at different pressures and under different conditions with runs made at a standard pressure. In what follows corrections have been made where necessary for varying light intensity. Intercomparisons were made usually by means of short runs in order to reduce error due to variation in light intensity to a minimum.

The variation of reaction rate with temperature was investigated, although high temperatures were impossible due to thermal decomposition of the germane. Table III gives a summary of results on two runs.

TABLE III

VARIATION OF RATE OF SENSITIZED DECOMPOSITION OF GERMANE WITH TEMPERATURE

Temperature, °C.	93	28
Initial pressure of germane, mm.	0.2121	0.1998
K, hrs.$^{-1}$	0.012	0.017

There is, therefore, no marked dependence on temperature.

The effect of added gases was investigated, as shown in Table IV.

TABLE IV

EFFECT OF ADDED GASES ON THE RATE OF SENSITIZED DECOMPOSITION OF GERMANE

Added gas	Pressure of added gas, mm.	Initial pressure of germane, mm.	K, hrs.$^{-1}$
H_2	0.0916	0.0943	0.044
..	....	.0937	.045
N_2	0.2092	.1095	.051
..	....	.1182	.052

Thus neither hydrogen nor nitrogen affects the rate of decomposition markedly.

(b) The Direct Photochemical Decomposition of Germane.—In these experiments the same phenomenon of hydrogen clean-up was observed. Since the radiation was not strictly monochromatic, only an approximate rate equation may be given. This should be of the form

$$-dP_g/dt = aI(1 - e^{-kP_g}) \qquad (4)$$

which upon integration gives

$$aI(t_2 - t_1) = P_{g_1} - P_{g_2} + (1/k) \log (e^{-kP_{g_1}} - 1)/(e^{-kP_{g_2}} - 1) \qquad (5)$$

From several runs an average value of k was found to be 12 if the pressure is expressed in millimeters. This value, even though it has no definite significance due to the fact that the radiation was not monochromatic, indicates a high absorption of the effective radiation even for a tube of the length used. It should be possible to evaluate aI from one time interval for a given run and calculate a theoretical curve. Direct calculation of pressures from equation (5) is rather laborious, so that a theoretical curve was plotted and comparison made between experimental values and values read from the curve. Table V shows the results of such a calculation for one run.

Table V

Rate of Direct Photochemical Decomposition of Germane

Time, min.	Total pressure observed, mm.	Total pressure calcd., eq. (5), mm.
0	0.0517	0.0517
10	.0661	.0671
15	.0762	.0769
20	.0822	.0826
25	.0896	.0905

(c) **The Sensitized Decomposition of Ammonia.**—Figure 3 shows typical curves of pressure of gas uncondensed by liquid air against time for the sensitized decomposition of ammonia. All runs show a rather rapid initial rate followed by a decided falling off.

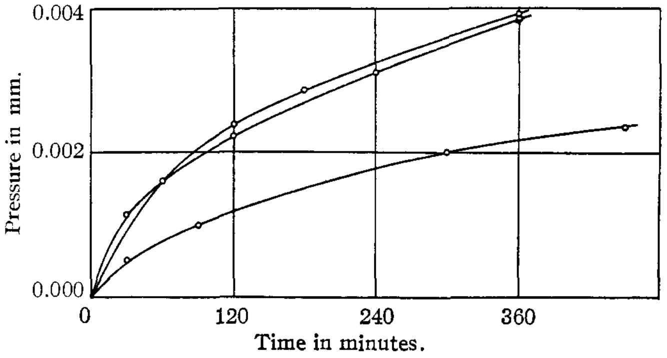

Fig. 3.—Photosensitized decomposition of ammonia.

III. Discussion of Results

(a) **Germane.**—The heat of dissociation of the germanium–hydrogen bond is not known. Mulliken[9] has summarized recently data derivable from band spectrum analysis for a large number of molecules. Inspection

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[9] Mulliken, *Rev. Modern Physics*, **4**, 1 (1932).

of data on hydrides indicates that the energy of dissociation of the GeH molecule will probably correspond to about 2 electron volts with a large uncertainty (probably at least a volt). The presence of three more hydrogen atoms in the germane molecule may be expected to modify somewhat the energy of dissociation of the germanium hydrogen bond, but we may accept this figure tentatively as the energy required to produce the reaction $GeH_4 = GeH_3 + H$. In any case the removal of one hydrogen should require much less energy in germane than in methane.[10]

The energy which a 2^3P_1 mercury atom is capable of giving up on collision corresponds to 4.86 electron volts, whereas the long wave length limit of the ultraviolet absorption of germane corresponds to more than 6 electron volts. The direct and sensitized decompositions of germane seem in every way to be similar and to involve the primary process $GeH_4 = GeH_3 + H$. At least in the direct unsensitized reaction the GeH_3 radical must be formed in either a high energy level or with high kinetic energy. In fact there is ample energy absorbed to cause the ejection of more than one hydrogen atom by a species of Auger effect. In any case reactions of the type $GeH_3 = GeH + H_2$ could take place spontaneously since the heat of dissociation of hydrogen is probably about twice the heat of dissociation of the germanium–hydrogen bond.

The experiments in which hydrogen was added and others toward the end when the hydrogen was in large excess showed that this gas did not affect markedly the rate of reaction. As will be shown later the effect of hydrogen in quenching the fluorescence of mercury is probably much less than that of germane, so that any inhibiting effect to be expected from this source might be difficult to detect with certainty. The reaction $H + GeH_4 = H_2 + GeH_3$ should be energetically possible and may account for the fact that hydrogen is not proved definitely to be an inhibitor. The lack of effect of nitrogen probably means that 2^3P_1 and 2^3P_0 mercury atoms are equally effective in initiating the reaction and that diffusion processes do not play an important part in determining the rate. We may state, therefore, that the initial removal of a hydrogen atom from germane either by excited mercury or by another hydrogen atom is followed by a sequence of events so rapid as not to be decisive in determining the rate of reaction. In this manner the data may be accounted for quantitatively up to pressures of several millimeters. For higher pressures peculiar effects seem to be taking place which may be analogous to those found by Bates[3] for methane.

As shown above the rate of the unsensitized reaction is at least approximately proportional to the intensity of the absorbed radiation. For the sensitized reaction we may write

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[10] Mecke, *Z. Elektrochem.*, **36**, 589 (1930), gives 5.4 electron volts for the reaction $CH_4 = CH_3 + H$. It seems probable that this figure is too high.

$$-\,dP_g/dt = Mk_1k_2IP_g/(k_2P_g + k_3P_H + k_4) \qquad (6)$$

M = no. of germane molecules used up per molecule dissociated by collision with excited mercury
k_1I = rate of formation of excited mercury atoms
$k_2P_gP_m$ = rate at which excited mercury atoms are used up by collision with germane molecules
$k_3P_HP_m$ = rate at which excited mercury atoms are used up by collision with hydrogen molecules
k_4P_m = rate at which excited mercury atoms are used up by fluorescence
P_m = pressure of excited mercury atoms in the steady state

This equation ignores the reaction $H + GeH_4 = H_2 + GeH_3$ except as a possible secondary step. Integration of equation (6) after substitution for P_H from equation (2) gives

$$1/Mk_1k_2I[(k_2 - 1.81k_3)(P_1 - P_g) + (1.81k_3P_1 + k_4)\log(P_1/P_g)] = t \qquad (7)$$

between the limits $t = 0$ and t, and P_1 and P_g. Since an appreciable fraction of the germane was decomposed in some of the runs shown graphically in Figure 2, it is necessary to use equation (7) to evaluate k_2. Values of this constant calculated in this manner show as good a constancy as could be expected and give for k_2 the value 4.7×10^7 if the unit of time is the second and the pressure is expressed in millimeters. The value of k_4 is assumed to be 9.7×10^6 sec.$^{-1}$ and that of k_3 to be 1.09×10^7 sec.$^{-1}$ mm.$^{-1}$.[11] It should now be possible to apply equation (7) to any run providing one point is used to calculate the quantity Mk_1I. Table VI shows how this equation applies to three runs. The bracketed pressures were used to calculate Mk_1I.

TABLE VI

APPLICABILITY OF COMPLETE RATE EQUATION TO THE DECOMPOSITION OF GERMANE

Time, min.	P(obs.)	P(calcd.)	Time, hrs.	P(obs.)	P(calcd.)	Time, min.	P(obs.)	P(calcd.)
0	0.0560	0.0560	0	0.1413	0.1413	0	0.2050	0.2050
61	.0605	.0612	1	.172	.159	30	.210	.208
122	.0645	.0650	2	.185	.173	60	.213	.213
182	.0677	.0681	4	.204	.196	90	.218	.217
245	.0708	[.0708]	10	.236	[.236]	120	.221	.221
			16	.244	.249	250	.237	[.237]
			21	.252	.253			

Equation (7) gives a fairly satisfactory representation of the course of the runs, probably as good as the data would warrant, although there are undoubtedly some factors which have not been included and which may be of importance. From the value of k_2 it should be possible to calculate an effective cross section for reaction between excited mercury atoms and germane molecules. This quantity may be defined as the square of the sum of the radii of the germane molecules and the excited mercury atoms.

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[11] Calculated from the data of Zemansky, *Phys. Rev.*, **36**, 219, 919 (1930).

Obtained in this manner the effective cross section is very large (about 1.4×10^{-14} sq. cm.). The validity of this calculation may be open to question for a variety of reasons. Comparison of the rate of germane decomposition with that of ammonia leads to one of two conclusions: either the quantity M (number of molecules decomposing in a chain) is quite large (> 10) or the effective cross section for reaction is quite large. Equation (7) assumes the latter to be the case, although the quantity M is not determined as such. Definite decision between these two possibilities must be left for the future. It seems quite probable that both M and the cross section may be fairly large. The effective cross section for quenching by methane[3] is very much smaller than that found for germane as would be expected.

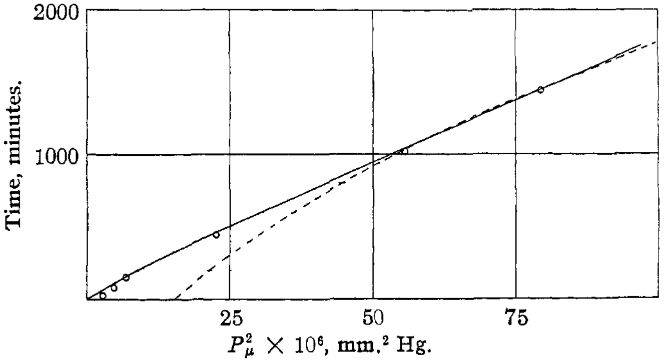

Fig. 4.—Solid curve is theoretical curve based on two methods of inhibition; lower curve assumes inhibition due to quenching only.

(b) **Ammonia.**—From the data of Zemansky[11] accurate values of the effective cross sections for quenching of ammonia, nitrogen and hydrogen are known. It should be possible to derive an equation for the rate of the sensitized decomposition of ammonia based on the assumption that the inhibiting effect of the hydrogen is due solely to its effectiveness in quenching the fluorescence of mercury. Using earlier and less satisfactory data on the quenching of fluorescence than now exist, Mitchell and Dickinson[12] have shown that hydrogen exhibits a larger inhibiting effect than could be accounted for by this mechanism. The equation derived in this manner is identical with equation (6) for germane. If the reaction $2NH_3 = N_2 + 3H_2$, which was found by Mitchell and Dickinson for the sensitized reaction[13] and by Wiig and Kistiakowsky for the unsensitized reaction, is assumed the equation may be integrated. Results of this type of equation are shown in Figure 4, in which the pressure of the gas uncondensed by

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

[13] Other workers have reported a higher percentage of hydrogen in the resulting gases than could be accounted for by this equation.

liquid air is plotted against the time. The dashed line is the theoretical curve for the equation analogous to equation (6). It was fitted arbitrarily to the two points shown in order to calculate a quantity proportional to the intensity.

It seems necessary to conclude, with Mitchell and Dickinson, that hydrogen exerts at least two inhibiting actions. Wiig and Kistiakowksy[6] have examined the entire question of the mechanism of this reaction. We do not feel justified, on the basis of the present experiments, in amplifying their discussion. It may be pointed out, however, that a satisfactory rate equation may be based on the following assumptions: (1) excited mercury atoms may lose their energy by collision with either ammonia or hydrogen molecules or by fluorescence; (2) the ammonia molecules are dissociated by collision with excited mercury; (3) one of the fragments produced may react either with ammonia to yield largely the final decomposition products (perhaps by a series of rapid steps) or with hydrogen to regenerate ammonia; (4) hydrogen atoms do not react with ammonia, but do combine with each other either by triple collision or on the walls. This mechanism leads to an equation of the type

$$-\mathrm{d}t/\mathrm{d}P_{\mathrm{N}} = K_1 + K_2P_1/P_{\mathrm{N}} + K_3/P_{\mathrm{N}} + K_4P_1/P_{\mathrm{N}}^2 \qquad (8)$$

where P_1 is the initial pressure of the ammonia and P_{N} is the pressure at time t. K_1, K_2, K_3 and K_4 are complex constants which are all inversely proportional to the light intensity. If the early stages of a run only are considered so that log (P_1/P_{N}) may be replaced by $(P_1/P_{\mathrm{N}} - 1)$, equation (8) upon integration and collection of terms becomes

$${}^1/_4K_1P_{\mathrm{u}}^2 - P_{\mathrm{u}}(A + t/2) + tP_1 = 0 \qquad (9)$$

where $2A = K_1P_1 + K_2P_1 + K_3 + K_4$ and P_{u} is the pressure of the gas uncondensed by liquid air. Having determined K_1 and A for any one run, it should be possible to fit this equation to any other run by using one point to calculate a coefficient depending on the light intensity by which both K_1 and A must be multiplied. For a complete solution of the equation the dependence of A on initial pressure must be determined, although the runs herein described were carried out mostly at approximately the same initial pressure. In Fig. 4 the solid curve is the theoretical curve for equation (9), the ratio between A and K_1 having been determined in an entirely different run.

Further details concerning the mechanism of the sensitized decomposition of ammonia would not seem to be of value at this point since from the method of deriving equation (8) several different steps might be postulated. In particular different behaviors for $2^3\mathrm{P}_1$ and $2^3\mathrm{P}_0$ mercury atoms may be postulated and a suitable equation derived. The temperature coefficient of this reaction seems to be exceedingly low. Several experiments were carried out at temperatures around 400° and in all cases the rate of increase of pressure of gas uncondensed by liquid air was within the experimental error of that obtained at room temperature.

It may be possible, therefore, that the sensitized reaction has a different mechanism from that of the unsensitized reaction. Since molecules are known which show more than one predissociation region for a given band system,[14] there is no *a priori* reason for believing that dissociation always takes place after absorption of radiation in the predissociation region. Whether the probability of dissociation could be quite low if the predissociation bands are very diffuse is a question which cannot be answered unambiguously at present for molecules even as complex as those of ammonia, but one should expect at least a variation of quantum efficiency with wave length if this is the case. Wiig and Kistiakowsky[6] found no variation greater than the experimental error between 1962 and 2144 Å. We wish to emphasize merely, in agreement with these authors, that neither the direct nor the sensitized reaction is as yet completely understood. In particular, derivations of satisfactory rate equations for the latter may be based on several different mechanisms and there is as yet very little definite reason for preferring any single one.

Summary

1. Germane shows no absorption bands between 2100 and 7000 Å. Radiation transmitted by thin layers of quartz will, however, cause photochemical decomposition of this gas.

2. Both the sensitized and unsensitized photochemical decompositions of germane lead largely to the reaction $GeH_4 = Ge + 2H_2$. Part of the hydrogen does not appear in the gas phase and is probably removed by adsorption. The removal of one hydrogen atom from germane seems to be followed by a series of steps too rapid to be decisive in determining the rate.

3. Brief remarks on the sensitized decomposition of ammonia have been made. While a satisfactory rate equation may be obtained, it is not possible to choose unambiguously a definite mechanism for this reaction.

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[14] Christy and Naude, *Phys. Rev.*, **37**, 903 (1931).