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ortho- to para-hydrogen at a space velocity of 60, while the results here recorded show that the hydrogen-deuterium reaction is comparatively much slower. It is evident, therefore, that the effect of the activated adsorption at this temperature on the ortho-para conversion is negligible as compared with the combined effect of van der Waals adsorption plus the paramagnetism of the surface. The reaction between hydrogen and deuterium does offer a method for the detection of activated adsorption in temperature regions in which it would be indistinguishable from van der Waals adsorption by the experimental methods customarily employed.

These results show that some of the hydrogen

adsorbed on Cr_2O_3 , Ni and undoubtedly other catalytic surfaces is in a chemically very reactive form even at liquid air temperatures and that, consequently, the reaction kinetics of a catalytic hydrogenation process is determined rather by the behavior of the substance hydrogenated than by the hydrogen.

Finally, the data give an experimental determination of the variation of the equilibrium constant, K , as a function of temperature from -190 to 270°C . The data are plotted in Fig. 5. The curve is that calculated from statistical mechanics by Urey and Rittenberg and the points represent values obtained in this investigation.

The Mercury Photosensitized Decomposition of the Deuteroammonias

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A method of preparation of ammonias in which one, two and three hydrogens are replaced by deuterium has been devised. It reveals that the preparation of magnesium nitride from magnesium and ammonia yields amido- or imido-compounds as intermediate stages of great stability. The physical properties of deuteroammonia preparations have been studied. Ultraviolet absorption spectra reveal the presence of all three substituted deuteroammonias in the preparations studied. The mercury photosensitized decomposition of trideuteroammonia is more than ten times slower than the corresponding reaction of ammonia.

THE isolation of deuterium oxide from water by processes of electrolytic separation offers the experimental chemist a large field of investigation into compounds in which deuterium has displaced hydrogen. It is evident that the choice of compounds to be studied is very large and choice will at first be best dictated by the use to which the products may be put in testing various physico-chemical theories. It is for reasons of this kind that we have prepared derivatives of ammonia and obtained products which contain ammonias in which one, two and three atoms of hydrogen have been replaced by deuterium. We shall show that this work has led

to interesting conclusions concerning the preparation of magnesium nitride, to important observations concerning the physical properties of the ammonias, to measurements of the absorption spectra of the ammonias for ultraviolet light and to a determination of the relative stabilities of the several ammonias towards collisions with excited mercury.

PREPARATION OF THE DEUTEROAMMONIAS

Three different preparations of the deuteroammonias have been made by allowing the vapor of deuterium oxide ($D_4^{20}=1.1052$) to interact with three different preparations of magnesium nitride. The vapor was allowed to diffuse into an evacuated tube containing the

¹ C. R. B. Fellow from Louvain University, 1933-1934.

magnesium preparation at room temperatures. Ready reaction occurred with evolution of heat, the resulting ammonia being pumped off and condensed in a trap cooled in liquid air. To ensure complete reaction of the water vapor the gas was passed backwards and forwards several times over the magnesium preparation which was finally heated during evacuation to remove any adsorbed gas. Specific gravity determinations by the ordinary gas density method of the dried and redistilled products showed that their densities, relative to that of ordinary ammonia, indicated them to contain 68, 90 and >99 percent of their hydrogen content as the deuterium isotope.

These differences in deuterium content are to be ascribed to the magnesium nitride preparations used. The 68 percent material was prepared from a product obtained by passing dry ammonia over heated magnesium filings. Prior to use it was subjected to evacuation with a good pumping system at ordinary temperatures. The second preparation leading to the 90 percent D product was from a similar magnesium preparation which was however evacuated for 40 hours at 400°C. It is quite evident that such methods of preparation do not yield pure Mg_3N_2 but material in which, depending on the degree of evacuation, greater or lesser amounts of hydrogen remain bound as amido- or imido-groups. This hydrogen would escape the normal analytical methods of identification, but the interaction with deuterium oxide at once exhibits its presence in such preparations. Similar observations as to intermediate stages of decomposition have been made by Frankenburger and Hodler,² by other methods in the case of tungsten powder. For the preparation containing >99 percent of the hydrogen in the form of the D isotope, the magnesium nitride was prepared by the interaction of magnesium filings and purified nitrogen.

PHYSICAL PROPERTIES OF THE DEUTEROAMMONIAS

The specific gravities ($\text{NH}_3=1$), freezing points and boiling points of ammonia and of the three preparations are exhibited in Table I.

TABLE I.

Percentage of Deuterium	0	68	90	99
Specific Gravity ($\text{NH}_3=1$)	1	1.12	1.158	1.174
Freezing Point, °Abs.	195.2	197.9	198.6	199
Boiling Point, °Abs.	239.75	241.7	242.1	242.3

By means of a differential tensimeter, using ammonia as reference, the vapor pressure data of Table II were obtained for the >99 percent ND_3 product.

TABLE II.

T°Abs.	202.3	213	226.1	232.1	238.6
P_{NH_3}	77	184	364	511	714
P_{ND_3}	63	154	313	445	628

Assuming the latent heat of vaporization of ammonia to be 5797 cal. per mole at 1 atmosphere, the vapor pressure curve of the product gives a value for the latent heat of vaporization of ND_3 of 5990 cal. per mole.

ABSORPTION SPECTRA OF THE DEUTERO-AMMONIAS

In Fig. 1 are shown spectrophotometric curves of the ultraviolet absorption of ordinary ammonia and the product containing 68 percent of the heavy isotope. In Fig. 2 similar curves are given for the 68 and 90 percent products. The figures also show the copper arc spectrum for reference purposes and the curves have been lined up therewith with respect to one another.

It is at once evident that the substitution of the heavy isotope has brought about a displacement of the absorption bands to shorter wavelengths. The more complex structure in the principal band of the 68 percent product has been analyzed by Dr. W. S. Benedict who ascribes the structure to the presence of the three deuteroammonia molecules NH_2D , NHD_2 and ND_3 , the displacement to shorter wavelengths being progressively greater with increased substitution in the ammonia molecule. On the laws of chance a product containing 68 percent D should contain approximately 34 percent ND_3 , 44 percent ND_2H , 19 percent NDH_2 and 3 percent NH_3 . A 90 percent D sample should contain on the same basis only 25 percent ND_3 , 3 percent NDH_2 and negligible amounts of NH_3 . It will be seen from a comparison of Figs. 1 and 2 that the spectrophotometric

² Frankenburger and Hodler, Trans. Faraday Soc. **28**, 229 (1932).

curves of the absorption bands are in fair agreement with this calculation and that we have in the ultraviolet absorption spectra a convenient semi-quantitative method of identification of the three deuterioammonias.

These spectra were made with the ammonias at room temperature and 40 mm pressure in quartz vessels 30 mm long. A more penetrating study of these absorptions at other pressures and temperatures is in progress.

THE MERCURY PHOTSENSITIZED DECOMPOSITION OF THE DEUTEROAMMONIAS

To compare the photochemical stabilities of the deuterioammonias relative to that of am-

monia, their decomposition under the influence of excited mercury was studied. The characteristics of the ammonia decomposition under such conditions are already well known.^{3, 4, 5}

APPARATUS

The measurements were carried out in an apparatus an outline of which is shown in Fig. 3. The gas to be studied was withdrawn from the reservoir *A* through the tube *B* to the quartz reaction vessel *D*. During illumination the

³ Dickinson and Mitchell, J. Am. Chem. Soc. **49**, 1487 (1927).

⁴ Bates and Taylor, J. Am. Chem. Soc. **49**, 2438 (1927).

⁵ Melville, Proc. Roy. Soc. **A138**, 384 (1932); Trans. Faraday Soc. **28**, 805 (1932).

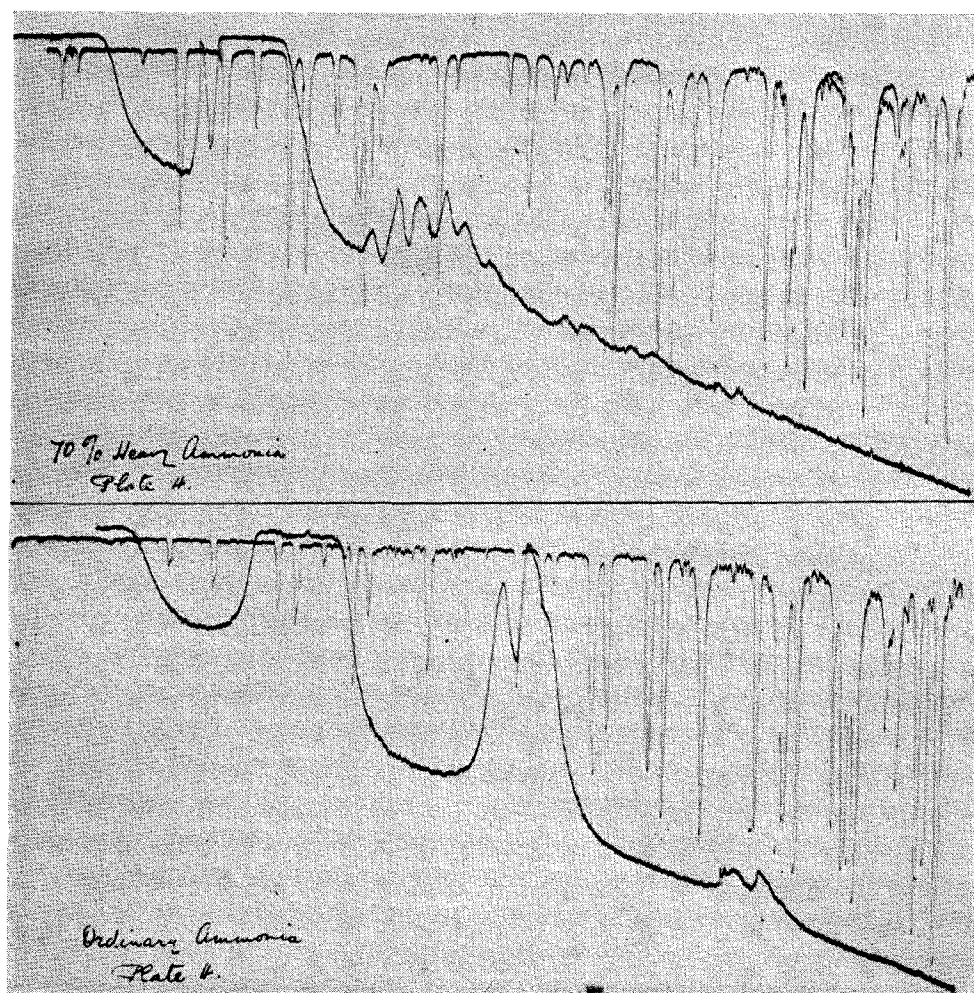


FIG. 1. Ultraviolet absorption spectra of ammonia and deuterioammonia (=68 percent ND₃).

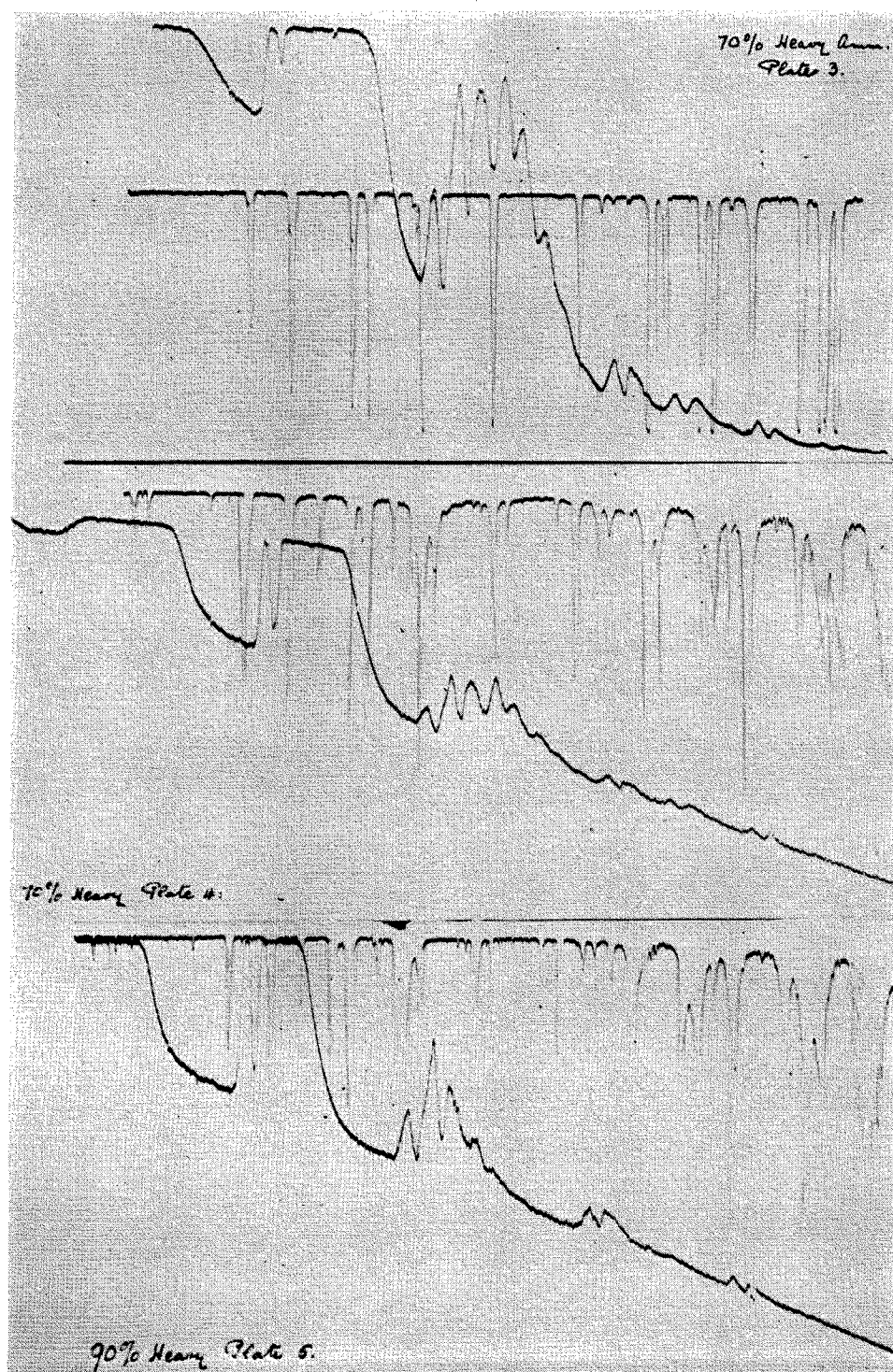


FIG. 2. Ultraviolet absorption spectra of deuteroammonias (=68 and 90 percent ND_3).

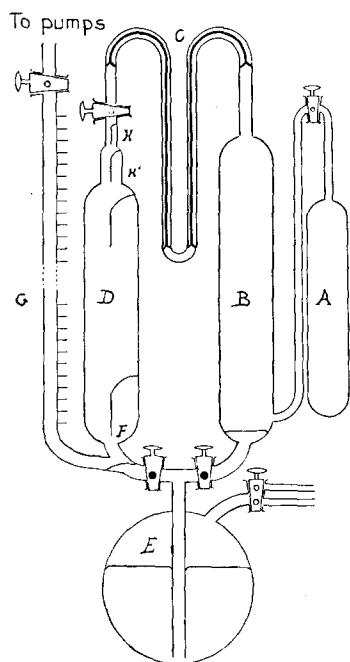


FIG. 3. Apparatus for photosensitized decomposition of ammonias.

mercury from the reservoir *E* was raised in *B* as far as the capillary U-tube, *C*. The pressure of gas in the quartz vessel was measured by means of the manometer *G* with the mercury level in *D* at the lowest pointer level *F*. The rate of decomposition was ascertained after a given period of illumination by condensing the ammonia in the U-tube *C* with the aid of liquid air, reading off the pressure of residual gas so produced on the manometer *G*, the sensitivity of the measurement being increased by raising the mercury level in *D* to the upper pointer level *H*. After this pressure measurement, the condensed gas was again vaporized, mixed by alternately raising and lowering the mercury levels in *B* and *D* and brought back for re-illumination to the quartz vessel as in the initial stages.

LIGHT SOURCE

As source of resonance radiation use was made of the new Hanovia quartz mercury vapor rare gas discharge tube, Sc-2537, developed initially for Raman effect determinations. The discharge tube used was a double-U grid type operating at 5000 volts delivered from the 110 volt a.c. lighting circuit through a 30 milliamper trans-

former. The advantage of this type of tube is that 85 percent of the generated light is in the band at 2537Å and the resonance line is non-reversed. The tube operates at little above room temperatures. With a 20 inch tube consuming 25 watts as much as 40 micro-watts of non-reversed radiation ($\lambda = 2537\text{Å}$) per square centimeter is obtained at 20°C. This is as great an intensity of light of this wave-length as is obtained from the d.c. Alpine Sun Lamp consuming 300 watts. The Sc-2537 type lamp is the most convenient source of mercury resonance radiation that we have thus far employed. The intensity of the light is constant and reproducible over many hours of illumination. Some diminution in light intensity results after the tube has been used during some hundreds of hours, due to the well-known deterioration of quartz in the presence of excited mercury atoms. Our experience in this research is paralleled by that of others in the laboratory with two other arcs of this type, one a 30, the other a 100 milliamper tube.

The light used was filtered through a layer, 1.5 cm thick of 25 percent acetic acid solution in a quartz vessel. This eliminates the light in the region of 2000–2300 to which the gases are photochemically sensitive.

COMPARATIVE RATES OF DECOMPOSITION OF NH_3 AND ND_3

The data in Table III show that the pure deuteroammonia is much less sensitive to photosensitized decomposition than is ordinary ammonia. The experiments were done under strictly comparable conditions at the same initial pressure of the two gases.

TABLE III. Photosensitized decomposition of NH_3 and ND_3 , initial gas pressure, 48.7 mm.

Gas	Time of illumination (min.)	Total press. of non-condensable gas (mm)	ΔP (mm)	$1/R$ (min./mm)	$1/R_0$ (min./mm)	$\bar{P}_{(\text{H}_2 \text{ or } \text{D}_2)}$ (mm)	$P_{(\text{H}_2 \text{ or } \text{D}_2)}$
NH_3	10	0.225	0.225	44.4	38.4	0.084	0.520
	20	0.561	0.336	59.5		0.295	
	20	0.831	0.270	74.0		0.522	
ND_3	30	0.057	0.057	522	410	0.019	0.072
	60	0.132	0.075	806		0.071	
	60	0.190	0.058	1022		0.121	

The successive intervals of illumination are shown in the second column. The cumulative residual gas pressure in mm resulting from the decomposition is shown in the third column, the increase in this pressure in mm for the given time interval is shown in the fourth column. In the fifth and seventh columns are shown the reciprocal rates of reaction and the mean hydrogen pressures during the period of illumination. The sixth column records the reciprocal of the initial rate of decomposition, $1/R_0$, for $P_{H_2}=0$ obtained by plotting the observed reciprocal rates against the mean \bar{P}_{H_2} for the interval and extrapolating the straight line joining the points to zero P_{H_2} . The final column shows the calculated hydrogen pressure at which the rate of reaction is reduced to one-half the initial rate of reaction, R_0 .

From these typical data it can be concluded that the ND_3 molecules are $410/38.4 = 10.7$ times less reactive than the NH_3 molecules under the given conditions of concentration and illumination. In each case, the reciprocal rate of reaction is directly proportional to the mean hydrogen (or deuterium) pressure. This confirms the previous finding of Dickinson and Mitchell for NH_3 . The ND_3 decomposition is, however, much more pronouncedly affected by deuterium pressure than is NH_3 by hydrogen. A deuterium pressure of 0.072 mm reduces the initial rate of ND_3 decomposition to half value whereas a hydrogen pressure of 0.52 mm is required for the NH_3 . This represents a ratio, $52:7.2 = 7.2:1$.

INFLUENCE OF CONCENTRATION OF DEUTERIUM IN THE AMMONIA MOLECULE

The velocities of decomposition of the four ammonias, NH_3 , and samples containing 68, 90 and >99 percent of the hydrogen as D, were illuminated under comparable conditions of light intensity at mean pressures of 40 mm. Table IV shows that the decomposition produced in (a) 30 minutes illumination and (b) 15 minutes illumination decreases progressively as the deuterium content increases. The two series are not comparable one with another since the light intensities differed in the two series.

TABLE IV. Influence of deuterium content on rate.

Percentage of hydrogen as deuterium		0	68	90	>99
Rate of decomposition in $mm \times 10^{-3}/min.$	(a)	16.9	3.83	2.23	1.6
	(b)	51.1	11.45	7.0	5.0

INFLUENCE OF THE PRESSURE OF DEUTEROAMMONIA

The velocity of photosensitized decomposition was studied under constant conditions of illumination, temperature and mercury pressure at pressures of deuterioammonia equal to 40.5, 21.3, 11.0 and 4.9 mm Hg. The deuterioammonia used had a velocity of decomposition relative to that of ammonia corresponding to a preparation containing 80 percent of the hydrogen present in the form of deuterium. The experimental data are presented in Table V in which the columns have the same significance as those of Table III.

Under the same experimental conditions the data of Table VI are typical of those obtained with ammonia.

The values for $1/R_0$ thus obtained, when plotted against the reciprocal of the deuterioammonia pressure, give a straight line. This result which was previously found by Mitchell and Dickinson for ammonia is also true of our ammonia preparation at the pressures used in these studies. The variation in $1/R_0$ is, however, much smaller with ammonia than with deuterioam-

TABLE V. Influence of pressure on reaction rate.

Deutero-ammonia press. (mm)	Time of illumination (min.)	Press. of non-condensable gas (mm)	ΔP (mm)	$1/R$ (min./mm)	$1/R_0$ (min./mm)	$\bar{P}(D_2)$ (mm)	$P(D_2)_\frac{1}{2}$ (mm)
40.4	15	0.189	0.189	79		0.094	
	31	0.365	0.176	176	34	0.277	0.060
	62	0.594	0.229	271		0.480	
21.3	15	0.108	0.108	138		0.054	
	30	0.205	0.097	311	44.5	0.156	0.028
	60	0.326	0.121	500		0.269	
11.0	15.5	0.069	0.069	224		0.035	
	32	0.130	0.061	526	67	0.100	0.014
	45.5	0.190	0.060	758		0.160	
4.9	15	0.042	0.042	358		0.021	
	30	0.080	0.038	794	125	0.061	0.011
	45.5	0.119	0.039	1158		0.099	

TABLE VI.

Ammonia press. (mm)	Time of illumination (min.)	Press. of non-condensable gas (mm)	ΔP (mm)	$1/R$ (min./mm)	$1/R_0$ (min./mm)	$P_{(H_2)}$ (mm)	$P_{(H_2)_i}$ (mm)
42.2	5	0.400	0.400	12.5		0.150	
	10	0.895	0.495	20.2	9.0	0.486	0.385
	15	1.409	0.514	29.2		0.864	
10.8	5	0.171	0.171	29.2		0.064	
	10	0.334	0.163	61.3	12.0	0.190	0.045
	15	0.493	0.159	94.3		0.310	

monia. For ammonia pressures of 10 and 40 mm Hg we find values for $1/R_0$ of 12 and 9 min./mm, respectively, as contrasted with 67 and 34 min./mm for the 80 percent deuterioammonia studied. With both types of ammonia, however, it is evident that the rate of sensitized decomposition increases with increasing ammonia pressure, the conditions of mercury sensitization being maintained constant.

THE KINETICS OF THE DECOMPOSITION PROCESS

The experimental data indicate that the kinetic expression must account for similar effects in the cases of both ammonia and deuterioammonia. The rate of sensitized decomposition increases with initial gas concentration and is inhibited by the hydrogen or deuterium produced. The kinetic picture should account for the quantitative differences in reaction rates, for the more pronounced influence of the deuterium on the decomposition of deuterioammonia than of hydrogen on ammonia, and also for the greater variation in initial rate of decomposition with change in initial deuterioammonia pressure.

Mitchell and Dickinson and Melville derived kinetic expressions both of which led to an equation of the same form for the initial rate of reaction in absence of hydrogen. Melville's approach was the simplest. He assumed that collision with excited mercury led to decomposition,

$$R = -d[NH_3]/dt = k_1[Hg'] [NH_3]. \quad (1)$$

He derived the concentration $[Hg']$ from a stationary state equation,

$$\begin{aligned} d[Hg']/dt &= K - k_1[Hg'] [NH_3] \\ &\quad - k_2[Hg'] [H_2] - k_3[Hg'] = 0, \end{aligned}$$

where K is proportional to the intensity of illumination and the mercury vapor concentration and the third and last terms take into account deactivation by collision with H_2 (k_2) and by radiation of resonance radiation (k_3). The rate then becomes

$$R = \frac{Kk_1[NH_3]}{k_1[NH_3] + k_2[H_2] + k_3} \quad (2)$$

or

$$\frac{1}{R} = \frac{1}{K} \left(1 + \frac{k_2[H_2] + k_3}{k_1[NH_3]} \right), \quad (3)$$

whence

$$\frac{1}{R_0} = \frac{1}{K} \left(1 + \frac{k_3}{k_1[NH_3]} \right). \quad (4)$$

These equations conform with the experimental observations that $1/R$ plotted against p_{H_2} or p_{D_2} for constant $[NH_3]$ or $[ND_3]$ gives a straight line and that $1/R_0$ plotted against $1/[NH_3]$ is also a straight line. The equation may be used to express the initial rate R_0 and the rate R_H at a given hydrogen (or deuterium) concentration $[H_2]$ or $[D_2]$ in the form,

$$(R_0 - R_H)/R_H = k_2[H_2]/(k_1[NH_3] + k_3). \quad (5)$$

If $[H_2]_i$ or $[D_2]_i$ is the hydrogen or deuterium concentration necessary to reduce R to $\frac{1}{2}R_0$ it follows that

$$k_2[H_2 \text{ or } D_2]_i = k_1[NH_3 \text{ or } ND_3] + k_3. \quad (6)$$

All our experimental data are in qualitative agreement with these kinetic equations but a quantitative correlation fails. We ascribe this in part to the experimental conditions of pressure under which we were forced to operate with the deuterioammonias owing to their low reactivity. These high gas pressures effect a broadening of the resonance line which prevents the exact application of the usual principles governing energy exchange between excited atom and colliding molecule.

Comparing ammonia and 80 percent deuterioammonia we find by application of Eq. (4) that the ratio k_1/k_3 obtained from the ratio of the intercept to the slope of the plot of $1/R_0$ against $1/[NH_3]$ gives the two values of 0.19 and 0.045 mm⁻¹, respectively. From these one deduces a ratio of $k_{1NH_3} : k_{1(80 \text{ percent } ND_3)} = 4.2 : 1$. On the other hand, from Eq. (6) with the data in

Tables V and VI we get values for $k_1/k_2=0.011$ for ammonia and 0.0016 for the 80 percent deuterioammonia. We are compelled to assume that k_2 is the same for both hydrogen and deuterium, since Dr. M. G. Evans has found that these gases have exactly the same effect in extinguishing the fluorescence of excited mercury. Hence we conclude that, calculated in this manner, $k_{1\text{NH}_3} : k_{1(80 \text{ percent HN}_3)} = 0.001 : 0.0016$ or approximately 7 : 1. When we compare the value for $k_1 : k_2 = 0.011$ for ammonia with that found by Melville from the data of Mitchell and Dickinson, namely 0.028, we can see that the ratio is dependent to some extent on the experimental conditions.

Whatever the actual magnitudes of k_1 for ammonia and deuterioammonia may be, it is clear that k_1 for the ammonia reaction is several times that for the deuterioammonia decomposition. It follows, therefore, from Eq. (6), that the inhibitory action of deuterium, since it has a quenching efficiency equal to that of hydrogen, must be more pronounced in the case of deuterioammonia than with ammonia. Tables III, V and VI show this quite effectively. Melville has already emphasized the same point in comparing the influence of hydrogen on the sensitized decomposition of ammonia and on the much faster reaction of excited mercury with phosphine. Similarly the relative values of k_1 account for the greater variation of $1/R_0$ for the deuterioammonia reaction with change in initial pressure.

We desire to call attention to the fact that our ratios for $k_1 : k_2$, 0.011 for ammonia and 0.0016 for deuterioammonia are very much less than the values that one derives for these quantities on the assumption that the efficiencies of quenching of resonance fluorescence are a measure of these quantities. Dr. Evans will record elsewhere the details of these measurements, which give him, for the quenching ratios, the values 0.18 for hydrogen and ammonia and 0.06 for deuterium

and deuterioammonia. The hydrogen-ammonia quenching ratio is several fold greater even than the value of 0.028 cited above for $k_1 : k_2$. Also the quenching ratio of ammonia and deuterioammonia is 3 : 1 as compared with the values of 4.2 and 7 : 1 obtained in the preceding calculations. We believe that this should be taken to indicate quite decisively that only a small fraction of the collisions with ammonia or deuterioammonia which are efficient for quenching of fluorescence lead to decomposition of the molecule. From the values of the intercepts in the plots of $1/R_0$ against $1/[\text{NH}_3]$ and $1/[\text{ND}_3]$ we believe that the probability of a molecule decomposing on collision is at least twice as great with NH_3 as with ND_3 . We conclude, therefore, that the bulk of the quenching by these gases must be ascribed to collisions involving the transfer of the excited mercury atom from the 3P_1 to the 3P_0 state. The energy thus accumulated by the ammonias, 0.218 volt, is quite inadequate to produce ammonia decomposition on subsequent collisions. We can assert this with confidence from our knowledge of the absence of homogeneous thermal decomposition of ammonia even at quite high temperatures. With Dr. Evans, we have made several attempts to amplify the theoretical approach to the kinetics of the problem on this basis. While we have been able thus to remove some of the difficulties in the simpler treatment of Melville employed above, we have not been able to bring all the experimental facts quantitatively within the framework of a theory. We are planning further photochemical studies of deuterioammonia which may assist in a final satisfactory solution. In the meantime we wish to express our indebtedness to Dr. Evans for his assistance in these attempts as well as for his courtesy in placing his data on quenching of resonance fluorescence immediately at our disposal.