

4. The primary salt effect upon the iodide-ion catalysis of hydrogen peroxide agrees remarkably well with the theoretical prediction.

5. The hydrogen-ion catalysis of ethyl acetate and the hydroxide-ion catalysis of decomposition of diacetone alcohol are too complicated to be computed by the simple theory. It is shown, however, that this is due to complicating factors involved in the calculation of W .

6. We are quite aware of the many difficulties confronting further advances in the interpretation of this complicated situation and realize that the simple theory is but an approximation. On the other hand, we believe that the factor of greatest importance is known.

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THE THERMAL DECOMPOSITION OF AMMONIA ON THE SURFACE OF OSMIUM

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While there have been many kinetic investigations of catalytic reactions in recent years, it cannot yet be said that there is universal agreement as to the precise function of the catalyst. For a surface reaction, the most likely major action of the catalyst is to lower the energy of activation¹ as compared with the requirement for the corresponding homogeneous reaction, since this is the dominant rate controlling factor for homogeneous reactions.² This action of a catalyst would be more evident were it not for the adsorption of products in some cases, which may have the effect of increasing the apparent energy of activation.³ This action of reaction products may go so far as to crowd the reactant almost completely off the surface and defeat the action of a catalyst which might lower the activation energy requirement to a degree sufficient for rapid reaction.

Thus, in addition to lowering the energy of activation, an effective catalyst must also preserve a suitable adsorption balance between reactants and products.

Osmium was found by Haber and Le Rossignol⁴ to be a very effective catalyst for the synthesis of ammonia, and therefore for its decomposition. We have found that the catalyst with a suitable preliminary treatment assumes a constant activity. The thermal decomposition of ammonia on

¹ Sixth Report of the Committee on Contact Catalysis, *J. Phys. Chem.*, **32**, 1601 (1928).

² "Material chains" would require further elaboration of this generalization.

³ Hinshelwood, "The Kinetics of Chemical Change in Gaseous Systems," 1929, 2d ed., p. 234.

⁴ Haber and Le Rossignol, *Z. Elektrochem.*, **19**, 53 (1913).

osmium seeded, therefore, a suitable case for establishing experimentally the adsorption balance for an effective catalyst.

Experimental Procedure

The apparatus used in carrying out the reactions is shown in Fig. 1. The pump system, not shown in the sketch, consisted of a two-stage mercury diffusion pump backed by an oil pump. The supply of liquid ammonia, kept in cylinder A, was purified by passing over barium oxide to remove moisture and condensed in storage bulb C, which was surrounded with liquid air. The ammonia was alternately frozen and liquefied several times, the solid ammonia being pumped each time to remove fixed gases held in solution.

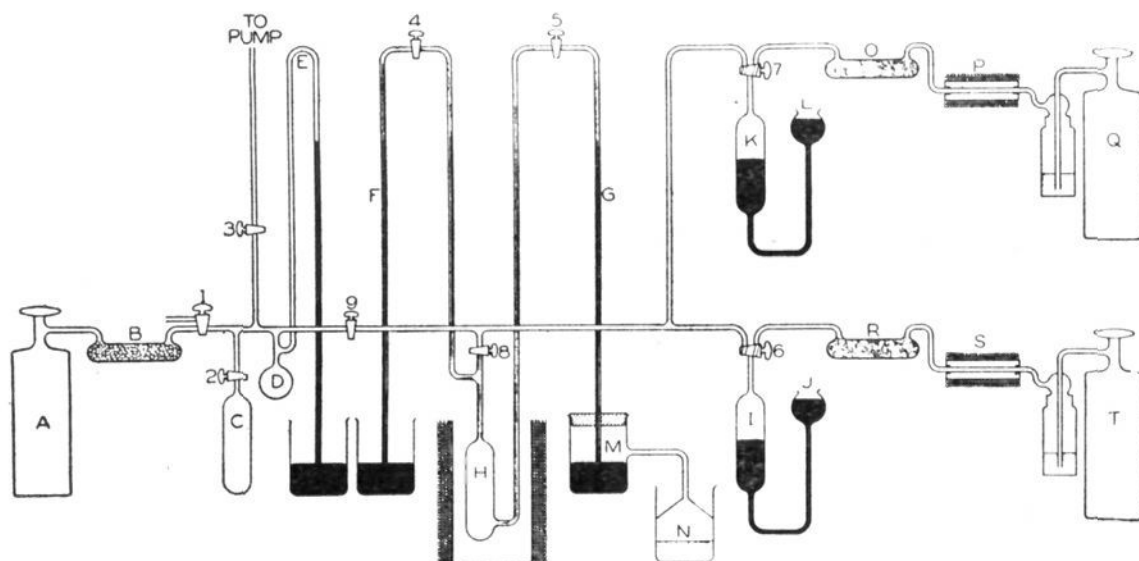


Fig. 1.

The hydrogen for retarding experiments was electrolytic hydrogen from a commercial cylinder T. It was purified by passing through concentrated sulfuric acid and then over finely divided copper maintained at a temperature of approximately 700° by a furnace S and finally over phosphorus pentoxide. The purified hydrogen was stored over mercury in bulb I. The storage bulb was filled and discharged three times in order to remove completely foreign gases which it previously contained.

The nitrogen, obtained from a commercial cylinder and purified in a train similar to that just described, was stored in bulb K.

Considerable difficulty was experienced, especially in the case of the faster reactions, in estimating the initial pressure in the reaction bulb. This difficulty was circumvented by means of the bulb D, which served as a measuring pipet. The pressure readings on barometer E obtained by means of a cathetometer, together with a previous calibration using hydrogen, enabled an accurate estimate of the initial ammonia pressure in the reaction bulb to be made.

The reaction bulb itself was made of quartz. At the outset, the minimum temperature was determined at which the quartz surface itself catalyzed the decomposition of ammonia. This temperature was found to be 610° and was verified from time to time during the course of the investigation.

All temperatures were measured with a platinum to platinum-rhodium thermocouple and a Leeds and Northrup Type K potentiometer. The couple was calibrated at the melting points of silver, zinc, antimony, lead and tin.

The osmium used was in the powdered form and was obtained from the American Platinum Works, its purity being given as better than 99.5%.

Some preliminary experiments indicated a slowly increasing activity of the catalyst. To drive this process of autoactivation to its limit in a reasonable time, the catalyst was seasoned by allowing the ammonia to flow in a slow stream through the reaction bulb with stopcock 5 opened. By regulating the heights of the mercury in the barometer wells the gas could be made to flow continuously over the catalyst and out of barometer G. It was found that after forty-eight hours of seasoning in this way, the activity of the catalyst was constant and results reproducible. The activity of the catalyst was frequently checked by running control reactions especially when the retarding effect of products was being investigated when control reactions were run between each pair of retarded reactions.

The last reaction of each day was allowed to run overnight and the reading next morning taken as the equilibrium reading. This continuous (day and night) operation of the furnace made for close temperature control. It is known that the equilibrium point for this reaction coincides with almost complete decomposition and the amount of ammonia that could be accounted for the next morning was always better than 95% of the ammonia added. Further, since the end-point was obtained on a different day from the early part of the reaction, the results speak for the tightness of the apparatus and for the attainment of thermal equilibrium between the thermocouple and the reaction zone.

Results

Order of Reaction.—In order to establish the apparent order of the reaction, a series of reactions was carried out at constant temperature and varying initial concentrations of ammonia. From these data, the half-life was determined graphically. Table I gives a summary of these results and Fig. 2 gives a series of characteristic reaction curves.

TABLE I
SUMMARY OF RESULTS

| Pressure of ammonia initially added, mm. | Temperature, °C. | Half-life, seconds | n from $t_{1/2} = 1/ka^n$ |
|--|------------------|--------------------|-----------------------------|
| 52.4 | 338 | 78 | -1.43 |
| 102.7 | 341 | 205 | -1.40 |
| 196.9 | 342 | 512 | -1.52 |
| 293.8 | 342 | 1102 | |

If these values are substituted in the equation

$$t_{1/2} = 1/ka^n \quad (1)$$

n has a value between -1.4 and -1.5. The ordinary method, therefore, of determining reaction order leads in this case to a negative value of approximately five-tenths, a result for which we know no precedent.

Temperature Coefficient.—The energy of activation was next determined by carrying out a series of reactions in which the pressure of am-

monia was held constant while the temperature was varied. In these cases, the half-life was again determined graphically. Table II gives the results so obtained.

TABLE II
RESULTS OF EXPERIMENTS

| Temperature (T), °A. | $1/T \times 10^3$ | Half-life ($t_{1/2}$), seconds | Log $t_{1/2}$ | Quarter-life ($t_{1/4}$), seconds | Log $t_{1/4}$ |
|-----------------------------|-------------------|-------------------------------------|---------------|--|---------------|
| 561 | 178.2 | 5970 | 3.776 | 692 | 2.840 |
| 590 | 169.5 | 695 | 2.841 | 99 | 1.996 |
| 614 | 162.9 | 205 | 2.312 | 36 | 1.556 |
| 640 | 155.9 | 37 | 1.568 | 8 | 0.903 |

These data are shown graphically in Fig. 3. As can be seen, the points lie on good straight lines and the best value for the energy of activation

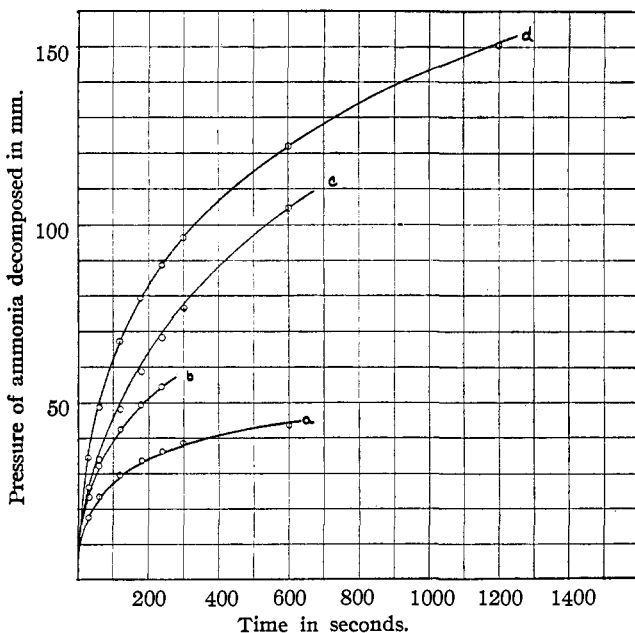


Fig. 2.—The effect of initial pressure on the decomposition of ammonia on osmium at 340°: curve a, initial ammonia pressure, 52.5 mm.; curve b, initial ammonia pressure, 102.7 mm.; curve c, initial ammonia pressure, 196.9 mm.; curve d, initial ammonia pressure, 293.8 mm.

calculated from half-lives and averaged by the method of least squares is 47,600 calories. This same constant evaluated from quarter-lives is 42,200 calories.

Retarding Effects.—The separate effects of added nitrogen, hydrogen and mixed nitrogen and hydrogen obtained as products from previous re-

actions were investigated by carrying out series of reactions in which the temperature and initial pressure of ammonia were held constant and the

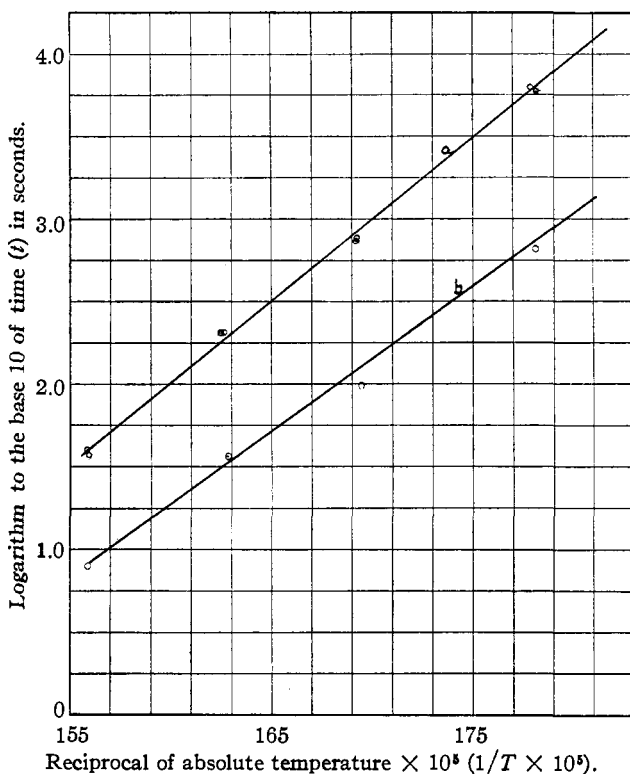


Fig. 3.—Temperature coefficient for the decomposition of ammonia on osmium between 561 and 640° A.; curve a, calculated from half-life; curve b, calculated from quarter-life.

pressure of the retarding gas varied. The results are give in Tables III, IV and V.

TABLE III
RETARDING EFFECT OF NITROGEN

Initial pressure of ammonia, 100 mm. Temperature, 340°

| | | | | | | |
|---|-----|------|------|------|-------|-------|
| Pressure of nitrogen initially added, mm... | 0 | 24.6 | 52.4 | 97.9 | 151.2 | 202.3 |
| Half-life, seconds..... | 205 | 291 | 380 | 565 | 765 | 925 |

TABLE IV
RETARDING EFFECT OF HYDROGEN

Initial pressure of ammonia, 100 mm. Temperature, 340°

| | | | | | | |
|---|-----|------|------|-------|-------|-------|
| Pressure of hydrogen initially added, mm. | 0 | 24.8 | 51.4 | 100.6 | 150.7 | 198.8 |
| Half-life, seconds..... | 205 | 405 | 589 | 1025 | 1805 | 3110 |

TABLE V
RETARDING EFFECT OF PRODUCTS FROM PREVIOUS REACTIONS
Initial pressure of ammonia, 100 mm. Temperature, 341°

| Pressure of products initially added, mm... | 0 | 37.1 | 81.4 | 128.4 | 169.6 |
|---|-----|------|------|-------|-------|
| Half-life, seconds..... | 205 | 415 | 740 | 1100 | 1610 |

These data are shown graphically in Fig. 4. These curves constitute an excellent check on the purity of the gases used since the retarding effect of products obtained by the decomposition of ammonia in the same bulb can

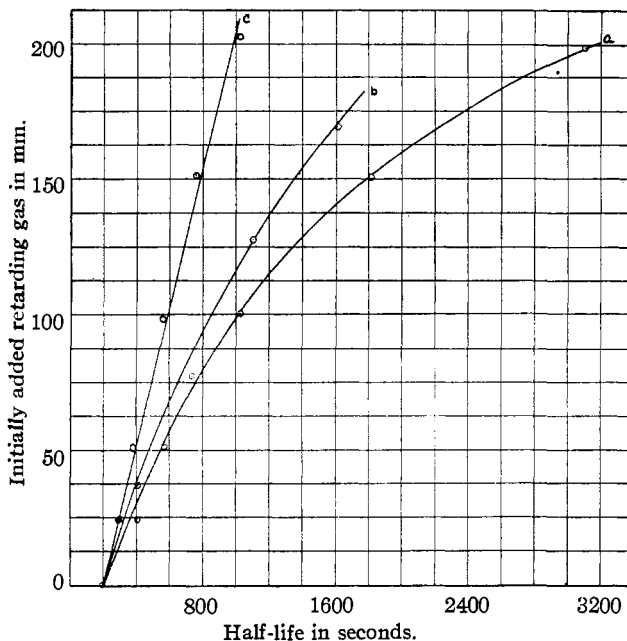


Fig. 4.—Retarding effects of products on the decomposition of ammonia on osmium at 340°: curve a, effect of added hydrogen; curve b, effect of added products; curve c, effect of added nitrogen.

be resolved into two separate retarding effects, one due to nitrogen and one due to hydrogen, and each falls in its proper place on the curves for the individual retarding effects. For instance, in the above table, 128.4 mm. of mercury pressure of products corresponds to partial pressures of hydrogen and nitrogen of 32.1 mm. and 96.3 mm. From the curve for the retarding effect of nitrogen, 32.1 mm. of nitrogen has the same retarding effect as 14.0 mm. of hydrogen. This, then, would make the retarding effect of 128.4 mm. of products equivalent to 110.3 mm. of hydrogen. The observed result taken from the curve is 107.8 mm.

The rate of any heterogeneous gas reaction is a function of the concentration of the reactant in the adsorbed film on the surface and also of the

amount of free surface at any time upon which such adsorption may occur. The rate may therefore be expressed by

$$dx/dt = kf(a - x) \cdot (\text{surface not covered by products}) \quad (2)$$

where x is the amount of reactant decomposed in any time t and a is the original concentration of the reactant.

In order to evaluate the function of concentration shown in equation (2) for this decomposition, Fig. 5 was drawn from the data for a number of characteristic reactions. The abscissas are the ratios $\Delta P/\Delta t$ where Δt is

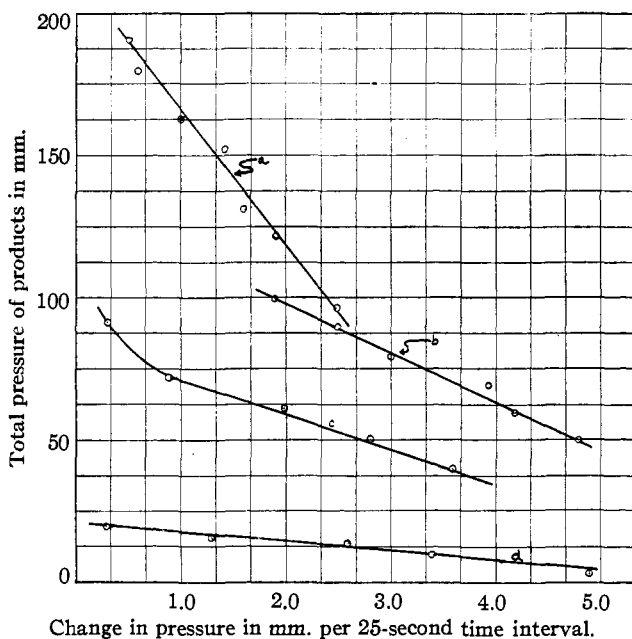


Fig. 5.—Rate of change of pressure—pressure of products for the decomposition of ammonia on osmium: curve a, 100 mm. of ammonia and 81 mm. of products at 340°; curve b, 100 mm. of ammonia and no retarding gas at 338°; curve c, 50 mm. of ammonia and no retarding gas at 316°; curve d, 100 mm. of ammonia and no retarding gas at 271°.

arbitrarily chosen as a twenty-five second time interval and the ordinates are the total pressures of products present. It will be seen that the average curves are all straight lines until near the end of the reaction, even though the pressure of ammonia is changing. This is equivalent to saying that the rate of the reaction is independent of the ammonia concentration and therefore the reaction is of zero order with respect to ammonia. Further, the slope of the lines is a negative one so that the influence of products should be represented by a term of the form

$$(1 - C \cdot \text{pressure of products})$$

The complete rate equation then becomes

$$dx/dt = k(1 - bx) \quad (3)$$

where the symbols have the same significance as before. When this equation is integrated between the limits $x = 0$ and $x = a/2$ and $t = 0$ and $t = t_{1/2}$,

$$kt_{1/2} = 1/b \ln(1 - ba/2) \quad (4)$$

The value of b was determined by substitution of values of $t_{1/2}$ and a from Table I and found to be 0.00585. When this value is substituted in equation (4) and the variation of initial pressure of ammonia on the half-life investigated, it is found that the half-life varies directly as the 1.4 power of the original concentration of ammonia. This is in good agreement with the observed result.

Discussion of Results

When the products of a reaction are so strongly adsorbed that they occupy practically all of the surface and the reactants do not interfere with their adsorption equilibrium which is assumed to be reached, then it may be shown⁵ that the apparent order of reaction is one less than that which would prevail if products were absent. We have presented evidence that the decomposition of ammonia on osmium is of zero order on the free surface. Consequently the maximum retarding effect of products might lead to an apparent reaction order of minus one. We have found values between minus four-tenths and minus five-tenths.

Apparently products are somewhat more strongly adsorbed than ammonia. A large part of the active surface is covered with ammonia and this is cut down as the pressure of products increases until at 316° (curve c, Fig. 5) at equal ammonia and product concentrations, about half of the active surface is covered by each. At a lower temperature (curve d, Fig. 5) the relative surface covering shifts over in favor of products. This state of affairs would exist if the heat of desorption of ammonia about equaled the heat of desorption of products, that for products being slightly the greater. That adsorption equilibrium was really reached with respect to products was established by introducing the additional hydrogen and nitrogen into the hot reaction bulb, first with the ammonia and then two hours before the ammonia. The retarding effects were the same in both cases.

In view of these arguments, the observed energy of activation calculated from the half-life—namely, 47,600 calories—is probably close to the true energy of activation and, remarkably enough, is almost equal to the value found by one⁶ of us and by Kunsman⁷ for the same reaction on tungsten where, for different reasons, the experimental and true values are probably the same.

⁵ Hinshelwood, Ref. 3, p. 212.

⁶ R. E. Burk, *Proc. Nat. Acad. Sci.*, **14**, 601 (1928).

⁷ C. H. Kunsman, *THIS JOURNAL*, **50**, 2100 (1928).

For an effective catalyst, one should have almost all of the active surface occupied and large covering of the surface by reactants as compared with products, *i. e.*, freedom from poisoning. However, an optimum compromise must exist between these absorptive relations in order that maximum reaction rate may be achieved.

Let the reactants be adsorbed in some given configuration. Reaction on the surface involves an endothermic disturbance of this configuration to give an active state, and then an exothermic transformation from the active state to adsorbed products. If the forces holding the reactants in the initial configuration are too strong, the activating step might become more difficult. This factor must be met in achieving large relative surface covering by reactants, which, if the gas phase concentrations are not too different, would imply a larger heat of adsorption for reactants than for products.

From a kinetic analysis of the thermal decomposition of ammonia on osmium, known to be effective for the reverse reaction, it appears that for the latter the active surface would be almost completely occupied, that the surface (up to more than 50% ammonia concentration in the gas phase) would be largely covered with reactants. This appears to be achieved without the heat of adsorption of reactants (nitrogen and hydrogen) rising much above that for ammonia.

These favorable adsorptive relations follow from the evidence already presented and may be seen to be consistent with the empirical equation (3) representing the velocity of the reaction.

Our experimental rate equation is

$$dx/dt = k(1 - bx)$$

where x is the pressure of ammonia decomposed in any time t . If s and s_1 are the fractions of the active surface covered with ammonia and products, respectively, when their pressures are p and p_1 , the adsorption equilibria may be represented by

$$k_1 p(1 - s - s_1) = k_2 s e^{-h/RT} \quad (5)$$

for ammonia, and

$$k_3 p_1(1 - s - s_1) = k_4 s_1 e^{-h'/RT} \quad (6)$$

for products, where h and h' are the heats of desorption of ammonia and products, respectively. If, as we observed, the rate is of zero order with respect to ammonia, $s \cong 1 - s_1$. Employing this relation and solving equations (5) and (6) simultaneously, taking into account that $p_1 = 2x$ and $p = a - x$, where a is the initial pressure of ammonia, gives

$$s_1 = \frac{2k_2 k_3 e^{-h/RT}(x)}{k_1 k_4 e^{-h'/RT}(a - x) + 2k_2 k_3 e^{-h/RT}(x)}$$

If, as assumed, $e^{-h/RT} \cong e^{-h'/RT}$ and $k_1 k_4 = 2k_2 k_3$, the required relations $s_1 = bx$ and $1 - s_1 = 1 - bx$ would follow, and the experimental rate equation $dx/dt = k(1 - bx)$ would thus be derived.

Summary

The thermal decomposition of ammonia on pure osmium has been investigated. The reaction was found to be of zero order with respect to ammonia between the temperatures 561 and 640° A. The retarding effect of products is such that the free surface may be represented by a term, $1 - (\text{concentration of products})$ so that the rate equation becomes

$$dx/dt = k(1 - bx)$$

The energy of activation for the given temperature range calculated from half-lives was found to be 47,600 calories per gram mole and calculated from quarter-lives 42,200 calories.

The physical interpretation of these results is that all gases, both products and reactants, are strongly adsorbed, the latter somewhat more strongly than the former.

Adsorption relations on an effective catalyst have been discussed and compared with those found on the effective ammonia catalyst, osmium.

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[CONTRIBUTION NO. 79 FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

PHOTOCHEMICAL DECOMPOSITION OF CHLOROFORM

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The correlation of the absorption spectrum of a substance with its photochemical behavior has been the subject of a number of recent investigations. The present work was undertaken to explain the absorption spectrum exhibited by chloroform, which is of a type which has so far been but little investigated.

A number of absorption spectrograms of chloroform vapor have been taken, using a small Gaertner spectrograph, and a hydrogen discharge tube as a light source. They confirm the work of Massol and Faucon¹ in showing absorption only in the far ultraviolet if the chloroform is sufficiently pure. Under the experimental conditions, using only moderate lengths (50 cm.) of chloroform vapor, the red bands found by Russell and Lepraik² and by Ellis³ would not be expected to appear. The absorption found is apparently perfectly continuous, and extends to the limit of transmission of quartz. The long wave length edge is not sharp, and moves toward longer wave lengths with increasing pressure. At the lowest pressures, less than 1 mm. of mercury, the absorption is recognizable at 2300 Å. and becomes total just below 2100 Å. Even with 1 cm. of liquid chloroform, the edge is not sharp, although much sharper, and falls about 2530 Å.

¹ Massol and Faucon, *Compt. rend.*, **159**, 314 (1914); *Bull. soc. chim.*, **19**, 350 (1916).

² Russell and Lepraik, *J. Chem. Soc.*, **39**, 168 (1881).

³ Ellis, *Phys. Rev.*, **32**, 906 (1928).