[Contribution from the Fertilizer and Fixed Nitrogen Investigations, Bureau of Chemistry and Soils, U. S. Department of Agriculture]

THE THERMAL DECOMPOSITION OF AMMONIA ON TUNGSTEN, MOLYBDENUM AND NICKEL. I

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The decomposition of ammonia on the surface of hot iron catalysts has been used in experiments to give further information regarding the role played by the catalysts in the ammonia reaction.[1] In order to compare the results of these experiments with the published results of similar tests on tungsten[2] and molybdenum,[3] it was necessary to make tests on drawn tungsten and molybdenum filaments, under the same conditions as for the catalysts. As these tests were made through a wider range in temperature and give results somewhat different from those previously reported, a detailed account of these tests will be given.

The impetus toward this method of studying a heterogeneous or surface reaction and the method of interpreting the experimental result are due primarily to Hinshelwood and his collaborators.[4] They studied the decomposition of ammonia on silica, platinum, tungsten and molybdenum with the view of interpreting the temperature coefficient of the surface reaction as a measure of the heat of activation somewhat as the analogous idea is applied to a homogeneous reaction. They were also interested in the magnitude of this apparent heat of activation in relation to the catalytic activity of the surface.

In some earlier work the homogeneous decomposition of ammonia was sought by Perman and Atkinson[5] and by Bodenstein and Kranendieck[6] in porcelain and quartz vessels, respectively, at temperatures from 677 to 1111°, with the result that all decomposition could be accounted for by a wall, or surface, reaction.

Very recently Schwab[7] has studied the decomposition of ammonia on platinum and tungsten at low pressures with the view to determining the order of the reaction and the effects of the products of the reaction.

The ammonia reaction is a surface reaction of the simpler form where

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[1] Jubilee Meeting, American Chemical Society, Philadelphia, September, 1926; *Science*, **65**, 527 (1927); Institute of Chemistry, Pennsylvania State College, July, 1927; Chemical Section, American Association for the Advancement of Science, Nashville, December, 1927.

[2] Hinshelwood and Burke, *J. Chem. Soc.*, **127**, 1105 (1925).

[3] Burke, *Proc. Nat. Acad. Sci.*, **13**, 67 (1927).

[4] Hinshelwood, "Kinetics of Chemical Changes in Gaseous Systems," Oxford Press, London, **1926**.

[5] Perman and Atkinson, *Proc. Roy. Soc. London*, **74**, 110 (1904).

[6] Bodenstein and Kranendieck, *Nernst-Festschr.*, **1912**, p. 99.

[7] Schwab, *Z. physik. Chem.*, **128**, 161 (1927).

both the reacting substance, ammonia, and the products, nitrogen and hydrogen, are gases and it lends itself to kinetic treatment.

Apparatus

The apparatus consisted of a decomposition chamber of 1 or 2 liters' capacity made of Pyrex glass with heavy tungsten leads. Fig. 1 shows a late type of the chamber in which the filaments were mounted horizontally. In an earlier design the filaments were mounted vertically. The tungsten, molybdenum and nickel filaments were attached directly at one end to heavy tungsten leads and at the other to a fourth common lead through molybdenum springs and platinum strips. The function of the springs was to keep the filaments taut, and of the platinum strips, which shunted the springs, to carry most of the current so that no part of the leads or filament connections became hot when current from the storage battery was used to heat the filaments. The chamber was attached to a high vacuum system and mounted so that it could be surrounded by an electric oven and baked to 500° and thoroughly evacuated to a pressure of 1×10^{-6} mm. of mercury. Ammonia gas from a liquid ammonia reservoir, previously dried in contact with sodium, was admitted into the system shown. The ammonia pressure, about one-third of an atmosphere, was read on a McLeod gage. Tank nitrogen and hydrogen were admitted to the system as desired after having been very thoroughly treated and dried by passing each gas over hot copper filings, calcium chloride, fused potassium hydroxide, a very hot tungsten spiral filament and through a liquid-air trap. A mercury trap, not shown in the figure, separated the decomposition chamber and McLeod gage from the rest of the system when the proper pressure of ammonia or gas mixture was obtained before current was applied to the filament. As the pressure in the chamber doubles when the ammonia is decomposed into N_2 and $3H_2$, the data sought were obtained by observing the rate of increase of pressure on the gage as a function of the temperature of the hot filament.

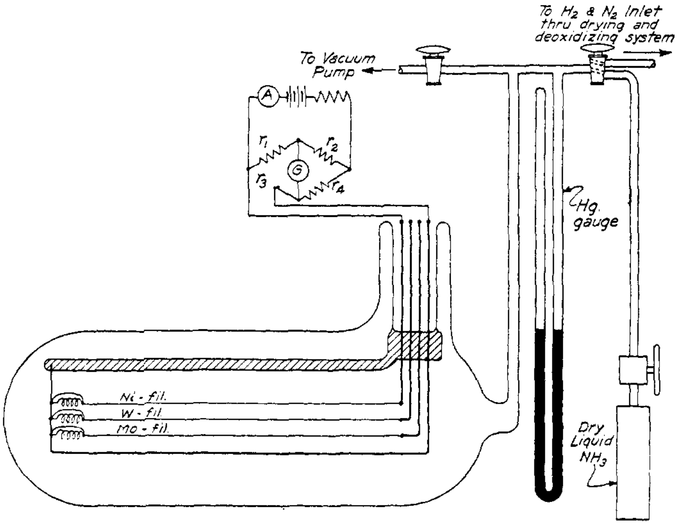

Fig. 1.—Apparatus for the study of the decomposition of ammonia on drawn filaments.

The temperature of the filament was determined by two methods: first, by direct observation with a Leeds and Northrup optical pyrometer, calibrated by the Bureau of Standards, and correcting for the emissivity of the surface and absorption of the glass;[8] second, by employing the temperature coefficient of the resistance of tungsten and molybdenum as determined by Jones[9] and Worthing.[10] These two methods were found to check within about 25° through the range of temperatures employed.

Any discrepancy in temperature was practically constant over the entire range of temperature used, and was therefore not a function of the individual observations or any part of the range.

The fact that the hydrogen formed as a decomposition product is a better conductor of heat than ammonia or nitrogen makes it necessary to increase the current through the filament in order to keep its temperature constant throughout the test or until the greater part of the ammonia is decomposed. The Wheatstone Bridge arrangement shown in Fig. 1 enables this to be done very easily and effectively. The filament is made one arm, r_3 of the bridge, which is comparable to r_4 and quite small in comparison to r_1 and r_2. As the decomposition takes place on the hot filament, the current (A) is increased, keeping r_3 constant. A sensitive galvanometer indicates when this balance is obtained.

The decomposition chamber was cooled by being immersed in a bath of continuously flowing tap water throughout all tests.

As the equilibrium concentration of ammonia with nitrogen and hydrogen at one atmosphere and at this temperature range is less than 1%, all tests were made far from equilibrium and the reaction velocities measured are, therefore, free from the effect of counter reaction.

Experimental Results

The decomposition of ammonia on hot surfaces is a chemical reaction no different from most surface reactions in that it can be expressed by Arrhenius' equation through a limited temperature range at least. Arrhenius stated that the rate of a chemical change $= A\ e^{-E/RT}$ holds equally well for a homogeneous gas phase, or a heterogeneous surface reaction, where R is the gas constant, 1.987 cal./deg.; T, the absolute temperature; e, the base of the Napieran logarithm, and A and E are constants.[11] In general A has to do with the number of reacting molecules at a given temperature T; E has the form of energy and is expressed in calories per gram molecule and can be obtained from the temperature coefficient of the reaction.

Arrhenius' equation may now be used to study the experimental results in order to see to what extent deductions can be made in regard to the relative significance of the A and E constants for a given reaction for various surfaces under identical experimental conditions; or to see to what extent A and E can be used to study catalysts in a heterogeneous system, rather than entering into a theoretical discussion of these constants.

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[8] Foote, Fairchild and Harrison, *Bureau of Standards Technical Paper No. 170,* "Pyrometric Practice," **1921.**

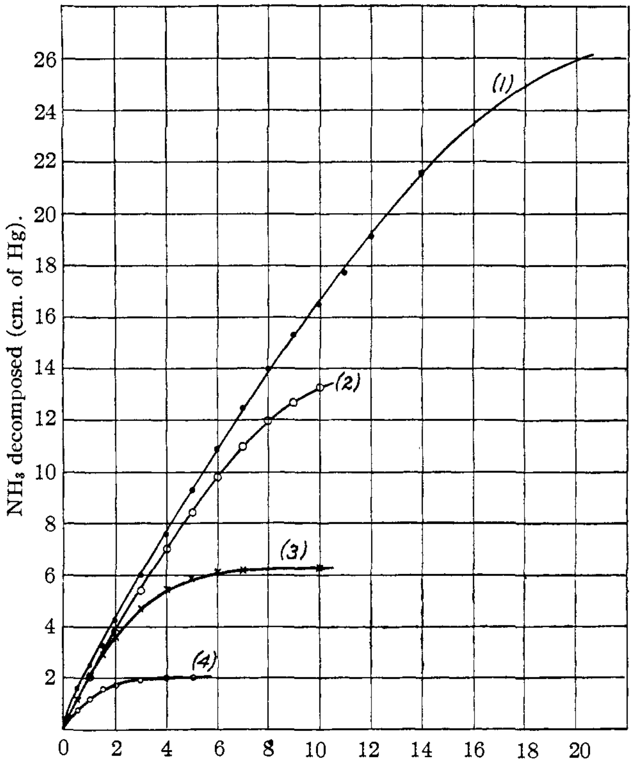
[9] Jones, *Phys. Rev.*, **28**, 202 (1926).

[10] Worthing, *Phys. Rev.*, **28**, 190 (1926).

[11] See Hinshelwood, "Kinetics of Chemical Changes in Gaseous Systems," for the meaning of these constants for the various types of reactions.

The Decomposition of Ammonia on Tungsten

The order of the reaction was determined by the usual method and found to be in general as reported by Hinshelwood and Burke, an apparent zero order. The zero order reaction is given by $dx/dt = k$, where x is the number of moles of ammonia per liter which have been changed to the resultants N_2 and $3H_2$ in time t, and k is the velocity constant which is independent of the concentration of the reactants at any time. Hinshelwood pictures the surface in the zero order as being nearly saturated with reacting gas and as molecules react and leave the surface others at once are adsorbed, so that the rate of reaction is constant regardless of the diminishing concentration in the gas phase. However, at sufficiently reduced pressure a point is reached where the surface is no longer saturated and the reaction becomes unimolecular.



Initial pressure: (1) 26.5 cm.; (2) 13 cm.; (3) 5.8 cm.; (4) 1.6 cm.
Fig. 2.—The decomposition of ammonia on a short tungsten filament at 1100°.

Typical examples of the results for tungsten are given in Fig. 2, where the ammonia decomposed as measured by the increase in total pressure in cm. of mercury is plotted against the time, for initial pressures of ammonia of 26.5, 13.0, 5.8 and 1.6 cm. Each experiment was started with pure ammonia, that is, free from excess of either H_2 or N_2. The time for one-half of the ammonia to decompose, which is a convenient measure of the rate, is 7.6, 3.7, 1.7 and 1.0 minutes for the respective pressures, instead of 7.6, 3.73, 1.66 and 0.46 minutes, which are calculated from the ratio of the initial ammonia pressures. In a unimolecular change all "half times" would be equal. There is a tendency in these data and all tests for the "half time" to become less dependent on pressure at the lower pressures, which may mean that at the lower pressures the reaction is tending toward a unimolecular form.

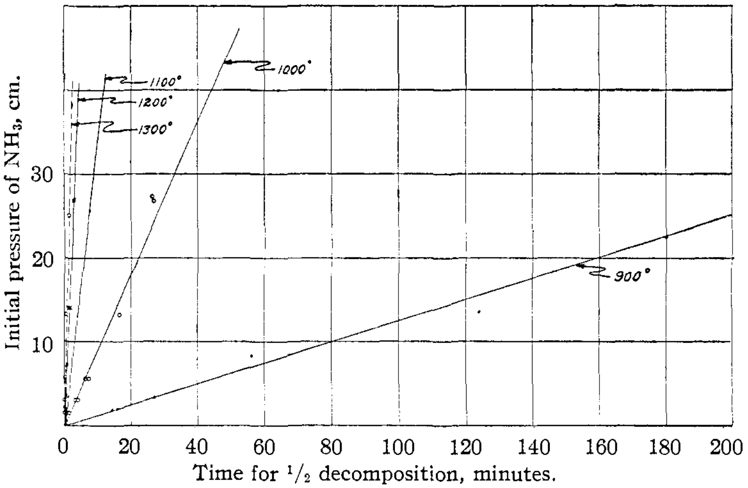
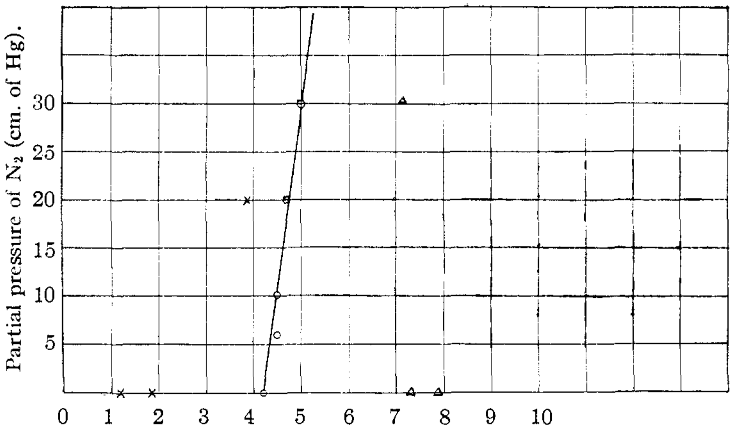


Fig. 3.—The decomposition of ammonia on a short tungsten filament from 900 to 1300°.

In Fig. 3 we have the results of tests at 900, 1000, 1200 and 1300°. The "half time" is here plotted against the initial ammonia pressure. This again shows that the zero order test holds throughout the entire temperature range.

Figs. 2 and 3 are from early data on short filaments and under conditions where the exact temperature was not well enough known to give dependable values of the temperature coefficient, although the temperature was kept constant in the test for the order of the reaction as the gas pressure was varied. The "half time" or relative activity from Figs. 2 and 3 cannot therefore be directly compared with the values obtained later under improved experimental conditions.

The next important point in regard to the reaction system is the extent to which the reaction rate is influenced by the products of the reaction, N_2 and H_2. Fig. 4 gives the times required for the decomposition of one-half of the ammonia where 10 cm. was the initial ammonia pressure. To this initial ammonia pressure of 10 cm. were added, in a series of experiments, varying quantities of very carefully deoxidized and dried nitrogen, representing, respectively, 5, 10, 20 and 30 cm., and the rate of decomposition of ammonia was noted for a given temperature, 950°. The pure tungsten filament was 0.18 mm. in diameter and 18 cm. long. We note that the large dilution with nitrogen has relatively little effect on the rate for a given state of activation of the surface. The slope of the curve drawn through the points is a measure of this effect. However, a far greater effect is caused by subjecting the surface to heat treatments. For example, the effect of glowing the tungsten filament in a vacuum at 1600°



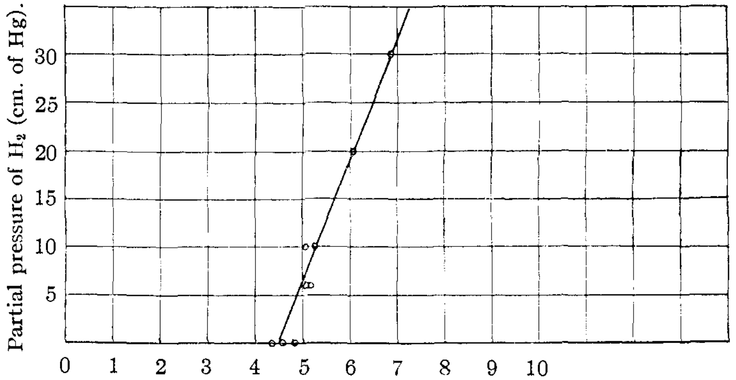
Time (min.) required for $^1/_2$ decomposition of NH_3 (initial pressure 10 cm.). OO A constant state of activity. XX Effect of glowing filament in N_2 at 1000°. ΔΔ Effect of glowing filament in vacuum at 1600°.

Fig. 4.—The effect of heat treatment and nitrogen on the rate of decomposition of ammonia on pure tungsten at 950°.

is to decrease the activity of the surface. This is shown by a doubling of the time for one-half decomposition, while an appreciable activation can be produced by glowing the tungsten filament in nitrogen at 1000°. This variation can best be compared by noting the points on the x-axis corresponding to the decomposition of one-half the ammonia where no nitrogen was present. The average time for the most active surface is 1.5 minutes. A value of 7.6 minutes after heat treatments in a vacuum may have been caused by a removal or modification of the active surface.

Fig. 5 shows a similar test on the same filament where the decomposition of ammonia was studied in the presence of hydrogen. In this case, for the given temperature 950°, hydrogen had a larger retarding effect than nitrogen, but the actual retarding effect was small at this temperature, 950°. Preliminary tests on the activation of the tungsten filament in hydrogen gave no change in activation comparable to those observed in nitrogen.

In general, the small retarding effect due to nitrogen or hydrogen decreased and disappeared at higher temperatures and increased at lower temperatures. The observation of a definite retarding effect of hydrogen and nitrogen is qualitatively in agreement with the results of Schwab.



Time (min.) required for $^1/_2$ decomposition of NH_3 (initial pressure, 10 cm.).

Fig. 5.—The effect of hydrogen on the rate of decomposition of ammonia on pure tungsten at 950°.

Determination of *E* for Tungsten

A very convenient way of representing the decomposition data is to plot the logarithm of the time for one-half decomposition against the reciprocal of the absolute temperature. Ordinarily in applying Arrhenius' equation, the velocity constant, which is the reciprocal of the time for one-half decomposition, is plotted against the reciprocal of the absolute temperature. Since the data for the entire temperature range can in no case be represented by a single straight line, we will adopt the method of resolving the data for a given filament surface into two straight lines, representing the two extremes of the temperature coefficient of the reaction. A smooth, unbroken curve can be drawn through all the points of a series of tests and is the best representation of the data. In this case *E* could be expressed as a function of *T*; then *E* would show a continuous decrease with increase in temperature. In this way a more accurate comparison of the values of *E* for the various surfaces could be made. Further studies will no doubt justify this form of presentation.

Fig. 6(a) gives the results from a very pure 7 mil (diam. 0.018, length 18 cm.) tungsten filament furnished by I. Langmuir of the General Electric Company. The total surface is 1.006 sq. cm., calculated from micrometer measurements of the filament. The value of *E*, which is proportional to the slope of the curve, Fig. 6, is obtained in the following way.

Arrhenius' equation states: rate = $A\ e^{-E/RT}$. Suppose the times for one-half decomposition for temperatures T_1 and T_2 are t_1 and t_2, respectively. Then $1/t_1 = A\ e^{-E/RT_1}$, and $1/t_2 = A\ e^{-E/RT_2}$. Taking logarithms, $\ln t_1 = -\ln A + E/RT_1$, and $\ln t_2 = -\ln A + E/RT_2$; by subtraction

$$\ln t_2 - \ln t_1 = E/R\ (1/T_2 - 1/T_1)$$

whence

$$E = \frac{R(\ln t_2 - \ln t_1)}{1/T_2 - 1/T_1}$$

or

$$E = \frac{2.3026\ R(\log t_2 - \log t_1)}{1/T_2 - 1/T_1}$$

E from the steeper straight line is 45,300, while E_2 from the other line is 36,470 calories.

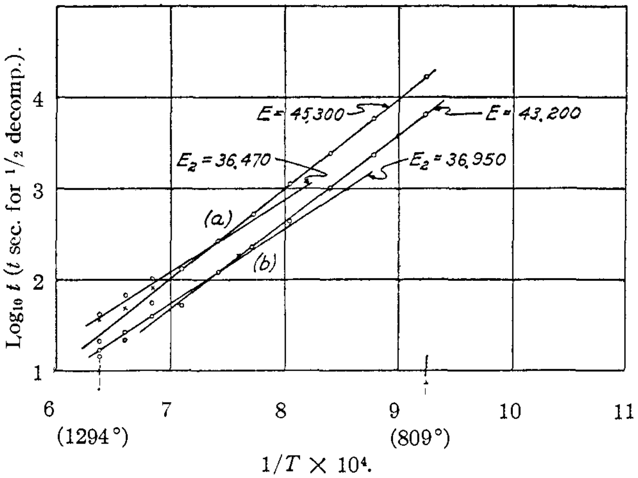


Fig. 6.—The temperature coefficient of the decomposition of ammonia on pure tungsten, for (a) "$^1/_2$ time" and (b) "$^1/_4$ time."

In Fig. 6(b) the time for one-fourth decomposition is taken from the original decomposition runs. The variation of E from that for one-half decomposition is comparable to the experimental error. This gives an added check on the method of determining E as to temperature control and effect of the products of the reaction as the reaction progresses. The temperature of the surface was obtained from a pyrometer calibration curve which was found to be 25° higher than, but parallel to, the calibration curve obtained from the temperature coefficient of tungsten by Jones. Since these two methods check so well, we are reasonably sure that although the exact temperature for a given point may not be known to within 25°, this error has no appreciable effect on the slope of the E curves.

The results for a 10 mil (diam. 0.025 cm., length 16.7 cm.) commercial tungsten filament are shown in Fig. 7, E_1 being 47,220 and E_2 34,800 calories. Similar tests were conducted on other grades of commercial tungsten and on a thoriated tungsten filament. Early tests made on the thoriated tungsten furnished by the General Electric Company and activated in a vacuum according to direction[12] showed no appreciable increase in activity over that of commercial tungsten, as was expected. However, no test, as the increase in electron emission of thoriated tungsten over tungsten, was made on the activity of the thoriated tungsten filament. Then again, as the thorium layer is very sensitive to gases, the ammonia

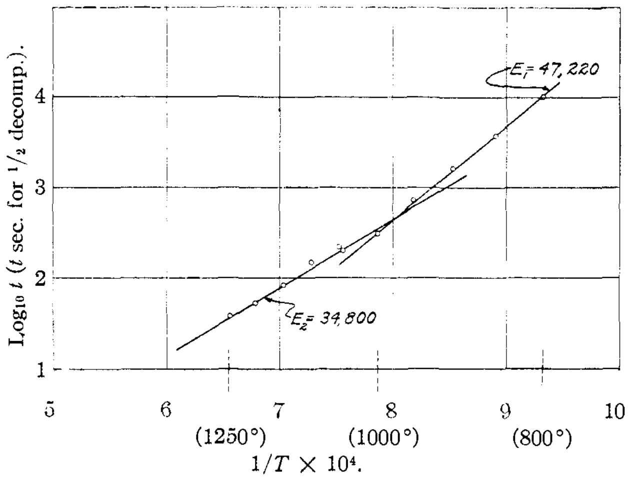


Fig. 7.—The temperature coefficient of the decomposition of ammonia on commercial tungsten.

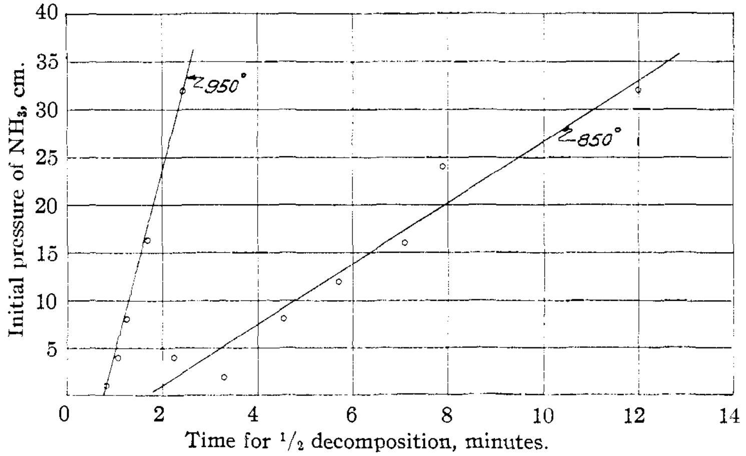


Fig. 8.—The decomposition of ammonia on molybdenum.

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[12] I. Langmuir, *Phys. Rev.*, **22**, 357 (1920).

may have destroyed the added increase in activity expected from the thoriated tungsten. Sufficient tests were not made under the best experimental conditions to say that a properly activated thoriated tungsten surface is not more active than a tungsten surface.

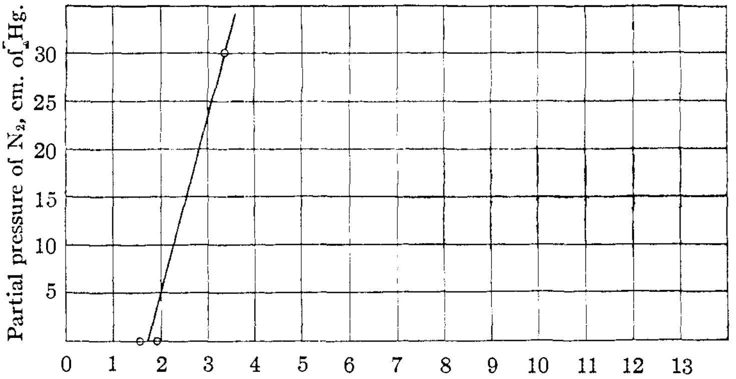

Fig. 9.—The effect of nitrogen on the rate of decomposition of ammonia on molybdenum at 850°.

Decomposition of Ammonia on Molybdenum

A 12 mil (diam. 0.030 cm., length 18 cm.) molybdenum filament from wire furnished by the Fansteel Products Company was used in these tests. Tests on the order of the reaction gave results very similar to those on tungsten, and an apparent zero reaction, Fig. 8. The effect of an initial concentration of nitrogen or hydrogen on the decomposition at 850° is shown in Figs. 9 and 10, respectively. Nitrogen has a much smaller effect than hydrogen. These results do not agree with those recently

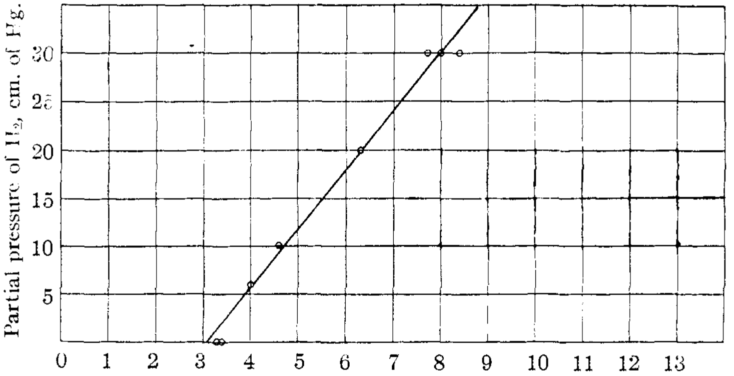

Fig. 10.—The effect of hydrogen on the rate of decomposition of ammonia on molybdenum at 850°.

published by Burke,[3] who finds no retarding effect for hydrogen and a very marked retarding effect for nitrogen. We do not know how to reconcile these two results. Water vapor or oxygen contaminations in the nitrogen used by Burke may have produced the progressive poisoning or retarding effect. Every effort was made to locate the discrepancy, but without success. Another difference has been noted in the value of E, Fig. 11. E_1 for the lower temperatures is 42,700 and at the higher temperature is 31,820 calories, while Burke's value is 53,200 between the temperatures of 824 and 955°. The experimental error is much less than 10,000 calories, the difference between these results and those of Burke.

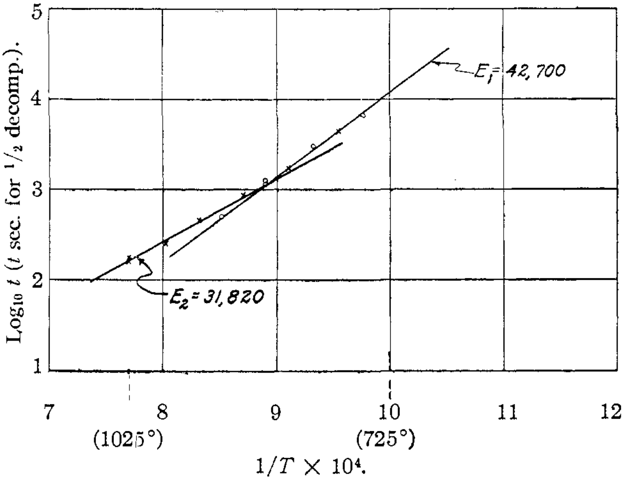

Fig. 11.—The temperature coefficient of the decomposition of ammonia on commercial molybdenum.

The Decomposition of Ammonia on Nickel

Only sufficient tests were made on a good grade of 12 mil commercial nickel wire (diam. 0.030 cm., length 16.5 cm.) to determine the relative position of nickel on a chart, Fig. 12, in respect to tungsten and molybdenum. Again we note a variation of E with temperature, starting at the low rates with values similar to tungsten and molybdenum and falling off with increase in temperature. In Fig. 12 the ordinates are based on one square centimeter of catalyst surface. Attention should be called to the general similarity of all curves and the relative activity of the respective metals for the ammonia reaction.

Discussion of Results

The experimental determinations of E for tungsten and molybdenum are not considered sufficiently reproducible for the lower temperatures to warrant deductions as to the relative values of E/T observed for a given rate of decomposition per square centimeter surface for the two materials. The observed values of E for the tests on tungsten were 45,300, 49,000, 45,250 and 49,750, with an average of 47,320; and for molybdenum, 44,200, 45,750, 44,600, 48,750 and 42,530, with an average of 45,170. Then again, at the lower temperatures, the retarding effects of the products are quite pronounced, so that although the reaction is of apparent zero order, the "true heat of activation" as expressed by Hinshelwood and Burke is not known. Tests are in progress toward a determination of more accurate values of E and a definite evaluation of the effects of the products of the reaction at the lower temperatures. There is no apparent relation between the catalytic activity of tungsten, molybdenum and nickel, and the observed temperature coefficients.

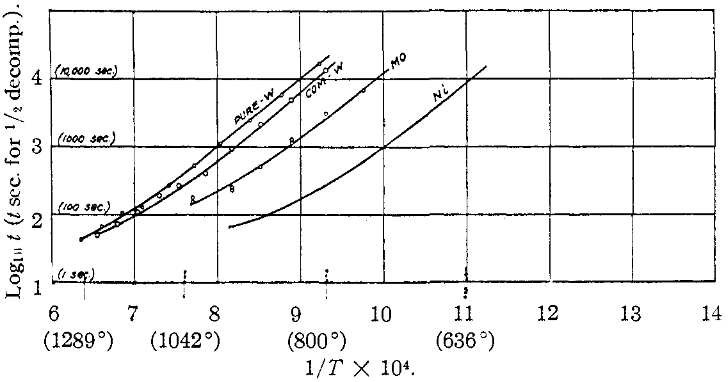

Fig. 12.—The relative activity of metal catalysts per square centimeter of surface for the decomposition of ammonia.

The catalyst surfaces were determined from careful measurements of the diameter and length of the drawn wire filaments in the absence of a better method of obtaining these surfaces. In so far as deductions can be made from the observed temperature coefficient and the measured surfaces, it would seem that the relative catalytic activity depended primarily on the catalyst surface and therefore on A, which is proportional to the number of molecules of ammonia decomposing per unit time per square centimeter surface. All curves, Fig. 12, are of the same general form and can be thought of as a shift to a higher or lower temperature, respectively.

In view of the fact that in general the log t against $1/T$ relation is curved rather than linear, and that the meaning of the heat of activation as applied to surface reactions is not too well understood, we prefer to speak of the results in terms of the temperature coefficient of the surface reaction expressed in terms of E, rather than a heat of activation. The answer to the question as to what extent the catalytic activity of a surface can be expressed in terms of the A or E constants of Arrhenius' equation is also not conclusive. At the lower reaction rates E has the value of about 45,000 calories, independent of the metal surface upon which decomposition takes place. The change of E with increase in temperature is no doubt due to a change of the surface upon which decomposition takes place. This may be due to (1) some change in the metal atoms of the surface with temperature; (2) a change in the amount or nature of the gas adsorbed on the surface with temperature; (3) not to be underestimated, a change of the physical and chemical properties of the composite surface with temperature, where the composite surface is the metal surface atoms in equilibrium with adsorbed gas molecules or atoms at any temperature; (4) a combination of (1), (2) and (3).

In dealing with surface catalysis, where the reactants need to be adsorbed before activation and reaction, the adsorbed gas no doubt has far different properties than in the gas phase. Likewise, the surface metal atoms in contact with gas would be expected to be different from atoms within the solid, so that the combination of the gas or gases on the metal surface presents a problem of the chemistry and physics of a fourth state, as considered by William B. Hardy, where the four states are: gases, liquids, solids and surfaces.

The results in Fig. 4, showing the activation of tungsten and similarly of molybdenum by glowing in an atmosphere of nitrogen, indicate the importance of the activation of a surface.

It seems of prime importance to know more of the physical and chemical properties of the catalyst surface at the temperature and conditions at which the catalyst is operating before much can be said as to the nature of the surface, mechanism of the reaction on the surface and the corresponding meaning of E. Experiments with the view of obtaining this information are now in progress at the Laboratory.

The recently reported work by Davisson and Germer[13] gives us a tool whereby surface phenomena can be investigated, namely, the analysis of diffraction patterns from slow speed electrons produced by potentials of 10 to 400 volts. These results have already shown that a thin film of adsorbed gas at room temperature has a definite solid lattice structure similar to the atoms in a nickel crystal, which lattice completely disappears at about 200° without a removal of the gas from the surface; that is, a solid or frozen lattice structure of adsorbed gas is changed into a 2-dimensional liquid structure by increasing the temperature of the surface from room temperature to 200 degrees or more.

The author wishes to express his appreciation for the interest shown and suggestions received in this work from the Laboratory staff, and especially to Mr. R. A. Nelson for constructing the apparatus and assisting through

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[13] Davisson and Germer, *Phys. Rev.*, **30**, 705 (1927); **31**, 307 (1928).

these studies; also to Messrs. E. S. Lamar and J. W. Westhaver, for assistance in the experimental work.

Summary

The decomposition of ammonia on tungsten, molybdenum and nickel has been investigated as a part of a program designed to give further information in regard to the ammonia reaction and the role played by the catalyst in this reaction. The results are expressed in terms of the A and E constants of Arrhenius' equation.

The decomposition of ammonia on tungsten and molybdenum was apparently of zero order. The reaction rate was decreased at the lower temperatures by both hydrogen and nitrogen.

The value of E as determined from the temperature coefficient was approximately constant for all surfaces at the lower reaction rates, about 45,000, decreasing for the higher temperatures to 35,000 for tungsten, 32,000 for molybdenum and 26,000 for nickel.

The relative catalytic activity of the surface investigated was not given by the observed temperature coefficient of the reaction expressed in terms of E but was given rather in terms of the surface, that is, in terms of A, in so far as comparisons can be made from the measured dimensions of the hot catalyst surfaces.

In general, the conclusions herein reached agree with the results obtained on promoted iron catalysts, which are to be published soon.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES. ORGANO-MOLECULAR INVESTIGATIONS]

INFRA-RED ABSORPTION BY THE S-H BOND

BY JOSEPH W. ELLIS

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The apparent possibility of identifying the carbon-hydrogen[1] and the nitrogen-hydrogen[2] atom pairs as the probable origins of certain series of absorption frequencies in the near infra-red spectra of organic molecules has suggested a search for corresponding frequencies characteristic of the sulfur-hydrogen linkage. The spectra of the mercaptans suggest possible sources in which to look for such absorption bands. Bell[3] has obtained the spectra of several alkyl and aryl mercaptans and sulfides in the spectral region from 1–12μ. The general appearance of these spectra is strikingly similar to that of the corresponding alkyl or aryl amines recorded by Bell.[4]

[1] (a) Ellis, *Phys. Rev.*, **23,** 48 (1924); (b) **27,** 298 (1926).

[2] (a) Ellis, THIS JOURNAL, **49,** 347 (1927); (b) **50,** 685 (1928).

[3] (a) Bell, *Ber.*, **60,** 1749 (1927); (b) private communication.

[4] (a) Bell, THIS JOURNAL, **47,** 2192 (1925); (b) **47,** 3009 (1925); (c) **48,** 813 (1926); (d) **48,** 818 (1926); (e) **49,** 1837 (1927).