warming for an hour the whole mixture was poured on to cracked ice. A solid was obtained. After three crystallizations from absolute alcohol nearly colorless crystals were obtained, which melted at 86°.

Analysis gave: C, 42.63; H, 3.99. Calculated for $C_9H_9O_6N_3$: C, 42.3; H, 3.5.

Therefore, we conclude that the compound is 2,4,6-trinitro-3-ethyltoluene, because we would expect the three nitro groups to take the symmetrical position with reference to each other by direct nitration. Furthermore, we were able to obtain a crystalline compound when equal molecules of the substance and aniline were mixed in alcoholic solution.

UNIVERSITY OF KANSAS,
    LAWRENCE, KANSAS.

THE DECOMPOSITION OF AMMONIA AT HIGH TEMPERATURES.

BY ALFRED H. WHITE AND WM. MELVILLE.

THE fact is well known that ammonia gas decomposes at a red heat into nitrogen and hydrogen, which recombine to only a very slight extent, if at all, on cooling. Deville and Troost[1] showed this very clearly. Ramsay and Young[2] in addition showed the very marked influence exerted by the character and extent of surface in contact with the gas, particularly at the higher temperatures. Their method of work was to pass dry ammonia gas through heated tubes of various materials and filled with various solid substances. Under circumstances to which some reference will be made later, decomposition became practically complete as the gas flowed through the hot tube. Recently Perman and Atkinson[3] have studied the decomposition of ammonia in a different manner. They used a porcelain globe placed in a constant temperature oven and keeping the volume constant, measured the decomposition by the increase in pressure. They found that at high temperatures, such as 1100° C., decomposition was practically complete in their apparatus in twenty minutes. They consider that the volume of the cold stem of their globe is suffi-

[1] *Compt. Rend.*, **56**, 895.
[2] *J. Chem. Soc.*, **45**, 88.
[3] *Proc. Roy. Soc.*, 1904, p. 110.

cient to account for the small trace of ammonia which escaped decomposition, and hold that there is no evidence of a state of equilibrium. They also note the effect of the nature of the contact surface in the markedly different action of an old and a new porcelain globe and the effect of platinizing the interior of the globe.

Practically, all the world's supply of ammonia comes from the destructive distillation of coal, mostly in retorts where it is exposed to the decomposing influence of the red-hot coke and the walls of the retort. Apparently, the decomposition is considerable, for it is calculated that only 12 to 14 per cent. of the nitrogen of the coal passes into the gas as ammonia, while from 25 to 30 per cent. gets into the gas as free nitrogen. There is no absolute proof that this free nitrogen is formed by the decomposition of the ammonia, but the fact that the yield of ammonia is four times as great in the Mond gas producer where the coal is subjected to distillation at a lower temperature and the products are diluted and rapidly swept out by a current of gas, gives considerable support to the theory that much ammonia is decomposed in the retorts of the gas works. Inasmuch, however, as illuminating gas contains nearly fifty times as much hydrogen as ammonia the presence of so large an amount of one of the decomposition products should, under the usual conditions of equilibrium, lessen the decomposition of the ammonia to a measurable degree. It might also be possible that equilibrium is already attained in ordinary practice in the manufacture of illuminating gas so that a longer stay of the gas in the retort would not further increase the decomposition of the ammonia. It was largely with a view to studying the technological points involved that the following experiments were undertaken to throw some light, if possible, on the question of the influence of change of temperature on decomposition, and also the effect of diluting the ammonia with one of the products of combustion and with other gases which are usually present in gas manufacture.

The following experiments were all made with one glass combustion tube and were terminated when the tube cracked in the attempt to investigate the effect of introducing a large amount of water vapor with the ammonia gas. In this apparatus were tested at various temperatures pure ammonia gas, and ammonia diluted with hydrogen, nitrogen, carbon monoxide and water

vapor.   The ammonia gas was generated by dropping pure aqua ammonia on solid caustic soda and was dried by soda-lime.   Its purity, as determined by absorption in acid, was 99.85 per cent. The dry ammonia was collected in a graduated 2-liter gas-holder, capable of being filled with dry mercury and provided with a manometer and an outlet stop-cock bearing a long sweep arm moving over a scale.   By setting the stop-cock at a given point and carefully watching the pressure, the flow of gas could be kept approximately constant.   A visual check on the rate of flow of gases was also afforded by a slightly inclined tube of mercury through which the gas bubbled.   The combustion tube itself was of Jena glass of an internal diameter of 16 mm.   At the exit end it was drawn down and fused to a glass tube of 6 mm. internal diameter in order to cool and convey the gases from the hot zone as rapidly as possible.   A side-arm was fused on near the inlet end provided for the introduction of the gases.   The LeChatelier pyrometer tube of glazed porcelain, 12 mm. in external diameter, passed through the open, large end of the tube. A gas-tight joint was assured by a layer of sealing-wax an inch thick, poured both into the annular space and around the platinum wires inside of the pyrometer tube.   The bare thermocouple was left exposed to the gases and was about 25 mm. from the drawn-down portion of the combustion tube.   The ammonia gas, therefore, passed through the annular space between the pyrometer tube and the combustion tube, and its temperature was measured just as it was leaving the large portion of the tube and was about to be rapidly withdrawn and cooled.   The glass combustion tube was wrapped with asbestos and placed in an iron jacket in a combustion furnace provided with an automatic gas-pressure regulator.   The glass tube was so placed that only about 200 mm. of its length was heated, and of this length about 25 mm. was of the 6 mm. tube and of 175 of the 16 mm.   The plan was that the gases should pass through a uniformly heated tube for about 175 mm. to the constriction, then about 25 mm. more through the hot constricted tube to prevent the thermocouple from being chilled by the cold tube and then be quickly cooled down.   An inspection of the tube, since it has been broken, shows that the result was as anticipated for the tube shows in just the portion planned, the milkiness characteristic of these tubes when heated for a long time to their softening-point.   At the outlet of the combustion tube was a three-way cock, one tip of which

opened into the air and was used during the preliminary manipu-
lations of each test. To the other tip was fused the nitrometer
for collecting the gas. Fused glass joints were used wherever
possible throughout the apparatus. In making an experiment
the furnace was allowed to heat until the temperature had be-
come stationary, and ammonia gas from the 2-liter gas-holder
was run in, the rate being held constant, as far as possible, by
keeping the pressure on the gas-holder constant, and the stop-
cock open at a definite angle. About 0.5 liter was run in first to
sweep out the train, the products passing through the final 3-way
cock into the open air. Then by turning the 3-way cock the
gases were passed into the nitrometer containing standard acid
until the nitrometer was nearly filled with unabsorbed gas, the
duration of the experiment being taken by a stop-watch. The
amount of undecomposed ammonia was determined by titration
of the standard acid, and the amount of ammonia decomposed
from the volume and composition of the gases in the nitrometer.
Since ammonia on decomposition gives three volumes of hydro-
gen to one of nitrogen this method allows the calculation of am-
monia decomposition when either of the gases, hydrogen or ni-
trogen, has been mixed with the ammonia before decomposi-
tion. All gas analyses were made in duplicate with the burette
for exact gas analysis, devised by one of us.[1] All data regarding
per cent. of decomposition and rate of flow have been figured
from the analysis of the contents of the nitrometer, the first grad-
uated gas-holder being merely used to obtain an approximation
of the conditions desired. Every result involves a determination
of the temperature of the furnace, a titration for undecomposed
ammonia, a measurement of the volume of the decomposed gases
in the nitrometer, an analysis of them and a determination of
the time required for their collection, usually considerably less
than a minute. Since every result thus involves these five ex-
perimentally determined factors and an error in any one of which
seriously affects the final figure, it is not strange that occasion-
ally figures are obtained which are not in harmony with the ma-
jority.

Thirteen series of experiments are presented here, each one
involving the measurement of decomposition of at least three tem-
peratures. The temperatures aimed for were 600° C., which rep-

[1] This Journal, **22**, 343.

resented only a small decomposition, 690°, which was about
the highest temperature which the furnace was certain to give,
and an intermediate point of 650°. Owing to the difficulty of
adjusting the furnace to exactly these points, the measure-
ments were made whenever the furnace had reached a fairly
constant temperature in the neighborhood of the point sought.
Practically, all the temperatures come within 13° of the desired
temperature. At first it was intended to keep the rate of flow
of gases constant while varying the temperature. When it was
found that this could not be done with sufficient accuracy wide
variations were purposely introduced in the rate of flow to fur-
nish the ground for the necessary correction. The three curves
of Plate I show the relation between speed and decomposition,
the number of cubic centimeters of gas entering the decomposi-
tion tube per minute being plotted as abscissae and the per cent.
decomposition of the ammonia as ordinates. Curve A gives the
results for the zone of temperature ranging from 587°-613°, and
will be alluded to from its mean temperature as the curve at 600°.
Similarly the mean temperature for Curve B is 650° and for Curve
C 690°. Thirty-six points are thus plotted in the three curves,
every point of all the experiments coming within the limits of
temperature being represented irrespective of whether the gas
was pure ammonia, or ammonia mixed with hydrogen, nitrogen,
carbon monoxide or water vapor. The only results from all the
series not included are those where water vapor and carbon mon-
oxide are simultaneously present, which have been omitted be-
cause there is evidently a secondary reaction taking place. The
numerical data from which Plate I was prepared are given in
Tables I, II and III. Although the points, especially those with
carbon monoxide, scatter somewhat there can be no mistaking
the general directions of the three curves. The fact that the
points range themselves on a curve at all shows very clearly that
the nitrogen, hydrogen and carbon monoxide are acting almost
completely as inert gases, for did the presence of its own volume
of hydrogen or nitrogen have any influence further than dilution
we would not find the same percentage of ammonia undergoing
decomposition in the two cases. Whatever might be the effect
of extreme rates of passage, the curves give us a fairly reliable
means of graphically correcting for the effect of speed within the
limits which our experiments covered.

Tables IV to IX, inclusive, give the numerical data of the experiments on pure ammonia, ammonia with approximately its own volume hydrogen, ammonia with approximately its own volume nitrogen, ammonia saturated with water vapor at room temperature, ammonia with approximately its own volume carbon monoxide, and ammonia with varying amounts of carbon monoxide and saturated with water vapor. The last column in each table gives the percentage decomposition of the ammonia when correction has been made for speed according to the curves of Plate I, to a uniform speed of 125 cc. gases entering the tube per minute. The results thus obtained from Tables IV, V and VI for pure ammonia, ammonia and hydrogen, and ammonia and nitrogen are plotted in Plate II with temperatures as ordinates and per cent. decomposition of ammonia as abscissae. The point at which the rate of decomposition begins to be appreciable is placed at 450° from other experiments and corresponds with Ramsay and Young's statement of "a little below 500°." The twenty-three points arrange themselves on the curve as sati - factorily as could be expected. So far as we can tell from the curve the nitrogen and hydrogen have behaved absolutely as
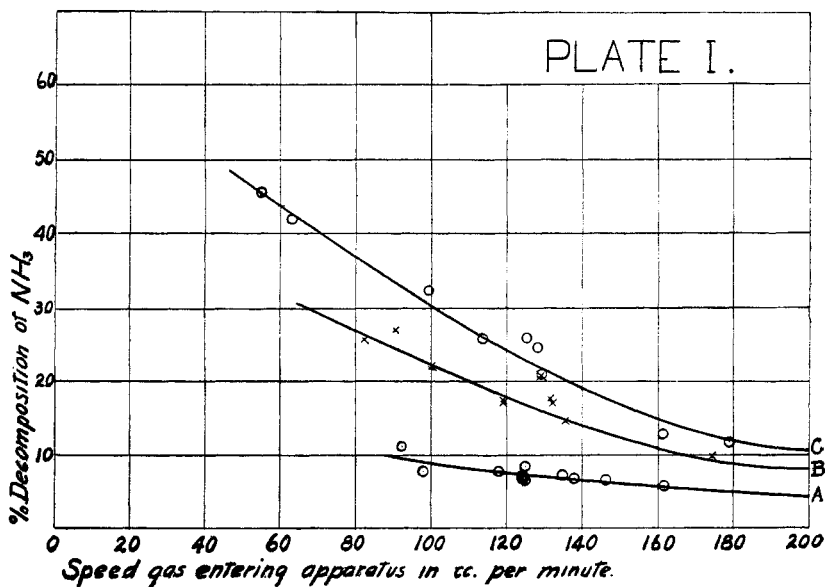
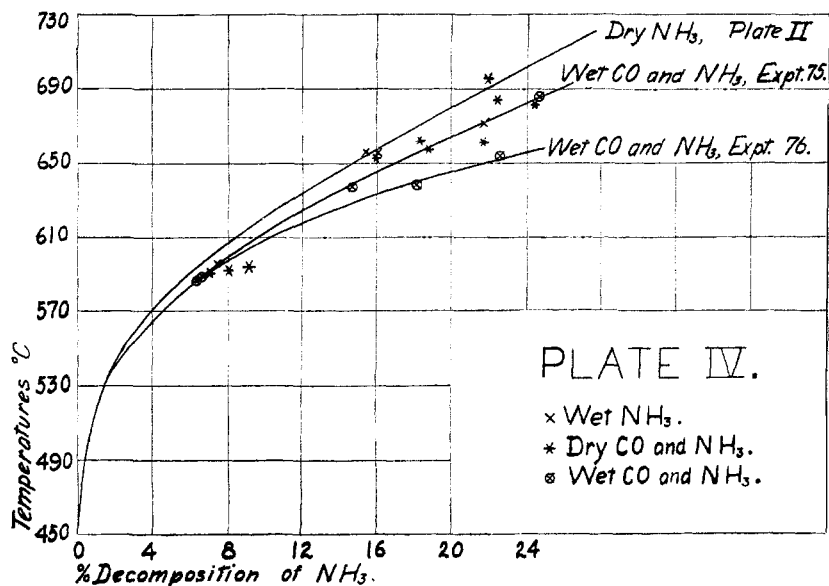Relation between speed and ammonia decomposition.   Curve A = 600° = 587-613°.
B = 650° = 637°-663°.   C = 690° = 677°-703°.
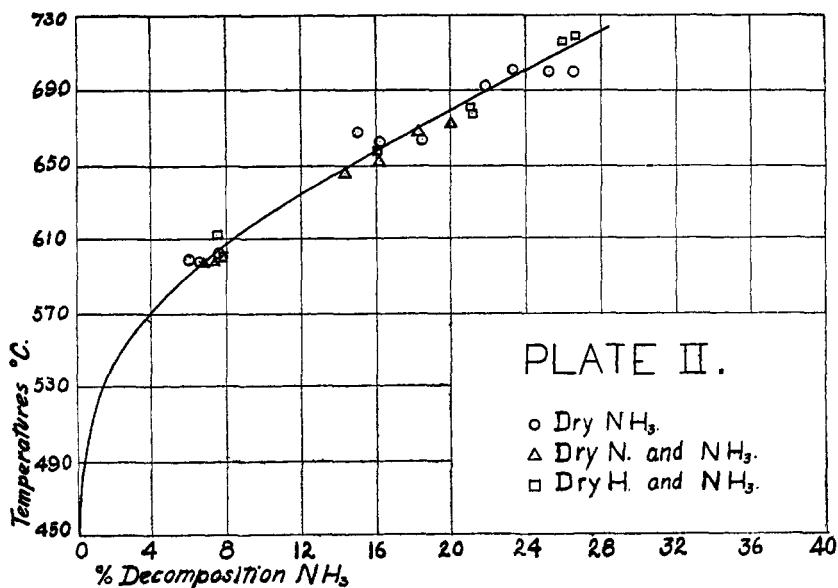
Relation between temperature and ammonia decomposition.
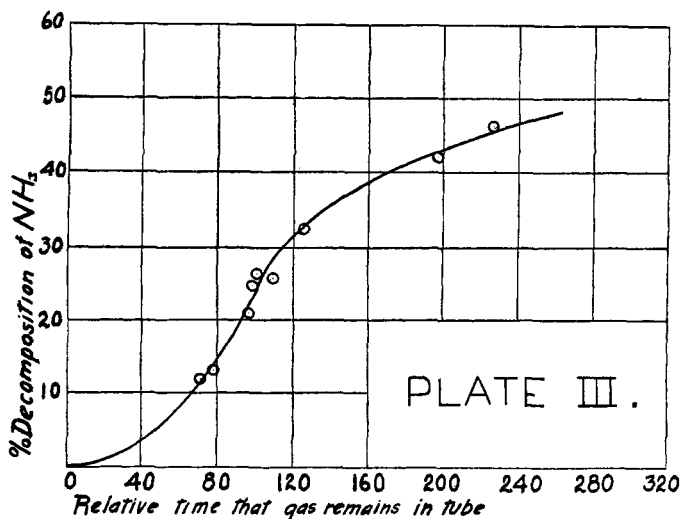
Influence of duration of heating at 690° upon ammonia decomposition.

Influence of carbon monoxide and water vapor upon ammonia decomposition.

indifferent gases. If there were any measurable tendency towards recombination of the nitrogen and hydrogen to form ammonia the equilibrium would be affected by the introduction into the ammonia of a large volume of one of the decomposition products. The proportion of ammonia decomposed does not appear to be affected by the introduction of an equal volume of hydrogen or nitrogen, therefore there is, apparently, no measurable tendency for nitrogen and hydrogen to recombine at these temperatures. If there is no equilibrium to limit the reaction, the decomposition of the ammonia should be complete at any temperature high enough to start decomposition, provided, only, that time enough be given.

The rate of decomposition is influenced to a very large extent by the physical state of the surface with which the gas is in contact. This was strikingly illustrated in one of our experiments. In the same apparatus, previously described, a new glass combustion tube was inserted, but this time the pyrometer tube was of glass instead of porcelain, all other conditions being the same. The decomposition was only about 2 per cent., as much as in the

former cases.   The figures are given below, those for the porcelain pyrometer tube being taken from Plate II.

PERCENT DECOMPOSITION.

Temp. °C.	Porcelain pyrometer tube.	Glass pyrometer tube.
456°	0.0	0.0
568	4.0	0.10
627	10.8	0.15
688	21.5	0.46
723	28.6	0.61

Ramsay and Young, in the paper before referred to, have made somewhat similar observations.   For instance, in their work they report that on passing ammonia through a glass combustion tube quite filled with fragments of broken glass tubing to increase the surface the decomposition amounted to 1.7 per cent., whereas on passing through a glass tube filled with ignited asbestos cardboard which, being porous, should expose a large surface to the gas, the decomposition was practically 100 per cent.

It is apparently not temperature then which is the important factor in causing decomposition, but the nature of the contact surface.   It does not seem probable that substances as inert and nearly alike chemically as glass, porcelain and asbestos would exert any chemical influence.   The difference would seem to be largely one of extent and physical nature of surface, and since surface is the all-important factor the inference follows that the decomposition must take place on the contact of the molecule with the surface.

This hypothesis is, in fact, entirely sufficient to explain all of our experimental results.   The experiments of Ramsay and Young, and of Perman and Atkinson are also in harmony with the theory, so that, although it is not proven, it appears to the authors as the most satisfactory hypothesis to explain the decomposition of ammonia at high temperatures.

TABLE I.—INFLUENCE OF RATE OF FLOW ON DECOMPOSITION OF NH_3 AT 600°.

Expt. No.	Gas used.	Temp. °C.	Speed per minute.	Decomposition NH_3. Per cent.
73.1	CO and NH_3	595	92	11.2
67.1	NH_3	600	98	7.8
71.1	CO and NH_3	591	118	7.7
72.1	CO and NH_3	593	125	8.15
65.1	N and NH_3	597	124	6.8
66.1	N and NH_3	598	124	7.4
63.1	NH_3	599	125	6.5
74.4	NH_3 wet	596	138	6.9
64.1	NH_3	603	135	7.15
61.1	H and NH_3	613	146	6.5
62.1	H and NH_3	602	162	5.7

TABLE II.—INFLUENCE OF RATE OF FLOW ON DECOMPOSITION OF NH_3 AT 650°.

Expt. No.	Gas used.	Temp. °C.	Speed per minute.	Decomposition NH_3. Per cent.
72.4	CO and NH_3	652	82.0	25.7
72.2	CO and NH_3	661	90.4	27.0
74.5	NH_3 wet	655	119.0	17.4
66.2	N and NH_3	646	117.0	16.6
65.2	N and NH_3	652	119.0	17.3
73.2	CO and NH_3	660	129.0	21.0
71.2	CO and NH_2	657	132.0	17.5
64.2	NH_3	663	132.0	17.1
63.2	NH_3	662	135.0	14.4
62.2	H and NH_3	657	174.0	9.8

TABLE III.—INFLUENCE OF RATE OF FLOW ON DECOMPOSITION OF NH_3 AT 690°.

Expt. No.	Gas used.	Temp. °C.	Speed per minute.	Decomposition NH_3. Per cent.	Relative time heated.
64.4	NH_3	700°	55.0	46.2	227.0
73.3	CO and NH_3	695	63.0	42.2	196.0
72.3	CO and NH_3	680	99.0	32.5	125.0
71.3	CO and NH_3	684	113.0	25.9	110.0
64.3	NH_3	700	125.0	26.3	100.0
63.3	NH_3	700	128.0	24.6	98.0
67.3	NH_3	691	129.0	20.9	97.0
61.2	H and NH_3	677	161.0	13.1	77.0
62.3	H and NH_3	680	179.0	12.0	70.0

TABLE IV.—DECOMPOSITION OF PURE NH₃.

Expt. No.	Temp. °C.	Flow NH₃ per minute.	Decomposition. Per cent.	Decomposition corrected by Plate I to 125 cc. per minute. Per cent.
63.1	599	125	6.5	6.5
63.2	662	135	14.4	16.2
63.3	700	128	24.6	25.1
64.1	603	135	7.1	7.6
64.2	663	132	17.1	18.4
64.3	700	125	26.3	26.3
64.4	700	55	46.2	23.2
67.1	600	98	7.8	6.1
67.2	668	122	15.7	15.0
67.3	691	129	20.9	21.7

TABLE V.—DECOMPOSITION OF APPROXIMATELY EQUAL VOLUMES OF H AND NH₃.

Expt. No.	Temp. °C.	Flow H per minute.	Flow NH₃ per minute.	Total flow per minute.	Decomposition of NH₃. Per cent.	Decomposition NH₃ corrected to total flow of 125 cc. per minute. Per cent.
61.1	613	70.3	76.0	146.0	16.5	7.5
61.2	677	75.5	85.5	161.0	13.1	21.1
61.3	719	75.1	79.4	154.5	19.5	26.5
62.1	602	74.6	87.2	161.8	5.7	7.7
62.2	657	85.2	88.4	173.6	9.8	16.0
62.3	680	85.1	93.8	178.9	12.0	21.0
62.4	716	78.8	80.1	158.9	18.3	25.8
62.5	717	20.8	21.7	42.5	44.3	

TABLE VI.—DECOMPOSITION OF APPROXIMATELY EQUAL VOLUMES N AND NH₃.

Expt. No.	Temp. °C.	Flow N per minute.	Flow NH₃ per minute.	Total flow per minute.	Decomposition of NH₃. Per cent.	Decomposition corrected to total flow of 125 cc. per minute. Per cent.
65.1	597	62.2	61.7	123.9	6.8	6.8
65.2	652	63.9	55.1	119.0	17.3	16.1
65.3	667	61.2	56.4	117.6	20.6	18.3
66.1	598	62.8	61.1	123.9	7.4	7.4
66.2	646	61.1	55.8	116.9	16.6	14.3
66.3	672	58.9	54.3	113.2	23.5	20.0

TABLE VII.—DECOMPOSITION OF NH_3 SATURATED WITH WATER VAPOR AT ROOM TEMPERATURE.

Expt. No.	Temp. °C.	Flow NH_3 per minute.	Flow H_2O vapor per minute.	Total flow per minute.	Decomposition of NH_3 Per cent.	Decomposition corrected to total flow of 125 cc. per minute. Per cent.
74.2	655	104	3.0	107.0	19.2	15.5
74.3	670	132	4.0	136.0	19.7	21.7
74.4	596	133	5.0	138.0	6.9	7.5
74.5	655	114	5.0	119.0	17.4	16.2

TABLE VIII.—DECOMPOSITION OF APPROXIMATELY EQUAL VOLUMES OF DRY CO AND NH_3.

Expt. No.	Temp. °C.	Flow CO per minute.	Flow NH_3 per minute.	Total flow per minute.	Decomposition NH_3. Per cent.	Decomposition corrected to total flow of 125 cc. per minute. Per cent.
71.1	591	63.6	54.7	118.3	7.7	7.2
71.2	657	68.7	63.7	132.4	17.5	18.8
71.3	684	57.0	56.0	113.0	25.9	22.4
72.1	593	60.2	64.4	124.6	8.1	8.1
72.2	661	45.1	45.3	90.4	27.0	19.3
72.3	680	50.7	48.7	99.4	32.5	24.5
72.4	652	42.1	39.9	82.0	25.7	16.0
73.1	595	48.8	43.2	92.0	11.2	9.2
73.2	660	68.6	60.4	129.0	21.0	21.7
73.3	695	30.8	32.5	63.3	42.2	22.0

TABLE IX.—DECOMPOSITION OF APPROXIMATELY EQUAL VOLUMES CO AND NH_3 SATURATED COLD WITH WATER VAPOR.

Expt. No.	Temp. °C.	Flow H_2O per minute.	Flow CO per minute.	Flow NH_3 per minute.	Total flow per minute.	Decomposition NH_3. Per cent.	Decomposition corrected to total flow of 125 cc. per minute. Per cent.
75.1	587	4.2	9.2	93.2	106.6	7.9	6.4
75.2	637	4.3	12.7	88.9	105.9	18.7	14.7
75.3	685	4.0	22.6	90.4	117.0	27.2	24.7
76.1	589	5.1	46.0	54.4	105.5	7.9	6.8
76.2	638	4.8	47.1	65.5	117.4	19.6	18.2
76.3	653	4.3	41.6	63.8	109.7	25.9	22.7

The influence of duration of heating upon decomposition of ammonia is shown graphically for one temperature, 690°, in Plate III. The data for this curve are given in Table III.

There remains to be considered the influence of gases like carbon monoxide and water vapor which affect the decomposition

differently from the nitrogen and hydrogen before considered. Some experiments on the influence of these gases, which are not entirely inert, are given in Tables VII, VIII and IX, and in Plate IV. We note that the influence of a small amount of water vapor apparently increases the percentage decomposition of the ammonia, although there is only one set of tests on this point. Dry carbon monoxide increases the decomposition noticeably and rather irregularly. The decomposing influence of moist carbon monoxide is much more marked, increasing with the higher temperature and the proportion of carbon monoxide, as shown in Plate IV, where, for instance, in Expt. 76, a mixture of approximately three volumes of ammonia and two of carbon monoxide saturated with moisture at room temperature shows a decomposition of approximately 22 per cent. at 650° C., as compared with 14 per cent., shown by dry ammonia. In all the tests with carbon monoxide the cyanogen formation was measured by passing the escaping gases into dilute alkali and titrating the cyanide by silver nitrate. The yield of cyanogen was larger with the dry gases than the wet, but was in all cases small, the highest result obtained showing only about 4 per cent. of the ammonia decomposed converted into cyanide. No especial attention was paid to this question, and it is possible that by use of a suitable contact substance the yield could be largely increased.

The results of the foregoing paper may be summarized as follows: The temperature of initial ammonia decomposition is about 450° C. The percentage decomposition of ammonia gas when passing through a hot tube is not affected by dilution of the ammonia by an inert gas like hydrogen or nitrogen, provided the time which each ammonia molecule stays in the hot tube is not changed. In other words, if a liter of ammonia gas is to be passed through a hot tube at the rate of a liter a minute as much of it will be decomposed as if it were diluted with 9 liters of hydrogen or nitrogen, and the mixture passed through at the same rate of a liter a minute. This is confirmatory evidence of the views advanced by others that the decomposition of ammonia is irreversible and that there is no recombination of the nitrogen and hydrogen. The decomposition will, therefore, theoretically, become complete in a sufficient time. Gases, like carbon monoxide and water vapor, increase the rate of decomposition somewhat. The amount of cyanogen formed under the conditions of our

tests is very small. The influence of the nature of the hot sur-
faces, like porcelain or glass, is so great as to warrant the assump-
tion that the decomposition takes place almost altogether on the
impact of the ammonia molecule against the solid surface. With
a rough surface a larger proportion of impinging molecules are
decomposed than with a smooth surface. Experimentally, it
has been found that ammonia gas in contact with a hot glass
tube may be decomposed only slightly, while at the same tem-
perature in contact with an equal extent of porcelain, the decom-
position may be fifty times as great.

It follows as a conclusion that in the destructive distillation
of coal, the decomposition of ammonia may be prevented by
keeping the temperature low, and by lessening, so far as possible,
the time which the red-hot gases remain in contact with rough
substances like coke or the fire-clay retort. The introduction
of blue water-gas into the retorts, as in the Lewes process, should,
by rapidly sweeping out the gases, lessen the ammonia decom-
position. The high yield of ammonia in the Mond gas producer
may be assigned to the combination of lower temperature and
rapid withdrawal of the gases.

CHEMICAL LABORATORY,
UNIVERSITY OF MICHIGAN.

NOTE ON THE CONSTITUTION OF CERTAIN ORGANIC SALTS OF NICKEL AND COBALT AS THEY EXIST IN AQUEOUS SOLUTION.

BY O. F. TOWER.

IN A former paper[1] it was shown that the nickel and cobalt
salts of succinic, malic and tartaric acids exist in a polymerized
state in aqueous solution, and that this polymerized condition
becomes more noticeable the more hydroxyl groups are present
in the molecule; that is, the tartrates are more polymerized than
the malates, and these latter than the succinates. These facts
were brought out by means of measurements of the electrical
conductivity and determinations of the depression of the freez-
ing-point of solutions of these salts. An extension of these de-
terminations[2] to the salts of malonic and tartronic acids showed

1 This Journal, 24, 1012 (1902).
2 Loc. cit., pp. 1020-1022.