Summary

The vapor pressures of zinc and lead have been determined by a direct method and from the values obtained together with those of other observers, satisfactory vapor-pressure equations have been set up.

The heats of vaporization and the entropy of the vapors have been calculated. The values for the entropies are in satisfactory agreement with the predicted values for the entropies of monatomic vapors.

URBANA, ILLINOIS

NOTES

The Dehydration of Ammonium Nitrate.—In the present note we wish (1) to direct attention to certain experiments of Pelouze which seem, for more than eighty years, to have escaped the attention of writers of textbooks and handbooks of inorganic chemistry, (2) to point out the necessary implications of his facts, (3) to show that they make clear the mechanism of the best known of the several modes of decomposition of ammonium nitrate, namely, of the decomposition into water and nitrous oxide, (4) and lastly to report experiments in which we have heated ammonium nitrate with concd. sulfuric, orthophosphoric, and metaphosphoric acid and have obtained nitrous oxide and nitrogen, the presence of which latter gas may be accounted for by a reaction reported by Pelouze and also not reported in the textbooks. The several reactions show much about the several modes of decomposition of ammonium nitrate.

When ammonium nitrate is heated with a large excess of concd. sulfuric acid, about 85% of all of its nitrogen is given off as nitrous oxide and a large part of the remaining nitrogen is evolved in the elementary state. When ortho- or metaphosphoric acid is used, the yield of nitrous oxide is much less and a large part of the total nitrogen is retained in non-volatile combination.

In 1841 Pelouze[1] reported (*a*) that ammonium nitrate heated with two equivalents of concd. sulfuric acid behaves in the normal manner and yields nitric acid, (*b*) that it gives off nitrous oxide (*protoxyde d'azote*) at about 150° when heated with 50 times its weight of concd. sulfuric acid, (*c*) that with a smaller amount of sulfuric acid it yields less nitrous oxide

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[1] Pelouze, *Ann. chim. phys.*, [3] II, 47 (1841). Abegg's "Handbuch der Anorganischen Chemie," Hirzel, Leipzig, 1907, vol. III, p. 314, cites the article but reports it wrongly to the effect that "beim Erwärmen auf 150° treten als Nebenprodukte N_2 und NO_2 auf." Pelouze also reported the abnormal behavior of ammonium nitrite, that it yields nitrogen when warmed with a large excess of concd. sulfuric acid, a reaction which suggests the existence of *nitroso-amide,* at present unknown. His observations on the conduct of ammonium nitrate with sulfuric acid explain the fact that the Kjeldahl method for the determination of nitrogen is not accurate in the presence of nitrates and in the case of certain nitro compounds.

and more nitric acid, and (*d*) that nitric acid may be distilled from a solution of ammonium nitrate in an "enormous" excess of concd. sulfuric acid by maintaining the temperature between 90° and 120°. It is also now known that the nitrate nitrogen of such a solution is quantitatively converted into nitric oxide in the nitrometer. He also reported (*e*) that pure nitrogen is produced by the interaction of nitric oxide (*deutoxyde d'azote*) and ammonia in hot, concd. sulfuric acid solution, and recommended the reaction as a convenient means of preparing nitrogen.

It appears, even without discursive expansion of logic, that the facts, *a, b, c* and *d* above, rigidly imply that a solution of ammonium nitrate in a large amount of concd. sulfuric acid contains some substance, not ammonium nitrate, not nitric acid, and not nitrous oxide, and this substance is derived from ammonium nitrate and is capable, according to the manner in which the solution is treated, of conversion either into nitric acid or into nitrous oxide. That is, the solution contains nitro-amide which, if the solution is heated, is dehydrated by the action of the strong sulfuric acid to produce nitrous oxide, or which is hydrated by the action of the sulfuric acid to yield nitric acid, slowly if the solution is digested at 90° to 120°, and rapidly at ordinary temperature in the nitrometer where mercury is present which reacts with the nitric acid as fast as it is formed.

$$NH_3.HONO_2 \text{ minus } H_2O \longrightarrow NH_2\text{—}NO_2 \begin{cases} \text{minus } H_2O \longrightarrow N_2O \\ \text{plus } H_2O \longrightarrow NH_3 + HONO_2 \end{cases}$$

When a solution of ammonium nitrate in a large excess of concd. sulfuric acid is heated, both hydration and dehydration of the nitro-amide would take place simultaneously, and the greater yield of nitrous oxide, when 50 parts of acid are used, appears to be evidence that under those conditions dehydration takes place more readily. The nitric acid produced in the hot liquid by the reaction of hydration would probably decompose in large part to yield water and oxygen, and nitric oxide which would not escape but would react with the ammonia present in the liquid to produce nitrogen (Pelouze, *e*, above): $4HNO_3 \longrightarrow 2H_2O + 4NO_2 + O_2$; $6NO_2 + 8NH_3 \longrightarrow 7N_2 + 12H_2O$.

We find that oxygen and nitrogen are present in the gas obtained in our experiments in almost precisely the proportions demanded by these equations, that is, 3 volumes of oxygen for 14 volumes of nitrogen.

The experiments reported below are typical of several experiments of each kind which we have carried out.

One g. of ammonium nitrate was dissolved in 30 cc. of cold, concd. sulfuric acid (c. p., d. 1.84) and the solution was immediately heated in an apparatus swept out before and after the experiment with carbon dioxide. Gas evolution commenced at 95° and ceased at 305°. The gas, collected over mercury and measured at laboratory temperature and pressure amounted to 321.5 cc., of which 34.5 cc. was absorbed by potassium hydroxide solution (carbon dioxide and nitrogen dioxide), 252.2 cc. was nitrous oxide (corresponding to about 84% of the ammonium nitrate), 6.4 cc. oxygen (corresponding to about 8.5% of the ammonium nitrate), and 28.4 cc. nitrogen (calculated on the basis of the oxygen, 29.6 cc.).

In a similar experiment, 258.8 cc. of gas was collected, 29.1 cc. absorbed by potassium hydroxide, 258.8 cc. nitrous oxide (about 86.3%), 6.9 cc. oxygen (about 9.2%), and 33.6 cc. nitrogen (calculated on the basis of oxygen 32.2 cc.).

In another experiment the solution of ammonium nitrate in sulfuric acid was allowed to stand for two hours before it was heated. At the end of this time it smelled strongly of nitric oxide. It gave off its gas between 158° and 250°, a total of 213.5 cc. of which 28.3 cc. was absorbed by potassium hydroxide, 157.7 cc. was nitrous oxide (about 53.6%), 6.9 cc. oxygen (about 9.2%), and 20.6 cc. of nitrogen (calculated on the basis of oxygen, 32.2 cc.). The disproportion between the volumes of oxygen and nitrogen indicates some other reaction than those mentioned above. In another experiment in which the solution was allowed to stand overnight before it was heated, only 5% of the calculated amount of nitrous oxide was obtained.

When 1 g. of ammonium nitrate and 30 cc. of 85% orthophosphoric acid were heated together in an apparatus swept out before and after the experiment with oxygen, 70.0 cc. of gas was obtained between 182° and 300°, of which 3.0 cc. was nitric oxide, 17.0 cc. nitrous oxide (about 5.7%), 11.5 cc. nitrogen, and the remainder oxygen. In a similar experiment with 35 g. of metaphosphoric acid, the gas, 254.9 cc., came off between 195° and 270°; 2.2 cc. was nitric oxide, 112.7 cc. nitrous oxide (about 37.6%), 56.7 cc. nitrogen, and the remainder oxygen. With the phosphoric acids the tendency toward dehydration is apparently less and that toward other reactions apparently greater.

CONTRIBUTION FROM THE
LABORATORY OF ORGANIC CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE A, MASSACHUSETTS

TENNEY L. DAVIS
ARMAND J. J. ABRAMS

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A Monochromatic Illuminator for Gas Flames.—When it is desired to examine the spectrum of a metal it is customary to dip a platinum wire into a salt of the metal and then hold it in the flame, repeating the action as need may arise. In making some spectrum photographs the writer recently found a more efficient means of illumination necessary. The essentials of the illuminator which was developed are indicated in the accompanying sketch.

The illuminator consists of a circular trough, made from porcelain or