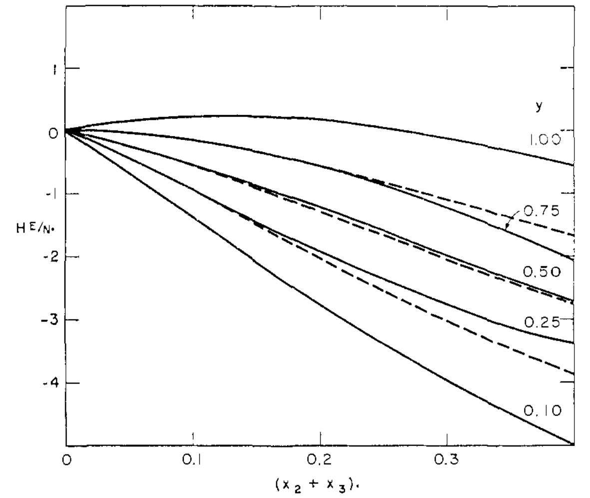

Fig. 4.—Excess enthalpy of α-silver–zinc–cadmium alloys.

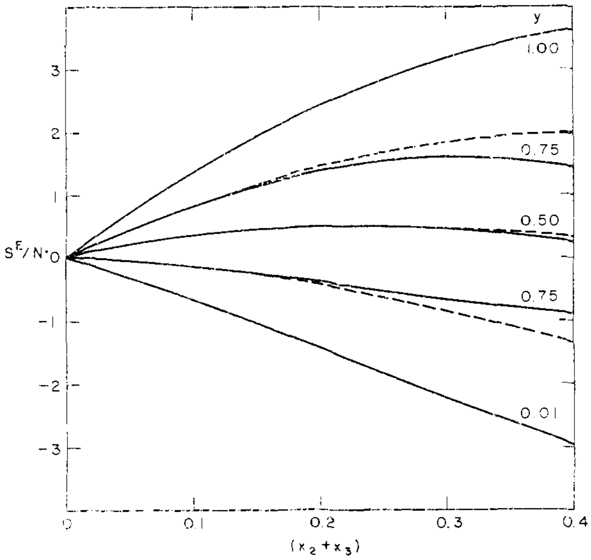

Fig. 5.—Excess entropy of α-silver–zinc–cadmium alloys.

ponents, at constant $(1 - y)x/(1 - x)$ or $yx/(1 - x)$.

The broken lines in Figs. 4 and 5 are y times the top curve plus $(1 - y)$ times the bottom one. The difference between any full curve and the corresponding broken one is the difference in excess enthalpy or entropy between one mole of the alloy and y moles of the silver–zinc alloy plus $(1 - y)$ moles of the silver–cadmium alloy, all with the same mole fraction of silver. In the dilute alloys these differences are extremely small. They are never large for $y = 0.5$. For $y = 0.25$ the differences in excess enthalpy and entropy are both positive, for $y = 0.75$ they are both negative.

$H_{23}^{(0)}$ is intermediate between $H_{12}^{(0)}$ and $H_{13}^{(0)}$, and $S_{23}^{(0)}$ is intermediate between $S_{12}^{(0)}$ and $S_{13}^{(0)}$, but we cannot take this relation too seriously. Assuming that $H_{123}^{(1)}$ was plus or minus 5% of the value which gives the best fit, instead of assuming that it is zero, would destroy this relation for one of the properties. Assuming plus 7% would change the sign of both $H_{23}^{(0)}$ and $S_{20}^{(0)}$. On the other hand $H_{23}^{(1)}$ and $S_{23}^{(1)}$ are an order of magnitude larger than the corresponding function for the binaries with silver. The two effects compensate in the excess free energy. The large values may arise from the fact that the parameters for silver–zinc were determined at higher temperatures and those for silver–cadmium at lower, or it may also be due to the difficulties of extrapolation. Although we have been successful in representing the thermodynamic properties of the α-alloys within their stability range, we have not obtained a unique function which warrants extrapolation.

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Ammonium Ozonide

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The new compound, ammonium ozonide, has been prepared by the low temperature ozonization of ammonia. It has the characteristic five-peaked ozonide spectrum which shows a maximum in the vicinity of 450 mμ. The salt is thermally unstable and starts to decompose above −126°. Its decomposition products are ammonium nitrate, oxygen and water.

Introduction

The reaction of ozone with some of the alkali metal hydroxides to yield orange-red products has been known for some time.[1–5] Kazarnovskii, Nikolskii and Abletsova[6] identified the product of the potassium hydroxide reaction as potassium ozonide. Strecker and Thienemann[5] also observed that the reaction of dilute gaseous ozone with liquid ammonia at −78° created a transitory red color. Upon evaporation of the ammonia, a solid consisting of 98% ammonium nitrate was found. Since all of the known ozonides are red, it was believed that ammonium ozonide had been formed and had subsequently decomposed. Therefore, it was decided to undertake the preparation, isolation and identification of this red product.

(1) Wurtz, "Dictionnaire de Chimie pure et appliquee," Vol. II, 1868, p. 721.

(2) A. Baeyer and V. Villiger, *Ber.*, **35**, 3038 (1902).

(3) W. Manchot and W. Kampschulte, *ibid.*, **40**, 4984 (1907).

(4) W. Traube, *ibid.*, **45**, 2201 (1912); **49**, 1670 (1917).

(5) W. Strecker and H. Thienemann, *ibid.*, **53**, 2096 (1920).

(6) I. A. Kazarnovskii, G. P. Nikolskii and T. A. Abletsova, *Doklady Akad. Nauk S.S.S.R.*, **64**, 69 (1949).

Results and Discussion

Preparation.—An initial reaction was carried out in which dilute gaseous ozone was bubbled through liquid ammonia at −78°. A red coloration, due to the formation of ammonium ozonide, appeared in the liquid ammonia at the initial point of contact, but as soon as the flow of ozone was stopped the color faded. As the temperature was lowered to −100°, a dark red solid was produced.

The reaction was repeated a number of times, but low yields always were obtained, the obvious difficulty of the method being that after about 15 minutes the ammonia froze and the reaction had to be stopped. In order to improve the yield, other methods of preparation were tried. The results of a number of different reactions are shown in Table I.

TABLE I

PREPARATION OF AMMONIUM OZONIDE

Run	NH_3 used, ml.	Temp., °C.	Time, min.	NH_4O_3 formed, mmole	Yield, %[a]
1	10	−100	10	0.48	0.12
2	1	−105	10	0.92	2.3
3	2	−105	15	4.12	5.1
4	3	−105	15	6.16	5.0
5	3	−100	15	5.91	4.8

[a] Based on the amount of ammonia used.

In Run 1, liquid ammonia was treated with dilute gaseous ozone. In Run 2, the inner walls of a U-tube were coated with solid ammonia, and then the dilute gaseous ozone was passed through the tube. As can be seen, the yield was improved.

In order to increase the surface area of the solid ammonia, in Runs 3 and 4 glass wool was placed in the U-tube and then ammonia was condensed into the system. Once again, the yields increased. The possibility of using a solvent for the reaction of ammonia and ozone also was studied. After various solvents had been tried, a solution consisting of 3 ml. of ammonia, 3 ml. of methyl chloride and 10 ml. of ethyl chloride was found to give the best results (Run 5). The yield, however, was not greater than those of Runs 3 and 4.

All attempts to remove the excess solvent by low temperature evaporation resulted in decomposition of the ammonium ozonide.

Characterization.—Since the ozonide ion contains an unpaired electron,[7] all ozonides should be paramagnetic. The electron paramagnetic resonance spectra of potassium ozonide, tetramethylammonium ozonide and the red compound obtained in this study were determined. All of these compounds show the presence of unpaired electrons of the same nature. The results of this study are summarized in Table II. A theoretical discussion of these results appears elsewhere.[8]

The visible absorption spectra of sodium, potassium, rubidium, cesium and tetramethylammonium ozonides have been observed in liquid ammonia solutions.[9] Figure 1 shows that the absorption in the region of 450 mμ is essentially the same for all ozonides and therefore is characteristic of the ozonide ion. These spectra also have been observed in dimethylformamide and the characteristic shape of the peaks is the same, but the maximum is shifted to 460 mμ. The spectrum of the red compound obtained in this study was observed in an ammonia–fluoroform solution. As is also shown in Fig. 1, the characteristic ozonide peak is evident. The use of the ammonia–fluoroform solvent was necessary to insure that the solution would remain liquid at the lower temperature required to stabilize the ammonium ozonide. The slight shift in the maximum of the absorption peak is due to the change in solvent.

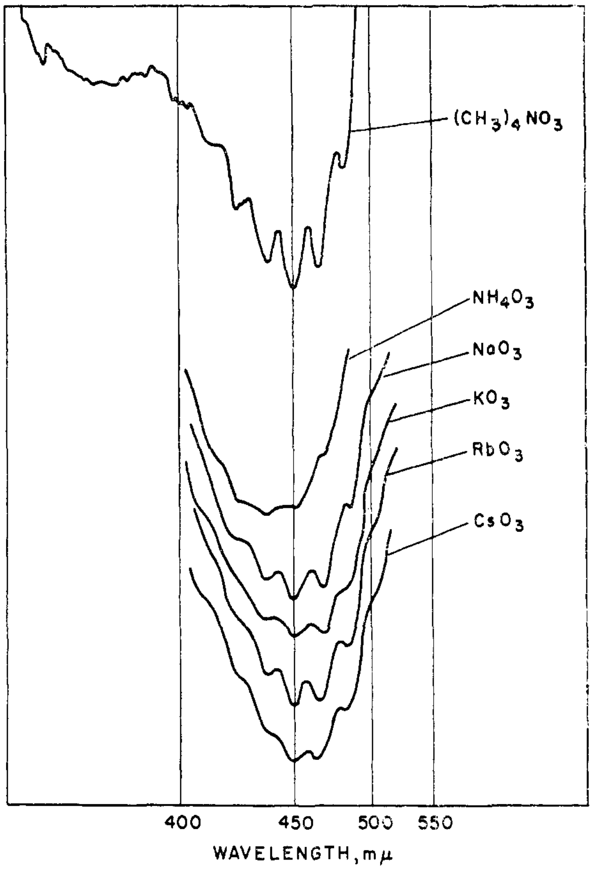

Fig. 1.—Visible spectra of ozonide compounds.

TABLE II

ELECTRON PARAMAGNETIC SPECTRA OF OZONIDES

Compound	g Value
KO_3	2.0124
$(CH_3)_4NO_3$	2.0144
NH_4O_3	2.0119

The empirical formula of ammonium ozonide was deduced from a quantitative decomposition study.

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(7) T. P. Whaley and J. Kleinberg, *J. Am. Chem. Soc.*, **73**, 79 (1951).

(8) S. A. Marshall and D. O. Van Ostenberg, *Phys. Rev.*, **117**, 712 (1960).

(9) I. J. Solomon, A. J. Kacmarek, J. M. McDonough and K. Hattori, *J. Am. Chem. Soc.*, **82**, 5640 (1960).

At first, qualitative observations indicated that water, oxygen and ammonium nitrate were the only decomposition products. The subsequent quantitative reaction, in which 2.92 mmoles of ammonium ozonide was allowed to decompose, produced 0.62, 3.65 and 1.58 mmoles of oxygen, water and ammonium nitrate, respectively. This analysis corresponds fairly closely to the values expected (0.73, 2.92, 1.46) from equation 1, which is postulated to represent the decomposition. The high value for water may be explained by the presence of some water that had been formed during the oxidation of some ammonia.

$$2NH_4O_3 \longrightarrow NH_4NO_3 + {}^1/_2O_2 + 2H_2O \qquad (1)$$

The above results are in agreement with the earlier work,[5] in that the product of the ammonia–ozone reaction at −78° and above is ammonium nitrate, and were confirmed by many other decomposition studies in which the initial quantity of ammonium ozonide was not measured. In these cases, the oxygen/water/ammonium nitrate ratio always was near 1/4/2. The empirical formula of the salt, as calculated from the above data, is $NH_{4.38}O_{3.08}$.

TABLE III

STABILITY OF AMMONIUM OZONIDE

Time, min.	Temp., °C.	Decomposition, %
90	− 78	74.1
90	− 86	65.4
210	− 95	17.3
210	−112	0.6
210	−126	0.0

Thermal Stability.—The decomposition of ammonium ozonide can be followed easily by the rise in oxygen pressure. Some typical results are given in Table III, from which it can be concluded that ammonium ozonide is unstable above −126°.

Experimental

The gaseous ozone, which was prepared by means of a Welsbach C-4 ozonizer, consisted of 3 to 5% by weight of ozone in oxygen. The ammonia was obtained from the Matheson Company and was used without further purification. The sodium, potassium, rubidium, cesium and tetramethylammonium ozonides were prepared by ozonization of the respective hydroxides and extraction with liquid ammonia.[6]

In the decomposition studies, the ammonium nitrate was identified by X-ray diffraction and was measured by independent analyses for ammonium and nitrate ions. The oxygen was characterized by its vapor pressure at −196° (which was 155 mm., compared with a reported value of 157 mm.) and was measured by standard vacuum line techniques. For the water determination, the ammonia solution was allowed to react with sodium hydride, and the hydrogen evolved was measured.

The electron paramagnetic resonance studies were performed with a Varian, 12-inch magnet, electron paramagnetic resonance spectrometer.

The visible absorption spectra were taken on a Beckman Model DK spectrophotometer, and specially designed, low temperature cells were used.[10]

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[10] I. J. Solomon and A. J. Kacmarek, *J. Phys. Chem.*, **64**, 168 (1960).