

QUANTITATIVE THERMOANALYSIS OF EVOLVED AMMONIA. APPLICATION TO AMMONIUM ZEOLITE Y AND SOME TRANSITION METAL AMMINE CHLORIDES

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ABSTRACT

Evolved ammonia is determined quantitatively as a function of temperature, with a suitably modified DuPont 950 thermogravimetric analyzer used in conjunction with a Radiometer automatic titrator. The new technique was applied to ammonium zeolite Y and hexamminenickel(II), tetrammineplatinum(II), and hexaminecobalt(III) chlorides. For the zeolite, the results show that true hydrogen or acid form of the zeolite is obtained after complete loss of ammonia and before the loss of constitutive water. The stoichiometries of the thermal decompositions of the metal amines are rapidly elucidated with this technique. Only the cobalt salt was free of impurity as shown by the experimental results. The quantities and some properties of the impurities in the nickel- and platinum-containing salts are determined. Evolved hydrogen chloride may also be measured with the same apparatus, and was determined during the spontaneous reduction of the intermediate $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, as well as during the reduction of CoCl_2 with hydrogen.

INTRODUCTION

Thermoanalytical methods include a wide variety of techniques ranging from conventional TG to high temperature X-ray diffraction analysis. Among these techniques is gas evolution detection (GE or GED) which utilizes thermal conductivity to indicate the presence of gases other than the carrier gas in effluent streams from conventional DTA or TG¹⁻³. Wendlandt⁴ stated that "perhaps the ultimate in thermoanalytical techniques for the study of gaseous thermal dissociation products is mass spectrometric analysis". These various techniques are essentially qualitative.

In the study of the thermochemistry of ammonium zeolite Y, a technique was developed for quantitatively determining the ammonia evolved as a function of sample temperature during TG of the zeolite samples. This technique was briefly described^{5a}. More recently the method was further refined. The capability of the method is demonstrated for the thermal decompositions of ammonium zeolite Y and of several transition-metal ammine chlorides.

A similar technique has been used by Ma for determination of evolved ammonia

during the decomposition of ammonium polymolybdates^{5b}. Ma apparently used a back-titration technique which is considerably less convenient than the technique presented here. In this paper, we demonstrate the wide applicability of this method for rapidly and simply obtaining basic information for thermal decomposition of ammonia-containing compounds.

EXPERIMENTAL

Two basic instrumental units were used: the standard Radiometer automatic titration unit comprising titrator, pH meter, automatic burette, and recorder (a schematic diagram of the system has been published⁶) and the DuPont 950 thermogravimetric analyzer. The novel purge gas inlet on the glass envelope of the 950 is shown in Fig. 1. This adaptation permits complete purging of the entire system

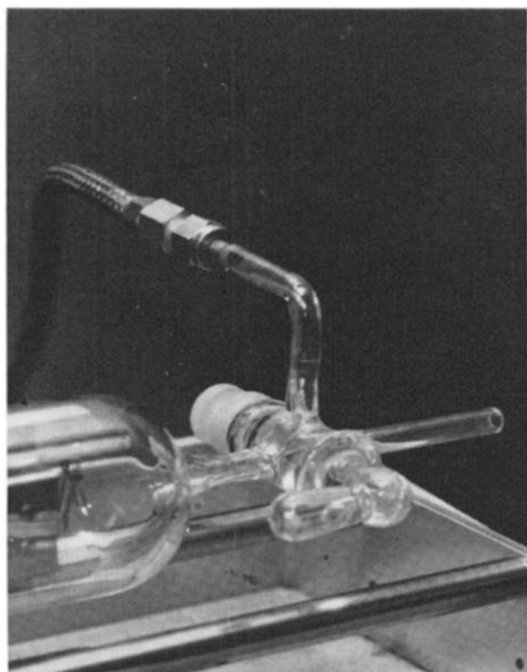


Fig. 1. Purge gas inlet on DuPont 950 thermogravimetric analyzer.

including the housing for the counterweights and servomotor together with the sample pan and reactor. Use of the purge gas inlet on the conventional DuPont 950 results in low ammonia analyses because of entrapment of ammonia in the glass envelope by back-diffusion. The titration vessel and the glass-Tygon tubing conduit for delivering effluent gas from the reactor into the titration vessel are shown in Fig. 2.

The thermobalance heating rate was $5^{\circ}\text{C}/\text{min}$ with a reactor helium purge of $150\text{ ml}/\text{min}$. The helium was first passed through a reactor containing copper wool at 450°C to remove traces of oxygen and then passed through a drying tower containing

“Granusic” brand pelletized P_2O_5 . Hydrogen flowing at ~ 150 ml/min was passed through the desiccant only.

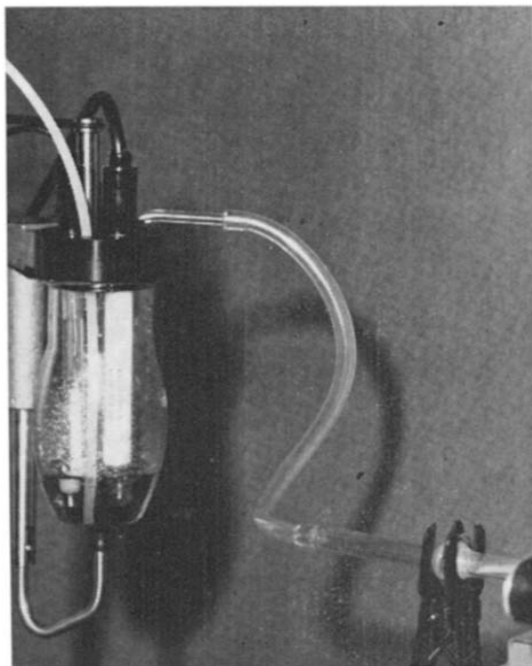


Fig. 2. Effluent gas delivery tube from thermogravimetric analyzer to automatic titrator vessel.

The titrator was set to maintain a pH of 5.00. The titration mixture consisted of 15 ml of 1 M NH_4Cl solution and 1 ml of saturated boric acid. The ammonium salt prevented a drifting pH as a result of dilution of the titration mixture by titrant. The boric acid insured against volatilization of ammonia from the titration mixture prior to neutralization by the titrant. The latter was sulfamic acid having a titre equivalent to 0.200 mg NH_3 /ml. The sizes of the Radiometer burette and sample and the standard solution can be varied so that the burette need not be refilled in the course of a run.

The automatic titrator plotted volume of titrant used *vs.* time. The time axis is readily converted to temperature by a variety of methods. Subsequent to the experiments reported here, the drive shaft of a potentiometer was connected to the cable of the Radiometer recorder. One axis of an X-Y recorder was driven by the EMF of the potentiometer, the other axis by the EMF of the sample thermocouple, thus achieving a direct plot of ml titrant *vs.* temperature.

A computer program was written to calculate and plot the derivative of the ammonia evolution curve and the non-ammonia weight loss (calculated by subtracting the ammonia evolved from the total weight loss at a given temperature). The slopes at each temperature were calculated by fitting three adjacent points to a parabola and calculating the slope at the central point (this procedure was developed

by R. H. Albert of this laboratory). Data points were taken at 5 or 10°C intervals, depending on the nature of the compound under study and the rates of decomposition over different temperature intervals. The computer plotted the original experimental data (TG and evolved ammonia), as well as the derived data.

Grammole ratios are used throughout this paper unless otherwise indicated. Corrections for non-linearity of the Chromel-Alumel thermocouple are unnecessary, since it is well-known that the various reactions studied here are non-equilibrium processes and the temperatures at which the reactions occur depend on such variables as sample size, sample geometry, heating rate, and purge gas flow rate.

Ammonium zeolite Y, and hexamminenickel(II) and tetrammineplatinum(II) chlorides, were prepared by standard published methods, while hexamminecobalt(III) chloride was obtained from Alfa Inorganics, Inc. The purities are discussed below.

The ammonium zeolite Y had the composition 0.42% Na₂O, 23.7% Al₂O₃, and 75.1% SiO₂ (ash basis). The unashed sample contained 4.22% NH₃ and 56.7% ash. The ammonia was determined by the conventional Kjeldahl method. Our results show that the sample lost some moisture after the conventional analysis and prior to the mass-loss studies. The TG curve indicates 65.5% ash and 4.85% NH₃. The ratio of NH₃/AlO₂⁻ calculated from our results and the conventional analyses agreed exactly at 0.94. The Na/Al ratio was 0.03 giving the total cation to aluminium ratio of 0.97, in good agreement with the theoretical value of unity.

RESULTS AND DISCUSSION

Ammonium zeolite Y

The thermogravimetric data for ammonium zeolite Y are shown in Fig. 3. The derivative curve for the ammonia loss shows the two peaks at 270 and 360°C, reported by Cattnach *et al.*⁷. The derivative curve for non-ammonia (water) shows the loss of moisture, peaking at 60°C, and the loss of sorbed or zeolitic water, peaking at 120°C. The loss of constitutive water from the hydrogen zeolite is shown as the peak with the maximum at 670°C.

In Table I are summarized the results of the thermoanalysis of ammonium zeolite Y. Determination of the ratio of chemical water evolved to ammonia evolved is the most definitive method for establishing a sample of "hydrogen" zeolite Y to be

TABLE I
THERMOANALYSIS OF AMMONIUM ZEOLITE Y

	<i>Found</i>	<i>Calc.^a</i>
NH ₃ /AlO ₂ ⁻	0.94	0.94
NH ₃ /H ₂ O ^b	1.94	2.00
H ₂ O ^b /AlO ₂ ⁻	0.475	0.470

^aBased on the conventional analyses and the reactions: 2NH₄⁺ → 2NH₃ + 2HY, 2HY → H₂O + Y⁻ (acid anhydride). ^bConstitutive (chemical) water evolved from 500 to 1000°C.

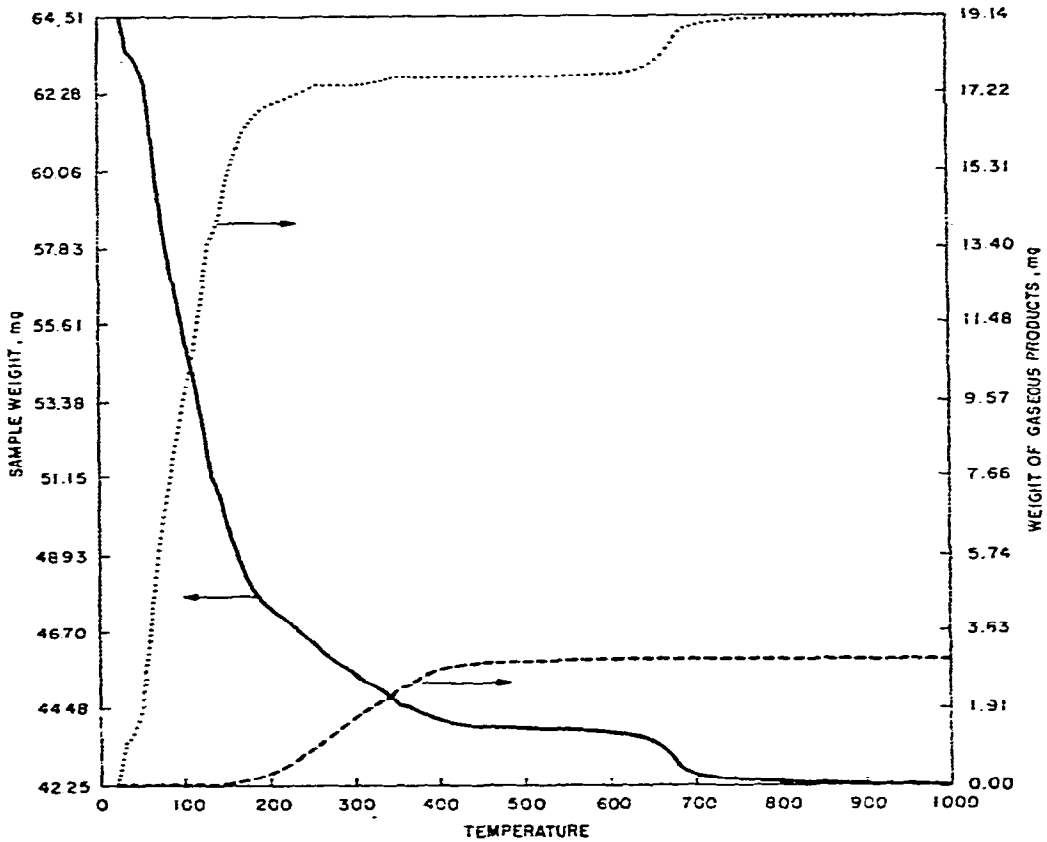
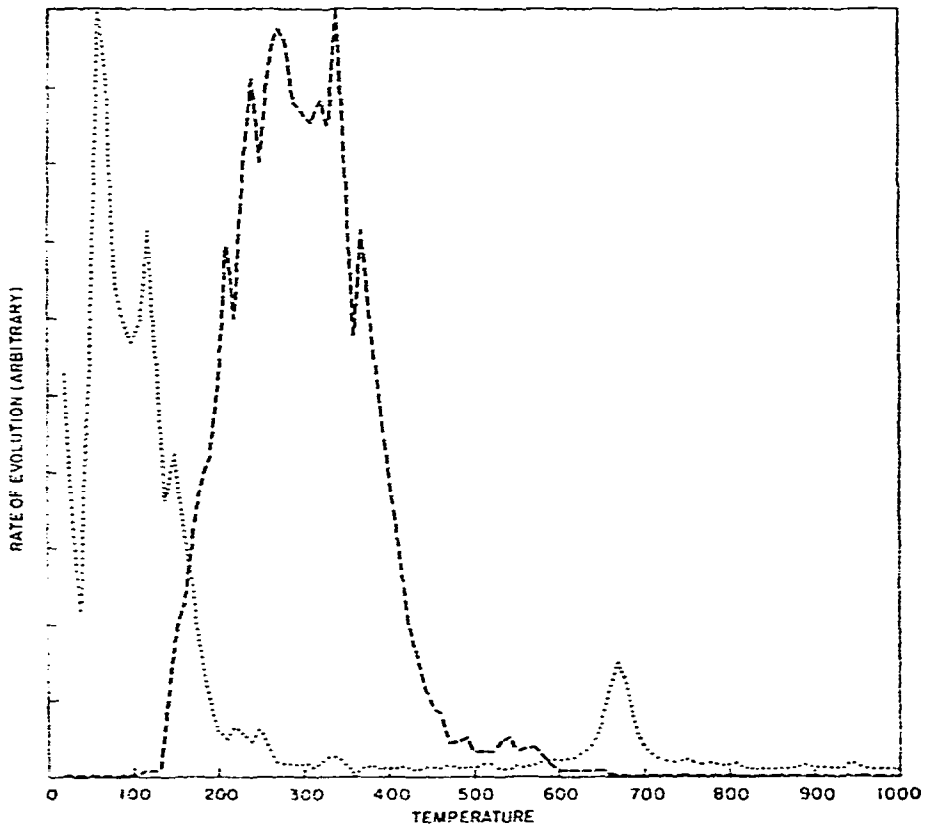


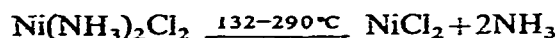
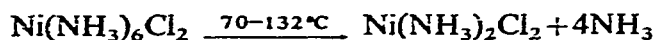
Fig. 3. Thermoanalytical data for ammonium zeolite Y; — TGA, - - - ammonia, non-ammonia.

the true or normal acid form of the zeolite. The so-called ultrastable faujasite or zeolite Y has been assumed by some authors as being the hydrogen form of the zeolite. It has already been shown that the ultrastable form contains considerably less chemical water, relative to the ammonium ion content of the initial ammonium zeolite, than the theoretical value of 0.50⁸.

Many studies have already been reported on the catalytic properties of calcined ammonium zeolite Y in which the authors assumed they were relating these properties to protonic sites. In many cases, the authors were unknowingly studying the properties of the ultrastable zeolite. We urge that future catalytic studies of this type include thermoanalyses of the calcined ammonium zeolite catalysts showing the chemical water content relative to the ammonium ion content of the initial salt.

Hexamminenickel(II) chloride

The thermogravimetric data are shown in Fig. 4. The purge gas was changed from He to H₂ at 325°C. Four plateaus are evident on the TG curve, corresponding to Ni(NH₃)₆Cl₂ at 25, Ni(NH₃)₂Cl₂ at 132–135, NiCl₂ at 290–410, and finally metallic nickel from 475°C. The ratio of ammonia evolved from 70–132°C to that evolved from 132–290°C is 2.01 compared with the calculated value of 2.00 for the reactions:



These results indicate that in the initial salt, each nickel is coordinated to 6.0 molecules of ammonia. The wt. percent nickel found was 27.1% compared with the calculated value of 25.3%, indicating an impurity in the original salt which is, at least in part, non-volatile. The ratio of NH₃/Ni(NH₃)₆Cl₂ and NH₃/Ni are 5.84 and 5.47, respectively. To obtain the calculated values of 6.00, the nickel and the hexammine-nickel(II) chloride weights should each be 0.03 mg less than the observed values. Thus, it seems probable that the initial sample, weighing 10.43 mg, contains 0.03 mg (2.9%) of a non-volatile impurity which does not react with hydrogen in the range of 300 to 500°C.

Tetrammineplatinum(II) chloride

The curves in Fig. 5 show that the initial sample contained a small amount of water; the two plateaus at 105–120 and above 550°C correspond to the anhydrous salt and metal ash, respectively. The inflection in the region of 250 to 275°C indicates the formation of the intermediate, Pt(NH₃)₂Cl₂. The ash amounts to 54.3% compared with 58.4% calculated for platinum metal, suggesting a volatile impurity in the initial sample. The total weight loss from 25 to 275°C was 5.35 mg while over this range only 2.83 mg of ammonia was evolved, indicating that 2.52 mg of a volatile impurity, probably ammonium chloride, was present. The weight loss is clearly evident in the

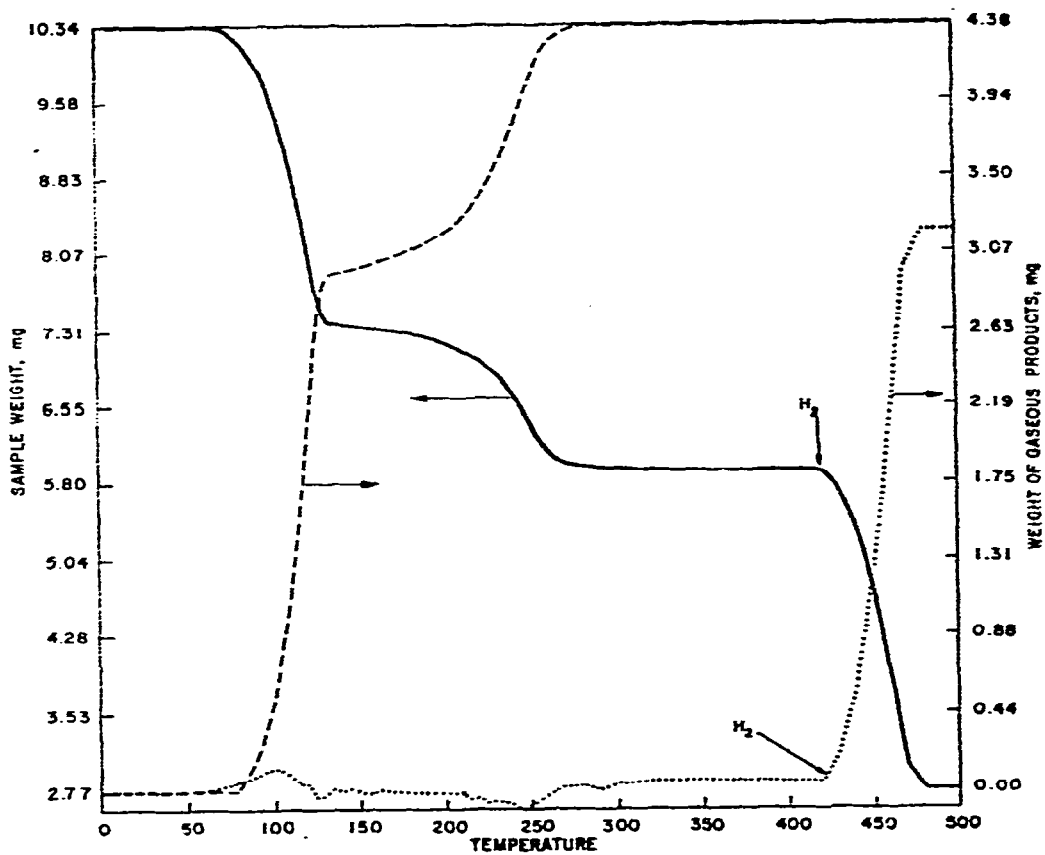
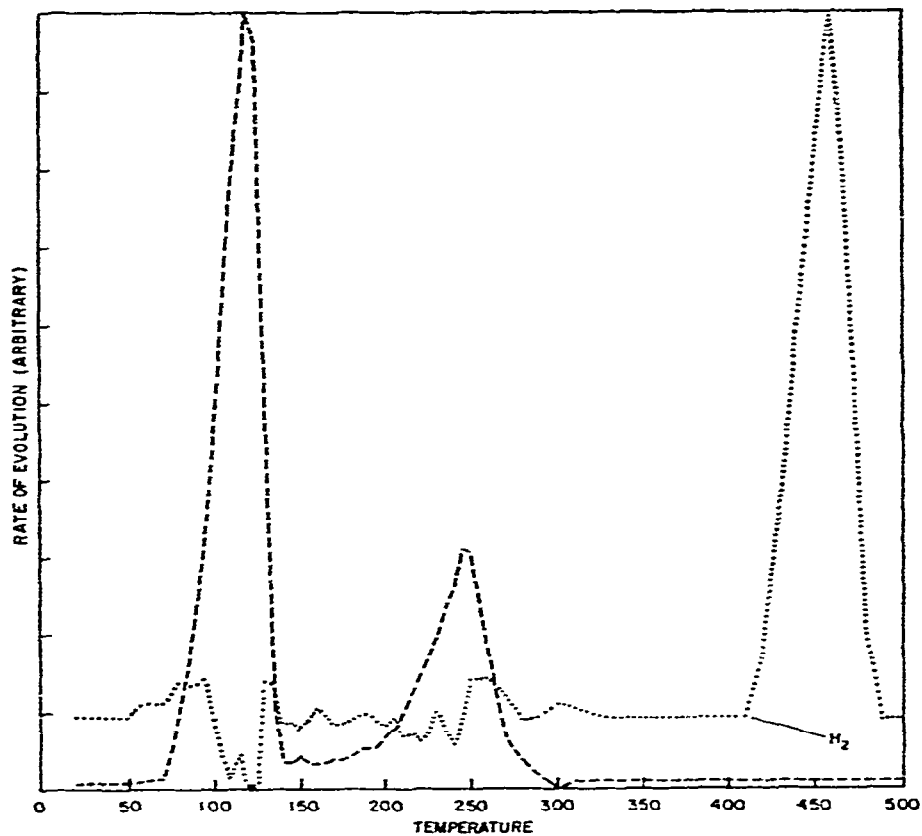


Fig. 4. Thermoanalytical data for hexamminickel(II) chloride; — TGA, --- ammonia, non-ammonia.

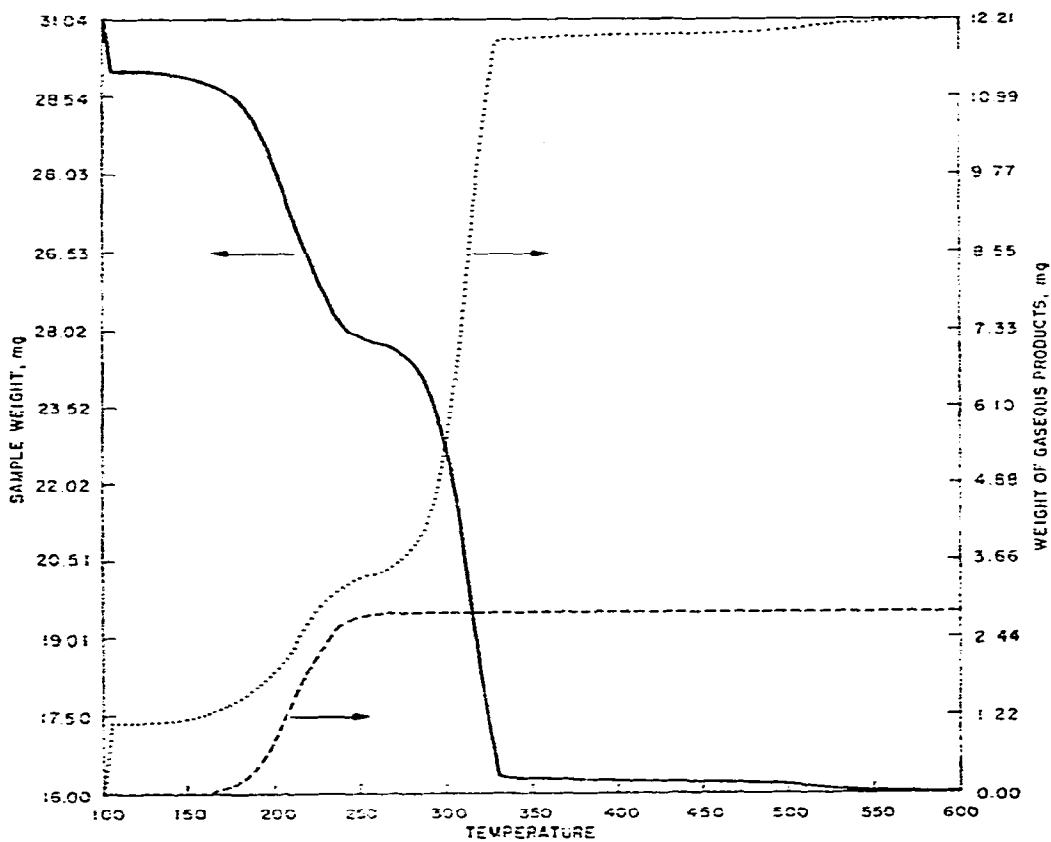
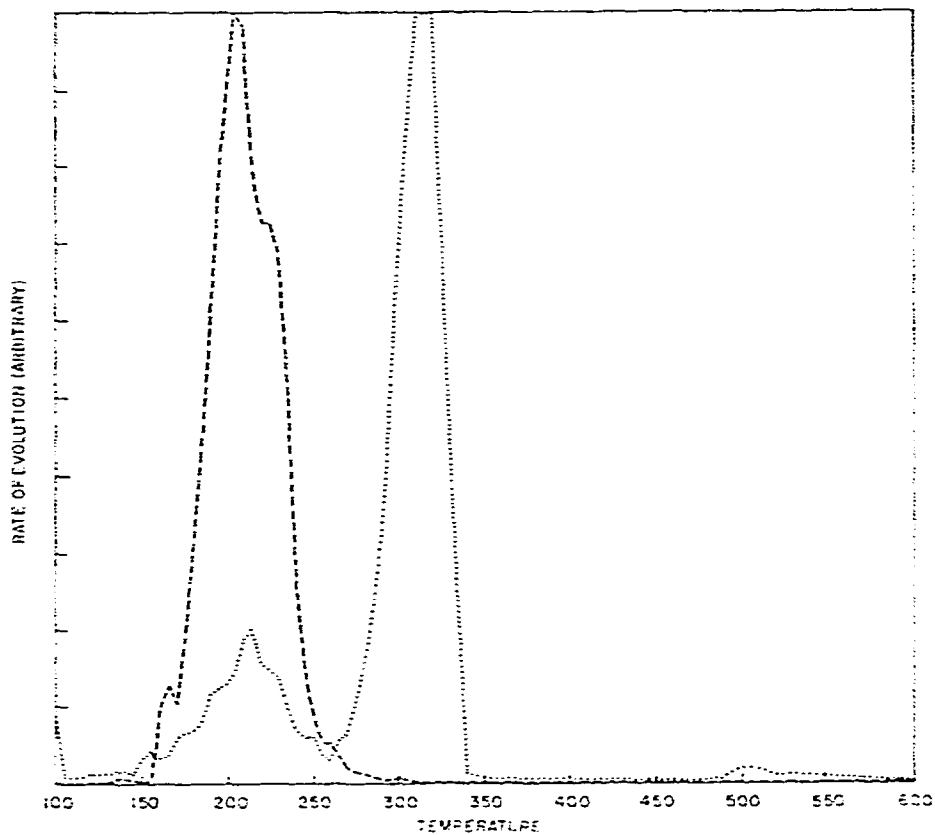
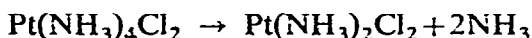


Fig. 5. Thermoanalytical data for tetrammineplatinum(II) chloride; — TGA, --- ammonia, non-ammonia.

derivative curve for non-ammonia, amounting to 8.4% impurity in the anhydrous tetrammineplatinum(II) chloride. From the weight of ash (assumed to be pure platinum), the atomic weight of platinum and the weights of the initial sample and intermediates, the various formula weights can be computed. This computation applied to the sample weight at 105°, less the weight of volatile impurity, gives a formula weight of 335; the calculated value for $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ is 334. The ratio of ammonia evolved to platinum is 2.03, in excellent agreement with the value calculated from the equation:



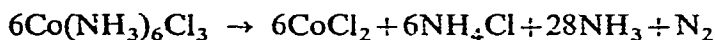
During another run, heating at 3°C/min, the effluent gas stream was passed through water over the range of 290 to 500°C using a sintered glass-cylinder at the end of the gas delivery tube. The titrator was set to maintain pH 7.00 and the effluent hydrogen chloride was titrated with 0.0100 *N* sodium hydroxide solution. The ratio of hydrogen chloride evolved to platinum was 0.77, in good agreement with the equation:



This stoichiometry has been reported for tetramminepalladium(II) chloride by Wendlandt and Funes⁹, but had not been verified previously for the platinum compound. Unlike ammonia, which is swept from the reactor almost immediately upon release from the sample, hydrogen chloride is not completely removed until 10 to 20 min after release.

Hexamminecobalt(III) chloride

Thermogravimetric curves are presented in Fig. 6. The evolution of ammonia begins at 190 and is complete at 285°C. At 325°C, hydrogen replaced the helium. Reduction was complete at 435°C; during and after reduction the hydrogen chloride was titrated as described for the platinum compound. The ratio of hydrogen chloride evolved to ash (assumed to be pure cobalt) was 1.95, in good agreement with the calculated value of 2.00. The weight percent cobalt was 21.8%; calculated for the anhydrous hexamminecobalt(III) chloride, 22.0%. The ratio of total ammonia evolved to cobalt was 4.71. According to the equation, the value should be 4.67:



The derivative curves for ammonia and non-ammonia ($\text{NH}_4\text{Cl} + \text{N}_2$) show that all of these substances are released from the sample more or less simultaneously. However, the derivative for the non-ammonia weight loss shows a small evolution prior to evolution of ammonia. This might be nitrogen, indicating that reduction begins to occur before the loss of ammonia. The weight loss below 185°C (the temperature where ammonia is evolved to a measurable level) amounts to about 1% of the total weight loss during thermoanalysis. The calculated loss for nitrogen is 3.4% of the total weight loss.

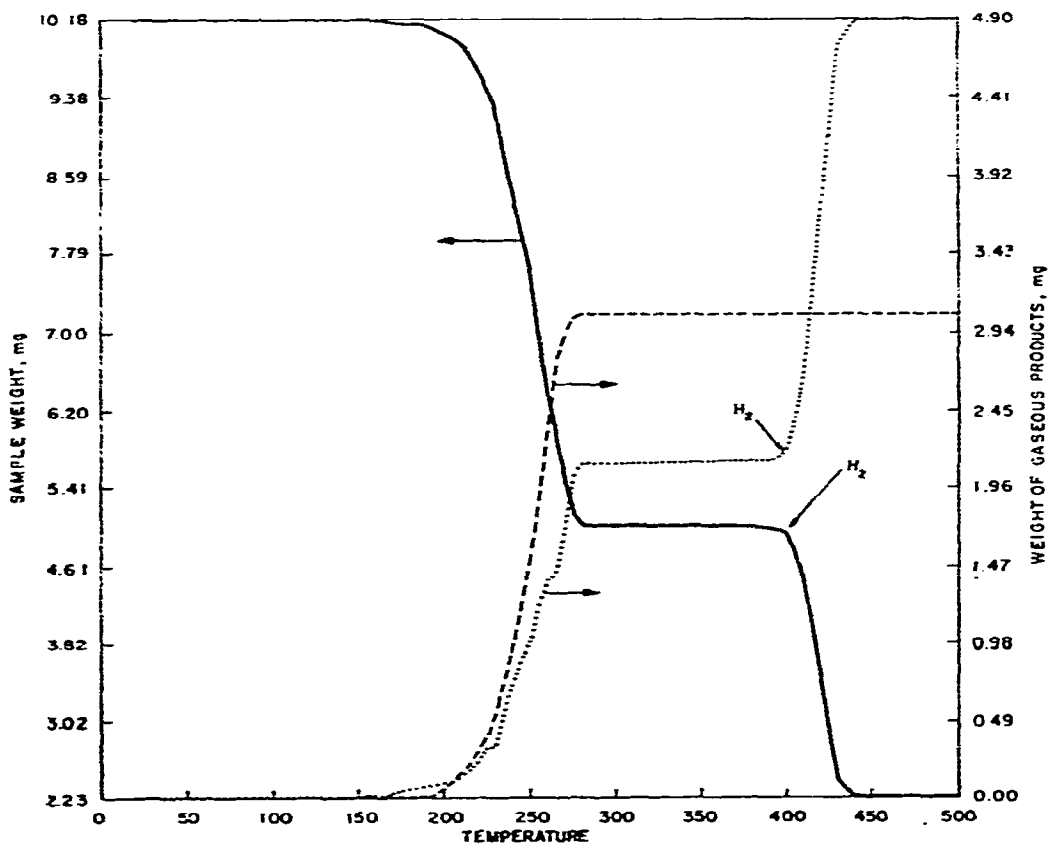
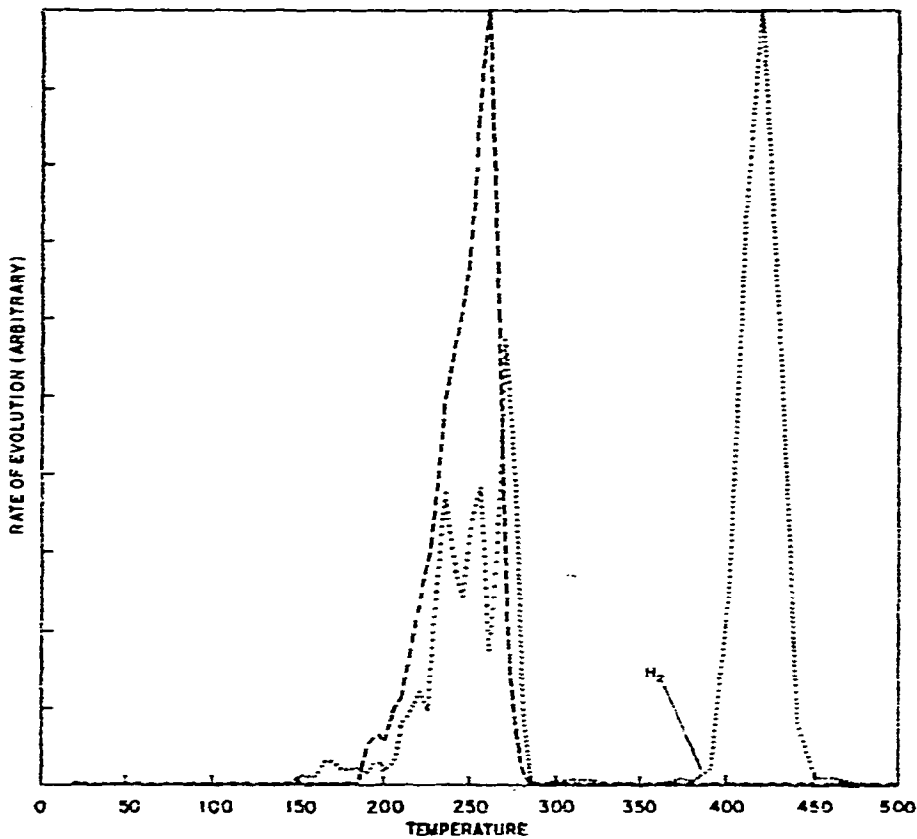
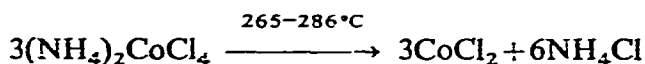
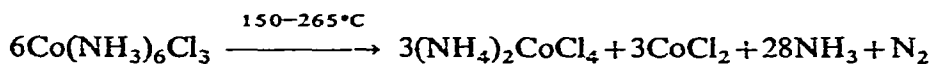


Fig. 6. Thermoanalytical data for hexamminecobalt(III) chloride; — TGA, --- ammonia, non-ammonia.

At 260–265°C, a small inflection appears on the evolution curve for the non-ammonia. The ratio by weight of loss above 260–265°C to loss below these temperatures is 0.695. For the reactions



the calculated weight ratio of the loss of ammonium chloride to the loss of ammonia and nitrogen is 0.635. The formation of the intermediate $(\text{NH}_4)_2\text{CoCl}_4$, which decomposes at 280°C, was proposed by Simmons and Wendlandt¹⁰.

CONCLUSIONS

The results reported here show that TG and an automatic titrator, used jointly, are powerful analytical tools for establishing the natures of ammonia-containing compounds and the stoichiometries of their thermal decompositions. Additionally, the purities of the compounds can, in many cases, be determined quantitatively. It has also been shown that the evolution of acidic gases, such as hydrogen chloride, can be determined quantitatively with this apparatus. While ammonia is swept from the reactor almost instantaneously upon release from the samples, hydrogen chloride is not completely removed from the reactor and/or gas delivery tube until 10 to 20 min after release.

NOTE ADDED IN PROOF

(Received August 31st, 1971). Paulik and Paulik have recently reported a technique essentially identical to that reported above [J. Paulik and F. Paulik, *J. Therm. Anal.*, 3 (1971) 63]. Their results for hexamminenickel(II) chloride, the only compound investigated in both papers, differ in details of resolution and temperature. These differences can be attributed to differences in sample size, sample configuration, and heating rate.

ACKNOWLEDGMENTS

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