begun several years ago. Practically all of the work was, however, executed in the summer during his absence. It is a pleasure to express my thanks to Professor G. P. Baxter for having put the facilities of the Harvard laboratory at my disposal.

Summary.

The specific heats of eleven salts and of ice between —190° and +22°, and —78.4° and +22° are determined adiabatically.

From these figures the molecular heats are calculated between —190° and —78.4°, and —78.4° and +22°

Comparisons are made at both ranges between the molecular heats of hydrated and double salts and those of their factors.

It is shown that these are almost the same except in the case of copper sodium sulfate.

An outline of further work on the subject is given.

CAMBRIDGE, MASS.

THE PREPARATION OF PERCHLORIC ACID.

BY H. H. WILLARD.

Among the various methods used for preparing perchloric acid only two deserve serious consideration. The first is that of Kreider,[1] which consists in treating sodium perchlorate with concentrated hydrochloric acid, filtering off the sodium chloride formed, and evaporating to expel all hydrochloric acid. The details of this method have been carefully worked out by Mathers.[2] The acid thus obtained is contaminated with sodium perchlorate, together with impurities present in the materials. To obtain a pure product, the crude acid must be distilled under diminished pressure. The second method is that of Mathers,[3] which consists in the distillation of potassium perchlorate with concentrated sulfuric acid in a current of steam under diminished pressure. The only advantage of this method over the preceding is in the use of the cheaper potassium salt, but this is more than counterbalanced by its disadvantages. Only comparatively small quantities can be used at a time, the distillation is rather troublesome, and the acid obtained contains 20–25% of sulfuric acid, so that, if a reasonably pure acid is required, it must be redistilled or the sulfuric acid precipitated by barium carbonate.

In trying to find a cheaper method of preparing perchloric acid, attention was directed to the ammonium salt, which is not much more expensive than the potassium salt, and considerably cheaper than the sodium

[1] Z. anorg. Chem., 9, 343; Am. J. Sci., [3] 49, 443.
[2] THIS JOURNAL, 32, 66.
[3] Indiana University Studies, 9, 173; Trans. Am. Electrochem. Soc., 21, 331.

salt. Since it is not difficult to oxidize ammonium compounds, a study was made of ammonium perchlorate, with this in view.

It was found that Schlösing,[1] in 1871, had already suggested the use of this salt with aqua regia, as a means of separating potassium and sodium, the ammonium being oxidized and thus giving practically a solution of perchloric acid; but he gave no details regarding the reaction. Experiments showed that ammonium perchlorate could easily be converted into pure perchloric acid in this way, and a careful study was made of the conditions necessary to obtain complete removal of the ammonium with minimum consumption of nitric and hydrochloric acid.

It would appear from Schlösing's statement that, since aqua regia is used, chlorine must be the oxidizing agent; but this is not true. The gas may be passed into a boiling ammonium perchlorate solution for hours with almost no effect. Although nitric acid itself does not oxidize ammonium salts, its reduction product, nitrous acid, decomposes them readily, and it seemed likely that this was the basis of the reaction. Accordingly, the gas obtained by treating sodium nitrite with sulfuric acid was passed into a boiling solution for some time. The action was very slow, but quite an appreciable amount of ammonium was decomposed and free perchloric acid formed.

On this theory, any reagent capable of reducing nitric acid fairly readily, and not acted upon by nitrous acid, could be substituted for hydrochloric acid. Formic acid, therefore, was slowly run into a boiling solution of ammonium perchlorate and nitric acid. Every trace of ammonium could thus be eliminated from the solution, indicating that nitrous acid is the active reagent. If, however, hydriodic acid, which is quickly oxidized by nitrous acid, was used, the ammonium salt was not decomposed. Although it is possible to use a reducing agent like formic acid, practically this is not advisable, for the oxidation of the ammonium proceeds much less rapidly and efficiently than with hydrochloric acid. It might be expected that nitrogen would be the principal product of the reaction, as is the case with ammonium nitrite, but, as will be seen later, this is not true.

A large number of experiments were made to determin the influence of temperature, volume, and relative concentrations of hydrochloric and nitric acids. The ammonium perchlorate used was purified by recrystallization, and some of it was prepared by neutralizing distilled perchloric acid with ammonia. It is readily prepared from the sodium salt by treatment with ammonium nitrate, and easily purified by recrystallization with excellent yields. If potassium perchlorate is present, however, it cannot be removed by this process. The salt was dried at 100° and

[1] *Compt. rend.*, **73**, 1269.

was not at all hygroscopic. The acids used were the ordinary chemically pure reagents, the nitric being labelled 69%, and the hydrochloric 37%, though the latter was probably a trifle weaker. In each experiment 500 grams of ammonium perchlorate were added to the water and nitric acid, contained in a two-liter flask, the solution heated to boiling, and the hydrochloric acid, previously diluted, was added, either in portions or continuously through a dropping funnel.

Effect of Temperature.—This is very pronounced; the solution must be kept boiling vigorously, or the action will be slow.

Effect of Rate of Adding Hydrochloric Acid.—When added all at once, more of each acid was required than when it was added in portions or through a dropping funnel. The latter method was preferred; most of the acid was run in during the first ten minutes, all of it within twenty-five minutes, and occasionally this time could be shortened without requiring more acids.

Effect of Volume.—The amount of water added was increased from 600 cc. to 900 cc. without any appreciable change in the quantity of nitric and hydrochloric acids required, but the reaction became slower. When reduced to 500 cc. the consumption of acids increased slightly, and with less than that the increase was very rapid, the two acids reacting on each other with comparatively little effect on the ammonium salt. It is necessary to keep the volume fairly constant by replacing the water lost by evaporation until most of the reaction is over, usually for about an hour, after which the solution was evaporated to remove excess of nitric or hydrochloric acid.

Yield.—The yield is the theoretical, since the perchloric acid takes no part in the reaction. To test this point, 500 grams of the ammonium salt were converted into the acid, evaporated until free from hydrochloric and nitric acids, diluted, neutralized with ammonia, evaporated, dried at 100° and weighed. In three experiments 498.5, 499, 499 grams were obtained, corresponding to a yield of 99.7–99.8%, the slight deficiency being due to a loss of perchloric acid during the evaporation to expel the other acids, and to a slight spattering during the evaporation of the ammonium perchlorate solution.

The amounts of the substances used when conditions were most favorable, were: ammonium perchlorate, 500 grams, water 600 grams, nitric acid 410 grams, and hydrochloric acid 105 grams.

Occasionally, it was possible to use about 2% less nitric acid, but as a rule these figures could not be decreased appreciably, without leaving a little ammonium in solution. Expressing these quantities in mols (assuming the hydrochloric acid to be 36% and the nitric 69%), they become:

$$\begin{array}{l} NH_4ClO_4 \quad 4.25 \\ HNO_3 \quad \cdot \; 4.49 \\ HCl \quad \quad 1.04 \end{array} \left.\right\} \text{ or in round numbers} \left\{\begin{array}{l} 17 \text{ mols.} \\ 18 \text{ mols.} \\ 4 \text{ mols.} \end{array}\right.$$

If all the nitrogen were liberated in elemental form, the proportions would be:

$$\begin{array}{ll} NH_4ClO_4 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots & 28^2/_3 \text{ mols.} \\ HNO_3 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots & 18 \text{ mols.} \\ HCl \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots & 4 \text{ mols.} \end{array}$$

It is evident, therefore, that the nitrogen must be combined with a certain amount of oxygen. If the numbers actually found by experiment as given in the first table are used to form an equation, the latter exactly balances, if nitrous oxide is formed, thus:

$$34NH_4ClO_4 + 36HNO_3 + 8HCl = 34HClO_4 + 4Cl_2 + 35N_2O + 73H_2O.$$
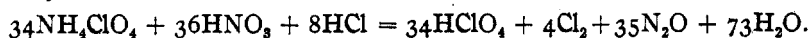
Accordingly, some of the gas evolved was collected over sodium hydroxide solution to remove chlorine and nitrogen dioxide, and analyzed by exploding with hydrogen. It was found to contain about 90% nitrous oxide, the rest being apparently nitrogen. It seemed to be free from nitric oxide. Some N_2O_3 or $NOCl$ is also apparently formed during the reaction, for the gas above the boiling solution is often faintly brownish.

The acid obtained contains only the impurities present in the materials or derived from the vessel used. Since ammonium perchlorate, if free from potassium, can readily be prepared chemically pure, and C. P. hydrochloric and nitric acids are always at hand, it is obvious that without any distillation, chemically pure perchloric acid can quickly be prepared by using a container which is not attacked.

As the result of this investigation, the following method is recommended: In a two-liter flask place 500 grams of ammonium perchlorate, add 600 cc. of water, 410 grams of 68–70% nitric acid, heat to boiling, and run in rapidly through a long-stemmed dropping funnel, 105 grams of 37% hydrochloric acid, previously diluted to 400–500 cc. or sufficiently so that the volume of the solution in the flask remains fairly constant. The acid is run in rapidly at first, then more slowly, but may all be added within 25 minutes, or it may be added more slowly. The boiling must be very vigorous throughout the entire operation. Water is then run in to replace that lost by evaporation, keeping the volume constant for about one hour, by which time the reaction is nearly over. The solution is then rapidly boiled down until fumes of perchloric acid appear. The acid should now be free from ammonium as shown by Nessler's test. Usually there will be a slight excess of nitric acid and this requires a somewhat higher temperature for its complete removal than does hydrochloric acid, where 135° suffices. It may in some cases be advisable to add a little more hydrochloric acid to react with the nitric acid present, leaving an excess of the former. A casserole or evaporating dish is more efficient

in the last evaporation. When the acid fumes copiously, its composition is nearly that of the dihydrate, $HClO_4.2H_2O$, this being the constant-boiling product obtained by distillation. The yield is the theoretical—580 grams of the dihydrate, and the entire process is easily completed within two and a half hours. If the hydrochloric acid used contains arsenic, this would probably remain with the perchloric acid, from which it could readily be precipitated, but no experiments were made along this line.

The distillation of the acid obtained in this way from impure materials is so easy that this method of purification will probably be the cheapest where a perfectly pure product is required. A pressure of 200 mm. is very satisfactory; at higher pressures, decomposition becomes noticeable, until at atmospheric pressure a loss of perhaps 10% is inevitable; at lower pressures, the acid tends to bump badly. The apparatus used in this laboratory consists of a one-liter distilling flask, with a ground joint between the side tube and condenser, for greater flexibility. The distance from flask to condenser jacket should be at least 40 cm., forming an air condenser, otherwise, when the vapor at 160–165° strikes the water-cooled portion of the tube, the latter is liable to crack. The neck of the flask is drawn out so that into it may be snugly fitted a thermometer, over which is slipped a short piece of rubber tubing, the latter fitting inside the neck like a thin rubber stopper. If this point is 20 cm. above the side tube, the rubber is scarcely attacked. The condenser tube is made tight in the receiver by passing through a rubber stopper. To prevent bumping, three or four capillary tubes, about 3 cm. in diameter, as described by Scudder,[1] were found very satisfactory. Five hundred grams of acid can easily be distilled in one hour. The distillate smells of chlorine and its oxides, from which it may be readily and completely freed by aspirating through it a current of air, keeping it gently warmed.

The following data will give an idea of the cost of the acid, using commercial chemicals: ammonium perchlorate is quoted in Germany at 155 marks per 100 kilos. To produce one kilo of commercial 70% perchloric acid would require about 865 grams of the ammonium salt, 710 grams of nitric acid and 185 grams of hydrochloric acid, which would cost at retail in Germany about forty cents. The cost for labor would be small, owing to the simplicity of the process. There is no reason, therefore, why, if a demand is created, the acid should not be available in large quantities at a reasonable price, instead of being quoted at some such figure as $5 a pound for 20% acid, when it is quoted at all. If produced by Kreider's method, the cost of materials is more than twice as great, while the product is more impure and the labor much greater.

In conclusion, it may be well to call attention to some of the valuable

[1] THIS JOURNAL, 25, 163.

properties of this acid. It is neither poisonous nor explosive and is perfectly stable (unlike the anhydrous acid). It is, as a rule, non-oxidizing except near its boiling point, 203°, and by reason of the latter being so high, it is capable of displacing completely from their salts, nitric, hydrofluoric, hydrochloric and other volatil acids. Most of its salts are readily soluble not only in water, but also in organic solvents like alcohol and acetone, and they are very suitable for electrochemical work, since they suffer no reduction by electrolysis. Its principal use in the laboratory is in the separation of potassium and sodium, but other uses will suggest themselves when it becomes cheaper. Andrews[1] has suggested it as a solvent for barium chromate in the volumetric determination of sulfur. It is very suitable for use in electrolytic analyses.[2] It makes an excellent standard solution for use in acidimetry where a non-volatil acid is required and sulfuric is not suitable. It may be substituted for sulfuric acid in permanganate titrations; the evaporation of ferric chloride solutions with perchloric acid to complete removal of chloride is not attended with the formation of difficultly soluble basic salts, as frequently occurs with sulfuric acid, and the addition of a little water causes immediate solution of the residue. In technical work, its extended use seems already assured, especially in electrochemical processes, judging from the number of such patents issued.

Summary.

1. A method is given for preparing pure $HClO_4.2H_2O$ from ammonium perchlorate by boiling with the proper quantity of dilute nitric acid, to which a certain amount of hydrochloric acid is gradually added.

2. The principal gaseous products are nitrous oxide and chlorine.

3. The superiority of this process lies in its simplicity, rapidity, and the cheapness of materials.

4. The distillation of the acid is briefly described.

5. Some of its most striking properties and a few new uses for it are mentioned.

ANN ARBOR, MICH.

THE INFLUENCE OF NON-VOLATIL ORGANIC MATTER AND CERTAIN ACIDS ON THE PRECIPITATION OF THE AMMONIUM SULFIDE GROUP OF METALS.[3]

BY LOUIS J. CURTMAN AND HARRY DUBIN.

As is well known, there are two classes of substances whose presence

[1] Am. Chem. J., 32, 476.

[2] THIS JOURNAL, 34, 389; Trans. Am. Electrochem. Soc., 9, 375.

[3] Published in abstract in the original communications of the Eighth International Congress of Applied Chemistry, Vol. 1, p. 153.