is seen to be 12.2, in good agreement with Kopp's number. The atomic volume of divalent carbon in the carbon monoxide is 23. It is interesting to note that, if acetylene be assumed to have a divalent and a tetravalent carbon atom, *i. e.*, the acetylidene structure, its atomic volume agrees exactly with that found experimentally.

We have endeavored to produce addition compounds of acetylene and hydrobromic at low temperatures. Acetylene is quite soluble in this acid, but solutions containing even 50% of acetylene show no tendency to precipitate compounds at temperatures as low as —115°.

With liquids having high vapor pressures at their freezing points, such as hydrobromic and hydriodic acid, but particularly with acetylene, the phenomenon of freezing and boiling occurring simultaneously is shown in a striking way. Liquid acetylene in a sealed tube can be supercooled about 5°. As crystallization takes place the remaining liquid boils furiously.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY.]

THE PREPARATION AND PROPERTIES OF THE NEUTRAL AMMONIUM SALTS OF ORGANIC ACIDS.

BY LEROY MCMASTER.

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As stated in two previous papers,[1] most of the ammonium salts of organic acids described in the literature are the acid salts instead of the neutral salts Many of the "neutral" salts purchased have also been found to be "acid." This is due to the fact that they have been prepared by neutralizing the aqueous solution of the organic acid with ammonia water or ammonium carbonate and the solution allowed to evaporate to crystallization. The salts thus formed are generally hydrolyzed and the acid salt results. Many of these salts also contain water of crystallization. Neutral ammonium salts free from water of crystallization can be obtained by passing dry ammonia gas into an absolute alcohol or ether solution of the organic acids. Most of the organic ammonium salts are insoluble in alcohol or ether and are thus precipitated. Keiser and McMaster prepared, by this method, the neutral ammonium salts of fumaric, maleic, mesaconic and citraconic acids. I prepared also, by this method, the neutral ammonium salts of propionic, isobutyric, benzoic, cinnamic, malonic, succinic, malic, tartaric, *o*-phthalic and *m*-phthalic acids and studied some of their properties. Many of the properties of the salts made by this method were found to be different

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[1] Keiser and McMaster, *Am. Chem. J.*, 49, 84–87 (1913); *Chem. News*, 108, 136–137 (1913); McMaster, *Am. Chem. J.*, 49, 294–301 (1913); *Chem. News*, 108, 182–183, 193–194 (1913).

from those as described in the literature. This has also been found to be the case with some of the ammonium salts of the organic acids described in this paper.

The work on the preparation and study of the properties of the neutral ammonium salts of organic acids has been continued. They were prepared in both absolute ethyl alcohol and ether. Several were prepared also in methyl alcohol. In several cases the salts were more or less soluble in the alcohols, and, under this condition, they were prepared only in ether. When the experiments were carried out in ethyl alcohol it was generally necessary to keep the flasks surrounded by cold water, for, when the ammonia was passed into the solution, heat was set free due to the action of ammonia on the alcohol and also to the heat of neutralization. Very little, if any, heat was developed when ether was used as the solvent for the acid.

Whenever the ammonium salts are only slightly soluble in ethyl alcohol, they were prepared in this medium rather than in ether, since from an alcoholic solution of the acid they are generally precipitated in a crystalline form. From an ethereal solution they are mostly precipitated in an amorphous state. The neutral ammonium salts were all filtered and washed by suction on alundum crucibles. The organic acids used in this investigation were obtained from Kahlbaum or Schuchardt.

Ammonium Butyrate.—No record can be found of the preparation of this salt other than being mentioned by Pelouze and Gélis[1] as being a deliquescent compound. When dry ammonia gas was run into an ethereal solution of normal butyric acid, a white, granular, crystalline precipitate of neutral ammonium butyrate was formed. The precipitate was quickly filtered by suction on an alundum crucible, washed with ether, and then placed in a vacuum desiccator for a few minutes. The salt is deliquescent and loses ammonia readily on standing in the air. On first dissolving the salt in water, the solution is neutral. The solution soon turns acid, due to hydrolysis. The salt is readily soluble in methyl alcohol, ethyl alcohol and acetic acid, and appreciably so in acetone.

Calc. for $C_4H_7O_2NH_4$: 13.33%; found: 13.31% N.

Ammonium Isovalerianate.—Beilstein states that an acid salt of isovalerianic acid of the formula $NH_4C_5H_9O_2 + 2C_5H_{10}O_2$ is used in medicine. The U. S. Dispensatory describes the commercial valerianic acid as a mixture of two isomeric acids—isovaleric acid and optically active valeric acid. This is true of the valeric acid that is obtained from the *Valeriana officinalis*, the *Angelica archangelica*, and that which results from the oxidation of the amyl alcohol of fermentation with the aid of chromic acid. The "ammonium valerianate" described in the Dispensatory is evidently a mixture of ammonium valerianate and ammonium iso-

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[1] Pelouze and Gélis, *Ann.*, **47**, 249.

valerianate. It is also acid. Hager[1] states that commercial ammonium valerianate is always the acid salt, as is proved by the acid reaction and the strong rotation of the crystals when placed upon cold water; the neutral salt is obtained only with difficulty, is in prismatic crystals, and is easily liquefied by moderate temperatures. A sample of ammonium valerianate purchased from Kahlbaum was found to be acid. The neutral ammonium salt of isovalerianic acid was prepared by conducting dry ammonia gas into an ethereal solution of the acid. There was formed a snow-white crystalline precipitate which is very deliquescent, and which has an odor like that of the free acid. The salt is very soluble in water. On first dissolving the salt in water, the solution is neutral, but soon becomes acid due to hydrolysis. It is readily soluble in methyl alcohol, ethyl alcohol, acetic acid, and somewhat so in acetone.

Calc. for $C_5H_9O_2NH_4$: 11.76%; found: 11.77% N.

Ammonium Caproate.—No record can be found of the preparation of this salt. Caproic acid, was dissolved in ether, and ammonia passed into the solution. A white precipitate formed which at first was somewhat gelatinous, but soon became crystalline and translucent. The salt is very deliquescent and has to be filtered and washed very quickly by suction. When dissolved in water a neutral solution is formed, which soon becomes acid. The salt is very soluble in methyl alcohol, ethyl alcohol and acetic acid. On standing in the air, it readily loses ammonia. Analysis proved it to be the neutral ammonium caproate.

Calc. for $C_6H_{11}O_2NH_4$: 10.52%; found: 10.53% N.

Ammonium Crotonate.—On passing ammonia gas into a saturated alcoholic solution of crotonic acid, a beautiful glistening white precipitate formed. The precipitate was quickly filtered, washed with ether and dried for a short time in a vacuum desiccator. The ammonium salt was also prepared in ether When ammonia gas was passed into an ethereal solution of the acid, there was first formed a very gelatinous precipitate which soon became an amorphous powder. The salt prepared in either medium is not hygroscopic, but is very soluble in water. The aqueous solution is neutral, but soon hydrolyzes. The neutral ammonium salt, both crystalline and amorphous, has the odor characteristic of crotonic acid. It is readily soluble in methyl alcohol, ethyl alcohol and acetic acid, but insoluble in ether and chloroform.

Prepared in alcohol: Calc. for $C_4H_5O_2NH_4$: 13.60%; found: 13.61% N.
Prepared in ether: Found: 13.60% N.

Although many of the salts of crotonic acid have been prepared and studied, no mention of the neutral ammonium salt can be found.

The Ammonium Salt of Ethyl Malonic Acid.—When ammonia gas was run into an alcoholic or an ethereal solution of ethyl malonic acid,

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[1] U. S. Dispensatory, 18th edition, p. 463. *Pharm. Centralb.*, 1879, p. 465.

there was first formed a white precipitate which is somewhat mucilaginous. This precipitate, after a short time, changed to a semi-crystalline one, when prepared in alcohol, and to an amorphous powder when prepared in ether. The salt prepared by either method is somewhat hygroscopic, and loses ammonia readily in moist air. The salt was filtered by suction, washed with ether, and dried in a desiccator. When dry the salt has the appearance of dry paper pulp. The aqueous solution was neutral to sensitive litmus paper. It is slightly soluble in ethyl alcohol, readily soluble in methyl alcohol and acetic acid, but insoluble in acetone. A solution of the salt is not precipitated by ferric chloride. No mention of this salt is made in the literature.

Prepared in alcohol: Calc. for $C_5H_6O_4(NH_4)_2$: 16.86%; found: 16.87% N.
Prepared in ether: Found: 16.87% N.

Ammonium Glutarate.—When ammonia is passed into an alcoholic solution of glutaric acid there is formed a white amorphous precipitate, which soon becomes crystalline and granular in appearance. This salt can also be prepared in ether. The salt thus formed is the neutral ammonium glutarate, soluble in water, methyl alcohol and acetic acid. It is insoluble in ether. The salt is not deliquescent.

Calc. for $C_5H_6O_4(NH_4)_2$: 16.86%; found: 16.85% N.

Ammonium Adipate.—This salt has been prepared by Dieterle and Hell[1] by treating an aqueous solution of adipic acid with an excess of ammonia water and evaporating the mixture to crystallization. Small, glittering leaflets were formed. Larger crystals of the neutral salt were obtained by allowing the aqueous solution to evaporate spontaneously in an atmosphere of ammonia. The salt is described as being stable in the air. It loses one molecule of ammonia when dried at 100°, forming the acid salt. Upon heating the salt to 120–150°, all of the ammonia is driven off and the free adipic acid is formed. This salt has also been described by Arppe[2] as forming monoclinic crystals.

Ammonia was passed into an alcoholic solution of adipic acid and a white crystalline salt was formed. It was filtered, washed with alcohol and ether and dried in a desiccator. The salt is stable in the air and an aqueous solution of it is neutral. It is slightly soluble in ethyl alcohol and insoluble in ether. It is appreciably soluble in methyl alcohol, from which it crystallizes in small, beautiful leaflets. Determination of the nitrogen proved it to have the composition of the neutral salt.

Calc. for $C_6H_8O_4(NH_4)_2$: 15.55%; found: 15.50% N.

Ammonium Pimelate.—This salt would not precipitate when ammonia gas was run into an alcoholic solution of pimelic acid, due to its solubility in alcohol. When ammonia gas was passed into an ethereal solution

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[1] Dieterle and Hell, *Ber.*, 17, 2221 (1884).

[2] Arppe, *Z. Chem.*, p. 301 (1865).

of the acid a white, gummy precipitate was formed which would not crystallize. Ammonia was then passed into a solution of the acid dissolved in alcohol and ether. A fine, white powder was formed which was filtered, washed with ether and dried in a desiccator. This salt gave a neutral solution when dissolved in water, in which it is very soluble. It is not hygroscopic, but loses ammonia very readily in both dry and moist air, passing to the acid salt. It is quite soluble in methyl alcohol and acetic acid. It crystallizes from ethyl alcohol in leaflets. Analysis showed it to be the neutral ammonium pimelate.

Calc. for $C_7H_{10}O_4(NH_4)_2$: 14.43%; found: 14.40% N.

Ammonium Sebate.—Neison[1] states that the ammonium salts of sebacic acid can be obtained in solution, but they are invariably partially decomposed, with loss of ammonia, on attempting to obtain them in the solid state, whether the evaporation is conducted *in vacuo*, at the heat of a water bath, over sulfuric acid, or spontaneously in a current of dry air.

The neutral ammonium salt of this acid was prepared in a *solid state* by the usual method in both alcohol and in ether. When precipitation takes place in alcohol, there is first formed a slightly gelatinous precipitate which changes to a white, crystalline powder. When prepared in ether the white powder is not crystalline. The precipitate in each case was filtered, washed with ether and dried for a short time over sulfuric acid in a vacuum desiccator. The salt is readily soluble in water to which it imparts a neutral reaction. The salt was still neutral to litmus after standing for one month in a tightly stoppered bottle. It is not deliquescent but loses ammonia in moist air. It is slightly soluble in ethyl alcohol. The salt crystallizes from methyl alcohol in small crystalline flakes.

Analysis of the salt prepared in alcohol showed it to be the neutral ammonium salt of sebacic acid.

Calc. for $C_{10}H_{16}O_4(NH_4)_2$: 11.86%; found: 11.86% N.

Ammonium Tartronate.—Petriew[2] describes this salt as needles which decompose at 100°. Tartronic acid was dried at 100°, at which temperature it loses its water of crystallization, dissolved in alcohol and ammonia conducted into the solution. A fine, glistening, white, crystalline precipitate formed. This salt was filtered, washed with ether and dried in a desiccator. It is not deliquescent and an aqueous solution of it is neutral to different indicators. It is insoluble in methyl alcohol and ether. When treated with acetic acid, free tartronic acid is formed.

Calc. for $C_3H_2O_5(NH_4)_2$: 18.18%; found: 18.17% N.

Ammonium Racemate.—Racemic acid was dried at 100°, and ammonia passed into an alcoholic solution of it. A white precipitate, somewhat flocculent at first, was formed. This changed to a crystalline powder,

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[1] Neison, *J. Chem. Soc.*, **27**, 301.

[2] Petriew, *J. Russ. Chem. Soc.*, **10**, 152.

which as soon as neutral, was filtered and washed with alcohol and ether. An aqueous solution of the salt was neutral towards different indicators. The salt is not deliquescent. It is insoluble in methyl alcohol, ethyl alcohol and ether.

Calc. for $C_4H_4O_6(NH_4)_2$: 15.21%; found: 15.21% N.

Ammonium Itaconate.—Baup[1] states that, like many other ammonium salts, neutral ammonium itaconate does not crystallize since on evaporation or standing in the air it loses ammonia and the acid salt forms.

When ammonia gas is passed into an alcoholic solution of itaconic acid, until a portion of the salt on being dissolved in water shows a neutral solution, there is formed a white, granular, crystalline precipitate of neutral ammonium itaconate. When the ammonia is first passed in, the precipitate formed is slightly gelatinous. The salt was washed with alcohol and ether, and dried for a short time over sulfuric acid in a vacuum desiccator. It is very hygroscopic. In dry air the salt is stable, but loses ammonia in moist air. It is soluble in acetic acid, but insoluble in methyl alcohol, ethyl alcohol and acetone.

The neutral ammonium salt of itaconic acid can also be precipitated in ether as an amorphous compound. The salt prepared in either alcohol or ether readily hydrolyzes when dissolved in water.

Prepared in alcohol: Calc. for $C_5H_4O_4(NH_4)_2$: 17.07%; found: 17.07% N.
Prepared in ether: Found: 17.07% N.

Action of Ammonia on some other Organic Acids.—Attempts to prepare the neutral ammonium salts of isosuccinic, pyrotartaric, aconitic and several other acids have so far given unfavorable results. The precipitates formed were usually very mucilaginous and would not crystallize, even if the ammonia was conducted into the alcoholic or ethereal solution for a long time. Methyl alcohol was tried as a medium in which to precipitate these salts but without success. Work on these acids is being continued. A number of neutral ammonium salts of the higher fatty acids and of the aromatic series have been prepared and analyzed. The results will be given in a future paper. This investigation is being continued with other organic acids.

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THE DOUBLE AURIC IODIDES OF SUBSTITUTED AMMONIUM BASES.

BY SATYARANJAN DAS GUPTA.

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The application of the method of double decomposition in the formation of double salts is being systematically studied by Datta and already some interesting results have been obtained by him. Though there are a few

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[1] Baup, *Ann.*, 19, 29.