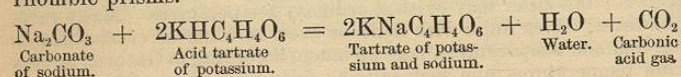


Tartrate of Potassium and Sodium.

Fifth Synthetical Reaction.—To some hot strong solution of carbonate of sodium (about three parts) in a test-tube or larger vessel add acid tartrate of potassium (about four parts), till no more effervescence occurs; when the solution is cold, crystals of the tartrate of potassium and sodium (*Potassii et Sodii Tartras*, U. S. P.), the old *Rochelle Salt*, will be deposited—($\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$). The crystals are usually halves of right rhombic prisms.

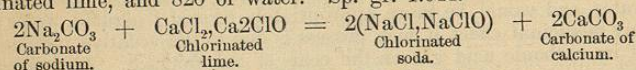
**FORMULÆ OF TARTRATES.**

Tartaric acid	HH C ₄ H ₄ O ₆
Acid tartrate of potassium	KH C ₄ H ₄ O ₆
Tartrate of potassium and sodium	KNaC ₄ H ₄ O ₆

Very close analogy will be noticed in the constitution of the molecules of these salts. When the other tartrates come under notice, it will be found they also have a similar constitution.

Hypochlorite of Sodium.

Liquor Sodæ Chloratæ, U. S. P., "Labbaraque's Solution," is made by decomposing solution of carbonate of sodium by solution of chlorinated lime; 100 parts of the carbonate, 80 of chlorinated lime, and 820 of water. Sp. gr. 1.044.

**Iodide and Bromide of Sodium.**

These salts (NaI, NaBr), *Sodii Iodidum* and *Sodii Bromidum*, are similar to the iodide and bromide of potassium in constitution, and are prepared with the same manipulations, soda being used instead of potash. The bromide of sodium, however, must be crystallized from warm solutions or rhombic prisms containing water ($\text{NaBr}, 2\text{H}_2\text{O}$) will be deposited.

Other Sodium Compounds.

Synthetical Reactions portraying the chemistry of the remaining official compounds (namely, nitrate, sulphate, hyposulphite, borate, arseniate, and valerianate of sodium) are deferred until the several acidulous radicals of these salts have been described.

Phosphate of Sodium.—The preparation and composition of this salt will be most usefully studied after bone-ash, the source of it and other phosphates, has been described. Bone-ash is phosphate of calcium (see page 109).

The *Citro-Tartrate* (*Sodæ Citro-tartras Effervescens*, B. P.) is a mixture of bicarbonate of sodium (17 parts), citric acid (6), and tartaric acid (8), heated (to 200° or 220° F.) until the particles

aggregate to a granular condition. When required for a medicinal use, a dose of the mixture is placed in water; escape of carbonic acid gas at once occurs and an effervescing liquid results. This substance may be regarded as the official representative of the popular "Effervescing Citrate of Magnesia," which will be further noticed in connection with the salts of magnesium (page 118).

Soda powders are formed of 30 grains of bicarbonate of sodium and 25 of tartaric acid wrapped separately in papers of different color. When mixed with water, tartrate of sodium ($\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$) results, a little bicarbonate also remaining.

In the manufacture of *Carbonate of Sodium* from chloride, the source of the sodium is chloride of sodium, and of the carbonic radical carbonate of calcium in the form of limestone. By one process the chloride is first converted into sulphate, the sulphate is then roasted with coal and limestone, and the resulting *black-ash* lixiviated (*lixivia*, from *lix*, lye—water impregnated with alkaline salts; hence *lixivation*, the operation of washing a mixture with the view of dissolving out salts). The lye, evaporated to dryness, yields crude carbonate of sodium (soda-ash). By another process the carbonate of sodium is obtained by heating bicarbonate of sodium, and the latter by mixing strong solutions of chloride of sodium and bicarbonate of ammonium. The last-named results from the action of carbonic acid gas (liberated on heating bicarbonate of sodium) on carbonate of ammonium, and this again from the reaction of heated mixture of chloride of ammonium and limestone. By either process common salt and limestone are the prime sources respectively of the sodium and carbonic radical in carbonate of sodium. The process will be further described in connection with Carbonates.

Deliquescence and Efflorescence.—The carbonates of sodium and potassium, chemically closely allied, are readily distinguished physically. Carbonate of potassium quickly absorbs moisture from the air and becomes damp, wet, and finally fluid—it is *deliquescent* (*deliquescent*, melting away). Carbonate of sodium, on the other hand, yields some of its water of crystallization to the air, the crystals becoming white, opaque, and pulverulent—it is *efflorescent* (*efflorescent*, blossoming forth).

Analogy of Sodium Salts to Potassium Salts.—Other synthetical reactions might be described similar to those given under Potassium, and thus citrate, iodate, bromate, chlorate (*Sodii Chloras*, U. S. P.), NaClO_3 , manganate and permanganate of sodium, and many other salts be formed. But enough has been stated to show how analogous sodium is chemically to potassium. Such analogies will constantly present themselves. In few departments of knowledge are order and method more perceptible; in few is there as much natural law, as much science, as in chemistry.

Substitution of Potassium and Sodium Salts for each other.—Sodium salts being cheaper than potassium salts, the former may sometimes be economically substituted. That one is employed rather than the other is often merely a result due to accident or fashion. But it must be borne in mind that in some cases a potassium salt

will crystallize more readily than its sodium analogue, or that a sodium salt is stable when the corresponding potassium salt has a tendency to absorb moisture, or one may be more soluble than the other, or the two may have different medicinal effect. For these or similar reasons, a potassium salt has come to be used in medicine or trade, instead of the corresponding sodium salt, and *vice versa*. Whenever the acidulous portion only is to be utilized, the least expensive salt of the class would nearly always be selected.

(b) *Reactions having Analytical Interest.*

1. The chief analytical reaction for sodium is the *flame-test*. When brought into contact with a flame in the manner described under potassium (page 79), an intensely yellow color is communicated to the flame by any salt of sodium. This is highly characteristic—indeed, almost too delicate a test; for if the point of the wire be touched by the fingers, enough salt (which is contained in the moisture of the hand) adheres to the wire to communicate a very distinct sodium reaction. These statements should be experimentally verified, the chloride, sulphate, or any other salt of sodium being employed.

2. Sodium salts, like those of potassium, are not volatile. Prove this fact by the means described when treating of the effect of heat on potassium salts (p. 79).

QUESTIONS AND EXERCISES.

98. How is the official Solution of Soda prepared? Give a diagram or equation.
99. Explain the action of sodium or potassium on water. What colors do these elements respectively communicate to flame?
100. How much bicarbonate of sodium can be obtained from 2240 pounds of crystallized carbonate? Ans. 1316 lbs., nearly.
101. Acetate of Sodium: give formula, process, and equation.
102. Give a diagram showing the formation of Bicarbonate of Sodium.
103. Why is a mixture of dried and undried carbonate of sodium employed in the preparation of the bicarbonate?
104. State the difference between anhydrous and crystallized carbonate of sodium.
105. Define the terms *anhydrous*, *hydrous*, *hydrate*, *anhydride*.
106. What do you understand by *water of crystallization*?
107. What is the nature of "Soda-water"?
108. How many volumes of gas (reckoned as at ordinary atmospheric pressure) are contained in any given volume of the British official "Soda-water"?
109. What is the general law regarding the solubility of gases in liquids under pressure?
110. What is the systematic name of Rochelle salt, and how is the salt prepared?

111. What is the relation of Rochelle salt to cream of tartar and tartaric acid?

112. Give the mode of preparation and composition of Solution of Chlorinated Soda, and express the process by a diagram.

113. How is the granular effervescing Citro-tartrate of Sodium prepared?

114. Define *Deliquescence*, *Efflorescence*, and *Lixiviation*.

115. What is the general relation of potassium salts to those of sodium?

116. How are sodium salts analytically distinguished from those of potassium?

AMMONIUM.

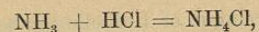
Symbol NH_4 . Atomic weight 18.

Memoranda.—The elements nitrogen and hydrogen, in the proportion of one atom to four (NH_4), are those characteristic of all the compounds about to be studied, just as potassium (K) and sodium (Na) are the characteristic elements of the potassium and sodium compounds. Ammonium is a univalent nucleus, root, or radical, like potassium or sodium; and the ammonium compounds closely resemble those of potassium or sodium. In short, if, for an instant, potassium or sodium be imagined to be compounds, the analogy between these three series of salts is complete. Ammonium is said to have been isolated by Weyl, as an unstable dark-blue liquid possessing a metallic lustre.

Source.—The source of nearly all the ammoniacal salts met with in commerce is ammonia-gas (NH_3) obtained in distilling coals in the manufacture of ordinary illuminating gas and of coke. It is doubtless derived from the nitrogen of the plants from which the coal has been produced. It is possible, however, to produce ammonia from its elements. Thus, coal-dust, air, and vapor of water, all at a red heat, yield, according to Rickman and Thompson, gaseous ammonia. Salt added to the mixture prevents the further combustion of the formed ammonia, and chloride of ammonium sublimes. Nitrogen and hydrogen passed over spongy platinum yields traces of ammonia.

Ammonia.—When this gas (NH_3) comes into contact with water (H_2O), in the process of washing and cooling coal-gas, hydrate of ammonium (NH_4HO) is believed to be formed, the analogue of hydrate of potassium (KHO) or sodium (NaHO). The grounds for this belief are the observed analogy of the well-known ammoniacal salts to those of potassium and sodium, the similarity of action of solution of potash, soda, and ammonia on salts of most metals, and the existence of crystals of an analogous sulphur salt (NH_4HS).

Chloride of Ammonium.—The ammonia of the "ammoniacal liquor" of the gas-works, liberated by heat and the concurrent action of lime on sulphhydrate, carbonate, and other salts present, and passed into hydrochloric acid, yields crude *chloride of ammonium* (sal-ammoniac),



and from this salt, purified, the others used in pharmacy are directly or indirectly made. Chloride of ammonium (*Ammonii Chloridum*, U. S. P.) occurs in colorless, inodorous minute crystals or in translucent fibrous masses, tough, and difficult to powder, and as a snow-white crystalline powder, soluble in water [1 in 10 is the "Solution of Chloride of Ammonium," U. S. P.] and in rectified spirit. Chloride of ammonium generally contains slight traces of oxychloride of iron, tarry matter, and possibly chlorides of compound ammoniums (vide "Artificial Alkaloids" in Index).

Sulphate of Ammonium, $(\text{NH}_4)_2\text{SO}_4$, results when the ammonia from "ammoniacal liquor" is neutralized by oil of vitriol. It is largely used as a constituent of artificial manure in England, and when purified by recrystallization is employed in pharmacy (*Ammonii Sulphas*, U. S. P.).

Volcanic Ammonia.—A very pure form of ammonia is that met with in volcanic districts, and obtained as a by-product in the manufacture of borax; the crude boracic acid as imported contains from 5 to 10 per cent. of ammonium salts, chiefly sulphate, and double sulphates of ammonium with magnesium, sodium, and manganese (Howard).

REACTIONS HAVING (a) GENERAL, (b) SYNTHETICAL, AND (c) ANALYTICAL INTEREST.

Ammonium-Amalgam. (?)

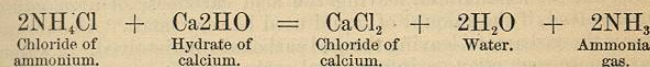
(a) *General Reaction*.—To forty or fifty grains of dry mercury in a dry test-tube, add one or two small pieces of sodium (freed from adhering naphtha by gentle pressure with a piece of filter-paper), and amalgamate by gently warming the tube. To this amalgam, when cold, add some fragments of chloride of ammonium and a strong solution of the same salt. The sodium amalgam soon begins to swell and rapidly increase in bulk, probably overflowing the tube. The light spongy mass produced is the so-called ammonium-amalgam, and the reaction is usually adduced as evidence of the existence of ammonium; the sodium of the amalgam unites with the chlorine of the chloride of ammonium, while the ammonium is supposed to form an amalgam with the mercury. As soon as formed the amalgam gives off hydrogen and ammonia gases; this decomposition is nearly complete after some minutes, and impure mercury remains.

(b) Reactions having Synthetical Interest.

Hydrate of Ammonium. Ammonia.

First Synthetical Reaction.—Heat a few grains of sal-ammo-

niac with about an equal weight of hydrate of calcium (slaked lime) dampened with a little water in a test-tube; ammonia gas is given off, and may be recognized by its well-known odor. It is very soluble in water. Pass a delivery-tube, fitted to the test-tube as described for the preparation of oxygen and hydrogen, into a second test-tube, at the bottom of which is a little water; again heat, the end of the delivery-tube being only just beneath the surface of the water (or, possibly, all the water might rush into the generating-tubes, water absorbing ammonia gas with great avidity); solution of ammonia will be thus formed.



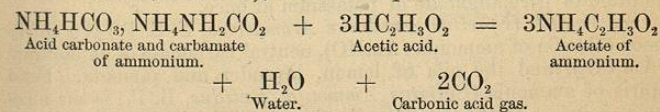
Ammonia gas is composed of one atom of nitrogen with three atoms of hydrogen; its formula is NH_3 ; two volumes of it contain one volume of nitrogen combined with three atoms or volumes of hydrogen. Its constituents have therefore in combining suffered condensation to one half their normal bulk. Its conversion into hydrate of ammonium may be thus shown:—



Solutions of Ammonia, prepared by this process on a large scale and in suitable apparatus, are met with in pharmacy—the one (sp. gr. 0.900) containing 28 per cent., the other (sp. gr. 0.959), 10 per cent., by weight, of ammonia gas, NH_3 (*Aqua Ammoniae Fortior* and *Aqua Ammoniae*, U. S. P.). On the large scale, bottles are so arranged in a series as to condense all the ammonia evolved during the operation.

Acetate of Ammonium.

Second Synthetical Reaction.—To acetic acid and water in a test-tube, add powdered commercial carbonate (acid carbonate and carbamate) of ammonium till effervescence ceases; the resulting liquid, made of prescribed strength, is the official solution of Acetate of Ammonium ($\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$) (*Liquor Ammonii Acetatis*, U. S. P.), the old "Spirit of Mindererus."

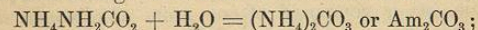


Carbonates of Ammonium.

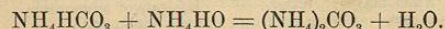
Commercial carbonate of ammonium is made by heating a mixture of chalk and sal-ammoniac; chloride of calcium (CaCl_2) is produced, ammonia gas (NH_3) and water (H_2O) escape, and the ammoniacal

carbonate distils, or rather sublimes,* in cakes (*Ammonii Carbonas*, U. S. P.). The best form of apparatus to employ is a retort with a short wide neck and a cool receiver. On the large scale the retort is usually iron and the receiver earthenware or glass; on the small scale glass vessels are employed. The salt is purified by resublimation at a low temperature; 150° F. is said to be sufficient.

This salt, the empirical formula of which is $N_3H_7C_2O_5$, is probably a mixture of one molecule (sometimes two) of acid carbonate or bicarbonate of ammonium (NH_4HCO_3) and one of a salt termed carbamate of ammonium ($NH_4NH_2CO_2$). The latter belongs to an important class of salts known as carbamates, but it is the only one of interest to the pharmacist. Cold water extracts it from the commercial carbonate of ammonium, leaving the acid carbonate of ammonium undissolved, if the amount of liquid used be very small. Alcohol extracts the carbamate, leaving the acid carbonate undissolved. In water, carbamate soon changes into neutral carbonate of ammonium,



so that an aqueous solution of commercial carbonate of ammonium contains both acid carbonate and neutral carbonate of ammonium. If to such a solution some ordinary solution of ammonia be added, a solution of *neutral carbonate of ammonium* is obtained; and this is the common reagent always found on the shelves of the analytical laboratory.



Neutral carbonate of ammonium is the salt formed on adding strong solution of ammonia to the commercial carbonate in preparing a pungent mixture for toilet smelling-bottles; but it is unstable, and on continued exposure to air is reduced to a mass of crystals of the acid carbonate or bicarbonate of ammonium. Bicarbonate of ammonium (NH_4HCO_3) is also produced on passing carbonic acid gas into an aqueous solution of commercial carbonate.

According to Divers, the sublimed product of the first distillation of chalk and sal-ammoniac is a mixture of carbamate and carbonate of ammonium, the latter losing some ammonia gas on redistillation, and carbamate with bicarbonate forming the resulting commercial salt.

If carbonate of ammonium contain more than traces of empyreumatic matters (derived primarily from the gas-liquors), an aqueous solution, with excess of sulphuric acid added, will decolorize a dilute solution of permanganate of potassium at once.

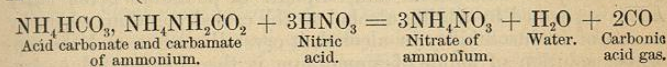
Sal Volatile (*Spiritus Ammoniae Aromaticus*, U. S. P.) is a spirituous solution of ammonia ($AmHO$), neutral carbonate of ammonium (Am_2CO_3), and the oils of lemon, lavender and pimenta. Fetid spirit of ammonia (*Spiritus Ammoniae Fetidus*, B. P.) is an alcoholic solution of the volatile oil of asafetida mixed with solution of ammonia. "Solution of Carbonate of Ammonia," B. P., is formed

* Sublimation (from *sublimis*, high). Vaporization of a solid substance by heat, and its condensation on an upper and cooler part of the vessel or apparatus in which the operation is performed.

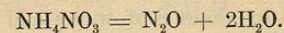
by dissolving 1 part of the salt in 10 of water. *Spiritus Ammoniae*, U. S. P., is an alcoholic solution of ammonia containing 10 per cent., by weight, of gas (NH_3).

Nitrate of Ammonium.

Third Synthetical Reaction.—To some diluted nitric acid add carbonate of ammonium, until, after well stirring, a slight ammoniacal odor remains. The solution contains Nitrate of Ammonium (*Ammonii Nitras*, U. S. P.)



From a strong hot solution of nitrate of ammonium crystals may be obtained containing much water ($NH_4NO_3 \cdot 12H_2O$). On heating these to about 320° F. the water escapes. The anhydrous salt remaining (NH_4NO_3) may be poured on to an iron plate. On further heating the powdered nitrate, at 350°–450° F., it is resolved into *nitrous oxide* gas (the so-called laughing gas) and water.



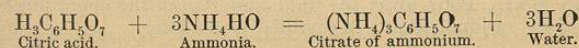
Nitrous oxide is thus prepared for use as an anaesthetic. When required for inhalation, it should be washed from any possible trace of acid or nitric oxide, by being passed through solution of potash, and through solution of ferrous sulphate, the former absorbing acid vapors and the latter nitric oxide.

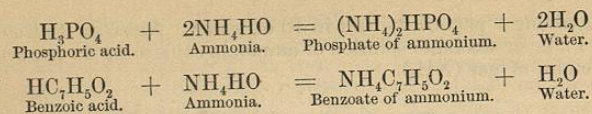
Nitrous oxide is slightly soluble in warm water, more so in cold. It supports combustion almost as well as oxygen. By pressure it may be liquefied to a colorless fluid, and by simultaneous cooling solidified.

Citrate, Phosphate, and Benzoate of Ammonium.

Fourth Synthetical Reaction.—To solution of citrate acid ($H_3C_6H_5O_7$) add solution of ammonia (NH_4HO) until the well-stirred liquid smells faintly of ammonia. Solutions having the specific gravities, respectively, of 1.062 (four times the strength) and 1.209 form the official Solutions of Citrate of Ammonium ($(NH_4)_3C_6H_5O_7$, *Liquor Ammoniae Citratis*, B. P., and *Liquor Ammonii Citratis Fortior*, B. P.

Phosphate of Ammonium, NH_4HPO_4 (*Ammonii Phosphas*, U. S. P.), and *Benzoate of Ammonium*, $NH_4C_7H_5O_2$ (*Ammonii Benzoas*, U. S. P.), are also made by adding solution of ammonia to phosphoric acid (H_3PO_4) and benzoic acid ($HC_7H_5O_2$) respectively, evaporating (keeping the ammonia in slight excess by adding more of its solution), and setting aside for crystals to form.





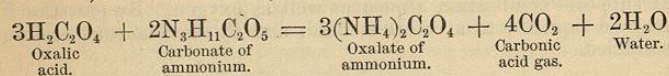
Phosphate of ammonium occurs in transparent colorless prisms, soluble in water, insoluble in spirit; benzoate in crystalline plates, soluble in water and in spirit.

Ammonii Iodidum, U. S. P., may be made by decomposing the two bodies iodide of potassium and sulphate of ammonium, which give iodide of ammonium and sulphate of potassium; the latter salt is separated by adding alcohol to the cooled solution, when, by reason of its insolubility in alcohol, it crystallizes out, and the separated solution of iodide of ammonium is then evaporated to dryness. It occurs usually in minute white crystalline cubes.

Bromide of Ammonium (*Ammonii Bromidum*, U. S. P.) will be noticed in connection with Hydrobromic Acid and other Bromides.

Oxalate of Ammonium.

Fifth Synthetical Reaction.—To a nearly boiling solution of 1 part of oxalic acid in about 8 of water add carbonate of ammonium until the liquid is neutral to *test-paper* (see following paragraph), filter while hot, and set aside for crystals to form. The product is oxalate of ammonium, $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$. The mother-liquor is useful as a reagent in analysis; 1 of the pure salt in 20 of water constitutes "Solution of Oxalate of Ammonium," U. S. P.



Neutralization.—Thus far, in reactions, the methods by which the student has avoided excess of either acid matter on the one hand, or alkaline matter on the other, have been the rough aid of taste, cessation of effervescence, presence or absence of odor, etc. More delicate aid is afforded by *test-papers*.

Test-papers.—*Litmus* is a blue vegetable pigment, prepared from various species of *Roccella* lichen, exceedingly sensitive to the action of acids, which turn it red. When thus reddened, alkalies (potash, soda, and ammonia) and other soluble hydrates readily turn it blue. The student should here test for himself the delicacy of this action by experiments with paper soaked in solution of litmus and dipped into very dilute solutions of acids, acid salts ($\text{KHC}_4\text{H}_4\text{O}_6$, *e. g.*), alkalies, and such neutral salts as nitrate of potassium, sulphate of sodium, or chloride of ammonium.

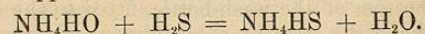
Solution of Litmus (U. S. P.).—This is prepared from purified litmus. Gently boil litmus with three times its bulk of spirit of wine for an hour. Pour away the fluid and repeat the operation twice. Digest the residual litmus in distilled water-filter.

Blue litmus paper (U. S. P.) is "unsized white paper colored with solution of litmus." *Red litmus paper* (U. S. P.) is "unsized white paper colored with solution of litmus previously reddened by the smallest requisite quantity of sulphuric acid."

Turmeric paper (U. S. P.), similarly prepared from Tincture of Turmeric (1 of turmeric root or rhizome to 6 of diluted alcohol, macerated for seven days), is occasionally useful as a test for alkalies, which turn its yellow to brown; acids do not affect it.

Sulphydrate of Ammonium.

Sixth Synthetical Reaction.—Pass sulphuretted hydrogen gas (H_2S) through a small quantity of solution of ammonia in a test-tube, until a portion of the liquid no longer causes a white precipitate in solution of sulphate of magnesium (Epsom salt); the product is solution of sulphydrate (or sulphide) of ammonium (NH_4HS), the "Solution of Sulphide of Ammonium," U. S. P., a most valuable chemical reagent, as will presently be apparent.



"*Test-Solution of Sulphide of Ammonium*," U. S. P., is made by passing the gas prepared in the apparatus described below into 3 fluidounces of Water of Ammonia so long as the gas continues to be absorbed, then adding 2 more ounces of the ammonia, and preserving the solution in a well-stoppered bottle.

Sulphuretted hydrogen is a compound of noxious odor; hence the above operation, and many others, described further on, in which this gas is indispensable, can only be performed in the open air, or in a fume-cupboard, a chamber so contrived that deleterious gases and vapors shall escape into a chimney in connection with the external air. In the above experiment, the small quantity of gas required can be made in a test-tube, after the manner of hydrogen itself. To two or three fragments of sulphide of iron (FeS), add water and then sulphuric acid; the gas is at once evolved, and may be conducted by a tube into the solution of Ammonia. Sulphate of iron remains dissolved in the water.



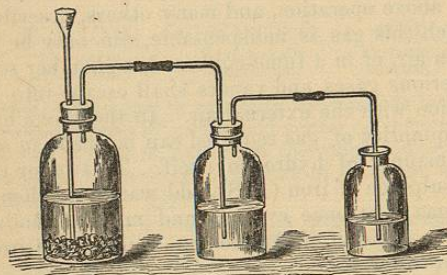
Crystals of sulphydrate of ammonium (NH_4HS) may be obtained on bringing ammonia gas (NH_3) and sulphuretted hydrogen (H_2S) together at a low temperature. They are soluble in water without decomposition.

Sulphuretted-Hydrogen Apparatus.—As no heat is necessary in making sulphuretted hydrogen, the test-tube of the foregoing operation may be advantageously replaced by a bottle,

especially when larger quantities of the gas are required. In analytical operations the gas should be purified by passing it through water contained in a second bottle.

The most convenient arrangement for experimental use is prepared as follows: Two common wide-mouthed bottles are selected, the one having a capacity of about half a pint, the other a quarter pint; the former may be called the generating-bottle, the latter the wash-bottle. Fit two corks to the bottles. Through each cork bore two holes by a round file or other instrument of such a size that glass tubing of about the diameter of a quill pen shall fit them tightly. Through one of the holes in the cork of the generating-bottle pass a funnel-tube, so that its extremity may nearly reach the bottom of the bottle. To the other hole adapt a piece of tubing, 6 inches long, and bent in the middle to a right angle. A similar "elbow-tube" is fitted to one of the holes in the cork of the wash-bottle, and another elbow-tube, one arm of which is long enough to reach to near the bottom of the wash-bottle, fitted to the other hole. Removing the corks, two or three ounces of water are now poured into each bottle, an ounce or two of sulphide of iron put into the generating-bottle, and the corks replaced. The elbow-tube of the generating-bottle is now attached by a short piece of India-rubber tubing to the long-armed elbow-tube of the

Fig. 18.



Sulphuretted-Hydrogen Apparatus.

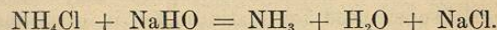
wash-bottle, so that gas coming from the generator may pass through the water in the wash-bottle. The delivery-tube of the wash-bottle is then lengthened by attaching to it, by India-rubber tubing, another piece of glass tubing several inches in length. The apparatus is now ready for use. Strong sulphuric acid is poured down the funnel-tube in small quantities at a time, until brisk effervescence is established, and more added

from time to time as the evolution of gas becomes slow. The gas passes through the tubes into the wash-bottle, where, as it bubbles up through the water, any trace of sulphuric acid, or other matter mechanically carried over, is arrested, and thence the gas flows out at the delivery-tube into any vessel or liquid that may be placed there to receive it. The generator must be occasionally dismounted and the sulphate of iron washed out.

Luting (lutum, mud).—If the corks of the above apparatus are sound, and tube-holes well made, no escape of gas will occur. If rough corks have been employed, or the holes are not cylindrical, linseed-meal lute may be rubbed over the defective parts. The lute is prepared by mixing linseed-meal with water to the consistence of dough. A neat appearance may be given to the lute by gently rubbing a well-wetted finger over its surface.

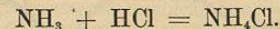
(c) *Reactions having Analytical Interest (Tests).*

First Analytical Reaction.—To a solution of any salt of ammonium (the chloride, for example) in a test-tube, add solution of caustic soda (or solution of potash, or a little slaked lime); ammonia gas is at once evolved, recognized by its well-known odor.



Though ammonium itself cannot be kept in the free state, its compounds are stable. Ammonia is easily expelled from these compounds by action of the stronger alkalies, caustic potash, soda, or lime. As a matter of exercise, the student should here draw out equations in which acetate ($\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$), sulphate ($(\text{NH}_4)_2\text{SO}_4$), nitrate (NH_4NO_3) or any other ammoniacal salt not already having the odor of ammonia, is supposed to be under examination; also representing the use of the other hydrates, potash (KHO) or slaked lime (Ca_2HO).

The odor of ammonia gas is perhaps the best means of recognizing its presence; but the following tests are also occasionally useful. Into the test-tube in which the ammonia gas is evolved insert a glass rod moistened with hydrochloric acid (that is, with the solution of hydrochloric acid gas, conveniently termed hydrochloric acid, the *Acidum Hydrochloricum* of the Pharmacopœias); white fumes of chloride of ammonium will be produced.



Hold a piece of moistened red litmus paper in a tube in which ammonia gas is present; the red color will be changed to blue.

Second Analytical Reaction.—To a few drops of a solution of an ammonium salt add a drop or two of hydrochloric acid

and a like small quantity of solution of perchloride of platinum (PtCl_4); a yellow crystalline precipitate of the double chloride of platinum and ammonium ($\text{PtCl}_4 \cdot 2\text{NH}_4\text{Cl}$) will be produced, similar in appearance to the corresponding salt of potassium, the remarks concerning which (p. 78) are equally applicable to the precipitate under notice.

Third Analytical Reaction.—To a moderately strong solution of an ammonium salt add a strong solution of tartaric acid, and shake or well stir the mixture; a white granular precipitate of acid tartrate of ammonium will be formed.

For data from which to draw out an equation representing this action, see the remarks and formulæ under the analogous salt of potassium (p. 77).

Fourth Analytical Fact.—Evaporate a few drops of a solution of an ammonium salt to dryness, or place a fragment of a salt in the solid state on a piece of platinum foil, and heat in a flame; the salt is readily volatilized. As already noticed, the salts of potassium and sodium are fixed under these circumstances, a point of difference of which advantage will frequently be taken in analysis. A porcelain crucible may often be advantageously substituted for platinum foil in experiments on volatilization.

Salts of ammonium with the more complex acidulous radicals seldom volatilize unchanged when heated. The oxalate, when warmed, loses its water of crystallization, and at a higher temperature decomposes, yielding carbonic oxide, carbonic acid gas, ammonia gas, water (the three latter sometimes in combination), and several organic substances. The phosphate yields more or less phosphoric acid as a residue.

Fig. 19.

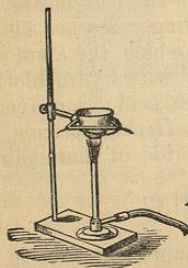


Fig. 20.

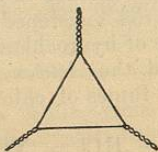
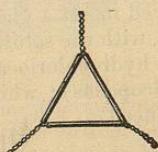


Fig. 21.



Triangular Supports for Crucibles.

A wire triangle may be used in supporting crucibles. It is made

by twisting together each pair of ends of three (5 or 6 inch) crossed pieces of wire (Fig. 20). A piece of tobacco-pipe stem (about 2 inches) is sometimes placed in the centre of each wire before twisting, the transference of any metallic matter to the sides of the crucible being thus prevented (Fig. 21).

Practical Analysis.

With regard to those experiments which are useful rather as means of detecting the presence of potassium, sodium, and ammonium, than as illustrating the preparation of salts, the student should proceed to apply them to certain solutions of any of the salts of potassium, sodium, and ammonium, with the view of ascertaining which metal is present; that is, proceed to practical analysis.* A little thought will enable him to apply these reactions in the most suitable order and to the best advantage for the contemplated purpose: but the following arrangements are perhaps as good as can be devised:—

DIRECTIONS FOR APPLYING THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF A SALT OF ONE OF THE METALS, POTASSIUM, SODIUM, AMMONIUM.

Add caustic soda to a small portion of the solution to be examined, and warm the mixture in a test-tube; the odor of ammonia gas at once reveals the presence of an ammonium salt.

If ammonium be not present, apply the perchloride-of-platinum test to another portion of the liquid; a yellow precipitate proves the presence of potassium.

(It will be observed that potassium can only be detected in the absence of ammonium, salts of the latter radical giving similar precipitates.)

The flame-test is sufficient for the recognition of sodium.

* Such solutions are prepared in educational laboratories by a tutor. They should, under other circumstances, be mixed by a friend, as it is not desirable for the student to know previously what is contained in the substance he is about to analyze.

The analysis of solutions containing only one salt serves to impress the memory with the characteristic tests for the various metals and other radicals, and familiarize the mind with chemical principles. Medical students seldom have time to go further than this. More thorough analytical and general chemical knowledge is only acquired by working on such mixtures of bodies as are met with in actual practice, beginning with solutions which may contain any or all the members of a group. Hence in this Manual two Tables of short directions for analyzing are given under each group. Pharmaceutical students should follow the second Table.

DIRECTIONS FOR APPLYING THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS OF ONE, TWO, OR ALL THREE OF THE ALKALI METALS.

Commence by testing a small portion of the solution for an ammonium salt. If present, make a memorandum to that effect, and then proceed to get rid of the ammoniacal compound to make way for the detection of potassium: advantage is here taken of the volatility of ammonium salts and the fixity of those of potassium and sodium. Evaporate the original solution to dryness in a small basin, transfer the solid residue to a porcelain crucible, and heat the latter to a low redness, or until dense white fumes (of ammoniacal salts) cease to escape. (See Fig. 19.) This operation should be conducted in a fume-cupboard, to avoid contamination of the air of the apartment. When the crucible is cold, dissolve out the solid residue with a small quantity of hot water, and test the solution for potassium by the perchloride-of-platinum test, and for sodium by the flame test.

If ammonium is proved to be absent, the original solution may, of course, at once be tested for potassium and sodium.

Flame-test.—The violet tint imparted to flame by potassium salts may be seen when masked by the intense yellow color due to sodium, if the flame be observed through a piece of dark-blue glass, a medium which absorbs the yellow rays of light.

Note on Nomenclature.—The operations of *evaporation* and *heating* to redness, or *ignition*, are frequently necessary in analysis, and are usually conducted in the above manner. If vegetable or animal matter be also present, carbon is set free, and ignition is accompanied by *carbonization*; the material is said to *char*. When all carbonaceous matter is burnt off, the crucible being slightly inclined and its cover removed to facilitate combustion, and mineral matter, or *ash*, alone remains, the operation of *incineration* has been effected.

Note on the Classification of Elements.—The compounds of potassium, sodium, and ammonium have many analogies. Their carbonates, phosphates, and other common salts are soluble in water. The atoms of the radicals themselves are univalent—that is, displace or are displaced by one atom of hydrogen. In fact, these radicals constitute by their similarity in properties a distinct group or family. All the elements thus naturally fall into classes—a fact that should constantly be borne in mind, and evidence of which should always be sought. It would be impossible for the memory to retain the details of chemistry without a system of classification and leading principles. Classification is also an important feature in the art as well as in the science of chemistry; for without it practical analysis

could not be undertaken. The classification adopted in this volume is founded on the quantivalence of the elements and on their analytical relations.

QUESTIONS AND EXERCISES.

117. Why are ammoniacal salts classed with those of potassium and sodium?

118. Mention the sources of the ammonium salts.

119. Describe the appearance and other characters of Chloride of Ammonium.

120. Give the formula of Sulphate of Ammonium.

121. Adduce evidence of the existence of ammonium.

122. How are the official Waters of Ammonia prepared? Give diagrams.

123. How is the official Solution of Acetate of Ammonium prepared?

124. What is the composition of commercial Carbonate of Ammonium?

125. Define *sublimation*.

126. What ammoniacal salts are contained in *Spiritus Ammoniac Aromaticus*?

127. Give diagrams or equations illustrating the formation of Citrate, Phosphate, and Benzoate of Ammonium?

128. Give the formula of Oxalate of Ammonium.

129. Show how Hydrate of Ammonium may be converted into Sulphhydrate.

130. Describe the preparation of Sulphuretted Hydrogen gas.

131. Enumerate and explain the tests for ammonium.

132. How is potassium detected in a solution in which ammonium has been found?

133. Give equations illustrating the action of hydrate of sodium on acetate of ammonium; hydrate of potassium on sulphate of ammonium; and hydrate of calcium on nitrate of ammonium.

134. What are the effects of acids and alkalies on litmus and turmeric?

135. Describe the analysis of an aqueous liquid containing salts of potassium, sodium, and ammonium.

136. What meanings are commonly assigned to the terms *evaporation*, *ignition*, *carbonization*, and *incineration*?

137. Write a short article descriptive of the analogies of potassium, sodium, and ammonium, and their compounds.