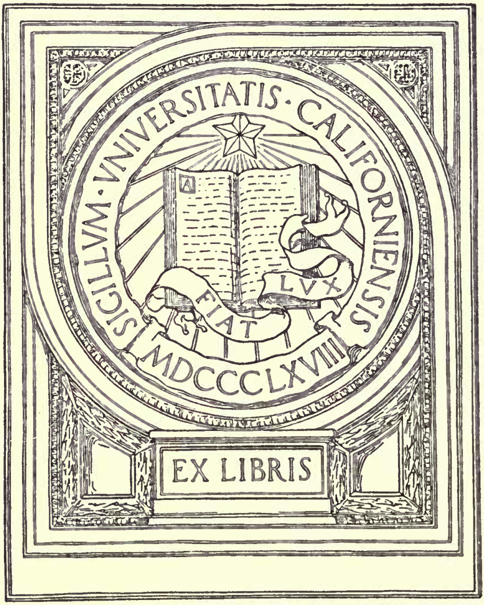

# ACETIC ACID AND VINEGAR, AMMONIA, AND ALUM.

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Three volumes have appeared under the editorship of Mr. JOHN GARDNER, F.I.C., F.C.S., who has had large experience in work of this kind, having been interested in the preparation of recent editions of "Cooley's Cyclopædia of Practical Receipts."

Mr. GARDNER, finding that, owing to other engagements, he is unable to continue this work, the co-operation as editor has been secured of Mr. JAMES CAMERON, F.I.C., Analyst in the Laboratory, Somerset House.

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CHURCHILL'S TECHNOLOGICAL HANDBOOKS.]

# ACETIC ACID AND VINEGAR,

# AMMONIA,

AND

# ALUM.

J. Gardner

$C_2H_5\text{-}OH + O = CH_3CHO + H_2O$

$CH_3CH_2OH + O = CH_3CHO + H_2O$

$CH_3CHO = O = CH_3COOH$

LONDON:
J. & A. CHURCHILL,
11 NEW BURLINGTON STREET.
1885.

# EDITOR'S PREFACE.

In the compilation of the present, as in the preceding volumes of the series, it has been the aim of the Editor to combine conciseness with practical utility. He hopes his endeavours may have been successful.

The Editor takes this opportunity of thanking his friends, Mr. James Taylor and Mr. John Linford, for many valuable suggestions; as well as for having given the sheets the benefit of their revision.

John Gardner, F.I.C., F.C.S.

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WATTS' "Dictionary of Chemistry."

# CONTENTS.

# ACETIC ACID AND VINEGAR, ALUM AND AMMONIA.

## CHAPTER I.

### ACETIC ACID.

ACETIC ACID, $HC_2H_3O_2$ or $C_2H_4O_2$.* *Syn.* ACID OF VINEGAR, NORMAL ACETIC ACID, REAL ACETIC ACID, HYDRATED ACETIC ACID, ABSOLUTE ACETIC ACID.

ACETIC ACID is the sour principle of vinegar.

Mention of vinegar occurs both in "Numbers" and "Proverbs." HIPPOCRATES employed it in medicine, and the alchemists obtained acetic acid in a concentrated form by distilling verdigris. LÖWITZ was the first to procure pure hydrated or normal acetic acid; and Dr. JOHN DAVY first pointed out that acetic acid was produced when spongy platinum was brought into contact with the vapour of alcohol.

Commercial acetic acid is met with under the forms of the pure glacial and dilute acids of the chemist and

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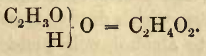
* GERHARDT regarded acetic acid as the hydrated oxide of an unisolated radicle, which he named *acetyl.* To acetyl he assigned the formula, $C_2H_3O$. That for acetic acid would therefore be:



$$\left.\begin{matrix} C_2H_3O \\ H \end{matrix}\right\} O = C_2H_4O_2.$$

pharmacist, and of vinegar, of which there are many varieties.

Its sources are—Fermented liquors; the vinegars of commerce; alcoholic liquors; wood, from which it is obtained, as pyroligneous acid, by distillation; the commercial acetates of soda, potassa, lime, lead, copper, &c. The acetic acid of the chemist and of commerce is almost wholly obtained from the acetates, either by the action of a strong acid, which seizes on the base, setting the acid free; or by dry distillation, in which the high degree of heat employed separates the acetic acid from the base in the form of vapour. It is also obtained by the oxidation of alcohol.

Acetic acid is produced either by the partial dehydrogenation and subsequent oxidation of bodies containing its elements, or by their destructive distillation. The first is effected—by their exposure, in a finely divided state, to the action of air or atmospheric oxygen, as in the quick process of making vinegar; or—by submitting them, in combination with ferments, to contact with a free supply of atmospheric air, as in the old field process of making vinegar; or—by exposure to the direct action of chemical or mechanical oxidizing agents, as condensed air (platinum-black process), chromic and nitric acid, &c.; in which latter case pure acetic acid is obtained. In general it is alcohol more or less dilute, particularly as it exists in fermented liquors, which is thus converted into acetic acid. In the second process—viz., by destructive distillation—wood is the substance usually employed, and heat is the agent which develops the acid.

The conversion of alcohol into acetic acid * is not immediate

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* 130½ lbs. of hydrated acetic acid contain 110·92 lbs. of anhydrous acetic acid; from which datum, it may be said, theoretically, that 100 lbs. of absolute alcohol will yield 111 lbs. of anhydrous

and direct. The atmospheric oxygen first oxidizes two atoms of its hydrogen, aldehyd and water being formed; and this aldehyd, uniting with one atom of oxygen, produces one molecule of acetic acid. The changes are represented in the following equations:—

Alcohol. Oxygen. Aldehyd. Water.

$$1.\quad C_2H_6O + O = C_2H_4O + H_2O$$

Aldehyd. Oxygen. Acetic Acid.

$$2.\quad C_2H_4O + O = HC_2H_3O_2$$

After the first formation of aldehyd, the two processes, unless artificially checked, go on simultaneously, as long as any undecomposed alcohol is present.

The conversion of alcohol into acetic acid, although greatly accelerated by the presence of yeast or of other ferments,* is rather a case of slow combustion than of fermentation. Acetification effects combination, as shown by the foregoing equations; whereas fermentation resolves complex bodies into simpler ones, as when sugar is converted into alcohol and carbonic anhydride. Moreover, the presence of ferments is not essential to the change, since pure alcohol becomes acidified when exposed to the oxidizing agents already named.

Another remarkable distinction between acetification and

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acetic acid. One pound of monohydrated acetic acid is generated from 0·77 lb. of absolute alcohol, and 1 lb. of anhydrous acetic acid from 0·9 lb. of absolute alcohol. These results, however, are higher than those obtained in practice, when there is always more or less loss arising from evaporation of the alcohol.

* Pasteur refers acetification of alcoholic solutions by the processes of fermentation to the presence of a fungus, which he calls the *mycoderma aceti*—the *mycoderma vini* of Mulder, or vinegar plant. Pasteur thinks this organism acts, like platinum black, by absorbing oxygen from the air, and imparting it in the nascent condition to the alcohol. His method of manufacturing vinegar by means of this mycoderm is described further on.

fermentation is, that the former requires the continuous presence of atmospheric oxygen, whilst the vinous fermentation, after being once established, proceeds perfectly without it.

During the oxidation of the alcohol of vegetable solutions, some of the other organic matters present also suffer change. A white gelatinous mass known as *Mother of Vinegar* is commonly deposited, but this is a secondary result of the process, and not, as formerly supposed, one essential to it. In ordinary cases acetification occurs only at or near the surface of the liquid; which accounts for the length of time required for the operation under the old process of *fielding*, and the shorter time in which it is accomplished under HAM's process.

Acetification proceeds favourably at temperatures ranging from 60° Fahr. (15·5° Cent.) to 90° Fahr. (32·2° Cent.), and, according to LIEBIG, most rapidly at 95° Fahr. (35° Cent.). In the quick process of vinegar-making, a temperature of 90° (32·2° Cent.) to 92° Fahr. (33·3° Cent.) is generally aimed at; but it often rises to 100° (37·7° Cent.), or even to 105° Fahr. (40·5° Cent.). As the temperature falls, acetification proceeds more slowly, and at 46° (7·7° Cent.) to 50° Fahr. (10° Cent.) it ceases altogether.

The following are processes for obtaining acetic acid:—

I. From the acetates* in the moist way.

*a.* From acetate of soda.

1. Commercial acetate of soda (*i.e.*, the "pure acetate" of the pyroligneous acid works), in crystals, is put into the body of a stout copper still, and a deep cavity being made in the centre of the mass, about 35 per cent. of sulphuric

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* When sulphuric acid is used for decomposing the acetates, it must be free from nitrous acid.

acid of a sp. gr. of not less than 1·84 is poured in; the walls of the cavity are then thrown in upon the acid, and the whole briskly agitated, for a very short time, with a large wooden spatula; the head of the still is next luted on, and the distillation conducted at a gentle heat, the receiver being changed as soon as the distillate begins to acquire a slight empyreumatic odour. The product, when the process is well managed, is an almost colourless acid of the sp. gr. of fully 1·05, containing about 40 per cent. of glacial acid, or between 34 and 35 per cent. of anhydrous acid (acetic anhydride, $C_4H_6O_3$). Any trace of colour or empyreuma is removed by agitation with some well-washed and recently ignited vegetable charcoal, or with a very small quantity of recently ignited purified animal charcoal, and subsequently passing it through a prepared calico bag-filter; or by allowing it to stand, for about a fortnight, in barrels containing some beech-wood chips; after which it is ready for sale, either as the ordinary acetic acid or pure pyroligneous acid of commerce; or on dilution with 5 times its weight of water, and after the addition of a little burnt sugar and acetic ether, as vinegar.

2. The acid of sp. gr. 1·05 obtained as above is distilled with fused chloride of calcium, the distillate being run into a refrigerator; the crystals that form are drained at a temperature below 40° or 45° Fahr. (4·4°—7·2° Cent.), and after removal to a warmer temperature, where they liquefy, and agitation with a little peroxide of lead, are submitted to a second distillation, as before; and this is repeated until the whole of the acid crystallizes at 55° Fahr. (12·7° Cent.). The product is the glacial acetic acid of commerce.

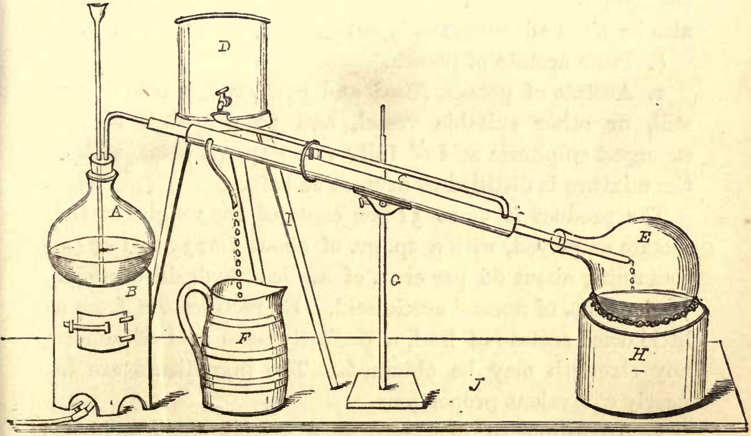
3. (MOLLERAT'S process—without distillation.)—Pure commercial acetate of soda, in coarse powder, is placed in a hard glazed stoneware or glass pan or receiver set in a cool situation, and 35 or 36 per cent. of concentrated sulphuric

acid, of the sp. gr. 1·843, added in such a manner that the acid may flow under the powder, and little heat be generated by the operation; the whole being covered up, is then allowed to remain in contact for some hours, when crystalline grains of sulphate of soda are found covering the bottom and sides of the vessel, and hydrated acetic acid, partly liquid and partly in crystals, the upper portion. The temperature being now slightly raised to a point just sufficient to cause the liquefaction of the crystals of acetic acid (*i.e.*, to from 62° to 65° Fahr.) (16·6°—18·3° Cent.), the fluid is poured off, and a very small quantity of pure acetate of lime added to it gradually, until it ceases to yield any trace of free sulphuric acid on evaporation. After sufficient repose it is carefully decanted for use. An excellent commercial strong acetic acid is thus obtained, without distillation, owing to the insolubility of sulphate of soda in acetic acid; and from which glacial acid may be procured by refrigeration. If, however, the process be badly managed, or the proportions of the ingredients be not carefully observed, the product will be contaminated with either a little sulphuric acid or saline matter. It is also important to the success of this process that it be performed in a cool apartment, and in well-cooled vessels. Perfectly-pure acetic acid may easily be obtained by rectification from this acid.

4. (LIEBIG'S process.)—Pure acetate of soda, thoroughly dried at 212° to 248° Fahr. (100° to 120° Cent.), and finely powdered, 3 parts, is placed in a capacious retort, and pure concentrated sulphuric acid, 9·7 parts, poured over it through the tubulure. One-eighth of the acetic acid passes over by the heat developed by the reaction of the ingredients. The heat of a sand-bath is next applied and continued until the contents of the retort become quite liquid. The distillate, carefully rectified, yields two parts of pure acid,

containing only 20 per cent of water. On exposing the latter portion which comes over in a closed vessel to a temperature below 40° Fahr., crystals of hydrated acetic acid are deposited. The weaker or liquid portion being poured off, the crystals are again melted and re-crystallized by cooling. The crystals of the last operation, separated from the liquid, and carefully drained in a cool and closed vessel, are perfectly pure glacial acetic acid.

FIG. I.



A is a flask containing the sodic acetate. The cork is perforated by two tubes, through one of which the sulphuric acid is introduced, whilst through the other the acetic vapours as they are evolved pass into the receiver E, through the condenser C, which is kept cooled by means of a stream of water flowing from the vessel D. B contains the gas-lamp for heating the mixture of sodic acetate and sulphuric acid. F is a jug placed to catch the heated water as it flows from the condenser. G is the support for the condenser.

The above is an excellent process for obtaining a chemically pure acid. The excess of sulphuric acid left from the process may be recovered by distillation; or the whole residuum may be employed in a second distillation with fresh acetate.

Although a retort is recommended by LIEBIG for the distillation, and is usually adopted, on the small scale, for the purpose, a flask closed by a cork perforated by two tubes, as shown in the engraving on the previous page, will be found more convenient and safe, as the product is then less likely to be contaminated by the "spurting" of the ingredients over the brim of the vessel. The heat of a diffused gas-flame may also be often advantageously substituted for a sand-bath.

*b.* From acetate of potash.

1. Acetate of potash, fused and powdered, is placed in a still, or other suitable vessel, and 50 per cent. of the strongest sulphuric acid of fully 1·840 sp. gr. being added, the mixture is distilled to dryness as before.

The product is 50 to 51 per cent. of the weight of the acetate employed, with a sp. gr. of about 1·0735 to 1·0740, containing about 66 per cent. of acetic anhydride, or about 75 per cent. of normal acetic acid. By rectification from a little dried acetate of lead, a perfectly pure acid of almost any strength may be obtained. The ingredients are in nearly equivalent proportions.

2. According to MELSENS, pure glacial acetic acid is most advantageously obtained by distilling pure and dry acetate of potash with an excess of strong and moderately pure acetic acid, rejecting that which first passes over.

The potassium acetate is mixed with a quantity of pure acetic acid of 7°—8° Baumé, sufficient to form the acid salt, which is then heated in a suitable vessel. Dilute acid at first comes over, but as the temperature increases, the acid salt is decomposed, and a distillate is obtained which solidifies on cooling. The residue is again treated with acetic acid, and a further quantity of acid salt is thus obtained. By rectifying the distillate over freshly fused potassium acetate, pure glacial acid is obtained.

*c.* From acetate of lead.

1. (URE.)—Take of dried acetate of lead 4 parts; strongest oil of vitriol, 1 part. Distil slowly to dryness. Nearly equal to the last.

2. (LIEBIG.)—Acetate of lead, 3 parts; sulphuric acid, 8 parts; as before.

3. (DOLFUS. Concentrated acetic acid.)—Take of dried acetate of lead, 12 oz.; sulphuric acid, 6 oz.; distil, 7 oz.

*d.* From acetate of lime.

1. (CHRISTL.)—Raw acetate or pyrolignite of lime (prepared by VÖLCKEL'S process),* 100 parts, is mixed with hydrochloric acid (20° Baumé, or sp. gr. 1·1515), 120 parts; and, after 12 hours, distilled in a copper vessel with a gradually applied heat. The product is 100 parts or lbs. of acetic acid of 8° Baumé (sp. gr. 1·0556), containing about 45 per cent. of hydrated acid only slightly

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* VÖLCKEL'S process is as follows:—The crude pyroligneous acid (that is, not previously distilled) is first saturated with lime, whereby part of the resinous matters are carried down with the excess of lime, and part remains in the supernatant liquid. This being either filtered or cleared by being kept at rest, is next evaporated in an iron pot to one-half its bulk. Hydrochloric acid is then added, in proportions (varying with the strength and quality of the pyroligneous acid) of from 80 to 50 parts of the latter to 1 part by weight of hydrochloric acid, or until the liquid acquires a faintly acid reaction. The hydrochloric acid liberates the resin, the creosote, and the volatile oils. The first rises to the surface, and is removed by skimming, while the creosote and oils are dissipated during the evaporation of the liquid. The solution of acetate of lime is then evaporated to dryness, the drying being conducted at a high temperature, to effectually remove the adhering empyreumatic matters, the presence of which would impart a very objectionable smell to the acid obtained from it.

coloured and empyreumatic, fit for various manufacturing purposes,* such as for making acetate of lead. The advantages of employing hydrochloric acid are the freedom of the product from contamination with sulphuric or sulphurous acid, besides which the deposition of a hard crust of sulphate of lime on the bottom of the retort is avoided.

It will be found that pyrolignite of lime generally contains 60 to 70 per cent. of neutral acetate; a proportionate quantity must therefore be employed, according to the amount contained in the sample. When the proper proportions are used the distillate gives a scarcely perceptible turbid cloud when tested with nitrate of silver. If the hydrochloric acid used has the sp. gr. 1·16, a smaller quantity being employed the product will have the sp. gr. of 1·058 to 1·061, and will then contain from 48 to 51 per cent. of the hydrated acetic acid, or 41 or 42 per cent. of acetic anhydride. The resin sometimes found floating upon the surface of the mixed ingredients should be carefully removed, by skimming, before distillation.

As acid of the above strength is rarely required, and as the distillation is more easily conducted when the ingredients are less concentrated, a little water may be conveniently added either before or towards the end of the distillation. Hence the following proportions have been recommended:—

2. (Völckel.)—Acetate of lime (as last), 100 parts; hydrochloric acid (sp. gr. 1·16), 90 to 95 parts; water, 25 parts; mix, and proceed as before. The product will be 96 to 98 parts of an excellent acid, well adapted to trading purposes, having a sp. gr. about 1·050 and containing nearly 40 per cent. of hydrated acetic acid. It has been correctly remarked

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* There is frequently a great difference in the specific gravity of the crude pyroligneous acid obtained from acetate of lime and hydrochloric or sulphuric acid.

that the acetic acid produced with hydrochloric acid is always of better quality than that produced with sulphuric acid, being not only less coloured but also entirely free from sulphurous acid. If necessary it may be rectified by redistilling with carbonate of soda, and any remains of empyreuma may be removed by distillation with 1 or 2 per cent. of bichromate of potash. The distillation uniformly proceeds with ease and regularity, and the whole of the acetic acid passes over between 212° and 248° Fahr. (100°—120° Cent.), by which the danger of contamination with other products, resulting from a high degree of heat, is obviated.

3. An acetic acid sufficiently strong and pure for many ordinary purposes may be obtained without distillation, by pouring strong sulphuric acid, 60 parts, diluted with water, 5 parts, on well-dried acetate of lime, 100 parts; digesting, with occasional agitation in a close vessel, decanting the clear liquid, and straining the remainder.

4. In 1868, H. B. CONDY took out a patent for the preparation of acetic acid from the double salt of chloride of calcium and acetate of lime (the aceto-chloride of calcium) and hydrochloric or sulphuric acid.

The aceto-chloride of calcium is first prepared either from the commercial, or, as it is technically called, the "distilled," acetate,* or from the brown acetate of lime. If brown

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[*] As the commercial acetate of lime contains more or less impurities, these are in great measure got rid of by roasting it for forty-eight hours in a large iron retort. The retort used for this purpose is usually about 6 feet long and 3½ feet in diameter, and furnished with an iron grating placed near the bottom, but with as few points of contact with the sides as possible. The acetate of lime is placed in sheet-iron trays, arranged on the grating one above the other, until they fill the retort, the trays being kept apart by iron rods, and as much as possible kept from touching the retort. The retort being then closed, a moderate heat is applied to it from a fire underneath, which is kept up until the water and volatile contamina-

distilled acetate, one part of the salt is dissolved in 5½ parts of boiling water, and to this solution, after it has been filtered or allowed to become clear by rest, dry chloride of calcium, in the proportion of $\frac{7}{10}$ths of the weight of acetate of lime used, is dissolved by the aid of heat and agitation. The liquid is then cautiously reduced by heat until it has a specific gravity of 30° Baumé. The aceto-chloride crystallizes out as the liquid becomes cold. The mother liquor is then drawn off, and evaporated down until it reaches 31° Baumé, when it is again drawn off and left to crystallize. These processes are repeated until three other crystallizations have been obtained. For the third crystallization, the liquid which is drawn off boils at about 30° Baumé, for the fourth at about 35°, and for the fifth at about 36° Baumé. An inferior acid is obtained from the final mother liquor by distillation with sulphuric or hydrochloric acid. The five batches of crystals, after being washed and drained, are next dissolved in twice their weight of water, and to the solution, after being filtered through animal charcoal, is added 10 per cent. of chloride of calcium.

The liquid is then evaporated till it reaches 29° Baumé, when pure white crystals are formed. By evaporating down the respective mother liquors from this last salt, the first at 30° Baumé, the second at 31°, and the third at 32° Baumé, three other crops of crystals may be procured. The results

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tions of the acetate are expelled, which may be known by the exit-pipe becoming cool.

When the aceto-chloride has been prepared from acetate of lime obtained from crude pyroligneous acid, it is roasted in the same manner before being redissolved and recrystallized. Sometimes, instead of being roasted, the aceto-chloride when in solution, or the acetate of lime alone, is filtered through animal charcoal; or the commercial acetate may be used without roasting for making the aceto-chloride, and this may be roasted.

are not so satisfactory or economical when the brown acetate of lime is employed in making the aceto-chloride. In this case it is requisite to use 20 per cent. more of the brown acetate than of "distilled" acetate for a given weight of chloride of calcium. The uncertain strength of the brown acetate renders it necessary to test the solution of aceto-chloride after it is evaporated down to 30° Baumé, to ascertain whether or no it yields a good crop of crystals. If it do not, the evaporation must be continued until it does.

Crude pyroligneous acid is sometimes used for preparing the aceto-chloride. The acid is first neutralized with lime, and the strength of the resulting solution ascertained by evaporating a small portion to dryness, weighing, and then apportioning the chloride of calcium according to the above ratio, and proceeding as before stated, with the exception that, for the first crop of crystals, the solution must be brought to 32° Baumé. In most cases the mother liquors are evaporated to half their bulk before they yield an additional crop of crystals. To obtain acetic acid from the aceto-chloride, it is distilled either with sulphuric or hydrochloric acid.

When sulphuric acid is used, 24 parts of sp. gr. 1·840, diluted with twice its volume of water, and 112 parts of the aceto-chloride, are taken. With hydrochloric acid the proportions are 100 parts of aceto-chloride and 50 parts of acid diluted with water.

As before stated, the acetic acid is obtained from the purified aceto-chloride of lime by distilling this with sulphuric, hydrochloric, and, we may add, with any other acid having a greater affinity for the lime than the acetic. To free the resulting acid from hydrochloric acid it is redistilled with an alkali or with acetate of soda; 1 lb. of either to every 10 gallons of acid.

Whichever the acid used, it will be found that the process of distillation goes on most satisfactorily if the mixture in the retort is largely diluted with water.

5. (KUHLMANN'S Process).—When crude pyroligneous acid is saturated by natural carbonate of baryta, or sulphide of barium, an acetate is obtained which it is necessary to roast with moderation in order not to decompose it; but, however, raising the temperature sufficiently high to drive off the tarry matter. It is important in every case, during this calcination, not to exceed an incipient red heat. The operation may be repeated several times.

The acetate of baryta thus obtained is decomposed by one equivalent of sulphuric acid; the decomposition is complete only when the solution is not too concentrated.

The result is sulphate of baryta and weak acetic acid, which however has sufficient density to be directly used in some manufactures. Thus it can be immediately employed in the fabrication of white lead, acetate of lead and other acetates.

When to produce the decomposition of the acetate of baryta by sulphuric acid, too much of the concentrated solution of acetate is used, the sulphate of baryta does not separate in its ordinary form; but then contains acetic acid, and presents a gelatinous, half transparent appearance, which it is difficult to destroy.

To obtain a purer acid, the acetate of baryta can be transformed into acetate of soda by the addition of sulphate of soda.

It is scarcely necessary to say that when a more concentrated acid is required, it is sufficient to distil the acetate of baryta with sulphuric acid.

The acetate of baryta is prepared by mixing finely powdered natural carbonate of baryta with pyroligneous acid, until all foaming ceases, and the resulting slightly acid solution is neutralized by sulphide or carbonate of baryta. After settling, the clear liquid is evaporated in a flat dish. The crystals as they form are removed, and deposited on an inclined surface, where they remain to drain. When drained the crystals are calcined in a large dish about three inches deep, and having a surface of 9 to 10 square feet, set in masonry in such a manner, as to be uniformly heated at the bottom without becoming red.

The crystals are spread in the dish to the depth of about 2 inches, and constantly stirred without being allowed to stick to the bottom. They are, lastly, heated until empyreumatic vapours cease to be given off, and a sample when dissolved in water gives a colourless solution. The crystals effloresce to a homogeneous powder, which must be removed from the fire into another dish, and constantly stirred till quite cold. In order to prevent a too great pulverization during the calcination, there may be mixed with the crystals some acetate of soda, which by melting renders the acetate of baryta damp. The calcined mass is dissolved in water, and the white acetate of baryta obtained by evaporation can be used to prepare acetic acid and acetates. It is claimed for the acetic acid and acetates prepared by the above process that they are of very pure quality.

II. From the acetates by dry distillation with a sulphate.

*a.* From acetate of lead.

1. Dried acetate of lead, 5 parts, and sulphate of iron, gently calcined, 2 parts, are separately powdered, and, after thorough mixture, carefully distilled, by the heat of a sand-bath, into a well-cooled receiver. This is an economical process for a strong acid, but is now seldom adopted.

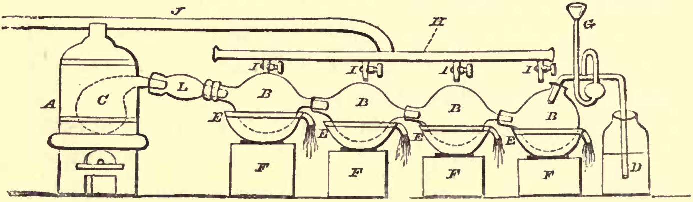
2. (Bardollier's strong acetous acid.)—Dried acetate of lead, 10 ozs.; calcined green vitriol, 12 ozs.; as the last.

*b.* From the acetates of copper.

By substituting acetate or diacetate of copper, in equivalent proportions, or, better still, with excess of the sulphate. Seldom used.

*c.* From acetate of potash; as the last.

FIG. 2.



*A*, Furnace.
*B B B B*, Glass receivers.
*C*, Stoneware retort.
*D*, Bottle containing vinegar
*E E E E*, Basins containing water.
*F F F F*, Supports for basins.
*G*, Welter safety-tube.
*H*, Supply-pipe of cold water.
*I I I I*, Cocks to supply water to the basins.
*J*, Water main.
*L*, Adapter connecting retort and globes.

III. From the acetates *per se.*

*a.* From acetate of copper.

AROMATIC VINEGAR; SPIRIT OF VERDIGRIS; SPIRITUS VENERIS; ESPRIT DE VÉNUS, Fr.; ACIDUM ACETICUM, Ph. L. 1787.—Dry carefully, crystallized verdigris (diacetate of copper) by a very gentle heat, and introduce it into a large stoneware retort (such as shown in the engraving), the bottom of which has been previously coated with a mixture of clay and horse-dung, to render it more capable of standing the fire. Next place it in a suitable furnace, and connect it, by an adapter, with three or four double tubulated globes (B, B, B, B,), the last of which must be furnished with a vertical tubulure, to which a double Welter's safety-tube should be adapted; the other end being immersed in a basin half-filled with distilled vinegar or water, while the funnel portion communicates with the atmosphere. The joinings are then to be coated with a paste composed of pipe-clay and linseed oil, and covered with glue-paper. Now place each globe in a basin of water, kept cool by a stream constantly passing through it; and cover the upper portion with cloths kept continually wet with cold water. After fifteen or twenty hours, fire may be applied, and must be so regulated that the drops follow each other with considerable rapidity from the end of the adapter, whilst the bubbles of air cause no inconvenience at the other end of the apparatus. If otherwise, the fire must be damped a little. The operation should be continued, and the fire gradually increased, until vapour ceases to come over, known by the globes gradually cooling, notwithstanding the heat of the furnace. The operation being concluded, the whole may be allowed to cool, and the acid collected preparatory to rectification. This may be effected in a similarly arranged apparatus, except that it must be wholly of glass; and the retort should not be much more than half filled. The operation must now be very carefully conducted, and discontinued before barely the whole of the acid has distilled over, as the last portion is apt to injure the flavour and colour of the rest. The first portions which come over are very weak, and should be kept separate until the sp. gr. reaches to about 1·072, when the receiver should be changed, and the product collected in separate portions, as noticed below.

Good diacetate of copper yields, by careful management, at a temperature of 400° to 560° Fahr. (204·4°–293° Cent.), fully one-half its weight of a greenish-coloured acid, of the sp. gr. of about 1·061, containing above 50 per cent. of hydrated acetic acid, or 40 per cent. of acetic anhydride. 20 lbs. of the ordinary acetate yields 9¾ lbs. of this rough acid, leaving a residuum of about 6½ lbs. of metallic copper mixed with a little charcoal in the retort; the remainder (nearly $\frac{2}{10}$ths of the acid in the acetate) being decomposed by the heat, and lost. This 9¾ lbs. of crude acid yields by rectification, and dividing the products, ½ lb. of acid of the sp. gr. 1·023; 3 lbs. of the sp. gr. 1·042; and 6 lbs. of the sp. gr. 1·065; exclusive of a little acetone which comes over with it. In the first distillation, the strongest acid is found in the third receiver, and the weakest in the first. The acid obtained in this way, is always accompanied with a little fragrant pyro-acetic spirit, which renders it preferable for aromatic vinegar* and perfumery. It dissolves camphor, resins, and essential oils with facility. This is one of the oldest methods of obtaining glacial acetic acid, and the product is still preferred for some purposes. It is the "radical vinegar" of the alchemists, and it is that which is said to be preferred by the perfumers. Well-dried acetate of lead, or of iron, as well as several other acetates, may be substituted for acetate of copper in the above process, but are less economical and convenient. In all cases great care must be taken to avoid over-firing, as thereby the quantity obtained is lessened, and the quality injured. The residuum of the distillation is pyrophoric, and frequently inflames spontaneously on exposure to the air. Due caution must be therefore observed regarding it. Until of late years, the above method of procuring acetic acid was that almost universally employed.

IV. From wood by destructive distillation. PYROLIGNEOUS ACID. *Syn.* VINEGAR OF WOOD. CRUDE ACETIC ACID.—Impure acetic acid, obtained by the destructive distillation of wood in close iron retorts. The acid comes over along with tar, creasote, wood spirit, and other liquid and gaseous matters, charcoal being left behind. In this state it con-

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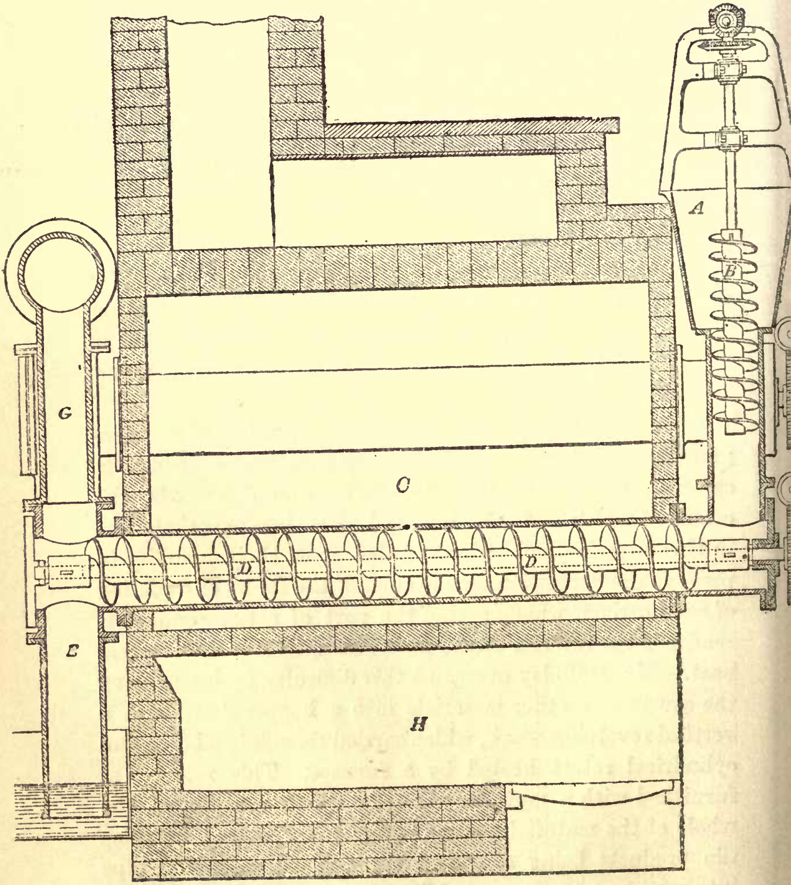
* The following formula from the Paris Codex yields a fragrant and refreshing aromatic vinegar:—Camphor, 2 ozs.; oil of lavender, 10 grains; oil of cinnamon, 20 grains; oil of cloves, 30 grains; concentrated acetic acid, 1 pint; macerate for seven days.

tains much empyreumatic matter in solution; but by separation from the tar, saturation with slaked lime or chalk, defecation and evaporation, an impure acetate or pyrolignite of lime is obtained, which, after being gently heated to destroy part of its empyreumatic matter, without injuring its acetic acid, is either used as the direct source of the acid or is again dissolved and defecated, and then precipitated by a solution of sulphate of soda, when a solution of acetate of soda and a precipitate of sulphate of lime are formed by double decomposition. The solution is next evaporated to dryness, the dry mass (pyrolignite of soda) dissolved in water, and the new solution filtered and recrystallized. The crystals of acetate of soda obtained by the last process yield nearly pure acetic acid by distillation with sulphuric or hydrochloric acid. Pyroligneous acid is largely manufactured in this country, France, Germany, and Belgium.

Some years ago, HALLIDAY, of Salford, patented an ingenious method for the manufacture of pyroligneous acid from sawdust, spent bark from tan-yards, and dye-woods, the colour of which had been removed. Previous experimenters in this direction had hitherto failed, from their inability to prevent the deposition on the sides of the retort of a coating of solid carbon, which, acting the part of a non-conductor, rendered the interior of the mass inaccessible to the external heat. Mr. Halliday overcame this difficulty by introducing the sawdust or other materials into a hopper fitted with a vertical revolving screw, which carried them into a horizontal cylindrical retort heated by a furnace. This retort was furnished with a movable worm, by which contrivance the whole of the material became perfectly carbonized, its volatile products being conveyed through an ascending pipe into a proper condenser, whilst the charcoal is discharged through a descending pipe into a cistern of water.

**Halliday** and **Hadfield** assert that the coniferous woods, which in ordinary retorts afford but a poor yield of

Fig. 3.



A. Hopper. B. Vertical screw. C. Retort. D. Movable worm. G. Ascending pipe. E. Descending pipe.

pyroligneous acid, yield a very considerable amount, when employed in the form of sawdust in this apparatus.

The sawdust of spent dye-wood, so treated, gave an amount of acid equal to that of ordinary woods.

Eight of Halliday's retorts, 14 inches in diameter, will, it is stated, produce in 24 hours the same amount of acid as 16 ordinary retorts, 3 feet in diameter, worked during the same time.

Eight of Halliday's retorts worked for many weeks, and converting into charcoal 22 tons of sawdust per week, gave an average product of :—

| | |
|---|---|
| Pyroligneous acid, 10° Tw. = 1·05 sp. gr. ... | 2,484 gallons. |
| Tar... ... ... ... ... ... ... | 240 ,, |

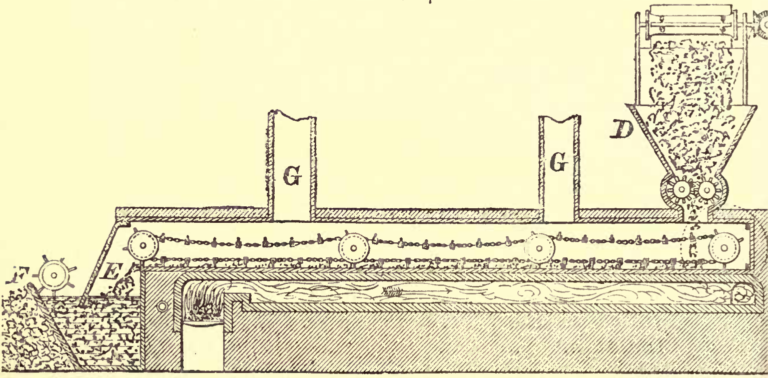
From 1 ton of oak, carbonized in ordinary cylinders, was obtained :—

| | |
|---|---|
| Pyroligneous acid, 6° Tw. = 1·03 sp. gr. ... | 1,277 lbs. |
| Charcoal ... ... ... ... ... ... | 600 ,, |

BOWER's apparatus is a modification of the above, and consists of a rectangular retort, placed at an angle of about 25°, and heated along its entire length by outside flues. Like HALLIDAY's, it is adapted to the distillation of sawdust, spent dye-woods, tan, &c.; which before being introduced into the retorts are dried by being propelled along a drying floor, by scrapers fixed on a revolving chain which is worked by drums turned by steam.

After the dried wood leaves the drying floor, it is raised by machinery and made to fall into the retort through a hopper, so constructed, as to prevent the escape of the products of distillation. When in the retort, the woody substances are kept in movement by an arrangement of chains, scrapers, and drums similar to that employed in the drying bed; and by the time they reach the end of the retort furthest from the hopper they have become charcoal, and as such are discharged into a receptacle full of water. At the top of the retort are two pipes, through which the volatile products of distillation are carried off, and are condensed in the ordinary manner. Bower's apparatus effects

Fig. 4.



D. Hopper. E. Receptacle containing water, into which the charcoal falls. F. Scraper for removing charcoal. GG. Pipes for carrying off products of distillation.

a considerable saving in steam power, provided the drying floor and the furnace are so arranged that the waste heat of the latter can be utilized for the former. The apparatus, owing to the slow movement of the machinery, suffers but little from wear and tear.

The drawbacks to the use of this and the previous apparatus are said to be the very inferior character of the charcoal, and the presence in the resulting acid of a large excess of resinous and oily substances, which are difficult of removal. The charcoal having to be dried, this involves another item of expense for fuel. The large demand for sawdust and its consequent high price, militate against its utilization for this purpose.

Solomon and Azulay's patent consists in passing superheated steam into a mass of sawdust, in such a manner that the sawdust becomes entirely and effectively carbonized. The volatile products largely diluted with steam when they leave the retorts, are made to traverse a coil of metal pipe placed in a pan of the distillates, which being thereby heated, the pyroligneous acid and other volatile products become volatilized, and pass into the adjoining condenser.

By another process, which has formed the subject of several patents, acetic acid, associated with wood naphtha, resin, and other products, is obtained from woody fibre, before this is used for paper-making. Under these circumstances, the wood is not of course, carbonized. By Fry's process, patented in 1869, the wood, after being cut into small pieces of from half an inch to an inch and a half long, and from $\frac{1}{8}$th to $\frac{1}{4}$ inch thick, is placed in cages made of copper wire or perforated zinc. The cages are next put into a cylindrical, jacketted iron boiler, and are of such dimensions as to exactly fill the boiler. The boiler being then filled with cold water, steam is admitted into the jacket from a second boiler connected with the first by a pipe, so that the steam can be regulated at pleasure. By this means the pieces of wood are heated to about 330° F. (165° Cent.), at which temperature, according to the description and size of wood, they are kept for 3, 4, or 5 hours, after which time the water surrounding them being removed from the boiler under proper precautions, is placed in a still, and the acetic acid separated from the other substances by fractional distillation. It is then neutralized with an alkali, carefully evaporated to dryness, and separated from the base by the usual treatment with sulphuric or hydrochloric acid. The difficulty of separating the acetic acid from the wood naphtha, resin, &c., has been a serious barrier to the successful working of this process.

In 1873, STEEDMAN patented a process for the purification of pyroligneous acid by passing it through paraffin, fat, or some hydrocarbon which possessed the power of absorbing and removing its impurities. The acetic acid in the state of vapour is conducted by a pipe into a rectangular copper vessel, 5 feet long, 1 foot wide, and about 3 feet deep. This vessel is filled with the liquefied hydrocarbon kept at a little higher temperature than the acetic acid, whereby the condensation and consequent loss of the latter is prevented. The interior of the vessel is so contrived as to cause the acid vapours as they issue from the distilling apparatus, to traverse it on their way to the condensing apparatus, and thus to be brought into contact with as large a body of the paraffin or other hydrocarbon as possible. The paraffin or other depurator in the copper vessel. is heated either by a coil of steam pipe or by a steam jacket, and is removed when saturated with the impurities.

By STOLTZE'S method the crude acetic acid is partially purified by distillation. He thus obtains 10 per cent. of a liquid which he uses for the production of wood naphtha, and 80 per cent. of impure acetic acid, the empyreumatic contaminations of which he destroys either by chlorine or ozone.

Wood distillation is conducted in various ways. In some works cast or wrought iron retorts * are used, and in others large square sheet iron ovens. These ovens are set in brickwork, so as to allow the flames from the naked fire underneath to play spirally around them; whilst the smoke

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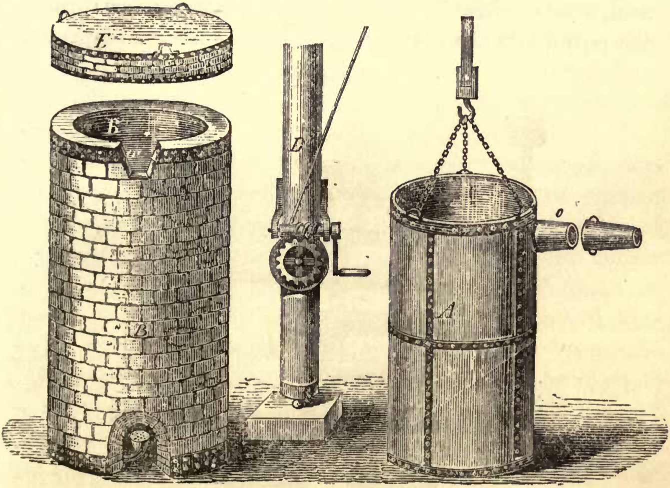
* Cylindrical retorts or ovens should not be made of cast iron. It is a disputed point among pyroligneous acid-makers whether wrought or cast iron is the better adapted for the distillation of wood. The advantage of using wrought is its much less tendency to crack, a quality which admits of the retorts being made thinner, and, therefore, causes them to be more quickly and economically heated. On

is carried off by flues into the chimney. A vertical retort, fitted at the upper part with a tube *o* as shown at A in the accompanying figure is used in France.

FIG. 5.



When A is charged with wood, the lid is tightly screwed on, so that the retort is made air-tight, and it is then raised by means of the crane D, and placed in the furnace B, which is afterwards closed by a lid E constructed of fire-brick. The products of the distillation are carried into the pipe *f*,

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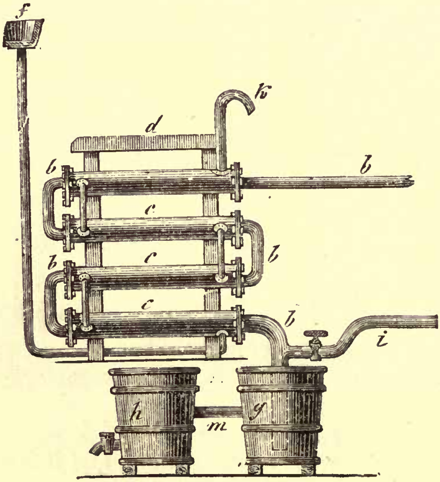
the other hand, retorts made of wrought iron, when overheated soon get out of shape, and occasionally leak at the joints. Owing to the liability of the acid vapours to condense, and consequently to act upon wrought iron, the exit pipes and doors of such retorts are *always* constructed of cast iron. The advantage of this latter is that the retorts being in one piece, the great inconvenience of leakage is avoided.

(Fig. 6) which passes through a series of iron condensers *c c c*, as shown in the engraving.

These condensers, which are supported on a framework *d*, are kept continually supplied with cold water* by the pipe *f*; whilst the heated water passes off by the pipe *k*. Acetic acid, wood spirit, and tar become condensed, and flow through the pipe *b* into the vessel *g*, when the tar becomes separated and remains, whilst the vinegar and wood spirit run through the pipe *m* into the receptacle *h*. The pipe *i* is for carrying off the uncondensable gases which result from the distillation, into the fire, where they are consumed, and thereby effect a considerable saving of fuel. This description of apparatus is employed, when the yield of acid is the first consideration.

FIG 6.



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* In some works the volatile products are condensed by means of cold air. This method, however, is very rarely adopted.

A similar condensing apparatus is employed when the distillation is carried out in ovens.

A rude form of distillation is carried on in some parts of France and Germany, where brushwood and heather are abundant. The wood is packed in a wrought iron retort resembling an inverted cone, and is set fire to, care being taken to admit no more air than is needed to effect carbonization. To the apex of the cone is attached a pipe through which the products of combustion pass into the condensers.

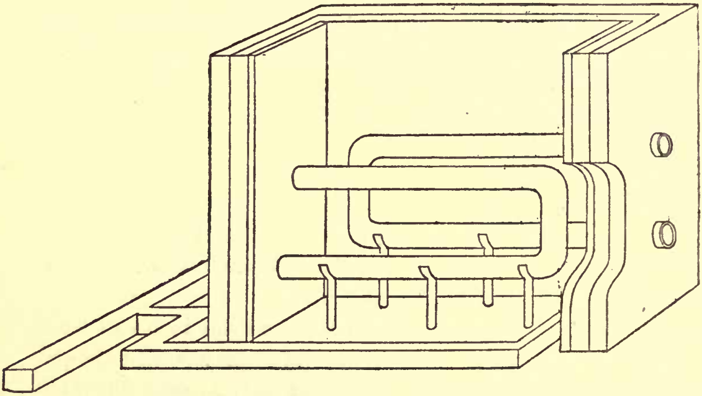
SCHWARTZ's carbonizer, which is largely used in France and Belgium, where the charcoal is the principal product required, consists of a fire-brick furnace, with a fireplace at the bottom having direct communication with the chamber or space containing the wood intended for distillation. In some cases the walls of the furnace are hollow, and filled with a mixture of sand and aluminous schist. When the fire is well alight, the flames play around the blocks of wood, causing them to become speedily carbonized, whilst the products of distillation are correspondingly rapidly liberated.

These last are carried through exit pipes, in their passage through which they part with their tar, whilst the acetic acid and oily matters together with the smoke, pass into wooden condensers, where the acid and oily substances remain, whilst the smoke escapes by the chimney.

When the carbonization is finished, as indicated by the colour of the smoke, from black to light blue, the chimneys and all the apertures are carefully closed, and when the furnace has cooled down, water is thrown upon the charcoal, the air being meanwhile excluded, until the charcoal ceases to show signs of ignition. SCHWARTZ's apparatus is so contrived as to admit only just sufficient air to carbonize the charcoal. It also possesses the advantage of enabling small wood to be utilized in the manufacture of the acid. "The cost of this furnace is about £120, the capacity being about 6,000 cubic feet."* This apparatus gives the best charcoal.

Reichenbach's carbonizer is a large square oven, the interior walls of which are of fire-brick. Running longitudinally through the oven from end to end and doubling back, are large tubes, around which the wood is placed. These tubes are from 1 to 2 feet in diameter, and are heated by means of a fire lighted inside them at their exterior orifice. When they become red-hot, the wood is carbonized, and the products of distillation run off, through openings in the bottom of the oven, into covered channels, where they deposit the tar, whilst the acetic acid in the state of vapour passes into a condensing apparatus. This and Schwartz's carbonizer are frequently made of a capacity of 5,000 or 6,000 cubic feet.

Fig. 7.



The English pyroligneous acid-makers usually employ

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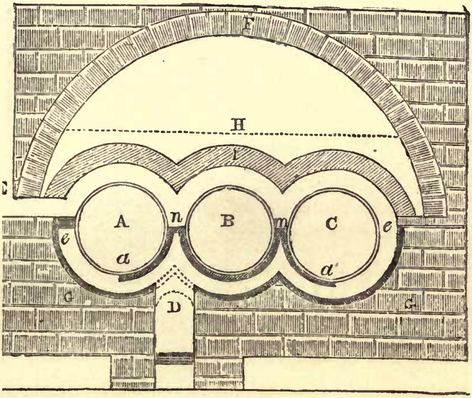
[*] "Chemistry, Theoretical, Practical, and Analytical." Mackenzie, London and Edinburgh.

cylindrical iron retorts built into brickwork. Eight such retorts constitute a good-sized work. Over the range of ovens is the drying house, on the floor of which the acetate of lime is dried. The retorts vary in length in different works, usually from 4 to 9 or 10 feet, and in breadth from $2\frac{1}{2}$ to 4 feet,* which experience, has shown to be a maximum diameter. The smaller the diameter the

FIG. 8.



A B C. Cylinders. D. Fire. e, e. Flues. H. Drying house.

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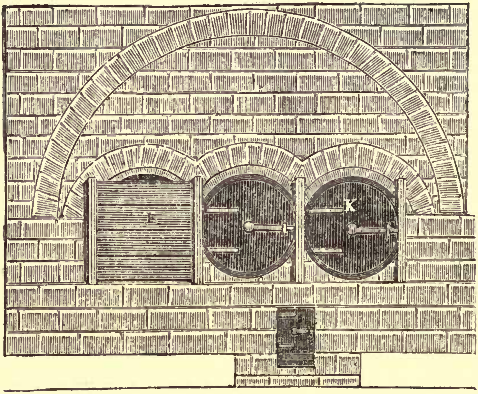
* Satisfactory results have been obtained by cylinders having the following dimensions:—No. 1, 7 feet long, 5 feet in diameter, 5 feet deep, and 5 feet broad (this was of wrought iron). No. 2, 10 feet long, $3\frac{1}{2}$ feet in diameter, $3\frac{1}{2}$ feet deep, and $3\frac{1}{2}$ feet broad (this was of cast iron). No. 3, 10 feet long, $3\frac{1}{10}$th feet in diameter, $3\frac{1}{10}$th feet deep, $3\frac{1}{10}$th feet broad (this was also of cast iron). No. 4, $9\frac{1}{2}$ feet long, $2\frac{1}{2}$ feet in diameter, 5 feet deep, and $3\frac{2}{3}$ feet broad (this was of rectangular shape, and of cast iron). Experience has shown that it is advantageous to let the end of the retort to which the pipe is attached, stand in about 5 inches, and to surround the exit pipe with a $4\frac{1}{2}$-inch brick wall.

more rapid the distillation. They are arranged horizontally, sometimes in sets of twos or threes or fives, with flues around each, and are heated by a fire underneath, which is not in direct contact with them. Very frequently each retort is heated by a separate fire, an arrangement which permits of the repair of a cylinder if needful. Rectangular retorts are heated by a separate furnace. The wood cut up into suitable lengths is packed into the retorts as closely as possible, so as to economize space. The average charge of each cylinder is about 24 cwt. of dry wood. One end of the retort is closed, sometimes by a massive iron door, which swings on stout hinges; and at others by an iron plate fastened by strong iron screws, or by cross bars, all being covered externally with a luting of clay or loam. To the other and further end of each retort is attached an iron pipe, which conducts the products of distillation into the condensers, which are metal pipes surrounded by cold water.

FIG. 9.



**Iron door of retort closed.**

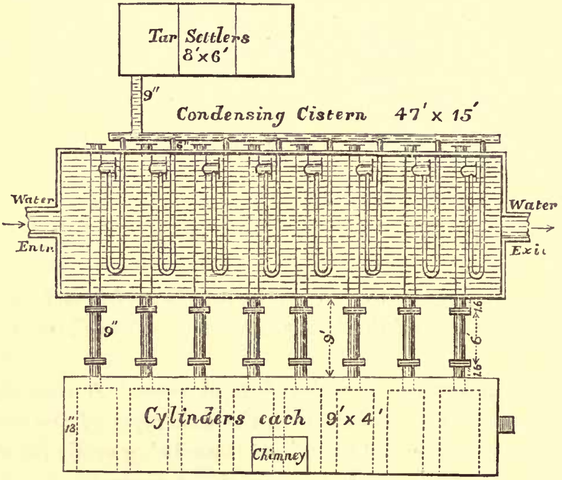
Here the vaporized tar, pyroligneous acid, naphtha, &c., assume the liquid form, and in this state reach the tar settlers. These are large tanks, about 20 feet in length, 5 feet in breadth, and 5 feet in width, constructed of strong 3-inch deal boards, bound together with iron rods.

The tar which falls to the bottom, is removed from the settlers by stop-cocks, to the tar still; whilst the supernatant fluid in which is contained the pyroligneous acid, naphtha, &c., undergoes different treatment according to the nature of the particular product required. If, for instance, pyroligneous acid, or white or grey acetate of lime be desired, the naphtha is first distilled off at a gentle heat, leaving the acid in the retort, this being obtained and in great measure deprived of its impurities by after distillation.

When the object is to procure the brown acetate, the fluid is pumped into the neutralizer in which it is mixed with lime, the naphtha being afterwards removed by distillation.

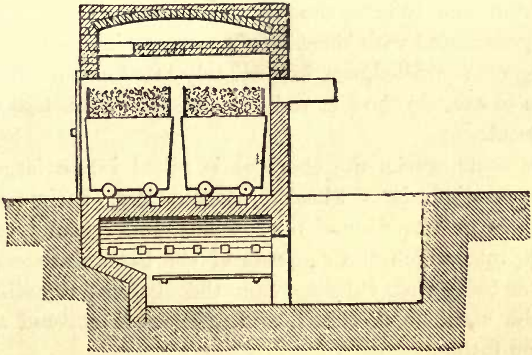
There are many varieties of condensers. A very useful form of one is connected with the exit pipes of the retorts in such a manner as to admit of these being easily detached when necessary. Each exit pipe has a separate condenser, although in some works two retorts have only one condenser, which arrangement is found to work less satisfactorily than when one retort is used. The condensers, which consist of one large pipe of about 10 inches in diameter, in connection with two pipes of half that diameter, and are so curved as to expose a large amount of surface, are placed in a large cistern fixed at the back of the retorts, and corresponding in length with the line of furnaces which heat the retorts. The water supply is so managed as to ensure its being in constant movement. The smaller condensers dip considerably so as to prevent the tar accumulating in them, and stopping them up. The incondensable gases, consisting of carbonic acid, and oxide, marsh and olefiant gases, are carried off by a pipe, whence they are conveyed to the furnace and there burnt. Should the least quantity of the volatile liquids generated during distillation have escaped condensation, this may be known by placing the palm of the hand in the stream of out-coming gas, when moisture will be deposited upon the hand. When no more liquid issues from the condensers, and the exit pipes from the retorts become cool, the distillation is known to be completed.

FIG. 10.



In the Forest of Dean and elsewhere, instead of cylindrical retorts, large square ovens of wrought iron are in use. The charge of wood (usually consisting of about half a cord) is placed in a waggon made of sheet iron, which is run by means of a tramway into the oven, and removed in the same manner when the carbonization is over. The wood is so piled above the top of the waggon as to enable it to enter the oven. Each oven is about 8 feet long, by 5 high, and 5 wide, and holds two waggons. The oven doors are fastened and luted in the usual manner. These square ovens are generally found to answer best for the distillation of small timber, which is mostly used in the Welsh works; whereas for the larger and heavier kinds the cylinder is preferable.

FIG. 11.



Chests made of wrought iron are sometimes employed, and are said to act satisfactorily. The heat is conveyed into the interior by an iron pipe, 6 inches in diameter, carried through the centre of the chest.

At some of the South Wales works they use large cylindrical carbonizers, divided in the interior into six compartments, into each of which a large sheet iron vessel, 4 feet high, and 2 feet wide, for holding the wood, fits. The carbonizer has but one opening at the top, through which the vessels containing the wood are lowered in succession by a crane, each being removed into the interior, to make way for the next, by a movable framework at the bottom of the carbonizer. When full, the opening is bolted and luted. This apparatus, which is placed in brickwork, is directly over the fire which heats it. The wear and tear to which it is subjected is very great.

The charcoal is sometimes removed at one operation, and in an unbroken condition, from the cylindrical retorts, by dragging through them from end to end, by means of an iron chain or rod, an iron plate, which fits into the interior of the retort. By this means the charcoal, in as whole a condition as possible, is drawn out.

From the retorts, the charcoal falls into deep iron waggons, fitted with sheet iron covers, which as soon as the waggons are filled, are immediately luted down with clay, so as to exclude the air, and prevent the combustion of the charcoal.

In some works the charcoal is raked into a large iron barrow, when it is wheeled without loss of time to the manhole or trap-door of a capacious underground tank or vault, into which the contents of the barrow are emptied. Water being then thrown upon the charcoal to extinguish it, the manhole is closed, and afterwards covered with a strong luting.

The yield of acid, charcoal, tar, and the other useful products, varies with different woods,* and is largely dependent upon their state of dryness or the reverse. Wood which has been felled about six months, gives about one-fifth its weight of charcoal. "A cord of such wood," says Mr. RANDALL, "yields from 120 to 130 gallons of liquor, consisting of pyroligneous acid, water, and tar." The yield is also largely influenced by the temperature at which the

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* PAYEN states that the larger the amount of incrusting matter, and the smaller that of the cellulose a wood contains, the greater will be its yield in acid. According to this chemist the hard woods give from 4 to 5 per cent. of hydrated acid, and soft woods only about 3½ per cent.

distillation is conducted. The retorts should be gently heated at the commencement to drive off the moisture contained in the wood, and the heat cautiously increased, so that only just as the operation is being finished, should a commencing red heat be reached.

The length of time for distilling wood in metallic retorts varies from eight to forty-eight hours; but on an average twelve hours for small retorts, and twenty-four hours for large ones is sufficient, and includes the time for charging the retorts, the distillation proper, and the extraction of the charcoal.

It has been conclusively shown that the largest amount of charcoal is obtained at a low temperature, and of acid also, when the distillation is performed at a low temperature in large ovens. On the contrary, when the distiller desires naphtha as his chief product, he must work with small retorts, and heat them very highly.

The following tables by Stoltze show the relative amount and strength of products yielded by various woods :—

| One pound of Wood. | | Weight of Acid. | Carbonate of Potassa neutralized by one ounce of Acid. | Weight of Charcoal. |
|---|---|---|---|---|
| | | ozs. | grs. | ozs. |
| White birch . . . | Betula alba . . . . . . . . . | 7⅛ | 55 | 3⅞ |
| Red beech . . . | Fagus Sylvatica . . . . . . . | 7 | 54 | 3⅞ |
| Large-leaved linden | Tilia plataphylla . . . . . . | 6⅞ | 52 | 3⅝ |
| Oak . . . . . | Quercus robur . . . . . . . . | 6⅞ | 50 | 4⅛ |
| Common ash . . | Fraxinus excelsior . . . . . | 7½ | 44 | 3¾ |
| Horse chestnut . . | Æsculus hippocastanum . . . | 7⅜ | 41 | 3½ |
| Lombardy poplar . | Populus dilatata . . . . . . | 7⅜ | 40 | 3¾ |
| White poplar . . | Populus alba . . . . . . . . | 7⅜ | 39 | 3¾ |
| Bird cherry . . . | Prunus padus . . . . . . . . | 7 | 37 | 3½ |
| Basket willow . . | Salix . . . . . . . . . . . | 7⅜ | 35 | 3½ |
| Buckthorn . . . | Rhamnus . . . . . . . . . | 7½ | 34 | 3½ |
| Logwood . . . . | Hæmatoxylon campechianum . | 7⅛ | 35 | 2 |
| Alder . . . . . | Alnus . . . . . . . . . . | 7⅜ | 30 | 3½ |
| Juniper . . . . | Juniperis communis . . . . | 7¼ | 29 | 3⅝ |
| White fir . . . . | Pinus abies . . . . . . . . . | 6⅝ | 29 | 3⅜ |
| Common pine . . | Pinus sylvestris . . . . . . | 6¾ | 28 | 3½ |
| Common savine . | Juniperus sabina . . . . . . | 7 | 27 | 3⅝ |
| Red fir . . . . . | Abies pectinata . . . . . . | 6⅜ | 25 | 3¾ |

| 84 lbs. of Wood. | Charcoal. | Charcoal per cwt. of Wood. | Acid Liquor. | Specific Gravity of Acid Liquor. | Specific Gravity of Acid Liquor saturated with Lime. | Measures of Soda to neutralize Acid Liquors. | Incondensable Products. | Real Acid. |
|---|---|---|---|---|---|---|---|---|
| Birch | 23½ | 31·33 | 45 | 1·046 | 1·080 | 70 | 15 | 1·86 |
| Elm | 21½ | 28·66 | 45½ | 1·036 | 1·075 | 83 | 17½ | 2·26 |
| Willow | 18 | 24·00 | 49 | 1·029 | 1·045 | 29 | 17 | 0·77 |
| Beech, low temp. | 24 | 32·00 | 46 | 1·039 | 1·090 | 115 | 14 | 3·06 |
| Ditto, high temp. | 20 | 26·64 | 47 | 1·034 | 1·067 | 90 | 17 | 2·40 |
| Laburnum | 20 | 26·64 | 46 | 1·030 | 1·055 | 75 | 18 | 2·00 |
| Ash | 23 | 30·68 | 48 | 1·035 | 1·078 | 92 | 13 | 2·45 |
| Alder | 20 | 26·64 | 48 | 1·030 | 1·065 | 70 | 16 | 1·86 |
| Hawthorn | 20 | 26·64 | 27 | 1·040 | 1·100 | 140 | 37 | 3·73 |
| Young Oak | 28 | 37·33 | 39 | 1·038 | 1·085 | 115 | 14 | 3·06 |

| 336 lbs. of Wood. | Charcoal. | Charcoal per cwt. of Wood. | Acid Liquor. | Specific Gravity of Acid Liquor. | Grains of Bicarbonate of Potash neutralized by one ounce. | Dry Acetate of Lime produced. |
|---|---|---|---|---|---|---|
| Beech | 84 | 28·00 | 180 | 1.029 | 9½ | 25 |
| Walnut | 72 | 24·00 | 150 | 1·018 | 7 | 14½ |
| Birch, cut three years | 70 | 23·33 | 120 | 1·031 | 11 | 13 |
| Oak | 91 | 30·33 | 190 | 1·022 | 8 | 24 |
| Ash | 90 | 30·00 | 190 | 1·024 | 8 | 22 |
| Apple | 70 | 23·33 | 200 | 1·017 | 6 | 18 |
| Witch-elm | 70 | 23·33 | 180 | 1·018 | 8 | 16 |
| Maple | 77 | 25·66 | 145 | 1·018 | 6 | 20 |

In this country pyroligneous acid and its accompanying products are chiefly obtained from the lesser branches of large trees, known as "lop," or from the timber of smaller ones called "coppice wood," the coppice being a plantation consisting of trees of various kinds, mostly alder, ash, hazel, maple, birch, and oak. The trees are in the best condition for felling when they are about sixteen or eighteen years old, although they are frequently cut when only of six years' growth. Beech is the only tree of large size used in England. The timber is first sawn into blocks the length of the retorts. These blocks are afterwards divided into smaller ones, by blasting with gunpowder. Thorn, apple, holly, and yew are also occasionally employed.

Of the above woods yielding the purest acid, is birch; then follow thorn and applewoods.

The "lop," or small branches of oak trees, and oak saplings afford an excellent charcoal, as well as a good yield of tar, naphtha, and acid, in which particular, beech is nearly as valuable, beside being the source of the best creasote.

The *Coniferæ* furnish the worst quality of acid, and in the smallest quantity, although by cautious distillation and complete carbonization the quantity may be increased. These trees, however, afford good quantities of tar and naphtha.

Sound roots are sometimes distilled with good results, but because of the trouble and expense of breaking them up, they are sometimes put into the ovens intact, and heated for forty-eight hours. Gunpowder is employed when necessary to divide them. Large pieces of wood are preferred by the wood-distiller, provided their complete carbonization can be effected in twenty-four hours.

Rotten wood of all kinds, or wood affected with dry-rot, is very unprofitable, and should never be used. Timber derived from trees of slow growth, and flourishing on dry soils, affords, as might be expected, the best acid. Branches less than three inches in diameter are seldom distilled, as the resulting charcoal is too small, and their yield in acid is inferior.

Different woods contain very varying proportions of water, as will be seen in the following table, compiled by Schübler and Hartig, whose experiments were conducted with freshly cut wood :—

| | | | | |
|---|---|---|---|---|
| Hornbeam | contains | 18·6 | per cent. | of water. |
| Willow | ,, | 26·0 | ,, | ,, |
| Sycamore | ,, | 27·0 | ,, | ,, |
| Mountain Ash | ,, | 28·3 | ,, | ,, |
| Ash | ,, | 28·7 | ,, | ,, |
| Birch | ,, | 30·8 | ,, | ,, |
| Oak | ,, | 34·7 | ,, | ,, |
| White Fir | ,, | 37·1 | ,, | ,, |
| Horse Chestnut | ,, | 38·2 | ,, | ,, |
| Pine | ,, | 39·7 | ,, | ,, |
| Red Beech | ,, | 39·7 | ,, | ,, |
| Alder | ,, | 41·6 | ,, | ,, |
| Elm | ,, | 44·5 | ,, | ,, |
| Red Fir | ,, | 45·2 | ,, | ,, |
| Lime | ,, | 47·1 | ,, | ,, |
| Italian Poplar | ,, | 48·2 | ,, | ,, |
| Larch | ,, | 48·6 | ,, | ,, |
| White Poplar | ,, | 50·6 | ,, | ,, |

It will be evident the larger the amount of water a wood contains, the greater will be the waste of fuel expended in distilling it, and the less concentrated the various products derived from it. The shoots and twigs of trees contain more water than the stems, and as during the season of the rising of the sap, the water is in excess, it is unadvisable to fell the tree at this particular time. It has been estimated that wood arranged in stacks or exposed to the air, loses in moisture about a third of its weight. Before the cut wood is fit for distillation it must be stripped of its bark, an operation which is termed "peeling," the removed bark being kept in the coppice until required for use. The bark is sold to the tanner, and generally realizes a sufficient sum to pay for cutting and peeling the wood. The cost for cutting this up and conveying it to the ovens, averages about 7*s.* per ton. An acre of coppice yields on an average 15 tons of timber, and this, taking the wet and dry seasons together, gives about 2 tons of bark.

The following were the quantities of crude and acid liquors obtained in a well-arranged English works by the distillation of :—

| | | | | | | |
|---|---|---|---|---|---|---|
| 174 | cords which | produced | 23·923 | gallons of | about 10 lbs. | each. |
| 160 | ,, | ,, | 27·720 | ,, | ,, | ,, |
| 252 | ,, | ,, | 30·424 | ,, | ,, | ,, |
| 318 | ,, | ,, | 40·584 | ,, | ,, | ,, |
| 330 | ,, | ,, | 55·900 | ,, | ,, | ,, |
| 400 | ,, | ,, | 50·700 | ,, | ,, | ,, |

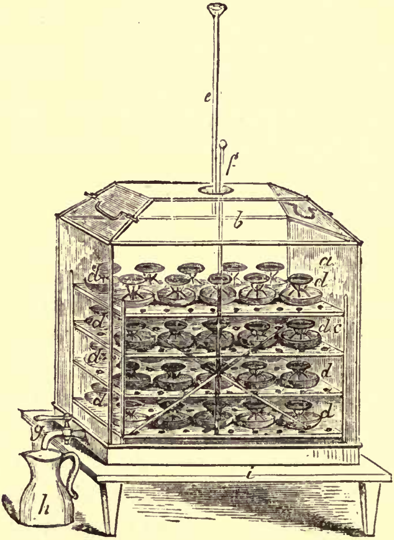
M. Mollerat obtained at his works at Nuits from 1,000 stères of wood, equal to 5,120 cwts., as follows :—

| | |
|---|---|
| Charcoal . . . . . . . . . . . | 1280 cwts. |
| Pyroligneous Acid . . . . . . . | 850 ,, |
| Acetic Acid . . . . . . . . . | 54 ,, |
| Acetate of Lead . . . . . . . . | 152 ,, |

In this country the chief seats of the acetic acid industry are in Yorkshire, Lancashire, and South Wales. There are a few works around London, and also in Somersetshire and Gloucestershire. Large quantities are also manufactured in France, Germany, Belgium, Russia, Sweden and America.

V. From Alcohol. Alcohol Vinegar, German Acetic Acid. In a bell-glass, or an oblong glass case, perforated shelves are arranged, 12 inches apart, one above another, on which are placed a number of small flat dishes of porcelain, earthenware, or wood (*d*). These dishes are filled with spirit of wine or dilute alcohol; and over each is suspended a watch-glass or capsule containing a portion of platinum black; the whole being arranged so that the platinum black and the surface of the alcohol are not more than 1½ to 2 inches apart. Strips of porous paper are next so hung in the case that their bottom edges are immersed in the spirit, to promote evaporation; and, lastly, the apparatus, loosely covered, is set in a light place, preferably the sunshine, when convenient, at a temperature of from 70° to 90° Fahr. (21·1°—32·2° Cent.). In a short time the temperature of the platinum rises, and the formation of acetic acid begins; and the condensed vapour trickles down the sides of the glass and collects at the bottom of the case, whence it is drawn off once or twice a day into the jug (*h*). The product of a case of twelve cubic feet content, with 7 or 8 oz. of platinum in powder, is capable of producing daily, if well managed, nearly 1·31 lb. of hydrated acetic acid from 1 lb. of absolute alcohol; 25 lbs. of platinum in powder and 300 lbs. of alcohol, will, in a case of proportionate capacity, in like manner, furnish a daily supply of nearly 350 lbs. of pure acid, and of other strengths in proportion. Theoretically, the product should be 130 parts of hydrated acid for every 100 parts of alcohol consumed; but

FIG. 12.



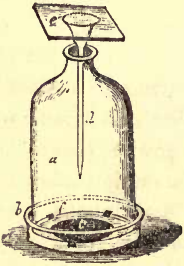
this is never quite obtained in practice, owing to a small portion of the alcohol mixing with the newly formed acid, and escaping decomposition; and from another small portion of both the alcohol and of the newly formed aldehyd being carried off by the air that permeates the apparatus. The platinum-powder does not waste, and the most inferior spirit may generally be employed.

In this process, the alcohol, as in other cases of acetification, is first converted into aldehyd; and this, as rapidly as formed, absorbs oxygen and passes into hydrated acetic acid. The simultaneous formation of aldehyd during the oxygenation of that already formed, may be detected by its odour.

During the mutual action of the platinum-black and the vapour of alcohol, the temperature increases, and continues to do so until all the oxygen contained in the air enclosed in the case is consumed, when the acetification stops. On opening the case for a short time, to admit a fresh supply of air, the operation recommences, thus showing its dependence on the oxygen of the atmosphere. For this transmutation, 100 grains of alcohol require 70 grains (equal to 200 cubic inches) of oxygen, or about 1,000 cubic inches of atmospheric air. To render the process continuous and rapid, a fresh supply of air must, therefore, be constantly provided. This may be effected by either having a loosely covered opening at the top of the case, and several much smaller ones near its lower part; or, preferably, by means of two small glass tubes passing through the lid or cover, one of which (*e*) terminates just below the point of insertion, whilst the other (*b*) divides into branches which reach to within a short distance from the bottom, as shown in the engraving. In this way a very slow current of fresh air will always be kept up in the apparatus.

In practice we find, that by loosely spreading the platinum black on pieces of platinum-gauze, and supporting these on small tripods or bars of glass, porcelain, or wood, the watch-glasses and their troublesome suspension may be dispensed with, as well as the strip of porous paper, provided a temperature of not less than 90° Fahr. (32·2° Cent.) be maintained in the case or acetifier, which may easily be done by the application of artificial heat in the absence of sunshine. On the large scale, a case of wood with a glass roof, or even a well-seasoned cask or vat may be employed, in which case the temperature of the apparatus must be kept up either by means of steam-pipes or flues, or by the supply of warm air. On the small scale, a hand bell-glass, placed on a dish, with a single watch-glass or piece of platinum-gauze, and a single capsule containing alcohol, may be used, provided the bell-glass be supported on three very small wedges, to admit of a supply of air. A modification of this is sometimes employed, in which the alcohol is supplied, in drops, to the platinum black in *c* by means of a long, tubular funnel (*d*), passing through the mouth of the bell-glass (*a*), and having its lower extremity drawn to a very fine point, as shown in the engraving; *b* is the dish into which the bell-glass fits, *f* is an orifice serving for the circulation of the air. To ensure success, the platinum-black should be either freshly prepared, or recently washed and very gently heated, before placing it in the acetifier. Spongy platinum does not answer well for this process. Previous to its being poured into the bell-glass the alcohol should be heated to about 90° Fahr. (32° Cent.)

FIG. 13.



By this second method perfectly pure acetic acid of considerable strength may be produced from even impure alcohol; but it is impossible in this way to obtain a concentrated acid without a subsequent operation, because the action of platinum black on absolute alcohol, or even on strong alcohol, is so violent that the platinum soon begins to glow, and inflammation ensues. The obstacles to the adoption of this process in Britain are the high price of alcohol as well as the great loss occasioned by its becoming converted into, and volatilized as aldehyd; and the large quantity of platinum required to work the process on a large scale.

VI. MISCELLANEOUS FORMULÆ:—

1. An excellent acetic acid of considerable strength may be made by soaking freshly burnt and perfectly dry charcoal in common vinegar, and then subjecting it to distillation. The water comes over first, and on increasing the heat, the acid follows. Vinegar-bottoms and waste vinegar may be used.

2. By exposing vinegar or dilute acetic acid to the air in very cold weather, or to freezing mixtures, the water separates in the form of ice, and the strong acetic acid may be obtained by draining it into suitable glass vessels, observing to do so at a temperature sufficiently low to keep the water solid. This method is said to answer well in cold climates, but it entails a considerable loss of acid.

3. LIEBIG. Acetic acid containing 20 per cent. of water may be deprived of a good deal of its superfluous water by standing over dry sulphate of soda. It may then be used either with or without distillation.

4. Acetic acid of ordinary strength may be concentrated to any degree, by rectification once, or oftener, from dry acetate of potash or soda, rejecting the first and last portions. The same acetate may be used repeatedly. The temperature need not exceed 400° (204° Cent.), and must not rise above 570° Fahr. (299° Cent.).

The acetic acid of the British Pharmacopœia consists of water mixed with 33 per cent. of hydrated acetic acid. It is prepared by distilling acetate of soda with sulphuric acid. It is a colourless sour liquid; its sp. gr. being 1·044. As acetic acid acts readily upon the lead and copper of the vessels in which it is prepared, the dilute acid employed by the pharmacist and the concentrated from which it is obtained, should always be examined for lead and copper.

5. STEIN says very strong acetic acid may be obtained from vinegar by distilling 100 parts of vinegar with 30 of salt.

6. The late Dr. STENHOUSE, by fermenting different varieties of sea-weed in presence of lime, obtained acetate of lime in such quantities as to yield 1·8 per cent. of absolute acetic acid for the sea-weed employed.

8. The glacial acetic acid of the British Pharmacopœia contains 84 per cent. of acetic anhydride. Like the previous acid, it is obtained by distilling acetate of soda with sulphuric acid.

9. Vinegar obtained from brandy contains from 14 to 18 per cent. of acetic acid. By treating the brandy vinegar with lime, straining and evaporating the solution and drying the salt, VÖLCKEL obtained it in a colourless condition. He distilled the dried acetate of lime so obtained, with hydrochloric acid, in the proportion of 130 parts of acid to 100 of salt.

The synthetic preparation of acetic acid has been accomplished by BERTHELOT, WANKLYN, and HARNITZKY. The first chemist obtained potassium acetate by heating acetylene dichloride with aqueous or alcoholic potash for some hours. WANKLYN procured sodium acetate by the direct union of carbonic anhydride and sodium methyl. HARNITZKY formed acetic acid by causing carbonyl chloride mixed with marsh gas, to be passed into a heated retort. Hydrochloric acid was evolved and acetyl chloride formed, which, on the addition of water, yielded hydrochloric and acetic acids.

The acetates yield by a comparatively inexpensive, and a not difficult operation, an acid sufficiently strong and pure for commercial purposes, without the necessity of rectification. In this process, shallow vessels of wood or of copper, formed without rivets or solder (unless it be silver solder) in those parts exposed to the action of the acid, are generally employed for the purpose of the distillation. A coil of drawn copper pipe, heated by steam having a pressure of 30 to 40 lbs. to the inch, traverses the bottom of the apparatus, to impart the necessary heat. The refrigerator consists of well-cooled earthenware, Berlin ware, or glass vessels; and the adapter pipe is also of the same materials. Another common form, which is even still more convenient, is a stout copper still, furnished with a cast-iron jacket to hold high-pressure steam, the usual refrigeratory being employed, and a stop-cock fixed to the lower part of the jacket for the removal of the condensed water. In a few instances the space between the still and jacket is filled with sand, oil, tallow, or fusible metal; in which case the apparatus is set in brickwork, and heated by a naked fire, a safety-tube for carrying off the gases that might be generated when oil or tallow is employed, being attached to the apparatus. Stills of earthenware are also frequently employed; and even worms and condensers of silver, or silvered copper, are sometimes used, and with advantage. If a leaden worm is used the product is always contaminated with a little of that metal. When a lute is required, it is best made of linseed meal and water, with or without a little powdered plaster of Paris; but flat bands and short tubes of well-seasoned vulcanized india rubber are infinitely more convenient and efficacious. The acetate of soda and oil of vitriol being placed in the still, and rapidly, but thoroughly stirred together with a wooden spatula, the head is luted on, and the distillation soon afterwards commenced.

The heat must be very cautiously and gradually increased as the distillation proceeds; and when a steam-heat is not used, over-firing must be carefully avoided, particularly towards the close of the operation. A little acetic ether is added by some manufacturers to the product. In this way 4 lbs. of acid of the sp. gr. 1·050 is obtained for every 3 lbs. of acetate of soda employed. Should rectification be had recourse to, the addition of about 2 or 3 per cent. of bichromate of potash, peroxide of manganese, or red oxide of lead, will remove empyreuma, if present. The first of these substances is the most effective, the efficiency of the others being in the order in which they are printed; or very frequently the acid is digested with animal charcoal, or kept in a tub containing beechwood shavings, for eight or ten days. In distilling the weaker acids and vinegars, it is found useful to add from 25 to 30 per cent. of chloride of sodium, which, by raising the boiling point of the liquid, causes the acid to pass over more freely; but this addition proves disadvantageous when any sulphuric acid is present, in which case sulphate of soda may be employed instead. If this addition be not made, the whole of the acid cannot be obtained without distillation to dryness, and the consequent generation of empyreuma.

On the small scale, glass retorts are usually directed to be used, but glass alembics or flasks are more convenient and safe, as already noticed. In the preparation of the pure acid, care should be taken that the acetate of soda does not contain common salt, as the carbonate of soda prepared by calcination, and frequently used to form the acetate, is generally contaminated with it, and yields up its hydrochloric acid or chlorine during the process of distillation, thus vitiating the product. In all the methods given, the product becomes more concentrated in proportion to the dryness of the acetate and the strength of the oil of vitriol or hydrochloric acid employed. By using the one dry, and the other concentrated, glacial acid may always be obtained by collecting separately the last two-fifths that come over, and submitting this to refrigeration.

A process for the preparation of the acetates—the source of acetic acid—was some years back devised by PAUER. By this method, the use of retorts, as well as the operation of distillation, and many of the steps usually followed in making this acid, were got rid of. One of the processes by which wood charcoal is obtained, consists, as is well known, in surrounding with earth, rough logs or piles of wood, placed upon a layer of brushwood, and erected into a mound or stack. At the base of, as well as at different heights about the stack, holes are made, the first for the admission of air after the brushwood has been set light to, the second for the escape of the various products generated by the combustion of the wood. Into the latter orifices PAUER placed small tubes, which, penetrating into the stack, collected the evolved products and carried them off into casks placed outside. The casks which act as receivers are more or less filled either with lime, potash, soda, magnesia, or their carbonates. The pyroligneous acid and other volatile bodies which are given off by the wood, are carried by pipes to the bottom of the cask, when the acid ascending through the contents, becomes fixed by them, whilst the other products escape at the top of the cask.

By PAUER's process, owing to the high temperature in the interior of the cask, there is a considerable diminution in the yield of tar, whereby the after-purification of the acid is said to be facilitated; but the process has been found an unsatisfactory and uncertain one.

Acetic acid on the large scale is made from the acetates of lime and soda, which are prepared as follows:—

The crude pyroligneous acid, after separation of the naphtha, is run off into tanks, where, after depositing part of its impurities, it is pumped into a large pan. Hydrate, or caustic lime, made into a stiff paste with water, is then added, slightly in excess, and the mixture boiled.

It is then drawn off into another vessel, where it is kept at rest for ten or twelve hours, and then conveyed to the evaporating pan.

Sometimes the crude acid is distilled previous to being neutralized with lime,* in which case the lime is added to the distillate, the mixture allowed to settle, and, when clear, run into the evaporating pan. The evaporating pans are sometimes constructed of wood, and lined with lead. Sometimes the contents are heated by steam passing through a coil of iron pipe, and at others, in shallow sheet-iron pans over the naked fire. During evaporation the liquid is frequently stirred with a wooden spatula, and kept constantly skimmed. The crystals of acetate of lime which in time form upon the surface of the evaporating fluid, are scooped or ladled into baskets suspended over the pan, whereby the drainings are prevented from cooling.

Acetate of soda is obtained as follows:—A solution of grey acetate of lime in water having a sp. gr. 1·200 is first prepared and filtered. To the filtered liquid, sulphate of soda in powder is added, in the proportion of four parts to one part of acetate of lime employed,

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* The resulting acetate is then called *grey* acetate of lime; if, on the contrary, the crude and undistilled acid has been used, the product is called *brown* or *black* acetate of lime. Previous to its being used for the production of acetate of soda, the brown acetate is dried in a furnace, or on heated iron plates at a temperature of 450° Fahr. (232° Cent.). This chars and removes resinous and other impurities. Acid-makers give the preference to brown over the grey acetate, for this reason:—the crude acid being saturated with lime before distillation, the excess of lime carries down and removes some of the impurities.

and the whole thoroughly mixed by vigorous stirring. When the excess of sulphate of soda and the sulphate of lime* have subsided the solution of acetate of soda is drawn off and evaporated down till it acquires the sp. gr. of 1·300, any impurities floating on the surface being carefully removed. The crystals of acetate of soda which soon form in the liquid are removed in the same manner as the acetate of lime. The different mother liquors are successively evaporated down till they have a specific gravity of 1·300 (care being taken to remove the tarry matters), and until they cease to give crystals of acetate of soda.†

The different crops of crystals are mixed and dissolved in water, and the solution concentrated by evaporation until it has the density of 1·500, and, after remaining at rest for ten hours, the resinous bodies are removed, and the acetate of soda again crystallized, the mother liquor being treated as above described.

Acetate of soda may be safely dried at a temperature of 400° to 450° Fahr. (204°—232° Cent.), provided care be taken to avoid ignition from contact with sparks. A less heat is, however, quite sufficient to drive off the whole of its water of crystallization. It is known to be dry by its assuming the appearance of a smooth, oily liquid whilst hot, and by the subsidence of frothing.

The drying is generally conducted in an iron pot, the

---

* These are washed with the water till the liquid is nearly tasteless, the washings being used in decomposing fresh acetate of lime.

† By evaporating the mother liquors to dryness, and calcining the residue at a red heat, carbonate of soda results. This may be extracted by treating the ignited residue with water. If the residue be, in the first place, roasted at a temperature of 450° Fahr. (204° Cent.) acetate of soda remains, and this may be removed by treatment with water.

contents of which must be stirred during the whole time. If whilst being heated it emits white fumes, the acetate is suffering decomposition, and directly this occurs, the pot must be cooled by raking out the fire. The same applies to the other acetates.

Crystallized acetate of soda loses about $\frac{2}{5}$ths of its weight by thorough drying.

PROPERTIES, TESTS, USES, &c., of ACETIC ACID. Pure normal, or hydrated acetic acid is a thin colourless liquid above 62° Fahr. (16·4° Cent.); at 50° to 55° Fahr. (10° to 12·70° Cent.) it crystallizes in large, brilliant, colourless, transparent needles and plates, and even at 60° Fahr. (15·5° Cent.) if a crystal of acid be dropped in. In the glacial condition, litmus is not reddened by it, water being necessary to produce the acid reaction. The specific gravity of the liquid acid, according to MOLLERAT, is 1·063; and, according to MOHR, 1·0635 at 59° Fahr. (15° Cent.); that of the crystallized at 55° Fahr. (12·7° Cent.) being 1·135. Its odour is intensely pungent when concentrated; but grateful, fragrant, and refreshing when diffused. It has an intensely sour and acrid taste, but on sufficient dilution with water it is agreeable and refreshing to the palate. Its vapour is volatile and extremely inflammable. Acetic acid dissolves camphor, resins, gum resins, volatile oils, gelatin, gliadin, various albuminous substances, and fibrin. It coagulates casein, but not liquid albumen, as exemplified in the serum of the blood and white of egg. It is miscible in all proportions with water, alcohol, and ether. According to KOPP, it boils at 242·6° Fahr. (117° Cent.) and is partially decomposed at a red heat, the products of combustion being carbon, acetone, naphthalin, benzol, and some combustible gaseous compounds. In its concentrated state it chars organic bodies when poured on them, and is consequently a corrosive and acrid poison if taken internally, and acts as a powerful caustic if applied to the skin. With chlorine, acetic acid forms chloracetic ($C_2H_3ClO_2$) and trichloracetic acid ($C_2HCl_3O_2$); and with bromine, bromacetic acid ($C_2H_3BrO_2$) and dibromacetic acid ($C_2H_2Br_2O_2$).

Acetic acid may be readily recognized by its odour and volatility. When perchloride of iron is added to an aqueous solution, and the acid then nearly saturated with a solution of ammonia, the fluid acquires a deep, dark, red colour; when a solution of mercurous nitrate is added to acetic acid, mercurous acetate is precipitated in white scales, which become partially resolved into metallic mercury by heat. The mercurous acetate dissolves in excess of the precipitant. Terchloride of gold mixed with excess of potash is reduced to metallic gold when treated with acetic acid.

Pure acetic acid is completely vaporized by heat, and should give no precipitate upon the addition of nitrate of silver, chloride of barium, or sulphuretted hydrogen. It is sometimes contaminated with sulphurous acid, which may be recognized by putting a fluid drachm of the suspected acid, mixed with an ounce of distilled water and half a drachm of pure hydrochloric acid, with a few pieces of granulated zinc, into a flask. If, when the gas begins to be disengaged, a slip of white blotting-paper, moistened with a solution of subacetate of lead, be placed in the upper part of the flask above the liquid for about five minutes, and no discolouration of the paper takes place, no sulphurous acid is present.

Acetic acid which has been obtained from acetate of lime is very likely to contain sulphuric or hydrochloric acid. Besides which, these latter are often added by the maker, under the erroneous impression that they assist to preserve the acetic acid.

Besides the above, another convenient qualitative test for sulphuric or hydrochloric acid, consists in boiling for a few minutes a small quantity of the previously diluted acetic acid, with a little potato starch. When cold, a few drops of solution of iodide of potassium are added to the mixture, when, if either sulphuric or hydrochloric acid are present, no change of colour takes place; if they be absent the liquid changes to a blue colour. Acetic acid is not affected by nitric acid.

Acetic acid is largely employed by the varnish and paint-maker, the chemist, the pharmaceutist, and perfumer, and by the calico printer, in the form of acetates. It is also in great demand in the preparation of caoutchouc; and, as pyroligneous acid, is extensively used in the preservation of wood and of flesh. Concentrated and diluted, it is employed in medicine as an antiseptic, stimulant, alterative, refrigerant, and escharotic. Aromatic vinegar is acetic acid in which are dissolved certain fragrant essential oils, or in which have been macerated, various sweet-smelling flowers and herbs.

For the estimation of acetic acid see ACETIMETRY, page 82.

ACETATES. In general these may all be formed by direct solution of the carbonate, hydrate, or oxide of the metal whose acetate it is desired to form, in dilute acetic acid; or from a solution of an acetate and another salt of the metal by double decomposition. In either case, the resulting solution must be carefully evaporated by a gentle heat and, when possible, crystallized. All the neutral acetates, except those of molybdenum, tungsten, mercury, and silver, are more or less soluble in water, several so much so, as to be uncrystallizable; many dissolve in alcohol; they all suffer decomposition at a dull red heat; at a full red heat, those of potassium, sodium, barium, strontium, calcium, and magnesium are converted into carbonates, whilst the other metallic acetates leave behind the pure metal, or its oxide.

The acetates are known:—By evolving, on the addition of concentrated sulphuric acid, fumes of acetic acid, recognizable by its odour, and giving off the vapour of acetic ether when heated with a mixture of about equal parts of concentrated sulphuric acid and alcohol.

We append a list of the technically most important Acetates:—

ACETATES OF ALUMINA. Pure hydrate of aluminium is digested to saturation in strong acetic acid in the cold; and the resulting solution, after being filtered or decanted, is either evaporated by a very gentle heat to a gelatinous semi-solid consistence, which is its usual form, or is preserved in the liquid state. By spontaneous evaporation it may be obtained in long transparent crystals.

*Red liquor.*—1. From alum in powder, 4 parts; warm water, q. s. to dissolve; acetate of lead in powder, 3 parts. The solution is effected by lengthened agitation in a tub or other wooden vessel, and the clear liquid, after repose for a sufficient time, is decanted or drawn off from the sediment.

2. Alum, 2 parts, dissolved in a sufficient quantity of warm water; solution of pyrolignite of lime, at 20° Baumé, 3 parts. As before, but allowing a longer time for the subsidence of the precipitate, and taking more care in the decantation than when acetate of lead is employed.

3. Acetate of lead in fine powder, 100 lbs.; to be added to 100 lbs. of alum previously dissolved in 50 gallons of boiling water.

4. 100 lbs. alum; 5 lbs. of soda crystals; 50 lbs. of acetate of lead, and 50 gallons of water.

10 lbs. alum; soda crystals, 1 lb.; acetate of lead, 7½ lbs.; and 2½ gallons of water.

5. (CRACE CALVERT). 453 lbs. of ammonia alum (or 383 lbs. of sulphate of alumina), 1132 lbs. of water; and 379 lbs. of acetate of lead.

In the manufacture of red liquor, it should be remembered that acetate, or pyrolignite of lime, is less certain in its action than lead acetate; besides which the resulting sulphate of lime is more troublesome to deal with than sulphate of lead. Ammonia alum is more variable in composition than potash alum.

Red liquor is extensively employed by the dyer and calico-printer.

ACETATE OF AMMONIA, $NH_4C_2H_3O_2$. Take of acetate of lime or of potash, and sal ammoniac, equal parts; mix, and distil at a gentle heat. The liquid in the receiver which is binacetate of ammonium forms a radiated crystalline mass on cooling. Dry gaseous ammonia passed into this salt, melted by a gentle heat, transforms it into the inodorous neutral acetate.

It occurs in long, slender crystals, or in a crystalline mass freely soluble in both alcohol and water, and deliquescent in the air. Mindererus' spirit is an aqueous solution of this salt.

ACETATES OF COPPER. ACETATE OF COPPER (NEUTRAL), $Cu(C_2H_3O_2)2$. *Syn.* NORMAL CUPRIC ACETATE, ACETATE OF COPPER, CRYSTALLIZED VERDIGRIS, DISTILLED VERDIGRIS. This name is applied to the normal acetate of copper, which is prepared in the wine districts by dissolving ordinary verdigris, 1 part, in good distilled vinegar, 2 parts; the operation being performed in a copper vessel by the aid of a gentle heat and agitation. The solution is afterwards slowly evaporated until a pellicle begins to form on the surface, when it is transferred into glazed earthenware pans, called *oulas*, in each of which are placed two or three cleft sticks, and it is then left in a warm apartment for fourteen or fifteen days to crystallize.

It occurs in beautiful dark bluish-green prisms, which dissolve in 14 parts of cold and 5 parts of boiling water.

It is often made by adding a solution of sulphate of copper, 12½ lbs., to a solution of sugar of lead, 19 lbs., or q. s., and then filtering and evaporating the liquid, and crystallizing.

BASIC ACETATES OF COPPER. *Syn.* SUBACETATES OF COPPER, VERDIGRIS (VERTE DE GRIS, Fr.). This is a mixture of several basic acetates of copper, which have a green or blue colour. It is obtained in the wine districts of the South of Europe by the action of refuse grapes (from which the juice has been expressed) on thin sheets of copper.

The verdigris of commerce should not contain more than 4—or at the utmost—5 per cent of impurity, mostly in the form of insoluble substance. It is frequently sophisticated with chalk and sulphate of copper. It should dissolve almost entirely in diluted hydrochloric or sulphuric acid.

The presence of sulphate of copper may be detected by treating the filtered solution of the suspected sample with chloride of barium.

An inferior quality of verdigris is prepared from *pomage* or apple marc in the cider districts of England.

SESQUIBASIC ACETATE OF COPPER is obtained by digesting powdered verdigris in tepid water, filtering, and leaving the soluble part to spontaneous evaporation.

TRIBASIC ACETATE OF COPPER is the green insoluble residue of the verdigris left after it has been treated with tepid water. It may be formed by digesting the neutral acetate of copper with the hydrated oxide.

All the acetates of copper are used as pigments, and also in dyeing, calico-printing and in medicine.

The distilled verdigris is often employed as a source of aromatic vinegar.

Annexed is the composition of three kinds of verdigris compared with BERZELIUS' centesimal analysis of the tribasic acetate of copper :—

| | Bibasic Acetate. | French Verdigris. | English Crystallized Verdigris. | English Compressed Verdigris. |
|---|---|---|---|---|
| Anhydrous Acetic Acid | 27·45 | 29·30 | 28·30 | 29·62 |
| Oxide of Copper | 43·24 | 43·50 | 43·25 | 44·25 |
| Water | 29·21 | 25·20 | 28·45 | 25·51 |
| Impurities | 00·10 | 2·00 | — | 0·62 |
| | 100·00 | 100·00 | 100·00 | 100·00 |

ACETATES OF IRON. FERROUS ACETATE, $Fe(C_2H_3O_2)_2$. 1. From freshly precipitated ferrous carbonate dissolved in dilute acetic acid. 2. By adding a solution of calcium acetate to another of ferrous sulphate, and evaporating the filtered liquid out of contact with the air. It occurs in small, colourless, or pale-greenish needles or prisms, very soluble and prone to oxidation.

In the arts, ferrous acetate is obtained by covering old iron, as free as possible from rust, with distilled pyroligneous acid in iron or wooden tanks, and keeping the whole at a heat of about 150° Fahr. (66° Cent.) for several days, until the solution has a specific gravity of 1·09 to 1·10 at the temperature of 69° Fahr. (15·5° Cent.)

FERRIC ACETATE.—The pure acetate may be prepared by dissolving recently prepared hydrate of sesquioxide of iron in acetic acid, or by the double decomposition of ferric sulphate and acetate of baryta or lead.

IRON LIQUOR. *Syn.* PYROLIGNITE OF IRON, DYERS' ACETATE OF IRON, BLACK LIQUOR, TAR IRON.—This article, which is extensively used in dyeing, is a crude mixed acetate of the protoxide and sesquioxide of iron.

It is usually prepared by one or the other of the following methods:—

1. Old scraps of iron, such as hoops, worn-out tin-plate, &c., are left in a cask of pyroligneous acid of the sp. gr. of 1·035, at a temperature of about 66° Fahr., occasional agitation being had recourse to, until a sufficiently strong

solution is obtained. By keeping the acid moderately warm at the above temperature, in a few days it will become saturated with the iron. With cold acid on a large scale, forty days or more are required to complete the process.

2. A solution of pyrolignite or crude acetate of lime is added to another of green copperas as long as a precipitate is formed; after repose the clear liquor is decanted.

Acetate of Lead, $Pb(C_2H_3O_2)_2, 3H_2O$. *Syn.* Diacetate of Lead, Sugar of Lead.—This is the most important of the lead acetates, and is extensively employed in dyeing, and calico-printing, in the manufacture of acetate of alumina and chrome yellow, as well as in making sulphide of lead, which is in great demand by the manufacturers of india-rubber articles.

Acetate of lead is also employed in medicine, and possesses astringent, styptic and hæmostatic properties.

It is met with in commerce under the three forms of *white*, *grey* and *brown* acetate, the white being the purest. It is mostly prepared by dissolving litharge in acetic acid, and sometimes by exposing thin sheets of lead in closed chambers to the action of air and acetic vapours.

1. The British pharmacopœia gives the following formula for the preparation of a pure white acetate:—Litharge in fine powder, 24 parts; distilled water, 20 parts; acetic acid, 40 parts. Mix the acetic acid and the water, add the litharge, and dissolve by the acid of a gentle heat, filter, evaporate until a pellicle forms, and crystallize. Drain and dry the crystals.

2. Another method employed by manufacturers, is as follows:—230 parts of acetic acid of sp. gr. 1·0843 are gently heated in a copper boiler rendered electro-negative by means of a large flat piece of lead soldered within it, and 130 parts of pure litharge in fine powder is sprinkled in; the heat is then continued with constant stirring,

until the acid is saturated, when the mother waters of a former process, if any, are added, and the whole is heated to the boiling point, and allowed to settle until cold. The clear portion is now decanted, and evaporated in a similar vessel until the liquor has the sp. gr. 1·266 or 1·267, when it is run into salt-glazed stoneware vessels (the edges of which have been well smeared with candle grease) and allowed to crystallize. The product is 360 to 380 parts of crystallized sugar of lead. It is found advantageous to preserve a very slight excess of acid during the boiling and crystallization, to prevent the formation of any basic acetate, the presence of which impedes the formation of regular crystals.

Sometimes, instead of using the mother waters of a former process, water in proportion to about half the acid taken, is added to the lead solution, whereby the impurities are brought to the surface, and skimmed off.

The mixture is then carefully and slowly evaporated until it acquires a density of about 1·500, the proper degree of condensation being reached when a sample of the liquid placed in a small shallow vessel affords a compact mass of crystals upon cooling. When this occurs, the liquid is siphoned into the crystallizing pans, and when the crystals which form are sufficiently solid, they are removed in a mass to the drying house, and drained, by being placed on a sloping bench, the drainings being collected in a cistern, and used in subsequent operations.

When dry, the crystals are carefully scraped, broken up, and put into casks, when they are ready for sale.

Crystallizing vessels of copper are often used as well as stoneware ones, over which they possess the advantage of not being breakable.

The temperature of the drying room should be about 90° Fahr. (32° Cent.), and the fire-place or stove for heating it should be outside the room, since dry wood, matting, and other materials used in the drying, are readily combustible when they become impregnated with acetate of lead.

3. When prepared by the action of the vapour of acetic acid and atmospheric air upon metallic lead, a mixture of carbonate and acetate forms upon the surface. This coating, when sufficiently thick, is scraped off and dissolved in a slight excess of acetic acid. The solution is then evaporated down till of the sp. gr. of 2·30. If small, needle-shaped crystals are required, the solution is rapidly cooled.

When the evaporation is slowly conducted, truncated flattened prisms are obtained.

The above is a more expensive method than the previous one, and in consequence, is but seldom had recourse to.

The crystals of pure acetate of lead are slightly efflorescent in dry air; they are soluble in 8 parts of alcohol and in about 1¼ parts of cold water. The aqueous solution has a sweet astringent taste, and feebly reddens litmus, but turns the juice of violets green; when gently heated it melts in its water of crystallization; by continuing the heat the whole of the water is expelled, and the anhydrous acetate obtained. At a higher temperature the salt suffers decomposition, and acetic acid, carbonic acid, and acetone are given off. Commercial acetate of lead is in general a confused crystalline mass, somewhat resembling broken lump sugar. It is powerfully poisonous.

Grey acetate of lead is obtained from the dirty mother-liquors which are left after the preparation of the white. Blocks of crystals which have become soiled are also used in its manufacture. It is very impure, and nearly or wholly destitute of crystalline form.

In making brown-acetate, or sugar of lead, distilled pyroligneous acid placed in a large tub is first saturated with litharge. From the tub, the thick mixture, after being well stirred, is ladled into a large cask and allowed to settle, after which the clear liquid is siphoned or run off into a pan of wrought or cast iron, 6 feet by 4 and having a depth of about 12 inches, heated at the bottom, and in which, after being brought to the boiling point, it is left to settle. The fluid is next conveyed into a hemispherical pan of about 500 gallons capacity, where it is evaporated down until it about reaches the point of crystallization. About three times its bulk of water is then added to it, with constant stirring, the solution meantime being kept boiling, whilst the impurities which rise to the surface are removed by skimming. If the solution is too highly coloured, this must be remedied by the addition of more water. The requisite quantity of water having been added, the solution is again evaporated until it is of such a strength that it will crystallize. It is then transferred into wrought iron crystallizing pans of about 4 feet long by 3 wide and 6 inches deep. After the crystals are "set," they are removed from the pans by inverting the latter, drained, dried, and broken up for sale.

A more satisfactory product than the above, is said to be obtained, if the liquid before dilution and evaporation, is first brought to the point of ebullition, and then allowed to settle.

The following analyses represent good commercial samples of neutral acetate or sugar of lead :*—

| | White. | Brown. |
|---|---|---|
| Acetic Acid | 27·6 | 21·8 |
| Oxide of Lead | 58·4 | 59·9 |
| Water | 14·0 | 15·5 |
| Carbonate of Lead and Insoluble Matter | — | 2·8 |
| | 100·0 | 100·0 |

**Basic Acetates of Lead.**—There are several of these salts. They are mostly procured by dissolving powdered

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* Spon's "Cyclopædia of the Industrial Arts." E. & F. N. Spon, Charing Cross.

litharge in hot solutions of the neutral acetate. Some of these basic acetates contain as much as six times the normal quantity of oxide of lead. They are employed in dyeing and calico-printing.

TRIBASIC ACETATE OF LEAD, $Pb(C_2H_3O_2)_2 2PbO,H_2O$. *Syn.* TRIPLUMBIC DIACETATE, SUBACETATE OF LEAD, GOULARD'S EXTRACT OF LEAD.—Made by digesting 7 parts of litharge in fine powder, and 6 parts of neutral acetate of lead in 30 parts of water, at a moderate temperature. This is the salt employed in the manufacture of carbonate of lead, or white lead, by the Clichy method, which consists in passing carbonic acid into a solution of tribasic acetate of lead, which thereby becomes converted into carbonate and neutral acetate. Tribasic lead acetate occurs in large needles. It has a strongly alkaline reaction, is very soluble in water, and insoluble in alcohol.

Goulard water is an aqueous solution of hexabasic acetate of lead.

ACETATE OF MANGANESE, $Mn(C_2H_3O_2)_2$. 1. May be prepared by neutralizing concentrated acetic acid with manganous carbonate, and evaporating the solution, so that crystals may form. The crystals when pure are of a pale red colour, permanent in the air; soluble in alcohol, and in 3½ parts of water.

2. The best commercial acetate, employed in dyeing and calico-printing, is made by mixing in their equivalent proportions manganous sulphate and crystallized lead acetate, both previously dissolved in water.

ACETATE OF TIN. Obtained by dissolving metallic tin in acetic acid. It is a very unstable compound. The commercial acetate, used in dyeing and calico-printing, may be prepared by mixing 103 parts of chloride of tin with 190 of brown lead acetate, well stirring the mixture, allowing it to settle, and drawing off the supernatant acetate of tin.

ACETATE OF ZINC. The following is the formula of the British pharmacopœia for the preparation of this salt:—Add 2 oz. carbonate of zinc in successive portions to 3 fluid ounces of acetic acid, previously mixed with 6 fluid ounces of distilled water, in a flask; heat gently, add by degrees 2 fluid ounces more of acid, or q. s., till the carbonate is dissolved; boil for a few minutes, filter whilst hot, and set it aside for two days to crystallize. Place the crystals in a funnel to drain, then spread them on filtering paper on a porous tile, and dry them by exposure to the air at an ordinary temperature.

The acid used by the calico-printer is made by dissolving 4 parts of sulphate of zinc and 7½ parts of acetate of lead, each in 3 parts of hot water, mixing the solutions, allowing the sulphate of lead to precipitate, and decanting or siphoning off the clear acetate.

ANHYDROUS ACETIC ACID. *Syn.* ACETIC ANHYDRIDE. Acetic acid deprived of the elements of water, thus

$$2\,C_2H_4O_2 - H_2O = C_4H_6O_3$$

It may be prepared by distilling 3 parts of phosphoryl chloride with 6½ parts of anhydrous acetate of soda, pouring back the distillate upon the residue, and redistilling until the odour of the chloride has disappeared, and, lastly, rectifying the liquid. Acetic anhydride is a colourless mobile liquid, of high refracting power, and possessing a very pungent smell, like that of a mixture of acetic acid and hawthorn blossom.

## VINEGAR.

Vinegar is dilute acetic acid, more or less contaminated with gum, sugar, and vegetable matter.

1. English vinegar was formerly almost wholly obtained from malt and unmalted grain; but of late years, besides these, artificial glucoses, cane sugar, and molasses have been largely used in its manufacture. The explanation of the fact that a mixture of malted and unmalted grain gives rise to a vinegar superior in keeping properties, and therefore of better quality than that made from unmalted alone, is as follows:—

In malted grain, the diastase which converts the starch into sugar, is in considerable excess of the quantity required for that purpose, and is left to set up putrefactive changes in the resulting vinegar. By the addition, however, to the malted, of unmalted grain in quantities which must have been previously determined by calculation, the superfluous, and as such detrimental, diastase is removed, since it is expended in converting the starch of the unmalted variety into sugar. The unmalted grain usually employed, is either barley, oats, maize, or rice.

In the manufacture of malt, or grain vinegar, the malt, or grain, or both, as the case may be, previously thoroughly kiln-dried, is first crushed (grinding being particularly avoided) by being made to pass between cast-iron rollers. From the crushing apparatus it is carried by machinery to hoppers, whence it is transferred to the mash tun, and mixed with water * at a temperature of about 170° Fahr. (76·6° Cent.).

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* In the manufacture of vinegar the purest water should be used; hence it is essential the water should be free from organic matter of

In this vessel the mixture of malted and unmalted grain and water is kept in a state of agitation by means of revolving forks, which are carried around the tun whilst they are revolving. After being sufficiently stirred, the *wort*, as the liquid is now called, is left to settle, after which it is pumped into boilers, where it is kept in brisk ebullition for some time. The grain remaining in the mash tun is then subjected to a second treatment with water, at the same temperature as that employed for the first maceration, to exhaust it of its saccharine constituent, the water in this case being supplied to it, and regulated by means of a revolving pipe fixed in the mash tun, and called a *sparge.*

When the boiling is finished, the wort cooled by being passed through a refrigerator, is carried to the fermenting tuns. Here large quantities of yeast at frequent intervals are added to it, and the fermentation which ensues, under proper conditions as to temperature, &c.,* is continued until the glucose is converted into alcohol and carbonic acid. From the fermenting tuns the liquid is pumped into the

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every kind, since this latter is a fruitful source of putrescence. Muddy water, even if the mud be free from organic impurity, should always be discarded. This may, however, become clear by being left to settle.

The presence in the water of the carbonates of lime, magnesia, and iron, acts also prejudicially.

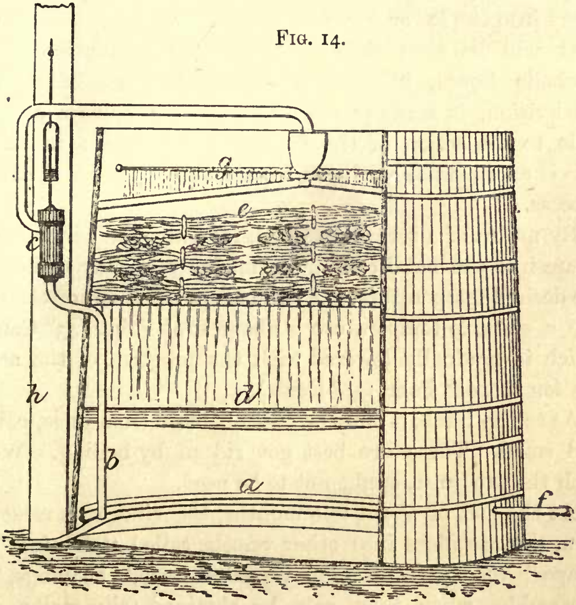
DUSSAUCE recommends those vinegar-makers who are compelled to use water which contains any of the above impurities, to first boil it, to drive off the carbonic acid, when the lime and magnesia salts will fall to the bottom; and then to filter it through alternate layers of gravel and charcoal, whereby suspended matters and organic compounds will be separated.

A temperature of 68° to 86° Cent. is the best suited for the conversion of the alcohol into acetic acid.

* PASTEUR has shown that fermentation is always brisker in the presence of light.

fining vats, where it remains for some days, at the end of which time it has become clear, owing to the deposition of the exhausted yeast and other matters.

FIG. 14.



*a*, Coil of block-tin piping for passage of steam for heating; *b*, intake of pump to feed sparges; *c*, pump; *d*, surface of the liquid in course of manufacture, above which is a space for dripping; *f*, escape-pipe at bottom of steam coil; *g*, sparges for distributing finely divided wash over the birch bed; *h*, support for pump.

From the fining vats it passes to the acetifiers (which are immense vessels having a capacity of from 8,000 to 10,000 gallons) where its alcohol is converted by oxidation into vinegar. The acetifier is heated by means of steam passed through a coil of metal tubing which runs at the bottom. The wash or alcoholic liquor from the fining vats is pumped to the top of the acetifier into a horizontal pipe perforated with very small holes, from which it falls in a finely divided state upon a layer of bundles of birch wood about 4 feet deep, after percolating which it falls in a small shower of spray into the lower part of the acetifier.

It will be seen that by the above arrangement the alcoholic liquid, in consequence of its state of minute subdivision, is made to expose as large a surface as possible to the action of the atmospheric oxygen; in short, this is an essential condition for the successful issue of the process.

By means of a screw tap which regulates the admission of steam into the metal coil, or worm, the wash may be kept at the desired temperature. At the commencement of the process a suitable temperature is about 110° Fahr. (43° Cent.), which is gradually lowered with the progress of the acetification to 100° Fahr. (38° Cent.).

As to the birch, it must be entirely freed from juice, colour and smell. These are best got rid of by boiling. Wood with the sap in it, ought not to be used.

At the end of about two months, the vinegar is removed from the acetifiers into other vessels, called "refining" or, "rape" vessels, containing prepared wood shavings, or, preferably, when they can be obtained, the stalks and skins of raisins, occurring as refuse in the manufacture of British wines. The vinegar being subjected to several filtrations through one or the other of these substances, becomes what is termed "cleansed," and assumes a bright appearance; and, after being coloured * and flavoured, is fit for sale.

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* The colouring may be effected either by admixture of a light with a dark vinegar, or by the addition of a small quantity of caramel. In America, burnt onion, chicory, and coffee are used. The desired

In vinegar-making it should be borne in mind that the greater the proportion of alcohol in the wash the stronger of course, will be the vinegar; the larger the amount of ferment the quicker the acetification, and the greater the surface of contact with the air the more rapid the operation.

The vinegar-maker must use discretion and judgment, however, in availing himself of the knowledge conveyed by these facts, and should remember—that the process of acetification is retarded by the presence of too much alcohol, and that a loss of the latter from evaporation and conversion into aldehyd is incurred; also that too much ferment impairs the flavour and keeping qualities† of the vinegar, and gives rise to the production of those organisms known as *vinegar eels;* and, lastly, that when there is an excess of air, particularly combined with too elevated a temperature, not only will there be a loss of alcohol from evaporation, but that the ethers, to which vinegar owes its pleasant smell and flavour, will escape also.

In some works the acetification is carried out in a series of casks or barrels. The malt wort, after treatment with yeast for 36 hours, is run into casks or barrels placed on their sides in a chamber the temperature of which ranges from 70° to 77° F. (21° to 24° C.). In addition to the bung-hole, each cask has a hole bored in the front and another at the end, near its upper edge. By this arrangement, when the orifices are kept open, a

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colouration may be gained by using brown malt in the manufacture of the vinegar. Highly coloured vinegars in France and Spain are decolourized by mixing with them 4 or 5 per cent. of hot milk. The casein coagulates and carries down the greater part of the colouring matter.

† A small quantity of alcohol, added to a vinegar that does not keep well, will often be found to preserve it.

constant current of air circulates over the top of the liquid, and effects its acetification. This is known as the *stoving* process.

Another method of vinegar-making, occupying a much longer time than the above, and known as *fielding*, instead of being carried on within doors, is effected in the open air. Both plans are, however, often adopted in the same works. In the *fielding* process the casks, resting upon massive supports, which are arranged in parallel rows, with a narrow pathway between every two rows, are filled by means of a large hose which conveys the wash from the brew-house.

The bung-holes are kept open in fine weather, but are lightly covered with a slate or tile when it rains. The casks are only two-thirds filled, the better to ensure their acetification, and when this is judged to be satisfactorily accomplished, their contents are siphoned off into a sluice which conveys them into the storeroom. Here the vinegar is refined and cleared by being filtered through a layer of grape stalks and skins, or raisins, or, failing these not being obtainable, of wood shavings, spent tan or straw, as before stated. This operation is performed in large casks with false bottoms called " rapes."

Vinegar by the fielding process cannot be manufactured in less than three months. Both the above varieties of malt vinegar are used for pickling purposes.

The following proportions of ingredients may be taken for making malt vinegars :—

Malt and barley, both crushed, of each 15 quarters, mashed three times, 183 barrels or 6,588 gallons of water, at the usual temperature, being used in the three mashings. For the total wort from the three mashings, 50 gallons of thick barm are required.

The above 30 quarters of grist should produce 150 barrels.

Sour ale or beer does not yield good vinegar, but a product very liable to undergo putrid fermentation, a very disagreeable smell being imparted to the vinegar in consequence. Besides, such vinegar very often loses its acidity when kept.

The general properties of malt vinegar are well known. Its pleasant and refreshing odour is chiefly derived from acetic acid and acetic ether.

Its strength is distinguished by makers as Nos. 18, 20, 22, and 24, from the fact that 1 fluid ounce of each variety requires as many grains of dry carbonate of soda to neutralize it. The last, which is called "proof vinegar," is the strongest, and usually contains about 5 per cent. of hydrated acetic acid. Its density varies according to the quantity of foreign matter which it contains, but averages about 1·0085. Until of late years, the vinegar maker was allowed to add $\frac{1}{1000}$th of its weight of sulphuric acid, under the erroneous impression that it acted as a preservative. Such addition now constitutes a legal offence under the "Food and Drug Adulteration Act."

It may be well to mention that—with the exception of those made of silver, perfectly clean copper and enamelled iron—metallic vessels are very unsuitable for keeping vinegar in.

Leaden vessels are readily attacked and acted on by it. Common pottery, which is almost always glazed with oxide of lead, should, for the same reason, never be used. Salt glazed stoneware is, however, perfectly safe.

(1) Paper written on or smeared with pure vinegar is not charred when strongly warmed before the fire; if it is, the sample examined contains fully 2 per cent. of oil of vitriol.

(2) If a solution consisting of 1 part sugar in 30 times its weight of water, in a small capsule or china cup, be heated to a temperature of about 200° Fahr., it should not be materially discoloured when a drop of pure vinegar is poured on to it; but a spot of an intensely brown or black colour is formed if the sample contains only $\frac{3}{100}$th part of sulphuric acid; if it contains only $\frac{1}{1000}$th part, the spot is olive green; and if a less quantity, then only of a pale green colour.

(3) The heavy white precipitate given with chloride of barium shows the presence of sulphuric acid; each grain, after being dried, and gently ignited, represents ·344 grs. of dry sulphuric acid.*

(4) If a solution of nitrate of silver gives a cloudy white

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* Allowance should always be made for the presence in vinegar of soluble neutral sulphates, derived, in the first place, from the malt used for the preparation of the wash, or, when the vinegar is prepared from wine, from the grapes. These sulphates may be determined as follows:—8 or 10 ozs. of the vinegar, in a platinum or porcelain basin, is evaporated over a water-bath to 1 oz., and then, when the liquid becomes cool, 5 or 6 ozs. of strong alcohol are added to it. This precipitates the natural neutral sulphates, which are removed by filtration. The filtrate, with the washings of the precipitate (it must be washed with dilute alcohol), is then placed over a water-bath until the greater part of the alcohol is driven off, what remains being diluted with 10 or 12 times its bulk of distilled water, and the free sulphuric acid in it, determined by means of a standard solution of chloride of barium. For determining free acetic acid in presence of free sulphuric acid HILGER carefully neutralizes 20 c.c. of the vinegar with standard potash (1 c.c. = 0·060 acetic acid). The number of potash c.c. used, is at present only noticed, as a direct calculation of free acetic acid cannot possibly be made. The sulphuric acid is next determined as sulphate of barium, and the acid formed, calculated on the potash. The quantity of potash belonging to sulphuric acid is now deducted from the original quantity used for neutralization, and the remainder calculated as belonging to free acetic acid.

precipitate, hydrochloric acid is present. Previous to applying this test, the vinegar must be distilled in a glass retort, and the nitrate of silver solution added to the distillate.

(5) If, after the addition of 2 or 3 grs. of carbonate of potash, and evaporation of the sample to dryness, the residuum deflagrates when ignited, the sample under examination contains nitric acid. Or, if a portion of the vinegar be evaporated, and the residue boiled with hydrochloric acid and copper turnings, the characteristic red fumes of nitrous acid will be generated if nitric acid be present in the vinegar.

(6) If the vinegar be blackened by sulphuretted hydrogen or hydrosulphide of ammonium, it contains either lead or copper; if the precipitate be yellow, tin is present. If it gives a yellow precipitate with iodide of potassium or chromate of potash, the metal is lead. If ferrocyanide of potassium gives a bronze-brown coloured precipitate, or a little olive oil, when agitated with some of the vinegar, be turned green, the metal is copper. Zinc is present if, on the addition of ammonia, a white precipitate is formed.

(7) If a small sample, gently evaporated to dryness, leaves more than 1 per cent. of residuum, and this has a sweet taste, it is undecomposed sugar. The presence of acrid substances, as capsicum, chillies, grains of paradise, mustard seed, pellitory of Spain, pepper, &c., may be detected by neutralizing the acidity of the vinegar with carbonate of soda, when the acrid taste of the adulterant will be readily perceived.

2. WINE VINEGAR. *Syn.* FRENCH VINEGAR, ORLEANS VINEGAR.—This is prepared in wine countries from sour wine, that which is full flavoured and clear, producing the best vinegar. Sometimes the wines are worked up with wine lees. In Orleans, the principal seat of the manufacture

of this variety of vinegar, the factories have a southern aspect, and the apartments in which acetification is carried on, are found to favour the process best, if they are low-roofed. It is also very important they should be amply supplied with atmospheric air; and so constructed as to allow of unimpeded ventilation, an essential condition in all varieties of vinegar-making. The casks in which the process is conducted are called *mothers*, and vary in capacity from 50 to 100 gallons, as little iron as possible being used in their construction. Every new cask is first one-third filled with strong boiling vinegar, to which the wine is added in instalments of 2½ gallons every eight days, by which time each charge of wine becomes acetified. This addition of wine is continued until each cask becomes more than half filled, when one-third of its contents is siphoned off into the store tuns, when the mothers are again recharged every eight days as before. It occasionally happens that in some of the mothers the charge does not become acetified in eight days. When this occurs, such mothers must be emptied, then filled to one-third of their capacity with hot strong vinegar, and then the charges of wine added as usual.

The acetification is known to be completed, when a white thick foam is found adhering to a white rod bent at one end, which has been plunged into the mothers and withdrawn horizontally. Should the foam be of a reddish brown colour, more wine must be run into the mother, and the temperature raised, until the froth becomes white.

The temperature that is found to answer best is one between 75° and 80° Fahr. (24° and 26·6° Cent.).* When

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* DUSSAUCE says that to cause the establishment of the acetic fermentation the wine must be exposed to a temperature between 50° and 86° Fahr. (10° and 30° Cent.), and that the most favourable temperature is that between 68° and 86° (20° and 30° Cent.). DEMACHY

weak wines are employed in the Orleans process, it often happens that the vinegar is ropy and wanting in transparency. When this is the case, it must undergo the fining process.

Vinegar prepared from white wine by the above process is the most esteemed, being purer and of a more pleasant flavour than malt vinegar. It usually contains from 5 to 6 per cent. of acetic acid. According to SOUBEIRAN, 100 parts of good Orleans vinegar should require 10 parts of dry carbonate of potash for saturation.

In some parts of France, Germany, and Holland, BOERHAAVE'S process of vinegar-making is still largely practised.

Two large casks or vats are raised on supports about ten or twelve inches high. These casks are open at the top, and are each fitted with a false perforated bottom, about a foot from the floor of the vat. Vine cuttings, willow twigs and the footstalks and skins of grapes are placed upon the perforated bottoms and pressed closely down. One of the casks is then filled, and the other half filled with wine. The contents of each vessel are then allowed to remain at a temperature of 75° Fahr. (23·90° Cent.) for twenty-four hours, at the end of which time the half-filled cask is filled up from the full one, and in this manner each cask is alternately filled and half-emptied every twenty-four hours. The process of acetification progresses most rapidly in the half-filled cask, and in this a decided elevation of temperature occurs after the first three or four days; but this rise of temperature is not allowed to exceed 80° Fahr. (26·7° Cent.).

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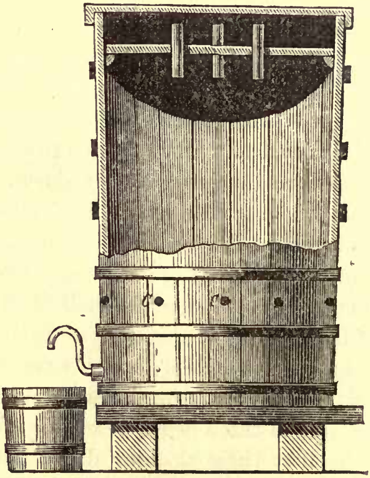
affirms that the alcoholic liquid must reach a temperature of 77° to 81° Fahr. (25° to 27° Cent.), and that it must not exceed 88° Fahr. (31° Cent.). Opposed to DEMACHY'S statement is the fact, that in the South of France vinegar is made in cellars the temperature of which is constantly at 50° Fahr.

The process requires from two to three weeks for completion, according to the atmospheric temperature. The vinegar is, lastly, drawn into casks, when, after settling and becoming clear, it is ready for use.

3. German or quick method of making vinegar; process of Ham. This method is based upon the fact that acetification is the mere oxidation of alcohol in contact with organic matter. Hence, by employing dilute alcohol, or liquors containing it, and by vastly enlarging the surface of the liquid exposed to the air at a proper temperature, and replacing the air as rapidly as possible, we may reduce the period occupied in acetification, from weeks to as many hours. In practice this is effected by causing the dilute spirit, previously mixed with $\frac{1}{1000}$th part of sugar or malt extract, or the fermented and clarified malt-wort, to

Fig. 15.



slowly trickle down through a mass of beech shavings,* through which strong and very pure vinegar has been previously run, and contained in a vessel called a vinegar-generator, or graduation vessel, and known in Germany as *essigbilder*. The generator is an oaken tub, narrower at the bottom than at the top, furnished with a loose lid or cover, below which is a perforated shelf, a sort

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* Instead of beech shavings some makers employ charcoal, because of its superior power of rapidly oxidizing the alcohol and converting it into acetic acid. The charcoal must be previously freed from saline substances by soaking in hydrochloric acid, the acid being afterwards carefully washed out.

Another formula, given in TOMLINSON'S "Cyclopædia," for the vinegar mixture, and mode of conducting the operation, is as follows :—"The vinegar mixture consists of 20 quarts of alcohol, 40 of vinegar, and 120 water ; or 15½ quarts of alcohol, 20 vinegar, and 137 of water. The water is first heated to 100° or 104° Fahr. (37·7°—40° Cent.), and then the vinegar and alcohol are added so that the temperature of the mixture may be about 86° or 90° Fahr. (30°—32·3° Cent.) before it is poured into the generator.

"From 2½ to 5 quarts of the mixture, according to the size of the generator, are poured upon the shavings every half hour. The cover is then put on, but the hole in the centre is left open. When all the mixture is filtered through, it is drawn off into the mixing vessel, and a few quarts of alcohol are added. It is passed a second time through the shavings, then drawn off and a second quantity of alcohol added; it is then sent through the shavings a third time. The supply of air to the casks should be abundant. With a vinegar room at 77° Fahr. (25° Cent.), and the mixture at 82° (27·1° Cent.), the interior of the casks will often be 98° or 100° Fahr. (36·6° to 37·7° Cent.); the internal temperature of the casks should not be less than 95° (35° Cent.). In general it may be remarked that the higher the temperature, and the larger the quantity of air conveyed in the shortest time to the mixture, the more rapidly is the hydrogen of the alcohol oxidized and vinegar formed. The more alcohol there is in the mixture, the stronger will be the vinegar, but the quantity of alcohol in the mixture ought not to exceed 10 per cent.; the temperature must not be below 72° (22·2° Cent.), nor above 113° Fahr. (45° Cent.)."

of colander, or false bottom having a number of small holes, which are loosely filled with packthread about six inches long, and prevented from falling through by a knot at the upper end. The shelf is also perforated with four open glass tubes, as air vents, each having its ends projecting above and below the shelf. This arrangement is repeated a second and a third time, or even oftener, according to the size of the vessel. The tube or graduator at its lower part is pierced with a horizontal row of eight equidistant round holes, to admit atmospheric air. One inch above the bottom is a syphon-formed discharge pipe, whose upper curvature stands one inch below the level of the air-holes in the side of the tub. The floors or partitions of the tub or generator being covered with birch twigs or beech chips to the depth of a few inches, the alcoholic liquor (first heated to between 75° and 83° Fahr. (23·9° and 28·3° Cent.), is introduced at the upper part of the apparatus. The fluid immediately commences trickling slowly down through the holes by means of the packthreads, diffuses itself over the chips or twigs forming the respective strata, slowly collects at the bottom of the tub, and then runs off by the syphon-pipe. The air enters by the circumferential holes, circulates freely through the tub, and escapes by the glass tubes. As the acetification proceeds, the temperature of the liquid rises to 100° or 105° Fahr. (37·7° or 40·8° Cent.), and remains stationary at that point while the action goes on favourably. The alcoholic solution or wort requires to be passed three or four times through the cask before acetification is complete, which is, in general, effected in from twenty-four to thirty-six hours. The larger the graduator the more quickly will the process be completed.

For the production of a superior vinegar by this process, it is necessary that the spirit employed be sufficiently pure, so as not to contaminate the product with its flavour or odour, and that the malt-wort should be fermented * and treated with all the care usually employed in the production of beer. The best English manufacturers who have adopted this process are in the habit of filtering or clarifying their fermented wash, and also of storing it away for several months before they subject it to acetification in the graduator. The most favorable temperature for the process is about 90° Fahr. (32·2° Cent.), and this should be preserved as much as possible by artificial means. A malt-wort of the sp. gr. 1·072, or, in "technical language, weighing about 26 lbs. per barrel, afforded a vinegar containing 5·4 per cent. of pure acetic acid and a residuary extract of 10 lbs., for 36 gallons. The former of these would indicate 35 lbs. of sugar, or 13·7 lbs. per barrel of gravity; whilst the latter shows 3·8 lbs. per barrel; the two united being only 17·5 lbs., instead of 26, the original weight. The loss, therefore, has been 8·5 lbs., or from a sp. gr. of 1·072 to less than 1·050." Thus, about one-third of all the extractive matter of the malt is lost or dissipated during the processes of fermentation and acetification. According to KNAPP, a mixture of about 80 gallons of water, 9 gallons of spirit of from 44 to 45 per cent. *Tralles* (18 or 20 u. p.), and 3 gallons of vinegar containing 3·5 per cent. of real acid, forming together 92 gallons, yield, on an average, an almost equal quantity of vinegar, or about from 90 to 91 gallons of

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* In localities where yeast cannot be procured, wheaten flour and water, made into a thick paste will be found a very efficient substitute. The mixture should be lightly covered, and left in a warm situation to undergo spontaneous decomposition. At the end of six or seven days a vinous smell will be developed; and if some of the decomposed flour, or leaven, previously mixed with a little tepid water, be now added to the wort, the temperature of which should range from 90° to 100° Fahr. (32° to 38° Cent.) alcoholic fermentation will be set up in a few hours.

the above-stated strength. When obtainable, good spring water should be used in this process, and, failing this, well filtered river-water.

In the above process the great loss alluded to, arises from volatilization of the alcohol and aldehyd. Great care must therefore be taken to duly regulate the temperature, as well as the supply of air during acetification. When this loss, which is always considerable on the quick process, is owing to too high a temperature, it may be diminished by passing the heated air, as it escapes from the acetifier, through a porcelain or silvered copper worm or refrigerator, set in a chamber containing water of a temperature not higher than 40° to 45° Fahr. (4·4°—7·2° Cent.), the connection being made at the lower end of the worm, whilst the upper end is open to the air. On the small scale, as in the platinum-black process, the loss may be almost entirely prevented, by causing the upper air-tube to pass through a vessel containing ice or a freezing mixture; or by uniting it with the lower end of a LIEBIG'S condenser. When the loss arises from a deficient supply of atmospheric air, more holes must be bored in the graduator.

The advantages of this process are the small capital required for working it, no large factory or expensive apparatus being required.

The *per contras* are the loss of alcohol by evaporation and the necessity of operating upon clear liquids. The quick process is not well adapted for malt washes and highly coloured wines, which abound in gummy, nitrogenous, and colouring matters, since these impurities clog the pores of the shavings, and thereby render them useless.

4. VINEGAR BY MEANS OF THE VINEGAR FUNGUS.—In 1862 a new method of making vinegar was devised by PASTEUR. The vinegar fungus (the *Mycoderma Aceti*), which is the agent by means of which acetification is brought

about, is first propagated and cultivated in a fluid composed of water, with 2 per cent. of alcohol, 1 per cent. of vinegar, and a small quantity of the phosphate of potash, magnesia and lime. The surface of the fluid soon becomes completely covered with the fungus, a part of the alcohol becoming at the same time acetified. When half the alcohol has become converted into acetic acid, small quantities of beer and wine are added to the fluid every day, and the process carried on until all the alcohol has become oxidized. The vinegar is then removed from the containing vessel, and the fungus employed in the manufacture of a second batch. Vinegar prepared by this process is said to possess the agreeable aroma of wine vinegar. The vessels in which the vinegar is made are of wood, and in the form of round or rectangular shallow tanks. The prepared liquid, contained in a vessel having an area of about 10¾ square feet and a capacity of from 90 to 100 pints, yields about 9 to 10 pints of vinegar daily. The tanks are covered by means of lids, and air is admitted to their contents through holes bored at the ends of the vessel, whilst the alcohol is conveyed to the bottom of the fluid through perforated gutta-percha tubes, an arrangement which gets rid of the necessity of opening the lids. When alcohol alone is employed, Pasteur makes the addition to the fluid of about $\frac{1}{10000}$th of its weight of sulphate of ammonia and phosphate of potash and magnesia, as well as some vinegar.

The above salts constitute the food of the fungus, and as they are contained in beer and wine, they are dispensed with when these fluids are employed instead of alcohol.

A successful result can only be obtained by paying great attention to the healthy development and growth of the *mycoderma* at starting.

5. Vinegar from Sugar Beet.—The roots of the sugar beet, thoroughly washed, deprived of shoots and tops, and

rasped into a pulp, are submitted to considerable pressure in strong cloth bags, until exhausted of juice. The expressed juice is then diluted with water until the mixture has a sp. gr. of 1·025. After being boiled for a short time, the liquid is then run into coolers, and when its temperature has fallen to 60° Fahr. (45° Cent.), it is conveyed into proper receptacles and fermented with yeast, in the proportion of 1 gallon of yeast to every 200 gallons of wort. When the fermentation is complete, the wash is mixed with an equal volume of vinegar, and exposed at a suitable temperature to the air, when acetification soon takes place. By NEALE'S and DUYCK'S process the wash is conveyed to a strong and large vat having a capacity of several thousand gallons, where it is mixed with an equal measure of vinegar. A little yeast being now added to the mixture, acetification is soon started. When this commences, air is injected into the liquid through a perforated nozzle or rose at the bottom of the vat. By this contrivance, the oxidation of the fluid is effected in a few days, the contents of the vat meanwhile being kept at a temperature of from 70° to 80° Fahr. (21° to 27° Cent.), maintained, if necessary, by means of a steam worm which runs through the bottom of the vat.

6. VINEGAR BY WIDEMANN'S PROCESS.—WIDEMANN'S process consists in the rapid oxidation of alcohol by ozone, and the consequent conversion of the alcohol into acetic acid. WIDEMANN found that by adding water to maize whisky, and passing ozonized air over it, the alcohol was completely converted into acetic acid in 8 minutes. Works for making vinegar upon this principle were established at White Plains in 1871 and 1872, which turned out in the first year 30 barrels, and in the second, 90 barrels of pickling vinegar.

7. Other varieties of vinegar of minor importance, chiefly domestic, and commonly worked as malt vinegar, are :—(1) *Crystal Vinegar*.—Pickling vinegar decolourized with

freshly-burnt animal charcoal. 2. *Cider Vinegar.*—From cider worked as malt vinegar. 3. *German Household Vinegar.*—From soft water 7½ gallons, honey or brown sugar 2 lbs., cream of tartar 2 oz., corn spirit or whisky 1 gallon. 4. *Gooseberry Vinegar.*—From bruised gooseberries and brown sugar of each 1¼ lbs., water 1 gallon. Other fruits may be substituted for gooseberries. 5. *Raisin Vinegar.*—From the marc left from making raisin wine; 1 cwt. to every 12 or 15 gallons of water along with a little yeast. 6. *Sugar Vinegar.*—From brown sugar 4 lbs. to each gallon of water. 7. *Whisky Vinegar.*—From whisky 1 pint, sugar 2 oz., yeast a dessert-spoonful.

## CULINARY VINEGARS.

1. BLACK PEPPER VINEGAR, CAPER VINEGAR, CAPSICUM VINEGAR, CELERY SEED VINEGAR, CHILLI VINEGAR, CRESS SEED VINEGAR, GARLIC VINEGAR, GINGER VINEGAR, HORSERADISH VINEGAR, ONION VINEGAR, RED ROSE VINEGAR, SEVILLE ORANGE PEEL VINEGAR, SHALLOT VINEGAR, TRUFFLE VINEGAR, WHITE PEPPER VINEGAR, with several others of a similar kind, are made by steeping about an ounce of the respective articles in a pint of good vinegar for fourteen days and straining.

2. BASIL VINEGAR, BURNET VINEGAR, CELERY VINEGAR, CHERVILLE VINEGAR, ELDER FLOWER VINEGAR, GREEN MINT VINEGAR, TARRAGON VINEGAR, are prepared by adding to each pint of vinegar 2 to 3 oz. of the leaves, the whole being frequently shaken for fourteen days, then strained or filtered, and bottled.

3. CAMP VINEGAR.—Take of sliced garlic, 8 oz.; cayenne pepper, soy and walnut ketchup, of each 4 oz.; thirty-six chopped anchovies; vinegar, 1 gallon; powdered cochineal, ½ oz. Macerate for a month, strain, and bottle.

Currie Vinegar.—Good currie powder, ½ lb.; vinegar, 1 gallon. Infuse for a week. Used as a flavouring.

Raspberry Vinegar.—Bruised ripe raspberries and white wine vinegar, of each 3 pints. Macerate for three days, press, strain, and to each pint add of white sugar, 1 lb. Boil, skim, cool, and bottle at once. 2 oz. of brandy to each pint is sometimes added.

In a similar manner may be made, Cherry Vinegar, Strawberry Vinegar, and the vinegars of similar fruits.

## ACETIMETRY.

The art or process of determining the quantity of pure acetic acid in vinegar or in any other liquid. The plans adopted for this purpose are:—

*a.* From the saturating power of the acid, as in the common methods of acidimetry. This is the most satisfactory method of assay.

1. The molecular weight of commercially pure bicarbonate of potash in crystals being 100, whilst that of absolute acetic acid is 60, it is evident that every 10 grains of the bicarbonate will exactly equal 6 grains of the acid. To apply this practically, we have only to exactly neutralize 100 grains of the vinegar or solution under examination with the bicarbonate, observing the usual precautions, such as well boiling the solution after the addition of the potash salt to drive off the carbonic acid, and using litmus or some other suitable indicator. Then as 10 is to 6 so is the number of grains used to the percentage strength required.

In this, as in similar cases, it is convenient to form a test solution with the bicarbonate by dissolving it in sufficient distilled water to fill the 100 divisions of any simple form of acidimeter,* when the quantity of the

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* A very convenient form of acidimeter is Binks' (No. 1).

Gay-Lussac's burette (No. 3) consists of a graduated glass solution, and consequently of the salt used, may be read off at once from the graduated portion of the tube. Still

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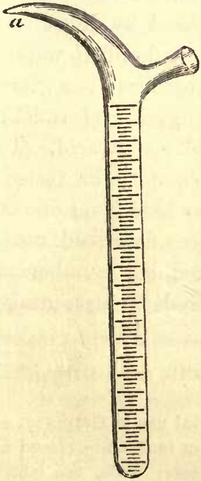
cylinder, to which is attached, and having connection with it, a thin glass tube of nearly equal height, through which the test liquid is dropped. The quantity consumed is read off on the graduated and larger cylinder.

Mohr's burette (No. 2), however, will be found more convenient than any of these instruments for acetimetrical operations. It consists of a cylindrical glass tube, open at top and bottom. "0" being at the top and "100" at the bottom of the tube. To the bottom, which is slightly contracted, is attached a small piece of flexible india-rubber tubing, into which is inserted a little glass exit pipe, which is opened or closed by means of a nipper clip, by manipu-

No. 1.



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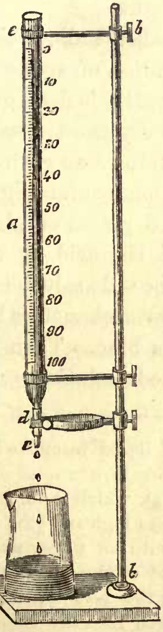

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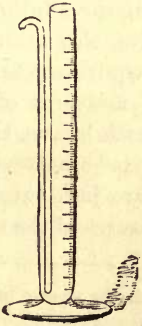

No. 4.

greater accuracy may be obtained by dissolving the bicarbonate in exactly 1,000 grains of distilled water contained in an alkalimeter previously very carefully weighed, in which case each grain of the test solution will indicate $\frac{1}{10}$th of a grain or 0·1 per cent. of absolute acetic acid, whilst every 10 grains will be equal to 1 grain or 1 per cent.

2. The test solution may also be prepared from bicarbonate of soda, or from the carbonates of soda or potash, care being taken that the quantity of salt dissolved be in proportion to its molecular weight.

3. The hydrated alkalies, soda, potash, and ammonia are also used for the estimation of acetic acid. When soda is employed, a normal solution is first prepared by dissolving 40 grains of pure and dry caustic soda in distilled water, and making the solution to 1,000 grain measures: 100 grain measures of this solution containing 4 grains of caustic soda are equivalent to 6 grains of glacial acetic acid. To 100 grain measures of the acid or vinegar to be tested, coloured with litmus, the soda solution is added from one of the graduated burettes or acetometers before described, until the mixture just turns blue. Then from the number of grain measures of the soda solution required, the percentage

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lating which the stream of liquid from the burette can be regulated at pleasure.

Otto's acetometer (No. 4), which is in general use in Germany, is a glass tube about 14½ inches high and $\frac{3}{5}$ths of an inch wide, closed at one end, and graduated into an upper and lower scale, the latter being for the measurement of the vinegar coloured by litmus, and the upper for measuring the test liquor. When used, a certain quantity of litmus is poured into the tube, and then vinegar up to the beginning of the second division; afterwards the test liquor is added until the blue colour of the litmus is restored, the quantity used being indicated on by the upper scale. The test liquor is a solution of ammonia containing 1·369 per cent. of ammonia.

of glacial acetic acid is arrived at by a very simple calculation.

Thus, suppose for the sample under examination 70 measures of the solution of soda have been taken, then as:—

$$\frac{6 \times 70}{100} = 4{\cdot}20 \text{ per cent. of absolute acid.}$$

When potash is used as a test liquid the normal solution is made by adding 56 grains of pure and dry caustic potash to 1,000 grain measures of distilled water, and proceeding precisely as with soda.

When ammonia is employed, the following process, recommended by URE, will be found a convenient and expeditious one:—100 grains of the sample under examination are slightly reddened with tincture of litmus, and ammonia of sp. gr. 0·992 is added drop by drop (from an acetometer holding 1,000 water-grain measures, divided into 100 divisions), until precise neutralization is effected, as indicated by the blue colour of the litmus being restored. The number of the divisions of the acetometer used, multiplied by 60, and the first two right-hand figures of the product cut off as decimals, gives a number which represents the exact quantity of absolute acetic acid in the sample. In practice it is found more convenient to keep the test ammonia ready tinged with litmus.

The ammoniacal test liquor is very liable to become weaker by keeping. To ascertain if this be the case, two hydrostatic beads are placed in the bottle containing it. When the solution is of the proper strength, one of the beads assumes a position very near the bottom of the bottle, and the other just under the surface of the liquid. Upon the evaporation of the ammonia and the consequent increase in the sp. gr. of the liquid, the beads rise in it, the lower one higher above the bottom and the other partially above the surface. When this takes place, as much ammonia must be added as will restore the beads to their original position.

The mode of estimating the percentage of acetic acid in beers, when finding their original gravities, is a slight modification of the above.

A test-solution of ammonia is prepared of such a strength that a given bulk of it will exactly neutralize one per cent. of absolute acetic acid in an equal bulk of beer, so that if 100 fluid grains of the solution are sufficient to neutralize the acid in 1,000 fluid grains of beer, such beer contains $\frac{1}{10}$th per cent. of acid. A solution of ammonia diluted with distilled water until it has the sp. gr. ·9986 at 60° Fahr. (15·5° Cent.) is of the exact strength required.

An acetometer holding 1,000 grains, and graduated downwards to 100 equal divisions, is filled to "*O*" of the scale with the test ammonia; which is then added drop by drop to 1,000 measured grains of the beer until neutralization takes place. Every division of the acetometer (corresponding to ten fluid grains) so emptied, indicates ·01 per cent. of acetic acid in the beer. The progress of the neutralization is tested from time to time with a slip of reddened litmus paper, which should be suffered to become faintly blue before ceasing to add the ammonia. By this method the exact percentage of absolute acetic acid in any sample may be accurately determined. The only precaution necessary is to be certain that the test ammonia has the required specific gravity, viz., ·9986.

The above methods will be found appropriate to acetic acid of all strengths, unadulterated with mineral acids.

Owing to the circumstance that the normal or neutral acetates exhibit a slight alkaline reaction, none of the above methods are strictly accurate.

Otto has shown, however, that the error arising from this cause is a very insignificant one, and does not exceed 0·1 per cent. for an acid containing 10 per cent. of absolute acid.

*b.* Mr. GREVILLE WILLIAMS suggests the employment of lime saccharate for acetic acid testing :—

A moderately strong solution of sugar being prepared with distilled water, lime is dissolved in this, and the strength of the mixture ascertained by titration with a standard solution of sulphuric acid. The lime saccharate is then diluted so that 5 burette divisions shall be equivalent to 1 grain of absolute acetic acid. The assay is made as follows: Fifty grains of the sample to be examined are diluted to about two ounces with water, and a few strips of litmus paper put into the solution, the test liquid being then carefully added, with constant stirring, until the blue colour of the liquid is restored. This is an accurate method, if carefully performed, and, even where much expedition is required, gives results within 0·25 per cent.

*c.* From the specific gravity of the liquid after it has been neutralized with hydrate of lime :—

Common hydrate of lime (freshly slaked lime), in powder, is added gradually to the sample under examination, until it is saturated, when the sp. gr. of the resulting clear solution of acetate of lime is taken by TAYLOR'S acetometer. This instrument is so adjusted and graduated as to float at the mark on the stem called "proof," in a solution containing 5 per cent. of absolute acetic acid (No. 24 vinegar). For vinegars stronger than proof, small weights are provided, each of which indicates an additional 5 per cent. To ascertain the percentage of real acid, 5 per cent. must therefore be added to the acetometer number. Thus, without being loaded, the instrument, floating at the "proof mark," indicates a vinegar of 5 per cent.; with one weight, a vinegar of 10 per cent.; with two weights, 15 per cent. and so on. According to this system of notation, each 5 per cent. is called a "vinegar." An acid of 10 per cent. is said to contain two vinegars; one of 15 per cent., three vinegars, &c. It is also common to speak of the degrees of the acetometer as "proof" or "over-proof." Thus, No. 24 vinegar is said to be proof; one of 5 acetimeter degrees, 5 over-proof; one of 10 degrees, 10 over-proof, &c. For malt and wine vinegars, which contain gluten and mucilage, this method is not strictly accurate, as a portion of these substances escapes precipitation by the lime, and consequently alters the specific gravity. A small weight marked "M" is generally supplied with the acetometers for trying such vinegars.

*d.* From the specific gravity. The specific gravity of the sample, carefully determined by an acetometer or any of the usual methods, is sought in the following tables, when the corresponding percentage content of acetic acid is at once seen.

This method furnishes reliable results only with pure or nearly pure solutions, which do not contain much above 50 per cent. of absolute acid, or which have a sp. gr. not higher than 1·062. It is also more to be depended on for weak solutions than strong ones. By carefully diluting a strong acid with an equal weight, or twice or thrice its weight of water, and allowing the mixture to again acquire its normal temperature, the sp. gr. may be taken as a guide in all cases in which great accuracy is not required. When such dilution is made it only becomes necessary to multiply the indication furnished in the Tables by 2, 3, or 4, as the case may be. As, however, authorities are not agreed as to the precise sp. gr. of the monohydrate or glacial acid, and of its solutions, extreme accuracy must not be expected by this method.

TABLE I.—*Adapted to the Specific Gravities of Common Vinegar.*
By Messrs. J. and P. TAYLOR.

| sp. gr. | | | per cent. |
|---|---|---|---|
| 1·0085 | contains of anhydrous or real acetic acid | | 5 |
| 1·0170 | ,, | ,, | 10 |
| 1·0257 | ,, | ,, | 15 |
| 1·0320 | ,, | ,, | 20 |
| 1·0470 | ,, | ,, | 30 |
| 1·0580 | ,, | ,, | 40 |

TABLE II.—*The following table refers to an acid composed of* 95 *per cent. of pure glacial acetic acid* (*hydrated acetic acid*) *and* 5 *per cent. of water. It was the result of a series of determinations undertaken by* Messrs. MOHR *for* OUDEMANN'S.

| Acetic Acid $C_2H_4O_2$ Per cent. | Density. | | Acetic Acid $C_2H_4O_2$ Per cent. | Density. | |
|---|---|---|---|---|---|
| | 15° C. | 40° C. | | 15° C. | 40° C. |
| 1 | 1·0007 | 0·9936 | 29 | 1·0400 | 1·0246 |
| 2 | 1·0022 | 0·9948 | 30 | 1·0412 | 1·0255 |
| 3 | 1·0037 | 0·9960 | 31 | 1·0424 | 1·0264 |
| 4 | 1·0052 | 0·9972 | 32 | 1·0436 | 1·0274 |
| 5 | 1·0067 | 0·9984 | 33 | 1·0447 | 1·0283 |
| 6 | 1·0083 | 0·9996 | 34 | 1·0459 | 1·0291 |
| 7 | 1·0098 | 1·0008 | 35 | 1·0470 | 1·0300 |
| 8 | 1·0113 | 1·0020 | 36 | 1·0481 | 1·0308 |
| 9 | 1·0127 | 1·0032 | 37 | 1·0492 | 1·0316 |
| 10 | 1·0142 | 1·0044 | 38 | 1·0502 | 1·0324 |
| 11 | 1·0157 | 1·0056 | 39 | 1·0513 | 1·0332 |
| 12 | 1·0171 | 1·0067 | 40 | 1·0523 | 1·0340 |
| 13 | 1·0185 | 1·0079 | 41 | 1·0533 | 1·0348 |
| 14 | 1·0200 | 1·0090 | 42 | 1·0543 | 1·0355 |
| 15 | 1·0214 | 1·0101 | 43 | 1·0552 | 1·0363 |
| 16 | 1·0228 | 1·0112 | 44 | 1·0562 | 1·0370 |
| 17 | 1·0242 | 1·0123 | 45 | 1·0571 | 1·0377 |
| 18 | 1·0256 | 1·0134 | 46 | 1·0580 | 1·0384 |
| 19 | 1·0270 | 1·0144 | 47 | 1·0589 | 1·0391 |
| 20 | 1·0284 | 1·0155 | 48 | 1·0598 | 1·0397 |
| 21 | 1·0298 | 1·0166 | 49 | 1·0607 | 1·0404 |
| 22 | 1·0311 | 1·0176 | 50 | 1·0615 | 1·0410 |
| 23 | 1·0324 | 1·0187 | 51 | 1·0623 | 1·0416 |
| 24 | 1·0337 | 1·0197 | 52 | 1·0631 | 1·0423 |
| 25 | 1·0350 | 1·0207 | 53 | 1·0638 | 1·0429 |
| 26 | 1·0363 | 1·0217 | 54 | 1·0646 | 1·0434 |
| 27 | 1·0375 | 1·0227 | 55 | 1·0653 | 1·0440 |
| 28 | 1·0388 | 1·0236 | 56 | 1·0660 | 1·0445 |

TABLE II.—*continued.*

| Acetic Acid $C_2H_4O_2$ Per cent. | Density. | | Acetic Acid $C_2H_4O_2$ Per cent. | Density. | |
|---|---|---|---|---|---|
| | 15° C. | 40° C. | | 15° C. | 40° C. |
| 57 | 1·0666 | 1·0450 | 79 | 1·0748 | 1·0499 |
| 58 | 1·0673 | 1·0455 | 80 | 1·0748 | 1·0497 |
| 59 | 1·0679 | 1·0460 | 81 | 1·0747 | 1·0495 |
| 60 | 1·0685 | 1·0464 | 82 | 1·0746 | 1·0492 |
| 61 | 1·0691 | 1·0468 | 83 | 1·0744 | 1·0489 |
| 62 | 1·0697 | 1·0472 | 84 | 1·0742 | 1·0485 |
| 63 | 1·0702 | 1·0475 | 85 | 1·0739 | 1·0481 |
| 64 | 1·0707 | 1·0479 | 86 | 1·0736 | 1·0475 |
| 65 | 1·0712 | 1·0482 | 87 | 1·0731 | 1·0469 |
| 66 | 1·0717 | 1·0485 | 88 | 1·0726 | 1·0462 |
| 67 | 1·0721 | 1·0488 | 89 | 1·0720 | 1·0455 |
| 68 | 1·0725 | 1·0491 | 90 | 1·0713 | 1·0447 |
| 69 | 1·0729 | 1·0493 | 91 | 1·0705 | 1·0438 |
| 70 | 1·0733 | 1·0495 | 92 | 1·0696 | 1·0428 |
| 71 | 1·0737 | 1·0497 | 93 | 1·0686 | 1·0416 |
| 72 | 1 0740 | 1·0498 | 94 | 1·0674 | 1·0403 |
| 73 | 1·0742 | 1·0499 | 95 | 1·0660 | 1·0388 |
| 74 | 1·0744 | 1·0500 | 96 | 1·0644 | 1·0370 |
| 75 | 1·0746 | 1·0501 | 97 | 1·0625 | 1·0350 |
| 76 | 1·0747 | 1·0501 | 98 | 1·0604 | 1·0327 |
| 77 | 1·0748 | 1·0501 | 99 | 1·0580 | 1·0301 |
| 78 | 1·0748 | 1·0500 | 100 | 1·0553 | 1·0273 |

Before applying the above processes, account should be taken of any mineral acid which may be present in the sample, such being not unfrequently added to vinegar to impart artificial strength. The methods depending on the saturating power of the acid, will be found appropriate to acetic acid of all strengths, when unadulterated with the mineral acids. The method based on the sp. gr. is also very convenient, and is sufficiently accurate for distilled vinegars and for pure acids of moderate strength, although neither this, nor the saturation by lime, give perfectly reliable results.

It is found that the decimal fraction of the sp. gr. of pure or nearly pure vinegar, is doubled by its conversion into acetate of lime. Thus, 1·0085 in vinegar becomes 1·0170 when converted into a solution of acetate of lime. In malt vinegar, however, 0·005 may be deducted from the sp. gr. for mucilage and gluten. The quantity of foreign matter present in vinegar may therefore be approximatively ascertained, by deducting the decimal of the sp. gr. of the solution of acetate of lime from double that of the decimal part of the sp. gr. of the vinegar. Thus:—the sp. gr. of a sample of vinegar being 1·014, and after saturation with hydrate of calcium, 1·023, the sp. gr. of the pure vinegar would be 1·009, and that due to foreign matter ·005. For—

$$·028 — ·023 = ·005$$

and—

$$1·014 — ·005 = 1·009.$$

# CHAPTER II.

# AMMONIA.

($NH_3 = 17$.) *Syn.* AMMONIA GAS, AMMONIACAL GAS, ANHYDROUS AMMONIA, TERHYDRIDE OF NITROGEN; VOLATILE ALKALI, PRIESTLY'S ALKALINE AIR.—This compound derives its name from Jupiter Ammon, in consequence of its having been first procured from the salt obtained by the ignition of camel's dung, near a temple of that mythological deity in Libya.

In the uncombined state ammonia exists in the juices of certain plants, and is freely developed during the decomposition of azotised vegetable substances and the putrefaction of animal matter, very probably owing to the combination of the nascent hydrogen liberated during the process of decay, with the nitrogen of the atmosphere which in small quantity occurs in solution. Ammonia is also largely given off when nitrogenous substances, except when in the form of nitrates and cyanides, are heated with the hydrated alkalies. It is also produced when nitric acid becomes deoxidized by acting on certain metals, preferably zinc, iron, and tin. It is likewise formed when moist iron filings are exposed to the atmosphere and is found in the resulting oxide. When nitric oxide and hydrogen, in the proportion of two volumes of the former to five of the latter, are passed over gently heated spongy platinum, ammonia and water are generated; and when an excess of hydrogen is ignited in the atmosphere, the product is ammonium nitrate.

Ammonia is likewise evolved during certain industrial processes, as in the preparation of caustic soda from ball soda, whilst cooling; during the formation of cyanogen and cyanide of potassium, in blast furnaces; and in considerable quantities when caustic soda is purified by the nitrate.

In nature, ammonia, in a state of combination, is found in variable quantities among the saline product of volcanoes; in sea and rain water; in bituminous coal; in urine; in guano; in the excretæ of animals and reptiles, especially of serpents; and in the atmosphere, especially that of large towns.

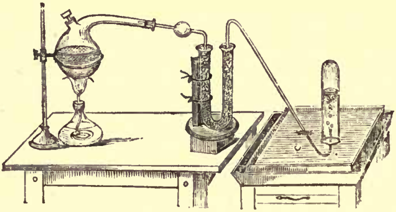
Many unsuccessful attempts have been made to directly convert the nitrogen of the atmosphere into ammonia. Of these we may mention one, which consisted in passing a mixture of air, carbonic oxide, and steam over red-hot hydrate of lime, whereby ammonia and carbonic acid are formed. A plan for the indirect application of atmospheric nitrogen in the preparation of ammonia was suggested by MARGUERITTE, in which it was proposed that cyanide of barium should be prepared, and its nitrogen converted into ammonia by the aid of a current of superheated steam at 572° Fahr. (300° C.). According to the description of this process in a patent—not, however, in practice—native carbonate of baryta is calcined with about 30 per cent. of coal tar, for the purpose of rendering the mass porous, as well as more readily convertible into caustic baryta at a lower temperature. The carbonaceous mass is, after cooling, placed in a retort and kept at a temperature of 572° Fahr. (300° C.), while air and aqueous vapour are forced in, the result being the formation of ammonia in considerable quantity, and carbonate of baryta, which is again used.

The ammonia of commerce and its salts, are chiefly prepared from the ammoniacal liquor of the gas-works, as well as that obtained from bone and animal charcoal factories.

By the addition to the crude ammoniacal liquid of sulphuric or hydrochloric acid, the corresponding salts are procured, which are more or less purified by evaporation and crystallization. The carbonate is prepared by sublimation from the sulphate or chloride, and chalk. The largest quantity of ammonia is obtained when the gas-retorts are kept at an orange-red heat, and the distillation is prolonged as long as practicable.

Ammoniacal gas for the laboratory may be prepared as follows:—a mixture of fresh hydrate of lime with an equal weight of sal ammoniac (both substances being dry and in fine powder) is introduced into a glass flask or retort, the beak of which communicates with one end of a U-shaped tube filled with small fragments of recently burnt quicklime. To the U-shaped tube another glass tube, about 10 inches long is attached, having its further end bent so that it can be placed under a gas-jar, on the shelf of a mercurial pneumatic trough, as shown in the annexed engraving. The joints being made air-tight by collars of india rubber, heat is gradually applied by means of a spirit-lamp, and as soon as the air contained in the apparatus is expelled, the gas is collected for use; powdered quicklime may be substituted for the hydrate in the above process, but a much greater heat will then be required for its liberation. Or it

FIG. 16.



may be more easily collected by displacement. In this case, the mercurial trough may be dispensed with, and the glass jar be suspended mouth downward on a retort stand; it must be so arranged that the end of the bent tube shall pass about half-way up it. As the ammonia is given off from the flask it displaces the air from the jar, which may be known to be full when a piece of turmeric paper placed near the neck turns brown. The jar must be perfectly dry.

Ammonia is a compound of three volumes of hydrogen and one volume of nitrogen, condensed into two volumes; and consists by weight of 82·35 parts of nitrogen, and 17·65 parts of hydrogen. Its formula is $NH_3$.

Ammonia is a gaseous, colourless, invisible gas; highly pungent, acrid, and irritating, and with a strongly alkaline reaction. It is irrespirable, unless very largely diluted with air; extinguishes combustion; and burns slowly in oxygen. Its specific gravity is 0·589; 100 cub. inches weigh 18·26 gr. Under a pressure of 6·5 atmospheres, at 50° Fahr. (10° C.), it forms a transparent, colourless liquid of the sp. gr. 0·731; at 60° Fahr. (15·5° Cent.) this liquid becomes expanded into 1,009 times its volume of ammoniacal gas; at −40° F. (−40° C.) and under ordinary atmospheric pressure, it forms a colourless liquid which at −108° Fahr. freezes into a white translucent crystalline substance.* It is highly basic, and neutralizes the strongest acids; its salts are either volatilized or become decomposed at a red heat or below it, those with a volatile acid subliming unchanged and those with a fixed acid losing their ammonia. Ammonia is decomposed into its elements by transmission through a red-hot tube; and when brought into contact with metallic oxides or spongy platinum at the same high temperature, the newly evolved

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* FARADAY.

hydrogen unites with the oxygen of the oxide or of the atmosphere and forms water. Water at 50° Fahr. (10° C.) absorbs 670 times its volume of this gas; hence it cannot be collected over water. The saturated solution has a sp. gr. of 0·875. Its concentrated aqueous solution boils at 130° (54·4° C.) and freezes at −40° Fahr. ( −40° C.). It is also largely soluble in alcohol. When the electric spark is passed through the gas, it is resolved into its constituent elements.

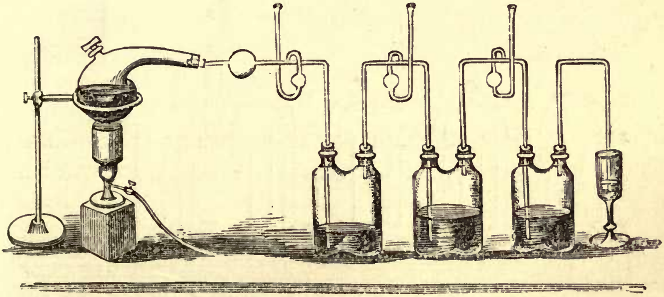
Ammonia may be recognized by—1. Its pungent odour. 2. By turning vegetable blues green, and vegetable yellows brown; the original colour, however, being quickly restored, particularly by the application of heat. 3. By producing dense white fumes when brought into contact with gaseous hydrochloric acid. 4. By the Nessler test, which occasions in solutions containing the smallest quantity of ammonia, a yellow or brown tinge. 5. If a saturated solution of arsenious acid is mixed with a solution of nitrate of silver, containing 2 per cent of the salt, a trace of ammonia causes the formation of a tri-argentic arsenite of a canary yellow colour. 6. A very delicate test for ammonia is afforded by an aqueous solution of carbolic acid. On adding to a liquid containing the smallest quantity of ammonia, or an ammoniacal salt, a few drops of this solution, and then a small quantity of a filtered solution of chloride of lime, the liquid becomes green, especially when warmed.

Ammonia when inhaled, undiluted with air, is an irritant poison, producing spasm of the glottis, convulsions, and death. Even when diluted, it acts as a powerfully acrid and local irritant. Applied to the skin it causes vesication. The use of the pungent odour of common "smelling salts," in syncope, headache, &c., is well known. Largely diluted with air, it has been extolled in chronic hoarseness, asthma, &c., and as an antidote to the fumes of bromine, chlorine, and hydrocyanic acid.

Ammonia is employed in numerous processes in chemistry and the arts; chiefly in the form of "liquor of ammonia," "spirits of hartshorn," &c., and in combination under the form of salts. In the industrial arts, liquid ammonia is mostly used for the preparation of archil from various species of lichen; for the purification of coal-gas; and, as in CARRÈ's machine, for the artificial production of ice. In its pure or gaseous state it possesses little practical interest.

**AMMONIA, SOLUTION OF.** *Syn.* SOLUTION OF AMMONIA, LIQUOR AMMONIÆ, AMMONIUM HYDRATE, AMMONIA. Ammoniacal gas readily dissolves in water, one volume of which absorbs about 670 volumes of ammonia, much heat being liberated during combination, and the solution increasing greatly in volume.

FIG. 17.

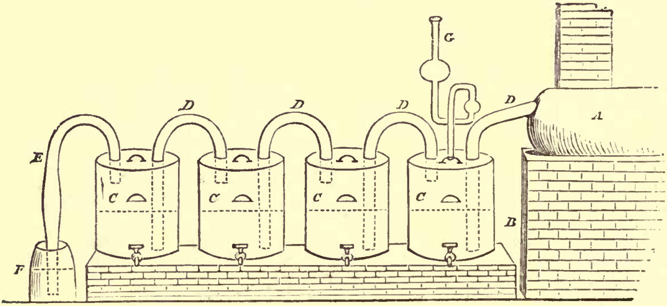


Solution of ammonia may be prepared for the laboratory by distilling, in a tubular retort, equal weights of sal ammoniac and freshly burned quicklime. The lime is slaked and made into a paste with water before admixture, and the gas evolved is passed through a set of WOULFE's bottles partially filled with water, as shown in the drawing above.

In conducting the operation, the heat should be cautiously applied during the evolution of the ammonia; and on no account should the bottom of the retort become red-hot. The balloon or bulb interposed between the neck of the retort and the first bottle is for the purpose of arresting any sublimed chloride of ammonium that may have escaped decomposition. When the gas has all passed over, the retort should be heated so as to fuse the residue of chloride of calcium, which should then be poured out.

If pure, solution of ammonia leaves no residue when evaporated to dryness; this shows the absence of lime compounds, and if it give no precipitate or cloudiness when after neutralization with nitric acid it is treated with barium chloride or argentic nitrate, it contains neither a sulphate nor a chloride. It should not be coloured by sulphuretted hydrogen. A more or less brown tint denotes the presence of organic compounds, derived from the substances from which it has been produced. The best method for the removal of these is the filtration of the ammoniacal solution through charcoal. The charcoal should afterwards be washed, and the washings added to the retorts when these are charged for a fresh distillation.

FIG. 18.



*A*, Cylindrical Iron Retort.
*B*, Furnace for ditto.
*C C C C*, Stoneware Receivers.
*D D D D*, Connecting Pipes.
*E F*, Waste Pipe and Receiver.
*G*, Safety Tube.

Solution of ammonia is prepared on the large scale, from a mixture of about equal parts of freshly-slaked lime and sal-ammoniac or sulphate of ammonia, which is heated in an iron cylinder or retort connected with a set of refrigerators; the latter consisting of a row of stoneware bottles with double necks, containing water, and kept very cold. The general arrangement of the apparatus used in this manufacture is exhibited above, and with the accompanying references will be easily understood. The condensers, when in use, are surrounded with cloths (not shown in the engraving) kept wet by means of very cold water, a constant current of cold air being at the same time made to pass over them. The pipe *D* leading from the retort is several feet long, and is advantageously passed through a wooden screen, in order that the radiated heat of the retort and brickwork of the furnace, may be intercepted as much as possible.

There are two methods of carrying out the process. In one the dry pulverulent ingredients are mixed together, and the resulting gas passes over into the water placed in the receivers. In the other the lime is made into a pap with water, and the ammonia salt, in coarse powder, being added to it, the whole is rapidly blended together, before closing the retort and applying heat. In either case a proportionate quantity of water is put into the condensers, and the operation is nearly similar; but the latter method requires the least heat, and so far as the receivers and refrigerators are concerned is perhaps more easily managed. It is that always followed when sulphate of ammonia is employed.

An aqueous solution of ammonia is in constant demand in the laboratory, both as a reagent and for precipitating the oxides of the heavy metals. Liquid ammonia is now very frequently made by distilling the sulphate with caustic soda, the value of the residual sulphate of soda, and the ease of manipulation, compensating for extra cost.

Among the plans having for their object the production of an ammoniacal solution, more or less concentrated, for many technical purposes, and for the preparation of salts, may be mentioned :—

1. That of WATSON (patent dated 1838), in which gas-liquor mixed with a proper quantity of freshly slaked lime is distilled from a spacious retort or still into a receiver containing cold water, until a large amount of steam passes over with the gas, when the strong alkaline liquor forming the distillate, and called the first portion, is drawn off. The distillation is then continued, when a weaker and impurer solution is obtained, called the second portion The first portion is then re-introduced into a retort or still with a small quantity of fresh lime, and the distillation repeated. The patentee calls the product the first portion of the second distillation. It is a strong ammoniacal liquor, sufficient for all the purposes of scouring, cleaning, and conversion into commercial ammonia-salts. It may be further purified by a third distillation; the second portion of each operation being transferred again to the still with the next fresh charge of gas-liquor.

2. A modification of COFFEY's still,* patented by Mr. W. E. NEWTON (1841), under the name of the AMMONIA STILL, is extensively employed in the manufacture of liquid ammonia. By NEWTON's process, which is a continuous one, solution of ammonia, of varying density and of considerable purity, can be obtained from gas-liquor, bone-spirit, ammoniacal salts and liquids. The body of the apparatus is of

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* An engraving and description of this still as employed in spirit-making are given under *Stills*, vol. i. of "Churchill's Technological Handbooks."

wood, the chambers are lined with lead, and the diaphragms are of perforated sheet-iron. The management of the apparatus varies with the form in which it is desired to obtain the product. When the ammonia is required to leave the upper chamber of the rectifier in the form of gas, either pure or impure, the steam which ascends, and the current of ammoniacal liquor which descends, are regulated in such relative proportions that the latter remains at or near the atmospheric temperature during its passage through some of the upper chambers, becoming successively hotter as it descends, until at length it enters into ebullition; in which state it passes through the lower chambers, either to make its escape or to enter a cistern provided to receive it. If, on the contrary, the ammonia is required to leave the upper chamber in combination with the vapour of water, the supply of steam entering below must be in such proportion to that of the ammoniacal liquor supplied from above, that the latter may be at or near the boiling temperature in the upper part of the apparatus. Crude liquor and ammonia-salts, before being submitted to distillation, are first treated with the requisite quantity of quicklime, which in the first case removes most of the impurities of the crude liquid; and in the second, by combining with the acid of the salt, liberates the ammonia. In addition to ammonia, carbonic acid and other volatile substances may be generated during the distillation. Sometimes the carbonate of ammonia produced under these circumstances may not be objected to; but when gaseous ammonia alone is desired, means must be taken to keep the carbonic acid out.*

3. Mallet's Apparatus. This, which is employed in many of the large gasworks, is shown in vertical section in

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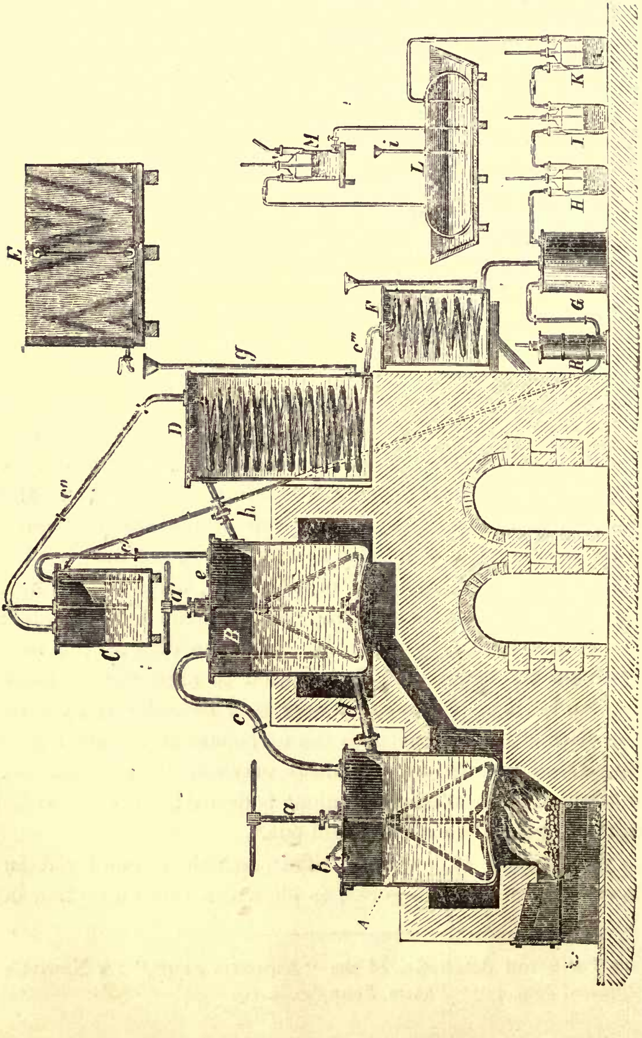
* For a full description of the "Ammonia-still," *see* Newton's "Patent Jour.;" "Pharm. Jour.," xiii. 64.

FIG. 19.



the accompanying woodcut. Steam is forced into large receptacles, which are filled with gas-water, by which means the carbonate of ammonia is volatilized. When lime is added, ammonia gas is evolved, and if this is conveyed into weak sulphuric acid, sulphate of ammonia will be the resulting product.

The apparatus consists of two cylindrical boiler-plate vessels, A and B. A is heated directly by the fire, and has a leaden tube, *c*, which dips into the liquid contained in B, this vessel being so placed as to catch the waste heat from the fire. *b* and *e* are man-holes; *a* and *a′* are stirrers. By means of the tube *d* the fluid from B can be run off into A. Gas-water is poured into both vessels, and lime added; ammonia is liberated, whilst carbonate of lime and sulphide of calcium are formed, and these latter remain in the vessels after the volatilization of the ammonia. The vessel D is also filled with ammoniacal water, and when the operation is in action this water, already warmed, is run by the aid of the tube *h* from D into B. E is a gas-water tank, from which D is filled by means of *g*. The ammonia set free in A is, with the steam, conveyed by the pipe *c* into B, thence through *c′* into the wash-vessel C, and thence again through *c″* into the first condenser D. The partially condensed vapour now passes into the condensing vessel F, the worm of which is surrounded by cold water. The dilute ammonia is collected in G, and forced by means of the pump R into C, from whence it is occasionally removed by means of a syphon into either A or B. The non-condensed ammoniacal gas is carried from G through a series of WOULFE's bottles, the first bottle (H) containing olive-oil, which retains any hydrocarbons that may be present in the gas; the bottle I contains caustic soda ley, in order to retain other impurities; the bottle K is half-filled with distilled water. The ammoniacal gas, having passed through K, is conveyed to the large wooden tank (lined with lead) L, filled with diluted sulphuric acid, if it is intended to prepare sulphate of ammonia, or with water, if solution of ammonia be required. The vessel L is placed in a tank of water; *i* is a small pipe for introducing acid, while the tube leading to M serves to carry off any unabsorbed ammonia, M being likewise filled with acid.

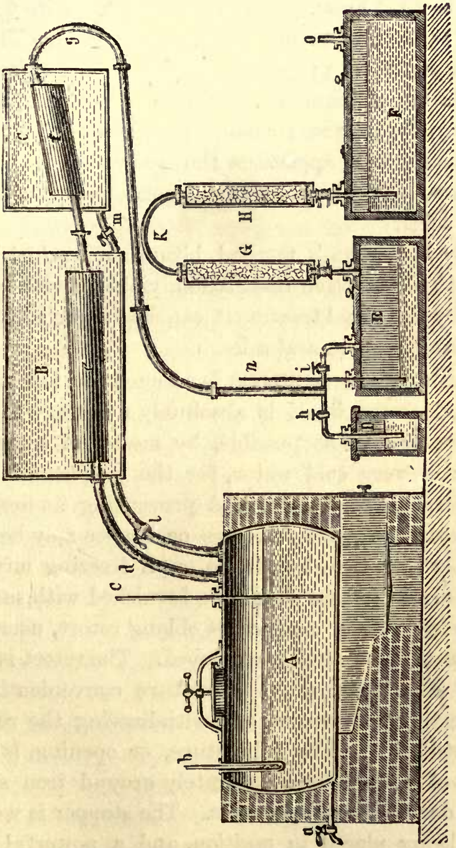
4. ROSE's apparatus consists of A, a boiler; B and C, two vessels in which the gas-liquor is warmed by means of the tubes *e* and *f*, through which and *g* the steam and ammonia gas evolved in A pass to the absorption vessels D, E, and F, the connexion between E and F being made by means of the gas-filters G and H. By means of the tubes *l* and *m*, each of which is fitted with a stop-cock, the gas-liquor can be run into the boiler A. A is filled two-thirds with gas-liquor and one-third with slaked lime. The gas-filters G and H are filled with freshly-burnt charcoal, which retains any empyreumatic substances that might be carried over by the ammoniacal gas. The vessel D is filled with hydrochloric acid, and pure water is poured into E and F. A, being two-thirds filled with the gas-liquor, and the rest of the apparatus put into working order, the fire is lighted. The ammoniacal gas evolved in A passes with the steam into *e* and *f*, where a portion of the steam is condensed and retained as water.

Into the boiler A is fitted a tube *b*, containing a thermometer surrounded by brass fittings, for the better conduction of the heat. When this thermometer indicates 197·6 Fahr. (92° Cent.) to 201·2° Fahr. (94° Cent.), the tap *h* is opened, and the tap *i* (which up to this time has been kept open) shut, so that the gas may pass into the hydrochloric acid contained in D, until the vessels G and H have been filled with fresh charcoal, an operation which is required at the beginning of the working as well as when the temperature has risen in A to 204·8° Fahr. (96° Cent.), 208·4° Fahr.

(98° Cent.), and 212° Fahr. (100° Cent.). This having been done, the tap *i* is again opened.

When the temperature has reached 217·4° Fahr. (103° Cent.), taking the boiling-point of the liquid at 212° Fahr. (100° Cent.), all the ammonia is expelled, and the liquid is

FIG. 20.



then run off by opening the stop-cock *a*. A fresh charge of gas-liquor and slaked lime is then put into the boiler, and the operation repeated. When the temperature in A reaches 217·4° Fahr. (103° Cent.) the liquid in B becomes heated to 194° Fahr. (90° Cent.), and that in C from 77° Fahr. (25° Cent.) to 86° Fahr. (30° Cent.). The vessel F holds from 26 to 33 gallons of water, which is converted into solution of ammonia, having a specific gravity varying from 0·910° to 0·920°: *c* and *n* are glass safety-tubes.

5. In LUNGE's apparatus the gas-water is heated in a boiler, and the liberated ammoniacal gas passed into sulphuric acid.

6. By HOMPESCH's method, bituminous schist being subjected to destructive distillation, yields gaseous ammonia, which by the usual treatment can be employed for the preparation of ammoniacal salts.

Whatever form or process is adopted for the preparation of liquid ammonia, it is absolutely necessary to keep the receivers as cool as possible, by means of snow, ice, or a current of very cold water, for the purpose of promoting the absorption of the gas and preventing its loss. On the small scale, the glass receivers or bottles may be most conveniently surrounded with ice, or a freezing mixture, and two or more of them should be furnished with safety-tubes. On the large scale, a capacious oblong retort, usually of iron and sometimes of lead, is employed. The retort is furnished with a large opening or tubulature conveniently situated for inserting the charges, and withdrawing the residuum of the distillation. The tubulature, or opening, is closed by means of a large and accurately ground iron stopper, or with a door secured by screws. The stopper is well greased before being placed in position, and a powerful lever employed when it is required to be taken out. Should it become fixed, a cloth moistened with cold water, and carefully wrapped round it, without touching the neck of the retort, by causing it to contract, will enable the operator to remove it with facility. Sometimes a large iron kettle is employed instead of a retort. The kettle has a moveable and accurately fitting lid secured in its place like that of a Papin's digester, and a large and long iron tubulature in its centre, in which is inserted another cast-iron tube, bent at right angles, for conveying the gaseous ammonia to the receivers. This form of vessel has the advantage over the retort of exposing a larger opening for the removal of the residuum of the process. In either case the distillatory vessel is imbedded in sand supported by fire-brick, and is not exposed directly to the heat of the furnace. Before commencing the distillation, the joints are all well luted, to avoid leakage. The following are good lutings:—1. Wax, resin, and turpentine melted together. 2. Freshly slaked lime made into a paste with bullock's blood or thin size. An excellent plan is to pass the gas, as it leaves the retort, through a silver or pewter worm or refrigerator set in a tub supplied with a stream of very cold water, by which it will be sufficiently cooled before it reaches the receivers, to obviate the necessity of any further attention to them than keeping the cloths wrapped round them constantly moistened with cold water. The upper end of the worm should be connected, by means of a balloon-shaped adapter, with the still, and the lower end with the first receiver; the use of the balloon being to intercept any volatilized ammonia-salt that might be accidentally driven over by the heat being too high, or raised too suddenly.

The heat should be gradually applied, and very cautiously raised, so as to prevent any of the sal ammoniac or sulphate being volatilized and passing over in an undecomposed state. Even towards the end of the process the heat should never be allowed to approach redness.

When the lime is slaked and papped with about four parts of water, a lower heat is required to expel the gas, and it passes over more easily and completely than when less water is employed. This plan should always be adopted, and is absolutely necessary when sulphate of ammonia is used; or the residuum of sulphate of lime would become so hard that it could only be removed from the retort with difficulty.

The gas being wholly expelled from the retort, or other distillatory vessel, the receivers are disconnected, and the heat is raised sufficiently high to fuse the residual chloride of calcium, which remains if sal ammoniac has been employed, which is then baled or poured out. Glass retorts often suffer fracture at this stage; but should they escape, it generally happens that they are broken when they are heated for a second operation. Hence, it is rarely that a retort, even when carefully handled, can be used more than twice.

When crude sulphate of ammonia is employed it is advisable that the first receiver should contain only a small quantity of water, the use of which is to purify the gas which passes through it, and to retain any traces of volatile empyreumatic or oily matter which may be carried over with it.

Pure solution of ammonia is most easily obtained from sal ammoniac; but crystallized sulphate of ammonia, often in the crude state, is commonly employed, on account of its lower price. When the sulphate is used, the addition of a few spadefuls of common salt to the mixture of sulphate and lime before distillation will prevent the caking of the residue left in the retort, should the distillation be carried to dryness.

AMMONIUM, SESQUICARBONATE OF. *Syn.* CARBONATE OF AMMONIA, SAL VOLATILE, SALT OF HARTSHORN, AMMONIÆ

CARBONAS. B.P. Probably $2NH_4HCO_3 + NH_4, NH_2CO_3$, a mixture or compound of bicarbonate of ammonium and carbamate of ammonium.

The commercial salt is prepared as follows:—1 part of sulphate of ammonium and 1½ or 2 parts of chalk, both dry and in coarse powder,* are mixed together and put into iron retorts, similar to those used in the manufacture of coal-gas, in which they are heated to redness. Double decomposition takes place, and the liberated sesquicarbonate of ammonia ascends into cooled receivers, where it becomes condensed. The receivers are lined with lead or earthenware. Very frequently the receiver is connected by iron or lead pipes with a second one containing a stratum of water, which absorbs the free ammonia evolved during the process.

The sesquicarbonate of ammonia of commerce usually occurs in the form of white, fibrous, translucent, or semi-translucent cakes, generally about two inches thick. It is less volatile and pungent than the neutral carbonate; it is soluble in 4 parts of water at 55° Fahr. (12·77° Cent.), 3·3 parts at 62° (16·66° Cent.), 2·5 parts at 90° (32·22° Cent.), and 2 parts at 120° (48·88° Cent.); boiling water and alcohol decompose it, with the evolution of carbonic acid and ammonia; by age or exposure to air, the surface assumes an opaque white colour, owing to the loss of part of its carbonate by volatilization, and the less volatile bicarbonate being left behind and forming a spongy crust on the remaining sesquicarbonate. Unlike the carbonate, it can neither be re-sublimed nor digested or distilled with either alcohol or water, without suffering decomposition. Its sp. gr. is 0·966.

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* Some portion of the chalk should be in small lumps, the better to allow of the passage of the gas.

The composition of this salt varies according to its method of preparation.

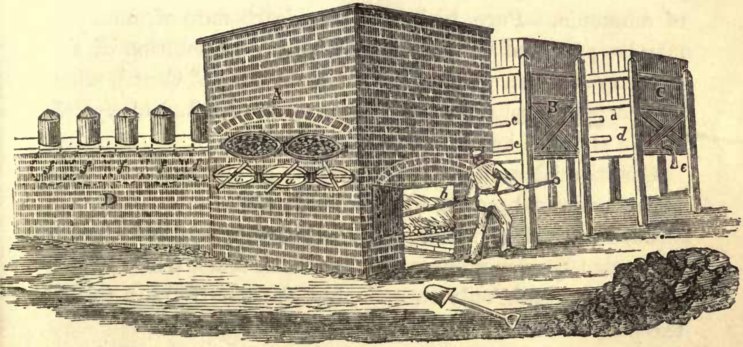
Commercial sesquicarbonate of ammonia is largely employed for the removal of grease from woollen goods; by bakers to give lightness to their fancy goods, and to make extemporaneous bread and pastry; by the chemist and pharmaceutist for the preparation of other salts of ammonia, for the preparation of smelling-salts, and in analysis.

In the manufacture of sesquicarbonate of ammonia on a large scale the distillation is usually carried on in cast-iron retorts, similar in size, shape, and character to those employed in the manufacture of coal-gas, five or more being commonly set horizontally in the same furnace, as shown in the engraving; each retort has its mouth (*a*), through which the charge is introduced, closed with a movable door, which is securely fastened, as seen in the plate. Each retort is furnished, at the upper part of its further end, with an iron pipe (*c*), to carry off the evolved vapours to the condenser or receiver. The latter consists of two large square leaden chambers (B, C), fitted with movable covers luted on, and movable bottoms, so as to permit of the easy removal of the sublimed salt. The first receiver communicates with the second by means of two large leaden tubes (*d*) near its centre. The second receiver contains a stratum of water, the object of which, as before explained, is to absorb the free ammoniacal gas. To the bottom of the chambers is attached a leaden pipe, as shown at *e*, for drawing off the liquid product of distillation. During the process of sublimation the pipe is closed with a wooden plug. The solution which is drawn contains carbonate of ammonia. It is evaporated and crystallized. Both chambers are placed on strong wooden supports or scaffolding, so as to bring them on a level with the retorts.

The sublimation is generally carried on night and day for about fourteen days, a fresh charge being inserted in the retorts daily. At the end of the fourteen days the covers of the chambers are lifted, the bottoms let down to the ground, and the crude carbonate is detached by heating the outsides of the lead chambers.

The substances employed produce monocarbonate of ammonia; but it is practically impossible to prevent loss of ammonia in the process, as a portion is always dissociated into nitrogen and hydrogen gases, by passing along the red-hot surface of the top of the retort. It sometimes happens that an explosion occurs when the doors of the retort are opened, owing to a stream of hot air passing into the chambers and mixing with the hydrogen, which then becomes fired by the heat. When impure sulphate or other ammonia-salt is used in the manufacture of the sesquicarbonate, the resulting salt, being impure and discoloured, is resublimed in iron pots (*f, f, f*), furnished with movable leaden heads, which are kept cool by means of a current of air circulating over them, a little water drawn from the bottoms of the chambers being introduced into the subliming-pots to render the product translucent. These pots are

Fig. 21.



arranged in sets, as shown at D in the engraving. The heat is applied either by means of a flue passing from the retort-furnace (A, *b*), or by a water bath heated in the same manner; the latter being the preferable method, as the temperature should not be greater than about 140° Fahr. (60° Cent.), and never exceed 150° Fahr. (65·5° Cent.) to 155° Fahr. (68·33° Cent.).

The charge of a retort usually consists of about 70 to 72 lbs. of ammonium sulphate, or 57 to 58 lbs. of the chloride, to 1 cwt. of chalk; or about these proportions. The product is about 40 lbs. of the crude salt, which by careful re-sublimation, yields about 39 lbs. of marketable carbonate of ammonia. Pure hydrated sesquicarbonate of ammonia may be prepared by exposing a saturated solution of the ordinary salt to a temperature of 32° Fahr. (0° Cent.), when it becomes deposited in large transparent octahedral crystals with a rhombic base.

Commercial carbonate of ammonia is also obtained from bones or animal matter by dry distillation.

Carbonate of ammonia, like the chloride and sulphate, is now scarcely ever prepared on the small scale, that of commerce being not only cheaper, but sufficiently pure for all the purposes of medicine and the arts.

Bicarbonate of ammonium in conjunction with chloride of sodium is employed in the manufacture of carbonate of soda, by what is known as the "ammoniacal soda process," the only one which has hitherto sustained competition with the well-known "Leblanc method."

The ammoniacal soda process was first patented by DYAR and HEMMING in June 1838, and although the patentees used equal weights of chloride of sodium made into a saturated solution, and powdered commercial carbonate of ammonia (which was a mixture of carbonate and sesquicarbonate), they suggest as preferable the employment of bicarbonate of ammonia. The following equation explains the decomposition :—

$$NaCl + (NH_4)H,Co_3 = NH_4Cl + NaH,Co_3.$$

The resulting bicarbonate of soda being but very slightly soluble in the chloride of ammonium solution, is precipitated in crystals, which, after removal of the supernatant liquor, are exposed to a temperature of about 700° Fahr.

This drives off half the carbonic anhydride of the bicarbonate, as well as a small quantity of carbonate and chloride of ammonium, both of which are condensed in a leaden chamber, whilst mono-carbonate of sodium remains behind. The solution of chloride of ammonium, consisting in great measure of that salt with small quantities of carbonate and chloride of sodium and carbonate of ammonium, is then boiled, whereby the carbonate of ammonium is driven off and also condensed in the leaden chamber. The solution is next evaporated to dryness, and the residue being mixed with carbonate of lime and heated, the ammonium chloride is converted into carbonate, which is carried into the same leaden chamber, the contents of which are again employed for acting upon a fresh quantity of salt, chloride of calcium remaining behind. This regeneration of carbonate of ammonium makes the process a continuous one. Of the various methods founded on the above, that by SOLVAY, of Couillet, near Charleroi, is the only one which has proved remunerative.

AMMONIUM, CHLORIDE OF. $NH_4Cl$. *Syn.* MURIATE OF AMMONIA, SAL AMMONIAC, HYDROCHLORATE OF AMMONIA. This salt appears to have been originally obtained in Egypt by sublimation from the soot of camels' dung. It has been found native in Bucharia, and is sometimes met with in the vicinity of coal-mines in which conflagrations have taken place, as well as in volcanic districts, where it is associated with lava. In this country it is manufactured chiefly from the crude ammoniacal liquors obtained as secondary products in the manufacture of coal-gas,* and animal charcoal.

1. From GAS-LIQUOR.—The crude ammoniacal liquor of the gasworks is, either before or after distillation,† neutralized with hydrochloric or sulphuric acid, choice being made of that acid which is the cheaper and more easily obtainable. When hydrochloric acid is employed, the saturation is usually effected by allowing the acid to flow from a wooden vessel or tank, lined with lead or gutta-percha, into an underground reservoir or tank containing the ammoniacal liquor. This vessel has an exit tube passing into the chimney or shaft, which carries off the sulphuretted hydrogen and other offensive gases liberated during the mixing of the liquids. Sometimes the gas liquor is accumulated in enormous covered wooden tuns, holding from 10,000 to 20,000 gallons or more, and the acid is poured in from gutta-percha carboys, raised by cranes, and mixed with the liquor by means of powerful agitators, the offensive fumes being got rid of either by being carried into the steam-engine chimney, or by being made before doing so, to traverse the boiler fire. The quantity of acid employed of course depends on the ammoniacal strength of the gas-liquor. The usual proportions are 1½ to 2 lbs. of the former to each gallon of the latter; but in all cases sufficient acid should be added to impart a very faint acid reaction to the mixture. This done, the saline solution, now containing chloride of am-

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* It has been calculated that every million tons of coal consumed in the London gasworks yields, 9723 tons of ammonium chloride.

† The distillation is generally conducted in a large wrought-iron boiler, connected with a rude modification of Coffey's still; the object being to obtain the concentrated liquor as free from tar as practicable.

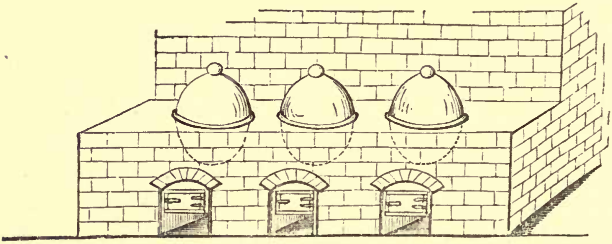
monium, is, after repose, ready to be pumped or run off into the evaporators.

The evaporation of the crude saline solution is usually carried on in large square or rectangular cast-iron vats, of very moderate depth, and from 1000 to 1500 gallons or more capacity. These are encased in brickwork, and are heated by a furnace, of which the flues pass in a sinuous course beneath the lining of brickwork on which the vats or pans rest. During the concentration of the liquid the tar, &c., which separates and floats upon the surface, and which seriously impedes evaporation, is from time to time removed by skimming. As soon as the sp. gr. reaches 1·25, any excess of acid in the solution is exactly neutralized with a little fresh ammoniacal liquor, which not only prevents any waste of acid, but precipitates any ferric salt that may be present, and would contaminate the ultimate product. After being allowed a short time to settle, the hot liquor is ready to be transferred to the crystallizers.

The vessels employed in the crystallization are pans or tubs, usually circular, and about seven or eight feet wide by two and a half to three feet deep; they are generally set on the ground, but sometimes embedded either partially or wholly. The saline liquor being pumped or run into these vessels at a little below the boiling temperature, crystallizes as it cools. Whilst cooling it is occasionally stirred or agitated, to prevent the formation of large crystals, which would prove inconvenient in the subsequent part of the process. The time occupied in the crystallization varies, according to the size of the crystallizers and the weather, from three or four to eight or even ten days. The mother-liquor of the crystallizers is pumped back into the evaporating-pans for further concentration. The crude blackish chloride of ammonium obtained as above is contaminated with tarry and oleaginous matter, free acid, water, &c.; from part of which it is freed by exposing it in a layer about four inches deep, on a cast-iron plate gently heated by a zigzag flue of a small furnace, until all the water is expelled; care being taken that the heat never rises high enough to volatilize the salt. This operation is generally performed under a dome, or the expanded throat of a large chimney. The salt will now have become of a greyish-white colour, and is ready for the next operation.

The crude dried salt of the last process is finally purified by sublimation. For this purpose cast-iron pots lined with clay are employed. These pots, which are heated from below and by means of flues running round their sides, are shown in the annexed engraving. The crude grey salt is beaten down into them until they are about two-thirds filled, when the heads or capitols are fitted on, and heat applied. The heads, which are very heavy and usually made of lead, but less frequently of iron, have the form of a dome or a hemispherical cup, with a small tube or hole at the apex, in which a plug is loosely placed, to permit the escape of steam. They are so made as to fit closely and firmly on the flat rim or flange of the sublimers, and are retained in their places during use both by their weight and by two or three clamps provided for the purpose. They are also furnished with three rings, set at equal distances, to allow of their

FIG. 22.



being lifted off, or moved by means of a pulley and chains. Economy both in time and labour is gained by the use of subliming pots as large as practicable; instead of being flat, the bottoms of these pots should be raised in the centre.* The regulation of the heat is of the utmost importance. If the temperature employed be too high, the sublimed salt will be contaminated with empyreumatic matter, while some of it will be carried beyond the dome and lost; and if it be extreme, the head may be altogether blown off, and the contents of the pan scattered about the building; whilst, on the other hand, if the heat employed be too low, the resulting cake of sal ammoniac will be soft, spongy, and either grey or yellowish. The proper temperature is said to be known by two or three drops of water readily boiling, and being dissipated in vapour, when placed on the head or cover of the sublimer; but the water should not spit or dance about, or be raised by the heat from contact with the metal. The usual practice is to keep the fires "briskly up until the sublimers and their surroundings attain a sufficient degree of heat; they are then slackened, and maintained at a mean temperature."† The sublimation occupies from five to nine days; but it is customary to raise the heads once, or even twice a week, to ascertain the progress made; the fires having been purposely neglected or checked for some hours previously. The process is finally stopped before the whole of the crude salt in the pots is volatilized; since the heat required for that purpose would lead to the decomposition of the carbonaceous impurities, and cause them to give off volatile hydrocarbons, which would materially lessen the purity and beauty of the product. The unsublimed portion

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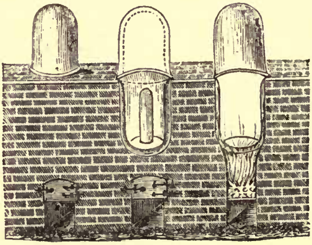
* "Chemistry as applied to the Arts and Manufactures."

† MUSPRATT.

in the pots forms a conical mass, which is technically called the "yolk." This is shown in the accompanying plate.

The sublimation having been carried to a sufficient extent, the fires are allowed to die out. The domes, after cooling, are lifted off, and the attached hemispherical cakes or "bells" of sal ammoniac or hydrochlorate of ammonia are at once removed. These vary from two to five inches in thickness, and from 45 or 50 lbs. to 1000 lbs. and upwards in weight, according to the size of the sublimers in which they have been condensed. They are generally nearly pure, except in the outer part which has been in contact with the metal. From the subliming-house they are taken to the store or packing-house, and after having been scraped, to remove the discoloured portion, are either preserved entire, or are broken up into convenient pieces, which are then packed in casks or barrels. In either state they are then ready for the market.

FIG. 23.



When sulphuric* acid is used to neutralize the ammoniacal liquor, the process is generally the same as when hydrochloric acid is employed; but the brown salt obtained by the crystallization, and subsequent desiccation, is of course crude

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* Sp. gr. 1·33 to 1·38.

sulphate of ammonium, instead of chloride. Before being put into the sublimers, the crude sulphate is intimately mixed with about an equal weight of common salt.

When the ammoniacal liquor is found to be rich in carbonate of ammonium, gypsum is employed as a source of sulphuric acid.

Another method consists in converting the solution of the crude sulphate into a solution of the chloride, during the process, by the addition of chloride of sodium. Both these methods are described further on.

2. From BONE-LIQUOR, &c.*—The ammoniacal liquor, technically called " bone-liquor " or " bone-spirit," and formerly known under the name of " spirit of hartshorn," is essentially a solution of carbonate of ammonia more or less contaminated with volatile empyreumatic oil. Its conversion into sal ammoniac may be easily effected by saturating it with hydrochloric acid, after first removing the empyreumatic oil floating on the top. Upon the addition of the acid a great many solid impurities separate, and these must be got rid of by filtration of the liquid through canvas, which retains most of them. Two or three filtrations are necessary. When by this means the liquor has become clear, it is pumped or conveyed into leaden or iron boilers, and

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* The bone-liquor employed in England is chiefly obtained from the manufacturers of bone-black or animal charcoal; but on the Continent, the liquor obtained by the destructive distillation of animal offal, such as blood, flesh, horn, hoofs, woollen rags and waste, hair, scrapings of hides, leather cuttings, is employed for the purpose. The preparatory process by which this liquor is procured is essentially the same in each case; save that with the animal offal the temperature should not exceed a red-brown heat, for if it does the resulting charcoal is not suited for the manufacture of ferrocyanide of potassium and Prussian blue. These bone-liquors have usually a density ranging between 8° and 9° Baumé (Ure; = sp. gr. 1·056 to 1·063).

evaporated until a pellicle begins to form, when it is pumped or run off into the crystallizers, the resulting crystals being properly drained and dried. The salt thus obtained may be purified either by sublimation or by recrystallization. The whole series of processes closely resemble those already described, but they are less troublesome, owing to the absence of the tarry and other foreign matters which impede and complicate the operation when gas-liquor is employed.

Another method in use, more especially on the Continent, and one equally applicable to any crude ammoniacal liquor rich in free ammonia or its carbonates, consists in the employment of sulphate of lime instead of sulphuric acid to neutralize the alkali. For this purpose the ammoniacal liquor is passed through a series of three or four covered wooden filters lined with lead, each containing a layer of crushed gypsum to the depth of three or four inches. These filters are usually set on stages one above another, and each communicates with a cistern placed beneath it by means of a leaden pipe furnished with a stop-cock. This last is not opened until the liquor has remained some little time in the filter ; and a pump throws back once, or oftener, upon each filter, what has already passed through it, before it is allowed to run into the next lower one. The liquor in each filter is not allowed to stand higher than from two to three inches above the surface of the gypsum ; and the lowest or last filter is supplied with fresh gypsum at each separate charge of fresh liquor. A little water is lastly passed through the filters to wash out the portion of sulphate of ammonia absorbed or retained by the filtering media. In this way the gypsum of the filters is converted into carbonate of lime at the expense of the carbonate of ammonium in the solution ; whilst the ammonia of the latter decomposes the gypsum, and becomes converted into sulphate of ammonium, which, with some free ammonia, is found in the filtrate. Sulphuric acid is next added to the filtered liquor to completely neutralize the free and carbonated alkali still existing in it; after which it is evaporated in a leaden boiler, with frequent skimming to remove floating oil, until of the sp. gr. 1·160. Common salt, in sufficient quantity to convert all the sulphate of ammonium in the liquid into chloride by double decomposition, is now added, with constant stirring; after which the clear portion is either pumped or syphoned off into a somewhat deep reservoir or tank, where it is allowed to settle. The liquid, after sufficient repose, is pumped from the reservoir to the boilers and evaporated, with frequent agitation, so long as the sulphate of sodium now existing in it falls to the bottom in granular crystals. These crystals are at intervals scraped to the cooler portion of the pan or boiler, whence they are removed by copper rakes and shovels into draining-hoppers placed near the edges of the pan. The liquor in the boiler is now a strong solution of sal ammoniac, but still containing a little sulphate of soda, from which it has to be freed by crystallization. With this object it is further concentrated, and then run or pumped into the crystallizers. In thirty or forty hours, or longer, the mother-liquor is run or pumped off. The mass of newly formed crystals is then drained and slightly washed, first with a little weak solution of sal ammoniac, and next with a very little cold water, after which they are again well drained. The crude chloride of ammonium thus obtained is converted into the pure salt by desiccation and sublimation, as before described.

In France, where this method is very generally employed, the sublimation is commonly conducted in stoneware or earthenware balloons or bottles coated with loam. These bottles, about eighteen to twenty inches in height in the body, are either surmounted with inverted cups or heads ten or twelve inches high, or simply covered with a tile, in which latter case the sublimate collects in the upper part or neck of the balloon, which is so situated as to be above the action of the fire. A number of these vessels are set on the dome of a furnace, which is perforated with holes or slits, to allow the heat to pass through; whilst their necks or heads are sheltered from the action of the fire by plates of iron or earthenware, having semicircular indentations on their edges, so that when placed together they form a level surface, through which the necks of the sublimers protrude and fit closely. The fire is nicely regulated, so as to cause the salts to condense in the upper and cooler part of the vessels, or in the heads, as the case may be; and great care is taken to clear the necks occasionally with a skewer, to prevent choking and consequent bursting of the vessels.

In Scotland, where a similar process is also commonly pursued, the sublimers are generally "cast-iron pots, lined with fire-proof tiles; the condensation being effected in globular heads of green glass, with which each of the iron pots is capped." *

Gas-liquor is chiefly composed of carbonate of ammonium, with chloride, sulphate, sulphide, cyanide, and sulphocyanide of the same radicle. On neutralization with hydrochloric acid or sulphuric acid, these are converted into chloride or sulphate of ammonium, according to the acid used. By sublimation with chloride of sodium, the sulphate of ammonium is converted, by double decomposition, into chloride of ammonium, which sublimes; and sulphate of sodium, which remains in the subliming-pot. A similar change occurs when the solution of the sulphate, prior to crystallization, is decomposed by the addition of chloride of sodium, or any other chloride. When the gas-liquor is at once converted into chloride of ammonium by the addition of hydrochloric

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* Ure's "Dict. of Arts, M. and M.," 5th ed. i. p. 143.

acid, the sublimation merely purifies the salt. Similar changes occur when bone-spirit is employed.

Chemically considered, this salt consists of equal volumes of gaseous ammonia and hydrochloric acid gas condensed into the solid form; or by weight, according to the ammonia theory, of—

| | Atoms. | Equiv. wt. | Per cent. |
|---|---|---|---|
| Ammonia ($NH_3$) | 1 | 17 | 31·78 |
| Hydrochloric acid ($HCl$) | 1 | 36·5 | 68·22 |
| Hydrochlorate of Ammonia ($NH_3\,HCl$) | 1 | 53·5 | 100 |

Or, according to the ammonium theory, of—

| | Atoms. | Equiv. wt. | Per cent. |
|---|---|---|---|
| Ammonium ($NH_4$) | 1 | 18 | 33·65 |
| Chlorine ($Cl$) | 1 | 35·5 | 66·35 |
| Chloride of Ammonium ($NH_4Cl$) | 1 | 53·5 | 100 |

The sal ammoniac of commerce is found under the form of large white hemispherical cup-like cakes or masses, or in large fragments, which are sections of them. It possesses a tough, fibrous, crystalline texture, and is very difficult to powder. It is odourless, has a saline taste somewhat sharp or acrid, and sublimes without either fusion or decomposition. It does not attract moisture upon exposure to the atmosphere. It slightly reddens litmus; dissolves in rather less than 3 parts of cold water, the temperature of which suffers considerable reduction, and in about 1 part of boiling water; it is soluble in alcohol; and when carefully crystallized from water forms distinct octahedra or cubes, usually small and aggregated together in rays or feathery masses. By slowly evaporating its aqueous solution, it may be sometimes obtained in cakes an inch in thickness. It is anhydrous. Sp. gr. 1·450 (1·570) (MILLER).

The cakes of commercial chloride of ammonium always contain some iron in the form of protochloride when freshly sublimed. This speedily becomes converted into perchloride on the outside by exposure to the air. Owing to this cause the cakes are generally yellow on the exposed surfaces.

Chloride of ammonium, when pure, should form a colourless solution with water; wholly sublime upon the application of heat; and neither chloride of barium nor sulphuretted hydrogen should affect its solution. A solution, to which a few drops of nitric acid have been added, should not yield a blue precipitate with ferrocyanide of potassium. It often contains sesquichloride of iron, and sometimes lead; both of which may be readily detected by the above tests. Its complete volatility may be easily determined by heating in the flame of a candle a small fragment held on the point of a knife.

In the arts, chloride of ammonium, combined with carbonate, is chiefly used in the coating and soldering of metals, in the preparation of alloys, and in dyeing. It is often mixed largely with snuff, to give it a factitious pungency. It is constantly employed in the chemist's laboratory as a reagent; and owing to the cold produced during its solution, forms an important ingredient in most frigorific mixtures.

The methods previously described are those by which commercial chloride of ammonium is usually if not almost entirely obtained; the various improvements or modifications from time to time introduced into its manufacture chiefly being confined to minor details, and the form or size of the apparatus and machinery employed, do not therefore affect the general principles on which the processes are based. Under this latter head may be mentioned the process which has for its object the entire removal of the iron present in the crude salt, part of which, if it be not removed before sublimation, becomes volatilized and contaminates the ultimate product. To obviate this evil, Mr. Brewer passes a few bubbles of chlorine through the hot concentrated solution of the salt, previous to its crystallization, by which the protochloride of iron is converted into the perchloride, which, being acted on by the ammonia always present in the liquor, is precipitated as ferric hydrate, with the formation of a small additional quantity of sal ammoniac. In the application of this method, the only precaution necessary is to avoid employing more chlorine gas than is necessary to peroxidize the iron, lest a portion of the ammonia salt becomes decomposed with the evolution of nitrogen. The temperature of the liquor is kept up, after the action of the chlorine has ceased, until the whole of the brown flocculent oxide of iron has subsided, when it is at once decanted or filtered into the crystallizers.

Another modification devised by Wilson is to effect neutralization of the crude ammoniacal liquor by distilling it, and passing the fumes in at the lower end of a hollow shaft or column filled with coke, down which the acid trickles; the resulting solution of sulphate or chloride of ammonium being received in proper cisterns, conveniently situated near the base of the column.

In Mr. Spence's method of obtaining ammonia-salts from gas-liquor or bone-spirit, a series of cylindrical boilers or reservoirs, usually four in number, are so placed that the contents of each upper one may be drawn off into the one next below it. Each boiler has an exit-pipe which carries the vapour generated in it to that next above it, whilst that of the highest boiler passes off to a tank containing the acid necessary to form the salt. The top boiler is connected with the reservoir of gas-liquor, which is already mixed with milk of lime, by a charging pipe furnished with a stop-cock turned by a floating ball, so as to keep the surface of the liquor constantly at the same height. High-pressure steam enters the lower boiler, by which its ammonia is driven through the connecting-pipe into the next boiler, and so on in succession, until it leaves the highest boiler in a concentrated state, and thus enters the acid-tank. When this last contains moderately strong hydrochloric or sulphuric acid, the resulting solution of chloride or sulphate of ammonium (as the case may be) is sufficiently concentrated to be at once run off into the crystallizers. As soon as the liquor in the lowest boiler is exhausted of its ammonia, its contents are drawn off, and replaced by that of the next boiler, which is followed by a like descent throughout the whole series.

Among improvements having for their object the substitution of cheap chlorides * for the more expensive commercial acids, may be mentioned those of—

1. Mr. LAMING (patent dated 1843), who employs a strong solution of chloride of calcium for converting the ammonia of gas-liquor into the chloride.

2. Mr. HILLS (patent dated 1846) employs chloride of magnesium † in the same way; and by a subsequent patent proposes to convert the ammonia eliminated in the distillation of coal into the chloride, by mixing chloride of magnesium with the coal in the retorts, or by introducing the chloride into a retort appropriated for the purpose. The heat dispels the chlorine of the chloride in the form of hydrochloric acid, and this, uniting with the ammoniacal vapour, forms chloride of ammonium, which is retained in the liquor of the condenser. From this liquor the salt is obtained by evaporation and crystallization in the usual way. Mr. HILL'S process, it is stated, did not prove a commercial success.

3. Mr. CROLL (patent dated 1849) converts the crude ammoniacal vapours that issue with the coal-gas from the

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* Particularly such chlorides as are the "waste or by-products" of other manufactures.

† Of the Epsom salt-works, &c.

retorts into the chloride, a solution of which he obtains by passing the gas through a solution of crude chloride of manganese,* consisting of 1 cwt. of the salt in 40 gallons of water; this solution being run into one of the ordinary vessels used for purifying the gas. The manganic solution absorbs the free ammonia and its salts, converting them into the chloride, whilst a corresponding proportion of oxide of manganese is precipitated. As soon as the liquor in the purifier is fully saturated, it is drawn off, and replaced by a fresh quantity; whilst the saturated liquor containing the chloride, after subsidence or filtration, is evaporated, and treated as usual. The resulting manganic oxide can be reconverted into chloride by heating three parts of it with four parts of common salt to redness in a furnace for two hours or more; 140 lbs. of the mixture thus produced are added to 140 gallons of water, and ammoniacal gas is passed into the resulting liquid, with the formation of chloride of ammonium. The manganic oxide left in this second operation, by treatment with the required acid, can thus be employed for the production of another quantity of the salt. Crude chloride of iron may be substituted for the chloride of manganese in the above process, or sulphate of manganese, in which case, the product of course will be sulphate of ammonia, instead of the chloride.

4. Mr. LAMING (patent dated 1850) also proposes the use of various salts and mixtures for retaining and condensing the ammoniacal vapour of coal-gas as it passes from the retorts through the purifiers. Of these, the principal are chloride of calcium, obtained by decomposing chloride of iron by means of hydrate of lime; chloride of iron, obtained by decomposing sulphate of iron with chloride of

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* Owing to the re-generation of this substance into manganic oxide by Mr. Weldon's chlorine process, its utilization for the above purpose becomes impracticable.

sodium; chloride of magnesium; a mixture of sulphate of lime and sulphate of iron; or of moist precipitated oxide of iron with carbonate of lime, carbonate of magnesia, or magnesium limestone; or one containing sulphate of magnesia, or chloride of magnesium or calcium, or one or more of them, in combination with oxide of copper, either with or without lime or magnesia, or with both or either of them, or their carbonates. These salts or compounds are mingled with sawdust, or some other porous substance not acted on by the gas, before being put into the purifiers; and after they become saturated with the vapour, the newly formed chloride or sulphate is washed out of the mass with water.

Besides the usual sources of commercial sal ammoniac and other ammonia-salts, it has been proposed to obtain them from guano, peat,* and shale, as noticed under SESQUICARBONATE OF AMMONIA, the substance employed to effect the neutralization or decomposition of the ammoniacal liquor being in this case either hydrochloric acid or a chloride. In France large quantities of ammoniacal salts are manufactured from ammonia obtained during the conversion of coal into coke, in coke-ovens. This process, as well as that for condensing the ammonia given off from blast furnaces, is at present attracting much attention amongst chemists and manufacturers.

In YOUNG'S Patent (1841) for "obtaining ammonia and its salts," a mixture of 2 parts of guano and 1 part of hydrate of lime, or other caustic alkali, after thorough admixture, is distilled in a vertically placed retort, at a moderate heat, gradually increased until the bottom of the retort becomes red hot. The ammoniacal portion of the fumes evolved is absorbed by the cold water contained in a suitable

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* Peat yields from 22 to 25 lbs. of ammonium salts per ton.—Sir R. KANE.

condenser, whilst the other gases eliminated by the process pass off uncondensed. By subsequently passing carbonic acid gas into the liquor of the condenser, a solution of carbonate, bicarbonate, or sesquicarbonate of ammonia is formed. By nearly filling the condenser with diluted hydrochloric or sulphuric acid, instead of with water, a solution of chloride or of sulphate of ammonia is obtained. In the above process ammonium carbonate and hydrocyanic acid are frequently the two principal products of the distillation, and these pass over and are absorbed by the water in the receiver, which then becomes a solution of ammonium carbonate and cyanide. By neutralizing this liquid with hydrochloric acid, and adding to it the necessary quantity of ferrous chloride, Prussian blue is formed and precipitated. This being separated by filtration, the filtrate which is an aqueous solution of ammonium chloride, after the precipitation of the iron by ammonia, is evaporated and crystallized in the usual manner; whilst the Prussian blue, being boiled with the requisite amount of caustic potash, and afterwards evaporated and crystallized, is converted into ferrocyanide, or yellow prussiate of potash.

Stale urine, saturated with hydrochloric acid or with sulphuric acid diluted with about twice its weight of water, yields on evaporation chloride or sulphate of ammonia, according to the acid used.

Chloride of ammonium is now wholly prepared on the large scale, and never by the dealer or retailer, by whom it is only occasionally refined or purified in small quantities, for chemical and medical purposes. The sal ammoniac of commerce is found to be sufficiently pure for all its ordinary applications in the arts; but when wanted of greater purity, it is broken into pieces, and re-sublimed from an earthenware vessel into a large receiver of earthenware or glass. The product, which is in a finely divided crystalline state, is popularly known as "refined sal ammoniac," "double-refined sal ammoniac," and "flowers of sal ammoniac."

The chemically pure chloride of ammonium may be prepared :—1. By bringing its gaseous constituents—ammonia and hydrochloric acid—into contact. During the combination much heat and even light are generated, and the anhydrous solid salt is precipitated in a minutely divided state, which under the microscope is seen to be crystalline.

2. By boiling a saturated solution of the commercial salt with $\frac{1}{10}$th of its volume of strong nitric acid, till no more chlorine is evolved, redissolving the salt which crystallizes out on cooling, and again heating the solution with $\frac{1}{20}$th of its volume of strong nitric acid.

3. It may be also easily and conveniently prepared by saturating pure and moderately dilute hydrochloric acid with ammonia or its carbonates, and evaporating the solution until a pellicle forms, when crystals of the chloride separate as the liquid cools. A similar but rather more violent reaction occurs when gaseous chlorine is brought into contact with gaseous ammonia, or is passed into a nearly saturated solution of ammonia or its carbonates; but in this case nitrogen is evolved at the expense of the ammonia; moreover, the process is attended with considerable danger.

The manufacture of sal ammoniac is usually a distinct business, and is carried on to a very great extent in the neighbourhood of London, the London makers supplying the chief portion of that used in England. A large quantity is, however, made at Manchester and Liverpool. A small quantity is imported from Germany. That from Brunswick is in the form of sugar-loaves. An inferior quality is also imported in chests from the East Indies.

The red bands frequently seen in the sal ammoniac of commerce are said to arise from the workmen falling asleep and allowing the fire to go down, and then suddenly raising the heat too high.* They consist chiefly of ammonio-chloride of iron. To obtain chloride of ammonium free from iron, about 5 per cent. of superphosphate of lime, or 3 per cent. of phosphate of ammonia are added to the crude salts before sublimation.

**Ammonium, Citrate of.** $(NH_4)_2HC_6H_5O_7$. *Syn.* DIAMMONIUM CITRATE, CITRATE OF OXIDE OF AMMONIUM. A concentrated solution of citric acid, gently heated, is slightly supersaturated with sesquicarbonate of ammonium, in fine powder, and the resulting liquid is crystallized by refrigeration in close vessels, or by evaporation in vacuo. If heat be employed in the evaporation of the solution, an acid citrate will be formed.

Chiefly used as a chemical test. An extemporaneous citrate, made with lemon-juice and drunk effervescing, is employed as a saline draught and a mild aperient and diaphoretic.

**Ammonium, Ferrocyanide of.** $(NH_4)_4FeC_6N_6.3$ Aq. 1. Saturate a solution of hydroferrocyanic acid with sesquicarbonate of ammonium in slight excess; evaporate the solution at a heat below ebullition, and crystallize by refrigeration.

2. Digest ferrocyanide of lead or of iron in a solution of sesquicarbonate of ammonium, at a gentle heat, for some time; then filter, evaporate, and crystallize.

It is isomorphous with ferrocyanide of potassium; it is easily crystallizable, very soluble in water, and is decomposed by ebullition.

**Ammonium, Molybdate of.** $(NH_4)_2MoO_4$. 1. Native sulphide of molybdenum, after being well roasted, is reduced to fine powder, digested with solution of ammonia, and the mixture filtered, and the filtrate evaporated to dryness;

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* MUSPRATT.

the residue, molybdate of ammonium, is then dissolved in water, and purified by crystallization.

2. Molybdic anhydride is treated with excess of strong ammonia in a closed vessel. Alcohol is then added when the molybdate is precipitated. This is then dried over quicklime.

Molybdate of ammonium occurs in small white scales, soluble in 570 parts of water; the solution reddens litmus paper; and dissolves in the alkalies, forming alkaline molybdates. It is used in the preparation of molybdenum blue and in calico-printing, but the scarcity of the acid precludes its extensive employment in the arts. Molybdate of ammonium is the salt principally used in dyeing. Silks and cottons passed through a solution of this salt, then through a bath soured with hydrochloric acid, and, lastly, without washing, through another of protochloride of tin, are dyed of a rich and permanent blue colour. A solution of molybdate of ammonium in excess of nitric acid forms a valuable agent as a test for phosphates, with which it gives a beautiful yellow precipitate of phospho-molybdate of ammonia.

**Ammonium, Nitrate of.** $NH_4NO_3$. 1. Let nitric acid be diluted with 3 or 4 times its weight of water, then saturate the mixture with sesquicarbonate of ammonium, evaporate by a gentle heat, and crystallize. When the salt is not required in a crystalline form, it should be evaporated to dryness at about 212° Fahr. (100° Cent.), and the heat carefully raised to about 250° Fahr. (121° Cent.); the fused salt is then poured on to a polished slab of iron or stone, and when solidified, broken up and put into bottles. In this form it is best fitted for the preparation of nitrous oxide gas.

2. Or it may be obtained by the double decomposition of ammonium sulphate and potassium nitrate. The potassium sulphate separates first, and the solution of ammonium nitrate is concentrated, and left to crystallize.

When the evaporation of the solution is conducted at a heat under 100° Fahr. (37·7° Cent.), the salt is obtained in beautiful hexagonal prisms; when at 212° Fahr. (100° Cent.), in long silky fibres; when by rapid evaporation and fusion, it forms a white, compact, and usually foliated mass. It dissolves in about twice its weight of water; is slightly deliquescent; melts at 230° Fahr. (110° Cent.), and is decomposed into nitrous gas and water at 460° Fahr. (238° Cent.). It deflagrates, like nitre, on contact with heated combustible matter.

Ammonium nitrate is mostly used as a source of nitrous oxide or laughing gas; 1 lb. avoir. yields nearly 4½ cubic feet of gas; mixed with water, it forms a useful freezing mixture. By evaporating its solution to dryness, the salt may be recovered unaltered, and employed for another refrigeration. Care, however, should be taken not to expose it to too great a heat, as at a certain temperature it deflagrates with violence.

**Ammonium, Oxalate of,** $(NH_4)_2C_2O_4$, may be prepared by neutralizing a hot solution of oxalic acid with sesquicarbonate of ammonia; evaporating and crystallizing.

Oxalate of ammonium crystallizes in beautiful, colourless, long, rhombic prisms, which effloresce in the air; it is slightly soluble in cold and freely soluble in hot water; heated in a retort, it yields ammonia, carbonate of ammonia, cyanogen, and carbonic acid, and oxamide, which sublimes.

Chiefly used as a test for calcium, with which it produces a white precipitate soluble in nitric acid; also to separate lime from magnesium, as it does not precipitate the salts of this latter metal.

**Ammonium, Sulphate of.** $(NH_4)_2SO_4$. *Syn.* SULPHATE OF AMMONIA. Crude sulphate of ammonia exists in considerable quantity in the soot from pit-coal; and it is obtained, as a secondary product, from the ammoniacal liquor of gasworks and animal charcoal manufactories. It is also found native, associated with sal ammoniac, in the neighbourhood of volcanoes, under the name of *mascagnine*, *massagnine*, or *mascagnite;* and a considerable quantity is obtained in Tuscany as a by-product in the manufacture of native boracic acid.

1. Saturate dilute sulphuric acid with sesquicarbonate of ammonia in slight excess; filter, gently evaporate, and crystallize.

2. Heat the commercial salt with $\frac{3}{4}$ths its weight of strong sulphuric acid till decomposition ensues, then add a small quantity of nitric acid, and heat the liquid until it is decolourized.

The common method of making crude sulphate of ammonia consists in putting gas-liquor into an iron boiler, and passing superheated steam through it into sulphuric acid of about 1·36 to 1·40 sp. gr., till the acid is saturated, or nearly so, when the somewhat acid solution is run into tanks lined with lead, and crystallizes as it cools.

Ammonium sulphate crystallizes in long, flattened, six-sided prisms; soluble in 2 parts of cold and 1 of boiling water; fuses, with loss of one atom of water, at about 280° Fahr. (137° Cent.); and is volatilized, with entire decomposition, at about 534° Fahr. (279° Cent.), giving as result, sulphite of ammonium, free sulphurous acid, and nitrogen: by long boiling, its solution becomes acid from loss of ammonia.

The crude sulphate of ammonium is principally used in the preparation of sal ammoniac and sesquicarbonate of ammonia, and for manure. "A mixture of 10 per cent. of this sulphate with 20 per cent. of bone-dust, some gypsum, and farm-yard manure, forms a very fertilizing compost, applicable to a great variety of soils." * It is also largely employed in the manufacture of alum.

The manufacture of commercial sulphate of ammonia has been already explained under AMMONIUM CHLORIDE. All that is necessary is to saturate with sulphuric acid the solution of ammonia, crude or otherwise, obtained in the manner before described, and then to evaporate the solution until the salt crystallizes out. At other times, however, instead of adding the acid to the ammoniacal liquor, the latter, either at once or after treatment with lime, is submitted to distillation, and the evolved alkaline vapour is passed into the acid (previously somewhat diluted), contained in a large receiver or cistern, or a series of them; the salt being obtained by evaporation and crystallization. The evaporating pans are sometimes heated by steam and sometimes by direct exposure to the fire. When the last method is used, unless great vigilance be exercised in regulating the temperature, decomposition of the sulphate of ammonia may take place, either with the formation of a sulphide which attacks the pan, or the evolution of sulphuretted hydrogen. This quickly manifests itself by its odour, and necessitates the lowering or putting out of the fire.

By re-solution and a second crystallization the sulphate is generally obtained sufficiently pure for all commercial purposes. The mother-liquor, after being drained from the crystals, is returned to the acid cistern. When the salt is intended for use as manure, or (unless very rough) for conversion into sal ammoniac, this need not be had recourse to. When it is required in a higher condition of purity, it should be dissolved in hot water, filtered through animal charcoal, and re-crystallized. As soon as the crystals form they must

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* URE.

be removed from the solution, drained, and dried on a heated fire-clay slab.

Among modifications and improvements not previously noticed may be mentioned—

1. That of Dr. Richardson (patent dated January 1850), who mixes sulphate of magnesia with the crude ammoniacal liquor, and thus forms a double sulphate of magnesia and ammonia, from which he obtains the sulphate of ammonia by sublimation.

2. That of Michiel (patent dated April 1850), who prepares sulphate of ammonium by means of oxysulphate of lead obtained from galena or native sulphide of lead, by exposing it in a crushed state and in thin layers for two or three hours, to the heat of a reverberatory furnace. The resulting mixture of sulphate and oxide of lead is reduced to coarse powder, and well worked up with the ammoniacal liquor, when sulphate of ammonium and sulphide and carbonate of lead are formed. The first is removed by treatment with water, and the residuum serves for the manufacture of lead compounds, or may be reduced to the metallic state by fusion with charcoal.

3. That of Mr. Laming (patent dated August 1852), in which a stream of sulphurous acid is transmitted through the liquor containing the ammonia, either in the free state or as carbonate, by which sulphite of ammonium is formed. This salt he oxidizes and converts into the sulphate of ammonia, by agitation and free exposure to the air.

In the manufacture of beet-root sugar, large quantities of ammonia are given off during the boiling of the root. Renard, who has suggested the utilization of this by converting it into sulphate of ammonium, has estimated that in a beet-sugar factory, in which 200,000 cwts. of the root are used yearly, there might be obtained 887 cwts. of the salt.

**Ammonium, Sulphide of (neutral).** $(NH_4)_2S$. Saturate strong solution of ammonia with pure sulphuretted hydrogen gas; then add a second portion of solution of ammonia equal to that first used, and preserve the resulting liquid in a well-stoppered bottle.

**Ammonium, Sulphydrate of.** $NH_4HS$. *Syn.* SULPHIDE OF AMMONIUM, HYDROSULPHIDE OF AMMONIUM, HYDROSULPHATE OF AMMONIA. By passing sulphuretted hydrogen gas, to saturation, through a mixture composed of strong solution of ammonia, 1 part, and distilled water, 4 parts.

Prepared as above, sulphydrate of ammonium has a very fetid odour. When pure, it is wholly volatilized by heat, and does not render turbid a solution of sulphate of magnesium. Mineral acids decompose it, with the evolution of sulphuretted hydrogen. By keeping, it decomposes and acquires a yellow colour. This yellow coloration does not, however, render it unfit for use as a reagent; but it must be borne in mind that it will now deposit sulphur when mixed with acids. In this state it proves valuable as a reagent to detect hydrocyanic acid, and as a solvent to separate metallic sulphides thrown down by sulphuretted hydrogen. It is also employed by hairdressers for dyeing hair.

**Ammonium, Sulphocyanide of.** $NH_4CNS$. *Preparation*—1. Neutralize hydrosulphocyanic acid with ammonia, and gently evaporate the solution to dryness by the heat of a water-bath.

2. Digest hydrocyanic acid with yellow sulphydrate of ammonium, and after a time evaporate as before.

A deliquescent white saline mass, very soluble in water, but seldom employed out of the laboratory in a pure state. Of late it has been obtained in considerable quantity as a crude product of the gas liquors.

**Ammonium.** $NH_4$ or $(NH_4)_2$. The name given to a group of atoms which play the part of a compound basic-radicle or metallic element. Although several attempts have been made to isolate this substance, they have hitherto not been successful. When sodium amalgam is added to a solution of ammonium chloride, sodium chloride is formed, and ammonium set free; but this instantly unites with the mercury, giving rise to a light, bulky amalgam, which is quickly spontaneously resolved into ammonia, mercury, and hydrogen.

ESTIMATION OF AMMONIA AND ITS SALTS.—The estimation of the strength of ammonia solutions in commerce, is known as AMMONIMETRY, and depends upon their specific gravities. The percentage richness of solutions of ammonia, or of its carbonates, may be most accurately determined by ALKALIMETRY. For all the ordinary purposes of commerce and of the laboratory, the strength of pure solutions of ammonia may, however, be inferred with sufficient correctness from their density; and to this the term AMMONIMETRY is usually restricted.

The specific gravity of the sample being found either by the hydrometer or specific gravity bottle, in the usual manner, its percentage strength may be seen by inspection of the table on opposite page.

If the precise specific gravity sought cannot be found in the table, the difference between it and the next greater specific gravity must be taken for the numerator of a fraction, having for its denominator the difference between the greater and the next less specific gravity in the table.

This fraction, added to the percentage of ammonia in the column of the table opposite the greater specific gravity, will give the true percentage sought.

A simple means of ascertaining the strength of liquid ammonia during its manufacture, is to note the expansion the water undergoes by the absorption of the gas. This may be easily calculated when it is borne in mind, that water fully saturated with ammonia expands from three

TABLE.—*Exhibiting the relations between the* SPECIFIC GRAVITY *of Solution of Ammonia and the* PERCENTAGE STRENGTH *for every variation of* ·00125 *sp. gr., from* ·87500 *to* 1·00000, *at* 62° Fahr. Abridged from the larger Table of Mr. J. J. GRIFFIN.

| Sp. gr. of the Liquid Ammonia. | Pure Ammonia per cent., by Weight. | Sp. gr. of the Liquid Ammonia. | Pure Ammonia per cent., by Weight. | Sp. gr. of the Liquid Ammonia. | Pure Ammonia per cent., by Weight. |
|---|---|---|---|---|---|
| ·87500 | 34·694 | ·91750 | 21·837 | ·96000 | 10·119 |
| ·87625 | 34·298 | ·91875 | 21·477 | ·96125 | 9·790 |
| ·87750 | 33·903 | ·92000 | 21·118 | ·96250 | 9·462 |
| ·87875 | 33·509 | ·92125 | 20·760 | ·96375 | 9·135 |
| ·88000 | 33·117 | ·92250 | 20·403 | ·96500 | 8·808 |
| ·88125 | 32·725 | ·92375 | 20·046 | ·96625 | 8·483 |
| ·88250 | 32·335 | ·92500 | 19·691 | ·96750 | 8·158 |
| ·88375 | 31·946 | ·92625 | 19·337 | ·96875 | 7·834 |
| ·88500 | 31·558 | ·92750 | 18·983 | ·97000 | 7·511 |
| ·88625 | 31·172 | ·92875 | 18·631 | ·97125 | 7·189 |
| ·88750 | 30·785 | ·93000 | 18·280 | ·97250 | 6·867 |
| ·88875 | 30·400 | ·93125 | 17·929 | ·97375 | 6·547 |
| ·89000 | 30·016 | ·93250 | 17·579 | ·97500 | 6·227 |
| ·89125 | 29·633 | ·93375 | 17·231 | ·97625 | 5·908 |
| ·89250 | 29·252 | ·93500 | 16·883 | ·97750 | 5·590 |
| ·89375 | 28·871 | ·93625 | 16·536 | ·97875 | 5·273 |
| ·89500 | 28·492 | ·93750 | 16·190 | ·98000 | 4·956 |
| ·89625 | 28·133 | ·93875 | 15·846 | ·98125 | 4·641 |
| ·89750 | 27·736 | ·94000 | 15·502 | ·98250 | 4·326 |
| ·89875 | 27·359 | ·94125 | 15·158 | ·98375 | 4·011 |
| ·90000 | 26·984 | ·94250 | 14·816 | ·98500 | 3·698 |
| ·90125 | 26·610 | ·94375 | 14·475 | ·98625 | 3·386 |
| ·90250 | 26·237 | ·94500 | 14·135 | ·98750 | 3·074 |
| ·90375 | 25·865 | ·94625 | 13·795 | ·98875 | 2·763 |
| ·90500 | 25·493 | ·94750 | 13·456 | ·99000 | 2·453 |
| ·90625 | 25·123 | ·94875 | 13·119 | ·99125 | 2·144 |
| ·90750 | 24·754 | ·95000 | 12·782 | ·99250 | 1·835 |
| ·90875 | 24·386 | ·95125 | 12·446 | ·99375 | 1·527 |
| ·91000 | 24·019 | ·95250 | 12·111 | ·99500 | 1·220 |
| ·91125 | 23·653 | ·95375 | 11·777 | ·99625 | ·914 |
| ·91250 | 23·288 | ·95500 | 11·444 | ·99760 | ·609 |
| ·91375 | 22·924 | ·95625 | 11·111 | ·99875 | ·304 |
| ·91500 | 22·561 | ·95750 | 10·780 | 1·00000 | 0<br>or Water. |
| ·91625 | 22·198 | ·95875 | 10·449 |  |  |

The specific gravity of mixtures of pure solution of ammonia and pure water is precisely the mean of the specific gravities of their constituents (Davy; Dalton; Christison). In all solutions of ammonia, a quantity of anhydrous ammonia, weighing 212½ gr., displaces exactly 300 gr. of water, and reduces the sp. gr. of the liquid to the extent of ·00125 (Griffin). The strongest solution of ammonia which it is possible to prepare at 62° Fahr. has the sp. gr. ·87500, and contains 34·694% of pure ammonia, by weight, or 21,251 gr. per gallon (Griffin).*

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* Mr. Griffin, in his "System of Ammonimetry," calls every

volumes to five. If each receiver be furnished with a gauge-pipe, the degree of expansion can be noted. On the small scale graduated glass receivers may be used.

The above method can be controlled by drawing off a small quantity of the solution of ammonia under examination, taking its specific gravity and referring to the above table.

When the ammoniacal substance consists of pure solution of ammonia, or of a salt of ammonia with a feebly volatile acid, the percentage content of ammonia may be easily determined by saturating the substance with hydrochloric acid, driving off the excess of acid and moisture over a water-bath at 212° Fahr. (100° Cent.), until the residue ceases to lose weight, and calculating the ammonia from the amount of chloride of ammonium found. The operation is, where practicable, preferably performed in a platinum dish.

When the sample consists of an impure or mixed substance, the mode of procedure is different. It is as follows:—

A given weight of the sample is placed in a small retort, the end of which is made to dip into a vessel containing dilute hydrochloric acid. A strong solution of caustic potash is then poured into the retort, and heat applied by means of a small spirit lamp. When all the ammonia has passed over, the acid solution is evaporated to dryness by the heat of a water-bath, and the residuum (chloride of ammonium) weighed. Each grain of the chloride thus found represents ·31804 gr. of ammonia; 53·5 parts of the

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212½ gr. of anhydrous ammonia a TEST-ATOM; and every 7 water gr. measures a SEPTEM. Thus, a gallon of water (= 10 lbs.) contains 10,000 septems. The degrees of his AMMONIA-METER range from 1 to 100, and indicate the number of test-atoms of ammonia in one gallon of the liquid.

former being equivalent to 17 of the latter. If the article for examination be a solid substance (as a salt), it may be dissolved in water, or in dilute acid, before being put into the retort.

Or a known quantity of a standard solution of sulphuric acid diluted with water may be put into the receiver, and the gas passed into it. When this ceases to be evolved, the distilled liquid is poured from the receiver into a beaker, and a few drops of tincture of litmus being added, it is titrated with a standard soda solution, the quantity of which shows the amount of acid neutralized, from which data the percentage of ammonia may be easily computed.

If in the above process, the mixture in the retort shows any disposition to frothing, milk of lime may be used for the caustic potash solution.

In accurate experiments in the laboratory, ammonia is usually weighed either as chloride of ammonium or as ammonio-platinic chloride $(NH_4Cl)_2$, $PtCl_4$; every gr. of the latter representing ·07614 gr. of pure ammonia.

The process is performed as follows:—The ammonia salt is dissolved in a little water, and hydrochloric acid added to faintly acid reaction. The solution is then evaporated over a water-bath to dryness. The resulting chloride of ammonium is then dissolved in a little water, and neutral solution of tetra-chloride of platinum added in not too great excess.

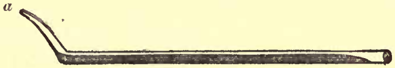
The double chloride of platinum and ammonium thus formed is then carefully evaporated in a porcelain dish, at a temperature a little under 212° Fahr. (100° Cent.), nearly to dryness. Rectified spirit is then poured upon it, and it is allowed to stand for some time.

The yellow salt which remains undissolved, is then poured with the spirit upon a weighed and previously dried filter; and washed with rectified spirit until the washings cease to give a yellow colour. It is then dried at a temperature of 212° Fahr. (100° Cent.) and weighed; the weight of the filter deducted from the substance *plus* the filter gives the amount of ammonio-platinic chloride found.

The above results may if necessary, be controlled by wrapping up the platino-ammonio chloride in the filter and igniting in a covered crucible. From the residue of the combustion, which consists of metallic platinum, the ammonia may be calculated. In conducting this experiment the heat must be very gradually raised.

For the determination of the ammonia in those ammoniacal compounds which are insoluble, recourse must be had to the "combustion method."

FIG. 24.



This is conducted as follows:—The sample is first carefully dried over sulphuric acid, in the exhausted receiver of an air-pump. Ten or twenty grains are then intimately mixed in a warm unglazed porcelain mortar (standing on a sheet of clean paper) with ten times its weight of soda-lime.* This mixture is introduced into a combustion tube of hard Bohemian glass, about 16 or 18 inches long and ½ inch in diameter, with the end drawn out, and sealed as shown at *a* in the engraving.

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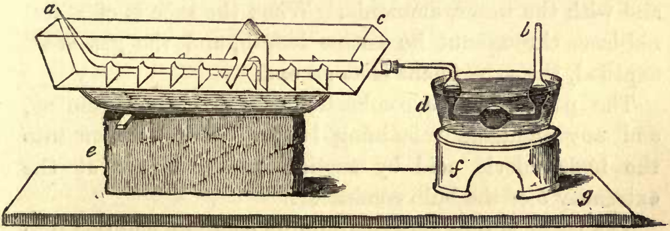
* Soda-lime may be made by slaking two parts of freshly burnt lime with an aqueous solution containing one part of caustic soda, and evaporating to dryness in an iron vessel. The substance so obtained is next moderately heated to redness for some time in a Hessian crucible; after which, while still warm, it is reduced to a moderately fine powder, and passed through a metal sieve. The powder should be preserved in a well-stoppered bottle.

Into the posterior part of this tube, soda-lime to the extent of about an inch has been previously introduced, then the mixture.

The tube is then filled to within about 2 inches of its orifice with soda-lime; this last addition being made in small quantities at a time, after having been used to rinse out the mortar. The tube is then loosely plugged with a piece of previously ignited asbestos, and afterwards gently tapped on a table or bench, being held meanwhile in a horizontal position. By this means, a free passage is afforded for the gases which are given off during the combustion.

FIG. 25.



The tube is then connected by means of a perforated cork with a tubular bulb condenser (as shown in the engraving) containing moderately strong hydrochloric acid, or a known volume of titrated sulphuric acid, as noticed above.

It is of the utmost importance that the apparatus should be perfectly air-tight. To ascertain this, a piece of burning charcoal is held to the bulb *d*; if on withdrawing the charcoal, after the escape of some bubbles of air into the middle bulb, the liquid assumes its original position, the connection is sound. The tube is then placed in the combustion-furnace with the bulbs arranged, as shown in the engraving.* The furnace is gradually surrounded with glowing charcoal by means of the screen *c;* the charcoal being first applied to the fore part of the tube, and so carried towards its end or beak. By this contrivance the ammonia is gradually expelled. Its disengagement should take place uninterruptedly, and not too rapidly, since directly the evolution of the gas ceases, if the tube be allowed to cool ever so little, the hydrochloric acid will ascend into the combustion-tube and spoil the experiment. During the combustion, it is necessary to keep the anterior part of the tube tolerably hot, which not only prevents the formation of certain troublesome liquid hydrocarbons, that would pass over into the bulbs, but raises the asbestos to such a temperature that it cannot retain water, and with the water, ammonia. When the tube is of a full red-heat throughout its entire length, and the gas is all expelled, the experiment is at an end.

The point *a* of the combustion-tube is then broken off, and any ammonia remaining in the tube is drawn into the hydrochloric acid by suction gently applied at the extremity *b* of the bulb condenser.

The latter is then detached, and its contents emptied into a small platinum dish and rinsed out with water, and afterwards evaporated to dryness; the resulting chloride of ammonium is dissolved in a little water, and by the addition of tetra-chloride of platinum is converted into the platino-ammonio chloride as before described, and weighed as such. From the amount of this, the centesimal quantity of ammonia is easily arrived at.

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* Instead of the above, Hoffman's combustion-furnace is now principally employed in this analysis, as it allows the heat to be more easily and equably regulated, than can be done with the charcoal one.

For the estimation of very small quantities of ammonia the Nessler test is frequently had recourse to.

This test is applied as follows:—

Two clear white glass cylinders, as nearly as possible of the same height and width, each of 100 cubic centimetres capacity, and graduated, are taken. One cylinder being filled up to the 100 cubic centimetre mark with the solution containing the ammonia diluted with water, if necessary, two cubic centimetres of the Nessler solution are dropped into it by means of a pipette, and the whole well mixed. The liquid immediately becomes of a yellow or brownish tinge, according to the amount of ammonia in it.

Into the other cylinder is dropped from a pipette a certain measured quantity of a very feeble solution of chloride of ammonium of known strength; after which the cylinder is filled up to the 100 cubic centimetre mark with distilled water, and 2 cubic centimetres of the Nessler solution added, the whole well stirred together. The colours of the two liquids are then compared, and if they are judged to be precisely the same, the operation is finished. If, however, they differ in tint, another experiment with fresh water, standard ammoniacal solution, and Nessler solution, must be performed, and this must be repeated until the two solutions agree in colour. The quantity of ammonia which has been used to produce this result will of course denote the amount of ammonia in 100 cubic centimetres of the ammoniacal solution under examination. In applying this test it is always best to distil off the ammonia, and to add the Nessler to the distillate. If more than 1 milligramme of ammonia be present in 100 cubic centimetres of the sample, this will become of too dark a colour for the comparison to be satisfactorily made.*

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* The plan generally adopted is to prepare standard solutions containing 1, ·09, ·08, ·07 to ·01 or ·005 milligrammes in 100 c.c.,

Nessler's test is made as follows:—

Potassic iodide, 35 grammes.
Mercuric chloride, 13 grammes.
Distilled water, 800 cubic centimetres.

Heat the above together to boiling, and stir until solution has taken place. To the liquid thus obtained, add a cold saturated solution of mercuric chloride, till the precipitate produced, just ceases to be dissolved by stirring. Then add to this, 160 grammes of solid potassic hydrate, and when this has dissolved, dilute with water until the whole measures 1 litre. Nessler's solution should have a slightly yellowish tint. When colourless it is not sensitive, and more mercuric chloride must be added.

The standard solution of ammonia is prepared by dissolving 3·15 grammes of ammonium chloride in 1 litre of distilled water. This solution contains 1 milligramme of ammonia in 1 cubic centimetre of solution.

Sometimes, though rarely, the quantity of ammonia is determined from the volume of nitrogen eliminated from it, of which 14 parts represent 17 parts of ammonia.

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and, having Nesslerized them, to dilute solutions of caramel to the same tint, and keep them for standards. The caramel solution keeps unaltered for any length of time.

## CHAPTER III.

# ALUM AND ALUM-MAKING.

ALUM is found native, either effloresced on the surface of bituminous alum-schist, as at Göttwigg, in Austria; or united with the soil in the neighbourhood of volcanoes, as at Naples, Solfatara, Sicily, and the South of France; where it is obtained by simple lixiviation and evaporation, a little potash being commonly added to convert the excess of sulphate of alumina into alum. Native alum is also found in certain mineral waters in the East Indies.

The principal sources of alum are—aluminous shales or schists, various kinds of clays, cryolite, bauxite, and felspar; also certain mineral phosphates. In Britain the aluminous shales or schists are chiefly used. In the neighbourhood of Manchester, coal shale is extensively employed. At Tolfa, near Civita Vecchia, where the best Roman alum is produced, the source is stratified alum-stone. The manufacture of alum is technically said to be conducted according to the natural process when prepared from alum-schist or alum-ore; and according to the artificial process, when made by acting on clay with sulphuric acid, and adding a potassium salt to the resulting lixivium.

ALUM FROM ALUM-ROCK OR ALUM-STONE.—Alum-rock is composed of the elements of potash-alum with an excess of alumina in the form of aluminic hydrate, and varying proportions of silica. It also frequently contains *alunite* in the crystalline form, and sometimes iron pyrites and manganese. It is of volcanic origin, and has been produced by the action of sulphurous anhydride upon substances which contain much felspar. Alum-rock is a frequent constituent of the soil at Tolfa, near Civita Vecchia, at Muszag in Hungary, in some parts of France, and in some of the islands of the Grecian Archipelago. It is by far the most abundant source of commercial alum. To obtain alum from the alum-rock it is necessary to free it from the silica and other foreign substances, as well as from the alumina existing in it as hydrate. The mineral is first burnt in kilns or iron furnaces, care being taken during the ignition to avoid the employment of too high a temperature, as well as the direct contact of the rock with the fuel. To attain this end the furnace is so arranged that the flame only shall be directed upon and through the material. When the vapours of sulphuric or sulphurous acid begin to be given off, this points to the decomposition of the aluminic sulphate, and the mineral must be removed from the furnace. By the above process of calcination, water has been expelled from the aluminic hydrate contained in the alum-rock, and the formation of an insoluble or basic sulphate of aluminum thus prevented. After its withdrawal from the furnace, the ore is either arranged in long heaps on a clay floor, or thrown into brick cisterns, where it is constantly moistened with water for two or three months, or until it has attained the condition of a soft mud. This mud being put into proper vessels, is lixiviated, and the clear solution evaporated down till it attains a density of about 1·115; at 45° C. (113° Fahr.) when it yields alum in crystals. The alum produced by this method, which is that followed at Tolfa, is known as *Roman alum.*

The first crop of crystals, owing to the presence of a minute quantity of peroxide of iron, are of a slight red colour. Upon recrystallization, however, they are obtained colourless. The insoluble alumina is left behind at the bottom of the lixiviating vessels. The proportion of the constituents of alum-rock varies with the localities whence it is obtained. Some samples are deficient in potash, in which case there is mostly an undue preponderance of alumina and sulphuric acid.*

ALUM FROM ALUM-ORE, ALUMINOUS SCHIST OR SHALE.—Alum-ore, schist, or shale, is a bituminous clay slate with iron pyrites diffused through it, sometimes in the form of bright yellow, golden, or brassy-looking crystals, but more frequently in minute black particles. Large beds of alum schist are met with near Dusseldorf, in the Harz, in Bohemia, Belgium, and the Uralian mountains.

In this country it occurs in large quantity in the lower beds of the coal formation at Whitby, in Yorkshire; and at Campsie and Hurlet, near Glasgow. The English and Scotch alum-schists are generally deficient in potash; the German ones, on the contrary, usually contain it in much larger quantity. Hence, whilst the British ores require the addition of variable quantities of alkali before they can be converted into alum, this is mostly unnecessary with the shales and alum earths of Germany.

The following is the percentage composition of certain alum shales:—

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* According to KLAPROTH, alum-stone from Tolfa, near Civita Vecchia, consists of—Silica, 56·5; alumina, 19; sulphuric acid ($SO_3$), 16·5; potassa, 4; water, 3; loss 1 = 100. This exhibits an excess of about 3 per cent. of sulphuric acid, and about 14 per cent. of alumina more than are requisite to form alum with the 4 per cent. of potash; proportions which therefore require to be supplemented with a potassium or ammonium salt during the process of manufacture. According to CORDIER, the alum-stone of Mont d'Or contains 1·4 per cent. of oxide of iron.

| | Whitby, Yorkshire. (RICHARDSON.) | |
|---|---|---|
| | Top rock. | Bottom rock. |
| Sulphide of iron (*pyrites*) | 4·20 | 8·50 |
| Silica | 52·25 | 15·16 |
| Protoxide of iron | 8·49 | 6·11 |
| Alumina | 18·75 | 18·30 |
| Lime | 1·25 | 2·15 |
| Magnesia | ·91 | ·90 |
| Oxide of manganese | traces | traces |
| Sulphuric acid ($SO_3$) | 1·37 | 2·50 |
| Potassa | ·13 | traces |
| Soda | ·20 | traces |
| Chlorine | traces | traces |
| Coal | 4·97 | 8·29 |
| Water | 2·88 | 2·00 |
| Loss | 4·60 | (?) |
| | 100 | 100 |

| | Campsie, near Glasgow. (RONALDS.) | | |
|---|---|---|---|
| | Top rock. | Top rock. | Bottom rock. |
| Sulphide of iron (*pyrites*) | 40·52 | 38·48 | 9·63 (?) |
| Silica | 15·40 | 15·41 | 20·47 (?) |
| Protoxide of iron | ... | ... | 2·18 |
| Alumina | 11·35 | 11·64 | 18·91 (?) |
| Lime | 1·40 | 2·22 | ·40 |
| Magnesia | ·50 | ·32 | 2·17 |
| Oxide of manganese | ·15 | ... | ·55 |
| Sulphuric acid | ... | ... | ·05 |
| Potassa | ·90 | ... | 1·26 |
| Soda | ... | ... | ·21 |
| Carbon or bituminous matter | 27·65 (?) | 28·80 | (?) |
| Coal | ... | ... | 8·51 |
| Water | ... | ... | 8 54 |
| Loss | 2·13 | 3·13 | 1·59 (?) |
| | 100 | 100 | 100 |

The mineral is placed in long heaps in the open air, and moistened from time to time with water, when it becomes gradually hot, and falls into a powdery condition. This decomposition commonly occurs either wholly or partially on the floor of the mine. If the ore does not possess this property on mere exposure to the air and moisture, it is broken into pieces, and laid upon a bed of brushwood and small coal to the depth of about four feet, when the pile is fired and fresh lumps of the alum mineral thrown on, until the mass becomes of considerable height and size. The combustion, as soon as established, is conducted with a smothered fire, until the calcination is complete, care being taken to prevent fusion or the disengagement of either sulphurous or sulphuric acid, from contact between the ignited stones and the carbonaceous fuel.*

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* The generality of alum-minerals require roasting, and their own bituminous matter is in many cases sufficient to produce the heat

To promote these ends, the heap at the proper time is mantled or covered with a layer of already calcined and exhausted ore, in order to protect it from high winds and heavy rains, as well as to moderate the heat, and let it proceed gradually, so that the sulphur present may not be lost or wasted by volatilization. The roasting is finally checked by a thicker "mantling," and the whole allowed to cool. When the roasting is completed, the pile is usually reduced to about half its original bulk, and has become open and porous in the interior, so that the air can circulate freely through it. To promote the draught, as the heap cools, a little water is sprinkled upon it, which, by dissolving out and carrying down some of the saline matter, renders the interior still more pervious to the atmosphere. The whole, when cold, or nearly cold, is, if necessary, still further exposed to the action of air and moisture. The time required to calcine the heap properly, including that taken by the burned ore to cool, varies, according to its size and the state of the weather, from three to nine, or even twelve months.

In order to ensure a continuous supply of calcined ore for the lixiviating vessels, the different mounds or ridges are kept in all degrees of progress toward completion, from being only just kindled, to being thoroughly roasted and weathered.

Dr. RUDOLPH WAGNER says that alum-earths are unfit for calcination, unless they have been previously subjected to a year's weathering; otherwise there will be a loss of sulphate of aluminum amounting to one-sixth.

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required, which need not necessarily exceed 600° to 650° Fahr. (315°–343° Cent.), provided it be continued for a sufficient period. It is only when they are less bituminous or carbonaceous, that slack or sawdust, &c., is employed.

A method of roasting alum-schist, invented by Wilson, consists in exposing the purest obtainable ore to the air until it becomes disintegrated, and then placing it in an ordinary lime-kiln; the calcined earth being removed from the bottom, and its place supplied with unburnt shale at the top. In this process, great care is necessary to prevent the mass from fusing over. The process of calcination completed, the burnt ore is next placed in a series of tanks, where it is lixiviated. In some parts of Germany certain aluminous minerals are lixiviated without previous roasting. The ores being arranged in heaps, are exhausted by water, and the resulting solution collected in brickwork or clay reservoirs at the base of the mound. The crude liquor being condensed until it has a density of 1·160, the alum, sometimes as potash, sometimes as ammonia alum, crystallizes out. The lixiviating vessels are sometimes made of wood lined with lead, and sometimes of stone. They are oblong in shape, and in England, France, and Germany, are mostly placed one above another. They are usually from 8 to 10 yards in length, 6 or 7 in breadth, and 1½ high. In Scotland they are arranged on the same level. The lixiviation process requires to be conducted with great care and judgment, for if too much water be employed, unnecessary time, trouble, and expense will be incurred in the subsequent evaporation. The objects of the alum-maker are to obtain a ley as concentrated as possible, and at the same time to exhaust the ore of its saline ingredients. When the tanks, usually arranged in sets of 4 or 5, are placed one above the other, they are two-thirds filled with roasted ore, and the one at the top filled with water, which after from eight to twelve hours is let off through a plug in the bottom to the next lower tank, and so on in succession through the series, by which means the lixivium becomes gradually stronger.

From the last vessel it is drawn off into a large cistern. The lixiviating tanks being meantime recharged with a fresh supply of the burnt earth, the first lixivium is pumped up into the top tank, and again passed through the series, after which it is drawn off into the clarifying vessels. Before it is ready for evaporation the lixivium should have a specific gravity ranging from 1·113 to 1·157 or 1·160. When the specific gravity is lower, more shale must be added. The exhausted shale is mostly used for mantling fresh heaps or ridges.

In Germany unexhausted shale is economized by subjecting it to another lixiviation, either alone or mixed with fresh earth.

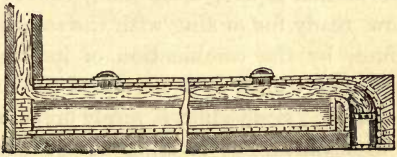
The subsequent treatment of the lixivium depends upon the amount of sulphate of iron or copperas it contains. If this salt, which is an unvarying constituent in all alum-leys, should have been found by examination not to be present in quantities sufficient to make its collection remunerative, the ley is evaporated until of the density of 1·40, at which degree of concentration it deposits the sulphate of iron as a basic salt. The liquor, the colour of which is brick-red, is then run off into proper receptacles, where, after depositing suspended matters, it is conveyed into the precipitation tanks. When, as very frequently happens, the copperas is equal, or nearly equal, in quantity to the alum, it pays the alum-maker to collect it, and the preparation of the two is carried on together. The iron sulphate, instead of being precipitated as a basic salt, is then collected in the crystalline form, after the lixivium, having reached the proper point of concentration, has become cool. The following is the rationale of the process :—The ley is first evaporated with scraps of old iron. The basic sulphate which is thereby formed is partly precipitated, setting free, sulphuric acid, which acting on a portion of the metallic iron, converts it into sulphate with liberation of hydrogen, which gas converts the ferric to ferrous sulphate, and prevents during the evaporation the further oxidation of the latter into the insoluble basic salt. The mother-liquor which is left after the removal of the copperas crystals contains the sulphate of alumina. The formation of the crystals of green vitriol is frequently facilitated by placing branches of trees or sticks in the lixivium. By another method, the ley is evaporated until it has a specific gravity of 1·35 to 1·37, at which point the solution becomes a saturated one, and any further evaporation causes the rapid deposition of a portion of the copperas in the form of very small anhydrous or slightly hydrated crystals. Meanwhile the loss of water by evaporation is constantly replaced by fresh water. By this arrangement, whilst the quantity of dissolved copperas cannot accumulate, the amount of aluminic sulphate increases simultaneously with the precipitation of the copperas, until the liquid is saturated with it. To obviate supersaturation, which would lead to the deposition of the aluminic with the ferrous sulphate, the strength of the liquid at this stage is vigilantly noted by means of the hydrometer. The precipitated sulphate of iron is then removed, and purified by crystallization, when it acquires its 7 molecules of water; whilst the aluminic sulphate can be easily obtained from the concentrated mother-liquor by crystallization.

By WEISMAN'S method, the ferric salts are precipitated by the addition of a solution of ferrocyanide of potassium; after which the supernatant clear liquor, which is now a solution of nearly pure sulphate of alumina, is decanted and evaporated for future operations, until it either forms on cooling, a concrete mass, which is moulded into bricks or lumps, for the convenience of packing; or until it is sufficiently concentrated to be converted into alum by the addition of a salt of potash or ammonia in the usual manner.

The product in each case is perfectly free from iron. By a similar addition of the ferrocyanide to a solution of ordinary sulphate of alumina or alum, the dyer may render them free from iron or iron-alum; when, as mordants for even the most delicate colours, they are equal to the very best Roman alum.

The above plans of removing the iron salt are sometimes replaced by precipitating the alum instead of the sulphate of iron, by the addition of alkaline matter to the lixivium. The crystalline precipitate is purified by draining, re-solution, and recrystallization; whilst the sulphate of iron and Epsom salts contained in the mother-liquor, are obtained by subsequent evaporation and crystallization; after which a fresh crop of alum may be got from it by the use of an alkaline precipitant as before.

FIG. 26.



When the ley or lixivium does not contain an excess of copperas, it is run from the clarifying vessels into the evaporating pans. The former are made of tinned or wrought iron, or lead. The liability of the tinned pans to corrode in contact with the ley, of the iron ones to crack, and of the leaden ones to melt, has led to the adoption in many alum-works of large cisterns of masonry, arched over with the same material.

In the Hurlet works, near Glasgow, these pans are of enormous capacity.

The ley from the calcined shale being first put into the pan, and the furnace-fire at the end lighted, as shown in the engraving, the flame and heated air sweep over the whole surface of the ley, and cause its rapid evaporation, the evolved vapours and products of combustion escaping by the chimney. The evaporation is continued until the liquor has a density of 1·40. A lower density is best for those lyes which contain a large preponderance of aluminic sulphate. It is of great importance, after the evaporation and subsequent cooling of the liquor, that no crystals of aluminic sulphate should be found in the liquid.

The concentrated liquid, being next conveyed to the cooling-vats, deposits basic sulphate of iron and sulphate of lime, whilst the clear or mother-liquor contains sulphate of alumina.

The clear mother-liquor, after being conveyed to other pans, is now ready for mixing with the salts of potassium or ammonium, by the combination of its aluminum sulphate with one of which, it is converted either into potash or ammonia-alum. Soda-alum is rarely prepared, as it possesses the disadvantage of forming a salt very soluble in cold water. The potassium salts preferably used for this purpose, are the chloride or sulphate. Of the ammoniacal salts, the sulphate obtained from the ammoniacal liquor of the gas-works is generally employed. 100 parts of aluminum sulphate require for precipitation—

| | |
|---|---|
| Potassium chloride . . . | 43·5 parts |
| ,, sulphate . . . | 50·9 ,, |
| Ammonium ,, . . . | 47·8 ,, |

In this country the alum-maker gets his potash salts from kelp, carnellite, kainite, and as a waste product in the manufacture of beet-root sugar.

The potassic sulphate occurs as an acid salt, as a secondary product in nitric acid making, as well as when caustic potash and carbonate of potassium are purified. It needs conversion into neutral sulphate before it can be employed in alum manufacture. In Germany potassic sulphate for this purpose, is obtained in abundance from kainite, which occurs among the Stassfurt salts.

Stale urine and the ley of wood-ashes were formerly used as precipitants, but these have been abandoned. Before the addition of the precipitant to the mother-liquor it is necessary to ascertain the amount of the former that will be required. To learn this, an assay of the mother-liquor is made by adding to a known quantity, so much of the alkaline salt in solution as shall form a liquor of a certain density. The mixture is then set aside for a day, and the resulting alum being carefully washed in cold water, dried, and weighed, affords a criterion as to the amount of alkaline salt required for every gallon of mother-liquor. This test, however, owing to various modifying circumstances, can only be considered an approximate one. According to KNAPP, more satisfactory results may be obtained by testing the mother-liquor with a volumetric solution of one of the alkaline salts to be used as precipitants. KNAPP considers a solution of ammonium sulphate as the best test liquid. One part of ammonium sulphate is equivalent to 1·32 parts of potassium sulphate, and 1·13 of potassium chloride.

A saturated solution of the ammonium sulphate being prepared, and its strength ascertained, is run from a burette on to a measured quantity of the aluminic mother-liquor, the mixture being actively stirred after each addition. The solution of the ammonium salt must be added as long as a precipitate is thrown down. When this no longer falls, the number of measures is read off, and by an easy calculation the amount of alkaline salt required for a given measure of mother-liquor can be arrived at.

The mother-liquor having been drawn from the evaporating-pans into the cooling or precipitating stone cisterns, and its strength in aluminic sulphate having been ascertained, the requisite quantity of the alkaline salt in solution is next added to it, the powdery precipitate which is in consequence formed, being kept diligently stirred until no more powder is deposited.

The powder technically known as "flour," is afterwards shovelled from the cisterns on to planks adjoining the cisterns; the planks being arranged on the incline, so that the mother-liquor which drains from the powder shall run back into the cistern. As this, however, is not sufficient to free the flour from adhering impurities,* it is afterwards twice washed by being thrown into a suitable tub or tank, containing a small quantity of very cold water, the whole being gently stirred. By this means the adhering colouring matter is removed from the powder, and passes into the supernatant water, which is syphoned off from the flour as soon as this has subsided.

The washing water, which contains a small quantity of alum, is run back into the cistern. Sometimes the hydro-extractor or centrifugal machine is used for washing the alum powder. In some alum-works the ley containing the aluminum-sulphate is drawn from the evaporating-pans into the cisterns upon the precipitant. When this method is adopted, the resulting alum, which is called "first alum," after being drained and washed on sieves, in tubs containing second alum mothers, or liquor which has been employed in washing in a subsequent stage of the operation, is thrown into a second boiler filled with the same kind of mother-

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* These chiefly consist of the chlorides and sulphates of iron and magnesia. In some works the liquor containing them is used for making impure alum, copperas, or ammonium sulphate. Epsom salt or magnesium sulphate is sometimes manufactured from the mother-liquor.

liquor, and the mixture heated by steam until it acquires a certain density. When all the impurities of the boiler have subsided, the clear liquor is run off by means of a plug, and conveyed to a second series of stone cisterns. After remaining in these for some four or five days, the alum deposits several inches in thickness on the sides and bottom, in the form of crystals, which are broken up, rinsed with very pure cold water, and drained.

The next stage in the process is the conversion of the alum flour, or of the broken-up crystals, as the case may be, into large ones; these latter being very generally preferred by the purchaser on account of their greater purity and freedom from contamination. To accomplish this, the flour is first placed in large covered wooden vessels lined with lead, and boiling water added in quantity only just sufficient to dissolve it; the hot saturated solution which results being, next conveyed into the crystallizing vessels, or "roaching-tubs," as they are called. Very frequently, instead of boiling water, steam, injected through a pipe let into the bottom of the vessel, is used to dissolve the flour, which is so arranged on perforated shelves as to expose as large a surface as possible to the ascending steam. In some alum factories the

FIG. 27.

vessels are covered with a lid, in which are two openings, one of which is for the entrance of the steam, whilst in the other a large leaden funnel, with numerous small holes or perforations, is fitted. The flour being placed in the funnel, the steam is forced into the vessel, and in escaping through the funnel dissolves the flour, the concentrated hot solution of which falls to the bottom of the vessel, and is conveyed to the roaching-casks. In this operation some undissolved basic aluminum-sulphate, which is always left in the funnel, is added to the first ley, and precipitated. The roaching-casks are large wooden, somewhat conically shaped, vessels, lined with lead, 6 to 8 feet in height, and 3 or 4 in diameter at the top. They are composed of staves, which fit very accurately one into the other, and are kept together by strong iron hoops. The above engraving will convey an idea of their construction.

A week or so (depending on temperature) after the hot saturated alum solution has been run into them, the hoops and staves are removed, any remaining mother-liquor is carried off by gutters into cisterns, and is subsequently utilized.

The alum is then cut into square blocks, and being placed in casks, is ready for the market.

In the previous processes, which may be described as the old methods of alum-making, the sulphuric acid of the salt, as has been shown, is obtained by the oxidation of the sulphur of the iron pyrites present in the alum-earths, schists, or shales. Within late years, however, other and more expeditious modes of preparing alum have largely come into use, particularly in this country.

These methods, which consist in the direct treatment of certain aluminous minerals with sulphuric acid, comprise the manufacture of ALUM FROM CLAY:—

1. Process of ALLAN & CHAPTAL.—ALLAN & CHAPTAL

were the first who obtained alum from clay. The process occupies a much longer time if uncalcined instead of burnt clay be employed. Pipe-clay makes the best alum. The more quickly the clay is decomposed by the acid, the sooner of course is the operation completed. In some works there are contrivances for mixing the clay and the acid. Sometimes the two are put into shallow troughs lined with lead, and heated from beneath with flues, the mixture being at the same time kept well stirred. In some places the necessary quantity of acid is supplied in jets from a pipe pierced with small holes, attached to a cistern placed over a tank containing the clay, into which the acid falls, the two being mixed by an agitator worked by machinery. By the process of TAYLOR, of Bristol, the pipe-clay after being previously calcined and mixed with about an equal weight of sulphuric acid of specific gravity, 1·20 is run into a tub, in which it is heated for twelve hours, or until it attains a density of 1·3, by means of a coil of leaden pipe at the bottom of the vessel. The pipe is heated by steam, and the temperature maintained at a point a little below that of boiling water. When the liquor is of the requisite gravity, it is run off into vats and treated with the alkaline liquid in the customary way.

2. Clay free, or nearly free from carbonate of lime and oxide of iron, is chosen for this purpose. It is moderately calcined in lumps in a reverberatory furnace, until it becomes friable, great care being taken that the heat is not sufficient to indurate it, which would destroy its subsequent solubility. It is next reduced to powder, sifted, and mixed with about 45 per cent. of its weight of sulphuric acid (sp. gr. 1·45), the operation being conducted in a large stone or brick basin arched over with brickwork. Heat is then applied, the flame and hot air of a reverberatory furnace being made to sweep over the surface of the liquor. The heat and

agitation are continued for two or three days, when the mass is raked out and set aside in a warm place for six or eight weeks, to allow the acid to combine more intimately with the clay. At the end of this time the newly formed sulphate of aluminum is washed out, the solution evaporated until of a sp. gr. of about 1·38 if for potash-alum, and 1·24 if for ammonia-alum, and the alkaline salt added. The remaining operations resemble those already described. Good alum may be produced by this process, at about two-thirds the cost of rock or mine alum.

3. Process of POCHIN.—Fine china clay is heated in a furnace with access of air, and mixed with a suitable proportion of sulphuric acid of sp. gr. 1·52; the latter being considerably diluted with water, in order to moderate its action, which would otherwise be far too violent. The mixture is then passed into cisterns furnished with movable sides, where in a few minutes it heats violently and boils. The thick liquid gradually becomes thicker, until it is converted into a solid porous mass; the pores being produced by the bubbles of steam which are driven through it, owing to the heat resulting from the reaction of the ingredients on each other. This porous mass, known as "alum-cake" or "concentrated alum," appears perfectly dry, although retaining a large amount of combined water. It also contains all the silica of the original clay, but in such a state of fine division that the whole appears homogeneous; whilst it imparts a dryness to the touch which can scarcely be given by pure sulphate of aluminum. From this substance a solution of pure sulphate of aluminum is easily obtainable by lixiviation and allowing the resulting solution to deposit its silica before using it, but for many purposes the presence of the finely divided silica is not objectionable. The sulphate of aluminum solution is adapted to all the purposes of dyeing

for which alum is employed; the sulphate of potash or of ammonia in the latter being an unnecessary constituent, and one merely added to facilitate the purification and subsequent crystallization of the salt. To obtain alum from the porous alum-cake, the proper proportion of acid having been used in its preparation, or subsequently added, it is only necessary to precipitate its concentrated solution with a strong solution of a salt of potash, or of ammonia, or a mixture of them, and to proceed then as before.

THE MANUFACTURE OF ALUM UNDER PRESSURE.—M. FAUDEL proposes for the use of paper-makers, alum-cake obtained by heating china clay with sulphuric acid under a pressure of 2 to 2½ atmospheres in leaden vessels.

1·5 parts of clay, heated to 135° to 140° Cent. under a pressure of 3 to 3½ atmospheres with 1·8 parts of sulphuric acid of 1·525 sp. gr., yielded a cake which dissolved almost entirely in water. Its composition was—

| | |
|---|---|
| Water and impurities . . . . | 37·5 |
| Sulphate of alumina . . . . | 37·0 |
| Silicic acid . . . . . . | 19·5 |
| Free sulphuric acid . . . . | 6·0 |

The free acid may be neutralized by the addition of alumina. (*Dingl. Polyb.*)

FROM FELSPAR (by TURNER'S patent, dated 1842).—By this process potash felspar is ground in an edgestone-mill until it is as fine as sand, the felspar* being previously heated to redness, then plunged in cold water, by which its disintegration is greatly aided.

The powdered substance is then treated with its own weight of potassium sulphate in a reverberatory furnace, previously raised to a red heat.

---

* Felspar is a double silicate of aluminum and potassium.

When the mixture is in a state of fusion, potassium carbonate, in quantity equal to the sulphate, is next thrown into the furnace, and the whole fused to a glass. By boiling with water this glass decomposes into a soluble silicate of potash, which dissolves, and an insoluble double silicate of aluminum and potassium which remains. This double silicate, after being well washed with water, is put into a leaden cistern, and boiled with sulphuric acid of sp. gr. 1·20; potash-alum being formed and silica liberated. The silica falls to the bottom of the cistern, whilst the supernatant liquor containing the alum is run off into coolers, when four-fifths of it crystallize out. The mother-liquor from the crystals, containing some silica, is next evaporated to dryness, and, the dry mass being treated with water, alum alone dissolves out, leaving the insoluble silica behind. The alum-liquor so obtained is afterwards sufficiently evaporated to produce crystals.

By employing ammonium or sodium salts, instead of potash ones, the corresponding alums may be obtained.

ALUM FROM CRYOLITE.—1. THOMPSON'S method.—Cryolite or Greenland spar is a double fluoride of aluminum and sodium. When decomposed by ignition with calcium carbonate it yields sodium aluminate and calcium fluoride. From the ignited mass the aluminate of sodium is obtained by lixiviation with water, and carbonic acid gas is passed into the solution, when there result precipitated hydrated gelatinous alumina and carbonate of soda, which remains in solution. If it be desired to obtain the alumina as an earthy compact precipitate, bicarbonate of soda is used instead of carbonic acid. While the clear liquor is boiled down for the purpose of obtaining carbonate of soda, the precipitated alumina is dissolved in dilute sulphuric acid; this solution is evaporated for the purpose of obtaining sulphate of aluminum (the so-called concentrated alum), or the solution, after having been treated with a potassa or an ammonia salt, is converted into alum.

2. Sauerwein's method is based upon the decomposition of cryolite by caustic lime by the wet way. Very finely ground cryolite is boiled in a leaden pan with water and lime, the purer the better, and as free from iron as possible. The result is the formation of a solution of aluminate of sodium and insoluble fluoride of calcium. When the fluoride of calcium has deposited, the clear liquid is decanted, and the sediment washed, the first wash-water being added to the decanted liquor, and the second and third wash-waters being used instead of pure water in a subsequent operation. In order to throw down the alumina from the clear solution very finely powdered cryolite in excess is added to the liquid, while being continuously stirred: alumina thereby deposits, and fluoride of sodium passes into solution. When no more caustic soda can be detected in the liquid, it is left to stand until it becomes clear. The clarified solution of fluoride of sodium is then drawn off, and the alumina treated as described above (1. Thompson's method). The solution of fluoride of sodium having been boiled with caustic lime, yields a caustic soda solution, which having been decanted from the sediment of fluoride of calcium, is evaporated to dryness. Recently the fluoride of calcium occurring as a by-product, has been used in glass-making.

3. The decomposition of cryolite by sulphuric acid yields sulphate of soda, convertible into carbonate by Leblanc's process, and sulphate of aluminum free from iron. This method of decomposing cryolite is, however, by no means to be recommended, as owing to the liberation of hydrofluoric acid peculiarly constructed apparatus is required, whilst the sulphate of sodium has to be converted into carbonate.

ALUM FROM BAUXITE.—This mineral, occurring in some parts of Southern France, in Calabria, near Belfast in Ireland, and in other parts of Europe, contains about 60 per cent. of hydrate of aluminum, more or less pure. In order to prepare alum and sulphate of aluminum from bauxite, the mineral is first disintegrated by being ignited with carbonate of sodium, or with a mixture of sulphate of sodium and charcoal; in each case the lixiviation of the ignited mass yields aluminate of sodium, from which, by the processes already described under "Cryolite," alum or sulphate of aluminum and sodium are prepared.

ALUM FROM BLAST-FURNACE SLAG.—LÜRMANN recommends the slag to be decomposed by means of hydrochloric acid. From the resulting solution of chloride of aluminum the alumina is precipitated by carbonate of lime, any dissolved silica being precipitated at the same time. The alumina thus obtained is dissolved in sulphuric acid, the silica being precipitated and thus separated. 220 lbs. of slag, containing 25 per cent. of alumina, yield 400 lbs. of alum and 68 lbs. of silica.

ALUM FROM COAL SHALES OR SCHISTS.—By SPENCE's method (patent dated 1845) alum is obtained from the aluminous schists occurring under the coal measures of South Lancashire. A number of bricks, placed in parallel lines about 4 inches apart, are so arranged as to form a series of air currents. A bed of burning coals is then made upon the bricks, and upon these the schist, previously broken into small pieces, is piled to the height of 3 or 4 feet.

More shale is added every day, care being taken to avoid allowing the combustion to cease on the one hand, and to rise above a red heat on the other, so that the alumina may not be rendered insoluble in its subsequent treatment with sulphuric acid.

The calcination requires about 10 days, and if it has been properly conducted, the burnt ore has become soft and porous, and of a pale brick colour. The calcined shale is put into covered receptacles, each capable of holding 20 tons, and digested from 36 to 48 hours in sulphuric acid of specific gravity 1·35 at a temperature of 230° Fahr. (110° Cent.), the vapour from a boiler containing gas-liquor being at the same time passed into the mixture, in which the acid must be kept in excess. The ammoniacal salts thus carried into the digesters are decomposed by the acid. Any excess of ammonia is got rid of by the addition of lime.

When the liquor has been found by experiment to be of the proper degree of concentration, it is removed to the coolers, large leaden vessels about 30 feet long, 17 wide, and 1·9 deep. Here it is stirred continuously, with the object of causing small crystals to be formed. These crystals are washed with the mother-liquor dripping from blocks of alum, drained, and then thrown into a cylindrical box open at the bottom. Here they encounter a current of steam issuing from a perforated lead pipe.

They are thus rapidly dissolved, the solution flowing into wooden tanks lined with lead, where it remains for three hours.

From the tanks it is conveyed to large vessels, in which the greater part crystallizes; the liquid, which by condensation yields more crystals, being run off by a hole made in the bottom of the crystallizing tub or cylinder.

ALUM FROM RHODONDA PHOSPHATES.—In 1870 SPENCE patented a process for making alum from the Rhodonda phosphate, a native compound consisting of alumina with phosphate of iron in varying amount, occurring in Rhodonda, one of the West Indian Islands. The mineral is mixed with coal or coke, and calcined in a kiln in a red heat, like lime; or it may be ground and passed through a 20 mesh to the inch sieve. SPENCE prefers the first method, since it renders the ore more soluble, and oxidizes part of the iron, thereby rendering it insoluble.

The phosphate prepared by either of the above methods, is then placed in leaden vessels and mixed with sulphuric acid of the specific gravity 1·6, the proportion of acid varying with the richness of the mineral in alumina. If it contains 20 per cent. of alumina, it will require an equal weight of acid; if 12 per cent., ⅗ths of its weight; and so on in proportion.

The mixture is then heated by means of steam being blown into it, which causes the ore to dissolve and the liquor to acquire an increase of specific gravity. The liquid, however, must be carefully diluted so that it does not exceed 1·45 specific gravity, or 90° Twaddle. This is done by adding water, or the weak liquids which are obtained as the operation goes on, the mixture meantime being kept in constant ebullition until all the mineral is dissolved, and nothing but an insoluble residue is left. The clear liquid being then conveyed into closed leaden vessels, steam charged with ammonia, and derived from the boiling ammoniacal liquor of the gas-works, is next passed into it, from 600 to 900 gallons of gas-liquor being required for every ton of the phosphate, according to its richness in alumina. The liquid having been charged with the requisite quantity of ammonia, is then left at rest for a few hours, after which the clear solution, which now has a specific gravity of 1·4 (80° Twaddle), is run into leaden coolers, in which the alum crystallizes out. By keeping the liquid in these coolers for some days and frequently stirring, the yield of alum is increased. Spence states that every ton of the phosphate containing 20 per cent. of alumina, produces about 1½ tons of alum. After the removal of the alum from the mother-liquors, these, which chiefly contain free phosphoric acid, and the phosphates and sulphates of ammonia, with a small amount of sulphate of iron, can be used for manurial purposes, either properly diluted or previously mixed with sawdust, the mixture being afterwards dried at a low heat. Salts of potash, either alone or in combination with ammonia, may be substituted for the gas ammonia; the sulphate of potash being preferable to the chloride for this purpose, since the latter is a deliquescent salt.

ALUM FROM BOGHEAD COAL-ASH.—A process for the manufacture of alum from the ash or residue of the combustion of Boghead coal was patented in 1851 by BARLOW and GORE ; but although this material contained 20 per cent. of alumina, it was not found a convenient one for the purpose.

ALUM FROM BEET-ROOT SUGAR SOLUTIONS.—DUNCAN and NEWLANDS' method.—The *Beta alba* contains a considerable quantity of potash salts, which it is essential should be removed, when this root is used as a source of sugar. In 1871 Messrs. DUNCAN and NEWLANDS, BROTHERS patented a process for getting rid of these salts by treating the syrup obtained from the white beet-root with solution of sulphate of aluminum. The sulphate of aluminum combines with the potash to form alum, which crystallizes out, and is thus separated from the saccharine solution. The process is conducted as follows :—The percentage of ash in the syrup is first estimated in the usual manner, by treatment with concentrated sulphuric acid and subsequent incineration and weighing, one-tenth being deducted from the weight of the ash. Two-fifths of the weight of the ash, after making the deduction, are calculated as potash found, and for every 1 part of potash, 9½ parts of sulphate of aluminum are required, unless it has been previously ascertained that the saccharine liquid, or the solution of sulphate of aluminum, contains sulphuric acid, either free or combined, in which case the quantity of sulphate of aluminum necessary to convert the potash into sulphate is, according to the amount of the free or combined acid, either entirely or proportionately dispensed with. Of the 9½ parts of the sulphate of aluminum, 2½ parts are required to convert the potash into sulphate. The amount of dry sulphate of aluminum having been calculated upon the above data, the quantity of solution corresponding to this may be easily ascertained by consulting the following Table :—

TABLE *giving the percentage of sulphate of aluminum in solutions of different densities.*

| Baumé. | Specific gravity. | Per cent. | Baumé. | Specific quantity. | Per cent. |
|---|---|---|---|---|---|
| 22½ | 1·184 | 34 | 28 | 1·225 | 43 |
| 24 | 1·188 | 35 | 29 | 1·235 | 44 |
| 24½ | 1·190 | 36 | 30 | 1·245 | 45 |
| 25 | 1·197 | 37 | 31 | 1·256 | 46 |
| 25½ | 1·201 | 38 | 31½ | 1·261 | 47 |
| 26 | 1·206 | 39 | 32 | 1·267 | 48 |
| 26½ | 1·211 | 40 | 32½ | 1·277 | 49 |
| 27 | 1·216 | 41 | 34 | 1·288 | 50 |
| 27½ | 1·218 | 42 | ... | ... | ... |

The percentage amount of potash in the syrup to be operated upon having been estimated, the cold saccharine liquid is run into a tank, and there is added to it the corresponding quantity of solution of sulphate of alumina, the mixture being kept in brisk agitation for from 15 minutes to an hour, by means of a mechanical stirring contrivance. It is then allowed to remain at rest for 4 or 5 hours, at the end of which time, the bottom of the tank is found covered with small crystals of potash alum, known as "alum-flour."

In carrying out this part of the process, in order to obtain satisfactory results, as well as to avoid the production of glucose, the operation should be conducted—(1) as rapidly as possible, compatible with the proper deposition of the alum; (2) at as low a temperature as possible; and (3) the two solutions should be at the greatest specific gravity compatible with the deposition of the alum. This last condition is best fulfilled by using syrup having a density of 38° B. and sulphate of aluminum solution at 27° B.

The crystals of alum having deposited at the bottom of the tank, the supernatant liquid is run off by means of taps fixed at different heights in the tank, into another vessel at a lower level. Here chalk made into a paste with water is added to it, and subsequently milk of lime, to complete saturation.

To wash and dry the precipitated alum-crystals, a centrifugal machine is used, but a small quantity of syrup is always found adhering to the crystals after they have been subjected to the action of the machine. However, after being mixed with a little cold water, and being a second time subjected to the action of the machine, the crystals lose the whole of the adhering syrup, and are fit for the market.

In alum-making the least possible quantity of boiling water or liquor is employed for making the solutions, so that they may crystallize without evaporation, and thus economize fuel; and the mother-liquors of previous operations are constantly employed for this purpose, when possible. Nor is anything which is convertible to use, from the drainage of the heaps to the liquor and slime of the roaching-casks, allowed to be wasted.

By whatever process or from whatever materials alum is obtained, it is absolutely necessary for the successful and economical conduct of its manufacture, that the precise composition of the mineral or minerals employed, should be exactly known. This can only be determined by actual analysis, which should be extended to several parts of the same bed of shale or earth, and particularly to the upper and lower strata, which frequently differ in composition from each other, and thus require different subsequent treatment, or to be so apportioned as to afford a mixture, the essential ingredients of which, shall bear the proper ratio to each other. The necessity of this will be seen by reference to the composition of certain alum shales, as given in the table at page 150, wherein is shown the variation in the amounts of iron pyrites, &c., in the top and bottom rocks.

The presence of lime in alum-ore is most prejudicial, owing to its affinity for sulphuric acid being greater than that of either aluminum or iron. Ores containing it in any quantity, are therefore unfitted for the manufacture of alum. Magnesia is also prejudicial; but in this case the sulphate of magnesia left in the mother-liquors is not wholly valueless, as it may often be crystallized and sold as "Epsom salt."

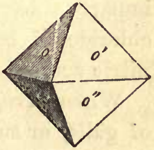
The ammonia-salt used in making alum is, as previously stated, generally the crude sulphate prepared from the ammoniacal liquor of gas-works, or that from the manufacture of sal-ammoniac by the destructive distillation of animal matter. Both these liquors may be used without previous conversion into sulphate of ammonia whenever there is an excess of sulphuric acid in the aluminous solution.

Soda-salts are seldom, if ever, used as precipitants in the manufacture of alum, on account of the easy solubility of the resulting soda-alum—a property which unfits them for this purpose.

In estimating the strength of his solution, the alum-maker takes as a standard a measure, or specific gravity bottle, capable of holding exactly 80 pennyweights of distilled water. The excess of the weight of liquor, in pennyweights, over 80, or that of water, is called so many "pennyweights strong." Thus one of 90 pennyweights (90 dwt.) is said to be "10 dwt. strong;" or simply, "one of 90 dwt." These numbers correspond to 2½ degrees of Twaddle's hydrometer, and may easily be found by dividing Twaddle's degrees by 2·5 or 2½: or by multiplying them by 4, and pointing off the right-hand figure of the product for a decimal. The result is in alum-makers' pennyweights.

Potassium alum crystallizes in regular octahedrons, often with truncated edges and angles; and sometimes in cubes, but only when there is a deficiency of acid in its composition, with the alkali in slight excess of the proper quantity.* It is slightly efflorescent in dry air: soluble in 18 parts of cold water, and in rather less than its own weight of boiling† water. It is insoluble in alcohol. Alum has a sweet, acidulous and very astringent taste, is styptic, and reddens litmus. Its solution dissolves zinc and iron, with evolution of hydrogen. When heated at 197° Fahr. it melts, loses its water of crystallization, and becomes white and spongy, forming the substance known as *burnt alum.* White heat decomposes it, with the evolution of oxygen, sulphurous anhydride, and steam; calcined with carbonaceous matter out of contact of air it suffers decomposition, and furnishes a pyrophoric residuum (HOMBERG'S pyrophorus). When alum is ignited with alkaline chlorides, hydrochloric acid is liberated; this reaction also occurs when a concentrated solution of alum is boiled with the alkaline chlorides. Am-

FIG. 28.



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* LÖWEL.

| | | | | Potash Alum. |
|---|---|---|---|---|
| † 100 parts of water at | 32° Fahr. | (0° Cent.) | dissolve | 3·9 parts |
| ,, ,, ,, | 68° ,, | (20° Cent.) | ,, | 15·8 ,, |
| ,, ,, ,, | 104° ,, | (40° Cent.) | ,, | 31·2 ,, |
| ,, ,, ,, | 212° ,, | (100° Cent.) | ,, | 360·0 ,, |

monia precipitates pure hydrate of aluminum from potassium alum, but only a subsulphate from the simple sulphate of aluminum; sp. gr. of the crystallized alum, 1·724, but when containing ammonia, often so low as 1·710.

Potassium alum is easily recognized by its crystalline form, its taste, and by its complete solubility in water. With soda or potash its aqueous solution gives a white gelatinous precipitate soluble in excess; a platinum wire moistened with the solution, and some solution of nitrate of cobalt, imparts a deep sky-blue colour to the blowpipe flame; and chloride of barium gives a white precipitate insoluble in nitric acid.

When pure, solution of alum is not darkened by tincture of galls, or sulphuretted hydrogen, or altered in colour by ferrocyanide of potassium; nor does it give any precipitate with solution of nitrate of silver.

The principal impurity, and one which renders alum unfit for the use of the dyer, is iron. This may be readily detected by the blue precipitate it gives with ferrocyanide of potassium, or the black precipitate with sulphide of ammonium, both of which are very delicate tests.* Lime, another very injurious contamination, may be detected by precipitating the alumina and iron, if there be any present, with ammonia, and then adding oxalate of ammonia to the boiled and filtered liquid. The liquid filtered from the last precipitate (oxalate of lime) may still contain magnesia, which may be detected by the white precipitate caused, on the addition of an alkaline phosphate. Common alum frequently contains ammonia, from urine or the crude sulphate of the gas-works having been employed in its manufacture.

---

* Good English alum contains less than $\frac{1}{10}$th per cent. of iron; the best Roman or Italian alums seldom contain more than $\frac{5}{1000}$ths per cent. of iron alum, notwithstanding their exterior colour.

Powdered alum is frequently adulterated with common salt, in which case it gives a white curdy precipitate with nitrate of silver, turning black by exposure to the light.

The applications of alum in the arts and manufactures are numerous and important. It is extensively used in the preparation of mordants for dyeing and calico-printing; also to harden tallow and fats; to render wood and paper incombustible; to remove greasiness from printers' blocks and rollers; in the manufacture of the commoner kinds of paper; for whitening silver and silvering brass in the cold; to aid in the separation of butter from milk; to purify turbid water: to dress skins; to make lake and pyrophorus; and as a lining, in conjunction with sulphate of lime, for fireproof safes.

It is also employed by the dishonest baker and the publican—the latter using it as an adulterant for gin and beer. It is likewise an ingredient in spurious port-wine.

In medicine, alum is used as a tonic and astringent, in doses of from 5 to 20 grains. One drachm of alum to half-a-pint of water forms a useful collyrium. In lead colic it is administered in doses of ½ drachm to 1 drachm dissolved in gum water, every three or four hours. Dr. MEIGS says, a teaspoonful in water forms one of the best emetics in croup.

It is also extensively used for clarifying liquors, and for many other purposes connected with the arts and wants of every-day life.

**Alum, Ammonia.** $H_4N,Al,(SO_4)_2,12H_2O$. *Syn.* AMMONIO-ALUMINIC SULPHATE. This is an alum in which the sulphate of potassium is replaced by an equivalent of sulphate of ammonium. As explained, it is mostly prepared by adding crude sulphate of ammonium to solution of sulphate of aluminum.

Much of the common alum, especially that prepared on the Continent, contains both potassium and ammonium; in England it is manufactured in enormous qnantities. As an astringent, and as a source of alumina in dyeing, it resembles potash-alum. It may, however, be readily distinguished from the latter by the fumes of ammonia which are evolved when it is moistened and triturated or heated with caustic potash or quicklime, and by the residuum of its exposure to a white heat, being pure alumina; sulphate of ammonia, sulphuric acid, and water having been driven off.

| | | | | | Ammonia alum. | |
|---|---|---|---|---|---|---|
| 100 parts of water at | 32° | Fahr. | (0° Cent.) | dissolve | 5·22 | parts |
| ,, ,, | 68° | ,, | (20° Cent.) | ,, | 13·66 | ,, |
| ,, ,, | 104° | ,, | (40° Cent.) | ,, | 27·27 | ,, |
| ,, ,, | 212° | ,, | (100° Cent.) | ,, | 421·90 | ,, |

**Alum, Basic.** $Al_2K_2(SO_4)_2$. A variety of alum found native at Tolfa. On calcination and subsequent lixivation it yields ordinary alum. A similar substance falls as a white insoluble powder, when newly precipitated alumina is boiled in a solution of alum. Basic alum is soluble in acetic acid.

**Alum, Chrome.** See page 178.

**Alum, Iron.** $KFe(SO_4)_2,12H_2O$.

*Preparation.*—Take of peroxide of iron, 9 lbs.; sulphuric acid, 14 lbs.; dissolve, dilute the mixture with a sufficient quantity of water, and add of potassium sulphate, 10 lbs.; evaporate and crystallize.

It occurs in beautiful octahedral crystals of a pinkish or pale violet colour. It has been employed as a mordant in dyeing black.

**Alum, Cubical.** *Syn.* NEUTRAL ALUM.

(1) Boil 12 parts of alum and 1 part of slaked lime together in water; let settle; filter, and evaporate the filtrate. (2) Add to a solution of alum so much potassium or sodium carbonate as will begin to separate the alumina.

Neutral or cubical alum is frequently preferred by the dyer to common alum, since it has no chemical effect on ordinary colours.

**Alum, Roman.** *Syn.* ROACH ALUM, ROCHE ALUM. Roman alum is much esteemed by dyers as being nearly free from iron. That sold for it in England, is sometimes only ordinary alum coloured with Venetian red, Armenian bole, or rose-pink.

The ordinary alum is coloured by shaking the lumps in a sieve over a vessel of hot water, and then stirring them up with the colour until the surface is uniformly tinged with it. In genuine Roman alum the colour not only covers the surface, but also partially pervades the substance of the crystals.

**Alum, Sodium.** $Al,NaSO_4,12H_2O$. Soda-alum is a natural product. It also occurs crystallized in the mother-liquor of alum, when soap-makers' ley, which contains sodium chloride, is used in its preparation. ZELLUCA says it may be obtained by the spontaneous evaporation of sulphate of aluminum and sulphate of sodium. It does not occur in commerce for the reasons already stated.

**Alum, Sulphate.**—The preparation of the crude aluminum sulphate has been previously described.

Crude aluminum sulphate is known as "concentrated alum." The commercial salt always contains free sulphuric acid, and frequently small quantities of potassium or ammonium alum. Sulphate of sodium has been found in that prepared from cryolite.

VARRENTRAPP's analyses show that commercial aluminium sulphate varies greatly in composition.

Four samples yielded the following results:—

| | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Alumina | 15·3 | 12·5 | 15·1 | 13·0 |
| Sulphuric acid | 38·0 | 30·6 | 38·0 | 34·0 |

According to the formula, the quantity of sulphuric acid in these samples should have been :—

| 1 | 2 | 3 | 4 |
|---|---|---|---|
| 35·8 | 29·2 | 43·3 | 30·5 |

In different parts of the same cake, the quantity of water was found to vary between 56 and 48 per cent.

**Alum, Sulphite.** $Al_2O_3,SO_3,4H_2O$. Dissolve recently precipitated aluminic hydrate in cold aqueous sulphurous acid; or pass sulphurous anhydride into water in which aluminic hydrate is suspended. When the solution is heated, the aluminium sulphite separates as a white earthy powder, which must be collected on a filter whilst hot, as it redissolves on cooling. Aluminium sulphite is insoluble in pure water, and becomes converted into sulphate when exposed to the air. This salt has been employed for purifying beet-root juice.

**Alums, other Varieties of.**—The aluminium of common alum may be replaced by any other metal of the same group, such as iron, chromium, or manganese, giving rise to a series of salts having potassium alum for their type.

Further, in the newly formed compound, as in potassium-alum, the second sulphate may also be replaced under similar conditions. The following are some of the chief salts of the series :—

| | |
|---|---|
| Potassium alum . . | $KAl(SO_4)_2,12H_2O$ |
| Sodium ,, . . | $NaAl(SO_4)_2,12H_2O$ |
| Ammonium ,, . . | $H_4NAl(SO_4)_2,12H_2O$ |
| Iron ,, . . | $KFe(SO_4)_2,12H_2O$ |
| Chrome ,, . . | $KCr(SO_4)_2,12H_2O$ |
| Manganese ,, . . | $KMn(SO_4)_2,12H_2O$ |

All these alums may be prepared by mixing together solutions of the respective sulphates in equivalent proportions, when crystals may be obtained by evaporation in the usual manner. The presence of sulphuric acid in slight excess assists their crystallization.

All the alums crystallize in octahedrons or cubes, and they all contain the same number of molecules of water.

**Aluminium.** Al=27·5. *Syn.* ALUMINUM. This metal in various forms of combination, is very abundantly distributed throughout nature. Combined with silica it forms the basis of all clays. Bauxite is a native hydrate of aluminum, and cryolite a double chloride of aluminium and sodium. Plants contain it in minute quantity.

Aluminium was first isolated by WÖHLER from its chloride in 1827, by igniting the latter with potassium; OERSTEDT having previously, in 1826, failed to obtain it by the same method. WÖHLER's aluminium occurred as a grey metallic powder mixed with malleable tin-white globules. In 1854, DEVILLE, who obtained it in a compact form, and in much larger quantity, substituted sodium for potassium, over which latter, the sodium possesses the advantages of being more easily prepared, and of effecting the reduction of the chloride with less violence, added to which, a smaller quantity is required.

1. DEVILLE's process for obtaining aluminium was as follows:—200 to 300 grammes (about 7 to 10 oz.) of dry chloride of aluminium are introduced into a hard glass tube, and kept in position by two plugs of asbestos. A current of hydrogen, previously dried by being passed first through concentrated sulphuric acid, and afterwards through a tube containing fused chloride of calcium, is then transmitted through the tube, the chloride of aluminium being at the same time gently heated, so as to get rid of any free hydrochloric acid or chloride of sulphur, and quite free from air. Two or three small porcelain boats or trays, each containing about 3 grammes (about 46 or 47 grains) of sodium, carefully freed from naphtha by pressure between folds of

blotting-paper, are now placed in the tube, and the current of hydrogen re-established and continued throughout the operation. Heat is then applied to that part of the tube containing the sodium, at the same time that the chloride of aluminium at the other end of the tube is subjected to a regulated heat. When the chloride becomes volatilized and the sodium melts, a violent reaction, accompanied with the disengagement of much heat and vivid incandescence, takes place between the two. The chloride is partially reduced to metallic aluminium in the form of small globules, which are condensed in the boats, together with the double chloride of sodium and aluminium. In conducting the process, it is desirable that the end of the tube in which the sodium is situated, should be slightly raised, otherwise the melted chloride of aluminium will run down upon the fused sodium, and in combining with this latter set up so much heat, as to crack the tube.

When the mass in the boat is cold, and is withdrawn from the glass tube, it is transferred to a porcelain one, through which hydrogen is passed; the volatile chloride of sodium and aluminium is driven over, and the residuum, consisting of small globules of aluminium, is lastly reduced to a solid mass or button, by fusion at a strong heat, under a layer of the fused double chloride of aluminium and sodium.

The above process is more particularly suited for obtaining small quantities of aluminium for the laboratory. When the metal is required in large quantity, instead of the glass or porcelain tube just referred to, two cast-iron cylinders are employed, the anterior one of which contains the chloride of aluminium, and the posterior one a tray holding the sodium, of which 10 or 12 lbs. are commonly operated on at once. These cylinders are united by means of a smaller intermediate one, filled with clean scraps of iron, which serve to separate iron, free hydrochloric acid, and chloride of sulphur, from the vapour of chloride of aluminium, as it passes through them. During the passage of the vapour of the chloride the smaller cylinder or tube is kept heated to from 400° to 600° Fahr. (204·4°–260° Cent.), but the two other cylinders are only very gently heated, since the chloride is volatilized at a comparatively low temperature, and the reaction between it and the fused sodium, when once commenced, usually generates sufficient heat for the completion of the process.

Amongst the several processes, many of them patented, that have from time to time been employed with varied success for the preparation of aluminium on a large scale, may be instanced the following:—

2. MM. ROUSSEAU FRÈRES, & MORIN (patent dated 1856).—10 parts of pulverized chloride of aluminium and sodium, and 5 parts of pulverized fluorspar or cryolite, are mixed with 2 parts of sodium in small ingots, and the mixture thrown on to the hearth of a reverberatory furnace previously raised to the required temperature, the dampers and doors of the furnace being closed, to exclude air. Energetic action soon takes place, accompanied with the extrication of so much heat, that the walls of the furnace, as well as the mixture, become heated to bright redness. The reduction being finished, the mass in a state of fusion is run out through an aperture at the back of the furnace. The slag flows out first, and this is followed by the aluminium, which collects in a mass below the molten slag. With a reverberatory furnace and a hearth having a superficies of 16 square feet, 16 lbs. of metallic aluminium may be obtained at one operation. From the lower layer of slag, which consists chiefly of fluoride of aluminium, an additional quantity of aluminium in globules may be procured by pulverizing the fluoride, and passing it through a sieve. Alumina may be prepared from the fluoride. The great

advantage of this process is, that the metallic aluminium is scarcely contaminated with silicon.

The process of Messrs. **Bell**, of Newcastle, is similar. They prepared the aluminium and sodium salts as follows:—Starting with a trisodic aluminate, which they obtain from bauxite, they decompose this by carbonic or hydrochloric acid, and by this means obtain hydrate of aluminium. The hydrate of aluminium is next mixed with common salt and charcoal, and the mass rolled into balls about the size of an orange, which are dried. The balls are then placed in vertical clay retorts heated to redness, and dried chlorine is passed through them. The result of the distillation is the double chloride of aluminium and sodium, which is carried over into the receiver.

3. **Professor Rose**, of Berlin, obtained aluminium by fusing cryolite (a natural double fluoride of aluminium and sodium) with sodium and common salt. Pulverized cryolite, 2 parts by weight, is mixed with 1 part of common salt, and the mixture is arranged in a perfectly dry earthen or iron crucible, in layers alternating with sodium; 2 parts of sodium being used for every 5 parts of cryolite, a layer of cryolite is placed at top, and the whole covered with common salt. The crucible and its contents are then rapidly heated in a wind-furnace, until the contents are entirely melted, and after being stirred with an iron rod, are left to cool. The aluminium generally separates in globules of considerable size. The processes of **Percy** and **Dick** are nearly the same. This method differs from the previous one in dispensing with the use of the double chloride of aluminium and sodium, the process for the preparation of which is a very tedious and costly one. The aluminium, however, is not so pure. **Wöhler** proposed a modification of **Rose's** plan, which consisted in melting 7 parts of chloride of sodium with 9 parts of chloride of potassium. The fused

mass was then to be reduced to fine powder, and intimately mixed with its own weight of finely pulverized cryolite. This powder was then to be arranged in a dry earthen crucible, in alternate layers with sodium, in the proportion of 1 part of sodium to 5 or 6 parts by weight of powder. The crucible was next to be rapidly heated in a wind-furnace. A violent reaction takes place, during which part of the sodium is burnt off. The mixture was then to be heated for another quarter of an hour, until it became molten, after which it was allowed to cool. The aluminium was generally found at the bottom of the crucible in the form of a button, and sometimes amounted to a third of the proportion present in the cryolite.

4. In 1856 a process was patented by GERHARD for obtaining aluminium by the reducing action of hydrogen at a red heat. Fluoride of aluminium, or the double fluoride of aluminium and sodium, is placed in shallow glazed earthenware dishes. These dishes stand in larger dishes containing iron filings. The dishes are then put into an oven heated to redness, and hydrogen gas, by means of a tube, is passed into the oven, and the heat increased. By means of an exit-pipe with a stop-cock, the supply and pressure of the gas can be arranged. The hydrogen combining with the fluorine to form hydrofluoric acid, this is absorbed by the iron, and the aluminium is left in the metallic condition. Although this process is said to have given satisfactory results, it has of late years been abandoned by the inventor for the method by sodium.

5. Aluminium may also be obtained by electrolysis. BUNSEN first procured it by this means in 1854.

Into a red-hot porcelain crucible, divided in two by a porous diaphragm of earthenware, he put double chloride of aluminium and sodium in a fused state, and then in each division he placed the ends of the carbon poles of a Bunsen's battery, consisting of ten elements. The aluminium was reduced at the negative pole. In carrying out this operation, the aluminium is very liable to be deposited in the pulverulent form, unless the temperature in the crucible is considerably higher than the melting-point of the salt. It is also necessary, all the time the deposition of the metal is going on, to keep on adding chloride of sodium to the crucible, the temperature of which should ultimately be increased to the melting-point of silver.

By taking these precautions, the metal may be obtained in good-sized globules, which may be fused into a mass by throwing the globules into chloride of sodium, at a white heat.

Of the above methods for obtaining aluminium in large quantities, those only have been found to answer in which the metal is reduced from the double chloride of aluminium and sodium, or from cryolite by sodium. Some years back there were two manufactories in France for the production of aluminium, in one of which the process of Messrs. ROUSSEAU FRÈRES & MORIN was in operation. Messrs. BELL, of Newcastle, have given up its preparation for some years.

In the preparation of aluminium the employment of too high a temperature is a frequent cause of failure. Whilst this may be avoided by care, the difficulty of eliminating certain foreign matters is not so easily overcome, owing to the facility with which these are taken up during its preparation from the material of which the apparatus is made, and from the substances from which it is prepared, which are seldom absolutely pure.

Indeed, it is not too much to assert that chemically pure aluminium has not yet been obtained, and that even a very close approximation to it is of very rare occurrence. If a copper boat be used to hold the sodium, the product will be contaminated with copper. Again, chloride of aluminium always contains chlorides of iron and silicon, both of which are volatile, and probably it takes up a further portion of impurity from the porcelain or earthenware of which the apparatus is formed. Then sodium is seldom uncontaminated with carbon or some compound of it; in which case, and also when it is not carefully freed from the naphtha in which it has been preserved, the resulting aluminium will contain carbon. The crucible, whether of porcelain or iron, in which the final fusion is made, also contributes to contaminate the metal. Hence the inferior whiteness and brilliancy of commercial specimens of aluminium. Commercial aluminium contains from 88 to 94 per cent. only of pure aluminium, and from 1 to 4 per cent. of iron, ½ to 3 per cent. of silicon, and from 1 to 6 per cent. of copper.

Pure aluminium resembles silver in colour and appearance, but is not so white or lustrous. The less pure varieties have a slightly bluish tint, somewhat like that of zinc. Aluminium is capable of receiving a fine polish. It has a specific gravity of 2·56, which by hammering may be raised to 2·57. It is both ductile and malleable, and may be rolled into thin sheets or drawn out into fine wire. By rolling, it becomes hard and elastic.

Aluminium fuses at a temperature between the melting-points of zinc and silver, and when in the molten state may be easily run into moulds of metal or sand. Although when in the form of bars, it is an extremely sonorous metal, it does not possess this quality if cast into bells. It is a good conductor of electricity. It is not affected by either damp or dry air, or by oxygen at ordinary temperatures. Water, whether cold or boiling, has no action on it, and even steam at a red heat, only slowly oxidizes it. It is not acted on by concentrated nitric acid at ordinary temperatures, and only very slowly by the boiling acid; nor by dilute sulphuric acid, sulphuretted hydrogen, and the sulphides. It is, however, readily dissolved by hydrochloric acid, both concentrated and dilute, with the evolution of hydrogen, even in the cold, and by solutions of the alkalies, especially when assisted by heat. Commercial specimens of aluminium, owing to the presence of iron, silicon, and frequently of zinc, usually tarnish in damp air, and possess the properties of pure aluminium in a somewhat diminished degree. Those specimens which contain iron are more readily soluble in acids than the pure metal.

In a finely divided state, aluminium, when heated to redness, catches fire and burns with great rapidity in the air, and in oxygen gas with intense brilliancy, the product in each case being alumina.

Aluminium unites with many metals, and forms alloys, some of which give promise of technical value. An alloy of 100 parts of aluminium with 5 parts of silver, may be worked like the pure metal, but is harder and susceptible of a finer polish, whilst its property of not being affected by sulphuretted hydrogen and acids, remains unimpaired ; even 3 per cent. of silver is said to be sufficient to impart to it the full brilliance and colour of pure silver. An alloy containing 10 per cent. of gold is softer and scarcely so malleable as the pure metal. With 6 per cent. of iron or 10 per cent. of copper it still remains tough and malleable ; but a larger proportion of either of these metals renders it brittle.

The presence of 2 or 3 per cent. of zinc or tin destroys its ductility and malleability, and also impairs its colour and lustre ; whilst less than even $\frac{1}{4}$ per cent. of bismuth renders it brittle in a high degree. Small quantities of aluminium added to other metals, change their properties in a very remarkable manner. Thus, copper alloyed with 10 per cent. of aluminium has the colour and brilliancy of gold, is harder than bronze, very malleable, and may be worked at high temperatures easier than the best varieties of iron. Made in these proportions, it forms *aluminium bronze,* and is used as a substitute for gold; with 20 per cent. it is quite white, and closely resembles silver; with more than 12 per cent. of aluminium the alloy is harder, but brittle. The alloy formed of 100 parts of silver with 5 parts of aluminium is as hard as the silver of our coinage, whilst the other properties of the latter metal remain unaltered.

The alloys of aluminium may be obtained by the process of Benzon. This method, which was patented by the inventor in 1853, consists in (1) heating alumina with an oxide of the other metal, both in equivalent proportions; (2) or by heating alumina with the other metal in a free state, likewise in equivalent quantities, and with carbon in slight excess. The materials in both cases must be finely pulverized. The solder employed in working aluminium is an alloy consisting of copper 4 parts, aluminium 6, and zinc 90. No flux is required.

Hulot gets over the difficulty of directly soldering aluminium by coating the surface with copper by electrolysis, and then applying solder in the ordinary way.

Although, from its properties, aluminium seems adapted for many useful every-day purposes, its employment has of late years, fallen into comparative disuse. At one time the eagles which adorn the standards of the French army were made of it, as well as cornets-à-piston, for which latter articles, its sonorousness especially adapted it. It is now only occasionally used for certain articles of plate and jewellery. At present its chief applications are in the manufacture of optical and surgical instruments, and the smaller decimal weights employed in the chemist's laboratory.

## SALTS OF ALUMINIUM.

With the exception of the chloride, the ordinary aluminium salts are generally colourless. Their solutions have a strongly astringent, somewhat sweetish taste, and an acid reaction. This last characteristic, joined to the tendency of its oxide to unite with basic oxides, indicates the possession by alumina of acid properties. In solution, the salts of aluminium are distinguished as follows:—Ammonia and the alkaline carbonates throw down a bulky white precipitate of hydrate of aluminium, which is nearly insoluble in excess of the precipitant. Caustic potash and soda give gelatinous white precipitates, freely soluble in excess of the precipitant, from which the hydrate of aluminium is re-precipitated by chloride of ammonium, even in the cold.

Phosphate of ammonium gives a white precipitate; iodide of potassium also a white one, passing into a permanent yellow. Bisulphate of potassium added to concentrated solutions, causes a precipitate of octahedral crystals of potash-alum. The salts of aluminium part with some of their acid at a red heat, and with most, if not the whole of it, at a white one. Aluminium compounds ignited on charcoal before the blowpipe, and afterwards moistened with a solution of nitrate of cobalt, and again strongly ignited, give an unfused mass, which on cooling appears blue by day and violet by candlelight; a test, however, which is inapplicable to fusible compounds of aluminium, and such as are not free, or nearly free, from other oxides.

**Aluminium, Acetate of.** *Syn.* ACETATE OF ALUMINA.—1. Pure hydrate of aluminium is digested to saturation in strong acetic acid in the cold, and the resulting solution, after being filtered or decanted, is either evaporated by a very gentle heat to a gelatinous semi-solid consistence, or preserved in the liquid state.

By spontaneous evaporation it may be obtained in long transparent crystals. It is mostly met with in the gelatinous semi-solid form.

2. It may also be prepared by double decomposition from sulphate of aluminium and acetate of lead, baryta, or lime. The liquor separated from sulphate of lead is evaporated to dryness by a gentle heat.

When a solution of acetate of aluminium is evaporated in contact with air, a basic acetate, which is insoluble in water, is formed, acetic acid being driven off. The feeble attraction between its acid and base constitutes its value as a mordant.

**Aluminium, Chloride of.** $Al_2Cl_6$. *Syn.* SESQUICHLORIDE OF ALUMINUM. A thick paste made of dry precipitated alumina,* lamp-black, and oil, is made into pellets, and strongly ignited in a covered crucible, until all the organic matter is carbonized. The residuum, consisting of alumina and carbon, is then transferred to a porcelain tube or tubulated retort placed in a furnace; to the end of the retort next the furnace is attached a dry receiver. At the other end is an apparatus for evolving chlorine. The furnace being heated to redness, the chlorine, dried by being carried through calcic chloride, is passed into the retort, and the resulting aluminic chloride is condensed in the receiver as a solid mass.

2. On the large scale, chloride of aluminium may be made by passing dried chlorine gas into an iron retort or cylinder heated to redness, containing a mixture of alumina or clay, lamp-black, and tar, which has been previously calcined. The retort is connected with a cool chamber lined with tiles of earthenware. The vapours of the chloride of

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* Obtained by adding an alkaline carbonate to a hot solution of alum.

aluminium which are given off, condense in this chamber as a yellowish crystalline mass. Clay containing much iron must be previously roasted with coal or coke, and afterwards treated with a dilute acid. By this means the iron which becomes reduced to a metallic state, may be dissolved out.

Aluminic chloride is volatile at a dull red heat, extremely deliquescent, and very soluble in water. Its chief use is in the prepartion of aluminium.

Although alumina, like magnesia, is freely soluble in hydrochloric acid, the chloride of aluminium contained in this solution cannot be obtained in the anhydrous state, or even the solid form, by its evaporation; as the chloride then undergoes decomposition with the formation of hydrochloric acid, which is volatilized, and alumina, which is left behind.

**Aluminium, Oxide of.** ($Al_2O_3$.) In the native state, alumina, nearly pure, is met with as *corundum*. This mineral, which occurs crystallized in six-sided prisms, is generally regarded as a sesquioxide of aluminium. In this form it has a specific gravity of 3·95; ranks in hardness next the diamond, and will cut glass. The *ruby*, *sapphire*, and *topaz* are varieties of corundum, coloured with small quantities of potassium chromate. *Hyaline* is a colourless variety of corundum. *Emery*, another native product, consists of alumina coloured with iron and manganese oxides. The mineral *diaspore* is a monohydrate, and *turquoise* a hydrated native phosphate of alumina.

Alumina may be prepared artificially by any of the following formulæ:—

1. Alum is dissolved in about 20 times its weight of distilled water, and the solution is dropped slowly into pure solution of ammonia, until the latter is nearly but not entirely saturated, when the whole is set aside for some time. The clear supernatant liquid is then decanted, and the gelatinous precipitate is carefully and thoroughly washed

three or four times, with tepid distilled water; after which it is collected on a filter, again well washed with water, and lastly, pressed and dried between bibulous paper, either without heat, or at a temperature not higher than 120° Fahr. (49° Cent.). The product is hydrate of aluminium. This hydrate may be converted into anhydrous alumina by exposure to a white heat in a covered crucible. The residuum, after ignition, is pure anhydrous alumina, or sesquioxide of aluminium.

2. A boiling solution of alum is precipitated with carbonate of ammonia, excess of the latter being avoided, and the resulting precipitate, after being thoroughly washed, is ignited.

3. Ammonia alum, after being strongly ignited for some time, loses its water, ammonia, and sulphuric acid; anhydrous alumina being left.

Traces of sulphuric acid, however, are frequently present in alumina prepared by this method.

4. By the ignition of sulphate of alumina.

Alumina prepared by any of the above methods contains iron. To free it from this, **Deville** recommends the alumina to be dissolved in caustic alkali, and the iron to be precipitated by sulphuretted hydrogen. The supernatant liquid is then to be poured off, and reprecipitated by passing carbonic acid through it. The alkaline carbonate, which invariably accompanies the alumina so obtained, may be separated by digesting the alumina in a small quantity of dilute hydrochloric or nitric acid with the aid of heat.

At all temperatures below that of the flame of the oxy-hydrogen blowpipe, factitious alumina is incapable of fusion. When exposed to the heat of the inflamed mixed gases, it melts into a colourless transparent crystalline mass resembling corundum. If, before the artificial alumina is subjected to fusion, a small quantity of potassium chromate be placed in the crucible, the product of the fusion bears a great resemblance to the natural ruby. Similarly DEVILLE has produced artificial sapphire. Alumina exposed to a moderately red heat, assumes the form of a light powder, soft to the touch. Anhydrous alumina is absolutely insoluble in water, and also, after being strongly ignited, in most acids, concentrated hydrochloric or sulphuric excepted. In the crystalline state all acids fail to dissolve it. In both states it becomes soluble after fusion with caustic potash or soda.

**Aluminium Silicate.** A substance which in its hydrated form is the chief and characteristic constituent of common clay. According to BRONGNIART and MALAGUTI, the essential and predominant ingredient of most varieties of clay is a hydrated aluminic silicate, having the formula $Al_2O_3$ $(SiO_2)_2$, $2H_2O$. Clay is formed by the disintegration of felspathic and silicious rock, by the combined action of air and water. Its plasticity when moist, and its capability of being made hard by heat, are properties which render it available for many useful purposes. The purest kind of clay is *kaolin* or *china clay*, which consists almost entirely of aluminium silicate. It is found in China; but a precisely similar substance is obtained from deposits met with at St. Austel in Cornwall, and at St. Yrieix in France. *Pipeclay*, a white clay nearly free from iron, is found in large quantity in the Isle of Purbeck: as its name indicates, it is used in the manufacture of tobacco-pipes.

*Potters' clay*, known as *blue clay*, is found in many parts of the United Kingdom; that of Devonshire and Dorsetshire is much valued. It is used in porcelain-making. *Loam*, which is a much more mixed variety of clay, is used in making bricks; it contains a large quantity of ferric oxide. *Yellow ochre* and *red bole* mostly consist of aluminium silicate, coloured with varying quantities of ferric oxide.

*Fullers' earth* is a porous aluminic silicate or clay, found in large quantity at Reigate in Surrey. The constituents usually present in the ordinary varieties of clay used in the arts, are hydrated aluminic silicate, potash, lime, magnesia, and oxide of iron. The proportions in which these ingredients are present in different kinds of clay vary greatly, a circumstance which largely influences the character of the compound.

Thus, if lime, magnesia, or peroxide of iron predominate, the clay will be a very fusible, but not a plastic one. It will also be more easily acted upon by acids. An excess of silica, on the contrary, renders the clay less fusible.

Pure clay is insoluble in water, and is very slowly attacked by nitric, or hydrochloric acids. When heated with sulphuric acid, it is decomposed, aluminic sulphate being formed; this reaction being that which takes place in alum-making. Clay possesses considerable absorbent properties, by reason of which it is able to abstract and store up, as nutriment for growing crops, ammonia, applied in the form of manure to the surface. WAY found its attraction for ammonia so powerful, that whilst sulphate and chloride of aluminium in solution were partially decomposed by the lime of the clay, with formation of a corresponding amount of sulphate or chloride of calcium, which passed into the liquid, the ammonia was retained by the clay.

ALUMINIUM SULPHATE. $Al_2(SO_4)_3,H_2O_8$. *Syn.* SESQUISULPHATE OF ALUMINIUM, NEUTRAL SULPHATE OF ALUMINIUM. Pure aluminium sulphate may be prepared by saturating dilute sulphuric acid with hydrate of aluminium, gently evaporating and crystallizing.

The preparation of the crude sulphate is described under ALUM.

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THE END.

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