This smell is the same as that evolved on burning lucifer matches that have been tipped with sulphur. It is due, probably, not to the gas (SO_2), but to sulphurous acid (H_2SO_3), formed by the union of sulphurous acid gas with either the moisture of the air or that on the surface of the mucous membrane of the nose. The gas is highly suffocating.

Second Analytical Reaction.—To a sulphite add a little water, a fragment or two of zinc, and then hydrochloric acid; sulphuretted hydrogen will be evolved, known by its odor and by its action on a piece of paper placed like a cap on the mouth of the test-tube, and moistened with a drop of solution of acetate of lead, black sulphide of lead being formed. Sulphurous acid may be detected in acetic acid, or in hydrochloric acid, by this test.

$$H_2SO_3 + H_6 = H_2S + 3H_2O.$$

Other Analytical Reactions.

To solutions of neutral sulphites add nitrate or chloride of barium, chloride of calcium, or nitrate of silver; in each case white sulphites of the various metals are precipitated. The barium sulphite is soluble in weak hydrochloric acid; but if a drop or two of chlorine-water is first added, barium sulphate is formed, which is insoluble in acids. The other precipitates are also soluble in acids. The silver sulphite is decomposed on boiling, sulphuric acid being formed, and metallic silver set free, the mixture darkening in color.

To recognize the three radicals in an aqueous solution of sulphides, sulphites, and sulphates, add chloride of barium, filter, and wash the precipitate. In the filtrate, sulphides are detected by the sulphuretted hydrogen evolved on adding an acid. In the precipitate, sulphites are detected by the odor of sulphurous acid produced on adding hydrochloric acid, and sulphates by their insolubility in the acid.

QUESTIONS AND EXERCISES.

H_2SO_3
SO_2

508. What are the differences between sulphurous acid and sulphurous acid gas, sulphites and acid sulphites?
509. State the characters of sulphurous acid gas?
510. How is the official Sulphurous Acid prepared?
511. By what test may sulphurous acid be recognized in acetic acid?
512. Give a method by which sulphites may be detected in presence of sulphides and sulphates.

SULPHURIC ACID AND OTHER SULPHATES.

Formula of Sulphuric Acid, H_2SO_4. Molecular weight, 98.

Many sulphates occur in nature; but the common and highly important hydrogen sulphate, sulphuric acid, is made artificially.

Preparation of the Acid: General Nature of the Process.—Sulphur itself, or sometimes the sulphur in iron pyrites, is first converted into sulphurous acid gas by burning in air, and this gas, by moisture and oxygen, into sulphuric acid ($SO_2 + H_2O + O = H_2SO_4$).

Details of the Process.—The oxygen necessary to oxidize the sulphurous acid gas cannot directly be obtained from air, but indirectly, the agency of nitric oxide (NO) being employed—this gas becoming nitric peroxide (NO_2) by the action of the air, and the nitric peroxide again becoming nitric oxide by the action of the sulphurous acid gas, and so on. A small quantity of nitric oxide gas will thus act as carrier of oxygen from the air to very large quantities of sulphurous acid. Nitrous anhydride (N_2O_3) may also act as the carrier.

The following equations represent the chief successive steps:—

$$\underset{\text{Sulphur.}}{S_2} + \underset{\text{Oxygen (of the air).}}{2O_2} = \underset{\text{Sulphurous acid gas.}}{2SO_2}$$

$$\underset{\text{Sulphurous acid gas.}}{SO_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Sulphurous acid.}}{H_2SO_3}$$

$$\underset{\text{Nitric oxide.}}{2NO} + \underset{\text{Oxygen (of the air).}}{O_2} = \underset{\text{Nitric peroxide.}}{2NO_2}$$

$$\underset{\text{Sulphurous acid.}}{H_2SO_3} + \underset{\text{Nitric peroxide.}}{NO_2} = \underset{\text{Sulphuric acid.}}{H_2SO_4} + \underset{\text{Nitric oxide.}}{NO}$$

On the large scale the sulphurous acid gas is produced by burning sulphur in furnaces; it is carried, together with the nitric vapors, by flues into leaden chambers, where jets of steam supply the necessary moisture; the steam also, condensing, prevents other reactions. The resulting dilute sulphuric acid is concentrated by evaporation in leaden vessels.

The nitric oxide is in the first instance obtained from nitric acid, and this from nitrate of potassium or of sodium by the action of a small quantity of the sulphuric acid of a previous operation.

$$\underset{\text{Nitrate of sodium.}}{2NaNO_3} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Sulphate of sodium.}}{Na_2SO_4} + \underset{\text{Nitric acid.}}{2HNO_3}$$

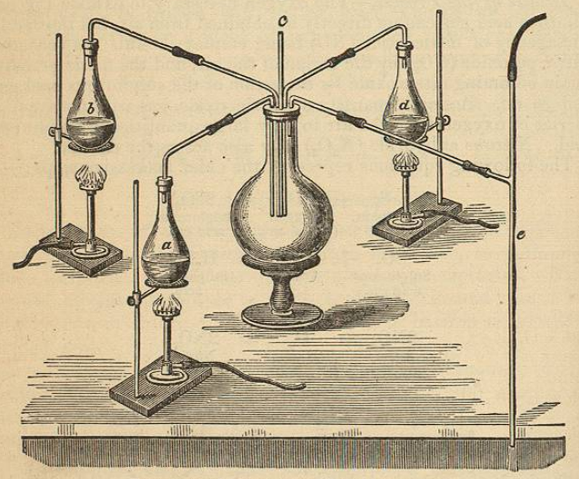
$$\underset{\text{Sulphurous acid.}}{3H_2SO_3} + \underset{\text{Nitric acid.}}{2HNO_3} = \underset{\text{Sulphuric acid.}}{3H_2SO_4} + \underset{\text{Water.}}{H_2O} + \underset{\text{Nitric oxide.}}{2NO}$$

Other Processes.—Sulphuric acid may be obtained by other processes, as by distilling the sulphate of iron resulting from the natural oxidation of iron pyrites by air; but it is seldom so made at the

present day. The sulphate of iron was formerly called *green vitriol* (p. 142), and the distilled product *oil of vitriol;* the latter in allusion to its consistence and origin.

Experiment.—For purposes of practical study, a small quantity may be made (as shown in fig. 39) by passing, *a*, sulphurous acid gas (p. 304), *b*, nitric oxide in small quantity (p. 288), *c*, air (forced through by aid of bellows or a gas-holder or drawn through by

Fig. 39.



Experimental Manufacture of Sulphuric Acid.

a *water-aspirator*, *e*), and occasionally, *d*, steam (generated in a Florence flask) through glass tubes, nearly to the bottom of a two- or three-quart flask.

$$SO_2 + H_2O = H_2SO_3; \quad | \quad 2NO + O_2 = 2NO_2;$$
$$H_2SO_3 + NO_2 = H_2SO_4 + NO.$$

A slow current of sulphurous acid gas, air, and steam, and a small quantity of nitric oxide, will furnish, in the course of a few minutes, enough sulphuric acid for recognition by the first of the following analytical reactions. The manufacturing process may be more exactly imitated by burning sulphur in a tube placed where the flask *a* is represented in the foregoing figure, or by burning it under a funnel there attached; but in either of these cases strong aspiration must be maintained.

Purification.—Sulphuric acid may contain arsenic, nitrous compounds, and salts (sulphate of lead, etc.). Arsenic may be detected by the hydrogen test (p. 171) or the stannous chloride test (p. 173),

nitrous compounds by powdered sulphate of iron (which acquires a violet tint if they are present), and salts by the residue left on boiling a little to dryness in a crucible in a fume-chamber. If only nitrous compounds are present, the acid may be purified by heating with about one-half per cent. of sulphate of ammonium—water and nitrogen being produced (Pelouze). If arsenic occurs, boil with a small quantity of hydrochloric acid, which converts the arsenic into chloride of arsenicum; or heat with a little nitric acid, which converts arsenious (As_2O_3) into arsenic anhydride (As_2O_5), then add sulphate of ammonium, and distil in a retort containing pieces of quartz and heat by an annular-shaped burner (to prevent "bumping;" see p. 279). The arsenic anhydride remains in the retort. (Arsenious anhydride would be carried over with the sulphuric acid vapors.) By distillation the acid is also purified from salts (such as $NaHSO_4$) which are not volatile.

Quantivalence.—The sulphuric radical being bivalent (SO_4''), acid as well as normal sulphates may exist. Acid sulphate of potassium ($KHSO_4$) is an illustration of the former, sulphate of sodium (Na_2SO_4) of the latter; *double sulphates* may also occur, such as that of potassium and magnesium ($K_2SO_4,MgSO_4,6H_2O$). Sulphates generally contain water of crystallization.

Pure sulphuric acid (H_2SO_4) is of specific gravity 1.848. The best "oil of vitriol" of commerce, a colorless liquid of oily consistence, is of specific gravity 1.843, and contains about 98 per cent. of real acid (H_2SO_4). A variety less pure than this "white" acid is known as "brown acid." The *Acidum Sulphuricum*, U. S. P., should contain not less than 96 per cent. of H_2SO_4, and have a sp. gr. not below 1.840. The *Acidum Sulphuricum Dilutum*, U. S. P., contains 10 per cent. of the strong acid, and should have a sp. gr. of nearly 1.067. The *Acidum Sulphuricum Aromaticum*, U. S. P., a dilute acid in which are dissolved oil of cinnamon and tincture of ginger, contains about 20 per cent. of strong acid, sp. gr. 0.955. There are some definite compounds of sulphuric acid with water; the first (H_2SO_4,H_2O) may be obtained in crystals.

Sulphuric anhydride (SO_3) is a white silky crystalline solid having no acid properties. It is made by distilling sulphuric acid with phosphoric anhydride ($H_2SO_4 + P_2O_5 = 2HPO_3 + SO_3$). On the large scale, sulphuric acid is dissociated by heat, and the dried sulphurous anhydride and oxygen made to recombine. It appears to unite with sulphuric acid and some other normal sulphates to form compounds (R'_2SO_4,SO_3) resembling in constitution red chromate of potassium or borax. The fuming sulphuric acid (H_2SO_4,SO_3), formerly made at Nordhausen in Saxony, seems to be such a body.

Note.—Sulphuric acid is a most valuable compound to all chemists and manufacturers of chemical substances. By its agency, direct or indirect, many, if not most, chemical transformations are effected. To describe all its uses would be to write a work on chemistry.

Analytical Reactions (Tests).

First Analytical Reaction.—To a solution of a sulphate add

solution of a barium salt; a white precipitate of sulphate of barium ($BaSO_4$) falls. Add nitric acid and boil the mixture; the precipitate does not dissolve.

This reaction is as highly characteristic of sulphate as it has been stated to be of barium salts (*vide* page 103). The only error likely to be made in its application is that of overlooking the fact that nitrate and chloride of barium are less soluble in strong acid than in water. On adding the barium salt to the acid liquid, therefore, a white precipitate may be obtained, which is simply the nitrate or chloride of barium. The appearance of such a precipitate differs considerably from that of the barium sulphate, hence a careful operator will not be misled. Should any doubt remain, water should be added, which will dissolve the nitrate or chloride, but not affect the sulphate.

Second Analytical Reaction.—Mix a fragment of an insoluble sulphate ($BaSO_4$, *e. g.*) with carbonate of potassium or of sodium; or, better, with both carbonates, and fuse the mixture in a small crucible. Digest the residue when cold, in water, and filter; the filtrate may be tested for the sulphuric radical.

This is a convenient method of qualitatively analyzing insoluble sulphates, such as those of barium and lead.

Third Analytical Reaction.—Mix a fragment of an insoluble sulphate with a little alkaline carbonate on a piece of charcoal, taking care that some of the charcoal-dust is included in the mixture. Heat the little heap in the blowpipe-flame until it fuses, and, when cold, add a drop of acid; sulphuretted hydrogen is evolved, recognized by its odor.

This is another process for the recognition of insoluble sulphates. Other preparations of sulphur, and sulphur itself, give a similar result. It is therefore rather a test for sulphur and its compounds than sulphates only; but the absence of other salts can generally, if necessary, be previously determined.

Note.—The presence of the sulphuric radical in a solution having been proved by the above reactions, its occurrence as the normal sulphate of a metal is demonstrated by the neutral, or nearly neutral, deportment of the liquid with test-paper, and the detection of the metal—its occurrence as sulphuric acid or an acid sulphate by the sourness of the liquid to the taste and the effervescence produced on the addition of a carbonate.

Antidote.—In cases of poisoning by strong sulphuric acid, solution of carbonate of sodium (common washing-soda), magnesia and water, etc., may be administered as antidotes.

QUESTIONS AND EXERCISES.

513. What is the formula of sulphuric acid, and what its molecular weight? H_2SO_4 weight 98

514. How is it related to other sulphates? It is the most import.

515. Write a short article on the manufacture of sulphuric acid, giving either diagrams or equations.

516. How may nitrous compounds be detected in, and eliminated from, sulphuric acid?

517. State the method by which the presence of arsenic is detected in sulphuric acid, and explain the process by which it may be removed.

518. Define sulphates, acid sulphates, and double sulphates.

519. What percentage of real acid is contained in commercial oil or vitriol?

520. State the strength of the official "diluted" and "aromatic" sulphuric acid.

521. By what process is sulphuric anhydride obtained from Nordhausen sulphuric acid?

522. Explain the reactions which occur in testing for sulphates.

523. Ascertain by calculation the weight of oil of vitriol (of 96.8 per cent.) necessary for the production of one ton of dry sulphate of ammonium.—*Ans.* 1718 pounds.

524. Name the antidotes in cases of poisoning by strong sulphuric acid.

CARBONIC ACID AND OTHER CARBONATES.

Formula of Carbonic Acid, H_2CO_3; molecular weight, 62. Formula of carbonic acid gas, or carbonic anhydride, commonly termed carbonic acid, CO_2; molecular weight, 44.

Sources.—Carbonates (compounds containing the grouping CO_3) are very common in nature, the calcium carbonate ($CaCO_3$) being widely distributed as chalk, limestone, or marble. The hydrogen carbonate, true carbonic acid, is not known, unless indeed carbonic acid gas assumes that condition on dissolving in water. Such a solution (see page 86) changes the color of blue litmus-paper, and the gas does not; this may be because only the true acid (H_2CO_3) affects the litmus, or because the gas (CO_2) cannot come into real contact with the litmus without a medium. From the commonest natural carbonate, carbonate of calcium, are derived the carbonic constituents of the one most frequently used in medicine and in the arts generally, carbonate of sodium.

Carbonate of sodium is prepared, by "the Leblanc process," from the chief natural salt, the chloride. After the chloride has been converted into sulphate (salt-cake) by sulphuric acid (or by sulphurous acid, air, and steam—Hargreave's modification)—

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl,$$

the sulphate is roasted with limestone and small coal, by which carbonate of sodium and sulphide of calcium are formed:—

$$Na_2SO_4 + C_4 + CaCO_3 = CaS + Na_2CO_3 + 4CO.$$

Carbonic oxide gas and a little carbonic acid gas from the excess of

chalk escape; the residual mass (black ash) is digested, in water, in which the carbonate of sodium dissolves, the sulphide of calcium with a little oxide remaining insoluble. The solution is evaporated to dryness, and yields true carbonate of sodium. This is roasted with a small quantity of sawdust, to convert any caustic soda resulting from the action of the lime on the carbonate into normal carbonate. The product is *soda-ash*. Dissolved in water and crystallized, it constitute the ordinary "soda" used for washing purposes; recrystallized and sometimes ground, it forms the official carbonate of sodium (*Sodii Carbonas*, U. S. P.) ($Na_2CO_3,10H_2O$). The reaction is rendered more intelligible by regarding it as occurring in two stages: 1st, the reduction of the sulphate of sodium to sulphide by the carbon of the coal—

$$Na_2SO_4 + C_4 = Na_2S + 4CO;$$

2d, the reaction of the sulphide of sodium and carbonate of calcium, giving soluble carbonate of sodium, thus—

$$Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

The sulphur in the residual sulphide (or, perhaps, oxysulphide) of calcium may be recovered by exposure to the waste carbonic acid gas of lime-kilns, carbonate of calcium being formed and the diluting nitrogen passing off, more carbonic acid afterward causing sulphuretted hydrogen to be set free. The latter is either burnt and converted into sulphuric acid, or is caused to react with air on ferric oxide, sulphur being set free.

Another Process.—To a strong solution of common salt bicarbonate of ammonium is added, when a precipitate of bicarbonate of sodium (*Sodii Bicarbonas*, B. P.) occurs. The resulting chloride of ammonium may be converted into carbonate by heating with chalk, and the carbonate be more fully carbonated by carbonic acid gas obtained by heating the bicarbonate of sodium, which is thereby reduced to the ordinary neutral carbonate (*Sodii Carbonas*, B. P.). This method is known as "the ammonia process."

Carbonic acid gas (CO_2) is a product of the combustion of all carbonaceous matters. It is constantly exhaled by animals and inhaled by plants, its intermediate storehouse being the atmosphere, throughout which it is equally distributed by *diffusion* (*vide* p. 24) to the extent of about 4 parts in 10,000. A larger proportion than that just mentioned gives to confined air depressing effects, 4 or 5 per cent. rendering the atmosphere poisonous when taken into the blood from the lungs. Carbonic acid, however, may be taken into the stomach with beneficial sedative effects; hence, probably, much of the value of such effervescing liquids as soda-water, lemonade, and solutions of the various granulated preparations and effervescing powders (*vide* p. 87). The gas liquefies on being compressed, and the liquid solidifies on being cooled. Carbonic acid gas is twenty-two times as heavy as hydrogen, and about half as heavy again as air. At common temperatures it dissolves in about its own volume of water, both being under the same pressure, the water retaining gas strongly if all air has previously been expelled.

Sulphocarbonates resemble carbonates in constitution, but contain sulphur in place of oxygen.

Sulphocarbonic anhydride, CS_2, commonly termed *bisulphide of carbon* or *disulphide of carbon* (*Carbonei Bisulphidum*, U. S. P.), is a highly volatile and inflammable liquid, easily made from its elements. Sp. gr. 1.272; boiling-point 46° C. It may be rendered almost scentless by digestion with lime and then with copper turnings. Its possible impurities are dissolved sulphur, sulphur oils, and sulphuretted hydrogen.

Reactions.

Synthetical and Analytical Reactions.—1. To a fragment of marble in a test-tube add water and then hydrochloric acid; carbonic acid gas (CO_2) is evolved, and may be conveyed into water or solutions of salts by the usual delivery-tube.

This is the process of the British Pharmacopœia, and the one usually adopted for experimental purposes. On the large scale the gas is prepared from chalk or marble and sulphuric acid, frequent stirring promoting its escape.

2. Pass the gas into lime-water; a white precipitate of carbonate of calcium ($CaCO_3$) falls. Solution of subacetate of lead may be used instead of, and is perhaps even a more delicate test than, lime-water.

The evolution of a gas on adding an acid to a salt, warming the mixture if necessary, the gas being inodorous and giving a white precipitate with lime-water, is sufficient evidence of the presence of a carbonate. Carbonates in solution of ammonia, potash, or soda may be detected by the direct addition of solution of lime. Carbonates in presence of sulphites or hyposulphites may be detected by adding acid tartrate of potassium, which decomposes carbonates with effervescence, but does not attack sulphites or hyposulphites.

3. Blow air from the lungs through a glass tube into lime-water; the presence of carbonic acid gas is at once indicated.

The passage of a considerable quantity of normal air through lime-water produces a similar effect. A bottle containing lime-water soon becomes coated with carbonate of calcium from absorption of atmospheric carbonic acid gas.

4. Fill a dry test-tube with the gas by pressing the delivery-tube of the above apparatus to the bottom of the test-tube. Being rather more than once and a half as heavy as the air (1.529), it will displace the latter. Prove the presence of the gas by pouring it slowly, as if a visible liquid, into another test-tube containing lime-water; the characteristic cloudiness and precipitate are obtained on gently shaking the lime-water.

In testing for carbonates by bringing evolved gas into contact with lime-water, the preparation and adaptation of a delivery-tube may

often be avoided by pouring the gas from the generating-tube into that containing the lime-water in the manner just indicated.

5. Pass carbonic acid gas through lime-water until the precipitate at first formed is dissolved. The resulting liquid is a solution of carbonate of calcium in carbonic acid water. Boil the solution; carbonic acid gas escapes, and the carbonate is again precipitated.

This experiment will serve to show how chalk is kept in solution in ordinary well-waters, giving the property of "hardness," and how the *fur* or stone-like deposit in tea-kettles and boilers is formed. It should be here stated that sulphate of calcium produces similar hardness, and that these, with small quantities of the sulphate and carbonate of magnesium, constitute the hardening constituents of well-waters, a curd (oleate of calcium or magnesium) being formed whenever soap is used with such waters. An enormous amount of soap is wasted through the employment of hard water for washing purposes. The hardness produced by the earthy carbonates is termed "temporary hardness," because removable by ebullition; that by the earthy sulphates "permanent hardness," because unaffected by ebullition. The addition of lime-water or a mixture of lime and water removes temporary hardness (reac. 2, page 313) and carbonate of sodium, "washing soda," both temporary and permanent hardness, in the latter case sulphate of sodium remaining in solution. Carbonate of barium (ground witherite) also decomposes sulphates of calcium and magnesium, sulphate of barium being precipitated and carbonates of calcium or magnesium formed; the latter and the carbonates originally in the water may then be precipitated by ebullition or by the action of lime-water. But the injurious effects of barium salts on man and the lower animals prevent the carbonate being used for purifying water for drinking purposes, as by accident or an unforeseen reaction a portion might become dissolved.

6. Add a solution of *carbonate* of potassium or sodium to a mercuric salt; a brownish-red precipitate results. Add a solution of *bicarbonate* of potassium or sodium to a mercuric solution; a white precipitate results, becoming red after some time.

QUESTIONS AND EXERCISES.

525. Name the chief natural carbonates.
526. What are the formulæ of carbonic acid and carbonic acid gas?
527. Adduce evidence of the existence of true carbonic acid.
528. Trace the steps by which the carbonic constituent of chalk is transferred to sodium by the process usually adopted in alkali-works—the manufacture of "soda."
529. Carbonic acid gas is constantly exhaled from the lungs of animals; why does it not accumulate in the atmosphere?

530. What is the effect of pressure on carbonic acid gas?
531. State the specific gravity of carbonic acid gas.
532. By what processes may carbonic acid gas be obtained for experimental and manufacturing purposes?
533. Describe the action of carbonic acid gas on the carbonates of potassium or sodium.
534. How may carbonic acid be detected in expired air?
535. To what extent is carbonic acid gas heavier than air?
536. Work sums showing what quantity of chalk (90 per cent. pure) will be required to furnish the carbonic acid necessary to convert one ton of carbonate of potassium (containing 83 per cent. of K_2CO_3) into acid carbonate, supposing no gas to be wasted?—*Ans.* 1500 lbs.
537. Define "hardness" in water.
538. How may the presence of carbonates be demonstrated?

OXALIC ACID AND OTHER OXALATES.

Formula of Oxalic Acid $H_2C_2O_4,2H_2O$. Molecular weight 126.

Source.—Oxalates occur in nature in the juices of some plants, as wood-sorrel, rhubarb, the common dock, and certain lichens; but the hydrogen oxalate (oxalic acid) and other oxalates are all made artificially. The carbon of many organic substances yields oxalic acid when those substances are boiled with nitric acid, and an alkaline oxalate when they are roasted with a mixture of the hydrates of potassium and sodium.

Experimental Process.—On the small scale, a mixture of nitric acid 10 parts, loaf sugar 2 parts, and water 3 parts, quickly yields the acid. Abundance of red fumes are at first evolved. On cooling, crystals are deposited. A more dilute acid, kept warm, acts more slowly, but yields a larger product.

Manufacturing Process.—On the large scale, sawdust is roasted with alkalies, resulting oxalate of sodium decomposed by lime with formation of oxalate of calcium, the latter digested with sulphuric acid, and the liberated oxalic acid (Oxalic Acid of Commerce, B. P.) made commercially pure by recrystallization.

Purified Oxalic Acid.—The acid made from sugar, recrystallized two or three times, is quite pure. Commercial acid should be mixed with insufficient water for complete solution, and the mixture occasionally shaken. Most of the impurities remain undissolved, and the saturated solution evaporated yields crystals which are fairly pure.

Quantivalence.—The elements represented by the formula C_2O_4 are those characteristic of oxalates. They form a bivalent grouping; hence normal oxalates ($R'_2C_2O_4$) and acid oxalates ($R'HC_2O_4$) exist.

Salt of sorrel is a crystalline compound of oxalic acid with acid potassium oxalate, the crystals containing two molecules of water of crystallization ($KHC_2O_4,H_2C_2O_4,2H_2O$).

Oxalate of iron (*Ferri Oxalas*, U. S. P., FeC_2O_4,H_2O) is a crys-

talline yellow powder. It may be made by precipitating a solution of sulphate of iron with an oxalate. When heated in contact with air it decomposes with a faint combustion, and leaves a residue of not less than 49.3 per cent. of red oxide of iron.

Analytical Reactions (Tests).

First Analytical Reaction.—To solution of an oxalate (oxalate of ammonium, *e. g.*) add solution of chloride of calcium; a white precipitate falls. Add to the precipitate excess of acetic acid; it is insoluble. Add hydrochloric acid; the precipitate is dissolved.

The formation of a white precipitate on adding a calcium or barium salt, insoluble in acetic but soluble in hydrochloric or nitric acid, is usually sufficient proof of the presence of an oxalate. The action of the liquid on litmus-paper, effervescence with carbonate of sodium, and absence of metals, would indicate that the oxalate is that of hydrogen, oxalic acid.

Note—The *barium* oxalate *is* slightly soluble in acetic acid (Souchay and Lenssen), and enough may be dissolved by this acid from a mixed barium precipitate (produced on adding chloride or nitrate of barium to a solution of mixed salts) to give the foregoing reaction on adding chloride of calcium to the filtered acetic liquid—an effect sometimes useful in the analysis of mixed substances (Davies).

Antidote.—In cases of poisoning by oxalic acid or salt of sorrel, chalk and water may be administered as a chemical antidote (with the view of producing the insoluble oxalate of calcium), emetics and the stomach-pump being used as soon as possible.

Second Analytical Reaction.—Heat a fragment of any dry common fixed metallic oxalate (an oxalate of potassium, for example) in a test-tube; decomposition occurs, carbonic oxide (CO) (a gas that will be noticed subsequently) is liberated, and a carbonate of the metal remains. Add water and then an acid to the residue; effervescence occurs.

This is a ready test for ordinary insoluble oxalates, and is trustworthy if, on heating the substance, no charring occurs, or not more than gives a gray color to the residue. Organic salts of metals decompose when heated, and leave a residue of carbonate, but except in the case of oxalate the residue is always accompanied by much charcoal. Insoluble oxalates and organic salts of such metals as lead and silver are, of course, liable to be reduced to oxide or even metal by heat. Such oxalates may be decomposed by boiling with solution of carbonate of sodium, filtering, and testing the filtrate for oxalates by the chloride-of-calcium test.

Other Analytical Reactions.—Nitrate of silver gives, with oxalates, white oxalate of silver ($Ag_2C_2O_4$).——Dry oxalates are decomposed when heated with strong sulphuric acid, carbonic oxide and carbonic acid gas escaping. If much of the substance be operated on, the gas may be washed with an alkali, the carbonic acid be thus removed, and the carbonic oxide be ignited; it will be found to burn with a characteristic bluish flame.——Oxalates, when mixed with water, black oxide of manganese (free from carbonates), and sulphuric acid, yield carbonic acid gas, which may be tested by lime-water in the usual manner.——Not only such insoluble oxalates as those of lead and silver, above referred, to, but any common insoluble oxalates, such as those of calcium and magnesium, may be decomposed by ebullition with solution of carbonate of sodium; after filtration the oxalic radical will be found in the clear liquid as soluble oxalate of sodium.

QUESTIONS AND EXERCISES.

539. Explain the constitution of oxalates.
540. State how oxalates are obtained.
541. What is the quantivalence of the oxalic radical?
542. Give the formula of "salt of sorrel."
543. Mention the chief test for oxalic acid and other soluble oxalates.
544. Name the antidote for oxalic acid, and describe its action.
545. By what reactions are insoluble oxalates recognized?

TARTARIC ACID AND OTHER TARTRATES.

Formula of Tartaric Acid $H_2C_4H_4O_6$. Molecular weight 150.

Source.—Tartrates exist in the juice of many fruits; but it is from that of the grape that our supplies are usually obtained. Grape-juice contains much acid tartrate of potassium ($KHC_4H_4O_6$), which is gradually deposited when the juice is fermented, as in making wine; for acid tartrate of potassium, not very soluble in aqueous liquids, is still less so in spirituous, and hence crystallizes out as the sugar of the grape-juice is gradually converted into alcohol. It is found with tartrate of calcium lining the vessels in which wine is kept; and it is from this crude substance, termed *urgal* or *argol*, also from the albumenoid yeasty matter or "lees" deposited at the same time, as well as from what tartrate may be remaining in the marc left after the juice has been pressed from the grapes, that by rough crystallization "tartar," still containing 6 or 7 per cent. or more of anhydrous tartrate of calcium ($CaC_4H_4O_6$), is obtained. From the latter tartaric acid and other tartrates are prepared. In old dried grapes (Raisins; *uvæ*, B. P.) crystalline masses of tartar and of grape-sugar are constantly met with.

Cream of Tartar, purified by crystallization (*Potassii Bitartras*,

U. S. P.), occurs as a "gritty white powder, or fragments of cakes crystallized on one surface;" of a pleasant acid taste, soluble in 180 parts of cold and 6 of boiling water, insoluble in spirit.* "If 1 gm. of Bitartrate of Potassium be digested with 5 c.c. of diluted acetic acid for half an hour, then diluted with distilled water to 500 c.c., the solution agitated and filtered, and 25 c.c. of the filtrate treated with 5 c.c. of test-solution of oxalate of ammonium, the liquid should not become cloudy in less than one minute, nor distinctly turbid in less than one minute and a half (absence of more than 6 per cent. of tartrate of calcium)."—U. S. P.

Quantivalence.—The elements represented by the formula $C_4H_4O_6$ are those characteristic of tartrates. They form a bivalent grouping; hence normal tartrates ($R'_2C_4H_4O_6$) and acid tartrates ($R'HC_4H_4O_6$) exist. Tartrate of potassium, the *Potassii Tartras* of the U. S. Pharmacopœia ($K_2C_4H_4O_6$), and Rochelle Salt, or tartrate of potassium and sodium ($KNaC_4H_4O_6,4H_2O$), the official *Potassii et Sodii Tartras* (*Soda Tartarata*, B. P.), are illustrations of normal tartrates, while Cream of Tartar is an example of acid tartrates. The only official tartrate not apparently included in these general formulæ is tartar-emetic (*Antimonium Tartaratum*, B. P., *Antimonii et Potassii Tartras*, U. S. P.), which is sometimes regarded as the double tartrate of potassium and a hypothetical radical, antimonyl (SbO), thus $KSbOC_4H_4O_6$. Probably, however, it is but an oxytartrate of antimony ($Sb_2O_2C_4H_4O_6$) with normal tartrate of potassium ($K_2C_4H_4O_6$); for there are several oxycompounds of antimony analogous to the oxycompounds of bismuth that have been described (p. 249), normal salts partially decomposed by water into oxides, and many of these oxycompounds readily unite with normal salts of other basylous radicals. Tartar-emetic would thus be oxytartrate of antimony, with tartrate of potassium ($Sb_2O_2C_4H_4O_6,K_2C_4H_4O_6$).

Tartaric Acid.

Tartaric Acid (*Acidum Tartaricum*, U. S. P.) is obtained by boiling cream of tartar (*Potassii Bitartras*, U. S. P.) with water, adding chalk till effervescence ceases, and then chloride of calcium so long as a precipitate falls; the two portions of tartrate of calcium thus consecutively formed are thoroughly washed, treated with sulphuric acid, the mixture boiled for a short time, resulting sulphate of calcium mostly separated by filtration, the filtrate concentrated by evaporation, any sulphate of calcium that may have deposited removed as before, and concentration continued until the solution is

* A boiling solution of tartar yields a floating crust of minute crystals on cooling—just as milk yields a floating layer of cream, hence the term *cream* of tartar.

"It is called *tartar*," says Paracelsus, "because it produces oil, water, tincture, and salt, which burn the patient as Tartarus does." *Tartarus* is Latin (Τάρταρος, Tartaros, Greek) for *hell*. The products of its destructive distillation are certainly somewhat irritating in taste and smell; and the "salt" (carbonate of potassium) that is left is diuretic, and, in larger quantities, powerfully corrosive.

strong enough to crystallize. Tartrate of calcium from 9 ounces of cream of tartar requires 5 ounces by weight of sulphuric acid for complete decomposition.

$$\underset{\text{Acid tartrate of potassium.}}{2KHC_4H_4O_6} + \underset{\text{Carbonate of calcium.}}{CaCO_3} = \underset{\text{Tartrate of calcium.}}{CaC_4H_4O_6} + \underset{\text{Tartrate of potassium.}}{K_2C_4H_4O_6} + \underset{\text{Water.}}{H_2O} + \underset{\text{Carbonic acid gas.}}{CO_2}$$

$$\underset{\text{Tartrate of potassium.}}{K_2C_4H_4O_6} + \underset{\text{Chloride of calcium.}}{CaCl_2} = \underset{\text{Tartrate of calcium.}}{CaC_4H_4O_6} + \underset{\text{Chloride of potassium.}}{2KCl}$$

$$\underset{\text{Tartrate of calcium.}}{2CaC_4H_4O_6} + \underset{\text{Sulphuric acid.}}{2H_2SO_4} = \underset{\text{Sulphate of calcium.}}{2CaSO_4} + \underset{\text{Tartaric acid.}}{2H_2C_4H_4O_6}$$

Tartaric acid occurs in trade in colorless crystals, or the same powdered It is strongly acid and readily soluble in water or spirit. One part in 8 of water and 2 of spirit of wine forms "Solution of Tartaric Acid," B. P. Its aqueous solution is not stable.

Parcels of tartaric acid often contain crystals of an allotropic or physically isomeric modification (*vide* "Allotropy" and "Isomerism" in Index). It is termed *Paratartaric acid* (*παρὰ*, *para*, beside) or *Racemic acid* (*racemus*, a bunch of grapes), and is a combination of ordinary tartaric acid, whose solution twists a ray of polarized light to the right hand (dextrotartaric or dextroracemic acid), and of lævotartaric or lævoracemic acid, whose solution twists a polarized ray to the left. Racemic acid is inactive in this respect, the opposite properties of its constituents neutralizing each other. Racemic acid is less soluble in alcohol than tartaric acid.

Reactions.

Tartrate of Potassium.

Synthetical Reaction.—To a small quantity of a strong solution of carbonate of potassium add acid tartrate of potassium so long as effervescence occurs; the resulting liquid is solution of normal tartrate of potassium (*Potassii Tartras*, U. S. P.) (K_2T), crystals of which may be obtained on evaporation.

Note.—This is a common method of converting an acid salt of a bivalent acidulous radical into a normal salt. The carbonate added need not be a carbonate of the same, but may be of a different metal; compounds like Rochelle salt ($KNaC_4H_4O_6$) are then obtained. Thus:—

Tartrate of Potassium and Sodium.

To a strong hot solution of carbonate of sodium add acid tartrate of potassium until effervescence ceases; the resulting liquid is solution of tartrate of potassium and sodium; on cooling, it yields crystals. This is the official process (*Soda Tartarata*, B. P.; *Potassii et Sodii Tartras*, U. S. P.) ($KNaC_4H_4O_6,4H_2O$).