

Table of the Chlorine Acids.

Hydrochloric acid	HCl.
Hypochlorous acid	HClO.
Chlorous acid	HClO ₂ .
Chloric acid	HClO ₃ .
Perechloric acid	HClO ₄ .

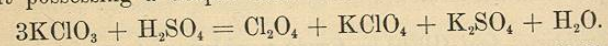
The chloric radical is univalent (ClO₃). The acidulous radicals of the other chlorine acids are also univalent, as indicated in the foregoing formulæ.

Analytical Reactions (Tests).

First Analytical Reaction.—To solution of a chlorate (*e. g.*, chlorate of potassium) add solution of nitrate of silver; no precipitate falls, showing that the chlorine must be performing different functions from those it possesses in chlorides. Evaporate the solution to dryness, and place the residue in a small dry test-tube, or at once drop a fragment of a chlorate into a test-tube, and heat strongly; oxygen is evolved, and may be recognized by its power of re-inflaming an incandescent match inserted in the tube. Boil the residue with water, and again add solution of nitrate of silver; a white precipitate falls, having all the characters of chloride of silver, as described under Hydrochloric Acid.

This is a trustworthy test, and, even omitting the recognition of the oxygen, may be applied in the detection of small quantities of chlorates.

Second Analytical Reaction.—To a fragment of a chlorate add two or three drops of strong sulphuric acid; an explosive gas (Cl₂O₄) is evolved, somewhat resembling chlorine in odor, but possessing a deeper color than that element.



Warm the upper part of the test-tube to 150° or 200° F., or introduce a hot wire; a sharp explosion ensues, due to decomposition of the gas, peroxide of chlorine, into its elements.

Third Analytical Reaction.—Heat a small fragment of a chlorate with hydrochloric acid: a yellowish-green explosive gas termed *euchlorine* is evolved. Its color is deeper than that of chlorine, hence the name (from εὖ, *eu*, well, and χλωρός, *chlōros*, green). In odor it resembles chlorine, and is probably a mixture of that element with one of the oxides of chlorine.

Fourth Analytical Reaction.—Direct the blowpipe-flame on to charcoal until a spot is red hot, and then place on the spot a fragment of a chlorate; deflagration ensues as with nitrates.

Bromates.

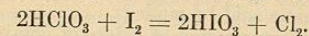
Bromates are salts closely resembling chlorates and iodates. The formula of Bromic Acid is HBrO₃. The presence of bromates in bromides is shown by the production of a yellow color on addition of diluted sulphuric acid, $5\text{KBr} + \text{KBrO}_3 + 3\text{H}_2\text{SO}_4 = 3\text{K}_2\text{SO}_4 + 3\text{H}_2\text{O} + 3\text{Br}_2$.

Iodates.

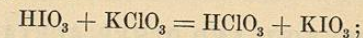
Iodic Acid (HIO₃).—Iodine is boiled in a flask with five times its weight of the strongest nitric acid (sp. gr. 1.5), in a fume-cupboard, until all action ceases. On cooling, iodic acid separates in small pyramidal crystals. These are removed, the residual liquid evaporated to dryness to remove excess of nitric acid, the residue and the first crop dissolved in a small quantity of boiling water, and the solution set aside to crystallize.

Iodate of Potassium (KIO₃).—Powder together equal weights of iodine and chlorate of potassium; to the mixture add twice its weight of water and about one-eighth of its weight of nitric acid; warm the whole until iodine disappears, and evaporate quite to dryness over a water-bath. The residue dissolved in water forms the reagent "Solution of Iodate of Potassium." It contains a little nitrate of potassium.

In this reaction the small quantity of nitric acid furnishes corresponding amounts of nitrate of potassium and chloric acid. The chloric acid with iodine gives iodic acid and chlorine, thus:—

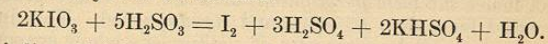


The iodic acid and some chlorate of potassium then yield chloric acid and iodate of potassium—



and the two reactions alternate until the whole of the iodine has displaced the whole of the chlorine.

Iodate of potassium and sulphurous acid decompose each other with elimination of iodine (or with formation of a blue color, if starch be present.) Sulphurous acid occurring as an impurity in acetic and other acids may thus be detected.



If iodic acid solution be mixed with mucilage of starch, and solution of sulphuretted hydrogen be added, a blue zone is formed at the junction of the liquids.

Ferric iodate, or rather **Oxyiodate** (Fe₂O₄IO₃·8H₂O), is precipitated on adding solution of ferric chloride to solution of iodate of potassium.

QUESTIONS AND EXERCISES.

462. How may hypochlorous acid be formed?

463. What are the relations of hypochlorous acid to common bleaching-powder?

464. By what reaction is chlorine eliminated from hypochlorites?
 465. State the general reaction by which chlorates are formed.
 466. Give details of the preparation of chlorate of potassium.
 467. Mention the properties of chlorate of potassium.
 468. What decompositions occur when chlorate of potassium is heated?
 469. Find the molecular weight of chlorate of potassium.
 470. What weight of oxygen is yielded when 1 oz. of chlorate of potassium is completely decomposed, and how much chloride of potassium remains?
 471. One hundred cubic inches of oxygen, at 60° F. and barometer at 30 inches, weighing 34.203 grains, and 1 gallon containing 277½ cubic inches, what weight of chlorate of potassium will be required to yield 10 gallons of the gas? *Ans.* 5½ ounces.
 472. How many cubic inches of oxygen are producible from 1 oz. of chlorate of potassium?
 473. Calculate the weight of chlorate of potassium theoretically obtainable from 100 parts of chloride.
 474. How is perchloric acid prepared?
 475. Enumerate the chlorine acids.
 476. How may the presence of chlorides in chlorates be demonstrated?
 477. Mention the tests for chlorates.
 478. Give the formula of peroxide of chlorine.
 479. What is euchlorine?
 480. How may iodic acid be made?
 481. Describe the preparation of iodate of potassium.

ACETIC ACID AND OTHER ACETATES.

Formula of Acetic Acid $\text{HC}_2\text{H}_3\text{O}_2$. Molecular weight 60.

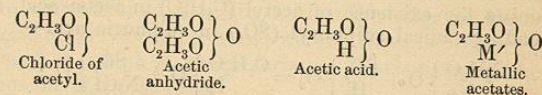
Source.—Acetic acid is said to occur naturally in certain plant juices and animal fluids in minute proportions, but otherwise is an artificial product. Much is furnished by the destructive distillation of wood, hence the term *pyroligneous acid* for the crude product, a hybrid word from *πῦρ*, *pῦr*, fire, and *lignum*, wood. This impure product, neutralized by carbonate of sodium, the whole evaporated, and the residue gently heated to drive off the volatile tarry matters, gives acetate of sodium, which after recrystallization furnishes by distillation with oil of vitriol and water acetic acid in a fair state of purity. In Germany and France large quantities of acetic acid are made by the spontaneous oxidation of the alcohol in inferior wines, in the presence, according to Pasteur, of a plant-ferment termed *Mycoderma aceti* (the *Bacterium mycodermi* of Cohn); hence the *white- and red-wine vinegar* (*vinegar*, from the French *vin*, wine, and *aigre*, sour). Indeed this bacterium may be propagated, and the artificial manufacture of vinegar from alcohol and water be carried out, by its acid, on a large scale. In England also the domestic form of acetic acid (brown vinegar) has a similar origin: infusion of

malt and unmalted grain is fermented, and the resulting oxidation of its sugar, instead of being arrested when the product is an alcoholic liquid, a sort of beer, is allowed to go on to the next stage, acetic acid; it usually contains from 3 to 6 per cent. of real acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$).

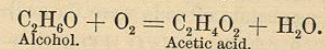
Vinegars.—Ordinary brown vinegar contains about 5½ per cent. of acid. The so-called Vinegar of Cantharides (*Acetum Cantharidis*, B. P.) is a solution of the active principle of cantharides in very strong acetic acid, not in vinegar. The Vinegar of Squill (*Acetum Scillæ*, U. S. P.) is also a solution of the active principle of squill in diluted acetic acid, not in true vinegar. The same may be said of *Acetum Lobeliæ*, U. S. P., and *Acetum Sanguinariæ*, U. S. P. (Vinegar of Blood-root). The *Acetum Opii*, U. S. P., or *Black Drop* of America, is made from nutmeg, saffron, and sugar, as well as Opium and Diluted Acetic Acid.

The Acetic Radical.—The group of elements represented by the formula $\text{C}_2\text{H}_3\text{O}_2$ is that characteristic of acetic acid and other acetates, and may, for the convenience of study, be assumed to be an acidulous univalent radical. But different strengths are sold under certain numbers which in the United States refer to the number of grains of bicarbonate of sodium neutralized by 1 fluidounce (wine measure), and in Great Britain refer to the number of grains of anhydrous carbonate of sodium neutralized by 1 Imperial fluidounce.

Acetyl.—The characteristic grouping in acetates, $\text{C}_2\text{H}_3\text{O}_2$, is frequently considered to contain, rather than to be, a radical— $\text{C}_2\text{H}_3\text{O}$, termed *acetyl*. Acetates yield a body having the composition $\text{C}_2\text{H}_3\text{OCl}$, which is regarded as chloride of acetyl; from this may be obtained acetic anhydride ($\text{C}_4\text{H}_6\text{O}_3$), which by absorbing water becomes acetic acid.



The relation of acetic acid to alcohol will be evident from the following equation representing empirically the formation of the acid:—



Acetates in aqueous solution are liable to decomposition. In solution of acetate of morphine a myceloid growth occasionally forms, acetic acid disappears, and morphine is deposited. Solution of acetate of ammonium is liable to a similar change, gradually becoming alkaline.

Synthetical Reaction.

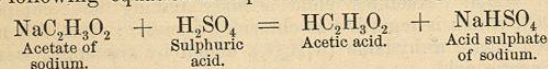
Acetic Acid.

Synthetical Reaction.—To a few grains of acetate of sodium, in a test-tube add a little water and some sulphuric acid, and heat the mixture; acetic acid is evolved, and may be con-

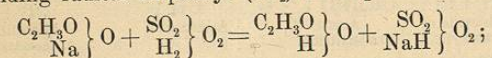
densed by a bent tube adapted to the test-tube by a cork in the usual way.

Acetic Acid.—This is the process by which acetate of sodium or calcium (the neutralized products of the distillation of wood) is made to yield acetic acid on the large scale. As with nitric and hydrochloric acids, the loose term "acetic acid" is that usually applied to aqueous solutions of acetic acid. The *Acidum Aceticum*, U. S. P., contains 36 per cent. of real acid, that is, of $\text{HC}_2\text{H}_3\text{O}_2$; for it contains only 30.6 per cent. of *acetic anhydride* ($\text{C}_4\text{H}_6\text{O}_3$)—still occasionally though somewhat obscurely termed *anhydrous acetic acid*. Its specific gravity is 1.048. *Acidum Aceticum Dilutum*, U. S. P., contains 6 per cent. of $\text{HC}_2\text{H}_3\text{O}_2$. Sp. gr. 1.0083. Glacial acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$) contains no water. It solidifies to a crystalline mass at and below 15°C . (59°F .), hence the appellation *glacial* (from *glacies*, ice). Sp. gr. from 1.056 to 1.058. Good commercial glacial acetic acid (*Acidum Aceticum Glaciale*, U. S. P.) does not contain more than 1 per cent. of water. Although water is lighter than this acetic acid, yet the addition of water at first renders the acid heavier; evidently, therefore, condensation or contraction in bulk occurs on mixing the liquids: after 10 per cent. has been added, the addition of more water produces the usual effect of dilution of a heavy liquid by a lighter—namely, reduction of relative weight. This matter will be better understood after the subject of specific gravity has been studied.

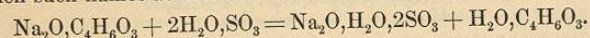
The following equation is expressive of the foregoing reaction:—



or, assuming the existence of acetyl ($\text{C}_2\text{H}_3\text{O}$) in acetic acid, and a corresponding radical sulphuryl (SO_2) in sulphuric acid—



or, thirdly, on the assumption that salts contain the oxide of a basylous radical united with the anhydride of an acid (the old view under which such names as acetate of soda were formed)—



Note on the Constitution of Salts.

Which of these three equations, or, more broadly, which of the three views of the constitution of salts illustrated by the equations, is correct, it is impossible to say. Whether it is $\text{C}_2\text{H}_3\text{O}_2$, $\text{C}_2\text{H}_3\text{O}$, or $\text{C}_4\text{H}_6\text{O}_3$, which migrates from one acetic compound to another, whether it is SO_4 , SO_2 , or SO_3 , which migrates from one sulphuric compound to another, and so on with other acidulous groupings, cannot at present be determined. There are strong objections to each view; and possibly neither is right. Either the given radicals cannot be isolated, or application of the forces of heat, light, and electricity do not confirm views arrived at by the results of opera-

tions with the chemical force; or a salt comes to be regarded as having so large a number of constituent parts that the view, however true, breaks down in practice from the sheer inability of the student to grasp the complicated analogies involved. Yet for the purposes of description, study, and conversation some system must be adopted. Let the first, then, be generally taken for the present, over-reliance on it being checked by the use of general instead of special names for the hypothetical radicals, and other systems be employed in other cases.

Analytical Reactions (Tests).

First Analytical Reaction.—To an acetate add sulphuric acid and heat the mixture; acetic acid, recognized by its odor, is evolved.

Note 1.—Iodine, sulphurous acid, and other substances of powerful odor, mask that of acetic acid; they must be removed, therefore, usually by precipitation or oxidation, before applying this test.

Note 2.—It will be noticed that this reaction is identical with the previous one; it has synthetical or analytical interest, according to the object and method of its performance.

Second Analytical Reaction.—Repeat the above action, a few drops of spirit of wine being first added to the acetate; acetic ether (acetate of ethyl, $\text{C}_2\text{H}_5\text{C}_2\text{H}_3\text{O}_2$), also of characteristic odor, is evolved.

The basylous radical ethyl (C_2H_5) will be referred to subsequently.

Third Analytical Reaction.—Heat a fragment of a dry acetate in a test-tube, and again notice the odor of the gaseous products of the decomposition; among them is *acetone* ($\text{C}_3\text{H}_6\text{O}$), the smell of which is characteristic. Carbonate of the metal remains in the test-tube.

Fourth Analytical Reaction.—To a solution of an acetate made neutral by the addition of acid or alkali, as the case may be, add a few drops of neutral solution of perchloride of iron; a deep-red liquid results, owing to the formation of ferric acetate ($\text{Fe}_2(\text{C}_2\text{H}_3\text{O}_2)_3$). Boil; a precipitate of oxyacetate of iron occurs, leaving the liquid colorless. Strong acids also decompose ferric acetate.

Analytical Note.—It will be noticed that the formation of characteristic precipitates, the usual method of removing radicals from solution for recognition, is not carried out in the qualitative analysis of acetates. This is because all acetates are soluble. Acetate of silver ($\text{AgC}_2\text{H}_3\text{O}_2$) and mercurous acetate ($\text{HgC}_2\text{H}_3\text{O}_2$) are only sparingly soluble in cold water, but the fact can seldom be utilized in analysis. Hence peculiarities of color and odor, the next best characters on which to rely, are adopted as means by which acetates

may be detected. Acetates, like other organic compounds, char when heated to a high temperature.

Note on Anhydrides.—Up to this point the student has regarded an anhydride as a body derived from an acid by removal of the whole of the hydrogen of the acid, together with as much of its oxygen as with the hydrogen forms water. The definition will scarcely apply to acetic anhydride, and must therefore be somewhat qualified. An *anhydride* is derived from an acid, the acid having lost the whole of its *basylous* hydrogen and so much oxygen as is necessary to form water with that hydrogen. Anhydrides are obtained by heating acids, and by other methods.

QUESTIONS AND EXERCISES.

482. What is the formula of acetic acid?
483. State the relation of acetic acid to other acetates.
484. What is the molecular weight of acetic acid?
485. Name the sources of acetic acid.
486. What is pyroligneous acid?
487. From what compound is the acetic acid of foreign and English vinegar immediately derived?
488. How much real acid is contained in official vinegar?
489. What is the nature of the "Vinegars" of Pharmacy?
490. How may acetic acid be obtained from acetate of sodium?
491. How much real acid is contained in the official acetic acid?
492. Mention the strength of commercial glacial acetic acid.
493. Give three or more views of the constitution of acetates, illustrating each by formulæ.
494. Enumerate the tests for acetates.

HYDROSULPHURIC ACID AND OTHER SULPHIDES.

Formula of Hydrosulphuric Acid H_2S . Molecular weight 34.

Source and Varieties of Sulphur.—The acidulous radical of *hydrosulphuric acid*, *sulphydric acid*, or *sulphuretted hydrogen*, and other sulphides, is the element sulphur (S). It occurs in nature in combination with metals, as already stated in describing the ores of some of the metals, and also in the free state. Most of the sulphur used in medicine is imported from Sicily, where it occurs chiefly associated with blue clay. It is purified by fusion, sublimation, or distillation. Melted and poured into moulds, it constitutes a crystalline mass termed *roll sulphur*. If distilled and the vapor carried into large chambers, so that it may be rapidly condensed, the crystals are so minute as to give the sulphur a pulverulent character; this is *sublimed sulphur* (*Sulphur Sublimatum*, U. S. P.) or *flowers of sulphur*: the same washed with dilute ammonia, to remove the traces of sulphuric acid (often 0.1 per cent., resulting from very slow oxidation in ordinary moist air), or, possibly, arsenious sulphide, constitutes *Sulphur Lotum*, U. S. P.

The third common form, *milk of sulphur*, will be noticed subse-

quently. Sulphur also occurs in nature in combination as a constituent of animal and vegetable tissues, as sulphurous acid gas (SO_2) in volcanic vapors, and as sulphuretted hydrogen in some waters, as those of Harrogate.

Plastic sulphur is one of the allotropic varieties of the element, obtained on heating sulphur considerably beyond its melting-point and pouring into cold water.

Quantivalence.—Sulphur is sexivalent, as seen in sulphuric anhydride (SO_3), a substance which will be noticed under sulphuric acid. It also occasionally exhibits quadrivalent (SO_2) and still oftener bivalent affinities (H_2S).

Molecular Weight.—At very high temperatures sulphur follows the rule that, under similar conditions of heat and pressure, atomic weights (in grammes, grains, etc.) of volatile elements occupy equal volumes of vapor; its formula therefore is S_8 , and molecular weight 64. At lower temperatures the volume weighs three times as much as it should do if following usual laws, and then the molecule would appear to contain six atoms (S_6).

Acid Salts.—Sulphur (S'') being the first acidulous radical of bivalent activity met with in these sections on acids, it is desirable here to draw attention to a new class of salts to which such a radical will generally give rise. These are acid salts, which are intermediate between normal salts and acids. Univalent radicals with an atom of hydrogen give an acid, and with an atom of other basylous radicals an ordinary or normal salt. But bivalent radicals, from the fact that they give with two atoms of hydrogen an acid, and with two atoms of univalent metals a normal salt, may obviously give intermediate bodies containing one atom of hydrogen and one atom of metal: these are appropriately termed acid salts: they are neither normal acids nor normal salts, but *acid salts*. (Examples: $KHCO_3$, $NaHSO_4$, $KHC_4H_4O_6$, Na_2HPO_4 , $CuHASO_3$, CaH_2PO_4 .) Whether or not these salts give an acid reaction with blue litmus-paper depends on the strength of the respective radicals. Usually they do redden the test-paper, but sometimes not; thus the acid sulphide or sulphydric acid of potassium (KHS), of sodium (NaHS), or ammonium (NH_4HS) has alkaline properties.*

The chemical analogy between sulphur and oxygen, already once alluded to (p. 173), is further illustrated by the compounds just mentioned. Sulphur is also closely related to the rarer element Selenium. Thus we have SeO_2 as well as SO_2 , H_2SeO_3 (selenious acid) as well as H_2SO_3 (sulphurous acid), H_2SeO_4 (selenic acid), as well as H_2SO_4 (sulphuric acid). The rare element Tellurium also seems to have similar analogies. The four hydrogen compounds of the group have the formulæ H_2O , H_2S , H_2Se , H_2Te . (*Vide Index*, "Periodic Law.")

* Chemists regard these sulphydrates as compounds of basylous radicals with HS, a univalent grouping termed hydrosulphyl (persulphide of hydrogen, H_2S_2), just as hydrates are similarly viewed as compounds of the univalent radical hydroxyl (HO) (peroxide of hydrogen, H_2O_2)— H_2S becoming HHS or HHs (hydrosulphylide of hydrogen), and H_2O becoming HHO or HHo (hydroxylide of hydrogen).

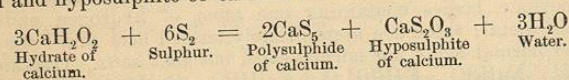
*Synthetical Reactions.***Sulphuretted Hydrogen.**

First Synthetical Reaction: The preparation of sulphuretted hydrogen.—This operation was described on page 95, and probably has already been studied by the reader.

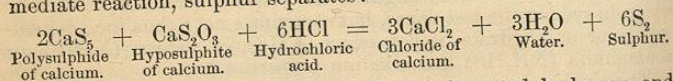
Precipitated Sulphur.

Second Synthetical Reaction.—Prepare the variety of the radical of sulphides known as *Precipitated Sulphur* (*Sulphur Præcipitatum*, U. S. P.), or *milk of sulphur*, by boiling a few grains of flowers of sulphur (100 parts) with slaked lime (66 parts) and some water (500 parts) in a test-tube (larger quantities in an evaporating-basin), filtering, and (reserving a small portion of the filtrate) adding diluted hydrochloric acid until the well-stirred milklike liquid has still a faint alkaline or scarcely acid reaction on test-paper; sulphur is precipitated, and may be collected on a filter, washed and dried (at about 120°). Excess of acid must be avoided, or some hydrosulphyl, the liquid persulphide of hydrogen (H_2S_2), will be formed, probably causing the particles of sulphur to aggregate to a gummy mass.

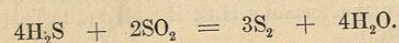
This is the process of the Pharmacopœias. Polysulphide of calcium and hyposulphite of calcium are formed:—



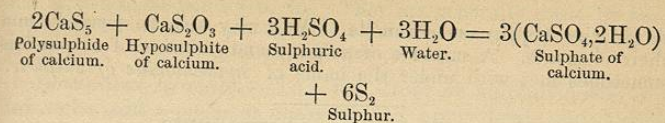
On adding the acid, both salts are decomposed and, after an intermediate reaction, sulphur separates:—



The polysulphide of calcium yields sulphuretted hydrogen and milk-white sulphur on the addition of acid. The hyposulphite of calcium then yields sulphurous acid gas as well as a yellowish sulphur. The gases react and give sulphur and water, very little sulphuretted hydrogen escaping: this is the intermediate reaction just alluded to. A little pentathionic acid (see Index) is also said to be formed.



Calcareous Precipitated Sulphur: The old "Milk of Sulphur."—To a sulphur solution prepared as before (or to the reserved portion) add a little dilute sulphuric acid; the precipitate is in this case largely mixed with sulphate of calcium:—



Place a little of each of these specimens of precipitated sulphur with a drop of the supernatant liquid on a strip of glass, cover each spot with a piece of thin glass, and examine the precipitates under a microscope; the pure sulphur will be found to consist of minute grains or globules, the calcareous to contain comparatively large crystals (sulphate of calcium).

Note.—A large proportion of the precipitated sulphur met with in trade in England still is thus mixed with sulphate of calcium, most of such specimens containing two-thirds of their weight of that substance. Many purchasers, indeed, are so accustomed to the satiny appearance of the mixed article as to regard the real sulphur with suspicion, sometimes refusing to purchase it. The mixed article is, certainly, more easily mixable with aqueous liquids;

Many English pharmacists have ceased to sell any sulphur which yields a white ash (the anhydrous sulphate) when a little is burnt off on the end of a table-knife or spatula. (No more damage is done to the steel than a rub on a knife-board will remove.)

To ascertain exactly the amount of sulphate of calcium in a specimen of calcareous precipitated sulphur, place a weighed quantity in a tared crucible and heat till no more vapors are evolved. The weight of the residual anhydrous sulphate of calcium ($CaSO_4 = 136$), with one-fourth thereof added, is the amount of crystalline sulphate of calcium ($CaSO_4, 2H_2O = 172$) present in the original quantity of calcareous sulphur.

Analytical Reactions (Tests).

To a sulphide add a few drops of hydrochloric acid; sulphuretted hydrogen will probably be evolved, well known by its smell. If the sulphide is not acted upon by the acid, or if free sulphur be under examination, mix a minute portion with a fragment of solid caustic potash or soda and fuse on a silver coin or old spoon. When cold, place a drop of dilute hydrochloric acid on the spot; sulphuretted hydrogen is evolved, and a black stain, due to sulphide of silver (Ag_2S) left on the coin.

Other sulphur reactions may be adopted as tests, but the above are sufficient for all ordinary purposes. The most convenient reagent for detecting a sulphide in solution of ammonia is ammonio-sulphate of copper, which gives a black precipitate of sulphide of copper if a sulphide be present.

The *Iodide of Sulphur* (S_2I_2) has been mentioned under "Iodine."

A chloride (S_2Cl_2) and bromide (S_2Br_2) may also be formed from their elements. A mixture of sulphur and chloride of sulphur is sometimes met with under the name of *hypochloride of sulphur*.

QUESTIONS AND EXERCISES.

495. In what form does sulphur occur in nature?
496. State the modes of preparation of the three chief commercial varieties of sulphur. *precipitate, from stone and flower*
497. To what extent does the atom of sulphur vary in quantivalence? *2-4*
498. State the relations of acid salts to acids and to normal salts.
499. Define sulphides and sulphhydrates.
500. Describe the preparation of sulphuretted hydrogen.
501. What are the characters of pure precipitated sulphur?
502. Give equations explanatory of the reactions which occur in precipitating sulphur according to the official process.
503. Describe the microscopic test for calcareous precipitated sulphur.
504. Mention a ready physical method of detecting sulphate of calcium in precipitated sulphur.
505. Mention the tests for sulphides, and the character by which sulphuretted hydrogen is distinguished from other sulphides.
506. How are sulphides insoluble in acids tested for sulphur?
507. Give a method for the detection of a trace of sulphur in solution of ammonia.

SULPHUROUS ACID AND OTHER SULPHITES.

Formula of Sulphurous Acid H_2SO_3 . Formula of sulphurous acid gas or sulphurous anhydride, sometimes termed sulphurous acid, SO_2 . Molecular weight of sulphurous acid 82; of the anhydride 64.

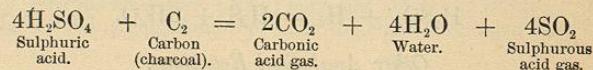
When sulphur is burned in the air it combines with oxygen and forms sulphurous acid gas (SO_2), more correctly termed sulphurous anhydride, or occasionally, but erroneously, sulphurous acid. It is a pungent, colorless gas, readily liquefied on being passed through a tube externally cooled by a *freezing-mixture* composed of two parts of well-powdered ice (or, better, snow) with one part of common salt. If sulphurous acid gas becomes moist or is passed into water, heat is evolved and true sulphurous acid (H_2SO_3) formed. The latter body may be obtained in crystals by freezing a strong aqueous solution; but it is very unstable, and hence the properties of the sulphurous radical must be studied under the form of some other sulphite; sulphite of calcium ($CaSO_3$) or sulphite of sodium (Na_2SO_3) may be used for the purpose.

Quantivalence.—The radical of the sulphites is bivalent ($SO_3^{''}$), and hence forms acid sulphites, such as acid sulphite of potassium ($KHSO_3$), and normal sulphites, such as sulphite of sodium (Na_2SO_3).

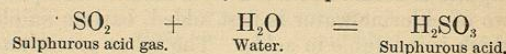
Note on Nomenclature.—The sulphites are so named from the usual rule, that salts corresponding with acids whose names end in

ous have a name ending in *ite*. They are generally made by passing sulphurous acid gas over moist oxides or carbonates; in the latter case carbonic acid gas escapes.

Synthetical Reaction.—To a few drops of sulphuric acid in a test-tube add a piece of charcoal and apply heat; sulphurous acid gas is evolved, and may be conveyed by a bent tube into a small quantity of cold water in another test-tube. Larger quantities may be made in a Florence flask. The product is the *Acidum Sulphurosum*, U. S. P. It contains about 4.5 per cent. of sulphurous acid (H_2SO_3) or about 3.5 per cent. of the gas (SO_2). The process is also that described in the Pharmacopœia, except that the gas is purified by passing through a small wash-bottle before final collection. Specific gravity 1.022 to 1.023.



Sulphurous acid gas may also be made by boiling copper, mercury, or iron with sulphuric acid, sulphate of the metals being formed. Also by boiling sulphur with sulphuric acid. The gas passed into water yields sulphurous acid.



If in this process the water were replaced by solutions of or solid metallic oxides or carbonates, sulphites of the various metals would be formed. The formula of sulphite of potassium (*Potassii Sulphis*, U. S. P.) is $K_2SO_3 \cdot 2H_2O$; of sulphite of sodium (*Sodii Sulphis*, U. S. P.), $Na_2SO_3 \cdot 7H_2O$; of the bisulphite or acid sulphite, $NaHSO_3$ (*Sodii Bisulphis*, U. S. P.). Under the name of *antichlor* the former is used for removing traces of chlorine from paper pulp. The sulphite of magnesium (*Magnesi Sulphis*, U. S. P., $MgSO_3 \cdot 6H_2O$) is deposited as a white crystalline powder from the aqueous solution containing excess of sulphurous acid. The so-called *Bisulphite of Lime*, employed by brewers for retarding or arresting fermentation and oxidation, and employed for various antiseptic purposes, is a solution of sulphite of calcium ($CaSO_3$) in free sulphurous acid (H_2SO_3), and is made by passing sulphurous acid gas (SO_2) into thin milk of lime. Its specific gravity varies from 1.050 to 1.070, and its potential strength of anhydride (SO_2) from 4 to 6 per cent. Sulphurous acid is very soluble in alcohol.

Analytical Reactions (Tests).

First Analytical Reaction.—To a sulphite (of sodium, for instance, made by passing sulphurous acid gas into solution of carbonate of sodium) add a drop or two of diluted hydrochloric acid; sulphurous acid gas escapes, recognized by a peculiar pungent smell.

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.



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.

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.

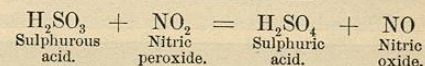
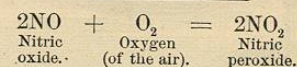
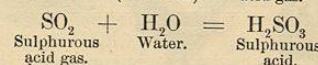
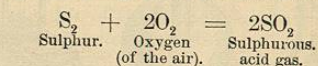
Formula of Sulphuric Acid, H_2SO_4 . Molecular weight, 98.

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 ($\text{SO}_2 + \text{H}_2\text{O} + \text{O} = \text{H}_2\text{SO}_4$).

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.

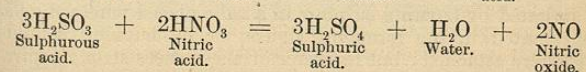
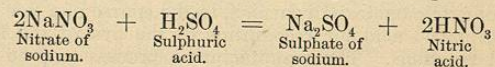
The following equations represent the chief successive steps:—



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.



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