Analytical Reactions (Tests).

First Analytical Reaction.—Dip a piece of turmeric-paper (paper soaked in tincture of turmeric tubers and dried) into a solution of boric acid; it is colored brown-red, as by alkalies.

The usual way of applying this test is as follows: Add to a solution of any borate a few drops of hydrochloric acid; immerse half of a slip of turmeric-paper in the liquid, then remove the hydrochloric acid by drying the paper over a flame. Concentrated hydrochloric acid and ferric chloride produce a somewhat similar effect.

Second Analytical Reaction.—To a fragment of a borate of metaborate (borax, for example) in a small dish or watch-glass add a drop of sulphuric acid, and then a little alcohol; warm the mixture and set light to the spirit; the resulting flame will be tinged of a greenish color at its edges by the volatilized boric acid or boric anhydride.

The liquid should be well stirred while burning. Salts of copper and some metallic chlorides produce a somewhat similar color. The flame test may also be applied to a little of a mixture of the borax with strong sulphuric acid on a platinum wire. Glycerin may be used in place of sulphuric acid (*Iles*), the reaction in this case being, according to Dunstan, the formation of borate of glyceryl, $C_3H_5BO_3$, water, and metaborate of sodium, the metaborate of glyceryl and water reacting immediately to form boric acid and glycerin.

Other Analytical Reactions.—In solutions of borax barium salts give a white precipitate of barium metaborate ($Ba2BO_2$) soluble in acids and alkaline salts. Nitrate of silver gives metaborate of silver ($AgBO_2$) soluble in nitric acid and in ammonia. Chloride of calcium, if the solution is not too dilute, gives white borate of calcium.

QUESTIONS AND EXERCISES.

573. Illustrate the relation of vanadium to nitrogen by formulæ of compounds of each element.
574. Describe the preparation of borax.
575. Give the formulæ of boric acid, metaboric acid, and borax.
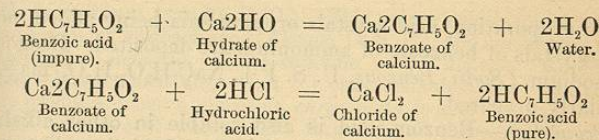576. Mention the tests for borates or metaborates.

The foregoing acids and other salts contain the only acidulous radicals that are commonly met with in analysis or in ordinary medical or pharmaceutical operations. There are, however, many others which occasionally present themselves. The chief of these will now be shortly noticed; they are arranged in alphabetical order to facilitate reference.

SALTS OF RARER ACIDULOUS RADICALS.

Anemonic Acid.—*Pulsatilla*, U. S. P., is the official name for the herbs of *Anemone Pulsatilla*, *A. pratensis*, and *A. patens*. These, together with several species of *Ranunculus*, on distillation with water yield a heavy, yellow, acrid oil, which, in contact with water, yields crystalline poisonous *anemonin* ($C_{15}H_{12}O_6$) and amorphous *anemonic acid* ($C_{15}H_{14}O_7$).

BENZOIC ACID ($HC_7H_5O_2$) AND OTHER BENZOATES.—Slowly heat a fragment of benzoin (Gum benzoinum) (*Benzoinum*, U. S. P.) in a test-tube; benzoic acid (*Acidum Benzoicum*, U. S. P.) rises in vapor and condenses in small, white, feathery plates and needles, on the cool sides of the tube. If the benzoin is first mixed with twice its weight of sand or roughly powdered pumice-stone, and the heat very cautiously applied, the product will be less likely to be burnt, and a larger quantity be yielded. By repeated sublimation 10 to 15 per cent. may be obtained.

A more economical process is to boil the benzoin with one fourth of its weight of lime, filter, concentrate, decompose the solution of benzoate of calcium by hydrochloric acid, collect the precipitated benzoic acid, press between paper, dry and sublime in a tube or other vessel.

$$2HC_7H_5O_2 \;+\; Ca2HO \;=\; Ca2C_7H_5O_2 \;+\; 2H_2O$$
Benzoic acid (impure).　Hydrate of calcium.　Benzoate of calcium.　Water.

$$Ca2C_7H_5O_2 \;+\; 2HCl \;=\; CaCl_2 \;+\; 2HC_7H_5O_2$$
Benzoate of calcium.　Hydrochloric acid.　Chloride of calcium.　Benzoic acid (pure).

There is always associated with the product a minute quantity of a mixture of volatile oils of agreeable odor, suggesting that of hay, and yielding, according to Jacobsen, methylbenzoate, guaiacol (methoxycatechol), catechol, acetylguaiacol, benzyl benzoate, benzophenone, and benzoylguaiacol.

Benzoic acid is also prepared on a large scale artificially from naphthalene, one of the crystalline by-products in the distillation of coal for gas. The naphthalene is oxidized by nitric acid to naphthalic or phthalic acid:—

$$C_{10}H_8 \;+\; 4O_2 \;=\; H_2C_8H_4O_4 \;+\; H_2C_2O_4$$
Naphthalene.　Oxygen.　Phthalic acid.　Oxalic acid.
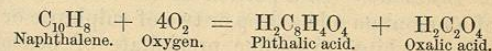
The phthalic acid is neutralized by lime, and the phthalate of calcium heated with hydrate of calcium in a covered vessel at a temperature of about 640° F. for several hours. Benzoate and carbonate of calcium are formed, and from the powder the benzoic acid is set free by action of hydrochloric acid.
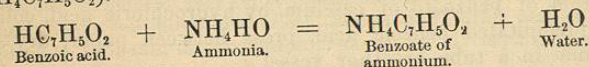
$$2CaC_8H_4O_4 \;+\; Ca2HO \;=\; Ca2C_7H_5O_2 \;+\; 2CaCO_3$$
Phthalate of calcium.　Hydrate of calcium.　Benzoate of calcium.　Carbonate of calcium.
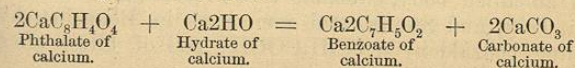
The crystalline deposit formed when essential oil of almonds, benzoic aldehyde, is exposed to the air is benzoic acid.

$$2C_6H_5COH \quad + \quad O_2 \quad = \quad 2C_6H_5COOH \text{ or } 2HC_7H_5O_2$$
Benzoic aldehyde. Oxygen. Benzoic acid.
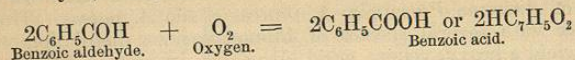
Pure sublimed benzoic acid is also obtained from hippuric acid (p. 336). Such acid, if not thoroughly purified, may have an urinoid odor. Jacobsen prepares benzoic acid from benzotrichloride (trichloromethyl-benzene, $C_6H_5CCl_3$), one of the trichlortoluenes, by heating with glacial acetic acid and chloride of zinc. This acid, if not very highly purified, may give a green color to flame when placed on platinum wire with a little oxide of copper. In artificial acid the fragrant volatile oil characteristic of the natural acid is, of course, absent, while in some specimens the odor of oil of bitter almond may be detected.

Benzoate of Ammonium.—To a little benzoic acid add a few drops of solution of ammonia; it readily dissolves, forming benzoate of ammonium (*Ammonii Benzoas*, U. S. P.) ($NH_4C_7H_5O_2$).

$$HC_7H_5O_2 \quad + \quad NH_4HO \quad = \quad NH_4C_7H_5O_2 \quad + \quad H_2O$$
Benzoic acid. Ammonia. Benzoate of ammonium. Water.

On evaporation, acid crystals or, ammonia being added, neutral crystals of benzoate of ammonium are deposited. Benzoate of sodium (*Sodii Benzoas*, U. S. P.), $NaC_7H_5O_2,H_2O$, may be similarly prepared.

Properties.—Benzoic acid is also soluble in other alkaline liquids, forming benzoates. It is slightly soluble in cold water, more so in hot, and readily soluble in rectified spirits. It melts at 248° F., and boils at 462°, volatilizing with only a slight residue. Heated with lime it yields benzene. It dissolves in cold oil of vitriol without decomposition, is again deposited on dilution, and the traces of odoriferous and other substances present in the acid from benzoin only slightly color the fluid, even on gently warming.

Tests for Benzoates.—To a portion of the above solution of benzoate of ammonium add a drop or two of sulphuric or hydrochloric acid; a white crystalline precipitate of benzoic acid separates. To another portion, carefully made neutral, add a drop or two of neutral solution of perchloride or persulphate of iron; reddish ferric benzoate is precipitated.

Cinnamic Acid (C_8H_7COOH).—Benzoic acid is distinguished from an allied body, cinnamic acid (occurring in Balsams of Peru, Tolu, and Storax, and sometimes in Benzoin), by not yielding benzaldehyde (C_6H_5COOH) (oil of bitter almonds)

when distilled with chromic acid—that is, with a mixture of red chromate of potassium and sulphuric acid—or when rubbed with half its weight of permanganate of potassium. Old hard balsam of tolu yields it on boiling with lime and water and precipitating by hydrochloric acid. Jacobsen makes it artificially by the prolonged reaction of glacial acetic acid and benzodichloride in the presence of chloride of zinc.

Carminic Acid ($C_{14}H_{14}O_8$).—This is the coloring principle (about ten per cent.) of the dried female *Coccus Cacti*, or cochineal (*Coccus*, U. S. P.). The *carmine* of trade, when unadulterated (*vide* Pharmaceutical Journal, 1859–60, p. 546), is carminic acid united with two or three per cent. of alumina and lime, or, occasionally, of oxide of tin or alumen. It should be wholly soluble in solution of ammonia, giving an apparently clear rich purple fluid. Carmine, with French chalk, or starch, constitutes *face-rouge* or *animal rouge*.

Merrick tests the relative value of several samples of cochineal or carmine by observing how much solution of permanganate of potassium is required to change the color of a decoction to faint pink. The silvery coating of cochineal is a wax, *coccerin*.

Cetraric Acid ($H_2C_{34}H_{30}O_{16}$) is the bitter principle of Iceland moss (*Cetraria*, U. S. P.). In the lichen it is associated with much starch.

Chrysophanic Acid ($C_{14}H_{10}O_4$).—This yellow acid is found in various species of rhubarb-root (*Rheum*, U. S. P.), and, under the name of *parietinic acid*, in various common yellow lichens. Kublé considers—Dragendorff also—that the chrysophanic acid of rhubarb is only produced when a glucoside, *chrysophan*, is acted on by a ferment in the presence of water. The formation of chrysophanic acid is probably in most, if not in all, cases preceded by the occurrence of chrysophan or an allied body. The author found it to form four-fifths of old "Chrysarobine," a name given by Kemp to the pith, etc. of a leguminous tree (*Andira Araroba*). Chrysarobine or *crysarobin* (*Chrysarobinum*, U. S. P.) is also known as Araroba Powder, Bahia Powder, Brazil Powder, Goa Powder, and Ringworm Powder. Recently chrysarobin has been shown by Liebermann and Seidler to have the formula $C_{30}H_{26}O_7$; this, by oxidation and elimination of water, yields the chrysophanic acid occurring in old chrysarobin. Chrysophanic acid may be obtained in crystals of of a golden-yellow color, hence the name (from χρυσὸς, *chrusos*, gold, and φαίνω, *phainō*, I shine). Its synonyms are *Rhaponticin, Rheic acid, Rhein, Rheumin, Rheubarbaric acid, Rheubarbarin, Rumicin.* Chrysophanic acid, actual or potential black, red-brown, and red resins (*Aporetine, Phœoretine,* and *Erythroretine*), a bitter principle, and tannic acid, are considered to be the conjoint source of the therapeutic properties of rhubarb. Chrysophanic acid may also be obtained from several species of *Rumex* or *Dock*. "Rumicin" is a name given to a preparation of the root of *Rumex crispus*, or Yellow Dock (*Rumex*, U. S. P.). *Cascara Sagrada*, or Sacred Bark (*Rhamni Purshiani Cortex*, B. P.), according to Limousin, contains chrys-

15

ophanic acid, a glucoside (?), and a ferment, and various resins are said to be present also.

Emodin, $C_{15}H_{10}O_5$, is, apparently, closely associated, chemically, with chrysophanic acid. It is obtained with chrysophanic acid in the preparation of the latter from rhubarb. It also occurs in Black Alder Bark (*Rhamni Frangulæ Cortex*, B. P.), according to Lieber-mann and Waldstein, is said to be derived, together with glucose, from *frangulin*, the glucoside of the dried bark.

CORNIC ACID, or CORNIN.—This is, according to Geiger, the crys-talline bitter principle of the bark (*Cornus*, U. S. P.) of *Cornus florida*. A crystalline resin is also present.

CYANIC ACID (HCyO) AND OTHER CYANATES.—The valu-able reducing power of cyanide of potassium (KCy) (or ferro-cyanide, K_4Fcy) on metallic compounds is due to the avidity with which cyanate (KCyO) is formed.
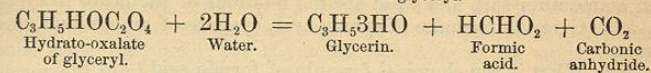
Process.—Fuse a few grains of cyanide of potassium in a small porcelain crucible, and add powdered oxide of lead; a globule of metallic lead is at once set free, excess of the oxide converting the whole of the cyanide of potassium into cyanate of potassium.

Urea.—Cyanate of potassium (KCNO), or, better, cyanate of lead (Pb2CNO), treated with sulphate of ammonium, yields cyanate of ammonium (NH$_4$CNO); and solution of cyanate of ammonium, when simply heated, changes to artificial *urea* (CH$_4$N$_2$O), the most important constituent of urine, and the chief form in which the nitrogen of food is eliminated from the animal system. The process will be more fully described subsequently in connection with Urea.

FORMIC ACID (HCHO$_2$).—The red ant (*Formica rufa*) and several other insects, when irritated, eject a strongly acid, acrid liquid, hav-ing a composition expressed by the above formula, and which has appropriately received the name of formic acid; it is also contained in the leaves of the stinging-nettle. (According to Church the sting of the wasp is alkaline.)

Process.—It may be artificially prepared by heating equal weights of oxalic acid and glycerin to a temperature of from 212° to 220° F. for fifteen hours, and then distilling the mix-ture with a considerable volume of water. The formic acid slowly passes over, the glycerin being regenerated. The dilute acid may be concentrated by neutralizing with carbonate of lead, filtering, evaporating to a small bulk, collecting the deposited crystalline formate of lead, drying, decomposing in a current of sulphuretted hydrogen, separating the resulting syrupy acid, and passing air through the product until all sul-

phuretted hydrogen is removed. The following are the chief reactions :—

$$C_3H_5 3HO \ + \ H_2C_2O_4 \ = \ C_3H_5HOC_2O_4 \ + \ 2H_2O$$
Glycerin.   Oxalic acid.   Hydrato-oxalate of glyceryl.   Water.

$$C_3H_5HOC_2O_4 \ + \ 2H_2O \ = \ C_3H_5 3HO \ + \ HCHO_2 \ + \ CO_2$$
Hydrato-oxalate of glyceryl.   Water.   Glycerin.   Formic acid.   Carbonic anhydride.

Formic acid may be instructively though not economically pre-pared by the oxidation of methylic alcohol (wood spirit), just as acetic acid and valerianic acid are obtained from ethylic alcohol and amylic alcohol respectively.

$$CH_3HO \ + \ O_2 \ = \ HCHO_2 \ + \ H_2O$$
Wood-spirit.   Oxygen.   Formic acid.   Water.
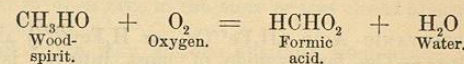
Tests.—Formic acid does not char when heated alone or with sul-phuric acid, but splits up into carbonic oxide gas and water. It is recognized by this property and by its reducing action on salts of gold, platinum, mercury, and silver. It is solid below 32° F.

GALLIC ACID.—See *Tannic Acid*.

HEMIDESMIC ACID.—The supposed active principle of hemi-desmus root (*Hemidesmi radix*, B. P.).

HIPPURIC ACID (HC$_9$H$_8$NO$_3$) is a constituent of human urine (much increased on taking benzonic acid), but is prepared from the urine of the horse (hence the name, from ἵππος, *hippos*, a horse), or, better, from that of the cow. To such urine add a little milk of lime, boil for a few minutes, remove precipitated phosphates by fil-tration, drop in hydrochloric acid until the liquid, after well stirring, is exactly neutral to test-paper, concentrate to about one-eighth the original bulk, and add excess of strong hydrochloric acid; impure hippuric acid is deposited. From a solution of the impure acid in hot water chlorine gas removes the color, and the liquid deposits crystals of pure hippuric acid on cooling.

Tests.—To a solution of hippurate add neutral solution of ferric chloride; a brown precipitate (ferric hippurate) results. Salts of silver and mercury give white precipitates. Heat hippuric acid in a test-tube; it chars, benzoic acid sublimes, and vapors of charac-teristic odor are evolved; they contain, amongst other bodies, hy-drocyanic acid and a substance smelling somewhat like Tonka bean. ——The crystalline form of hippuric acid is characteristic; it will be described in connection with the subject of urine.

## QUESTIONS AND EXERCISES.

577. Give the preparation, composition, properties, and tests of benzoic acid, employing equations or diagrams.

578. What is the nature of carmine?

579. Name the bitter principle of Iceland moss.

580. Mention the coloring principle of rhubarb.

581. To what is rhubarb considered to owe its medicinal activity?

582. How is cyanate of potassium prepared, how converted into an ammonium salt, and what are the relations of the latter to urea?

583. Give the formulæ of cyanic acid, cyanate of ammonium, and urea.

584. What is the chemical formula of formic acid?

585. Describe the artificial production of formic acid.

586. Describe the relation of formic acid to wood spirit.

587. State the sources, characters, and tests of hippuric acid.

HYDROFERROCYANIC ACID ($H_4Fe''Cy_6$, or H_4Fcy'''') AND OTHER FERROCYANIDES.—The ferrocyanide of most interest is that of potassium (*Potassii Ferrocyanidum*, U. S. P.), the yellow prussiate of potash ($K_4FeC_6N_6,3H_2O$), the formation of which was alluded to in connection with hydrocyanic acid (see page 278). It cannot be regarded as simply a double salt of cyanide of potassium with cyanide of iron ($FeCy_2,4KCy$), its chemical properties being entirely different from either of those substances; moreover, unlike cyanide of potassium, it is not poisonous. Most of its reactions point to the conclusion that its iron and cyanogen are intimately united to form a definite quadrivalent radical appropriately termed *ferrocyanogen* ($FeCy_6$, or Fcy). One part of ferrocyanide of potassium in 20 of water forms the official "Solution of Ferrocyanide of Potassium," B. P.
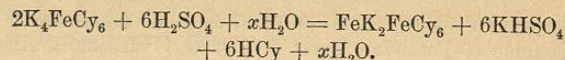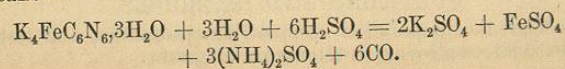
Tests.—Many of the ferrocyanides are insoluble, and are therefore precipitated when solution of ferrocyanide of potassium is added to the various salts. Those of iron and copper, being of characteristic color, are adopted as tests of the presence of the metals or of the ferrocyanogen, as the case may be.

To solution of ferrocyanide of potassium add a ferric salt; ferrocyanide of iron (Fe_4Fcy_3) (Prussian blue) is precipitated.

$$3K_4Fcy + 2(Fe_2,3SO_4) = Fe_4Fcy_3 + 6K_2SO_4.$$
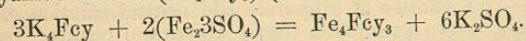
To another portion add solution of a copper salt; reddish-brown ferrocyanide of copper (Cu_2Fcy) is precipitated.

Note.—The ferrocyanogen in ferrocyanide of potassium is broken up when the salt is heated with sulphuric acid, *carbonic oxide* being evolved if the acid is strong (that is, ordinary oil of vitriol—H_2SO_4 with 3 to 4 per. cent of water), and *hydrocyanic acid* if weak:—

$$K_4FeC_6N_6,3H_2O + 3H_2O + 6H_2SO_4 = 2K_2SO_4 + FeSO_4$$
$$+ 3(NH_4)_2SO_4 + 6CO.$$

$$2K_4FeCy_6 + 6H_2SO_4 + xH_2O = FeK_2FeCy_6 + 6KHSO_4$$
$$+ 6HCy + xH_2O.$$

Hydrocyanic Acid has already been described. (*Vide* p. 278.)

Carbonic Oxide (CO).—Heat two or three fragments of ferrocyanide of potassium with eight or ten times their weight of sulphuric acid, and as soon as the gas begins to be evolved remove the test-tube from the flame; for the action, when once set up, proceeds somewhat tumultuously. Ignite the carbonic oxide at the mouth of the tube; it burns with a pale blue flame, the product of combustion being carbonic acid gas (CO_2).

Carbonic oxide is a direct poison. It is generated whenever coke, charcoal, or coal burns with an insufficient supply of air. Hence the danger of open fires in the more or less closed apartments of ordinary dwellings.

Carbonic oxide may also be obtained from oxalic acid. (*Vide* p. 316.)

HYDROFERRICYANIC ACID ($H_6Fe'''_2Cy_{12}$, or $H^I_6Fdcy^{VI}$) AND OTHER FERRICYANIDES.—Pass chlorine gas slowly through solution of ferrocyanide of potassium until the liquid, after frequent shaking, ceases to give a blue precipitate, when a minute portion is taken out on the end of a glass rod and brought into contact with a drop of a dilute solution of a ferric salt; it now contains ferricyanide of potassium (B. P.), ($K_6Fe'''_2Cy_{12}$, or $K^I_6Fdcy^{VI}$), *red prussiate of potash*, as it is termed from the color of its crystals. Excess of chlorine must be carefully avoided, as chloride of cyanogen and other compounds are then formed. Such a result does not ensue if bromine be used instead of chlorine, but the process is, of course, more expensive.

$$2K'_4Fe''Cy'_6 + Cl'_2 = 2K'Cl' + K'_6Fe'''_2Cy'_{12}.$$
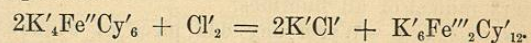
Another Process.—To a cold solution of yellow prussiate of potash so much hydrochloric acid is added as will take two atoms of potassium from two molecules of the salt, and then a cold clear solution of bleaching-powder till ferric chloride gives no reaction. Any excess of acid is then neutralized with chalk and the solution evaporated to crystallization (Rhien).

Note.—The removal of two atoms of potassium from the ferrocyanide is the only change of composition that occurs; but the ferrocyanogen is altered in quality, its iron passing from the ferrous to the ferric condition, from bivalent to trivalent activity, altered to a condition in which it no longer precipitates ferric salts, but, on the other hand, gives a dark blue precipitate with ferrous salts. The radical is distinguished as *ferricyanogen*.

Ferricyanide of potassium may also be prepared by a modification of the foregoing method in which nascent instead of free chlorine

is employed (Wenzell). Take of Bichromate of Potassium 1 part, Ferrocyanide of Potassium Cryst. 5.72 parts, Hydrochloric Acid, of spec. grav. 1.16, 3 parts by weight, Water 60 parts. Dissolve the two salts in hot water, add the acid, heat to boiling, continuing the ebullition, replacing the water evaporated during the process until a portion of the filtered liquid is not precipitated on the addition of solution of ferric chloride. When reaction is completed, filter the liquid and wash the hydrate of chromium, unite the liquids, and concentrate to crystallization. If the evaporated liquid possess an acid reaction, the addition of caustic potash, in sufficient quantity to cause a weak alkaline reaction, will greatly facilitate the subsequent crystallization.

$$6(K_4FeCy_6) + K_2Cr_2O_7 + 8HCl = 3(K_6Fe_2Cy_{12}) + 8KCl + H_2O + Cr_2 6HO.$$
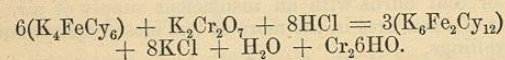
Test.—To a portion of the solution add solution of ferrous sulphate; a precipitate falls. This precipitate is ferricyanide of iron (Turnbull's blue), $Fe''_3Fe'''_2Cy'_{12}$, or $Fe^{II}_3Fdcy^{VI}$.

$$K_6Fdcy + 3FeSO_4 = Fe_3Fdcy + 3K_2SO_4.$$

It will be noticed that the change in the condition of the iron keeps up the balance of the atomic values of the various parts of the radicals or of the salts; the quantivalential equilibrium is maintained.

A solution of 1 part of ferricyanide of potassium in 20 of water constitutes the "Solution of Ferricyanide of Potassium," B. P.

HYDROFLUORIC ACID (HF) AND OTHER FLUORIDES.—Molecular weight of HF, 20. The chief use of hydrofluoric acid is in the etching on glass. The operation, performed on the small scale, also constitutes the best test for fluorine, the elementary radical of all fluorides.

Process and Test.—Warm any odd piece of window-glass, having an inch or two of surface, until a piece of beeswax rubbed on one side yields a thin oily film. When cool make a cross, letter, or other mark on the glass by pressing a pointed piece of wood, a penknife, or file, through the wax. Place a few grains of powdered fluor spar, the commonest natural fluoride, in a porcelain crucible (or a lead cup), add a drop or two of sulphuric acid, cover the crucible with the prepared glass, waxed side downwards, and gently warm the bottom of the crucible in a fume-chamber or in the open air, in such a way as not to melt the wax. After a few minutes remove the glass, wash the waxed side by pouring water over it, scrape off most of the wax, then warm the glass, and wipe off the remainder; the marks made through the wax will be found to be permanently etched on the glass; the acid has eaten into or *etched* (from the German *ätzen*, to corrode) the glass.

In the above operation the fluoride of calcium and sulphuric acid yield hydrofluoric acid, thus:—

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$

The hydrofluoric acid gas and the silica of the glass then yield gaseous fluoride of silicon (SiF_4), which escapes, and water, thus:—

$$4HF + SiO_2 = 2H_2O + SiF_4.$$
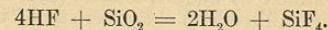
The silica, being removed from the glass, leaves furrows or etched portions.

Note.—In the experiment just described, the liberated hydrofluoric acid also attacks the siliceous glazing of the porcelain crucible; so that in important cases, where search is made for very small quantities of fluorine, vessels of platinum or lead must be employed.

Uses.—The aqueous solution of hydrofluoric acid used by etchers, and commonly termed simply hydrofluoric acid, or "fluoric" acid, is prepared in leaden stills and receivers, and kept in leaden or gutta-percha bottles. Except these materials, as well as platinum and fluor spar, hydrofluoric acid rapidly attacks any substance of which bottles and basins are usually made. It quickly cauterizes the skin, producing a painful, slow-healing sore. A mixture of hydrofluoric acid and fluoride of ammonium, known as "white acid," is also used for etching glass.

Quantivalence.—The atom of fluorine, like that of chlorine, bromine, or iodine, is univalent (F'). The great analogy existing between these radicals extends to their compounds.

Fluorine is said to be a colorless gas; but, from the avidity with which it combines with all elements (except oxygen), it is so difficult of isolation as hitherto to preclude satisfactory study of its physical properties.

HYPOPHOSPHOROUS ACID (H_3PO_2, or HPH_2O_2) AND OTHER HYPOPHOSPHITES.—Boil together, in a fume-chamber, two or three grains of phosphorus, three or four grains of slaked lime, and about a quarter of an ounce of water until phosphoretted hydrogen, a spontaneously inflammable, badly-smelling gas, ceases to be evolved. The lime must not be in great excess or the hypophosphite will be converted into phosphate as fast as formed. The mixture, filtered, and excess of lime removed by carbonic acid gas, yields solution of hypophosphite of calcium ($Ca2PH_2O_2$) (*Calcii Hypophosphis*, U. S. P.). The salt may be obtained in crystals by evaporating and slowly cooling.

$$2P_4 + 6H_2O + 3CaH_2O_2 = 3(Ca2PH_2O_2) + 2PH_3.$$
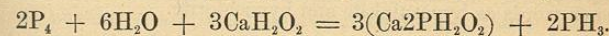
Phosphoretted Hydrogen (PH_3).—The above reaction is also that by which phosphoretted hydrogen, the third hydride of phosphorus, may be prepared. If the gas is to be collected, the phosphorus and water may first be boiled in a flask until a jet of spontaneously in-

flammable phosphorus vapor escapes, with steam, from the end of the attached delivery-tube. Strong solution of caustic potash or soda is next very gradually poured into the flask through a funnel tube previously fitted into the cork, the liquid being kept boiling. Phosphoretted hydrogen is then evolved, and, if the delivery-tube dip under water, may be collected, or allowed to slowly pass up through the water bubble by bubble, so as to form the peculiar rings of smoke (phosphoric anhydride) characteristic of the experiment.

The Hypophosphite of Potassium (*Potassii Hypophosphis*, U. S. P.) (KPH_2O_2) may be obtained in the same way from its hydrate, and many other hypophosphites ($Mg2PH_2O_2,6H_2O$, $Fe2PH_2O_2,6H_2O$, etc.) similarly from other hydrates, or by double decomposition of the calcium salt and carbonates.

Hypophosphite of sodium ($NaPH_2O_2,H_2O$) (*Sodii Hypophosphis*, U. S. P.) may be made by decomposing solution of hypophosphite of calcium by carbonate of sodium, filtering, and evaporating to dryness. It is a white, granular, deliquescent substance.

$$Ca2PH_2O_2 + Na_2CO_3 = 2NaPH_2O_2 + CaCO_3.$$
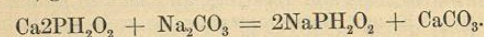
When heated, the water is first evolved, then hydrogen and spontaneously inflammable phosphoretted hydrogen, and a mixture of pyrophosphate and metaphosphate of sodium remains (Rammelsberg).

$$5NaPH_2O_2 = Na_4P_2O_7 + NaPO_3 + 2PH_3 + 2H_2.$$
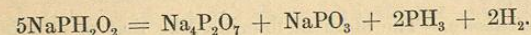
Hypophosphorous acid, the hydrogen hypophosphite, may be prepared by decomposing the barium salt with sulphuric acid or the calcium salt by oxalic acid; hypophosphite of quinine by dissolving the alkaloid in hypophosphorous acid, or by decomposing sulphate of quinine by hypophosphite of barium. The latter is obtained on boiling excess of pure hydrate of barium with hypophosphite of ammonium until all ammonia is evolved. The ammonium salt is formed on bringing calcium hypophosphite and oxalate of ammonium together in presence of a little ammonia. Hypophosphite of Iron ($Fe_26PH_2O_2$) (*Ferri Hypophosphis*, U. S. P.) may be obtained by dissolving ferric hydrate in cold aqueous hypophosphorous acid and evaporating the solution.

The hypophosphites are often used in medicine in the form of syrups (*Syrupus Hypophosphitum*, U. S. P., and *Syr. Hypophosphitum cum Ferro*, U. S. P.). The term hypophosphite is in allusion to the smaller amount (ὑπὸ, *hupo*, under or deficiency) of oxygen in these compounds (R'_3PO_2) than in the phosphites (R_3PO_3), a class of salts having again less oxygen in their molecules than exists in those of the phosphates (R_3PO_4). The prefix *hypo* has similar significance in such words as hyposulphite and hypochlorite.

Tests.—To a portion of the above solution of hypophosphite of calcium add solution of chloride of barium, chloride of calcium, or acetate of lead; in neither case is a precipitate obtained, whereas soluble phosphates and phosphites yield white

precipitates of phosphate or phosphite of barium, calcium, or lead. To other portions add solutions of nitrate of silver and mercuric chloride; the respective metals are precipitated as by phosphites. To another small portion add zinc and dilute sulphuric acid; hydrogen and phosphoretted hydrogen are evolved as from phosphites. To another portion add sufficient oxalic acid to remove the calcium; filter; to the solution of hypophosphorus acid add solution of sulphate of copper, and slowly warm the mixture; solid brown cuprous hydride (Cu_2H_2) is precipitated: increase the heat to the boiling-point; hydrogen is evolved and metallic copper set free. Add the ordinary nitric solution of a molybdate or tungstate to a hypophosphite solution, and then a very little sulphurous acid; a blue precipitate results, or, in very dilute solutions, a blue color, deepened on shaking or gently warming. Heat a small quantity of a solid hypophosphite on the end of a spatula in a flame; it splits up into pyrophosphate, a little metaphosphate, hydrogen, phosphoretted hydrogen, and, sometimes, water, burning with a phosphorescent light—the official hypophosphite of calcium yielding about 80 per cent. of residue.

$$7(Ca2PH_2O_2) = 3Ca_2P_2O_7 + Ca2PO_3 + 6PH_3 + H_2O + 4H_2$$
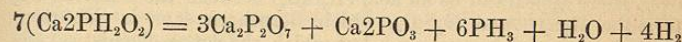
Five grains of hypophosphite of calcium, if of good quality, will almost decolorize a solution of twelve grains of permanganate of potassium on boiling the mixture for about ten minutes. Five grains of hypophosphite of sodium should almost decolorize eleven and a half grains of permanganate under similar conditions. The same effect follows the addition of the permaganate to an acid solution of a phosphite, but not to that of an ortho-, meta-, or pyrophosphate.

HYPOSULPHUROUS ACID ($H_2S_2O_3$) AND OTHER HYPOSULPHITES.—The only hyposulphite of much interest in pharmacy is the sodium salt (*Sodii Hyposulphis*, U. S. P.) ($Na_2S_2O_3,5H_2O$). Hyposulphites are now commonly termed *thiosulphates* (e. g., H_2SO_3S; Na_2SO_3S), being regarded as *sulphates* (e. g. Na_2SO_4) in whose molecules one atom of oxygen is displaced by one of *theion* (θεῖον, *sulphur*).

Process.—Heat together gently, or set aside in a warm place, a mixture of solution of sulphite of sodium (Na_2SO_3) and a little powdered sulphur; combination slowly takes place, and hyposulphite of sodium is formed. The solution, filtered from excess of sulphur, readily yields crystals. (The solution of sulphite of sodium may be made by saturating a solution of soda with sulphurous acid gas.)

Use of Hyposulphite of Sodium in Quantitative Analysis.—
In the British Pharmacopœia hyposulphite of sodium is given
as a reagent for the quantitative estimation of free iodine in
volumetric analysis. To a few drops of iodine-water add cold
mucilage of starch; a deep-blue color (starch iodide) is pro-
duced. To the product add solution of hyposulphite of sodium
until the blue color just disappears. This absorption of iodine
is sufficiently definite and delicate to admit of application for
quantitative purposes. It depends on the combination of the
iodine with half of the sodium in two molecules of the hypo-
sulphite, the hyposulphurous radicals of the two molecules
apparently coalescing to form a new radical, the tetrathionic
(from τέτρας, *tetras*, four, and θεῖον, *theion*, sulphur), tetrathio-
nate of sodium ($Na_2S_4O_6$) and iodide of sodium being formed.

Sulphur Oxyacids.—It will be as well here to give the formulæ of
other oxyacids of sulphur, forming with the four already mentioned
a series that is as useful as the series of compounds of nitrogen and
oxygen in illustrating the soundness of Dalton's atomic theory. The
first named (H_2SO_2) is now generally, in chemistry, termed hypo-
sulphurous acid, and the fourth ($H_2S_2O_3$) thiosulphuric acid. More-
over, there appears to be an acid ($H_2S_2O_4$) between those having the
formulæ $H_2S_2O_3$ and $H_2S_2O_6$, which Bernthsen says is Schützen-
berger's hydrosulphurous acid, but which the latter chemist says is
probably a distinct acid.

Hydrosulphurous Acid . .	H_2SO_2	?	$H_2S_2O_4$
Sulphurous Acid	H_2SO_3	Dithionic Acid	$H_2S_2O_6$
Sulphuric Acid	H_2SO_4	Trithionic Acid	$H_2S_3O_6$
Hyposulphurous or	} $H_2S_2O_3$	Tetrathionic Acid . . .	$H_2S_4O_6$
Thiosulphuric Acid		Pentathionic Acid . . .	$H_2S_5O_6$

Use of "Hypo" in Photography.—The sodium hyposulphite
is largely used in photography to dissolve chloride, bromide, or
iodide of silver off plates which have been exposed in the
camera. Prepare a little chloride of silver by adding a chloride
(chloride of sodium) to a few drops of solution of nitrate of
silver. Collect the precipitated chloride on a filter, wash, and
add a few drops of solution of hyposulphite of sodium; the
silver salt is dissolved, solution of double hyposulphite of so-
dium and silver being formed. The solution of this double hy-
posulphite has a remarkably sweet taste, sweeter than syrup,
if the solution is strong. The double hyposulphite of sodium
and gold is employed for giving a pleasant tint to photographic
prints.

Test.—To solution of a hyposulphite add a few drops of
dilute sulphuric or other acid; hyposulphurous acid is set free,
but at once begins to decompose into sulphurous acid, recog-

nized by its odor, and free sulphur ($2H_2S_2O_3 = 2H_2SO_3 + S_2$).
This reaction constitutes the best test for hyposulphites. An-
other test of a soluble simple hyposulphite is its power of dis-
solving chloride of silver with production of a more or less
sweet solution.

QUESTIONS AND EXERCISES.

588. Give the formula of ferrocyanide of potassium.

589. What is the supposed constitution of ferrocyanide of potas-
sium?

590. Enumerate the tests for ferrocyanogen.

591. What are the respective reactions of ferrocyanide of potas-
sium with strong and weak sulphuric acid?

592. Mention and explain a common source of carbonic oxide in
households. What is the product of its combustion?

593. Write equations or diagrams illustrative of the changes
effected on ferrocyanide of potassium during its conversion into fer-
ricyanide.

594. By what reactions may the presence of a ferricyanide in a
solution be demonstrated?

595. State the difference between Prussian blue and Turnbull's
blue.

596. Describe the source, mode of preparation, chief use of, and
test for hydrofluoric acid.

597. Illustrate by a diagram the preparation and composition of
hyposulphite of sodium.

598. Mention the uses and characteristic reactions of hyposulphite
of sodium.

599. Give the names and formulæ of eight acids, each containing
hydrogen, sulphur and oxygen.

LACTIC ACID ($HC_3H_5O_3$) AND OTHER LACTATES.—Lactic acid
occurs naturally in willow-bark (Dott). When milk turns sour its
sugar has become converted into an acid appropriately termed lactic
(*lac, lactis*). Other saccharine and amylaceous substances also by
fermentation yield lactic acid. The hydrogen lactate (lactic acid)
is official (*Acidum Lacticum*, U. S. P.).

Process.—Lactate of calcium and lactic acid may be pre-
pared as follows: Mix together eight parts of sugar, one of
common cheese, three of chalk, and fifty of water, and set
aside in a warm place (about 80° F.) for two or three weeks;
a mass of small crystals of lactate of calcium results. Remove
these, recrystallize from hot water, decompose by sulphuric acid,
avoiding excess, digest in alcohol, filter off the sulphate of calcium,
evaporate the clear solution to a syrup; this residue is lactic
acid; when of sp. gr. 1.212 it contains 75 per cent. of real acid.