

Lactate of Iron (*Ferri Lactas*, U. S. P.; $\text{Fe}_2\text{C}_3\text{H}_5\text{O}_3 \cdot 3\text{H}_2\text{O}$) may be made by digesting iron filings in warm diluted lactic acid (1 acid to 16 water) till effervescence of hydrogen ceases, filtering and setting aside to cool and crystallize. The crystals are collected, washed with alcohol, and dried. This ferrous lactate occurs in greenish-white crystalline crusts or grains, of a mild, sweetish, ferruginous taste, soluble in forty-eight parts of cold and twelve of boiling water, but insoluble in alcohol. Exposed to heat, it froths up, gives out thick, white, acid fumes, and becomes black, sesquioxide of iron being left. If it be boiled for fifteen minutes with nitric acid of the specific gravity 1.20, a white, granular deposit of mucic acid will occur on the cooling of the liquid.

Tests.—No single reaction of lactic acid is sufficiently distinctive to form a test. The crystalline form of the lactate of calcium, as seen by the microscope, is characteristic. The production of this salt, and the isolation of the syrupy acid itself, are the only means, short of quantitative analysis, on which reliance can be placed. It is soluble in water, alcohol, and ether, but almost insoluble in chloroform. It is only slightly colored by cold sulphuric acid; warmed with permanganate of potassium, it gives the odor of aldehyde.

A variety of lactic acid has been obtained from the juice of fish; it is termed *sarcocollactic acid* (from *σάρξ*, *σάρκος*, *sarx*, *sarcos*, flesh). Unlike lactic acid, it is precipitated by solution of sulphate of copper.

MALIC ACID ($\text{C}_4\text{H}_6\text{O}_5$) AND OTHER MALATES (from *malum*, an apple).—The juice of unripe apples, gooseberries, currants, rhubarb-stalks, strawberries, grapes, etc. contains malic acid and malate of potassium. When isolated it occurs in deliquescent prismatic crystals.

Tests.—Malate of calcium ($\text{CaC}_4\text{H}_4\text{O}_5$) is soluble in water; hence the aqueous solution of malic acid or other malate is not precipitated by lime-water or chloride of calcium; but on adding spirit of wine a white precipitate falls, owing to the insolubility of the calcium malate in alcohol. Malates are precipitated by lead-salts; on warming the malate of lead with acetic acid it dissolves, separating out in acicular crystals on cooling. If the mixture be heated without acid, the malate of lead agglutinates and fuses.

Hot strong sulphuric acid chars malic acid far less readily than it does nearly all other organic acids.

Asparagin ($\text{C}_4\text{H}_8\text{N}_2\text{O}_3 \cdot \text{H}_2\text{O}$).—This proximate principle of plants occurs in many vegetable juices, and doubtless plays a very important part in their nutrition. It is deposited in crystals when the fresh juices of asparagus, marshmallow, etc. are rapidly evaporated. It

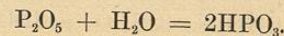
is noticed here because malic acid is readily obtained from it by oxidation, nitrogen being eliminated, and because its exact natural position among chemical substances is not yet well made out. The atoms of its molecule are those of aspartate of ammonium ($\text{NH}_4\text{C}_4\text{H}_5\text{NO}_4$), into which it is converted when its solution is long boiled. Decomposed by aid of ferments, asparagin, absorbing hydrogen, yields succinate of ammonium (NH_4) $_2\text{C}_4\text{H}_5\text{O}_4$. Such reactions as these and the formation of the lactic acid of willow-bark from sugars may suggest to the student possible modes in which chemical changes take place in the plant-department of the vast laboratory of nature.

MECONIC ACID ($\text{H}_2\text{C}_7\text{H}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$).—Opium contains meconic acid (from *μῆκων*, *mekōn*, a poppy) partially combined with morphine. To concentrated infusion of opium nearly neutralized by ammonia add solution of chloride of calcium; meconate of calcium is precipitated. Wash the precipitate, place it in a small quantity of hot water, and add a little hydrochloric acid; the clear liquid (filtered, if necessary) deposits scales of meconic acid on cooling (*Acidum Meconicum*, B. P.).

Tests.—To solution of meconic acid or other meconate, or to infusion of opium, add a neutral solution of ferric chloride; a red solution of meconate of iron is produced. To a portion of the mixture add solution of corrosive sublimate; the color is not destroyed; to another portion add hydrochloric acid; the color is discharged. (These reagents act on sulphocyanate of iron, which is of similar tint, in exactly the opposite manner.) To another portion add a drop of a dilute acid and boil; the color is not discharged. (A solution of ferric acetate, which is of similar color, is decomposed on boiling, giving a colorless fluid and a red precipitate of ferric oxyacetate.)

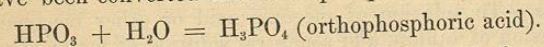
The normal meconates of potassium, sodium, and ammonium are soluble in water, the acid meconates very slightly soluble, the meconates of barium, calcium, lead, copper, and silver insoluble in water, but soluble in acetic acid.

METAPHOSPHORIC ACID (HPO_3) AND OTHER METAPHOSPHATES.—Prepare phosphoric anhydride (P_2O_5) by burning a small piece of phosphorus in a porcelain crucible placed on a plate and covered by an inverted test-glass tumbler, half-pint measure-glass, or some such vessel. After waiting a few minutes for the phosphoric anhydride to fall, pour a little water on the plate and filter the liquid; the product is solution of metaphosphoric acid (from *μετά*, *meta*, a preposition denoting change).

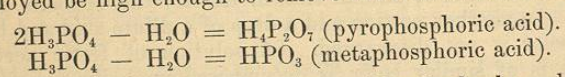


Tests.—To solution of metaphosphoric acid add ammonio-nitrate of silver, or to a neutral metaphosphate add solution

of nitrate of silver; a white precipitate (AgPO_3) is obtained. This reaction sufficiently distinguishes metaphosphates from the ordinary phosphates or orthophosphates (from *ὀρθός*, *orthos*, straight), as the common phosphates may, for distinction, be termed (which give, it will be remembered, a yellow precipitate with nitrate of silver). Another variety of phosphates shortly to be considered, the pyrophosphates, also gives a white precipitate with nitrate of silver. To the solution of metaphosphoric acid obtained as above, or by the action of acetic acid on a metaphosphate, add an aqueous solution of white of egg; coagulation of the albumen ensues. Neither orthophosphoric nor pyrophosphoric acid coagulates albumen. When mixed with an equal volume of Tincture of Chloride of Iron, meta- and pyrophosphoric acids give a precipitate after some time (U. S. P.). Boil the aqueous solution of metaphosphoric acid for some time; on testing the solution the acid will be found to have been converted into orthophosphoric acid:—



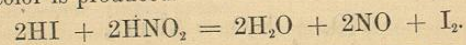
The ordinary medicinal phosphoric acid is made from phosphorus and nitric acid, the liquid being evaporated to a syrupy consistence to remove the last traces of nitric acid. It may contain pyrophosphoric and metaphosphoric acids, if the heat employed be high enough to remove the elements of water:—



On redilution the metaphosphoric acid only slowly reabsorbs water. If, therefore, on testing, metaphosphoric be found to be present, the solution should be boiled until conversion to orthophosphoric acid has occurred.

NITROUS ACID (HNO_2) AND OTHER NITRITES.—Strongly heat a fragment of nitrate of potassium or of sodium on a piece of platinum foil; oxygen is evolved and nitrite of potassium remains.

Test.—Dissolve the residue in water, add a few drops of dilute sulphuric acid, then a little weak solution of iodide of potassium, and, lastly, some mucilage of starch; the deep-blue compound of iodine and starch is at once produced. Repeat this experiment, using nitrate of potassium instead of nitrite; no blue color is produced.



Tests for Nitrites in Water.—This liberation of iodine by nitrites and not by nitrates is a reaction of considerable value in searching

for nitrites in ordinary drinking-waters, the occurrence of such salts being held to indicate the presence of nitrogenous organic matter in a state of oxidation or decay. The sulphuric acid used in the operation must be pure, and the iodide of potassium free from iodate. If much organic matter is present, however, the nitric acid liberated by the sulphuric may be reduced to nitrous acid. It is perhaps best, therefore, to add acetic acid, and (Fresenius) distil over 10 or 20 per cent. of the water and apply the test to this distillate. Very dilute solutions of nitrous acid may thus be distilled without the slightest decomposition.

Commercial Nitrous Acid.—The liquid commonly termed in pharmacy “nitrous acid” is simply nitric acid impure from the presence of nitrous acid.

The chief nitrites used in medicine are nitrites of organic basylous radicals; nitrite of ethyl ($\text{C}_2\text{H}_5\text{NO}_2$), or nitrous ether, is the most important constituent of “sweet spirit of nitre” (*Spiritus Ætheris Nitrosi*, U. S. P.; vide Index). Nitrite of amyl ($\text{C}_5\text{H}_{11}\text{NO}_2$) is also official (*Amyl Nitris*, U. S. P.). The double nitrite of cobalt and potassium is said to possess some therapeutic advantages over other nitrites. Nitrite of ammonium, on being heated, yields pure nitrogen gas, $\text{NH}_4\text{NO}_2 = 2\text{H}_2\text{O} + \text{N}_2$.

OPHELIC ACID ($\text{C}_{13}\text{H}_{20}\text{O}_{10}$).—This is one of the principles to which the herb *Ophelia chirata*, or Chiretta (*Chirata*, U. S. P.), owes its bitterness. It is an amorphous yellow body. Another is *Chiratin* ($\text{C}_{26}\text{H}_{48}\text{O}_{15}$), decomposable by hydrochloric acid into *Chiratogenin* ($\text{C}_{13}\text{H}_{24}\text{O}_3$) and ophelic acid (Höhn).

PHOSPHOROUS ACID (H_3PO_3 , or H_2PHO_3).—It is necessary to notice this compound in order that the reader may have brought before him the three acids of phosphorus, namely, phosphoric acid (H_3PO_4), phosphorous acid (H_3PHO_3), and hypophosphorous acid ($\text{H}_2\text{PH}_2\text{O}_2$): it will be noticed that in composition they differ from each other simply in the proportion of oxygen, the molecules containing four, three, and two atoms respectively. In constitution they differ by the hypothetical phosphoric radical or grouping being trivalent, the phosphorous bivalent, and the hypophosphorous radical univalent. These three acids and corresponding salts must not be confounded with pyrophosphoric and metaphosphoric acids and salts; the former are acids of phosphorus; the latter, varieties of phosphoric acid; the former, in composition, differ from each other in the proportion of oxygen they contain; the latter, by the elements of water:—

Acids of Phosphorus.

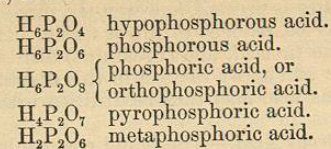
H_3PO_4 phosphoric acid.
 H_3PHO_3 phosphorous acid.
 $\text{H}_2\text{PH}_2\text{O}_2$ hypophosphorous acid.

Varieties of Phosphoric Acid.

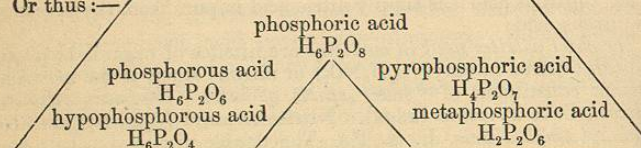
H_3PO_4 (ortho)phosphoric acid.
 $\text{H}_4\text{P}_2\text{O}_7$ pyrophosphoric acid.
 HPO_3 metaphosphoric acid.

When hypophosphorous acid is exposed to the air, oxygen is absorbed and phosphorous acid results; by prolonged exposure more oxygen is absorbed and phosphoric acid is obtained. When phosphoric acid, or rather, for distinction, orthophosphoric acid, is heated, every two molecules yield the elements and a molecule of water, and pyro-

phosphoric acid results; by prolonged exposure to heat more water is evolved, and metaphosphoric acid is obtained. These differences will be further evident if the formulæ be written empirically, nearly all being doubled, thus:—



Or thus:—



From the central compound, phosphoric acid, the acids of phosphorus differ by regularly diminishing proportions of the element oxygen (see previous page), the varieties of phosphoric acid by regularly diminishing proportions of the elements of water.

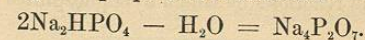
Prepare phosphorous acid by exposing a moist stick of phosphorus to the air; a thin stream of heavy white vapor falls, which contains the acid in question. The best method of collection is to place the stick in an old test-tube having a hole in the bottom, to support this tube by a funnel or otherwise, the neck of the funnel being supported in a bottle, test-glass, or tube, at the bottom of which is a little water. Having collected some phosphorous acid in this way, apply the various tests already alluded to under *Hypophosphorous Acid*, first carefully neutralizing the phosphorous acid by an alkali. The means by which the varieties of phosphoric acid are distinguished have been given under *Metaphosphoric Acid*. Associated with the phosphorous acid, prepared as above stated, there is said to be an acid having the formula H_2PO_3 , and termed *hypophosphoric acid*. Its anhydride would be P_2O_4 .

Other soluble phosphites are prepared by neutralizing phosphorous acid with alkalis, and the insoluble phosphites by double decomposition.

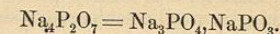
It is interesting to note that during the oxidation of phosphorus in moist air, not only are phosphoric, hypophosphoric, and phosphorous acids formed, but also oxygen (O_2), ozone (O_3), peroxide of hydrogen (H_2O_2), and a small quantity of nitrate of ammonium (NH_4NO_3).

PYROGALLIC ACID.—See *Tannic Acid*.

PYROPHOSPHORIC ACID ($\text{H}_4\text{P}_2\text{O}_7$) AND OTHER PYROPHOSPHATES.—Heat ordinary phosphate of sodium ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$) in a crucible; water of crystallization is first evolved and dry phosphate (Na_2HPO_4) remains. Continue the heat to redness; two molecules of the salt yield one molecule of water, and a salt having new properties is obtained:—



It is termed pyrophosphate of sodium, in allusion to its origin (*πῦρ, πῦρ*, fire). From its solution in water it may be obtained in prismatic crystals ($\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$), *Sodii Pyrophosphas*, U. S. P. Phosphoric acid itself is similarly affected by heat, $2\text{H}_3\text{PO}_4 - \text{H}_2\text{O} = \text{H}_4\text{P}_2\text{O}_7$ (pyrophosphoric acid), though metaphosphoric acid is also formed. Other pyrophosphates are produced in a similar way, or by double decomposition and precipitation, or by neutralizing pyrophosphoric acid by an oxide, hydrate, or carbonate. Possibly the pyrophosphates are only compounds of orthophosphates with metaphosphates:—



Tests.—To solution of a pyrophosphate add solution of nitrate of silver; white pyrophosphate of silver ($\text{Ag}_4\text{P}_2\text{O}_7$) falls as a dense white powder, differing much in appearance from the white gelatinous metaphosphate of silver or the yellow orthophosphate. To pyrophosphoric acid, or to a pyrophosphate mixed with acetic acid, add an aqueous solution of albumen (white of egg); no precipitate occurs. Metaphosphoric acid, it will be remembered, gives a white precipitate with albumen.

QUESTIONS AND EXERCISES.

600. What are the sources of lactic acid?
601. How is lactic acid usually prepared?
602. Name some of the plants in which malic acid is found.
603. Whence is meconic acid derived?
604. By what process may meconic acid be isolated?
605. Which is the best test for the meconic radical?
606. Distinguish meconates from sulphocyanates.
607. Give the mode of manufacture of hypophosphites.
608. How is phosphoretted hydrogen prepared?
609. By what ready method may metaphosphoric acid be obtained for experimental purposes?
610. Name the tests for metaphosphates.
611. How may meta- or pyrophosphoric acid be converted into orthophosphoric acid?
612. Describe the preparation of phosphorous acid.
613. State the relations which the acids of phosphorus bear to each other.

614. How are pyrophosphates prepared?
 615. Offer two views of the constitution of pyrophosphates.
 616. Define by formulæ, metaphosphates, pyrophosphates, orthophosphates, phosphites, and hypophosphites.
 617. Mention the tests by which meta-, pyro-, and orthophosphates are analytically distinguished.
 618. Name the reactions by which hypophosphites and phosphites are detected.

SILICIC ACID (H_4SiO_4) AND OTHER SILICATES.—Silicates of various kinds are among the commonest of minerals. The various *clays* are aluminium silicates; the volcanic substance termed *pumice-stone* is a porous silicate of aluminium and of alkali-metals or alkaline-earth metals; *meerschau* is an acid silicate of magnesium; the ordinary *sandstones* are chiefly silica; *sand*, *flint*, *quartz*, *agate*, *chalcidony*, and *opal* are silicic anhydride or silica (SiO_2). *Tripoli*, a polishing powder now found in many other countries than Tripoli, consists of infusorial skeletons of nearly pure silica. *Bath brick*, used in knife-polishing, is a silico-calcareous deposit found in the estuary at Bridgwater and other places. *Asbestos* or *amianth* is a fibrous silicate of calcium and magnesium, the length of the fibres being from less than one inch to five feet. A single silk-like fibre can easily be fused, but, even in very small masses, and for all practical purposes, asbestos is infusible and, of course, incombustible. It is also a bad conductor of heat. It is already largely used in piston-rods and joints and for steam apparatus generally; as a covering for boilers to prevent loss of heat by radiation; and for so lining ceilings, floors, and other partitions as to render rooms, etc. fire-proof. Artificial silicates are familiar under the forms of *glass* and *earthenware*. Common English window-glass is usually silicate of calcium, sodium, and aluminium; French glass, silicate of calcium and sodium; Bohemian, chiefly silicate of potassium and calcium; English flint or crystal-glass for ornamental, table, and optical purposes is mainly silicate of potassium and lead. Earthenware is mostly silicate of aluminium (clay), with more or less of silicate of calcium, sodium, and potassium, and, in the commoner forms, silicates of iron. The various kinds of *porcelain* (China, Sèvres, Meissen, Berlin, English), *Wedgwood-ware*, and *stoneware* are varieties of earthenware. *Kaolin* or *China Clay*, which is disintegrated *felspar*, not more common in China than in Devonshire and Cornwall, is the clay which yields the finest translucent porcelain. *Crucibles*, *bricks*, and *tiles* are clay silicates. *Mortar* is essentially silicate of calcium. *Portland*, *Roman*, and other hydraulic *cements* are silicates of calcium with more or less silicate of aluminium.

Mix together a few grains of powdered flint or sand with about five or six times its weight of carbonate of sodium and an equal quantity of carbonate of potassium, and fuse a little of the mixture on platinum-foil in the blowpipe-flame; the product is a kind of *soluble glass*. Boil the foil in water for

a few minutes, filter; to a portion add excess of hydrochloric acid, evaporate the solution to dryness, and again boil the residue in water and acid; oxide of silicon, *silicic anhydride*, or *silica* (SiO_2), remains as a light, flaky, insoluble powder.

The *soluble glass* or *glass liquor* of trade commonly contains 10 or 12 per cent. of soda (NaHO) to 20 or 25 per cent. of silica (SiO_2). When of sp. gr. 1.300 to 1.400 it satisfies official requirements (*Liquor Sodii Silicatis*, U. S. P.).

The foregoing operation constitutes the *test* for silicates. By fusion with alkali the silicate is decomposed, and a soluble alkaline silicate formed. On addition of acid, silicic acid (H_4SiO_4) is set free, but remains in solution if sufficient water is present. The heat subsequently applied eliminates water and reduces the silicic acid to silica (SiO_2), which is insoluble in water or acid. By the addition of hydrochloric acid to soluble glass, and removal of the resulting alkaline chloride and excess of hydrochloric acid by dialysis (a process to be subsequently described), a pure aqueous solution of silicic acid may be obtained; it readily changes into a gelatinous mass of silicic acid. Possibly some of the natural crystallized varieties of silica may have been obtained from the silica contained in such an aqueous solution, nearly all waters yielding a small quantity of silica when treated as above described.

A variety of silicic acid (H_4SiO_4) sometimes termed *dibasic*, to distinguish it from the normal or *tetrabasic* acid (H_4SiO_4), results when the aqueous solution of the latter is evaporated *in vacuo*.

Siliciuretted hydrogen, or hydride of silicon (SiH_4), is a spontaneously inflammable gas formed on treating silicide of magnesium with hydrochloric acid. It is the analogue of light carburetted hydrogen or methane (CH_4). A liquid chloride of silicon (SiCl_4) analogous to tetrachloride of carbon (CCl_4) and a gaseous fluoride (SiF_4) also exist. Many other analogies are traceable between the elements silicon, boron, and carbon, especially amongst organic compounds (see p. 332).

SUCCINIC ACID ($\text{H}_2\text{C}_4\text{H}_4\text{O}_4$).—Amber (*Succinum*) is a peculiar resin usually occurring in association with coal and lignite. From the fact that fragments of coniferous fruit are frequently found in amber, and impressions of bark on its surface, it is considered to have been an exudation from a species of *Pinus* now probably extinct. Heated in a retort, amber yields, first, a sour aqueous liquid containing acetic acid and another characteristic body appropriately termed *succinic acid*; second, a volatile liquid known as *oil of amber* (*Oleum Succini*, U. S. P.), resembling the oil yielded by most resinous substances under similar circumstances; and, third, a pitchy residue allied to asphalt. The succinic acid is a normal constituent of the amber; the acetic acid is produced during distillation. Succinic acid has also been found in wormwood, in several pine-resins, and in certain animal fluids, such as those of hydatid cysts, and hydrocele. It may be obtained artificially from butyric, stearic, or margaric acid by oxygen. Tartaric, malic, and succinic acids are also convertible the one into the other.