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

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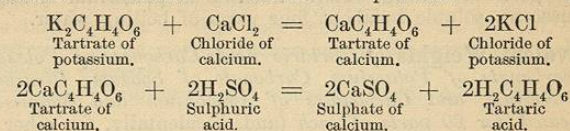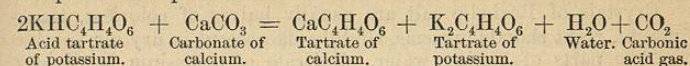
Tartaric Acid.

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

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

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

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

$$2KHC_4H_4O_6 + CaCO_3 = CaC_4H_4O_6 + K_2C_4H_4O_6 + H_2O + CO_2$$

Acid tartrate of potassium. Carbonate of calcium. Tartrate of calcium. Tartrate of potassium. Water. Carbonic acid gas.

$$K_2C_4H_4O_6 + CaCl_2 = CaC_4H_4O_6 + 2KCl$$

Tartrate of potassium. Chloride of calcium. Tartrate of calcium. Chloride of potassium.

$$2CaC_4H_4O_6 + 2H_2SO_4 = 2CaSO_4 + 2H_2C_4H_4O_6$$

Tartrate of calcium. Sulphuric acid. Sulphate of calcium. Tartaric acid.

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

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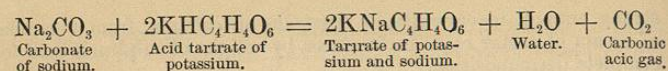
Reactions.

Tartrate of Potassium.

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

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

Tartrate of Potassium and Sodium.

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

$$Na_2CO_3 + 2KHC_4H_4O_6 = 2KNaC_4H_4O_6 + H_2O + CO_2$$

Carbonate of sodium.　　Acid tartrate of potassium.　　Tartrate of potassium and sodium.　　Water.　　Carbonic acic gas.

Crystals of Rochelle salt are usually halves of colorless, transparent, right rhombic prisms, slightly efflorescent in dry air, soluble in five parts of boiling water. Tartrate of potassium is slightly deliquescent, soluble in about four parts of boiling water.

Equivalent Weights *of Tartaric Acid, Carbonate of Potassium, Bicarbonate of Potassium, Carbonate of Sodium, Bicarbonate of Sodium, and Carbonates of Ammonium and Magnesium; repeated for 20 parts of each (and, incidentally, for other proportions).*

Tart. Acid	$H_2C_4H_4O_6$ = 150	**20**	$18\frac{1}{2}$	15	$10\frac{1}{2}$	$17\frac{3}{4}$	$28\frac{1}{2}$	$31\frac{1}{2}$
Carb. Potas	K_2CO_3 (of 84 per cent.) = 164	**22**	**20**	$16\frac{1}{2}$	$11\frac{1}{2}$	$19\frac{1}{2}$	$31\frac{1}{2}$	$34\frac{1}{2}$
Bicarb. Pot.	$2(KHCO_3)$ = 200	$26\frac{3}{4}$	$24\frac{1}{2}$	**20**	14	$3\frac{3}{4}$	$38\frac{1}{2}$	42
Carb. Soda (cryst.)	$Na_2CO_3,10H_2O$ = 286	38	$24\frac{1}{2}$	$28\frac{1}{2}$	**20**	34	$54\frac{1}{2}$	60
Bicarb. Soda	$2(NaHCO_3)$ = 168	$22\frac{1}{2}$	**20**	$16\frac{1}{2}$	$11\frac{1}{2}$	**20**	32	$35\frac{1}{2}$
Carb. Ammon	$(N_3H_{11}C_2O_5) \div 3 \times 2$ = 105	**14**	$12\frac{1}{2}$	$10\frac{1}{2}$	$7\frac{1}{2}$	$12\frac{1}{2}$	**20**	$21\frac{3}{4}$
Carb. Magnes	$(MgCO_3)_3Mg2HO,4H_2O$ = 95.5	$12\frac{3}{4}$	$11\frac{1}{2}$	$9\frac{3}{4}$	$6\frac{3}{4}$	$11\frac{1}{2}$	$18\frac{1}{2}$	**20**

Thus 20 parts (grains or other weights) of tartaric acid neutralize 22 of carbonate of potassium, $26\frac{3}{4}$ of bicarbonate of potassium, 38 of carbonate of sodium, $22\frac{1}{2}$ of bicarbonate of sodium, 14 of carbonate of ammonium, or $12\frac{3}{4}$ of carbonate of magnesium. Other quantities of tartaric acid ($18\frac{1}{4}$, 15, $10\frac{1}{2}$, $16\frac{3}{4}$, $28\frac{1}{2}$, $31\frac{1}{2}$) saturate the amounts of salts mentioned in the other columns, and *vice versâ*. A similar Table for Citric Acid will be found on page 322, and for both acids in the Appendix. These Tables afford good illustrations of the laws of chemical combination (page 48). The reader should verify a few of the numbers by calculation from the atomic weights of the elements concerned in the reactions, remembering that the salts formed are considered to be neutral in constitution. In medical practice effervescing saline draughts are often designedly prescribed to contain an amount of acid or alkali considerably in excess of the proportions required for perfect neutrality.

A common form of *Seidlitz Powder* consists of 3 parts of Rochelle salt (120 grains) with 1 (40 grains) of acid carbonate of sodium (the mixture usually wrapped in blue paper), and 1 (40 grains) of tartaric acid (wrapped in white paper). When administered, the one powder is dissolved in a tumbler rather more than half full of water, the other added, and the mixture drank during effervescence. It will be seen that the salts swallowed are tartrate of potassium and sodium ($KNaC_4H_4O_6$, $4H_2O$), tartrate of sodium ($Na_2C_4H_4O_6,2H_2O$), and acid tartrate of sodium or of potassium. The last-mentioned salt results because (for one reason) $11\frac{1}{4}$ per cent. ($4\frac{1}{2}$ grains) of the tartaric acid is in excess of the quantity necessary for the formation of neutral

tartrate of sodium; and, for another reason, while carbonic acid remains in great excess, a neutral tartrate containing potassium may be converted more or less into acid tartrate of potassium and bicarbonate. This amount of acid salt gives, according to the taste of some persons, agreeable acidity to the draught. The United States formula (*Pulvis Effervescens Compositus*, U. S. P.) includes rather less tartaric acid, so that only neutral salts are formed, and the occurrence or permanent occurrence of the gritty acid tartrate of potassium avoided.

"Double" Seidlitz Powder contains a double dose of Rochelle salt.

Analytical Reactions (Tests.)

First Analytical Reaction.—To solution of any normal tartrate, or tartaric acid made neutral by solution of soda, add solution of chloride of calcium; a white precipitate, tartrate of calcium ($CaC_4H_4O_6,4H_2O$), falls. Collect the precipitate on a filter, wash, place a small quantity in a test-tube, and add solution of potash; on stirring the mixture the precipitate dissolves. Heat the solution; the tartrate of calcium is again precipitated.

In the above reaction a fair amount of the chloride of calcium solution should be added at once, and the whole test performed without delay, or the calcium tartrate will assume a crystalline character, and be with difficulty dissolved by the potash.

The solubility of tartrate of calcium in cold potash solution enables the analyst to distinguish between tartrates and citrates, otherwise a difficult matter. Citrate of calcium is not soluble, or only to a very slight extent, in the alkali. The absence of much ammoniacal salt must be insured, citrate as well as tartrate of calcium being soluble in solutions of salts of ammonium.

Second Analytical Reaction.—Acidulate a solution of a tartrate with acetic acid, add acetate of potassium, and well stir the mixture; a crystalline precipitate of acid tartrate of potassium slowly separates.

This reaction is not applicable in testing for very small quantities of tartrates, the acid tartrate of potassium being not altogether insoluble. The precipitate being insoluble in alcohol, however, the addition of spirit of wine renders the test far more delicate. One part of acid should yield $1\frac{1}{4}$ of salt.

Third Analytical Reaction.—To a neutral solution of a tartrate add solution of nitrate of silver; a white precipitate of tartrate of silver, $Ag_2C_4H_4O_6$, falls. Boil the mixture; it blackens, owing to the reduction of the salt to metallic silver. Or, before boiling, add a drop, or less, of ammonia; a mirror will form on the tube—adhering well to the glass if the tube

was thoroughly cleansed. Even an insoluble tartrate, placed in a dry tube with a few fragments of nitrate of silver and a drop, or less, of ammonia added, gives a mirror-like character to each fragment of the silver salt when the tube is gently rotated some inches above a flame.

Fourth Analytical Reaction.—To a neutral or alkaline solution of a tartrate add a few drops of solution of permanganate of potassium, and slowly heat the test-tube; the color is discharged, an oxide of manganese being precipitated. Citrates only reduce the permanganate to green manganate.

Other Reactions.—Tartrates heated with strong sulphuric acid char immediately.——Tartaric acid and the soluble tartrates prevent the precipitation of ferric and other hydrates by alkalies, soluble double tartrates being formed (which on evaporation yield liquids that do not crystallize, but, spread on sheets of glass, dry up to thin transparent plates or scales). The *Ferri et Potassii Tartras*, U. S. P. (*Ferrum Tartaratum*, B. P.), is a preparation of this kind.——Tartrates decompose when heated, carbonates being formed and carbon set free, the gaseous products having a peculiar, more or less characteristic smell, resembling that of burnt sugar.

QUESTIONS AND EXERCISES.

546. State the origin of tartaric acid and other tartrates, and explain the deposition of argol, crude acid tartrate of potassium, during the manufacture of wine.

547. What is the chemical formula and what are the characters of "cream of tartar"?

548. Mention the formula and quantivalence of the tartaric radical.

549. Write formulæ of normal, acid, and double tartrates, tartar-emetic being treated as an oxytartrate of antimony with tartrate of potassium.

550. Give equations or diagrams illustrative of the production of tartaric acid from cream of tartar.

551. By what general process may normal or double tartrates be obtained from acid tartrate of potassium?

552. Work out sums proving the correctness of some of the figures given on p. 320 as showing the saturating power of tartaric acid for various quantities of different carbonates, and give diagrams or equations of the reactions.

553. State the names and work sums showing the quantities of the salts resulting from the admixture of 120 grains of tartrate of potassium and sodium, 40 grains of acid carbonate of sodium, and 40 grains of tartaric acid (Seidlitz powder).
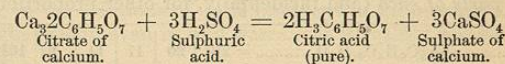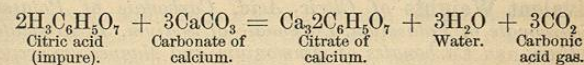
554. Enumerate the tests for tartrates, and explain the effects of heat on tartrates of the metals.

CITRIC ACID AND OTHER CITRATES.

Formula of Citric Acid $H_3C_6H_5O_7,H_2O$. Molecular weight 210.

Source.—Citric Acid (*Acidum Citricum*, U. S. P.) exists in the juice of the gooseberry, currant, cherry, strawberry, raspberry (*Rubus*, U. S. P.), and many other fruits, and in other parts of plants. The pulp of the fruit of *Tamarindus indica* (*Tamarindus*, U. S. P.) contains from 1 to 12 per cent. (in addition to 1.5 of tartaric acid, 5 of malic acid, and 3 per cent. of acid tartrate of potassium). But it is from the lemon or lime that the acid of commerce is usually obtained. For this purpose concentrated lemon-juice is exported from Sicily, concentrated bergamot juice from the Calabrian coast of South Italy, and concentrated lime-juice from the West Indies. The lime-fruit from *Citrus bergamia* is official in the Pharmacopœia of India.

Process.—The British Pharmacopœia directs that the hot lemon-juice (4 pints) be saturated by powdered chalk, that is, whiting (4½ ounces), the resulting citrate of calcium collected on a filter, washed with hot water till the liquor passes from it colorless (by which not only the coloring-matter, but the mucilage, sugar, and other constituents of the juice are got rid of), then mixed with cold water (1 pint) decomposed by sulphuric acid (2½ fluidounces in 1½ pints of water), the mixture boiled for half an hour, filtered, the solution evaporated to a density of 1.21, set aside for 24 hours, then poured off from any deposit of crystalline sulphate of calcium, further concentrated, and set aside to crystallize. If the quantity of citrate of calcium to be decomposed is indefinite, the sulphuric acid may be added until a little of the supernatant fluid gives, after a minute or two, a precipitate with solution of chloride of calcium. The concentrated citric solution generally crystallizes very slowly. Shaken violently, however, in a bottle, with a granule or two of solid acid, it quickly yields its citric acid in a pulverulent form, and this, drained and redissolved in a very small quantity of hot water, yields crystals fairly quickly (Warington).

$$2H_3C_6H_5O_7 + 3CaCO_3 = Ca_3 2C_6H_5O_7 + 3H_2O + 3CO_2$$
Citric acid (impure). Carbonate of calcium. Citrate of calcium. Water. Carbonic acid gas.

$$Ca_3 2C_6H_5O_7 + 3H_2SO_4 = 2H_3C_6H_5O_7 + 3CaSO_4$$
Citrate of calcium. Sulphuric acid. Citric acid (pure). Sulphate of calcium.

Quantivalence.—The elements represented by the formula $C_6H_5O_7$ are those characteristic of citrates. They form a trivalent grouping; hence three classes of salts may exist—one, two, or three atoms of the basylous hydrogen in the acid, $H_3C_6H_5O_7$, being displaced by equivalent proportions of other basylous radicals.

Citric acid itself is the only citric compound of much direct importance to the pharmacist. It usually occurs in colorless crystals soluble in half their weight of boiling and three-fourths of cold water, less soluble in spirit, and insoluble in ether. A solution of

about 34 grains in 1 ounce of water forms a sort of artificial lemon-juice. Citrates heated with strong sulphuric acid to about 212° F. evolve carbonic oxide gas, and at higher temperatures acetone and carbonic acid gas.

The artificial production of citric acid has been accomplished by Grimaux and Adam, who starting with glycerin, produce certain chloro- and cyano-derivatives, and ultimately citric acid itself.

Action of Heat on Citric Acid.—Citric acid slowly heated first loses its water of crystallization; afterwards (at 347° F.) the elements of another molecule of water are evolved and a residue obtained from which ether extracts *aconitic acid* ($H_3C_6H_3O_6$), identical with the aconitic acid (and the acid first termed *equisetic*) in various species of *Aconitum* and *Equisetum*.

The official Lemon Juice (*Limonis Succus*, U. S. P.) is to be freshly expressed from the ripe fruit, and to contain about 7 per cent. of citric acid. *Lime Juice* contains an average of 7.84 per cent. of citric acid, rarely rising to 10 per cent., and very seldom falling to 7 per cent. Containing but little sugar and mucilage, it requires no addition of spirit to preserve it. The acidity may be ascertained by adding solution of potash or soda (the strength of which has been previously determined with pure crystals of citric acid) till red litmus-paper is fairly turned blue. Before applying this test to commercial specimens, the absence of notable quantities of sulphuric, hydro-chloric, acetic, tartaric, or other acid must be insured by application of appropriate reagents. (See also "Lemon Juice," in Index.)

Mistura Potassii Citratis, U. S. P., is lemon-juice completely neutralized by bicarbonate of potassium. It is a slightly impure but flavored solution of citrate of potassium.

Lime Juice, as imported into England, contains an average of 7.84 per cent. of citric acid, rarely rising to 10 per cent., and very seldom falling to 7 per cent. Containing but little sugar and mucilage, it requires no addition of spirit to preserve it.

Lemon juice requires about 40 per cent. of proof spirit to prevent fermentation (Conroy).

Equivalent Weights *of Citric Acid, Carbonate of Potassium, Bicarbonate of Potassium, Carbonate of Sodium, Bicarbonate of Sodium, and Carbonates of Ammonium and Magnesium; repeated for 20 parts of each* (and incidentally, for other proportions).

Citric Acid............	$A_3C_6H_5O_7,H_2O$ ...... = 210	20	17	14	9¾	16¼	26¾	29¼
Carb. Potass.........	(K_2CO_3, of 84 p.ct.)÷2×3 = 246½	23½	20	16½	11½	19¾	31¼	34¼
Bicarb. Pot...........	3($KHCO_3$).................. = 300	28½	24½	20	14	24	38½	41¾
Carb. Sod. (cryst)....	($Na_2CO_3,10H_2O$)÷2×3... = 429	40	34½	28½	20	34½	54½	60
Bicarb. Sod.........	3($NaHCO_3$)................. = 252	24	20½	16½	11½	20	32	35
Carb. Ammon.......	($N_3H_{11}C_2O_5$÷3×2 .... = 157	15	12½	10¼	7½	12½	20	21¾
Carb. Magnes........	($MgCO_3)_3Mg2HO,4H_2O$ ÷8×3 = 143½	13¼	11¼	9¼	6½	11¼	18¼	20

Thus 20 parts (grains or other weights) of citric acid neutralize 23½ of carbonate of potassium, 28½ of bicarbonate of potassium, 40 of carbonate of sodium, 24 of bicarbonate of sodium, 16¼ of carbonate of ammonium, or 15 of carb. of magnesium. Other quantities of citric acid (17, 14, 9¾, 16¼, 26¾, 29¼) saturate the amount of salts mentioned in the other columns, and *vice versâ.*

This Table, the similar one for tartaric acid (p. 320), and that for both acids (*vide* Appendix) afford good illustrations of some of the laws of chemical combination (p. 47). The reader should verify a few of the numbers by calculation from the atomic weights of the elements concerned in the reactions, remembering that the salts formed are considered to be neutral in constitution. In medical practice, effervescing saline draughts are often designedly prescribed to contain an amount of acid or alkali considerably in excess of the proportions required for perfect neutrality.

Analytical Reactions (Tests).

First Analytical Reaction.—To a dilute solution of any neutral citrate, or citric acid carefully neutralized by alkali, add solution of chloride of calcium and boil; a white precipitate, citrate of calcium ($Ca_3 2C_6H_5O_7$), falls. Treat the precipitate as for tartrate of calcium (p. 321); it is not perceptibly dissolved by the potash.

A mixture of citrates and tartrates can be separated by this reaction. They are precipitated as calcium salts, and the rapidly washed precipitate mixed with solution of potash, diluted, and filtered; the filtrate contains the tartrate, which is shown to be present by reprecipitation on boiling. The precipitate still on the filter is washed, dissolved in solution of chloride of ammonium, and the solution boiled; the citrate of calcium is reprecipitated. The presence of much sugar interferes with this reaction. A dilute solution of a citrate is not precipitated by chloride of calcium until the liquid is heated; precipitation from a strong solution, also, is not thoroughly complete without ebullition of the mixture. This reaction is not thoroughly satisfactory, citrate of calcium being *slightly* soluble in alkalies, in the solutions of salts produced in the reaction, and, to a very slight extent, even in cold water. It is readily soluble in acetic acid.

Second Analytical Reaction.—To a neutral solution of a citrate add solution of nitrate of silver; a white precipitate of citrate of silver ($Ag_3C_6H_5O_7$) falls. Boil the mixture; the precipitate does not turn black as a tartrate of silver does, or only after long boiling.

Third Analytical Reaction.—To a neutral or alkaline solution of a citrate add a few drops of solution of permanganate of potassium and slowly heat the test-tube; reduction to man-

ganate only occurs, a green or reddish-green solution resulting. Tartrates reduce the permanganate entirely.

Other Analytical Reactions.—Citric acid forms no precipitate corresponding with the acid tartrate of potassium.——Lime-water, in excess, gives no precipitate with citric acid or citrates, unless the solution is boiled, citrate of calcium being slightly soluble in cold but not in hot water; it usually precipitates tartrates in the cold.——Citrates, when heated with strong sulphuric acid, do not char immediately.——Citric acid and citrates prevent the precipitation of oxide of iron by alkalies, soluble double compounds being formed. The *Ferri et Ammonii Citras*, U. S. P., is a preparation of this kind.——Metallic citrates decompose when heated, carbonates being formed and carbon set free: the odor of the gaseous products is not so characteristic as that of tartrates.——According to Cailletet, a cold saturated solution of red chromate of potassium turns a solution of tartaric acid dark brown, carbonic acid gas being evolved, while a solution of citric acid only slowly becomes of a light brown.

Pusch's Test for the Detection of Tartaric Acid in Citric Acid depends on the well-known difference in the action of sulphuric acid on tartaric action and citric acid. It consists in adding to 1 gramme of powdered citric acid in a dry test-tube 10 grammes of strong pure (colorless) sulphuric acid, and keeping the tube containing the mixture immersed in boiling water for an hour. The citric acid dissolves with the evolution of gas and frothing to form a lemon-colored liquid; and if the sample be pure, this color undergoes no change within half an hour, but if as much as half per cent. of tartaric acid be present, the lemon color becomes brownish within that time, and in an hour the mixture a red brown.


QUESTIONS AND EXERCISES.

555. What is the source of citric acid?

556. Describe the method by which citric acid is prepared, giving diagrams.

557. Illustrate by formulæ the various classes of tartrates and citrates.

558. State the average proportion of citric acid in lemon-juice.

559. Work out the sums proving the correctness of some of the figures given on page 324 as showing the saturating-power of citric acid for various carbonates.

560. What are the tests for citrates?

561. How are the tartrates separated from citrates?

PHOSPHORIC ACID AND OTHER PHOSPHATES.

Formula of Phosphoric Acid H_3PO_4. Molecular weight 98.

Source.—The source of the ordinary normal phosphates and of phosphorus itself (*Phosphorus*, U. S. P.) is the normal phosphate of calcium ($Ca_3 2PO_4$). It is the chief constituent of the bones of animals, being derived from the plants on which they feed, plants again obtaining it from the soil. Compounds of phosphorus are also met with in the brain, nerves, muscles, blood, saliva, and, according to Kirkes, even in tissues so simple that one must assume that the compounds are necessary constituents of the substance of the primary cell. They escape from the system both in the urine and in the fæces.

Process.—Phosphorus ($P = 31$) is obtained from bones by the following processes: The bones are burnt to remove all traces of animal matter. The resulting *bone-earth* is treated with sulphuric acid and water, by which an acid phosphate of calcium ($CaH_4 2PO_4$), often called *superphosphate of lime*, is produced:—

$$Ca_3 2PO_4 + 2H_2SO_4 = CaH_4 2PO_4 + 2CaSO_4.$$
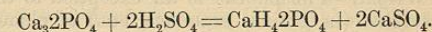
The acid phosphate (strained from the sulphate and evaporated to dryness) is mixed with charcoal and sand, and heated to dull redness in an iron pot. At this stage water escapes and metaphosphate of calcium ($Ca2PO_3$, see Index) remains:—

$$CaH_4 2PO_4 = Ca2PO_3 + 2H_2O.$$
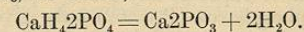
The mixture is then transferred to a retort, and distilled at a strong red heat; a silicate of calcium ($CaSiO_3$) is formed and remains in the retort, phosphorus vapor is evolved and condensed under water, and carbonic oxide gas escapes:—

$$2(Ca2PO_3) + 2SiO_2 + C_{10} = 2CaSiO_3 + 10CO + P_4.$$
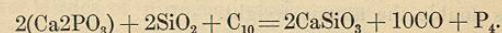
The phosphorus is purified by melting under water containing sulphuric acid and red chromate of potassium.

Properties.—Phosphorus is a "semi-transparent, colorless, wax-like solid (in sticks or cakes), which emits white vapors when exposed to the air. Specific gravity 1. 77. It is soft and flexible at common temperatures, melts at 110° F., ignites in the air at a temperature a little above its melting-point, burning with a luminous flame and producing dense white fumes. It is very poisonous. Insoluble in water, but soluble in ether and in boiling oil of turpentine," also in bisulphide of carbon. It is soluble in oil which has been previously heated for a short time to about 482° F. to expel moisture: 1 part in 90 parts of dried almond oil with 9 parts of ether constituting Phosphorated Oil, *Oleum Phosphoratum*, U. S. P. A mixture, or rather a solution, of phosphorus in chloroform, mixed with althea, acacia, and glycerin, forms the official Phosphorus Pills (*Pilulæ Phosphori*, U. S. P.).

Granulated or pulverulent phosphorus is obtained by placing a portion under equal parts of spirit and water in a bottle, standing

the bottle in warm water till the phosphorus melts, then inserting the stopper (glass, not cork), and shaking the whole till cold.

Red or Amorphous Phosphorus.—Ordinary phosphorus kept at a temperature of about 450° F., in an atmosphere from which air is excluded, becomes red, opaque, insoluble in liquids in which ordinary phosphorus is soluble, oxidizes extremely slowly, and only ignites when heated to near 500° F. It is used in the manufacture of several varieties of lucifer matches, not emitting the poisonous, jaw-destroying fumes given by ordinary phosphorus.

Quantivalence.—The atom of phosphorus is quinquivalent, as seen in the pentachloride (PCl_5) and oxychloride (PCl_3O); but it often exhibits trivalent activity, as seen in the trichloride (PCl_3) and trihydride (PH_3).

Phosphide of Zinc, Zn_3P_2 (*Zinci Phosphidum,* U. S. P.), occurs as a grayish-black powder or in crystalline fragments having a metallic lustre. It may be obtained by throwing phosphorus upon melted zinc.

Molecular Weight.—Phosphorus is an exception to the rule that the atomic weights (in grains, grammes, etc.) of elements occupy similar volumes of vapor at similar temperatures, the equivalent weight of phosphorus (31) only giving half such a volume. Hence while the molecular weights, that is, double the atomic weights, of oxygen ($O_2 = 32$), hydrogen ($H_2 = 2$), nitrogen ($N_2 = 28$), etc., give a similar bulk of vapor at any given temperature, the double atomic weight of phosphorus ($P_2 = 62$) only gives half this bulk; that is, four times the atomic weight of phosphorus must be taken to obtain the whole bulk. It would appear therefore that the molecule of phosphorus contains four atoms ($P_4 = 124$). As with sulphur, however, phosphorus in the state ordinarily known to us may be abnormal, and conditions yet be found in which the molecular weight is double the atomic weight.

Phosphoric Acid.

The chief use of phosphorus in pharmacy is the formation of Diluted Phosphoric Acid. Phosphorus is boiled with nitric acid and water until dissolved. The solution, evaporated to a low bulk to remove nitrous compounds, and diluted so as to contain 50 per cent. of acid (H_3PO_4), constitutes the *Acidum Phosphoricum,* U. S. P., a colorless liquid of specific gravity 1.347. If the necessary appliances are at hand, an ounce or two of this acid may be prepared by the official process as follows: Boil together, in a retort attached to a Liebig's condenser, 160 grains of phosphorus, 1000 grains of the official nitric acid, and 1000 grains of water. When about 1 oz. of water has distilled over, it should be returned to the retort, and the operation repeated until the phosphorus has disappeared.

$$3P_4 + 20HNO_3 + 8H_2O = 12H_3PO_4 + 20NO$$

Phosphorus.   Nitric acid.   Water.   Phosphoric acid.   Nitric oxide.
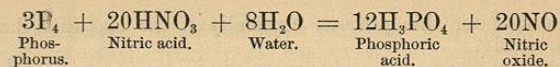
The liquid remaining in the retort is then transferred to a dish (preferably of platinum), evaporated down to about half an ounce, and, lastly, diluted with distilled water until the product weighs 1000 grains.

One part, by weight, of the official phosphoric acid with four of water yields *Acidum Phosphoricum Dilutum,* U. S. P. It contains 10 per cent. of H_3PO_4; sp. gr. 1.057.

The use of the water in the former part of this process is to moderate the reaction. Strong hot nitric acid oxidizes phosphorus with almost explosive rapidity, hence the acid must be diluted in the first instance, and be rediluted, from time to time, to prevent its becoming too strong by loss of water. Time is saved by using a strong acid, but in that case constant supervision is necessary in order that water may be added, or the temperature otherwise reduced, when the action becomes too violent. Deficiency of nitric acid must also be avoided, or some phosphorous acid (H_2PHO_3) will be formed.

Markoe, also, to economize time, modifies the process by adding, for every ounce of phosphorus, four or five grains of iodine, and, drop by drop, twenty-five or thirty drops of bromine. The iodine and bromine unite with the phosphorus with a readiness or even violence that would be explosive if not controlled by the presence of the cold fluid—further cooled, if necessary, by immersing the vessel in cold water. Iodide of phosphorus (PI_5) and bromide of phosphorus (PBr_5) are at once formed. These, in the presence of water, immediately yield hydriodic and hydrobromic acids (HI, HBr) and phosphoric acid. The nitric acid attacks the hydriodic and hydrobromic acids, forming the lower oxides of nitrogen, which escape as gas, water, and free iodine and bromine. The latter unite with more phosphorus, and the reactions are repeated. This carrying power of a little iodine or bromine, or both, would perhaps be indefinitely prolonged if no vapor of these elements or their acids escaped with the gases. The phosphorus having disappeared, excess of nitric acid is got rid of roughly by dropping in clean rags or paper (nitric oxide, carbonic acid gas, and water being formed), and the last portions by adding oxalic acid (which even still more readily yields similar products). Evaporation to a syrupy consistence finally removes all traces of iodine, bromine, oxalic acid, and moisture. The product is then diluted to any required extent.

Experimental Process.—A flask, in the neck of which a funnel is inserted, and a second funnel inverted, so that its mouth rests within the mouth of the first, is an efficient and convenient arrangement

Fig. 40.