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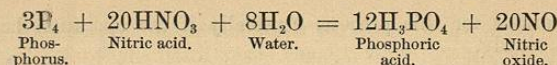
The liquid remaining in the retort is then transferred to a dish (preferably of platinum), evaporated down to about half an ounce, and, lastly, diluted with distilled water until the product weighs 1000 grains.

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.

Fig. 40.

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
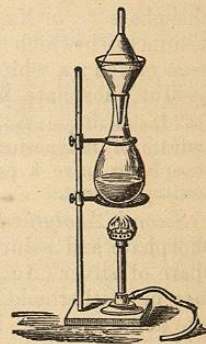
of apparatus for this process, especially if the operation be conducted slowly.

Solution of phosphoric acid evaporated to a specific gravity of 1.850 yields a mass of prismatic crystals of H_3PO_4, especially if a crystal or two be dropped into the fluid (Cooper). Further evaporated, it leaves a residue which melts at a low red heat, yielding *pyrophosphoric acid*, and, finally, *metaphosphoric acid* (*Glacial Phosphoric Acid*).

Phosphoric acid is also easily made from amorphous phosphorus (Mattison). Also by dissolving phosphoric anhydride in water, and boiling with a little nitric acid to oxidize any lower acids of phosphorus and to cause any lower phosphoric acids to take up the elements of water.

Prepared from bones, phosphoric acid is apt to develop fungoid deposits (Jensen). Not more than traces of arsenicum or of sulphur should be present in phosphorus, the former detected by sulphuretted hydrogen and the latter by chloride of barium solution after the phosphorus has been converted by nitric acid into phosphoric acid (U. S. P.).

Quantivalence.—The elements represented by the formula PO_4 are those characteristic of phosphates. The grouping is trivalent; hence there may exist trimetallic or normal phosphates (M'_3PO_4), dimetallic acid phosphates (M'_2HPO_4), monometallic acid phosphates ($M'H_2PO_4$), and, lastly, trihydric phosphate (H_3PO_4) or common phosphoric acid. These are the ordinary phosphates or *orthophosphates* met with in nature or used in pharmacy; the rarer pyrophosphates and metaphosphates, as well as the phosphites and hypophosphites, will be mentioned subsequently.

Analytical Reactions (Tests).

First Analytical Reaction.—To an aqueous solution of a phosphate (*e. g.* Na_2HPO_4) add solution of sulphate of magnesium with which chloride of ammonium and ammonia have been mixed; a white crystalline precipitate of ammonio-magnesium phosphate falls ($MgNH_4PO_4$).

Chloride of ammonium is added to prevent the precipitation of hydrate of magnesium. Arseniates, which have close analogy to phosphates, give a precipitate of similar character with the magnesium reagent.

Second Analytical Reaction.—To an aqueous solution of a phosphate add solution of nitrate of silver; light-yellow phosphate of silver (Ag_3PO_4) is precipitated completely if the mixture be neither acid nor alkaline. To a portion of the precipitate add ammonia; it dissolves. To another portion add nitric acid; it dissolves. By the former part of this reaction phosphates may be distinguished from their close allies the arseniates, arseniate of silver being of a chocolate color.

Third Analytical Reaction.—To solution (in a few drops

of acid) of a phosphate insoluble in water (*e. g.* $Ca_3 2PO_4$) add the acetate of an alkali-metal (easily made by adding to soda or ammonia in a test-tube excess of acetic acid), and then a drop or two of solution of perchloride of iron; yellowish-white ferric phosphate (Fe_2PO_4) is precipitated, insoluble in acetic acid. Too much of the ferric chloride must not be added, or ferric acetate will be produced, in which ferric phosphate is to some extent soluble.

To remove the whole of the phosphoric radical from the solution, add ferric chloride so long as a precipitate is produced, and boil; ferric phosphate and oxyacetate are precipitated.

To obtain confirmatory evidence of the presence of phosphate in this precipitate, and to separate the phosphoric radical as a pure unmixed phosphate, collect the precipitate on a filter, wash, drop some solution of ammonia on it, then sulphydrate of ammonium, and finally wash with water; black ferrous sulphide remains on the filter, while phosphate of ammonium occurs in the filtrate. To the filtrate add a mixture of solutions of sulphate of magnesium and chloride of ammonium, and well stir; ammonio-magnesian phosphate is precipitated.

Fourth Analytical Reaction.—To diluted nitric acid add a little phosphate of calcium (or any other phosphate), and then solution of molybdate of ammonium, and gently heat; a yellow precipitate falls.

This precipitate contains what is termed phospho-molybdic acid, but is a compound of molybdic acid with phosphoric acid (about 4 per cent. of H_3PO_4) and ammonia (nearly 7 per cent.).

Molybdate of ammonium is obtained by roasting the native sulphide of molybdenum (MoS_2) to molybdic oxide or anhydride (MoO_3), dissolving the latter in water, adding ammonia, evaporating, and crystallizing.

Molybdates having the following formulæ (M = 1 univalent atom of any metal) have been obtained: M_2MoO_4; $MHMoO_4$; $MHMoO_4$, H_2MoO_4. According to Carrington, commercial molybdate of ammonium is commonly the intermediate of these three salts. Molybdate of sodium has the formula Na_2MoO_4, H_2O.

Note.—The foregoing two reactions are useful in the analysis of bone-earth, other earthy phosphates, phosphate of iron, and all phosphates insoluble in water. Only arseniates give similar appearances; but the acid solution of these may be decomposed by agitation with sulphurous acid and subsequent treatment with sulphuretted hydrogen, arsenious sulphide, As_2S_3, being then precipitated.

Other Analytical Reactions.—Solutions of barium and calcium salts give, with aqueous solutions of phosphates, white precipitates of the respective phosphates $BaHPO_4$, or $Ba_3 2PO_4$, and $CaHPO_4$, or $Ca_3 2PO_4$, all of which are soluble in acetic and the stronger acids.

QUESTIONS AND EXERCISES.

562. State the source of phosphorus.

563. Give equations or diagrams explanatory of the isolation of phosphorus from its natural compounds.

564. What is the composition of farmers' "superphosphate," and how is it prepared?

565. Enumerate the properties of phosphorus.

566. Mention some solvents of phosphorus.

567. How are the varieties of official Phosphoric Acid made?

568. Describe the precautions necessary to be observed in making this acid.

569. What are the strengths of the official acids?

570. Write formulæ illustrative of all classes of orthophosphates.

571. Mention the chief tests for soluble and insoluble phosphates.

572. By what reactions may phosphates be distinguished from arseniates?

Vanadium, V. 51.3, is a very rare element, and is here mentioned only because of its exceedingly interesting relationship to nitrogen, phosphorus, and arsenicum. Discovered but not isolated by Sefström, and its compounds investigated by Berzelius, it has only of late years been obtained in the free state and fully studied by Roscoe.

Oxides of Nitrogen.		Oxides of Vanadium.	
N_2O_5, N_2O_4, N_2O_3, N_2O_2, N_2O.		V_2O_5, V_2O_4 V_2O_3, V_2O_2, V_2O.	
Orthophosphates	$R_3'PO_4$	Orthovanadates	$R_3'VO_4$
Pyrophosphates	$R_4'P_2O_7$	Pyrovanadates	$R_4'V_2O_7$
Metaphosphates	$R'PO_3$	Metavanadates	$R'VO_3$

Isomorphous Minerals.

Apatite	$3(Ca_3 2PO_4),CaFl_2$
Pyromorphite	$3(Pb_3 2PO_4),PbCl_2$
Mimetesite	$3(Pb_3 2AsO_4),PbCl_2$
Vanadinite	$3(Pb_3 2VO_4),PbCl_2$

BORIC ACID AND OTHER BORATES.

Formula of Boric Acid H_3BO_3. Molecular weight 62.

The composition of artificial boric acid, sometimes termed boracic acid, is expressed by the formula H_3BO_3 (*Acidum Boricum,* U. S. P.); but at a temperature of 212° F. this body loses the elements of water, and yields metaboric acid, HBO_2, which at higher temperatures becomes boric anhydride (B_2O_3). The latter acid exists in the jets of steam (*fumerolles* or *suffioni*) that issue from the earth in some districts of Tuscany and collects in the water of the *lagoni* (lagoons or little lakes) formed at the orifices of the steam-channels. This acid

liquid, evaporated by aid of the waste natural steam and neutralized by carbonate of sodium, gives common borax ($2NaBO_2,2HBO_2,9H_2O$), possibly an acid metaborate of sodium with water of crystallization, or, possibly, a metaborate of sodium with boric anhydride ($2NaBO_2,-B_2O_3,10H_2O$). It occurs "in transparent colorless crystals, sometimes slightly effloresced, with a weak alkaline reaction; insoluble in rectified spirit, soluble in water." Native borax, or *tincal,* and other borates are also found in Thibet, in Nevada, Peru, Chili, and recently in California, in the Clear Lake district. The introduction of the natural borax from California has reduced the price to about one-half its former amount. This borax is represented as forming large portions of the crystalline bed of a dried-up lake. Fused borax readily dissolves metallic oxides, as will have been already noticed in testing for cobalt and manganese. Hence, besides its use in medicine (*Sodii Boras,* U. S. P.), it is employed as a flux in refining and other metallurgic and ceramic operations.

Quantivalence.—The boric radical is trivalent (BO_3'''), the metaboric, univalent (BO_2'). *The element boron,* like carbon, occurs in the amorphous, graphitoidal, and crystalline conditions. It is a trivalent element (B'''), yielding definite salts, such as the chloride (BCl_3) and fluoride (BF_3). Its atomic weight is 11.

REACTIONS.

First Synthetical Reaction.—To a hot solution of a crystal of borax add a few drops of sulphuric acid and set aside; on cooling, crystalline scales of boric acid (H_3BO_3), *Acidum Boricum,* B. P., are deposited. They may be purified by collecting on a filter, slightly washing, drying, digesting in hot alcohol, filtering, and setting aside; pure boric acid is deposited. The acid may also be recrystallized from water. Fifty grains dissolved in one ounce of rectified spirit constitute "Solution of Boric Acid," B. P.

Boric acid is a very weak compound. Indeed, the alkalinity of borax is as great as if it contained no acidulous radical. The acid only slowly decomposes carbonates. Boric acid is said to be itself an antiseptic, but Endemann states that in preserving foods it acts by converting phosphates into acid phosphates, and that the latter are the antiseptic principles.

Second Synthetical Reaction.—Mix together 1 part of boric acid, 4 of acid tartrate of potassium, and 10 or 20 of water; evaporate to a syrupy consistence, spread on plates, and set aside for dry scales to form. The resulting substance is, in water, far more readily soluble than either of its constituents, and is known as *boro-tartrate of potassium* or *soluble cream of tartar.* The Prussian *tartarus boraxatus* differs from the foregoing French variety in containing 1 part of *borax* to 3 of acid tartrate of potassium.

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.
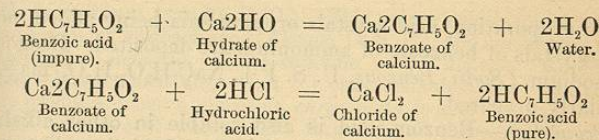

The foregoing acids and other salts contain the only acidulous radicals that are commonly met with in analysis or in ordinary medical or pharmaceutical operations. There are, however, many others which occasionally present themselves. The chief of these will now be shortly noticed; they are arranged 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.
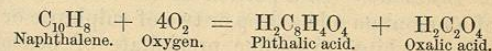
The phthalic acid is neutralized by lime, and the phthalate of calcium heated with hydrate of calcium in a covered vessel at a temperature of about 640° F. for several hours. Benzoate and carbonate of calcium are formed, and from the powder the benzoic acid is set free by action of hydrochloric acid.

$$2CaC_8H_4O_4 \ + \ Ca2HO \ = \ Ca2C_7H_5O_2 \ + \ 2CaCO_3$$

Phthalate of calcium.   Hydrate of calcium.   Benzoate of calcium.   Carbonate of calcium.