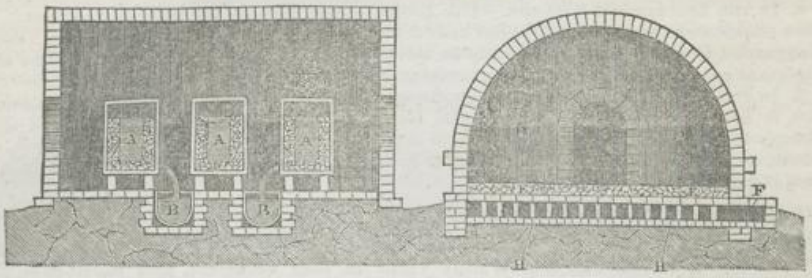
FIG. 57.



Crystallization and Drying Chambers.

A, A, A. Wooden tubs lined with lead, in which the acid crystallizes.
B, B. Mother liquor.
C. Basket in which the crystallized acid is placed to drain before it is conveyed to the drying chamber.
D, D. Drying chamber.
E, E. Boracic acid drying on the floor (F,) between which and the lower floor (H) the hot vapour circulates.

Boracic Acid may also be obtained by dissolving borax in hot water, and adding half its weight of oil of vitriol. As the solution cools, crystals of boracic acid (retaining a little sulphuric acid) are deposited, which must be well washed. Or borax may be decomposed by hydrochloric acid, by which a purer boracic acid is procured.

PROPERTIES.—Crystallized boracic acid occurs in the form of white, transparent, pearly, hexagonal scales, which are odourless, have a weak, scarcely acid, taste, and communicate a wine-red tint to litmus. At 60° the crystallized acid requires 25·66 times its weight of water to dissolve it, but only 2·97 times at 212.° It dissolves readily in spirit of wine. When sufficiently heated it evolves its water of crystallization, melts, forming a transparent liquid, which, by cooling, becomes a brittle glass (*vitrified boracic acid.*)

Characteristics.—An alcoholic solution of boracic acid burns with a beautiful green flame. A hot aqueous solution of the acid renders turmeric paper brown, like the alkalis. (Faraday, *Quarterly Journal of Science*, vol. ix. p. 403.) Before the blowpipe, boracic acid fuses, and forms a glass which may be tinged blue by chloride of cobalt, and rose-red by the terchloride of gold. A mixture of one part of vitrified boracic acid, finely pulverized, two parts of fluor spar, and twelve parts of oil of vitriol, evolves, by heat, the fluoride of boron, recognised by its forming dense white fumes in the air, and by its charring paper, wood, &c.

COMPOSITION.—The following is the composition of boracic acid:—

	Atoms.	*Eq. Wt.*	*Per Ct.*	*Berzelius.*
Boron	1	10	29·41	31·18
Oxygen	3	24	70·59	68·82
Dry Boracic Acid	1	34	100·00	100·00

	Atoms.	*Eq. Wt.*	*Per Ct.*	*Berzelius.*
Dry Boracic Acid	1	34	55·74	56
Water	3	27	44·26	44
Crystallized Boracic Acid	1	61	100·00	100

PHYSIOLOGICAL EFFECTS AND USES.—Though sedative properties were formerly ascribed to this acid, it is probably inert, or nearly so. Cullen (*Materia Medica*, p. 341.) gave it in large doses without observing that it produced any effect on the human body. It is, therefore, not employed in medicine; but it is extensively used in the manufacture of borax. (See *Sodæ Biboras.*)

ORDER IX. PHOSPHORUS AND PHOSPHORIC ACID.

1. PHOS'PHORUS, *L.*—PHOSPHORUS.

HISTORY.—This substance was discovered, in 1669, by Brandt, an alchymist at Hamburgh; and received its name from being luminous in the dark (from φως, *light*, and φερω, *I carry.*)

Natural History.—Phosphorus is found in both kingdoms of nature.

α. In the Inorganized Kingdom.—It is comparatively rare in the mineral kingdom. Various phosphates are found native, but in small quantities: those of Lime, Lead, Iron, Copper, Manganese, Uranium, and Yttria, may be mentioned as examples. Phosphate of Lime is an important constituent of the organic exuviæ entombed in the fossiliferous rocks.

β. In the Organized Kingdom.—Phosphoric acid, free, or combined with lime, potash, or iron, is found in various vegetables. (De Candolle, *Phys. Végét.* pp. 383, 387, and 390.) Phosphorus is a constituent of animals: in some cases it is in combination with oxygen, and a base, as in the bones, urine, &c.; in other instances, as in the brain, it is uncertain in what form it exists.

Preparation.—Phosphorus is obtained from bone-ash, which is principally composed of the sub- or six-eighths *phosphate of lime*. The bones of the sheep are preferred, as the ash which they yield is less compact, and more easily attacked by the acid. Sulphuric acid is gradually added to the bone-ash previously made into a thin pap with water. Carbonic acid is evolved, while sulphate and a soluble superphosphate of lime are formed. Water is added, and at the end of twenty-four hours the liquor is filtered and evaporated in leaden or copper pans to the consistence of sirup or honey. It is then mixed with charcoal, dried, and distilled in an earthen retort. The charcoal abstracts the oxygen from the phosphoric acid of the superphosphate, setting free the phosphorus, which is volatilized, and condensed in water contained in a copper receiver. It is afterwards purified by pressing it through shamoy leather under water. It is subsequently moulded for sale into cylinders, by melting it in water, and sucking it up a slightly conical glass tube, which is then immersed in cold water, when the solidified stick of phosphorus falls out.[1]

Properties.—It is a pale yellow, semitransparent, crystallizable, highly combustible solid. Mitscherlich says the crystals are rhombic dodecahedrons; so that they belong to the regular or cubic system. Light, especially violet light, reddens it.

Its sp. gr. is 1·77. At ordinary temperatures it is flexible, but at 32° is brittle. It melts at 108°, and boils at 550° F. It gives off a small quantity of vapour at ordinary temperatures. In the atmosphere its fumes are luminous in the dark, in consequence of a slow combustion: they have the odour of garlic. By keeping in water, phosphorus becomes coated by a white substance, by some regarded as an oxide, by others as the hydrate of phosphorus. By Rose it is considered to be phosphorus in a peculiar mechanical state. Phosphorus is insoluble in water, but soluble in ether, and the oils both fixed and volatile. It may be reduced to powder by melting it under water, and shaking in a closed vessel until cold. Its equivalent by weight is 16.

Characteristics.—Phosphorus, in substance, is easily recognised by its waxy appearance and garlic-like odour; by its fuming in the air, and being phosphorescent or luminous in the dark; by friction or gentle heat causing it to inflame; and, lastly, by its burning with a most intense white light and a white smoke of phosphoric acid, in air, or still better in oxygen gas. A solution of phosphorus in oil or ether, may be known by its garlic-like odour, and, when rubbed on the skin, by its rendering the latter luminous in the dark.

Physiological Effects. *α. On Vegetables.*—According to Marcet it is poisonous to plants.

β. On Animals generally.—Water impregnated with phosphorus acts as an aphrodisiac to drakes. (Alph. Leroy, quoted by Bayle, *Biblioth. de Thérap.* t. ii. p. 28. Paris, 1830.) Phosphuretted oil is a stimulant to horses: blood drawn from the veins of horses under its influence has a phosphoric odour. (Pilger. quoted by Bayle.) If phosphuretted oil be injected into the jugular vein, or into the cavity of the pleura of a dog, white vapours of phosphorus are evolved from

[1] For farther details consult Soubeiran, *Nouveau Traité de Pharmacie*, t. ii. p 260, 2de éd.: also Ure, *Dict. of Arts.*

the mouth, and death shortly takes place. The phosphorous acid (formed by the combustion of the phosphorus) inflames the lungs in its passage through the delicate pulmonary vessels. Introduced into the stomach of animals, phosphorus acts as a caustic poison. The corrosion is supposed to depend on the action of the phosphorous acid (formed by the combination of the phosphorus with the oxygen of the air contained in the pulmonary canal) on the tissue with which it is in contact. (Orfila, *Toxicol. Génér.*)

γ. *On Man.*—In *small doses*, phosphorus acts as a powerful and diffusible stimulant, exciting the nervous, vascular, and secreting organs. It creates an agreeable feeling of warmth at the epigastrium, increases the frequency and fulness of the pulse, augments the heat of skin, heightens the mental activity and the muscular powers, and operates as a powerful sudorific and diuretic. Its aphrodisiac operation has been recognised by Alphonse Leroy, and Bouttatz, (Bayle, *op. cit.*) by experiments made on themselves. In *somewhat larger doses* it causes burning pain, vomiting and purging, with extreme sensibility of the stomach, which lasts for several days. (See an experiment made by Sundelin on himself, *Handb. der. Heilmittellehre*, 2ᵉ. Bd. S. 213.) In *still larger doses*, it causes inflammation of the stomach and bowels. Its activity as a caustic poison depends, according to Orfila, on its absorbing oxygen, and thus becoming converted into an acid which acts as a corrosive, like the other mineral acids. Hence, therefore, etherial and oleaginous solutions are more active poisons, inasmuch as the oxidation of the phosphorus is effected more rapidly. Comparatively small doses have in some cases proved fatal. Dr. Christison (*Treatise on Poisons.*) mentions one instance in which 1½ grains, in another instance 3 grains, caused death.[1] Cases, however, are reported, in which 6, 10, and even 12 grains have been swallowed without any hurtful effects; but doubts have been entertained as to the correctness of the statements. Thus Merat and De Lens (*Dictionnaire de Matière Médicale.*) think that the phosphorus employed in these cases must have undergone some chemical change. I once administered 16 grains of apparently good phosphorus to a man without any injurious effect. The person here alluded to was Chabert, some years ago renowned in London under the name of the "*Fire King.*" I carefully weighed the above quantity, which was placed in a spoon, introduced into his mouth, and washed down by a tumblerful of water. He offered to take this dose daily. Within ten minutes after swallowing the phosphorus, he left the room for about a quarter of an hour.

Uses.—In this country, phosphorus is rarely employed, and therefore, it will be unnecessary to enter minutely into its uses. It has been strongly recommended in those cases attended with great prostration of the vital powers, as in the latter stages of typhus fever, dropsies, &c.; in some chronic diseases of the nervous system (as epilepsy, paralysis, melancholy, mania, amaurosis, &c.,) occurring in debilitated subjects. In some of the exanthemata, as measles, it has been administered to promote the re-appearance of the eruption when this, from some cause, had receded from the skin. In *impotentia virilis* of old and debilitated subjects, in cholera, and in some other maladies, it has also been exhibited. Paillard recommends phosphorus as a caustic, in the place of moxa, than which, he says, it is more convenient and safe. (*Lond. Med. Gaz.* vol. ii. p. 254.)

Administration.—Phosphorus cannot be given with safety in the solid form. It may be administered dissolved in ether, or, still better, in oil.

Antidotes.—In poisoning by phosphorus, large quantities of mild demulcent liquids are to be exhibited, so as to envelop the phosphorus and exclude it from the air contained in the alimentary canal. Magnesia should be given, in order to neutralize the phosphorous and phosphoric acids which may be formed. Parts

[1] In the *Morning Herald* of June 17, 1840, is a report of an inquest held on the body of a child killed by sucking the phosphoric ends of lucifer matches.

burned with phosphorus are to be washed with a weak alkaline solution, to remove any adhering acid which might serve to keep up irritation.

1. TINCTURA ÆTHEREA CUM PHOSPHORO, *French Codex.*—(Phosphorus 4 parts, Sulphuric Ether 200 parts by weight. Macerate for a month, in well-stoppered bottles covered with black paper, occasionally shaking. Preserve it in small bottles, well stoppered and covered with black paper. The quantity of phosphorus dissolved is about 4 grains for each ounce of ether. Dose from 5 to 10 drops. Some objection has been raised to the use of this preparation on the ground that, by the evaporation of the ether, the phosphorus will be set free in the stomach, and might ignite.

2. OLEUM PHOSPHORATUM, *Ph. Borussica.*—(Phosphorus dry and cut into small pieces, gr. xij.; Almond Oil, recently prepared, ℥j. Melt the phosphorus in the oil by the aid of warm water: then agitate until it appears to be dissolved.) One ounce of oil dissolves about 4 grs. of phosphorus. Dose from 5 to 10 drops. It should be administered in some mucilaginous liquid, or made into an emulsion. It may be *aromatized* by a few drops of some essential oil, as of bergamot.

2. ACIDUM PHOSPHORICUM DILUTUM, *L.*—PHOSPHORIC ACID.

HISTORY.—Phosphoric acid was first distinguished by Marggraf, in 1740.

NATURAL HISTORY.—(See *Phosphorus.*)

PREPARATION.—In the London Pharmacopœia, diluted phosphoric acid is ordered to be thus prepared:—

Take of Phosphorus, ℥j.; Nitric Acid, f℥iv.; Distilled Water, f℥x. Add the phosphorus to the nitric acid, mixed with the water, in a glass retort placed in a sand-bath; then apply heat until eight fluid ounces are produced [distilled.] Let these be again put into the retort that eight fluid ounces may distil, which are to be rejected. Evaporate the remaining liquor in a platinum capsule until only two ounces and six drachms remain. Lastly, add to the acid, when it is cold, as much distilled water as may make it accurately measure twenty-eight fluid ounces.

In this process six equivalents or 96 parts of phosphorus react on five equivalents or 270 parts of nitric acid, and abstract fifteen equivalents or 120 parts of oxygen, with which they form six equivalents or 210 parts of phosphoric acid, while five equivalents or 150 parts of the binoxide of nitrogen are evolved.

MATERIALS.		COMPOSITION.		PRODUCTS.	
5 eq. Nitric Acid	270	5 *eq. Nitrogen*	70	5 eq. Binox. Nitrogen	150
		10 *eq. Oxygen*	80		
		15 *eq. Oxygen*	120	6 eq. Phosphoric Acid	216
6 eq. Phosphorus	96				
	366				366

If strong nitric acid be employed, instead of the dilute acid ordered in the Pharmacopœia, the re-action is so energetic that explosion and combustion are sometimes the consequence. In such cases some nitrate of ammonia is usually developed: the ammonia being formed by the union of the nitrogen of the acid with the hydrogen of the water.

PROPERTIES.—The aqueous solution of phosphoric acid (*acidum phosphoricum dilutum*, Ph. L.) prepared as above, is a colourless and odourless liquid. It possesses the usual characteristics of an acid; that is, it is sour to the taste, reddens litmus, and neutralizes bases. Its sp. gr., according to the London Pharmacopœia, is 1·064. By evaporation it acquires the consistence of treacle (*hydrated phosphoric acid:*) and when exposed to a higher temperature, it loses water and becomes *pyrophosphoric acid.* At a dull red heat a farther evolution of water takes place, and a compound is formed, called *metaphosphoric acid;* this is fusible, and by cooling concretes into a transparent solid, called *glacial phosphoric acid.*

Characteristics.—If phosphoric acid be saturated with an alkali (soda) so as to

form a soluble phosphate, it may be distinguished from all other acids by the following characters: it throws down, with the soluble salts of lime, lead, and baryta, white precipitates (*phosphates*) soluble in nitric acid: with the nitrate of silver it causes a yellow precipitate (*subsesquiphosphate of silver*) soluble in nitric acid and in ammonia: hydrosulphuric acid causes no change of colour or precipitate with it: if the soluble phosphate be heated to redness, it is converted into a pyrophosphate, which gives, with the nitrate of silver, a white precipitate (*pyrophosphate of silver.*)

Purity.—The following are the qualities of this preparation, as given in the London Pharmacopœia:—

"Chloride of barium or nitrate of silver being added, whatever is thrown down is readily dissolved by nitric acid. Strips of copper and silver are not at all acted upon by it, nor is it coloured when hydrosulphuric acid is added. Its sp. gr. is 1·064; 42 grs. of [crystallized] carbonate of soda are saturated by 100 grs. of this acid, and nothing is thrown down."

The chloride of barium is to detect sulphuric acid: while the nitrate of silver detects hydrochloric acid. Should any free nitric acid be present, a portion of the copper and silver would be dissolved; and the solution would yield a dark precipitate with hydrosulphuric acid. The quantity of carbonate of soda saturated indicates the per-centage strength to be 10·5. The absence of any precipitate, on the addition of carbonate of soda, shows that no phosphate of lime or any other earthy phosphate is present.

Composition.—Pure anhydrous phosphoric acid is thus composed:—

	Atoms.	*Eq. Wt.*	*Per Cent.*	*Berzelius.*	*Dulong.*	*Davy.*
Phosphorus	1	16	44·44	44·05	44·8	4·26
Oxygen	2½	20	55·56	55·05	55·2	57·4
Phosphoric Acid	1	36	100·00	100·00	100·0	100·0

Mr. Phillips says, that 100 grains of the diluted acid of the Pharmacopœia saturate 42 grains of [crystallized] carbonate of soda. This indicates its composition to be as follows:—

	By Weight.
Phosphoric Acid	10·5
Water	89·5
Diluted Phosphoric Acid, *Ph. L.*	100·0

Physiological Effects. *α. On Vegetables.*—This acid is poisonous to plants. (Gœppert, quoted by De Candolle, *Phys. Végét.*)

β. On Animals.—Very few experiments have hitherto been made with it on animals. Orfila (*Toxicolog. Génér.*) found that a strong solution of it acted like sulphuric acid. Thrown into the veins of a dog, it coagulated the blood and killed the animal within ten minutes. Introduced into the stomach, it acted as a powerfully corrosive poison.

γ. On Man.—Diluted phosphoric acid produces the usual effects of the diluted mineral acids, and which I have before noticed (pp. 192, 198, and 207.) It is, therefore, denominated tonic and refrigerant, and may be employed wherever the mineral acids are indicated. It is milder, more assimilable, and, therefore, less likely to disagree with the digestive organs, than sulphuric acid, with which, in its action, it is usually compared. These qualities it perhaps derives from its being, as Burdach (*Arzneimittellehre*, Bd. 3. S. 395. 1809.) expresses it, "less heterogeneous to the human organism, since it has a considerable share in the composition of it." The same authority also observes, that besides fulfilling the indications of the mineral acids, "it much exalts the excitability when the organism is weak."

Various effects have been ascribed to this acid, which require to be farther investigated ere they are admitted. Thus Hecker (*Arzneimittel.* Bd. 2. S. 305.) says, it exerts a special influence over the nervous system, in virtue of which it possesses the power of allaying pain and spasm. Lentin (*Beitrage zur ausüb.*

Heilk. Bd. 2. S. 139.) considers it to be endowed with the specific power of influencing secreting surfaces and the bones, whereby it is enabled to ameliorate various morbid conditions of these parts. Sundelin (*Heilmittell.* Bd. 2. S. 234.) regards it as a stimulant and tonic to the sexual organs. Various effects have been ascribed to it by Herder. (*Hufeland's Journ.* Bd. 9. St. 3. S. 148.)

Uses.—Phosphoric acid has been employed in the same cases in which sulphuric and other mineral acids have been used, and under the same regulations. It may be employed for a longer period, without disturbing the digestive functions, than the other agents of this class.

It has been used in certain cases rather on theoretical than practical grounds. Thus its power of dissolving phosphate of lime has led to its employment in those forms of lithiasis attended with phosphatic deposites in the urine,—in ossification of the arteries and cardiac valves,—and in exostosis and other osseous tumours. Lentin used it as a local agent to check caries, from a notion that this disease depends on a deficiency of phosphoric acid in the part affected. Woulff applied it to promote the formation of bone.

There are several other diseases against which this acid has been administered. Thus it has been given in blennorrhœa and leucorrhœa, when the secreted fluid was thin and acrid (Sundelin,)—in profuse suppuration, to diminish the quantity and improve the quality of the secreted matter,—in hysterical affections of young and irritable subjects, Sundelin has found it useful,—in impotency of the male (Berends,)—in diabetes, and in jaundice. Dr. Paris (*Appendix to the 8th ed. of the Pharmacologia.* Lond. 1836.) has found it to assuage the thirst so commonly present in diabetes, more effectually than any other acidulated drink.

Administration.—Internally the dilute phosphoric acid should be given in doses of from ten minims to a fluid-drachm, properly diluted. Mixed with eight or ten times its volume of water, it may be employed as a wash in caries.

Antidote.—(See *Sulphuric Acid.*)

Order X. SULPHUR AND ITS NON-METALLIC COMPOUNDS.

1. SUL'PHUR, *L. E.*—SULPHUR OR BRIMSTONE.

History.—Sulphur has been known from the most remote periods of antiquity. It is mentioned by Moses, (*Genesis*, xix. 24.) Homer, (*Iliad*, lib. xvi.) and other ancient writers.

Natural History.—It is found in both kingdoms of nature.

α. In the Inorganized Kingdom.—*Native* or *virgin sulphur* occurs in two forms: either imbedded in rocks (*common native sulphur,*) or produced by sublimation (*volcanic sulphur.*) In Sicily[1] it is found in beds in a blue clay formation, which, in the opinion of Dr. Daubeny, is more recent than chalk, but is of the same age with the gypsum beds in the neighbourhood of Paris. Solfatara (called by the ancients *Forum Vulcani* or the *Court of Vulcan,*) a kind of half-extinct volcano, in the vicinity of Naples, is celebrated for its native sulphur, which is collected in considerable quantities for the purpose of commerce. (Sir W. Hamilton, *Campi Phlegræi*, 1776.) Sulphur is also found in the mineral kingdom in a state of combination. Thus sulphurous acid gas rushes out from volcanoes. Sulphuric acid is found native both in the free and combined states: hydrosulphuric acid gas is evolved from the pure sulphurous or hepatic waters (see p. 249,) and from the soil in some other places: lastly, sulphur is found in combination with metals. Dr. Thomson (*Outlines of Mineralogy*, &c. vol. i. p. 76.) mentions fourteen native sulphurets and seventeen sulphur salts.

β. In the Organized Kingdom.—Sulphur is found in *Liliaceæ* (as in garlic:) in *Cruciferæ* (as in mustard:) in *Umbelliferæ* (as in asafœtida,) and in many other orders of plants. The alkaline and earthy sulphates are frequently met with in vegetables. Sulphur is also a constituent of some animal substances (thus it is found in eggs, urine, &c.;) sulphates are found in the urine.

[1] Some mineralogists entertain the opinion that Sicilian sulphur is of organic (animal) origin. See *Athenæum* for December 1st, 1838; also Leonhard, *Handbuch der Oryktognosie*, S. 599. Heidelberg, 1826.