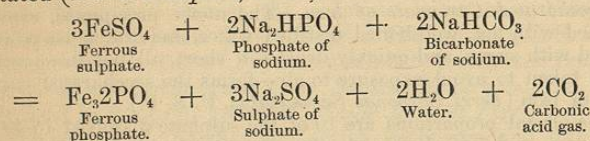


partially oxidized, is formed. This will be noticed again under Arsenicum.

Phosphates of Iron. a. Ferrous Phosphate.

Fourth Synthetical Reaction.—To a hot solution of ferrous sulphate in a test-tube add a hot solution of phosphate of sodium and a little of a solution of bicarbonate of sodium; the lower phosphate of iron, ferrous phosphate (Fe_3PO_4) is precipitated (*Ferris Phosphas*, B. P.).



Officially, solutions of 3 ounces of sulphate of iron in 30 of hot water and $2\frac{3}{4}$ ounces of phosphate in 30 of hot water, together with $\frac{3}{4}$ of an ounce of bicarbonate of sodium dissolved in a little water, are well mixed, filtered, the precipitate well washed with hot water, and, to prevent oxidation as much as possible, dried at a temperature not exceeding 120°F . These proportions will be found to fairly accord with the molecular weights of the crystalline salts, multiplied as indicated in the foregoing equation. $3(\text{FeSO}_4 \cdot 7\text{H}_2\text{O}) = 834$; $2(\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}) = 716$; $2(\text{NaHCO}_3) = 168$.

The above reaction also occurs in making *Syrupus Ferri Phosphatis*, B. P.

The use of bicarbonate of sodium is to ensure the absence of free sulphuric acid in the solution. Sulphuric acid is a powerful solvent of ferrous phosphate. It is impossible to prevent the separation of sulphuric acid if only ferrous sulphate and phosphate of sodium be employed. Ferrous phosphate is white, but soon oxidizes and becomes slate-blue. The official salt contains at least 47 per cent. of hydrous ferrous phosphate, $\text{Fe}_3(\text{PO}_4)_2(\text{H}_2\text{O})_8$, with ferric phosphate and some oxide.

l. Ferric phosphate (see page 153).

Sulphide of Iron. Ferrous Sulphide.

Fifth Synthetical Reaction.—In a gas- or spirit-flame strongly heat sulphur with about twice its weight of iron filings in a test-tube (or in an earthen crucible in a furnace); ferrous sulphide (FeS) is formed. When cold, add water to a small portion, and then a few drops of sulphuric acid; sulphuretted hydrogen gas (H_2S), known by its odor, is evolved.



Sticks of sulphur pressed against a white-hot bar of cast iron give a pure form of ferrous sulphide. The liquid sulphide thus formed

is allowed to drop into a vessel of water. Or melted sulphur may be poured into a crucible full of red-hot iron nails, when a quantity of fluid ferrous sulphide is at once formed, and may be poured out on to a slab.

Green Iodide of Iron. Ferrous Iodide.

Sixth Synthetical Reaction.—Place a piece of iodine, about the size of a pea, in a test-tube with a small quantity of water, and add a few iron filings, small nails, or iron wire. On gently warming, or merely shaking if longer time be allowed, the iodine disappears, and, on filtering, a clear light-green solution of iodide of iron (FeI_2) is obtained. On evaporation solid iodide remains.

Solid iodide of iron contains about 18 per cent. of water of crystallization, and a little oxide of iron. It is deliquescent and liable to absorb oxygen from the air, with formation of insoluble ferric oxyiodide or hydrate-iodide. Iodide of iron thus spoiled may be purified by re-solution in water, addition of a little more iodine and some iron, warming, filtering, and evaporating as before. Syrup of Iodide of Iron which has become brown may usually be restored by immersing the bottle in a water-bath and slowly warming.

Ferrous bromide (FeBr_2), occasionally used in medicine, could be made, as might be expected, in the same way as the iodide. *Syrupus Ferri Bromidi*, U. S. P., contains 10 per cent. of ferrous bromide.

Ferri Iodidum Saccharatum, U. S. P., is made by mixing 6 parts of iron, 17 of iodine, and 20 of water, shaking until reaction ceases, filtering into 40 parts of sugar of milk, evaporating to dryness with frequent stirring, and mixing the product in a mortar with 20 additional parts of sugar of milk. It is a grayish or yellowish-white hygroscopic powder.

Syrupus Ferri Iodidum, U. S. P., contains 10 per cent. of the iodide.

FERRIC SALTS.

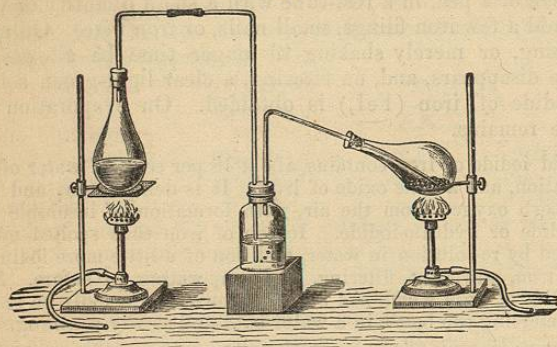
Anhydrous Perchloride of Iron. Ferric Chloride.

Seventh Synthetical Reaction.—Pass chlorine (generated as usual from black oxide of manganese and hydrochloric acid in a flask) through sulphuric acid contained in a small bottle, and thence by the ordinary narrow glass tubing quite to the bottom of a test-tube containing twenty or thirty small iron tacks (or a Florence flask containing 2 or 3 ounces of iron tacks), the latter kept hot by a gas-flame; the higher chloride of iron, ferric chloride, or the perchloride* of iron (Fe_2Cl_6), is formed, and condenses in the upper part of the tube or flask as a mass

* The prefixes *per* and *hyper* used here and elsewhere are from *ὑπὲρ*, *hyper*, over and above, and simply mean "the highest" of several. Thus perchloride, *i.e.* highest chloride.

of small dark, iridescent crystals. When a tolerably thick crust of the salt is formed, break off the part of the glass containing it, being careful that the remaining corroded tacks are excluded, and place it in ten or twenty times its weight of water; the resulting solution, poured off from any pieces of glass, is a

Fig. 31.



Preparation of Anhydrous Ferric Chloride.

pure neutral solution of hydrous ferric chloride, and will be serviceable in performing analytical reactions.

Precaution.—The above experiment must be conducted in the open air, or in a cupboard having a draught outwards.

Anhydrous Ferrous Chloride.—In breaking up the tube, small scales of a light buff color will be observed adhering to the nails; they are crystals of ferrous chloride (FeCl_2).

Note.—Solution of ferric chloride evolves some hydrochloric acid on boiling, while a darker colored solution of ferric oxychloride remains.

Formula of Ferric Chloride.—Qualitative analysis shows that ferric chloride contains iron and chlorine. Quantitative analysis shows that to 56 parts of iron there are 106.5 parts of chlorine; total, 162.5. And as 56 parts of iron are indicated by the symbol Fe, and 162.5 of chlorine by the symbol and figure Cl_3 , the formula for ferric chloride will, so far, be FeCl_3 . But equal volumes of gases and vapors contain equal numbers of molecules (see p. 53). A volume which, if water-vapor, weighs 18 grains, will, if ammonia, weigh 17 grains, or if carbonic acid gas, 44 grains, and if perchloride of iron vapor, 325 grains. And these respective volumes containing equal numbers of molecules, one molecule of each will be represented by the same figures respectively; that is to say, the equal volumes differing in weight as the figures 18, 17, 44, and 325 differ; and the volumes containing equal numbers of molecules, the respective molecules themselves will differ in weight as the figures 18, 17, 44, and 325 differ. Now, 325 parts by weight of perchloride of iron can only be represented by the formula Fe_2Cl_6 ; for FeCl_3

would only represent half the number thus obtained by actual experiment. Hence Fe_2Cl_6 is the formula for a molecule of perchloride of iron, and not FeCl_3 —at all events, at temperatures between 320° and 440°C .

Green Chloride of Iron. Hydrous Ferrous Chloride. Solution of Hydrous Ferric Chloride.

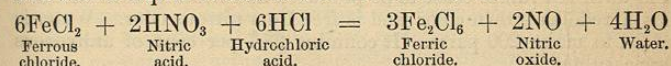
Eighth Synthetical Reaction.—Dissolve iron tacks, in a test-tube, in hydrochloric acid; hydrogen escapes, and the solution on cooling, or on evaporation and cooling, deposits crystallized ferrous chloride (FeCl_2), associated with four molecules of water ($4\text{H}_2\text{O}$) of crystallization ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$).

Through a portion of the solution of ferrous chloride pass chlorine gas; the ferrous chloride becomes ferric chloride.

The excess of chlorine dissolved by the liquid in this experiment may be removed by ebullition; but the ferric chloride is liable to be slightly decomposed. The free chlorine is better carried off by passing a current of air through the liquid for some time.

Hydrous Ferric Chloride (another process).

Ninth Synthetical Reaction.—To another portion of the solution of ferrous chloride, in a test-tube, add a little hydrochloric acid; heat the liquid, and continue to drop in nitric acid until the black color it first produces disappears; the resulting red-dish-brown liquid is solution of ferric chloride.



The black substance is a compound of nitric oxide gas (NO) with a portion of the ferrous salt; it is decomposed by heat.

This is the process for producing the *Liquor Ferri Chloridi*, U. S. P., definite weights of materials being employed and the solution of ferrous chloride being poured slowly into the nitric acid. The sp. gr. of the *Liquor* is 1.405. It contains some free hydrochloric acid. Percentage of anhydrous chloride, 37.8.

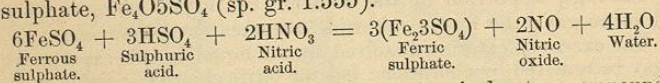
35 parts of this solution and 65 of alcohol form the *Tinctura Ferri Chloridi*, U. S. P.

Note.—The spirit in the tincture is unnecessary, useless, and deleterious; for it acts neither as a special solvent nor as a preservative, the offices usually performed by alcohol (*Tincturae et Succa*, B. P. and U. S. P.), but, unless the liquid contain excess of acid, decomposes the ferric chloride and causes the formation of an insoluble oxychloride of iron. Even if the tincture be acid, it slowly loses color, ferrous chloride and chlorinated ethereal bodies being formed. A *Liquor*, of similar strength, is doubtless destined to displace the tincture altogether.

A strong solution of ferric chloride, on standing, yields a mass of yellow crystals (*Ferri Chloridum*, U. S. P.) containing $\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$, or, rarely, red crystals having the formula $\text{Fe}_2\text{Cl}_6 \cdot 5\text{H}_2\text{O}$.

Persulphate of Iron. Ferric Sulphate.

Tenth Synthetical Reaction.—Dissolve ferrous sulphate with about a fifth of its weight of sulphuric acid in water in an evaporating-dish, heat the mixture and drop in nitric acid until the black color it first produces disappears; the resulting liquid, when made of a certain prescribed strength, is the solution of ferric sulphate, or higher sulphate, "Solution of Tersulphate of Iron" of the Pharmacopœia, a heavy dark-red liquid, sp. gr. 1.320 (*Liquor Ferri Tersulphatis*, U. S. P.). *Liquor Ferri Subsulphatis*, U. S. P. (Monsel's Solution), is a similar fluid, made with less acids, containing, therefore, ferric oxy-sulphate, $\text{Fe}_4\text{O}_5\text{SO}_4$ (sp. gr. 1.555).



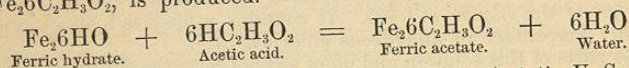
The black color, as in the previous reaction, is due to a compound of ferrous salt with nitric oxide ($2\text{FeSO}_4 + \text{NO}$).

Note.—In all the reactions in which iron passes from ferrous to ferric condition the element assumes different properties, the chief one being an alteration from bivalent to trivalent activity.

The official "Solution of Normal Ferric Sulphate" or Tersulphate, just mentioned, is made by heating a mixture of 15 parts of sulphuric acid, 11 of nitric, and 50 of water, and adding 80 of ferrous sulphate (about one-fourth at a time); then dropping in more nitric acid until red fumes cease to be produced and heating until the fluid has a reddish-brown color and is free from nitrous odor. Water is added to make 200 parts. It contains 28.7 per cent. of anhydrous ferric sulphate.

Acetate of Iron. Ferric Acetate.

Eleventh Synthetical Reaction.—Digest recently washed and drained ferric hydrate in glacial acetic acid; ferric acetate, $\text{Fe}_2\text{C}_2\text{H}_3\text{O}_2$, is produced.



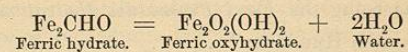
The Solution of Acetate of Iron (*Liquor Ferri Acetatis*, U. S. P.) is an aqueous solution of ferric acetate, containing 33 per cent. of $\text{Fe}_2\text{C}_2\text{H}_3\text{O}_2$. It is made by dissolving the ferric hydrate prepared from a known quantity of ferric sulphate in a definite weight of glacial acetic acid. Sp. gr. 1.160. 50 parts of this solution, 30 of alcohol, and 20 of acetic ether form the *Tinctura Ferri Acetatis*, U. S. P.

Ferric Oxyhydrate, or Hydrated Oxide of Iron.

Twelfth Synthetical Reaction.—Pour a portion of the solution of ferric sulphate into excess of solution of ammonia; moist ferric hydrate, Fe_2CHO , is precipitated (*Ferri Oxidum Hydratum*, U. S. P.).



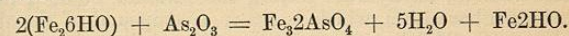
Wash the precipitate by decantation or on a filter, and dry it on a plate over boiling water; *ferric oxyhydrate*, $\text{Fe}_2\text{O}_2(\text{HO})_2$ (*Ferri peroxidum hydratum*, B. P.), remains. When rubbed to a fine powder it is fit for medicinal use.



Either of the other alkalies (potash or soda) will produce a similar reaction; soda is cheapest, ammonia most convenient.

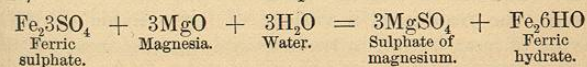
Ferric hydrate is an antidote to arsenic if administered directly the poison has been taken.

It converts the soluble arsenic (As_2O_3) into insoluble ferrous arseniate:—



Dried ferric hydrate (having become an oxyhydrate— $\text{Fe}_2\text{O}_4\text{HO}$) has less action on arsenic. Even the moist, recently prepared hydrate ($\text{Fe}_2\text{6HO}$) loses much of this power as soon as it has become converted into an oxyhydrate ($\text{Fe}_2\text{O}_3\text{6HO}$), a change which occurs though the hydrate be kept under water (W. Procter, Jr.). According to T. and H. Smith this decomposition occurs gradually, but in an increasing ratio; so that after four months the power of the moist mass is reduced to one-half and after five months to one-fourth. Now mere loss of water is not usually followed by any alteration of the essential chemical properties of a compound. It would seem, therefore, that ferric hydrate (two molecules) ($\text{Fe}_2\text{12HO}$) probably suffers, on standing, actual decomposition into oxyhydrate ($\text{Fe}_2\text{O}_3\text{6HO}$) and water ($3\text{H}_2\text{O}$), and does not merely lose water already existing in it as water. Ferric hydrate is also far more readily soluble in hydrochloric acid, tartaric acid, citric acid, and acid tartrate of potassium, than ferric oxyhydrate. Any formula exhibiting ferric hydrate ($\text{Fe}_2\text{6HO}$) as a combination of ferric oxide and water ($\text{Fe}_2\text{O}_3\text{,3H}_2\text{O}$), or the oxyhydrate ($\text{Fe}_2\text{O}_2\text{,2HO}$) as a similar combination ($\text{Fe}_2\text{O}_3\text{,H}_2\text{O}$) are apparently, for these and other reasons, scarcely correct.

Ferri Oxidum Hydratum cum Magnesia.—As a more trustworthy arsenical antidote, a mixture of solution of ferric sulphate and magnesia is recommended in the United States Pharmacopœia. Bottles containing (a) 100 parts of the official solution of ferric sulphate mixed with twice its weight of water, and (b) 15 parts of magnesia well mixed and diluted with water, are to be kept on hand ready for immediate use. Their contents are simply mixed, shaken together, and administered to the patient.



Peroxide of Iron. Ferric Oxide.

The six univalent atoms of the HO, the characteristic elements of all hydrates, are thus, by two successive steps, split up into water and oxygen. But between the hydrate and oxide there obviously may be another oxyhydrate, in which only 2HO is displaced by O^{''}; and such a compound is well known; it is a variety of brown iron ore. The other oxyhydrate, Fe₂O₃·2HO, is also native (needle iron ore), as well as being the *Ferri Peroxidum Hydratum*, B. P.

"Ferri Peroxidum Humidum"	Fe ^{'''} ₂ O ^{''} ₃ 6HO
A variety of brown iron ore	Fe ^{'''} ₂ O ^{''} ₃ 4HO
"Ferri Peroxidum Hydratum" (needle ore)	Fe ^{'''} ₂ O ^{''} ₃ 2HO
Ferric oxide	Fe ^{'''} ₂ O ^{''} ₃

The moist ferric hydrate, as already stated, when kept for some months, even under water, loses the elements of water, and is converted into an oxyhydrate having the formula Fe₂H₆O₉ (limonite or brown hæmatite), which is either a compound of the above oxyhydrates (Fe₂O₄HO) + (Fe₂O₃·2HO), or is a definite intermediate oxyhydrate (Fe₂O₃·6HO).

By ebullition with water for seven or eight hours, ferric hydrate is decomposed into water and an oxyhydrate having the formula Fe₂H₂O₇ (Saint Giles), which is either a mixture of the official oxyhydrate (Fe₂O₃·2HO) with ferric oxide (Fe₂O₃), or a definite intermediate body (Fe₂O₃·2HO). The relation of these bodies to each other will be apparent from the following Table, in which, for convenience, the formulæ of ferric hydrate and oxide are doubled:—

Ferric hydrate (B. P.) (as stalactite)	Fe ₂ 12HO
Kilbride mineral (?)	Fe ₂ O 10HO
Brown iron ore (Huttenrode and Raschau)	Fe ₂ O ₃ 8HO
Old, or frozen, ferric hydrate (limonite)	Fe ₂ O ₃ 6HO
Ferric oxyhydrate (B. P.) (göthite)	Fe ₂ O ₄ 4HO
Boiled ferric hydrate (turgite)	Fe ₂ O ₅ 2HO
Ferric oxide (red hæmatite)	Fe ₂ O ₃

A ferric oxycarbhydrate (Fe₂OCO₃·8HO) has been obtained by Rother.

The *English official ferric oxyhydrate* (Fe₂O₃·2HO) was formerly made by mixing solutions of ferrous sulphate and carbonate of sodium, and exposing the resulting ferrous carbonate to the air until it was nearly all converted into ferric oxyhydrate; hence its old names, still sometimes seen on old bottles, of *Ferri Carbonas* and *Ferri Subcarbonas*.

Ferric Oxide (another process).

Thirteenth Synthetical Reaction.—Roast a crystal or two of ferrous sulphate in a small crucible until fumes cease to be evolved; the residue is a variety of ferric oxide (Fe₂O₃) or peroxide of iron, known in trade as *red oxide of iron*, *colcothar*, *crocus*, *rouge* (mineral), or *Venetian red*. It has sometimes been used in pharmacy in mistake for the official oxyhydrates

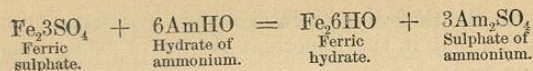
(vide 12th Synthet. Reac.), from which it differs not only in composition, but in the important respect of being almost insoluble in acids.

The Scale Compounds of Iron.

Fourteenth Synthetical Reaction.—Repeat the twelfth reaction, introducing a little solution of citric or tartaric acid, or acid tartrate of potassium, before adding to the alkali (soda, potash, or ammonia), and notice that now no precipitation of ferric hydrate occurs. This experiment serves to illustrate, not the manufacture of a scale compound, but the chemistry of the manufacture. The effect is due to the formation of double compounds, termed Ammonio-Citrate, Potassio-Citrate, Ammonio-Tartrate, Potassio-Tartrate, and similar Sodium compounds of Iron, which remain in solution along with the secondary product—sulphate of the alkali metal. Such ferric compounds, made with certain prescribed proportions of recently prepared ferric hydrate (from which all alkaline sulphate has been washed), and the respective acids (tartaric or citric) or acid salts (acid tartrate of potassium), etc., and the solutions evaporated to a syrupy consistence, and spread on flat plates till dry, form the scale preparations known as *Ferri et Ammonii Citras*, U. S. P., *Ferri Citras*, U. S. P. (also *Liquor Ferri Citratis*, U. S. P.), *Ferri et Ammonii Tartras*, U. S. P., and *Ferri Potassii Tartras*, or rather *Ferrum Tartaratum*, B. P., *Ferri et Potassii Tartras*, U. S. P. A mixture of citrate of iron and ammonium with citrate of strychnine yields, on evaporation, *Ferri et Strychninæ Citras*, U. S. P. A mixture of ferric citrate with citrate of ammonium and citrate of quinine yields, by similar treatment, the well-known scales of *Ferri et Quininæ Citras*, U. S. P.

Specimens of these substances may be prepared by attending to the following details. It is essential, first, that the ferric hydrate be thoroughly washed, or an insoluble oxysulphate will be formed; second, that the ferric hydrate be rapidly washed, or an insoluble ferric oxyhydrate will be produced; thirdly, that the whole operation be conducted quickly, or reduction to green ferrous salt will occur; fourthly, that the solutions of the salts be not evaporated at a higher temperature than that stated, or decomposition will take place; and fifthly, that the full quantities of ferric hydrate be employed.

In the pharmacopœial processes for the scale compounds, the ferric hydrate is in each case freshly made from solution of ferric sulphate by precipitation with solution of ammonia,



the solution of ferric sulphate being made of a definite strength (see p. 146) from a known weight of ferrous sulphate. The reason for adopting this course is that ferric hydrate is unstable and cannot be weighed, because it cannot be dried without decomposing and becoming insoluble, as explained under the 12th reaction.

Ferri Citras, U. S. P., and *Ferri et Ammonii Citras*, U. S. P.—Ferric hydrate is dissolved in solution of citric acid, and the whole evaporated to dryness without or with ammonia.

To prepare the ferric hydrate, dilute 105 parts of official solution of ferric sulphate with water; pour this into water containing excess of solution of ammonia. (If the opposite course were adopted, the alkaline liquid poured into the ferric solution, the precipitate would contain ferric oxysulphate, or hydrato-sulphate, which interferes with the brilliancy of the scales.) Thoroughly stir the mixture (it will smell strongly of ammonia, if enough of the latter has been added), allow the precipitate to subside, pour away the supernatant liquid, add more water, and repeat the washing until a little of the liquid tested for by-product (sulphate of ammonium) by solution of chloride or nitrate of barium ceases to give a white precipitate (sulphate of barium). Collect the ferric hydrate on a filter, drain, and place in it, while still moist, 30 parts of citric acid, in an evaporating-basin, over a water-bath; stir frequently, until the hydrate has dissolved. Filter, and either evaporate until the liquid weighs 100 parts (*Liquor Ferri Citratis*, U. S. P., sp. gr. 1.260; strength, 35.5 per cent. of $\text{Fe}_2\text{C}_6\text{H}_5\text{O}_7$) or evaporate to a syrup at 60°C . and spread on glass plates to dry (*Ferri Citras*, U. S. P., $\text{Fe}_2\text{C}_6\text{H}_5\text{O}_7 \cdot 6\text{H}_2\text{O}$), or to 3 parts of the *Liquor* add 1 of ammonia-water and evaporate to form scales (*Ferri et Ammonii Citras*, U. S. P.).

Ferri et Quininae Citras, U. S. P., is made by dissolving 12 parts of pure quinine (dried at 100°C .) and 88 parts of citrate of iron in water, evaporating and scaling. *Liquor Ferri et Quininae Citratis*, U. S. P., contains citrate of iron and ammonium and citrate of quinine.

Ferri et Strychninae Citras, U. S. P., is prepared by mixing one part of strychnine and one of citric acid with a solution containing 98 parts of citrate of iron and ammonium, evaporating the mixture at a temperature not exceeding 60°C . or 140°F . to a syrupy consistence, and scaling in the usual way by spreading it upon plates of glass.

Ferri et Potassii Tartras, U. S. P.—Ferric hydrate is dissolved in solution of acid tartrate of potassium with a little ammonia, and the whole evaporated to dryness.

The ferric hydrate obtainable from twelve parts of the official solution of ferric sulphate by the action of ammonia, in the manner detailed in the previous paragraphs, is mixed (in a mortar), while still moist but well drained, with four parts of acid tartrate of potassium. The whole is then heated in a dish over a water-bath to a temperature not exceeding 140°F ., and the mixture kept warm

until nothing more will dissolve; a little ammonia added and the clear fluid evaporated at a temperature not exceeding 140°F . (greater heat causes decomposition), and, when the mixture has the consistence of syrup, spread on panes of glass and allowed to dry (in any warm and open place shown by a thermometer to be not hotter than 140°F .). The dry salt is then obtained in flakes. It should be kept in well-closed bottles.

Ferri et Ammonii Tartras, U. S. P., is made by saturating solution of acid tartrate of ammonium with ferric hydrate, evaporating, and scaling. The acid tartrate is prepared by exactly neutralizing half of any quantity of tartaric acid by carbonate of ammonium, and then adding the other half.

The foregoing are the only official scale preparations of iron. Many others of similar character might be formed. The *Citrate* dissolves slowly in cold but readily in warm water. Few crystallize or give other indications of definite chemical composition. Their properties are only constant so long as they are made with unvarying proportions of constituents. Want of chemical compactness, the loose state in which the iron is combined, precludes their recognition as well-defined chemical compounds, yet possibly enables them to be more readily assimilated as medicines than some of the more definite ferrous and ferric salts.

A definite *ferrous tartrate* ($\text{FeC}_4\text{H}_4\text{O}_6$) and *ferrous citrate* ($\text{FeHC}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$) have been obtained by reaction of iron and acid in hot water. They occur as white masses of microscopic crystals. A *sodio-ferrous citrate* ($\text{FeNaC}_6\text{H}_5\text{O}_7$) and *hydrato-citrate* ($\text{FeNa}_2\text{HOC}_6\text{H}_5\text{O}_7$) may be obtained in scales (Rother).

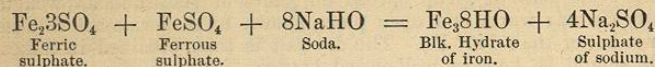
Ferric phosphate (Fe_2PO_4), when freshly precipitated, is soluble in solution of citrates of the alkali-metals, and the mixture, on evaporation on glass plates, yields scales. The official (U. S. P.) *Ferri Phosphas* is to be made by adding 6 parts of phosphate of sodium to an aqueous solution of 5 parts of citrate of iron, evaporating and scaling. It is a mixture of ferric phosphate and citrate of sodium.

Wine of Iron, or "Steel" wine (*Vinum Ferri*, B. P.), made by digesting iron wire in sherry wine, probably contains tartrate of potassium and iron and other iron salts, formed by action of the metal on the acid tartrate of potassium and tartaric, citric, malic, and acetic acid present in the wine. *Vinum Ferri Citratis*, U. S. P., contains ammomo-citrate of iron; *Vinum Ferri Amarum*, U. S. P., contains citrate of iron and quinine.

Black Hydrate of Iron. Ferroso-ferric Hydrate.

Fifteenth Synthetical Reaction.—To two-thirds of a small quantity of a solution of ferrous sulphate add a little sulphuric acid; warm, and gradually add nitric acid, as described in the tenth reaction, care being taken not to allow one drop more nitric acid than necessary to fall into the test-tube. Add the other third of ferrous sulphate, snake, and pour the liquid into

excess of an alkali; black (at first brown) hydrate of iron, or ferroso-ferric hydrate ($\text{Fe}_3\text{SHO} = \text{Fe}_2\text{HO}, \text{Fe}_2\text{HO}$), is produced.



It is so readily attracted by a magnet, even when moist, as to collect round the poles when the instrument is immersed in the supernatant liquid. Hence the name, *magnetic oxide of iron*.

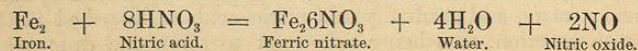
In this process the nitric acid oxidizes the hydrogen of the sulphuric acid, the sulphuric radical uniting with the ferrous sulphate, the iron of which is at the same time altered from the ferrous to the ferric condition, ferric sulphate being formed. If too much nitric acid be employed, the second portion of ferrous sulphate will also be converted into ferric salt, and the solution, on the addition of alkali, yield only red ferric hydrate. This result may be avoided by evaporating the solution of ferric sulphate nearly to dryness, thus boiling off excess of nitric acid, or by pouring first the ferric and then the ferrous liquid into the alkali and thoroughly stirring the mixture; any nitric acid is then neutralized and rendered incapable of oxidizing the ferrous sulphate subsequently added.

Black hydrate of iron is decomposed by heat, yielding, in a closed vessel, oxyhydrates, and, finally, black oxide of iron or ferroso-ferric oxide. Heated in the air it absorbs oxygen and gives ferric oxide. The black *forge-scales* which collect near the blacksmith's anvil have the composition of ferroso-ferric oxide: the black magma formed on exposing a mixture of iron and water to the air is ferroso-ferric hydrate; but these varieties are apt to contain particles of metal, and hence give hydrogen gas when dissolved in acids—a character which distinguishes them from the medicinal preparation.

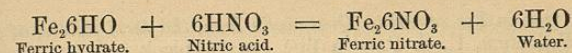
If a dried specimen of the black hydrate of iron be required, the mixture should be well boiled and then set aside for an hour or two to favor aggregation of the particles, the mixture filtered, and the precipitate washed until the washings contain no trace of sulphate (that is, until they no longer yield a white precipitate with chloride of barium). Black hydrate of iron absorbs oxygen even at the temperature of the water-bath; it should consequently be dried at 120° , a temperature at which only slight oxidation occurs.

Pernitrate of Iron. Ferric Nitrate.

Sixteenth Synthetical Reaction.—Place a few iron tacks in dilute nitric acid and set aside; solution of ferric nitrate, or pernitrate of iron, is formed ($\text{Fe}_2\text{6NO}_3$).



Precipitate ferric hydrate from solution of ferric sulphate, wash, and dissolve it in nitric acid.



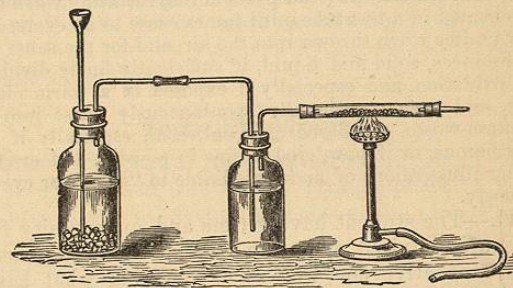
The latter is the official method for preparing *Liquor Ferri Nitrat*, U. S. P., definite quantities of solution of ferric sulphate and of nitric acid being employed. Sp. gr. 1.050. Strength, about 6 per cent. of anhydrous nitrate.

Ferric nitrate and ferric acetate unite to form various aceto-nitrates, amongst which is one having the formula $\text{Fe}_2(\text{C}_2\text{H}_3\text{O})_4\text{NO}_3, \text{HO}, 4\text{H}_2\text{O}$, crystallizing in hard, shining, brownish-red prisms.

Reduced Iron.

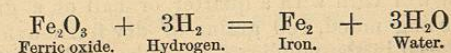
Seventeenth Synthetical Reaction.—Pass hydrogen gas (dried by passing over pieces of chloride of calcium contained in a

Fig. 32.



Preparation of Reduced Iron.

tube, or through sulphuric acid in a wash-bottle) into a small quantity of ferric oxyhydrate ("subcarbonate," U. S. P.) contained in a tube arranged horizontally (a test-tube the bottom of which has been accidentally broken answers very well), the oxyhydrate being kept hot by a gas-flame; oxygen is removed by the hydrogen, steam escapes at the open end of the tube, and after a short time, when moisture ceases to be evolved, metallic iron, in a minute state of division, remains. (See Fig. 32.)



While still hot throw the iron out into the air; it takes fire and falls to the ground as oxide.

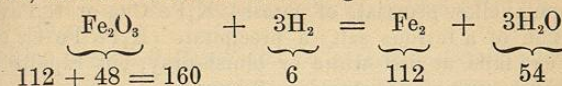
If the ferric oxide is reduced in an iron tube heated by a strong furnace, the particles of iron aggregate to some extent, and, when cold, are only slowly oxidized in dry air. This latter form of re-

duced iron is *Fer réduit* or *Quevenne's Iron*, the *ferri pulvis*, or *Ferum Reductum*, U. S. P.—“a fine grayish-black powder, strongly attracted by the magnet, and exhibiting metallic streaks when rubbed with firm pressure in a mortar.”

Note I.—The spontaneous ignition of the iron in the above experiment is an illustration of the influence of minute division on chemical affinity. The action is the same as occurs whenever iron rusts, and the heat evolved and amount of oxide formed is not greater from a given quantity of iron; but the surface exposed to the action of the oxygen of the air is, in the case of this variety of reduced iron, so enormous compared with the weight of the iron, that heat cannot be conducted away sufficiently fast to prevent elevation of temperature to a point at which the whole becomes incandescent. In the slow rusting of iron escape of heat occurs, but is not observed, because spread over a length of time; in the spontaneous ignition of reduced iron the whole is evolved at one moment. The mixture of lead and carbon (lead pyrophorus) resulting when tartrate of lead is heated in a test-tube until fumes cease to be evolved, spontaneously ignites when thrown into the air, and for the same reason. Many substances, solid and liquid, if sufficiently finely divided and liable to oxidation, and especially if exposed in a warm place, become hot, and even occasionally spontaneously burst into flame. Oil on cotton-waste, powdered charcoal, coal, especially if pyritic or if very porous, or if powdered, resins in powder, and even flour, are familiar illustrations of materials liable to “heat” or even burn spontaneously.

Note II.—The student having time and opportunity for the experiment is advised to make this seventeenth reaction a roughly quantitative one, by way of realizing what has been stated (see, again, the General Principles of Chemical Philosophy, pp. 36–59) respecting the action of chemical force on definite weights only of matter. Three tubes, similar to the oxide-tube shown in the engraving, should be prepared, the second being connected to the first and the third to the second by India-rubber tubing in the usual manner. The first tube should contain pieces of chloride of calcium to absorb any traces of moisture not retained by the sulphuric acid. The second tube (the ends of the small tube being temporarily closed by small corks) should be weighed in any ordinary scales which will turn with a quarter or half of a grain, and the weight being noted, 160 grains of dry ferric oxide should be neatly placed in the middle of the tube. (The oxide must be previously gently heated in a small crucible over a lamp to remove all traces of moisture.) The third tube should contain pieces of chloride of calcium to absorb the water produced in the reaction, and just before being connected should be weighed. The operation is now carried out. At its close, and when the middle tube is cold, the latter tube and the third tube are again

weighed. The oxide-tube should weigh 48 grains less than before, and the terminal tube 54 grains more than before.



The operation is more quickly and easily performed if one-half or one-quarter of the weight of oxide be taken; in that case one-half or one-quarter of the weight of iron and of water will be obtained. Indeed any weight of oxide may be employed; the amount of iron and water resulting will be *always exactly proportionate* to the weights just mentioned. Thus 16 parts of oxide yield 11.2 of iron and 5.4 of water. Iron, hydrogen, and oxygen always combine in proportions of 56, 1, and 16 respectively; hence our justification for agreeing that the symbol Fe shall stand for 56, more exactly 55.9, parts by weight of iron, H for 1 part by weight of hydrogen, and O for 16 parts by weight of oxygen.

Ferric Pyrophosphate.

Eighteenth Synthetical Reaction.—To solution of pyrophosphate of sodium add solution of ferric sulphate; a yellowish-white precipitate of ferric pyrophosphate ($\text{Fe}_2\text{P}_2\text{O}_7 \cdot 9\text{H}_2\text{O}$) separates.

The official (U. S. P.) *Ferri Pyrophosphas* is to be made by adding 10 parts of pyrophosphate of sodium to an aqueous solution of 9 parts of citrate of iron, evaporating and scaling. The apple-green product is a mixture of ferric pyrophosphate and citrate of sodium.

Dialyzed Iron.

“*Liquor Ferri Dialysatus*,” B. P.—This solution of Dialyzed Iron, so called, is a solution of highly basic ferric oxychloride or chloroxide of iron, from which most of the acidulous matter has been removed by dialysis. *Vide* “Dialysis” in Index.

(b) Reactions having Analytical Interest (Tests).

(The iron occurring as a ferrous salt.)

First Analytical Reaction.—Pass sulphuretted hydrogen (H_2S) through a solution of a ferrous salt (e. g., ferrous sulphate) slightly acidulated by hydrochloric acid; no precipitate occurs.

This is a valuable negative fact, as will be evident presently.

Second Analytical Reaction.—Add sulphhydrate of ammonium (NH_4HS) to solution of a ferrous salt; a black precipitate of ferrous sulphide (FeS) falls.