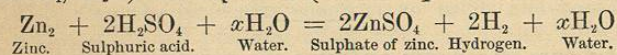


## REACTIONS HAVING (a) SYNTHETICAL AND (b) ANALYTICAL INTEREST.

(a) *Synthetical Reactions.***Sulphate of Zinc.**

*First Synthetical Reaction.*—Heat zinc (4 parts) with water (20 parts) and sulphuric acid (3 fl. parts) in a test-tube (or larger vessel) until gas ceases to be evolved; solution of sulphate of zinc ( $\text{ZnSO}_4$ ) results. Filter (to separate the particles of lead, carbon, etc., commonly contained in sheet zinc), and concentrate the solution in an evaporating-dish; on cooling, colorless, transparent, prismatic crystals of Sulphate of Zinc ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ) are deposited (*Zinci Sulphas*, U. S. P.).



Zinc does not displace hydrogen from the sulphuric acid alone, nor from the water alone, yet it does from the mixture. The possible explanation is that as sulphuric acid combines with several different quantities of water to form definite hydrous compounds ( $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ ;  $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ ; etc.), it is one or more of these that is decomposed with elimination of hydrogen. At present we can only say that an unknown ( $x$ ) amount of water is required in the reaction.

*Note.*—This reaction affords hydrogen and sulphate of zinc; it also develops electricity. Of several methods of evolving hydrogen, it is the most convenient; of the two or three means of preparing sulphate of zinc, it is the most commonly employed; and of the many reactions which may be utilized in the development of dynamic electricity, it is one of the most convenient. The apparatus in which the reaction is effected differs according to the requirements of the operator: if the sulphate of zinc alone is wanted, an open dish is all that is necessary, the action being, perhaps, accelerated by heat; if hydrogen, a closed vessel and delivery-tube; if electricity, square vessels called cells, and certain complementary materials, forming altogether what is termed a battery. In each operation for one product, the other two are commonly wasted. It would not be difficult for the operator, as a matter of amusement, to construct an apparatus from which all three products should be collected.

*Purification.*—Impure sulphate of zinc may be purified in the same manner as impure chloride (see next reaction).

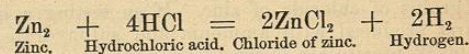
Sulphate of zinc is isomorphous with sulphate of magnesium, and like that salt, loses six-sevenths of its water of crystallization at  $212^\circ \text{F}$ .

**Chloride of Zinc.**

*Second Synthetical Reaction.*—Dissolve zinc in hydrochloric acid mixed with half its bulk of water; the resulting solution

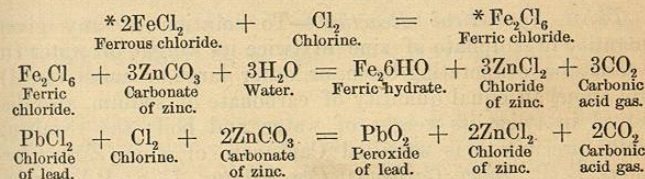
contains chloride of zinc. Evaporate the liquid till no more steam escapes; Chloride of Zinc ( $\text{ZnCl}_2$ ) in a state of fusion remains, and on cooling is obtained as an opaque white solid (*Zinci Chloridum*, U. S. P.).

It is soluble in water, alcohol, or ether.

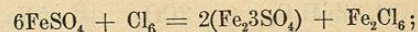


This reaction is analogous to that previously prescribed. The Burnett deodorizing or disinfecting liquid is solution of chloride of zinc.

*Purification of Chloride or Sulphate of Zinc.*—Zinc sometimes contains traces of iron or lead; and these, like zinc, are dissolved by most acids, with formation of soluble salts; they may be recognized in the liquids by applying the tests described hereafter to a little of the solution in a test-tube. Should either be present in the above solution, a little chlorine-water is added to the liquid till the odor of chlorine is permanent, and then the whole well shaken with some hydrate of zinc or the common official "carbonate" of zinc (really hydrate-carbonate—see p. 132). In this way iron is precipitated as ferric hydrate, and lead as peroxide:—



In the British Pharmacopœia the possible presence of impurities in the zinc is recognized, and the process of purification just described incorporated with the process of preparation of *Zinci Chloridum*, *Liquor Zinci Chloridi*, and *Zinci Sulphas*. In the purification of the sulphate of zinc the action of chlorine on any ferrous sulphate will result in the formation of ferric sulphate as well as ferric chloride:—



carbonate of zinc will then give chloride as well as sulphate of zinc, and thus the whole quantity of sulphate of zinc be slightly contaminated by chloride. On evaporating and crystallizing, however, the chloride of zinc will be retained in the mother-liquor. This process admits of general application.

For *Liquor Zinci Chloridi*, B. P., 1 pound of zinc is placed in a mixture of 44 fluidounces of hydrochloric acid and 20 of water, the

\* It will be noticed that the atom of iron is represented, in these equations, as exerting both bivalent and trivalent activity; this will be alluded to when iron comes under consideration.



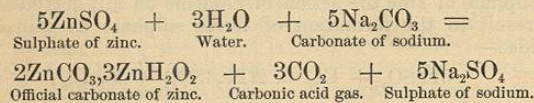
mixture ultimately warmed until no more gas escapes, filtered into a bottle, chlorine-water added until the liquid after shaking smells fairly of chlorine, about half an ounce or somewhat more of carbonate of zinc shaken up with the solution until a brown precipitate (of ferric hydrate or peroxide of lead, or both) appears, the whole filtered, and the filtrate evaporated to 40 fluidounces. One fluidounce contains 366 grains of chloride of zinc. If on testing a little of the solution first produced with ammonia and sulphhydrate of ammonium, no black precipitate is produced, neither iron nor lead was present in the zinc, and the treatment with chlorine-water and carbonate of zinc is to be omitted. The *Liquor Zinci Chloridi*, U. S. P., is prepared by a somewhat similar process; nitric acid, however, is used instead of chlorine-water; the solution contains "about 50 per cent. of the salt ( $\text{ZnCl}_2$ )," sp. gr. 1.555. It is miscible with alcohol in all proportions, indicating absence of basic chloride of zinc.

*Bromide of Zinc*,  $\text{ZnBr}_2$  (*Zinci Bromidum*, U. S. P.) may be made by the action of zinc on hydrobromic acid and evaporation to dryness. It is a white powder, but may be sublimed in needles.

*Iodide of Zinc*,  $\text{ZnI}_2$  (*Zinci Iodidum*, U. S. P.) may be made from its elements. It is a white powder, but when volatilized condenses in acicular prisms.

#### Carbonate of Zinc.

*Third Synthetical Reaction.*—To solution of any given quantity of sulphate of zinc in twice its weight of water (in a test-tube, evaporating-basin, or other large or small vessel), add about an equal quantity of carbonate of sodium, also dissolved in twice its weight of water, and boil; the resulting white precipitate is so-called Carbonate of Zinc (*Zinci Carbonas*, B. P., *Zinci Carbonas Præcipitatus*, U. S. P.), a mixture of carbonate ( $\text{ZnCO}_3$ ) and hydrate ( $\text{Zn}_2\text{HO}$ ), in the proportion of two molecules of the former and three of the latter. It may be washed, drained, and dried in the usual manner. It is used in the arts under the name of *zinc-white*.



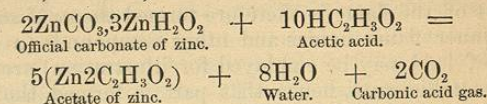
*Calamina Præparata*, B. P., *Prepared Calamine*, is ferruginous carbonate of zinc, or *calamine*, calcined, powdered, and freed from gritty particles by *elutriation*.

*Elutriation* (Lat. *elutriatus*, *elutrio*, *eluo*, to wash out) is the act of straining off water containing lighter particles in suspension from heavier and coarser particles which have become deposited. The decanted fluid yields a sediment of fine particles on standing.

#### Acetate of Zinc.

*Fourth Synthetical Reaction.*—Collect in a filter the precipitate

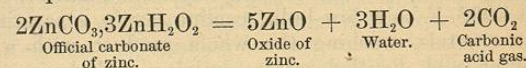
obtained in the last reaction, wash with distilled water, and dissolve a portion in strong acetic acid; the resulting solution contains acetate of zinc ( $\text{Zn}_2\text{C}_2\text{H}_3\text{O}_2$ ), and, on evaporating and setting aside, yields lamellar pearly crystals ( $\text{Zn}_2\text{C}_2\text{H}_3\text{O}_2, 3\text{H}_2\text{O}$ ) (*Zinci Acetas*, U. S. P.).



Another process consists in digesting oxide of zinc in acetic acid, heating the mixture to boiling-point, filtering while hot, and setting aside the clear solution to crystallize.

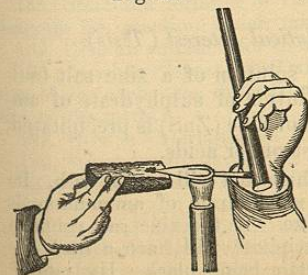
#### Oxide of Zinc.

*Fifth Synthetical Reaction.*—Dry the remainder of the precipitated carbonate (by placing the open filter on a plate over a dish of water kept boiling), and then heat it in a small crucible till it ceases to effervesce on the addition of water and acid to trial samples taken out of the crucible from time to time; the product is Oxide of Zinc (*Zinci Oxidum*, U. S. P.).



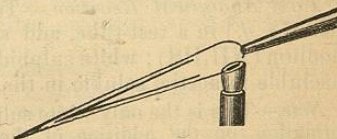
*Note.*—This oxide is yellow while hot, and of a very pale yellow or slight buff tint when cold, not actually white, like the oxides prepared by the combustion of zinc in air. The preparation of the latter variety, which also occurs in commerce, can only be practically accomplished on the large scale, but the chief features of the action may be observed by heating a piece of zinc on charcoal in the blow-pipe-flame (Fig. 29) till it burns; flocks escape, float about in the air, and slowly fall. These are the old *Flores Zinci*, *Lana Philosophica*, or *Nihilum Album*.

Fig. 29.



The Blowpipe.

Fig. 30.

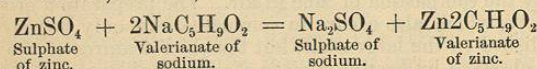




A clear blowpipe-flame consists more or less of two portions (see Fig. 30), an inner cone, at the apex of which are hot gases greedy of oxygen, and an outer cone, at the apex of which is excess of hot oxygen. At the latter point oxidizable metals, etc. are readily oxidized, as in the foregoing experiment, and that part of the flame is therefore termed the *oxidizing flame*; in the inner flame oxides and other compounds (a grain of acetate of lead may be employed for illustration) are reduced to the metallic state, hence that part is termed the *reducing flame*. A blowpipe-flame is much altered in character by slight variations in the position of the nozzle of the blowpipe, by the form of the nozzle, by the force with which air is expelled from the blowpipe, and by the character of the jet of gas. Oxide of zinc slowly absorbs carbonic acid from moist air, and is partly reconverted into hydrate-carbonate.

#### Valerianate of Zinc.

*Sixth Synthetical Reaction.*—Valerianate of Zinc ( $\text{Zn}2\text{C}_5\text{H}_9\text{O}_2, \text{H}_2\text{O}$ ) (*Zinci Valerianas*, U. S. P.) is prepared by mixing strong solutions of sulphate of zinc and valerianate of sodium, cooling, separating the white pearly crystalline matter, evaporating at  $200^\circ \text{F}$ . to a low bulk, cooling, again separating the lamellar crystals, washing the whole product with a small quantity of cold distilled water, draining, and drying by exposure to air at ordinary temperatures. Valerianate of zinc is soluble in ether, alcohol, or hot water.



*Note.*—The compounds of zinc described in the foregoing six reactions are the only ones mentioned in the British Pharmacopœia; the processes are also those of that work. *Sulphide and Hydrate of Zinc* are mentioned in the following analytical paragraphs. The formula of *Sulphite of Zinc* is  $\text{ZnSO}_3, 3\text{H}_2\text{O}$ .

#### (b) Reactions having Analytical Interest (Tests).

*First Analytical Reaction.*—To solution of a zinc salt (sulphate, *e. g.*) in a test-tube, add solution of sulphhydrate of ammonium ( $\text{NH}_4\text{HS}$ ); white sulphide of zinc ( $\text{ZnS}$ ) is precipitated, insoluble in acetic, soluble in the stronger acids.

*Note.*—This is the only white sulphide that will be met with. Its formation, on the addition of the sulphhydrate of ammonium, is therefore highly characteristic of zinc. If the zinc salt contains iron or lead as impurities, the precipitate will have a dark appearance, the sulphides of those metals being black. Hydrate of aluminium, which is also white and precipitated by sulphhydrate

of ammonium, is the only substance sulphide of zinc is likely to be mistaken for, and *vice versa*; but, as will be seen immediately, there are good means of distinguishing these from each other.

*Second Analytical Reaction.*—To solution of a zinc salt add ammonia; white hydrate of zinc ( $\text{Zn}2\text{HO}$ ) is precipitated. Add excess of ammonia; the precipitate is redissolved.

This reaction at once distinguishes a zinc salt from an aluminium salt, hydrate of aluminium being insoluble in dilute ammonia.

*Other Analytical Reactions.*—The fixed alkali-hydrates afford a similar reaction to that just mentioned, the hydrate of zinc redissolving if the alkali is free from carbonate. Carbonate of ammonium yields a white precipitate of carbonate and hydrate, soluble in excess. The fixed alkaline carbonates give a similar precipitate, which is not redissolved if the mixed solution and precipitate be well boiled. Ferrocyanide of potassium precipitates white ferrocyanide of zinc ( $\text{Zn}_2\text{FeCy}_6$ ).

Sulphate of magnesium, which is isomorphous with, and indistinguishable in appearance from, sulphate of zinc, is not precipitated from its solutions either by ferrocyanide of potassium or sulphhydrate of ammonium.

*Antidotes.*—There are no efficient chemical means of counteracting the poisonous effects of zinc. Large doses, fortunately, act as powerful emetics. If vomiting has not occurred, or apparently to an insufficient extent, solution of carbonate of sodium (common washing salt), immediately followed by white of egg and demulcents, may be administered.

#### QUESTIONS AND EXERCISES.

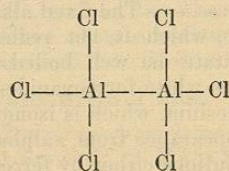
185. Give the sources and uses of metallic zinc.
186. Explain by a diagram what occurs when zinc is dissolved in diluted sulphuric acid.
187. How may solutions of Chloride and of Sulphate of Zinc be purified from the salts of iron? Give equations for the reactions.
188. State the formula of Carbonate of Zinc, and illustrate by a diagram the reaction which takes place in its production.
189. Give an equation for the synthesis of Acetate of Zinc.
190. In what respect does Oxide of Zinc, resulting from the ignition of the carbonate, differ from that produced during the combustion of the metal?
191. How is Valerianate of Zinc prepared?
192. What are the properties of Valerianate of Zinc?
193. Name the more important tests of Zinc.
194. How would you distinguish, chemically, between solutions of Sulphate of Zinc and Alum?
195. Describe the treatment in cases of poisoning by zinc salts.
196. Give reactions distinguishing Sulphate of Zinc from Sulphate of Magnesium.



## ALUMINIUM.

Symbol Al. Atomic weight 27.

*Note.*—In the formulæ of aluminium salts it will be observed that to one atom of metal there are three atoms of other univalent radicals; hence, apparently, the atom of aluminium is trivalent, Al<sup>'''</sup>. But possibly it is quadrivalent; for one molecule of aluminium compounds includes two atoms of the metal, three-fourths only of whose power may be supposed to be exerted in retaining the other constituents of the molecule, the remaining fourth enabling the aluminium atoms themselves to keep together. This is graphically shown in the following formula of chloride of aluminium (Al<sub>2</sub>Cl<sub>6</sub>), which represents each aluminium atom as a body having four arms



or bonds, three of which are engaged in grasping the arms of univalent chlorine atoms, while the fourth grasps the corresponding arm of its brother aluminium atom. Such graphic formulæ, as they are called, are useful in facilitating the acquirement of hypotheses regarding the constitution of chemical substances, especially if the error be avoided of supposing that they are pictures either of the position or absolute power of atoms in a molecule, or indeed, the true representation of a molecule at all; for on this point man knows little or nothing. AlCl<sub>3</sub> may be the formula at very high temperatures.

*Source.*—Aluminium is very abundant in nature, chiefly as silicate, in clays, slate, marl, granite, basalt, and a large number of minerals. *Mica* consists chiefly of silicates of aluminium, iron, and potassium. *Rotten-stone* is a soft and friable aluminium silicate containing a little organic matter. The sapphire and ruby are almost pure oxide of aluminium. The metal aluminium is obtained from the double chloride of aluminium and sodium, by the action of metallic sodium, the source of the chloride being the mineral *bauxite*—a more or less ferruginous hydrate of aluminium.

Aluminium readily alloys with other metals. One part fused with nine of copper gives *aluminium-bronze*.

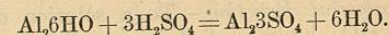
*Alum* (*Alumen*, U. S. P.), a double sulphate of aluminium and potassium (Al<sub>2</sub>SO<sub>4</sub>.K<sub>2</sub>SO<sub>4</sub>.24H<sub>2</sub>O), may be obtained from aluminous schist (from *σχιστός*, *schistos*, divided), a sort of pyritous slate or shale, by exposure to air; oxidation and chemical change produce sulphate of aluminium, sulphate of iron, and silica, from the silicate of aluminium and bisulphide of iron (iron pyrites) originally present in the shale. The sulphate of aluminium and sulphate of iron are dissolved out of the mass by water, and sulphate of potassium

added; on concentrating the liquid, alum crystallizes out, while the more soluble iron salt remains in the mother liquor.

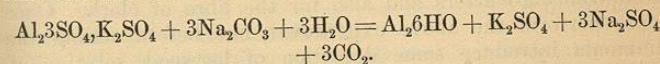
It is more frequently prepared by directly decomposing the silicate of aluminium in the calcined shale of the coal-measures by hot sulphuric acid, sulphate of potassium being added from time to time until a solution strong enough to crystallize is obtained. The liquid well agitated during cooling deposits alum, in minute crystals, termed *alum-flour*, which is afterwards recrystallized.

*Alums.*—There are several *alums*, iron or chromium taking the place of aluminium, and ammonium or sodium that of potassium, all crystallizing in an eight-sided form, the octahedron—a sort of double pyramid. These are apparently alike in chemical constitution, and their general formula (M=either metal) is M<sup>'''</sup><sub>2</sub>SO<sub>4</sub>.M'<sup>'</sup><sub>2</sub>SO<sub>4</sub>.24H<sub>2</sub>O. The alum of the manufacturer commonly occurs in colorless, transparent, octahedral crystals, massed in lumps, which are roughly broken up for trade purposes, but still exhibit the faces of octahedra. It is liable to contain sulphate of ammonium or sulphate of potassium, according as one or other is the cheaper.

*Sulphate of Aluminium* (Al<sub>2</sub>SO<sub>4</sub>.9H<sub>2</sub>O), or *Alum Cake*, prepared from natural silicates in the manner just described, is a common article of trade, serving most of the manufacturing purposes for which alum was formerly employed. It is official in the United States Pharmacopœia (*Aluminii Sulphas*). It may be made by dissolving hydrate of aluminium in diluted sulphuric acid, with subsequent removal of water by evaporation.



The hydrate of aluminium (*Aluminii Hydras*, U. S. P.) is to be prepared by the addition of solution of alum to solution of carbonate of sodium, the precipitated hydrate being collected on a filter and well washed.



*Preparation of Alum.*—Prepare alum by heating a small quantity of powdered pipe-clay (silicate of aluminium) with about twice its weight of sulphuric acid for some time, dissolving out the resulting sulphate of aluminium and excess of sulphuric acid by water, and adding carbonate of potassium to the clear filtered solution only until, after well stirring, the excess of acid is neutralized. (If too much carbonate be added, the hydrate of aluminium precipitated when the carbonate is first poured in will not be redissolved on well mixing the whole. Perhaps the readiest indication of neutrality in this and similar cases is the presence of a little precipitate after stirring and warming the mixture.) On evaporating the clear solution crystals of alum are obtained.

The *Ammonio-ferric Alum* or *Ammonio-ferric Sulphate* of American pharmacy (*Ferri et Ammonii Sulphas*, U. S. P.) may be made by adding sulphate of ammonium to a hot solution of persulphate of iron, and setting the liquid aside to crystallize. It forms pale



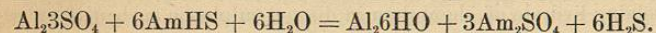
violet octahedral crystals expressed by the formula  $\text{Fe}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ .

*Dried Alum* (*Alumen Exsiccatum*, U. S. P.) is alum from which the water of crystallization has been expelled by heat, the temperature not exceeding  $205^\circ \text{C}$ . or  $400^\circ \text{F}$ . By calculation from the molecular weight of alum, it will be found that the salt contains between 45 and 46 per cent. of water. At temperatures above  $400^\circ$  ammonium alum is decomposed, sulphate of ammonium and sulphuric anhydride escaping, and pure oxide of aluminium ( $\text{Al}_2\text{O}_3$ ) remaining. Dried alum rapidly reabsorbs water from the atmosphere.

*Roche alum*, or *Rock alum* (*roche*, French, rock), is the name of an impure native variety of alum containing iron. The article sold under this name is sometimes an artificial mixture of common alum with oxide of iron.

#### REACTIONS HAVING ANALYTICAL INTEREST.

*First Analytical Reaction.*—To a solution of an aluminium salt (alum, for example, which contains sulphate of aluminium) add sulphhydrate of ammonium ( $\text{NH}_4\text{HS}$ ); a gelatinous white precipitate of hydrate of aluminium falls:—



*Second Analytical Reaction.*—To a solution of alum add ammonia,  $\text{NH}_4\text{HO}$ ; hydrate of aluminium falls: add excess of ammonia; the precipitate is, practically, insoluble.

*Principle of Dyeing by help of Mordants.*—The precipitated hydrate of aluminium, or alumina, has great affinity for vegetable coloring-matters and also for the fibre of cloth. Once more perform the above experiment, but before adding the ammonia introduce some decoction of logwood, solution of cochineal, or other similar colored liquid, into the test-tube. Add now the ammonia, and set the tube aside for the alumina to fall; the latter takes down with it all the coloring principle. In dye-works the fabrics are passed through liquids holding the alumina but weakly in solution, and then through the coloring solutions; from the first bath the fibres abstract alumina, and from the second the alumina abstracts coloring-matter. Some other metallic hydrates, notably those of tin and iron, resemble alumina in this property; they are all termed *mordants* (from *mordens*, biting); the substances they form with coloring-matters have the name of *lakes*.

*Third Analytical Reaction.*—To the alum add solution of potash; again hydrate of aluminium falls. Add excess of potash, and agitate; the precipitate dissolves.

Hydrate of aluminium may be precipitated from this solu-

tion by neutralizing the potash with hydrochloric acid, and adding ammonia until, after shaking, the mixture has an ammoniacal smell, or by adding solution of chloride of ammonium to the potash liquid. But the former way is the better; for it is difficult to know when a sufficiency of the chloride of ammonium has been poured in, whereas reaction with blue and red litmus-paper at once enables the operator to know when excess of hydrochloric acid or ammonia has been added.

Alkaline phosphates, arseniates, and salts of other acidulous radicals also decompose solutions of aluminium salts and produce insoluble compounds of that metal, with the several acidulous radicals, but the resulting precipitates are of no special interest.

#### QUESTIONS AND EXERCISES.

197. What is there remarkable about the quantivalence of aluminium?
198. Practically, what is the quantivalence of the atom of aluminium?
199. Enumerate the chief natural compounds of aluminium.
200. Write down a formula which will represent either of the Alums.
201. Which *alum* is official, and commonly employed in the arts?
202. State the source and explain the formation of alum.
203. What is the crystalline form of alum? Work a sum showing how much Dried Alum is theoretically producible from 100 pounds of alum. Ans. 52 lbs. 6 oz.
204. Show by figures how ordinary ammonium alum is capable of yielding 11.356 per cent. of alumina.
205. Why are aluminium compounds used in dyeing?
206. How are salts of aluminium analytically distinguished from those of zinc?

#### IRON.

Symbol Fe. Atomic weight 55.9.

*Sources.*—Compounds of iron are abundant in nature. *Magnetic Iron Ore*, or *Loadstone* (*Lodestone* or *Leadstone*, from the Saxon *lædan*, to lead, in allusion to its use, or rather to the use of magnets made from it, in navigation), is the chief ore from which Swedish iron is made; it is a mixture of ferrous and ferric oxides ( $\text{FeO}, \text{Fe}_2\text{O}_3$ ). Much of the Russian iron is made from *Specular Iron Ore* (from *speculum*, a mirror, in allusion to the lustrous nature of the crystals of this mineral). This and *Red Hæmatite* (from *αἷμα*, *haima*, blood, so named from the color of its streak), an ore raised in Lancashire, are composed of ferric oxide only ( $\text{Fe}_2\text{O}_3$ ). *Brown Hæmatite*, an



oxyhydrate, is the source of much of the French iron. *Spathic Iron Ore* (from *spatha*, a slice, in allusion to the lamellar structure of the ore) is a ferrous carbonate ( $\text{FeCO}_3$ ). An impure ferrous carbonate forms the *Clay Ironstone*, whence most of the English iron is derived. The chief Scotch ore is also an impure carbonate, containing much bituminous matter; it is known as *Black Band*. *Iron Pyrites* (from *πῖρ*, *pur*, fire, in allusion to the production of sparks when sharply struck) ( $\text{FeS}_2$ ) is a yellow lustrous mineral, of use only for its sulphur. As met with in coal it is commonly termed *coal brasses*. Ferrous carbonate ( $\text{FeCO}_3$ ), chloride ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ), and sulphate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) sometimes occur in springs, the water of which is hence termed *chalybeate* (*chalybs*, steel).

*Process*.—Iron is obtained from its ores by processes of roasting, and reduction of the resulting impure oxide with coal or charcoal in the presence of chalk, the latter uniting with the sand, clay, etc. to form a fusible slag. The *cast iron* thus produced may be converted into *wrought iron* by burning out the 4 or 5 per cent. of carbon, silicon, and other impurities present, by oxidation in a furnace, an operation which is termed *puddling*. *Steel* is iron containing from one to two per cent. of carbon, and is made by the now celebrated Bessemer process of burning out from cast iron the variable amount of carbon it contains, and then adding melted iron containing a known proportion of carbon. The official varieties of the metal are "metallic iron, in the form of fine, bright, and non-elastic wire" (*Ferrum*, U. S. P.); and "annealed iron wire," having a diameter about 0.005 of an inch (about No. 35 wire gauge), or wrought-iron nails, free from oxide (*Ferrum*, B. P.), the conditions in which it is most easily employed for conversion into its compounds. In the form of a fine powder (see 17 Reac.) metallic iron is employed as a medicine.

*Properties*.—The specific gravity of pure iron is 7.844, of the best bar iron 7.7; its color is bluish-white or gray. Bar iron requires the highest heat of a wind-furnace for fusion, but below that temperature assumes a pasty consistence, and in that state two pieces may be joined or *welded* (Germ. *wellen*, to join) by the pressure of blows from a hammer. A little sand thrown on to the hot metal facilitates this operation by forming with the superficial oxide of iron a fusible slag, which is dispersed by the blows: the purely metallic surfaces are thus better enabled to come into thorough contact and enter into perfect union. Iron is highly ductile, and of all common metals possesses the greatest amount of tenacity. At a high temperature it burns in the air, forming oxide of iron. *Rust of iron* is chiefly red oxide of iron, with a little ferrous oxide and carbonate; it is produced by action of the moist carbonic acid of the air and subsequent oxidation. Steam passed over scrap iron heated to redness gives hydrogen gas and black oxide of iron. Iron exposed at a high temperature to oxidation by a limited amount of steam (Barff) or air (Bower) becomes coated with magnetic oxide of so closely coherent and adherent a nature that the metal is more or less permanently protected from alteration by atmospheric and many other influences.

*Quantivalence*.—Iron combines with other elements and radicals in two proportions; those salts in which the atom of iron appears to

possess inferior affinities (in which the other radicals are in the less amount) are termed *ferrous*, the higher being *ferric* salts. In the former the iron exerts bivalent ( $\text{Fe}''$ ), in the latter trivalent activity ( $\text{Fe}'''$  or  $\text{Fe}_2'''$ ), as seen in the formulæ of the chlorides,  $\text{FeCl}_2$  (possibly  $\text{Fe}_2\text{Cl}_4$ ) and  $\text{Fe}_2\text{Cl}_6$  (perhaps  $\text{FeCl}_3$  at very high temperatures).

The atom of iron is also sometimes considered to be sexivalent, on account of the analogy of its compounds with those of chromium, which is sexivalent, if the formula of its fluoride ( $\text{CrF}_6$ ) be correct, and because the composition of *ferrate of potassium* ( $\text{K}_2\text{FeO}_4$ ), a deep purple salt (obtained on warming a mixture, in a test-tube, of a few fragments of solid hydrate of potassium and of perchloride of iron with a few drops of bromine), is best explained on the assumption of the sexivalence of its iron.

Why the quantivalence of the atom of iron should vary is not at present known.

*The Nomenclature of Iron Salts*.—For educational and descriptive purposes the two classes of iron compounds are very conveniently spoken of as *ferrous* and *ferric*, the syllable "*ferr*" common to all indicating their allied ferruginous character, the syllables *ous* and *ic* indicating the lower and higher class respectively—functions fulfilled by these two syllables in other similar cases (sulphurous and sulphuric, mercurous and mercuric). Officially the iron salts are known by other names, thus, *Sulphate of Iron* (*Ferri Sulphas*) and *Phosphate of Iron* (*Ferri Phosphas*), names which are chemically inexplicit, for there are two sulphates, and two phosphates, and the terms do not define which salt is intended. Consistency and uniformity would demand that the names Ferrous Sulphate, Ferrous Phosphate, or similar terms, should be employed. Practically, however, the old names cause no confusion, inasmuch as, commonly, only one sulphate, phosphate, etc. are used in medicine; moreover, the higher salts usually have the prefix *per* attached (as persulphate, perchloride). These names are already well known, can be easily rendered in Latin, and then admit of simple abbreviations and adaptations such as are employed in prescriptions, advantages not possessed by the more rational terms. While, therefore, the comprehension of the chemistry of iron is rendered simple and intelligible by the use of the terms ferrous and ferric, the employment of older and less definite names may very well be continued in pharmacy as being practically more convenient.

#### REACTIONS HAVING (a) SYNTHETICAL AND (b) ANALYTICAL INTEREST.

##### (a) *Synthetical Reactions.*

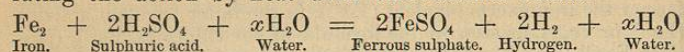
##### FERROUS SALTS.

##### Green Sulphate of Iron. Ferrous Sulphate.

*First Synthetical Reaction*.—Place iron (small tacks) in sulphuric acid diluted with eight times its bulk of water (in a

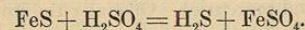


test-tube, basin, or other vessel of any required size), accelerating the action by heat until effervescence ceases.



The solution contains what is generally known as Sulphate of Iron, that is, Ferrous Sulphate, the lower of the two sulphates, and will yield crystals of that substance ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) (*Ferri Sulphas*, U. S. P.) on cooling or on further evaporation; or if the hot concentrated solutions be poured into alcohol, the mixture being well stirred, the sulphate is at once thrown down in minute crystals (*Ferri Sulphas Præcipitatus*, U. S. P.). At a temperature of  $300^\circ \text{F}$ . ferrous sulphate loses six-sevenths of its water, and becomes the *Ferri Sulphas Exsiccatus*, U. S. P., a salt used in the preparation of *Pilule Aloes et Ferri*, U. S. P. (For the nature of the chemical action with iron and diluted sulphuric acid see the analogous zinc reaction on p. 130.)

*Other Sources of Ferrous Sulphate.*—In the laboratory ferrous sulphate is often obtained as a by-product in making sulphuretted hydrogen:—



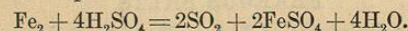
In manufactories it occurs as a by-product in the decomposition of aluminous shale, as already noticed (p. 135).

Ten grains of granulated sulphate of iron dissolved in one ounce of water constitute "Solution of Sulphate of Iron," B. P. "The solution should be recently prepared."

*Notes.*—Ferrous sulphate is sometimes termed *green vitriol*. *Vitriol* (from *vitrum*, glass) was originally the name of any transparent crystalline substance, but afterwards restricted to the sulphates of zinc, iron, and copper, which were, and still are, occasionally known as white, green, and blue vitriol. *Copperas* (probably originally *copper-rust*, a term applied to verdigris and other green incrustations of copper) is another name for this sulphate of iron, sometimes distinguished as *green copperas*, sulphate of copper being blue copperas. Solid sulphate of iron is a constituent of *Pilule Aloes et Ferri*, B. P. Ferrous sulphate forms a light-green double salt with sulphate of ammonium.

Ferrous sulphate, when exposed to the air, gradually turns brown through absorption of oxygen, ferric oxysulphate ( $\text{Fe}_2\text{O}_2\text{SO}_4$ ) being formed. The latter is not completely dissolved by water, owing to the formation of a still lower insoluble oxysalt ( $\text{Fe}_2\text{O}_3\text{SO}_4$ ) and soluble ferric sulphate,  $5(\text{Fe}_2\text{O}_2\text{SO}_4) = \text{Fe}_2\text{O}_3\text{SO}_4 + 3(\text{Fe}_2\text{SO}_4)$ .

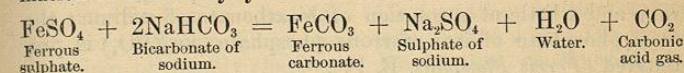
Iron heated with undiluted sulphuric acid gives sulphurous acid gas and ferrous sulphate:—



#### Carbonate of Iron. Ferrous Carbonate.

*Second Synthetical Reaction.*—To solution of ferrous sul-

phate, boiling, in a test-tube, add solution of bicarbonate of sodium ( $\text{NaHCO}_3$ ) in recently boiled water; a white precipitate of ferrous carbonate ( $\text{FeCO}_3$ ) is thrown down, rapidly becoming light green, bluish green, and, after a long time, red, through absorption of oxygen, evolution of carbonic acid gas, and formation of ferric oxyhydrate.

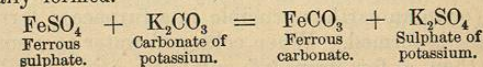


*Saccharated Carbonate of Iron.*—The above precipitate, rapidly washed with hot, well-boiled distilled water, and the moist powder mixed with sugar, and quickly dried—in short, all possible precautions taken to avoid exposure to air—forms the saccharated carbonate of iron (*Ferri Carbonas Saccharatus*, U. S. P.).

The official proportions are 10 of the sulphate dissolved in 40 of hot water, and 7 of the bicarbonate dissolved in 100 of warm water, and each filtered. The former is then added to the latter in a flask, the mixture shaken, the precipitate washed by decantation until the washings give only a very slight turbidity with chloride of barium, drained, and while still somewhat moist mixed with 16 parts of sugar, and finally dried over a water-bath.

Carbonate of iron, mixed with honey and sugar, forms the *Massa Ferri Carbonatis*, U. S. P.

Ferrous carbonate is said to be more easily dissolved in the stomach than any other iron preparation. It is so unstable and prone to oxidation, that it must be washed in water containing no dissolved air and mixed with the sugar (which protects it from oxidation) as quickly as possible. In making the official compound mixture of iron (*Mistura Ferri Composita*, U. S. P.), "Griffith's mixture," the various ingredients, including the carbonate of potassium, should be placed in a bottle of the required size, space being left for the crystals or solution of ferrous sulphate, which should be added last, the bottle immediately filled up with the rose-water, and securely corked; the minimum of oxidation is thus insured. More than 2 molecular weights of the carbonate of potassium to 1 of the sulphate of iron are ordered in the official mixture; hence, as the ferrous carbonate decomposes, the carbonic acid produced does not necessarily escape, but converts carbonate into bicarbonate of potassium. *Pilule Ferri Compositæ*, U. S. P., is made from myrrh, carbonate of soda, sulphate of iron, and syrup: carbonate of iron is gradually formed.



#### Arseniate of Iron. Ferrous Arseniate.

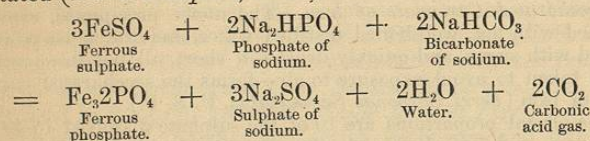
*Third Synthetical Reaction*, by which the lower arseniate of iron, ferrous arseniate (*Ferri Arsenias*, B. P.) ( $\text{Fe}_2\text{AsO}_4$ ), partially oxidized, is formed. This will be noticed again under



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 ( $\text{Fe}_3\text{PO}_4$ ) 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  $120^\circ\text{F}$ . 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 ( $\text{FeS}$ ) is formed. When cold, add water to a small portion, and then a few drops of sulphuric acid; sulphuretted hydrogen gas ( $\text{H}_2\text{S}$ ), 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 ( $\text{FeI}_2$ ) 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* ( $\text{FeBr}_2$ ), 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 ( $\text{Fe}_2\text{Cl}_6$ ), 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.