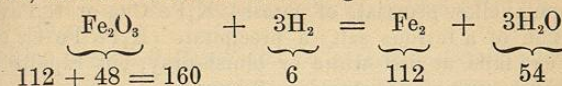


duced iron is *Fer réduit* or *Quevenne's Iron*, the *ferri pulvis*, or *Ferum Reductum*, U. S. P.—“a fine grayish-black powder, strongly attracted by the magnet, and exhibiting metallic streaks when rubbed with firm pressure in a mortar.”

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.

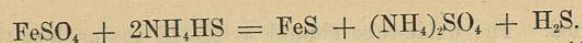
(b) Reactions having Analytical Interest (Tests).

(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.



Third Analytical Reaction.—Add solution of ferrocyanide of potassium (yellow prussiate of potash), $\text{K}_4\text{Fe}'''\text{Cy}_6$, or $\text{K}_4\text{Fcy}'''$, to solution of a ferrous salt; a precipitate ($\text{K}_2\text{Fe}'''\text{Fe}''\text{Cy}_6$, or $\text{K}_2\text{Fe}'''\text{Fcy}$) falls, at first white or bluish-gray, but rapidly becoming blue, owing to absorption of oxygen.

Fourth Analytical Reaction.—To solution of a ferrous salt add ferricyanide of potassium (red prussiate of potash), $\text{K}_3\text{Fe}'''\text{Cy}_{12}$, or K_3Fdcy ; a precipitate ($\text{Fe}'''\text{Fe}'''\text{Cy}_{12}$, or $\text{Fe}'''\text{Fdcy}$) (Turnbull's blue) resembling Prussian blue in color is thrown down.

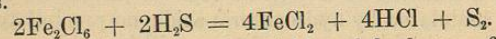
Other Analytical Reactions.—The precipitates produced from ferrous solutions on the addition of alkaline carbonates, phosphates, and arseniates, as already described in the synthetical reactions of ferrous salts, are characteristic, and hence have a certain amount of analytical interest, but are inferior in this respect to the four reactions above mentioned.

Note.—Alkalies (potash, soda, or ammonia) are incomplete precipitants of ferrous salts, hence are almost useless as tests. To solution of a ferrous salt add ammonia (NH_4HO); on filtering off the whitish ferrous hydrate and testing the solution with sulphhydrate of ammonium, iron will still be found. To another portion of the ferrous solution add a few drops of nitric acid or excess of chlorine-water, and boil; this converts the ferrous into ferric salt, and now alkalies will wholly remove the iron, as already twice seen during the performance of the synthetical experiments.

In actual analysis, the separation of iron as ferric hydrate is an operation of frequent performance. This is always accomplished by the addition of alkali, and, if the iron occurs as a ferrous salt, by previous ebullition with a little nitric acid. Ferrocyanide and ferridcyanide of potassium are the reagents used in distinguishing ferrous from ferric salts.

(The iron occurring as a ferric salt.)

Fifth Analytical Reaction.—Through a ferric solution (ferric chloride, *e. g.*) pass sulphuretted hydrogen; a white precipitate of the sulphur of the sulphuretted hydrogen falls, and the ferric is reduced to a ferrous salt, the latter remaining in solution. This reaction is of frequent occurrence in practical analysis.



Sixth Analytical Reaction.—Add sulphhydrate of ammonium to a ferric solution; the latter is reduced to the ferrous state, and black ferrous sulphide (FeS) is precipitated as in the second analytical reaction, sulphur being set free.

Seventh Analytical Reaction.—To a ferric solution add ferrocyanide of potassium (K_4FeCy_6 , or $\text{K}_4\text{Fcy}'''$); a precipitate of Prussian blue, the common pigment, occurs ($\text{Fe}'''\text{Fe}'''\text{Cy}_6$, or $\text{Fe}'''\text{Fcy}'''$).

Eighth Analytical Reaction.—To a ferric solution add solution of ferridcyanide of potassium; no precipitate occurs, but the liquid is darkened to a brownish-red or to a greenish or olive hue if the salts are not quite pure.

Ninth Analytical Reaction.—This is the production of a red precipitate of ferric hydrate, on the addition of alkalies to ferric salts, and is identical with the twelfth synthetical reaction.

Note.—This reaction illustrates the conventional character of the terms synthesis and analysis. It is of equal importance to the manufacturer and the analyst, and is synthetical or analytical according to the intention with which it is performed.

Other ferric reactions have occasional analytical interest. In neutral ferric solutions the tannic acid in aqueous infusion of galls occasions a bluish-black inky precipitate, the basis of most black writing inks. — *Sulphocyanide of Potassium* (KCyS) causes the formation of ferric sulphocyanide, which is of a deep blood-red color. — There is no ferric carbonate; alkaline carbonates cause the precipitation of ferric hydrate, while carbonic acid gas escapes.

Note.—Cyanogen (CN , or Cy'), ferrocyanogen (FeC_6N_6 , or FeCy_6 , or simply Fcy'''), and ferricyanogen ($\text{Fe}_2\text{Cy}_{12}$, or Fdcy''), are radicals which play the part of non-metallic elements, just as ammonium in its chemical relations resembles the metallic elements. They will be again referred to.

Memorandum.—The reader must on no account omit to write out equations or diagrams expressive of each of the reactions of iron, analytical as well as synthetical. It is presumed that this has already been done immediately after each reaction has been performed.

DIRECTIONS FOR APPLYING THE FOREGOING ANALYTICAL REACTIONS TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS CONTAINING ONE OF THE METALS, ZINC, ALUMINIUM, IRON.

Add solution of ammonia gradually:

A dirty-green precipitate indicates iron in the state of a ferrous salt.

A red precipitate indicates iron in the state of a ferric salt.

A white precipitate, insoluble in excess, indicates the presence of an aluminium salt.

A white precipitate, soluble in excess, indicates zinc.

These results may be confirmed by the application of some of the other tests to fresh portions of the solution.

TABLE OF SHORT DIRECTIONS FOR APPLYING THE FOREGOING ANALYTICAL REACTION TO THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS OF ONE, TWO, OR ALL THREE OF THE METALS, ZINC, ALUMINIUM, IRON.

Boil about half a test-tubeful of the solution with a few drops of nitric acid. This insures the conversion of ferrous into ferric salts, and enables the next reagent (ammonia) *completely* to precipitate the iron. Add excess of ammonia, and shake the mixture. Filter

Precipitate Al Fe.*		Filtrate Zn.
Dissolve in HCl, add excess of KHO, stir, filter.		Test by NH_4HS (white ppt.).
Ppt. Fe (red ppt.).	Filtrate Al.	
	Make slightly acid by HCl, and add excess of $\text{NH}_4\text{HO}^\dagger$ (white ppt.).	

Note I.—If iron is present, portions of the original solution must be tested by ferridecyanide of potassium for ferrous, and by ferrocyanide for ferric salts; dark-blue precipitates with both indicate both salts.

Note II.—If no ferrous salt is present, ebullition with nitric acid is unnecessary. It is, perhaps, therefore advisable always to determine this point by *previously* testing a little of the original solution with ferridecyanide; if no blue precipitate occurs, the nitric acid treatment may be omitted.

* The aluminium precipitate ($\text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$) is white, the iron ($\text{Fe}_2\text{O}_3\cdot \text{H}_2\text{O}$) red. If the precipitate is red, iron must be and aluminium may be present; if white, iron is absent, and further operations on the ppt. are unnecessary. This precipitate ($\text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$ and $\text{Fe}_2\text{O}_3\cdot \text{H}_2\text{O}$) may also, if sufficient is at disposal, be analyzed by simply well shaking a washed portion in a tube with solution of potash or soda; the hydrate of iron is not thereby affected, while the hydrate of aluminium is dissolved, and may be detected in the clear decanted fluid by neutralizing all alkali by a little excess of acid, and then adding excess of ammonia.

† Alumina, when in small quantity, is sometimes prevented from being precipitated by ammonia through the presence of organic matter derived from the filter-paper by action of the potash. In cases of doubt, therefore, before adding ammonia boil the liquid with a little nitric acid, which destroys any organic matter. Avoid *great* excess of ammonia.

TABLE OF SHORT DIRECTIONS FOR THE ANALYSIS OF AN AQUEOUS SOLUTION OF SALTS OF ANY OR ALL OF THE METALLIC ELEMENTS HITHERTO CONSIDERED.
Add NH_4Cl ; NH_4HO ; NH_4HS ; stir, filter.

Ppt. Fe (test orig. sol. by K. Fe ^y and K ₆ Fe ^y).	Precipitate Fe Al Zn. Wash, dissolve in HCl, * boil (to remove H_2S), filter (to remove S), add excess of KHO,† stir, filter.		Filtrate Ba Ca Mg NH ₄ Na K. Add $(\text{NH}_4)_2\text{CO}_3$, boil, filter.			
	Filtrate Al Zn. Neutralize with HCl. Add NH_4HO , stir, filter.	Ppt. Al (white).	Filtrate Zn. Add NH_4HS (white ppt.).	Ppt. Ba (yellow).	Filtrate Ca Add $(\text{NH}_4)_2\text{C}_2\text{O}_4$ (white ppt.).	Ppt. Mg (white).
				Ppt. Ba Ca. Dissolve in HCl , H_2O , Add K_2CrO_4 , filter.		Filtrate Mg NH ₄ Na K. Add $(\text{NH}_4)_2\text{HPO}_4$, stir, filter.
						Filtrate NH ₄ Na K. Evap., ignite, dissolve. Na by flame; K by PtCl_4 , orig. sol. for NH ₄ .

* Add, also, a few drops of HNO_3 if Fe be present—i. e., if the ppt. be black. (Vide notes on pp. 157 and 160.)
† Or add excess of ammonia, filter, and test filtrate for zinc. The hydrates of iron and aluminium may then be separated by an alkali, as described in the foot-note to the previous table, p. 160.

CHART FOR ALL METALS HITHERTO CONSIDERED.

The preceding Table (*vide* p. 161) is perhaps the best, but not the only, adaptation of the ordinary reactions to systematic analysis. In it the analytical scheme for the third group is added to that of the first two groups. As before, analysis is commenced by the addition of chloride of ammonium (NH_4Cl) to prevent partial precipitation of magnesium, and by ammonia (NH_4HO) to neutralize any acid. For acid destroys the group precipitant, sulphhydrate of ammonium (NH_4HS), preventing its useful action, and causing a precipitation of the free sulphur it commonly contains. Any precipitate by the ammonia may be disregarded, for the sulphhydrate attacks both solid and liquid.

Note.—When a test gives no reaction, absence of the body sought for may be fairly inferred. If a group-test (that is, a test which precipitates a group of substances) gives no reaction, the analyst is saved the trouble of looking for any of the members of that group.

QUESTIONS AND EXERCISES.

207. Name the chief ores of iron.
208. How is the metal obtained from the ores?
209. What is the chemical difference between cast iron, wrought iron, and steel?
210. Explain the process of welding.
211. What is the nature of chalybeate waters?
212. Illustrate by formula the difference between ferrous and ferric salts.
213. Under what different circumstances may the atom of iron be considered to exert bivalent, trivalent, and sexivalent activity?
214. Write a paragraph on the nomenclature of iron salts.
215. Give a diagram of the official process for the preparation of ferrous sulphate.
216. In what respects do Sulphate of Iron, Granulated Sulphate of Iron, and dried Sulphate of Iron differ?
217. How is ferrous sulphate obtained on the large scale?
218. Give the chemical names of white, green, and blue vitriol.
219. Why does ferrous sulphate become brown by prolonged exposure to air?
220. Show the formation of Ferrous Carbonate by a diagram.
221. Describe the action of atmospheric oxygen on ferrous carbonate. Can the effect be prevented?
222. In what order would you mix the ingredients of *Mistura Ferri Compositi*, and why?
223. Write out an equation illustrative of the formation of the Phosphate of Iron.
224. Why is bicarbonate of sodium used in the preparation of ferrous phosphate?
225. Which four compounds of iron may be formed by the direct union of their elements?

226. Give the official method for the preparation of Solution of Ferric Chloride.
227. Of what use is the spirit in Tincture of Perchloride of Iron?
228. How may Ferrous be converted into Ferric Sulphate?
229. What is the formula of Ferric Acetate? And how is it prepared for use in pharmacy?
230. Give the formula for *Ferri Peroxidum Hydratum*, B. P.
231. How does Ferric Hydrate act as an antidote to arsenic?
232. What are the properties of anhydrous ferric oxide?
233. What are the general characters and mode of production of the medicinal scale preparations of iron?
234. In what state is the iron in *Vinum Ferri Amarum*, U. S. P.?
235. What other form of Wine of Iron is official?
236. Give equations illustrating the chief steps in the artificial production of the so-called Magnetic Oxide of Iron.
237. How is precipitated magnetic oxide of iron distinguished from the varieties made directly from the metal?
238. Why is magnetic oxide of iron directed to be dried at a temperature not exceeding 120° Fahr.?
239. Give a diagram showing the formation of Ferric Nitrate.
240. Work out a sum showing how much ferric oxide will yield, theoretically, one hundred-weight of iron. Ans. 160 lbs.
241. What are the properties of anhydrous ferric oxide?
242. Explain the action of the following tests for iron, distinguishing between ferrous and ferric reactions, and illustrating each by an equation or a diagram:—*a.* Sulphhydrate of ammonium; *b.* Ferrocyanide of potassium; *c.* Ferridcyanide of potassium; *d.* Caustic alkalies; *e.* Sulphocyanide of potassium.
243. Describe the action of ammonia on salts of iron, aluminium, and zinc respectively.
244. What precautions must be used in testing for calcium a solution containing iron?
245. How is magnesium detected in the presence of zinc?
246. How is aluminium detected in the presence of magnesium?
247. Draw up a scheme for the analysis of an aqueous liquid containing salts of iron, barium, and potassium.
248. How may zinc, magnesium, and ammonium be consecutively removed from aqueous solution?

ARSENICUM AND STIBIUM OR ANTIMONY.

These elements resemble metals in appearance and in the character of some of their compounds; but they are still more closely allied to the non-metals, especially to phosphorus and nitrogen. Their atoms are quinivalent (As^V , Sb^V), as seen in arsenic anhydride (As_2O_5) and pentachloride of antimony (SbCl_5), but usually exert trivalent activity only (As^{III} , Sb^{III}), as seen in the hydrogen and other compounds (AsH_3 , AsCl_3 , AsBr_3 , AsI_3). A few preparations of these elements are used in medicine; but all are more or less powerful poisons, and hence have considerable toxicological interest. The

iodide (*Arsenii Iodidum*, U. S. P.) may be made by cautiously fusing together atomic proportions of arsenicum and iodine. It is an orange-red crystalline solid, soluble in water. The *Liquor Arsenii et Hydrargyri Iodidi*, U. S. P., or "Donovan's Solution," is made by dissolving iodide of arsenicum and red iodide of mercury in water, in the proportion of 1 per cent. of each. The old Donovan's Solution contained in each fluidounce (wine measure) the equivalents of 1 grain of white arsenic (As_2O_3), 2 grains of peroxide of mercury, and about 7 grains of iodine.

Arsenicum is an exception to the rule that the atomic weights (taken in grains, grammes, or other weight) of elements, under similar circumstances of temperature and pressure, give equal volumes of vapor, the equivalent weight (75) of arsenicum only occupying half such a volume. Hence, while the molecular weights (that is, double the atomic weights of oxygen ($\text{O}_2 = 32$), hydrogen ($\text{H}_2 = 2$), nitrogen ($\text{N}_2 = 28$), etc.) give a similar bulk of vapor at any given temperature and pressure, the double atomic weight of arsenicum ($\text{As}_2 = 150$), at the same temperature and pressure, only affords half this bulk. It would appear, therefore, that the molecule of arsenicum contains four atoms, and that its formula is As_4 . As in the case of sulphur, however, arsenicum, in the state ordinarily known to us, may be abnormal, and conditions yet be found in which the molecular weight is double (instead of quadruple) the atomic weight.

From observed analogy between the two metals, the molecular constitution of stibium is probably similar to that of arsenicum.

ARSENICUM.

Symbol As. Atomic weight 74.9.

Sources.—Arsenical ores are frequently met with in nature, the commonest being the arsenio-sulphide of iron (FeSAs). This mineral is roasted in a current of air, the oxygen of which, combining with the arsenicum, forms common white arsenic (As_2O_3 , possibly As_4O_6) (*Acidum Arseniosum*, U. S. P.), arsenious oxide, sometimes called anhydrous arsenious acid, or, better, arsenious anhydride, which is condensed in chambers or long flues. It commonly "occurs as a heavy white powder, or in sublimed masses, which usually present a stratified appearance, caused by the existence of separate layers, differing from each other in degrees of opacity." The vitreous or amorphous arsenic is far more soluble than the crystalline variety, and in other respects they differ in properties. Such differences between the crystalline and amorphous varieties of an element or compound are not unfrequent: they have not yet been satisfactorily explained. *Realgar* (red algar) is the red native sulphide (As_2S_2), and orpiment (*auripigmentum*, the golden pigment) the yellow native sulphide (As_2S_3) of arsenicum. The iodide of arsenicum (As_2I_2) (*Arsenii Iodidum*, U. S. P.) may be made from its elements or by dissolving white arsenic in aqueous hydriodic acid and evaporating.

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

(a) Reactions having Synthetical Interest.

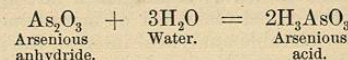
Alkaline Solution of Arsenic.

First Synthetical Reaction.—Boil a grain or two of powdered arsenic (As_2O_3) in water containing an equal weight of bicarbonate of potassium, and, if necessary, filter. The solution, colored with compound tincture of lavender, and containing 1 per cent. of arsenic, forms the *Liquor Potassii Arsenitis*, U. S. P. (*Fowler's Solution*).

Note.—This official solution does not generally contain arsenite of potassium; for the arsenic does not decompose the carbonate of potassium, or only after long boiling. From concentrated solutions carbonic acid gas is more quickly eliminated.

Arsenious Acids and other Arsenites.

Arsenic or *arsenious anhydride* (the so-called arsenious acid), when dissolved in water, is said to yield true arsenious acid (H_3AsO_3)—the arsenite of hydrogen.



When arsenic (As_2O_3) is dissolved in excess of solutions of potash or soda, arsenites are formed having the formulæ KH_2AsO_3 and NaH_2AsO_3 . Boiled with excess of arsenic, one molecule of these salts combines with one of arsenic. The usual character of such compounds is that of oily alkaline liquids. Arsenic fused with alkaline carbonates yields pyroarsenates ($\text{Na}_4\text{As}_2\text{O}_7$ or $\text{H}_4\text{As}_2\text{O}_7$) and metallic arsenicum. Arsenites have the general formula R_3AsO_3 .

Acid Solution of Arsenic.

Second Synthetical Reaction.—Boil arsenic with dilute hydrochloric acid. Such a solution made with prescribed proportions of acid (2 per cent.) and water, and containing 1 per cent. of arsenic (As_2O_3), forms the *Liquor Acidi Arseniosi*, U. S. P. (*De Valangin's Solution* contained a grain and a half per ounce.)

Note.—No decomposition occurs in this experiment. The liquid is simply a solution of arsenic in dilute hydrochloric acid. These two solutions may be preserved for analytical operations.

Mem.—The practical student should boil arsenic in water also, and thus have an acid, alkaline, and aqueous solution for analytical comparison.

Arsenicum.

Third Synthetical Reaction.—Place a grain or less of arsenic at the bottom of a narrow test-tube, cover it with about half an inch or an inch of small fragments of dry charcoal, and hold the tube, nearly horizontally, in a flame, the mouth being loosely covered by the thumb. At first let the bottom of the tube project slightly beyond the flame, so that the charcoal may become nearly red hot; then heat the bottom of the tube. The arsenic will sublime, become deoxidized by the charcoal, carbonic oxide being formed, and the element *arsenicum*, sometimes termed arsenicum, and also formerly called *arsenic*, be deposited in the cooler part of the tube as a dark mirror-like incrustation.

There is a characteristic odor, resembling garlic, emitted during this operation, probably due to a partially oxidized trace of arsenicum, which escapes from the tube; for arsenic does not give this odor; moreover, arsenicum being a freely oxidizable element, its vaporous particles could scarcely exist in the air in an entirely unoxidized state.

Metallic arsenicum may be obtained in large quantities by the above process if the operation be conducted in vessels of commensurate size. But performed with great care, in narrow tubes, using not charcoal alone, but *black flux* (a mixture of charcoal and carbonate of potassium obtained by heating acid tartrate of potassium in a test-tube or other closed vessel till no more fumes are evolved), the reaction has considerable analytical interest, the garlic odor and the formation of the mirror-like ring being highly characteristic of arsenicum. Compounds of mercury and antimony, however, give sublimes which may be mistaken for arsenicum.

Arsenic Acid and other Arseniates.

Fourth Synthetical Reaction.—Boil a grain or two of arsenic with a few drops of nitric acid until red fumes cease to be evolved; evaporate the solution in a small dish to dryness, to remove excess of nitric acid; dissolve the residue in water; the product is Arsenic acid (H_3AsO_4).

Arsenic acid, when strongly heated, loses the elements of water, and arsenic anhydride remains (As_2O_3).

Arsenic anhydride readily absorbs water and becomes arsenic acid (H_3AsO_4). Arsenic acid is reduced to arsenious by the action of sulphurous acid $\text{H}_3\text{AsO}_4 + \text{H}_2\text{SO}_3 = \text{H}_3\text{AsO}_3 + \text{H}_2\text{SO}_4$.

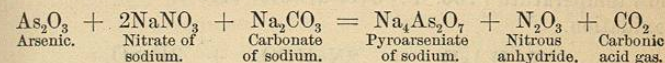
Salts analogous to arsenic acid, the arseniate of hydrogen, are termed *arseniates*, and have the general formula $\text{R}'_3\text{AsO}_4$. The ammonium arseniate (NH_4) HAsO_4 may be made by neutralizing arsenic acid with ammonia. Its solution in water forms a useful reagent.

—Arsenic acid is used as an oxidizing agent in the manufacture of the well-known dye, magenta.

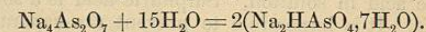
Arsenite and arseniate of sodium are used in the cleansing operations of the calico-printer.

Pyroarsenate and Arseniate of Sodium.

Fifth Synthetical Reaction.—Fuse two or three grains of common white arsenic (As_2O_3) with nitrate of sodium (NaNO_3) and dried carbonate of sodium (Na_2CO_3) in a porcelain crucible, and dissolve the mass in water; solution of arseniate of sodium (Na_2HAsO_4) results.



The official proportions (B. P.) are 10 of arsenic to $8\frac{1}{2}$ of nitrate of sodium and $5\frac{1}{2}$ of dried carbonate, each powdered, the whole well mixed, fused in a crucible at a red heat till effervescence ceases, and the liquid poured out on a slab. The product is pyroarsenate of sodium ($\text{Na}_4\text{As}_2\text{O}_7$). Dissolved in water, crystallized and dried, the salt has the formula $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (*Sodii Arsenias*, U. S. P.).



Heated to 300°F . the crystals lose all water. A solution of 1 part of the anhydrous salt (Na_2HAsO_4) in 99 of water forms the *Liquor Sodii Arseniatis*, U. S. P. The anhydrous salt is used in this preparation because the crystallized is of somewhat uncertain composition. The fresh crystals are represented by the formula $\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O}$ (= 53.7 per cent. of water); these soon effloresce and yield a stable salt having the formula $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (= 40.4 per cent. of water). To avoid the possible employment of a mixture of these bodies, the invariable anhydrous salt is officially used, constancy in the strength of a powerful preparation being thereby secured.

The student will find useful practice in verifying the above numbers representing the centesimal proportion of water in the two arseniates of sodium. This will readily be accomplished if what has already been stated respecting a symbol representing a number as well as a name, and the remarks concerning a molecular weight, be remembered.

The shape of each of the two varieties of arseniate of sodium ($\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O}$, and $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$) is identical with that of the corresponding phosphate of sodium ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, and $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$); the structure of the molecule of the 12-arseniate is the same as that of the 12-phosphate, and the 7-arseniate as that of the 7-phosphate; the two former are isomorphous, the two latter are isomorphous. This is only one instance of the strong analogy of arsenicum and its compounds with phosphorus and its corresponding compounds. The preparation and characters of the next substance, arseniate of iron, will remind the learner of phosphate of iron.

Arseniate of Iron. Ferrous Arseniate.

Sixth Synthetical Reaction.—To a hot solution of arseniate of sodium add a little solution of bicarbonate of sodium, and