the centre) the bromide fixed by the addition of a drop of solution of potash or soda, the chloroform or ether evaporated off, and the residue tested as described in the next reaction.

The above operation is frequently employed for synthetical purposes.

Third Analytical Reaction.—Liberate bromine from a bromide by the cautious addition of chlorine or chlorine-water, then add a few drops of cold decoction of starch; a yellow combination of bromine and starch, commonly termed "bromide of starch," is formed.

Decoction of starch is made by rubbing down two or three grains of starch with some drops of cold water, then adding much more water and boiling the mixture.

The above reaction may be varied by liberating the bromine by a little black oxide of manganese and a drop of sulphuric acid, the upper part of the inside of the test-tube being smeared over with some thick decoction of starch or thin starch-paste. Even sulphuric acid alone, if strong, liberates bromine from a bromide, the hydrogen of the hydrobromic acid first produced uniting with the oxygen of the sulphuric acid—the latter being reduced to sulphurous acid or even to hydrosulphuric acid.

HYDRIODIC ACID AND OTHER IODIDES.

Formula of Hydriodic Acid HI. Molecular weight 127.6.

Source.—The acidulous radical of hydriodic acid and other iodides is the element iodine (I). It occurs in nature as iodide of sodium and of magnesium in sea-water. Seaweeds, sponges, and other marine organisms, which derive much of their nourishment from sea-water, store up iodides in their tissues, and it is from the ashes of these that supplies of iodine (*Iodum*, U. S. P.) are obtained. Mineral iodides also are met with, and iodates occur in crude cubic nitre.

Process.—The seaweed ash or *kelp* is treated with water, insoluble matter thrown away, and the decanted liquid evaporated and set aside to allow of the deposition of most of the sulphates, carbonates, and chlorides of sodium and potassium. The residual liquor is treated with excess of sulphuric acid, which causes evolution of carbonic and sulphurous or sulphuretted gases, deposition of sulphur and more sulphate of sodium, and formation of hydriodic acid. To the decanted liquid is added black oxide of manganese, and the mixture is then slowly distilled; the iodine sublimes, and is afterwards purified by re-sublimation.

$$2HI + MnO_2 + H_2SO_4 = MnSO_4 + 2H_2O + I_2.$$

The analogy of chlorine, bromine, and iodine is well indicated by the fact that each is obtained from its compounds by the same reaction. Iodine is liberated from any iodide as bromine from bromides, or chlorine from chlorides—namely, by the action of black oxide of manganese and sulphuric acid.

Properties.—Iodine is a crystalline purplish-black substance; its vapor, readily seen on heating a fragment in a test-tube, is dark violet. Its vapors are irritating to the lungs, but a trace may be inhaled with safety (*Vapor Iodi*, B. P.). It melts at 239°, boils at about 392° F., and is entirely volatilized, the first portions containing any cyanide of iodine that may, though very rarely, be present. The latter body occurs in slender colorless prisms, emitting a pungent odor.

"A solution of Iodine in chloroform should be perfectly clear and limpid (abs. of moisture). When shaken with distilled water, it should not communicate to the latter more than a light brownish tinge, and no deep brown color (abs. of chloride of iodine). If the Iodine be removed from this dilute aqueous solution by agitation with disulphide of carbon, and, after the separation of the latter, some dilute solution of ferrous sulphate with a trace of ferric chloride be added, finally solution of soda, and the whole supersaturated with hydrochloric acid, no blue precipitate should make its appearance (abs. of cyanide of iodine). If Iodine be dissolved in sulphurous acid, the solution strongly supersaturated with ammonia, and completely precipitated by nitrate of silver, the filtrate, on being supersaturated with nitric acid, should not at once become more than faintly cloudy (abs. of more than traces of chlorine or bromine)." U. S. P.

This latter reaction is applied for the detection of chloride or bromide in Iodides, omitting the addition of sulphurous acid.

Quantivalence.—The atom of iodine, like those of bromine and chlorine, is univalent* (I′). The atomic weight of iodine is 126.6, its molecular formula I_2.

The Iodide of Hydrogen, or Hydriodic Acid, is a heavy, colorless gas. Its solution in water may be made by passing sulphuretted hydrogen through water in which iodine is suspended.

$$2H_2S + 2I_2 = S_2 + 4HI.$$

Hydriodic acid may also be prepared by placing 20 parts of iodine and 2 of water in a retort, the neck of which points upward, and the end of the neck of which is connected by a glass tube with a bottle

* There is a compound of iodine having the formula ICl_3. Iodine would at first sight, therefore, seem to be a trivalent element (I‴); and bromine and fluorine, from their close chemical analogy with iodine, would necessarily be regarded as trivalent also. From this aspect the position of chlorine would be anomalous. Possibly, however, the compound is only a molecular combination of chloride of iodine, ICl, with chlorine, Cl_2. Iodine also forms with iodide of potassium a periodide, or tri-iodide, KI_3, which may be obtained in lustrous prismatic crystals. This, too, may have the formula KI,I_2. A mercuric hexiodide (HgI_6, perhaps HgI_2,I_2,I_2) is also known; and a periodide of ammonium, NH_4I_2,I_2.

or other vessel containing a little water. Into the tubulure of the retort is passed, at first a drop at a time, a mixture of 1 part of red phosphorus with 2 of water. Abundance of hydriodic acid is evolved on the application of gentle heat, and falls into and dissolves in the water in the receiver. Phosphoric acid remains.

$$P_2 + 5I_2 + 8H_2O = 10HI + 2H_3PO_4.$$

Or iodine may be dissolved in bisulphide of carbon in a tall cylinder, water added, and sulphuretted hydrogen passed through the mixture. The water dissolves the hydriodic acid, the bisulphide retaining the separated sulphur. The aqueous solution only needs boiling for two or three minutes to remove excess of sulphuretted hydrogen.

Syrupus Acidi Hydriodici, U. S. P., contains 1 per cent. of real acid.

Iodide of potassium (KI) is largely used in medicine, and hence is the most convenient iodide on which to experiment in studying the reactions of this acidulous radical. Solid iodine itself might be taken for the purpose; but its use and action in that state have already been alluded to in describing the iodides of potassium, cadmium, and mercury; its analytical reactions in the combined condition are those which may now occupy attention.

Solution of Iodine.—Iodine is slightly soluble in water (iodine-water), and readily soluble in an aqueous solution of iodide of potassium. Five parts of iodine and 10 of iodide of potassium dissolved in 85 of distilled water, form *Liquor Iodi Compositus*, U. S. P. ("Lugol's Solution"); 4 parts of iodine and 1 of iodide of potassium, rubbed with 2 parts of water and 93 of benzoated lard form *Unguentum Iodi*, U. S. P. It is more soluble in spirit (*Tinctura Iodi*, U. S. P.), or in a spiritous solution of iodide of potassium (*Tinctura Iodi*, B. P.). It combines with sulphur, forming an unstable grayish-black solid iodide (S_2I_2), having a radiated crystalline structure (*Sulphuris Iodidum*, U. S. P.). If 100 parts be thoroughly boiled with water, the iodine will pass off in vapor, and about 20 parts of sulphur remain.—*B. P.* and *U. S. P.*

Analytical Reactions (Tests).

First Analytical Reaction.—To a few drops of an aqueous solution of an iodide (*e. g.*, KI) add solution of nitrate of silver; a light yellow precipitate of iodide of silver (AgI) falls. Pour away the supernatant liquid and treat the precipitate with nitric acid, it is not dissolved; pour away the acid and then add dilute ammonia, it is only sparingly dissolved.

This reaction is useful in separating iodine from most other acidulous radicals, but does not distinguish iodine from bromine.

The presence of chloride in iodide of silver may be detected by boiling with dilute solution of carbonate of ammonium, filtering off

the insoluble iodide of silver and saturating the filtrate with nitric acid; any chloride of silver is then precipitated.

Ammonia, it will be remembered, dissolves chloride of silver readily; hence the presence of chloride of potassium in bromide or iodide may be detected by dissolving in water, adding excess of nitrate of silver, collecting the precipitate, washing, digesting in ammonia, filtering, and adding excess of nitric acid to the filtrate; more than a trace of white curdy precipitate indicates a chloride (of potassium). Bromide and iodide of silver are, however, slightly soluble in ammonia. Better processes are given on page 275.

Second Analytical Reaction.—Liberate iodine from an iodide by the cautious addition of chlorine, then add cold decoction of starch; a deep-blue combination of iodine and starch, commonly termed "iodide of starch," is formed.

Starch is highly sensitive to the action of iodine; this reaction is consequently very delicate and characteristic. The reaction is not observed in hot liquids. Excess of chlorine must be avoided, or colorless chloride of iodine will be produced. Nitrous acid, or a nitrite acidulated with sulphuric acid, may be used instead of chlorine. Concentrated sulphuric acid also liberates iodine from iodides, the hydrogen of the hydriodic acid first produced uniting with the oxygen of the sulphuric acid—the latter (H_2SO_4) being reduced to sulphurous acid (H_2SO_3) or even to hydrosulphuric acid (H_2S).

In testing bromine for iodine the bromine must be nearly all removed by dilute solution of sulphurous acid, or be nearly all removed by solution of soda, before the decoction of starch is added.

Ozone (O_3).—Papers soaked in mucilage of starch containing iodide of potassium form a test for free chlorine and nitrous acid, and are also employed by meteorologists to detect an allotropic or physically polymeric and energetic form of oxygen termed by Schönbein *ozone* (from ὀζω, *ozō*, I smell). This substance liberates iodine from iodide of potassium (with formation of iodide of starch), and is supposed to occur normally in the atmosphere, the salubrity or insalubrity of which is said to be dependent to some extent on the presence or absence of ozone. The possible occurrence of nitrous or chlorinoid gases in the air, however, renders the test untrustworthy. Houzeau proposes to test for ozone by exposing litmus-paper of a neutral tint soaked in a dilute solution of iodide of potassium; the potash set free by action of the ozone turns the paper blue. The same paper without iodide would indicate the extent to which the effect might be due to ammonia vapor. Ozone, or rather ozonized air, is produced artificially in large quantities on passing air through a box (Beane's Ozone-generator) highly charged with electricity. In the latter operation condensation of the volume of air, or, rather, of the oxygen in the air, occurs. Small quantities are obtained by exposing in a loosely closed bottle a stick of phosphorus partially covered by water, but the product is mixed with peroxide of hydrogen. Ozone is a powerful bleaching, disinfecting, and general oxidizing agent; insoluble in water, soluble in oils of

turpentine, cinnamon, and some other liquids. From experiments that have been made by Soret on the specific gravity of ozone, its molecular formula would seem to be O_3, that of ordinary oxygen being O_2. Its smell is peculiar. (See p. 236, also "Blood.")

Third Analytical Reaction.—To a neutral aqueous solution of an iodide, add a solution containing one part of sulphate of copper to two and a half parts of green sulphate of iron, and well shake; a dirty-white precipitate of cuprous iodide (Cu_2I_2) falls.

$$2KI + 2CuSO_4 + 2FeSO_4 = Cu_2I_2 + K_2SO_4 + Fe_23SO_4.$$

Or to the liquid containing an iodide add the solution of copper sulphate and some solution of sulphurous acid, and warm the mixture, cuprous iodide falls.

$$2KI + 2CuSO_4 + H_2SO_3 + H_2O = Cu_2I_2 + 2KHSO_4 + H_2SO_4.$$

Separation of Chlorides, Bromides, and Iodides.—Chlorides and bromides are not affected in this way; the reaction is useful, therefore, in removing iodine from a solution in which chlorides and bromides have to be sought. The total removal of iodine by the former of the two modifications of the process is insured by supplementing the addition of the cupric and ferrous sulphates by a few drops of solution of potash or soda, any acid which might be keeping cuprous iodide in solution being thereby neutralized, ferric or ferrous hydrate, precipitated at the same time, not affecting the reaction. Occasionally, too, it may be necessary to repeat the process with the filtrate before the last traces of iodine are removed. The second modification of the process is, on the whole, to be preferred.

Chloride of the rare metal palladium performs a similar useful office in removing iodine, but not bromine or chlorine, from solutions.

Chlorides may be separated from bromides by taking advantage of the ready solubility of chloride of silver, and slow and slight solubility of bromide of silver in ammonia, especially in (a fair, not a great, excess of) ammonia containing chloride of silver.

The presence of much bromide of silver, however, considerably reduces the power of ammonia to dissolve chloride of silver.

Hart's Test.—(If nitrates, chlorates, bromates, or iodates are present, it is necessary to fuse the substance with a little sodium carbonate and charcoal to reduce them. If the haloids are united with silver, it is best to fuse with sodium carbonate and extract with water, although with iodine and bromine it is not absolutely necessary.) The substance is placed in the flask shown in the figure given in the section on quantitative analysis of oxide of manganese (*vide* Index), with some water and a few drops of solution of ferric sulphate. In the bulbs are poured a few drops of dilute starch paste. The bulbs are kept cool by immersing in water in a beaker. The

contents of the flask are then boiled, and if iodine is present the starch is colored blue. This test is extremely delicate. If iodine is found, the cork in the bulb-tube is removed and the solution boiled until on testing again in the same way no more iodine is found. If much iodine is present, it is necessary to add more ferric sulphate solution. The bulb-tube is now cleaned, charged with a few drops of water and a drop or two of chloroform, and a very small crystal of potassium permanganate added to the solution in the flask. The contents of the flask are boiled again, and if bromine is present the chloroform becomes red. The tube is now moved and more potassium permangante and ferric sulphate added, little by little, boiling between each addition until the bromine has all been driven off. A few drops of alcohol are added to the contents of the flask to decolorize any excess of permanganate, and after filtration chlorine is tested for in the filtrate with silver nitrate.

Chlorides may also be detected in bromides and iodides by taking advantage of the formation of chlorochromic anhydride (page 237) and the non-occurrence of corresponding compounds of bromine or iodine, as follows:—

To a solution of a chloride with a bromide and an iodide add a concentrated solution of sulphite of sodium, and then a reagent prepared by mixing equal volumes of sulphuric acid and saturated solution of sulphate of copper, until no further precipitation of cuprous iodide occurs. Next add solution of soda to remove excess of sulphate of copper; filter and evaporate to dryness. Place the dried residue, together with an equal bulk of red chromate of potassium, in a dry test-tube fitted with a delivery-tube, or into a small retort, and cover the mixture with sulphuric acid. Distil into water. Chromic anhydride and hydrochloric and hydrobromic acids are liberated by the sulphuric acid, and reacting upon one another form chlorochromic anhydride, together with free bromine and chlorine.

$$CrO_3 + 2HCl = CrCl_2O_2 + H_2O.$$
$$2CrO_3 + 6HCl + 3H_2SO_4 = Cr_23SO_4 + 3Cl_2 + 6H_2O.$$
$$2CrO_3 + 6HBr + 3H_2SO_4 = Cr_23SO_4 + 3Br_2 + 6H_2O.$$

The chlorochromic anhydride is decomposed by the excess of water into which it falls, giving rise to chromic acid, which imparts its color to the liquid, and hydrochloric acid.

$$CrCl_2O_2 + 2H_2O = H_2CrO_4 + 2HCl.$$

The chlorine escapes and the bromine is dissolved by the water. The colored liquid is then shaken with chloroform, which removes the bromine—indicating bromine in the original substance. A yellow color remaining is due to chromic acid, indicating chlorides in the original substance. Or add

ammonia to the distillate—the color due to bromine is thereby entirely removed, while that of the chromic compound is only slightly modified.

Instead of eliminating the iodine as cuprous iodide, it may be expelled in vapor, obvious enough by its color and odor, by fusing the dry mixture of the salts with excess of powdered red chromate. The residue, broken into small fragments, may then be distilled with the sulphuric acid for the detection of the bromine and chlorine.

$$5K_2Cr_2O_7 + 6KI = 8K_2CrO_4 + Cr_2O_3 + 3I_2.$$

Fourth Analytical Reaction.—Iodides have been shown to be useful in testing for mercuric salts (see the Mercury reactions, p. 202); a mercuric salt (corrosive sublimate, for example) may therefore be used in testing for iodides, a scarlet precipitate of mercuric iodide (HgI_2) being produced.

This reaction may be employed where large quantities of an iodide are present; but its usefulness in analysis is much impaired by the fact that the precipitate is soluble in excess of the dissolved iodide or in excess of the mercuric reagent. Its color and insolubility in water distinguish it from mercuric chloride, bromide, and cyanide, which are white soluble salts.

Fifth Analytical Reaction.—Iodides have also (see the Lead reactions, p. 212) been shown to be useful in testing for lead salts; similarly a lead salt (acetate, for example) may be used in testing for iodides, in solutions which are either neutral or faintly acid with acetic acid, a yellow precipitate of iodide of lead (PbI_2), soluble in hot water and crystallizing in yellow scales on cooling, being produced.

Chloride, bromide, and cyanide of lead are white; hence the above reaction may occasionally be useful in distinguishing iodine from the allied radicals. But iodide of lead is slightly soluble in cold water; hence small quantities of iodide cannot be detected by this reaction. (For *Iodates* see p. 294.)

Analogies between Chlorine, Bromine, Iodine, and their Compounds.—These elements form a natural group or family, each distinct from the other, yet closely related. Moreover, their dissimilarities are so curiously gradational as to irresistibly suggest the idea that some day we may find the differences between these bodies to be in degree rather than in kind. Thus chlorine is a gas and iodine a solid, while bromine occupies the intermediate condition. The atomic weight of bromine is nearly midway between those of chlorine and iodine. The same may be said of the weight of equal volumes of each in the gaseous state. The specific gravity of fluid chlorine is 1.33, of iodine 4.95, while bromine is nearly 3. Liquid chlorine is transparent, iodine opaque, bromine intermediate.

The crystalline forms of the chloride, bromide, and iodide of a metal are commonly identical. One volume of either element in the gaseous state combines with an equal volume of hydrogen (at the same temperature) to form two volumes of a gaseous acid, very soluble in water (hydrochloric acid, hydrobromic acid, hydriodic acid). Many other analogies are traceable. (*Vide* Index, "Periodic Law.")

QUESTIONS AND EXERCISES.

419. State the method by which Bromine is obtained from its natural compounds.
420. Mention the properties of bromine.
421. How may the Bromides of Potassium and Ammonium be made?
422. By what reagents may bromides be distinguished from chlorides?
423. Whence is iodine obtained?
424. By what process is iodine isolated?
425. State the properties of iodine.
426. What is the nature of Iodide of Sulphur?
427. Give the analytical reaction of iodides.
428. Which three substances may indirectly be detected by a mixture of iodide of potassium and mucilage of starch?
429. Describe a method by which iodides may be removed from a solution containing chlorides and bromides.

HYDROCYANIC ACID AND OTHER CYANIDES.

Formula of Hydrocyanic Acid HCN or HCy.

Molecular weight 27.

History of Cyanogen.—The acidulous radical of hydrocyanic acid and other cyanides is a compound body, cyanogen (Cy). It is so named from κύανος, *kuanos*, blue, and γεννάω, *gennaō*, I generate, in allusion to its prominent chemical character of forming, with iron, the different varieties of Prussian blue. It was from Prussian blue that Scheele, in 1782, first obtained what we now, from our knowledge of its composition, term hydrocyanic acid, but which he called Prussic acid. Cyanogen was isolated by Gay-Lussac in 1814, and was the first compound radical distinctly proved to exist.

Sources.—Cyanogen does not occur in nature, and is only formed from its elements under certain circumstances. It is found in small quantities among the gases of iron-furnaces, and is produced to a slight extent in distilling coals for gas. In the form of ferrocyanide of potassium it is obtained abundantly by heating animal refuse containing nitrogen, such as the scrapings of horns, hoofs, and hides (5 parts), with carbonate of potassium (2 parts) and waste iron (filings, etc.) in a covered iron pot. The residual mass is boiled with

water, the mixture filtered, and the filtrate evaporated and set aside for crystals to form. The cyanogen, produced from the carbon and nitrogen of the animal matter, unites with the potassium, and afterwards, on boiling with water, with iron, to form what is often termed the yellow prussiate of potash or ferrocyanide of potassium ($K'_4Fe''Cy'_6,3H_2O$) (*Potassii Ferrocyanidum*, U. S. P.), a compound occurring in four-sided tabular yellow crystals. It contains the elements of cyanogen, yet it is not a cyanide, for it is not poisonous, and is otherwise different from cyanides; it will be further noticed subsequently. From this salt all cyanides are directly or indirectly prepared.

Cyanide of Potassium (KCy) (*Potassii Cyanidum*, U. S. P.), which is the most common, may be obtained by heating the ferrocyanide to redness until gas (chiefly nitrogen) ceases to be evolved; a carbide of iron settles to the bottom of the molten mass of almost pure cyanide. The product, carefully poured off and cooled, is an opaque crystalline mass containing about 95 per cent. of the salt. It also may be procured by fusing 8 parts of ferrocyanide with 3 of carbonate of potassium in a crucible; carbonic acid gas (CO_2) is evolved, iron (Fe) is set free, and cyanate of potassium (KCyO), a body that will be subsequently noticed, is formed at the same time:—

$$2K_4FeCy_6 + 2K_2CO_3 = 10KCy + 2KCyO + Fe_2 + 2CO_2.$$

Double cyanides exist, such as the cyanide of sodium and silver (NaCy,AgCy), formed in the process (subsequently described) of quantitatively determining the amount of hydrocyanic acid in a liquid by a standard solution of nitrate of silver; these compounds have, more or less, the properties of their constituents. But other cyanogen compounds, not double cyanides, occur in which the cyanogen is so intimately united with a metal as to form a distinct radical; such are ferrocyanides and ferricyanides—salts which will be noticed in due course.

Cyanogen, like chlorine, bromine, and iodine, is univalent (Cy'). It may be isolated by simply heating mercuric cyanide ($HgCy_2$) or cyanide of silver (AgCy). It is a colorless gas, burning, when ignited, with a beautiful peach-blossom-colored flame.

Mercuric cyanide is produced in crystals on dissolving 1 part of ferrocyanide of potassium in 15 parts of boiling water, adding 2 parts of mercuric sulphate, keeping the whole hot for ten or fifteen minutes, and then filtering and setting aside to cool. In addition to mercuric cyanide ($HgCy_2$), mercury (Hg), ferric sulphate (Fe_23SO_4), and sulphate of potassium (K_2SO_4), are formed. Any excess of ferrocyanide also gives Prussian blue by reaction with the ferric sulphate. It (*Hydrargyri Cyanidum*, U. S. P.) may also be made by dissolving red oxide of mercury in diluted hydrocyanic acid. A small flame of cyanogen may be obtained on heating a few crystals of mercuric cyanide in a short piece of glass tubing closed at one end, and applying a light to the other end as soon as evolution of gas commences; brown *paracyanogen* (C_3N_3) and mercury remain.

REACTIONS.

Diluted Hydrocyanic Acid.

Synthetical Reaction.—Dissolve 2 or 3 grains of ferrocyanide of potassium in 5 or 6 times its weight of water in a test-tube, add a few drops of sulphuric acid and boil the mixture, conveying the evolved gas by a bent glass tube (adapted to the test-tube by a cork) into another test-tube containing a little water; the product is a dilute solution of hydrocyanic acid. Made by this process in large quantities of a certain definite strength (2 per cent.), this solution is the *Acidum Hydrocyanicum Dilutum*, U. S. P. "A colorless liquid of a peculiar odor. Specific gravity 0.997."

$$2K_4FeCy_6 + 6H_2SO_4 = FeK_2Fe''Cy_6 + 6KHSO_4 + 6HCy.$$

The following are the details of the official (U. S. P.) process:—

Place 20 parts of Ferrocyanide of Potassium in coarse powder in a tubulated retort, and add to it *forty* (40) *parts* of Water. Connect the neck of the retort (which is to be directed upward), by means of a bent tube, with a well-cooled condenser, the delivery-tube of which terminates in a receiver surrounded with ice-cold water, and containing *sixty* (60) *parts* of Diluted Alcohol. All the joints of the apparatus, except the neck of the receiver, having been made air-tight, pour into the retort, through the tubulure, the Sulphuric Acid previously diluted with an equal weight of Water. Agitate the retort gently, and then heat it, in a sand-bath, until the contents are in brisk ebullition, and continue the heat regularly until there is but little liquid mixed with the saline mass remaining in the retort.* Detach the receiver, and add to its contents so much Distilled Water as may be required to bring the product to the strength of *two* (2) *per cent.* of absolute Hydrocyanic Acid. (*Vide* paragraphs on quantitative analysis.)

* This operation is peculiarly liable to those sudden and tumultuous evolutions of vapor, or "bumpings," or "*soubresauts*," which often interfere with successful distillation. Such phenomena occur, according to Tomlinson, whenever unaided heat has to overcome the great amount of adhesion naturally existing between certain liquids and vapors, or, rather, between the normal liquid and those particles of it which, becoming strongly heated at the heated part of the vessel, have assumed the condition of particles of dissolved vapor, and which would at once pass from this condition into that of permanent vapor but for adhesion. Ordinarily a glass or other surface is not absolutely clean, but is more or less covered with specks, traces of materials deposited from the air, the fingers, cloths, etc. Some liquids seem to have little or no adhesion for these materials, while certain vapors have greater adhesion for the films than for the liquids. Hence, in ordinary regular ebullitions the vapors accumulate on the films, and then at once become subject to the pressure of the mass of fluid, and so pass off in bubbles. But when the films are absent, or have become removed during distillation, the

The residue of this reaction is acid sulphate of potassium ($KHSO_4$), which remains in solution, and ferrocyanide of potassium and iron ($Fe''K_2FeCy_6$), an insoluble powder sometimes termed Everitt's yellow salt, from the name of the chemist who first made out the nature of the reaction. The latter compound becomes bluish-green during the reaction, owing to absorption of oxygen.

Diluted hydrocyanic acid may also be prepared by reaction of cyanide of silver (6 parts), hydrochloric acid (5 parts), and distilled water (55 parts).——Mix the hydrochloric acid with the distilled water, add the cyanide of silver, and shake the whole together in a glass-stoppered bottle. When the precipitate has subsided, pour off the clear liquid.

Pure anhydrous hydrocyanic acid is a colorless, highly volatile, intensely poisonous liquid, solidifying when cooled to a low temperature.* It may be made by passing sulphuretted hydrogen over mercuric cyanide. The official solution of the acid is fairly stable, but is said to be rendered more so by the presence of a minute trace of sulphuric or hydrochloric acid. A stronger acid is liable to assimilate the elements of water, and yield formate of ammonium (NH_4CHO_2). Solutions of hydrocyanic acid often become brown by formation of what is, apparently, *paracyanogen* (C_3N_3). According to Williams, aqueous hydrocyanic acid containing 20 per cent. of glycerin can be kept for an apparently indefinite length of time. The official acid should be preserved in small stoppered bottles in a cool dark place.

Note.—A few drops of diluted hydrocyanic acid so placed that its vapor may be inhaled, forms the *Vapor Acid Hydrocyanici*, B. P., or Inhalation of Hydrocyanic Acid.

Hydrocyanic acid also occurs in cherry-laurel water and bitter-almond water (*vide* Index). *Aqua Lauro-Cerasi*, B. P., is made to contain 0.1 per cent. of real hydrocyanic acid (KCy.).

The hydrocyanic acid used in pharmacy is extremely liable to variation in strength. It should frequently be tested volumetrically.

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heat accumulates until it is sufficient to overcome the adhesion of the superheated particles, and these are then, all of them at once, converted into vapor, the liquid commonly boiling over, sometimes even bursting the vessel. "Bumping" would be prevented by the introduction of fragments of substances for which vapor-particles have adhesion, but no known substance has this property in an absolute degree. Fragments of tobacco-pipe or pumice-stone, pieces of cork, thick paper, resin, sulphur, platinum wire, etc., are all useful when there is no chemical action between them and the liquid. Mr. Tomlinson very strongly recommends cocoanut-shell charcoal to be used whenever practicable. A slow current of gas, such as hydrogen, air, or carbonic acid gas, also usefully promotes escape of vapor from a liquid. A jet of steam prevents bumping, but is not always applicable. When the bumping cannot well be prevented, as in the distillation of sulphuric acid, it is somewhat reduced in violence if the retort be heated by an annular gas-burner rather than by a single central jet.

* Traces are formed when electricity passes between carbon poles in slightly moist air (Dewar).

Analytical Reactions (Tests).

First Analytical Reaction.—To a few drops of the hydrocyanic acid solution produced in the above reaction, or to any solution of a cyanide, add excess of solution of nitrate of silver; a white precipitate of cyanide of silver (AgCy) falls. When the precipitate has subsided, pour away the supernatant liquid, and place half of the residue in another test-tube: to one portion add nitric acid, and notice that the precipitate does not dissolve; to the other add ammonia, and observe that the precipitate, though soluble, dissolves somewhat slowly. (Chloride of silver, which is also white, is readily soluble in ammonia.) Cyanide of silver dissolves in solutions of cyanides of alkali-metals, soluble double cyanides being formed (*e. g.*, KCy,AgCy).

Solubility of precipitates in strong solutions of salts.—Cyanide of silver and many other precipitates insoluble in acids (similar remarks apply to precipitates insoluble in alkalies) are often soluble in the strong saline liquids formed by the addition of acids and alkalies to one another. Hence the precaution of adding the latter reagents to separate portions of a precipitate, or of not adding the one until the other has been poured away.

Cyanogen in an insoluble cyanide, such as cyanide of silver itself, is readily recognized on heating the substance in a short piece of glass tubing closed at one end like a test-tube and drawn out at the other end, so as to have but a small opening; on applying a flame, the escaping cyanogen ignites and burns with a characteristic peach-blossom tint. Metallic silver remains.

Antidote.

Second Analytical Reaction.—To a dilute solution of hydrocyanic acid, or a soluble cyanide, add a few drops of solution of a ferrous salt and a drop or two of solution of a ferric salt (ferrous sulphate and ferric chloride are usually at hand); to the mixture add potash or soda (magnesia or carbonate of sodium), and then hydrochloric acid; a precipitate of Prussian blue remains. The decompositions may be traced in the following equations:—

$$\begin{array}{llll} HCy & + KHO & = KCy & + H_2O \\ 2KCy & + FeSO_4 & = FeCy & + K_2SO_4 \\ 4KCy & + FeCy_2 & = K_4FeCy_6 & \text{or } K_4Fcy \\ 3K_4Fcy & + 2Fe_2Cl_6 & = 12KCl & + Fe_4Fcy_3. \end{array}$$

The test depends on the conversion of the cyanogen into ferrocyanogen by aid of the iron of a ferrous salt, and the combination of the ferrocyanogen, so produced, with the iron of a ferric salt.

Hence a mixture of green sulphate of iron, solution of perchloride of iron, and either magnesia or carbonate of sodium, is the recognized *antidote* in cases of poisoning by hydrocyanic acid or cyanide of potassium.

In such an alkaline mixture the poisonous cyanide, by reaction with ferrous hydrate, is at once converted into innocuous ferrocyanide of potassium or sodium, etc.; should the mixture become acid, the ferric salt present reacts with the soluble ferrocyanide, forming insoluble Prussian blue, which is also inert. From the rapidity of the action of these poisons, however, there is seldom time to prepare an antidote. Emetics, the stomach-pump, the application of a stream of cold water to the spine, and the above antidote, form the usual treatment.

Third Analytical Reaction.—To solution of hydrocyanic acid add ammonia and common yellow sulphydrate of ammonium, and evaporate the liquid nearly or quite to dryness in a small dish, occasionally adding ammonia till the excess of sulphydrate of ammonium is decomposed; add water and acidify the liquid with hydrochloric acid, and then add a drop of solution of a ferric salt; a blood-red solution of sulphocyanide of iron will be formed.

This is a very delicate reaction. Some free sulphur in the yellow sulphydrate of ammonium unites with the alkaline cyanide and forms sulphocyanate ($2NH_4Cy + S_2 = 2NH_4CyS$); the ammonia combines with excess of free sulphur, and forms, among other salts, sulphydrate of ammonium, the whole of which is removed by the ebullition. If the liquid has not been evaporated far enough, sulphydrate of ammonium may still be present, and give black sulphide of iron on the addition of ferric salt.

Hydrocyanic Acid in the Blood.—According to Buchner the blood of animals poisoned by hydrocyanic acid, instead of coagulating as usual, remains liquid and of a clear cherry-red color several days. In one case he obtained the reactions of the acid on diluting and distilling the blood fifteen days after death, and applying the usual reagents to the distillate. Aqueous solution of peroxide of hydrogen (p. 102) changes such blood to a deep-brown color.

Schönbein's test for hydrocyanic acid is said to be extremely delicate. Filtering-paper is soaked in a solution of 3 parts of guaiacum resin in 100 of alcohol. A strip of this paper is dipped in a solution of 1 part of sulphate of copper in 50 of water; a little of the suspected solution is placed on this paper and exposed to the air, when it immediately turns blue. Or the paper may be placed over the neck of an open bottle of medicine supposed to contain hydrocyanic acid, or otherwise exposed to the vapor of the acid.

QUESTIONS AND EXERCISES.

430. Write a paragraph on the history of cyanogen.
431. Mention the source of the cyanogen of cyanides.
432. How is Ferrocyanide of Potassium prepared?
433. What is the formula of ferrocyanide of potassium?
434. Is ferrocyanide of potassium poisonous?
435. Write an equation expressive of the reaction which ensues when ferrocyanide and carbonate of potassium are brought together at a high temperature.
436. What are the properties of cyanogen? How may it be obtained in a pure condition?
437. How is mercuric cyanide prepared?
438. How much real hydrocyanic acid is contained in the official liquid?
439. Give details of the preparation of hydrocyanic acid, and an equation of the reaction.
440. State the proportion of water that must be added to an aqueous solution containing 15 per cent. of hydrocyanic acid to reduce the strength to 2 per cent.—*Ans.* $6\frac{1}{2}$ to 1.
441. What are the characters of pure undiluted hydrocyanic acid? How may it be obtained?
442. Enumerate the tests for cyanogen, giving equations.
443. Explain the action of the best antidote in cases of poisoning by hydrocyanic acid or cyanide of potassium.

NITRIC ACID AND OTHER NITRATES.

Formula of Nitric Acid HNO_3. Molecular weight 63.

Introduction.—The group of elements represented by the formula NO_3 is that characteristic of nitric acid and all other nitrates; hence it is expedient to regard these elements as forming an acidulous radical, which may be termed *the nitric radical.* Like the hypothetical basylous radical ammonium (NH_4), this supposed acidulous radical (NO_3) has not been isolated. Possibly it is liberated when chlorine is brought into contact with nitrate of silver; but, if so, its decomposition into white crystalline nitric anhydride (N_2O_5) and oxygen (O) is too rapid to admit of its identification.

Sources.—The nitrogen and oxygen of the air combine and ultimately form nitric acid whenever a current of electricity (as in the occurrence of lightning) passes. The nitrates found in rain may partly or wholly thus originate. The oxidation of ammoniacal matter and of the nitrogenous constituents of animal and vegetable matter in the soil, favored by the darkness and by the presence of some low form of vegetable life acting as a ferment, result in the production of nitrates. Hence nitrates are commonly met with in waters, soils, and the juices of plants. In the concentrated plant-juices, termed medicinal "Extracts," small prismatic crystals of nitrate of potassium may occasionally be observed. (The