Rarer Acids.—The above acids contain the only acidulous groupings that commonly present themselves in analysis or in pharmaceutical operations. There are, however, several other acids (such as hypochlorous, nitrous, hypophosphorous, valerianic, benzoic, gallic, tannic, uric, hyposulphurous, hydroferrocyanic, hydroferridcyanic, lactic, etc.) with which it is desirable to be more or less familiar; reactions concerning these will therefore be described. Arsenious, arsenic, stannic, manganic, and chromic acids have already been treated of in connection with the metals they contain; in practical analysis they always become sufficiently altered to come out among the metals.

Quantivalence.—A glance at the foregoing Table is sufficient to show the quantivalence of the acidulous radicals. The first seven are clearly univalent, then follow six bivalent, leaving three trivalent.

These all combine with equivalent amounts of basylous radicals to form various salts; hence they may be termed monobasylous, dibasylous, and tribasylous radicals. The acids themselves were formerly spoken of as monobasic, dibasic, and tribasic respectively, or monobasic and polybasic, in reference to the amount of *base* (hydrates or oxides) they could decompose; but the terms are no longer definite, and hence but little used in mineral chemistry.

Antidotes.—The antidotes in cases of poisoning by the strong acids will naturally be non-corrosive alkaline substances, as soap and water, magnesia, common washing "soda," or other carbonates. Vinegar, lemon-juice, and weak or non-corrosive acids would be the appropriate antidotes to caustic alkalies.

Analysis.—The practical study of the acidulous side of salts will occupy far less time than the basylous. Salts will then be briefly examined as a whole.

Caution.—Once more: it is only for convenience in the division of chemistry for systematic study that salts may be considered to contain basylous and acidulous radicals, or separate sides, so to speak; for we possess no absolute knowledge of the internal arrangement of the atoms (admitting that there are such things) in the molecule of a salt. We only know that certain groups of atoms may be transferred from compound to compound in mass (that is, without apparent decomposition); hence the assumption that these groups are radicals. A salt is probably a whole, having no such sides as those mentioned.

QUESTIONS AND EXERCISES.

410. Mention the basylous radical of acids.

411. Give illustrations of univalent, bivalent, and trivalent acidulous radicals, or monobasylous, dibasylous, and tribasylous radicals.

412. What is the difference between an elementary and a compound acidulous radical?

413. Name the grounds on which salts may be assumed to contain basylous and acidulous radicals.

HYDROCHLORIC ACID AND OTHER CHLORIDES.

Formula of Hydrochloric Acid HCl. Molecular weight* 36.4.

The acidulous radical of hydrochloric acid and of other chlorides is the element chlorine (Cl). It occurs in nature chiefly as chloride of sodium (NaCl), either solid, under the name of *rock-salt*, mines of which are not unfrequently met with, or in solution in the water of all seas. Common table-salt is more or less pure chloride of sodium in minute crystals. Chlorine, like hydrogen, is univalent (Cl′); its atomic weight is 35.4. Its molecule is symbolized thus, Cl_2, chloride of chlorine.

Reactions.

Hydrochloric Acid.

First Synthetical Reaction.—To a few fragments of chloride of sodium in a test-tube or small flask add about an equal weight of sulphuric acid; colorless and invisible gaseous hydrochloric acid is evolved, a sulphate of sodium remaining. Adapt to the mouth of the vessel by a perforated cork a piece of glass tubing bent to a right angle, heat the mixture, and convey the gas into a small bottle containing a little water; solution of hydrochloric acid results.

$$\underset{\text{Chloride of sodium.}}{NaCl} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Hydrochloric acid.}}{HCl} + \underset{\text{Acid sulphate of sodium.}}{NaHSO_4}$$

Hydrochloric Acid.—The product of this operation is the nearly colorless and very sour liquor commonly called hydrochloric acid. When of certain given strengths (estimated by volumetric analysis) it forms *Acidum Hydrochloricum*, U. S. P. (*Acidum Muriaticum*), and *Acidum Hydrochloricum Dilutum*, U. S. P. The former has a specific gravity of 1.16 and contains 31.9 per cent. of real acid. The latter, specific gravity 1.049, with 10 per cent. of the real acid, is made by diluting 6 fluid parts of the strong acid with 13 of water. The above process is that of the manufacturer, larger vessels being employed, and the gas being freed from any trace of sulphuric acid by washing. Other chlorides yield hydrochloric acid when heated with sulphuric acid; but chloride of sodium is always used, because cheap and common.

Common yellow hydrochloric acid is a by-product in the manufacture of carbonate of sodium from common salt, a process in which the chloride of sodium is first converted into sulphate, hydrochloric acid being liberated. This impure acid is liable to contain iron, arsenic, fixed salts, sulphuric acid, sulphurous acid, nitrous compounds, and chlorine.

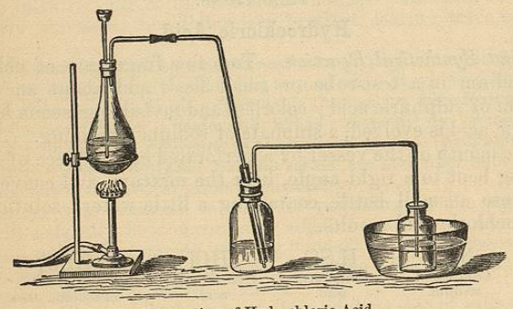
The process for the preparation of hydrochloric acid is as follows: it may be carried out by the student with about one-twelfth of the quantities mentioned:—

---

* The weight of a molecule is the sum of the weights of its atoms.

"Take of chloride of sodium, dried, 48 ounces, sulphuric acid 44 fluidounces, water 36 fluidounces, distilled water 50 fluidounces; pour the sulphuric acid slowly into 32 ounces of the water, and, when the mixture has cooled, add it to the chloride of sodium previously introduced into a flask having the capacity of at least one gallon. Connect the flasks by corks and a bent glass tube with a three-necked wash-bottle, furnished with a safety-tube, and containing the remaining 4 ounces of the water [or let the flask-tube pass loosely through a wider tube fixed in the cork of the wash-bottle, as shown in Fig. 37]; then, applying heat to the flask, conduct the

Fig. 37.



Preparation of Hydrochloric Acid.

disengaged gas through the wash-bottle into a second bottle containing the distilled water, by means of a bent tube dipping about half an inch below the surface, and let the process be continued until the product measures 36 ounces, or the liquid has acquired a specific gravity of 1.16. The bottle containing the distilled water must be kept cool during the whole operation."

The modification of wash-bottle shown in the figure allows of the easy insertion or removal of a delivery-tube. The wider tube there shown, or an ordinary tube-funnel, also acts as a *safety-tube* by admitting air the moment there is any tendency in the water in the receiver to be forced back on account of a too rapid absorption of the gas. The time of the student will be saved if hydrochloric acid already in stock be placed in the wash-bottle instead of water.

Invisible gaseous hydrochloric acid forms visible grayish-white fumes on coming into contact with air. This is due to combination with the moisture of the air. The intense greediness of hydrochloric gas and water for each other is strikingly demonstrated on opening a test-tube full of the gas under water; the latter rushes into and instantly fills the tube. If the water is tinged with blue litmus, the acid character of the gas is prettily shown at the same time. The test-tube, which should be perfectly dry, may be filled from the delivery-tube direct; for the gas is somewhat heavier than, and therefore readily displaces, air. The mouth may be closed by

the thumb of the operator. At low temperatures hydrochloric acid and water form a crystalline compound, $HCl,2H_2O$.

Note.—The process includes the use of as much sulphuric acid as is theoretically necessary for the production of acid sulphate of sodium ($NaHSO_4$), which remains in the generating vessel. A hot solution of this residue, carefully neutralized by carbonate of sodium, filtered, and set aside, yields normal sulphate (*Sodii Sulphas*, U. S. P.), "Glauber's Salt," in the form of transparent oblique efflorescent prisms ($Na_2SO_4,10H_2O$).

$$\underset{\text{Acid sulphate of sodium.}}{2NaHSO_4} + \underset{\text{Carbonate of sodium.}}{Na_2CO_3} = \underset{\text{Sulphate of sodium.}}{2Na_2SO_4} + \underset{\text{Water.}}{H_2O} + \underset{\text{Carbonic acid gas.}}{CO_2}$$

Chlorine.

Second Synthetical Reaction.—To some drops of hydrochloric acid (that is, the common aqueous solution of the gas) add a few grains of black oxide of manganese, and warm the mixture; *chlorine*, the acidulous radical of all chlorides, is evolved, and may be recognized by its peculiar odor or irritating effect on the nose and air-passages.

$$4HCl + MnO_2 = Cl_2 + 2H_2O + MnCl_2.$$

Chlorine-water.—This is the process of the Pharmacopœia for the production of chlorine-water (*Aqua Chlori*, U. S. P.), the gas being first washed and then passed into water. Chlorine slowly decomposes water, with production of hydrochloric acid and oxygen gas; hence, for medicinal purposes the solution should be freshly prepared; it is best preserved in a green-glass well-stoppered bottle in a cool and dark place. At common temperatures (60° F.), if fresh and thoroughly saturated, chlorine-water contains more than twice (2.3) its bulk of chlorine, or less than 1 per cent. (about 0.75) by weight. Chlorine passed into cold water yields crystals of hydrous chlorine ($Cl\,5H_2O$), and these when heated under pressure give an upper layer of chlorine-water and a lower layer of *liquid chlorine.*

Note.—To obtain the chlorine from other chlorides, sulphuric acid as well as black oxide of manganese must be added. Hydrochloric acid is first formed. The action described in the foregoing equation then goes on, except that half instead of the whole of the oxygen of the black oxide is available for the removal of the hydrogen from the chlorine of the hydrochloric acid, the other half being taken up by the hydrogen of the sulphuric acid. Thus, supposing common salt to be the chloride used, the following equations may represent the supposed steps of the process:—

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl,$$
$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O;$$

then the $2HCl + O = H_2O + Cl_2$

or the whole may be included in one equation:—

$$2NaCl + MnO_2 + 2H_2SO_4 = Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2.$$

This reaction may occasionally have analytical interest, a very small quantity of combined chlorine being recognized by its means. But the following test is nearly always applicable for the detection of this element, and leaves nothing to be desired in point of delicacy.

Analytical Reactions (Test).

To a drop of hydrochloric acid, or to a dilute solution of any other chloride, add solution of nitrate of silver; a white curdy precipitate falls. Pour off most of the supernatant liquid, add nitric acid and boil; the precipitate does not dissolve. Pour off the acid, and add dilute ammonia; the precipitate quickly dissolves. Neutralize the solution by an acid; chloride of silver is once more precipitated.

The formation of this white precipitate, its appearance, insolubility in boiling nitric acid, solubility in ammonia and in solution of its carbonate and reprecipitation by an acid, form abundant evidence of the presence of chlorine. Its occurrence as a chloride of a metal is determined by testing for the metal with the appropriate reagent; its occurrence as hydrochloric acid is considered to be indicated by the odor, if strong, and the sour taste, if weak, of the liquid, and the action of the liquid on blue litmus-paper, which, like other acids, it reddens. If hydrochloric acid be present in excessive quantity, it will, in addition to the above reactions, give rise to strong effervescence on the addition of a carbonate, a chloride being formed. The chlorine in insoluble chlorides, such as calomel, "white precipitate," etc., may be detected by boiling with caustic potash, filtering, acidulating the filtrate by nitric acid, and then adding the nitrate of silver.

Antidotes.—In cases of poisoning by strong hydrochloric acid, solution of carbonate of sodium (common washing soda) or a mixture of magnesia and water may be administered as an antidote.

QUESTIONS AND EXERCISES.

414. A specimen of official Hydrochloric Acid contains 31.8 per cent. by weight of gas, and its specific gravity is 1.16; work out a sum showing what volume of it will be required, theoretically, to mix with black oxide of manganese for the production of one gallon of chlorine-water, one fluidounce of which contains 2.66 grains of chlorine. *Ans.* 5½ fluidounces, nearly (5.4).

415. Why does hydrochloric acid gas give visible fumes on coming into contact with air?

416. How much chloride of sodium will be required to furnish one pound of chlorine?

417. Give the analytical reactions of chlorides.

418. What antidotes may be administered in cases of poisoning by hydrochloric acid?

HYDROBROMIC ACID AND OTHER BROMIDES.

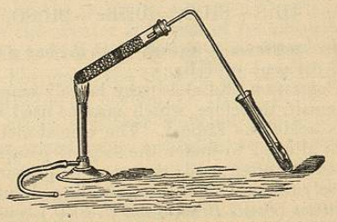
Formula of Hydrobromic Acid HBr. Molecular weight 80.8.

Bromine: Source, Preparation, and Properties.—The acidulous radical of hydrobromic acid and other bromides is the element bromine, Br (*Bromum*, U. S. P.). It occurs in nature chiefly as bromide of magnesium ($MgBr_2$) in sea-water and certain saline springs, and is commonly prepared from the *bittern*, or residual liquors of salt-works. It may be liberated from its compounds by the process for chlorine from chlorides—that is, by heating with black oxide of manganese and sulphuric acid (see page 265). It is a dark-red volatile liquid, emitting an odor more irritating, if possible, than chlorine—of specific gravity 2.990, boiling-point 135° to 145.4° F.

Test of purity, U. S. P.—If 3 gm. of Bromine be mixed with 30 c.c. of water and enough water of ammonia to render the solution colorless, the liquid then digested with carbonate of barium, filtered, evaporated to dryness, and the residue gently ignited, the latter [chiefly bromide of barium] should be soluble in absolute alcohol without leaving more than 0.26 gm. of residue [chloride of barium] (abs. of more than 3 per cent. of chlorine). If an aqueous solution of Bromine be poured upon reduced iron and shaken with the latter until it has become nearly colorless, then filtered, mixed with gelatinized starch, and a few drops of Bromine solution be now carefully poured on top, not more than a very faint blue zone should appear at the line of contact of the two liquids (limit of iodine).

Quantivalence.—The atom of bromine, like that of chlorine, is univalent (Br′). The atomic weight of bromine is 79.8. Free bromine has the molecular formula Br_2, bromide of bromine.

Fig. 38.



Preparation of Hydrobromic Acid.

Hydrobromic Acid.—The bromide of hydrogen, hydrobromic acid, may be made by decomposing bromide of phosphorus by water—$PBr_5 + 4H_2O = 5HBr + H_3PO_4$. A small quantity may be prepared by placing seven or eight drops of bromine at the bottom of

a test-tube, putting in fragments of glass to the height of about an inch or two, then ten or eleven grains of phosphorus, then another inch of glass, and finally a couple of inches of glass fragments slightly wetted with water, a delivery-tube being fitted on by a cork. The phosphorus combines readily, almost violently, with the bromine as soon as the vapor of the latter, aided by a little warmth from a flame, rises to the region of the phosphorus. The bromide of phosphorus thus formed then suffers decomposition by the water of the moist glass, phosphoric and phosphorous acids being produced. The hydrobromic acid gas passes over (heat being applied in the after part of the operation), and may be condensed in water or in solution of ammonia. The latter solution on evaporation yields bromide of ammonium.

Other Methods.—One hundred parts of sodium hyposulphite, fifty of bromine, and ten of water, are placed in a flask and the generated gas is conducted into the upper portion of 140 parts of water contained in another vessel. When the gas begins to come over slowly, gentle heat is applied. The product is nearly 190 parts of liquid containing 25 per cent. of real acid; specific gravity 1.204. It should be kept in a cool dark place (*Hager*). *Squibb* prefers to decompose solution of bromide of potassium by sulphuric acid, and, after removal of potassium sulphate by crystallization, to distil the residual fluid. *Wade* prescribes an almost pure clear solution of the acid made by shaking together 120 grains of bromide of potassium and 153 grains of crystallized tartaric acid in 1 ounce of distilled water, and setting aside till precipitation of acid tartrate of potassium ceases. *Goebel* decomposes bromide of barium by an equivalent weight of sulphuric acid; preparing the bromide of barium by heating a wet mixture of bromide of ammonium and carbonate of barium until carbonate of ammonium fumes cease to be evolved. *Fletcher* prefers to pass sulphuretted hydrogen gas through water containing bromine, and, when all bromine has disappeared, distilling the mixture. The distillate, when diluted until it has a sp. gr. of 1.300, contains 34 per cent. of HBr.

$$10Br_2 + 4H_2S + 8H_2O = 20HBr + 2H_2SO_4 + S_2.$$

Acidum Hydrobromicum Dilutum, U. S. P., has a sp. gr. of 1.077 and contains 10 per cent. of HBr.

Bromide of Potassium (KBr) is very largely employed in pharmacy, and is the salt, therefore, which may be used in studying the reactions of this acidulous radical. The official method of making the salt has been alluded to under the salts of potassium (page 76).

Other Bromides are often used; they may be prepared in the same way as, and closely resemble, the corresponding chlorides or iodides. *Bromide of Sodium* (*Sodii Bromidum*, U. S. P.) crystallizes in anhydrous cubes (NaBr) from solutions at 110° or 120° F., and in hydrous prisms ($NaBr,2H_2O$) at ordinary temperatures.

Bromide of Ammonium (NH_4Br) (*Ammonii Bromidum*, U. S. P.) is prepared by agitating iron wire with a solution of bromine until the odor of bromine can be no longer perceived, adding solution of ammonia, filtering, and evaporating the filtrate to dryness. It forms a

white granular salt, which becomes slightly yellow on exposure to air, is readily soluble in water, less so in spirit, and, when heated, sublimes. Bromide or Iodide of Ammonium may also be made by mixing equivalent quantities of strong hot, aqueous solutions of the corresponding potassium salts and of sulphate of ammonium. To the cooled liquids rectified spirit is added, which precipitates the sulphate of potassium. The spirit recovered by distillation of the clear liquid leaves the required salt as a residue in the retort.

Bromide of Calcium, $CaBr_2$ (*Calcii Bromidum*, U. S. P.), may be prepared by neutralizing hydrochloric acid by hydrate or carbonate of calcium, filtering, and evaporating to dryness; or by uniting bromine with iron, boiling the aqueous solution with lime until the mixture is red, filtering and evaporating. It is a white deliquescent granular salt, soluble in water and in alcohol.

Solution of Bromine, B. P., 10 minims in 5 ounces, is an aqueous solution, bromine being slightly soluble in water.

Hypobromites, Bromates, Perbromates, analogous to hypochlorites, chlorates, and perchlorates, are producible.

Bromates occurring as an impurity in bromides are detected by dropping diluted sulphuric acid on to the salt, when a yellow color, due to free bromine, is produced *immediately* if bromates are present.

Analytical Reactions (*Tests*).

First Analytical Reaction.—To a few drops of solution of a bromide (KBr, or NH_4Br) add solution of nitrate of silver; a yellowish-white precipitate of bromide of silver (AgBr) falls. Treat the precipitate successively with nitric acid and dilute ammonia, as described for the chloride of silver; it is only sparingly dissolved by the ammonia.

Second Analytical Reaction.—To solution of a bromide add a drop or two of chlorine-water or a bubble or two of chlorine gas; then add a few drops of chloroform or ether, or disulphide of carbon, shake the mixture, and set the test-tube aside; the chlorine, from the greater strength of its affinities, liberates the bromine, which is dissolved by the chloroform, etc., the solution falling to the bottom of the tube in the case of the heavy chloroform or bisulphide of carbon, or rising to the top in the case of the light ether. Either solution has a distinct yellow or reddish-yellow or red color, according to the amount of bromine present.

Note.—This reaction serves for the isolation of bromine when mixed with many other substances. Excess of chlorine must be avoided, as colorless chloride of bromine is then formed. Iodides give a somewhat similar but more violet appearance; the absence of iodine must therefore be insured by a process given in the next section. The above solution in chloroform or ether may be removed from the tube by drawing up into a *pipette* (small pipe—a narrow glass tube, usually having a bulb or expanded portion in

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.