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

cubical crystals often met with on extracts are chloride of potassium.) Nitric acid and other nitrates are obtained from nitrates of potassium and sodium, and these form the surface layers of the soil of tropical countries. *Nitrate of potassium* or *prismatic nitre* (from the form of its crystals) is chiefly produced in and about the villages of India. The natives simply scrape the surface of waste grounds, mud-heaps, banks, and other spots where a slight incrustation indicates the presence of appreciable quantities of nitre, mix the scrapings with wood ashes (carbonate of potassium, to decompose the nitrate of calcium always present), digest the mixture in water, and evaporate the liquor. The impure product is purified by careful recrystallizations, and is sent into commerce in the form of white crystalline masses or fragments of striated six-sided prisms. Besides its use in medicine (*Potassii Nitras*, U. S. P.), it is employed in very large quantities in the manufacture of gunpowder. *Charta Potassii Nitratis*, U. S. P., Nitrate-of-Potassium Paper, is made by immersing strips of white unsized paper in a solution of 1 part of the salt in 4 parts of water and drying them. *Nitrate of Sodium* (*Sodii Nitras*, U. S. P.) occurs in deposits from 3 inches to 3 yards in thickness on and near the surface, and at any depth down to about 30 feet, in many parts of Peru, Bolivia, and Chili, but more especially in the district of Atacama. The mineral is termed *caliche*, and commonly contains 50 per cent. of nitrate of sodium. The latter is distinguished as *Chili saltpetre* or *Chili nitre* or (from the form of its crystals—obtuse rhomboids) *cubic nitre*, and is chiefly used as a manure and as a source of nitric acid, its tendency to absorb moisture unfitting it for use in gunpowder. In many parts of Europe nitrate of potassium is made artificially by exposing heaps of animal manure, refuse, ashes, and soil to the action of the air and the heat of the sun: in the course of a year or two the nitrogen of the animal matter becomes oxidized to nitrates; the latter are removed by washing. According to Warington, the nitrifying ferment appears capable of existing in three conditions:—1, the nitric ferment of soil, which converts both ammonium salts and nitrites into nitrates; 2, the altered ferment, which converts ammonium salts into nitrites, but fails to change nitrites into nitrates; and, 3, the surface organism (a bacterium), which changes nitrites into nitrates. Similar nitrification goes on in impure well and river waters, which thereby tend to become pure.

Note.—The word *nitric* is from *nitre*, the English equivalent of the Greek νίτρον (nitron), a name applied to certain natural deposits of *natron* (carbonate of sodium), for which nitrate of potassium seems at first to have been mistaken. *Saltpetre* is simply *sal petræ*, salt of the rock, in allusion to the natural origin of nitrate of potassium. *Sal prunella* (from *sal*, a salt, and *pruna*, a live coal) is nitrate of potassium melted over a fire and cast into cakes or bullets.

The nitric radical is univalent (NO_3').

Constitution of Salts.

It is here necessary again to caution the reader against regarding salts as invariably possessing a known constitution, or supposing

that they always possess two or more sides or contain definite radicals. The erroneous conception which, of all others, is most likely to be imperceptibly formed is that of considering salts to be binary bodies. For, first, the names of salts are necessarily binary. A student hears the names "sulphate of iron," "sulphate of copper," and simultaneously receives the impression that each salt has two sides, copper or iron occupying one, and something indicated by the words "sulphate of" the other. Such words as "vitriol," green or blue, or "nitre," would perhaps implant unitary ideas in the mind; but it is simply impossible to give such names to all salts as will convey the impression that each salt is a whole, and therefore unitary. The name "sulphate of potash" produces binary impressions; and the less incorrect name, "sulphate of potassium," is in this respect no better. Secondly, it is impracticable to study salts as a whole. Teachers are almost unanimous in the opinion that students should first master the reactions characteristic of the metals in salts, and then the residues which, with those metals, make up the salts, or *vice versâ*. It is not only impracticable, but impossible, to study salts as a whole; binary ideas concerning them are therefore almost inevitably imbibed. We come to regard a salt as a body which splits up in one direction only, look upon nitre, for instance, and all other nitrates, as containing NO_3 and a metal K; whereas KNO_3 may be split up into KNO_2 and O; or into K_2O, N_2, and O_5; or may contain K_2O and N_2O_5. These are the chief disadvantages attending the employment of the binary hypothesis in studying chemical compounds; if they be borne in mind, the hypothesis may be freely used without much danger of permanent mental bias. Thus in nitre let the group of elements (NO_3) which, with potassium, makes up the whole salt be called the nitric radical, the name of the latter being directly derived from its hydrogen salt. Similarly allow the acidulous residues of other salts of metals to be termed respectively the chloric, acetic, sulphurous, sulphuric, carbonic, oxalic, tartaric, phosphoric, citric, boracic radicals. In short, these compound radicals should be regarded as groupings common to many salts, and which may usually be transferred without any apparent breaking or splitting; at the same time we must be prepared to find that occasionally a salt divides in other directions. In this way perhaps erroneous impressions will gain least hold on the mind, and a way be left open for the easy entrance of new truths should the real constitution of salts be discovered.

Formerly salts (such as sulphate of magnesium) were regarded as containing (*a*) an oxide of a metal (MgO) and an anhydride (SO_3), the latter being incorrectly called an acid (sulphuric acid); or (*b*) as containing two simple radicals (*e. g.*, KI, NaCl, KCy, HgS)—the former being called *oxyacid salts*, or *oxysalts*, and the latter *haloid salts* (from ἁλς, *als*, sea-salt, and εἶδος, *eidos*, likeness). Such distinction is no longer maintained, the two classes being merged. This is an important educational gain on the side of simplicity; for, whereas under the old system much time was necessarily expended before salts of a metal and salts of the oxide of that metal could be distinguished (*e. g.*, KI and K_2O,SO_3), now all salts being regarded

as salts of the metals themselves (*e. g.*, KI and K_2SO_4), no such distinction is necessary.

REACTIONS.

Nitric Acid.

Synthetical Reaction.—To a fragment of nitrate of potassium or nitrate of sodium in a test-tube add a drop or two of sulphuric acid, and warm; nitric acid (HNO_3) is evolved in vapor. The fumes may be condensed by a bent tube fitted to the test-tube, not by a cork as for hydrochloric acid—because the nitric vapors would strongly act on it—but by plaster of Paris, a paste of which sets hard on being set aside for a short time, and is unaffected by the acid.

On a somewhat larger scale nitric acid may be prepared by heating, in a stoppered or plain retort, a mixture of equal weights of nitrate of potassium and sulphuric acid; the acid distils over, and acid sulphate of potassium remains behind:—

$$\underset{\substack{\text{Nitrate of}\\\text{potassium.}}}{KNO_3} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Nitric}\\\text{acid.}}}{HNO_3} + \underset{\substack{\text{Acid sulphate}\\\text{of potassium.}}}{KHSO_4}$$
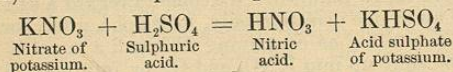
Half the quantity of sulphuric acid may be taken; but in that case neutral sulphate of potassium (K_2SO_4) is produced, which, from its hard, slightly soluble character, is removed with difficulty from the retort. On the manufacturing scale the less proportion is used; but instead of retorts iron cylinders are employed, from which the residual salt is removed by chisels. Moreover, the cheaper sodium salt is the nitrate, from which manufacturers usually prepare nitric acid, seven parts of nitrate of sodium and four of sulphuric acid being employed.
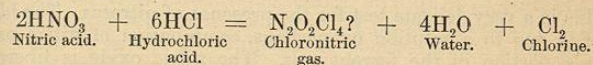
Note.—The acid sulphate of potassium is readily converted into neutral sulphate (*Potassii Sulphas*, U. S. P.) by dissolving in water, adding carbonate of potassium until effervescence ceases to occur, filtering, and setting aside to crystallize.

Pure nitric acid (HNO_3) is a colorless liquid, somewhat difficult of preparation; its specific gravity is 1.52. The strongest acid met with in commerce has a sp. gr. of 1.5, and contains 93 per cent. of real nitric acid (HNO_3); it fumes disagreeably, is unstable, and, except as an escharotic, is seldom used. The United States Pharmacopœia contains two acids: *Acidum Nitricum*, of sp. gr. 1.42, and containing 69.4 per cent. of real acid (HNO_3); and another, *Acidum Nitricum Dilutum*, sp. gr. 1.059, containing 10 per cent. The stronger liquid, although containing water, is usually simply termed "nitric acid." The official nitric acid, of sp. gr. 1.42, is a definite hydrous acid ($2HNO_3,3H_2O$); it distils at 250° F. without change. If a weaker acid be heated it loses water; if a stronger acid be heated it loses nitric acid, until the density of 1.42 is reached. *Aqua fortis* is an old name for nitric acid (*Aqua fortis simplex*, sp. gr. 1.22 to 1.25; *Aqua fortis duplex*, 1.36). The strength of a
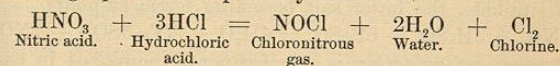
specimen of nitric acid is determined by volumetric analysis. *Nitric anhydride* (N_2O_5), sometimes but erroneously called *anhydrous nitric acid*, is a solid crystalline substance formed on passing dry chlorine over dry nitrate of silver. Metals reduce nitric acid to nitrous acid and to the various oxides of nitrogen, or even to nitrogen itself, according to the strength of acid, temperature, and amount of nitrate present. Not unfrequently nitrate of ammonium is simultaneously formed. Thus, with zinc:—

$$10HNO_3 + 2Zn_2 = 4(Zn2NO_3) + NH_4NO_3 + 3H_2O.$$
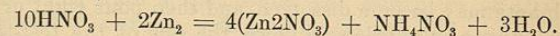
Aqua Regia.—Four parts of nitric acid and fifteen of hydrochloric acid by weight form the *Acidum Nitrohydrochloricum*, U. S. P., and the same weights with 76 of water, give the *Acidum Nitrohydrochloricum Dilutum*.

$$\underset{\substack{\text{Nitric acid.}}}{2HNO_3} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{6HCl} = \underset{\substack{\text{Chloronitric}\\\text{gas.}}}{N_2O_2Cl_4?} + \underset{\substack{\text{Water.}}}{4H_2O} + \underset{\substack{\text{Chlorine.}}}{Cl_2}$$

In the later stages of the reaction, the decomposition expressed in the following equation also probably occurs:—

$$\underset{\substack{\text{Nitric acid.}}}{HNO_3} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{3HCl} = \underset{\substack{\text{Chloronitrous}\\\text{gas.}}}{NOCl} + \underset{\substack{\text{Water.}}}{2H_2O} + \underset{\substack{\text{Chlorine.}}}{Cl_2}$$

The same reaction occurs if the acids are mixed after dilution, but is not complete for a week or a fortnight (Tilden). The undiluted mixture of acids is known as *aqua regia*, so called from its property of dissolving gold, "the king" of metals.

This "diluted nitrohydrochloric acid" is quite strong enough to attack organic matter, with evolution of nitrous gases, hence should not be dispensed with tinctures, etc. without further dilution.

Analytical Reactions (Tests).

First Analytical Reaction.—To a solution of any nitrate (*e. g.*, KNO_3) add sulphuric acid, and then copper turnings, and warm; colorless nitric oxide gas (NO) is evolved, which at once unites with the oxygen in the tube, giving *red fumes* of nitric peroxide or peroxide of nitrogen (NO_2).

$$2KNO_3 + 5H_2SO_4 + Cu_3 = 2NO + 3CuSO_4 + 4H_2O + 2KHSO_4;$$
$$\text{then,} \quad 2NO + O_2 = 2NO_2.$$
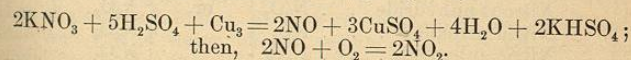
Performed on a larger scale, in a vessel to which a delivery-tube is attached, the reaction of nitric acid on copper becomes of synthetical interest, being the process for the preparation of nitric oxide gas for the purposes of chemical experiment.

Small amounts of a nitrate may be overlooked by this test, the color of the red fumes not being very intense.

Undiluted nitric acid poured on to copper turnings gives dense red vapors of *nitrous acid* (HNO_2), *nitrous anhydride* (N_2O_3), *nitric peroxide* (NO_2), *nitric oxide* (NO), and even *nitrogen* (N_2), the re-

action varying somewhat according to the temperature of the mixture and (Ackworth) the amount of nitrate of copper in solution. Diluted nitric acid gives nitric oxide, $Cu_3 + 8HNO_3 = 3(Cu2NO + 4H_2O + 2NO$.

Second Analytical Reaction.—To a cold solution of the nitrate, even if very dilute, add three or four crystals of sulphate of iron, shake gently for a minute in order that some of the sulphate may become dissolved, and then pour eight or ten drops of strong sulphuric acid down the side of the test-tube, so that it may form a layer at the bottom of the vessel ; a reddish-purple or black coloration will appear between the acid and the supernatant liquid.

This is a very delicate test for the presence of nitrates. The black color is due to a solution or, perhaps, combination of nitric oxide with a portion of the ferrous salt. The nitric oxide is liberated from the nitrate by the reducing action of the hydrogen of the sulphuric acid, the sulphuric radical of which is absorbed by the ferrous sulphate, the latter salt becoming ferric sulphate.

$$2HNO_3 + 3H_2SO_4 + 6FeSO_4 = 4H_2O + 3(Fe_23SO_4) + 2NO.$$
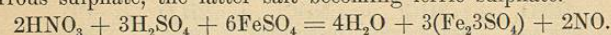
The process of oxidation is one frequently employed in experimental chemistry ; and nitrates, from their richness in oxygen, but more especially because always at hand, are the oxidizers usually selected for the purpose. In the operation they generally split up in one way, namely, into oxide of their basylous radical, nitric oxide gas, and available oxygen. Thus hydrogen nitrate (nitric acid) yields oxide of hydrogen (water) and the other bodies mentioned, as shown in the following equation :—

$$4HNO_3 = 2H_2O + 4NO + 3O_2.$$
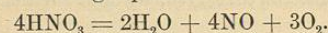
When nitrates, other than nitric acid, are used for the purpose of oxidation, a stronger acid, generally sulphuric, is commonly added in order that nitric acid may be formed ; the hydrogen nitrate splitting up more readily than other nitrates.

The five oxides of nitrogen have now been mentioned, namely—

Nitrous oxide	N_2O		N_2O
Nitric oxide*	NO		N_2O_2
Nitrous anhydride	N_2O_3	or	N_2O_3
Nitric peroxide*	NO_2		N_2O_4
Nitric anhydride	N_2O_5		N_2O_5

Nitrous oxide is a colorless gas not altered by exposure to air ; nitric oxide is also colorless, but gives red fumes in the air ; nitrous anhydride is a red vapor condensible to a blue liquid ; nitric peroxide is a red vapor condensible to an orange liquid ; nitric anhydride is a colorless crystalline solid. The two anhydrides by absorbing water yield respectively nitrous acid (HNO_2) and nitric acid (HNO_3).

---

* The specific gravities of these gases indicate that NO and NO_2 are the correct formulæ, and not N_2O_2 and N_2O_4.

Nitrous oxide is also probably an anhydride, the acid of which would doubtless have the formula HNO, while the silver and sodium salts certainly have the formulæ AgNO and NaNO,3H$_2$O (Divers ; Menke). The above series of compounds forms a good illustration of the doctrine of multiple proportions (p. 51).

Third Analytical Reaction.—Direct the blowpipe-flame on to charcoal until a spot is red hot ; now place on the spot a fragment of nitrate ; deflagration ensues.

This reaction does not distinguish nitrates from chlorates. It is insufficient for the recognition of very small quantities of either class of salts, especially when they are mixed with other substances.

Gunpowder is an intimate mechanical mixture of 75 parts of nitre, 15 to $12\frac{1}{2}$ parts of charcoal, and 10 to $12\frac{1}{2}$ parts of sulphur. In burning it may be said to give sulphide of potassium (the white smoke), (K_2S), nitrogen (N), carbonic oxide (CO), and carbonic acid (CO_2) gases, though the decomposition is seldom complete. The sudden production of a large quantity of heated gas from a small quantity of a cold solid is sufficient to account for all the effects of gunpowder.

Fourth Analytical Reaction.—To nitric acid or other nitrate add solution of " sulphate of indigo ; " the color is discharged.

Test-Solution of Indigo. U. S. P. (Sulphindylic or Sulphindigotic acid), is made by digesting 1 part of dry, finely powdered indigo in 12 parts of strong sulphuric acid in a test-tube for an hour, the mixture being kept hot by a water-bath ; the blue liquid is then poured into 500 parts of sulphuric acid, the whole well shaken, set aside, and the clear liquid decanted. Free chlorine also destroys the color of this reagent.

Indigo, U. S. P. (C_8H_5NO), is a blue coloring-matter deposited when infusion of various species of *Indigofera* is exposed to air and slight warmth. Under these circumstances *indican*, a yellow transparent amorphous substance, soluble in water, breaks up into indigo, which is insoluble and falls as a sediment, and a sort of sugar termed *indiglucin.* The indigo is collected, drained, pressed, and dried. By action of deoxidizing agents indigo is converted into soluble colorless *indigogen, reduced indigo* or *white indigo* (C_8H_6NO) ; 1 part of powdered indigo, 3 of green sulphate of iron, 3 of slaked lime, and 200 of water, shaken together and set aside in a well-closed bottle, give this colorless indigo. A piece of yarn, calico, or similar fabric dipped into such a solution, and exposed to air, becomes dyed blue, deposition of insoluble indigo-blue occurring within the cells and vessels of the fibre. This operation is readily performed on the small scale, and forms a good illustration of the characteristic feature of the art of dyeing, namely, the introduction of soluble coloring-matter into a fabric by permeation of the walls of its cellular and vascular tissue, and the imprisonment of that coloring-matter by conversion into a solid and insoluble form (*vide* also p. 138).

Pure indigo, or *indigotin*, may be obtained in beautiful needles by

13

spreading a paste of indigo and plaster of Paris on a tin plate, and when *quite* dry placing a lamp underneath, moving the latter from place to place as the indigo sublimes and condenses on the surface of the plaster. It may also be obtained in crystals by gently boiling finely-powdered indigo with aniline, filtering while hot, and setting aside; these crystals may be washed with alcohol. Hot paraffin may be employed instead of aniline. It is possible to obtain indigotin artificially; indeed, Baeyer states that indigo can be made economically from toluene.

Distinction between Nitric Acid and other Nitrates.—Presence of the nitric radical in a solution having been proved by the above reactions, its occurrence as the nitrate of a metal is demonstrated by the neutral, or nearly neutral, deportment of the liquid with test-paper and the detection of the metal, its occurrence as nitric acid by the sourness of the liquor to the taste and the effervescence produced on the addition of a carbonate.

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

QUESTIONS AND EXERCISES.

444. Trace the origin of nitrates.
445. In what does cubic nitre differ, chemically, from prismatic nitre?
446. Describe a process by which nitrate of potassium may be obtained artificially.
447. State the difference between nitrate of potassium, nitre, salt-petre, and sal prunella.
448. What group of elements is characteristic of all nitrates? and what claim has this group to the title of radical?
449. Mention the usual theory regarding the manner in which atoms are arranged with reference to each other in such salts as nitrate of potassium.
450. How is Nitric Acid prepared?
451. Give the properties of nitric acid.
452. What reactions occur when strong nitric and hydrochloric acids are mixed?
453. How is nitric oxide prepared?
454. Enumerate and explain the tests for nitrates.
455. Into what substances does nitric acid usually split when employed as an oxidizing agent?
456. How is nitrous oxide prepared?
457. Enumerate the five oxides of nitrogen.
458. What is the nature of gunpowder?
459. Write a few sentences on the chemistry of indigo, one of the tests for nitric acid.
460. How is nitric acid distinguished from other nitrates?
461. What quantity of cubic nitre will be required to produce ten carboys of official nitric acid, each containing 114 pounds?—*Ans.* 1076⅔ pounds.

CHLORIC ACID AND OTHER CHLORATES.

Formula of Chloric Acid $HClO_3$.   Molecular weight 84.4.
Chlorates are made from hypochlorites.

### Hypochlorous Acid ($HClO$) and other Hypochlorites.

Place a few grains of red oxide of mercury in a test-tube, half fill the tube with chlorine-water, and well shake the mixture; the resulting liquid is a solution of hypochlorous acid, mercuric oxychloride remaining undissolved:

$$2HgO + 2Cl_2 + H_2O = HClO + Hg_2OCl_2.$$
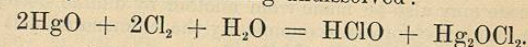
By the metathesis (double decomposition) of hypochlorous acid and oxides or hydrates, other pure hypochlorites are formed:—

$$HClO + NaHO = NaClO + H_2O.$$
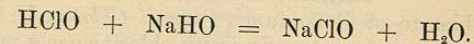
The direct action of chlorine on metallic hydrates and some carbonates is supposed to give a mixture of chloride and hypochlorite, as described in connection with the synthetical reactions of Calcium (p. 111, *Calx Chlorata*, U. S. P.)

$$Cl_2 + 2NaHO = NaCl,NaClO + H_2O;$$
$$2Cl_2 + 2CaH_2O_2 = CaCl_2,Ca2ClO + 2H_2O.$$
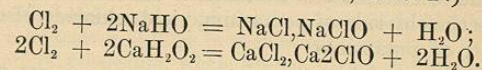
The condition of chlorides in these bodies is not satisfactorily made out; so that their constitution is not definitely determined. The action of acids on them results in the evolution of chlorine; hence the great value of the calcium compound (chlorinated lime, or chloride of lime) in bleaching operations:—

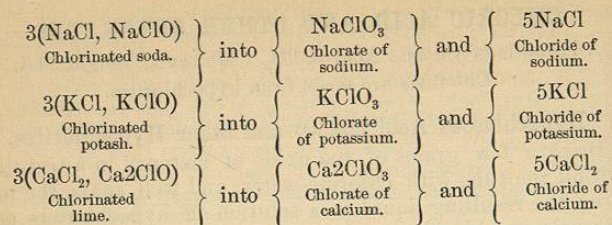$$CaCl_2,Ca2ClO + 2H_2SO_4 = 2Cl_2 + 2CaSO_4 + 2H_2O.$$

The solubility of hypochlorites in water, their peculiar odor, greatly intensified on the addition of acid, and their bleaching powers (see the above Calcium reaction) are the characters on which to rely in searching for hypochlorites.

Chlorates.

The group of elementary atoms represented by the formula ClO_3 is that characteristic of chloric acid and all other chlorates; hence it is expedient to regard it as being an acidulous radical, which may be termed the chloric radical. Like the nitric radical, it has not been isolated. Chloric anhydride (Cl_2O_5), unlike nitric anhydride, has not yet been obtained in the free condition.
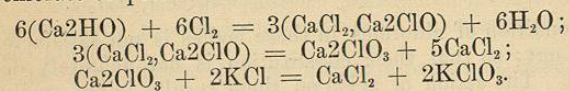
Chlorates are artificial salts. They are formed by simply boiling aqueous solution of the common bleaching salts (chlorinated lime, chlorinated soda, chlorinated potash). Heat thus converts

$$3(NaCl, NaClO) \begin{Bmatrix} \end{Bmatrix} \text{into} \begin{Bmatrix} NaClO_3 \\ \text{Chlorate of sodium.} \end{Bmatrix} \text{and} \begin{Bmatrix} 5NaCl \\ \text{Chloride of sodium.} \end{Bmatrix}$$

$$\text{Chlorinated soda.}$$

$$3(KCl, KClO) \begin{Bmatrix} \end{Bmatrix} \text{into} \begin{Bmatrix} KClO_3 \\ \text{Chlorate of potassium.} \end{Bmatrix} \text{and} \begin{Bmatrix} 5KCl \\ \text{Chloride of potassium.} \end{Bmatrix}$$

$$\text{Chlorinated potash.}$$

$$3(CaCl_2, Ca2ClO) \begin{Bmatrix} \end{Bmatrix} \text{into} \begin{Bmatrix} Ca2ClO_3 \\ \text{Chlorate of calcium.} \end{Bmatrix} \text{and} \begin{Bmatrix} 5CaCl_2 \\ \text{Chloride of calcium.} \end{Bmatrix}$$

$$\text{Chlorinated lime.}$$

One chlorate may also be made from another by double decomposition. In making chlorates economically the chlorinated salt is, of course, at once converted into chlorate.
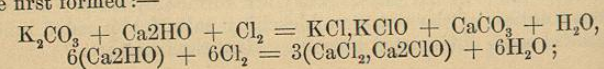
Chlorate of Potassium.

Thus Chlorate of Potassium (*Potassii Chloras*, U. S. P.) is commercially made by saturating with chlorine gas a moistened mixture of three parts of chloride of potassium and ten of slaked lime, and well boiling the product. Chlorinated lime is first formed; this, on continued boiling with water, splits up into chloride of calcium and chlorate of calcium, and the latter, reacting on the chloride of potassium, yields chloride of calcium and chlorate of potassium.

$$6(Ca2HO) + 6Cl_2 = 3(CaCl_2, Ca2ClO) + 6H_2O;$$
$$3(CaCl_2, Ca2ClO) = Ca2ClO_3 + 5CaCl_2;$$
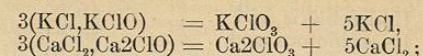$$Ca2ClO_3 + 2KCl = CaCl_2 + 2KClO_3.$$

This operation may be conducted on a small scale by rubbing together in a mortar the above proportions of ingredients in ounces or half ounces, adding enough water to make the whole assume the character of damp lumps, placing the porous mass in a funnel (loosely plugged with stones or pieces of glass), and passing chlorine gas (p. 27) through the mass by attaching the tube delivering the gas to the neck of the funnel. When the whole mass has become of a slight pink tint (due to a trace of permanganate), it should be turned into a dish, *well* boiled with water, filtered, the filtrate evaporated if necessary, and set aside; the chlorate of potassium crystallizes out in colorless rhomboidal plates, chloride of calcium remaining in the mother-liquor.

In the official process carbonate of potassium is alluded to as being used in place of the chloride; but otherwise the method is similar to that just described. Chlorinated potash and chlorinated lime are first formed :—
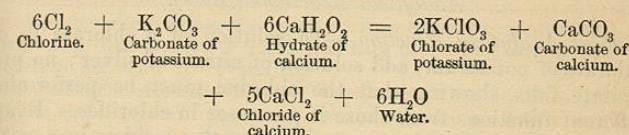
$$K_2CO_3 + Ca2HO + Cl_2 = KCl, KClO + CaCO_3 + H_2O,$$
$$6(Ca2HO) + 6Cl_2 = 3(CaCl_2, Ca2ClO) + 6H_2O;$$

these, on boiling with water, split up into chlorates and chlorides—

$$3(KCl, KClO) = KClO_3 + 5KCl,$$
$$3(CaCl_2, Ca2ClO) = Ca2ClO_3 + 5CaCl_2;$$

the whole of the chloride of potassium and chlorate of calcium finally yielding chlorate of potassium and chloride of calcium—

$$2KCl + Ca2ClO_3 = CaCl_2 + 2KClO_3.$$
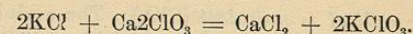
Neglecting intermediate decomposition, the reactions may be represented by the following equation :

$$6Cl_2 + K_2CO_3 + 6CaH_2O_2 = 2KClO_3 + CaCO_3$$
$$\text{Chlorine.} \quad \text{Carbonate of potassium.} \quad \text{Hydrate of calcium.} \quad \text{Chlorate of potassium.} \quad \text{Carbonate of calcium.}$$
$$+ 5CaCl_2 + 6H_2O.$$
$$\text{Chloride of calcium.} \quad \text{Water.}$$

Chlorate of Sodium (*Sodii Chloras*, U.S.P.), $NaClO_3$, is similarly prepared.

Chlorate of potassium is soluble in water to the extent of 6 or 7 parts in 100 at common temperatures. It must on no account be rubbed with sulphur or sulphides in a mortar or otherwise, friction of such a mixture resulting in violent explosion.

Chlorate of potassium, when heated, yields chloride of potassium and oxygen, and is the salt commonly employed in the preparation of the gas for experimental purposes. But if the action be carried on at as low a temperature as possible, and be arrested when 100 parts of the chlorate have (Teed) yielded 7.84 parts of oxygen, the residual salt will be found to contain only perchlorate of potassium ($KClO_4$), and chloride $10KClO_3 = 6KClO_4 + 4KCl + 3O_2$; a higher temperature causes decomposition of the perchlorate, $KClO_4 = KCl + 2O_2$. When the chlorate is heated with peroxide of manganese, no perchlorate is formed.

Perchloric Acid ($HClO_4$).—Crude perchlorate of potassium, obtained as just indicated, is boiled (in a fume-cupboard) with hydrochloric acid to decompose any chlorate that may be remaining, and then separated from chloride by washing and crystallization, chloride being far more soluble in water than the perchlorate. Perchloric acid is then obtained by distilling the perchlorate of potassium with sulphuric acid; it is quite stable, and is occasionally administered in medicine.

Chloric Acid ($HClO_3$) may be isolated, but is unstable, quickly decomposing into chlorine, oxygen, and perchloric acid; some other chlorate (*e. g.*, $KClO_3$) must therefore be used in studying the reactions of the chloric radical.

Table of the Chlorine Acids.

Hydrochloric acid . . . . HCl.
Hypochlorous acid . . . . HClO.
Chlorous acid . . . . . HClO$_2$.
Chloric acid . . . . . HClO$_3$.
Perchloric acid . . . . . HClO$_4$.

The chloric radical is univalent (ClO$_3$). The acidulous radicals of the other chlorine acids are also univalent, as indicated in the foregoing formulæ.

Analytical Reactions (Tests).

First Analytical Reaction.—To solution of a chlorate (*e. g.*, chlorate of potassium) add solution of nitrate of silver; no precipitate falls, showing that the chlorine must be performing different functions from those it possesses in chlorides. Evaporate the solution to dryness, and place the residue in a small dry test-tube, or at once drop a fragment of a chlorate into a test-tube, and heat strongly; oxygen is evolved, and may be recognized by its power of re-inflaming an incandescent match inserted in the tube. Boil the residue with water, and again add solution of nitrate of silver; a white precipitate falls, having all the characters of chloride of silver, as described under Hydrochloric Acid.

This is a trustworthy test, and, even omitting the recognition of the oxygen, may be applied in the detection of small quantities of chlorates.

Second Analytical Reaction.—To a fragment of a chlorate add two or three drops of strong sulphuric acid; an explosive gas (Cl$_2$O$_4$) is evolved, somewhat resembling chlorine in odor, but possessing a deeper color than that element.

$$3KClO_3 + H_2SO_4 = Cl_2O_4 + KClO_4 + K_2SO_4 + H_2O.$$
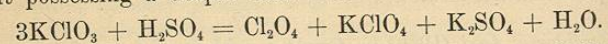
Warm the upper part of the test-tube to 150° or 200° F., or introduce a hot wire; a sharp explosion ensues, due to decomposition of the gas, peroxide of chlorine, into its elements.

Third Analytical Reaction.—Heat a small fragment of a chlorate with hydrochloric acid: a yellowish-green explosive gas termed *euchlorine* is evolved. Its color is deeper than that of chlorine, hence the name (from εὖ, *eu*, well, and χλωρός, *chlōros*, green). In odor it resembles chlorine, and is probably a mixture of that element with one of the oxides of chlorine.

Fourth Analytical Reaction.—Direct the blowpipe-flame on to charcoal until a spot is red hot, and then place on the spot a fragment of a chlorate; deflagration ensues as with nitrates.

Bromates.

Bromates are salts closely resembling chlorates and iodates. The formula of Bromic Acid is HBrO$_3$. The presence of bromates in bromides is shown by the production of a yellow color on addition of diluted sulphuric acid, $5KBr + KBrO_3 + 3H_2SO_4 = 3K_2SO_4 + 3H_2O + 3Br_2$.
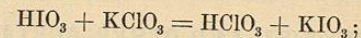
Iodates.

Iodic Acid (HIO$_3$).—Iodine is boiled in a flask with five times its weight of the strongest nitric acid (sp. gr. 1.5), in a fume-cupboard, until all action ceases. On cooling, iodic acid separates in small pyramidal crystals. These are removed, the residual liquid evaporated to dryness to remove excess of nitric acid, the residue and the first crop dissolved in a small quantity of boiling water, and the solution set aside to crystallize.

Iodate of Potassium (KIO$_3$).—Powder together equal weights of iodine and chlorate of potassium; to the mixture add twice its weight of water and about one-eighth of its weight of nitric acid; warm the whole until iodine disappears, and evaporate quite to dryness over a water-bath. The residue dissolved in water forms the reagent "Solution of Iodate of Potassium." It contains a little nitrate of potassium.

In this reaction the small quantity of nitric acid furnishes corresponding amounts of nitrate of potassium and chloric acid. The chloric acid with iodine gives iodic acid and chlorine, thus:—

$$2HClO_3 + I_2 = 2HIO_3 + Cl_2.$$
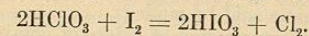
The iodic acid and some chlorate of potassium then yield chloric acid and iodate of potassium—

$$HIO_3 + KClO_3 = HClO_3 + KIO_3;$$

and the two reactions alternate until the whole of the iodine has displaced the whole of the chlorine.

Iodate of potassium and sulphurous acid decompose each other with elimination of iodine (or with formation of a blue color, if starch be present.) Sulphurous acid occurring as an impurity in acetic and other acids may thus be detected.

$$2KIO_3 + 5H_2SO_3 = I_2 + 3H_2SO_4 + 2KHSO_4 + H_2O.$$
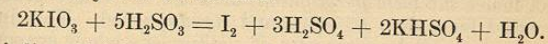
If iodic acid solution be mixed with mucilage of starch, and solution of sulphuretted hydrogen be added, a blue zone is formed at the junction of the liquids.

Ferric iodate, or rather *Oxyiodate* (Fe$_2$O4IO$_3$,8H$_2$O), is precipitated on adding solution of ferric chloride to solution of iodate of potassium.

QUESTIONS AND EXERCISES.

462. How may hypochlorous acid be formed?
463. What are the relations of hypochlorous acid to common bleaching-powder?