## Order II.—CHLORINE, AND ITS COMBINATIONS WITH OXYGEN.

### CHLORIN'IUM.—CHLORINE.

History, Synonymes, and Etymology.—This gas was discovered by Scheele in 1774, who termed it *dephlogisticated muriatic acid*. Berthollet, in 1785, named it *oxygenated muriatic acid*. Sir H. Davy called it *chlorine* (from χλωρος, *green*,) on account of its colour.

Natural History.—It is found in both kingdoms of nature.

α. In the Inorganized Kingdom it exists principally in combination with sodium, either dissolved in the water of the ocean or forming deposites of rock salt. Chlorine also occurs in combination with magnesium, calcium, lead, silver, &c. Free hydrochloric acid is met with in the neighbourhood of volcanoes, and is probably produced by the decomposition of some chloride.

β. In the Organized Kingdom it is found, in combination, in both animals and vegetables. Sprengel (De Candolle, *Physiol. Vég.* tom. i. p. 220.) says, maritime plants exhale chlorine, principally during the night. Hydrochloric acid in the free state, exists, according to Dr. Prout, in the stomach of animals during the process of digestion.

Preparation.—There are several methods of procuring chlorine gas:—

1. *By adding Diluted Sulphuric Acid to a mixture of Common Salt and Binoxide of Manganese.*—This is the cheapest and most usual method of preparing it. Mix intimately three parts of dried common salt with one part of the binoxide of manganese, and introduce the mixture into a retort. Then add as much sulphuric acid, previously mixed with its own weight of water, as will form a mixture of the consistence of cream. (Brande directs 8 salt, 3 manganese, 4 water, and 5 acid;—Thenard, 1½ salt, 1 manganese, 2 acid, and 2 water;—Graham; 8 salt, 6 manganese, and dilute acid as much as contains 13 parts of oil of vitriol.)

On the application of a gentle heat, the gas is copiously evolved, and may be collected over either warm or cold water.[1]

In this process two equivalents or 80 parts of sulphuric acid react on one equivalent or 44 parts of the binoxide, and on one equivalent or 60 parts of chloride of sodium, and yield one equivalent or 36 parts of chlorine, one equivalent or 76 parts of the sulphate of the protoxide of manganese, and one equivalent or 72 parts of the sulphate of soda.

| MATERIALS. | | COMPOSITION. | | PRODUCTS. | |
|---|---|---|---|---|---|
| 1 eq. Chloride Sodium | 60 | 1 eq. *Chlorine* | 36 | 1 eq. Chlorine | 36 |
| | | 1 eq. *Sodium* | 24 | 1 eq. *Soda* 32 | |
| 1 eq. Binoxide Manganese | 44 | 1 eq. *Oxygen* | 8 | | |
| | | 1 eq. *Protoxide Mang.* | 36 | | |
| 2 eq. Sulphuric Acid | 80 | 1 eq. *Sulphuric Acid* | 40 | 1 eq. Sulphate Soda | 72 |
| | | 1 eq. *Sulphuric Acid* | 40 | 1 eq. Protosulphate Manganese | 76 |
| | 184 | | 184 | | 184 |

2. *By heating a mixture of equal weights of common Hydrochloric Acid and Binoxide of Manganese in a glass retort over a lamp.*

In this process two equivalents or 74 parts of hydrochloric acid react on one equivalent or 44 parts of the binoxide, and yield one equivalent or 36 parts of chlorine, two equivalents or 18 parts of water, and one equivalent or 64 parts of protochloride of manganese.

| MATERIALS. | | COMPOSITION. | | PRODUCTS. | |
|---|---|---|---|---|---|
| 2 eq. Hydrochl. Acid | 74 | 1 eq. *Chlorine* | 36 | 1 eq. Chlorine | 36 |
| | | 1 eq. *Chlorine* | 36 | | |
| | | 2 eq. *Hydrog.* | 2 | 2 eq. Water | 18 |
| 1 eq. Binox. Mang. | 44 | 2 eq. *Oxygen* | 16 | | |
| | | 1 eq. *Mangan.* | 28 | 1 eq. Protochlo. Mang. | 64 |
| | 118 | | 118 | | 118 |

[1] For further information respecting the commercial mode of preparing chlorine, see *Hypochlorite of Lime*.

3. *By the action of Hydrochloric Acid on Chloride [Hypochlorite] of Lime.*—This method may be resorted to when binoxide of manganese cannot be procured. The products of the reaction of the ingredients are, chlorine, water, and chloride of calcium.

Properties.—Chlorine, at ordinary temperatures and pressures, is a gaseous substance, having a yellowish-green colour, a pungent, suffocating odour, and an astringent taste. 100 cubic inches weigh, according to Dr. Thomson, 77·8615 grs.; and its sp. gr., therefore, is 2·5 [2·47, Berzelius.] Its equivalent by weight is 36 (See Mr. Phillip's experiments in the *Philosophical Transactions*, for 1839.) [35·47 Berz.; 35·42 Turner] by volume 1; hydrogen being unity. It is not combustible, but is a supporter of combustion. Phosphorus and powdered antimony take fire spontaneously when introduced into it; and a taper burns in it, with the evolution of a red light and much smoke. When water is present it destroys vegetable colours, organic odours, and infectious matters.

1 eq. Chlorine = 36

By a pressure of 4 atmospheres, at the temperature of 60° F., chlorine is a yellow liquid, having a sp. gr. of 1·33 (water being 1·).

*Characteristics.*—The colour, odour, and bleaching property of chlorine readily distinguish it from other gases. It forms a white, curdy precipitate (*chloride of silver*) with the nitrate of silver: this precipitate blackens by exposure to light, from the escape of a little chlorine, and the formation of a subchloride of silver; (Wetzlar, in Landgrebe's *Versuch über das Licht*, p. 53, 1834.) is insoluble in nitric acid, cold or boiling; readily dissolves in liquid ammonia; when heated in a glass tube fuses, and, on cooling, concretes into a gray, semi-transparent mass (*horn silver*, or *luna cornea;*) and, lastly, when heated with Potash, it yields metallic silver, and a chloride of potassium. An aqueous solution of chlorine dissolves leaf-gold. The soluble *chlorides* react, as free chlorine, on the solution of nitrate of silver. They evolve hydrochloric acid (which also reacts on a solution of silver) when heated with liquid sulphuric acid. If a watery solution of a chloride, coloured blue by sulphate of indigo, be submitted to the action of a galvanic battery, the chlorine is evolved at the anode or positive pole, and destroys the colour of the sulphate of indigo in its immediate neighbourhood.

The *chlorates* when heated evolve oxygen, and are converted into chlorides. When mixed with strong sulphuric acid they become orange-red, and give out chlorous acid. They do not precipitate the salts of silver.

The *hyperchlorates* evolve oxygen, and are converted into chlorides when heated. They do not become red, or give out chlorous acid by the action of sulphuric acid. The soluble hyperchlorates precipitate the salts of potash.

Physiological Effects. *α. On Vegetables.*—The germination of seeds has been said to be promoted by watering them with a weak solution of chlorine; (De Candolle, *Physiologie Végétale*, t. ii. p. 632.) but the statement is, probably, erroneous.

*β. On Animals generally.*—Nysten (*Recherches*, p. 140.) injected a small quantity of chlorine gas into the jugular vein of a dog, and the only effect was howling. A larger quantity occasioned difficult respiration, apparently great agony, and death in three minutes. The body was opened four minutes afterwards: the blood was fluid and venous in the auricles and ventricles, which contained neither gas nor coagula. On another occasion he threw this gas into the pleura, and thereby produced inflammation of this membrane, and death. From these experiments, Nysten (*Op. cit.* p. 143.) concludes that it is a local irritant, but has no specific effect on any part of the system.

*γ. On Man.*—Chlorine gas acts as a *local* irritant. Mr. Wallace,[1] tells us, that diluted with air, or aqueous vapour, of 116° F., and applied to the skin, it produces peculiar sensations, similar to those caused by the bite or sting of insects: this effect is accompanied with copious perspiration, and a determination of blood

[1] *Researches respecting the Medical Powers of Chlorine, particularly in Diseases of the Liver.* Lond. 1822.

to the skin, sometimes attended with an eruption of minute papulæ, or even vesicles. Applied to the skin in a pure form, its action is similar, but more energetic.

If an attempt be made to inspire undiluted chlorine gas, it produces spasm of the glottis. If the gas be mixed with air, it enters into the bronchial ramifications, causes a sensation of tightness and suffocation, and violent cough. Twice I have suffered most severely from the accidental inhalation of it; and each time it gave me the sensation of constriction of the air-tubes, such as might be produced by a spasmodic condition of the muscular fibres of the bronchial tubes. The attack usually goes off in increased secretion from the mucous membrane. When diluted with a large quantity of air, chlorine may be inhaled without exciting cough: it occasions a sensation of warmth in the respiratory passages, and promotes expectoration.

The irritating effects of chlorine are less powerful on those accustomed to inhale it; as I have repeatedly seen in patients who were using the gas, and which is also proved by the following statement, made by Dr. Christison:—(*Treatise on Poisons*, p. 736.) "I have been told (says he,) by a chemical manufacturer at Belfast, that his workmen can work with impunity in an atmosphere of chlorine, where he himself could not remain above a few minutes."

The constitutional or *remote* effect caused by inhalations of chlorine, is increased frequency of the pulse and of respiration. But this effect may be in part owing to the augmented muscular efforts of the patient. Mr. Wallace states, that the application of chlorine to the skin also occasions soreness of the mouth, fauces, and œsophagus, increased vascularity, and even minute ulcerations of these parts, and an alteration in the quantity and quality of the salivary and biliary secretions. He thinks that it has a tranquillizing, and at the same time exciting, power, with respect to the nervous system. It would appear, from the observations of Professor Albers, (*British and Foreign Med. Review*, vol. iv. p. 212.) that, though the topical action of chlorine is stimulating, yet the remote action is antiphlogistic; for it diminished the frequency of the pulse, calmed excitement, and produced effects which may be termed antiphlogistic. Dr. Christison tells us, that at the Belfast manufactory above alluded to, the chief consequences of exposure to an atmosphere of chlorine, are acidity and other stomach complaints, which the men generally correct by taking chalk. Absorption of fat is also an effect observed in the manufactories at Glasgow, Manchester, and Belfast.[1]

When applied to the skin or bronchial membrane, chlorine gas, probably, becomes absorbed; for Mr. Wallace found that the urine acquired bleaching properties under its use.

Uses.—α. *As a fumigating agent, disinfectant, and antiseptic*, chlorine, I believe, stands unrivalled. Hallé, in 1785, appears to have been the first person who employed it as a disinfectant; but we are greatly indebted to Guyton-Morveau for the zeal and energy he manifested in his attempts to introduce it into use. For destroying miasmata, noxious effluvia, and putrid odours, it is the most powerful agent known; and is, therefore, well adapted for disinfecting prisons, ships, hospitals, dissecting-rooms, and all other places, the air of which requires purification. The best method of fumigating a large building is that adopted by Dr. Faraday, at the General Penitentiary at Milbank. (*Quarterly Journal of Science and the Arts*, vol. xviii. p. 92.) One part of common salt was intimately mixed with one part of the black or binoxide of manganese; then placed in a shallow earthen pan, and two parts of oil of vitriol, previously diluted with two parts by measure of water, poured over it, and the whole stirred with a stick. Chlorine continued to be liberated from this mixture for four days.

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[1] *An Experimental Essay on the relative Physiological and Medicinal Properties of Iodine and its Compounds.* By C. Cogswell, A. B., M. D. Edinb. 1837, p. 82.

The quantities of the ingredients consumed were 700 lbs. of common salt, 700 lbs. of binoxide of manganese, and 1400 lbs. of sulphuric acid. The disinfecting power of chlorine is supposed to depend on its affinity for hydrogen, by which it effects the decomposition of water or aqueous vapour, with the hydrogen of which it unites, while the nascent oxygen oxidizes the organic matter: or it may act merely by abstracting hydrogen from the putrid miasmata. Chlorine fumigations should be plentifully employed on board of ships off the Western coast of Africa, to prevent the deleterious effects of the miasm, which, according to Professor Daniell, is sulphuretted hydrogen.[1]

β. *As an antidote in poisoning by hydrocyanic acid, sulphuretted hydrogen, or hydrosulphate of ammonia*, chlorine gas is a very valuable agent. I believe, however, that chloride of lime will be found a more convenient, safe, and opportune substance. The beneficial influence of chlorine in the treatment of animals asphyxiated by sulphuretted hydrogen, doubtless arises in part at least from its chemical properties; for when mixed with sulphuretted hydrogen, it forms chloride of sulphur and hydrochloric acid. The best method of applying the remedy is to diffuse a little chlorine in the air, and then to effect artificial respiration.

γ. *Inhaled in chronic pulmonary diseases* it is sometimes a useful remedy. I have carefully watched its effects in phthisis and chronic bronchitis; and the result of my observation is, that chlorine is rarely serviceable. Frequently, after the first and second inhalations, the patients fancy their breathing much relieved, but the amendment is seldom permanent. I need hardly say it has no pretensions to the cure of tubercular phthisis; but it may be useful as a palliative (sometimes diminishing the sweating;) and I can readily believe that occasionally in ulceration of the lungs it may be, as Albers (*British and Foreign Medical Review*, vol. iv. p. 212.) declares it is, of essential service. This would agree with the effects observed, in surgical practice, of solutions of chlorine and of the hypochlorites on old ulcers.

I have before described the mode of administering the gas. (See p. 159.) Either the aqueous solution of chlorine, or a small portion of the chloride of lime, may be placed into the inhaling bottle: if the latter be not sufficiently strong, a few drops of muriatic acid are to be added, to develope free chlorine.

δ. *In diseases of the liver*, not attended with active inflammation, Mr. Wallace has successfully employed gaseous chlorine, either in the pure state or diluted with air or aqueous vapour. The benefit of chlorine in these cases has been confirmed by others. The temperature of the bath, and the time the patient ought to remain in it, will vary in different instances; but Mr. Wallace thinks, that, in the greater number, 150° F. will be found to answer best, and the proper time about half an hour. The benefit obtained is in part referrible to the heat employed, in part to the irritant effect of the chlorine on the skin, and (according to Mr. Wallace,) in part to the specific influence of chlorine on the liver. (For a sketch of the apparatus used, see *Lancet*, vol. i. for 1831–32, p. 859.) Ziese, an apothecary at Altona, has also employed chlorine baths in these cases with advantage.

Antidotes.—The inhalation of ammoniacal gas, of the vapour of warm water, of the spirit of wine, or of ether, has been recommended, to relieve the effects of chlorine. I tried them all when suffering myself, but without the least apparent benefit. In a case related by Kastner, and which is reported in Wibmer's work, (*Die Wirkung der Arzneim, u. Gifte.* 2er Bd. S. 109. München, 1832.) sulphuretted hydrogen gave great relief. If this agent be employed, it must be done cautiously, as it is itself a powerful poison.

**AQUA CHLORINII**, Ph. Dub. *Chlorinei Aqua*, Ph. Ed.—*Solutio Chlorinii; Chlorine Water; Aqua Oxymuriatica; Liquor Chlori; Liquid Oxymuriatic Acid.*—This is readily prepared by passing chlorine gas (prepared as above di-

[1] See p. 83.—Also *Lond. Edinb. and Dub. Philosophical Magazine*, for July 1841; and *Lond. Med. Gaz.* for July 16th and 23d, 1841.

rected) through water placed in a Woulfe's bottle. The gas may be generated in a clean Florence flask, to which a curved tube is adapted by means of a cork. The receiving vessel holding the water, may be, in the absence of a double-necked bottle, a six- or eight-ounce phial; or a wide-mouthed bottle closed by a cork having two perforations, through one of which passes a glass tube open at the top, and dipping into the water beneath; while through the other passes the end of the tube conveying the gas from the flask into the water.

In the *Dublin Pharmacopœia* the proportions of ingredients used are, Dried Muriate of Soda, 100 parts; Oxide of Manganese, 30 parts; Sulphuric Acid, 87 parts; Water, 124 parts. The gas is to be gradually evolved from this mixture, contained in a retort, and transmitted through 200 parts of Distilled Water.

In the *Edinburgh Pharmacopœia* the process is somewhat different. Muriate of Soda, 60 grs., and Red Oxide of Lead, 350 grs., are to be triturated together; then put into f℥viij. of Water, contained in a bottle with a glass stopper; afterwards the Acid added, and the mixture agitated until all the Red Oxide becomes white. The insoluble matter is to be allowed to subside before using the liquid. In this process, Chlorine and Sulphate of Soda are formed in solution, and White Sulphate of the Protoxide of Lead is precipitated. The sodium of the common salt is oxidized by the nascent oxygen evolved by the red lead, in consequence of the action of the sulphuric acid on it. This process has been contrived to obviate the necessity of having to pass the gas through water, the apparatus for which operation might not be at hand.

In the *Pharmacopœia Nosocomii Middlesexensis*, Lond. 1841, is the following formula for a solution of chlorine:—℞. Potassæ Chloratis ℥ij. Acidi Hydrochlorici, Aquæ destillatæ, ää. f℥ij. Misce. ℞. Hujus Solutionis f℥iij. Aquæ destillatæ f℥xij. Misce.—This solution contains besides chlorine, some chloride of potassium.

Properties.—At the temperature of 60° F. and when the mercury in the barometer is standing at 30 inches, water takes up about twice its bulk of chlorine gas (Gay-Lussac.) The solution has a greenish yellow colour, the strong and peculiar odour of the gas, and an astringent taste. Its sp. gr. is 1·003. It bleaches vegetable colours—as tincture of litmus, turmeric, &c. By exposure to light, the water is decomposed, the oxygen is evolved, while the hydrogen unites with the chlorine to form muriatic acid. Hence, the solution should be kept in bottles excluded from the light. Prepared according to the Edinburgh Pharmacopœia, the liquid holds in solution a little sulphate of soda, and deposites a white insoluble sulphate of lead.

*Characteristics.*—Its odour, its action on a solution of nitrate of silver (as before described for chlorine gas,) its power of dissolving leaf-gold, and its bleaching properties, readily distinguish this solution. It destroys the blue colour of iodide of starch and of sulphate of indigo. A piece of silver plunged into it is immediately blackened.

Physiological Effects.—In a concentrated form, the aqueous solution of chlorine acts as a corrosive poison. Somewhat diluted it ceases to be a caustic, but is a powerful local irritant. Administered in proper doses, and sufficiently diluted, it operates as a tonic and stimulant. The continued use of it causes salivation. Applied to dead organic matter it operates as an antiseptic and disinfectant.

Uses.—Chlorine water has been employed in medicine both as an external and internal remedy.

*α. Externally.*—It has been used, in the concentrated form, as a caustic application to wounds caused by rabid animals; diluted, it has been employed as a wash in skin diseases (itch and porrigo;) as a gargle in putrid sore-throat; as a local bath in liver diseases; and as an application to cancerous and other ulcers attended with a fetid discharge. In the latter cases I have repeatedly employed it with advantage, though I give the preference to a solution of the chloride [hypochlorite] of soda.

*β. Internally.*—It has been administered in those diseases denominated putrid; for example, in the worst forms of typhus, in scarlet fever, and in malignant

sore throat. It has also been employed in venereal maladies, and in diseases of the liver.

Dose.—The dose of this solution varies with the degree of concentration. I have frequently allowed patients to drink, *ad libitum*, water, to which some of this solution has been added. If made according to the directions of the Dublin Pharmacopœia, the dose is from one to two drachms, properly diluted.

Antidotes.—According to Devergie, (*Médecine Légale*, t. ii. p. 634. Paris, 1836.) the antidote for poisoning by a solution of chlorine is albumen. The white of egg, mixed with water or milk (the caseum of which is as effective as the albumen of the egg,) is to be given in large quantities. The compound, which albumen forms with chlorine, has little or no action on the animal economy, and may be readily expelled from the stomach. In the absence of eggs or milk, flour might be exhibited; or, if this cannot be procured, magnesia or chalk. The gastro-enteritic symptoms are, of course, to be combated in the usual way.

### COMPOUNDS OF CHLORIDE AND OXYGEN.

None of these are used in medicine. The concentrated aqueous solutions of all of them are oxidizing agents, and act on the organic tissues as caustics. Their remote effects are probably similar to the acids generally and chlorine. *Hypochlorous* (Cl. + O) and *Chlorous* (Cl. + 4O) *Acids* are bleaching agents: to the first, the substances called Chloride of Lime and Chloride of Soda owe their disinfecting properties. *Chloric Acid* (Cl. + 5O) has great analogy with nitric acid; combined with potash it constitutes Chlorate of Potash. *Perchloric Acid* (Cl. + 7O) is an excellent test for potash.

## Order III.—IODINE, AND ITS COMBINATIONS WITH OXYGEN AND CHLORINE.

IODIN'IUM, *L. D.*—IODINE.

(Iodineum, *E.*) (Iodinum, U. S.)

General History.—Iodine was discovered in 1811 by M. Courtois, a saltpetre manufacturer at Paris. It was first described by Clement in 1813, but was afterwards more fully investigated by Davy and Gay-Lussac. It was named *iodine*, from ἰώδης, *violet-coloured;* on account of the colour of its vapour.

Natural History.—It exists in both kingdoms of nature.[1]

*α.* In the inorganized kingdom.—Vauquelin met with iodide of silver in a mineral brought from Mexico, and Mentzel found Iodine in an ore of zinc which contained cadmium. It has also been met with in an ore of lead. (*Journ. de Pharmacie*, tom. xxiii. for 1837, p. 29.) It is said to have been found in coals. (*Lond. and Edinb. Philosoph. Mag.* for Nov. 1839.) In sea-water it has likewise been discovered, where it probably exists as an iodide of sodium or of magnesium. Many mineral waters contain it. It was detected by Mr. Copeland (*Edinburgh New Philosophical Journal*, vol. i. p. 159.) in the carbonated chalybeate of Bonnington. About one grain of iodine was found by Dr. Daubeny (*Phil. Trans.* 1830, Part 2, p. 223.) in ten gallons of the water of Robin's Well at Leamington, in Warwickshire. In the old well at Cheltenham the quantity was not more than one grain in sixty gallons. In a brine-spring at Nantwich, in Cheshire, there was about a grain of iodine in twelve gallons. In the sulphurous water of Castel Nuovo d'Asti, iodine was discovered by Cantu. In some of the mineral waters of Germany, Bavaria, and South America, it has also been detected.[2] Fuchs found it in the rock-salt of the Tyrol. (Gmelin, *Handbuch der Chemie*, Bd. i. S. 350.)

*β.* In the organized kingdom.—Of Animals containing iodine I may mention the genera *Spongia*, *Gorgonia*, *Doris*, *Venus*, &c.: likewise *Sepia*, the envelopes of the eggs of which contain it. An insect has been found near Ascoli, in Italy, which Savi has described under the name of *Julus fœtidissimus*, containing iodine. The animal emits, when disturbed, a

[1] Since the publication of the first edition of this work, I have met with S. E. Sarphati's *Commentatio de Iodio*, Lugduni, 1835, which contains the most extensive list of natural bodies containing iodine, of any work with which I am acquainted.

[2] Gairdner, *Essay on the Natural History, Origin, Composition, and Medicinal Effects of Mineral and Thermal Springs*, p. 27, Edinb. 1832.