Sub-Chapter III

HALOGEN OR SULPHUR COMPOUNDS OF NON-METALS

GENERAL

This sub-Chapter covers products which, although known by names (chlorides, sulphides, etc.) similar to those of the metal salts of hydracids classified in sub-Chapter V, are actually **non-metal** combinations such as :

(1) A halogen with a non-metal other than oxygen or hydrogen **(halogen compounds**).

(2) The same compounds as under (1) above, combined with oxygen (**halide oxides**).

or (3) Sulphur with a non-metal other than oxygen or hydrogen (**sulphur compounds**).

Sulphide oxides of non-metals (sulphur + oxygen + non-metal) are **excluded** from this sub-Chapter; they fall in **heading 28.53**.

Halides, halide oxides, and sulphides of metals (see the General Explanatory Note to sub-Chapter I) or of the ammonium ion (NH_4^+) fall in sub-Chapter V except in the case of compounds of precious metals (**heading 28.43**) and the compounds of **heading 28.44**, **28.45, 28.46** or **28.52**.

28.12 - Halides and halide oxides of non-metals.

2812.10 - Chlorides and chloride oxides

2812.90 - Other

(A) CHLORIDES OF NON-METALS

The most important of these binary compounds are :

(1) **Iodine chlorides**.

(a) **Iodine chloride** (ICl) results from direct action of chlorine on iodine. Dark brown liquid above 27 ºC; below that temperature, reddish crystals. Specific gravity about 3. Decomposed by water; it burns the skin badly. Used in organic synthesis as an iodinating agent.

(b) **Iodine trichloride** (ICl_3). Obtained by the same process as the monochloride, or from hydriodic acid. Yellow needles soluble in water. Specific gravity about 3. Used for the same purposes as the monochloride and also in medicine.

(2) **Sulphur chlorides**.

(a) **Disulphur dichloride** (S_2Cl_2). Obtained by the action of chlorine on sulphur. This is the commercial sulphur chloride, a yellow or reddish liquid, giving off fumes of a suffocating odour when exposed to air; decomposed by water. Specific gravity about 1.7. A solvent for sulphur, it is used in the cold vulcanisation of rubber or of gutta-percha.

(b) **Sulphur dichloride** (SCl_2). Prepared from monochloride. Reddish-brown liquid, also decomposed by water; rather unstable. Specific gravity about 1.6. Uses include : the cold vulcanisation of rubber, as a chlorinating agent in the manufacture of synthetic dyes (in particular thioindigo).

(3) **Phosphorus chlorides**.

(a) **Phosphorus trichloride** (PCl_3). Obtained by the direct action of chlorine on phosphorus. Colourless liquid, specific gravity about 1.6; corrosive, with an irritating odour, lachrymatory. Fumes in a humid atmosphere and decomposes on contact with water. Mainly used as a chlorinating agent in organic synthesis (e.g., manufacture of acid chlorides, dyes, etc.); also used in the manufacture of ceramics to produce a lustrous effect.

(b) **Phosphorus pentachloride** (PCl_5). Obtained from trichloride in the form of white or yellowish crystals. Specific gravity about 3.6. Like the trichloride, it fumes in a humid atmosphere; decomposes on contact with water and is lachrymatory. Used in organic chemistry as a chlorinating agent or a catalyst (e.g., to prepare isatin chloride).

Phosphonium chloride (PH_4Cl) is **excluded** (**heading 28.53**).

(4) **Arsenic chlorides**.

Arsenic trichloride ($AsCl_3$). Obtained by the action of chlorine on arsenic or of hydrochloric acid on arsenic trioxide. Colourless liquid of oily appearance. Fumes in moist air; very toxic.

(5) **Silicon chlorides**.

Silicon tetrachloride ($SiCl_4$). Obtained by the action of chlorine gas on a mixture of silica and coal, or on silicon, silicon bronze or ferro-silicon. Colourless liquid, specific gravity of about 1.5. Liberates suffocating white fumes (hydrogen chloride (HCl)) in the presence of atmospheric moisture. Decomposes in water with formation of gelatinous silica and liberation of HCl fumes. Used for preparing silica and very pure silicon, silicones and smoke screens.

Substitution products of hydrogen silicides, such as trichlorosilane ($SiHCl_3$) are **excluded** (**heading 28.53**).

The heading **does not include** carbon tetrachloride (tetrachloromethane) (CCl_4) hexachloroethane (carbon hexachloride) (C_2Cl_6), hexachlorobenzene (ISO) (C_6Cl_6), octachloronaphthalene ($C_{10}Cl_8$) and similar carbon chlorides; these are chlorinated derivatives of hydrocarbons (**heading 29.03**).

(B) **CHLORIDE OXIDES OF NON-METALS**

These ternary combinations include, *inter alia* :

(1) **Sulphur chloride oxides.**

(a) **Sulphur dichloride oxide** (sulphinyl chloride, thionyl chloride) ($SOCl_2$). Obtained by the oxidation of sulphur dichloride with either sulphur trioxide or sulphuryl chloride. Colourless liquid; specific gravity about 1.7. Gives off suffocating vapours; decomposed by water. Used in the manufacture of organic chlorides.

(b) **Sulphur dichloride dioxide** (sulphonyl chloride, sulphuryl chloride) (" dichloro-sulphonic acid ") (SO_2Cl_2). Obtained by the action of chlorine on sulphur dioxide either on exposure to sunlight or in the presence of a catalyst (camphor or activated carbon). Colourless liquid, specific gravity about 1.7. Fumes in the air; decomposed by water; corrosive. Used as a chlorinating and sulphonating agent in organic synthesis, e.g., in the manufacture of acid chlorides.

The heading **excludes** chlorosulphuric acid (" sulphuric chlorohydrin ") ($ClSO_2.OH$) (**heading 28.06**).

(2) **Selenium dichloride oxide.**

Selenium dichloride oxide, generally called " selenyl chloride " ($SeOCl_2$) is similar to thionyl chloride. Produced by the action of selenium tetrachloride on selenium dioxide. Above 10 ºC it is a yellow liquid, fuming in the air; below that temperature it forms colourless crystals; specific gravity is about 2.4. Decomposed by water. Used in organic synthesis or for decarbonising the cylinders of internal combustion engines.

(3) **Nitrosyl chloride** (nitrogen chloride oxide) (NOCl).

Orange yellow gas with a suffocating smell; toxic; used as an oxidising agent.

(4) **Phosphorus trichloride oxide** (phosphoryl chloride) ($POCl_3$).

Obtained from phosphorus trichloride treated with potassium chlorate, from phosphorus pentachloride treated with boric acid, or by the action of carbonyl chloride on tricalcium phosphate. Colourless liquid, specific gravity about 1.7. It has an irritating odour, fumes in a humid atmosphere and is decomposed by water. Used as a chlorinating agent in organic synthesis and also in the manufacture of acetic anhydride or chlorosulphonic acid.

(5) **Carbon chloride oxide** (carbonyl chloride, phosgene) ($COCl_2$).

Produced by the action of chlorine on carbon monoxide in the presence of animal black or charcoal, or by the action of oleum on carbon tetrachloride. Colourless product, liquid up to 8 °C and gaseous above that temperature; it is presented liquefied or under pressure in heavy steel containers. When dissolved in toluene or benzene, it is classified in **heading 38.24**.

A lachrymatory and very toxic product. It is a chlorinating agent, widely used in organic synthesis (e.g., in the manufacture of acid chlorides, amino derivatives, Michler's ketone and of intermediates in the organic dyestuff industry).

(C) OTHER HALIDES AND HALIDE OXIDES OF NON-METALS

This group includes all other halides of non-metals (fluorides, bromides and iodides).

(1) **Fluorides.**

(a) **Iodine pentafluoride** (IF_5), a fuming liquid.

(b) **Phosphorus fluorides and silicon fluorides**.

(c) **Boron trifluoride** (BF_3). Obtained by heating natural calcium fluoride and powdered boric oxide in the presence of sulphuric acid. Colourless gas. Fumes in moist air; carbonises organic products. Highly absorbent of water forming fluoroboric acid. Used as a dehydrating agent and as a catalyst in organic synthesis. It forms complex compounds with organic compounds (e.g., diethyl ether, acetic acid or phenol); these compounds, which are also used as catalysts, fall in **heading 29.42**.

(2) **Bromides**.

(a) **Iodine bromide** (monobromide) (IBr). Prepared by combining the constituent elements. Blackish-red crystalline mass, resembling iodine. Soluble in water. Used in organic synthesis.

(b) **Phosphorus bromides**.

Phosphorus tribromide (PBr_3). Obtained by the action of bromine on phosphorus dissolved in carbon disulphide. Colourless liquid. Fumes in moist air; decomposes in water. Specific gravity about 2.8. Used in organic synthesis.

The heading **excludes** phosphonium bromide (PH_4Br) (**heading 28.53**) and carbon bromides (**heading 29.03**).

(3) **Iodides**.

(a) **Phosphorus iodides.**

Phosphorus di-iodide (P_2I_4). Results from the action of iodine on phosphorus dissolved in carbon disulphide. Orange-coloured crystals, giving off coloured vapour.

Phosphorus tri-iodide (PI_3). Obtained by a similar method; crystallises into dark red tablets.

Phosphonium iodide (PH_4I) falls in **heading 28.53**.

(b) **Arsenic iodides.**

Arsenic tri-iodide (AsI_3). Red crystals; obtained from the constituent elements. Toxic and volatile. Used in medicine or as a reagent in laboratories.

(c) **Combinations of iodine with other halogens**. See paragraphs A (1), C (1) (a), C (2) (a) above.

(4) **Halide oxides other than chloride oxides**.

(a) **Fluoride oxides**, e.g., phosphorus trifluoride oxide (phosphoryl fluoride) (POF_3).

(b) **Bromide oxides**, e.g., sulphur dibromide oxide (thionyl bromide) ($SOBr_2$), an orange-coloured liquid, and phosphorus tribromide oxide (phosphoryl bromide) ($POBr_3$) in lamellar crystals.

(c) **Iodide oxides**.