

into a swollen, metal-grey compound of sulphide of cadmium with a small quantity of orpiment, which forms a deep-yellow powder. (Berzelius, *Pogg.* 7, 146.)

B. SULPHARSENATE OF CADMIUM.—Aqueous sulpharsenate of sodium gives a light yellow precipitate with cadmic salts. (Berzelius, *Pogg.* 7, 88.)

CADMIUM AND ANTIMONY.

SULPHANTIMONIATE OF CADMIUM.—The solution of Schlippe's salt gives a light orange-yellow precipitate with cadmic salts, if the former be in excess; but if the cadmic salt is in excess, the precipitate is darker in colour and becomes red-brown after remaining for some time immersed in the liquid. (Rammelsberg, *Pogg.* 52, 236.)

CADMIUM AND TELLURIUM.

SULPHOTELLURITE OF CADMIUM.—Analogous to the cerium-compound (IV. 425).

OTHER COMPOUNDS OF CADMIUM.

With Copper, Mercury, and Platinum.

CHAPTER XXX.

T I N .

Proust. *J. Phys.* 51, 173; also *Scher. J.* 8, 481.—*J. Phys.* 61, 338; also *N. Gchl.* 1, 249; also *Gilb.* 25, 440.

Berzelius. *Schw.* 6, 284.—Further: *Ann. Chim. Phys.* 5, 141; also *N. Tr.* 2, 2, 359.

J. Davy. *Schw.* 10, 321.

Gay-Lussac. *Ann. Chim. Phys.* 1, 40.

SYNONYMES: *Etain, Zinn, Stannum, Jupiter.*

History. Tin was known in the metallic state as early as the time of Moses; it was imported by the Phœnicians from Spain and England. Bichloride of tin was discovered in the sixteenth century by Libavius. The preparation of Mosaic gold was taught by Kunkel. The chief contributions to our knowledge of the compounds of tin have been made by Pelletier, Proust, J. Davy, and Berzelius.

Sources. Most frequently, as binoxide, in Tin-stone; rarely with sulphur and copper, in Tin-pyrites. In very small quantities, as binoxide, in the Seidschütz water, and in many meteoric stones (Berzelius); in Manganesian Epidote and native peroxide of manganese (*Braunstein*) from Piedmont, and in all Scandinavian Epidotes. (Sobrero.)

Preparation on the large scale. Tin-stone is broken up—roasted to drive off the sulphur and arsenic of the ores that are mixed with it, and convert the other metals into light oxides easily separated from the heavier tin-stone by washing—and then fused in contact with charcoal, either in smelting furnaces or in reverberatory furnaces, sometimes with the addition of a calcareous flux.—*Purification on the large scale.*—1. By gentle heating, whereby the purer tin fuses and runs off, while the more refractory alloys of tin and the foreign metals remain unmelted.—2. By fusion, with imperfect access of air, whereby the foreign metals, together with a portion of the tin, are oxidized first.—The purest varieties of tin are *Malacca* and *Banca tin* and *English Grain-tin*; then follows *Common English Grain-tin*; then *English Block-tin* and *Saxon* and *Bohemian Mine-tin* (*Bergzinn*); then *Tin-refuse* and *Tin-scum* (*Abgangs-und Abstrich-zinn*). The impurities consist of arsenic, antimony, bismuth, zinc, lead, iron and copper; they remain for the most part in the form of a black powder, on dissolving the tin in hydrochloric acid. The greater part of the arsenic is, however, evolved in the form of arseniuretted hydrogen gas, and may be detected by Marsh's process. Stüremberg (*Ann. Pharm.* 29, 216) found arsenic in all commercial tin, and likewise in tin-foil and tin-plate; a sample of Banca tin and likewise of English grain-tin were, however, found to be free from arsenic. Chevallier (*J. Chim. Méd.* 16, 250) likewise obtained arseniuretted hydrogen gas on dissolving Banca tin which was said to be free from arsenic and did not deposit any black powder when dissolved.—*Purification on the small scale.*—This is effected by oxidizing tin-filings with excess of nitric acid, washing the resulting binoxide with hydrochloric acid and water, and reducing it in a closed charcoal crucible at a low white heat. If pure water be used in the washing, the stannic oxide retains oxide of copper.

Properties. Crystalline system the square prismatic. When a feeble current from a Daniell's battery (I. 421) is passed through aqueous hydrochlorate of stannous oxide, the positive pole being formed of a plate of tin, the negative polar wire becomes covered, in the course of four days, with perfect crystals belonging to the square prismatic system. *Fig. 39*, without the *p* face, but having the four *a*-faces and likewise eight acumination-faces resting upon *e* and *a*. Macle-crystals are of frequent occurrence. (Miller, *Phil. Mag. J.* 22, 263.) Mather (*Sill. Ann. J.* 27, 254) likewise obtained right-angled four-sided crystals of metallic tin, upon a piece of the metal immersed in a solution of the protochloride. Brooke obtained eight-sided needles by slowly cooling melted tin, and pouring off the portion which remained liquid. Pajot, on the other hand (*J. Phys.* 38, 52), obtained rhombic tables by this process; and Breithaupt (*Schw.* 52, 171) saw tin from a Cornwall tin-furnace crystallized in short, regular, six-sided prisms. These crystals were regarded by Miller as CuSn^2 . Frankenheim (*Pogg.* 40, 456) concludes, from the angles of the dendrites in the tin-tree, that the crystals belong to the regular system.—Specific gravity of tin-crystals = 7.178, and after fusion and solidification, 7.293 (Miller); of tin solidified from fusion, 7.291 (Brisson), 7.2911 (Kupffer), 7.2905 (Karsten); of rolled tin, 7.299 (Brisson). Softer than gold, harder than lead; fracture indented. Decrepitates when bent. This crackling of tin (*Geshrei des Zinns*) is produced by the displacement of the crystals of which it is made up. Tin cannot be drawn out into fine wire, but may be beaten out into thin plates (*Tin-foil*). Bluish-white, with a strong lustre. Melts at 222.5°.

(G. A. Erman), at 238° (Crichton), at 230° (Kupffer), at 267° (Morveau), and contracts slightly in cooling (Marx). Boils at a white heat. The disagreeable odour ascribed to tin does not properly belong to the metal itself, but is solely due to its action on animal substances, the fingers for example, with which it comes in contact.—Nitric acid of moderate strength attacks tin with violence, but without dissolving it, and converts it into a white powder. Tin may also be easily distinguished from other metals by its behaviour with a solution of gold containing excess of hydrochloric acid; a bright surface of tin immersed in such a solution, is blackened without evolution of gas; zinc turns black and liberates gas; lead does not blacken. (Friedemann, *Repert.* 77, 224.)

Compounds of Tin.

TIN AND OXYGEN.

A. STANNOUS OXIDE. SnO.

Protoxide of Tin, Zinnoxidul, Oxyde Stanneux.

Formation. Tin slowly decomposes water mixed with hydrochloric acid, sulphuric acid, or potash, and dissolves in these substances in the form of stannous oxide. The hydrogen which is evolved contains arsenic, if that metal is present in the tin. The aqueous solutions of sal-ammoniac, common salt, bisulphate of potash, alum, cream of tartar and borax-tartar likewise dissolve small quantities of tin when heated, and form solutions of stannous oxide; tin is also dissolved, though in very small quantity, by the aqueous solutions of nitrate of soda, monotartrate of potash, and Rochelle salt. Solutions of carbonate of potash, sulphate of soda, chloride of barium or calcium, sulphate of magnesia, and tartrate of potash and ammonia do not retain tin in solution, but in contact with air produce a deposition of stannic oxide. Nitre, borax, and diphosphate of soda have no action upon tin. (Lindes, *Berl. Jahrb.* 32, 2, 99; Cludius, *J. pr. Chem.* 9, 161.)

Preparation. 1. Stannous oxide is precipitated in the form of hydrate from its solution in hydrochloric acid by the addition of carbonate of potash in excess—the hydrate quickly washed with thoroughly boiled water, and as much as possible out of contact of air—then dried at a temperature not exceeding 80°—and lastly freed from water by heating it in a retort completely filled with it, and having the air replaced by hydrogen or carbonic acid gas. (Berzelius.)—2. Hydrochlorate of stannous oxide is treated with excess of ammonia, and the precipitated hydrate of stannous oxide boiled quickly for awhile to convert it into the anhydrous oxide, which is then quickly washed and dried. (Gay-Lussac.)—3. Aqueous hydrochloric acid is saturated with tin; the solution evaporated in contact with a piece of metallic tin, till a residue of fused protochloride of tin is left; the metal then taken out; 1 At. of the chloride of tin (94.4 parts) mixed in a mortar with 1 At. (143.2 parts) or more of crystallized carbonate of soda; the fluid mixture heated in a basin—with constant stirring—till it has become black through and through; the chloride of sodium, after cooling, extracted with boiling water; the stannous oxide washed with boiling water on the filter, and

lastly dried at a gentle heat. (Sandall, *Phil. Mag. J.* 12, 216; also *J. pr. Chem.* 14, 254.) This is a very advantageous mode of preparation. (Böttger, *Ann. Pharm.* 29, 87.)

Properties. Black powder, of specific gravity 6.666; brown-greenish-grey when pounded. (Berzelius.) Olive-green. (Gay-Lussac.) Bluish-black or slate-grey. (Sandall.) When hydrate of stannous oxide is boiled with a quantity of potash not sufficient to dissolve it, the undissolved portion is converted into small, hard, shining, black crystals of anhydrous stannic oxide, which, when heated to 200°, decrepitate, swell up, and fall to pieces, and are converted into the olive-green protoxide like that obtained by Gay-Lussac. On evaporating a very dilute solution of sal-ammoniac in which hydrated protoxide of tin is diffused, that compound is converted, as soon as the sal-ammoniac crystallizes, into the anhydrous protoxide, having the form of a cinnabar-coloured powder, which, by friction with a hard body, is immediately converted into the greenish-brown binoxide. There are therefore three modifications of stannous oxide: crystallized, olive-green, and red. (Fremy, *Compt. rend.* 15, 1107; also *N. J. Pharm.* 3, 28.)—† Roth (*Ann. Pharm.* 60, 214) obtains the red modification by thoroughly washing the white hydrate of stannous oxide and digesting it at a temperature of 56° with a solution of that oxide in acetic acid, the acid being slightly in excess and the solution having a specific gravity of 1.06. The stannous oxide is then converted into heavy, hard, crystalline grains which yield a greenish-brown powder by trituration; they take fire when heated, and soon blacken by exposure to sunshine. With chemical re-agents, they behave like stannous oxide. †

| | Berzelius. | J. Davy. | Gay-Lussac. | Proust. |
|----------|------------|----------|-------------|---------|
| Sn | 59 | 88.06 | 88.028 | 88.01 |
| O..... | 8 | 11.94 | 11.972 | 11.99 |
| SnO..... | 67 | 100.00 | 100.000 | 100.000 |

(SnO = 735.29 + 100 = 835.29. Berzelius.)

Decompositions. Reduced to the metallic state, by charcoal at a strong red heat; by potassium at a moderate heat, and with combustion. By sulphur it is converted into sulphide of tin, with evolution of sulphurous acid; and by boiling with a small quantity of potash-ley, into metallic tin and stannic acid, the latter dissolving in the potash.

Combinations. a. With Water.—HYDRATE OF STANNOUS OXIDE. When a solution of protochloride of tin is mixed with excess of carbonate of potash, or with excess of ammonia, the hydrated protoxide is precipitated in the form of a brilliant white powder, containing, according to Proust, 5 per cent. of water, which, according to Berzelius, it gives up when gently heated, or even when boiled with water.—† According to Schaffner, the precipitate formed by ammonia is not the hydrate, but a basic salt. The composition of the hydrate is 2SnO, HO. ¶

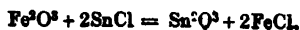
b. With Acids, forming the SALTS OF STANNOUS OXIDE OR STANNOUS SALTS.—*Protosalts of Tin.*—These salts are obtained by dissolving metallic tin, the protoxide, or its hydrate—which is more easily soluble—in acids. Most of them are either colourless or yellowish, redden litmus, and have a very disagreeable metallic taste. They rapidly abstract oxygen from the air and other oxygen compounds, and are thereby converted into stannic salts; hence they give a purple or brown

precipitate with chloride of gold, &c. [For a more detailed description of this, vid. *Protochloride of Tin*.] Those which contain a volatile acid, give it off at a red heat, and, if the air has access to them, are converted into stannic oxide. With carbonate of soda upon charcoal in the inner blowpipe-flame, they yield globules of metallic tin.—Zinc and cadmium immersed in the aqueous solutions of these salts precipitate the tin in an arborescent form: *the Tin-tree, Arbor Jovis*. Acetate of stannous oxide, however, is not reduced by tin or cadmium. Iron reduces the tin from the hydrochlorate and acetate, provided the iron is made to dip into water in which is likewise immersed a bladder containing the tin-solution, so that the latter may mix very slowly with the water by endosmose. Iron does not precipitate tin from the protochloride at a boiling heat. Lead, when first immersed, reduces a small quantity of tin in brilliant needles, but the action soon ceases. (Fischer, *Pogg.* 9, 263; 10, 603.) Hydrosulphuric acid gas and hydrosulphate of ammonia precipitate dark-brown hydrated protosulphide of tin. This precipitate dissolves in a large excess of hydrosulphate of ammonia—provided that compound likewise contains hydrosulphite of ammonia—and is precipitated from the solution by acids in the form of yellow bisulphide of tin. (H. Rose.)—Hydrosulphuric acid gives no precipitate in a solution containing less than 1 part of tin in 120,000 parts of water. (Pfaff.)—A solution of 1 part of crystallized hydrochlorate of stannous oxide in 100 parts of water, mixed with 15 parts of hydrochloric acid of specific gravity 1.168, is immediately precipitated by hydrosulphuric acid; with 25 parts of hydrochloric acid, not till after some time; with 40 parts of hydrochloric acid, not at all, but immediately on adding more water. (Reinsch. *J. pr. Chem.* 13, 132.)—Iodide of potassium gives a yellowish-white curdy precipitate, which, if the tin and iodine are in proper proportion and the solution duly concentrated, is soon converted into protiodide of tin. Ammonia, carbonate of ammonia, and carbonate of potash throw down the white hydrate of stannous oxide, insoluble in excess of these precipitants.—An excess of potash, on the contrary, re-dissolves the precipitated hydrate, forming a solution, which deposits metallic tin in the form of a black powder, slowly in the cold, rapidly when heated, stannate of potash being formed and remaining in solution.—Phosphate of soda throws down white phosphate of stannous oxide.—Oxalic acid throws down white oxalate of stannous oxide.—Croconate of potash gives an orange-yellow precipitate with stannous salts.—Succinic acid and the alkaline benzoates, according to Pfaff, give white precipitates to the ten-thousandth degree of dilution.—Tincture of galls produces, in solutions not containing a very great excess of acid, an abundance of light-yellow flakes.—Ferrocyanide and ferricyanide of potassium produce white precipitates soluble in hydrochloric acid.—Stannous salts which are insoluble in water, dissolve in hydrochloric acid—provided they have not been ignited—but not in sal-ammoniac.

c. With Potash and Soda.

Oxides of Tin, intermediate between Stannous and Stannic Oxide.

a. *Sesquioxide.* Sn^2O^3 .—1. Aqueous hydrochlorate of stannous oxide, somewhat in excess, is boiled with freshly precipitated hydrate of ferric oxide or hydrate of manganic oxide, and the precipitated sesquioxide of tin thoroughly washed. (Fuchs, *Kastn. Arch.* 23, 368.)—



The precipitate is frequently mixed with hydrated ferric oxide. (Berzelius.) The hydrated ferric oxide, even when recently precipitated, acts much less quickly in the cold than at a boiling heat; the dried hydrate requires continued boiling; finely pounded specular iron acts but very imperfectly at a boiling heat. Even when the hydrochlorate of stannous oxide contains no free acid, a small quantity of iron is dissolved at the beginning of the action, before the precipitation of the sesquioxide of tin takes place. If the hydrated ferric oxide be briskly boiled with excess of stannous hydrochlorate, the precipitate which forms at first is re-dissolved after a while, but appears again on the addition of water; under these circumstances, however, the sesquioxide of tin is contaminated with bibasic hydrochlorate of stannous oxide.—Pulverized Pyrolusite acts but very slowly, even on boiling; but if the liquid be boiled down nearly to dryness,—whereupon a large quantity of hydrochloric acid is evolved, but no chlorine—and the residue dissolved in water, sesquioxide of tin separates from the solution, mixed with pyrolusite. (Fuchs.)—2. Hydrochlorate of stannous oxide is mixed with hydrochlorate of ferric oxide, and as soon as the yellow-colour of the mixture has changed to greenish, the hydrated oxide is precipitated from it by adding carbonate of lime in excess, and applying a gentle heat. (Fuchs, *J. pr. Chem.* 5, 318.)—3. A solution of hydrochlorate of stannous oxide, saturated as far as possible with ammonia, is mixed in excess with the dark red solution of basic hydrochlorate of ferric oxide,—obtained by saturating aqueous hydrochlorate of ferric oxide with recently precipitated hydrate of ferric oxide, or by mixing the aqueous solution of the hydrochlorate of ferric oxide with as much ammonia as can be added to it without producing a permanent precipitate—and the mixture heated to 60° in a vessel completely filled with it. The liquid, which is dark brown at first, gradually loses its colour, and the hydrated sesquioxide of tin is precipitated free from iron. (Berzelius, *Pogg.* 28, 443.)—White, with a tinge of yellow. (Fuchs.) The precipitate, which is gummy and difficult to wash, dries up to a mass of yellow, translucent granules. The hydrate turns black when ignited out of contact of air. It dissolves completely in ammonia, and is therefore not a mere mixture of stannic and stannous oxides, inasmuch as the latter is insoluble in ammonia. (Berzelius.)—[Probably, however, it is a salt— SnO, SnO_2 , containing the soluble modification of stannic acid.]

b. Anomalous Stannate of Stannous Oxide.—When hydrated stannic oxide, obtained by treating tin with nitric acid, is digested in cold aqueous hydrochlorate of stannous oxide, it abstracts the whole of the stannous oxide, and is converted into an orange-yellow compound of anomalous stannic acid with stannous oxide. (Fremy, *N. J. Pharm.* 1, 344.) According to Fremy's statement, the composition of this substance is probably $\text{SnO}, 3\text{SnO}_2$.

B. STANNIC OXIDE. STANNIC ACID. SnO_2 .

Binoxide of Tin, Peroxide of Tin, Zinnoxid, Zinnsäure, Deutoxyde d'Etain, Oxyde stannique, Acide stannique.—Found native in the form of *Tin-stone* and *Wood-tin*.

Formation. Tin, when heated in the air to its boiling point, burns with a bright white flame, and is converted into stannic oxide: *Flowers of Tin, Zinnblumen, Flores Stanni s. Jovis*. When fused in the air, it

becomes covered with a grey film, and is converted into a grey mixture of metallic tin and stannic oxide—*Tin-ash*—which, by longer ignition, is converted into pure stannic oxide.—Tin immersed in water containing $\frac{1}{100}$ part of potash, becomes dull, and imparts a small quantity of stannic oxide to the liquid. (A. Vogel, *J. pr. Chem.* 14, 107.)—2. Stannic oxide is formed in the decomposition of aqueous vapour by red-hot tin. (Gay-Lussac, Regnault.)—3. By nitric acid tin is converted rapidly, and with violent evolution of heat, into hydrated stannic acid, nitrate of ammonia being at the same time produced. Proust states that the oxidation of melted tin by fuming nitric acid produces explosion.—4. With heated oil of vitriol tin produces sulphurous acid and stannic sulphate.—5. The deflagration of tin with nitre produces stannate of potash.—6. When tin is heated with mercuric oxide, stannic oxide and metallic mercury are formed.—7. Stannous oxide remains unaltered in dry air at ordinary temperatures; in damp air, it is converted, in the course of a year, into stannic oxide. (Proust.) When heated in the air, or when merely touched by a spark from the flint and steel, it burns like tinder, with great rapidity, and produces a small quantity of white smoke. Hydrated stannous oxide likewise burns in the flame of a candle, but less rapidly. (Berzelius.)—Hydrated stannous oxide placed in contact with carbonate of copper under water, liberates carbonic acid and forms a mixture of stannic oxide and crystalline laminae of copper. (Proust.)

Preparation. 1. By rapid or slow combustion of tin.—2. By precipitating the hydrate from hydrochlorate of stannic oxide by means of ammonia or carbonate of potash, and then washing and igniting.—3. By oxidating tin with nitric acid and igniting the hydrate after washing.—4. By heating 1 part of tin-filings in a retort with 4 parts of mercuric oxide. (Berzelius.)

Properties. Tin-stone belongs to the square prismatic system; Fig. 21, 29, 30, and other forms. $e:e' = 133^{\circ} 36' 18''$; $e:e'' = 67^{\circ} 42' 32''$. Cleavage parallel to e . (Haüy.)—Specific gravity 6.639 (Herapath), 6.96. (Mohs.) Harder than felspar; transparent, brownish-yellow. Often coloured black by ferric and manganic oxide.—The oxide prepared by method (1) is white; all the other artificial varieties are straw-yellow powders which redden litmus, and, when heated, acquire a transient orange-yellow and brown tint. Specific gravity of the artificial oxide—6.90 (Boullay); of that prepared by (3), 6.64 (Berzelius). Stannic oxide in all its forms is very refractory, and not volatile.

| | Proust. | | J. Davy. | | Thomson. | |
|------------------------|-------------|--------|------------|-------|-----------|--------|
| Sn | 59 | 78.67 | 78.1 | 78.4 | 78.34 | 78.38 |
| 2O | 16 | 21.33 | 21.9 | 21.6 | 21.66 | 21.62 |
| SnO ² | 75 | 100.00 | 100.0 | 100.0 | 100.00 | 100.00 |
| | Gay-Lussac. | | Berzelius. | | Klaproth. | |
| Sn | 78.6 | 78.62 | 79.5 | | | |
| 2O | 21.4 | 20.38 | 20.5 | | | |
| SnO ² | 100.0 | 100.00 | 100.0 | | | |

$$\text{SnO}^2 = 735.29 + 2 \cdot 100 = 935.29. \quad (\text{Berzelius.})$$

Decompositions. By potassium and sodium with the aid of gentle heat, stannic oxide is reduced to the metallic state, the reduction being attended with incandescence.—It is also reduced to the metallic state by

charcoal at a strong red heat (also before the blowpipe on charcoal, if carbonate of soda be added and the flame strongly urged); likewise by carbonic oxide gas (Despretz, *Ann. Chim. Phys.* 43, 222; Leplay & Laurent, *Ann. Chim. Phys.* 65, 404; Gmelin); also by a mixture of equal volumes of carbonic oxide and carbonic acid gases (Leplay & Laurent);—by the oxy-hydrogen blowpipe (Clark, Pfaff), and by a current of hydrogen gas at the temperature at which tin decomposes water (Despretz);—easily at a low red heat by cyanide of potassium, which is thereby converted into cyanate of potash. (Liebig).—By sulphur it is converted into bisulphide of tin, with evolution of sulphurous acid.

Combinations. Stannic acid exists—as discovered by Berzelius—in two isomeric states, and, accordingly, forms two series of compounds with water, acids, and bases. The hydrate obtained by the action of nitric acid upon tin contains the acid $a\text{SnO}^2$, which combines with the smaller quantity of base, and is, therefore, analogous to metaphosphoric acid:—*b*. The hydrate obtained by precipitating bichloride of tin with an alkaline carbonate contains the acid $b\text{SnO}^2$, which saturates three times as much base as the former, and is, therefore, analogous to ordinary phosphoric acid.—Berzelius calls the former of these modifications, *Oxydum stannicum*, and the latter *Oxydum parastannicum*; Fremy distinguishes the former as *Acide stannique*, and the latter as *Acide metastannique*. It would, however, be better to reverse these denominations, so as to make them agree with those of the modifications of phosphoric acid.*—For the present, the acid obtained by the action of nitric acid upon the metal may be distinguished by the epithet *Anomalous*.—¶ H. Rose is of opinion that there exist other modifications of stannic oxide besides those distinguished by Berzelius: in particular, he mentions *Tin-stone*, and the ignited oxide, with which the product obtained by heating stannic oxide to redness with alkaline carbonates, is probably identical. Rose is moreover inclined to regard the difference between the oxides *a* and *b* as due, not to any difference of saturating power which they may possess as acids, but to some other cause. (*Pogg.* 75, 1.) ¶

a. With Water. — *a. Anomalous Hydrate of Stannic Acid.*—Formed by completely oxidizing tin with moderately strong nitric acid, and washing the resulting white powder with water, till the liquid which runs through no longer reddens litmus-paper.—It is a white powder, which has a density of 4.933, and reddens litmus, even when thoroughly washed, although when ignited, it gives off nothing but pure water, without any nitric acid or nitrogen gas. (Berzelius.)—The hydrate dries up at 55°, in the form of colourless, translucent, friable lumps, having a conchoidal fracture. When dried at ordinary temperatures, it is white and opaque, with a silky lustre, and contains twice as much water as when dried at the higher temperature. (Thomson, *Ann. Phil.* 10, 149.)

| | | | | Berzelius. | Thomson. Dried at 55°. |
|---------------------------|----|-----|--------|------------|---------------------------|
| $a\text{SnO}^2$ | 75 | ... | 89.29 | 89 | 80.64 |
| HO..... | 9 | ... | 10.71 | 11 | 19.36 |
| HO, $a\text{SnO}^2$ | 84 | ... | 100.00 | 100 | 100.00 |

¶ According to Fremy (*N. Ann. Chim. Phys.* 23, 393), the anomalous hydrate of stannic acid [hydrate of metastannic acid] dried at ordinary temperatures in air free from moisture, consists of $\text{Sn}^2\text{O}^{10} + 10\text{HO}$; when

* In Fremy's later memoirs (c.g. *N. Ann. Chim. Phys.* 23, 393) this change is actually made.

dried in vacuo, it contains $\text{Sn}^{\circ}\text{O}^{10} + 5\text{HO}$; when kept for several hours at 130° , it is reduced to $\text{Sn}^{\circ}\text{O}^{10} + 4\text{HO}$; and at 160° it gives off another atom of water and becomes $\text{Sn}^{\circ}\text{O}^{10} + 3\text{HO}$. The most permanent of these hydrates is that which contains 5HO . [The composition per cent. of this hydrate is the same as that of the ordinary hydrate of stannic acid dried in vacuo, $\text{SnO}_2 \cdot \text{HO}$.] (*Comp. Schaffner, Ann. Pharm.* 56, 174.)—On dissolving any of the above-mentioned hydrates in caustic potash, and precipitating by an acid, a precipitate of stannic acid (*metastannic acid*) is obtained, insoluble in nitric acid, but soluble in ammonia. ¶

β. Ordinary Hydrate of Stannic Acid. 1. By precipitating hydrochlorate of stannic oxide with carbonate of lime, not in excess. The washed precipitate reddens litmus. (Fremy, *N. J. Pharm.* 1, 342; also *Pogg.* 55, 519). If carbonate of potash is used as the precipitant instead of carbonate of lime, the precipitate obtained consists of stannate of potash, which, under these circumstances, is insoluble in water. (Fremy.)—2. By precipitating with a caustic alkali and washing thoroughly. The gelatinous precipitate resembles pieces of glass when dry; it reddens moistened litmus-paper, and is slightly soluble in water. (Berzelius.)—The ordinary hydrate of stannic acid contains more water than the anomalous hydrate, and, when boiled in water, or dried for some time in vacuo over oil of vitriol at ordinary temperatures, gives off water, and is converted into the anomalous hydrate. (Graham, *Ann. Pharm.* 13, 146.) According to Fremy, also, this hydrate contains more water than the anomalous hydrate, and is converted into the latter by drying at a strong heat. [Fremy's later results have already been given, *vid. sup.*]

b. With Acids, forming the SALTS OF STANNIC OXIDE, or STANNIC SALTS.—The native oxide, and likewise the artificial oxide after ignition, are quite incapable of combining with acids. By ignition with excess of caustic or carbonated potash or soda, the oxide is rendered soluble in acids.

a. Anomalous Stannic Salts.—The anomalous hydrate of stannic acid does not dissolve in acids, but takes up some of them, *e. g.* sulphuric and hydrochloric acid, in small quantity. When the compound thus formed with sulphuric acid is digested in water, after the excess of acid has been removed by decantation, it gives up to the water the acid which it has taken up; the hydrochloric acid compound dissolves in water, but is precipitated from the solution by acids. (Berzelius.) [*vid. Anomalous Hydrochlorate of Stannic Oxide.*]—¶ The solutions obtained in the manner just described are decomposed by boiling, the stannic oxide being completely precipitated, and the more quickly in proportion as the quantity of free acid in the solution is less.—Caustic potash or soda added to the solution throws down a white precipitate of the hydrated oxide, soluble in a moderate excess of the re-agent, but re-precipitated on the addition of a larger quantity. The precipitate thus formed disappears on the addition of water; according to Weber, it contains, when dried at 100° , $\text{KO}, \text{Sn}^{\circ}\text{O}^{14} + 3\text{HO}$.—Ammonia gives a white precipitate insoluble in excess; the addition of tartaric acid does not prevent the precipitation.—Carbonate of potash also gives a white precipitate, insoluble in excess.—A solution of $a\text{SnO}_2$, in the smallest possible quantity of hydrochloric acid, gives no precipitate with phosphoric acid, but a copious white precipitate, in the course of 12 hours, with arsenic acid.—Nitrate of silver gives a white precipitate, from which ammonia dissolves out chloride of silver and leaves a residue of stannic oxide.—Tincture of galls gives,

after a few hours, a whitish-yellow precipitate.—Sulphuric acid, added to a solution of αSnO_2 in hydrochloric acid—even if the hydrochloric acid is in considerable excess—produces a copious precipitate, consisting of stannic oxide and sulphuric acid, the latter of which may be extracted by water. The precipitate, if heated with hydrochlorate or nitric acid, dissolves on the addition of water. The solution, when left to itself for a while, deposits a copious precipitate. ¶

β. Ordinary Stannic Salts. These salts are obtained : 1. By exposing stannous salts to the air, or treating them with chlorine, or heating them with nitric acid, care being taken not to use too much. Since 1 atom of stannous oxide requires but 1 atom of acid to form a normal salt, whereas 1 atom of stannic oxide requires 2 atoms of acid (II. 6), it follows that if a normal stannous salt is to be converted into a normal stannic salt by the action of the air or of nitric acid, it must first be mixed with a quantity of acid equal to that which it already contains ; in default of the requisite quantity of acid, a precipitate is formed during the oxidation, consisting either of hydrated stannic oxide or of a basic salt.—2. By dissolving the ordinary hydrate of stannic oxide in acids.—3. When any specimen of stannic oxide, natural or artificial—previously ignited with potash, and thereby rendered soluble—is treated with acids [a potash-salt is, however, formed at the same time].—Stannic salts are colourless or yellowish. Those which are soluble in water redden litmus strongly, and have a sour, metallic, and styptic taste. Those which contain a volatile acid readily give it off when ignited. Before the blowpipe they behave like stannous salts. When boiled with nitric acid, they deposit the anomalous hydrate of stannic oxide, or a salt of that base. According to H. Rose, the same result is produced on boiling a solution largely diluted with water.—Zinc and cadmium immersed in solutions of stannic salts, precipitate the tin in the dendritic form. Iron precipitates the tin only under the circumstances mentioned under the head of *stannous salts*; lead ceases to act as soon as it becomes covered with a coating of metallic tin. (Fischer.)—Hydrosulphuric acid throws down from these solutions, even when they contain excess of acid, a yellow precipitate of hydrated bisulphide of tin : the precipitate is formed immediately on boiling ; but at ordinary temperatures, and in dilute solutions, it takes some time to form. The same precipitate is formed by hydrosulphate of ammonia. It is soluble in hydrosulphate of ammonia, caustic ammonia, caustic potash, and carbonate of potash ; the solution in caustic potash or carbonate of potash deposits hydrated stannic oxide after a while. (H. Rose.)—Ammonia throws down a white bulky hydrate, which dissolves, with some turbidity, in a very large excess of ammonia ; the solution becomes clear after standing for some time, but subsequently deposits a copious precipitate. (Rose.) The precipitate dissolves readily if the solution of the tin-salt is dilute—imperfectly, if it is concentrated. (Gm.) Tartaric acid prevents the precipitation by ammonia. (H. Rose.)—Potash throws down a white bulky hydrate [containing potash ?], easily soluble in a slight excess of the alkali.—Monocarbonate of potash precipitates the hydrate [stannate of potash, according to Fremy] with some degree of effervescence ; the precipitate dissolves in excess of the re-agent, but separates again completely after standing for a while. The hydrate precipitated by sesquicarbonate of ammonia and bicarbonate of potash does not dissolve in excess of those re-agents. (H. Rose.)—Carbonate of baryta, strontia, lime, and magnesia precipitate the salts of stannic oxide, even in the cold (Demarçay) ; the hydrate thereby precipitated is free from

alkali. (Fremy.) Phosphate of soda throws down white phosphate of stannic oxide. ¶. When phosphoric acid (αPO^3) is mixed with hydrochlorate of stannic oxide, the mixture solidifies, in the course of a few days, to a colourless jelly: arsenious acid gives, after a while, a somewhat copious precipitate. ¶.—Tincture of galls shows no action at first, but the mixture, after a while, solidifies in a gelatinous mass. (H. Rose.) Succinate of ammonia precipitates stannic salts completely. (Gahn & Berzelius.)—Ferrocyanide of potassium produces a white turbidity after some time; subsequently the mixture solidifies to a stiff jelly, insoluble in hydrochloric acid: the greater the degree of dilution, the more slowly does the solidification take place. (H. Rose.) When hydrochlorate of stannic oxide is boiled with acetate of soda or formiate of potash, a precipitate is formed, which re-dissolves on cooling, or when washed with cold water. (Liebig.)—Phosphuretted hydrogen gas gives no precipitate with hydrochlorate of stannic oxide, but colours it yellow. (H. Rose.) Iodide of potassium, chloride of gold, oxalic acid, sulphuric, nitric, hydrochloric, and arsenic acid, and ferrocyanide of potassium, give no precipitate. ¶¶. If the solution be very largely diluted with water, sulphuric acid produces a slight precipitate, which, however, is soluble in hydrochloric acid. Nitrate of silver in excess gives a precipitate perfectly soluble in ammonia. ¶.—Those stannic salts which are insoluble in water, dissolve—provided they have not been ignited—in hydrochloric acid, but not in sal-ammoniac.

c. With Salifiable Bases, forming salts called STANNATES.

α. Anomalous Stannates. By dissolving the anomalous hydrate in aqueous alkalis. These salts are composed of 3 At. stannic acid, with 1 At. metallic oxide, $=\text{MO}, 3\text{SnO}^2$, and contain water as an essential constituent, by virtue of which the stannic oxide acquires the character of an acid; hence, when the salts are heated, the stannic oxide is separated in the anhydrous state. By ignition with an alkali, the anomalous stannates are converted into ordinary stannates. (Fremy.) Acids added to the solution of the hydrate in aqueous caustic alkalis, or alkaline carbonates, precipitate the hydrate in the anomalous state; consequently, the precipitate is not soluble in excess of the acid. (Berzelius.)

β. Ordinary Stannates. 1. By dissolving the ordinary hydrate of stannic acid in aqueous alkalis.—2. By fusing the anhydrous acid, or either of its hydrates, in a silver crucible, with caustic potash or carbonate of potash.—3. The stannates of the earthy alkalis, earths and heavy metallic oxides, are obtained by precipitating the soluble salts of these bases with the stannate of potash obtained by either of the preceding methods. (Berzelius.) The ordinary stannates contain at most 1 atom of base to 1 atom of acid, $=\text{MO}, \text{SnO}^2$. (Moberg, *Berz. Jahresber.* 22, 142; also *J. pr. Chem.* 28, 230; Fremy.) The stannates of the fixed alkalis, if they do not contain excess of alkali, are resolved, by ignition, into anhydrous stannic acid, and a compound of a small quantity of stannic acid with the whole of the alkali. Acids—even carbonic acid—decompose them, throwing down the ordinary hydrate of stannic acid. (Berzelius.)

According to Kastner (*Kast. Arch.* 19, 423) there exists a *Stannuretted Hydrogen gas*.

Carbonic acid does not combine with either of the oxides of tin. (Bergman, Proust.)

TIN AND BORON.

BORATE OF STANNOUS OXIDE.—Borax forms with hydrochlorate of stannous oxide, a white precipitate which fuses to a grey slag. (Wenzel.)

TIN AND PHOSPHORUS.

A. PHOSPHIDE OF TIN.—*a.* Formed by throwing phosphorus upon melted tin, or by fusing together equal parts of tin and glacial phosphoric acid, whereby phosphate of stannic or stannous oxide is likewise formed. (Pelletier, Landgrebe, *Schw.* 55, 106.) The compound may also be formed by heating in a blast-furnace for an hour: 6 parts of tin-filings or 8 of stannic oxide with 1 charcoal, 10 bone-ash, 5 pounded quartz, and 5 boracic acid. (Berthier, *Ann. Chim. Phys.* 33, 180.) Silver-white (lead-coloured: *Berthier*). May be cut with the knife; extends under the hammer, but at the same time splits into laminae. Contains from 13 to 14 per cent. of phosphorus, which burns away on the application of heat. (Pelletier.) *b.* When the compound of bichloride of tin with phosphuretted hydrogen is decomposed by water, the phosphuretted hydrogen, as it escapes, reduces the bichloride of tin to the state of protochloride, and at the same time precipitates phosphide of tin in the form of a yellow powder, which remains for a long time suspended in the liquid, and oxidizes readily in the air. When washed and dried out of contact of air, it exhibits the phosphorus flame before the blowpipe. When ignited in hydrogen gas, it gives up its phosphorus, amounting to 55.43—56.88 per cent., and is converted into metallic tin. (H. Rose, *Pogg.* 24, 326.)

B. PHOSPHITE OF STANNOUS OXIDE, or STANNOUS PHOSPHITE.—Hydrochlorate of stannous oxide is precipitated by phosphite of ammonia, and the white precipitate washed till the wash-water, after boiling with nitric acid, no longer gives a turbidity with solution of silver. The salt, when heated in a retort, blackens without tumefaction, fuses without glowing, gives off hydrogen rich in phosphorus, and yields a sublimate of phosphorus. It is readily oxidized, with formation of a jelly, by warm nitric acid, and, on subsequent evaporation and ignition, yields 109.54 per cent. of stannic phosphate, containing 74.16 stannic oxide and 35.38 phosphoric acid. Its solution in hydrochloric acid exerts a powerful reducing action on several metals. (H. Rose, *Pogg.* 9, 45.)

| | H. Rose. | | | |
|----------------------------------|----------|------|--------|--------------|
| 2SnO | 134.0 | | 67.54 | 66.24 |
| PO ³ | 55.4 | | 27.92 | 27.44 |
| HO | 9.0 | | 4.54 | 6.32 |
| 2SnO, PO ³ + Aq. | 198.4 | | 100.00 | 100.00 |

In consequence of the difficulty of drying the salt, the analysis gave too much water. (H. Rose.)

C. PHOSPHITE OF STANNIC OXIDE, or STANNIC PHOSPHITE.—The aqueous solution of bichloride of tin gives, with phosphite of ammonia, a white precipitate which dries up to a glassy, brittle mass. This, when heated, gives off merely water, without any gas, because the binocide of tin is converted into protoxide: hence the residue is soluble in hydrochloric

acid. According to this, the precipitate appears to consist of $2\text{SnO}^2\cdot\text{PO}^2$. (H. Rose, *Pogg.* 9, 47.)

D. PHOSPHATE OF STANNOUS OXIDE, or STANNOUS PHOSPHATE.—Diphosphate of soda added to a solution of protochloride of tin, throws down a white powder, insoluble in water and in aqueous sal-ammoniac, but soluble in hydrochloric acid: it vitrefies in the fire.

TIN AND SULPHUR.

PROTOSULPHIDE OF TIN.—STANNOUS SULPHIDE.—SULPHOSTANNOUS ACID.—Tin-foil in narrow strips takes fire in sulphur vapour. (Winkelblech.)—The protosulphide is formed when sulphur is mixed with tin heated above its melting point. Since the mass thus formed still contains uncombined tin, it must be pounded and heated with fresh sulphur in a close vessel. Dark lead-grey; of laminar texture; crystallizable; somewhat tough; not easily pulverized (Berthier); much less fusible than tin. By electrolysis, Becquerel obtained sulphide of tin in white cubes possessing the metallic lustre. (I. 395.)

| | | | | J. Davy, Berzelius. | Bergman. Proust. | Pelletier. | Vauquelin. | | | | |
|-----------|----|------|--------|------------------------|---------------------|------------|------------|------|-----|------|-------|
| Sn | 59 | | 78·67 | | 78·6 | | 80 | | 85 | | 85·9 |
| S | 16 | | 21·33 | | 21·4 | | 20 | | 15 | | 14·1 |
| SnS | 75 | | 100·00 | | 100·0 | | 100 | | 100 | | 100·0 |

At a red heat, it slowly converts hydrogen gas into hydrosulphuric acid. (H. Rose.) If the hydrogen be passed over it for a longer time, nothing but metallic tin remains. (Elsner, *J. pr. Chem.* 17, 233.)—With phosphuretted hydrogen gas at a gentle heat, it is slowly decomposed, yielding hydrosulphuric acid, sublimed phosphorus, and a residue of tin. (H. Rose, *Pogg.* 24, 235.)—When fused with cyanide of potassium, it yields metallic tin and sulphocyanide of potassium. (Liebig.)—Chlorine at ordinary temperatures converts it into liquid bichloride of tin and a crystalline compound of that substance with bichloride of sulphur. (H. Rose.)



75 parts (1 At.) of stannous sulphide heated to whiteness in a charcoal crucible with 53·2 parts (1 At.) of dry carbonate of soda, yield 29·37 parts ($\frac{1}{2}$ At.) of tin and a grey slag containing sulphide of tin, sulphide of sodium, and carbonate of soda. With a larger quantity of carbonate of soda, the quantity of tin reduced does not exceed three-fourths of the whole. Carbonate of soda without charcoal decomposes part of the sulphide of tin at a red heat by oxidating the metal. (Berthier, *Ann. Chim. Phys.* 43, 169.)—Aqueous hydrochloric acid readily dissolves protosulphide of tin, evolving sulphuretted hydrogen and forming hydrochlorate of stannous oxide. Potash-ley has no action upon it. (Proust.)—The protosulphide appears to be capable of mixing with tin by fusion in all proportions.

Hydrated Protosulphide of Tin, or Hydrosulphate of Stannous Oxide.—The black-brown precipitate which hydrosulphuric acid or alkaline hydrosulphates produce with protochloride of tin, washed with boiling water.—Black when dry.—When heated, it gives off water and a small quantity of sulphur(?), and is converted into the anhydrous protosulphide. With hydrochloric acid, it behaves like the anhydrous sulphide. (Proust.) Not soluble in aqueous sulphurous acid. (Berthier.)

B. SESQUISULPHIDE OF TIN.—By gently igniting an intimate mixture of 3 parts of stannous sulphide and 1 part of sulphur in a retort. 100 parts of stannous sulphide thus treated take up 10.5 parts of sulphur.—Greyish-yellow, with metallic lustre.—When strongly ignited in a close vessel, it gives off one-third of its sulphur.—With potash-ley it yields a solution of sulphostannate of potassium and stannate of potash, and a residue of protosulphide of tin. Concentrated hydrochloric acid converts it into bisulphide of tin, leaving $\frac{1}{4}$ [$\frac{1}{4}$?] of the tin in the form of protoxide.

| Berzelius. | | | | | |
|--------------------------------------|-----|------|--------|-------|-----|
| 2Sn | 118 | | 71.08 | | 71 |
| 3S | 48 | | 28.92 | | 29 |
| Sn ² S ³ | 166 | | 100.00 | | 100 |

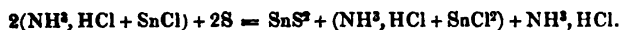
Hydrated Sesquisulphide of Tin.—Separates in the form of a liver-coloured powder on digesting a saturated solution of sulphostannate of potassium with bisulphide of tin. By digestion with caustic potash it is converted into black protosulphide. (Berzelius.)

C. BISULPHIDE OF TIN.—STANNIC SULPHIDE.—SULPHOSTANNIC ACID.
—*Mosaic Gold, Aurum mosaicum s. musivum.*—*Comp. Woulfe (Crell. Chem. J. 1, 149); Bullion (Crell. Ann. 1793, 1, 89); Pelletier (Crell. Ann. 1797, 1, 46); Proust (N. Gehl. 1, 250).*

Formation. 1. By heating sulphur with protochloride or ammonio-protochloride of tin, whereupon one-half of the tin combines with the sulphur, and bichloride of tin or chlorostannate of ammonium volatilizes.—In the preparation of mosaic gold from tin, sal-ammoniac, and sulphur, the reaction appears to pass through the two following stages: First, there is formed, with evolution of hydrogen gas and ammonia, a compound of protochloride of tin with sal-ammoniac (*chlorostannite of ammonium*):



Afterwards, when the temperature rises higher, the sulphur abstracts half the tin, while a compound bichloride of tin with sal-ammoniac (*chlorostannate of ammonium*) sublimes, together with free sal-ammoniac.



If amalgam of tin is used, cinnabar likewise sublimes.—2. By heating protoxide [in which case, according to Proust, incandescence is produced] or binoxide of tin with silver.—3. When protosulphide of tin is heated with cinnabar, whereupon mercury is set free (Pelletier) [This mode of formation is denied by Proust];—or with corrosive sublimate—whereby bichloride of tin and cinnabar are produced at the same time (Woulfe);—or with sal-ammoniac and sulphur.—4. By heating hydrated protosulphide of tin.

Preparation. a. Protochloride of tin and sulphur (Proust);—b. Equal parts of sifted tin-filings, sulphur, and sal-ammoniac (Pelletier) [Gives a less beautiful preparation than c (Woulfe)];—c. 4 parts of tin-filings, 3 sulphur, 2 sal-ammoniac (Woulfe);—d. A pulverized amalgam of 2 parts tin and 2 mercury, with $1\frac{1}{2}$ sulphur and 1 sal-ammoniac (Thénard);—e. A pulverized amalgam of 12 parts tin and 6 mercury, with 7 sulphur and 6 sal-ammoniac [whereby $1\frac{1}{4}$ pt. volatile liver of sulphur, $13\frac{1}{4}$ sublimed matter, and 16 parts of fine, and for the most part sublimed, mosaic gold are obtained] (Woulfe).—f. A pulverized amalgam of 12 parts tin and 3 mercury with 7 sulphur

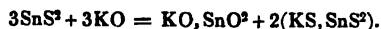
and 3 sal-ammoniac;—*g.* 2 parts stannous oxide and 1 sulphur (Proust) [yields 2·4 mosaic gold];—*h.* 8 parts stannic oxide, 7 sulphur, and 4 sal-ammoniac (Woulfe);—*i.* 10 parts protosulphide of tin, 5 sulphur, and 4 sal-ammoniac (Woulfe);—*k.* 5 parts protosulphide of tin, 1 protochloride, and 2 sulphur (Woulfe);—*l.* 5 parts protosulphide of tin and 8 corrosive sublimate (Woulfe) [gives a very beautiful preparation];—*m.* Hydrated bisulphide of tin [obtained by deflagrating tin with nitre, dissolving the stannic oxide in hydrochloric acid, and precipitating with solution of liver of sulphur] (Van Mons).

Either of these mixtures or compounds is heated in a retort or a loosely-closed flask placed in the sand-bath, or in an inverted Passau crucible, having its mouth closed with a tile and its upturned base perforated with an aperture, which is covered with aludels. (Woulfe.) A gentle heat is first applied for some hours; afterwards the heat is raised, but not quite to redness.—The greater part of the mosaic gold is found at the bottom of the vessel—the smaller, but purer and finer portion, sublimes.

Properties.—Gold-coloured, translucent, delicate scales or six-sided laminae, unctuous to the touch. Specific gravity 4·425 (P. Boullay); 4,600 (Karsten).

| | J. Davy. | | Berzelius. | |
|------------------------|----------|--------|------------|-----|
| Sn | 59 | 64·84 | 63·6 | 65 |
| 2S | 32 | 35·16 | 36·4 | 35 |
| SnS ² | 91 | 100·00 | 100·0 | 100 |

Decompositions. By ignition it is resolved into sulphur and protosulphide of tin, a portion of the bisulphide, however, subliming at the same time in a very beautiful form. If the action of the heat has not been long continued, protosulphide of tin is found at the bottom, above it a thin layer of sesquisulphide, and undecomposed mosaic gold at the top. (Berzelius.) The sulphurous acid gas observed by Proust, and previously also by Berzelius, is not evolved unless air has access to the heated substance. (Gay-Lussac, Berzelius.)—2. Boiling aqua-regia converts it into sulphuric acid and stannic oxide. Hydrochloric acid or nitric acid alone has no action on it.—3. Deliquesces in chlorine gas at ordinary temperatures, forming a brown liquid, and afterwards solidifies in yellow crystals of SnCl²·2SCP². (H. Rose.)—Mosaic gold dissolves in a heated solution of potash [also in carbonate of potash, with evolution of carbonic acid], forming stannate of potash and sulphostannate of potassium:



(For the decomposition by litharge, vid. *Lead-oxide.*)

Hydrated Bisulphide of Tin, or Bi-hydrosulphate of Stannic Oxide.—

1. By precipitating hydrochlorate of stannic oxide with sulphuretted hydrogen or an alkaline hydrosulphate.—2. By precipitating aqueous sulphostannate of potassium with hydrochloric acid.—Light yellow, loosely-coherent flakes, which dry up to dark yellow, hard lumps, having a conchoidal fracture. When gently heated, it gives off water, sulphur, and sulphurous acid (?), and is reduced to mosaic gold. (Proust.) At a higher temperature, it gives off the rest of its water with violent decrepitation, and is at the same time reduced to sesquisulphide by the loss of $\frac{1}{2}$ At. sulphur; or at a still higher temperature, to protosulphide. (Ber-

zelius.) Dissolves in boiling hydrochloric acid with evolution of sulphuretted hydrogen, and is thereby converted into hydrochlorate of stannic-oxide. (Proust.)

Bisulphide of tin unites with the more basic metallic sulphides, forming salts called *Sulphostannates*. These compounds are obtained: 1. By dissolving either the anhydrous or the hydrated bisulphide of tin in aqueous alkaline hydrosulphates or caustic alkalis. The hydrated sulphide dissolves more readily than the anhydrous; with the latter, a boiling heat is required, to insure complete saturation. If the alkaline hydrosulphates contain 2 atoms of hydrosulphuric acid, 1 atom of the latter is expelled with effervescence. When caustic alkalis are used, the resulting solution likewise contains stannate of potash. (*vid. sup.*)—2. By precipitating a heavy metallic salt with aqueous sulphostannate of potassium. Those sulphostannates which contain an alkali-metal are not decomposed by ignition in close vessels.

D. TETRATHIONATE OF STANNOUS OXIDE.—Tetrathionic acid gives a white precipitate with hydrochlorate of stannous oxide. (Fordos and Gélis.)

E. *Hyposulphite of Stannous oxide?*—Aqueous sulphurous acid and metallic tin produce protosulphide of tin in the form of a black powder, and a solution of stannous hyposulphite, from which acids evolve sulphurous acid and precipitate sulphur. (Fourcroy & Vauquelin.) According to Berzelius, and likewise according to Fordos & Gélis, this process yields but very little hyposulphite of stannous-oxide, together with the sulphide, but on the other hand, a large quantity of sulphite,—the tin, in fact, behaving exactly like cadmium under similar circumstances (p. 57).

F. SULPHITE OF STANNOUS OXIDE, OR STANNOUS SULPHITE.—Sulphite of ammonia added to hydrochlorate of stannous oxide throws down, at ordinary temperatures, the greater part, and at a boiling heat, the whole of the stannous oxide, in the form of a white basic salt. This salt gradually gives up all its acid to boiling water, and is converted into pale yellow, anhydrous protoxide of tin. (Berthier, *N. Ann. Chim. Phys.* 7, 81; *Comp. Böttinger, Ann. Pharm.* 51, 408.)

¶ G. STANNOUS HYPOSULPHATE.—Known only in solution. When concentrated in vacuo, it deposits protosulphide of tin. (Bouquet.) ¶

H. SULPHATE OF STANNOUS OXIDE, OR STANNOUS SULPHATE.—*a. Basic.*—Precipitated on mixing *b* with an alkali. (A. Berthollet.)

b. Monosulphate.—1. Protosulphide of tin heated with red oxide of mercury yields the anhydrous salt, which bears a dull red heat without decomposition.—2. By heating tin in oil of vitriol slightly diluted.—3. By dissolving hydrated stannous oxide in sulphuric acid.—4. Sulphuric acid added to solution of hydrochlorate of stannous oxide throws down a white powder. The liquid obtained by (3), and the solution of the saline mass (1), (2), or of the white powder (4), all yield needles on cooling. (A. Berthollet.) At a red heat the salt is resolved into sulphurous acid, oxygen gas, and stannic oxide. (Gay-Lussac.) When ignited in hydrogen gas, it leaves metallic tin with a small quantity of sulphide. (Arrvedson, *Pogg.* 1, 74.) ¶ According to Bouquet (*N. J. Pharm.* 11, 459), the salt

SnO , SO^3 crystallizes in laminæ from a hot saturated solution of recently precipitated stannous oxide in dilute sulphuric acid. It is very soluble in water; the solution soon becomes turbid from deposition of a basic salt, but its transparency is restored by adding a few drops of sulphuric acid. When ignited it leaves stannic oxide. Combines with the sulphates of potash and ammonia, forming crystallizable compounds. ¶

I. SULPHATE OF STANNIC OXIDE, OF STANNIC SULPHATE.—*a. Ordinary.* 1. By dissolving ordinary hydrate of stannic oxide in aqueous sulphuric acid.—2. By heating tin with excess of oil of vitriol, whereupon sulphurous acid and sulphur are given off, and stannic sulphate remains behind. Kraskowitz (*Pogg.* 35, 518) heats 1 part of granulated tin with 3 parts of oil of vitriol in a capacious iron vessel; whereupon slight effervescence is at first produced, with formation of a white scum; then suddenly great heat is developed, and sulphurous acid mixed with sulphur vapour is given off; the vessel should therefore be cooled to prevent frothing over. After the frothing has ceased, the excess of oil of vitriol is driven off by the application of a stronger heat, which is continued till the residue becomes friable, and thereby separable from the metallic tin mixed with it. The aqueous solution (1) yields no precipitate on boiling. (Berzelius.)

b. Anomalous. The oxide of tin produced by the action of nitric acid does not dissolve in sulphuric acid either concentrated or dilute; a portion of the acid is, however, absorbed by it, with tumefaction, and may be extracted by water. (Berzelius.)

K. SULPHOCARBONATE OF STANNOUS SULPHIDE, and SULPHOCARBONATE OF STANNIC SULPHIDE.—Aqueous sulphocarbonate of calcium gives a dark brown precipitate with stannous salts and brownish-yellow with stannic salts. (Berzelius.)

TIN AND SELENIUM.

A. SELENIDE OF TIN.—*a.* Tin combines with selenium, on the application of heat, forming a grey, metallic, shining substance, which, when heated in the air, is readily decomposed without fusion, yielding selenium which volatilizes, and stannic oxide which remains behind.—*b. Biselenide of Tin* may be obtained by precipitating hydrochlorate of stannic oxide with hydroselenic acid.

B. SELENITE OF STANNIC OXIDE.—White powder, insoluble in water, but soluble in hydrochloric acid, and precipitated from the solution on the addition of water. When heated, it first gives off water, and then the whole of its acid. (Berzelius.) Formula of the dry salt, $\text{SnO}^3, 2\text{SeO}^3$. (Muspratt.)

TIN AND IODINE.

A. PROTIODIDE OF TIN, OF STANNOUS IODIDE.—*Iodostannous Acid.*
1. When tin-filings are heated with a twofold quantity of iodine, a brown-red, translucent compound is formed, which yields a dingy orange-yellow powder, and fuses very easily (according to Sir H. Davy, it volatilizes when heated more strongly); the combination is attended with

noise and ignition. (Gay-Lussac, Rammelsberg, *Pogg*, 48, 169.) ¶ According to Henry (*Phil. Trans.* 1845, 363), tin heated with twice its weight of iodine, yields two compounds, the protiodide SnI , and the biniodide SnI^2 , which may be separated by sublimation, the latter volatilizing at 180°C . while the former remains fixed at a red heat. ¶ 2. A dilute solution of protochloride of tin mixed with a very slight excess of iodide of potassium soon deposits a large quantity of yellowish-red crystalline tufts. If the mixture was warm, the iodide of tin is deposited, on cooling, in fine yellowish-red needles. (Boullay, *Ann. Chim. Phys.* 34, 372.) Gay-Lussac likewise obtained orange-yellow silky crystals, by treating the iodide of tin (1) with a small quantity of water, and pouring off the liquid from the separated hydrate of stannous oxide—that liquid containing stannous oxide with excess of hydriodic acid. According to Gay-Lussac, these crystals consist of acid hydriodate of stannous oxide, but, according to Boullay's analysis, they are formed of protiodide of tin.

Protiodide of tin, when heated in the air in contact with stannic oxide, leaves a substance, which, when treated with water, is resolved into stannic oxide and hydriodic acid which dissolves. (Boullay.) The iodide prepared by (1) is easily decomposed by water—especially with the aid of heat, and the more completely in proportion as the quantity of water is greater—yielding hydrated stannous oxide which is precipitated, and aqueous hydriodic acid containing a trace of tin. (Gay-Lussac, Rammelsberg.) ¶ Dissolves in water sparingly, but without decomposition; fuses readily and forms a dark-red mass, having a crystalline texture; yields a powder of a red colour and considerable lustre, like red lead. (Henry.) ¶ The iodide (2) dissolves in water without decomposition, and more abundantly in warm than in cold water; it is likewise soluble in hydrochlorate of stannous oxide. Hence it is not precipitated from a solution of that compound by small quantities of iodide of potassium. (Boullay.) Iodide of tin combines with the more basic metallic iodides. (Boullay.)

| | | Boullay (2.) | |
|-----------|-----|--------------|--------------|
| Sn | 59 | | 31·89 |
| I..... | 126 | | 68·11 |
| SnI | 185 | | 100·00 |
| | | | 32·01 |
| | | | 67·99 |
| | | | 100·00 |

When tin is heated in excess with iodine and a large quantity of water, violent action ensues, the tin is rapidly oxidated, and a solution of hydriodic acid is formed, containing but a trace of tin. (Gay-Lussac.)

On dissolving in aqueous iodide of potassium half as much iodine as it already contains, and adding protochloride of tin to the solution, the colourless mixture yields no precipitate, but on evaporation deposits a yellow powder, slightly soluble in water, probably Sn^2I^2 . (Boullay.)

¶ B. BINIODIDE OF TIN.— SnI^2 .—1. Separated by sublimation from the mixture of protiodide and biniodide obtained by heating tin with twice its weight of iodine (*supra*).—2. By boiling equal parts of protochloride of tin and iodine with a small quantity of water. By (1): orange-yellow, shining crystals; by (2): red crystals. Sublimes at 180° . Easily decomposed by water. (Henry.) ¶

C and D. STANNOUS and STANNIC IODATES.—Iodic acid and iodate of potash give white precipitates both with hydrochlorate of stannous oxide

and with hydrochlorate of stannic oxide. (Pleischl.) When hydrochlorate of stannous oxide is dropped into iodate of soda, iodate of stannous oxide is precipitated, white at first, but turning brown in a few minutes, and then grey, from liberation of iodine and formation of stannic hydrochlorate. If, on the contrary, the iodate of soda be added to the stannous hydrochlorate, the white precipitate which forms at first is quickly re-dissolved, and the solution acquires a yellow colour; with a larger quantity of iodate of soda, a separation of iodine takes place. (Rammelsberg, *Pogg.* 44, 567.)

TIN AND BROMINE.

A. PROTObROMIDE OF TIN, OR STANNOUS BROMIDE.—*Bromostannous Acid.*—Formed by heating tin in hydrobromic acid gas (Balard), or with protobromide of mercury (Löwig).—Greyish-white, with considerable lustre; when heated, it fuses to a yellowish oil.—When heated in the air or in contact with nitre, it gives off bibromide of tin and leaves the binoxide.

Aqueous Protobromide of Tin, or Hydrobromate of Stannous Oxide.—1. By dissolving stannous bromide in water.—2. Tin dissolves in aqueous hydrobromic acid with evolution of hydrogen, very slowly when the liquid is cold, more quickly when it is raised to the boiling point.—The colourless solution, which reddens litmus, becomes gelatinous when evaporated, but does not crystallize; when more strongly heated, it gives off hydrobromic acid. (Löwig.)

B. BIBROMIDE OF TIN, OR STANNIC BROMIDE.—*Bromostannic Acid.*—Tin takes fire in contact with bromine and is converted into stannic bromide. (Balard.)—2. Protobromide of tin with bromine yields the same compound. (Löwig).—White, crystalline, easily fusible and volatile; gives off a faint white cloud when exposed to the air. In heated oil of vitriol, it fuses, without visible decomposition, into oily drops. With nitric acid, after a few seconds, it gives off bright-coloured vapours of bromine. Dissolves in water without apparent decomposition. (Balard.)

Bromine-water converts stannous oxide, with evolution of heat, into mono-hydrobromate of stannic oxide; on stannic oxide, bromine exerts no action. (Balard.)

C. BROMATE OF STANNOUS OXIDE, OR STANNOUS BROMATE.—Bromate of potash gives a yellowish-white precipitate with hydrochlorate of stannous oxide. (Simon, *Repert.* 65, 207.)

D. BROMATE OF STANNIC OXIDE, OR STANNIC BROMATE.—Aqueous bromic acid dissolves but a small quantity of the ordinary hydrate of stannic acid, even after digestion for weeks. The hydrate separated from the liquid becomes translucent and glassy when dried over oil and vitriol, and loses 18 per cent. when heated to 180°. (Rammelsberg, *Pogg.* 55, 87.)

TIN AND CHLORINE.

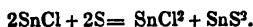
PROTOCHLORIDE OF TIN, OR STANNOUS CHLORIDE.—*Chlorostannous Acid.*—*Butter of Tin.*—1. By gradually heating tin or amalgam of tin with calomel, or with at most two parts of corrosive sublimate, the mercury

volatilizing.—2. By heating tin in hydrochloric acid gas, hydrogen being set free.—3. By heating hydrochlorate of stannous oxide in close vessels—whereupon, when the heat is gradually raised to redness and the receiver changed, the chloride of tin passes over after the water. Capitaine (*J. Pharm.* 25, 552) gently heats commercial *tin-salt* in a capacious crucible (to prevent frothing over) as long as it froths up and gives off water and sulphuric acid—pours the mass, as soon as it is brought to a state of tranquil fusion, into a small crucible—then pounds it up coarsely, and distils it from a coated glass retort. The first portions of stannous chloride which pass over are perfectly pure; the last portions contain a small quantity of iron, from which they may be freed by a second distillation.

Translucent, almost pure white (frequently grey), with a fatty lustre and conchoidal fracture. Fuses at 250° to an oily liquid which penetrates the crucibles and makes them crack; boils at a heat near redness, but always with some degree of decomposition. (J. Davy, *Schw.* 10, 321; Capitaine.) When cooled after fusion, it remains liquid for a long time, but afterwards becomes syrupy and solidifies. (Marx.)

| | | | | |
|------------|------|------|-------|----------|
| | | | | J. Davy. |
| Sn | 59·0 | | 62·5 | 62·22 |
| Cl | 35·4 | | 37·5 | 37·78 |
| SnCl | 94·4 | | 100·0 | 100·00 |

When heated to bright redness, it gives off bichloride of tin and afterwards unaltered protochloride, leaving a black shining mass which dissolves in aqueous hydrochloric acid with evolution of hydrogen gas, and forms a solution of stannous hydrochlorate. (A. Vogel, *Schw.* 21, 68.) When heated to the boiling point, it passes over in company with bichloride of tin, and leaves yellow, earthy stannous oxychloride, SnCl, SnO. (Capitaine.)—When heated with sulphur, it yields bichloride and bisulphide of tin. (Proust.)

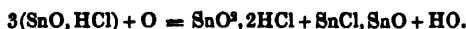


When heated in the air, or with nitre, chlorate of potash, or mercuric oxide, it gives off bichloride of tin and leaves binoxide.—At ordinary temperatures, it does not suffer much alteration by exposure to the air; in the course of three weeks, however, it becomes somewhat disintegrated, but still dissolves completely in water.

Hydrated and Aqueous Protochloride of Tin, or Crystallized and Aqueous Mono-hydrochlorate of Stannous Oxide.—Tin-salt.—1. Protochloride of tin dissolves without turbidity in water [freed from air?]. (Capitaine.) The solution is commonly turbid, partly perhaps from the presence of air in the water, partly because the chloride of tin may have been mixed with oxychloride.—2. Tin dissolves very slowly in cold, more quickly in warm hydrochloric acid, and with evolution of hydrogen gas. The preparation on the large scale is performed in copper vessels, which, so long as any portion of tin remains undissolved, are not attacked by the acid.—3. If granulated tin be covered with hydrochloric acid, then the acid poured off, and the tin exposed to the air—afterwards the acid poured on again, and so on alternately—the tin takes up oxygen from the air, whereby it becomes heated, and dissolves much more quickly than by the simple action of the acid. (Berard.)—¶ 4. In the preparation of *Tin-salt* on the large scale, Nöllner recommends that the hydrochloric acid, as it is evolved from the retorts, be made to act

directly upon granulated tin contained in stone-ware receivers adapted to the retorts, and that the concentrated solution of tin-salt thus formed be afterwards evaporated in tinned pans with the addition of granulated tin. (*Arch. Pharm.* 63, 120.)—¶ The solution, when evaporated and cooled, yields large, transparent, and colourless prisms (and octohedrons: *Dumas*), having a disagreeable metallic taste. According to Berzelius, their composition is SnCl_2HO ; according to Henry, they contain 2 atoms of water, $\text{SnCl}_2\cdot 2\text{HO}$. The crystals when heated evolve water and hydrochloric acid containing a small quantity of tin, and leave protochloride and protoxide of tin. Cold oil of vitriol separates from them but a small quantity of hydrochloric acid; heated oil of vitriol separates hydrochloric acid—together with small quantities of stannous chloride, sulphurous acid, and sulphuretted hydrogen [the two latter substances partly decomposing each other and yielding a precipitate of sulphur]—and forms stannic sulphate. (*A. Vogel.*)

The crystals generally give a turbid solution with water, which, however, may be rendered transparent by the addition of hydrochloric acid [partly, perhaps, because the crystals have become oxidated by exposure to the air, partly because the air contains water]. The turbidity of the solution increases with excess of water, and diminishes with excess of the tin-salt. (*Fischer.*)—The solution absorbs oxygen from the air, and if it does not contain an excess of hydrochloric acid, becomes turbid, from formation of bi-hydrochlorate of stannic oxide and precipitation of stannous oxychloride. Probably in this manner:



By longer exposure to the air, the solution recovers its transparency and acquires a yellow colour—the change being slower as the solution is more concentrated. (*Fischer, Kastn. Arch.* 13, 225; *Capitaine.*) [Does there exist a mono-hydrochlorate of stannic oxide, which forms a yellow solution in water?]
—The solution of stannous hydrochlorate mixed with sulphurous acid, becomes yellow and turbid, especially when warmed, and yields a deep-yellow precipitate of hydrated bisulphide of tin, the odour of sulphurous acid being at the same time destroyed, and hydrochlorate of stannic oxide formed. (*Hering, Ann. Pharm.* 29, 90.) Probably thus:



The stannic oxide formed remains dissolved in the excess of hydrochloric acid.—According to Girardin (*Ann. Chim. Phys.* 61, 286), if the hydrochloric acid contains even a small quantity of sulphurous acid, the solution of the tin-salt in it is attended with the formation of a yellow cloudiness; and if water be afterwards added, a faint smell of sulphuretted hydrogen is evolved and a yellowish-brown precipitate formed, which is a mixture of stannic sulphide and stannic oxide.—Trithionic acid added to the heated tin-solution throws down sulphide of tin. (*Persoz.*)—The solution reduces hypochlorous acid, evolving chlorine and being itself converted into a stannic salt. (*Balard.*) It likewise reduces nitric acid to nitric oxide, and this again, by longer contact, to nitrous oxide;—tungstic acid, even when united with an alkali, to blue oxide of tungsten;—molybdic acid to blue oxide of molybdenum;—chromic acid to chromic oxide;—manganic acid to manganous oxide;—hydrated peroxide of manganese, on boiling, to manganous oxide, with precipitation of sesquioxide of tin (*Fuchs*);—arsenic acid to arsenious acid, and this, by longer digestion, to metallic arsenic (*Woulfe, Crell. Chem. J.* 1, 155);—antimonious acid to

antimony (Woulfe);—mononitrate of bismuth-oxide to black suboxide (A. Vogel);—the red and brown peroxides of lead to chloride of lead (A. Vogel);—ferric salts to ferrous salts (with formation of hydrochlorate of sesquioxide-of-tin, (Fuchs, *comp.* p. 80);—cupric oxide and its salts to dichloride of copper;—the protoxide, dichloride, protochloride, and cyanide of mercury to metallic mercury (A. Vogel, *Kastn. Arch.* 23, 78);—silver-salts to metallic silver;—with gold-salts, the stannous solution forms a precipitate which is brown or purple according to circumstances. —Copper immersed in the stannous solution mixed with a large quantity of hydrochloric acid, throws down metallic tin in the form of a greyish-black powder, only however when the solution is exposed to the air and boiled. (Reinsch, *J. pr. Chem.* 24; 248.)

Protochloride of tin unites with the chlorides of the alkali-metals, forming salts which may be called *Chlorostannites*.—According to Kuhlmann, it forms definite compounds with nitrous, hyponitric, and nitric acid. It is easily soluble in absolute alcohol. (Capitaine.)

B. HYDRATED STANNOUS OXYCHLORIDE, or DI-HYDROCHLORATE OF STANNOUS OXIDE.—By precipitating hydrochlorate of stannous oxide with an insufficient quantity of potash.—White powder. (Proust.)—At a red heat, it yields water containing hydrochloric acid and hydrochlorate of stannous oxide, a sublimate of protochloride of tin and a residue of stannous oxide.—Froths up violently with strong nitric acid; gives off hydrochloric acid gas when treated with oil of vitriol; and dissolves without effervescence in hydrochloric acid, acetic acid, and dilute nitric or sulphuric acid, forming stannous salts. (J. Davy, *Schw.* 10, 325.)

| | | Or: | | | J. Davy. | | | |
|------------------|-------|------|--------|------------|----------|-------|--------|------|
| SnCl | 94·4 | | 50·11 | 2SnO 134·0 | | 71·13 | | 70·4 |
| SnO | 67·0 | | 35·56 | HCl.... | 36·4 | | 19·32 | |
| 3HO | 27·0 | | 14·33 | 2HO | 18·0 | | 9·55 | |
| SnCl, SnO + 3Aq. | 188·4 | | 100·00 | | 188·4 | | 100·00 | |

C. AQUEOUS SESQUICHLORIDE OF TIN, or HYDROCHLORATE OF SESQUIOXIDE-OF-TIN.—Hydrated sesquioxide of tin dissolves readily in hydrochloric acid. (Fuchs.) It dissolves with difficulty in cold dilute hydrochloric acid, and the concentrated acid does not become saturated with it till after long digestion, which, to prevent oxidation, must be performed in close vessels. The solution has a purely astringent taste, yields, with hydrosulphuric acid, a lighter brown precipitate than the stannous-salt, and a remarkably fine purple with gold-salts. (Fuchs.)

D. BICHLORIDE OF TIN, or STANNIC CHLORIDE.—*Chlorostannic Acid.*
—*Fuming Spirit of Libavius, Spiritus fumans Libavii.*

Formation. 1. Tin-foil takes fire after a while in chlorine gas, and burns with emission of red sparks, forming bichloride of tin.—2. Protochloride of tin likewise takes fire in chlorine gas at ordinary temperatures.—3. Tin heated with protochloride of mercury volatilizes in the form of bichloride. 4. Protosulphide of tin heated with sulphur or with oxidized bodies is converted into bisulphide.

Preparation. 1. When dry chlorine gas is slowly passed through the retort *d*, *App.* 52, containing tin-foil or melted tin, the bichloride distils over into the receiver *e*, which must be kept cool.—2. By distilling 1 part of tin with 5 parts of protochloride of mercury.—3. By distilling

concentrated hydrochlorate of stannic oxide with fuming oil of vitriol. (J. Davy.)—4. By distilling common salt with stannic sulphate :



The stannic sulphate prepared by method 2, page 82, is pounded in a mortar while still warm—then sifted—intimately mixed with an equal weight of common salt—and heated in an iron retort with glass receiver (or in a glass retort—in which, however, it is difficult to effect complete decomposition)—the heat being gradually raised as long as anything passes over. The bichloride of tin which distils over—together with hydrochloric acid gas—contains chloride of iron and crystals of hydrated bichloride of tin. To free it from iron and water, it is rectified in a glass retort with from twice to four times its weight of oil of vitriol. (Von Kraskowitz, *Pogg.* 35, 518.)

Properties. Thin, colourless liquid, which does not freeze at -29° , boils at 120° under a pressure of 0.767 met., and yields a vapour whose density is 9.1997 (Dumas); gives off white fumes in the air at ordinary temperatures.

| | | | Berzelius. | | J. Davy. | |
|-------------------------|-------|-----|------------|-----|----------|-----|
| Sn | 59.0 | ... | 45.45 | ... | 54.43 | ... |
| 2Cl | 70.8 | ... | 54.55 | ... | 45.57 | ... |
| SnCl ² | 129.9 | ... | 100.00 | ... | 100.00 | ... |

| | Vol. | Sp. gr. |
|-----------------------------------|------|--------------|
| Tin vapour | 1 | 4.0905 |
| Chlorine gas | 2 | 4.9086 |
| Vapour of SnCl ² | 1 | 8.9991 |

Decomposed by sulphuretted hydrogen with the aid of heat, the products being hydrochloric acid gas and bisulphide of tin. (H. Rose, *Pogg.* 24, 339.)



When heated with nitric acid, it gives off chlorine and nitric oxide, and deposits stannic oxide. (Gay-Lussac.) To mercury it slowly gives up chlorine, so that calomel and stannous chloride are produced. (Dumas.)—Alcohol decomposes it, with formation of hydrochloric ether and deposition of stannous oxychloride. With oil of turpentine it becomes strongly heated, the turpentine sometimes taking fire, and deposits stannic oxide. (J. Davy.) Not decomposed by olefiant gas. (Wöhler.)

Hydrated Bichloride of Tin, or Crystallized Hydrochlorate of Stannic Oxide.—22 parts of bichloride of tin solidify with 7 parts of water, forming a colourless mass of crystals fusible by heat. (Adet.)—¶ If this crystalline mass be treated with an additional quantity of water, and the liquid gently evaporated, deliquescent crystals are obtained, which appear to contain 5 atoms of water: $\text{SnCl}^2, 5\text{HO}$. When dried over sulphuric acid, they give off 3 At. water, and are converted into $\text{SnCl}^2, 2\text{HO}$. (Lewy, *Compt. rend.* 21, 369.) ¶

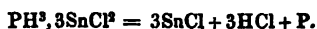
Aqueous Bichloride of Tin, or Aqueous Hydrochlorate of Stannic Oxide.—a. *Ordinary.*—Colour-makers' Composition.—1. By dissolving bichloride of tin in water.—2. By saturating an aqueous solution of stannous chloride with chlorine gas.—3. By mixing the same solution with a quantity of hydrochloric acid twice as great as that which it already contains, and exposing it to the air for some time,—or by heating

it with nitric acid not in excess.—4. By dissolving tin in aqua-regia not containing too much nitric acid. A mixture of nitric acid with sal-ammoniac or common salt, or of hydrochloric acid with nitre may likewise be used.—The solution obtained by the agency of nitric acid always retains a portion of that acid, and therefore deposits anomalous hydrate of stannic oxide when boiled (Bolley, *Ann. Pharm.* 39, 103); according to H. Rose, this effect is not produced till the solution has attained a somewhat high degree of concentration.—The compound may likewise be obtained by dissolving ordinary hydrate of stannic oxide in hydrochloric acid. The anomalous hydrate of stannic oxide, when distilled with hydrochloric acid, is partly converted into ordinary hydrochlorate of stannic oxide, which passes over, while the rest remains behind, as anomalous hydrochlorate of stannic oxide, in the form of a yellow mass, which, when digested in water, partly dissolves and partly swells up. (Berzelius.)—Colourless liquid, not decomposable by boiling; yields crystals when evaporated and cooled.

b. Anomalous.—The hydrate of stannic oxide produced by the action of nitric acid does not dissolve in hydrochloric acid even when boiling and concentrated, but takes up a portion of that acid and acquires a yellowish tint, and is thereby converted—after the excess of acid has been poured off, and the residue dried on bibulous paper—into a soft yellow mass perfectly soluble in water. Nevertheless, the resulting solution, even when largely diluted, coagulates at a boiling heat, and if concentrated becomes as thick as white of egg. It likewise yields a precipitate when mixed with concentrated hydrochloric acid,—but the precipitate dissolves again in water, after the acid is poured off. When this compound is distilled, aqueous hydrochloric acid passes over first, then hydrochloric acid gas, with a small quantity of stannic chloride, while anhydrous stannic oxide is left behind. (Berzelius.)—Ammonia or potash added to the aqueous solution yields a white precipitate slightly soluble in excess of the alkali. (H. Rose.)

E. and F.—Bichloride of tin dissolves sulphur and phosphorus, forming oily liquids.

G. CHLOROSTANNATE OF PHOSPHURETTED HYDROGEN.—Bichloride of tin absorbs both the more inflammable and the less inflammable phosphuretted hydrogen gas without decomposition, thereby acquiring a yellow colour, and being subsequently converted into a yellow solid body which fumes in the air and absorbs moisture with avidity. When heated out of contact of air, it gives off hydrochloric acid gas with a sublimate of phosphorus, and leaves protochloride of tin:



Ammoniacal gas colours the compound black, even in the cold, and appears to form ammonio-bichloride of tin together with several other products.—Water added to this compound gives off non-spontaneously inflammable phosphuretted hydrogen gas with effervescence, and forms hydrochlorate of stannous and of stannic oxide, together with a precipitate of terphosphide of tin (p. 88). Aqueous solution of potash, carbonate of ammonia, or carbonate of potash, and hydrochloric acid likewise give rise to the evolution of the less inflammable variety of phosphuretted hydrogen; but aqueous ammonia evolves the spontaneously inflammable gas. (H. Rose, *Pogg.* 24, 159.)

| | | | | H. Rose. |
|--|-------|-----|--------|----------|
| PH ³ | 34.4 | ... | 8.12 | 8.64 |
| 3SnCl ² | 389.4 | ... | 91.88 | 91.36 |
| PH ³ , 3SnCl ² ... | 423.8 | ... | 100.00 | 100.00 |

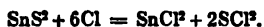
H.—Bichloride of tin may be mixed with terchloride of phosphorus.

I. CHLOROSULPHIDE OF TIN.—SnS², 2SnCl².—Sulphuretted hydrogen is rapidly absorbed by bichloride of tin, with formation of hydrochloric acid gas:



The liquid obtained by perfect saturation with sulphuretted hydrogen is transparent, of a yellowish or reddish colour, and heavier than water. When heated, it leaves bisulphide of tin, while the bichloride volatilizes. Water added to the liquid dissolves out the latter compound and throws down 25.07 per cent. of bisulphide of tin. (Dumas, *J. Chim. Méd.* 8, 478; also *Schw.* 66, 409.)

K. CHLORIDE OF SULPHUR AND TIN.—Produced by the action of chlorine gas on bisulphide of tin at ordinary temperatures:



A bulb is blown on a glass tube and filled with mosaic gold; a cylindrical enlargement is also blown on the tube, the end drawn out, and passed into a chloride of calcium tube, to keep out the moisture of the air. As soon as the dried chlorine gas passed into the bulb has decomposed the mosaic gold, the bulb is gently heated till the compound sublimes into the cylindrical enlargement; air is passed over it to drive out the excess of chlorine; and the cylinder sealed at both ends. Protosulphide of tin likewise yields this compound, mixed however with free bichloride (p. 78).

Large yellow crystals, which fuse when heated, and sublime without decomposition; they fume in the air more strongly than bichloride of tin.—The crystals dissolve gradually but completely in dilute nitric acid, with evolution of nitrous fumes; the solution contains stannic oxide, together with the whole of the sulphur in the form of sulphuric acid. With fuming nitric acid they form a thick white mass, perfectly soluble in water.—With water they form a solution which is milky from separated sulphur, but does not smell of sulphurous acid. The solution when boiled yields a deposit of stannic oxide soluble in hydrochloric acid; with hydrosulphuric acid it forms bisulphide of tin, and the filtered liquid treated with chloride of barium yields sulphate of baryta. With nitrate of silver-oxide, it yields a white curdy precipitate, which contains hyposulphite of silver-oxide, together with chloride of silver, and therefore turns black. Hence it appears that the aqueous solution contains bichloride of tin, sulphuric acid, hyposulphurous acid, and hydrochloric acid. [But whence the precipitation of stannic oxide on boiling?—Aqueous ammonia separates sulphur and part of the stannic oxide from the crystals, but takes up a large proportion of the stannic oxide, together with hyposulphurous, sulphuric, and hydrochloric acid.—The crystals absorb ammoniacal gas with great evolution of heat, and are converted into a yellowish-brown mass; and when this mass is digested in water, the whole of the stannic oxide is left undissolved together with sulphur

in the form of white flakes. The filtrate, which is neutral at first, acquires after a while, the property of reddening litmus, and contains hyposulphite, sulphate, and hydrochlorate of ammonia. (H. Rose, *Pogg.* 42, 517.)

| | | | | | |
|--|-------|-----|--------|-------|----------|
| Sn..... | 59.0 | ... | 19.44 | | H. Rose. |
| 2S..... | 32.0 | ... | 10.55 | | 19.82 |
| 6Cl..... | 212.4 | ... | 70.01 | | 11.38 |
| <hr/> | | | | | |
| SnCl ² , 2SnCl ³ | 303.4 | ... | 100.00 | | 68.19 |
| <hr/> | | | | | |
| | | | | | 99.39 |

Bichloride of tin may likewise be mixed with dichloride of sulphur, and forms crystals with it in the cold. (H. Rose, *Pogg.* 16, 67.)

I. SULPHATE OF STANNIC CHLORIDE.—Bichloride of tin absorbs the vapour of anhydrous sulphuric acid in large quantity, and without evolution of sulphurous acid, and when perfectly saturated with it, solidifies in a transparent and colourless mass. It dissolves clearly in a small quantity of water, with milky turbidity in a larger quantity.

On distilling this mass, a colourless syrup (a) passes over and hardens into a transparent, colourless, brittle mass; a white mealy sublimate b collects in the neck of the retort; and an unfused mass (c) remains in the retort.

a. The brittle mass forms with water a very turbid solution containing stannic oxide, hydrochloric acid, and sulphuric acid, with separation of white flakes mixed with heavy oily drops; these dissolve but slowly in water, as sulphate of terchloride-of-sulphur; the flakes which remain behind dissolve readily in hydrochloric, sulphuric, or nitric acid.



| | | | | | | | | | |
|--------------------------|--------|-----|--------|-----------|----------|-----|--------|-----|-------|
| | | | | Or: | H. Rose. | | | | |
| 6SnCl ² | 778.8 | ... | 27.43 | 12Sn..... | 708.0 | ... | 24.93 | ... | 25.07 |
| 6SnO ² | 450.0 | ... | 15.85 | 30S..... | 480.0 | ... | 16.90 | ... | 17.40 |
| 5SnCl ³ | 611.0 | ... | 21.51 | 27Cl..... | 955.8 | ... | 33.66 | ... | 33.96 |
| 25SO ² | 1000.0 | ... | 35.21 | 87O..... | 696.0 | ... | 24.51 | ... | |
| <hr/> | | | | <hr/> | | | | | |
| | 2839.8 | ... | 100.00 | | 2839.8 | ... | 100.00 | | |

Sometimes the compound contains less (SnCl², SnO²), and in that case it dissolves in water with little or no turbidity.

b. The mealy sublimate contains less quintosulphate of chloride-of-sulphur than a, and therefore forms no oil-drops or only a few, when put into water.

c. The residue in the retort, after being sufficiently heated, contains nothing but stannic oxide with sulphuric acid. The large quantity of stannic oxide arises from the simultaneous formation of terchloride of sulphur from the sulphur of the sulphuric acid. (H. Rose, *Pogg.* 44, 320.)

¶ M. IODOCHLORIDE OF TIN.—SnCl, SnI.—When a concentrated solution of stannous chloride is boiled with iodine, a deposit of stannous iodide is formed, and the liquid, after filtration and cooling, yields straw-yellow, silky crystals of the iodochloride.—These crystals are decomposed by contact with water; they are not volatile. They contain 12.63 per cent. of chlorine, 45.86 iodine, and 42.16 tin. (Henry, *Phil. Trans.* 1845, 363.) ¶

TIN AND FLUORINE.

HYDRATED PROTOFLUORIDE OF TIN, or HYDROFLUATE OF STANNOUS OXIDE.—Aqueous hydrofluoric acid, even when warmed, has no sensible action upon tin. The solution of stannous oxide in aqueous hydrofluoric acid, when evaporated out of contact of air, yields small, white, very brilliant crystals, which have a very sour taste, and are easily soluble in water. (Gay-Lussac & Thénard.)—Opaque prisms which taste first sweet and then bitter; and when exposed to the air, are readily converted by oxidation into SnF_3 , SnO^2 . (Berzelius, *Pogg.* 1, 34.) According to Unverdorben (*N. Tr.* 1, 36), hydrofluates of ammonia gives, with hydrochlorate of stannous oxide, a precipitate consisting of glimmering, metal-shining laminae, soluble in dilute potash.

B. AQUEOUS BIFLUORIDE OF TIN, or HYDROFLUATE OF STANNIC OXIDE.—Aqueous hydrofluoric acid forms with stannic oxide a solution, which, when evaporated, gives off hydrofluoric acid, and is converted into an insoluble (basic ?) salt. (Gay-Lussac & Thénard.) The solution when boiled coagulates like white of egg. (Berzelius.)

TIN AND NITROGEN.

A. NITRATE OF STANNOUS OXIDE, or STANNOUS NITRATE.—1. Very dilute nitric acid, at ordinary temperatures, dissolves tin in the form of stannous oxide, the action being attended, not with evolution of nitrous gas, but with formation of ammonia. (Proust.)—2. By dissolving hydrated stannous oxide in dilute nitric acid, a salt is obtained not mixed with nitrate of ammonia. (Berzelius.)—3. By precipitating protochloride of tin with nitrate of lead, and filtering to separate the chloride of lead. The solution is less liable to change, if mixed with excess of nitrate of lead. (Fischer, *Schw.* 56, 360.)—Yellow solution, which if left to itself for some time, deposits a small portion of stannous oxide (gelatinous hydrate of stannous oxide, according to Berzelius), but if heated with fresh nitric acid, deposits the whole of the tin in the form of stannic oxide [anomalous hydrate of that oxide]. (Proust.)

B. NITRATE OF STANNIC OXIDE, or STANNIC NITRATE.—The ordinary hydrate of stannic oxide dissolves abundantly in nitric acid, and neutralizes it completely. The solution has a bitter taste. If the acid used is rather strong, a portion of the salt separates from it in silky crystals.—At 50° , it deposits nearly all the oxide in the hydrated state, in gelatinous lumps, which dry up to a transparent and colourless mass; the oxide thus obtained behaves like ordinary hydrate of stannic oxide, excepting that it will not again dissolve freely in nitric acid, unless it be previously treated with ammonia. If the solution contains nitrate of ammonia, it does not decompose at ordinary temperatures; if it does not contain that substance, and especially if it be much diluted, it deposits stannic oxide, which, however, disappears again on the addition of nitrate of ammonia. (Berzelius.)

The anomalous hydrate of stannic oxide is completely insoluble in nitric acid, even if previously digested in ammonia. (Berzelius.)

C. NITRIC OXIDE WITH STANNIC CHLORIDE.—Crystalline; easy to distil; decomposable by water. (Kuhlmann.)

Hydrated stannous oxide is nearly insoluble in aqueous ammonia, (Berzelius, *Pogg.* 28, 444.)—In a large quantity of carbonate of ammonia, it dissolves almost completely. (Wittstein, *Repert.* 63, 334.)

D. STANNATE OF AMMONIA.—1. The ordinary hydrate of stannic acid dissolves in aqueous ammonia. The saturated solution evaporated over oil of vitriol in a receiver containing air leaves a yellowish jelly, containing $NH^4O, 2SnO^2$, together with water. (Moberg.)—2. Aqueous stannate of potash precipitates stannate of ammonia from a solution of sal-ammoniac. The gelatinous precipitate dissolves in pure water, but is reprecipitated by ammonia. The aqueous solution, when spontaneously evaporated, becomes viscid, but does not lose its transparency. (Berzelius.)—The anomalous hydrate of stannic oxide does not dissolve in ammonia.

E. SULPHOSTANNATE OF AMMONIUM.—By dissolving hydrated stannic oxide in aqueous bihydrosulphate of ammonia.—No stannate of ammonia is thereby produced. (Berzelius.)

F. AMMONIO-PROTIODIDE OF TIN.—100 parts of stannous iodide absorb 20.9 parts of ammonia, evolving heat, and forming a white compound. (Rammelsberg, *Pogg.* 48, 169.)

| | | | | | | Rammelsberg. |
|--------------------|-----|-----|--------|-------|--|--------------|
| $2NH^3$ | 34 | ... | 15.52 | | | 17.29 |
| SnI | 185 | ... | 84.48 | | | 82.71 |
| <hr/> | | | | | | |
| $2NH^3, SnI$ | 219 | ... | 100.00 | | | 100.00 |

G. IODOSTANNITE OF AMMONIUM.—By precipitating tolerably concentrated hydrochlorate of stannous oxide with hydriodate of ammonia.—Greenish-yellow needles, decomposed by water, with separation of red iodide of tin. (P. Boullay.)

| | | | | | | Boullay. |
|---------------------|-----|-----|--------|-------|--|----------|
| | | | | | | Dried. |
| NH^3, HI | 144 | ... | 28.01 | | | 29.02 |
| $2SnI$ | 370 | ... | 71.99 | | | 70.98 |
| <hr/> | | | | | | |
| $NH^4I, 2SnI$ | 514 | ... | 100.00 | | | 100.00 |

H. AMMONIO-PROTOCHLORIDE OF TIN.—2 At. protochloride of tin absorb, when heated, 1 At. ammoniacal gas. (Persoz.)

I. AMMONIO-BICHLORIDE OF TIN.—The fuming spirit of Libavius absorbs ammoniacal gas at ordinary temperatures, causing evolution of heat. (H. Davy.)—The solid mass, as it forms, must be assiduously pulverized, and again exposed to the ammoniacal gas, if we would ensure its complete saturation. (H. Rose.) The white mass may be sublimed without decomposition (even in hydrogen gas: *H. Rose*), and when heated in the air, evaporates in white pungent fumes. (H. Davy.) When dissolved in water it reddens litmus strongly. (Grouvelle.) After sublimation, it is crystalline and has a somewhat yellowish white tint. When heated with sodium, it emits a brilliant violet light, and is resolved into granules of tin, chloride of sodium, and ammoniacal gas. It dissolves completely in cold water (Grouvelle, *H. Rose*), only that which has not been sublimed forming a turbid solution. The solution, if evaporated in vacuo over oil of vitriol, leaves the unde-

composed compound in the form of a mass of crystals, which sublime without decomposition. But if the cold solution (which gives no turbidity with ammonia) be heated, or left to itself for a few days, it deposits a jelly. Sulphuric acid likewise gives a gelatinous precipitate, soluble in a larger quantity of water. The same character is exhibited by aqueous bichloride of tin, to which a small quantity of ammonia has been added. The compound is not altered by phosphuretted hydrogen gas in the cold; when heated, it gives off ammonia and turns red on the surface, probably from formation of a small quantity of chlorostannate of phosphuretted hydrogen. (H. Rose, *Pogg.* 24, 163.)

| | H. Rose. | | | | Persoz. | Grouvelle. | | | | | |
|-------------------------------------|-----------|-----|---------------|-----|---------|------------|--------|-----|--------|-----|--------|
| | sublimed. | | not sublimed. | | | | | | | | |
| NH ³ | 17.0 | ... | 11.58 | ... | 10.92 | ... | 13.27 | ... | 20.45 | ... | 20.94 |
| SnCl ² | 129.8 | ... | 88.42 | ... | 89.08 | ... | 86.73 | ... | 79.55 | ... | 79.06 |
| NH ³ , SnCl ² | 146.8 | ... | 100.00 | ... | 100.00 | ... | 100.00 | ... | 100.00 | ... | 100.00 |

The unsublimed compound yields a larger quantity of ammonia, because free ammonia adheres to it. (H. Rose.) According to Grouvelle and Persoz (*Ann. Chim. Phys.* 44, 322), the compound = 2NH³, SnCl².

K. CHLOROSTANNITE OF AMMONIUM.—This is the residue obtained when tin-flings are heated with sal-ammoniac, ammonia and hydrogen gas being evolved; at a higher temperature it sublimes. (Proust, *N. Gehl.* 1, 249; Berzelius.) Regular octohedrons, which are permanent in the air, and redden litmus; their solution in water becomes turbid on boiling. (Apjohn.)

| | Apjohn. | | | | |
|-------------------------------------|---------|-----|--------|-------|-------|
| NH ⁴ Cl | 53.4 | ... | 34.06 | | 34.1 |
| SnCl | 94.4 | ... | 60.20 | | 60.3 |
| HO | 9.0 | ... | 5.74 | | 5.6 |
| NH ⁴ Cl, SnCl + Aq. | 156.8 | ... | 100.00 | | 100.0 |

† Poggiale (*Compt. rend.* 20, 1180) has formed a compound containing 2NH⁴Cl, SnCl + 3Aq; it crystallizes in needles grouped in tufts, permanent in the air and decomposed by water. †

L. CHLOROSTANNATE OF AMMONIUM.—*Pink Salt.*—1. Precipitated in the form of a white powder, on mixing concentrated solutions of bichloride of tin and sal-ammoniac. When a dilute mixture of the two solutions is slowly evaporated, the compound is deposited in small regular octohedrons and cubo-octohedrons. (Bolley, *Ann. Pharm.* 39, 100.) It may also be obtained by mixing a solution of 40 parts of tin in aqua-regia with 35 parts of sal-ammoniac at 100°, evaporating to dryness, dissolving the perfectly dried residue, which amounts to 120 parts, in water, and leaving the solution to crystallize. (Wittstein, *Repert.* 64, 7.)—2. Sublimes in transparent octohedrons during the preparation of mosaic gold with tin, sal-ammoniac, and sulphur, and may be purified by solution, filtration, and crystallization. (Gm.) The crystals decrepitate when heated, then evolve bichloride of tin, and afterwards sublime in white laminae. (Wittstein.) Dissolves in 3 parts of water at 14.5°. The concentrated solution does not decompose on boiling; the dilute solution, when boiled, deposits the whole of the stannic oxide in white flakes. (Bolley.)

| | | | | Boley. |
|---|-------|------|--------|--------|
| NH ⁴ | 18.0 | | 98.2 | 9.9 |
| Cl | 35.4 | | 19.33 | 19.2 |
| SnCl ² | 129.8 | | 70.85 | 70.9 |
| <hr/> | | | | |
| NH ⁴ Cl, SnCl ² | 183.2 | | 100.00 | 100.0 |

M. HYDROCHLORATE AND STANNITE OF AMMONIA.—By supersaturating aqueous protochloride of tin with ammonia till the precipitated stannous oxide is redissolved, and evaporating the solution in vacuo, this compound is obtained in crystals. (Berzelius.)

N. NITRATE OF STANNIC OXIDE AND AMMONIA.—Nitrate of ammonia increases the solubility of stannic oxide in nitric acid; hence it is easier to dissolve tin without precipitation in nitric acid containing nitrate of ammonia. (Vid. *Nitrate of Stannic Oxide*, p. 92; also *Ann. Chim.* 42, 218.)

TIN AND POTASSIUM.

A. ALLOY OF TIN AND POTASSIUM.—*a.* Seven volumes of tin-flings unite with 2 volumes of potassium, with faint incandescence, and form an alloy, which is somewhat less white than tin, brittle, of fine-grained fracture, and easily fusible. Oxidizes quickly in the air, effervesces with water, and still more with aqueous acids.—*b.* With a larger quantity of potassium an alloy is obtained, which often, especially during pulverization, takes fire in the air. (Gay-Lussac & Thénard).—*c.* When granulated tin is ignited with cream of tartar, or 100 parts of stannic oxide with 60 parts of tartar carbonized by roasting, and 8 parts of lamp-black (with 16 lamp-black a pyrophorus is formed), the tin takes up a small quantity of potassium, so that when thrown into water, it slowly evolves hydrogen gas. (Serullus, *Ann. Chim. Phys.* 21, 200.)

B. STANNITE OF POTASH.—Hydrated stannous oxide dissolves readily in caustic potash. The solution is resolved, especially when heated, into crystallized tin and stannate of potash. (Proust.) Zinc separates the tin from it in soft laminae. (Klaproth.) When solution of potash is completely saturated with hydrate of stannous oxide, and then left to evaporate in vacuo, the potash, at a certain degree of concentration, withdraws the water from the hydrated oxide, which thereupon becomes insoluble and falls to the bottom. (Fremy.)

C. STANNATE OF POTASH.—*a. Ordinary.*—*a. Monostannate.*—1. By fusing stannic oxide or either of its hydrates with hydrate or carbonate of potash. If the fusion with carbonate of potash be interrupted before the carbonic acid is completely expelled, the same effect is produced as with titanic acid and carbonate of potash. (III. 484; H. Rose.) The fused mass generally contains an excess of potash.—2. By dissolving stannic oxide, or the ordinary or anomalous hydrate in hot, strong potash-ley. The solution saturated with hydrated stannic oxide and then evaporated in vacuo over oil of vitriol to a considerable degree of concentration, yields colourless, shining, oblique rhombic prisms, whose very acute lateral edges are often truncated; they have a caustic alkaline taste, do not deliquesce in the air, but absorb carbonic acid from it. Easily soluble in water whether hot or cold. (Moberg, *Ber. Jahresber.* 22, 142; *Ber. über d. Versamml. d. Naturf. in Prag.* 1837.) The

crystals turn red when heated, but do not melt. (Proust.) Lead immersed in the aqueous solution precipitates the whole of the tin. (Fischer, *Pogg.* 9, 263.) Copper in contact with tin is quickly tinned by the solution. (Böttger, *Ann. Pharm.* 39, 171.) Alcohol added to the solution precipitates the salt β .—¶ Ordinary stannate of potash does not lose its solubility in water by ignition; acids added to the solution of the ignited salt, throw down stannic acid, perfectly soluble in nitric acid. (Fremy.) ¶

| <i>Anhydrous.</i> | | <i>Crystallized.</i> | | <i>Moberg.</i> |
|------------------------|-------------------|------------------------|-------------------------|----------------|
| KO | 47.2 38.62 | KO | 47.2 31.64 | 31.88 |
| SnO ² | 75.0 61.38 | SnO ² | 75.0 50.27 | 49.00 |
| | | 3HO | 27.0 18.09 | 18.06 |
| KO, SnO ² | 122.2 100.00 | + 3Aq. | 149.2 100.00 | 98.94 |

β . *Acid Salt*.—1. By precipitating the aqueous solution of α with alcohol.—2. When stannic salt is precipitated by carbonate of potash, hydrated stannic oxide containing potash is precipitated; and this, after the saline solution has been removed by decantation, dissolves in pure water, forming a milky liquid, which gives a precipitate with carbonate of potash. (Berzelius.)

b. Anomalous.—*Fremy's Metastannate of Potash*.—When the anomalous hydrate of stannic oxide is boiled with a very dilute solution of potash, a solution is formed, containing 16 parts of stannic oxide to 1 part of potash. The liquid, which appears bluish-white and opalescent by reflected, and deep yellow by transmitted light, becomes gelatinous on evaporation, and afterwards dries up to a deep yellow substance, which re-dissolves when treated with water. This substance is resolved by ignition into insoluble stannic oxide and a compound of potash with a small quantity of stannic oxide, which may be extracted by water. (Berzelius.) The anomalous hydrate dissolves imperfectly in aqueous potash, and, when the solution is left to itself for some time, partly separates out again. It does not dissolve in aqueous carbonate of potash. (H. Rose, *Anal. Chem.*) ¶ Fremy prepares metastannate of potash by dissolving metastannic acid (p. 73) in dilute potash-ley and adding solid caustic potash, whereupon the compound separates in the form of a white granular precipitate. This precipitate, when dried upon a porous porcelain plate, becomes resinous and translucent; it dissolves completely in water, forming an alkaline liquid which cannot be made to crystallize by evaporation, but on the addition of an acid, yields a precipitate of metastannic acid insoluble in nitric acid. Metastannate of potash, when heated with excess of caustic potash or left in contact with it for several days, is converted into stannate of potash. By ignition it is dehydrated and decomposed. From the ignited salt, water extracts potash and only a small quantity of metastannic acid; 100 parts of the salt, after ignition and treatment with water, yield 79 parts of metastannic acid. Fremy assigns to this salt the formula $\text{KO,Sn}^5\text{O}^{10} + 4\text{HO}$. (*N. Ann. Chim. Phys.* 23, 393.) ¶

D. *SULPHOSTANNATE OF POTASSIUM*.— KS,SnS^2 .—By dissolving anhydrous or hydrated bisulphide of tin in hydrosulphate of potash. If the bihydrosulphate be used, the second atom of hydrosulphuric acid is given off with effervescence; if the sulphide of tin is anhydrous, a boiling heat is required to insure saturation. Caustic potash with bisulphide of tin yields the same solution, likewise, however, containing stannate of potash.



Pale yellow liquid. When digested with excess of hydrated bisulphide of tin, it converts the latter into sesquisulphide, tin being deposited and sulphur dissolved, and a solution of polysulphide of potassium formed. Acids added to the solution of sulphostannate of potassium evolve hydro-sulphuric acid and precipitate bisulphide of tin:



For every 2·12 parts of bisulphide of tin (in the anhydrous state) which hydrochloric acid throws down from the liquid, there are formed 1·63 parts of chloride of potassium. Alcohol added to the yellow solution throws down a more concentrated solution of the same compound, in the form of a light yellow thickish liquid. (Berzelius.)

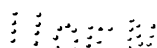
E. IODOSTANNITE OF POTASSIUM.—Concentrated solutions of proto-chloride of tin and iodide of potassium solidify when mixed, in consequence of the formation of yellowish silky needles; the same may be obtained, but in a finer state of crystallization, from a solution in hot alcohol. When chlorine gas is passed over the anhydrous salt, the tin burns with emission of light and forms bichloride of tin, leaving a residue of chloride of potassium. A small quantity of water withdraws iodide of potassium from the salt; the remaining iodide dissolves on the addition of more water. The compound dissolves in hot alcohol, leaving but a small quantity of iodide of tin behind, and the solution yields crystals on cooling. (P. Boullay.)

| | | | | Or: | | | | | Boullay. |
|---------------|-------|------|--------|----------|-------|------|--------|-------|----------|
| K..... | 39·2 | | 7·33 | KI..... | 165·2 | | 30·87 | | 33·76 |
| 2Sn | 118·0 | | 22·05 | 2SnI ... | 370·0 | | 69·13 | | 66·24 |
| 3I | 378·0 | | 70·62 | | | | | | |
| KI, 2SnI..... | 535·2 | | 100·00 | | 535·2 | | 100·00 | | 100·00 |

F. CHLOROSTANNITE OF POTASSIUM.— $2\text{KCl}, \text{SnCl} + 3\text{HO}$. Needles. (Poggiale.)

G. CHLOROSTANNATE OF POTASSIUM.—By evaporating aqueous bichloride of tin with chloride of potassium. Jacquelain (*Ann. Chim. Phys.* 66, 130) dissolves equal numbers of atoms of chloride of potassium and bichloride of tin in water. Wittstein (*Repert.* 64, 7) adds 5 parts of chloride of potassium to a solution of 4 parts of tin in aqua-regia, or fuses 1 At. anomalous hydrate of stannic oxide in a silver crucible with 1 At. hydrate of potash, and dissolves in hydrochloric acid. Bolley (*Ann. Pharm.* 39, 100) mixes dilute hydrochlorate of stannic oxide with excess of chloride of potassium.—Regular octohedrons (Bolley, Wittstein); rhombohedrons (Jacquelain). The crystals, which are permanent in the air, decrepitate when heated, give off bichloride of tin, and leave chloride of potassium mixed with a small quantity of stannic oxide (Bolley), or chloride (Wittstein).

| | | | | Jacquelain. | | | | | Or: | | | | | Bolley. |
|------------------------|-------|------|--------|-------------|-------|------|-------------------|-------|-------|------|-------|------|--|---------|
| K..... | 39·2 | | 19·18 | | 19·42 | | KCl... | 74·6 | | 36·5 | | 36·3 | | |
| Sn | 59·0 | | 28·86 | | 28·67 | | SnCl ² | 129·8 | | 63·5 | | 63·7 | | |
| 3Cl | 106·2 | | 51·96 | | 51·85 | | | | | | | | | |
| KCl, SnCl ² | 204·4 | | 100·00 | | 99·94 | | 204·4 | | 100·0 | | 100·0 | | | |



H. HYDROCHLORATE AND STANNITE OF POTASH.—The liquid obtained by supersaturating hydrochlorate of stannous oxide with potash till the precipitate is re-dissolved, yields crystals when evaporated in *vacuo*. (Berzelius.)

TIN AND SODIUM.

A. ALLOY OF TIN AND SODIUM.—Four volumes of tin-filings unite with 1 volume of sodium at the melting point of tin—the combination being attended with evolution of light and heat—and form a white, very brittle, fine-grained alloy, which oxidizes in the air, and effervesces with water and with aqueous acids. (Gay-Lussac & Thénard.) The alloy may likewise be formed by igniting tin with charred soap. (Serullus.)

B. STANNITE OF SODA.—Hydrated stannous oxide dissolves in aqueous solution of soda.

C. STANNATE OF SODA.—*a. Ordinary.*—Solution of soda saturated with ordinary hydrate of stannic oxide yields—though not without difficulty—six-sided tabular crystals, which are lighter than the potash-salt and soluble in water. (Moberg.)

| <i>Anhydrous.</i> | | <i>Crystallised.</i> | | <i>Moberg.</i> | |
|----------------------------|-------|------------------------|-------|----------------|------|
| NaO | 31·2 | NaO | 31·2 | 23·42 | 23·5 |
| SnO ² | 75·0 | SnO ² | 75·0 | 56·31 | 56·0 |
| | | 3HO | 27·0 | 20·27 | 20·2 |
| <hr/> | | <hr/> | | <hr/> | |
| NaO,SnO ² | 106·2 | +3Aq | 133·2 | 100·00 | 99·7 |

If hydrochlorate of stannous oxide be precipitated at a temperature above 40° with excess of carbonate of soda, the filtrate, on cooling, deposits a compound, which effervesces with acids after being washed, and is therefore probably a carbonate of stannous oxide and soda. (Leykauf, *J. pr. Chem.* 21, 317.)—*¶. b. Metastannate.*—Obtained by the action of concentrated soda-ley on metastannic acid. The salt is very difficultly soluble in water, white, granular, and crystalline. It is resolved at 60° (or at a boiling heat, if in solution) into metastannic acid and soda. Its composition appears to be : NaO,Sn²O¹⁰ + 4Aq. (Fremy.) ¶.

D. SULPHOSTANNATE OF SODIUM.—Similar to the potassium-compound. (Berzelius.)

E. IODOSTANNITE OF SODIUM.—When a solution of iodide of sodium in concentrated hydrochlorate of stannous oxide is left to stand for some hours, it first deposits iodide of tin, and then pale yellow crystals of the iodostannite, decomposable by water. (P. Boullay.)

F. CHLOROSTANNATE OF SODIUM.—By evaporating a mixture of bichloride of tin and common salt. According to Wittstein, 1 part of common salt with 1 part of tin dissolved in aqua-regia; or 1 At. anomalous hydrate of stannic oxide fused with 1 At. hydrate of soda, and dissolved in hydrochloric acid. Anhydrous, deliquescent cubes, which, when ignited, leave common salt with a small quantity of chloride of tin. (Wittstein.) Rhombic laminae, which are permanent in cold air, effloresce in warm air, give off 12 or 13 per cent. of water at 100, and the chloride of tin at

a red heat. (Bolley.) It remains to be determined by analysis, whether the salts obtained by Wittstein and by Bolley differ in anything besides their quantity of water. Lewy has formed a compound containing $\text{NaCl}, \text{SnCl}^2 + 5 \text{ Aq.}$

G. HYDROCHLORATE AND STANNITE OF SODA.—Analogous to the potash-compound. Delicate needles. (Berzelius.)

TIN AND BARIUM.

By heating tin to whiteness with baryta, strontia or lime, and charcoal, Gay-Lussac and Thénard did not succeed in forming alloys of tin with the metals of these alkalis.

A. STANNATE OF BARYTA.—Precipitated on mixing baryta-water or a baryta-salt with aqueous stannate of potash. The precipitate produced by baryta-water contains 20.9 (1 At.) baryta to 79.1 (4 At.) stannic acid. (Berzelius.) Moberg, by precipitating chloride of barium with stannate of potash, obtained a heavy white powder = $\text{BaO}, \text{SnO}^2 + 6 \text{ Aq.}$

B. SULPHOSTANNATE OF BARIUM.—Sulphostannate of potassium forms with baryta-salts, a light yellow precipitate soluble in water. (Berzelius.)

C. IODOSTANNITE OF BARIUM.—By dissolving stannous iodide in aqueous iodide of barium. Very soluble salt. (P. Boullay.)

† D. CHLOROSTANNITE OF BARIUM.— $\text{BaCl}, \text{SnCl} + 4 \text{ Aq.}$ Prepared by Poggiale.

E. CHLOROSTANNATE OF BARIUM.— $\text{BaCl}, \text{SnCl}^2 + 5 \text{ Aq.}$ Prepared by Lewy. †.

F. HYDROCHLORATE AND STANNITE OF BARYTA.—Analogous to the potash-compound.

TIN AND STRONTIUM.

A. STANNATE OF STRONTIA.—By precipitating stannate of potash with strontia-water or a strontia-salt.

B. SULPHOSTANNATE OF STRONTIUM.—As with barium.

C. IODOSTANNITE OF STRONTIUM.—As with barium.

† D. CHLOROSTANNITE OF STRONTIUM.— $\text{SrCl}, \text{SnCl} + 4 \text{ Aq.}$ —Prepared by Poggiale.

E. CHLOROSTANNATE OF STRONTIUM.— $\text{SrCl}, \text{SnCl}^2 + 5 \text{ Aq.}$ —Prepared by Lewy. †.

F. HYDROCHLORATE AND STANNITE OF STRONTIA.—Analogous to the potash-compound. Delicate needles. (Berzelius.)

TIN AND CALCIUM.

A. STANNATE OF LIME.—Slowly precipitated when a lime-salt is mixed with stannate of potash. Contains $\text{CaO}, \text{SnO}_2 + 4 \text{ Aq.}$ (Moberg.)

B. SULPHOSTANNATE OF CALCIUM.—Analogous to the barium compound.

TIN AND MAGNESIUM.

A. STANNATE OF MAGNESIA.—Stannate of potash precipitates from magnesia-salts a magma, which stops up the filter and cannot be washed. (Moberg.)

† B. CHLOROSTANNATE OF MAGNESIUM.— $\text{MgCl}, \text{SnCl}_2 + 5 \text{ Aq.}$ Prepared by Lewy. †

C. HYDROCHLORATE AND STANNITE OF MAGNESIA.—Similar to the potash-salt. Deliquescent.

TIN AND SILICIUM.

A. SILICIDE OF TIN.—Tin fuses with silicium before the blowpipe, forming a ductile alloy, which, when dissolved in acids, leaves a small quantity of silica. (Berzelius, *Pogg.* 1, 220.)

Quadrosilicate of soda precipitates bichloride of tin, but not the protochloride. (Walcker.)

B. SILICO-FLUORIDE OF TIN.—Long prisms, very easily soluble in water. On evaporating the solution in the air, the stannous oxide is converted into stannic oxide, and is precipitated in combination with silica. (Berzelius.) According to Berzelius (*Pogg.* 1, 200), this salt contains protofluoride of tin; according to Berzelius's *Lehrbuch* (4, 532), on the contrary (writing the formula in accordance with the numbers adopted in this *Hand-book*), it is $\text{SnF}_2, \text{SiF}_2$.

TIN AND TUNGSTEN.

A. TUNGSTATE OF STANNOUS OXIDE, OR STANNOUS TUNGSTATE.—Monotungstate of potash added to hydrochlorate of stannous oxide throws down a yellow powder, which gives off water and turns brown when heated, and bakes together at a red heat. Hydrochloric acid extracts from the powder the stannous oxide, which then converts the separated tungstic acid into blue oxide. The salt dissolves in oxalic acid and in potash, slowly in boiling phosphoric acid, and not at all in water. (Anthon, *J. pr. Chem.* 9, 341.)

| | Ignited. | | Anthon. | | Unignited. | | Anthon. | |
|----------------------------|----------|--------|---------|--------|------------|-------|---------|-----|
| SnO | 67 | 35·83 | 35·9 | 67 | 27·8 | 29 | 67 | 29 |
| WO ³ | 120 | 64·17 | 64·1 | 120 | 49·8 | 50 | 120 | 50 |
| | | | | 6HO | 22·4 | 22 | | |
| SnO, WO ³ | 187 | 100·00 | 100·0 | + 6Aq. | 241 | 100·0 | 100 | 100 |

B. STANNOUS SULPHOTUNGSTATE.— SnS, WS^2 .—Voluminous brown flakes. (Berzelius.)

C. STANNIC SULPHOTUNGSTATE.— $\text{SnS}^2, \text{WS}^2$.—Greyish-yellow flakes. (Berzelius.)

TIN AND MOLYBDENUM.

A. MOLYBDATE OF STANNIC OXIDE, OR STANNIC MOLYBDATE.—Grey powder, insoluble in water, but soluble in dilute hydrochloric acid with a blue, in concentrated hydrochloric acid with a green, and in aqueous potash with a brown colour; not altered by nitric acid. (Berzelius.) The blue precipitate, obtained by mixing an alkaline molybdate with stannous hydrochlorate, or by placing tin in contact with molybdic acid, water, and a very small quantity of hydrochloric acid—Richter's *Blue Carmine*, which was regarded by Bucholz as a molybdanite of stannic oxide—is, according to Berzelius, nothing more than a mixture of stannic molybdate and blue oxide of molybdenum.

B. STANNOUS SULPHOMOLYBDATE.—Formed by precipitating a stannous salt. Black precipitate.

C. STANNIC SULPHOMOLYBDATE.—By precipitating a stannic salt. The translucent brown precipitate becomes brownish-grey on drying.

D. STANNOUS PERSULPHOMOLYBDATE.—Hydrochlorate of stannous oxide is completely precipitated by an aqueous solution of the potassium-salt. The dark brown precipitate, when immersed in the liquid and exposed to the air, is converted into E, and dissolves gradually, forming a red solution.

E. STANNIC PERSULPHOMOLYBDATE.—Red precipitate, slightly soluble in water, in which it forms a red solution; hence, when it is precipitated, a portion remains dissolved. (Berzelius, *Pogg.* 7, 287.)

Alkaline *Vanadates* give no precipitates with tin-salts. The yellow mixture of vanadate of ammonia with hydrochlorate of stannous oxide loses its colour after a while; the mixture of vanadate of ammonia with hydrochlorate of stannic oxide remains yellow. (Berzelius.)

TIN AND CHROMIUM.

A. *Stannate of Chromic Oxide?*—a. By heating chromate of stannic oxide to bright redness, a dark violet mass is obtained, which communicates to glazings a variety of tints, from rose-red to violet. (Leykauf, *J. pr. Chem.* 19, 127.)—b. *Hyper-acid Salt.*—*Mineral lac, Lacque minérale.* 50 parts of stannic oxide very strongly ignited with 1 part of chromic oxide, yield a mass consisting of fine crystals and vitreous globules, of beautiful and very durable colour.—c. *Hyperacid Salt containing Stannate of Lime.*—*Pink-colour.*—100 parts of stannic oxide are strongly ignited for some hours with 34 parts of chalk and from 1 to 1½ pt. chromic oxide, or 3 to 4 chromate of potash (perhaps also with the addition of 1 part silica and 1 part alumina). The dingy-red mass is washed with water containing hydrochloric acid, and thereby acquires a beautiful rose-red colour. It is soluble in rather strong hydro-

ehleric acid, which is not the case with mineral lac; it is used to produce a red colour on *Fayence*. (Malaguti, *Ann. Chim. Phys.* 61, 433.)—*d. Hydrated?*—Monochromate of potash added to hydrochlorate of stannous oxide throws down a green mixture of chromic oxide and stannic oxide. (Gronvelle.)

B. CHROMATE OF STANNOUS OXIDE.—When hydrochlorate of stannous oxide is added to chromate of potash, the latter being in excess and the liquid agitated, chromate of stannous oxide is precipitated in yellow, curdy flocks. (Berzelius.) On the contrary, when dilute chromate of potash is added by small portions at a time, and with constant agitation, to hydrochlorate of stannous oxide, a greenish-white precipitate is produced, probably consisting of stannate of chromic oxide. If the tin-solution contains free acid, the whole remains dissolved, forming a green solution.

C. CHROMATE OF STANNIC OXIDE.—Bi-hydrochlorate of stannic oxide, not containing any further excess of acid, forms a yellow precipitate with chromate of potash. The liquid above the precipitate acquires an orange-yellow colour, in consequence of the liberation of chromic acid.—The precipitate, after drying, is brownish-yellow and translucent, and is converted by ignition into violet-coloured stannate of chromic oxide.

TIN AND MANGANESE.

STANNATE OF MANGANOUS OXIDE.—White powder, which gradually becomes dark brown by exposure to the air. (Berzelius.) According to Moberg, it acquires a yellow colour.

Permanganate of potash gives no precipitate with hydrochlorate of stannic oxide. (Fromherz.)

TIN AND ARSENIC.

A. ARSENIDE OF TIN.—1. When pulverized arsenic is stirred about in melted tin, combination takes place, attended with evolution of light and heat. (Gehlen, A. Vogel.)—2. By heating tin with arsenious acid. (Gehlen.)—White, sonorous, and brittle, if the tin be not in too great excess; of laminar texture, and less fusible than tin.—Gives off its arsenic when fused in an open vessel. With hydrochloric acid it evolves arseniuretted hydrogen gas.—When it is dissolved in hydrochloric acid, there remains a black compound of tin with excess of arsenic, which gives off its arsenic when ignited, and then dissolves again in acids. An alloy containing excess of arsenic is not attacked by hydrochloric acid. (Soubeiran.)

B. Arsenite of Stannic Oxide or Arseniate of Stannous Oxide?—1. Arsenic acid with acetate of stannous oxide, or arseniate of potash with hydrochlorate of stannous oxide, forms a white precipitate, insoluble in water.—2. Tin dissolves in aqueous arsenic acid—arseniuretted hydrogen being evolved—and forms a gelatinous mass. (Scheele.)

C. STANNOUS SULPHARSENITE.—By precipitating hydrochlorate of stannous oxide with a saturated solution of orpiment in hydrosulphate of

soda. The dark brown precipitate does not fuse when heated, but gives off part of its orpiment, and leaves a grey, metallic, porous mass.

D. STANNIC SULPHARSENITE.—The yellow, gummy precipitate obtained with hydrochlorate of stannic oxide, becomes orange-yellow on drying, yields a powder of a fine yellow colour, and behaves like C when heated. (Berzelius, *Pogg.* 7, 147.)

E. STANNOUS SULPHARSENATE.—Both the bibasic and the terbasic sulpharsenite of sodium give dark chestnut-brown precipitates with hydrochlorate of stannous oxide.

F. STANNIC SULPHARSENATE.—Both the bibasic and terbasic sodium-salts form, with hydrochlorate of stannic oxide, pale yellow, gummy precipitates, which stop up the filter, and become orange-yellow on drying. (Berzelius, *Pogg.* 7, 28.)

G. Bichloride of tin combines with terchloride of arsenic, the combination being attended with evolution of heat. (J. Davy.)

TIN AND ANTIMONY.

A. ANTIMONIDE OF TIN.—Formed by fusing the two metals together—in which case the combination takes place without evolution of light and heat—or by fusing sulphide of antimony with excess of tin.

a. 12 pts. tin to 1 antimony. The alloy called *Peuter*, used for making vessels to hold liquids.

b. 10 pts. tin to 1 antimony. Perfectly ductile. (Chaudet.)

c. 7 pts. tin to 1 antimony. Produces a fine tone. (Kastner, *Kastn. Arch.* 19, 324.)

d. 3 pts. tin to 1 antimony. Less ductile than tin; sp. gr. 7.059. (Chaudet.)

e. 1.5 pts. tin to 1 antimony. Brittle, less laminar than antimony. (Gehlen.)

f. 1 pt. tin to 1 antimony. Extremely brittle; easily pulverized; sp. gr. 6.803. (Chaudet.)

The ductile alloys are rendered brittle by the addition of a small quantity of lead. If the quantity of tin be not less than 9 times as great as that of the antimony, boiling hydrochloric acid extracts the whole of it (with evolution of antimoniuretted hydrogen?), and leaves the antimony in the form of a black powder. (Chaudet, *Ann. Chim. Phys.* 3, 376; also *N. Tr.* 2, 1, 167.)

B. ANTIMONIATE OF STANNIC OXIDE.—When hydrochloric acid in which antimonious acid and stannic oxide are dissolved together, is diluted with water, the two metallic acids are precipitated in combination, and the liquid loses nearly all the metal that it contained. (Thénard.)—If tin on the one hand, and antimony on the other, be heated with excess of nitric acid, till red fumes are no longer given off, and the two liquids be then mixed, the two white powders therein contained are converted into a yellow powder, with fresh evolution of nitrous vapours,—because the antimoniante of antimonious oxide [nitrate of antimonious oxide] formed from the antimony, becomes oxidized and converted into antimonious acid,

which then unites with the stannous oxide [stannic oxide]. (Levol, *N. Ann. Chim. Phys.* 1, 504; also *J. pr. Chem.* 24, 253.)

C. STANNOUS SULPHANTIMONIATE.—Schlippe's salt gives a dark brown precipitate with hydrochlorate of stannic oxide. (Rammelsberg.)

TIN AND TELLURIUM.

A. TELLURIDE OF TIN.—Tellurium fuses with tin.

B. STANNOUS SULPHOTELLURITE.—The brown precipitate turns black on drying, and, when heated in a retort, gives off sulphur, and is converted into a grey mass having the metallic lustre.

C. STANNIC SULPHOTELLURITE.—The precipitate is dark brown. (Berzelius.)

TIN AND BISMUTH.

A. ALLOYS OF TIN AND BISMUTH.—An alloy of 177 parts (3 At.) of tin and 213 parts (1 At.) of bismuth, when cooled from a state of fusion, exhibits but one solidifying point—inasmuch as it first cools regularly down to 143°, and then remains at that temperature for a considerable time, till the latent heat set free in the solidification of the alloy, has had time to escape. But all other alloys of these metals likewise exhibit a higher solidifying point (which may be distinguished as the *Point of Separation*), inasmuch as the excess of the one or the other metal [or rather—since the point is variable—another definite alloy containing an excess of one of the two metals] solidifies first, and afterwards, at 143°, the hitherto fluid alloy containing Sn³Bi. The higher solidifying point, or point of separation, is 190° for Sn⁶Bi, 160° for Sn⁴Bi, 150° for Sn²Bi, 170° for Sn⁴Bi³, and 190° for SnBi. (Rudberg, *Pogg.* 18, 240.)

a. 40 parts tin to 1 bismuth; perfectly ductile; the addition of 1 part of lead diminishes its extensibility.

b. 25 parts of tin to 1 bismuth. Slightly ductile. (Chaudet.)

c. 8 parts tin to 1 bismuth. Fuses at 199°. (Lewis.)

d. 3 parts tin to 1 bismuth. Pulverizable; of dull grey fracture, and specific gravity 7.776. Gives up all its tin with a small quantity of bismuth to heated hydrochloric acid. (Chaudet.)

e. 2 parts tin to 1 bismuth. Fuses at 166°. (Lewis.)

f. 236 parts (4 At.) tin to 213 parts (1 At.) bismuth. Sp. gr. 8.085. (Regnault.)

g. 1 part tin to 1 bismuth. Perfectly brittle; pulverizable; of fine-grained fracture; sp. gr. 8.345. (Chaudet.) Fuses at 138°. (Lewis.) Expands strongly in solidifying. (Marx.) With hydrochloric acid it behaves like d. (Chaudet, *Ann. Chim. Phys.* 5, 142; also *N. Tr.* 2, 2, 349.)

h. 177 pts. (3 At.) tin to 213 pts. (1 At.) bismuth. Fuses between 131° and 137°. (Dobereiner, *Kastn. Arch.* 3, 90.)

i. 118 pts. (2 At.) tin to 213 pts. (1 At.) bismuth. Sp. gr. 8.759. (Regnault.)

B. ALLOY OF ANTIMONY, BISMUTH, AND TIN.—236 parts (4 At.) tin to 213 pts. (1 At.) bismuth, and 129 pts (1 At.) antimony. Sp. gr. 7.883 at 20°. (Regnault, *Ann. Chim. Phys.* 76, 186.)

TIN AND ZINC.

A. ALLOYS OF TIN AND ZINC.—These two metals fuse together with ease; the alloy is harder than either tin or zinc, and less extensible than tin. Sn^6Zn has but one solidifying point, viz., at 204° . (Compare the observations made with reference to *Bismuth and Tin*.) The other alloys exhibit in addition a higher solidifying point, which varies according to the nature of the alloy. (Rudberg.)

| | Sn^{12}Zn | Sn^6Zn | Sn^4Zn | Sn^3Zn | Sn^2Zn | SnZn | | | |
|---------------------|---------------------------|------------------------|------------------------|------------------------|------------------------|---------------|-------------|------|-------------|
| Variable point | 210° | | 230° | | 250° | | 280° | | 320° |
| Fixed point | 204° | | 204° | | 204° | | 204° | | 204° |

B. STANNATE OF ZINC-OXIDE.—Stannate of potash yields, with zinc-salts, a white precipitate composed of $\text{ZnO}, \text{SnO}^3 + 2\text{Aq}$. (Moberg.)

OTHER COMPOUNDS OF TIN.

With Lead, Iron, Cobalt, Nickel, Copper, Mercury, Silver, Gold, Platinum, Palladium, and Iridium. As tin makes these metals brittle, it was called by the alchemists, *Diabolus Metallorum*.

CHAPTER XXXI.

L E A D .

Bucholz. Lead-oxide and its salts. *A. Gehl.* 5, 253.

Thomson. Oxides of lead. *A. Gehl.* 4, 92.

Berzelius. *Gilb.* 166 and 186; 46, 131. Further: *Schw.* 7, 71.

Winkelblech. Oxides of lead. *Ann. Pharm.* 21, 21; also *J. pr. Chem.* 10, 227.

Bromeis. On the salts produced by the action of lead on the nitrate of lead-oxide. *Ann. Pharm.* 72, 38.

SYNONYMS:—*Blei, Plomb, Plumbum, Saturnus.*

History.—Known from the earliest times.

Sources.—In the metallic state [?]—as red lead; as peroxide; as carbonate, phosphate, sulphate, selenite, tungstate, molybdate, vanadate, chromate, and arseniate of lead-oxide; as aluminate of lead-oxide; as chloride of lead, sometimes united with oxide or carbonate; as selenide of lead; as sulphide of lead, either alone or associated with other metals, as