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Chemistry, theoretical, practical, and analytical, as applied to the Arts and Manufactures

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Bismuth.

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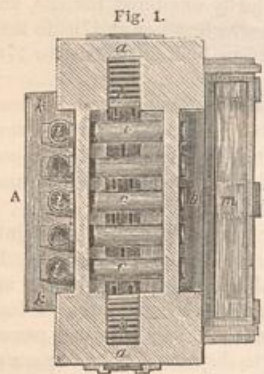
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BISMUTH.—*Etain de Glace*, French; *Wismuth*, German: symbol, Bi; atomic weight, 208 (SCHNEIDER), 210 (DUMAS).—This comparatively rare metal has been known for about three centuries, GEORGE AGRICOLA having described it in 1546 as a metal "somewhat different from lead." In nature, bismuth occurs principally in the metallic state, generally associated with the ores of cobalt, nickel, copper, and silver; and in combination as *Bismuth glance* or *bismuthine*, Bi_2S_3 ; *bismuth ochre*, Bi_2O_3 ; *bismuthite*, $\text{Bi}_2\text{S}_3\text{CO}_3$; *bismuth blende*, Bi_2SiO_3 ; *cupreous bismuth*, $3(\text{Cu}_2\text{S})\text{Bi}_2\text{S}_3$; and combined with copper, silver, lead, cobalt, and nickel, in several other more complex minerals, among which may be mentioned *aciculate* or *needle ore*, *kobellite*, and *bismuthic silver*. It is found with tellurium in *tetradymite*, and with vanadium in *pucherite*.

Bismuth ores occur most plentifully in Saxony, Bohemia, and Transylvania; but they are also found in Norway, Sweden, and the United States, and in England in Cornwall and Cumberland, and Stirlingshire in Scotland.

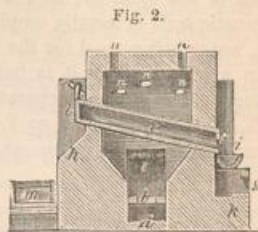
Metallurgy.—Bismuth is almost wholly obtained from ores containing the native metal, its extraction from which is rendered exceedingly simple by its ready fusibility. The ancient method was to fire a mixture of ore and fuel, when the metal melted and subsided to the bottom of the heap. At Schneeberg, in Saxony, where the greater part of the bismuth in the market is produced, it is obtained from cobalt ores previously to their employment in the manufacture of smalt.

The operation is conducted in cast-iron retorts placed obliquely, and heated by a furnace beneath them. When the bismuth of the ore with which these retorts are charged is fused, it flows down into an appropriate receiver, leaving behind it the siliceous and other impurities. The furnace used at Schneeberg is represented in the annexed Figs. 1, 2, 3; the first of which is a plan; the second a section at A B, Fig. 1; and the third a front elevation at k k, Fig. 1.



In the plan—Fig. 1—the fire-door is represented by a, the grate by b, and the cylindrical retorts by c c c, which incline towards the iron pans, i i i, where the fused metal is collected. A wall, k k, supports the pans; and to prevent the metal from forming an alloy with the latter, and also to obviate its oxidation, it is customary to throw a little charcoal powder into each. The slag remaining in the pipes after the metal is separated from it, is drawn off into a tank of cold water situated at m. In doing this the heated matter does not splash at once into the water, but falls gently down the declivity,

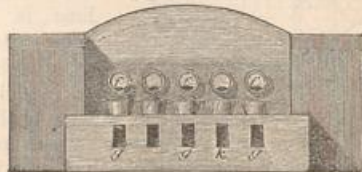
h. This arrangement is shown in elevation—Fig. 2—which is a section of the preceding, the same objects being distinguished by the foregoing letters. The pipes, c c, are closed at the depressed end by clay plates, f, with the exception of a small opening through which the fused metal issues to the receivers, c. A stout cast-iron door-plate, l, secures them at the other end.



The retorts are heated by the fire, e, with the assistance of flues passing from it round each severally, as seen in Fig. 2 and Fig. 3, at g g. The draught of the furnace is increased at will by opening the holes shown at n n, Fig. 2, placed between each pair of retorts.

The ore is prepared by breaking it up and removing the very impure portions; this being effected, about half a hundredweight is introduced into each of the retorts, the door-plates, l, made secure, and the fire stirred up to communicate the required degree of heat. The charge should only be about

Fig. 3.



three-eighths of the capacity of the retorts, in order that it may be conveniently stirred. After the application of the heat for ten minutes the metal begins to run out by the small space in the clay plate, f, at the end; and as soon as the flow slackens the contents of the retort are stirred with a rake till the whole of the metal is obtained, which is usually the case in half an hour. The slag, deprived of all the metal, is then raked out of the retorts into the water tank in front, and replaced by a fresh charge. When the pans, i i i, are nearly full, the fused metal is ladled out and cast into bars, weighing each from 20 to 50 lbs.

At Schneeberg, where about 10,000 pounds of bismuth are annually produced, wood is the fuel employed, 50 cubic feet of which is sufficient to work off a ton of ore.

At Joachimsthal, in Bohemia, a process devised by VOGEL, for extracting bismuth from other ores than those containing the native metal, has latterly been employed. The ore is powdered, mixed with 28 per cent. of small scrap iron, 15 to 50 per cent. of soda ash (according to the amount of silica in the ore), 5 per cent. of lime, and 5 per cent. of fluor spar. Crucibles, 2 feet in height and 16 inches in diameter, are each charged with about 1 cwt. of this mixture, closed, and strongly heated till the mass

becomes pasty. The contents are then well stirred to effect complete mixture, reheated till perfectly liquid, and then ladled into conical moulds. The bismuth, together with the cobalt speiss, subsides to the bottom, and on cooling is separated from the speiss, which, however, still retains about 2 per cent. of bismuth.

Refining.—The bismuth obtained by these methods is contaminated with arsenic, iron, copper, and silver.

The greater part of the arsenic may be removed by strongly heating the bismuth in a crucible under a layer of charcoal, when the arsenic passes off in vapour. TAMM recommends immersing strips of iron in bismuth fused under a layer of borax. He states that the arsenic unites with the iron, and on cooling the still fluid bismuth may be decanted from the iron arsenide, which solidifies more rapidly.

Copper, according to the same authority, may be removed by treating the fused metal with one-sixteenth part of a mixture of 8 parts potassium cyanide, with 3 parts of sulphur, the crucible being kept covered during the deflagration that ensues. The metal is then well stirred and the flux allowed to set, upon which the metal is poured out.

Antimony may be removed by heating the bismuth with about 3 parts of teroxide of bismuth for each part of antimony present, the antimony being converted into oxide, while the oxide of bismuth is at the same time reduced to the metallic state.

Bismuth, when required pure, may be prepared by dissolving ordinary bismuth in just sufficient nitric acid, filtering from arseniate of bismuth and other insoluble impurities, and then largely diluting with water, which precipitates the bismuth as basic nitrate. This precipitate is washed and digested with potash, after which it is again washed, and finally reduced to the metallic state by heating with charcoal in a crucible.

Properties.—Bismuth is a white metal with a tinge of red. It crystallizes in rhombohedra closely resembling cubes, which are obtained artificially in the following manner:—A large quantity of bismuth is fused in a crucible; while still red hot the crucible is embedded in hot sand, so as to cool slowly. When part of the metal has solidified and there is a firm crust on the surface, two holes are made in the crust with a red-hot rod, and through one of them the metal still remaining liquid is poured off; the other hole serves to admit air. Upon breaking the crust the solidified portion will be found beautifully crystallized, the crystals having an iridescent tarnish, caused by contact with the air while yet hot. Bismuth is exceedingly brittle, and it has so little tenacity that a rod one-tenth of an inch in diameter only sustains 40 lbs.

Pure bismuth melts at 264° C. (607° Fahr.); at a high temperature it volatilizes, and may, though with great difficulty, be distilled. Its specific gravity is variously given at from 9.6 to 9.8, the higher number being probably the more correct. When subjected to pressure, instead of being rendered denser, it is reduced in specific gravity. Thus MARCHAND and SCHEERER, by submitting a cylinder of the metal to

powerful pressure, succeeded in reducing its specific gravity from 9.799 to 9.556. It is the most diamagnetic substance known. Its diamagnetic repulsion being nevertheless only $\frac{1}{2500000}$ of the attraction of an equal mass of iron.—(WEBER.)

Bismuth, like water, expands on solidification; but while water expands on cooling from 4° C. to the freezing point, bismuth only expands at the moment of solidification.—(TRIBE.) When fused it can be cooled several degrees below its melting point without solidifying, but the instant that solidification begins, the temperature rises to the fusing point, and remains so till the whole has solidified.—(URE.)

Bismuth is not affected by dry air, and is only slightly acted on by a moist atmosphere; its vapour decomposes steam (REGNAULT), and the solid metal at a white heat decomposes water. When strongly heated in the air, it burns with a bluish flame, evolving light yellow fumes of bismuthous oxide, Bi_2O_3 . In chlorine gas, divided bismuth takes fire, forming bismuthous chloride, BiCl_3 . It is attacked with difficulty by hydrochloric and sulphuric acids, but is readily dissolved by slightly dilute nitric or nitrohydrochloric acids, forming bismuthous nitrate and chloride respectively. It also enters into combination with most of the non-metallic elements, and with many inorganic negative radicles.

Uses in the Arts.—Bismuth is too brittle to be useful by itself, and hence is chiefly employed in the arts for alloying with other metals, generally lead and tin, in order to communicate to the resulting alloy, either fusibility or the property of expansion on solidification above referred to. In bell-founding, bismuth is of considerable value, its alloy with tin being very sonorous.

Bismuth is sometimes employed in stereotype metal to communicate its expansive property, which causes the alloy to take a very exact impression, and for the same reason it is used by die sinkers in the fusible metal employed to test the accuracy and finish of a die.

Fusible metal is an alloy of bismuth, tin, and lead. Thus, an alloy of 8 parts bismuth, 5 of lead, and 3 of tin melts at 202° Fahr.; and another, consisting of 2 parts bismuth, 1 of lead, and 1 of tin, liquefies at 200.75 Fahr.—(ROSE.) Both these alloys are liquid in boiling water.

These fusible metals are rendered still more fusible by the addition of small quantities of mercury; such alloys are serviceable for taking casts of anatomical preparations.

The soft solder employed by pewterers consists of 1 part bismuth, 2 of tin, and 1 of lead; and the same composition has been proposed as a bath for tempering steel instruments, and has also been used in making the cake moulds for fancy toilet soaps.

An alloy for electrotype moulds is composed of 8 parts bismuth, 8 lead, and 3 tin. It melts at 228° Fahr. It is allowed to cool till it acquires a pasty consistency, and the warmed medal, or other article, pressed upon it and kept under pressure till cold.

If 2 parts of hot mercury be added to 1 part of

fused bismuth, a pasty amalgam is obtained, which after a time becomes granular, hard, and partly crystalline. Since a small quantity of bismuth only slightly diminishes the fluidity of mercury, it is occasionally used to adulterate the latter. This fraud may be detected by shaking the mercury with air, when a black powder separates.—(GMELIN.)

Bismuth and silver, when fused together in equal proportions, form a bismuth-coloured alloy. The silver may be extracted by cupellation, in the same manner as from argentiferous lead. Gold may also be extracted from its alloy with bismuth by cupellation.

Platinum and also palladium readily alloy with bismuth; 1 part of platinum or 2 parts of palladium form severally with 2 parts of bismuth, grey, brittle, fusible alloys.

Bismuth when alloyed with copper renders the copper harder, but at the same time brittle: 4 parts of bismuth and 1 of copper form an alloy having the red colour of copper and the crystalline texture of bismuth.

If a small quantity of bismuth be added to lead, it makes the latter tougher without becoming brittle. Equal weights of each give an alloy which resembles bismuth in all its properties, being of red tint, brittle, and laminar.

Oxides.—Four oxides are known, viz.:—The dioxide, Bi_2O_2 ; bismuthous oxide, or the trioxide, Bi_2O_3 ; tetroxide, Bi_2O_4 ; and bismuthic oxide, or the pentoxide, Bi_2O_5 .

Bismuthous oxide, or the trioxide (Bi_2O_3) is the most important of these, and the only one which has received any industrial application. It occurs in nature as bismuth-ochre, associated with oxide of iron, carbonic acid, and water, at Schneeberg and Joachimsthal, and with gold in Siberia. It may be readily prepared by heating the neutral or basic nitrate until nitric fumes cease to be evolved. When pure, this oxide is of a straw yellow colour; at a red heat it fuses to an opaque glass, which, while hot, is dark brown or black, but on cooling again becomes yellow. In the arts it is used for fixing the gilding on porcelains, since at a high temperature it acts as a powerful flux towards siliceous matters. It is also employed to destroy the colours which would be given by many substances used as fluxes.

Hydrated bismuthous oxide ($\text{Bi}_2\text{O}_3 \cdot \text{H}_2\text{O}$) forms as a white precipitate, when an alkali is mixed with a solution of any bismuthous salt, and as a white powder, when the basic nitrate or chloride is triturated with an alkali. When boiled with potash, it is converted into the yellow oxide through loss of its water of hydration. Heated with an alkaline solution of metallic sulphides, it converts them into the corresponding oxides.

The oxide and hydrate when treated with acids form bismuthous salts, of the general formula Bi_2R_3 , R being univalent.

Bismuthous salts, with the exception of the yellow chromate, are white or colourless; most of those which contain oxygen are non-volatile, and decom-

pose at a red heat. The chloride is, however, volatile. The neutral salts redden litmus paper, and are decomposed by a large quantity of water.

Nitrates.—Ternitrate, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$. To prepare this salt the metal is dissolved in nitric acid with the aid of heat, and the solution concentrated by evaporation; on cooling it deposits in deliquescent transparent prisms. The crystals dissolve easily in dilute nitric acid, and on mixing this solution with water an insoluble basic nitrate precipitates, an acid salt remaining in solution.

Basic Nitrate or Trinitrate of Bismuth (*Bismuthum Album, Magistery of Bismuth, Flake White*). This compound is formed in the manner just mentioned, but to obtain the maximum yield, it is recommended to add 24 parts of hot water for each part of ternitrate; by this treatment 45 per cent. of the basic nitrate is obtained. Too much water should not be used in washing the precipitate, as it is rendered more basic by this treatment. The filtered liquid from the precipitate may be evaporated to dryness, or nearly so, and again decomposed by addition of water, when a further quantity of the basic salt is obtained. The washings from the first precipitation may be used for decomposing this second quantity. The purified metal must be used in the first instance if a pure product be desired, since the subnitrate is liable to contain arsenic and other impurities if this precaution be not taken.

Basic nitrate of bismuth thus obtained is a pearly white powder of a loose texture, presenting the appearance of crystalline scales under the microscope. Prepared from acid solutions with but little water it has a silky lustre, and the crystals are acicular. The salt manifests an acid reaction with litmus. It varies to some extent in composition, according to the temperature and the quantity of the water employed in its preparation, but it agrees pretty closely with the formula $\text{Bi}(\text{NO}_3)_3 \cdot \text{Bi}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$.

Oxychloride of bismuth may be prepared by adding water to a solution of the chloride, or by pouring a solution of ternitrate into a solution of common salt. It is used as a paint, and is known as *pearl white*.

Basic nitrate of bismuth has been advantageously employed in medicine. It is administered principally in affections of the stomach which are unaccompanied by any organic disease. It has been particularly prescribed to relieve gastrodynia and cramp of the stomach, to allay sickness and vomiting, and as a cure for pyrosis. Dr. PEREIRA gave it in the form of powder in conjunction with hydrocyanic acid mixture, and remarked that the patient seldom failed to obtain benefit from its use. Dr. THEOPHILUS THOMSON recommends it in doses of 5 grains, usually combined with 3 of gum arabic and 2 of magnesia, given every four or six hours in the diarrhoea accompanying phthisis. He thinks that both for efficacy and safety it surpasses our most approved remedies for that complaint. It has also been administered in intermittent fever and spasmodic asthma. HAHNEMANN directed a portion of it to be introduced into a hollow tooth to allay tooth-

ache. It was also used with advantage by Dr. PEREIRA, in the form of ointment applied to the *septum nasi* in ulceration of that part, and as a local remedy in chronic skin diseases.

In small doses it acts as an astringent, diminishing the secretion; but in large doses it is undoubtedly poisonous. It disorders the digestive organs, causing pain, vomiting, and purging, sometimes affecting the nervous system, producing giddiness, insensibility, cramp of the extremities, and even death.

Upon the lower animals it acts as a local irritant and caustic poison, and appears to exercise a specific influence over the lungs and nervous system.

It was formerly extensively employed as a cosmetic; but even here its use is dangerous, since when thus employed it produces spasmodic trembling of the face, commonly ending in paralysis.

Detection and Estimation.—Bismuth in solution is thus characterized:—

Sulphuretted hydrogen, in slightly acid or in alkaline solutions, throws down the black tersulphide.

Alkalies precipitate white bismuthous hydrate, insoluble in excess of the precipitant.

Potassium chromate throws down the yellow chromate, soluble in nitric acid and insoluble in potash.

Soluble sulphates produce no precipitate, which fact, in conjunction with the insolubility of the hydrate and chromate in potash, distinguishes bismuth from lead.

Water throws down a white basic salt in solutions of the chloride and nitrate, unless a large quantity of free acid be present. Where such is the case, or where the solution is very dilute, it is evaporated nearly to dryness previously to the addition of water; and if sulphuric acid be present, some sodium or ammonium chloride should be added. The basic salt being insoluble in tartaric acid, distinguishes it from antimony. This reaction with water is very characteristic. Before the blow-pipe, bismuth, with reducing agents on charcoal, gives a brittle metallic bead and a yellow incrustation.

Estimation.—When bismuth has to be estimated in those of its compounds which are free from admixture with other metals, the body is brought into the state of nitrate by acting on it with nitric acid, diluting the solution with water, heating almost to ebullition, and precipitating with carbonate of ammonia. In presence of hydrochloric acid the precipitate thus produced would contain some oxychloride, which on ignition would decompose, and part of the bismuth volatilize as chloride. In such a case the bismuth is first precipitated from the acid solution with sulphuretted hydrogen, and the tersulphide washed, removed while moist, together with the filter, to a beaker glass, and converted into nitrate by means of nitric acid. The end of the decomposition is indicated by the separated sulphur assuming a yellow colour. The remains of the filter paper are then filtered off, after addition of dilute nitric acid, and the filter well washed. The filtrate and washings are then mixed, and the bismuth precipitated with ammonium carbonate, the solution being heated as above mentioned. The precipitate is to be col-

lected in a filter, washed with water, dried, transferred as much as possible from the paper to a porcelain crucible, and ignited. The filter is then burned separately, and the ash added to the oxide in the crucible and weighed. If highly ignited the oxide fuses, but does not decompose. As the teroxide contains 89.6 per cent. of metal, the amount of bismuth may easily be calculated. Bismuth being usually found associated with other metals—generally lead, silver, copper, arsenic, and iron—it may be interesting to give the process whereby the quantity of bismuth is ascertained in mixtures of these metals. The method also serves to detect adulteration in the preparations of bismuth, particularly when compounds of those metals are used.

The ore or compound is treated with nitric acid till dissolved, and this solution filtered and diluted with water; the washings of the residue, if any, are added, and a stream of sulphuretted hydrogen passed through it as long as a precipitate is produced. The vessel is then gently heated upon the sand-bath till the whole of the sulphides fall down; these are filtered and washed with water impregnated with sulphuretted hydrogen. The substance upon the paper is next digested with a strong solution of sulphide of potassium, which dissolves the sulphide of arsenic, leaving the sulphides of lead, silver, copper, and bismuth, which are separated from this solution by filtration and washing. These sulphides are then dissolved in nitric acid, the solution thus produced largely diluted, and the silver precipitated by hydrochloric acid. When the silver chloride has subsided, it is filtered, and the filtrate and washings evaporated with excess of sulphuric acid till the latter begins to be evolved. Sulphate of lead is thus formed, which is removed by filtering rapidly while hot, and washing the precipitate with water acidulated with sulphuric acid. The filtered solution now contains copper and bismuth. To separate the latter mix the diluted solution with carbonate of soda, in slight excess, add solution of cyanide of potassium, heat gently for some time, filter, and wash. The compound of bismuth on the filter contains some alkali, to remove which it is dissolved in nitric acid and reprecipitated by ammonium carbonate, as above directed. The precipitated bismuth is then treated in the same manner as before.

The quantity of each of the other constituents may be ascertained by weighing the precipitates already procured in the case of lead or silver. By adding ammonia to the filtrate containing the iron this body is thrown down as sesquioxide, which may be collected, dried, ignited, and weighed. The copper in solution, after the precipitation of bismuth, is ascertained by evaporation with strong sulphuric acid, to decompose the cuprocyanide of potassium, after which the copper may be thrown down by addition of caustic potash in excess and boiling. The black precipitate, consisting of oxide of copper, is well washed with boiling water, dried, separated from the filter, ignited, and weighed. This gives the amount of oxide of copper.