

strongly basylous; metals of group 2 are only slowly attacked, with formation of relatively feebly basylous and practically insoluble hydrates. Disregarding the rarer elements (as we propose to do in this section), the metals not named so far may be said to be proof against the action of pure water in the absence of free oxygen (air).

By the conjoint action of water and air, thallium, lead, bismuth are oxidized, with formation of more or less sparingly soluble hydrates (ThHO , PbO_2H_2 , BiO_3H_3), which, in the presence of carbonic acid, pass into still less soluble basic carbonates.

Iron, as everybody knows, when exposed to moisture and air, "rusts," that is, undergoes gradual conversion into a brown ferric hydrate, $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$; but this process never takes place in the absence of air, and it is questionable whether it ever sets in in the absence of carbonic acid. What is known is that iron never rusts in solutions of caustic alkalies or lime (which reagents preclude the presence of free carbonic acid), while it does so readily in ordinary moist air containing CO_2 . When once started the process proceeds with increasing rapidity, the ferric hydrate produced acting as a carrier of oxygen; it gives up part of its oxygen to the adjoining metal, being itself reduced to (perhaps) Fe_3O_4 , which latter again absorbs oxygen from the air to become ferric hydrate and so on (Kuhlmann).

Copper, in the present connexion, is intermediate between iron and the following group of metals.

Mercury, if pure, and all the "noble" metals (silver, gold, platinum, and platinum-metals), are absolutely proof against water even in the presence of oxygen and carbonic acid.

The metals grouped together above under 1 and 2 act on steam pretty much as they do on liquid water. Of the rest, the following are readily oxidized by steam at a red heat, with formation of hydrogen gas,—zinc, iron, cadmium, cobalt, nickel, tin. Bismuth is similarly attacked, but slowly, at a white heat. Aluminium is barely affected even at a white heat, if it is pure; the ordinary impure metal is liable to be very readily oxidized.

Aqueous Sulphuric or Hydrochloric Acid, of course, readily dissolves groups 1 and 2, with evolution of hydrogen and formation of chlorides or sulphates. The same holds for the following group (A):—[manganese, zinc, magnesium] iron, aluminium, cobalt, nickel, cadmium. Tin dissolves readily in strong hot hydrochloric acid as SnCl_2 ; aqueous vitriol does not act on it appreciably in the cold; at 150° it attacks it more or less quickly, according to the strength of the acid, with evolution of sulphuretted hydrogen or, when the acid is stronger, of sulphurous acid gas and deposition of sulphur (Calvert and Johnson). A group (B), comprising copper, are, substantially, attacked only in the presence of oxygen or air. Lead, in sufficiently dilute acid, or in stronger acid if not too hot, remains unchanged. A group (C) may be formed of mercury, silver, gold, and platinum, which are not touched by either aqueous acid in any circumstances.

Hot (concentrated) oil of vitriol does not attack gold, platinum, and platinum-metals generally; all other metals (including even silver) are converted into sulphates, with evolution of sulphurous acid. In the case of iron, ferric sulphate, $\text{Fe}_2(\text{SO}_4)_3$, is produced; tin yields a somewhat indefinite sulphate of its binoxide SnO_2 .

Nitric Acid (Aqueous).—Gold, platinum, iridium, and rhodium only are proof against the action of this powerful oxidizer. Tin and antimony (also arsenic) are converted by it (ultimately) into hydrates of their highest oxides SnO_2 , Sb_2O_5 , (As_2O_5),—the oxides of tin and antimony being insoluble in water and in the acid itself. All other metals, including palladium, are dissolved as nitrates, the oxidizing part of the reagent being generally reduced to nitric

oxide, NO , or sometimes to N_2O_3 or N_2O_4 . Iron, zinc, cadmium, also tin under certain conditions, reduce the dilute acid, partially at least, to nitrous oxide, N_2O , or nitrate of ammonia, $\text{NH}_4\text{NO}_3 = \text{N}_2\text{O} + 2\text{H}_2\text{O}$.

Aqua Regia, a mixture of nitric and hydrochloric acids, converts all metals (even gold, the "king of metals," whence the name) into chlorides, except only rhodium, iridium, and ruthenium, which, when pure, are not attacked.

Caustic Alkalies.—Of metals not decomposing liquid pure water, only a few dissolve in aqueous caustic potash or soda, with evolution of hydrogen. The most important of these are aluminium and zinc, which are converted into aluminate, $\text{Al}_2\text{O}_3 \cdot 3(\text{K}_2 \text{ or } \text{Na}_2)\text{O}$, and zincate, $\text{ZnO} \cdot \text{RHO}$, where $\text{R} = \text{K}$ or Na respectively. But of the rest the majority, when treated with boiling sufficiently strong alkali, are attacked at least superficially; of ordinary metals only gold, platinum, and silver are perfectly proof against the reagents under consideration, and these accordingly are used preferably for the construction of vessels intended for analytical operations involving the use of aqueous caustic alkalies. For preparative purposes iron is universally employed and works well; but it is not available analytically, because a superficial oxidation of the empty part of the vessel (by the water and air) cannot be prevented. According to the writer's experience basins made of pure malleable nickel are free from this drawback; they work as well as platinum, and rather better than silver ones do. There is hardly a single metal which holds out against the alkalies themselves when in the state of fiery fusion; even platinum is most violently attacked. In chemical laboratories fusions with caustic alkalies are always effected in vessels made of gold or silver, these metals holding out fairly well even in the presence of air. Gold is the better of the two. Iron, which stands so well against aqueous alkalies, is most violently attacked by the fused reagents. Yet tons of caustic soda are fused daily in chemical works in iron pots without thereby suffering contamination, which seems to show that (clean) iron, like gold and silver, is attacked only by the conjoint action of fused alkali and air, the influence of the latter being of course minimized in large-scale operations.

Oxygen or Air.—The noble metals (from silver upwards) do not combine directly with oxygen given as oxygen gas (O_2), although, like silver, they may absorb this gas largely when in the fused condition, and may not be proof against ozone, O_3 . Mercury, within a certain range of temperatures situated close to its boiling point, combines slowly with oxygen into the red oxide, which, however, breaks up again at higher temperatures. All other metals, when heated in oxygen or air, are converted, more or less readily, into stable oxides. Potassium, for example, yields peroxide, K_2O_2 or K_2O_4 ; sodium gives Na_2O_2 ; the barium-group metals, as well as magnesium, cadmium, zinc, lead, copper, are converted into their monoxides MeO . Bismuth and antimony give (the latter very readily) sesquioxide (Bi_2O_3 and Sb_2O_3 , the latter being capable of passing into Sb_2O_4). Aluminium, when pure and kept out of contact with siliceous matter, is only oxidized at a white heat, and then very slowly, into alumina, Al_2O_3 . Tin, at high temperatures, passes slowly into binoxide, SnO_2 .

Sulphur.—Amongst the better known metals, gold and aluminium are the only ones which, when heated with sulphur or in sulphur vapour, remain unchanged. All the rest, under these circumstances, are converted into sulphides. The metals of the alkalies and alkaline earths, also magnesium, burn in sulphur-vapour as they do in oxygen. Of the heavy metals, copper is the one which exhibits by far the greatest avidity for sulphur, its subsulphide Cu_2S being the stablest of all heavy metallic sulphides in opposition to dry reactions. See METALLURGY.

Chlorine.—All metals, when treated with chlorine gas at the proper temperatures, pass into chlorides. In some cases the chlorine is taken up in two instalments, a lower chloride being produced first, to pass ultimately into a higher chloride. Iron, for instance, is converted first into FeCl_2 , ultimately into Fe_2Cl_6 , which practically means a mixture of the two chlorides, or pure Fe_2Cl_6 as a final product. Of the several products, the chlorides of gold and platinum (AuCl_3 and PtCl_4) are the only ones which when heated beyond their temperature of formation dissociate into metal and chlorine. The ultimate chlorination product of copper, CuCl_2 , when heated to redness, decomposes into the lower chloride, Cu_2Cl_2 , and chlorine. All the rest, when heated by themselves, volatilize, some at lower, others at higher temperatures.

Of the several individual chlorides, the following are liquids or solids, volatile enough to be distilled from out of glass vessels:— AsCl_3 , SbCl_3 , SnCl_4 , BiCl_3 , HgCl_2 , the chlorides of arsenic, antimony, tin, bismuth, mercury respectively. The following are readily volatilized in a current of chlorine, at a red heat:— Al_2Cl_6 , Cr_2Cl_6 , Fe_2Cl_6 , the chlorides of aluminium, chromium, iron. The following, though volatile at higher temperatures, are not volatilized at dull redness:— KCl , NaCl , LiCl , NiCl_2 , CoCl_2 , MnCl_2 , ZnCl_2 , MgCl_2 , PbCl_2 , AgCl , the chlorides of potassium, sodium, lithium, nickel, cobalt, manganese, zinc, magnesium, lead, silver. Somewhat less volatile than the last-named group are the chlorides (MCl_2) of barium, strontium, and calcium.

Metallic chlorides, as a class, are readily soluble in water. The following are the most important exceptions:—chloride of silver, AgCl , and subchloride of mercury, Hg_2Cl_2 , are absolutely insoluble; chloride of lead, PbCl_2 , and subchloride of copper, Cu_2Cl_2 , are very sparingly soluble in water. The chlorides AsCl_3 , SbCl_3 , BiCl_3 , are at once decomposed by (liquid) water, with formation of oxide (As_2O_3) or oxychlorides (SbClO , BiClO) and hydrochloric acid. The chlorides MgCl_2 , Al_2Cl_6 , Cr_2Cl_6 , Fe_2Cl_6 , suffer a similar decomposition when evaporated with water in the heat. The same holds in a limited sense for ZnCl_2 , CoCl_2 , NiCl_2 , and even CaCl_2 . All chlorides, except those of silver and mercury (and, of course, those of gold and platinum), are oxidized by steam at high temperatures, with elimination of hydrochloric acid.

The above statements concerning the volatilities and solubilities of metallic chlorides form the basis of a number of important analytical methods for the separation of the respective metals.

For the characters of metals as chemical elements the reader is referred to the article CHEMISTRY and to the special articles on the different metals. (w. d.)

METAL-WORK. Among the many stages in the development of primeval man, none can have been of greater moment in his struggle for existence than the discovery of the metals, and the means of working them. The names generally given to the three prehistoric periods of man's life on the earth—the Stone, the Bronze, and the Iron age—imply the vast importance of the progressive steps from the flint knife to the bronze celt, and lastly to the keen-edged elastic iron weapon or tool. The length of time during which each of these ages lasted must of course have been different in every country and race in the world. The Digger Indians of South California have even now not progressed beyond the Stone Age; while some of the tribes of Central Africa are acquainted with the use of copper and bronze, though they are unable to smelt or work iron.

The metals chiefly used have been gold, silver, copper and tin (the last two generally mixed, forming an alloy called bronze), iron, and lead. The peculiarities of these

various metals have naturally marked out each of them for special uses and methods of treatment. The durability and the extraordinary ductility and pliancy of gold, its power of being subdivided, drawn out, or flattened into wire or leaf of almost infinite fineness, have led to its being used for works where great minuteness and delicacy of execution were required; while its beauty and rarity have, for the most part, limited its use to objects of adornment and luxury, as distinct from those of utility. In a lesser degree most of the qualities of gold are shared by silver, and consequently the treatment of these two metals has always been very similar, though the greater abundance of the latter metal has allowed it to be used on a larger scale and for a greater variety of purposes.

Bronze is an alloy of copper and tin in varying proportions, the proportion of tin being from 8 to 20 per cent. The great fluidity of bronze when melted, the slightness of its contraction on solidifying, together with its density and hardness, make it especially suitable for casting, and allow of its taking the impress of the mould with extreme sharpness and delicacy. In the form of plate it can be tempered and annealed till its elasticity and toughness are much increased, and it can then be formed into almost any shape under the hammer and punch. By other methods of treatment, known to the ancient Egyptians, Greeks, and others, but now forgotten, it could be hardened and formed into knife and razor edges of the utmost keenness. In many specimens of ancient bronze small quantities of silver, lead, and zinc have been found, but their presence is probably accidental.

In modern times, after the discovery of zinc, an alloy of copper and zinc called brass has been much used, chiefly for the sake of its cheapness as compared with bronze. In beauty, durability, and delicacy of surface it is very inferior to bronze, and, though of some commercial importance, has been of but little use in the production of works of art.

To some extent copper was used in an almost pure state during mediæval times, especially from the 12th to the 15th century, mainly for objects of ecclesiastical use, such as pyxes, monstrances, reliquaries, and croziers, partly on account of its softness under the tool, and also because it was slightly easier to apply enamel and gilding to pure copper than to bronze (see fig. 1). In the mediæval period it was used to some extent in the shape of thin sheeting for roofs, as at St Mark's, Venice; while during the 16th and 17th centuries it was largely employed for ornamental domestic vessels of various sorts.

Iron.—The abundance in which iron is found in so many places, its great strength, its remarkable ductility and malleability in a red-hot state, and the ease with which two heated surfaces of iron can be welded together under the hammer combine to make it specially suitable for works on a large scale where strength with lightness are required—things such as screens, window-grills, ornamental hinges, and the like.

In its hot plastic state iron can be formed and modelled under the hammer to almost any degree of refinement, while its great strength allows it to be beaten out into leaves and ornaments of almost paper-like thinness and delicacy. With repeated hammering, drawing out, and annealing, it gains much in strength and toughness, and the addition of a very minute quantity of carbon converts

¹ Some recent analyses of the iron of prehistoric weapons have brought to light the interesting fact that many of these earliest specimens of iron manufacture contain a considerable percentage of nickel. This special alloy does not occur in any known iron ores, but is invariably found in meteoric iron. It thus appears that iron was manufactured from meteorolites which had fallen to the earth in an almost pure metallic state, possibly long before prehistoric man had learnt how to dig for and smelt iron in any of the forms of ore which are found on this planet.

it into steel, less tough, but of the keenest hardness. The large employment of cast iron is comparatively modern, in England at least only dating from the 16th century; it is not, however, incapable of artistic treatment if due regard be paid to the necessities of casting, and if no attempt is made to imitate the fine-drawn lightness to which wrought iron so readily lends itself. At the best, however, it is not generally suited for the finest work, as the great contraction of iron in passing from the fluid to the solid state renders the cast somewhat blunt and spiritless.

Among the Assyrians, Egyptians, and Greeks the use of iron, either cast or wrought, was very limited bronze being the favourite metal for almost all purposes. The difficulty of smelting the ore was probably one reason for this, as well as the now forgotten skill which enabled bronze to be tempered to a steel-like edge. It had, however, its value, of which a proof occurs in Homer (*Il.* xxiii.), where a mass of iron is mentioned as being one of the prizes at the funeral games of Patroclus.

Methods of Manipulation in Metal-Work.—Gold, silver, and bronze may be treated in various ways, the chief of which are (1) casting in a mould, and (2) treatment by hammering and punching (French, *repoussé*).

The first of these, casting, is chiefly adapted for bronze, or in the case of the more precious metals only if they are used on a very small scale. The reason of this is that a repoussé relief is of much thinner substance than if the same design were cast, even by the most skilful metal-worker, and so a large surface may be produced with a very small expenditure of valuable metal.

Casting is probably the most primitive method of metal-work.

This has passed through three stages, the first being represented by solid castings, such as are most celts and other implements of the prehistoric time; the mould was formed of clay, sand, or stone, and the fluid metal was poured in till the hollow was full. The next stage was, in the case of bronze, to introduce an iron core, probably to save needless expenditure of the more valuable metal. The British Museum possesses an interesting Etruscan or Archaic Italian example of this primitive

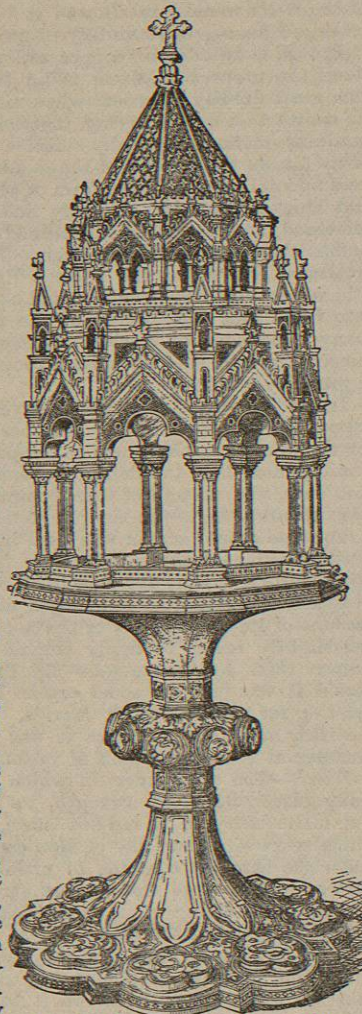


FIG. 1.—Monstrance of Copper Gilt; Italian work of the 15th century.

device. It is a bronze statuette from Sessa on the Volturno about 2 feet high, of a female standing, robed in a close fitting chiton. The presence of the iron core has been made visible by the splitting of the figure, owing to the unequal contraction of the two metals. The forearms which are extended, have been cast separately and soldered or brazed on to the elbows.

The third and last stage in the progress of the art of casting was the employment of a core, generally of clay, round which the metal was cast in a mere skin, only thick enough for strength, without waste of metal. The Greeks and Romans attained to the greatest possible skill in this process. Their exact method is not certainly known, but it appears probable that they were acquainted with the process now called *à cire perdue*—the same as that employed by the great Italian artists in bronze, and still unimproved upon even at the present day. Cellini, the great Florentine artist of the 16th century, has described it fully in his *Trattato della Scultura*. If a statue was to be cast, the figure was first roughly modelled in clay—only rather smaller in all its dimensions than the future bronze; all over this a skin of wax was laid, and worked by the sculptor with modelling tools to the required form and finish. A mixture of pounded brick, clay, and ashes was then ground finely in water to the consistency of cream, and successive coats of this mixture were then applied with a brush, till a second skin was formed all over the wax, fitting closely into every line and depression of the modelling. Soft clay was then carefully laid on to strengthen the mould, in considerable thickness, till the whole statue appeared like a shapeless mass of clay, round which iron hoops were bound to hold it all together. The whole was then thoroughly dried, and placed in a hot oven, which baked the clay, both of the core and the outside mould, and melted the wax, which was allowed to run out from small holes made for the purpose. Thus a hollow was left, corresponding to the skin of wax between the core and the mould, the relative positions of which were preserved by various small rods of bronze, which had previously been driven through from the outer mould to the rough core. The mould was now ready, and melted bronze was poured in till the whole space between the core and the outer mould was full. After slowly cooling, the outer mould was broken away from outside the statue, and the inner core as much as possible broken up and raked out through a hole in the foot or some other part of the statue. The projecting rods of bronze were then cut away, and the whole finished by rubbing down and polishing over any roughnesses or defective places. The most skilful sculptors, however, had but little of this after-touching to do, the final modelling and even polish which they had put upon the wax being faithfully reproduced in the bronze casting.

The further enrichment of the object by enamels and inlay of other metals was practised at a very early period by Assyrian, Egyptian, and Greek metal-workers, as well as by the artists of Persia and mediæval Europe.

The second chief process, that of hammered work (Greek, *sphyrelata*; French, *repoussé*), was probably adopted for bronze-work on a large scale, before the art of forming large castings was discovered. In the most primitive method thin plates of bronze were hammered over a wooden core, rudely cut into the required shape, the core serving the double purpose of giving shape to and strengthening the thin metal.

A further development in the art of hammered work consisted in laying the metal plate on a soft and elastic bed of cement made of pitch and pounded brick. The design was then beaten into relief from the back with hammers and punches, the pitch bed yielding to the protuberances which were thus formed, and serving to pre-

vent the punch from breaking the metal into holes. The pitch was then melted away from the front of the embossed relief, and applied in a similar way to the back, so that the modelling could be completed on the face of the relief, the final touches being given by the graver. This process was chiefly applied by mediæval artists to the precious metals, but by the Assyrians, Greeks, and other early nations it was largely used for bronze.

The great gates of Shalmaneser II., 859–824 B.C., from Balawat, now in the British Museum, are a remarkable example of this sort of work on a large scale, though the treatment of the reliefs is minute and delicate. The "Siris bronzes," in the same museum, are a most astonishing example of the skill attained by Greek artists in this repoussé work (see Brönsted's *Bronzes of Siris*, 1836). They are a pair of shoulder-pieces from a suit of bronze armour, and each has in very high relief a combat between a Greek warrior and an Amazon. No work of art in metal has probably ever surpassed these little figures for beauty, vigour, and expression, while the skill with which the artist has beaten these high reliefs out of a flat plate of metal appears almost miraculous. The heads of the figures are nearly detached from the ground, their substance is little thicker than paper, and yet in no place has the metal been broken through by the punch. They are probably of the school of Praxiteles, and date from the 4th century B.C. (see fig. 2).

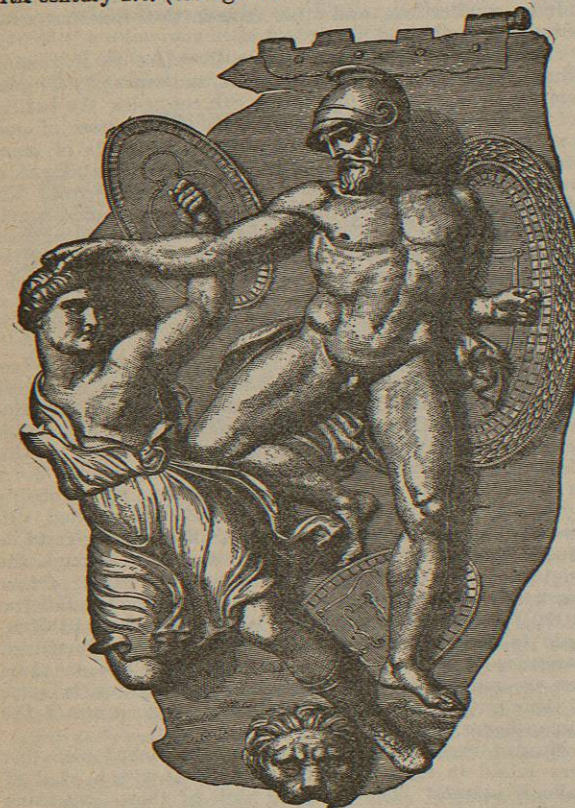


FIG. 2.—One of the Siris Bronzes.

Copper and tin have been but little used separately. Copper in its pure state may be worked by the same methods as bronze, but it is inferior to it in hardness, strength, and beauty of surface. Tin is too weak and

brittle a metal to be employed alone for any but small objects. Some considerable number of tin drinking-cups and bowls of the Celtic period have been found in Cornwall in the neighbourhood of the celebrated tin and copper mines, which appear to have been worked from a very early period. The existence of these mines was known to the Phœnicians, who carried on a considerable trade in metals with the south-west corner of England and the Scilly Isles—probably the Cassiterides of Pliny and other classical writers.

The use of lead has been more extended. In sheets it forms the best of all coverings for roofs and even spires. In the Roman and mediæval periods it was largely used for coffins, which were often richly ornamented with cast work in relief. Though fusible at a very low temperature, and very soft, it has great power of resisting decay from damp or exposure. Its most important use in an artistic form has been in the shape of baptismal fonts, chiefly between the 11th and the 14th centuries. The superior beauty of colour and durability of old specimens of lead is owing to the natural presence of a small proportion of silver. Modern smelters carefully extract this silver from the lead ore, thereby greatly impairing the durability and beauty of the metal.

As in almost all the arts, the ancient Egyptians excelled in their metal-work, especially in the use of bronze and the precious metals. These were worked by casting and hammering, and ornamented by inlay, gilding, and enamels with the greatest possible skill.

From Egypt perhaps was derived the early skill of the Hebrews. Further instruction in the art of metal-working came probably to the Jews from the neighbouring country of Tyre. The description of the great gold lions of Solomon's throne, and the laver of cast bronze supported on figures of oxen, shows that the artificers of that time had overcome the difficulties of metal-working and founding on a large scale. The Assyrians were perhaps the most remarkable of all ancient nations for the colossal size and splendour of their works in metal; whole circuit walls of great cities, such as Ecbatana, are said to have been covered with metal plates, gilt or silvered.

Herodotus, Athenæus, and other Greek and Roman writers have recorded the enormous number of colossal statues and other works of art for which Babylon and Nineveh were so famed. The numerous objects of bronze and other metals brought to light by the excavations of the last forty years in the Tigris and Euphrates valleys, though mostly on a small scale, bear witness to the great skill and artistic power of the people who produced them; while the recent discovery of some bronze statuettes, shown by inscriptions on them to be not later than 2200 B.C., proves how early was the development of this branch of art among the people of Assyria.

The Metal-Work of Greece.—The poems of Homer are full of descriptions of elaborate works in bronze, iron, gold, and silver, which, even when full allowance is made for poetic fancy, show clearly enough a very advanced amount of skill in the working and ornamenting of these metals among the Greeks of his time. His description of the shield of Achilles, made of bronze, enriched with bands of figure reliefs in gold, silver, and tin, could hardly have been written by a man who had not some personal acquaintance with works in metal of a very elaborate kind. Again, the accuracy of his descriptions of brazen houses—such as that of Alcinous, *Od.* vii. 81—is borne witness to by Pausanias's mention of the bronze temple of Athena Χαλκίονος in Sparta, and the bronze chamber dedicated to Myron in 648 B.C., as well as by the discovery of the stains and bronze nails, which show that the whole interior of the so-called treasury of Atreus at Mycenæ was once