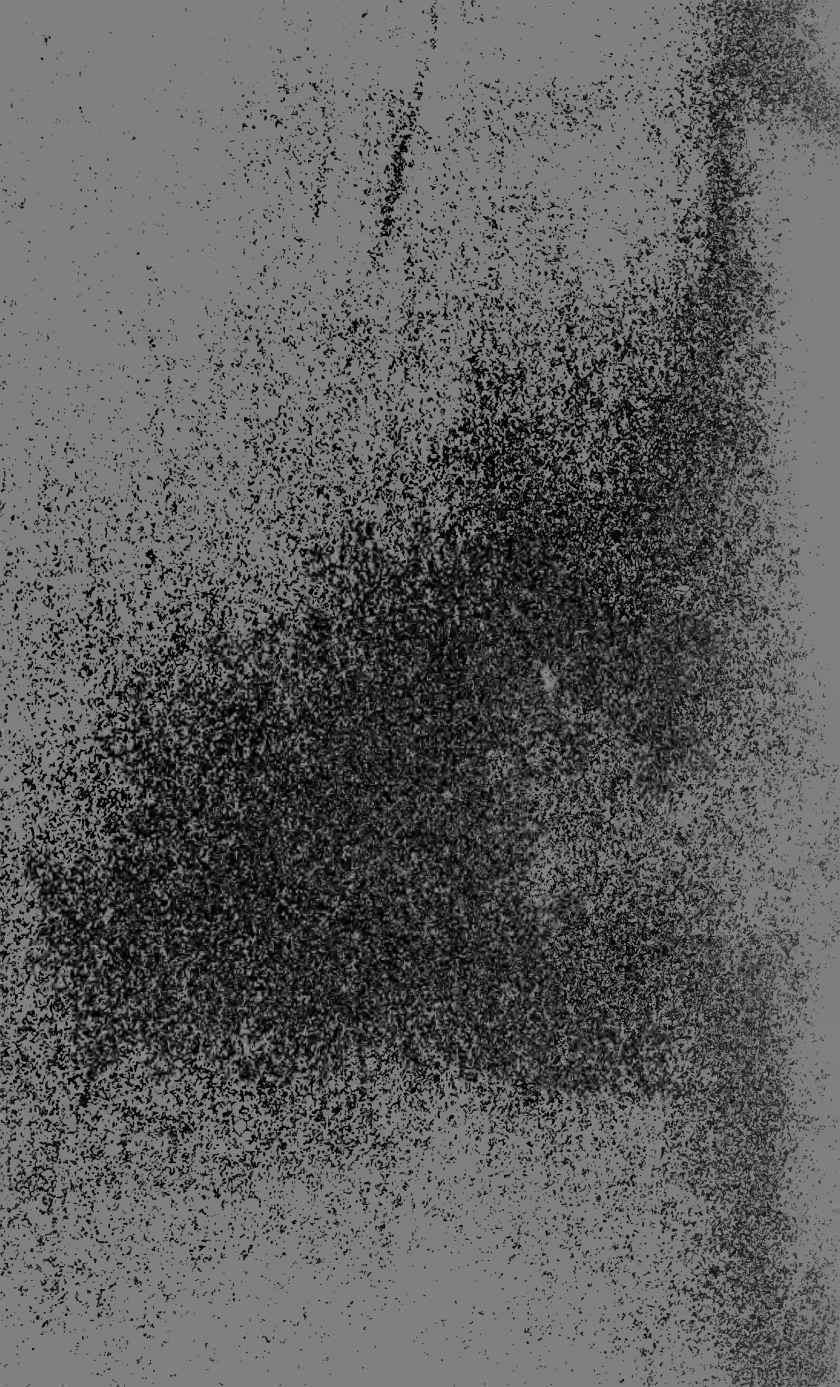






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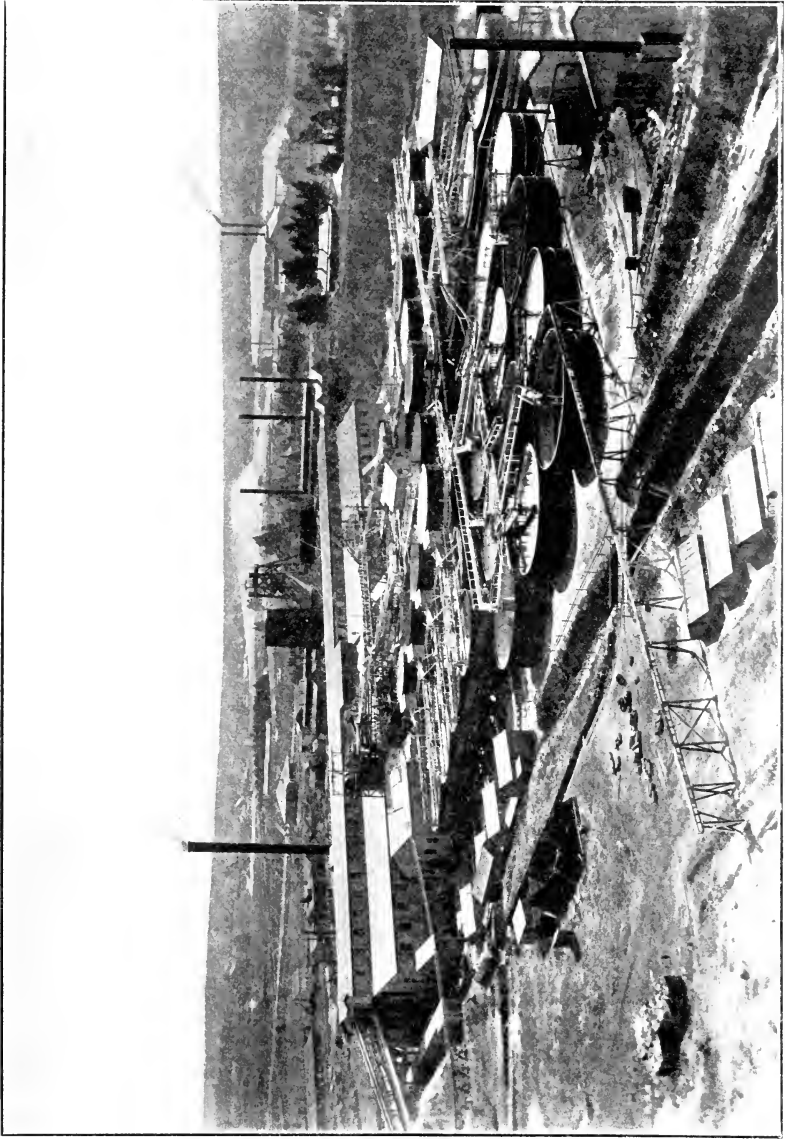
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Knight's Deep and Shimmer East Joint Plant. View from Sand Dump. (See p. 117.)

(From a photograph kindly supplied by Mr. W. A. Caldercroft.)

*Frontispiece.*

# THE PRECIOUS METALS

COMPRISING

GOLD SILVER AND PLATINUM

BY

T. KIRKE ROSE A.R.S.M. D.Sc.

CHEMIST AND ASSAYER OF THE ROYAL MINT; VICE-PRESIDENT  
OF THE INSTITUTION OF MINING AND METALLURGY; HONORARY  
MEMBER OF THE CHEMICAL, METALLURGICAL AND MINING  
SOCIETY OF SOUTH AFRICA; FELLOW OF THE CHEMICAL  
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## PREFACE

THE term "precious metals" has usually been applied to gold and silver only, its use dating back to a time when no regard was paid to platinum. As platinum is now in common use and is more valuable, weight for weight, than gold, it may very well rank as a precious metal. Other metals of high price come under the heading of rare metals.

In the preparation of this work, the aim has been to provide an introduction to the study of the precious metals, and an elementary book of reference for those who do not wish to pursue the subject further. With these objects in view details have been generally omitted and a wide extent of ground has been covered, including the technical processes of minting and the manufacture of gold and silver wares. It need hardly be mentioned, however, that all questions of currency and finance have been left untouched. It is also perfectly obvious that the book is not intended to be a substitute for the larger treatises on metallurgy, some of which devote the whole of a bulky volume to the full consideration of a section of the subject dealt with here in the course of a few pages.

The author desires to express his thanks to Mr. Edward

Rigg, I.S.O., Superintendent of the Operative Department of the Royal Mint, to Mr. Arthur Westwood, Assay Master of the Birmingham Assay Office, and to others for kindly reading the proofs of various chapters and for their valuable suggestions.

NORTHWOOD,  
*February 1st, 1909.*

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# THE PRECIOUS METALS

## CHAPTER I

### HISTORY OF GOLD

It is probable that gold was the first metal to attract the attention of primitive man, although no traces of it have been found in the dwellings and other relics of the Stone Age. It must be noted, however, that flint daggers with gilt handles have been found in Egypt. Whether gold was the first metal observed or not, however, it is certain that its lustre, bright colour, and toughness, and its wide distribution in a native state as pieces of all sizes in loose sands and gravels, must have led to the collection of gold in very early times.

Professor Gowland considers<sup>1</sup> that the order in which the metals were discovered was not the same for every region, but that the metals which occur as such in Nature must have been the first known to the men inhabiting the localities in which they occurred. According to his view, although gold cannot have escaped the observation of the men of the Stone Age, it must generally have been found in the form of fine particles which could not have been applied to any useful purpose until after the invention of the art of melting. Even melted lumps or naturally occurring nuggets

<sup>1</sup> Presidential Address, Anthropological Institute, 1906.

of gold would have been too soft to be of value as weapons or implements, and must have been used only as personal ornaments. Hence gold could have played only a very small part, if any, in the development of culture in Neolithic times.

It was well known in Egypt some 5,500 years ago, and had probably at that time already passed into use as a standard of value. Thus in the code of Menes, B.C. 3600, one part of gold was declared equal in value to two and a half parts of silver.

The words originally used to denote gold seem to have been connected with its glittering appearance, and indicate the ideas associated with it in the minds of the early observers. Such words are the Egyptian *nub*, the Hebrew *zahab*, and the Sanscrit *jvalita* and *hiranya*. In later times the alchemists called gold *sol*, and denoted it by the same symbol as the sun, ☉, not on account of its appearance, but because it was the most perfect of the noble metals, the King of Metals. Silver was *luna*, the moon, and the other known metals were named after the planets.

The ancient methods of obtaining gold in Egypt are illustrated in rock carvings which date back to 2500 B.C. The auriferous gravels were washed with water in stone basins, and the gold melted in little furnaces with the aid of mouth blowpipes. The earliest furnaces being adapted from camp fires were urged no doubt by the wind only, and the introduction of artificial bellows marked a great advance in metallurgical skill. An ancient Egyptian furnace closely resembling a camp fire, but fitted with bellows, is shown in Fig. 1. This is from a wall painting at Thebes and is reproduced from the *Journal of the Anthropological Institute*,



Vol. XXXVI., 1906, by kind permission of Professor Gowland and of the Royal Anthropological Institute.

Sloping tables of stone were also used, as well as basins, for washing gold ores, and sheepskins spread on the tables or on sloping rocks for entangling the particles of gold and helping in its collection were employed at an early date. The Golden Fleece seized by Jason in B.C. 1200 doubtless typified the gold obtained from the rivers by its use.

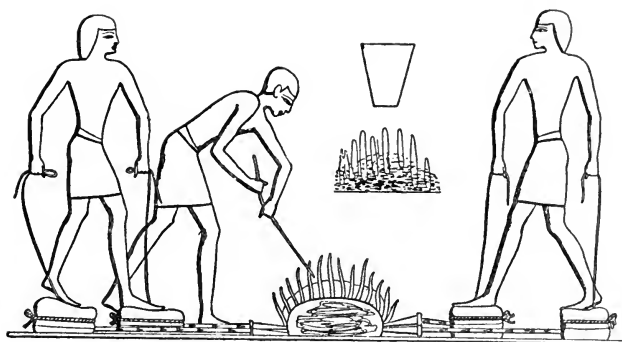


FIG. 1.—Ancient Egyptian Furnace.

The introduction of ore-crushing to obtain gold contained in solid rock took place at some unknown time, but it was well established in Egypt in B.C. 59, when it was described by Diodorus the Sicilian as follows<sup>1</sup> :—

“The parts of Egypt near Ethiopia and Arabia are rich in gold mines. . . . The ore is a black mineral, marked with white veins and shining specks. The chiefs of the undertaking employ a great number of workmen who are all either condemned criminals or prisoners of war. Even

<sup>1</sup> Diodorus Siculus, Bk.-IV., c. 11 and 12.



the parents of the condemned are summoned when the number of workmen is insufficient. They work day and night without rest, and under the surveillance of barbarous soldiers, who speak languages different from those of the miners, so that they cannot be won over either by promises or by prayers.

“The man who recognises the veins of gold is placed at the head of the workmen, and points out to them the place to excavate. The rocks are broken by iron wedges. The miners follow, in their labours, the direction of the metallic threads, and are assisted by the light of lamps in the subterranean darkness. The stones are carried outside, and are there crushed and reduced to small fragments.

“The workmen never cease from their toil; they are forced incessantly to the work by bad treatment and by blows of the whip. Even children are not spared; some are set to carry the blocks of stone, others to break them into fragments. The fragments are taken by older workmen, of over thirty years of age, and crushed in iron mortars. The fragments thus crushed are then ground in mills with arms, which are turned by women and aged men. Two or three people work at each mill. It is impossible to describe the sufferings of these unhappy ones; exposed naked to cold and rain, they are allowed no repose; there is no feeling of pity, either for a weakly woman or for an old man on the verge of the tomb; no regard to the sick, who may be a prey to the shivering of fever; they are all struck indiscriminately with repeated blows until they die of their sufferings on the very spot where they have worked.”

When the ore had been reduced to powder, it was spread on wide, slightly inclined tables, and a stream of water

flowing over the tables carried off the earthy materials, and left the gold separated by its weight. This operation was repeated by the workmen several times; they rubbed the powdered ore with their hands for some time, then they wiped it with little sponges in order to remove the impurities which water alone could not carry off. By this means the gold dust became clean and shining.

Diodorus adds that these methods were very ancient and had been discovered by the first Kings of Egypt.

Hollowed-out stone mortars and also stone grinding-mills have been found in many parts of the world besides Egypt, in proximity to ancient gold workings, and the methods described above were probably carried by the Romans to some of these countries. The use of sieves, which were originally made of hair and fibres, was also probably introduced by the Egyptians, but heavy pestles or stampers, requiring the efforts of several men to raise them and let them fall, had their origin in later times.

The gold produced by these simple mechanical methods was naturally very impure, containing varying proportions of silver and other metals. When the silver was in sufficient proportion (20 to 35 per cent.) to affect the colour perceptibly, the alloy was called *electrum*. This natural mixture of gold and silver was used for some of the earliest gold coinages, but the removal of silver by cementation was begun in very ancient times. Gold, *electrum* and silver were all recognised and mentioned by Homer, and Dr. Schliemann found all three among the ruins of Troy.

The purification of gold was effected, according to Agatharcides, by enclosing it in an earthenware vessel with

lead (proportionate in amount to the quantity of gold), salt, a little tin and some barley husks. The vessel was luted up and heated in a furnace for five days and five nights, and was then allowed to cool and opened. The gold, though it had lost a little of its weight, was very pure, and retained neither lead nor tin. Such gold was called *aurum obryzum*, and the process itself was called *obrussa*.<sup>1</sup> It seems to have been a combination of cupellation and cementation. The lead and the base metals in the gold would be eventually oxidised and absorbed by the pot, and the silver chloride, formed by the action of the common salt, would also fuse and pass into the pot. The use of the tin is obscure, but the bran would prevent the lead from being oxidised and absorbed too rapidly. This process was well known to the Romans and is mentioned by Cicero, Suetonius, and others.

Strabo describes the use of cementation in Spain, and Pliny gives a still more exact description. The process differed from *obrussa* in the omission of lead and the addition of *misy* or sulphate of iron. The removal of silver from the gold was more perfect by this method.

The Middle Ages were characterised more by the work of the alchemists than by any great progress in the metallurgy of gold. "Chemia" was defined by Suidas as the art of making gold and silver. It had its origin in Egypt at the beginning of our era, and great powers were attributed to the Egyptian priests, who carefully guarded their reputed secrets and made their experiments a part of the mystic rites of their religion.

The history of alchemy affords very curious reading.

<sup>1</sup> "Histoire de la Chimie," F. Hoefler, Vol. I., p. 116.

The alchemists were familiar with a number of chemical changes which seemed to them no less remarkable than the transmutation of mercury or copper into gold would be. For example, they knew that the addition of antimony to copper produced a beautiful violet-coloured substance, and that the incineration of lead yielded a bright yellow body. Why, they asked, should not the "projection" of some substance into the base metals give them the yellow colour and the other properties of gold? They sacrificed everything to experiments with this end in view and repeatedly announced that they had discovered the secret. Nevertheless no one seems to have prepared the transmuting agent for himself, but to have received it from a mysterious stranger. The credulity and desire for gold of the rich and powerful kept the alchemists supplied with funds to continue their researches, their patrons including many reigning monarchs. Alchemy continued to flourish throughout Europe for over a thousand years, and the claims of the gold-makers were not generally discredited until about the end of the seventeenth century.

Few improvements were introduced in the extraction of gold from its ores for several hundreds of years previous to the beginning of the sixteenth century. In 1519 stamp batteries for crushing ore were introduced at Joachimsthal, and screens set at the outlet of the mortars were described by Agricola in 1556 and were in use in the Hartz in 1767.<sup>1</sup>

A stamp mill for dry crushing in use in the sixteenth century is shown in Fig. 2, which is taken from Agricola, "De Re Metallica," Lib. VIII. Here A is a screen frame, and B a screen which consists of iron wire and is fastened

<sup>1</sup> "Voyages Metallurgiques," Jars, Vol. II., p. 309.

to the frame by iron rods D. The screen E is used for separating the fine material from the coarse ore which is



FIG. 2.—German Stamp Mill of the sixteenth century.

fed to the stamps. The crushed material is sieved at F. The stamps are raised by water power.

The use of mercury for separating gold from other materials was described by Pliny and was probably never

forgotten. Thus Geber, who died in 777, was aware that mercury would dissolve gold and silver but not earthy materials, and Theophilus in the eleventh century described the extraction of gold from the sands of the Rhine by means of quicksilver. In the Tyrol the method of gold ore treatment included crushing in stamp batteries and the stirring of the crushed ore in circular bowls with large quantities of mercury. A stream of water passing through the bowl carried off the tailings, leaving the gold to sink to the bottom of the bowl and unite with the bath of mercury kept there. This process is of great antiquity, and its principle is still used in the modern amalgamating machines of Hungary.

The catching of amalgam by means of copper plates is more modern, and was probably suggested by the Cazo process, which was introduced in Peru in 1609.<sup>1</sup> No mention is made of charging mercury into stamp batteries and catching the gold amalgam on copper plates before the year 1850. The chlorination process of gold ore treatment originated in 1848, and the cyanide process in 1887.

As for the parting of gold from silver, the cementation process continued in use by the side of some other furnace processes until it was displaced by the use of nitric acid, which dissolves silver and other metals and leaves gold unattacked. The process was described by Albertus Magnus in the thirteenth century, but was not used on a large scale until about 200 years later in Venice. It was introduced into Paris in 1514, and has become obsolete only within the last hundred years. The sulphuric acid method was established in 1802 in Paris, and has flourished

<sup>1</sup> Barba, "Arte de los Metales," Lib. III., cap. xxi.

for about a century. It is now being superseded by the electrolytic process, which has already replaced it throughout America. In Australia the chlorine process of refining and parting, introduced in 1867, is the only one that has ever been used, owing to the high price of acids on that continent.



## CHAPTER II

### THE PROPERTIES OF GOLD

#### PHYSICAL PROPERTIES.

GOLD has a characteristic yellow colour, the so-called golden yellow. If it contains silver the colour is paler yellow, and if it contains copper the colour is a more reddish-yellow. The colour of pure gold is seldom seen, although it is closely imitated by certain mixtures of gold, silver, and copper, used for wares of 18- and 22-carat gold. Some specimens of gold-leaf consist of nearly pure gold. Finely divided gold is often red or purple, as may be seen in purple of Cassius (*q.v.*) and in some ruby glass, although most specimens of ruby glass are now coloured by oxide of copper instead of by metallic gold. Gold-leaf is green by transmitted light. Gold precipitated from solution varies in colour from black to bright red (see Faraday's gold). Volatilised gold condenses as a reddish-purple stain. Molten gold is green.

Gold is softer than silver, but harder than pure tin. It is the most malleable and most ductile of metals. Leaf gold can be made only one three-hundred-thousandth of an inch thick by hammering, and an ounce of gold can be drawn out into fifty miles of wire. The tenacity of gold is seven tons per square inch, or less than that of silver or copper. A wire of 0·1 inch in diameter is broken by a

weight of 123 lbs. Gold has an elongation of 30·8 per cent. before rupture.

Gold crystallises in the cubic system, but large, well-formed crystals are only occasionally found in Nature, and are difficult to produce artificially. There are some large cubic crystals of pure gold preserved in the Mint, which remained in a crucible when the molten charge was poured out.

The density of cast gold is about 19·3, and this can be raised by rolling to 19·48, and by hammering to 19·65. The density of precipitated gold is usually somewhat higher, and one specimen was found to be as high as 20·72. The melting point of gold is 1,064° C., and it begins to volatilise at about the same temperature. The amount of volatilisation, however, remains small at the temperatures attained in ordinary industrial furnaces. Gold boils readily in electric-arc furnaces, and its boiling point has been estimated by Krafft and Bergfeld to be about 2,530° C. under atmospheric pressure.

Its electrical conductivity at ordinary temperatures is 76·7, that of silver being 100. Its conductivity for heat is also less than that of silver and of copper. It is non-magnetic.

#### CHEMICAL PROPERTIES.

Originally gold was called by the alchemists a noble metal, because it was not affected by fire. When put into the fire, and even melted, it emerged unchanged, whereas the "base" metals were oxidised and "destroyed" (*i.e.*, they lost their metallic character) under the same conditions. In the cupellation process the furnace was observed to

remove the base metals from admixture with gold, leaving the noble metal unscathed. The other noble metal recognised by the alchemists was silver, but it was deemed less perfect in its nobility than gold, because it could be dissolved in aqua fortis, by which gold is unaffected. Hence gold was called the more noble and silver the less noble or less perfect metal. This identification of physical with moral qualities still has its effect on our nomenclature.

The symbol of gold is Au (from *aurum*), and its atomic weight is 197.2, taking that of oxygen as 16. In its solution in mercury it is apparently monatomic. It bears a close relation to the heavy platinum metals, osmium, iridium, and platinum. Silver is similarly related to ruthenium, rhodium, and palladium, the light platinum metals. Thus the atomic weights of gold and the heavy platinum metals are not very different; their densities are all very high, and they all form lower oxides which are feebly basic, and higher oxides which are both acidic and basic in a slight degree.

At the same time gold is also related to silver and copper, compounds of the type RX existing in each case. The substances aurous chloride, AuCl, silver chloride, AgCl, and cuprous chloride, CuCl, resemble each other in several respects. They are insoluble in water (although AuCl is decomposed by it), but are soluble in potassium cyanide, hydrochloric acid, and ammonia. Gold differs from silver and copper in the extreme facility with which its compounds are decomposed and the metal isolated. At a gentle heat chlorine and oxygen are expelled from the chlorides and oxides of gold, and metallic gold alone remains. These compounds, therefore, act as oxidising agents.

Gold is not appreciably attacked at any temperature by water or by air, and consequently it does not become tarnished. Molten gold gradually absorbs oxygen from the atmosphere, and retains at least part of the oxygen after solidification. According to Neumann, finely divided gold absorbs from 32 to 48 volumes of oxygen at  $450^{\circ}$ , or 0.24 to 0.36 per cent. by weight. Gold also occludes hydrogen and carbon monoxide under suitable conditions.

Gold is not perceptibly attacked by alkalis or by hydrochloric, nitric, or sulphuric acid. Finely divided gold is slightly soluble in boiling hydrochloric acid and in boiling nitric acid. It dissolves readily at the ordinary temperature in water containing chlorine, bromine, or a mixture of iodine and potassium iodide. It also dissolves readily in a boiling concentrated solution of ferric chloride, and in any mixture producing nascent chlorine, bromine, or iodine. It is slowly dissolved by a solution of potassium cyanide at the ordinary temperature. This action depends on the presence of oxygen or an oxidising agent. The most rapid solvent for gold is hot aqua regia (a mixture of three parts of hydrochloric acid with one part of nitric acid). Another convenient method of dissolving it is to pass a current of electricity through a solution of an alkaline cyanide, using an anode of gold.<sup>1</sup>

The compounds of gold are not numerous and have not been fully studied. One of the chief chemical characteristics of gold is the difficulty with which its compounds are formed and the ease with which they are decomposed.

<sup>1</sup> For further information on the solvents of gold see "The Metallurgy of Gold," T. K. Rose, 5th edition, 1906, pp. 9 and 12.

## IDENTIFICATION OF GOLD.

Gold in the metallic form can be readily identified by its colour, its great density, and by the fact that it is not attacked by hot nitric acid. For confirmation, the gold may be dissolved in aqua regia, and the yellow liquid evaporated to dryness with the occasional addition of hydrochloric acid. The residue, which must not be heated above  $100^{\circ}$ , is redissolved in water, and sulphurous acid gas is passed through the liquid. A black or brown precipitate insoluble in nitric acid denotes the presence of gold.

Cupellation is also a good test of the presence of gold (see chapter on Assaying). The lead remaining on the cupel must be tested further, as it may consist of silver or the platinum metals.

Gold in solution may be identified by acidifying with hydrochloric acid and passing sulphuretted hydrogen or sulphurous acid. If nitric acid or other oxidising agents are present they must be destroyed before  $\text{SH}_2$  or  $\text{SO}_2$  is passed through the solution. The precipitate with sulphuretted hydrogen is black if the solution is cold, brown if it is boiling. The precipitate is soluble in ammonium sulphide, and if it is cupelled or merely ignited it yields metallic gold. Sulphurous acid gives a black precipitate of metallic gold, insoluble in nitric acid, and yielding a yellow bead when cupelled. In these points it differs from tellurium, which also gives a black precipitate with sulphurous acid.

Other reactions of gold in solution as chloride, in the absence of nitric acid, are as follows:—

A mixture of protochloride and perchloride of tin gives a precipitate of purple of Cassius.

Ferrous salts yield a black or brown precipitate of metallic gold. In very dilute solutions, the liquid becomes blue by transmitted light and brown by reflected light.

Oxalic acid and alkaline oxalates precipitate metallic gold, especially on the application of heat.

Ammonia gives a yellow precipitate of fulminating gold.

Potash and soda give a precipitate of oxide of gold soluble in excess. If a large quantity of hydrochloric acid is present the precipitate is not formed.

In the absence of an excess of hydrochloric acid potassium cyanide gives a yellow precipitate soluble in excess.

Solutions containing aurocyanides of the alkalies and thiosulphates of gold do not give the ordinary reactions of gold, although sulphuretted hydrogen precipitates sulphide of gold from thiosulphates. Solutions containing cyanides or thiosulphates may be tested for gold by heating them with aqua regia, evaporating to dryness, taking up with water and a little hydrochloric acid, and testing the solutions in the ordinary way.

#### COLLOIDAL GOLD.

Colloidal gold suspended in water may be obtained in various ways by precipitating dilute solutions of gold chloride. Such gold was first prepared by Faraday, and the ruby-coloured liquids containing it are known as "Faraday's gold." A good method of preparation is to raise to boiling a solution containing from 0.01 to 0.001 per cent. of gold chloride, made slightly alkaline by the

addition of a little magnesia, and then to add a few drops of formaldehyde or oil of turpentine, or a solution of acetylene, or of phosphorus dissolved in carbon disulphide. The red liquid may also be prepared cold, and in that case the action is much more rapid if a drop of liquid containing colloidal gold is added to "inoculate" the solution.

The gold is in the form of minute particles, which are far too small to settle in water under the influence of gravity, so that the liquids remain unchanged even if left undisturbed for years. Nevertheless, the gold is not in solution, as is shown by the fact that it can be removed from the liquid by shaking with freshly precipitated barium sulphate and other precipitates.

These particles of gold are rendered visible under the microscope by means of a powerful ray of light thrown from the side. The smallest particles that become visible are rather less than one hundred-thousandth of a millimeter in diameter, or about six times the diameter of a molecule, so that they are aggregates of about 200 atoms of gold.

The gold is collected and the solutions decolorised by shaking with mercury. Larger aggregates of gold are formed and the liquid gradually changed to a blue colour by the action of acids, neutral salts, alcohol in excess, etc. The blue colour in time changes to violet and then to black, and the gold settles to the bottom.

The same red colour is seen in ruby glass containing gold.

The gold purples, such as the well-known *purple of Cassius*, also owe their colour to finely divided metallic gold or a "colloidal solution" of gold. Purple of Cassius is prepared by adding  $\text{SnCl}_2$  and  $\text{SnCl}_4$  to a solution of

gold chloride. A purple precipitate of hydrated stannic oxide is formed, mixed with finely divided metallic gold. The same colour is seen when alloys of silver, tin and gold are attacked by nitric acid. Recently it has been found by H. Moissan<sup>1</sup> that when a gold-tin alloy is raised to its boiling point in an electric furnace and the metallic vapours allowed to escape into the air, the tin burns and a substance is obtained with the properties of purple of Cassius, and containing tin dioxide, calcium oxide and gold. Similar purples are obtained by distilling mixtures of gold with lime, alumina, magnesia, silica, etc. Müller also prepared in the wet way a number of purples, containing magnesia, lime, baryta and alumina instead of oxide of tin.

#### THE PREPARATION OF PURE GOLD.

“Parted” gold, which contains little except a small proportion of silver, is dissolved in nitro-hydrochloric acid, and the excess of nitric acid is expelled by evaporation on a waterbath with additional HCl. The product consists chiefly of chloro-auric acid,  $\text{HAuCl}_4$ . As soon as scales of gold begin to appear on the surface of the black fused liquid and a smell of chlorine is perceived, the vessel is allowed to cool, when the contents solidify. The gold chloride is then dissolved in a little distilled water and poured into a larger volume of water. A yellow solution is produced with a white cloud of silver chloride suspended in it. This is allowed to settle and the solution is siphoned off, diluted to about 150 c.c. for each gram of dissolved gold, and precipitated by sulphur dioxide or oxalic acid. The former

<sup>1</sup> *Comptes Rendus*, Vol. CXXI. (1905), p. 977.



is the more convenient reagent, as it acts at the ordinary temperature. The brown precipitate of gold (largely consisting of scales and plates, if oxalic acid is used) is allowed to settle; washed at first by decantation, and then, when the smell of  $\text{SO}_2$  has been removed, by shaking with pure cold distilled water in a large flask. After shaking with many fresh additions of water, the flask is heated. As soon as it can be boiled for twenty-four hours with distilled water without showing a trace of hydrochloric acid in the liquid (tested by a considerable excess of silver nitrate), the gold is dried, melted in a plumbago or clay crucible and cast in a blackleaded mould. No scum should appear on the surface of the molten gold, but if a scum appears, it is advisable to clear it away by adding a pinch of borax. The ingot is scratch-brushed and cleaned in acid. It is rolled down between carefully cleaned rolls. The gold may sometimes be still not quite pure, and in that case it can be improved by passing it again through the whole process, redissolving and reprecipitating it.

This method is used at the Royal Mint in the preparation of fine gold trial plates. The most convenient amount of gold to work on is from 10 to 20 oz. Larger amounts than these must be subdivided, and smaller amounts may give less satisfactory results owing to the introduction of impurities in melting and casting.

## CHAPTER III

### THE COMPOUNDS OF GOLD

THERE are two series of simple compounds of gold, corresponding to the general formulæ  $AuR$  and  $AuR_3$ , in which  $R$  is a negative monovalent radicle. There are also some complex compounds which do not exhibit the ordinary reactions of gold. In these gold is regarded as forming part of certain complex ions (see below under "Cyanides of Gold," p. 28).

#### GOLD CHLORIDES.

There are two well-known chlorides,  $AuCl$  and  $AuCl_3$ . As their densities in the gaseous condition have not been determined their molecular formulæ are not certainly known. The formulæ given above are the simplest that can be assigned to these compounds. They are formed simultaneously by the action of chlorine on metallic gold at moderate temperatures, and are split up into gold and chlorine at slightly higher temperatures. Gold and chlorine unite at the ordinary temperature in the presence of moisture, and this property is taken advantage of in the extraction of gold from its ores in the Plattner and other chlorination processes. The rate of action increases as the temperature rises to about  $225^\circ C.$ , when the rapidity of absorption of chlorine by gold in the presence of water vapour is at a maximum. At this temperature a mixture of about 20 per

cent. of AuCl and 80 per cent. of AuCl<sub>3</sub> is formed in an atmosphere of chlorine, approximately corresponding to the empirical formulæ Au<sub>2</sub>Cl<sub>5</sub>. Meanwhile the opposing tendency of the chlorides of gold to decompose into gold and chlorine begins to be apparent at about 70° in an atmosphere of chlorine, and the rate of decomposition increasing with the temperature becomes very rapid at about 300°, so that above this temperature, even in an atmosphere of chlorine, gold chloride is not formed to any great extent.

In the air, the decomposition of gold chloride takes place at far lower temperatures. At 100°, 25 per cent. of AuCl<sub>3</sub> is converted into AuCl in seven days. At 190°, AuCl<sub>3</sub> is completely converted into AuCl in ten hours, and into metallic gold in six days.

The volatilisation of chloride of gold is of importance in connection with the loss of gold in the roasting of ores with salt. It was found by the author<sup>1</sup> that volatilisation begins at about 180° and rapidly increases to a maximum at about 290°. It then falls off gradually until the temperature reaches 800°, when it again begins to increase rapidly. The rate of volatilisation depends partly on the vapour tension of gold chloride and partly on its pressure of dissociation, which is at a maximum between 300° and 800°.

The volatilisation between 500° and 800° (very dull red to red heat) is small. The gold volatilises chiefly in the form of AuCl<sub>3</sub>, with which a little AuCl is mixed.

*Aurous chloride*, AuCl, can be best prepared by heating AuCl<sub>3</sub> to 190° in air. It is a lemon-yellow hygroscopic powder, insoluble in water and ether, but soluble in potassium cyanide. It is decomposed by water at the

<sup>1</sup> *Chem. Soc. Jour.*, Vol. LXVII. (1895), p. 881.

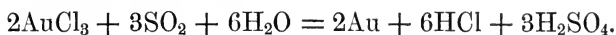
ordinary temperature into gold, which remains as a fine powder, and  $\text{AuCl}_3$ , which dissolves in the water. The density of aurous chloride is 7.4. For its behaviour when heated see above.

*Auric chloride*,  $\text{AuCl}_3$ , can be prepared by acting on finely divided gold with chlorine, especially at about  $200^\circ$ , or by dissolving gold in aqua regia. In the latter case the excess of acid is removed as far as possible by evaporation or a water bath, and the reddish-black liquid is allowed to crystallise. Some chloro-auric acid,  $\text{HAuCl}_4$ , remains mixed with the auric chloride. Pure auric chloride is difficult to prepare. The product obtained by acting on gold with chlorine at  $200^\circ$  to  $300^\circ$  always contains less chlorine than corresponds to the formula  $\text{AuCl}_3$ . If the product is dissolved in water, the metallic gold separated by decantation, and the solution evaporated to the crystallising point, large orange crystals of the hydrate  $\text{AuCl}_3 \cdot 2\text{H}_2\text{O}$  separate. These can be partly dehydrated by standing on a porous tile over concentrated sulphuric acid for some days.

Auric chloride is brilliant red to dark red in colour. It crystallises in needles and leaflets. Its melting point is  $288^\circ$  and its density is 4.3. It is deliquescent and dissolves in water readily with evolution of heat. It is also soluble in ether and alcohol. Water dissolves about five times its weight of  $\text{AuCl}_3$ . The strongest solutions are dark red, but weaker solutions are of a bright lemon-yellow colour.

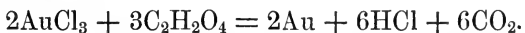
These solutions are decomposed and gold precipitated by many reducing substances, such as sulphurous acid, oxalic acid,  $\text{FeSO}_4$ ,  $\text{FeCl}_2$ , phosphorus, hypophosphites, nitrites and nitrous acid,  $\text{NO}$ ,  $\text{N}_2\text{O}_4$ , arsenious and antimonious

acids. The reaction in the case of precipitation by  $\text{SO}_2$  may be expressed as follows:—



Pure hydrogen, unless nascent, does not appear to act on chloride of gold, but most of the metals decompose it at once. Mercury forms a gold amalgam, lead gives dendritic gold, and tin often yields a purple-coloured precipitate resembling purple of Cassius as well as gold in the form of brown powder. Many organic compounds also precipitate gold, their action being assisted by light and heat. Charcoal acts best on boiling. Solutions of gold chloride leave a violet stain on the skin, which can be removed by cyanide solutions. Cyanide of potassium, if added to gold chloride in solution, produces at first a yellow precipitate soluble in excess; if much free hydrochloric acid is present, no precipitate is formed.

Sulphuretted hydrogen precipitates metallic gold at  $100^\circ$ , but at lower temperatures mixtures of gold, sulphur and sulphides of gold are thrown down. Oxalic acid reduces gold chloride very slowly at ordinary temperatures, but rapidly at  $100^\circ$ . The reaction may be expressed by the following equation:—



The detection of minute quantities of gold chloride in solution is usually effected either by means of protochloride of tin or of ferrous sulphate. Protochloride of tin,  $\text{SnCl}_2$ , gives a brown precipitate of ill-defined composition with concentrated solutions of auric chloride. A mixture of  $\text{SnCl}_2$  and  $\text{SnCl}_4$ , however, prepared by digesting a piece of metallic tin in a solution of  $\text{SnCl}_2$ , with the addition of

a little hydrochloric acid, gives a purple precipitate of purple of Cassius.

The test may be made a very delicate one. The best method of carrying it out is to heat the solution of gold chloride to boiling, and then to mix it suddenly with a few cubic centimetres of a solution of stannous chloride. This is most easily effected by pouring the auric chloride solution into a large beaker containing the stannous chloride. A yellowish-white flocculent precipitate of tin hydrate is formed, and this settles rapidly, and can be separated and transferred, together with a few cubic centimetres of liquid, to a Nessler's tube. In this way the author has detected the presence of one part of gold in solution as chloride in 100,000,000 parts of water (or one grain of gold in six tons of water). The amount of solution used in this case was about three litres, and the colour of the precipitate was a faint greyish-violet, the difference between it and stannous chloride precipitated by pure water being just visible. The presence of one part of gold per million is signalled by a purplish-red to blackish-purple colour.

The ferrous sulphate test is less delicate, but more easily and quickly applied. In comparatively strong solutions a brown precipitate of metallic gold is formed, and in weaker solutions the colour of the solution becomes blue by transmitted light. By comparing two Nessler tubes, one containing distilled water and the other a solution of gold chloride, the presence of one part of gold in about 720,000 parts of water can be detected by the addition of ferrous sulphate.

*Chloro-auric acid*,  $\text{HAuCl}_4$ . When gold is dissolved in aqua regia and evaporated with excess of hydrochloric acid

to the point of crystallisation, long yellow needles are formed on cooling, having the composition  $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ . When heated these needles fuse and then decompose, yielding hydrochloric acid, chlorine, and a mixture of aurous and auric chlorides. The crystals are deliquescent and readily soluble in water. The solutions are in general reduced by the same agents as auric chloride.

A number of double salts of the same type are known and are distinguished by the name *chloro-aurates*. They are prepared by adding a slight excess of metallic chloride to a solution of  $\text{HAuCl}_4$ , evaporating to dryness, taking up with pure water and crystallising out by evaporation in a vacuum. They may be purified by redissolving and recrystallising them. They are all soluble in water and alcohol, and may be represented by the general formula,  $\text{AuCl}_3 \cdot \text{RCl} \cdot n\text{H}_2\text{O}$ .

Potassium chloro-aurate crystallises in yellow needles, having the composition  $2\text{KAuCl}_4 \cdot 5\text{H}_2\text{O}$ . Sodium chloro-aurate,  $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$ , which also forms yellow needles, is used in photography in the toning bath. When pure it contains 49·5 per cent. of gold.

Chloro-aurates of ammonium, barium, strontium, lithium, magnesium ( $\text{MgAu}_2\text{Cl}_8 \cdot 6\text{H}_2\text{O}$ ), calcium, manganese, nickel, cobalt, zinc, cadmium, rubidium and caesium are also known in crystalline form. They are all dehydrated at  $100^\circ$ .

Double chlorides of gold and phosphorus, gold and sulphur and gold and selenium have also been prepared.

#### GOLD BROMIDES.

Two bromides,  $\text{AuBr}$  and  $\text{AuBr}_3$ , have been isolated corresponding to the chlorides. Their vapour density has

not been determined, so that their molecular formulæ are unknown.

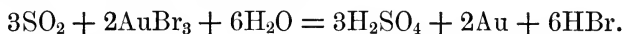
*Aurous bromide*,  $\text{AuBr}$ , is obtained by heating auric bromide, or better still bromo-auric acid, to about  $115^\circ$ . If bromo-auric acid,  $\text{HAuBr}_4 \cdot 5\text{H}_2\text{O}$ , is heated in a porcelain basin, it melts and gives off  $\text{HBr}$  and water. After being kept at  $115^\circ$  for some time, the colour becomes yellowish-grey, and nearly pure  $\text{AuBr}$  remains. Thus prepared it is a yellowish-grey amorphous powder, not deliquescent and insoluble in water, but decomposed by it on boiling into gold and auric bromide. Hydrobromic acid converts it into metallic gold and bromo-auric acid. At temperatures above  $115^\circ$  it is decomposed into gold and bromine.

*Auric bromide*,  $\text{AuBr}_3$ , is prepared by acting on finely divided gold with bromine in the presence of water. The action is slow and may be somewhat expedited by heat. Gold is more readily soluble in a mixture of nitric and hydrobromic acids, but in this case the nitric acid must be subsequently expelled by evaporating at a gentle heat, if auric bromide is to be prepared. In evaporating solutions containing either bromide or chloride of gold, the bottom only of the porcelain basin must be heated, while the sides are kept cool. If this precaution is not taken, the salt creeps up the sides and over the edge, and is found in part on the outside of the vessel.

Auric bromide crystallises in black needles and in scarlet plates. It also occurs as a brownish-black powder. It is not deliquescent and is not very soluble in water, dissolving in about 100 parts of water at the ordinary temperature. Even highly dilute solutions are coloured red, and as the proportion of auric bromide increases the solution darkens,



and concentrated solutions are nearly black. Auric bromide is soluble in ether, and resembles auric chloride in many of its properties. It is split up into gold and bromine at about  $140^{\circ}$ . Its solutions are reducible in the same way as those of chloride of gold. Sulphur dioxide completely decolorises a solution of auric bromide before any gold is precipitated. The final result of the action may be represented by the following equation :—



Auric bromide forms double bromides or bromo-aurates with bromides of some other metals. The bromo-aurates are of reddish-brown colour, and are similar in properties to the chlor-aurates.

#### GOLD IODIDES.

Iodine combines with gold less readily than either chlorine or bromine. Gold dissolves in a solution of potassium iodide containing iodine, forming a solution of potassium iodo-aurate,  $\text{KAuI}_4$ . This salt crystallises in black, lustrous, quadrangular prisms which decompose on heating. Auric iodide,  $\text{AuI}_3$ , is obtained as a dark green precipitate by adding  $\text{AuCl}_3$  little by little to a solution of potassium iodide. Auric iodide is very unstable, and breaks down into aurous iodide and iodine at the ordinary temperature. It is decomposed by potash with precipitation of metallic gold. Aurous iodide,  $\text{AuI}$ , is obtained as a pale yellow precipitate by adding potassium iodide little by little to a solution of auric chloride. It is decomposed into gold and iodine at a temperature of about  $120^{\circ}$ .

Some double iodides or iodo-aurates are also known, as, for example,  $\text{KAuI}_4$ .

## GOLD CYANIDES.

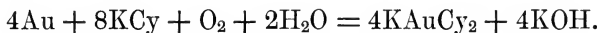
The only simple cyanide known is aurous cyanide,  $\text{AuCy}$ . A number of double cyanides corresponding to a hypothetical auric cyanide,  $\text{AuCy}_3$ , are also known, but no such compound as  $\text{AuCy}_3$  has been isolated.

*Aurous cyanide* is prepared by evaporating down a solution of potassium aurocyanide,  $\text{KAuCy}_2$ , with hydrochloric or nitric acid and washing it with water in the dark. The residue when dried consists of yellow crystalline grains of aurous cyanide. It is insoluble in water, alcohol and ether, and is unaffected by exposure to air and light provided that it has been well dried. It is not attacked by nitric, hydrochloric or sulphuric acid, but dissolves in aqua regia. When heated, cyanogen is given off and metallic gold remains. It is soluble in ammonia, sodium thiosulphate, yellow ammonium sulphide, and in alkaline cyanides.

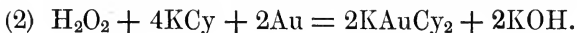
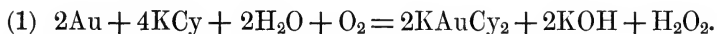
*Aurocyanides* of ammonium, potassium, sodium, barium, strontium, calcium, cadmium, zinc and cobalt have been isolated. These compounds when in solution contain the ion  $\text{AuCy}_2$ , "aurocyanidion," and not the simple ion  $\text{Au}$ . They are colourless and do not show the ordinary reactions of gold. When a solution of potassium aurocyanide,  $\text{KAuCy}_2$ , is electrolysed, it is believed that potassium is set free at the cathode and the ion  $\text{AuCy}_2$  at the anode. The potassium acts on water, liberating hydrogen and forming potash, and also perhaps in part replaces the gold in solution directly, precipitating the gold at the cathode and forming potassium cyanide. The  $\text{AuCy}_2$  set free at the anode immediately breaks down into  $\text{AuCy}$  and  $\text{Cy}$ . The  $\text{AuCy}$  is either precipitated in the anode

sludge or is redissolved in excess of KCy if that is present, and the nascent cyanogen generally attacks the anode, dissolving or oxidising it.

*Aurocyanide of potassium*,  $\text{KAuCy}_2$ , is formed by dissolving AuCy, fulminating gold or  $\text{Au}_2\text{O}$  in a solution of cyanide of potassium. It is also formed by passing a current of electricity through a solution of cyanide of potassium, using a gold anode. Soon after this was discovered it was found by Bagration<sup>1</sup> that plates of gold are slowly dissolved by cyanide solutions without the aid of an electric battery. This is due to the presence of oxygen, as was pointed out by Elsner.<sup>2</sup> The amount of oxygen required was shown by Maclaurin<sup>3</sup> to be in accordance with the equation—



According to Bodländer<sup>4</sup> the action takes place in two stages, the first stage being accompanied by the production of hydrogen peroxide, which then acts as an oxidiser and enables the cyanide to dissolve more gold, thus:—



Oxygen can be replaced by many other oxidisers in this reaction. Among these may be mentioned sodium dioxide, barium dioxide, hydrogen peroxide, potassium permanganate, potassium ferricyanide, chlorine, bromine, etc. The

<sup>1</sup> *Bull. de l'Acad. des Sciences de St. Petersbourg*, Vol. II. (1843), p. 136.

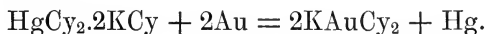
<sup>2</sup> *Erdm. Jour. Prak. Chem.*, Vol. XXXVII. (1846), p. 441.

<sup>3</sup> *Jour. Chem. Soc.*, Vol. LXIII. (1893), p. 724.

<sup>4</sup> *Zeit. für Angewandte Chemie*, 1896, p. 583.

dissolution of gold is assisted in all cases by heat, if the oxidiser is not destroyed by it too rapidly.

Aurocyanide of potassium is also formed without the presence of an oxidiser by the action of the double cyanide of mercury and potassium on metallic gold. In this case the gold directly replaces the mercury in solution according to the equation—



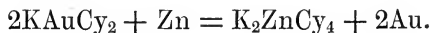
The action is greatly expedited by boiling the solution.

Aurocyanide of potassium crystallises in colourless rhomboidal octahedra, which remain unchanged in air at the ordinary temperature, but are decomposed by heat, cyanogen being given off and a mixture of gold and potassium cyanide remaining. The aurocyanide is soluble in seven parts of cold water and in half a part of boiling water. When it is heated with nitric, hydrochloric or sulphuric acid, hydrocyanic acid is given off and aurous cyanide is precipitated. On boiling with aqua regia all the cyanogen is removed and gold chloride remains.

Ferrous salts are without action on solutions of  $\text{KAuCy}_2$ , but according to Lindbom oxalic acid and sulphur dioxide precipitate aurous cyanide from hot solutions.

Gold is precipitated from solutions of potassium aurocyanide by the passage of a current of electricity or by the action of certain metals, notably zinc, copper and aluminium.

The reaction is probably mainly one of simple displacement, thus:—



When cyanide of potassium is not present in excess, the action stops almost at once, owing to the formation of a

layer of zinc hydrate or zinc cyanide on the zinc, or perhaps to the "polarising" action of a layer of hydrogen. When  $\text{KCy}$  is present in excess the zinc dissolves in it, hydrogen is freely evolved, and potash is formed. In the cyanide process, the zinc shavings used to precipitate the gold tend to become coated with a "white precipitate," which consists of a mixture consisting mainly of zinc hydrate, zinc cyanide, and ferrocyanide of zinc and potassium.<sup>1</sup>

Gold is also precipitated from solutions of  $\text{KAuCy}_2$  by charcoal, and  $\text{AuCy}$  is precipitated by the addition of copper sulphate after acidification with  $\text{SO}_2$ . Aurous cyanide is also precipitated by neutralising a solution of  $\text{KAuCy}_2$  by means of sulphuric acid and adding cuprous chloride.

Aurocyanide of potassium is used in gold baths for electro-plating. The baths may be prepared by passing an electric current through a solution of potassium cyanide, using a large anode of gold and a small cathode.

Aurocyanides of ammonium,  $\text{NH}_4\text{AuCy}_2$ , and sodium,  $\text{NaAuCy}_2$ , are similar in their properties to the potassium salt. The ammonium salt is easily soluble in water, but the sodium salt is only slightly soluble.

All these aurocyanides, when acted on by chlorine, bromine, or iodine, yield compounds, of which  $\text{KAuCy}_2 \cdot \text{Cl}_2 + 2\text{H}_2\text{O}$ , may be taken as a type. These compounds are very soluble in water, and are decomposed by heat.

*Auricyanides* are salts of auricyanhydric acid,  $\text{HAuCy}_4$ , which can be prepared as follows:—A solution of  $\text{AgNO}_3$  is added to a solution of auricyanide of potassium. A

<sup>1</sup> Prister and Bay, *Jour. Chem. Met. and Mng. Soc. of S. A.*, Vol. V. (1904), p. 75.

precipitate of auricyanide of silver is obtained, and this is washed and then treated with a small quantity of HCl. The liquid is then filtered, to remove the silver chloride, and evaporated in a vacuum, when colourless tabular crystals of  $\text{HAuCy}_4 + 1\frac{1}{2}\text{H}_2\text{O}$  result.

Auricyanide of potassium,  $\text{KAuCy}_4 + 1\frac{1}{2}\text{H}_2\text{O}$ , is formed by adding a perfectly neutral solution of  $\text{AuCl}_3$  to a warm concentrated solution of KCy. On evaporating down, large tabular colourless crystals of the auricyanide are formed. They are easily soluble in hot water, and are less soluble in cold water. Auricyanide of potassium begins to decompose when heated to  $200^\circ$ , but fuses at a red heat long before its decomposition is complete.

Auricyanides of ammonium, silver and cobalt are also known.

*Sulphocyanides of gold* are known only as double sulphocyanides, such as aurous potassium sulphocyanide,  $\text{KAuS}_2\text{Cy}_2$ , formed by adding  $\text{AuCl}_3$  to KSCy at  $80^\circ$ . This salt forms insoluble precipitates with many metallic salts. Selenocyanates of gold are also known, but cyanate of gold has not been prepared.

#### OXIDES OF GOLD.

Three oxides have been isolated,  $\text{Au}_2\text{O}$ ,  $\text{AuO}$  and  $\text{Au}_2\text{O}_3$ . These are obtained by precipitating the haloid compounds. They are not readily formed by the action of oxidising agents on metallic gold, and are all reduced at a moderate temperature by heat alone, oxygen being given off and metallic gold left as a residue. *Auric oxide*,  $\text{Au}_2\text{O}_3$ , is obtained by the action of potash or magnesia on a boiling solution of gold chloride. The orange-coloured precipitate

of hydrate of gold,  $\text{AuO}_3\text{H}_3$ , is dehydrated by drying at about  $100^\circ$ . At about  $110^\circ$  oxygen is given off, and at  $160^\circ$  the dark chestnut *auro-auric oxide*  $\text{AuO}$  is produced, soluble in hydrochloric acid. *Aurous oxide*,  $\text{Au}_2\text{O}$ , is produced by the action of potash on  $\text{AuBr}$ . It is a violet-coloured powder, soluble in cold water and in alkalies, and decomposed by hydrochloric acid. It breaks down into gold and oxygen at about  $250^\circ$ . Nevertheless, at  $450^\circ$  gold absorbs and retains from 0.24 to 0.36 per cent. of its weight of oxygen, an amount which corresponds to from 6 to 9 per cent. of  $\text{Au}_2\text{O}$ . In cupellation (*q.v.*) it is possible that some aurous oxide is produced and absorbed as such by the cupel.

Auric oxide dissolves in hydrochloric acid, forming  $\text{HAuCl}_4$ , and it is also soluble in sulphuric and nitric acids. On dilution, hydrated auric oxide is reprecipitated, but by cooling the solution in nitric acid by means of a freezing mixture a *nitrate of gold*,  $\text{Au}(\text{NO}_3)_3 \cdot \text{HNO}_3 \cdot 3\text{H}_2\text{O}$  may be crystallised out. Schottländer also obtained sulphate of gold from the nitrate. When metallic gold dissolves in nitric acid the nitrate is probably directly produced. Several crystallisable double nitrates have also been prepared.

Auric oxide also dissolves in alkalies, forming *aurates*, whence auric oxide is sometimes called auric acid. Potassium aurate,  $\text{KAuO}_2 \cdot 3\text{H}_2\text{O}$ , has been obtained in yellow crystals, and from its aqueous solutions various insoluble aurates have been obtained by precipitation with metallic salts. The aurates are readily reduced by heat, or by organic compounds with the production of metallic gold.

When a solution of gold chloride is precipitated by

ammonia, *fulminating gold* is produced, but this is perhaps better regarded as an amine than an aurate. Raschig states that if prepared in this way it is a mixture of auric diamine,  $(\text{AuN.NH}_3)_2 \cdot 3\text{H}_2\text{O}$ , with auric imidochloride,  $\text{NH.AuCl}$ . It is also produced by the action of ammonia on moist auric oxide. It is of a yellow colour, is soluble in potassium cyanide and in hydrochloric acid, and detonates when struck or heated to  $143^\circ$ . Sometimes it explodes spontaneously at ordinary temperatures. The products of its decomposition are gold, ammonia, nitrogen and water. Other fulminates are obtained by the action of ammonia on aurous oxide,  $\text{Au}_2\text{O}$ .

The aurates also give rise to double sulphites of gold and the alkalies (or *aurosulphites*), when alkaline aurates are acted on by means of alkaline sulphites. The ammonium, sodium, potassium, and barium salts are known.

*Thiosulphate of gold and sodium*,  $\text{Au}_2\text{S}_2\text{O}_3 \cdot 3\text{Na}_2\text{S}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ , crystallises in fine colourless needles, readily soluble in water. Its solutions are sweet to the taste. It is prepared by adding neutral chloride of gold to thiosulphate of soda, and precipitating the salt with alcohol, in which it is very slightly soluble. It was formerly used, under the name "Sel de Fordos et Gélis," for intensifying the images of daguerreotype pictures, gold being deposited on the silver amalgam. The salt still plays an important part in photography in "toning" silver prints, as it exists in combined toning and fixing baths. The solution of the salt exhibits neither the characteristic reactions of gold nor those of thiosulphates. Neither ferrous sulphate, stannous chloride nor oxalic acid precipitates gold from thiosulphate solutions, and sulphuric or hydrochloric acid does not at

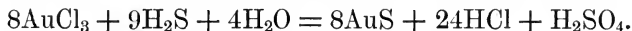


once precipitate sulphur or disengage sulphurous acid. On heating for some time with these acids, or on passing sulphuretted hydrogen through the solution it yields sulphide of gold.

*Silicates of gold* are prepared by fusion of an aurate or of gold chloride mixed with an oxidiser, such as antimony oxide or nitre, with a large excess of a glass rich in silica. The result is a clear yellow glass containing about 0·2 per cent. of gold.

### SULPHIDES OF GOLD.

Two sulphides are known,  $\text{Au}_2\text{S}$  and  $\text{AuS}$ , corresponding to the lower oxides, and a number of double sulphides or thio-salts corresponding to the aurates have also been prepared. When  $\text{H}_2\text{S}$  is passed into a cold solution of  $\text{AuCl}_3$  a black precipitate of  $\text{AuS}$  mixed with sulphur is obtained, the action being partly represented by the following equation:—



If the solution is heated variable mixtures of sulphur, metallic gold and gold sulphides are obtained. Sulphide of gold begins to decompose at  $140^\circ$ , and loses all its sulphur at about  $270^\circ$ . It is unattacked by mineral acids except aqua regia, but is soluble in alkaline sulphides, forming thio-salts which are decomposed by mineral acids.

*Gold selenide* and *gold telluride* are similarly obtained by precipitation from a solution of  $\text{AuCl}_3$  by means of  $\text{H}_2\text{Se}$  and  $\text{H}_2\text{Te}$ .

*Phosphide of gold* is a grey, readily fusible substance formed by gently heating gold in phosphorus vapour or by passing phosphoretted hydrogen into a solution of gold chloride. It burns when heated in air to about  $115^\circ$ .

*Arsenide of gold* is a similar grey, brittle body obtained by heating together gold and arsenic or by acting on gold with the vapour of arsenic. On being heated in air most of the arsenic is expelled. On grinding arsenide of gold with mercury, the gold is amalgamated and the arsenic expelled, but the mercury and amalgam become subdivided into a number of little globules coated with a greyish powder, and it is difficult to collect them again.

*Antimonide of gold* is similar. See also pp. 50 and 51.

## CHAPTER IV

### THE ALLOYS OF GOLD

#### GOLD AND SILVER.

GOLD and silver unite in all proportions when melted together, forming homogeneous alloys. On solidification no separation of the constituents takes place, and the microscopic structure resembles that of pure gold or pure silver. If the mixture is kept melted for some time without stirring, a partial separation of the two metals takes place under the action of gravity, gold settling to the bottom.

The colour of gold becomes paler when small quantities of silver are added to it, and is white with a scarcely perceptible tinge of yellow when 50 per cent. of silver is present. Alloys containing more than 60 per cent. of silver are silver-white. Gold containing small quantities of silver (10 to 20 per cent.) are stated by some observers to be of a green colour ("green gold").

The melting point of alloys containing less than 5 per cent. of silver is the same as that of pure gold, and further moderate additions of silver lower the melting point only slightly. The alloy containing 35 per cent. of silver melts at  $1,061^{\circ}$ , or only three degrees below the melting point of gold. As the percentage of silver increases the melting point falls more rapidly, but if there is only a trace of gold in silver, its melting point is still above that of pure silver,<sup>1</sup> see Fig. 3.

<sup>1</sup> Roberts-Austen and Rose, *Proc. Roy. Soc.*, Vol. LXXI. (1903), p. 161.

All the alloys are soft, malleable and ductile, being intermediate in these properties between pure gold and pure silver. The densities of the alloys are also intermediate between those of the metals, and show no marked expansion or contraction due to the mixing of the metals, although Hoitsema<sup>1</sup> found evidence of slight contraction of about

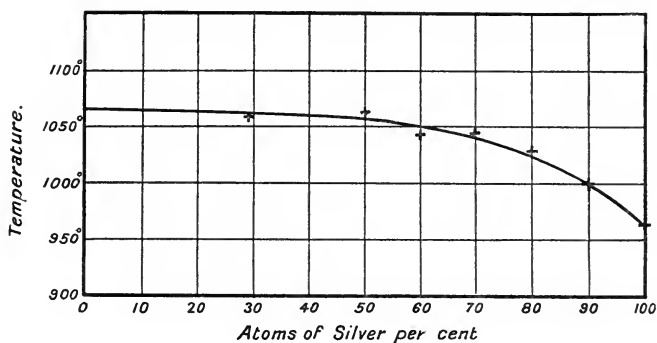


FIG. 3.—Curve showing Freezing Points of the Alloys of Gold and Silver.

0.4 per cent. in some of the alloys. At 15° the densities of unworked cast alloys are as shown in the table on p. 39.

The electric conductivity of alloys of gold and silver was found by Matthiessen<sup>2</sup> to be below that of either gold or silver. The electric conductivity of silver being taken at 100, that of gold is 78, and that of the 50 per cent. alloy only 15.

There is no chemical compound of gold and silver known to be formed, but they appear to form isomorphous mixtures,

<sup>1</sup> *Zeitschrift für Anorgan. Chem.*, Vol. XLI. (1904), p. 66.

<sup>2</sup> *Chem. Soc. Jour.*, Vol. IV. (1867), p. 201.

the crystalline structure of all the alloys being precisely similar.

The behaviour of these alloys when treated with nitric or sulphuric acid is of interest, as upon it are based the usual methods of refining gold. Alloys containing at least 60 per cent. of silver are completely "parted" by boiling in nitric acid, the silver being dissolved and the gold left behind in a brown porous state. The gold obstinately retains about

TABLE OF DENSITIES OF THE ALLOYS OF GOLD AND SILVER.

Gold.	Density.
100 per cent. . . . .	19·31
91·6 „ . . . . .	18·04
79·8 „ . . . . .	17·54
78·4 „ . . . . .	16·35
75·0 „ . . . . .	16·03
66·7 „ . . . . .	15·07
50·0 „ . . . . .	13·60
33·3 „ . . . . .	12·38
25·0 „ . . . . .	11·78
16·7 „ . . . . .	11·28
0 „ . . . . .	10·47

0·1 per cent. of its weight in silver, and if boiling is continued in strong acid, gold dissolves whilst the amount of silver is not appreciably reduced. If the alloy originally contains less than 60 per cent. of silver, the parting is not complete, but the alloy of gold 1 to silver 1·25, containing 55·5 per cent. of silver, yields gold containing only 0·3 per cent. of silver. With equal parts of gold and silver, however, nitric acid leaves half the silver in the gold, and with smaller proportions of silver the acid has less and less

effect. Copper or other base metals can replace silver without materially affecting the results.

Alloys of gold and silver containing over 50 per cent. of gold are difficult to dissolve in acid, and should be melted with more silver if it is required to part them. Nitric acid has little effect on them, and nitro-hydrochloric acid, which dissolves the gold, converts the silver into insoluble chloride, which protects the alloy from further attack. The alternate action of nitro-hydrochloric acid and ammonia eventually results in the dissolution of all the gold, but the method is a tedious one. A mixture of aqua regia and common salt is also sometimes used in the dissolution of these alloys, the silver chloride being dissolved by the salt. A large volume of liquid must be used, as only 0.127 gram  $\text{AgCl}$  can be held in solution by 100 c.c. of a saturated solution of common salt.

Alloys of gold and silver have been used from very early times in jewellery and for coins. Phidon, King of Argos, struck coins of *electrum* in Ægina about the year 720 B.C. Electrum includes pale coloured alloys, containing from 15 to 35 per cent. of silver. A little later pure gold and electrum were being coined side by side in Lydia, with different money values, the electrum being taken as worth 25 per cent. less than pure gold.<sup>1</sup> The addition of copper to harden both gold and electrum was made in Roman coins some time before the Christian era.

#### GOLD AND COPPER.<sup>2</sup>

These metals are miscible in all proportions when molten, and on solidification, separate only to a slight degree. The

<sup>1</sup> Lenormant, "La Monnaie dans l'Antiquité," Vol. I., p. 194.

<sup>2</sup> Roberts-Austen and Rose, *Proc. Roy. Soc.*, Vol. LXVII. (1900), p. 105.

first additions of copper to gold cause a rapid lowering of the melting point. Standard gold, containing gold 91·6 per cent., copper 8·3 per cent., solidifies at 951°, or 103° below the melting point of pure gold, and gold of the French standard coinage alloy containing 90 per cent. of gold, solidifies at 946°. The alloy containing 82 per cent. of gold and 18 per cent. of copper has the lowest melting point, viz., 905°, and this alloy may be a true eutectic. The melting point curve rises continuously with the increase of copper from the eutectic alloy to pure copper, which melts at 1,083°. The densities of the alloys are as follows <sup>1</sup> :—

Gold.	Density.
100 per cent. . . . .	19·31
91·7 „ . . . . .	17·35
90·0 „ . . . . .	17·17
83·3 „ . . . . .	15·86
75·0 „ . . . . .	14·74
58·3 „ . . . . .	12·69
25·0 „ . . . . .	10·03
0 „ . . . . .	8·7

These densities refer, however, to cast specimens. When hardened by rolling or hammering the densities of the alloys become greater. Thus the usual density of an English sovereign (containing 91·66 per cent. of gold) is about 17·48, but these coins for the most part contain a small and variable percentage of silver. From the densities it is evident that gold and copper contract slightly (from 0·5 to 1·0 per cent.) on being alloyed.

<sup>1</sup> Roberts-Austen, *Ann. Chim. Phys.*, [5] XIII. (1878), p. 118; Hoitsema, *Zeit. An. Chem.*, Vol. XLI. (1904), p. 65.



The colour of gold becomes redder when copper is added to it, and if silver is added at the same time, the two metals counteract the effect of each other, so that triple alloys can be formed having a colour closely resembling that of pure gold.

The electric conductivity of alloys of gold and copper is less than that of either gold or copper,<sup>1</sup> and is even less than that of the silver-gold alloys (see above). The chemical compound of gold and copper is known to exist, and the alloys in general show no marked change in properties when the proportions of the metals are slightly varied.

Copper hardens gold and decreases its malleability, these effects continually increasing until the eutectic alloy is reached. This alloy (containing 18 per cent. of copper) is distinctly brittle, breaking under the hammer with a conchoidal fracture, and showing an elongation before rupture of 3·3 per cent., that of pure gold being 30·8 per cent., and that of pure gold alloyed with 0·24 per cent. of lead being 4·9 per cent. The tensile strength of pure gold is 7 tons per square inch, that of standard gold (containing 8·3 per cent. of copper) 16 tons, and that of the eutectic alloy 7·87 tons per square inch.

According to Kurnakoff and Schemtchuschny<sup>2</sup> the two metals are isomorphous, and form a continuous series of mixed crystals. In Fig. 4, which gives the results of their work, the curve of electric conductivity of the alloys is shown in the line PQR. The line ALML<sub>1</sub>B is the liquidus curve connecting the points at which solidification begins, and ASMS<sub>1</sub>B is the solidus curve, denoting the completion of solidification. The minimum M, corresponding to the

<sup>1</sup> Matthiessen, *Chem. Soc. Jour.*, Vol. IV. (1867), p. 201.

<sup>2</sup> *Jour. Russ. Phys. Chem. Soc.*, Vol. XXXIX. (1907), p. 211.



alloy containing about 40·5 atoms per cent. of copper, is coincident with the eutectic observed by Roberts-Austen and Rose. At this point the two curves meet, and there is no pasty stage. When copper is in excess, that is, when

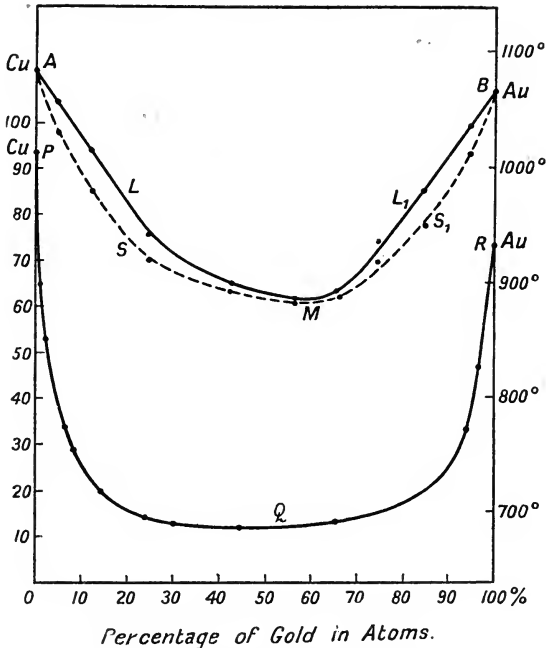


FIG. 4.—Curves showing Freezing Points and Electric Conductivity of the Alloys of Gold and Copper.

more than 18 per cent. by weight or 40·5 atoms per cent. of copper is present, the part first solidified is rich in copper, forming crystallites, which are darkened by a mixture of chloride of iron and hydrochloric acid. The peripheral layers of the crystallites and the matrix are richer in gold

and remain unattacked: see Fig. 5, which is a photomicrograph, after Kurnakoff, of the alloy containing 25 per cent. gold magnified 90 diameters.

The gold-copper alloys are used extensively for coinage and jewellery, pure gold and the gold-silver alloys being too soft, so that they soon become defaced by wear. In jewellery some silver is usually added to the copper and gold (see Chapter XVI.).



FIG. 5.—Gold, 25 per cent.; Copper, 75 per cent.  $\times 90$ .

When alloys of gold and copper are heated in the air they blacken from the formation of oxide of copper, but the black scale can be removed by dissolving in hot dilute sulphuric acid.

#### GOLD AND MERCURY.

These alloys are known as *amalgams*, and are formed, although with difficulty, by the direct union of the two metals at the ordinary temperature. According to Kasentsof,<sup>1</sup> mercury dissolves 0.11 per cent. of gold at 0°, 0.126 per cent. at 20° and 0.65 per cent. at 100°. The mixtures containing less than these quantities of gold are the alloys, liquid at ordinary temperatures, silver-white like mercury, and passing through cloth or other filtering material unchanged.

On the other hand, gold will absorb about six times its

<sup>1</sup> *Bull. Soc. Chem.*, [2] Vol. XXV., p. 20.

weight of mercury, forming a silver-white solid alloy. If this solid amalgam, which contains about 13·5 per cent. of gold, is mixed with more mercury, the result is not a homogeneous body, but a saturated solution of gold in mercury, in which solid particles of gold amalgam are suspended. These solid particles are heavier than mercury and settle to the bottom. They can be separated from mercury by filtration under pressure, but usually retain a small excess of mercury.

The amalgams recovered in gold-mills, in which ores are treated by the amalgamation process, are not true alloys. Before straining they consist of mercury containing a number of little "nuggets" of gold into which mercury has penetrated to some extent. On straining, these nuggets coated with mercury are separated, and the gold miner's amalgam is consequently of variable composition, generally containing from 25 to 50 per cent. of gold, the percentage of gold being highest when the average size of the gold particles is greatest.

When mercury is applied to the clean surface of a piece of solid gold, it "wets" it and at once penetrates through it, passing between the crystalline faces, making it brittle and of silver-white colour. A gold coin or ring is immediately whitened by mercury, and can be broken in the fingers, the fractured surfaces (crystalline faces) being as white as the outside. The amount of mercury so taken up is, however, small, and most of it can be removed by careful heating below a red heat, when the mercury volatilises and, unless air is excluded, the coin blackens.

At 440°, or about 150° below red heat, a large part of the mercury is removed from amalgam by distillation, and a

mixture containing about 75 per cent. of gold remains. At a bright red heat almost all the remainder of the mercury is expelled, but about 0.1 per cent. is retained and cannot be driven off below the melting point of gold.

Amalgams are all attacked by hot nitric acid, the mercury being dissolved and the gold left as a spongy mass. If the action of the acid is kept very slow by dilution and cooling, the gold is left behind, nearly pure, in the form of crystalline needles.

No evidence has been adduced of the existence of any true compounds of gold and mercury.

#### GOLD AND ZINC.

The alloys containing less than 14 per cent. of zinc are pale yellow and of about the same hardness as gold. They increase gradually in brittleness with the increase in percentage of zinc. The first additions of zinc rapidly reduce the melting point and give rise to a long pasty stage during solidification, so that gold containing one or two per cent. of zinc can be readily welded. The alloy, gold 85.6, zinc 14.4 (approximately corresponding to the formula  $\text{Au}_2\text{Zn}$ , that is, containing gold 66.6 atoms, Zn 33.4 atoms, see Fig. 6), is a eutectic, solidifying at  $648^\circ$ . As zinc increases from 14 to 25 per cent. (33.4 to 50 atoms per cent.), the colour of the alloy gradually changes from pale yellow to a beautiful reddish-lilac tint, and the melting point rises from  $648^\circ$  to a maximum of about  $750^\circ$ . This is the melting point of a distinct compound,  $\text{AuZn}$ , containing 25 per cent. of zinc. It forms lustrous crystals and is brittle. With further additions of zinc the lilac colour fades, the alloys containing from 25 to 30 per cent. of zinc consisting of

lilac polygonal crystals of AuZn set in a white matrix. The compound AuZn<sub>2</sub>, containing 39·8 per cent. of zinc (66·6 atoms per cent.) is a hard, white, homogeneous alloy, and will scratch steel, but is as brittle as glass and breaks with a conchoidal fracture, which has a brilliant lustre. It solidifies at 650°. According to Vogel<sup>1</sup> this compound is

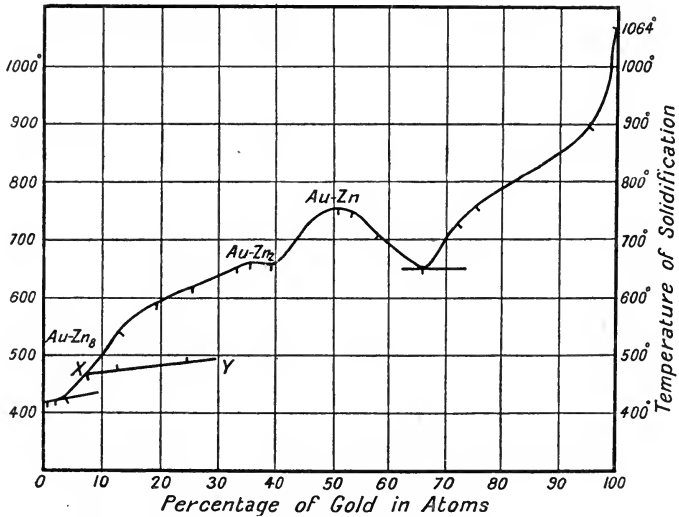


FIG. 6.—Freezing Point of the Alloys of Gold and Zinc.

Au<sub>3</sub>Zn<sub>5</sub> and contains 35·5 per cent. of zinc. The alloys containing more than 40 per cent. of zinc (67 atoms per cent.) become less brittle and less lustrous as the proportion of zinc increases. They are not homogeneous, and present a dull bluish-white appearance resembling zinc. The compound AuZn<sub>8</sub>, containing 72·6 per cent. of zinc (88·9 atoms per cent.), makes its appearance in these alloys. It is a

<sup>1</sup> *Zeit. Anorg. Chem.*, Vol. XLVIII. (1906), p. 319.

hard white substance solidifying with surfusion at about  $470^{\circ}$  (along the line XY, Fig. 6), and probably occurs in the zinc crusts which are formed in Parke's process. The alloys containing more than 72 per cent. of zinc melt at temperatures between  $419^{\circ}$  and  $470^{\circ}$  (see Fig. 6).

All the alloys of gold and zinc are brittle, but those containing from 30 to 80 per cent. of gold (13 to 58 atoms per cent.) are more brittle than the others. The alloys poor in gold are best prepared by adding solid gold to molten zinc below a red heat. The gold is taken up by the zinc quietly. In preparing the alloys containing over 50 per cent. of gold which solidify above a red heat, the metals ignite with momentary incandescence, and a small part of the zinc is volatilised and lost. On heating these alloys to about  $1,000^{\circ}$  the zinc can be boiled off for the most part.

#### GOLD AND CADMIUM.

These alloys present a general resemblance to the alloys of gold and zinc. Heycock and Neville,<sup>1</sup> by distilling off the excess of cadmium from an alloy of the two metals, obtained residues which corresponded approximately in composition with the formula AuCd, but Vogel<sup>2</sup> believes that the compound is  $Au_4Cd_3$ , containing 30 per cent. of cadmium. The compound is greyish or silver-white, somewhat like cadmium, and is very brittle. It solidifies at  $623^{\circ}$ . Another compound,  $AuCd_3$ , containing 63 per cent. of cadmium, melts at  $493^{\circ}$  and is extremely hard and brittle. There is a eutectic alloy containing 87 per cent.

<sup>1</sup> *Chem. Soc. Jour.*, Vol. LXI. (1892), p. 914.

<sup>2</sup> *Zeit. Anorg. Chem.*, Vol. XLVIII. (1906), p. 333.

of cadmium, and freezing at  $303^{\circ}$ , the melting point of cadmium being  $320^{\circ}$ . The alloy containing 31.5 per cent. gold and 68.5 per cent. cadmium, etched with concentrated nitric acid, is shown under a magnification of 25 diameters in Fig. 7. It consists of white crystallites of  $\text{AuCd}_3$  set in a black eutectic mixture. The photomicrograph is after Vogel.

The hardness of this series attains to a maximum in the alloys containing 18 to 30 per cent. and 51 to 63 per cent. of cadmium respectively. The remaining alloys have about the same degree of hardness as the metals themselves. The metals when melted together unite with incandescence to form the alloys, some of the cadmium being volatilised and oxidised.

Like the alloys of gold and copper and of gold and zinc, these alloys can be "parted" by nitric acid and are completely dissolved by aqua regia. The zinc-gold and cadmium-gold alloys are also readily parted by dilute sulphuric acid.



FIG. 7. — Gold, 31.5 per cent.;  
Cadmium, 68.5 per cent.  $\times 25$ .

### GOLD AND TIN.

Three definite compounds of gold and tin have been found to exist.<sup>1</sup> They are  $\text{AuSn}$ , containing 62.4 per cent.

<sup>1</sup> R. Vogel, *Zeit. Anorg. Chem.*, Vol. XLVI. (1905), p. 60.

of gold,  $\text{AuSn}_2$ , containing 45.5 per cent. of gold, and  $\text{AuSn}_4$ , containing 29.4 per cent. of gold.  $\text{AuSn}$  is a metallic silver-grey alloy, harder and more brittle than the other alloys, and having a higher electrical conductivity than other gold-tin alloys except those containing over 95 per cent. of gold.  $\text{AuSn}_2$  is also silver-grey, but consists of large crystals, which are often 10 millimetres long.  $\text{AuSn}_4$  is coloured gold-brown by nitric acid, while  $\text{AuSn}_2$  is unchanged.  $\text{AuSn}$  is as resistant as pure gold to the action of acids.

The curve of fusion falls sharply from the melting point of gold to a eutectic point at  $280^\circ$  and 20 per cent. of tin. It then rises less rapidly to a maximum at  $418^\circ$ , the melting point of  $\text{AuSn}$ , and again falls to a second eutectic point at  $217^\circ$  and 90 per cent. of tin, finally rising to the melting point of tin,  $226^\circ$ .

When alloys of gold and tin are treated with aqua regia the colour of purple of Cassius is seen, and when a gold-tin alloy is heated in an electric arc furnace and the metallic vapours allowed to escape into the air, the tin burns and a substance is obtained having the properties of the purple of Cassius and containing tin oxide, calcium oxide and gold.<sup>1</sup> The residual ingot of gold and tin in the furnace is richer in gold than the original alloy. The alloy containing 8 per cent. of tin is brittle and has a pale whitish-yellow colour externally, with a yellowish-grey earthy fracture. Gold containing only 1 or 2 per cent. of tin is, however, perfectly ductile.

#### GOLD AND ANTIMONY.

About 1 per cent. of antimony makes gold brittle when it is not annealed, and none of the alloys are malleable.

<sup>1</sup> H. Moissan, *Comptes Rendus*, Vol. CXLI. (1905), p. 977.



One definite compound,  $\text{AuSb}_2$ , exists, containing 45 per cent. of gold.<sup>1</sup> This substance is of the same colour as antimony and is extremely brittle and harder than its components. It melts at  $460^\circ$ . The lowest freezing point of the series of alloys is at  $360^\circ$ , corresponding to a eutectic which contains 76 per cent. of gold. A small quantity of antimony greatly reduces the melting point of gold and gives rise to a long pasty stage. Hatchett showed that molten gold absorbs the vapours of antimony and is made brittle thereby. All the alloys are formed with contraction. They are not easily attacked except by aqua regia. According to Cosmo Newbery, when they are finely powdered and triturated with mercury they are slowly decomposed, yielding gold-amalgam and black metallic antimony.

#### GOLD AND ARSENIC.

These alloys have been little studied, but appear to resemble the antimony alloys. They are easily fusible, brittle, pale yellow or grey alloys. Owing to the volatility of arsenic they are not readily formed above a dull red heat. See also p. 36.

#### GOLD AND BISMUTH.

Bismuth alloys with gold, forming pale yellow or greyish alloys which are readily fusible and are all very brittle, although none are hard. Of all metals bismuth has the greatest effect in decreasing the ductility of gold. Even 0.25 part of bismuth in 1,000 parts of fine gold is enough to make the metal fragile,<sup>2</sup> so that it breaks under the hammer. This is due to the fact that bismuth is not

<sup>1</sup> R. Vogel, *Zeit. Anorg. Chem.*, Vol. L. (1906), p. 151.

<sup>2</sup> 33rd Annual Report of the Mint, 1902, p. 72.

dissolved by gold, and no definite compound of gold and bismuth exists. The freezing-point curve of the series of alloys consists of two straight branches which meet in a eutectic point at  $240^{\circ}$ .<sup>1</sup> The eutectic mixture contains 82 per cent. of bismuth. Molten gold absorbs the vapours of bismuth and becomes brittle. All the alloys have a strong tendency to segregate. Small quantities of bismuth do not lower the melting point of gold rapidly as in the cases of antimony and cadmium, but when the bismuth exceeds about 5 per cent. there is a long pasty stage terminating at  $240^{\circ}$ .

#### GOLD AND LEAD.

These alloys are readily fusible, and very brittle, ranging in colour from pale yellow by yellowish-grey to bluish-white. About 0.15 per cent. of lead makes pure gold somewhat brittle. There are two definite compounds of gold and lead,  $\text{AuPb}_2$  and  $\text{Au}_2\text{Pb}$ , containing 32 and 65.5 per cent. of gold respectively.<sup>2</sup> The former forms long white needle-shaped crystals, which are readily distinguished under the microscope from the large well-shaped crystals of  $\text{Au}_2\text{Pb}$ .

Large white crystals of  $\text{Au}_2\text{Pb}$  set in the eutectic are shown in Fig. 8, which is a photomicrograph after Vogel of the alloy containing 70 per cent. of gold, slowly cooled and magnified 70 diameters.

There are three eutectic alloys, containing mixtures of lead and  $\text{AuPb}_2$ ,  $\text{AuPb}_2$  and  $\text{Au}_2\text{Pb}$ , and  $\text{Au}_2\text{Pb}$  and gold respectively. The first of these (D, Fig. 9) has the

<sup>1</sup> R. Vogel, *Zeit. Anorg. Chem.*, Vol. L. (1906), p. 145.

<sup>2</sup> R. Vogel, *Zeit. Anorg. Chem.*, Vol. XLV. (1905), p. 11.

composition gold 14·8 per cent., lead 85·2 per cent., and solidifies at  $215^{\circ}$  or  $111^{\circ}$  below the melting point of lead. The second (C, Fig. 9) solidifies at  $254^{\circ}$  and the third (B, Fig. 9) at  $418^{\circ}$ . All the alloys containing no more than 70 per cent. of gold solidify below a red heat. The freezing-point curve is shown in Fig. 9, which is after Vogel.

Lead is separated from gold by solution in nitric acid, but is still more readily removable by exposure of the molten alloys to a current of air at a red heat (cupellation, *q.v.*). Under these conditions the lead is oxidised, and the litharge,  $PbO$ , so formed can be removed by absorption by a porous substance, such as bone-ash or compacted magnesia, or may be allowed to flow away

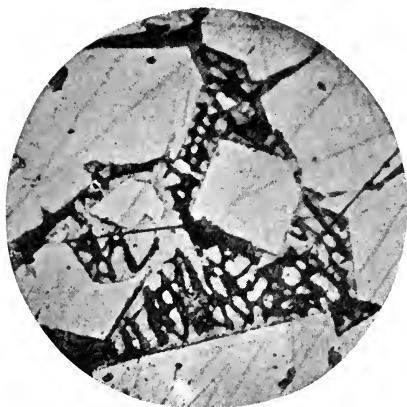


FIG. 8.—Gold, 70 per cent. ; Lead, 30 per cent.  $\times 70$ .

in shallow channels in the furnace bed, the molten metal being held together by its higher surface tension. Almost the last traces of lead are removable in this way, although it is oxidised only when at the surface of the molten gold. Moreover, the molten litharge dissolves and carries away the oxides of other metals which are not readily fusible alone, and consequently a convenient method of removing base metals from gold is to melt it with lead and subject the whole to cupellation. The method is used in refining and

in assaying. Silver, platinum and other metals remain with the gold, and from this cause, as already stated, silver

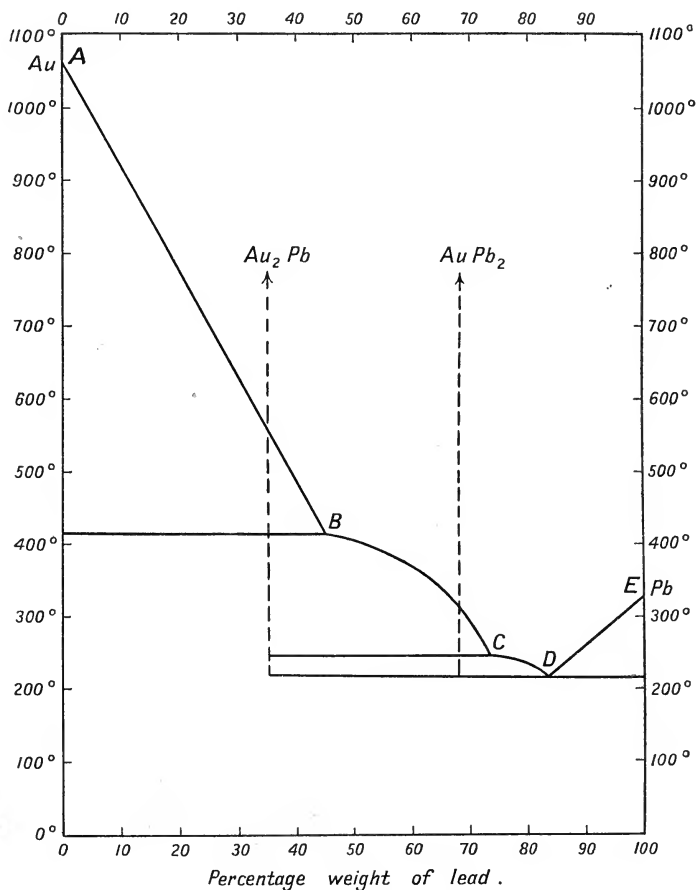


FIG. 9.—Freezing Points of Alloys of Gold and Lead.

and gold were known as “noble metals,” because they would resist the fire, whilst the “base metals” were destroyed as

such. The art of cupellation is of great antiquity, and was known to the ancient Hebrews.

### GOLD AND IRON.

Gold and iron unite without much difficulty and in all proportions, forming alloys which are hard but malleable and ductile, so long as the proportion of iron does not exceed 80 per cent. The only difficulty encountered in preparing the alloys is caused by the high temperature at which iron melts, but it is gradually taken up by molten gold at a temperature of  $1,100^{\circ}$  to  $1,200^{\circ}$ . If cast iron is used, melting at about  $1,130^{\circ}$ , this difficulty disappears. The freezing-point curve of gold and iron has been determined by Isaac and Tammann.<sup>1</sup> It is shown in Fig. 10. The first additions of iron to gold cause a fall in the melting point, the lowest point reached being  $1,040^{\circ}$ , when 5 per cent. of iron is present. With a further increase in the proportion of iron the melting point rises again and reaches  $1,168^{\circ}$ , when 26 per cent. of iron is present. This temperature marks the completion of solidification of all mixtures containing between 26 and 74 per cent. of gold. The gold does not affect the temperatures of the critical points (changes in allotropic form) of iron.

The alloys containing 8 to 10 per cent. of iron are pale yellow, very ductile and susceptible of receiving a high polish. Alloys containing between 15 and 20 per cent. of iron are used in jewellery in France under the name *or gris*. They are greyish-yellow and very hard, but are easily worked. The alloy with 25 per cent. of iron is also employed by jewellers under the name *or bleu*. Those

<sup>1</sup> *Zeit. Anorg. Chem.*, Vol. LIII. (1907), p. 291.

containing from 75 to 80 per cent. of iron are silver-white, extremely hard, and are attracted by the magnet. The gold

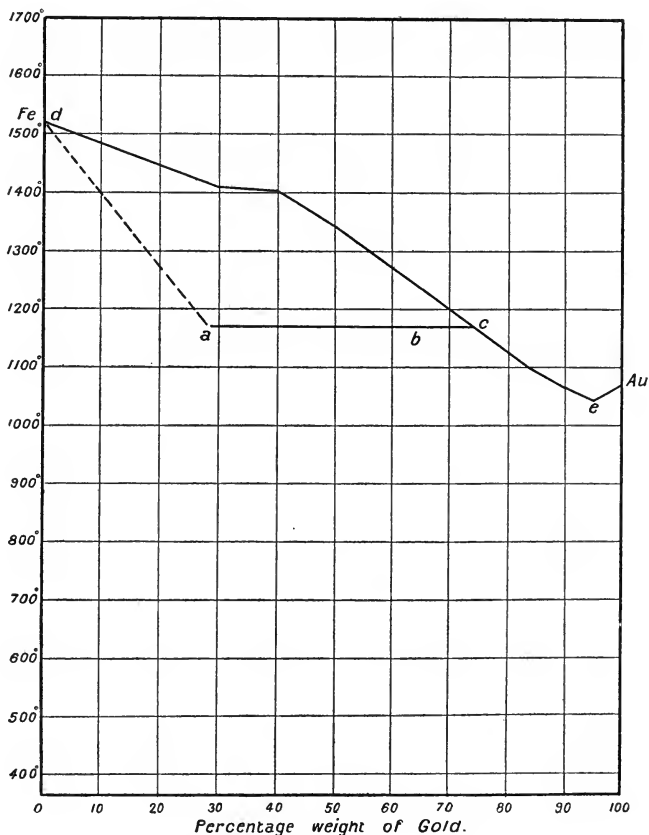


FIG. 10.—Freezing Points of Alloys of Gold and Iron.

and iron in these alloys are not easily separated by cupellation, but they are readily soluble in aqua regia. If the percentage of iron is not too small it is readily removed by

dissolution in hot dilute sulphuric acid, or less conveniently by hydrochloric acid or nitric acid. The alloys of gold and iron are formed with expansion.

### GOLD AND NICKEL.

Small quantities of nickel alloyed with gold produce pale yellow, hard, very ductile alloys, which are magnetic and take a good polish. Hatchett<sup>1</sup> found that 8 per cent. of nickel made gold brittle with a coarse-grained earthy fracture. The two metals form a eutectic,<sup>2</sup> which contains about 22 per cent. of nickel and melts at 950°. The freezing-point curve of the alloys is shown in Fig. 11, which is after Levin.

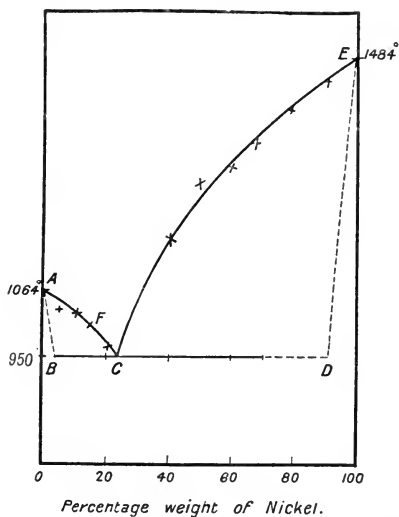


FIG. 11.—Freezing Points of Alloys of Gold and Nickel.

### GOLD AND COBALT.

Cobalt has a far greater effect than nickel in making gold brittle. According to Hatchett, standard gold becomes brittle if only one-eightieth part of cobalt is melted with it.

<sup>1</sup> *Phil. Trans.*, 1803, p. 43.

<sup>2</sup> Levin, *Zeit. Anorg. Chem.*, Vol. XLV. (1905), p. 238.

## GOLD AND MANGANESE.

These alloys are very hard and melt at a higher temperature than gold. The alloy containing about 12 per cent. of manganese is of a pale greyish-yellow colour with a lustre like that of polished steel. It is somewhat malleable, and shows a coarse-grained fracture. The manganese can be removed by cupellation with lead. The alloy containing 67 per cent. of manganese is grey, hard, very slightly ductile, and has a coarsely granulated fracture. The alloy of gold 10 per cent., manganese 90 per cent., is pale grey in colour, and is very ductile with a fine-grained fracture.

## GOLD AND PLATINUM.

These metals are not known to form any definite compounds, but can be alloyed in all proportions. The first additions of platinum at once raise the melting point of the alloy above that of gold, and the alloys formed are malleable and ductile. When the proportion of platinum exceeds 50 per cent. the alloys are brittle and greyish in colour.

A thermal study of the alloys containing up to 60 per cent. platinum has been made by Doerinckel<sup>1</sup> with the results shown in Fig. 12. The curve ABC marks the beginning and the curve ADC the end of solidification. The two metals appear to form a continuous series of mixed crystals. When examined under high powers of the microscope the alloys are seen to consist of crystals of which the cores, richer in platinum than the edges, appear in relief. By annealing at the temperatures indicated by the curve ADC, the alloys become completely homogeneous.

<sup>1</sup> *Zeit. Anorg. Chem.*, Vol. LIV. (1907), p. 345.



The yellow colour of gold disappears rapidly on the addition of platinum, and only a slight yellow colour remains when 30 per cent. of platinum is present. If the platinum is above 40 per cent. the colour is that of platinum. The alloy of gold 10, platinum 90, has a

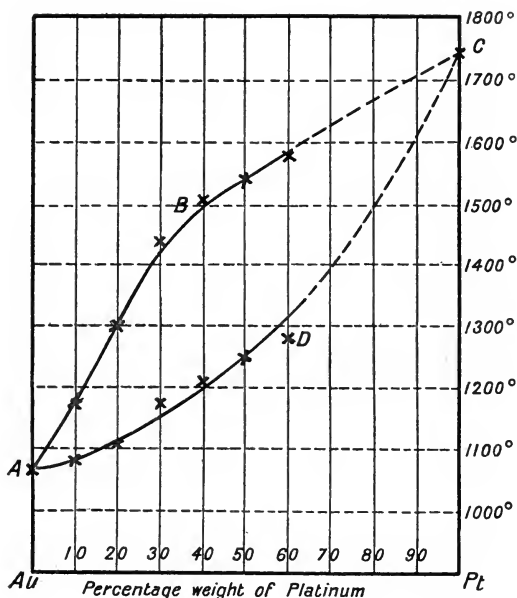


FIG. 12.—Freezing Points of Alloys of Gold and Platinum.

brilliant white crystalline structure, and the alloy gold 25, platinum 75, is hard and brittle, resembling grey cast iron. (E. Matthey).

E. Matthey has shown<sup>1</sup> that the alloys containing from 5 to 20 per cent. of platinum are not uniform in composition,

<sup>1</sup> *Phil. Trans.*, Vol. CLXXXIII. (1892), p. 629.

the platinum moving towards the centre of the ingot on solidification. These alloys cannot be separated into their constituents by cupellation and parting in acid in the ordinary way. They are not attacked by single acids, but are dissolved by aqua regia.

#### GOLD AND PALLADIUM, RHODIUM, IRIIDIUM, ETC.

These alloys have been very little studied. The gold-palladium alloys form a continuous series of mixed crystals (see Fig. 13, which gives the curves of fusibility after Ruer). Gold containing from 10 to 20 per cent. of palladium is nearly white and is hard but ductile. The alloy of gold 50 per cent., palladium 50 per cent., is said to be iron-grey in colour and deficient in ductility.

Gold forms difficultly fusible but ductile alloys with osmium and rhodium. It is doubtful whether any real alloy with iridium is formed. When gold containing iridium is melted, the iridium sinks to the bottom. On treatment with aqua regia the gold is dissolved and the iridium left in the form of a black powder which is mainly if not entirely oxide of iridium.

#### GOLD AND ALUMINIUM.

These metals form at least two definite compounds. One of them,  $Au_2Al$ , containing 6.4 per cent. of aluminium, is a hard white substance melting at  $622^\circ$ .<sup>1</sup> The eutectic alloy between this compound and pure gold contains only 4 per cent. of aluminium but melts at  $525^\circ$ , over  $500^\circ$  below the melting point of pure gold. The other compound,  $AuAl_2$ ,

<sup>1</sup> *Phil. Trans.*, Vol. CXCIVA. (1900), p. 201.

containing 21·5 per cent. of aluminium, solidifies at a higher temperature than the melting point of pure gold itself.<sup>1</sup> This compound is of a beautiful purple colour which resembles but is deeper in tint than the compound

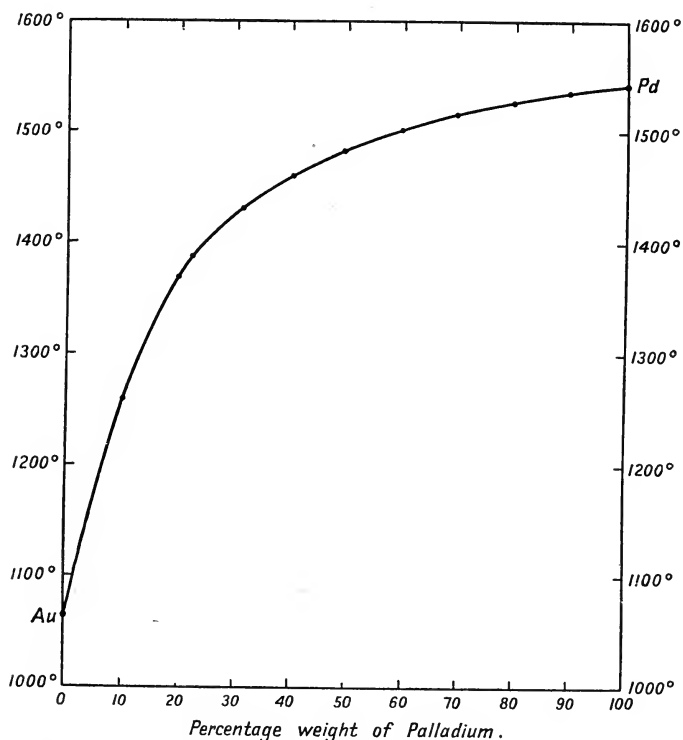


FIG. 13.—Freezing Points of Alloys of Gold and Palladium.

AuZn. It is formed whenever gold and aluminium are fused together, provided that at least 10 per cent. of aluminium is present. The purple compound is readily seen in any of these alloys, occurring in patches in a white

<sup>1</sup> *Proc. Roy. Soc.*, Vol. L. (1892), p. 367.

matrix consisting of the excess of aluminium or of the white compound of aluminium. There is little evidence of the existence of any other compounds of gold and aluminium except these two.

#### GOLD AND TELLURIUM.<sup>1</sup>

The curve of fusibility is shown in Fig. 14. A compound,  $\text{AuTe}_2$ , containing 43·6 per cent. of gold exists, freezing at  $452^\circ$ . This corresponds in composition to the mineral species sylvanite and calaverite. There are two eutectics, one containing 60 per cent. of gold and fusing at  $432^\circ$ , and the other containing 20 per cent. of gold and fusing at  $397^\circ$ . The presence of 0·05 per cent. of tellurium is enough to cause the formation of a small quantity of the gold-rich eutectic, and gold containing this amount of tellurium is accordingly deficient in ductility. When more tellurium is present, the alloys are very brittle.

The alloys rich in gold consist of crystals of gold set in the greyish-white eutectic. Gold containing 2·4 per cent. of tellurium is of a pale brass-yellow colour, but even when 40 per cent. of tellurium is present, a faint yellowish tinge is still perceptible, which disappears before the pure compound  $\text{AuTe}_2$  is reached. The behaviour of tellurides of gold on roasting is partly explained by the remarkably low temperatures of fusion of these alloys, all mixtures containing less than 60 per cent. of gold being completely fused before a red heat is reached. The production of spherical globules of gold must therefore accompany the roasting of gold ores containing tellurides, however carefully the operation may be carried out. These globules will not be free from tellurium.

<sup>1</sup> T. K. Rose, *Trans. Inst. of Mng. and Met.*, Vol. XVII. (1908), p. 285.

GOLD AND THALLIUM.<sup>1</sup>

These metals form neither compounds nor homogeneous solid solutions. There is a eutectic alloy containing 27 per cent. of gold and melting at 131°. This eutectic occurs in

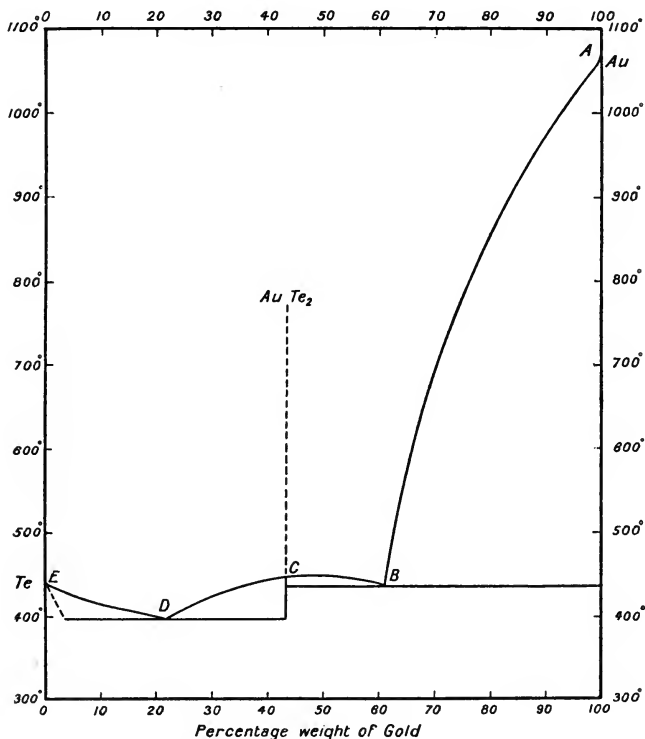


FIG. 14.—Freezing Points of Mixtures of Gold and Tellurium.

all the alloys, so that the addition of a small amount of thallium to gold gives rise to a long pasty stage, terminating at 131°. The alloys are all brittle.

<sup>1</sup> Levin, *Zeit. Anorg. Chem.*, Vol. XLV. (1905), p. 31.

## CHAPTER V

### THE OCCURRENCE OF GOLD IN NATURE : GOLD ORES

GOLD generally occurs in Nature in the metallic state alloyed with a varying proportion of silver and smaller quantities of copper and other metals. Native gold is never found pure, but sometimes contains less than 1 per cent. of impurities. According to Furman,<sup>1</sup> the finest native gold which has been met with is that from the Pike's Peak mine, at Cripple Creek, Colorado, which contained 99·9 per cent. of pure gold.

Gold occurs in the form of nuggets, grains and "dust" in many river gravels. In this form it was known to the ancients, and, as already pointed out, was probably the earliest metal known to man, although it is unlikely that any use was made of it until long after its first discovery. In some gravels masses of gold of considerable size occur. The largest piece recorded was the "Welcome" nugget which was found in Victoria. It weighed 2,195 oz., and yielded gold to the value of £8,376 10s. 6d. Large nuggets have also been found in other parts of Australia, in Russia, and in California. Auriferous deposits consisting of sands and gravels formed by the erosion of older rocks are known as placer deposits or *placers*. The gold in these deposits is rounded by attrition, all its sharp angles having been worn off. The nuggets of gold are often larger and purer

<sup>1</sup> *Colliery Manager and Metal Miner*, October, 1896, p. 89.

than the masses found in lodes in the same localities; but there is now little doubt that the gold in placer deposits previously existed in ores in veins and has been derived from them by the action of running water, or in rare cases by the waves of the sea. A large proportion of the gold production of the world was formerly obtained from placers by washing, but placer gold is now of secondary importance, most of the present enormous output of gold coming from gold ores which require to be crushed before the values can be extracted.

The occurrence of well-defined crystals of gold is rare, but has been noted in lodes in Transylvania, California, Australia and Brazil. The usual forms are cubes and octahedra, with rod- and plate-like forms. The crystal faces are frequently striated, and the crystals are generally rounded, uneven, or even curved. Twinning gives rise to dendritic and reticulated groups, but individual crystal faces and edges are usually very small. Moss-gold, leaf-gold and wire-gold are forms occurring sometimes. The interior of nuggets when polished and etched shows a crystalline structure similar to that of fused masses. No traces have been observed of a laminated, concentric structure such as might be expected if the nuggets had grown by accretion by means of deposition from solution. It is of course arguable that the deposited gold may have been rearranged after deposition by the slow effects of solid diffusion.

Gold ores are usually found in veins or lodes in rock formations. The greater part of the material ("gangue") forming the lodes is usually quartz, but various silicates also occur, and sulphides, arsenides or antimonides of base

metals are almost invariably present. The upper portions of these veins near the surface of the ground are often found to have undergone oxidation from the influence of the atmosphere, so that the sulphides of iron, etc., have been converted into oxides. These *gossans*, or oxidised portions, may extend downwards to a considerable depth, and the gold contained in them, associated as it is with a loose mixture of silica and oxide of iron, is often readily separated. When the oxides pass into sulphides with increase of depth, the extraction of gold may become more difficult. The great deposit of ferruginous sinter, mainly composed of silica, found at Mount Morgan in Queensland, from which gold to the value of several millions of pounds has been extracted, is the richest gossan known.

Generally, below the water level in the rocks of the district gold is found associated with metallic sulphides.

According to Dr. Don<sup>1</sup> gold is always present in lodes, in the districts of Australia which he examined, when pyrites occurs, and is absent when no pyrites is observable. According to L. Wagoner, however, gold sometimes occurs in Western America in rocks free from sulphides. The gold in lodes is in the form of minute scales, threads or grains disseminated through the ore. It is sometimes visible to the eye without magnification, but is more often in too fine a state of division to be seen. It also occurs in copper and iron pyrites, gilding the faces of the crystals or otherwise associated with them, probably in the metallic state, not as a sulphide.

If sulphides of gold are rare or unknown, on the other hand tellurides of gold, containing the compound  $\text{AuTe}_2$ ,

<sup>1</sup> *Trans. A. I. M. E.*, Vol. XXVII. (1897), p. 564.



are very common. They occur in considerable quantities in Western Australia, Colorado and Transylvania, and have been reported from many other localities. Various mineralogical names have been assigned to the tellurides from different localities, the best known being calaverite, which has the composition  $\text{AuTe}_2$ , sylvanite or graphic tellurium, which appears to be a variable mixture of  $\text{AuTe}_2$  and  $\text{Ag}_3\text{Te}_4$ , petzite ( $\text{Ag}_2\text{Te}$ , in which some silver is replaced by gold) and nagyagite, or foliated tellurium, which contains a considerable percentage of lead.

The tellurides are for the most part dark grey or black in colour, rarely silver-grey. They are often mixed with metallic gold, which sometimes gives them a brassy-yellow colour. When heated in air they oxidise, fuming and giving off  $\text{TeO}_2$ , and fuse below a red heat. The removal of most of the tellurium leaves the gold in the form of round pellets which have solidified from fusion. Calaverite has a density of about 9, and contains about 44 per cent. of gold, part of which is usually replaced by silver. Sylvanite has a density of about 8.1. Analyses of two specimens from South Dakota and Cripple Creek respectively gave the following results<sup>1</sup>:—

(1) Gold . . . 7.64 per cent.	(2) Gold . . . 5.61 per cent.
Silver . . . 32.39     ,,	Silver . . . 34.23     ,,
Tellurium 59.96     ,,	Tellurium 60.16     ,,
<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>
99.99	100.00
<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>

Petzite, or  $\text{Ag}_2\text{Te}$ , has a density of 8.86 (Miers). A specimen from California contained 25.6 per cent. of gold

<sup>1</sup> F. C. Smith, *Trans. A. I. M. E.*, Vol. XXVI. (1896), p. 485.

and 41·86 per cent. of silver (Genth). Nagyagite is foliated like graphite, but has a density of about 7. It contains only a few per cent. of gold.

The proportion of gold present in ores or gravels which can be treated profitably for its extraction is very small. The mean return from the Rand ores is less than half an ounce per ton, or about one part of gold in 70,000 parts of worthless material. Auriferous gravels which do not require to be crushed are sometimes treated at a profit when they contain only two or three grains of gold per ton, or say one part of gold in five millions.

Beyond the limits of profitable extraction gold is very widely disseminated. Minute quantities of gold appear to occur in all ores of silver, copper, lead, antimony and bismuth.<sup>1</sup>

It has also been detected in igneous rocks in almost every case in which a diligent search for it has been made. It is perhaps even more generally distributed throughout metamorphic rocks, and sedimentary rocks are seldom quite free from it. L. Wagoner found<sup>2</sup> an average of 0·37 part of gold per million, or 5 grains per ton in granites, 0·03 part per million in sandstones, and 0·007 part per million in limestones. It also occurs in many clays and shales. For example, the bed of clay on which the city of Philadelphia is built is an auriferous deposit. It has been suggested that the gold in sedimentary deposits has been derived from the sea, but it seems at least equally probable that the gold previously existed in the older rocks from which these deposits were formed. The comparatively small quantity of gold in limestones which are formed in clear

<sup>1</sup> "Metallurgy of Gold," T. K. Rose, 5th edition, p. 36.

<sup>2</sup> *Trans. A. I. M. E.*, November, 1901.

water far from land points rather to the land as the place of origin of the gold.

Gold was first detected in sea water by Sonstadt,<sup>1</sup> who states that the amount in British waters is far less than one grain per ton. Liversedge found<sup>2</sup> between one-half and one grain per ton in various samples of water taken from the sea off the coast of Australia. L. Wagoner<sup>3</sup> found from 0·6 to 3·7 grains of gold per ton of water from the depths of the Atlantic, and only 0·2 grains per ton in Chesapeake Bay. The total quantity of gold in the sea is evidently enormous, amounting, on the figures given by Liversedge, to about £10,000,000 to each inhabitant of the globe, but there appears to be no prospect of its successful extraction on a large scale. It is not known how gold came to be present in sea water. /

The origin of gold ores is not yet certainly determined. Gold is usually contained in quartz veins which pass through rocks of many different kinds. The effects of segregation, by which solid crystals of definite composition grow in a fluid containing a number of different constituents, seem to be quite enough to account for the existence of quartz veins in igneous and metamorphic rocks and of gold in quartz veins. Given a molten mass of rock, there would be nothing surprising in nearly pure silica beginning to solidify at certain points and receiving additions of more silica by the operations of diffusion. When the whole mass had become solid, the segregated silica would readily become converted into quartz and also receive still further

<sup>1</sup> *Chem. News*, Vol. XXVI. (1872), p. 159.

<sup>2</sup> *Roy. Soc. N.S.W.*, October 2, 1895.

<sup>3</sup> *Trans. A. I. M. E.*, 1907.

additions by the agency of heated water, by which silica would be dissolved, transferred and re-precipitated. The concentration of gold in quartz veins and other ores may have been effected in a similar manner.<sup>1</sup> It is of course well known that when a crystalline nucleus of any mineral, such as gold, has been formed, there is a tendency for all particles of the same mineral which are brought near the nucleus by diffusion or in other ways to be fixed to it, so that the crystal grows. The almost universal dissemination of gold throughout rocks of all sorts and in the waters passing through them would thus afford an unfailing source for the creation of gold ores by the enrichment of certain zones. The length of time required for the formation of the gold ores which have been discovered is not known.

The veins containing gold ores mainly traverse metamorphic rocks, especially slates or schistose rocks, such as hydromica and chlorite schists. Valuable gold ores are sometimes met with in basalt, rhyolite, and other igneous rocks, and also occur "in many different forms, as replacement-deposits in limestones, as disseminations in igneous and sedimentary rocks, and as contact-deposits near intrusive masses . . ." <sup>2</sup>

Gold-bearing gravels are, generally speaking, valuable when they occur in river-beds in districts containing gold ores, and consequently they are for the most part confined

<sup>1</sup> For a full discussion of the origin of gold ores, see papers by Posepny, Spurr, Rickard, Weed, Wagoner, Don, and others, in the *Transactions of the American Institute of Mining Engineers*, and elsewhere. For a short *résumé* with references, see "Metallurgy of Gold," T. K. Rose, 5th edition, pp. 42—44.

<sup>2</sup> "Igneous Rocks as related to Occurrence of Ores," J. E. Spurr, *Trans. A. I. M. E.*, 1902.

to rivers flowing through metamorphic rocks, especially slates and schists. The beds of ancient rivers which have long ceased to flow are sometimes very rich. Such river gravels have been covered by thick masses of eruptive basalt and other deposits in California and Victoria. In the latter country they are known as "deep leads."

The geographical distribution of gold ores corresponds roughly with what has been said as to the geological distribution. Mountainous districts and the streams flowing from them are frequently auriferous. Wide, flat, alluvial plains generally contain no gold. In Europe the chief gold mines are in Hungary and Transylvania. Some gold is produced in North Italy, Norway, Wales, etc. The Russian gold production is mainly from the placers of Siberia. In India gold occurs at Colar, in Mysore, and in small quantities in Madras. The other goldfields of Asia are in Borneo, Celebes, Sumatra, and some other East Indian islands, in China, Korea, Japan, and in the Malay Peninsula. In Africa the greater part of the gold produced is from the Transvaal and Rhodesia, but deposits of less importance occur in West Africa, in Egypt, and in Abyssinia. Gold is widely distributed in the western mountains of North America, alike in Canada, the United States, and Mexico. Minor goldfields exist in the Appalachians and in Eastern Canada. The goldfields of Central and South America were formerly more important than at present. They occur both on the Pacific and the Atlantic slopes. Gold occurs in many parts of Australia and in several districts in New Zealand.

The production of gold for different countries is given in Chapter XVIII.

## CHAPTER VI

### EXTRACTION OF GOLD FROM ITS ORES : GOLD WASHING

WHEN the treatment of gold ores is under consideration they fall naturally into two divisions—(a) loose aggregations, from which the gold can be removed by concentration in virtue of its high specific gravity, and (b) relatively hard ore, which must be crushed before the gold can be extracted. It is convenient to include in the first division gravels which have been cemented by infiltration of silica, oxide of iron, lime, etc., so that they have become too coherent to be treated without crushing. Many examples of such “cement gravels” occur in California. The second division includes some quartzose ores, in which the gold is mainly in the form of grains of moderate size, so that after crushing most of the gold can be collected by simple concentration. Ores of this character have been met with chiefly in Australia. Gold in a finer state of division escapes under such treatment, but is caught by mixing the crushed ore with mercury. The gold then becomes “amalgamated,” and the small particles of gold-amalgam are recoverable by taking advantage of their tendency to coalesce with one another, or with fresh mercury, so as to form large globules, which readily sink in pulp diluted with water. Gold-amalgam may also be separated from the crushed ore or pulp by bringing it into contact with a metal plate, the surface of which has been previously amalgamated by

rubbing with mercury. In the latter case the gold-amalgam adheres to the amalgamated plate, and is removed at intervals by scraping. Mercury is also largely used in the treatment of auriferous gravels.

Very finely divided gold, however, may escape amalgamation, and the resistance to amalgamation is still more marked in the case of compounds of gold, such as tellurides, which show little or no tendency to yield up their gold when brought into contact with mercury. Many ores, too, contain materials which exercise a deleterious effect on mercury, preventing its globules from coalescing, so that they are lost in the tailings, together with the gold which they have picked up. All such ores which do not yield a satisfactory percentage of their values on treatment with mercury are known as "refractory" ores, as distinguished from "free-milling" ores.

In a sense all ores are partly refractory, inasmuch as a part of the gold contained in them is not in a condition to be recovered by means of mercury, however carefully the treatment is carried out. Accordingly it is now customary to treat the tailings from the amalgamation process by mixing them with a solution of cyanide of potassium. Very finely divided gold is dissolved by cyanide solutions, which are then separated from the ore. The gold is obtained from them by precipitation. Sometimes tailings containing rich pyrites or other sulphides are treated by concentration, and the concentrates are smelted with lead, or roasted and subjected to the action of a solution of chlorine in water by which the gold is dissolved, with a view to subsequent precipitation.

Refractory ores are treated by smelting, cyaniding, or

chlorinating, according to their nature and to various other considerations. When the gold has been obtained, whatever methods have been employed, it is melted and cast into bars and afterwards refined to fit it for use in the arts.

The methods of treatment of gold ores may accordingly be tabulated as follows:—

1. Simple “washing” or concentration, with or without the aid of mercury. This is suitable for auriferous sands and gravels (placer deposits).

2. Crushing and concentration, usually with the aid of mercury: suitable for free-milling quartzose ores.

3. Subjecting crushed ores, usually without roasting, to the action of cyanide of potassium: suitable for the tailings from free-milling ores and for certain refractory ores.

4. Roasting and chlorination: suitable for concentrates from free-milling ores which have already been amalgamated, and for certain refractory ores.

5. Smelting in blast furnaces to obtain the gold as an alloy of lead: suitable for certain refractory ores and concentrates. This is described under the treatment of silver ores, Chapter XI.

The methods given above will now be briefly described, and some of their chief modifications touched upon.

### 1. GOLD WASHING.

Small quantities of rich sands are washed in the *miner's pan*, which was originally the cooking-pan of the prospector. It is a flat-bottomed pan of sheet-iron, about 16 inches in diameter, with sloping sides 4 or 5 inches wide. It is often made with one or more “riffles” or shallow trenches in the



side or on the bottom near the angle to catch mercury and amalgam. When used, it is nearly filled with sand and water, and is first well shaken to enable the gold to settle to the bottom, and then dipped in and out of water in an inclined position to enable the sand to escape over the edge by degrees. The final operation of separating the last remaining sand from the gold requires a considerable degree of skill. This implement was much used in early days in California and Australia, when a single panful of dirt sometimes yielded several ounces of gold. A somewhat similar wooden (usually mahogany) bowl, the *batea*, is especially favoured by the negro race. It is a conical vessel about 18 inches in diameter, and 2 inches deep in the centre (see

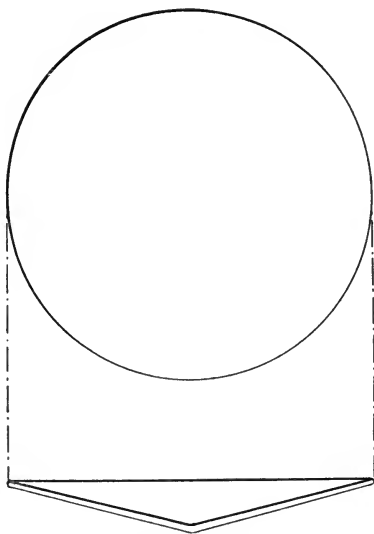


FIG. 15.—Batea.

Fig. 15). The gold clings to the wood when it would slide over iron. In the East a wooden trough is used.

For concerted work by a small party of diggers, the *cradle*, or rocker, is more advantageous. It consists of a wooden box, resting on two rockers DD, like a baby's cradle (see Fig. 16, which is a sectional elevation). One man shovels gravel into the box A, the bottom of which

consists of a sieve, while another pours on water with one hand and rocks the cradle with the other. Mercury is sprinkled on at intervals. The fine sands and gold pass through the sieve and over some inclined plates B, to which cross-bars of wood, C, are nailed. The heavy materials—gold, mercury, amalgam, pyrites, etc.—accumulate behind the cross-bars, or “riffles,” and every now and then are scraped out and panned. The amalgam is heated on a shovel and the mercury driven off, leaving the gold behind.

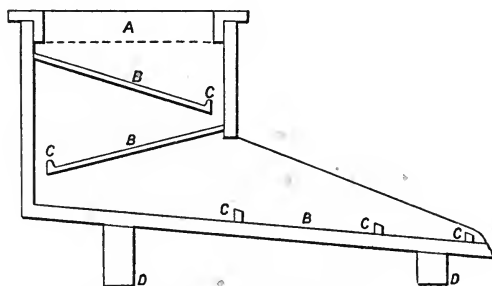


FIG. 16.—Cradle.

When larger quantities of auriferous gravel are available, a *sluice* is generally used. A sluice-box is a slightly inclined trough made of wood, through which the gravel is carried by a stream of water. Mercury is sprinkled on at short intervals of time. A large number of boxes are sometimes fitted together, making a sluice which may be some hundreds of yards long.

The methods of conveying the auriferous material to the sluices vary with the scale of the operations and the other conditions. When small sluices or rocking cradles are used the gravel is piled near at hand and shovelled into them. In Siberia, where the valleys are shallow and the

inclination of the ground small, the gravel is carried in carts up an inclined plane to an elevated wooden platform whence the sluice starts.

In California, where the "gulches" are deep, the fall of the ground rapid, water plentiful, and the auriferous deposits of great thickness, the banks of gravel are sometimes attacked by jets of water under high pressure, and the earth washed down and carried through the sluices without being touched by hand. This is called *hydraulic mining*, or "hydraulicking." When the gravel beds are below the general level of the country they may be raised by the "hydraulic elevator," a jet of water under a head of as much as 400 or 500 feet, carrying water, sand and boulders alike up a pipe inclined at some 60 degrees to the horizon, so as to deliver them all at the head of the sluice, the vertical lift being sometimes over 50 feet. When gravels are buried beneath great thicknesses of lava or other materials, as in the case of the "deep leads" of Bendigo, Ballarat and other places in Victoria, the gravel is mined and raised through shafts. If the gold-bearing material is hard and compacted, it is coarsely crushed in a stamp mill resembling those described in Chapter VII., but sometimes called a "cement mill."

The sluice is paved in various ways to take up the wear and to catch the gold and amalgam. An irregular bottom is required with plenty of depressions, chinks and crannies into which the gold can settle. The obstructions are known as *riffles*. The simplest contrivances are fir poles about four inches in diameter, left rough with the bark on. These poles are cut to the required length and nailed or wedged in the bottom of the sluice either transverse to the

direction of the current or longitudinally. The latter is generally preferred. Other riffles in use consist of cut slats of wood nailed to the bottom of the trough or sluice. In Siberia square "pigeon-hole" depressions have been continuously used for more than fifty years. In California the sluice is sometimes paved with 6-inch square blocks of wood placed about two inches apart, or with large rounded stones, or ordinary iron rails placed longitudinally. All these afford plenty of crevices where the amalgam can lodge. In later years the use of perforated iron plates and of "expanded metal" has largely increased. To catch light spangles of gold, blankets are spread, the loose fibres of which become charged with pyrites and gold, and in New Zealand plush is a favourite gold-catcher. Amalgamated plates, both stationary and shaking, are also used.

On dredges, where the sluice is necessarily short, a number of different kinds of riffles are often used in the same sluice. The view has been expressed<sup>1</sup> that this is advantageous because "the ripple in the water as it flows down the box is altered, and consequently the material being treated is tossed about, its course altered, and the gold which may be adhering to the stones or grit has more chance of being liberated." There are, of course, two somewhat opposed operations to be carried out in a sluice. The process of disintegration of the gravel, if not previously completed, must be finished in the sluice by "tossing about" the auriferous material, but the main function of the sluice must be to save gold. This is done by affording opportunities to the denser particles of matter to settle to

<sup>1</sup> E. S. Marks and G. N. Marks, *Trans. Inst. of Mng. and Met.*, Vol. XV. (1906), p. 479.

the bottom, and any eddies in the water, "boiling-up" or disturbances of any kind interfere with the process. The flakes of gold, instead of continuing to settle towards the bottom of the sluice, are in such cases carried up again towards the surface of the stream. Consequently, where further disintegration is not required the water is allowed to flow as smoothly as possible.

Sometimes disintegration in the sluice is necessary, and this is effected partly by the boulders occurring in the gravel and partly by arranging drops of a few feet in the sluice. When boulders are allowed to work down the sluice, the wear of the pavement is increased.

At the La Grange hydraulic mine in North California,<sup>1</sup> the sluice-boxes are 6 feet wide and 4 feet deep, and are paved with steel rails weighing 40 lb. per yard, but the number of boulders passing through the sluice is large, and the rails are worn out in about six months.

In some sluices the larger stones and lumps of clay are removed by passing the stream of gravel and water through a set of parallel iron bars (a "grizzly"), or in small operations by means of a fork or by hand.

The dimensions of the sluice and its angle of slope vary with the quantity and nature of the material to be treated and the amount of water available. The art of sluicing consists in arranging that the heavy materials—gold, mercury, amalgam, and "black sand"—shall sink to the bottom of the stream and lodge in the irregularities in the sluice-bed, but that the lighter worthless sand shall be carried away by the water. If sand accumulates in the sluice, the object is defeated and the amount of water must

<sup>1</sup> *Mining and Scientific Press*, October 10, 1908, p. 492.

be increased or the angle of inclination raised. The difficulty lies chiefly in catching finely divided gold, which is liable to be swept away with the sand. With this object the stream is kept as shallow as possible, and various special devices have been introduced, such as the *undercurrent*. In this, a part (say one-fourth to one-third) of the fine material and water are drawn off through a sieve placed in the bed of the sluice and spread in a thin, even stream over the surface of a wide, inclined table, sometimes supplied with transverse riffles. After flowing over the table the material is returned to the main sluice. The fine gold settles on the table and is caught by the "burlap" or other material with which it is covered.

At intervals the work is stopped, and a "clean up" takes place to recover the gold caught in the sluice. The water is allowed to run until it passes through clear, and it is then deflected from the sluice, and the material lodged in the riffles, etc., is scooped out and panned or ground in a revolving barrel with more mercury and a few cannon balls. The amalgam and quicksilver collected in this way are squeezed through chamois leather or canvas, as in the days of Pliny. Nearly pure mercury passes through, and pasty amalgam containing 30 or 40 per cent. of gold remains in the bag. Pliny describes the process in the following words: "ut et ipsum [*i.e.*, argentum vivum] ab auro discedat, in pellis subactas effunditur, per quas sudoris vice defluens purum relinquit aurum." The pasty amalgam is retorted, the mercury driven off and condensed by cold water, and the residue melted and cast into bars.

The tailings, or refuse material from which the gold has been extracted, are carried off by the water and discharged

into the nearest river or collected and impounded in brushwood dams.

One of the main difficulties in hydraulic mining is in the disposal of the tailings, which may amount to millions of cubic yards in a year from a single mine. Vast quantities of débris were discharged by the hydraulic miners into the rivers of California between 1862 and 1884, with the result that the river-beds were gradually filled up and floods became more frequent and extensive. The farmers' lands were being covered more and more by deposits of barren gravel and sand and their industry was threatened with destruction. They accordingly obtained an injunction from the Courts which put an end to hydraulic mining in a great part of California in 1884.<sup>1</sup>

Within the last few years the use of *dredges* has been rapidly extending. A dredge is a flat-bottomed boat, with machinery for raising gravel from the bottom of a stream or pond, hoisting it on board, washing it over inclined tables to save the gold, and then throwing or "dumping" the tailings overboard at the stern. A dredge may thus work its way up-stream, or may proceed across a flat plain floating in a pond, cutting out the bank in front of it and piling up the tailings behind. The latter method is known as "paddock dredging." A continuous supply of clear water is necessary for washing in the latter case, as very muddy water is found to interfere with the gold-saving. Dredges were first successfully used on the rivers of New Zealand, but are now at work in many countries. Sometimes suction pumps or grab-bucket dredges are used to lift

<sup>1</sup> See *Production of Precious Metals in the United States*, 1884, pp. 524—530.

the gravel, but ladder-bucket dredges similar to those used in ordinary dredging operations are much more common.

The following is a description of a typical New Zealand ladder-bucket dredge<sup>1</sup>:—The pontoon is 119 feet long and 50 feet wide at the stern, and its greatest draught is 9 feet 6 inches. The engine is of 25 h.p. nominal. The capacity of the buckets is 7 cubic feet, and they are worked at a speed of ten buckets per minute. The ladder carrying the buckets can be raised and lowered by means of a winch. The pontoon is moored to the bank and moved from place to place by a head-line and four side-lines, each of which is supplied with a separate winch. The buckets empty the gravel into a trommel, or revolving screen, which is 31 feet long and 4 feet 6 inches in diameter. The coarse material is delivered into the buckets of the main tailings elevator, and the fine material falling through the screen passes to the washing tables, where the gold is saved. The tailings are deposited in a settling tank, whence they are lifted out and delivered to the main tailings elevator, which is 145 feet long and capable of stacking tailings at a height of 80 feet above the water level. The capacity of the dredge is reckoned at about 120 cubic yards per hour.

Some dredges are not supplied with a revolving screen, and the material is tipped from the buckets direct into a sluice. In either case the length of the gold-saving tables is strictly limited, and the gravel must be thoroughly disintegrated and an opportunity afforded for the gold to settle in a short distance. The tables are supplied with expanded metal or perforated plates placed on cocoanut

<sup>1</sup> "Report of the Department of Mines, New Zealand, for 1899—1900," p. 43.



matting or other material. Angle-irons and Hungarian riffles are also used, but the losses of finely divided gold are frequently heavy.

Tailings in river dredging are often discharged into the water over the stern of the pontoon. In paddock-dredging it is of course necessary to stack them on the bank. One of the drawbacks is that stacked tailings do not usually form ground capable of cultivation, and arable land is often laid waste by dredging operations.

Cleaning-up usually takes place weekly. The expanded metal or other plates are lifted and the mats washed in tubs until free from all gold, grit, etc. The concentrates may be again washed on a "streaming-down" table, which is covered with plush or green baize, and the final concentrates are amalgamated and panned.

Dredges are very economical in work, some large ones treating from 3,000 to 6,000 cubic yards or more per day, at a total cost of 2*d.* or 3*d.* per cubic yard, as in the subjoined table.

	No. 1 Dredge.	No. 2 Dredge.
Actual time worked .	6,161 hours	5,572 hours
Time lost . . . . .	17·7 per cent.	25·6 per cent.
Capacity of dredge .	130 cub. yds. per hour	112·5 cub. yds. per hour
Material treated . .	325,896 cub. yds.	303,360 cub. yds.
Gold recovered . . .	1,198·6 oz.	1,393·9 oz.
Net value . . . . .	£4,816	£5,104
Working expenses . .	£3,322	£3,150
Profit . . . . .	£1,494	£1,954
Value per cubic yard	1·76 grains or 3·5 <i>d.</i>	2·2 grains or 4 <i>d.</i>
Cost of treatment per cubic yard . . . . .	2·4 <i>d.</i>	2·4 <i>d.</i>

The above figures for a year's work on two dredges

are given by E. S. and G. N. Marks.<sup>1</sup> The first is from a dredge working on the Buckland river, Victoria, and dealing with gravel containing a quantity of sunken logs, which delayed the operations. The second worked in the Australian Alps on the Encumbene river at an altitude of 5,000 feet, and time was lost in the winter by the dredge being frozen up.

<sup>1</sup> "The Bucket Dredging Industry," *Trans. Inst. of Mng. and Met.* Vol. XV. (1906), p. 491.

## CHAPTER VII

### TREATMENT OF GOLD ORES BY CRUSHING AND AMALGAMATION

Most gold ores are crushed in stamp-mills, which consist of heavy stampers or pestles raised by machinery and let fall in cast-iron mortars.

A stamp consists of the stem (A, Fig. 17), a rod of wrought iron or mild steel, 12 or 15 feet long and 3 or 4 inches in diameter, the head B, and the shoe C. The stamp is raised by the double cam D, acting on the tappet E, which is keyed to the stem. The stem moves in guides F, of which there are two. The total weight of the stamp is generally from 1,000 to 1,500 lb., but even heavier stamps, up to a ton in weight, are now preferred. The stamps are raised and let fall 6 or 8 inches about 90 or 100 times a minute. The ore is crushed between the shoe C and the die G. Five stamps are let fall side by side in each mortar.

A section of a mortar is shown in

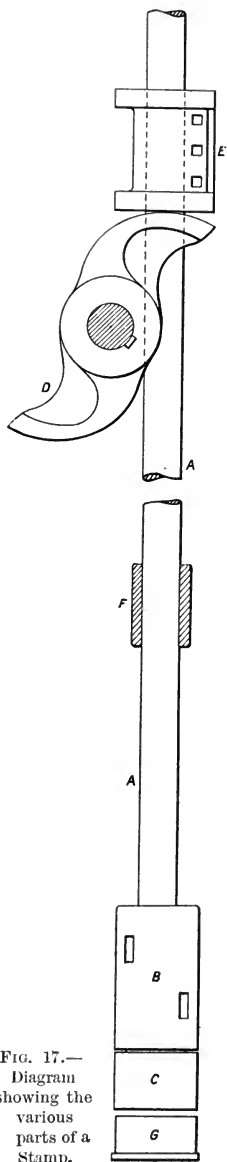


FIG. 17.—  
Diagram showing the  
various  
parts of a  
Stamp.

Fig. 18, where *a* is the aperture through which the ore and water are fed-in constantly, *b* is the screen opening set in the side of the mortar, and *d* is the die. An amalgamated copper plate is often bolted to the inside of the mortar at *c* just below the screen. This is called the "chuck-plate." The fall of the stamps splashes the pulp against the screens. The water and fine particles of ore pass through and are then allowed to run over the amalgamated tables where the gold is saved.

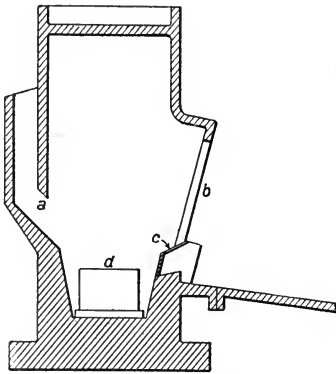


FIG. 18.—Section of Mortar.

The ore to be fed to a stamp-mill is now usually broken to moderate size by being passed through a *rock-breaker*. These machines have approaching and receding jaws which crush the rock. They are divisible into two classes, the reciprocating jaw breakers, such as the Blake crusher, and the gyrating breakers, which are continuous in action, such as the Gates crusher. In the Blake machine a steel plate or jaw, pivoted above and having a swinging motion, alternately advances towards and recedes from a fixed vertical jaw. When the swinging jaw advances some rock is crushed. When it recedes the opening at the bottom between the jaws is widened and the crushed ore drops through. This machine can be set to break rock down to about two-inch cubes, and a large size machine can easily break 500 tons of ore per day to this size. The ore is usually shovelled into the mouth of the breaker by hand.

The gyrating machines contain a spindle carrying a crushing head, which rotates inside conical crushing faces when the machine is empty and gyrates when ore is fed in. The largest of these machines are of greater capacity than the reciprocating machines, and work at a lower cost.

The ore from the rock-breakers is usually broken down in them to pass a 2-inch ring. Such ore is in the right condition to be fed to the stamps. It is stored in a bin with sloping bottom, and sliding down on to the table of an automatic feeding machine is passed forward into the mortar.

A typical automatic feeder is *Hendy's Challenge Feeder*, which consists of a circular tray inclined towards the mortar at an angle of about  $12\frac{1}{2}$  degrees and slowly revolved by bevelled gearing placed below it. The ore is delivered into a sheet-iron hopper and slides thence on to the tray, the amount being regulated by an adjustable door. When the level of the ore on the dies in the mortar is low enough, the tappet of the stamp-stem strikes a bumper-rod which moves the bevelled gear-wheel and partly rotates the tray. As the tray rotates, some of the ore is scraped off by stationary side-plates and falls into the mortar. One feeder is usually supplied to each battery of five stamps.

The *foundations* of a stamp battery are of the first importance, for if they are badly made, the battery shakes itself to pieces. A trench is dug out to receive the vertical timbers or *mortar blocks*, which usually rest on concrete, and are surrounded by concrete or masonry. Sometimes the mortar blocks consist of concrete or iron instead of wood. The mortars rest on and are bolted to these blocks,

but are separated from them by sheet-rubber or blanketing, to reduce the vibration.

The *mortars* themselves are of cast iron, usually cast in one piece, and vary considerably in width and in depth of discharge—that is, in the vertical distance from the bottom of the screen to the top of the die. If the depth of discharge is low, the ore is thrown more directly and with greater violence against the screens than if the depth of discharge is high. The result is that the screens wear out sooner, but, on the other hand, the capacity of the mill is increased and the discharged pulp is coarser. The shorter time during which the ore remains in the mortar when the depth of discharge is low, checks amalgamation inside the battery ; but the practice is now growing, and finds general acceptance on the Rand, of adding no mercury in the mortar. In this case the battery proper is used as a crushing machine only, and not as an amalgamator. This method is a reversion to the older practice which was universal before 1850.

The mortars are lined with plates of chilled iron or steel to take up wear and preserve the mortar. The lining plates are about 1 inch thick and last for some months. The open top of the mortar is covered with planking which surrounds the stamp stems, and is provided with holes for feeding-in the water.

The *screen-openings* are usually at the front of the mortar only, as in Fig. 18, and are more rarely provided at both front and back, when maximum crushing capacity is desired and inside battery amalgamation is not practised. The *screens* are carried in wooden frames and consist either of iron plates with holes or slots cut in them or of wire

cloth. In the latter case the proportion of the opening to the area of the screen is greater than in punched plates, so that the crushed ore is more readily discharged from the battery. On the other hand, wire screens have a shorter life than plates. Sheet-iron or steel plates or wire cloth are in wide use, but suffer very rapid corrosion if the water in the battery is acid from the oxidation of pyrites in the ore. This is especially the case when the water used in the battery is pumped from a mine. The acidity can be neutralised by the addition of quicklime, and it is not so rapid in its action on brass wire screens or on aluminium or phosphor bronze, which are sometimes used. Richards cites a case<sup>1</sup> where aluminium bronze cloth lasted seventeen weeks while Russia iron lasted only three weeks.

The slope of the screens is generally 10 degrees from the vertical. Gravity thus assists the splash in passing the grains of ore through the screen. Outside the screen is fixed a canvas shield or a splash-board of wood to stop the splashes caused by the fall of the stamps. The crushed ore and water, striking the canvas, drips down and is enabled to flow evenly on to the amalgamated plates.

The cam-shafts, stamp-guides, etc., are supported by a framework usually consisting of heavy timbers, which are better able to withstand the jarring than iron or steel. The *guides* are required to keep the stamps vertical in spite of the side-thrust of the cams. Sectional guides are best, so that those belonging to any single stamp can be renewed when worn out. The cam-shaft is made long enough to

<sup>1</sup> "Ore Dressing," Vol. I., p. 178. This case is quoted from a paper by T. A. Rickard. *Trans. Am. Inst. Mng. Eng.*, Vol. XXIII. (1893), pp. 137, 545.

carry the cams for ten stamps. The lifting faces of the *cams* are made in the form of the involute of a circle modified at the end so as to allow the upward motion of the stamp to stop gradually. The radius of the circle is equal to the distance between the centres of the stamp stem and the cam-shaft. The cams rotate the stamp as well as lift it, and this gives a more even wear to the head than would otherwise be the case. Cams are fastened to the cam-shaft by means of tapered keys which are driven into slots placed opposite each other in the shaft and cams. Cams are removed by driving out the keys, but there are self-tightening cams, such as the Blanton cam, by which the operation of replacing a broken cam is made much less tedious. The Blanton cam is fastened to the shaft by a tapered wedge which wraps round the shaft and is kept in position by two pins. When the cam lifts the shaft it slips up the inclined plane of the wedge and makes itself tighter. It is loosened by being knocked backwards.

The cam-shaft is driven by a belt and pulley, and as the stamps are dropped alternately it is not difficult to arrange that the strain on the cam-shaft shall be nearly constant. The order of drop of the stamps in a battery is often 1, 3, 5, 2, 4, but other orders are in use. The distribution of ore on the dies depends partly on the order of drop, the blow of a stamp throwing ore upon the adjacent dies in readiness for the next blows. The wave of water must be prevented from heaping ore on certain dies and leaving others bare. It is laid down that two adjacent stamps should not fall in succession, and that when a stamp falls its neighbours should be rising.

The *jack*, or finger, is a bar of wood which is pivoted below



on a subsidiary beam, and is used for hanging up the stamp. When this has to be done, a piece of wood is laid upon the cam as it rises, so that the stamp is lifted above its usual level, and when the stamp reaches its highest point the finger is pushed under the tappet and supports the stamp out of reach of the cam. The stamp is brought into action again by a reversal of this proceeding.

The wear of crushing falls upon the stamp heads and dies. The tappets are moved on the stamp stems when required by the wearing down of the dies, and false dies are also put underneath worn dies to raise them and prolong their life.

In running a stamp-mill, the best thickness of ore to be arranged for on the die when a blow is struck is such that the ore may be crushed without injury to the die. If the layer of ore is too thick, part of the force of the blow is spent in packing the particles together without crushing them. If the layer is too thin, the stamp head clashes on the die.

The amount of ore crushed by a stamp in a day depends on the nature of the ore, the size of the mesh of the screens, the height of drop of the stamp and the number of drops per minute, as well as on the weight of the stamp. Clayey ores are troublesome to crush, and soft friable ores are crushed most easily. Fast-running stamps cannot be given so high a drop as slow-running ones. Time must be given to raise the stamp, let it fall and allow a short period of rest before beginning to lift it again. From D. B. Morison's researches<sup>1</sup> it appears that the maximum safe lifting velocity of a stamp is 31·9 inches per second, and that about 0·15 second must be allowed, after the stamp has completed

<sup>1</sup> *N. E. Coast Inst. Eng. and Shipbuilders*, Vol. XIII, April 30, 1897. Richards' "Ore Dressing," Vol. I., p. 216.

its descent, for rebound and repose, in order that the rising cam may not strike a falling tappet. These figures afford data for calculating the maximum number of blows possible for any given height of drop. With a fall of 5 inches, 115·2 drops per minute may be given, a fall of 6 inches corresponds to 105·4 drops per minute, a fall of 7 inches to 97·6 drops per minute, 8 inches to 91·3 drops per minute, and 9 inches to 85·5 drops per minute. These are the usual heights of drop, and the numbers of drops per minute arranged for in practice are not far short of the theoretical maxima given above.

The amount of water supplied in a stamp-mill is proportioned to the ore as the occasion requires. A larger proportion of water corresponds to more rapid stamping owing to the discharge being facilitated. When inside amalgamation is practised, rapidity of discharge is not the only point to be considered, and the ore treatment outside the battery also limits the amount of water to be used. In a number of cases cited by Richards<sup>1</sup> the water used varied from 2·92 to 15·97 tons of water per ton of ore stamped. The average was 6·68 tons of water per ton of ore.

Mercury is still often sprinkled into the battery. The amount depends on the quantity of gold and silver contained in the ore. The average quantity added is about 1½ oz. to each ounce of gold contained in the ore. If too much mercury is added the outside amalgamated plates become soft with excess of quicksilver. The use of amalgamated plates inside the battery and the sprinkling of mercury in the mortar, which originated about 1850, have of late years been tending to fall into disuse, especially since regrinding

<sup>1</sup> "Ore Dressing," Vol. I., p. 222.

in tube-mills has been introduced. On the Rand goldfield, battery amalgamation has been entirely discontinued.

The "pulp," or crushed ore and water issuing from the battery screens, is led in a very thin stream over inclined tables where the gold is caught. These tables were formerly covered with blanket material, in which the heavy particles of gold, pyrites, etc., became entangled. The blankets were taken up and washed at intervals. About the year 1860, however, the blankets began to be replaced by amalgamated copper plates, the use of which became almost universal soon after 1870. Similar copper plates had been placed inside the mortars about 1850, and the practice of feeding mercury into the mortars with the ore and water began at about the same time. The gold amalgam accumulates on the copper plates, and the stamps are occasionally stopped and the amalgam is scraped off and squeezed in a filter-bag to separate the excess of mercury. The pasty amalgam, containing from 25 to 50 per cent. of gold, is then placed in a retort and heated gradually to redness. The mercury distils and is condensed by means of water, and the residue of gold is ready to be melted.

The *amalgamated plates* are made of the purest and softest copper, usually Lake or electrolytic copper. It is annealed in order to make the surface porous and so enable it to absorb mercury readily. In annealing, the plate is supported at a little distance from the ground and a fire kindled underneath. The plate is made hot enough to char paper placed on it, and is then allowed to cool. Any buckling is removed by the blows of a mallet, and the plate is cleaned by scrubbing with sand and ammonia or alkali. Cyanide of potassium is even more often used for

removing the oxide of copper, grease, etc., which would prevent the mercury from adhering to the surface of the copper. The cyanide may be painted on the plate and washed off after a day, or less, or it may be used in conjunction with a brush and some fine sand. Plates are also cleaned with emery cloth, but however prepared they are liable to become tarnished, and so to make amalgamation difficult. The clean plate is sprinkled with mercury and rubbed with a cloth, sal ammoniac or cyanide of potassium solution being added to dissolve any oxide of copper that may make its appearance. The mercury then coats the plate, giving it a uniformly bright silvery appearance. Gold amalgam or silver amalgam is rubbed on to give the plate a better "catching" surface, and the plate is ready for use. According to Roskelley,<sup>1</sup> 16 oz. mercury and 6 oz. gold amalgam are enough for the preparation of a plate 16 feet by 4 feet 9 inches.

Copper plates are often electro-plated with silver before being amalgamated. This prevents the appearance of green spots, the so-called "verdigris," due to the oxidation of copper, which greatly reduces the value of the plate as a gold-saver. The plates are prepared for electro-plating by coating the back with asphalt varnish and cleaning the face with acid, followed by scrubbing with pumice powder and final washing with cyanide of potassium. The plate is then immersed in a bath made by dissolving chloride of silver in cyanide of potassium, and a current of electricity passed from silver anodes to the copper plate as cathode. The bath contains about 3 oz. of silver per gallon, and the plating is complete when about 1 oz. of silver

<sup>1</sup> *Jour. Chem. Met. and Mng. Soc. of S. A.*, February, 1904, p. 286.

is deposited per square foot of cathode. The plate is then amalgamated as before. Electro-silvered plates are more easily kept in good condition than plain copper ones.

Amalgamated plates are supported on wooden tables, to which they are fastened by copper screws or by buttons or wedges at the sides to make them easily removable. A number of plates are laid on each table, either overlapping or laid side by side. The main catching plates are called *apron plates*, or simply amalgamated tables. They are laid on a slope to enable the pulp to run over them by gravity, the inclination varying from about 1 to 2½ inches per foot. If the slope is too great the pulp runs over it too fast, and the gold has less opportunity of settling down and coming into contact with the plate. If the slope is insufficient, sulphides accumulate on the plate and interfere with its proper working. The variation of the slope is due to differences in the ore, pyritic ores requiring more slope than those nearly free from sulphides. Coarsely crushing batteries with a high output require a high angle of inclination of the plates, but the greater the proportion of water used, the less the slope.

When pulp flows over the plates, the gold settles through the stream, and coming in contact with the amalgamated surface, adheres to it. It would appear from this that the stream should be as thin as possible, and should flow smoothly and uniformly without any tumbling action. In practice, however, these conditions are probably unattainable. The discharge through the screens is intermittent, and the pulp flows down in a series of little waves which tumble over and over and bring all the grains in the pulp in contact with the plate irrespective of the action of

gravity. With the idea of increasing the tumbling action, many amalgamated tables are broken up by steps or drops placed transversely, so that the pulp falls from the lower edge of one plate upon the upper end of the next plate from a height of from 1 to 3 inches. If the fall is of the correct height, the amalgam builds up under it faster than anywhere else, float gold being caught there. If the fall is too great, the amalgam is scoured away instead of being saved. These drops act as distributors of the pulp, and are sometimes placed every 2 feet, but are often entirely omitted. In the latter case the area of the plates is made greater.

The apron plates are usually as wide as the mortar is long, and their length varies from about 6 to 21 feet. When *sluice plates*, or narrower plates below the apron plates, are used, the apron plates may be even shorter, but in sluice plates the stream of pulp is necessarily deeper, and they are falling into disuse.

The depth of the pulp on the plates is given by Richards<sup>1</sup> at from 0.19 inch downwards. At the trough of the wave it may be as little as 0.014 inch at the lower end of the plates. He gives the velocity of the waves at from 19 to 42 inches per second.

*Mercury traps* are sometimes placed between the plates instead of drops. In one form they consist of simple transverse troughs or riffles, 2 or 3 inches wide and deep. Sometimes they are made wider and deeper, and partitions or gates are placed in them, under which the pulp passes. The intention is to catch mercury and amalgam and to let the sand and pyrites pass through.

<sup>1</sup> "Ore Dressing," Vol. II., p. 746.

Sometimes they have a pool of mercury placed in them, when they become *mercury wells* or riffles. If a gate is placed in the well almost or quite touching the surface of the mercury, the pulp in escaping must pass over the surface of the mercury, or even through it. A mercury well acts as a trap for mercury, but has little other advantage to recommend it, and such wells are not now used much. They are useful in catching very coarse free gold, but large particles are not likely to escape whatever method of gold-saving is adopted.

Amalgamated plates are in the best condition to catch and retain gold and silver when they are clean and bright and the amalgam is soft enough to be marked by the pressure of the finger, but not soft enough for the mercury to gather into drops and run off. If the amalgam becomes hard it tends to flake off under the scouring action of the pulp, and fresh mercury is sprinkled on, or the amount of mercury fed into the battery is increased. On the Rand<sup>1</sup> mercury is sprayed over the upper 3 feet of the plates (the part that is scraped daily) every four hours, when the plates are dressed, and this mercury oozing downwards supplies the lower part.

*Dressing* is necessitated by the discoloration of the plates, and is designed to make them more active in catching gold. In dressing, the stamps are hung up, the water turned off and the sand brushed off the plates. If they are discoloured they are cleaned with potassium cyanide. On the Rand mercury is sprayed over first, and then a solution containing 0.08 per cent. of cyanide is sprinkled on, and the mercury is rubbed in with a hard

<sup>1</sup> Roskelley, *Chem. Met. and Mng. Soc. of S. A.*, Vol. IV. (1904), p. 286.

brush. Afterwards the amalgam is brushed smooth with a soft brush, and the plates are finally washed down. Cyanide is used to a less extent than formerly, as it makes the mercury drain away from the amalgam and so tends to cause the plates to become hard and dry.

*Cleaning-up*, or the removal of amalgam from the plates, takes place at intervals, which may be as short as two hours if extraordinarily rich ore is being treated, or as long as a month. A daily clean-up is very common. In cleaning-up the amalgam is softened by the addition of mercury well rubbed in, and the amalgam is then removed with a scraper of rubber or iron, care being taken not to scratch the plates. A thin layer of amalgam is left on the plate to form a good catching surface, and the plates are then dressed. Hard amalgam accumulates on the plates and cannot be entirely removed even by means of a chisel. It is removed at long intervals of two months or more by long scraping, or by steaming or "sweating" the plates before scraping, or by buckling the plates with a hammer, a procedure which causes the amalgam to strip off. Old worn-out plates are scaled by being heated over a fire and plunged into water, or they may be dissolved in acid or melted up and sold to a refinery.

The dirty amalgam obtained from the plates and battery, containing sand, sulphides, metallic iron and base metal amalgam, is mixed with more mercury and treated in a rotating iron *clean-up barrel* with water and cannon balls. The water is then poured off and the mercury squeezed through chamois leather or canvas. The squeezing is often by hand, but hydraulic amalgam-squeezers are also in use. The amalgam retained by the filter contains from 10 to



50 per cent. of gold and silver, coarse gold yielding richer amalgam than finely divided gold. Hard amalgam contains more gold and silver than the soft amalgam obtained in the usual way by cleaning the plates.

*Retorting* is carried out in cast-iron retorts, of which there are two kinds, the pot retorts and the cylindrical retorts. The pot retorts are smaller than the others and are placed on any fire. The cylinders are placed horizontally in special furnaces. Both kinds have a delivery pipe leading to a Liebig's condenser. The amalgam is squeezed into ball- or cake-shaped masses and placed in the retorts on trays, or simply on paper or lime-wash linings. The fire is lighted after the retort is in position, and at first a gentle heat is used which is increased gradually. The mercury is volatilised, and after condensation in the cooled pipe is received in a vessel of water. When no more mercury comes over, the retort is heated to redness for a few minutes, and is then allowed to cool. The residue in the retort contains gold, silver, base metals, sulphides and some mercury. It is cut up, if necessary, and melted in graphite crucibles with borax, soda carbonate, nitre and sand. The base metals are partly oxidised by the nitre and partly left in the molten gold and silver. The metallic oxides form a fusible slag with the borax and sand, and the carbonate of soda takes up sulphur from the sulphides, and makes the slag more liquid. When the charge is melted it is well stirred and poured into ingot moulds, which are overturned into water as soon as the charge is solid in order to detach the metal readily from the slag. The fineness of the bullion and the methods of sampling are dealt with in Chapter XIV.



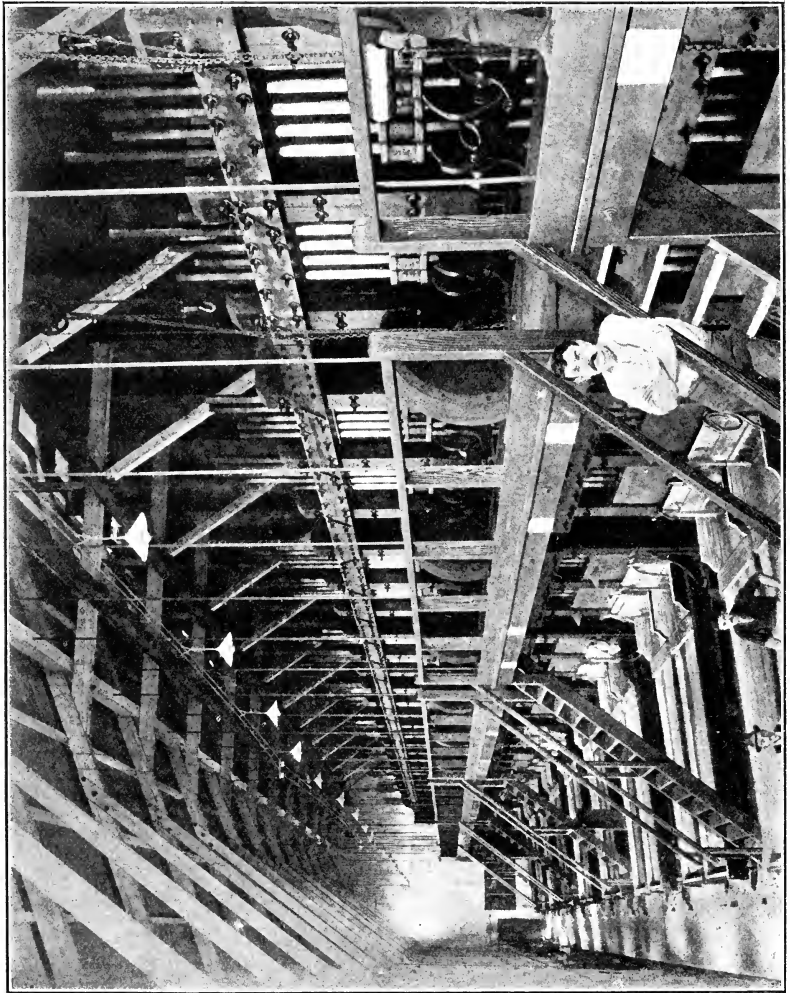


Fig. 19. — Simmer East Stamp-mill.

Fig. 19 shows a general view of a stamp battery in operation. It is a reproduction of a photograph (kindly supplied by Mr. W. A. Caldecott) of the interior of the

Simmer East Mill, Witwatersrand, Transvaal. It shows the guide-posts, the guide-timbers, the stamp-stems, cams and tappets, the cam-shafts and the cam-pulleys. The stamp heads are hidden inside the mortar boxes. The screens are shown and the amalgamated tables in front of them. The weight of the stamps is 1,550 lb. in this battery, and the amount of ore crushed per stamp is about 6.3 tons per day of twenty-four hours.

On the Rand the ore is sorted by hand before delivery to the stamp-mill and the waste or barren rock picked out and discarded. In Fig. 20<sup>1</sup> the sorting table and trommel at the Knight's Deep and Simmer East joint plant are shown. The trommel delivers large pieces of ore on to the rotating tables, where it is sorted.

The ordinary stamps described above are known as gravitation stamps or gravity stamps. There are other forms of stamp in which power in addition to the weight of the stamp is used to deliver the blow. Steam stamps are lifted and forced down by a steam piston. In pneumatic and spring stamps the power is applied by a crank with an air piston or a spring to take up part of the shock to the machine. These forms of stamp are not much used in crushing gold or silver ores.

A number of other pulverisers are also in use. Arrastras and amalgamating pans are described in Chapter XI., which deals with the treatment of silver ores. Ball-mills and roller-mills are more often applied to the crushing of gold ores. Like stamps they can be used for either wet or dry crushing. The *Krupp ball-mill* is widely used, and is a very

<sup>1</sup> This figure is also from a photograph kindly supplied by Mr. W. A. Caldecott.

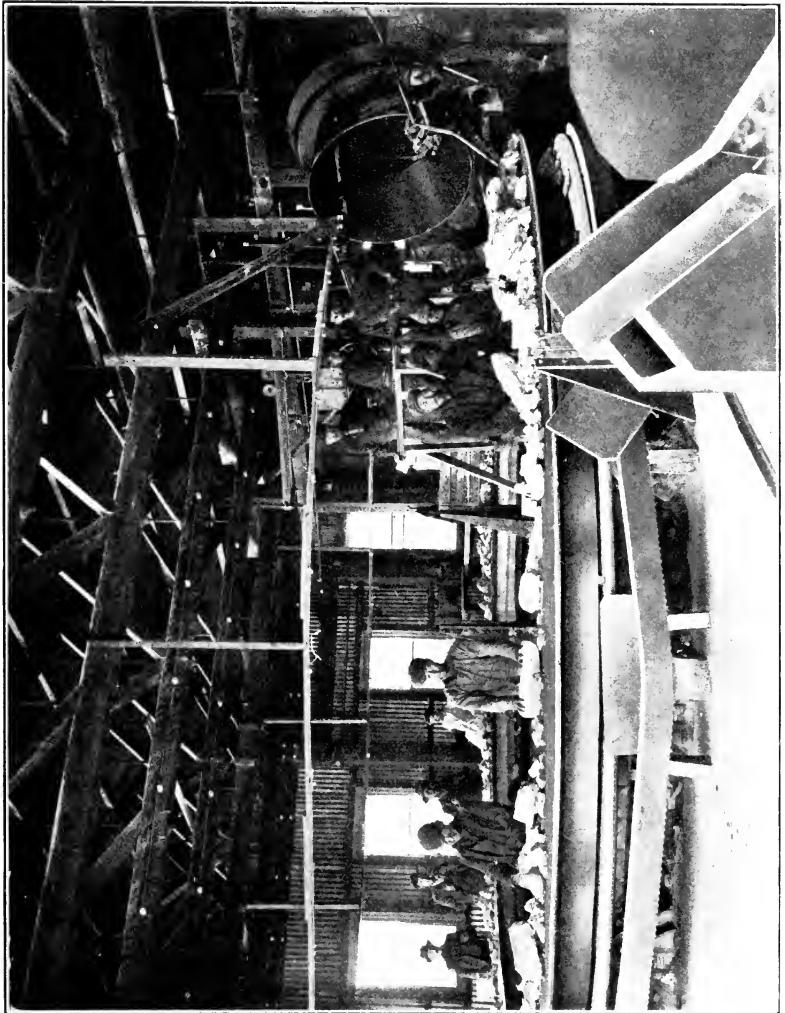


Fig. 20.—Trommel and Sorting Table. Knight's Deep and Simmer East Joint Plant.

efficient machine. It consists of a cylindrical drum containing a number of chilled-iron or cast-steel balls of

different sizes, and is rotated on a horizontal axis. The ore is crushed by the grinding of the balls against each other and against the inside of the periphery of the drum, which is composed of five or more overlapping steel plates so arranged that the balls drop a few inches in passing from one plate to the next. The crushed ore passes out between the plates on to a screen, and the oversized particles are returned to the interior of the mill. The Krupp mill is applicable to soft ores, especially in preparing them for treatment by the cyanide or chlorination process.

Among roller-mills, the *Huntington mill* has perhaps been more used than any other. It is applicable to the crushing of soft gold ores as a substitute for the stamp battery. It consists of a pan, inside which an iron ring revolves in a horizontal plane, and hanging from the ring are three stems, each having a roller attached to its lower extremity. When the ring rotates, the stems swing outwards by centrifugal force, and the rollers press against and roll round inside a ring-die near the bottom of the pan. The ore, previously broken to less than  $\frac{3}{4}$ -inch pieces, is fed into the mill with water and is crushed between the rollers and the ring-die. Mercury is used in the mill, and the pulverised ore passes out through peripheral screens placed above the ring-die, and is allowed to run over amalgamated plates. The Huntington mill is much used in America, and with careful feeding gives excellent and economical results.

*Amalgamating machines*, designed to do the work generally assigned to amalgamated copper plates, are numerous, but not so much used as formerly. Amalgamating pans are referred to elsewhere. In Transylvania the old system

of crushing in stamp batteries and amalgamating in separate machines is still followed to a considerable extent. The so-called Austrian theory of amalgamation is that gold-saving is best effected by giving the particles of metal an opportunity of settling by gravity through the pulp and of coming into contact with the surface of mercury lying underneath. In the old Tyrolean bowls described by Agricola in 1556, the crushed ore was kept in agitation by revolving stirrers above a bath of mercury, and according to him<sup>1</sup> the machines "separated even very minute flakes of gold from the crushed ore. These flakes, settling to the bottom, are drawn to itself and cleansed by the quicksilver (lying in the tubs), but the water carries off the dross." The modern forms of Hungarian amalgamators, such as the *Schemnitz mill* and the *Lazzlo amalgamator*, resemble the old bowls. They have revolving mullers which force the ore to come in contact with the pool of mercury, but do not, as in ordinary amalgamation pans, stir the mercury itself so as to mix and grind it with the ore.

*Shaking amalgamated plates* have lately been used to a great extent for the treatment of reground ore coming from tube-mills in the Transvaal. They are sometimes placed on old Frue vanner frames, and are given a slight rapid side-shake of about 200 throws per minute of half an inch or so each. The pulp is kept by this device from settling on the plate, so that the inclination of the plate can be reduced to about half an inch per foot, or even less. Silver-plated copper is the material usually employed. A longitudinal shake is sometimes given instead of a side-shake. The width of the plates is made as great as possible

<sup>1</sup> "De Re Metallica," Lib. VIII., p. 233.

to reduce the depth of the film of pulp flowing over them, but their length need not be very great, as they are efficient gold-catchers. Since the introduction of regrinding and treatment with shaking plates, the proportion of gold extracted by amalgamation from ordinary Rand blanket ore has greatly increased, and is now nearly 70 per cent. on a number of the mines. The extraction by means of cyanide has suffered a corresponding diminution.

The *loss of mercury* in amalgamation varies with the kind of ore as well as with the method of treatment. The chief cause of loss is the flouring or sickening of mercury—that is, its subdivision into minute globules which are too small to settle in mercury traps, etc. The globules of mercury are prevented from coalescing by a film of some foreign material, such as grease, oxides of base metal, sulphides, arsenides, hydrous silicates, etc. The loss by flouring is increased by using impure mercury containing amalgams of base metals, which are readily oxidised. It is also increased by stamping or grinding ore and mercury together, especially when the ore contains arsenides, antimonides, etc., or soapy materials, such as clay, serpentine, talc, or other hydrous silicates. Base oxides are removed from quicksilver by sodium amalgam, but as the base metals re-enter the mercury the improvement is only temporary. Apart from flouring, a considerable loss of mercury takes place in the pan-amalgamation process, and also in the patio process, from the formation of sulphates and chlorides of mercury. The loss owing to this cause is trivial in the stamp battery. In the treatment of gold ores in stamp mills the loss of mercury is given by Richards<sup>1</sup>

<sup>1</sup> "Ore Dressing," Vol. I., p. 206.

as 0.339 oz. per ton of ore crushed. This was the average at sixteen American mills, but it is much less in the Transvaal, where mercury is not charged into the mortar.

Mercury is purified by distillation with lime and iron filings. An addition of charcoal prevents the formation of volatile oxides. Floating impurities may be removed by running quicksilver through a funnel and rejecting the last portion. The most effectual method of purifying mercury is to cover it with dilute nitric acid and force air through the mercury. The base metals are then oxidised, and rising to the surface are dissolved by the acid.

#### TREATMENT OF TAILINGS FROM THE STAMP BATTERY.

After treatment in the stamp battery, the crushed ore and water flowing from the amalgamated plates still contains some of the gold, either embedded in the pyrites or locked-up inside coarse grains of sand, or even in the form of finely divided free flakes of native metal. The treatment of these "tailings" for the extraction of the remainder of the gold varies according to the nature of the ore.

The older method of treatment was generally some form of concentration, the heavier particles being separated from those of lower density and saved, whilst the lighter particles, being comparatively poor in gold, were allowed to be carried away in the stream of water and lost. Blankets were stretched on sloping tables, and the pyrites, grains of gold, etc., which adhered to the fibrous surface were washed off every now and then and sent to a smelter or amalgamated in grinding pans or chlorinated. Canvas tables have been substituted for blankets, and sloping wooden tables were also used, but some form of "vanner"



or shaking table has now generally superseded these devices.

The Frue vanner is the best known of the vanners. It consists of an endless rubber belt, slightly inclined to the horizontal, and subjected to a rapid side-shake. The belt has a continuous slow motion up the slope. The pulp coming from the amalgamated plates is fed on to the upper end of the inclined table formed by the belt, together with some additional water. The pulp runs down the belt in a thin stream, and the particles of high density settle to the bottom of the stream of pulp, and, adhering to the surface of the belt, are carried up against the stream and over the top. They are washed off into a tank by means of jets of water. The side-shake keeps the ore loose, and so assists the heavy minerals to settle to the bottom. Finely divided sulphides are saved on this machine even better than very large particles, which tend to roll or slide down the belt with the worthless material. Two Frue vanners are generally sufficient to treat the product of a battery of five stamps.

The *Wilfley table* has no travelling belt, but is provided with a number of wooden strips nailed on the surface of the table. The lighter grains are washed down across these wooden riffles, and the sulphides, etc., of any size whatever, travel along the riffles under the influence of a side-jerk and over the side of the table. The Wilfley table is stated not to be of the highest efficiency in saving fine slimes, and is sometimes supplemented by other machines. It has largely replaced other forms of shaking tables and vanners of late years.

For certain purposes it is desirable to classify the pulp

according to the size of the particles before other treatment. This may be done by inclined shaking or revolving screens or by the use of *hydraulic classifiers*, which generally consist of some form of pyramidal box or inverted roof-shaped trough. The apex of the box or trough is, of course, downwards. A stream of pulp enters at one side of the box, which is full of water, and overflows at the other side. The current slackens when it enters the box, and the larger and heavier particles of ore settle in the box and accumulate in the apex, where they are discharged either continuously or intermittently. Successive boxes are used, each larger than the previous one, so that two or three or more grades of material are collected, besides the slimes which do not settle in such boxes. In order to clean the separated classes of material an ascending current of clear water is sometimes introduced at the apex. The sand falls through the upward current, but cannot carry down any slimes with it. The slimes can be collected in large pits or tanks.

Classified material is better fitted than unclassified pulp for some methods of concentration, such as jiggling, and also for treatment in leaching vats, as, for example, by the cyanide process. The concentration of gold ores is, however, less generally practised than formerly now that the cyanide process has come into almost universal use.

Concentrates usually amount to 1, 2, or 3 per cent. of the original ores. They consist of sulphides, oxides of iron, flakes of gold, coarse grains of sand, etc., and may be very rich. Their values can often be extracted in great part by grinding with mercury in iron pans. The ordinary amalgamating pan described in Chapter XI. answers the

purpose sufficiently well, but its capacity is often too great for the small quantities of concentrates collected, and a smaller type of pan is used. This method, however, is not now very widely used. When amalgamation of concentrates is not adopted, they may be roasted and chlorinated or simply cyanided. Extremely rich concentrates can be treated by smelting with lead in reverberatory furnaces, followed by cupellation, but finely divided material is not suitable for reduction in blast furnaces, so that the smelting of concentrates is exceptional.

## CHAPTER VIII

### TREATMENT OF GOLD ORES BY WET METHODS

#### THE CYANIDE PROCESS.

At the present day the usual method of treating the tailings from stamp battery amalgamation is by means of the cyanide process without any previous concentration. Rough classification of the pulp is, however, necessary. The tailings are run into large vats, from which the surplus water overflows, carrying with it the "slimes," or fine mud. The vat may be originally filled with clean water, in which case the slimes overflow from the beginning, leaving the sands to settle quietly to the bottom, or some kind of rising gate may be used, beginning with an empty vat and raising the height of the overflow from time to time as the sand accumulates. When the vat is filled with sand, it may be drained and discharged into trucks and the sand conveyed to another vat for leaching with cyanide. This is the method of *intermediate filling* with the use of a collecting vat, which may be of any depth. The cyanide vat may of course be placed vertically below the intermediate filling vat to facilitate transference. As an alternative, *direct filling* may be employed, the sands being collected in the cyanide vat itself and leached without being disturbed.

In leaching, dilute solutions are used, usually containing from 0.05 to 0.35 per cent. of cyanide of potassium. The

sand rests on a false bottom placed inside the vat, and consisting of a filter-frame of wood covered by cocoa-nut fibre matting and hessian, or some other kind of filter-cloth. The vats are round and contain as much as 400 tons of ore. The cyanide solutions are either run on from above, or are introduced below the false bottom and rise up through the charge. When the ore contains partially oxidised pyrites, which act as "cyanicides," decomposing the cyanide, the acidity may be removed by treatment with caustic lime. This may be mixed with the ore before it is crushed, or an alkali wash of lime or soda may be applied to the ore in the vat, before the cyanide solution is run on.

Two strengths of solution are often applied in succession, a "strong" solution and a "weak" solution. The strong solution is usually left on for some time before being allowed to run through, but the solution is not pumped back again to the surface of the ore. Three or four additions of solution are usually sufficient, the time of treatment by the strong solution being often one or two days. The solution is sometimes applied continuously, that is to say, as soon as the liquid has sunk below the surface of the ore, fresh solution is run on. Sometimes the solution is allowed to drain away completely before the next charge is applied. This causes air to be drawn into the interstices of the ore, and the fresh oxygen enables subsequent dissolution of the gold to be more rapidly effected (see p. 29).

Some ores absorb oxygen and require to be re-oxygenated. This difficulty has been met by the method of *double treatment*, the ore being treated with cyanide solution in one

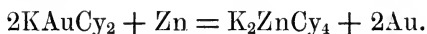
vat, then allowed to drain, and removed to another vat and again leached. The turning over and exposure to air of the charge during transference affords an opportunity for its thorough oxygenation. The treatment of concentrates is made especially difficult owing to the absorption of all free oxygen by the sulphides. In the Transvaal, concentrates formerly often underwent cyanidation during three or four weeks, the charge being drained and spaded over frequently to facilitate aeration between the applications of cyanide solution.

When the strong solution has been drawn off, the weak solution is run on, and finally a number of water washes are applied, each wash being small in amount. Washing is discontinued when cyanide can no longer be detected in the water issuing from the vat.

The vats are discharged through doors in the bottom into trucks which are often hauled up inclines and emptied on the top of a heap of tailings. The heap thus grows higher and higher as its area is extended. The sand in the vat is sampled for assay before being discharged.

The auriferous solution drawn from the charge is passed to the zinc-boxes for the precipitation of the gold. These are usually troughs containing shavings of zinc coated with precipitated lead, formed by dipping the shavings into a strong solution of acetate of lead. The boxes are divided into compartments by partitions, and the solutions generally flow upwards through each compartment in succession, the overflow from one compartment being conveyed through a small passage to the bottom of the next. The zinc shavings are very thin and light, and are carried on iron gratings through which the solution passes. The gold is precipitated

on the zinc which displaces it in solution according to the equation—



The lead forms a galvanic couple with the zinc and strengthens its action as a precipitant, but the lead itself remains unchanged. The zinc is, however, also dissolved by the cyanide solution direct, potash being formed and hydrogen set free. A white precipitate tends to form on the zinc, checking its action (see above, p. 31). It consists in part of cyanide of zinc, which would be dissolved by a large excess of cyanide of potassium. If the percentage of free cyanide of potassium in the solution is too small, the precipitation of gold is incomplete or is entirely stopped. The gold forms a black mud on the surface of the shavings, which disintegrate as the action proceeds.

In cleaning-up, the shavings are washed and filtered in order to separate the residue of zinc and soluble salts, and the sludge is charged into a large tub with dilute sulphuric acid or bisulphate of sodium. Finely divided zinc is dissolved and the cyanides decomposed with violent frothing, owing to the disengagement of gas. After all action has ceased the charge is allowed to settle and the clear liquid decanted off. The slimes are then washed with hot water and separated by a vacuum filter or a filter-press. They may then be dried, calcined and fused with fluxes in graphite crucibles. The fluxes used are soda carbonate, borax and sand. Nitre or manganese dioxide are also added sometimes to oxidise some of the base metals and produce purer bullion.

Another method, the Tavener process, consists in mixing the slimes, after filter-pressing, with fluxes and litharge, and

smelting for auriferous lead in a reverberatory furnace. Sawdust is used as a reducing agent. The slags are very poor, and the lead may be regulated so as to contain as much as 8 per cent. of gold. This is cupelled in a second operation in an English cupellation furnace. The cupelled gold is allowed to solidify on the test, and is then detached, broken up while still hot, and melted in graphite crucibles for casting into bars.

The treatment of the slimed ore separated from the sands before the latter are cyanided differs considerably from the method described above. In the Transvaal the *decantation process* is in general use. Milk of lime is added to the water from the separating plant containing the slimes, in order to coagulate them and assist them to settle, which they do in a flocculent form when lime is added. Large pointed boxes are used for settling the slimes, which are drawn off at the bottom and pumped to the treatment vats, about 90 per cent. of the water contained in them having been separated. The cyanide solution used to dissolve the gold contains about 0.01 per cent. KCy. Dissolution is rapid and is aided by agitating the charge, which is done by means of pumps. The slimes are then allowed to settle, and the clear liquid is withdrawn and sent to the zinc precipitation boxes. Slimes cannot be washed by the ordinary method of percolation, as they resist the passage of liquids through them, even when a vacuum is created underneath the filter-bed. They are accordingly washed by decantation, the vats being repeatedly filled up with fresh water with which they are stirred. The charge is then allowed to settle and the supernatant liquid removed by decantation until it is too poor to pay for treatment.



The solutions are poor, both in gold and in cyanide, and are treated either by passage through zinc-lead shavings or by electrical precipitation, in which the smallness of the percentage of cyanide present is not disadvantageous. The cathodes consist of sheet-lead and the anodes of iron plates or of sheet-lead coated with peroxide of lead. The current used is not great, in order to avoid the destruction of cyanide as far as possible. The gold gilds the lead, or is deposited in a black granular form, and to recover the gold it is merely necessary to melt and cupel the lead, which contains from 2 to 12 per cent. of gold. The electrical method of precipitation was introduced as the *Siemens-Halske process*.

In Western Australia slimed ore is treated by *filter-pressing* instead of by the decantation process. The pulp is usually partly freed from water by settlement or by a filter-press, and is then treated with cyanide solution in vats by agitation applied by means of paddles. The mixture is then pumped into filter-presses and the liquid forced through the filter-cloths under high pressure applied by compressed air. Dissolution of the gold may also be effected either wholly or partially in filter-presses by forcing cyanide solution through them. In any case the ore is washed clean in the presses. Filter-presses consist of a series of parallel ribbed or corrugated iron flanged plates tightly fitting together at their planed margins. Each pair of plates is separated by filter-cloths, which constitute the packing between the planed margins. The liquid is forced through the cloth into the corrugations of the plate and is drawn off in a series of channels. The cakes of slimes are removed from the presses by opening them individually. The whole operation of filter-pressing

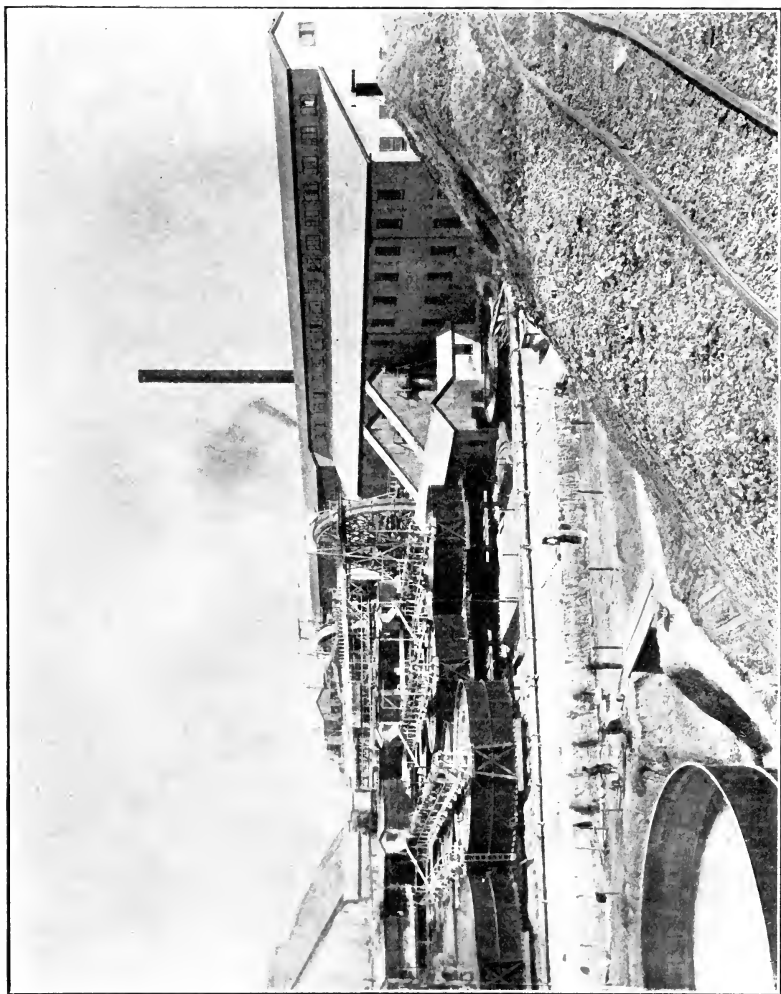


Fig. 21.—Cyanide Plant and Battery House. Knight's Deep and Simmer East Joint Plant.

occupies only about two hours, so that the treatment is far more expeditious than the method of decantation. The precipitation of the gold from solution is effected as usual.

Cyanide plants are now of great capacity and very complicated on the Rand. A general view of a portion of the reduction works (stamp battery and cyanide plant combined) of the Knight's Deep and Simmer East joint plant is shown in Fig. 21. The battery house is on the right of the picture.

Another view of the same plant is shown in the frontispiece, which is taken from the top of the enormous sand heap or dump where the tailings, or ore after treatment, are thrown.

In Fig. 22 a view is given of the interior of the extractor house at the same works. On the right the zinc-boxes divided into compartments are shown, and on the left a filter-press and the pumping machinery.

The slimes tailings cannot be piled up like the sands, and are settled and caught in huge dams, one of which, the Knight's Deep and Simmer East dam, is shown in Fig. 23. Figs. 21, 22 and 23 are reproduced from photographs kindly supplied by Mr. W. A. Caldecott.

There are numerous modifications of the cyanide process in use at different mines. The strength of the cyanide solutions, the time of treatment, and the method of leaching vary with almost every ore.

Latterly it has become apparent that the tailings from stamp-mills are often too coarse to yield their gold without previous *regrinding*, and they are accordingly reduced to fine slime by being passed through *tube-mills* or other machines. Tube-mills (see Fig. 24)<sup>1</sup> are rotating iron cylinders lined with flint or chert and half filled with round flint pebbles, or more rarely with iron rods. The

<sup>1</sup> Fig. 24 is from a photograph kindly supplied by Mr. W. A. Caldecott.

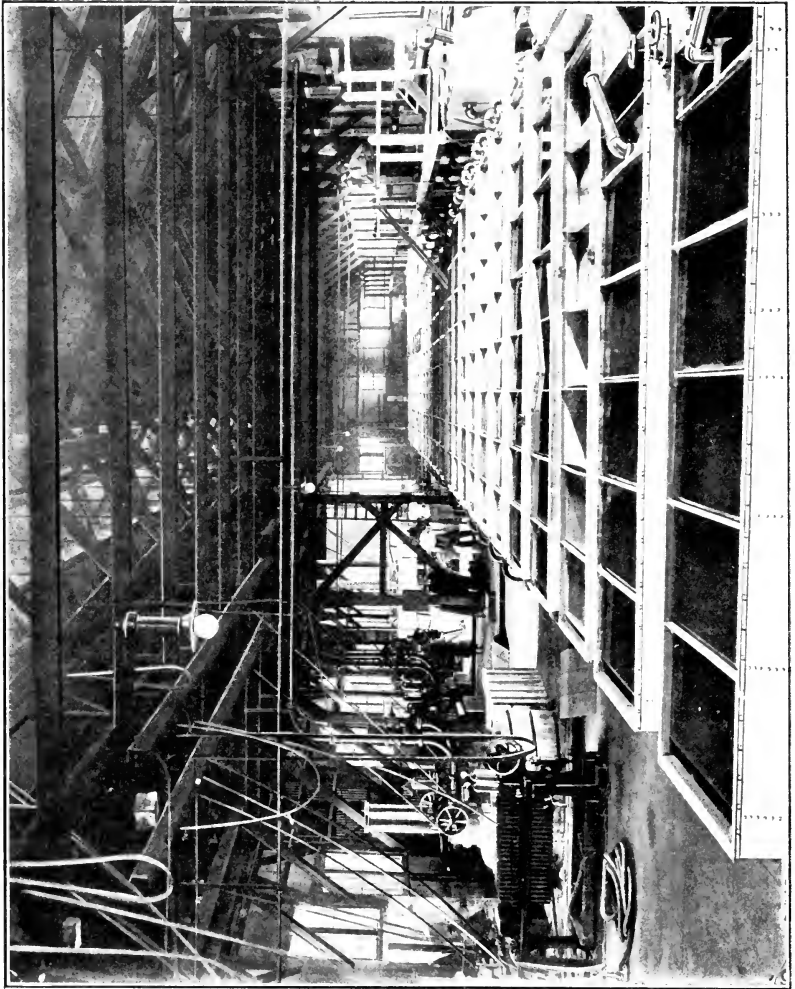


FIG. 22.—Interior of Extractor House. Knight's Deep and Simmer East Joint Plant.

tailings are fed in at one end of the cylinder, ground between the pebbles and discharged at the other end. Any coarse material which escapes from the mill is returned to

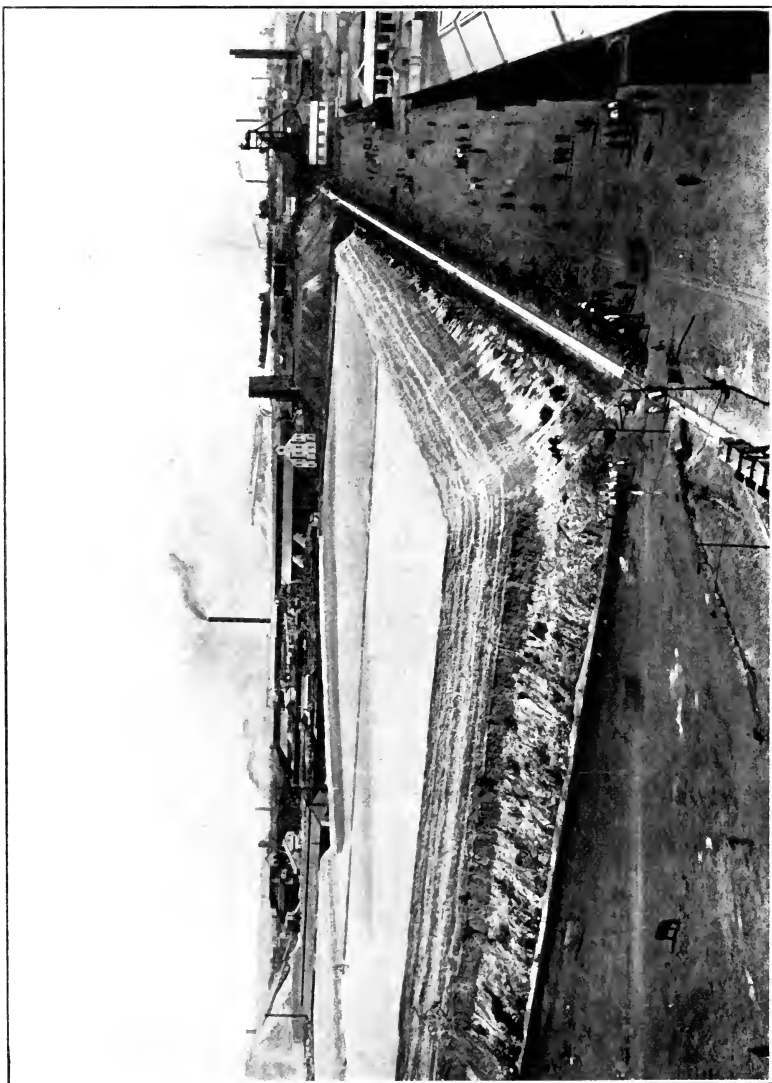


FIG. 23.—Slimes Dam. Knight's Deep and Simmer East Joint Plant.

it. A photograph of one of the three tube-mills in use at the Knight's Deep and Simmer East joint plant is reproduced in Fig. 24.

The silica lining of tube-mills may be replaced by steel, and in the Transvaal the flint pebbles have been discarded in favour of banket ore, which consists of quartz pebbles set in a siliceous cement. This material is found to answer very well and contains a little gold which is set free as the pieces of ore are ground up.

The speed of revolution of tube-mills is such that the pebbles, carried up the side of the mill by the friction of the lining, in part roll over one another and in part fall freely through the air and strike the bed of pebbles at the bottom. For a mill 5 feet in diameter the speed is about twenty-eight revolutions per minute. The pulp is thickened as much as possible by the removal of water before it is fed to the mill. No screen is used at the discharge aperture, but the product is classified in *spitzkasten* (pointed boxes), and the coarser material is returned to the mill.

Since the introduction of tube-mills in the Transvaal (where there were 103 at work in September, 1908) the stamp-mill screens have been made coarser, so that the output of the stamps has materially increased and the tailings from the stamp-mills consist of particles of greater average size than was formerly the case. Thus at the Luipaard's Vlei Estate mill in August, 1908, the duty per stamp was 9.67 tons of ore per day, and the average duty on the Witwatersrand in September, 1908, was 6.49 tons per day, while the average duty in the early part of 1904 was only 4.78 tons per day. Part of this change is, however, due to the increase in weight of the stamps. The

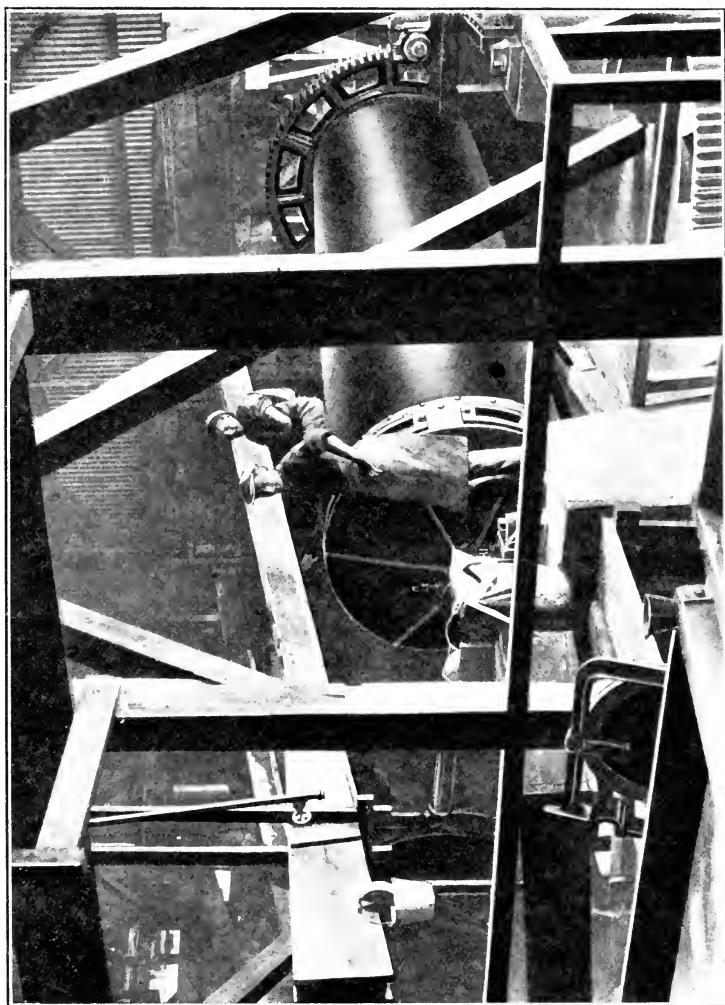


FIG. 24.—Tube-mill. Knight's Deep and Simmer East Joint Plant.

product of the tube-mills is of course finer than the former product of the stamps.

The fine material from the mills is passed over shaking amalgamated copper plates, which have already been described. The extraction of gold by mercury on these and on the ordinary stationary plates is as great as was the case before the introduction of regrinding, so that the material for cyaniding is poorer than formerly, and the proportion of the gold obtained in the cyanide plant is about the same in spite of the fact that, owing to the finer grinding the tailings after being treated by cyanide are poorer than before. "All-sliming" of ore appears to be almost impossible. Even after very fine grinding in tube-mills, the pulp can still be separated into easily leached sands and slimes which cannot be leached by percolation.

The telluride ores of Cripple Creek, Colorado, and of Kalgoorlie, West Australia, cannot be treated successfully by the cyanide process or by amalgamation without special precautions. Telluride of gold is acted on by cyanide of potassium only very slowly, and is not amalgamable at all. Two methods have been used largely. In the *Diehl process* the ore is crushed with water in stamp-mills, amalgamated, concentrated, and the tailings separated by classifiers into sands and slimes. The concentrates are dried, roasted and sent back to the crushing mill. The sands are reground in tube-mills, and the whole of the fine material is then agitated with cyanide solution, to which some bromocyanide is added, and filter-pressed. In the *Marriner process* the ore is crushed dry in roller-mills or ball-mills (*q.v.*) and roasted dead. The product is ground with mercury and cyanide solutions in pans, and the tailings are agitated with dilute cyanide of potassium and filter-pressed.

At Cripple Creek the telluride ores are crushed dry by



means of rolls, roasted and treated with cyanide by percolation in large vats.

*Dry crushing* has not been previously dealt with, but is generally required as a preliminary to roasting or smelting. Stamp batteries can be used, the discharge screens being placed on both sides of the mortar instead of on one side only. *Rolls* are more generally employed. They are revolving cylinders of steel or cast iron, placed with their axes parallel and their peripheries a short distance apart. Pieces of ores are drawn between two rolls and crushed by compression. Ore is generally passed through two or more pairs of rolls in succession, the last pair having their revolving faces placed close together. Rolls are not adapted for very fine crushing, and are seldom used in conjunction with screens finer than about 20-mesh. The ore which will not pass the screen is returned for another passage through the rolls.

*Roasting furnaces* for use in conjunction with the cyanide or chlorination process are of many different designs. The old-fashioned hand-worked reverberatory furnace has now almost passed out of use for such purposes. It consists of a large hearth, on which the ore is spread, surmounted by a low roof. The flame from a fire passes over the hearth, heating the ore, which is stirred by iron tools or rabblies introduced through doors at the sides of the furnaces. Air is supplied through the working doors. The sulphur in the ore is oxidised and partly removed as sulphur dioxide.

Automatic furnaces are now almost universal. In one type, which has many forms, the rabblies are carried by endless moving chains and the ore is stirred and pushed forward towards the hot end of the hearth by the rabblies,

and finally drops through a hole in the hearth near the fire. In another type the ore is fed in at the upper end of an inclined rotating cylinder, and, tumbling over and over as it is carried up the sides of the cylinder, gradually finds its way to the lower end, where it is discharged. The flame from a fire enters, together with air, at the lower end, and passing through the cylinders escapes into the stack at the upper end. In both types of furnace the inclination of the hearth, the arrangements for moving the ore, and the heat from the fire are adjusted so that the ore is roasted as nearly completely as is required before it is discharged.

The cyanide process, which was introduced in South Africa in 1890, and has since spread to all parts of the world, is now of the highest importance in the treatment of gold ores. In the Transvaal 2,264,994 oz. of gold were produced by its use in 1907, as against 4,142,939 oz. by means of amalgamation. The importance of the cyanide process is even higher than might be deduced from these figures, as few of the mines could be worked profitably if the gold extracted by amalgamation represented their total output. The same thing can be said of most of the gold-fields in other parts of the world.

#### THE CHLORINATION PROCESS.

Chlorination has been to some extent displaced by the cheaper cyanide process, but is still used for the treatment of certain ores and concentrates, and is applicable in certain cases in which cyanide is useless.

Ores must always be roasted before chlorination, to prevent the waste of chlorine in acting on oxidisable materials. The roasted ore is sometimes damped and

subjected to the action of chlorine gas in closed vessels, the soluble chloride of gold being afterwards washed out by percolating water (Plattner process). It is now more usual to treat the ore with a solution of chlorine in water, either in vats open to the air (vat solution process) or in closed rotating barrels (barrel process).

The *Plattner process* was that originally employed, and is chiefly applicable to small quantities of rich concentrates. These contain much pyrites and are roasted dead. If copper pyrites is present, salt is added towards the end of the roasting operation to chloridise the copper, which would otherwise absorb chlorine in the vat. Chloridising roasting of gold ores is, however, liable to be attended by a heavy loss of gold by volatilisation. The roasted ore is damped by sprinkling with water and thorough mixing, the amount of water being kept low enough to allow the mass to be porous, so that chlorine gas can pass through it readily. The vat is lead-lined and has a filter-bed and false bottom, and the gas, made by the action of common salt, manganese dioxide and sulphuric acid in a separate generator, is passed upwards into the ore through the filter-bed. When the whole charge smells strongly of chlorine, the vat is closed and allowed to remain for twenty-four hours or more, fresh gas being added if required. The cover is then removed and water poured on the ore and drawn off at the bottom until gold can no longer be detected in the wash-water. The gold chloride is precipitated by ferrous sulphate, the equation being—



The brown precipitate of metallic gold is allowed to settle,

and is collected by filtering. It is then washed, dried and melted.

The *barrel process* of chlorination was originally introduced in the United States, and has never been used for any great length of time in any other country. The chlorine is applied under pressure with a view to shorten the time of action. The gas was originally pumped into the barrel through one of its trunnions, but the later practice is to generate the chlorine inside the barrel by means of sulphuric acid and bleaching powder. Care is taken to prevent these chemicals from coming into contact with each other until the manhole of the barrel has been closed and rotation begun. More water is used than in the Plattner process, the charge being required to be an easily flowing pulp. Iron barrels lined with lead and holding a charge of from five to ten tons of ore are used, and are rotated for about five hours, when the dissolution of the gold is usually complete. The rotation is of value in mixing the charge and bringing all parts of it equally under the action of the chlorine, and also in scouring and brightening the particles of gold and laying them open to attack.

When dissolution is complete, the charge is emptied into a false-bottomed vat to be washed, or the washing is sometimes carried out in the barrel itself, which in this case is provided with a filter-bed forming the chord of an arc of the circle of the barrel. The precipitation of the gold is effected by sulphuretted hydrogen, and the sulphide of gold is filter-pressed, roasted on iron trays and melted with fluxes. If much base metals are present in the solution, the gold is precipitated by ferrous sulphate.

The *vat solution process* is in use at the Mount Morgan

Mine, Queensland, the largest chlorination mill in the world. The vats are oblong, and of a capacity of 100 tons of ore each. They are constructed of concrete lined with cement and faced with pitch and tar, which are unattacked by chlorine. The solution is run on to the ore through earthenware pipes, and is drawn off through the filter-bed as soon as the vat is full. Fresh chlorine solution is added continuously until the gold is completely dissolved, which appears to take about thirty-six hours. Water for washing is then applied and passed through the ore until ferrous sulphate gives no precipitate of gold in the issuing liquid. The tailings are discharged from the tanks into trucks.

The gold solution is heated to expel all free chlorine, and the liquid while still hot is allowed to run through tanks filled with coarsely powdered charcoal resting on a filter-bed and covered with perforated sheet-lead to keep the charcoal from floating. The gold is precipitated on the charcoal, and when the latter is sufficiently coated it is burnt in small furnaces, and the ashes melted with fluxes in a reverberatory furnace.

## CHAPTER IX

### SILVER AND ITS ALLOYS

*Historical.*<sup>1</sup>—Silver was known to the ancients, probably almost as soon as gold itself. Although it did not attract so much attention as gold, the name which it carried in ancient languages was founded on its colour and appearance. Thus in Hebrew “khesef” (silver) was derived from the verb “khasaf,” *to be pale*, and the Latin *argentum* was derived from its Greek equivalent, which meant *white*.<sup>2</sup>

Silver was in use as money probably as early as gold. It is recorded that Abraham paid Ephron in silver for the land bought as a burial place.<sup>3</sup> Pliny states that mines of silver occurred in the mountains in almost all the Roman provinces, and that Spain contained the richest deposits.<sup>4</sup> Strabo<sup>5</sup> describes the treatment of silver ore at New Carthage in Spain as consisting of roasting, followed by washing through sieves. This operation was repeated five times. The residue was fused with lead and cupelled, with the result that pure silver was obtained.

According to Hoefer the only compound of silver known to the ancients was silver chloride, which was formed in refining gold and thrown away with the refuse.

<sup>1</sup> Some notes on the history of silver are given in Chapter I.

<sup>2</sup> Hoefer, “Histoire de la Chimie,” p. 43.

<sup>3</sup> Genesis, chap. xxiii., v. 15.

<sup>4</sup> “Hist. Nat.,” Lib. XXXIII., cap. 31.

<sup>5</sup> “Geogr.,” Lib. III.

## THE PROPERTIES OF SILVER.

Silver is pure white in colour and is capable of receiving a brilliant polish. When in the form of fine powder, as for instance when reduced from the state of chloride by iron and acid, silver is grey and earthy in appearance. It is extremely malleable and ductile, though less so than gold. It is hardened by hammering or rolling, but its softness is restored by annealing at a red heat. It is harder than gold and softer than copper. It is the most perfect conductor of heat and electricity known, and its conductivity is increased by annealing. Its specific gravity is 10·50 after having been cast, and 10·57 after being struck in a coining press. Pure silver, however, is difficult to cast quite solid, and generally contains minute cavities which reduce its density. The density of English silver coin (925 fine) is 10·37. The specific gravity of molten silver is 9·51. The atomic weight of silver is 107·93 (taking  $O = 16$ ), and its symbol is Ag.

Silver melts at  $962^{\circ}$  (Berthelot), and volatilises when heated by the oxy-hydrogen blow-pipe, yielding a pale blue vapour. It can be distilled in quantity by a hydrogen flame in a suitable furnace, or by being heated in the electric arc furnace, when it boils vigorously. Molten silver absorbs about twenty-two volumes of oxygen from the air, and the gas is given off again during solidification, usually with much vigour. The solidified crust of silver is generally broken and blistered, and particles of metal are projected by the gas disengaged from the interior (the so-called "spitting" or "sprouting"). This effect can be prevented by stirring the metal under a cover of charcoal,

or by adding a small quantity of copper, zinc or other oxidisable metal, by which the oxygen is retained. It is probable that the oxygen exists in the molten silver in the form of the oxide,  $\text{Ag}_2\text{O}$ , as this substance has been shown to be stable at very high temperatures, although it is instantly decomposed at a red heat.

Silver is not oxidised at ordinary temperatures either in dry or moist air, and is only slowly oxidised at high temperatures. It is rapidly dissolved by boiling nitric acid, and if it is slightly impure it is attacked at the ordinary temperature. It is soluble in boiling, concentrated sulphuric acid, but is not attacked by the dilute acid unless alloyed with such a metal as iron. Hydrochloric acid acts very slowly, if at all, on pure silver, but at a red heat silver chloride is readily formed by the action of  $\text{HCl}$  gas. The formation of silver chloride by the action of aqua regia, chlorine, or hydrochloric acid on silver is soon stopped by the formation of a protective layer of  $\text{AgCl}$ , which is insoluble in acid.

Sulphide of silver is readily formed by throwing sulphur on to molten silver, or by exposing silver to the action of sulphurous fumes at the ordinary temperature. It is for this reason that silver blackens in the air in towns, a film of sulphide of silver being formed on the surface, presumably by the action of  $\text{H}_2\text{S}$ . The blackening of silver egg-spoons is also due to the formation of sulphide of silver.

#### PREPARATION OF PURE SILVER.

The simplest method of preparing pure silver is to dissolve commercial silver in nitric acid, allow the liquid to



stand, syphon off from precipitated gold, etc., precipitate silver chloride in a hot solution with hydrochloric acid, stir well, allow to settle and wash by decantation. The silver chloride becomes granular by continuous stirring and settles readily. When the decanted liquid no longer shows a trace of impurity, the silver chloride is transferred to a porous pot which has been previously steeped in hydrochloric acid for some days and thoroughly washed by long, continued standing in clean distilled water frequently renewed. The porous pot is placed in water in an outer vessel, in which carbon electrodes are dipped. A cathode of platinum or pure silver is plunged into the silver chloride and connected with the carbon anodes through an electric battery. The white chloride at once begins to blacken next the cathode, and is entirely converted into silver in the course of a few days. The outer liquid becomes strongly impregnated with chlorine gas and should be renewed once or twice a day.

The carbon anodes may be replaced by a cylinder of wrought iron, and a little hydrochloric acid added to start the action. No chlorine is then evolved, and the action is far more rapid. In this case the chloride of iron diffuses into the inner pot and contaminates the silver, but may be removed by washing.

The grey silver powder, after being carefully washed by shaking it with pure water renewed many times, is dried and melted under a little carbon in a graphite or clay crucible and poured into a blackleaded iron mould.

This method is used in the preparation of pure silver for trial plates at the Royal Mint.

## ALLOYS OF SILVER.

The *Silver-copper* alloys are by far the most important of these bodies commercially. The addition of copper to silver lowers its melting point, prevents it from "sprouting" on solidification, and makes it harder without sensibly impairing its malleability or altering its colour. The melting points

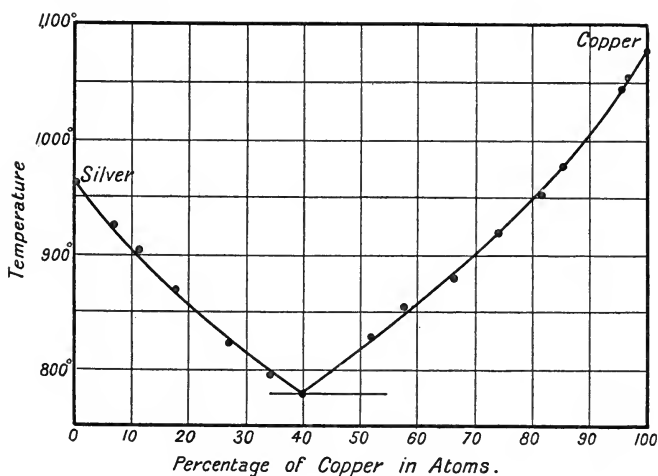


FIG. 25.—Freezing Points of the Alloys of Silver and Copper.

of the series of alloys as determined by Roberts-Austen<sup>1</sup> and by Heycock and Neville<sup>2</sup> are shown in Fig. 26. Levl's alloy, containing 71·89 per cent. of silver or 60 atoms of silver per cent., is the eutectic alloy, melting at 778°, the lowest temperature of any of the series. This alloy is perfectly homogeneous, and has been used for coinage purposes for circulation in the Dutch Indies. It is not, however,

<sup>1</sup> *Jour. Soc. Arts*, March, 1897.

<sup>2</sup> *Phil. Trans. Roy. Soc.*, Vol. CLXXXIX. (1897), p. 25.

especially well fitted for manufacture into coin, as it is harder and less ductile than the other silver-copper alloys.

Alloys containing more silver than is contained by the eutectic alloy consist of non-homogeneous mixtures, and on solidification become richer in silver in the interior than on the outside. The difference, however, never exceeds a few parts per 1,000. These alloys are largely used for coinage and for wares of all kinds. In England the standard for both is 92.5 per cent. silver, with 7.5 per cent. copper. This is known as "standard silver." In the United States, France, Germany and most other countries the principal coinage alloy contains 90 per cent. silver, and melts at a lower temperature than the English standard alloy and is slightly harder. The colour of these alloys is almost the same. English silver coin melts at  $890^{\circ}$  and American coin at  $873^{\circ}$ . For full details as to the standards of alloys used for coinage in various countries, see Chapter XV., on Minting. The silver-copper alloys blacken on being heated in the air owing to the formation of oxide of copper, which can be removed by hot dilute sulphuric acid. They dissolve completely in nitric acid and in boiling concentrated sulphuric acid, but are scarcely affected by hydrochloric acid.

The *Silver-zinc* alloys rich in silver present some resemblances to the corresponding silver-copper alloys. They are malleable and ductile, and take a high polish. The freezing-point curve of the series according to Heycock and Neville<sup>1</sup> and Petrenko<sup>2</sup> is shown in Fig. 26. The addition of zinc lowers the freezing point of silver, and this continues throughout the series, pure zinc having a lower melting point than any

<sup>1</sup> *Jour. Chem. Soc.*, Vol. LXXI. (1897), p. 407.

<sup>2</sup> *Zeit. Anorg. Chem.*, Vol. XLVIII. (1906), p. 347.

of the alloys. The alloys with less than 20 per cent. of zinc are malleable, but those with 20 to 30 per cent. are brittle. These alloys contain the first eutectic, which melts

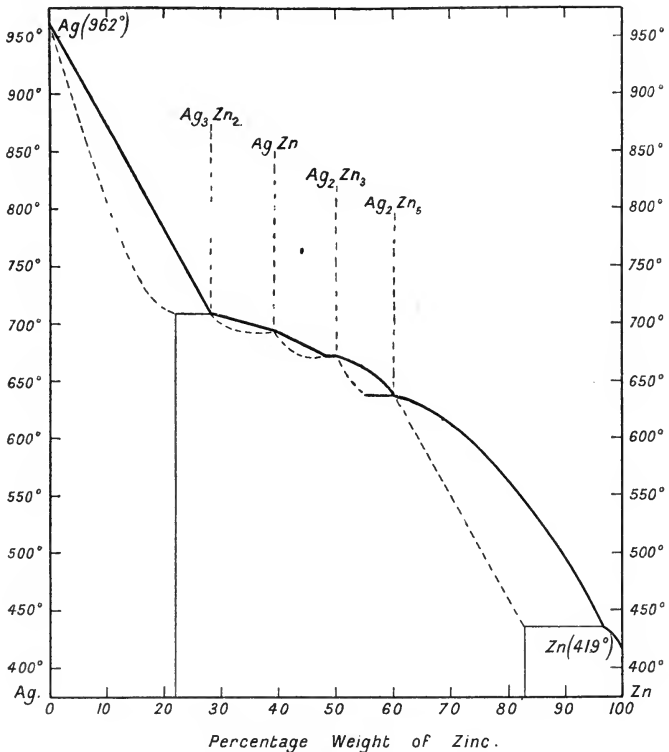


FIG. 26.—Freezing Points of the Alloys of Silver and Zinc.

at 705° and contains 28 per cent. of zinc. The alloy corresponding to the formula  $AgZn$ , and containing 37.7 per cent. of zinc, shows a lilac-red tint when heated to 300° and suddenly cooled, resembling in its colour the alloys  $AuZn$  and  $AgCd$ . This colour disappears if the alloy is heated

with dilute nitric acid, and hence is probably due to a superficial layer of oxide. The alloys containing about 48 to 50 per cent. of zinc have a conchoidal fracture with a brilliant glassy surface, and are very brittle. These alloys contain the compound  $\text{Ag}_2\text{Zn}_3$ . All the alloys, except those whose composition is nearly equivalent to  $\text{AgZn}$ , are of a silver-white colour. The best method of preparing them, as in the case of the silver-cadmium alloys, is to pour molten silver into molten zinc. The latter is kept at a low red heat, considerably below its boiling point. When this method of preparation of the alloy is adopted the loss of zinc by volatilisation or oxidation is very small. Besides  $\text{AgZn}$  and  $\text{Ag}_2\text{Zn}_3$ , the compounds  $\text{Ag}_2\text{Zn}_3$  and  $\text{Ag}_2\text{Zn}_5$  and one of about the composition  $\text{AgZn}_{12}$  have been shown to exist.

*Silver and Cadmium.*—These alloys are softer, whiter and more malleable and ductile than the silver-copper alloys. They consist of isomorphous mixtures of various compounds of silver and cadmium, and the alloys rich in silver are homogeneous and suitable for the manufacture of trial plates for assay purposes. The compounds  $\text{Ag}_4\text{Cd}$ ,  $\text{Ag}_2\text{Cd}$ ,  $\text{Ag}_3\text{Cd}_2$ ,  $\text{AgCd}$ ,  $\text{Ag}_2\text{Cd}_3$  and  $\text{AgCd}_3$  have been shown to exist.<sup>1</sup> The alloy containing 40 per cent. of silver ( $\text{Ag}_2\text{Cd}_3$ ) has a brilliant lustre and a conchoidal fracture, and is intensely hard and brittle. The compounds  $\text{Ag}_2\text{Cd}_3$  and  $\text{Ag}_2\text{Zn}_3$  thus bear strong resemblances to each other, as do the compounds  $\text{AgZn}$  and  $\text{AgCd}$ . A violet colour distinguishes the alloys with composition nearly equivalent to  $\text{AgCd}$ , and these alloys, like those near in composition to  $\text{AgZn}$ , undergo allotropic changes at temperatures considerably below their melting points.

<sup>1</sup> T. K. Rose, *Proc. Roy. S. c.*, Vol. LXXIV. (1904), p. 218.

*Silver and Lead.*—Silver and lead mix together in all proportions while they are molten, but on solidification they separate, so that the alloys are not homogeneous. The freezing-point curve is shown in Fig. 27, which is after Petrenko,<sup>1</sup> and is remarkable for the persistence of the

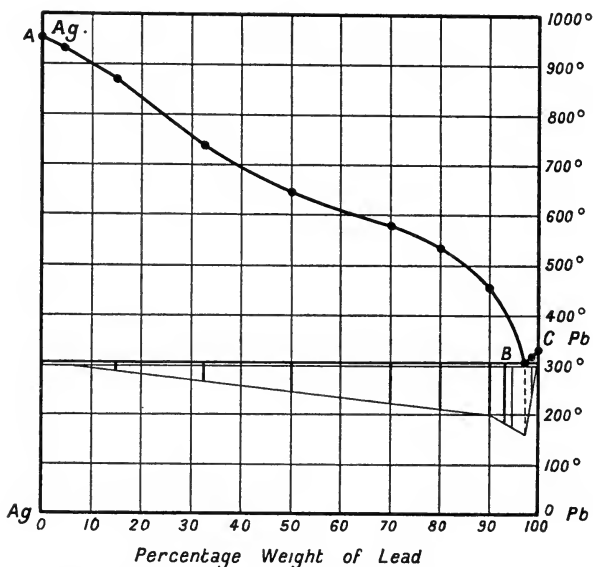


FIG. 27.—Freezing Points of the Alloys of Silver and Lead.

eutectic point, which is observable in an alloy containing over 99 per cent. of silver. The two metals are in fact quite insoluble in each other in the solid state. The eutectic alloy, B, contains 2.5 per cent. of silver and solidifies at 303°. There is no evidence that any compounds of silver and lead exist. These properties explain the effects of the Pattinson process (*q.v.*) for concentrating the silver

<sup>1</sup> *Zeit. Anorg. Chem.*, Vol. LIII. (1907), p. 200.

contained in lead. The curve AB is of a remarkable shape.

Molten lead takes up silver readily, removing it from its compounds such as the chloride, sulphide, arsenide, etc. Lead also removes silver from its alloys with copper at temperatures between the melting point of lead and those of the silver-copper alloys. This property was used in the old liquation process, now abandoned. On the other hand, zinc removes silver from molten lead, forming a zinc-silver compound, probably  $\text{AgZn}_{12}$ , which is lighter than lead and floats to the top with the dross and surplus zinc, so that it can be skimmed off the lead. This is the basis of Parke's process (*q.v.*).

When silver-lead alloys are melted in the air, the lead is oxidised and the silver remains unaltered. At a red heat the action is rapid and the litharge produced becomes molten and is far less viscous than the molten metals. The cupellation process is based on these properties.

In 1853 it was shown by Level<sup>1</sup> that alloys of silver and lead undergo segregation and are not uniform in composition. A result of this is that the valuation of argentiferous lead produced in smelting operations is a matter of difficulty. According to A. C. Claudet,<sup>2</sup> satisfactory samples cannot be cut from pig lead, and it is necessary to remelt the alloy and to take dip samples.

*Silver and Mercury.*—The alloys are called amalgams like the other alloys of mercury. Surface action between silver and mercury is easy and rapid at the ordinary temperature,

<sup>1</sup> *Ann. de Chim. et Phys.*, Vol. XXXIX. (1853), p. 173; Percy's "Silver and Gold," p. 173.

<sup>2</sup> *Trans. Inst. of Mng. and Met.*, Vol. VI. (1898), p. 29.

so that silver is at once "wetted" by mercury. The interpenetration of the metals is, however, exceedingly slow, though more rapid at the boiling point of mercury than at the ordinary temperature. The crystalline amalgam  $\text{AgHg}$  (containing 35 per cent. of silver and 65 per cent. of mercury) is produced in the branching form known as *Arbor Diane*, by prolonged contact of an amalgam of silver and mercury with a saturated solution of silver and mercury nitrates in nitric acid (see Percy's "Silver and Gold," p. 176). If too much mercury is present a liquid amalgam only is formed.

The amount of silver dissolved by liquid mercury, and remaining in it after the solid amalgam has been filtered off, is stated to vary with the pressure to which the amalgam is subjected. This seems to be improbable. The amount of dissolved silver is variously stated at from 0.05 to 1.5 per cent. The composition of solid amalgam undoubtedly varies with the pressure during filtration and with the size of the particles of silver, which are rarely fully amalgamated to their centre. Before filtering, the solid amalgam floats to the top of the mercury.

Mercury decomposes a number of compounds of silver, such as the chloride and bromide, forming mercury chloride, bromide, etc., and amalgams of silver.

*Silver-tin Alloys.*—These alloys are silver-white in colour and are in general somewhat brittle and hard. The alloys containing between 40 and 60 per cent. of silver are used by dentists.<sup>1</sup> They are mixed with about an equal weight of mercury, and amalgams are formed which are pasty at first and subsequently become hard. The full degree of hardness is not attained until 24 or 48 hours after the

<sup>1</sup> E. A. Smith, "Silver Alloys of Industrial Importance," 1901.



mixing with mercury, and some molecular change evidently takes place gradually.

The thermic study of these alloys by Petrenko<sup>1</sup> shows that only one compound,  $\text{Ag}_3\text{Sn}$ , exists, containing 26.7 per cent. of tin, and that there is only one homogeneous

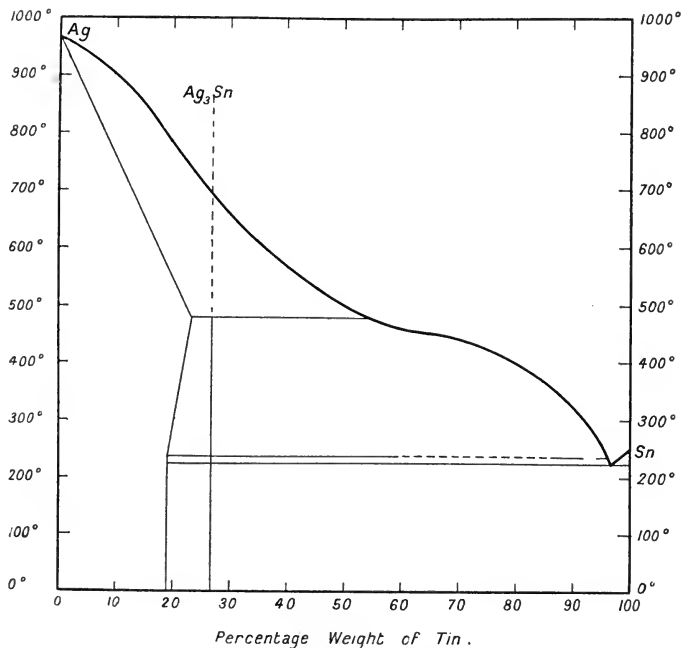


FIG. 28.—Freezing Points of the Alloys of Silver and Tin.

alloy, the eutectic mixture, which contains 3.5 per cent. of tin and solidifies at 220°, or 8° below the melting point of tin. The thermic diagram of these alloys is shown in Fig. 28. The compound  $\text{Ag}_3\text{Sn}$  undergoes a polymorphic change at 232°. Fig. 29 shows the structure of the 20 per

<sup>1</sup> *Zeit. Anorg. Chem.*, Vol. LIII. (1907), p. 204.

cent. tin alloy, after attack by hydrogen peroxide and ammonia, magnified twenty-four diameters. Both these diagrams are after Petrenko.

*Silver and Platinum.*—These alloys are also used in dentistry. The first additions of platinum to silver raise the melting point of the latter, and the dental alloys which contain from 25 to 35 per cent. of platinum require a high temperature for their preparation. They are hard but ductile,



FIG. 29.—Silver, 80 per cent. ;  
Tin, 20 per cent.  $\times 24$ .

and do not readily tarnish. The alloy containing 33.3 per cent. of platinum has been used as a standard of electrical resistance. The platinum-silver alloys are also used in jewellery. As the proportion of platinum is increased the alloys formed are less ductile and harder. The metals do not readily mix, the platinum having a strong tendency to

settle to the bottom in molten mixtures on account of its high density. Platinum in its alloys with silver is soluble to some extent in nitric acid, so that it can be partly separated from gold by the nitric acid parting process (see below under "Assay of Platinum," Chapter XVII.). When these alloys are attacked by boiling concentrated sulphuric acid, the silver dissolves and the platinum remains undissolved.

The freezing-point curves of the alloys have been examined by Doerincel,<sup>1</sup> who melted them in a carbon-

<sup>1</sup> *Zeit. Anorg. Chem.*, Vol. LIV. (1907), p. 338.

resistance electric furnace, and measured temperatures by a thermocouple of platinum and platinum-rhodium. The alloys containing more than 80 per cent. platinum were

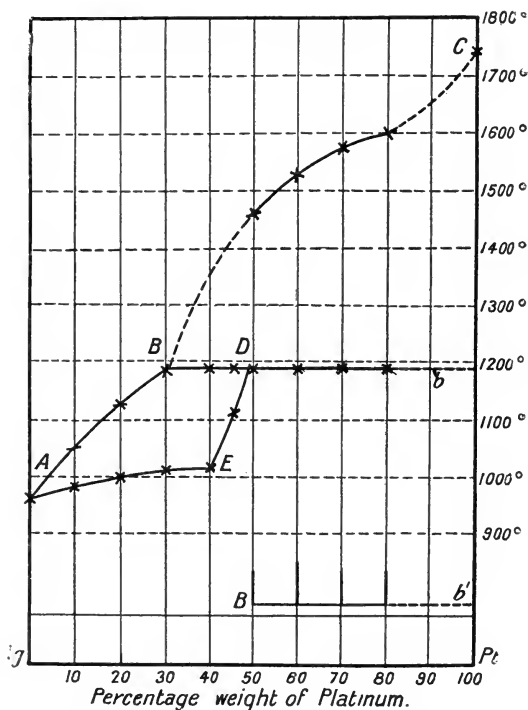


FIG. 30.—Freezing Points of Alloys of Silver and Platinum.

not examined. The diagram of freezing points is shown in Fig. 30. The curve ABC gives the initial freezing points of the alloys (liquidus curve), and AEDb the points where solidification is completed. It is uncertain whether pure platinum or mixed crystals rich in platinum separate

along the line BC. It is clear that the alloys when solidified from fusion are not homogeneous, but separate into two constituents. When alloys containing between 30 and 45 per cent. of platinum are reheated at  $1,150^{\circ}$  to  $1,180^{\circ}$  for six hours, they tend to become homogeneous.

*Silver and Aluminium.*—The preparation of the alloys



FIG. 31.—Ag, 94 per cent. ; Al, 6 per cent.  $\times 30$ .

rich in silver presents some difficulties owing to the low density of aluminium and the tendency it has to cover itself with a skin of oxide which is not easily broken through. The best method is to melt aluminium and to pour molten silver into it. The alloys containing from 0 to 4 per cent. of

aluminium and also those containing from 7.72 to 11.3 per cent. easily receive a fine polish, because they contain only one structural element.<sup>1</sup> Most of the alloys are not homogeneous (see Fig. 31, which is the alloy containing 6 per cent. aluminium magnified thirty diameters). There is a eutectic melting at  $567^{\circ}$  and containing 30 per cent. of aluminium, and two compounds have been found to exist,  $AlAg_2$  and  $AlAg_3$ .

<sup>1</sup> Petrenko, *Zeit. Anorg. Chem.*, Vol. XLVI. (1905), p. 49.

*Silver and Bismuth* form a series of alloys similar in properties to the silver-lead alloys. There is a eutectic melting at  $262^{\circ}$  and containing 2.5 per cent. of silver. The eutectic persists almost to the pure silver end of the series, making all the alloys brittle. By annealing for two or three hours at  $260^{\circ}$  to  $270^{\circ}$ , however, the bismuth is dissolved in the silver if less than 5 per cent. of bismuth is present,<sup>1</sup> and under these circumstances these alloys become ductile. When copper is added to the alloys, however, bismuth is no longer soluble in the silver, and annealing is not in that case sufficient to cure the brittleness if more than a trace of bismuth is present. Gowland found some silver ingots (received at the Japanese Mint from certain Japanese refineries) to be brittle owing to the presence of bismuth.<sup>2</sup>

*Silver and Nickel* form homogeneous alloys if the silver does not exceed 4 per cent. These alloys fuse at temperatures above  $1,464^{\circ}$ . If more silver is present, the alloys separate into two layers, the nickel with 4 per cent. of silver floating on the top of nearly pure silver. Silver does not mix at all with *iron* or *cobalt*.

*Silver and Palladium* mix in all proportions, forming a series resembling the gold-palladium alloys.

*Silver and Thallium*.<sup>3</sup>—The series of alloys closely resemble those of silver and lead and of silver and bismuth. The eutectic alloy contains 2.5 per cent. of silver and solidifies at  $287^{\circ}$ . As much as 10 per cent. of thallium, however, dissolves in silver, forming homogeneous ductile alloys. When alloys rich in silver are melted, thallium is rapidly volatilised.

<sup>1</sup> Petrenko, *Zeit. Anorg. Chem.*, Vol. I. (1906), p. 136.

<sup>2</sup> *Jour. Chem. Soc.*, Vol. LI. (1887), p. 410.

<sup>3</sup> Petrenko, *Zeit. Anorg. Chem.*, Vol. I. (1906), p. 133; Poitevin, *Revue de Metallurgie*, 1908, p. 159.

## CHAPTER X

### COMPOUNDS AND ORES OF SILVER

*Silver oxide*,  $\text{Ag}_2\text{O}$ , is formed by heating finely divided silver with cupric oxide, red lead, or manganese dioxide, and in presence of one of these oxides is not decomposed even at a bright red heat. When heated alone it is decomposed into silver and oxygen at temperatures between  $250^\circ$  and  $300^\circ$ , but Troost and Hautefeuille showed that at about  $1,400^\circ$  silver unites with oxygen with the formation of  $\text{Ag}_2\text{O}$ .<sup>1</sup> At a red heat  $\text{Ag}_2\text{O}$  is immediately decomposed, and cannot be formed in the absence of other metallic oxides. Wait showed<sup>2</sup> that in a rich litharge containing 2·94 per cent. of silver, about 19 per cent. of the silver was soluble in acetic acid, and must be assumed to have been in the form of oxide, as metallic silver is not attacked by acetic acid. Silver oxide may be prepared by adding baryta water to a solution of silver nitrate, and washing and drying the precipitate. Thus prepared, it is a powder of a deep brownish-olive colour, and has a density of 7·1.

*Silver sulphide*,  $\text{Ag}_2\text{S}$ , is prepared in the dry way by melting together silver and sulphur, when a dark grey crystalline substance results, resembling the native sulphide, argentite, in its properties. It has a feebly metallic lustre,

<sup>1</sup> *Comptes Rendus*, Vol. LXXXIV. (1877), p. 948.

<sup>2</sup> *Trans. Am. Inst. Mng. Eng.*, Vol. XV. p. 423.



and is opaque, easily sectile and slightly malleable. Its density is 6.85.

It is also formed by the action of aqueous solutions of alkaline sulphides on metallic silver, although far less rapidly than in the dry way at high temperatures. Silver is rapidly tarnished with the formation of  $\text{Ag}_2\text{S}$  by the action of sulphuretted hydrogen gas or by being rubbed with sulphur. Silver sulphide is precipitated from silver solutions by  $\text{H}_2\text{S}$  or by soluble sulphides.

It is soluble in cyanide of potassium, especially in hot strong solutions. This property is useful in removing the tarnish from silver articles when polishing is impossible or undesirable. Sulphide of silver is acted on by nitric acid with the formation of nitrate of silver and the separation of sulphur. "Oxidised" silver is silver coated with  $\text{Ag}_2\text{S}$ . It is prepared by dipping the articles to be "oxidised" into a hot solution of potassium sulphide.

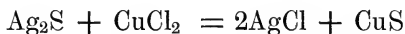
Friedrich and Leroux have shown<sup>1</sup> that silver sulphide solidifies at  $806^\circ$ , and that all mixtures of silver and sulphide of silver containing more than about 13 per cent. of  $\text{Ag}_2\text{S}$  solidify at  $906^\circ$ , any excess of  $\text{Ag}_2\text{S}$  over 13 per cent. solidifying at  $806^\circ$ . If more than 13 per cent.  $\text{Ag}_2\text{S}$  is present, the two substances are not miscible even in the liquid state, but separate into layers.

Sulphide of silver readily mixes with other metallic sulphides when they are melted together, so that in smelting, silver is readily concentrated in a matte. When fused by itself, sulphide of silver loses a little sulphur, and the remainder of the sulphur may be removed by fusion with metallic iron, when sulphide of iron and metallic silver

<sup>1</sup> *Metallurgie*, Vol. III. (1906), p. 361.

results. Copper reduces silver from its fused sulphide only imperfectly, but the sulphide is reduced to metallic silver when heated in air, steam or hydrogen. When copper sulphide is mixed with silver sulphide and the mixture is heated in air, sulphate of copper is produced, and at a red heat gaseous  $\text{SO}_3$  is given off and silver sulphate and oxide of copper remain. If the temperature is too high, or if the action is prolonged for some time, the silver sulphate is split up and metallic silver remains.

Silver sulphide is converted into chloride by being roasted with common salt in the presence of air, or by the action of chlorine water, chlorine gas or hydrochloric acid, especially with the aid of heat. Even in cold solutions cuprous chloride and cupric chloride act similarly on silver sulphide, the reactions being partly represented by the following equations :—



The action is facilitated by boiling. Some metallic silver is also produced, according to the equation—



Sodium - copper thiosulphate ( $4\text{Na}_2\text{S}_2\text{O}_3 \cdot 3\text{Cu}_2\text{S}_2\text{O}_3$ ) was shown by Russell to decompose silver sulphide, the silver going into solution as thiosulphate, with the formation of copper sulphide. Ordinary sodium thiosulphate, however, does not act on silver sulphide. Alkaline cyanides dissolve  $\text{Ag}_2\text{S}$ , and it is decomposed by mercury, the action being rapid in the presence of metallic iron, especially on heating.

These properties of silver sulphide are of importance in the extraction of silver from its ores.



*Silver chloride*, AgCl. This compound is usually prepared by adding hydrochloric acid or a soluble chloride such as common salt to a solution of silver nitrate. It is thrown down as a white, curdy, amorphous precipitate which can be made to settle by shaking, or less readily by stirring and heating. It is readily washed by decantation.

Silver chloride is also formed by the action of chlorine gas on metallic silver and on certain compounds of silver. This action takes place at ordinary temperatures, but is expedited by heat, and at a red heat most of the compounds of silver are converted into the chloride.

Silver chloride precipitate is a white anhydrous powder. Its density is 5.5. It fuses at  $360^{\circ}$  to a reddish-yellow liquid, which is readily absorbed by unglazed clay crucibles. It is volatilised without decomposition at a bright red heat. When solidified after fusion it is waxy in appearance, and is translucent, sectile and tough. Thin plates of it are flexible and almost transparent, and have a horn-like appearance. In this state it is sometimes called *horn-silver*. The mineral *Kerargyrite*, which consists of AgCl, resembles horn-silver in appearance.

Silver chloride is darkened by exposure to light owing to the formation of oxychloride of silver,  $\text{Ag}_2\text{ClO}$ . The darkening is checked by the presence of an excess of hydrochloric acid, and increased by an excess of silver nitrate in solution. It is entirely prevented by the presence of chloride of mercury.

Silver chloride is very insoluble in water. Silver can be readily detected in water containing one-millionth of its weight of silver in solution as nitrate, by the addition of hydrochloric acid. Stas detected far smaller quantities of

silver in solution than this. Silver chloride is, however, perceptibly soluble in strong nitric acid, especially when the acid is hot, and is more readily soluble in hydrochloric acid and in a number of chlorides, as shown in the following table<sup>1</sup> :—

Solution.	Percentage of Salt contained in the Solution.	Temperature.	AgCl contained in one Litre.
Water . . .	—	18° C.	0·0015 gram.
KCl . . .	24·95	19·6° C.	0·914 "
NaCl . . .	25·96	19·6° C.	1·270 "
NH <sub>4</sub> Cl . . .	28·45	30·0° C.	3·673 "
CaCl <sub>2</sub> . . .	41·26	30·0° C.	8·350 "
MgCl <sub>2</sub> . . .	36·35	30·0° C.	7·095 "
FeCl <sub>2</sub> . . .	37·48	21·4° C.	0·085 "
Fe <sub>2</sub> Cl <sub>6</sub> . . .	30·70	20·0° C.	2·395 "
CuCl <sub>2</sub> . . .	44·48	30·0° C.	0·833 "

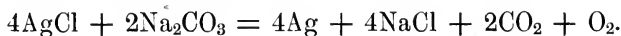
The solubility in hot solutions is greater. Silver chloride is freely soluble in ammonia, in cyanides of the alkalis and in thiosulphate of sodium. After fusion it dissolves with much difficulty.

It is decomposed by mercury with the formation of mercurous chloride and silver amalgam, and is also reduced by many other metals, such as zinc, iron, etc. Zinc or iron in the presence of water and a little hydrochloric or sulphuric acid reduces silver chloride rapidly at the ordinary temperature. The end of the action is signalled by a vigorous evolution of hydrogen, which is prevented from making its appearance by being converted into hydrochloric acid so long as some silver chloride remains undecomposed.

Silver chloride is also reduced by alkalis and the

<sup>1</sup> Vondracek, *Revue de Metallurgie*, September, 1908, p. 678.

alkaline carbonates at a red heat. The reaction may be represented as follows:—



It is also reduced by cuprous chloride in ammoniacal solution or by being heated with charcoal.

*Silver bromide*, AgBr, is a pale yellow powder of density 6.25, melting at 434° to a red liquid. It can be prepared by precipitating silver nitrate with a soluble bromide. Its properties resemble those of silver chloride, but it is less soluble in water and other solvents. Sodium bromide has long been used instead of sodium chloride at the Utrecht Mint for the precipitation of silver in the volumetric process of assay. Silver bromide is dissolved by potassium bromide. It darkens rapidly when exposed to light.

*Silver iodide*, AgI, is a pale yellow powder, melting at 527° to a red liquid. On solidification a substance is produced which is yellow, transparent and flexible above 142°, and pale green, opaque, brittle and crystalline below 142°. Silver iodide is almost insoluble in water and in alkaline chlorides, and is only slightly soluble in ammonia (one part in 2,510 parts), but it is soluble in cyanide and thiosulphate solutions, and in a concentrated solution of potassium iodide.

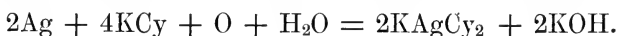
*Silver cyanide*, AgCy, is obtained as a white curdy precipitate by the addition of a soluble cyanide to a solution of silver nitrate. In its properties it resembles the haloid silver salts, but it is not darkened by light. It is soluble in molecular proportions in potassium cyanide, thus—



It is decomposed, like the haloid salts, by strong sulphuric

acid. It is also decomposed by hydrochloric acid and by nitric acid with evolution of HCy. When heated it is decomposed, cyanogen being given off and metallic silver remaining as a residue. Its density is 3·95.

*Silver-potassium cyanide*,  $\text{KAgCy}_2$ , is crystalline, forming anhydrous transparent regular octahedra, soluble in 4·7 parts of water at  $20^\circ$  and in 25 parts of alcohol. It is formed in solution by dissolving  $\text{AgCy}$  or  $\text{AgCl}$  in  $\text{KCy}$ , and also by the action of cyanide solutions on metallic silver in the presence of air or certain other oxidising agents. The reaction may be represented as follows:—



Silver potassium cyanide is decomposed by acids,  $\text{AgCy}$  being precipitated. The silver is precipitated from a solution of  $\text{KAgCy}_2$  by a current of electricity and by certain metals, such as zinc, copper, etc., of which zinc is used on the large scale in the cyanide process. The solution of this salt is used for electro-plating.

*Silver nitrate*,  $\text{AgNO}_3$ , occurs in colourless transparent crystalline plates, unalterable at ordinary temperatures in the air and having a density of 4·35. It melts at  $198^\circ$ , and the fused salt after solidification is the form of silver nitrate commonly known as *lunar caustic* which is used by surgeons. At a low red heat silver nitrate is reduced to the metallic state. It dissolves in 0·783 of its weight of water at  $11^\circ$ , and in half its weight of water at the boiling point.

*Silver telluride*,  $\text{Ag}_2\text{Te}$ , and *Silver selenide*,  $\text{Ag}_2\text{Se}$ , resemble the sulphide in their properties, and occur native. Like the sulphide, when roasted in air they offer considerable resistance to oxidation.

*Silver sulphate*,  $\text{Ag}_2\text{SO}_4$ , is formed at a red heat by the action of sulphates on silver sulphide. Copper sulphate is particularly suitable for effecting this conversion. It is also formed when silver is dissolved in sulphuric acid, and when it is heated with acid sulphates. Silver sulphate is freely soluble in hot concentrated sulphuric acid, but is far less soluble in cold acid and in water. Copper, iron or zinc precipitates silver from solutions of the sulphate.

Silver sulphate is decomposed at a bright red heat into silver, oxygen and sulphur dioxide. It is converted into silver chloride by being roasted with common salt at a red heat.

*Silver antimonate* and *Silver arsenate* are formed in the roasting of antimonial and arsenical silver ores. They are stable at high temperatures, but can be reduced by heating with charcoal or metallic lead. They are also convertible into silver chloride by roasting with salt, but are not reduced by mercury at the ordinary temperatures.

### SILVER ORES.

Silver occurs native, but unlike gold it is generally combined with other elements in its ores. Native silver, together with horn-silver,  $\text{AgCl}$ , bromite,  $\text{AgBr}$ , etc., are found in the oxidised portions of lodes near the surface. At deeper levels these are replaced by argentiferous sulphides, arsenides and antimonides.

*Native Silver*,  $\text{Ag}$ , occurs in cubes and octahedra, usually in aggregates which take a filiform or dendritic shape. It also occurs massive and in laminæ. It has been found in considerable masses at Kongsberg, in Norway, where it

is the principal ore. The largest mass recorded by Daubr e weighed 697 kilograms, or 22,409 oz. Troy. Large amounts of native silver were also found in the great Comstock lode, and great quantities have been extracted in various localities in Mexico and South America, at Freiberg and at Broken Hill. Native silver is sometimes over 990 fine, but it generally contains such impurities as gold, copper, etc. The alloy of silver and mercury (silver amalgam) occurs native.

*Argentite*,  $\text{Ag}_2\text{S}$ , is one of the most important ores of silver. It occurs in black, soft, sectile crystals and masses, which are usually pure, containing 87.1 per cent. of silver. Its density is 7.2 or 7.3. It occurs in great quantities at the Comstock lode, Nevada, in Mexico, and in many other localities.

Other widely distributed sulphides are the ruby silver ores, *proustite*,  $3\text{Ag}_2\text{S} + \text{As}_2\text{S}_3$ , *pyrargyrite*,  $3\text{Ag}_2\text{S} + \text{Sb}_2\text{S}_3$ , and brittle silver ore, or *stephanite*,  $5\text{Ag}_2\text{S} + \text{Sb}_2\text{S}_3$ . *Fahlore*, or grey silver, another important ore, is a mixture of antimony and arsenic sulphides with sulphides of silver, mercury, copper, zinc and iron. Its formula is  $4(\text{Ag}_2\text{Hg.CuFeZn})\text{S} + (\text{SbAs})_2\text{S}_3$ . It may contain any proportion of silver up to 31 per cent., arsenical grey silver being poorer than the antimonial varieties. It occurs in Germany, the Tyrol, Bolivia, Nevada, Mexico, Colorado, etc.

*Polybasite*,  $9(\text{Ag}_2\text{Cu})\text{S} + (\text{SbAs})_2\text{S}_3$ , is also a commonly occurring mineral, especially in America.

Other sulphide minerals containing silver, but less important as ores than those given above, are *castillite*,  $(\text{CuAg})_2\text{S} \cdot 2(\text{CuPbZnFe})\text{S}$ ; *cosalite*,  $2(\text{Ag}_2\text{Pb})\text{S} \cdot \text{Bi}_2\text{S}_3$ ; *dyscrasite*,  $\text{Ag}_3\text{Sb}$ ; *freieslebenite*,  $5(\text{Ag}_2\text{Pb})\text{S} \cdot 2\text{Sb}_2\text{S}_3$ , and *stro-*

*meyerite*,  $\text{Ag}_2\text{S} \cdot \text{Cu}_2\text{S}$ . *Hessite*,  $\text{Ag}_2\text{Te}$ , and *petzite*, a telluride of gold and silver, are also of some importance as ores.

The haloid ores, *Kerargyrite*,  $\text{AgCl}$ , and *embolite*,  $\text{Ag}(\text{ClBr})$  are also very abundant in the upper oxidised zones of lodes in South America, Mexico, etc. Many of these have now been worked out. *Bromite*,  $\text{AgBr}$ , and *iodite*,  $\text{AgI}$ , are not very abundant.

There are many other minerals containing silver described by mineralogists, but they are not important to miners or metallurgists. Among these are *Naumannite*,  $\text{Ag}_2\text{Se}$ , and other selenides, *chilenite*,  $\text{Ag}_6\text{Bi}$ , and a number of complex sulphides. Several silver minerals often occur together in the same mine.

Silver also occurs in the ores of lead, copper, zinc, nickel, etc. Galena often contains considerable amounts of silver (up to 5 per cent.), and zinc blende,  $\text{ZnS}$ , chalcopyrite,  $\text{CuS} \cdot \text{FeS} \cdot \text{FeS}_2$ , bournonite and other minerals also yield much silver. Sometimes the silver replaces one of the base metals in these minerals, but it is often not an essential part of the mineral, occurring in the form of thin films which separate the crystal faces or are situated along the cleavage planes.

## CHAPTER XI

### THE EXTRACTION OF SILVER FROM ITS ORES

SILVER is extracted from its ores by methods which may be classified as follows:—

1. Amalgamation processes.
2. Lixiviation                   ,,
3. Smelting                       ,,
4. Electrolytic                   ,,

These are described in succession below.

#### 1. AMALGAMATION PROCESSES.

Native silver, together with chloride, bromide, chlorobromide and iodide of silver can be amalgamated direct by grinding with mercury without any special preparation. The haloid salts are decomposed with the formation of silver amalgam and haloid compounds of mercury.

Owing to its lower density and its habit of being in combination, however, silver cannot be extracted from its ores by amalgamation so easily and completely as gold. When crushed in stamp batteries and passed over amalgamated tables silver ores yield only small percentages of their silver contents. More prolonged and intimate contact with the mercury is required, and this is obtained in various ways.

Silver sulphide is decomposed by mercury, metallic silver being set free and amalgamated and sulphide of mercury being produced, but the action is very slow.



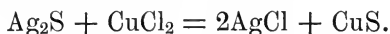
Arsenical and antimonial silver compounds are still less easy to amalgamate, and the action is always incomplete. Ores containing sulphides, arsenides and antimonides are accordingly treated by roasting with salt, or by the use of various chemicals, in order to convert the refractory silver compounds into silver chloride or metallic silver, before they are subjected to amalgamation.

*Direct amalgamation* has been used on rich ores containing native silver and silver chloride and only small quantities of sulphides. In the *tina* process, formerly employed at Kongsberg, Norway, and in Chile and Peru, the ore was crushed in edge-runner or Chilian mills and then amalgamated in tinas or wooden tubs with iron bottoms. The charge was stirred and ground by means of iron agitators with water and a large quantity of mercury, most of which remained as a pool at the bottom of the tub. The agitation was continued for a few hours, and the mercury was then drawn off and filtered through canvas for the separation of the amalgam. The ore and water was run off into settling pits for further treatment if necessary.

The *arrastra* was also used for direct amalgamation. It consists of a shallow circular pit, with its floor constructed of a layer of hard stones, over which other stones are dragged. The drag-stones are attached to horizontal arms projecting from a vertical revolving shaft in the centre. The ore is ground between the drag-stones and the pavement with mercury and a little water. Very small quantities of mercury were used, because liquid mercury would escape through the pavement. This machine was introduced into America in 1557, at the same time as the patio process.

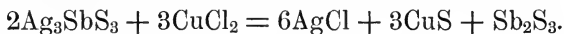
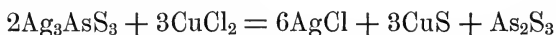
In the *patio process*, which has been used in Mexico for over 300 years, the ore is coarsely crushed in stamp-mills or Chilian mills, and subsequently ground fine in arrastras. Mercury is added to the pulp in the arrastra to collect the gold and the native silver. The fine pulp is then diluted to allow the amalgam to separate by settling, and the pulp is subsequently run off or baled out and conveyed to a paved courtyard called the patio. Here it is allowed to dry partly and is then spaded over and additions made of mercury, common salt, and either sulphate of copper or *magistral*, a mixture of  $\text{CuSO}_4$ ,  $\text{FeSO}_4$  and oxides, formed by roasting copper carbonate ores with pyrites. After each addition the heap of ore, or *torta*, is mixed with the chemicals, usually by being trodden over by mules. The torta becomes hot owing to the chemical actions, and water is sometimes sprinkled on if the mixture becomes too dry. After the lapse of some time and much mixing, the sulphides of silver are decomposed by the cupric chloride formed from the interaction of  $\text{CuSO}_4$  and  $\text{NaCl}$ .

The reaction may be expressed thus :—



The chemical action is due entirely to the difference of the solubilities, which explains the facts that pure sulphate of copper reacts only feebly with sulphide of silver, and that the reaction is accelerated by sodium chloride.<sup>1</sup>

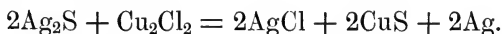
As to complex sulphides, they are decomposed as follows, under favourable conditions :—



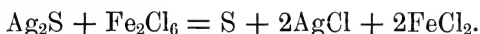
<sup>1</sup> Vondracek, *Revue Universelle des Mines et de Metallurgie*, Vol. XIII. (1908), 4th series, p. 105; *Revue de Metallurgie*, September, 1908, p. 678.

Generally, however, some sulphur is set free.<sup>1</sup>

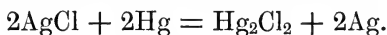
In a similar way cuprous chloride can decompose silver sulphide, thus:—



There is also chloride of iron present in the torta, and this gives the equation—

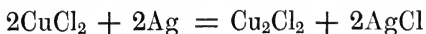
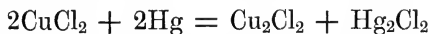


Finally the silver chloride is reduced by mercury with the production of silver amalgam and calomel, thus:—

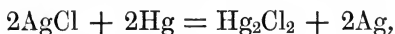


Although all the compounds of silver, when in solution, can be reduced by mercury as well as by zinc, copper and iron, this is not of much use in practice, because the sulphide and sulphantimonide of silver are almost insoluble, and are decomposed by mercury very slowly. It is necessary to hasten the operation by previous conversion of these compounds into the chloride.

Some action takes place in the following manner:—



but Vondracek does not consider these reactions to be important, partly because the loss of mercury which they would entail would be greater than that found in practice. The loss of mercury, according to the equation given above,



corresponds to 400 parts of mercury for each 216 parts of silver recovered. In practice the loss is only about 330

<sup>1</sup> *Loc. cit.*

parts of mercury to 216 parts of silver obtained,<sup>1</sup> owing doubtless to the presence of metallic silver in the ores and also to the fact that cuprous chloride reduces some sulphide of silver directly to the metallic state. The action of cuprous chloride, however, is never great.

The period of amalgamation in the torta usually lasts from two to four weeks, samples being examined daily to determine the progress of the reactions. The process is suitable only to countries with a warm dry climate. Even in Mexico cold weather sometimes delays the amalgamation, and falls of rain dilute the pulp, so that further additions of chemicals are required.

When the amalgamation is complete, some more mercury is incorporated with the torta to assist in collecting the amalgam. The mixture is then washed in tanks or tubs generally supplied with revolving stirring-arms. The amalgam and heavier parts of the ore settle to the bottom and the remainder is run off through plug-holes. The amalgam is washed free from sulphides in bateas, and the concentrates in later times were shipped to smelting works. The amalgam is strained through filter-bags to separate the excess mercury, and it is then pressed into cakes and retorted.

The patio process is now becoming obsolete partly as a result of the introduction of better means of communication into Mexico, but it has been of vital importance in that country in the past. Many ores yield about 75 per cent. of their silver when treated by the process, without the use of much fuel or of expensive machinery.

The *cazo* or *caldron process* is a simple method of

<sup>1</sup> *Loc. cit.*

treating surface ores containing silver, either native or in the form of chloride or bromide. It was formerly in use in Peru and Mexico, but has now been discarded in most localities. The ore, after being crushed in stamp-mills and ground fine in arrastras, was charged into amalgamating vessels with mercury and common salt. The small vessels originally employed were called *cazos* and consisted entirely of copper, but in later times vessels of larger size with wooden sides and copper bottoms came into use. The larger-sized vessel was called *fondon* in Mexico, and was 6 or 7 feet in diameter and  $2\frac{1}{2}$  to 3 feet deep. The vessel was heated over a fire, and the charge of ore and water raised to boiling. Common salt was then added with continuous stirring and when it was dissolved several successive additions of mercury were made. In the *fondon*, two copper blocks fastened to arms attached to a vertical revolving shaft were dragged round on the copper bottom by mule power. The boiling and stirring was continued for about six hours, and the charge was then run off and washed for the recovery of the mercury and amalgam. Efforts were made to prevent the adherence of the mercury to the copper.

In this method the silver chloride dissolved in common salt is reduced to metallic silver by the copper, but sulphide of silver is not decomposed and remains in the tailings.

It was the tendency of the amalgam to adhere to the copper plates in this process which probably furnished the idea of using amalgamated copper plates in gold-mills.

The *Francke-tina process* is another process of amalgamation, the use of which is confined to South and Central America. The ore after being crushed is roasted

with salt in reverberatory furnaces, with the object of converting sulphides of silver into chloride. The chloridised pulp is then treated in *tinas*, or pans with wooden sides and copper or bronze bottoms. A solution of 10 per cent. of sea salt is added to the pulp, and the charge is stirred with wooden or iron mullers provided with copper shoes and is heated by means of steam. Mercury is added at intervals, but soluble copper salts are not added, as they are contained in the roasted ore and are dissolved from the copper bottom or sole-plate and the copper side-plates which are fixed to the wood inside. The silver chloride and metallic silver are amalgamated. The chemical reactions which take place have the effect of causing metallic copper to be dissolved, and the sole-plate is worn out and requires renewal in a few months.

The *Krönke process*, which was introduced into Chile in 1860, depends on the use of a hot solution of cuprous chloride in common salt for the decomposition of the refractory silver compounds. The silver is finally reduced to the metallic state by means of an amalgam of zinc or lead.

The crushed ore is treated in rotating wooden barrels with about 40 per cent. of its weight of the solution, which makes a thick mud with the ore. The solution is prepared by adding common salt to a strong solution of copper sulphate until no more is dissolved. The cupric chloride so formed is afterwards converted into cuprous chloride by heating it with metallic copper. The cuprous chloride remains dissolved in the common salt. The solution is then slightly acidulated with sulphuric acid and used at once, being charged-in hot.

After the barrel has been rotated for about half an hour,

mercury is added, with a small quantity of lead or zinc amalgam dissolved in it. The amount of mercury is 10 per cent. or more of the weight of the ore. After rotating for four to six hours longer, the barrel is filled with cold water and rotated less rapidly for an hour or more to collect the mercury and amalgam. The barrel is then emptied, and the amalgam is purified by a hot solution of cupric chloride and finally by treatment with ammonium carbonate. The process is suitable for treating highly refractory ores.

The *pan amalgamation process* is doubtless an outcome of the *cazo* and *fondon* processes, although it also bears some resemblance to the obsolete *Freiberg barrel amalgamation process*, in which ores, after being roasted with salt, were treated in rotating barrels with mercury, iron and water. The ore is generally crushed in stamp batteries, either wet or dry, double-discharge mortars being used in either case. In the *Washoe process* the pulp is charged into amalgamating pans (see Fig. 32) with water and mercury. The pan is a flat-bottomed circular vessel about 5 feet in diameter and 2 feet 6 inches deep, with a capacity of about  $1\frac{1}{2}$  tons of ore at a charge. The bottom is of iron, with an iron flange reaching about to the top of the muller, and the rest of the sides are of wood. In the centre is a vertical revolving shaft carrying horizontal iron arms or mullers. These can be lowered so as to touch the bottom, or raised some distance. At first they are lowered, and the pulp is ground fine between them and the bottom, detachable shoes and dies being used to take up the wear. After the pulp has been completely slimed, the mullers are raised by about half an inch, mercury

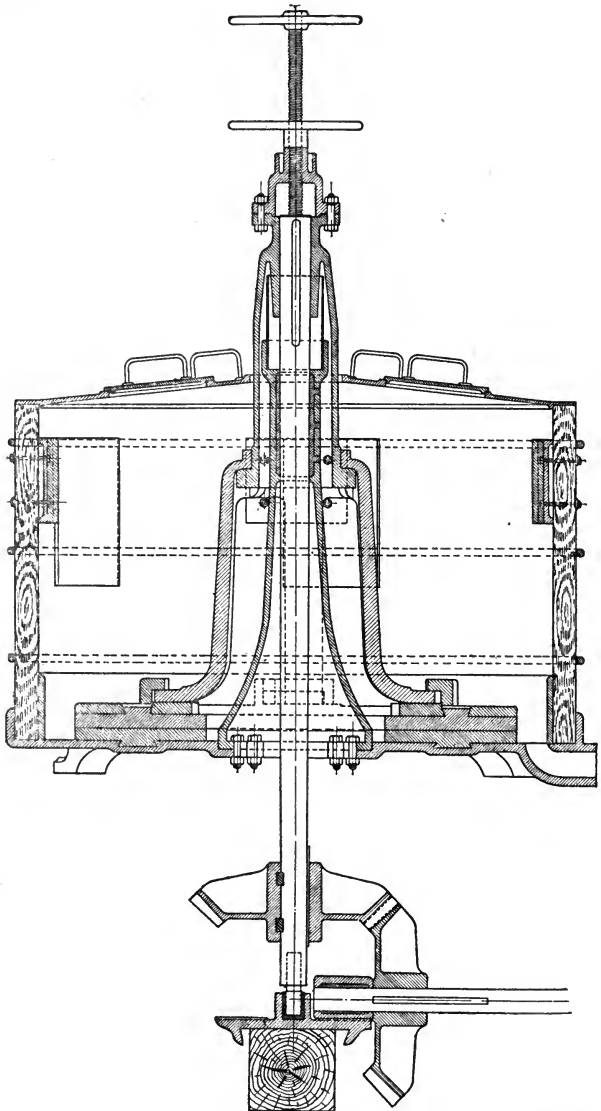


FIG. 32.—Amalgamating Pan: Fraser and Chalmers Pattern.



is added, and the charge is stirred by the mullers for some time longer. The thickness of the pulp is such that globules of mercury become dispersed through it without sinking to the bottom. The amalgamating pans are heated by steam jackets at the bottom, and amalgamation is also promoted by the addition of chemicals, such as sulphate of copper and common salt. These act in the same way as in the patio process, but far more rapidly owing to the higher temperature in the pan. The metallic iron of the pan is also serviceable in decomposing sulphide and chloride of silver. Caustic alkalies are sometimes used to remove grease which may have been introduced into the ore from the machinery.

When the amalgamation is complete—that is, after about four hours—the speed of the mullers is reduced from their ordinary rate of 60 or 80 revolutions per minute to about 30 or 40 revolutions per minute, and the pulp is diluted by filling the pan to the top with water. A few minutes later the amalgam, now for the most part collected at the bottom of the pan, is drawn off into a bowl, and the pulp is run off through plug-holes into the settling pan. This is a vessel similar to the amalgamating pan, but larger (8 feet or more in diameter), and provided with wooden shoes to the mullers. The bottom of the settling pan slopes down from the middle towards the periphery, where an annular groove is provided to collect the mercury. This is drawn off either at intervals or continuously through a mercury trap.

In the settling pan the pulp is further diluted and the pulp is stirred, the mullers revolving at the rate of 10 or 20 revolutions per minute. The lighter parts of the pulp are thus kept in suspension, whilst the mercury, amalgam,

particles of iron, and the heavier portions of the ore settle to the bottom. The settling process is usually arranged so that the settler can be discharged and prepared for the next charge as soon as it is ready for transference from the amalgamating pan. Plugs at different levels in the side of the settler are withdrawn successively and the muddy liquid run off, stirring being continuous. The amalgam and mercury from the settler are mixed with that from the pan, and the whole is treated together. Sometimes no mercury is separated in the amalgamating pan, but the whole charge is transferred to the settler.

In some mills the *continuous process* of pan amalgamation is in use, the pulp passing automatically through a series of pans, the first two or three of which are arranged for grinding.

The treatment of the amalgam, by whichever process it is obtained, begins with the addition of more mercury, and it is then stirred with water in a clean-up pan or rotating barrel for some hours. The impurities in the amalgam are thus removed and carried off suspended in the water, and the mercury is then strained through conical bags of canvas. These are suspended from an iron ring and kept in a lock-up safe. The excess mercury passes through the filter-bag, leaving the amalgam in a pasty condition, containing about six or seven parts of mercury to one of silver. By the use of pressure more mercury could be squeezed out. The amalgam is distilled in horizontal iron cylindrical retorts, which sometimes take a charge of as much as a ton. The amalgam is usually placed in sheet-iron trays which fit the retort. The temperature is raised gradually to a bright red heat, and the mercury is distilled off and

condensed in water. The silver residues, still containing about 1 per cent. of mercury, are melted in crucibles and cast into bars.

Oxidised ores are usually treated in pans without previous roasting, as described above, but sulphide ores are generally roasted with salt to convert the sulphides of silver into silver chloride before being amalgamated (*Reese river process*). In this case the ore is crushed dry and roasted in rotating tube furnaces, reverberatories, or shaft furnaces. The rotating furnaces are large iron tubes lined with firebrick. The ore is tumbled over and over by the movement of the furnace, so that hand-stirring is unnecessary. The heat is supplied by flames passing into the tube. In another type of furnace the hearth is stationary, and the ore is stirred and moved towards the discharge end by the passage of iron ploughs attached to an iron chain. The salt is usually added after most of the sulphur in the ore has been oxidised, as otherwise the loss of silver by volatilisation becomes considerable. After roasting, the ore is allowed to cool before being charged into the amalgamation pans.

The amalgamation of roasted ore is far more rapid and effective than the treatment of sulphide ore before roasting. Mercury acts slowly on sulphide of silver, forming silver amalgam and separating the sulphur. The action is quickened by the presence of iron, which is supplied by the wear of the stamps in a finely divided form and also by the inside of the pan. Amalgamation is also promoted by heat. Nevertheless the action on metallic silver and silver chloride, which exist in roasted ore, is far more rapid than that on unroasted sulphides. The disadvantages

in roasting before amalgamation are the extra expense of roasting, the difficulties of dry as compared with wet crushing, and the greater impurity of the amalgam, which contains more base metals if the ore is roasted.

## 2. LIXIVIATION PROCESSES.

In these processes the silver is obtained in solution, and after filtering is precipitated from the clear liquid in the metallic form or as a sulphide. In the *Ziervogel process*, which is only applicable to argentiferous copper mattes (see below under "Smelting"), the material is roasted in an oxidising atmosphere, and the silver is converted into silver sulphate, the copper being transformed into cupric oxide. The charge is then washed in tubs with hot water, in which the silver sulphate is dissolved, and metallic silver is precipitated by scrap copper.

The roasting must be carefully performed, the temperature being gradually raised and not allowed to become too high. Iron sulphate is formed at first by the oxidation of iron sulphide. Oxides of iron and copper are also formed simultaneously with the sulphate of iron. As the temperature rises, the sulphate of iron is decomposed, sulphurous anhydride and oxygen are evolved, and copper sulphate is produced. At a still higher temperature copper sulphate is decomposed and silver sulphate formed. This is stable at the temperature of decomposition of copper sulphate, but if the heat becomes too intense the silver sulphate is split up and the charge is spoilt. If the matte contains lead, bismuth, arsenic or antimony, some silver remains insoluble even after the roasting, and the process is unsuitable. The

finish of the roast is denoted by the presence of a very faint blue colour in the liquid on treatment of a sample with water, and the appearance of a thick, curdy precipitate of silver chloride on the addition of common salt.

The roasted matte is extracted with hot water, and afterwards with copper sulphate solutions resulting from the precipitation of the silver by copper, acidulated with sulphuric acid. The cement or precipitated silver is washed, pressed, dried and melted.

Another group of processes depends on the conversion of the silver into chloride, which is then dissolved by common salt (Augustin process), sodium thiosulphate (Patera process) or calcium thiosulphate (Kiss process). The silver is converted into chloride by roasting with common salt, as in the Reese river pan amalgamation process (see above).

The *Augustin process* has been superseded almost everywhere by other methods.

The solubility of silver chloride in brine solutions is comparatively slight (about 0.12 part AgCl in 100 parts of saturated solution of NaCl, see above, p. 148), and other compounds of silver, as well as metallic silver existing in the roasted ore, are not dissolved at all. Ores seldom yield more than 75 or 80 per cent. of their silver to treatment by this process. Lixiviation is commonly carried out in wooden tubs, and the liquids are run through a layer of granulated copper on which the silver is precipitated. Cuprous chloride is formed and dissolved in the salt solution, and the copper is recovered by precipitation with scrap-iron. The cement silver is washed first in hot water and then in hydrochloric acid before being dried and melted.

Sometimes this process is followed by treatment with thiosulphate solutions.

The *Patera process* is more efficacious than the Augustin process, as silver chloride is far more soluble in thiosulphate solutions than in brine. A soluble double thiosulphate of silver and sodium is formed from which the silver is precipitated as sulphide by sodium sulphide, sodium thiosulphate being regenerated. The roasted ores are treated in large wooden vats holding fifty tons or more, with false bottoms consisting of filter-beds. The precipitation of the silver is effected in a separate vat, and the sulphides are filter-pressed, dried carefully and charged into a bath of molten lead, which is then usually cupelled.

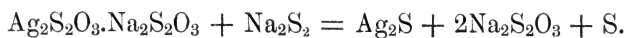
The roasting of the ore with salt must be carried out with greater care than when it is a preliminary to amalgamation, for the reason that metallic silver, which is readily amalgamable, is only slowly dissolved by sodium thiosulphate. Undecomposed sulphide of silver is unattacked by thiosulphate, but, unlike brine, thiosulphate solutions dissolve the silver from arsenate and antimonate of silver, and accordingly the process is applicable to ores containing some arsenic and antimony. Lead and copper are injurious, going in part into solution and being precipitated with the silver in the form of sulphides, so that the bullion is contaminated. The ill effects of these metals in the ore may be in part removed by lixiviation with cold water before the application of the thiosulphate solution. Sulphates and chlorides of copper, iron and zinc and chloride of lead are dissolved by the water and removed. If hot water is used a considerable amount of silver is dissolved in the wash water and has to be precipitated separately.

The lixiviation with thiosulphate takes place in the same vat as the washing with water, the solution containing from 0·25 to 2 per cent. of sodium thiosulphate. The solution of silver chloride proceeds in accordance with the following equation:—



The solubility of silver chloride is reduced by the presence of caustic alkalies and alkaline earths. Arsenate and antimonate of silver, silver oxide and metallic silver and gold are also dissolved, especially in hot solutions. Sodium thiosulphate is slowly decomposed on exposure to the air, absorbing oxygen and forming sulphate of sodium and sulphur, with the result that the solvent power of the solution is reduced. This effect is partly counteracted by the method introduced by Hofman of precipitating silver with calcium sulphide instead of sodium sulphide. This destroys sodium sulphate, producing sodium thiosulphate, calcium sulphate and silver sulphide. Some calcium thiosulphate is also produced.

The solution is run through the bed of ore until silver cannot be detected in the effluent liquid. Water-washes are then applied, and run with the solution into the precipitating vats. The sodium sulphide for precipitation is made by adding sulphur to a strong hot solution of caustic soda. The silver is thrown down in accordance with the equation—



Care is taken to avoid an excess of sodium sulphide. The excess sulphur is removed from the precipitate by treatment with caustic soda or by distillation or careful

roasting, but care is taken not to allow the temperature to rise sufficiently for the sulphides to become ignited. The dried sulphides, which contain from 25 to 40 per cent. of silver, are then usually charged into a bath of lead already molten on a cupellation hearth.

In the *Kiss process*, calcium thiosulphate is used instead of the sodium salt, the methods and plant being similar to those used in the *Patera process*.

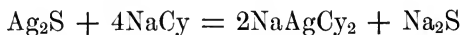
In both processes, however, undecomposed sulphide of silver as well as most of the metallic silver is left undissolved, and in the *Russell process* a solution of sodium-copper thiosulphate is applied after the simple thiosulphate has been run through. This so-called *extra* solution contains the salt  $4\text{Na}_2\text{S}_2\text{O}_3 \cdot 3\text{Cu}_2\text{S}_2\text{O}_3 + x\text{H}_2\text{O}$ . The extra solution quickly dissolves metallic silver and decomposes silver sulphide, copper sulphide being precipitated and silver passing into solution. The copper-sodium salt is not regenerated, as the copper is precipitated with the silver when sodium sulphide is added. The *Russell process* has not been uniformly successful, and has never passed into wide use.

The *cyanide process* has been applied to the treatment of silver ores in Mexico, and has proved very successful during the last few years. The result has been that the patio process and lixiviation by thiosulphate solutions have been displaced and are now mainly of historical interest.<sup>1</sup> The principles are the same as in the treatment of gold ores, and the methods employed do not differ essentially from

<sup>1</sup> "Some Features of Silver Ore Treatment in Mexico," by W. A. Caldecott, *Jour. Chem. Met. and Mng. Soc. of S. A.*, Vol. VIII. (1908), p. 204.



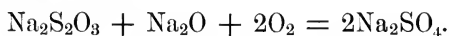
those already described on pp. 110—124. The ore is crushed in stamp-mills and on some mines converted into slimes by regrinding in tube-mills. The pulp is then separated into sands and slimes by water-classification, the sands being treated with cyanide by percolation and the slimes by agitation, either by means of mechanical stirrers or by air-blowing. The length of time of treatment is considerable, owing to the slow rate of solution of silver in cyanide solutions.<sup>1</sup> The solutions of cyanide in use are much stronger than those employed in gold extraction. Solutions containing 1 per cent. KCy are not unusual, and even in slime treatment, according to Caldecott, solutions containing 0·1 per cent. are frequently used. The values in the ores are chiefly in the form of sulphide of silver, although some metallic silver, silver chloride and gold are also present. The last-named bodies are readily dissolved, but silver sulphide is comparatively slowly acted on and requires strong solutions. Caldecott has shown<sup>2</sup> that its dissolution depends on secondary reactions by which soluble sulphides are removed from the cyanide solution. The primary reaction



is stopped by the sulphide of sodium, which would reprecipitate silver if present in excess, and soon establishes an equilibrium. Of the secondary reactions the following is the most important:—



This is followed by



<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Jour. Chem. Met. and Mng. Soc. of S. A.*, Vol. VIII. (1908), p. 266

Like the other secondary reactions, this involves the absorption of oxygen, so that aeration is as important in the treatment of silver ores as it is in that of gold ores. Soluble sulphides are also removed or rendered harmless by the addition of lead acetate.

Largely owing to the considerable strength of the solutions used, the consumption of cyanide is very great, amounting to from two to five pounds per ton of ore. The silver is precipitated on zinc shavings which are not coated with lead, and in cleaning-up the black silver slimes are briquetted and melted in crucibles with fluxes without any preliminary treatment with acid.

In the treatment of gold and silver ores alike, the practice is growing of using dilute cyanide solutions instead of merely water in the stamp battery, and thus to begin to dissolve the valuable metals from the outset. Even in the treatment of some gold ores the amalgamated plates are dispensed with, and reliance placed entirely on cyanide to extract the values. After the gold and silver have been dissolved, the liquid is now often removed through vacuum filter frames, which are lowered into the vats and immersed in the solution. This method is used in the Moore, Ridgway and other filters.

### 3. SMELTING PROCESSES.

These processes, which are largely carried on in North America, and to a less extent in Germany, have for their object the concentration of the silver in lead. The smelting is carried out in blast furnaces of moderate size into which a mixture of ore, fuel and fluxes are charged. The composition of the charge is determined beforehand, and the

quantities of ingredients required can then be calculated. The lead usually amounts to about 10 or 12 per cent. and the coke to from 7·5 to 15 per cent. of the charge. The slag is a fusible silicate of iron and lime with a number of other bodies present as impurities. It is usual to mix a number of ores together so as to obtain a charge of the required composition. Great heaps are formed consisting of thin layers of sulphide ores, ferruginous ores, lead ores, zinciferous ores, and even quartzose ores, and vertical slices are taken for charging into the furnaces together with coke and limestone. If gold ores require smelting, they are mixed with the heaps. Sometimes the ores or part of them are roasted to reduce the percentage of sulphur before they are smelted. Sometimes poor sulphide ores are smelted without lead and a matte (sulphides of iron, copper, etc.) formed in which the silver is contained. The matte is then separated from the slag and treated like a sulphide ore.

The reduced lead accumulates in the hearth at the bottom of the blast furnace, and is run off either continuously or at intervals of time. The pigs of lead are assayed and passed forward for desilverisation. The slags are also assayed, and if sufficiently poor in silver and lead are thrown away, but a portion of them is often returned to the blast furnace.

The blast furnaces employed are either circular or rectangular in section. The latter shape is preferred for the reason that much larger furnaces can be employed, the rectangular section being as much as 12 feet by 3 feet 6 inches at the tuyer level, while the round furnaces are not more than about 5 feet in diameter. Both types widen from the tuyer level to the mouth. If larger round

furnaces were used, the blast would not penetrate to the middle, which would not be sufficiently heated. Cold air is used for the blast to prevent the temperature of the furnace from rising too high, as in that case losses of lead by volatilisation take place. The pressure of the blast is usually from two to four pounds per square inch. The number of tuyers varies with the size of the furnace, round furnaces often having eight tuyers, and large rectangular furnaces six on each of the long sides. The height of the tuyer level above the hearth is 2 or 3 feet, and the total height of the furnace from 12 to 30 feet. The walls of the furnace in the neighbourhood of the zone of fusion consist of water-jackets, which are constructed of iron or steel. The hollow space in the water-jackets is about 6 inches wide, and water circulates through them.

The continuous discharge of the lead from the furnace is effected by a *syphon tap*, the molten part of the charge inside the furnace forming one leg of the syphon, the other being an inclined passage leading up from the bottom of the hearth to the outside of the furnace, where it terminates in a bowl which becomes full of molten lead. The lead can be ladled from this bowl, or tapped from it, or run off it continuously. Cuprififerous ores are not fitted for smelting with the use of the syphon tap, as alloys of lead and copper are formed which are liable to freeze in the comparatively cool passages and obstruct them.

The slag may be run off continuously through slag notches placed one in each of the short sides in rectangular furnaces, or tapped off at intervals. In either case it is usually run into slag-pots, which consist of cast iron and are carried on wheels and are cone-shaped with the apex downwards.

There is a tap-hole at a few inches from the bottom. The matte or speiss in the slag settles to the bottom, and after a time the slag can be tapped off, leaving the matte in the apex of the cone. This is saved for further treatment. Generally the slag contains from 0·2 to 0·5 per cent. of lead and only one or two ounces of silver per ton. The loss of lead by volatilisation may also be considerable, and is kept down by working at a moderate temperature with the upper part of the furnace charge at a black heat. The escaping gases are carried through condensing chambers, where some of the volatilised lead is caught.

The smelting of silver ores with lead is most satisfactory in places where fuel and limestone are cheap and large quantities of lead ores are available. It is best adapted to the treatment of ores at large centres where considerable quantities of ores of all sorts require treatment. It is not suitable for cupriferous ores and ores poor in silver and free from lead. Such ores are better adapted for treatment by wet processes or by amalgamation. The proportion of zinc in a charge must not be allowed to become excessive, as zinciferous slags are somewhat infusible.

The pig lead, which is sometimes called "base bullion," contains from about 0·1 per cent. of silver upwards. The proportion of silver in the lead is generally kept below 2 per cent. in order to avoid undue losses in the slag. The distribution of the silver in the lead is not uniform, and difficulties are encountered in obtaining trustworthy samples for assay. The silver is concentrated towards the bottom of the pig, and also to a limited extent towards the outside. Samples are taken by drilling and also by means of sawcuts, but neither method is quite satisfactory (see above, p. 137).

## TREATMENT OF ARGENTIFEROUS LEAD.

The pig lead, if impure, is refined first and desilverised afterwards either by Pattinsonisation or by Parke's process, or it may be cupelled. If it is sufficiently pure, lead is desilverised before being refined. The impurities commonly contained in the pig lead are arsenic, antimony, sulphur, copper, zinc, etc.

The *Pattinson process* depends on the fact that the eutectic alloy of silver and lead, that is, the alloy of lowest melting point, contains 2·5 per cent. of silver. If an alloy of this composition is melted and allowed to cool, it sets as a whole, the portions solidifying first having the same composition as the part remaining molten. If molten alloys containing less than 2·5 per cent. of silver are allowed to cool slowly, the crystals first formed in the liquid contain much less silver than the part remaining molten. In the original Pattinson process, these crystals are ladled by hand out of a large iron pot in which the silver-lead alloy is slowly cooling, and an enriched silver-lead alloy is left molten in the pot. Friedrich has shown<sup>1</sup> that the iron pot has no influence on the result, which can be equally well attained in an earthenware vessel, and that pressure up to five atmospheres has no effect on the crystallisation of the lead. The crystals are removed by perforated ladles, and either two-thirds or seven-eighths of the contents of the pot are ladled out into a neighbouring pot. The operation is repeated until the rich lead contains about 1 per cent. of silver and the

<sup>1</sup> *Metallurgie*, Vol. III., "Blei und Silber."

poor lead about 0·001 or 0·002 per cent. of silver. The limit of richness that could be reached would be lead containing 2·5 per cent. of silver. This process is now seldom used.

In an alternative method, the liquid alloy is drawn off, leaving the solidified portion behind. The charge is stirred by horizontal iron arms attached to a vertical rotating axle worked by bevel gearing (mechanical Pattinson process), or by means of jets of steam under a pressure of about three atmospheres (Rozan process). It is usual to tap off about one-third of the lead, leaving two-thirds in the form of crystals. The operation is repeated until the rich lead contains about 2 per cent. of silver, and the poor lead from 0·001 to 0·003 per cent. The Rozan process is the cheapest method of Pattinsonisation, but it is more expensive than desilverisation by means of zinc.

*Parke's process* depends on the formation of compounds of zinc and silver when these metals are melted together. When zinc is in excess, the compound formed probably corresponds to the formula  $\text{AgZn}_{12}$ , containing about 12 per cent. of silver. If molten zinc is stirred with a bath of argentiferous lead, which is afterwards allowed to cool, a crust forms on the surface containing zinc and lead together with the silver and any gold and copper that may be present. The lead retains about 0·6 per cent. of zinc dissolved in it at temperatures but little above its melting point. At  $650^{\circ}$  lead dissolves about 3 per cent. of zinc, but as the temperature falls zinc is separated, and as its alloys are lighter than lead they rise to the surface. Arsenic, antimony and tin remain

with the lead, and if large quantities of these elements are present, the lead must be refined before the zinc is added.

The zinc is thrown solid on the surface of the molten lead and the temperature is raised until it melts, or in the alternative molten zinc is poured into the lead bath. The mixture is then thoroughly stirred and allowed to cool slowly. The total amount of zinc added is usually from  $1\frac{1}{2}$  to 2 per cent. of the weight of the lead, but it is added in two or three lots, the crusts being kept separate. The first crust contains practically all the gold and copper, and if the first addition of zinc is small, hardly any silver is removed by it.

The crusts are removed from the surface as soon as they are formed by means of perforated ladles, and the ladling is continued until the lead begins to solidify. Fresh additions of zinc are made until the lead contains only about 0.0005 per cent. of silver (or one-sixth of an ounce per ton). This is much poorer than can be profitably attained by the Pattinson process.

The zinc crusts or scums contain a high percentage of lead, for the most part mechanically mixed with the other constituents. The lead is partly separated by liquation, the mixture being raised to a temperature above the melting point of lead, but below that of the zinc alloys. The lead is then allowed to flow away, leaving the enriched scum behind. The liquated lead must be again desilverised.

The rich scums are usually treated by retorting, the zinc being distilled and condensed so that it is available for further use. The residue consists chiefly of lead, and



contains from 5 to 10 per cent. of silver. It is passed to the cupellation furnace.

Parke's process is carried out in large cast-iron pots holding as much as 50 tons, as against 10 or 15 tons, the usual charge in the Pattinson process. Besides its cheapness, desilverisation by zinc has the advantage of quickness, so that the poor lead is soon available.

The *cupellation* of argentiferous lead is a very ancient operation, being referred to in the book of Jeremiah (B.C. 600). It consists in melting the lead in a reverberatory furnace, and oxidising it by means of a blast of air directed on to its surface. The litharge accumulates round the edge of the molten metal and is allowed to flow away. Finally silver only is left unoxidised.

The operation is carried out on hearths of bone-ash, marl or magnesia, covered by a movable hood (German cupellation furnace), or on smaller movable hearths, the roof being fixed (English cupellation furnace). The use of bone-ash in the hearth is not on account of its absorptive properties, as in assaying, but because it resists the corrosive action of molten litharge. It is now seldom used, as marl is cheaper. The litharge first formed contains such impurities as iron, zinc, arsenic, antimony, tin, cobalt and nickel, which oxidise readily. Towards the end of the cupellation the litharge contains copper, bismuth and silver. Cupelled silver may be as fine as 997 or 998, but must often be cupelled again with fresh lead to raise it to marketable fineness. The gold remains with it and must be removed by parting.

The *German cupellation furnace*, which is usually round, takes from 10 to 50 tons of argentiferous lead. In the larger

furnaces the work is not carried on until all the lead is removed, as there would be a difficulty in keeping the temperature high enough to prevent the silver from freezing if it were nearly pure. The fuel used is coal, wood, or peat, and the oxidation is effected by a blast of air from two or three tuyers directed on to the surface of the lead bath. The first products of oxidation consist largely of arsenate and antimonate of lead, which form a dark-coloured scum (*abstrich*). This is not readily melted, and is raked off. Then nearly pure litharge begins to form, and is drawn off through a channel cut in the hearth. As the operation continues, and the molten charge is diminished, the channel is deepened. At the end of the operation the litharge clears off from the surface of the charge, which becomes a bright mirror reflecting the roof of the furnace. The *blicksilber* thus obtained contains a few per cent. of impurities, chiefly lead. It is broken up and recupelled in a smaller furnace for the production of fine silver. After each charge has been worked the hearth is broken up and smelted for lead, and a new hearth is prepared.

The *English cupellation furnace* is used for richer silver-lead alloys than the German furnace. As a rule the first cupellation of lead, containing, say, 10 per cent. of silver, is partial only, the charge being enriched until it contains 60 or 70 per cent. of silver, when it is ladled out and fresh lead charged into the furnace. The blast is usually supplied through one tuyer, the oval *test* or hearth being only 3 or 4 feet long and 2 or 3 feet wide. The final cupellation is carried out at a higher temperature, and when oxidation is finished the silver is cast with the help of ladles. The tests are used continuously until worn too thin for further

use. A worn-out test can be withdrawn and another one substituted in the furnace with very little delay. The test is contained in a movable test-frame, in which the marl is rammed. A new test, however, requires very careful drying before it can be used.

The English cupellation furnace is used for the production of silver from rich lead, and the litharge produced generally contains too much silver for it to be sold without further treatment. In the German cupellation furnace, poorer lead is cupelled, and quantities of marketable litharge are usually produced. The German furnace is useful when it is required to treat rich gold or silver-bearing materials by charging them into a bath of molten lead.

#### 4. ELECTROLYTIC PROCESSES.

The only electrolytic process which has passed into wide use is that used for the separation of silver from argentiferous copper obtained by smelting. The copper is cast into slabs which form the anodes, the bath consisting of sulphuric acid and sulphate of copper. The copper is dissolved at the anodes together with iron and other metals electro-positive to it, the electro-negative metals—gold, platinum, silver, etc.—remaining undissolved if the current is of the proper density. The copper is deposited at the cathodes, and the electro-positive metals accumulate in the solution, which must be drawn off and renewed after a time.

If the current density is too great, silver will be dissolved at the anode with the copper and reprecipitated at the cathodes. Some free acid in the bath is necessary, as silver goes into solution more readily in neutral solutions.

The anode slime may contain over 50 per cent. of silver. It is purified in various ways, such as by cupellation with lead or by the Moebius electrolytic process, or by dissolving it in sulphuric acid and reprecipitating the silver with copper.

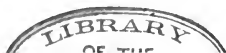
In the *Moebius process* the electrolyte is a mixture of nitric acid and silver and copper nitrates. About one per cent. of free nitric acid is kept in the bath. Silver and copper are dissolved at the anodes, leaving the gold undissolved. Silver is precipitated at the cathodes, leaving the copper in solution. If too much copper accumulates in the solution (more than 4 or 5 per cent.) it would precipitate on the cathodes simultaneously with the silver, and part of the liquid is in that case withdrawn and water is added to reduce the percentage of copper present. An addition of more nitric acid also assists in preventing the copper from being deposited. Very large amounts of silver are now refined by this process in the United States.

## CHAPTER XII

### REFINING GOLD AND SILVER

THE gold bullion produced by the methods of ore treatment described in Chapters VI. to VIII. is impure and unfit for use in the arts until after it has been refined. Retorted metal from the amalgamation process often contains 2 or 3 per cent. of copper and iron, besides some mercury and smaller amounts of other base metals. Silver is always present, in amounts varying from about one per cent. up to more than half the total weight. Sometimes bullion is sold to the Australian mints containing only a few per cent. of gold, the remainder being chiefly lead, zinc and silver. This is produced by means of the cyanide process. The presence of 20 or 30 per cent. of iron, lead and zinc in gold bullion gives it a worthless appearance, bearing some resemblance to cast iron, but with an earthy fracture. Most bullion, even if it has the outward appearance of gold, is brittle before it is refined.

The bullion is often subjected to rough refining operations at the mine before being sold. For example, at some American gold-mills the bullion is melted in a crucible and a blast of air directed on its surface. The base metals are oxidised and form dross which can be skimmed off. Sometimes oxidising agents such as nitre or manganese dioxide are melted with the bullion. Care is taken, however, to leave part of the copper, etc., unoxidised in order to avoid



losses of silver in the slag or dross. In South Africa and elsewhere the gold precipitate from the cyanide process is often refined by cupellation with an excess of lead (Tavener process, *q.v.*).

When the bullion is brought to London, Philadelphia, Melbourne, St. Petersburg and other great centres, it is in the first instance melted and assayed in order that its value may be ascertained. The assay pieces sometimes consist of a small portion dipped out of the molten gold, and sometimes of portions cut from the cast ingots.

After the value has been agreed upon, the bullion is at once refined, the base metals being removed, the gold and silver separated and fine bars of each obtained.

There are a number of different processes for parting gold from silver, some of them of great antiquity, but only three are now in use on a large scale. These are the sulphuric acid process introduced in Paris in 1802, the chlorine process, introduced at the Sydney Mint in 1870, and the electrolytic process, introduced at Hamburg in 1888. Until recently nitric acid was used as an adjunct to the sulphuric acid process in Philadelphia, and it formed by far the most important parting agent during the three centuries before the introduction of sulphuric acid. It is still used for parting gold from silver in assaying, as in that case the extra cost is of no importance. Sometimes gold is dissolved in aqua regia, and precipitated by ferrous chloride or some other suitable agent, the impurities being left in solution. This method does not separate tellurium from the gold, and is too costly to be widely used.

At the present day gold to the value of more than £50,000,000 is refined annually by the sulphuric acid

process in London and on the Continent, an amount of about £12,000,000 is treated by the chlorine process in Australia, and about £14,000,000 in the United States by electrolysis.

### THE SULPHURIC ACID PROCESS OF REFINING.

In this process an alloy of silver and gold is prepared by melting and granulating, the granulations are boiled in sulphuric acid by which the silver is dissolved, and the residue of gold is washed and melted. The silver is precipitated from solution by metallic copper, and the sulphate of copper is recovered by evaporation and crystallisation. The parting alloy is made up to contain one part of gold to about two and a half parts of silver. The addition of some copper is advantageous in promoting the dissolution of the silver, and the presence of lead is supposed to aid the solution of the copper, but large quantities of base metals in the alloy are disadvantageous. The copper must not exceed 10 per cent. nor the lead 1 per cent.

When gold bullion containing a large percentage of lead, zinc and other metals (*e.g.*, some bullion produced by the cyanide process) is to be refined, it is subjected to a preliminary operation called "toughening." The gold is melted, and saltpetre is thrown upon its surface and stirred in. Much oxygen is evolved and vigorous bubbling ensues. The base metals are oxidised and skimmed off the surface of the molten metal, and more saltpetre is added until the gold is sufficiently pure, according to the judgment of the operator, who is guided partly by the increasing pastiness of the metal. Some more nitre is then stirred in and the pot covered over and its temperature

raised for pouring. Toughening is a tedious operation, and involves considerable losses of precious metal by spiriting and volatilisation. The losses are mainly temporary, as most of the gold can be recovered by grinding and washing the ashes, and by the use of condensing chambers between the furnace flue and the stack.

The mixture of nitre and oxides of the heavy metals which forms on the top of the charge rapidly attacks the pot in which the bullion is contained, corroding it in a ring just above the surface of the metal. In order to prevent this, bone-ash is sometimes thrown into the crucible and pushed back from the centre of the charge towards the periphery so as to form a ring round the inside of the pot, and so to protect it from the action of the molten oxides. The bone-ash does not melt but absorbs the oxides, clearing the surface of the metal. The nitre is projected on to the eye of metal within the ring of bone-ash.

The gold after toughening still contains copper as well as silver, but most of the other base metals have been removed. The metal is rarely of such a composition that it can be parted by acid without any addition. If less than about two parts of silver to one of gold are present, the dissolution of the silver would not be complete. After the acid had acted for some time, it would have no further effect, the remainder of the silver being protected by the gold. The best proportion of gold in the bullion is from 18 to 25 per cent., according to Dr. Rossler,<sup>1</sup> but parting is still possible with 33 per cent. of gold, and hardly any difficulties are introduced by an excess of silver. The silver used for mixing with the gold consists of ingots containing some

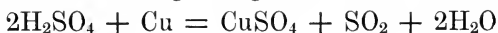
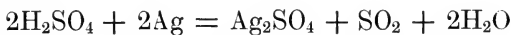
<sup>1</sup> Percy's "Metallurgy of Silver and Gold," p. 471.



gold if they can be obtained, but in London it often happens that such silver is scarce, and the parting silver is used over and over again. The copper is sometimes already contained in the silver, as when Mexican dollars are used for parting; and sometimes old amalgamated copper plates which contain some gold are available for making the necessary addition of copper to the parting alloy.

The alloy for parting is melted in graphite crucibles, well mixed and dipped out by means of ladles. The ladle is held about three feet above the surface of a copper vessel filled with cold water, and the molten metal is poured into it in a thin stream with a wavy or circular motion. Under these conditions the metal is broken up and solidified in the form of small beads, hollow spheres and leafy granulations. They are caught in a perforated copper pan, which is lifted out and drained after the pouring is completed.

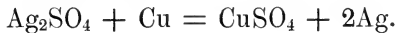
The granulations are heated in cast-iron kettles with concentrated sulphuric acid, of S.G. 1.85, which is raised to boiling point cautiously. Air is excluded from the kettles as far as possible, and the sulphurous acid gas which is given off in large quantities is carried away through leaden pipes. The amount of acid required is four or five times the weight of the granulations, but only about half this amount is added at first. The reactions involved are represented by the following equations:—



The sulphates are soluble in hot concentrated acid, but tend to be precipitated when the acid is cooled or diluted. When the evolution of  $\text{SO}_2$  is at an end, the liquid is

removed to a settling pot and fresh acid added. After three boilings the gold residue is strained and washed with boiling water in filter-boxes until free from acid. The "brown gold" is then dried and melted with nitre. Unless great care is exercised in washing and melting the gold, some lead remains with it, and the resulting bars are brittle.

The clear silver solution is poured into large lead-lined tanks containing hot water and sheet or scrap copper, and stirred until precipitation is complete. The chemical action is one of simple replacement—



The copper is not attacked by the dilute acid. The precipitated silver crystals are washed, dried, and strongly compressed by hydraulic power before being melted. The copper solution is evaporated down and allowed to cool three times, a crop of crystals of sulphate of copper (blue-stone) being obtained each time, and the acid mother-liquor when sufficiently purified is used to dilute the solution of silver sulphate before it is precipitated.

The net cost of refining by sulphuric acid is stated to be about one penny per ounce of gold in Europe. In the United States the cost in the San Francisco refinery was between four and five cents per ounce of gold in the year 1905-6, exclusive of salaries and rent, and at New York the cost was still greater.<sup>1</sup>

Modifications in the sulphuric acid process were introduced in the United States by F. Gutzkow in 1867. They

<sup>1</sup> "Report of the Director of the United States Mint," 1906, pp. 22, 24, 40, 66.

consist mainly in the removal of the silver sulphate from the acid by crystallisation, so that the acid can be used again, and in the reduction of silver from the crystals of  $\text{Ag}_2\text{SO}_4$  direct by a solution of ferrous sulphate. The removal of the silver from the acid without too great dilution enables the acid to be used over again, so that a greater quantity can be used in the first instance for parting, with the result that sufficiently pure gold can be obtained in a short time. The Gutzkow process, however, was not adopted in Europe, and with the abandonment of sulphuric acid for parting in America it has come to an end.

The gold produced by sulphuric acid parting is generally from 996 to 998 fine, and is usually fairly free from lead and other deleterious constituents. The silver is also about 996 or 998 fine if care is taken to remove all small particles of metallic copper from the precipitate.

#### REFINING BY MEANS OF CHLORINE GAS.

This method is applicable especially to the refining of gold bullion containing only small quantities of silver and base metals, in places where the supply of silver bullion for parting purposes is limited. It has been used continuously only in Australia, where it appears to be suited to the local conditions. Chlorine gas is forced through clay tubes to the bottom of clay crucibles containing molten gold, and rises through it. The chlorine is absorbed by base metals and silver, and chlorides are formed which rise to the surface and are skimmed off. The gold is not attacked perceptibly by chlorine at such high temperatures.

When very large quantities of base metals are present, it is more economical to remove them in part either by

treatment with nitre, as in the sulphuric acid process, or by passing oxygen or air through the clay tubes before chlorine is used. The oxides formed by the oxygen attack the pots and tubes, and it is necessary to add sand and a little borax to the charge and to use thick-walled clay tubes. When the oxygen begins to pass freely through the gold, the preliminary operation is concluded, the slag is skimmed off, more borax is added and the passage of chlorine is begun. As the chlorides do not attack the clay tubes, thin-walled tubes are used. The chlorine is generated from manganese dioxide, sulphuric acid and common salt. A depth of about 10 inches of gold is used in the pot, corresponding to a charge of about 700 oz. A rapid stream of chlorine is admitted at first and is entirely absorbed. After about an hour, when the bulk of the silver has been removed, the stream of gas is reduced, and the operation is stopped when the gas comes through the metal freely without being absorbed. The liquid chlorides are then ladled out and cast in iron moulds, and the gold is afterwards poured.

The chlorides contain from 5 to 10 per cent. of gold, and are remelted on the same day in graphite pots which hold 300 oz. of silver chloride. The gold is removed from the chlorides by means of carbonate of soda, which is thrown upon the molten charge. Effervescence ensues and the gold is reduced, together with about an equal weight of silver, and settles to the bottom of the pot. Two successive additions of carbonate of soda are made, amounting together to about 10 per cent. by weight of the chlorides. The metal is allowed to solidify, and the fluid chlorides are then poured off and cast into slabs which contain less than 0.1

per 1,000 of gold and are ready for reduction. The slabs of chloride, encased in flannel bags, are first boiled in water for some days to remove chlorides of copper and other base metals, and the silver is afterwards reduced by electrolytic action by means of iron plates, fairly pure metallic silver and chloride of iron being produced.

The gold produced by this process is about 996 fine, and is of excellent quality, all the metals which produce brittleness being removed in the early stages of the refining operations. The silver is usually about 990 fine, but if the cakes of chloride are not boiled in water, although the losses of silver are reduced, the resulting bullion is sometimes very impure, containing 20 per cent. or more of copper. The losses of gold are small, and the cost for materials, wear and tear, treatment of sweep, and wages is about one farthing per ounce of gold at the Melbourne Mint.<sup>1</sup>

Since the introduction of the process at Sydney, in 1870, it has been continuously at work in Australia, where it is favoured by the high price of sulphuric acid and the absence of auriferous silver suitable for mixing with the gold for parting purposes. It remains to be seen whether parting by chlorine will be displaced by the electrolytic process.

#### THE ELECTROLYTIC PARTING PROCESS.

Two electrolytic methods are in use which are both necessary, neither being sufficient without the help of the other. They are the Moebius and the Wohlwill processes, called after the names of their inventors. In the *Moebius process* (see above, p. 182), the electrolyte consists of dilute nitric acid.

<sup>1</sup> Rose's "Metallurgy of Gold," 5th edition, 1906, p. 422.

Silver, copper and some other metals are dissolved at the anodes, and pure silver is deposited at the cathodes. The gold remains in the anodes undissolved, but cannot be made sufficiently pure by this process to be fit for use in the arts. The anode mud is accordingly melted down and used as the anodes in the *Wohlwill process*, in which the electrolyte is hydrochloric acid. In this process, when the electric current is passed through the bath, gold, copper, etc., are dissolved at the anodes and pure gold is deposited at the cathodes, silver remaining undissolved in the anodes.

The Moebius process was successfully used for some years for the treatment of doré silver, which contains only a few parts of gold per 1,000 of silver, before it was applied in 1904 to the treatment of impure gold bullion at the Philadelphia Mint.

The Moebius and Wohlwill processes are now used together, to the exclusion of the sulphuric acid process, at the United States Mints at Philadelphia, Denver and San Francisco, and at the New York Assay Office.

In preparing the bullion for treatment at these establishments, gold and silver bullion are melted together to form a parting alloy containing 30 per cent. of gold and 70 per cent. of silver, copper, lead, etc. The base metals sometimes amount to 20 per cent. of the alloy. This alloy is cast into slabs to be used as anodes, which are suspended in earthenware tanks by means of gold hangers attached to copper rods. At the Denver Mint there are eight earthenware tanks, each 47 inches long, 26 inches wide and 22 inches deep, arranged in two sets of four tanks.<sup>1</sup> In each

<sup>1</sup> "Report of the Director of the United States Mint for 1906," p. 59.

set the liquid circulates by gravitation, being syphoned from the uppermost cell into the next, and finally pumped up from the lowest cell to a distributing tank above the highest cell. The cathodes are rolled sheets of pure silver one-hundredth of an inch thick, alternating with the anodes. By the addition of a small quantity of a colloid, such as gelatine, to the electrolyte, the silver is deposited in a coherent form on the cathodes, instead of in a granular non-adherent form, which would fall to the bottom of the cell, or form bridges between the electrodes.<sup>1</sup> This discovery obviates the necessity of the frequent scraping or renewal of the cathodes. The electrolyte contains 2 per cent. of free nitric acid and 3 per cent. of silver in solution as nitrate. The current density is 7.5 amperes per square foot of cathode surface at Philadelphia and as high as 20 amperes per square foot at Denver.<sup>2</sup> The resistance in the cells is from one to two volts per cell. The deposited silver is stripped off the cathodes, which are then straightened and used over again. The gold remains a hard spongy mass of the original form of the anodes, and obstinately retaining a small amount of silver, even if subjected to the current after the point at which oxygen is freely evolved from its surface. After being washed free from nitrate of silver, the anodes are dried, melted, and cast into anodes for the gold cells, if they contain over 950 parts of gold per 1,000. Sometimes the anodes are boiled in sulphuric acid before being melted. The copper, lead, zinc, etc., accumulate in the electrolyte, which is renewed at frequent intervals.

In the *Wohlwill process* the anodes consist of gold 940

<sup>1</sup> "Report of United States Mint for 1905," p. 62.

<sup>2</sup> "Report of United States Mint for 1906," p. 59.

to 950 parts, silver not more than 50 parts, and a few parts per 1,000 of base metals. The electrolyte consists of a solution containing from 2 to 10 per cent. of hydrochloric acid and from 2.5 to 6 per cent. of gold chloride, heated to a temperature of 60° or 70° C. The higher strengths are those used at the Denver Mint, where a high current density is used. If the hydrochloric acid is insufficient in amount, or if the baths are not hot enough, chlorine is given off at the anodes and the gold is not dissolved. The cathodes are sheets of pure gold, about one-hundredth of an inch thick. Under the action of the current all the metals in the anodes are converted into chlorides, the silver chloride remaining undissolved for the most part, and the other chlorides dissolving. Nearly pure gold is precipitated on the cathodes, so that the gold in solution is gradually replaced by copper, lead, zinc, tellurium, etc., and additions of gold chloride are made to the electrolyte at intervals. When the electrolyte has become charged with base metals it is renewed, and the gold in the old electrolyte is precipitated with ferrous sulphate. The anodes recommended by Dr. Wohlwill were 4 mm. thick, but are half an inch thick at Philadelphia. The current density employed is from 30 to 60 amperes per square foot, and the E.M.F. required is little more than half a volt per cell. The anodes are dissolved in from 24 to 36 hours. The anode mud contains gold, but consists chiefly of silver chloride. It is boiled in sulphuric acid, which converts the  $\text{AgCl}$  into  $\text{Ag}_2\text{SO}_4$ . The average fineness of the fine gold returned from the refinery of the Denver Mint during the year ended June 30, 1906, was 999.85. In this period 1,085,733 oz. of standard gold were refined at a total cost,



exclusive of salaries and rent of building, of \$44,712 or 4·1 cents per ounce.<sup>1</sup> It is probable that future costs will be lower, and it is stated that they need not exceed 1 cent per ounce.

The advantages claimed for the process are:—

(1) The small amount of acid consumed. This is stated to be only about 2 per cent. of that which would be required to dissolve the gold without the aid of the current of electricity.

(2) The absence of acid fumes. At the Philadelphia Mint the battery of cells is placed in an ordinary room without any special method of ventilation, but no inconvenience is experienced. In both the sulphuric acid and chlorine processes the fumes are disagreeable and unhealthy.

(3) Platinum, palladium, etc., are recovered instead of being left mixed with the gold. In the Wohlwill process these metals are dissolved with the gold, but are not precipitated at the cathodes, and accumulate in the solution. When the amount of platinum in solution reaches about 5 per cent., or the palladium in solution exceeds 0·5 per cent., these metals begin to be precipitated at the cathodes. The operation is then stopped, and the platinum is precipitated with ammonium chloride and recovered. In a period of twelve months, in 1899-1900, the Hamburg refinery recovered 1·5 kilograms of platinum from 2,000 kilograms of gold. The platinum was stated to be worth more than the cost of refining.

(4) Floor space is saved and few vats are required. The space required for the treatment of gold of the value of £2,500,000 per annum is put at 50 feet by 30 feet.

<sup>1</sup> "Report of United States Mint for 1906," p. 22.

(5) The gold and silver produced are of the highest possible quality. All the elements which make the gold-copper alloys brittle are entirely eliminated. Since the final installation of the process in the United States Mints, brittle coinage bars have become unknown, and it has been found possible to discontinue the annealing of coinage bars in the course of rolling.

On the other hand, there are difficulties and limitations of the process. Bars containing less than 850 per 1,000 of gold cannot be treated by the Wohlwill process, and in practice the successive use of the Moebius and Wohlwill processes is found to be most satisfactory. The double treatment makes the whole process of refining gold somewhat slow, and this is serious if a loss of interest is occasioned. Interest at 3 per cent. per annum amounts to one-twelfth of a penny per fine ounce of gold per day. The exact length of time required to refine gold by the electrolytic process has not been published, but it appears to take about a week, against two or three days by the sulphuric acid process.

## CHAPTER XIII

### THE ASSAY OF GOLD AND SILVER ORES

THE quantity of gold contained in ores is too minute to allow of its being accurately determined by wet methods, and the usual method of assay is to melt the sample with materials yielding metallic lead, which takes up all the gold and silver and sinks to the bottom of the molten charge. Suitable fluxes are added to make the ore readily fusible at a moderate temperature. After the charge has been allowed to solidify, the lead is detached from the slag and subjected to cupellation. In this operation the lead is melted in a cupel or little cup of a porous material (bone-ash or magnesia) and oxidised by a current of air. The litharge,  $PbO$ , so formed is absorbed by the cupel, but the gold and silver, the "noble" metals, resist the fire and are not oxidised, and, although melted, their high surface tension prevents them from being carried into the pores of the bone-ash. They remain as a bead of metal on the surface of the cupel, and after cooling can be detached and weighed. The silver is parted from the gold by boiling in nitric acid.

The process of ore assay is divisible into the following sections:—

- (1) Preparation of the ore for assay by sampling and crushing.
- (2) Concentration of the precious metals in a button of lead by fusion in a crucible, or by "scorification."

- (3) Cupellation.
- (4) Inquartation and parting.
- (5) Weighing the gold.

(1) *Sampling* the ore from a mine is partly carried out underground by taking pieces from different parts of the lode. In order to sample a heap of uncrushed ore it is all broken down to a moderate size, thoroughly mixed, and a portion set on one side either by machinery or by "coning and quartering," or by dividing the heap into two halves repeatedly by taking alternate shovelfuls. In coning and quartering the ore is heaped up into a cone, flattened down, and divided by two vertical planes at right angles to each other. This divides the heap into four right-angled sectors or quarters, and the opposite quarters are removed, mixed together, and the operation repeated as often as necessary. Sampling machines either take a definite portion, say one-sixteenth, of a falling or sliding stream of ore, continuously, or take the whole stream of ore momentarily at intervals, say during one second in each sixteen seconds. The latter is considered most satisfactory.

When the sample has been taken, it is crushed finer and again sampled, and finally a weighed quantity is crushed with pestle and mortar or otherwise to very fine powder. It is usually considered fine enough if all passes through an 80-mesh sieve, that is, one containing eighty holes to the linear inch; but some ores, such as those containing tellurides, must be crushed through a 100-mesh or even a 200-mesh sieve. If flakes of gold are caught on the sieve ("metallics"), they are collected and cupelled with lead and parted separately.

Finally the crushed sample is well mixed and a portion weighed out, usually one or two assay-tons. An assay-ton contains 29·166 grams, or as many milligrams as there are ounces Troy in a ton of 2,000 lbs. Then, if the resulting gold weighs, say, 1·5 milligrams, the result is at once reported as 1·5 oz. of gold per ton of ore without calculation. In the assay of very poor materials, such as tailings, as much as 12 A.T. (assay-tons) are taken, fused in several portions, and the gold and silver added together before parting.

(2) *Fusion or Scorification.*—The ore is usually mixed with an equal weight of litharge ( $\text{PbO}$ ), or red lead ( $\text{Pb}_3\text{O}_4$ ), and enough charcoal to reduce from 25 to 30 grams of lead to the metallic state, and to reduce all iron oxides to the ferrous condition. The fluxes to be added depend on the nature of the ore. Carbonate of soda is added to form a fusible silicate with quartz or sand, and it is also useful in taking up and removing sulphur when sulphides are contained in the ore. Borax is needed to form fusible borates with the oxides of the metals if these are present in excess and is advantageous in increasing the fluidity of almost any charge. Sand is added in the comparatively rare cases in which the ore is deficient in silica. Sand forms fusible silicates with alumina, lime, oxides of iron, etc., and protects the clay pot from corrosion, but even when silica is added, a little carbonate of soda is added also, as the double silicates of soda and other bases are more fusible than silicates free from soda. Iron in the form of nails or strips is used when sulphides are present. A cover of common salt is sometimes added. It protects the charge from the air and diminishes the chance of loss by spurting.

The quantities of the fluxes must be judged from the appearance of the ore and the experience of the assayer. A quartzose ore requires about  $1\frac{1}{4}$  A.T. of soda carbonate and 5 or 10 grams of borax to 1 A.T. of ore. The amount of charcoal will be about 1.25 grams. Oxidised ores require more charcoal, up to 3 grams or even more, and basic ores less carbonate of soda.

The charge is thoroughly mixed in a basin or on rubber cloth and charged into a cold clay crucible which must not be much more than half full. The crucible is put into the furnace when the temperature is low. If coke is used, all fuel touching the pot should be in the first instance at a black heat. The temperature is slowly raised, and after twenty minutes the charge should have just reached a very low red heat. At this time the lead is all reduced, and remains entangled in the charge in the form of minute liquid beads. Chemical action now begins between the carbonate of soda and the silica. Carbonic acid gas is given off and effervescence results. The temperature is gradually raised to a full red heat, and the lead beads coalesce and sink through the liquefying charge, which is continually stirred up by the disengaged gas. After a period of forty or fifty minutes from the time of charging in, the charge is in a state of quiet fusion, and the lead containing the gold is collected at the bottom. The nails are then withdrawn, all adhering lead shaken off them into the pot, and the charge poured into a warm iron mould, or allowed to solidify in the pot, which is broken when quite cold. The lead is found at the bottom of the pot or mould, and is detached from the slag by hammering. If the charge is melted too quickly part of the gold remains in the slag.

An older method, *scorification*, is still largely used, especially for silver ores. Finely-divided granulated lead is used instead of litharge and charcoal, and no fluxes are used except a little borax. The mixture of about 0.1 A.T. of ore and ten to twenty times its weight of lead<sup>1</sup> is placed in a clay dish (a scorifier) and melted in a hot muffle. The lead is oxidised by the air, and the silica in the ore is fluxed by the litharge. The precious metals are taken up by the lead, which diminishes in amount as oxidation proceeds until the slag forms a continuous layer over the lead. The charge is then poured into an iron mould, and the lead detached for cupellation.

(3) *Cupellation*.—The cupels (see below for description) are placed in a muffle furnace, which consists essentially of a clay oven or muffle, constructed so that it can be heated to bright redness, and can be either closed up or left open to the air. Care must be taken to prevent the products of combustion of the fuel from entering the muffle. Gas muffles are now used wherever possible.

Fig. 33 is from a photograph of one of the gas muffle furnaces in use at the Assay Department of the Royal Mint. The furnace is covered with a thick layer of magnesia lagging. The figure shows the tube at the back, fitted with a regulating damper, through which the air passes from the muffle. The supply of air to the muffle is through the mouth, which is shown open.

*Cupels* are little cups made of bone-ash or magnesia, and are usually round as in Fig. 34, but are sometimes square.

<sup>1</sup> See Rose's "Metallurgy of Gold," Chap. XIX., for full details as to quantities of lead required for different ores; also for composition of charges in pot fusion.

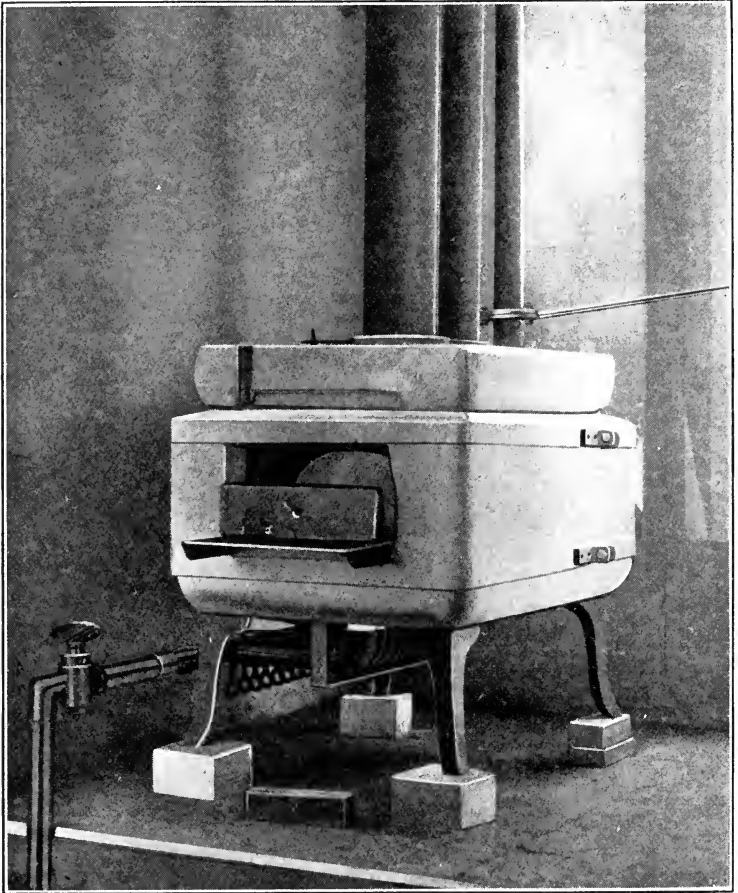


FIG. 33.—Assay Furnace.

The bone-ash is made by calcining bones and treating the crushed ashes with ammonium chloride. It is ground fine, slightly moistened with water, and compressed by the blows of a mallet in a cupel mould, which is also shown in Fig. 34.



The mould is made of gun-metal or steel. The cupels are dried very slowly to prevent cracking, and are heated for fifteen minutes or more in the furnace before the assay-pieces are charged in. Sometimes several cupels are made in one piece in a large mould, as at the Royal Mint.

When the cupels are at a good red heat (about  $700^{\circ}$ ), the lead buttons are placed in them by means of tongs and the door of the muffle closed while the lead melts. Air is then admitted, and the temperature gradually raised. The lead bath in the cupel becomes smaller and smaller as litharge is formed and absorbed until all the lead has disappeared, and the button of gold and silver remains dull and motionless on the cupel. It is then withdrawn and the button or *prill* is detached, cleaned, and weighed.

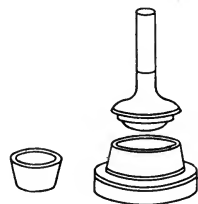


FIG. 34.—Cupel and Mould.

The losses of gold and silver in cupellation are mainly due to absorption by the cupel. They amount to about 1 per cent. of the gold and 10 per cent. of the silver in gold ores of moderate value containing small quantities of silver, if the lead button is free from impurities when charged in. The presence of copper, bismuth, thallium, and especially of tellurium and selenium in the lead increases the losses of precious metal.<sup>1</sup> Care must be taken in the pot fusion to prevent these metals from entering the lead, which can best be done by leaving a considerable proportion of the lead unreduced in the slag. If the lead is hard or brittle in spite of this, it should be scorified with fresh lead before being cupelled. It is also advisable to fuse the

<sup>1</sup> *Jour. Chem. Met. and Mining Soc. of S. Africa*, Jan., 1905.

cupel with litharge, charcoal, and fluxes, including some fluor-spar, and to cupel the resulting lead. Lead is more often contaminated by copper than by other metals.

(4) *Inquartation and parting*.—The bead of silver and gold is weighed, flattened, and dropped into nitric acid of specific gravity 1·16 heated nearly to boiling. The silver is dissolved, leaving the gold as a black scale of the same size and shape as the original flattened bead. If there is too high a proportion of gold, some silver is retained by it. The most suitable proportions of silver for different weights of gold are as follows :—

Weight of Gold.	Proportion of Silver to Gold.
Less than 0·1 milligram.	20 or 30 to 1
About 0·2     ,,	10 to 1
,,     1·0     ,,	6 to 1
,,     10·0    ,,	4 to 1
More than 200·0    ,,	2 $\frac{1}{4}$ to 1

If the silver is deficient, the prill is cupelled with more silver after having been weighed. This operation is called *inquartation*, the word coming from the old view that the gold should be a quarter of the whole. Prills containing less than one milligram of gold are parted in a few seconds, but are generally heated further for a minute or two. With large quantities of gold and silver, a second boiling in fresh acid may be necessary. The parting vessel is usually either a glass test tube or a glazed porcelain crucible.

(5) *Weighing*.—The parted gold is washed by decantation, dried, and annealed by being raised to a red heat. It then assumes the ordinary yellow colour of gold, shrinks,

and becomes harder. It is placed in the pan of a delicate assay balance by the point of a pen-knife or other instrument and weighed. The silver is determined by the difference between this weight and that of the gold and silver together. The balance should turn with  $\frac{1}{200}$  milligram or less. If 1 A.T. of ore has been taken for assay, the unit of weight will then be equivalent to  $\frac{1}{200}$  or 2.4 grains per ton. If 12 A.T. are taken, as in the case of the poorest tailings, the unit of weight will be 0.2 grain per ton. This is sufficiently accurate for almost all cases.

## CHAPTER XIV

### THE ASSAY OF GOLD AND SILVER BULLION

UNREFINED gold bullion contains some silver and variable quantities of base metals, and it is usually necessary to determine the proportion of both gold and silver. In the case of refined gold bullion, the gold alone is determined, silver, if any, being disregarded. Gold is always determined by the "parting assay," which consists in cupellation with from two to three parts of silver, followed by the removal of silver by boiling in nitric acid and the weighing of the gold residue. The silver in refined silver bullion is determined in one of four ways—by cupellation, by conversion into chloride, which is then weighed (India Mint method), by titration with common salt (Gay-Lussac method), or by titration with thiocyanate (Volhard method). Silver in gold bullion is usually determined by difference, the gold and silver being estimated together, and the gold determined separately in the same or another estimation. Small quantities of gold in silver bullion are determined by parting in nitric acid and subsequent collection and weighing of the finely-divided gold.

#### THE PARTING ASSAY OF GOLD IN BULLION.

A clean piece is cut off the ingot, or a small quantity is dipped out of the molten metal. The sample is then

flattened by hammering, and a portion of it, usually amounting to half a gram in weight, is weighed out on a delicate balance, the weight of the assay piece being adjusted by cutting with shears and filing. The piece is then wrapped in lead foil together with about a gram of silver and a few milligrams of copper, if none is contained in the gold bullion. Four or five grams of lead are enough for bullion containing no more than 10 per cent. of base metals, the object of the cupellation being less to remove the whole of the base metals than to provide a clean and perfectly mixed button or prill of gold and silver.

The alloy for parting should not contain less than two nor more than three parts of silver, copper, etc., to one part of gold. After a long series of experiments at the Royal Mint, it has been found that the most exact results are obtained by using a ratio of silver to gold of about  $2\frac{1}{6}$  to 1. If silver is contained in the gold bullion, it is allowed for in calculating the quantity of silver to be added. Thus, for example, bullion containing 315 parts of gold and 685 of silver per 1,000 would not require the addition of any more silver. An alloy containing 500 parts of gold and 500 of silver would require the addition of about 600 parts of pure silver. Base metals such as copper can replace part of the silver in the parting alloy, but in practice most of the copper is removed during cupellation. In the assay of bullion of unknown composition, the percentage of gold is judged by the operator, who is guided by the colour and hardness of the alloy and by his experience of bullion from the same source. In doubtful cases a preliminary assay may be made with twice the weight of silver. Approximately accurate results are obtained with

any amount of silver between two and three times the weight of the gold.

The assay piece of gold, silver, copper, and lead is charged into a muffle furnace in which cupels have previously been raised to a full red heat. The mixture at once melts on the cupel and begins to be oxidised, fumes of litharge rising slowly in the furnace. The molten metal is gradually reduced in size by the oxidation and removal of the lead, and towards the end of the operation bright spots of litharge are seen to be formed and to move to the edge of the lead and disappear. At last no more such spots are formed and the metal becomes dull and motionless. A few minutes later the cupel is withdrawn by tongs and the bead allowed to solidify, when the setting free of the latent heat causes it to brighten or "flash." If no copper had been added, the disengagement of oxygen at the moment of solidification would cause the button to spurt or "spit," and the assay would be spoilt by the loss of some metal. Spitting is more likely to occur the higher the percentage of silver in the button. When the cupel is cool the prill is removed, cleaned from bone-ash by brushing, and flattened by hammering. It is then annealed by heating to redness, rolled out into a strip about two inches long by a passage through a pair of jewellers' rolls, and again annealed. The strip is coiled up by the fingers and dropped into hot nitric acid of S.G. 1.16 to S.G. 1.26.

If large numbers of assays are made together, each coiled strip or cornet is placed in a little platinum cup, contained in a platinum tray which is plunged bodily into nitric acid for parting. At the Royal Mint the platinum trays contain 144 cups, and 80 oz. (about 2.25 litres) of nitric acid of

S.G. 1·20 are used. For a smaller number of assays a larger amount of acid for each assay piece is required, a single assay requiring about  $1\frac{1}{2}$  oz. Assay pieces containing more than about three parts of silver to one of gold generally break up in the acid and must therefore be boiled separately in small glass vessels—"parting flasks." When the temperature of the acid reaches about  $95^{\circ}$  the silver is attacked and brown nitrous fumes are disengaged. After about half an hour, the brown fumes having disappeared and the acid boiling freely, the assays are removed, washed in hot distilled water, and again boiled for half an hour in nitric acid free from silver. At the Royal Mint 80 oz. of acid of S.G. 1·20 are used for 144 assays in the second boiling. At the end of this time most of the silver has been dissolved, and the cornets consist of gold about 999 parts, silver about one part. They are then washed, dried, and heated to redness.

The cornets are weighed on a delicate balance and their exact weight recorded. It is to be observed that gold is lost during cupellation, chiefly by being carried into the cupel. The amount varies with the proportion of copper, being about 0·3 or 0·4 per 1,000 when the copper in the gold does not exceed 10 per cent., and more if large quantities of copper are present. On the other hand, about 1 per 1,000 of silver is retained by the gold, which could be reduced to about 0·5 per 1,000 by a third boiling. Consequently it is necessary to subject pieces of fine gold (called "proofs" or "checks") to the various operations side by side and under identical conditions with the assay pieces, and thus to determine the "surcharge" or net sum of the losses and gains incurred in the various operations. The

surcharge is usually positive, a proof weighing 1,000 at the beginning attaining a weight of about 1,000·5 at the end. The accuracy of the results depends on treating all the assay pieces alike, and this can be judged by the agreement between two or more proofs. At the Royal Mint a batch of 72 assays, including six proofs, is charged into the furnace simultaneously by means of a charging tray and withdrawn simultaneously. They are also annealed and boiled in acid together. A high degree of accuracy is attained and results can be obtained correct to within 0·05 per 1,000.

#### PARTING ASSAY OF GOLD AND SILVER IN BULLION.

A small quantity of gold, such as 10 per cent. or less, does not materially interfere with the accuracy of the assay of silver bullion described in the sequel. The gold is determined by parting, the alloy being boiled in nitric acid in a parting flask. The gold residue breaks up into a number of fine particles, and when the silver is completely dissolved the gold is allowed to settle, and is washed twice by decantation with hot water. It is then transferred to an unglazed porcelain cup in the following manner. The flask is filled to the brim with water, the cup is inverted over its mouth, and flask and cup are then turned over together. A little water flows out into the cup and then forms a seal, and the particles of gold fall into the cup. The flask is best withdrawn after immersing the whole in a vessel of water, when the gold particles are not disturbed. The gold is then dried and annealed in the cup and is ready for weighing. It is in the form of a coherent cake, which can be removed from the cup to the balance pan by means of a pair of forceps.



The presence of a small proportion of silver in gold bullion is a source of greater difficulty, although the determination of the gold is not interfered with. The silver is usually determined by difference, the gold and silver being weighed together after cupellation and the gold estimated in another portion. An alternative method is to melt the assay piece with two and a half times its weight of cadmium under a cover of potassium cyanide in a porcelain cup, dissolve the cyanide in water, and part the alloy in nitric acid. The cadmium and silver are dissolved and the silver is precipitated by hydrochloric acid and weighed as chloride. The gold residue is also weighed. Proofs of similar composition are required if extreme accuracy in the results is desired.

#### THE CUPELLATION ASSAY OF SILVER BULLION.

In this process the base metals are removed by cupellation and the silver prill is cleaned and weighed. The weight of silver bullion taken is generally about 10 grains. The amount of lead required varies with the composition of the silver bullion, the minimum quantity being about six times the weight of the silver. This is suitable for silver not less than 925 fine (925 parts per 1,000). More lead is required for silver of lower fineness. D'Arcet recommended ten times the weight for silver 800 fine and twelve times for silver 700 fine. The cupellation furnace is kept at a lower temperature than is required for gold bullion assaying, but must be raised to above the melting point of silver (962°) at the end, as otherwise the metal may set in the furnace before all the lead has been removed. When the cupellation is complete the door of the furnace is closed.

All chinks are stopped by means of bone-ash, and the furnace is allowed to cool down slowly and evenly. If the molten beads were removed before solidification, spitting would result, but as soon as they have solidified they are withdrawn from the furnace, cleaned, and weighed.

The absorption of silver by the cupel is large, amounting to about 10 per 1,000, and varies considerably, being increased by a higher temperature of the furnace and by the presence of a larger amount of copper or of lead. It is therefore necessary to use several proofs in different parts of the muffle, and to make them up of the same composition as the assay pieces.

This process is very ancient and was described by Agricola in 1556. It has been largely displaced by the wet processes introduced in the nineteenth century, but is still in wide use. It is accurate to about 0.5 per 1000 when nearly pure silver is being assayed.

#### THE GAY-LUSSAC PROCESS OF SILVER BULLION ASSAYING.

This is a volumetric process in which the volume is measured of a standard solution of common salt (NaCl) or of sodium bromide required for the precipitation of a known amount of silver nitrate. No indicator is used, and the end of the operation is judged from the appearance of an exceedingly faint cloud produced by sodium chloride in a solution from which almost all the silver has been precipitated. It is the most accurate method of silver bullion assaying at present known, capable, with proper precautions and the expenditure of sufficient time, of giving results accurate to about one part in 100,000. As ordinarily carried out it is accurate to one part in 10,000.

The usual method is to make up a solution of common salt of such a strength (5.416 grams NaCl per litre) that 100 c.c. of it will precipitate one gram of silver. This is

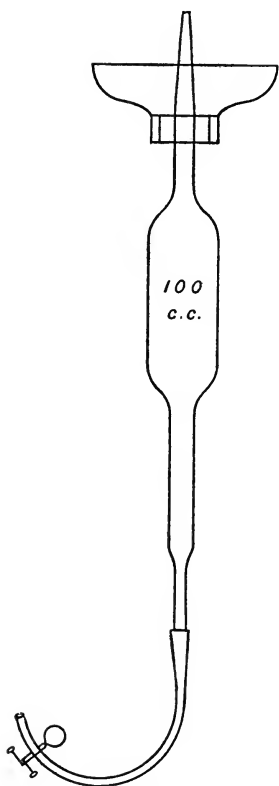


FIG. 35.—Stas Pipette.



FIG. 36.—Hand Pipette for Decinormal Solution, Gay-Lussac Process.

called the “normal solution.” An amount of silver bullion containing about 1.003 grams of silver is then weighed accurately, transferred to an 8 oz. glass bottle, and dissolved in nitric acid on a hot plate. The composition of the

bullion must be known approximately before the weight to be taken can be determined. If the composition is, say, 900 fine, then the weight to be taken is  $\frac{1.003}{900}$  grams, or

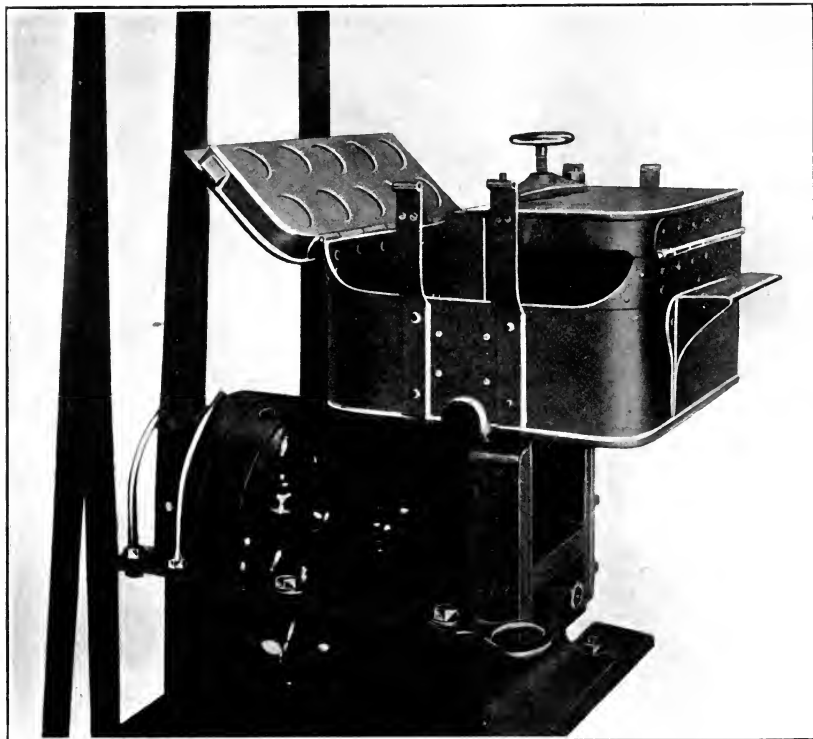


FIG. 37.—Shaking Machine used in Gay-Lussac Process of Silver Bullion Assay.

1.115 grams. The normal solution is then run into the bottle from a pipette containing 100 c.c. (see Fig. 35), and the contents are shaken until the silver chloride has curdled and will settle to the bottom, leaving the supernatant liquid

clear. One of the shaking machines in use in the assay laboratory of the Royal Mint is shown in Fig. 37. It holds twenty bottles. After the liquid has been shaken it is tested by the addition down the side of the bottle of 1 c.c. of a decinormal solution of salt, from a hand pipette shown in Fig. 36. This is equivalent to the addition of one-thousandth (a millième) of the 100 c.c. of solution originally added. If a cloud is formed near the surface of the liquid the amount of salt solution required in the judgment of the operator, based on the density of the cloud, to precipitate the rest of the silver is added, and the bottle is shaken again and tested once more. The end reaction is marked by the gradual formation in the course of about ten minutes of a faint cloud, the value of which in tenths of a millième is judged by the assayer. For example, the first addition of salt precipitated 1·000 gram of silver, the second addition of say 4 c.c. in all of decimal solution precipitated 0·004 gram silver; then suppose that the cloud produced by the third addition was declared to be equivalent to five ten-thousandths or 0·0005 gram silver. It follows that the total amount of silver present in the assay piece must have been 1·0045 gram, whence its composition can be calculated.

Mercury interferes with the method, as it is precipitated with the silver, but its presence is detected by its prevention of the darkening of silver chloride when exposed to light. The effects on the assay result caused by a small proportion of mercury are removed by the addition of acetate of soda.

It is, of course, necessary to use check-assays in order to test the strength of the solution. The method was invented by Gay-Lussac in 1832, and has displaced the cupellation process in almost all mints and in many private assay offices.

## THE VOLHARD METHOD OF SILVER BULLION ASSAYING.

This method was proposed by J. Volhard in 1878, and is particularly suitable for the assay of silver plate at the hall-marking offices. In this work the exact composition of the silver bullion is not required, but tests are made to ascertain that the proportion of silver in the bullion is not less than the standard prescribed by law. In England there are two standards containing 925 parts per 1,000 and 958·3 parts per 1,000 respectively.

At the Sheffield Assay Office,<sup>1</sup> where the method is in use, a quantity of bullion is taken, such that about one gram of silver is present. It is dissolved in 10 c.c. of dilute nitric acid (S.G. 1·2) in a bottle of about 250 c.c. capacity and heated in a water bath until all traces of nitrous acid are expelled. The solution is then diluted with 50 c.c. of water containing 2 c.c. of a saturated solution of iron alum decolorised by nitric acid, and 100 c.c. of "normal" ammonium thiocyanate is added from a pipette. This solution contains about 7·04 grams of  $\text{NH}_4\text{CNS}$  per litre, and 100 c.c. is sufficient to precipitate about one gram of silver. The bottle is then well shaken for about two minutes, when the white precipitate of silver thiocyanate settles to the bottom and leaves the liquid clear. If some silver is still in solution, the liquid retains the pale green colour due to the dissolved copper originally contained in the silver bullion. If, however, the ammonium thiocyanate is in excess, the liquid is coloured red from the action on it of the ferric salt. Proofs are used consisting of the same

<sup>1</sup> "Assay of Silver Bullion by Volhard's Method." E. A. Smith. *Trans. Inst. of Mining and Metallurgy*, Vol. XVI. (1907), p. 154.

weight of a standard silver trial plate as is taken of the bullion to be tested. The strength of the solution of thiocyanate is adjusted so that the liquid becomes of a pale red colour in the proof bottle. Then, if the other bottles contain green or still paler red liquids, the silver in the bullion tested is of higher standard than the trial plate, and the wares are passed. If the liquid in an ordinary assay is of a deeper red than that in the trial plate bottle, the bullion is below standard and the wares are condemned.

By making use of a "decinormal" solution of thiocyanate, and adding it little by little, the colour in all the bottles can be made the same, and the exact composition of the bullion ascertained correctly to about 0·2 per 1,000, or even more closely.

#### THE INDIA MINT METHOD OF SILVER BULLION ASSAY.

This method was introduced by Dr. Dodd, of the Calcutta Mint, in 1851. It consists in adding an excess of hydrochloric acid to a solution of nitrate of silver and weighing the silver chloride produced. The weight of silver bullion taken is 18·817 grains, which is equivalent to 25 grains of silver chloride if the bullion consists of pure silver. After precipitation, the bottle is well shaken, and the chloride is allowed to settle and is washed by decantation. The chloride of silver is transferred to a Wedgwood cup by placing the latter over the mouth of the bottle and inverting it. Afterwards the excess water is poured off, the chloride broken up by a glass rod, and dried. The drying is finished on a hot plate, and the cake of chloride

is weighed while still warm. A set of weights is used in which the "1,000" weighs 25 grains, and the smaller weights are in proportion, so that the composition of the alloy is indicated without calculation.

In this method the gold remains unchanged and is weighed with the chloride of silver.



## CHAPTER XV

### MINTING

MINTING is the manufacture of coins from gold, silver, and other metals under the authority of the State. In early times the exchange of commodities was carried on by means of barter, but the difficulties met with under this system caused attempts to be made to establish a medium of exchange by which the values of all commodities might be expressed in terms of one of them. In pastoral communities cattle and skins were used for this medium, and the origin of the Latin word *pecunia* (money) may be traced in this way from *pecus* (cattle). There are certain necessary properties which money must possess, such as high intrinsic value, indestructibility, divisibility, etc., and these appertain to metals in a far greater degree than to other commodities. Accordingly pieces of metal were used for money in Egypt at an early period, and subsequently, about 700 B.C., the manufacture of coins was begun in the island of Ægina and in Lydia. The art of minting spread among the Greeks and was carried by them to Italy and other countries around the Mediterranean, and also into Asia. Coining of silver began in Rome in 269 B.C. and was introduced by the Romans throughout a large part of Europe.

The earliest coins were made by casting in spherical or conical moulds. The cast metal was then placed on a little anvil and marked with a bronze die by means of heavy

blows of a hammer. The lower side or reverse of the coin was also marked by the sharp edges of the anvil (*ambos*), which was smaller than the coin. Subsequently the anvil was engraved with various devices and was ultimately replaced by a reverse die. The "blank" was made red hot and struck between cold dies which were held in position by tongs or by a roll of lead to protect the hand of the workman. One of the great improvements introduced by the Romans was the use of iron dies, which were sufficiently hard and durable to allow of the coins being struck while cold. Later, strip-shaped bars of metal were cast, and square pieces cut from them and hammered round. The discs prepared in this way were then struck between dies, and their edges sometimes trimmed with shears. The smaller coins, such as the silver pennies made in England in the Middle Ages, were made from sheet metal reduced in thickness by hammering and were cut approximately round by shears. Such "hammered money" continued to be manufactured in England until 1662 and was in circulation until 1696.

In 1662 the "mill and screw" were finally established in London, after having been tried for a short time in 1561. The "mill" was a rolling mill used to reduce the thickness of the cast bars, and the "screw" was a screw-press used for applying the power in striking the coins. A collar to surround the coin whilst it was being struck was introduced at the same time. The inside of the collar was sometimes smooth and sometimes marked with corrugations or inscriptions. The money was known as "milled money," and the chief noticeable difference between it and "hammered money" was that its size was invariable and

its edge marked. Hence arose the phrases "milled edge" and "milling," referring to the graining on the edge, although the rolling mill had nothing to do with the marks on the edge. As had been hoped, the practice of clipping money fell into disuse on the introduction of the milled edge. An even greater improvement than the new collar, introduced at the same time, was the cutting machine by which the blanks were punched out from the flattened bars.

All these machines had been originally introduced in Paris in 1553, and they were finally set up at the French Mint in 1640. The power used to drive the machinery was supplied by workmen at first, but their place was soon taken by horses, which were finally displaced by steam in Birmingham in 1788, in London in 1810, and in Philadelphia in 1835. Numerous minor improvements in minting were made in the nineteenth century, chiefly having for their object the saving of time in manufacture rather than the production of better-executed coins. Among the chief improvements were the introduction of the lever press for striking in 1839, and the invention of automatic balances for weighing single coins in 1843.

The manufacture of coin from gold and silver bullion involves a number of operations which may be ranged under the following heads:—

1. Valuation of the bullion received at the Mint.
2. Melting the metal and casting it into bars.
3. Rolling out the bars into strips or "fillets."
4. Cutting discs or blanks from the strips.
5. Adjusting the weight of each blank.
6. Edge-rolling the blanks.

7. Annealing and "blanching" the blanks.
8. Striking the coins.
9. Weighing each coin.
10. "Telling" and packing the coin.

#### VALUATION OF BULLION.

Gold may be sent in to the London Mint for coinage by any one who has some in his possession, the only restrictions being that the average fineness must not be less than 916·6 per 1,000, the standard fineness of sovereigns and half-sovereigns, and that the gold must be suitable for conversion into coin without further refining. There is no refinery in the Mint, and unrefined gold is not received. The gold is converted into coin at the rate of £3 17s. 10½*d.* per standard ounce troy without any charge or deduction whatever. The price of standard gold in the London market varies from £3 17s. 9*d.* to about £3 18s., but it is never profitable for ordinary owners of gold bullion to send it to the Mint, because the conversion into coin usually takes some weeks and the interest on the value of the gold amounts to over 2*d.* per oz. per month. The result is that the Bank of England alone sends gold into the Mint. The metal is usually in the form of refined ingots, each weighing about 400 oz. and containing over 99 per cent. of gold. The ingots are weighed in the presence of a representative of the Bank of England on scales turning easily to 0·005 oz. A piece is then cut from the ingot and is assayed as described in Chapter XIV. The number of standard ounces of gold in each ingot is calculated from the weight and the assay, and a notification

of the estimated value of each consignment sent to the Bank. Unless an objection is made, the ingot is then passed for melting. The number of ingots usually sent to the Mint at one time is 200, of the value of about £340,000, and four times this amount is sometimes received in a week.

At the three Australian mints, which are situated at Sydney, Melbourne, and Perth, unrefined gold is received for treatment. It is weighed and assayed (usually after being melted), and the value is then calculated. This is paid to the owner of the gold a short time later, less a deduction made to cover the cost of refining and coining. The charges vary somewhat at the different mints, and are higher for small consignments and for bullion containing considerable quantities of base metals. The actual amount of the charges at the Perth Mint in 1907 was equal to 2·65*d.* per oz. of the gross weight of metal sent in.<sup>1</sup> But inasmuch as only a part of the silver contained in the bullion is paid for, the real total of the deductions was equal to about 4·78*d.* per standard ounce of gold sent in.

In the United States unrefined gold is also received at the mints and Government assay offices. It is valued, and a charge for treatment made to cover the cost of refining, etc., including the waste of metal. The charges usually amount to about 6 or 8 cents per ounce of gold.

Silver bullion is no longer received for free coinage at any mint. The usual practice at mints at the present day, with currency on a gold basis, is to purchase silver bullion with Government funds and to coin it into pieces required

<sup>1</sup> "Thirty-eighth Annual Report of the Mint," p. 137.

for circulation at rates giving a large percentage of profit. The silver coins then circulate at values which are far greater than that of the metallic silver contained in them, and can only be kept from depreciation by strictly limiting the supply and by withdrawing from circulation any unnecessary coins at their full "face" value at the expense of the State. In England one ounce of standard silver is coined into 5s. 6d. in silver money, and similar rates are in force in many other countries.

Refined silver bullion is usually sold in the form of ingots which weigh from 1,000 to 1,200 oz., and often contain over 99.9 per cent. of silver.

#### MANUFACTURE OF COIN.

The bullion is melted in plumbago crucibles, together with the copper required to produce bars of the correct composition. In England standard gold consists of 916.6 parts of gold and 83.3 parts of alloy metal, and standard silver contains 925 parts of silver and 75 parts of alloy. Abroad the 900 standard is generally used, with some exceptions. The crucible was formerly heated in coke furnaces, but latterly the use of gas or oil fuel has been spreading rapidly.

One of the disadvantages of coke for fuel is that the fire has to be made up afresh for each charge. At the Royal Mint, London, where coke is still in use, when the charge is ready to be poured, some of the firebars are taken out and all the coke is raked down into the ashpit. The crucible is then lifted out, and as soon as possible the same or another crucible is put in its place and the furnace is again filled with coke.

This involves a great loss of heat, and restoking with cold fuel is also necessary in some cases before the melting of the charge can be completed, so that further loss of heat takes place. The result is that the work of the furnace is delayed. With oil or gas for fuel the heating is continuous and more charges can be melted in a day.

The greatest disadvantage in the use of solid fuel, however, lies in the production of ashes which become enriched with particles of the precious metals. The mint "sweep" consists of these, together with the crucibles and floor sweepings. They are ground up (sometimes with the addition of mercury) in edge-runner mills resembling mortar-mills, and washed for the recovery of the flattened pellets of gold and silver or of the amalgam. The residues, which still have some value, are sold to smelters, a course which involves some loss to the mints. The greater part of the "sweep" results from the ashes of the fuel, and when oil or gas is used, the inconvenience due to this portion is avoided. A blast of air is generally used with oil or gas, and a flame produced like that from a blowpipe. Care must be taken to prevent the flame from impinging directly on the crucibles or they will be rapidly burnt through. Checker-work of brick is sometimes used to receive the direct flame, which afterwards spreads out round the crucible.

At the London Mint gold is melted in crucibles about  $10\frac{1}{2}$  inches in height, containing 1,200 or 1,300 oz. of metal, and silver in larger crucibles containing over 5,000 oz. In some foreign mints larger crucibles are used, holding 500, 600, and even 1,000 kilograms (32,000 oz.). When such large pots are used, the molten metal is ladled out for

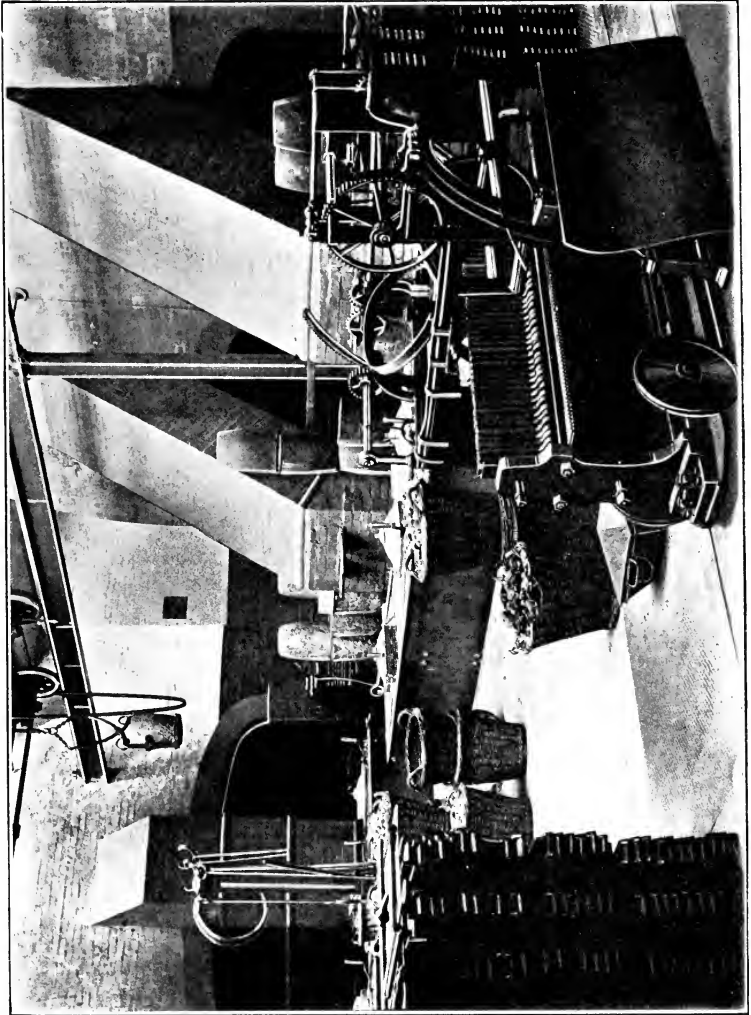


FIG. 38.—Silver Melting House, Royal Mint.

casting, but in the Royal Mint the crucibles are lifted out of the furnace by basket tongs, and their contents, after being



well stirred, are poured into moulds by tilting the crucible. The crucibles containing silver, bronze or nickel are lifted by a travelling electric crane and placed in a tilting cradle, shown at the front in Fig. 38.<sup>1</sup> A pot is shown in Fig. 38, held in the basket tongs and suspended from the crane. The iron moulds are shown on their wheeled truck close to the cradle in the same figure. The dimensions of the moulds vary somewhat, sovereign bars, for example, being 22 inches long,  $1\frac{5}{8}$  inches wide, and  $\frac{1}{2}$  inch thick. The cradle is tilted by a hand crank working through geared wheels.

After assay, the cast bars, having been cleaned, their ends cropped and the rough edges filed off, are reduced in thickness by rolling. Heavy pinches between the "breaking down" rolls, which are 15 inches in diameter, are applied at first, and subsequently lighter pinches are given in the smaller "thinning" and "finishing" rolls. The bars increase in length as their thickness is diminished, but their width is hardly affected.

In Fig. 39 the breaking-down rolls in the silver and gold rolling room at the Royal Mint are shown. The illustration is from a photograph taken by Mr. S. W. Smith. The rolls are driven by an electric motor placed under the floor and connected by chain gearing. The apparatus for adjusting the space between the rolls is shown at the top of the framework. A truckload of bars is in front. The distance between the faces of the rolls is reduced after each passage of the bars through them. A number of spare rolls is shown on the wall of the room, but the breakage of a roll is of rare occurrence.

After repeated passages through the rolls, the silver bars

<sup>1</sup> Figs. 38, 41, 43, 44, 45, and 46 are from photographs taken by Mr. J. E. Barnard.

become hard and are usually annealed by subjection to a low red heat in gas furnaces before the rolling can be completed. At the Vienna Mint the silver bars are



FIG. 39.—Rolling Room, Royal Mint.

annealed several times, in London only once, and in the United States, since the introduction of the electrolytic refining process, the improvement in the purity of the metal has enabled annealing to be dispensed with.

When the rolled-out bars or "fillets" are of the correct

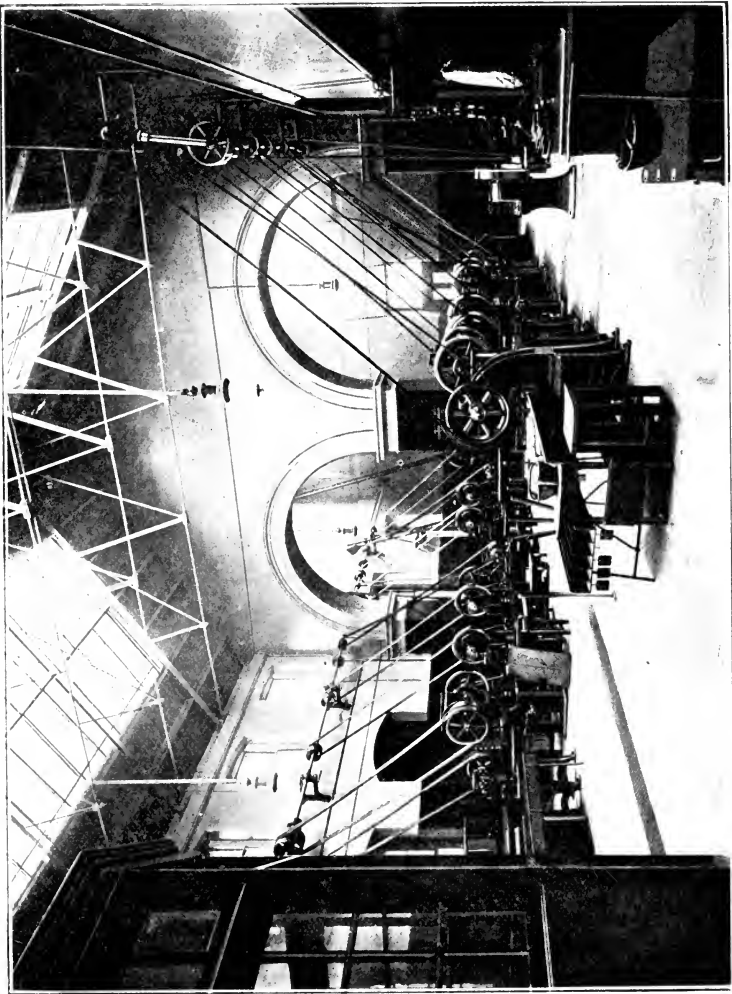


Fig. 40.—Cutting Room, Royal Mint.

thickness, as evidenced by the use of a gauge and the weight of a trial blank, they are passed through the cutting

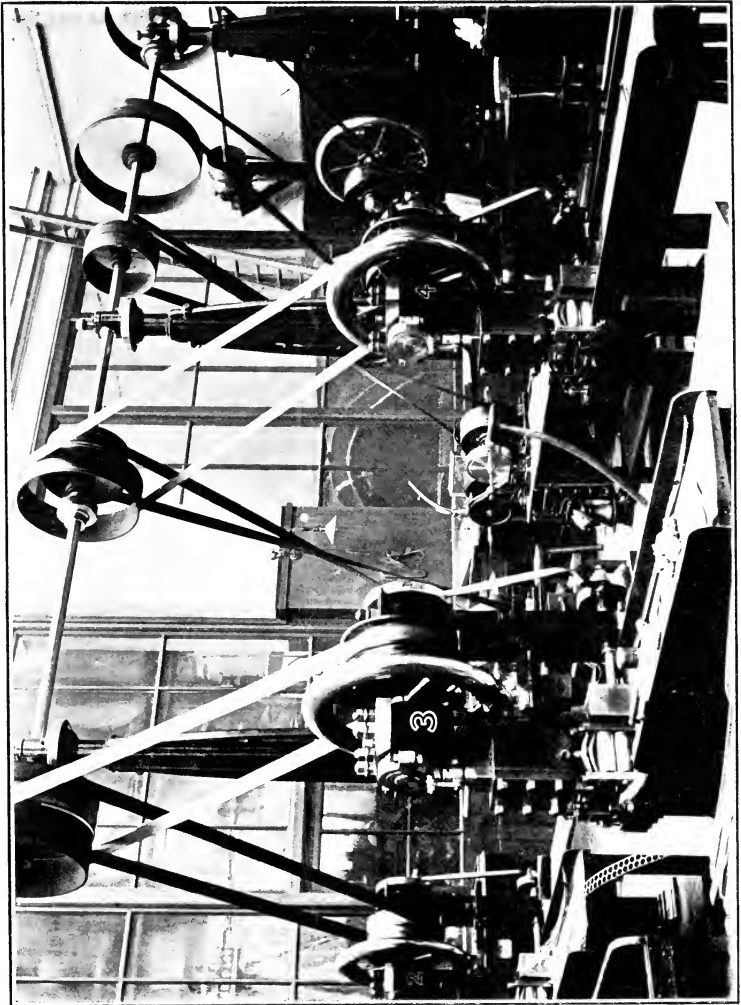


FIG. 41.—Cutting Machines, Royal Mint.

machines, by which one, two or more blanks are punched out at each revolution.

The cutting room at the Royal Mint is shown in Fig. 40, which is from a photograph taken and kindly lent by Mr. Edward Rigg, I.S.O., the Superintendent of the Operative Department.

Some of the cutting machines are shown at closer quarters in Fig. 41. The punches or cutters descend owing to the revolution of an eccentric, and the pieces of metal are cut from the strip between the edge of the cutter and that of a hole in a steel plate which the cutter fits accurately.

The "scissel" or residual metal (see Fig. 42) is returned to the melting house.

In Fig. 42 the arrangement used when two rows of blanks are cut from a fillet is shown. This is the usual number,

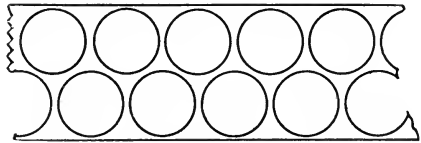


FIG. 42.—Scissel.

but only a single row of large coins, such as dollars or crowns, is cut from a fillet, whilst three rows of pennies and five of farthings are cut from each strip.

The blanks are passed through an "upsetting" machine (called the marking machine) for the purpose of rolling up and thickening their edges, and are afterwards again annealed. In the case of gold and bronze, furnaces are used from which air is carefully excluded by a water-seal so as to prevent the blanks from being discoloured by oxidation. Silver blanks, however, are heated with free access of air, and their surfaces become blackened owing to the formation of oxide of copper. The rotary gas furnaces in use for this purpose are shown in Fig. 43. A bag of

blanks is emptied into the mouth of the furnace, and the pieces are conveyed to the other end of the furnace by means of an internal Archimedean screw. They fall through an

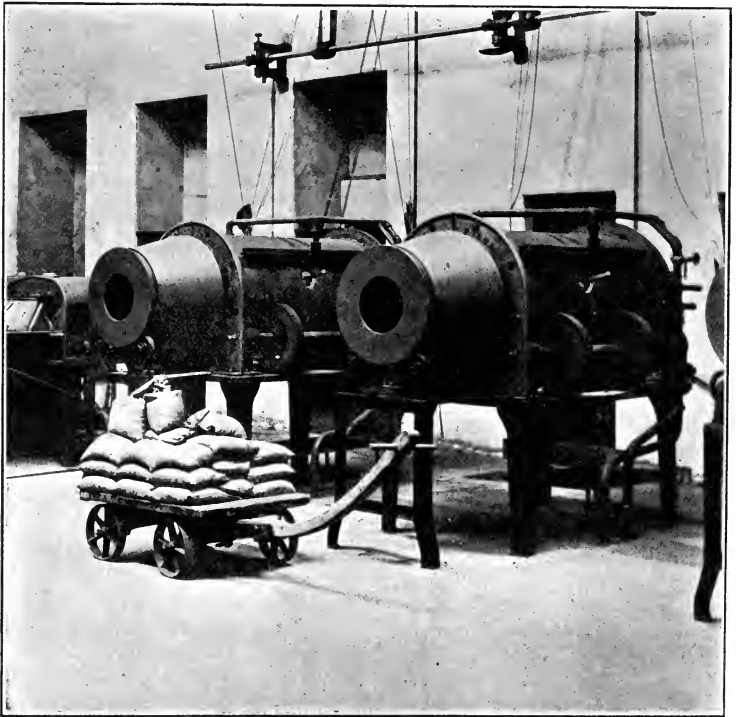


FIG. 43.—Annealing Furnaces for Silver Blanks, Royal Mint.

aperture into a copper tray placed to receive them, having been raised to a dull red heat during their passage through the hot zone.

The blackened silver blanks are pickled or “blanched” by dipping in hot dilute sulphuric acid. Any oxide of

copper formed on the surface during annealing is removed in this way and a film of pure frosted silver remains, coating the blank. In many mints the blanks are weighed before being struck, and those of incorrect weight are eliminated. Light blanks are returned for melting, and heavy ones are adjusted by filing by hand or in a machine. In the Royal Mint the process of adjusting blanks was abandoned in 1869, and individual pieces are not weighed until they have been struck.

The modern coining press was invented by Uhlhorn in Germany in 1839, and altered or independently devised by Thonnelier in Paris immediately afterwards. The blank is placed by the machine on the lower die, and is surrounded by a collar which is either plain or crenated, according to the denomination of the coin to be struck. The upper die is then brought down on the blank by the straightening of a toggle-joint, which is effected by the movement of a bent lever. A single blow is sufficient for the manufacture of each coin, the designs on both sides being made simultaneously, while the metal is forced laterally by the enormous pressure into the corrugations of the collar.

The press-room at the Royal Mint is shown in Fig. 44. There are 19 presses, and each of them can strike from 90 to 125 coins per minute. The force of the blow varies with the coin to be struck. The pressure required by a hydraulic press to strike an American dollar (1.529 in. diam.) was found at the Philadelphia Mint to be 160 tons, and in the case of a rupee (1.205 in. diam.) it was found at the Bombay Mint to be 135.7 tons. The pressures exerted in the screw coining press

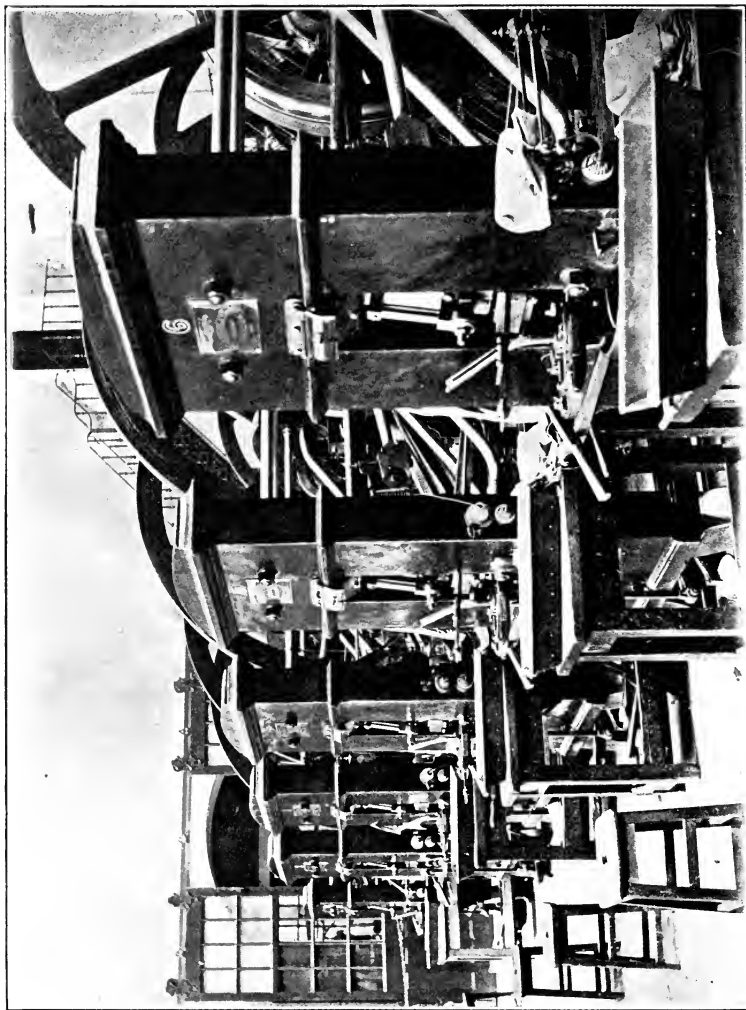


FIG. 44.—Press Room, Royal Mint.

were found by Capt. Bourke to be 178·84 tons for the dollar and 145·56 tons for the rupee. The dollar was raised in



temperature about  $20^{\circ}$  C., and the rupee about  $25^{\circ}$  by the blow.<sup>1</sup>

After being struck, each individual coin is weighed separately to determine whether it is within the legal limits of weight. It is not possible to make all coins of exactly the same weight, and the maximum difference from the standard weight allowed by law is called the "remedy." It amounts to 0.2 grain above or below the standard weight of 123.274 grains in the case of the English sovereign, or about 1.62 parts per 1,000. The remedies on silver coins and on foreign coins are proportionally greater. The coins are weighed on automatic balances which were invented in 1843 and have undergone some changes. The modified Cotton-Pilcher balance used at the Royal Mint consists of a steel beam with steel knife-edges supporting two "pans," one for the coin, the other for the counterpoise weight. The beam is allowed to move freely for about a second under the influence of the weight of the coin acting against the counterpoise, and it is then seized by forceps and held firmly in its new position. By an ingenious arrangement of levers, the position of a shoot down which the weighed coin falls is determined by the final position of the beam. According to the weight of the coin the shoot stops above one of three slots, and heavy, light, and good coins are discharged through different orifices and make their way into different compartments of a box.

These automatic balances are shown in Fig. 45. Each balance weighs about 22 coins per minute, and is sensitive to 0.01 grain. The proportion of rejected coin was formerly

<sup>1</sup> See pamphlet by Capt. J. J. Bourke and W. G. Nichols. Privately printed.

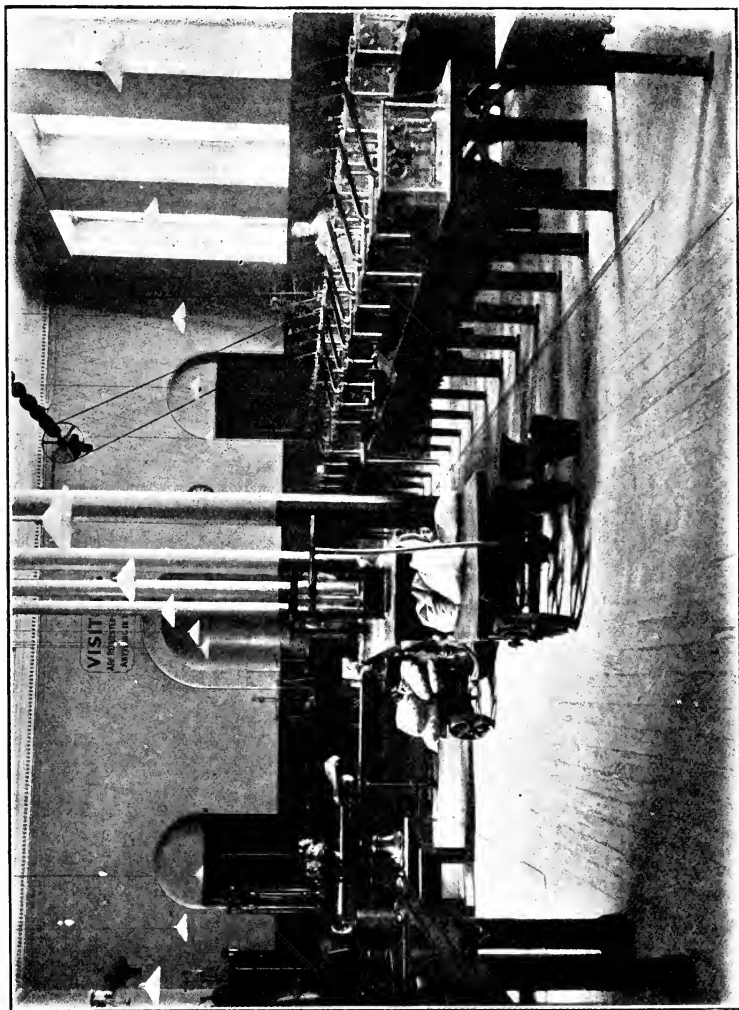


FIG. 45.—Weighing Room, Royal Mint.

large, but has been greatly reduced of late years. It sometimes exceeds 10 per cent. in the case of gold coin,

and is usually below 1 per cent. in that of silver coin. This difference is due to the comparatively small remedies allowed for gold.

The finished coin is examined for superficial defects, dumb pieces are eliminated by testing the "ring," and the

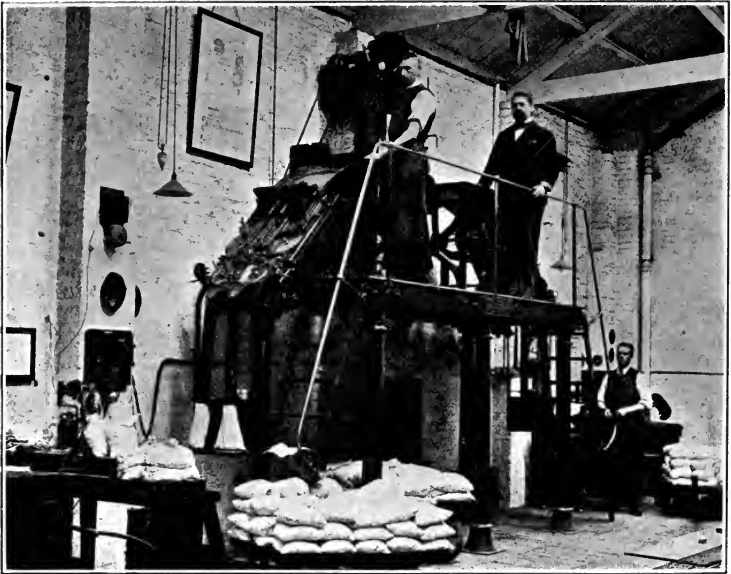


FIG. 46.—Telling Machine, Royal Mint.

good pieces are counted and packed in bags by "telling" or counting machines, one of which deals with 3,000 pieces per minute. This is shown in Fig. 46. The machines contain a serrated wheel on an inclined table, with semicircular notches on its periphery. The coins are made to pass down a narrow shoot in single file and are gripped by a pair of india-rubber driving wheels which force the coins forward

and so cause the wheel to rotate, but only one coin is passed forward by each notch, so that with each revolution of the wheel a definite number of coins pass down the shoot and fall into a bag. When the correct number of coins have passed the wheel and entered the bag, the machine stops automatically. For example, 1,200 pence are counted into one bag. The bag is then removed, a new one substituted for it, and the machine is restarted. There are four such serrated wheels on the machine shown in the illustration.

#### COMPOSITION OF GOLD AND SILVER COINS.

The earliest gold alloy used for purposes of currency was *electrum*, a naturally occurring silver-gold alloy containing 60 to 80 per cent. of gold. In the Hellenic world, however, the coins of gold and silver were remarkably pure, the gold coins sometimes containing only 3 per 1,000 of silver.<sup>1</sup> Some of the Greek silver coins contained 30 per 1,000 of copper, but others were from 983 to 986 fine. The Romans in Republican times used pure gold and silver. Under the Empire, copper was intentionally added, and in some reigns the coinage became very debased, containing only a few parts of precious metal per 1,000. In England after the Conquest the gold standard was 994·8 for a long time, but the last coins of this composition were struck in 1637. The present standard of 916·6 was first instituted in 1525, the ostensible object of the lowering of the standard being to prevent the exportation of the coin to Flanders. The view that the copper preserves the coin from rapid wear is of far more recent date. The silver standard of silver 925 parts, copper

<sup>1</sup> Lenormant, "La Monnaie dans l'Antiquité," Vol. I., p. 187.

75 parts, has been in use since Anglo-Saxon times, except for a brief period of debasement in the reigns of Henry VIII. and Edward VI., when the gold coinage was also debased. The 900 standard for both gold and silver was introduced in France in 1794 and has been adopted in many other countries. For subsidiary silver coins, however, lower standards (especially 835 fine) have been introduced, in the Latin Union and elsewhere, the alloy in use containing most copper being that adopted by Scandinavia and Denmark for small coins (10 öre pieces), which contain 400 parts of silver and 600 parts of copper.

The following table gives the legal standards now in force for gold and silver coin in the principal countries of the world. The standards given are in parts of precious metal per 1,000, the remainder being copper.

	Gold Coin.	Silver Coin.
Abyssinia . . . . .	—	835
Argentina . . . . .	900	900
Austria-Hungary . . . . .	900	900 and 835
Belgium . . . . .	900	900 and 835
Bolivia . . . . .	—	900
Brazil . . . . .	916·6	916·6
Bulgaria . . . . .	900	900 and 835
Canada . . . . .	—	925
Ceylon . . . . .	—	800
Chile . . . . .	916·6	500
China . . . . .	—	900, 866, and 820
Colombia . . . . .	900	900 and 835
Congo . . . . .	900	900 and 835
Corea . . . . .	900	800
Costa Rica . . . . .	900	900
Crete . . . . .	900	900 and 835
Curaçao . . . . .	—	640
Cyprus . . . . .	—	925
Denmark . . . . .	900	800, 600, and 400

	Gold Coin.	Silver Coin.
Dominica . . . . .	—	900 and 835
Dutch East Indies . . . . .	—	720
Ecuador . . . . .	900	900
Egypt . . . . .	875	833·3
Finland . . . . .	900	868 and 750
France . . . . .	900	900 and 835
Germany . . . . .	900	900
Greece . . . . .	900	900 and 835
Guatemala . . . . .	900	900 and 835
Hayti . . . . .	900	900 and 835
Holland . . . . .	900	945 and 640
Honduras (British) . . . . .	—	925
Honduras . . . . .	—	900
Hong Kong . . . . .	—	800
India . . . . .	916·6	916·6
Italy . . . . .	900	900 and 835
Japan . . . . .	900	800
Mauritius . . . . .	—	800
Mexico . . . . .	—	902·7 and 800
Morocco . . . . .	—	900 and 835
Newfoundland . . . . .	916·6	925
Nicaragua . . . . .	—	800
Norway . . . . .	900	800, 600, and 400
Panama . . . . .	900	900
Paraguay . . . . .	—	900
Persia . . . . .	900	900
Peru . . . . .	916·6	900
Portugal . . . . .	916·6	916·6
Roumania . . . . .	900	900 and 835
Russia . . . . .	900	900 and 500
Salvador . . . . .	900	900 and 835
Servia . . . . .	900	900 and 835
Siam . . . . .	—	900
Spain . . . . .	900	900 and 835
Sweden . . . . .	900	800, 600, and 400
Straits Settlements . . . . .	—	900 and 800
Switzerland . . . . .	900	900 and 835
Turkey . . . . .	916·6	830
United States . . . . .	900	900
Uruguay . . . . .	—	900
Venezuela . . . . .	900	900 and 835

Many of the countries enumerated in the table have no actual gold coins, but have merely made provision for them.

In addition to the standards given above, others are in use for coins used for trade purposes. Thus, for example, the Austrian gold ducat, the coin of highest standard in the world now in use, contains  $986\frac{1}{9}$  parts of gold and only  $13\frac{8}{9}$  of copper. It is not current in Austria. The Maria Theresa thaler, containing  $833\frac{3}{4}$  parts of silver per 1,000, is also struck at Vienna, principally for use in Africa and the Levant.

## CHAPTER XVI

### THE MANUFACTURE OF GOLD AND SILVER WARES

#### COMPOSITION OF GOLD WARES.

IN England the carat system is still employed for denoting the standard of fineness of gold wares. Under this system, which was formerly in use for the assay of gold at the Mint, the troy pound of 5,760 grains is divided into 24 parts, called carats. A carat is divided into 4 carat grains, each of which contains 60 ordinary grains. Gold bullion, consisting of 22 parts of pure gold mixed with 2 parts of other metal or "alloy," is called 22-carat gold. The standards recognised by law in England are those containing 22, 18, 15, 12 and 9 parts of gold in 24 parts. The usual composition of wares made of these standards is as follows, in parts per 1,000:—

Standard.	Gold.	Silver.	Base Metal, chiefly Copper.
22 carat . . .	916·6	20	63·3
18 „ . . .	750	125	125
15 „ . . .	625	100	275
12 „ . . .	500	100	400
9 „ . . .	375	100	525

Wares of these standards, after manufacture or partial manufacture, are taken to one of the assay offices appointed for the purpose, and a portion of the ware is removed by



cutting or scraping and assayed for gold. If the fineness is below standard the wares are broken, but if of full standard they are hall-marked. Offices for hall-marking are at London (Goldsmiths' Hall), Birmingham, Chester, Sheffield, Dublin (where 20-carat gold is marked), Edinburgh, and Glasgow. Offices formerly existing at Exeter, Newcastle, Norwich, and other places have now been closed. The marks on the wares include a number giving the standard (22 for 22-carat, etc.), a distinctive mark showing the town where the marking was done, and a date mark, usually a single letter of special design.

Hall-marking offices are provided by most of the governments of the civilised world, the most noteworthy exception being that of the United States.

The following table gives the legal standards of gold plate in use in some of the principal countries in the world:—<sup>1</sup>

Austria-Hungary . . . . .	920, 840, 750, and 580.
Belgium . . . . .	800 and 750.
Denmark . . . . .	585 and upwards.
France . . . . .	920, 840, 750, and 583.
Germany . . . . .	583 and upwards.
Italy . . . . .	900, 750, and 500.
Netherlands . . . . .	916, 833, 750, and 583.
Portugal . . . . .	.916·6 and 750.
Russia . . . . .	990, 920, 820, 720, and 560.
Spain . . . . .	.916·6 and 750.
Sweden and Norway . . . . .	975·7, 847·2, and 763·9.
Switzerland . . . . .	750 and 583.

<sup>1</sup> "Return to House of Commons as to Foreign Countries (Gold and Silver Marking)," February 25, 1890.

In England the 22-carat standard is used almost exclusively for wedding rings, and was formerly used for mourning rings. A few watch cases are made of this standard. The best jewellery and almost all watch cases are made of 18-carat gold, which is manufactured into all kinds of personal ornaments, as the beauty of its colour is not much altered by wear. Fifteen-carat gold is also used extensively for "coloured" jewellery, and has greater strength and durability than most other standards. Gee states<sup>1</sup> that 13-carat gold is largely used in Birmingham for jewellery, as it is the lowest standard that can be readily coloured to look rich and beautiful. It is not presented for hall-marking, and very little 12-carat jewellery is manufactured. The lowest standard, 9-carat, is now very largely used for cheap jewellery, and Gee states that even more jewellery is made of slightly inferior material, which cannot be hall-marked, although it is usually called 9-carat. This standard contains some zinc, but for the higher standards the base metal is usually copper, which gives the wares a better and more durable colour.

#### COMPOSITION OF SILVER WARES.

Silver wares in the United Kingdom are almost always of the same composition as silver coin, containing 925 parts of silver and 75 of copper per 1,000 or 11 oz. 2 dwt. silver and 18 dwt. copper in the pound troy. Another standard, Britannia silver, containing 11 oz. 10 dwt. silver in the pound troy, or 958·3 parts per 1,000, is occasionally used, while in Austria-Hungary there are four standards, ranging from 950 to 750 fine.

<sup>1</sup> "Goldsmiths' Handbook." Fifth edition, p. 45.

The following table gives the legal standards for silver plate in use in some of the principal countries in the world:—<sup>1</sup>

	Fine Silver per 1,000 parts.
Austria-Hungary. . . .	950, 900, 800 and 750.
Belgium . . . . .	900 and 800.
Denmark . . . . .	826.
France. . . . .	950 and 800.
Germany . . . . .	800 for plate. Any degree of fineness for jewellery, etc.
Netherlands. . . . .	934 and 833.
Italy . . . . .	950, 900 and 800.
Norway and Sweden . . . .	828·1 and 812·5.
Portugal . . . . .	916·6 and 833. Various standards down to 800 for export.
Russia . . . . .	910, 880 and 840. For silver wire, 940 to 960.
Spain . . . . .	916·6 and 750.
Switzerland . . . . .	875 and 800.
Turkey <sup>2</sup> . . . . .	900.

#### MELTING AND ROLLING GOLD AND SILVER FOR WARES.

For 22-carat gold it is usual to melt down sovereigns. For other standards refined gold or coin is used. The gold, silver and copper are melted together in plumbago crucibles, and if zinc is to be added it is charged in last, after the other metals are melted, in order to reduce loss. The charge is covered with charcoal, and borax is frequently added to remove dross. If it is feared that the metal will be brittle, sal ammoniac or corrosive sublimate is added to the charge in the crucible. The deleterious elements are in that way removed as chlorides and the residue of flux is

<sup>1</sup> "Return to House of Commons as to Foreign Countries (Gold and Silver Marking)," February 25, 1890.

<sup>2</sup> E. A. Smith, "On Silver Alloys of Industrial Importance," p. 4.

sublimed. Nitre and carbonate of soda or potash are also sometimes used to remove tin, lead, etc. The charge is well stirred with a graphite rod, which is better than iron, before being poured. In the United States it is customary to add cadmium as a deoxidant to sterling silver, the mixture being made up as follows :—<sup>1</sup>

Fine silver	.	.	.	.	925 parts.
Shot copper	.	.	.	.	70 „
Cadmium	.	.	.	.	5 „

This mixture gives sound malleable castings.

The metal is cast in warm cast-iron well-oiled moulds, no attempt being made to fill up the hollow formed by shrinkage. Charcoal, flux, etc., are kept from entering the mould by a piece of wood held in the hand. The bar is cooled by plunging it into water, and it is trimmed, cropped and cleaned before being rolled. In rolling frequent annealing is desirable, especially of gold of 18 carats and under.

After annealing, silver plate is plunged into a pickling solution of dilute sulphuric acid. This is usually done while the plate is still red hot from the furnace. Oxide of copper is dissolved and the plate is left with a uniform dead-white surface. Both before and after rolling the plate is carefully “overlooked,” and imperfections such as pieces of charcoal, slag, etc., embedded in the plate are removed by scraping, generally by a machine similar to a planer, called an overlooking machine.<sup>2</sup>

For the production of wire, a rolled plate after annealing

<sup>1</sup> *Jour. Franklin Institute*, Vol. CLXIII. (1907), p. 118.

<sup>2</sup> *Idem*, p. 119.

is passed through a pair of slitting rolls, which have a number of parallel square grooves, the projecting edges on one roll fitting into the depressions of the other, so forming a number of cutting edges. The plate is cut up into square strips by this machine, and these, after passing through a pair of wire-rolls, which make them approximately round, are annealed, their ends are pointed and they are dragged through the draw-plate. The draw-plate contains about ten conical holes of different sizes, and the wire is passed through them in succession until it is of the required thickness. Square, oval, half-round and oblong wires are also made with the aid of special draw-plates. Oblong wires are also made by flattening square wire by rolling. Hollow half-round wires are made from flat wire by pulling it through half-round holes with the point of a tapered steel punch held against the wire. Two oblong gold wires placed one on each side of a piece of steel wire and drawn through a plate produce hollow-square or hollow-round wires. The wires are used for the manufacture of gold and silver chains and other purposes. The pieces of wire cut to length are put together in innumerable ways and soldered by hand.

#### MANUFACTURE OF WARES FROM PLATE.

The ancient method of making spoons and forks was to hammer them out from a rod by hand, finishing them by sawing and filing. This has now almost entirely given place to machine processes, in which the metal is stamped out from plates, and shaped by striking between dies. The general method of cutting by means of punches and striking between dies has been applied to the manufacture of

numberless articles. The presses for striking are generally of the falling-weight type, the weight being raised by steam or electric power and released by hand, the feeding of the pieces of plate on to the dies and their removal being also done by hand. Much work is also done by turning, and by "spinning" or burnishing into the desired shape on a lathe by means of special burnishing tools. The metal must of course be soft and malleable for spinning.

Decorative work in the case of "wrought" wares is carried out by hand hammering. Other decorative methods are engraving and chasing, the raised pattern in the latter case being applied by means of punches having their surface in *intaglio*.

#### SOLDERING.

The pieces of gold or silver, whether cut out or stamped or otherwise prepared, are fitted together by hand, usually by means of soldering. The best solders for "coloured" gold articles, that is for gold of 13 carats and upwards, are given by Gee<sup>1</sup> as follows:—

—	Fine Gold.	Fine Silver.	Copper.
Best solder . . .	12½ parts	4½ parts	3 parts
Medium solder . .	10    ,,	6    ,,	4    ,,
Common solder . .	8½    ,,	6½    ,,	5    ,,

These solders may be rolled flat and cut with shears into "pallions," or filed into dust.

Solders for silver wares and also for the lower standards of gold usually consist of alloys of silver, copper and zinc,

<sup>1</sup> "Goldsmiths' Handbook," p. 136.

but tin and arsenic are also used with some solders. The solder should fuse at a lower temperature than the metal-work to which it is applied, but the less difference there is between the two fusing points the more tenacious the joint will be.

The compositions of a large number of solders are given by E. A. Smith<sup>1</sup> and by Gee,<sup>2</sup> among which are the following:—

—	Silver.	Copper.	Zinc.	Tin.
	per cent.	per cent.	per cent.	per cent.
Hard solder . . . .	80	13·2	6·8	—
Medium solder . . . .	66·7	23·3	10	—
Easy solder for chains	62·5	20·87	16·63	—
Quick-running solder	62·5	20·87	10·38	6·25
Common solder . . . .	57·1	34·3	8·6	—

The zinc used for making solders is generally added in the form of brass. Soldering is carried out with the help of fused borax as a flux so as to keep the work clean and free from oxides.

### COLOURING GOLD WARES.

By this process the base metals are removed from the surface of wares so as to leave a film of pure gold of a rich yellow colour. Gold of low standards may thus be given the appearance of fine gold. The dry colouring process consists in dipping the wares for a few seconds in a fused mixture of certain salts, followed by immersion in a pickling solution. The articles to be coloured must first be thoroughly cleaned and polished, and marks or scratches

<sup>1</sup> "On Silver Alloys of Industrial Importance," *Proc. Sheff. Soc. of Eng. and Metallurgists*, November, 1901.

<sup>2</sup> "Silversmiths' Handbook."

removed. If the required colour is not obtained in the first dip, they are dried and dipped again. Several colouring mixtures are in use, the composition of one of them being as follows:—

Nitre . . . . .	2 parts.
Common salt . . . . .	1 part.
Alum . . . . .	1 „

The pickling solution usually consists of hot nitric acid, and after immersion in this the work is rinsed in a very weak solution of potash to remove the acid, and then in boiling water. After drying in warm sawdust, the wares are often burnished, *i.e.*, rubbed with steel or agate implements of various shapes.

Dry colouring is said by Gee not to be suitable for gold of lower standard than 18 carats.

In wet colouring, a small quantity of water is added to the other ingredients of the colouring pot. The wares are prepared by careful cleaning and polishing, followed by annealing or heating to redness on an iron or copper plate. The blackened wares are boiled in dilute nitric or sulphuric acid and well washed, and are then ready for the colour-pot. The ingredients of the colouring mixture vary, the composition of one of them being given by Gee as follows:—<sup>1</sup>

Nitrate of potassium . . . . .	14 oz.
Common salt . . . . .	7 „
Alum . . . . .	7 „
Spirits of salts (HCl) . . . . .	2 „
	<hr/>
	30 oz.

<sup>1</sup> "Goldsmiths' Handbook," p. 168.



The salts are crushed fine, well mixed, heated in a crucible and the acid added when the mixture begins to effervesce. The wares are then immersed in the mixture for a few minutes, well rinsed in boiling water, and again immersed in the colouring-pot, the operation being repeated until the desired colour is obtained. Water is added to the colouring-pot every now and then to make up for the loss by evaporation.

The colour of silver wares is also improved by various methods, the simplest being the same as that employed in the blanching of coins (*q.v.*).

#### IMITATION GOLD AND SILVER WARES.

The chief of these are "gold plate," "rolled gold," "gold filled," and electroplate.

*Gold plate* can be made from any quality of gold. A little bar of gold of the required standard is united by soldering to a bar of base metal, and the combined bar can be rolled out, stamped, drawn into wire and otherwise manipulated, the gold still covering the surface of the alloy. Even the relative thickness of, say, one of gold to 25 of alloy may be retained in great part. The value of gold plate is of course very small, 9-carat gold plate costing less than 2s. per ounce. Old Sheffield silver plate was made similarly.

*Electro-plating* is a comparatively recent invention, not having been used until 1840. Before that time the ordinary method of gilding metals was to apply gold amalgam to the surface by means of a brush previously dipped in a solution of nitrate of mercury. The amalgamated article was then rinsed and dried and the mercury expelled by evaporation over a charcoal fire. Afterwards the article

was scratch-brushed and burnished, or coloured or treated by one of the ormolu processes,<sup>1</sup> which consisted in heating the articles, after covering them with a paste of alum, oxide of iron, saltpetre, common salt, and other ingredients.

Electro-gilding is almost always carried out in cyanide baths. The bath is usually made by the battery process. For this Philip recommends<sup>2</sup> dissolving one pound of pure cyanide of potassium in a gallon of hot distilled water. Electrodes consisting of plates of pure gold are immersed in the liquid and a current of electricity from two Daniel cells is then passed through the solution until one ounce of gold has been dissolved, a point determined by weighing the anode. The condition of the bath may be ascertained at any time by trying if a clean cathode of German silver can be gilded promptly, when cathode and anode are of about the same size. Gold chloride may be used to strengthen the solution in gold if required. The bath is used hot, at about 130° F., and is frequently stirred. The hotter the solution the deeper becomes the colour of the deposit. The articles to be gilded are previously cleaned by scrubbing with soap and water and dipping into potash or ammonia solution followed by rinsing and scratch-brushing. If the deposit is at all uneven or patchy the wares are taken out, rinsed, and again scratch-brushed. The anode is kept of about the same dimensions as the article to be gilded, the size of the anode being varied by keeping it partly immersed and raising or lowering it. If the anode is too small, the deposit may become too pale; if

<sup>1</sup> See "Electro-plating and Electro-refining of Metals," by A. Philip, for full details of these processes.

<sup>2</sup> *Idem*, p. 179.

it is too large, the deposit becomes dark coloured. Impurities in the bath are to be avoided, but a very little organic matter, such as grease, is not disadvantageous, as it gives a deeper and richer colour to the deposit. Hot distilled water is added from time to time to make up for the loss by evaporation. When the deposit is thick enough, the article is taken out and well rinsed and scratch-brushed.

Silver-plating is also almost exclusively carried out by means of cyanide baths, which may be prepared similarly to gold-plating baths. About three ounces of potassium cyanide are used to one gallon of water, and one ounce of silver is dissolved in this. The deposit from such a bath will be dead-white, and requires to be scratch-brushed. By adding a little carbon bisulphide, however (about one part of  $CS_2$  to 50,000 parts of the bath) a bright deposit of silver may be obtained. Fresh bisulphide must be added every day.

*Manufacture of Gold Leaf.*—Gold leaf is of various qualities, containing from 90 to 98 per cent. of gold and the rest silver and copper. The metal is cast into flat ingots, weighing 2 oz. each, and these are rolled out with frequent annealings until about 0.0013 in. thick. The ribband of gold is then cut into inch-square pieces, a packet of which interleaved with vellum is beaten with a 16-lb. convex-faced hammer until each gold leaf is 4 inches square. They are again cut into inch-square pieces and beaten between gold-beaters' skins with a 10-lb. hammer until about  $3\frac{1}{4}$  in. square, when they are put up in small books between paper leaves. Each book of 25 leaves contains from 4 to 10 grains of gold. Gold leaf is commonly from  $\frac{1}{125000}$  to  $\frac{1}{300000}$  in. thick.

## CHAPTER XVII

### PLATINUM

*History.*—Platinum occurs in so many alluvial beds mixed with grains of gold, that it would be surprising if it had never been observed by the ancients. There is little doubt that Pliny refers to it<sup>1</sup> under the name “aluta” as occurring in gold mines, and presenting itself in the form of rounded black concretions varied with white specks, of the same weight as gold, and remaining with it after the washing has been completed.

It attracted the attention of Don Antonio de Ulloa when he was at Choco, in Colombia, in 1735, with a French expedition. It was brought to Europe in 1740, from Jamaica, and was described by Watson in the *Philosophical Transactions for 1750*. It had apparently been long known in South America, and was called by the Spaniards “platina del Pinto,” “platina” being the diminutive of “plata,” silver, and the Pinto the river where it was first discovered. The Spanish Government had forbidden its export and ordered it to be thrown into the sea, to prevent it from being fraudulently used to alloy with gold. In 1788, however, the Spanish Government offered 8s. per pound for platinum (perhaps for the same purpose of mixing it with gold), and according to Don Vincente Restrepo of Bogota,

<sup>1</sup> Book XXXIV., c. 47.



3,280 lb. were obtained in that year.<sup>1</sup> All platinum came from South America until 1823, when it was recognised in certain white metallic grains from the Urals which had been found in 1819. Production in Russia began in 1824, and since that time most of the platinum in the world has been derived from these "placers," which at present show no signs of exhaustion.

#### PROPERTIES.

Platinum is not so white as silver and has a greyish tinge, but its lustre is not much less brilliant than that of silver in polished specimens. Finely divided platinum is black. Its hardness is 4·3, or greater than that of copper, silver, or gold, and slightly more than that of phosphor bronze. Its tenacity is between those of silver and copper. It is malleable and ductile, but the presence of small quantities of certain impurities greatly impairs these qualities. Thus the presence of 0·3 per 1,000 of silicon makes it hard and brittle, and small quantities of the other metals of the platinum group (palladium, rhodium, iridium, etc.) reduce its ductility.

The density of cast platinum is given by Deville and Debray as 21·50 at 17·6° after melting in hydrogen, and by Tilden as 21·323 at 18°. The density of platinum foil and wire varies from 21·2 to 21·7, and that of platinum sponge from 16·32 to 21·24 (Landolt-Börnstein Physikalisch-Chemische Tabellen, 1905, p. 227). The addition of iridium increases the specific gravity of platinum. Pure platinum, according to G. Matthey, has a density of 21·46.

The coefficient of expansion of platinum is given by

<sup>1</sup> "Mineral Industry for 1892," p. 373.

Fizeau as 0·00000907 at 50°, and by Le Chatelier as 0·00001130 at 1,000°. This is less than that of other metals and is about the same as some kinds of glass, such as Crown glass. In consequence, it can be placed in molten glass without causing the latter to crack on cooling, and platinum wire is therefore used to lead electric currents through glass, without allowing the passage of air.

Platinum melts at about 1,710°, according to Harker (*Proc. Roy. Soc.*, Vol. LXXVI.A, 1905), and at 1,730° according to the Bureau of Standards at Washington (1907). An older determination by Violle gave it as 1,775°. The melting point of platinum is lowered by arsenic, carbon, and most other impurities. In the electric furnace Moissan found that platinum volatilises readily, but its boiling point is unknown, although obviously above those of gold, copper, etc.

The specific heat of platinum is 0·0323 between 0° and 100°. Its conductivity for heat is 19, taking that of silver as 100, but according to Dewar and Fleming its electric conductivity is only about 13·4 at 0° when silver = 100.

Platinum is not affected by heating in dry or moist air. When molten it absorbs oxygen which is given off on cooling, sometimes with sufficient rapidity to cause the metal to spit like silver. Oxygen is also occluded by platinum foil, which can absorb as much as 80 volumes of the gas at a moderate temperature. Hydrogen is occluded in still greater quantity, from 80 to 200 volumes being absorbed under varying conditions. The whole of these gases can be removed by strongly heating the metal *in vacuo*. At a bright red heat, hydrogen rapidly passes through platinum. At 180° platinum foil quickly absorbs

oxygen and hydrogen and enables them to combine, so that it causes electrolytic gas ( $H_2 + O$ ) to explode.

*Platinum black*, which is platinum in the form of a finely divided black powder produced by precipitation from alkaline platinum solutions by means of certain substances such as formic acid, absorbs still larger quantities of gases, especially of oxygen, with great rapidity. When charged with oxygen, platinum black acts as an oxidiser, and by its action hydrogen, CO, vapours of alcohol, ether, etc., are rapidly oxidised and usually ignited. This is one of the best known examples of catalytic action. The property is used in making machines for the spontaneous ignition of gas, alcohol vapour, etc. Platinum black charged with hydrogen is a powerful reducing agent. Platinum black becomes lustrous and greyish-white when burnished. Its density varies from 15·8 to 17·6.

Platinum is not acted on by either pure hydrochloric, nitric or sulphuric acid. It is dissolved (with the formation of  $PtCl_4$ ) by aqua regia and other mixtures which evolve chlorine, but far less readily than gold, so that gold after being fused so as to be firmly adherent to a platinum crucible can be slowly dissolved by dilute aqua regia at moderate temperatures without much injury to the crucible. Platinum is dissolved more rapidly by aqua regia or solutions of chlorine under pressure. Dry chlorine is without action on it at the ordinary temperature, but at  $230^\circ$  to  $250^\circ$   $PtCl_2$  is formed.

When platinum is alloyed with silver, copper, lead, zinc and some other metals, it is attacked and partly dissolved by nitric acid, with the formation of platinum nitrate.

When platinum black is heated with sulphur,  $PtS$  is

formed in the absence of air, and if platinum is heated with sulphur and an alkali (dry),  $\text{PtS}_2$  is formed. Both sulphides are decomposed at a red heat, even in the absence of air.

When platinum is heated strongly in phosphorus vapour, phosphide of platinum is formed, and the phosphorus is not entirely driven off even at a white heat in the absence of air. Arsenic attacks platinum at a red heat, forming a fusible arsenite. Platinum is oxidised at high temperatures by molten alkali in the presence of air, and by nitrates even if air is excluded. It is also attacked at high temperatures by cyanides (forming platinocyanides), by carbon (forming a carbide), and by silicon, or carbon and silica acting together (forming silicides of platinum).

The atomic weight of platinum is 194.8 taking oxygen as 16. It is closely allied chemically with iridium and less closely with osmium. Platinum forms two sets of compounds corresponding with the oxides  $\text{PtO}$  and  $\text{PtO}_2$ . In each case the oxide of platinum can act either as an acidic or basic radicle, forming salts such as  $\text{Pt}(\text{SO}_4)_2$  and platinates such as  $\text{Na}_2\text{O} \cdot 3\text{PtO}_2$ . The compounds in which platinum is tetravalent have been studied most. Platinum also forms a large number of complex compounds such as  $\text{H}_2\text{PtCl}_6$ ,  $\text{H}_2\text{PtCy}_4$ , etc.

#### COMPOUNDS OF PLATINUM.

*Platinum dichloride* or platinous chloride,  $\text{PtCl}_2$ , is formed by heating platinum black in chlorine until no more of the gas is absorbed. It can also be obtained by heating  $\text{H}_2\text{PtCl}_6$  to about  $230^\circ$ , or by heating  $\text{PtCl}_4$  in a stream of dry  $\text{HCl}$ .



It is a greenish-brown powder, insoluble in water but soluble in hydrochloric acid in the absence of air. It is decomposed at a red heat into platinum and chlorine, and is readily reduced to metallic platinum by  $\text{FeSO}_4$  and other reducing agents. Platino-chlorides are formed by dissolving  $\text{PtCl}_2$  in solutions of metallic chlorides. They are highly soluble compounds of the general formula,  $\text{R}_2\text{PtCl}_4$ , obtained as dark red crystals by crystallising from concentrated solutions. Platino-chlorhydric acid,  $\text{H}_2\text{PtCl}_4$ , is probably obtained by dissolving  $\text{PtCl}_2$  in  $\text{HCl}$ , but has not been isolated.

*Platinum tetrachloride*,  $\text{PtCl}_4$ , is formed by heating  $\text{H}_2\text{PtCl}_6$  to  $165^\circ$  in a stream of dry  $\text{HCl}$ . It forms  $\text{H}_2\text{PtCl}_6$  by dissolving in hydrochloric acid, and platini-chlorides by dissolving in solutions of metallic chlorides. Bromides and iodides of platinum are known corresponding to these chlorides.

*Platini-chlorhydric acid*,  $\text{H}_2\text{PtCl}_6$ , is formed by dissolving platinum in aqua regia. It may be crystallised out after expelling the nitric acid by evaporation with  $\text{HCl}$ . It forms red-brown deliquescent crystals, soluble in alcohol, and decomposed by heating to about  $230^\circ$ . Its solution is the starting point for the formation of most of the platinum compounds. It forms *platini-chlorides* of many metals when their chlorides are added to it in solution. Most of these platini-chlorides are yellow-red crystalline substances, readily soluble in water and alcohol, but the salts of potassium and ammonium are only slightly soluble in water and are insoluble in alcohol. These properties are made use of for the estimation of potassium and ammonium and also for the separation of platinum from its ores and

residues. By passing  $\text{SO}_2$  through a solution of  $\text{H}_2\text{PtCl}_6$ , some reduction to  $\text{H}_2\text{PtCl}_4$  takes place, but there is no precipitation of Pt or  $\text{PtCl}_2$ . Platinum is precipitated by long continued boiling with  $\text{FeSO}_4$ , and by formic acid and soda carbonate acting together.

*Ammonium platini-chloride*,  $(\text{NH}_4)_2\text{PtCl}_6$ , occurs in yellow octahedral crystals. At  $20^\circ$ , 0.665 gram and at  $100^\circ$  1.25 gram dissolves in 100 c.c. of water. The substance is nearly insoluble in alcohol. The solubility of *potassium platini-chloride*,  $\text{K}_2\text{PtCl}_6$  is greater, 1.12 gram dissolving at  $20^\circ$  and 5.13 grams at  $100^\circ$  in 100 c.c. of water. When these two salts are heated to redness they are reduced and platinum sponge remains, mixed, in the case of potassium platini-chloride, with potassium chloride.

When platini-chlorides are electrolysed the platinum moves towards the anode and the solution around the cathode becomes weaker in platinum. Nevertheless platinum is deposited at the cathode by being reduced by hydrogen which is liberated there.

*Carbonyls* of platinous chloride are formed by passing carbon monoxide over  $\text{PtCl}_2$ . Of these,  $\text{PtCl}_2\cdot\text{CO}$  volatilises at  $250^\circ$  without decomposition, thus contrasting strongly with almost all other compounds of platinum, which decompose when heated without volatilising. However,  $\text{PtCl}_4$  sublimes to some extent when heated in a current of chlorine, like  $\text{AuCl}_3$ .

#### ALLOYS OF PLATINUM.

*Platinum and Gold.* See above, p. 58.

*Platinum and Silver.* See above, p. 140.

*Platinum and Copper.*—These metals mix in all proportions, but require a high temperature for their production, like all platinum alloys, which are usually prepared in an oxy-hydrogen or oxygen-coal gas furnace, or in an electric furnace. As the proportion of platinum increases, the colour of the alloy passes from reddish-yellow to golden-yellow and finally to white. The alloys also become harder, and less ductile. They are less easily tarnished by the atmosphere than ordinary brasses or bronzes. The alloy containing platinum 18·75 per cent., copper 81·25 per cent. (Cooper's gold) is of a golden-yellow colour and is malleable and ductile, although hard. It is susceptible of a high polish and closely resembles 18-carat gold. When the metals are present in equal parts the alloy is still yellow, but is somewhat brittle. The alloy of 3 parts platinum to 2 parts copper is nearly white and is very hard and brittle, without ductility.

About 4 per cent. of zinc is sometimes added to alloys of platinum and copper, for use in jewellery, ornaments, mathematical instruments, chronometer wheels, etc.

*Platinum and Nickel.*—Platinum unites with nickel, forming malleable alloys susceptible of a high polish and not readily tarnished. Alloys of nickel, platinum and tin have been manufactured under the name of platinum-bronze, but generally contain very small percentages of platinum. Equal parts of platinum and nickel yield a yellowish-white malleable magnetic alloy, as fusible as copper.

*Platinum and Iridium.*—Alloys containing these metals are very hard and elastic. They are unalterable in air and take a high polish. They fuse at very high temperatures,

much above the melting point of platinum. When not more than about 20 per cent. of iridium is present the alloys are malleable and ductile, but the 25 per cent. alloy "can only with great difficulty and waste be worked into sheet and wire when heated at low temperatures."<sup>1</sup> Alloys containing more than 25 per cent. of iridium seem to be of very little value. The alloy of iridium 10, platinum 90, prepared by Messrs. Johnson and Matthey in 1870 for the Comité International des Poids et Mesures, was chosen after exhaustive trials as the material for standard weights and measures. Subsequently G. Matthey<sup>2</sup> recommended the alloy containing 15 per cent. of iridium for standard measures of length, made in the tubular form, and the 20 per cent. alloy for standard weights. The densities of platinum-iridium alloys, according to Deville and Debray, are as follows:—

Platinum.	Iridium.	Specific Gravity.
90	10	21·575
85	15	21·618
66·67	33·33	21·874

These densities are reduced by the presence of rhodium, ruthenium and other impurities, and the actual alloys used for standards are of lower density.

*Platinum and Iron.*—Platinum unites with steel in all proportions, forming hard white alloys, some of which are malleable. The presence of two or three per cent. of platinum prevents steel from rusting, and this alloy has been used in the manufacture of cutlery.

<sup>1</sup> G. Matthey. *Proc. Roy. Soc.*, Vol. XXVIII. (1879), p. 468.

<sup>2</sup> *Loc. cit.*

The alloys containing from 15 to 20 per cent. of platinum were shown by Daubr e to exhibit magnetic polarity. Some native grains of platinum containing similar proportions of iron are also natural magnets.

The alloys containing a large proportion of iron are attracted by the magnet, but show no polarity. Stodart and Faraday found that equal parts of steel and platinum gave an alloy of density 9.862, taking a beautiful polish, but not very malleable.

*Platinum and Zinc alloys* when treated with hydrochloric acid sometimes leave an explosive platinum residue. Cohen and Strengers have shown that the metal is heavily charged with occluded hydrogen and oxygen, and that the explosion is caused by the union of these elements.

*Platinum and Lead* form readily fusible grey, brittle alloys, from which the platinum can be extracted by cupellation. In ordinary furnaces, however, the platinum freezes before the whole of the lead has been removed, and it is necessary to finish the operation with the aid of the oxy-hydrogen flame.

*Platinum and Tin* unite in all proportions, forming brittle alloys, of which the melting point is higher, as in the other alloys, in proportion as the percentage of platinum is increased. A small quantity of platinum interferes with the malleability of tin. Ten per cent. of platinum yields a white ductile alloy which takes a beautiful polish. Equal parts of tin and platinum yield a brittle, dark grey alloy, with a coarse-grained fracture.

*Platinum and Antimony* unite with incandescence and yield brittle, hard, dark grey alloys with fine-grained fracture. A trace of antimony makes platinum brittle.

*Platinum and Arsenic* also unite with incandescence. According to Friedrich and Leroux<sup>1</sup> they combine to form the compound  $\text{Pt}_2\text{As}_3$ , which contains 36·7 per cent. of arsenic, and melts at about 1,400°. The alloy of lowest melting point contains 86·8 per cent. of platinum and 13·2 per cent. of arsenic. This eutectic alloy melts at 597° and can be detected in all the alloys containing from 97 to 63 per cent. of platinum. The remarkably low melting point of this alloy accounts for the readiness with which platinum vessels are destroyed when heated with substances containing arsenic. At high temperatures arsenic is volatilised and spongy platinum left behind in a fit state for working. The alloy was used for a long time after 1784 as the only means of preparing platinum in a suitable condition to be worked.

*Platinum and Bismuth* form brittle alloys with a foliated fracture, taking a purple or violet colour when exposed to the air. They can be partly separated by liquation at a moderate heat.

*Platinum and Cadmium* are said to unite to form the compound  $\text{PtCd}_2$ , from which any excess of cadmium can be removed by volatilisation. It is a brittle, fine-grained substance.

*Platinum and Mercury* do not unite directly.

#### OCCURRENCE OF PLATINUM IN NATURE.

Platinum occurs in flattened or angular grains in beds of gravel or sand which resemble gold placers, and have been formed in the same way by the erosion of older deposits.

<sup>1</sup> *Metallurgie*, February, 1908, p. 148.

The richest and most extensive platinum placers occur in or near the Ural Mountains in gravels about 3 or 4 feet thick and buried below thicker layers of barren material. Usually, but not invariably, the gravels are also auriferous, and other minerals occurring with the platinum are zircon, spinel, corundum, magnetite, and osmiridium. The deposits, besides quartz grains, contain fragments of basic magnesian volcanic and metamorphic rocks, such as serpentine, olivine rock, porphyries, etc.

Platinum alluvial deposits also occur in Brazil, New Granada, California, British Columbia, New South Wales, and in many other localities, but the quantities derived from these places are small.

Platinum occurs *in situ* in serpentine in the Urals and elsewhere, and in other metamorphic rocks in various parts of the world, but the quantities so found are insignificant. It is also found in the form of *Sperrylite*, arsenide of platinum,  $PtAs_2$ , associated with sulphide of nickel at Sudbury in Ontario. Platinum sometimes occurs in fahlerz, zinc blendes, lead ores, etc.

The amount of platinum occurring in placers is usually only a few grains per cubic yard. Sometimes nuggets are found, but according to Schnabel and Louis the largest lump of platinum found up to the present in the "alluvials" of the Ural Mountains is in the Demidoff Museum at St. Petersburg and weighs 21.64 lbs.

The platinum grains occurring native are alloys containing iridium, rhodium, palladium, osmium, iron and copper. The chief impurities are iridium, which may form more than half the alloy, and iron, which has been known to amount to 19 per cent. of the mass. Usually,

however, the grains contain from 70 to 80 per cent. of platinum.

The following analyses of native platinum concentrates are quoted by Thorpe ("Dict. of Applied Chemistry," Vol. II., pp. 253, 254) from Deville and Debray.

—	Platinum from the Urals.	Platinum from Choco (S. America).	Platinum from California.
Platinum . . . . .	76.4	86.20	79.85
Iridium . . . . .	4.3	0.85	4.20
Rhodium . . . . .	0.3	1.40	0.65
Palladium . . . . .	1.4	0.50	1.95
Gold . . . . .	0.4	1.00	0.55
Copper . . . . .	4.1	0.60	0.75
Iron . . . . .	11.7	7.80	4.45
Osmiridium . . . . .	0.5	0.95	4.95
Sand . . . . .	1.4	0.95	2.69
	100.5	100.25	99.95

—	Platiniridium from the Urals (Roscoe and Schorlemmer).	Osmiridium from the Urals (Roscoe and Schorlemmer).
Platinum . . . . .	19.64	10.08
Iridium . . . . .	76.85	55.24
Rhodium . . . . .	—	1.51
Palladium . . . . .	0.89	tr.
Copper . . . . .	1.78	tr.
Iron . . . . .	—	tr.
Osmium . . . . .	—	27.23
Rutherfordium . . . . .	—	5.85
	99.16	100.00

#### EXTRACTION OF PLATINUM FROM ITS ORES.

The platiniferous sands and gravels are washed in the same way as gold-bearing sand and a concentrate obtained which is treated with mercury for the extraction of gold.



The residue consists of platinum grains (which are not attacked by mercury) together with some iridosmine, sand, etc. These are treated for the production of commercially pure platinum, very occasionally by cupellation with lead, but usually by wet methods.

The *Wollaston process*, which came into use in London about the year 1808, is as follows:—The crude platinum is heated with 10 to 15 times its weight of aqua regia for several hours. In this way a solution is obtained of most of the metals of the platinum group, but osmiridium remains undissolved with the sand, etc. The solution is evaporated to a syrupy consistency to remove the greater part of the excess of acid, and is then diluted with water and syphoned off from the insoluble residue. The clear red solution is treated with a solution of ammonium chloride, and the double chloride of ammonium and platinum precipitated. The precipitate is washed, dried and heated to dull redness to drive off the ammonium chloride and chlorine, and spongy platinum is obtained. This is broken up by rubbing, sieved, and the finer particles made into a paste with water and strongly compressed. The solid cake is heated strongly and then hammered while still red hot. The metal thus obtained can be worked by heating and hammering or rolling, but always contains about 2 per cent. of iridium, which is precipitated with the platinum and can be removed only by a second refining.

The mother liquor, after precipitation of the ammonium platini-chloride, still contains some platinum. The metals are precipitated by means of iron, and the precipitate, after digestion with hydrochloric acid, is redissolved in aqua regia for further treatment.

Some modifications have been introduced in this method. Heræus of Hanan evaporates the aqua regia solution to dryness and heats to  $125^{\circ}$  in order to convert the chlorides of iridium, rhodium and palladium to sesquichlorides and so to prevent their precipitation by ammonium chloride.

Deville and Debray about the year 1856 introduced the method of melting the spongy platinum in a lime furnace by means of the oxy-hydrogen blowpipe. The furnace consists of a hollow block of lime, made in two pieces so that the upper half acts as a lid. The nozzle of the blowpipe, in which coal gas is now generally used instead of hydrogen, passes through the lid, and the flame impinges directly upon the metal. An oxidising flame is used, and some refining effect takes place, oxides of iron and copper being formed and absorbed by the lime, and osmium being volatilised as oxide. The products of combustion pass out through an aperture in the furnace, which also serves as an outlet for the molten platinum.

Another method introduced by Deville and Debray has for its object the preparation of platinum direct from its ores in a furnace. A small reverberatory furnace with a hollowed-out bed of firebrick lined with marl is raised to a bright red heat and a charge of about 200 lbs. of crude platinum with an equal weight of galena is added little by little. The iron in the metal is sulphurised and metallic lead is set free and forms a fusible alloy with the platinum. About 200 lbs. of litharge and some glass are then added, the matte is oxidised, and a fusible slag results. The osmiridium is not taken up by the lead but sinks to the bottom and is separated. The platinum-lead alloy is cupelled and the platinum melted in the oxy-

hydrogen furnace. Thus prepared it contains iridium and rhodium, but is suitable for making vessels for chemical purposes.

G. Matthey adopted the following process for the preparation of pure platinum:—<sup>1</sup>

Commercial platinum is melted with six times its weight of pure lead, and after granulation it is dissolved slowly in nitric acid diluted with eight times its volume of water. The solution contains most of the lead, copper, iron, palladium and rhodium.

The black amorphous residue is digested with weak aqua regia, by which the platinum and lead are dissolved and the iridium left unattacked. After evaporation the lead is precipitated by sulphuric acid and the platinum chloride is dissolved in distilled water and treated with an excess of chloride of ammonium and sodium. The whole is then heated to about 80°, and in the course of a few days the ammonio-chloride of platinum settles down as a firm deposit at the bottom of the vessel.

The precipitate is washed first with a saturated solution of chloride of ammonium and afterwards with hydrochloric acid. Rhodium is separated by mixing the dried precipitate with bisulphate of potash together with a small proportion of bisulphate of ammonia and subjecting the mixture to a gradual heat brought by degrees to a dull red in a platinum basin. The platinum is reduced and the rhodium remains as bisulphate of rhodium and potash, which is dissolved out in boiling water. The platinum, a black spongy residue, is now in a high state of purity and merely requires to be washed and melted.

<sup>1</sup> *Proc. Roy. Soc.*, Vol. XXVIII. (1879), p. 464.

## USES OF PLATINUM.

In 1828 the Russian Government began the coinage of platinum, striking 3, 6 and 12 rouble pieces. These were demonetised and called in in 1845, as it was found that the cost of making the coins was very great owing to the difficulty of melting the metal. Moreover, great changes in the value of platinum occurred rapidly owing to the extremely limited supply. The unsuitability of platinum for coinage purposes is due to these causes.

Owing to its high temperature of fusion and its resistance to attack at a red heat by acids, salts, etc., it is used largely for the manufacture of crucibles, basins, foils, wire gauze, etc., for chemical laboratory purposes. It is also used for the manufacture of weights for scientific purposes, and to serve as standards.

A far larger amount is used annually in the manufacture of stills for the concentration of sulphuric acid. The first still for this purpose was made in 1809, and Messrs. Johnson, Matthey & Co. have used as much as 40,000 oz. of platinum in a single year in the manufacture of improved forms of such apparatus.<sup>1</sup>

The dental industry requires even more platinum, which is used for the manufacture of pins for attaching artificial teeth to the plate, and for other purposes.

Platinum is also used in the electrical industry to connect the inside filament of incandescent lamps with the outside copper wire through the glass. Its suitability for this purpose is due to the fact that its coefficient of expansion is nearly the same as that of glass.

<sup>1</sup> "Thorpe's Dict. of Applied Chem.," Vol. III., p. 257.

Among other uses may be mentioned the manufacture of platinised incandescent gas mantles, platinised paper for photographic purposes, and platinised asbestos, etc., for igniting gases. It is also employed in obtaining a silver colour on porcelain, in watch-making, in jewellery, in stylographic pens, in surgical and philosophical instruments, and for "oxidising" silver. Of late years the demand for platinum for the electrical, incandescent light, and dental industries has increased largely whilst the new supplies have not increased. The high price has caused very large supplies of old material to become available.

#### ASSAY OF PLATINUM.

The determination of platinum may be made by weighing it as the platini-chloride of ammonium or potassium or as metallic platinum. The aqua regia solution containing platinum is evaporated to dryness cautiously and then redissolved with the smallest possible quantity of water. Twice the volume of absolute alcohol is then added and a large excess of pure crystallised ammonium chloride. The liquid is warmed, stirred, and left for twenty-four hours and the precipitate of  $\text{Am}_2\text{PtCl}_6$  is collected on a weighed filter paper and washed with alcohol. The washings must be evaporated to dryness and the residue cupelled, as they contain platinum.

The precipitate may be ignited and weighed as platinum instead of being weighed as the platini-chloride, but during ignition part of the platinum is carried away with the volatilising ammonium chloride.

A small quantity of iridium usually remains with the platinum. It may be removed by redissolving in aqua regia and reprecipitating the platinum.

The use of alloys of platinum in jewellery makes it necessary for assays of such alloys to be often made. The methods in use have been worked out by Chaudet, Riche and Forest.

The alloys of platinum with base metals present no difficulty. They are dissolved in a suitable acid which removes the base metal and leaves the platinum as a residue. If the platinum exceeds 30 per cent. of the alloy it is not completely freed from base metal in this way, and must be cupelled with silver and parted by means of sulphuric acid.

*Platinum, Gold, Silver, Copper.*—The most complicated case for assay is an alloy containing platinum, gold, silver, and copper or other base metal. Here it is necessary to determine first of all the approximate composition of the alloy and then to make an exact assay.

In the *approximate assay*, the amount taken is usually 100 half-milligrams, or 100 millièmes, where "1,000" is equal to 0.5 gram. This is cupelled with one gram of lead at a very high temperature, and if the button is flat it is again cupelled with more lead. When a rounded button has been produced it is weighed and the weight accepted as that of the gold, silver and platinum together.

The button is then inquarted by cupellation with twice its weight of silver and is attacked by boiling in concentrated sulphuric acid, which dissolves the silver and leaves the gold and platinum as a residue.

The separation of gold from platinum is effected by nitric acid, but it is necessary for the amount of gold to be at least ten times that of the platinum, in order that the result may be satisfactory. This proportion of gold is accordingly added with  $2\frac{1}{2}$  times its weight of silver, and the cupelled

button is parted in nitric acid as in the ordinary gold bullion assay. The cornet represents the original gold contents (after allowing for the amount added) and the platinum is taken by difference.

Thus, to take an example:—

Weight of alloy taken for assay, 100 half-milligrams.

„ after cupellation (Au+  
Pt+Ag) . . . . . 85 „

To this is added 170 of silver, and the whole is cupelled. The weight after second cupellation and parting in sulphuric acid (Au+Pt) is . 75 „

To this 750 half-milligrams of gold and  $2\frac{1}{2} \times 825$  or 2,062.5 half-milligrams of silver are added, and the whole is cupelled.

Weight after third cupellation and parting in nitric acid = 800 half-milligrams, of which 750 had been added in the form of pure gold. The approximate composition of this alloy is thus determined to be as follows:—

Gold . . . . .	50
Platinum . . . . .	25
Silver . . . . .	10
Copper . . . . .	15
	100
	100

The *final assay* cannot conveniently be made on a single assay piece, because in the sulphuric acid parting it is desirable for the assay piece to contain one and a half to two parts of gold to one part of platinum. In the nitric acid parting, on the other hand, ten parts of gold are required to each part of platinum.

Riche and Forest accordingly recommend that 0·5 gram (“1,000” in gold bullion assay weights) of the alloy be taken for the sulphuric acid parting if the platinum does not exceed 300 millièmes, and that a little less weight be taken if a greater proportion of platinum is present. Gold is added, if necessary, to give a maximum of two parts of gold to one of platinum.

The amount of lead required for cupellation is about double the amount of lead which would be required in a gold assay, or in the case under consideration, as the copper amounts to 150 per 1,000, about 15 grams of lead would be used for 0·5 gram of the alloy. In cases where the platinum exceeds 200 per 1,000 of the alloy, d’Arcet and Chaudet recommend a second cupellation with one or two grams of lead.

The weight of the cupelled button is, of course, compared with a check assay-piece made up in accordance with the approximate composition of the alloy, previously determined, and this is done step by step through all the operations. If there is a surcharge<sup>1</sup> in the check of more than one or two parts per 1,000 in the first cupellation, showing retention of copper, the prills are re-cupelled with fresh lead. The corrected weight of Au+Pt+Ag is then, say 853.

The cupelled button or prill in this case does not require the addition of gold, and is re-cupelled with  $2\frac{1}{2}$  parts of silver to one part of gold and platinum taken together, that is to say—

Gold + platinum =	750 approximately
Silver already present =	100                   ,,
Silver required to be added =	1,775, or 0·877 gram.

<sup>1</sup> See above, p. 209.



The amount of lead required for this second cupellation is 5 grams.

The button is worked as described above in the assay of gold bullion and the cornet boiled in concentrated sulphuric acid for ten minutes. This is a delicate operation, as the boiling point of sulphuric acid ( $325^{\circ}\text{C}.$ ) is so high that glass vessels are liable to be cracked by cold draughts. Moreover, the acid boils explosively with heavy bumping, and boiling sulphuric acid is terribly corrosive and inflicts dangerous wounds. It is advisable to use a platinum boiler, if possible, but if glass is used it must be protected from the air by being wrapped in asbestos, and heated at the sides more than at the bottom. Sometimes pieces of carbon are added to assist the acid to boil quietly. After boiling, the vessel is allowed to cool almost completely, as otherwise it would crack during decantation. The liquid is then decanted into a dry vessel, or into a considerable bulk of cold water, to avoid danger from the heat generated by mixing sulphuric acid and water. The decantation must be as complete as possible, to avoid heating on the addition of the washing water, which should be warm in order to dissolve the sulphate of silver. After washing twice, the cornet is again boiled for ten minutes in sulphuric acid and washed, dried, and annealed. Its weight gives the amount of gold + platinum, in this case, say 752.5.

For the determination of the gold, 0.25 gram or 500 half-milligrams of the original alloy is taken, containing

250 gold  
125 platinum  
50 silver  
75 copper.

This is cupelled with 0.5 gram of pure gold (making ten parts of gold to one part of platinum) and 1.412 grams of silver and 5 grams of lead. The resulting button is worked and parted in nitric acid as described in the assay of gold bullion. If, as generally happens, there is a surcharge in the check assays of more than one or two parts per 1,000, showing the retention of platinum, the inquartation and parting is repeated. The final weight is then, say 1,248 half-milligrams, and after deducting 1,000 and doubling the remainder, the result 496 is obtained for the amount of gold present in 1,000 parts of the original alloy.

The final result of the assay will then be reported as follows :—

Gold . . . . .	496.0
Platinum . . . . .	256.5
Silver . . . . .	100.5
Copper (by difference) . . .	147.0
Total	<u>1000.0</u>

If necessary as small a quantity as 0.1 gram may be taken for assay. This is a convenient amount for alloys containing 900 to 950 platinum and the remainder gold.

It is, of course, obvious that alloys of platinum and silver only can be assayed by sulphuric acid parting without the other methods, and platinum-gold alloys do not require the sulphuric acid parting. The cupellation requires a higher temperature in proportion as the percentage of platinum is greater, and alloys containing over 50 per cent. of platinum cannot be freed from lead without the help of the oxygen-gas blowpipe.

## CHAPTER XVIII

### PRODUCTION AND CONSUMPTION OF THE PRECIOUS METALS

#### PRODUCTION OF GOLD IN THE WORLD.

No means exist of estimating the amount of gold produced in ancient times. Doubtless it was small compared with the output during the last half-century. The consumption, however, was much less, and considerable stocks accumulated in the hands of certain monarchs. Thus the treasure of Pytheus, 470 B.C., has been estimated at £3,600,000, derived from the sands of the Pactolus in Phrygia; and Jacob states that Alexander acquired in Persia gold probably amounting in value to over £50,000,000.

Production of gold in the Middle Ages was very small, most of the old goldfields in Egypt, Spain, Phrygia, India, etc., having been exhausted and no new ones discovered. After the discovery of America in 1492, gold reached Europe from the West in a steady and increasing stream. The following table gives Soetbeer's estimates of the annual production between 1492 and 1885, and the estimates of the Bureau of the United States Mint for the years 1886 to 1906.

The total amount of gold produced in the period is given as 603,781,000 fine ounces of the value of £2,412,750,000.

## PRODUCTION OF GOLD IN THE WORLD.

Period.	Annual Average.	
	Ounces (fine).	Value.
		£
1493—1520 . . . . .	186,000	790,000
1521—1544 . . . . .	230,000	977,000
1545—1560 . . . . .	273,000	1,165,000
1560—1600 . . . . .	228,000	968,000
1601—1640 . . . . .	270,000	1,152,000
1641—1680 . . . . .	290,000	1,232,000
1681—1720 . . . . .	379,000	1,610,000
1721—1740 . . . . .	613,000	2,605,000
1741—1760 . . . . .	791,000	3,362,000
1760—1800 . . . . .	618,000	2,626,000
1801—1810 . . . . .	571,000	2,426,000
1811—1820 . . . . .	368,000	1,564,000
1821—1830 . . . . .	457,000	1,942,000
1831—1840 . . . . .	652,000	2,771,000
1841—1850 . . . . .	1,760,000	7,480,000
1851—1860 . . . . .	6,450,000	27,410,000
1861—1870 . . . . .	6,110,000	25,960,000
1871—1880 . . . . .	5,570,000	23,670,000
1881—1885 . . . . .	4,790,000	20,360,000
1886—1890 . . . . .	5,461,000	23,209,000
1891—1895 . . . . .	7,882,000	33,490,000
1896—1900 . . . . .	12,447,000	52,900,000
1901—1905 . . . . .	15,581,000	66,200,000
1906 . . . . .	19,366,550	82,260,000
1907 . . . . .	19,958,874	84,825,000

The production of gold for the year 1906 for different countries is given by the Director of the United States Mint as follows:—

Country.	Ounces (fine).	Value.
North America—		£
United States . . . . .	4,565,333	19,392,000
Canada . . . . .	581,657	2,470,000
Mexico . . . . .	896,615	3,808,000
Carried forward . . . . .	6,043,605	25,670,000

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Country.	Ounces (fine).	Value.
		£
Brought forward . . . . .	6,043,605	25,670,000
Africa . . . . .	6,553,484	27,837,000
Australasia . . . . .	3,985,684	16,930,000
Europe—		
Russia . . . . .	943,056	4,005,000
Austria-Hungary . . . . .	126,519	537,000
Germany . . . . .	3,890	16,500
Sweden . . . . .	643	2,700
Italy . . . . .	1,993	8,500
Turkey . . . . .	289	1,200
Great Britain . . . . .	1,414	6,000
Servia . . . . .	2,893	12,300
Asia—		
Japan . . . . .	156,016	663,000
China . . . . .	88,961	378,000
Korea . . . . .	108,844	462,000
Siam . . . . .	2,572	10,900
India . . . . .	584,744	2,483,000
East Indies . . . . .	142,064	604,000
South America . . . . .	527,447	2,244,200
Central America . . . . .	92,432	392,500
	19,366,550	82,263,800

The production of gold in the United States in 1906 and 1907 was divided between the following States, according to the Director of the United States Mint:—

State.	1906. Ounces (fine).	1907. Ounces (fine).
Colorado . . . . .	1,109,452	990,398
Alaska . . . . .	1,033,537	882,923
California . . . . .	911,041	841,454
Nevada . . . . .	448,852	711,339
South Dakota . . . . .	319,512	197,634
Utah . . . . .	248,208	225,086
Montana . . . . .	218,752	203,482
Arizona . . . . .	132,891	122,849
Oregon . . . . .	63,860	57,082
Idaho . . . . .	50,102	52,616
Other States or Territories	29,126	29,879
	4,565,333	4,314,742

The production of Canada in 1906 came chiefly from the Yukon (250,000 oz.) and from British Columbia (296,000 oz.). A little is produced in Ontario and Nova Scotia.

The output of Africa in 1906 and 1907 is divided as follows<sup>1</sup> :—

—	1906. Ounces (fine).	1907. Ounces (fine).
Witwatersrand . . .	5,559,534	6,451,494
Rest of Transvaal . . .	227,083	
Rhodesia . . . . .	479,089	545,082
Madagascar . . . . .	56,585	54,012
West Coast . . . . .	199,432	272,277

The production of the individual Colonies of Australasia in 1906 and 1907 was as follows :—

Colony.	1906. Ounces (fine).	1907. Ounces (fine).
West Australia . . .	1,794,547	1,697,553
Queensland . . . . .	544,636	466,476
Victoria . . . . .	772,290	695,576
New Zealand . . . . .	534,617	477,312
New South Wales . . .	253,987	247,363
Tasmania . . . . .	60,023	65,354
South Australia . . .	25,584	11,871
	3,985,684	3,661,505

Russia furnishes official accounts of her production of gold, which is derived from Siberia and the Urals. The official figures give the amounts deposited in the Imperial Treasury. It is estimated, however, that 10 or 15 per cent. of the output does not find its way to the Treasury and

<sup>1</sup> "Mineral Industry for 1907," p. 473.

is smuggled out of the country. It is probable that this gold is not reckoned in the output of any country.

PRODUCTION OF SILVER IN THE WORLD.

The following table is from the Annual Report of the Director of the United States Mint for 1907, p. 142. It gives the annual average production of silver in the world since the discovery of America in 1492 :—

Period.	Annual average. Ounces (fine).
1493—1520 . . . . .	1,510,000
1521—1580 . . . . .	7,040,000
1581—1640 . . . . .	13,240,000
1641—1700 . . . . .	11,200,000
1701—1760 . . . . .	14,140,000
1761—1820 . . . . .	24,100,000
1821—1830 . . . . .	14,807,000
1831—1840 . . . . .	19,175,000
1841—1850 . . . . .	25,090,000
1851—1860 . . . . .	28,791,000
1861—1870 . . . . .	39,226,000
1871—1880 . . . . .	71,046,000
1881—1890 . . . . .	100,457,000
1891—1895 . . . . .	157,581,000
1896—1900 . . . . .	165,693,000
1901—1905 . . . . .	167,450,000
1906 . . . . .	165,755,000

The production of silver is given by the “Mineral Industry for 1907,” p. 474, as 184,552,343 fine ounces for 1906, and 193,542,381 fine ounces for 1907.

The production of silver for the year 1906 for different countries is given by the Director of the United States Mint as follows:—

Country.	Ounces (fine).
North America—	
United States . . . . .	56,517,900
Canada . . . . .	8,568,665
Mexico . . . . .	55,225,268
Africa . . . . .	702,464
Australasia . . . . .	14,237,246 <sup>1</sup>
Europe—	
Russia . . . . .	166,183
Austria-Hungary . . . . .	1,806,322
Germany . . . . .	5,696,433
Norway and Sweden . . . . .	207,850
Italy . . . . .	672,449
Spain . . . . .	4,064,532
Greece . . . . .	829,025
Turkey . . . . .	37,874
France . . . . .	890,555
Great Britain . . . . .	137,216
Asia—	
Japan . . . . .	2,451,357
East Indies . . . . .	182,889
South America—	
Peru . . . . .	7,404,238
Bolivia . . . . .	3,096,998
Carried forward . . . . .	<u>162,895,464</u>

<sup>1</sup> The estimate of the Deputy Master of the Melbourne Mint is 8,075,959 refined ounces.



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Country.	Ounces (fine).
Brought forward . . . . .	162,895,464
South America— <i>continued</i> .	
Colombia . . . . .	763,335
Chile . . . . .	397,853
Argentine . . . . .	14,440
Ecuador . . . . .	13,592
Central America . . . . .	1,670,159
Total . . . . .	<u>165,754,843</u>

The production of silver in the United States is divided between the following States and Territories :—

	Ounces (fine).
Montana . . . . .	12,540,300
Colorado . . . . .	12,447,400
Utah . . . . .	11,508,000
Idaho . . . . .	8,836,200
Nevada . . . . .	5,207,600
Arizona . . . . .	2,969,200
California . . . . .	1,517,500
New Mexico . . . . .	453,400
Texas . . . . .	277,400
Alaska . . . . .	203,500
Michigan . . . . .	186,100
South Dakota . . . . .	155,200
Oregon . . . . .	90,700
Other States and Territories . . . . .	125,400
Total . . . . .	<u>56,517,900</u>

## CONSUMPTION OF THE PRECIOUS METALS.

One of the difficulties in estimating the amounts of gold and silver used in the Arts is that variable proportions of old material (jewellery, etc.) are used with new material. In 1880 Dr. Adolf Soetbeer estimated the consumption of the precious metals by the civilised nations of the world at 2,689,000 oz. of gold and 15,142,000 oz. of silver, reckoning new material only. The following are estimates made by the Director of the United States Mint :—

Year.	Gold. Ounces (fine).	Silver. Ounces (fine).
1901 . . .	3,834,000	44,068,000
1904 . . .	3,870,000	57,377,800
1905 . . .	4,117,777	50,718,000
1906 . . .	5,882,458	85,196,100

In these estimates only new material is taken into account.

They do not include the exports of gold and silver to India, China, etc., where they are converted into jewellery or hoarded. The exports of silver to these countries are sometimes very large, having amounted in 1906, for example, to about 120,000,000 oz.

The precious metals used for the coinage of the world sometimes exceed the total production for the year, but this is due to the remelting of foreign coin in many mints, and to the withdrawal and remelting of worn coin in certain countries. In the year 1906, 17,721,058 fine ounces of gold were used for coinage in the mints of the world,<sup>1</sup> of which 3,537,000 fine ounces were supplied by

<sup>1</sup> " Report of the Director of the United States Mint " (1907), p. 102.

remelting old coin. In the same year 120,339,500 oz. of silver were used in coinage, of which 34,200,000 oz. consisted of old coin.

*World's Stock of Precious Metals.*—The stock of gold and silver in the world has increased largely in recent years, but was formerly very small. Jacob estimated the amount of gold and silver in circulation in Europe in 1492 at only £34,000,000, and MacCulloch estimated that this had risen to £400,000,000 in 1850. In 1894 the amount of gold coin only was put at £813,500,000.<sup>1</sup> According to the Director of the United States Mint, the world's stock of gold on December 31, 1906, was of the value of \$6,888,900,000, or about £1,425,000,000, of which \$3,764,900,000, or about £779,000,000, was in banks and public treasuries. It is probable that the estimate of the amount in circulation (£646,000,000) is too high. The total stock of silver at the same date is put at \$3,260,200,000, or about £674,000,000 at coining value. The stock of gold coin in the United Kingdom is estimated to be about £100,000,000, and that of silver coin to be about £25,000,000.

#### PRODUCTION OF PLATINUM.

The greater part of the annual production of platinum is obtained from Russia. It is estimated that the total amount produced in that country from its discovery in 1819 down to 1907 was 7,500,000 oz., including 1,500,000 oz., stolen by the miners, which has secretly found its way to the market and is not accounted for by the Government statistics.<sup>2</sup> The production, at first small, rose to 110,000 oz.

<sup>1</sup> "Report of the Director of the United States Mint for 1894."

<sup>2</sup> "Mineral Industry for 1892," p. 388, and subsequent years.

per annum in 1846, but after the coining of platinum by the Russian Government had been discontinued, the output fell in 1852 to 6,400 oz.<sup>1</sup> Subsequently the amount gradually increased and reached an average of 53,000 oz. per annum in 1876,<sup>2</sup> 139,000 oz. in 1886, and 200,000 oz. in 1896. The output has been stationary for some years, and amounted to 210,318 oz. in 1906.<sup>3</sup> In that year 120 platinum placers were being exploited, employing 6,200 workmen who washed 1,886,000 tons of alluvium and obtained an average of 0·09 oz. crude platinum per ton of gravel.<sup>1</sup>

The production in other countries is insignificant. Colombia produces about 4,000 oz. per annum, the United States a few hundred ounces, and Australia, Canada, Borneo, etc., smaller quantities.

The price of platinum has risen in an extraordinary manner in the past few years. After being between 30s. and 40s. per oz. for many years prior to 1894, it rose to £4 10s. per oz. in 1905, and reached a maximum of £8 per oz. in 1906. This great increase in price led to no unusual activity on the part of the producers in the Urals, because the entire output for a number of years to come is stated to have been bought at fixed prices by the dealers in platinum.

The consumption of platinum is put at 325,000 oz. per annum, or much more than the production. The deficiency is made up by old platinum which comes into the market, partly owing to the high price of the metal.

<sup>1</sup> "Mineral Industry for 1906," p. 656.

<sup>2</sup> "Ore Deposits," J. A. Phillips, 1884, p. 402.

<sup>3</sup> "Mining Journal," May 4, 1907, "Mineral Industry for 1907," p. 784.

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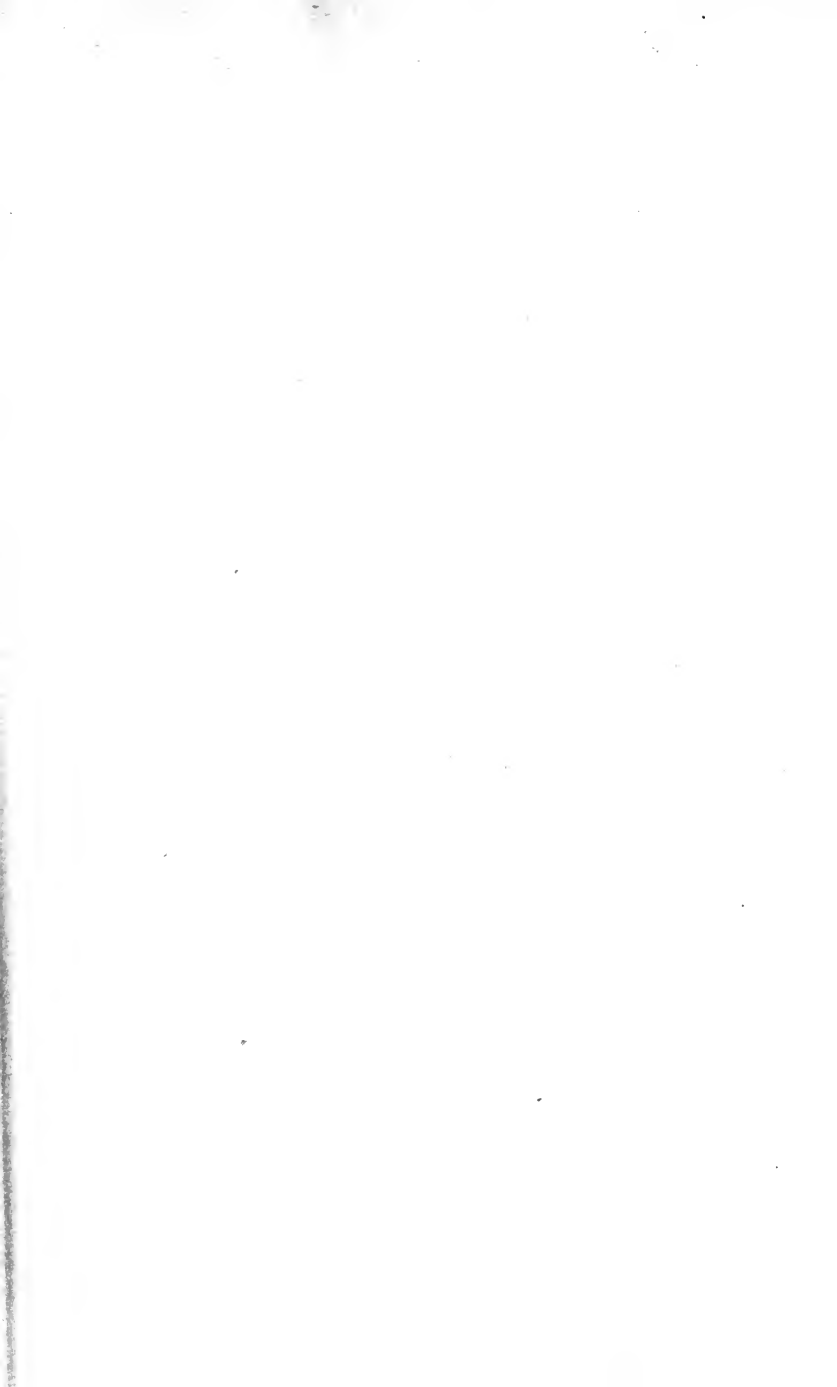
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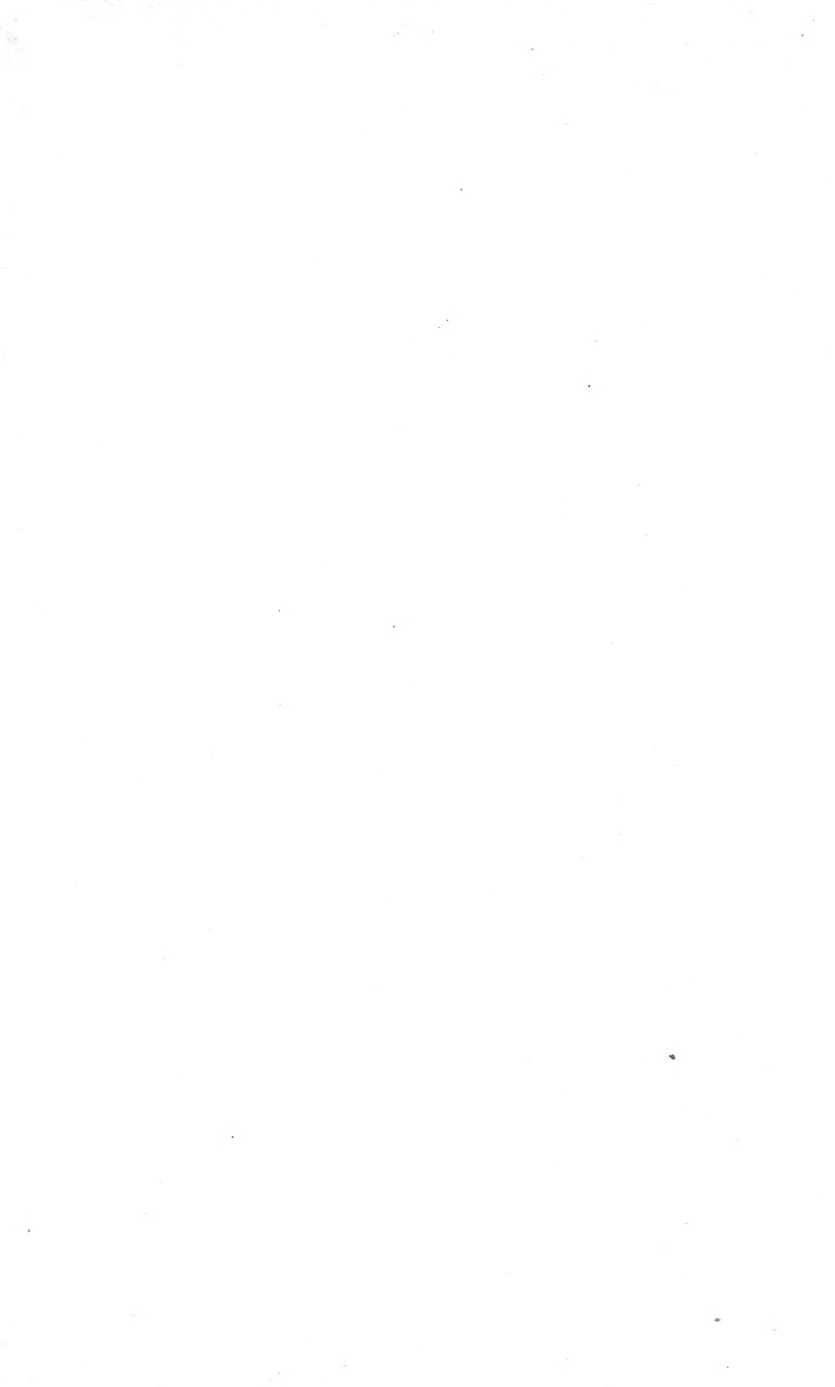
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